SOIL STERILANTS PROGRAM:
PROJECT REPORT COMPILATION

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EXECUTIVE SUMMARY

Soil sterilants were commonly used from the 1960s to late 1990s to control weeds on rangelands, pipeline right of ways, oil and gas wells, railways, sawmills, pulp mills, and other industrial sites across Alberta. Sterilants are typically non-selective, residual, and persistent; they control all plants they contact and because they persist in soil, vegetation growth on sterilant-impacted sites is often inhibited. Sterilants tend to be highly mobile, which can result in off-site contamination via leaching, surface runoff, and wind. Two of the most used soil sterilants in Alberta are bromacil and tebuthiuron.

This report is a compilation of the final technical reports from the research projects, plus the associated fact sheets and presentations from annual knowledge sharing events. Each of the sections includes the report citation, and the executive summary to provide a general overview of the project objectives and findings. Note that some of the projects produced more than one report.

The full reports, and associated fact sheets and presentations are included as Appendices.

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ACRONYMS

AC	Activated Carbon
ASE	Accelerated Solvent Extraction
ELISA	Enzyme-linked Immunosorbent Assays
foc	Fraction of soil Organic Carbon
GC/TID	Gas Chromatography/Thermionic Ionization Detector
GC-MS	Gas Chromatography coupled to Mass Spectrometry
HPC	Heterotrophic Plate Count
IC_p	Inhibition Concentration
Koc	Water–organic Carbon Partition Coefficient
LC-HRMS	Liquid Chromatography coupled to High-resolution Mass Spectrometry
LC-MS	Liquid Chromatography coupled to Mass Spectrometry
LC-UV	Liquid Chromatography with Ultraviolet detection
LIBS	Laser-induced Breakdown Spectroscopy
NIRS	Near Infrared Reflectance Spectroscopy
SPE	Solid-phase Extraction
SPLP	Synthetic Precipitation Leaching Procedure
ssDNA MRE	Single-stranded DNA Molecular Recognition Element
S/V	Surface area to Volume ratio
UW	University of Waterloo
XRF	X-ray Fluorescence
ZVI	Zero Valent Iron

1.0 INTRODUCTION

1.1 Background

Soil sterilants were commonly used from the 1960s to late 1990s for non-selective vegetation control on industrial sites in Alberta. Many of these industrial sites are either starting to be decommissioned or stalled at the remediation phase resulting in delayed reclamation and certification. Soils treated with sterilants often become a source of contamination to adjacent land and waterbodies through leaching, surface runoff, and wind dispersion.

A 5-year Soil Sterilants Program (SSP), funded by both government and industry (Figure 1), was established to develop proven, technical, and cost-effective strategies and best management practices for management of sites impacted by residual soil sterilants, with the goal of achieving regulatory site closure.

Figure 1. Soil Sterilant Program funders.

Bromacil and tebuthiuron were identified as the primary sterilants of concern in Alberta based on a literature review (Drozdowski et al., 2018a), a stakeholder workshop (Drozdowski et al., 2018b), and consultation with industry. The SSP was designed to address knowledge gaps in the areas of: (1) Identification and Delineation, (2) Risk Assessment and Management, and (3) Remediation of these two sterilants (Table 1). A Knowledge Transfer component was included to ensure technical information derived from the research projects was provided to project funders and eventually to all stakeholders.

Table 1. Intended outcomes of the Sterilants Program.

Program Area	Intended Outcome of the Program
Identification and Delineation	a) The uncertainty associated with the methods used to identify when/where sterilant impacts occur is reduced. b) Technologies, best practices, and analytical methods are developed to assess and delineate impacts more accurately and cost-effectively.
Risk Assessment and Management	a) Uncertainty associated with empirical data inputs to risk assessment models for protection of ecological pathways is reduced. b) Conclusive evidence is generated regarding long-term effectiveness of immobilization technologies.
Remediation	a) Optimal, state-of-the-art technologies and/or processes are demonstrated under Alberta conditions to address specific challenges faced by the community of practice.
Knowledge Transfer	a) A community of practice consisting of practitioners, industry, and government representatives is developed and retained. b) Technical information is disseminated through annual workshops and external presentations.

Given the nature of the challenges surrounding these contaminants of concern, and the variety of sites and media where they are found, a single solution was not available for substantially improving the management of sites impacted with sterilants. The SSP aimed to synthesize information so that practitioners, site owners and regulators have the tools needed to assess, remediate, reclaim, and effectively manage risk surrounding sterilant impacts.

1.2 Sterilants Program Delivery

InnoTech Alberta handled management and execution of the SSP with direction from a Steering Committee comprising program funders and input from an Expert Advisory Committee comprising technical experts (

Figure 2). The knowledge gaps associated with bromacil and tebuthiuron impacts were addressed through a series of 13 projects completed by multiple project service providers, including InnoTech Alberta, over a 5-year period (2020 to 2024; Table 2).

The Program Director generated project-specific Requests for Proposals in collaboration with the Steering Committee and Expert Advisory Committee to address the specific knowledge gaps and contribute to the overall objective of the program. The Expert Advisory Committee reviewed and ranked proposals, and the Steering Committee selected Project Service Providers. All projects had clearly defined milestones, budgets, and deliverables. The Program Director and applicable Expert Advisory Committee members reviewed all project reports; individual Project Service Providers conducted internal reviews prior to report submission.

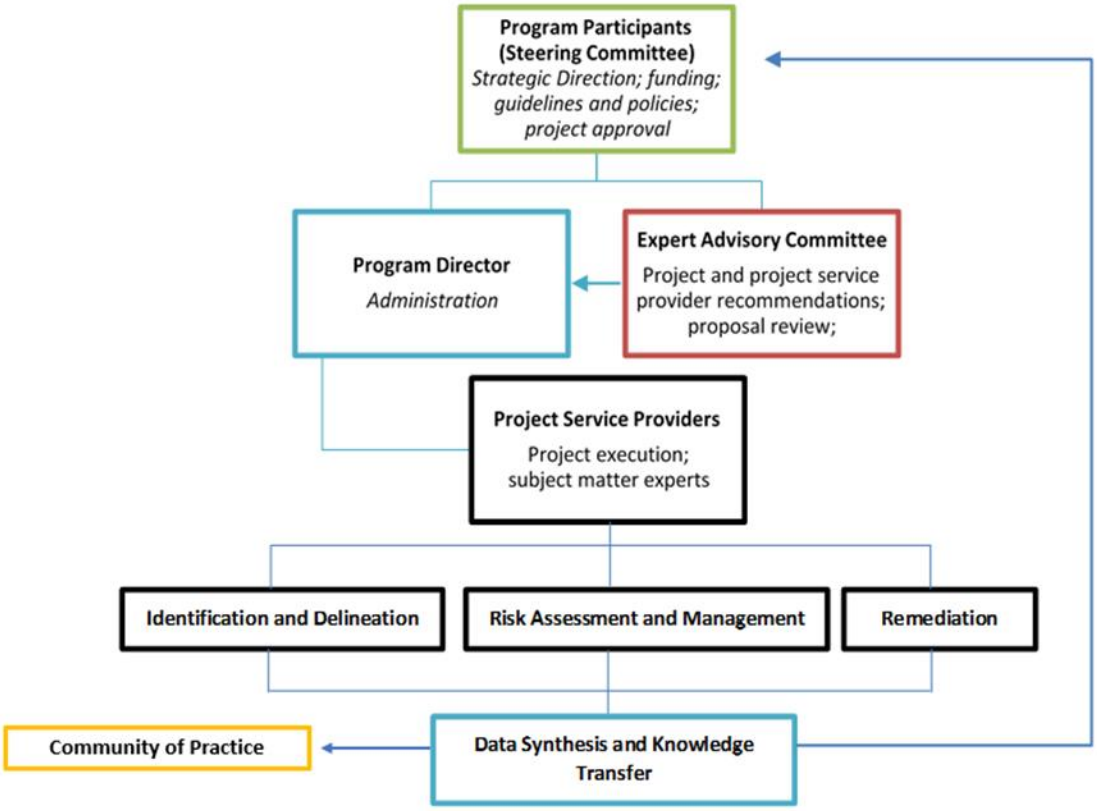


Figure 2. Soil Sterilants Program governance model.

Table 2. List of projects and service providers under the Soil Sterilants Program.

Project	Project Description	Project Service Provider(s)
Identification and Delineation		
Sampling Best Management Practices	Develop best management practices for sampling methodologies to ensure quality analytical results are available to inform management decisions.	TetraTech
Laboratory Method Investigation	Develop a method to increase effectiveness and/or efficiency in laboratory analysis for detection of total bromacil and tebuthiuron in soil and water.	InnoTech Alberta
Detection of Bioavailable Sterilants	Develop and validate laboratory analytical method(s) for detection of bioaccessible bromacil and tebuthiuron, required for evaluating effectiveness of immobilization technologies and for supporting risk assessment.	University of Alberta InnoTech Alberta
Field Screening Technologies	Investigate the potential to develop field screening or proxy lab analytical methods to minimize costs associated with delineation of bromacil and/or tebuthiuron.	Vertex Environmental Inc.
Risk Assessment and Management		
Sterilant-Specific Model Input Data [1]	Develop sterilant-specific model input data relevant to Alberta (soil half-life, mobility, etc.).	Advisian
Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life	Determine appropriate risk model(s) and model parameters to develop screening guidelines for bromacil and tebuthiuron deemed to be protective of the irrigation watering and freshwater aquatic life pathways and better reflect the contaminant's "real-world" fate and mobility in the subsurface under Alberta field conditions.	Millennium EMS Solutions
Investigating Sterilant Fate and Mobility in Alberta [1]	Investigate bromacil mobility in groundwater under Alberta conditions to inform guideline modification and/or acceptance for Tier 2 approaches.	Advisian

Project	Project Description	Project Service Provider(s)
Native Species Toxicity Evaluation	Undertake Alberta native plant species toxicity evaluation.	InnoTech Alberta Millennium EMS Solutions
Remediation		
Investigation of Long-term Effects of Activated Carbon	Investigate longevity of immobilized bromacil and/or tebuthiuron with activated carbon, a common historical amendment for preventing migration of soil sterilants.	InnoTech Alberta
Bench-scale Testing of Sterilant Remediation Technologies	Identify and test candidate technologies for immobilization or remediation of bromacil and/or tebuthiuron in soil and water.	Chemco Inc. Mount Royal University and InnoTech Alberta Vertex Environmental Inc.
Remediation Demonstration(s)	Undertake operational-scale demonstration of management of representative sterilant-impacted site:multiple technology approach.	InnoTech Alberta
Data Synthesis/ Knowledge Transfer		
Technology Evaluation and Comparison	Evaluate and compare remediation technologies, including cost and benefit analysis (including treatment logistics).	InnoTech Alberta
Knowledge Synthesis and Extension	Hold Annual sharing events to update project status. Present non-proprietary information through publications and conferences. Prepare a series of Program Summary reports for Sterilant Program members and, where approved, for public dissemination.	InnoTech Alberta Enviro Q&A Services

[1] These two projects were combined because of the synergies and dependencies in their objectives and methods.

1.3 Knowledge Coordination and Sharing

The intent of the Sterilants Program was to develop strategies for management of sterilant-impacted sites. This required integration of information from multiple projects; thus, Project Service Providers were requested to participate in collaborative discussions with others to synthesize and transfer learnings and advance the collective state of knowledge.

To facilitate this collaboration, knowledge sharing events were held in 2021, 2022, and 2024, at which the Program Director provided updates on the overall SSP, and Project Service Providers presented updates to ongoing projects and their findings from completed projects.

The SSP aimed to synthesize information in ways that were digestible and, in some cases, to provide quick reference guides for field activities and decision making. Each project had an associated Fact Sheet for dissemination, along with final project reports containing all applicable data, for broad distribution as required.

1.3.1 Public Presentations

In addition to the presentations at the Annual Sharing events, some of the researchers and the Program Manager gave presentations at various conferences:

Management of Soil Sterilant Impacted Sites – Bonnie Drozdowski, SMART Remediation – March 11, 2020 – https://smartremediation.com/wp-content/uploads/2022/09/SMART-Remediation-Edmonton-2020-Bonnie-Drozdowski.pdf

Soil Sterilants Program – Bonnie Drozdowski and Simone Levy, ESAA Webinar, May 6, 2020 – https://www.youtube.com/watch?v=GM_yc9bJpmo

Management of Soil Sterilant Impacted Sites – Bonnie Drozdowski and Simone Levy, RemTech 2020, October 15, 2020 – https://esaa.org/wp-content/uploads/2021/04/RT2020-Drozdowski.pdf

The Soil Sterilants Program: Collaboration and Engagement Key to Addressing Challenging Contaminants – Simone Levy, Alberta Chapter, Canadian Land Reclamation Association 2022 Conference and AGM, May 4, 2022 – https://static1.squarespace.com/static/5977ae4ef14aa1a84a5f2bad/t/62966cc8bfa123749568aa67/1654025421430/san_1600_SES7CW0CCS81NV1RM_InnoTech_Sterilants_Program_CLRA_0522.pptx.pdf

Remediation of Bromacil and Tebuthiuron – Optimization and De-risking – Simone Levy, EnviroWorkshops, September 13, 2022.

Development of an Extraction Method for Estimating Phytoaccessible Concentrations of Soil Sterilants Bromacil and tebuthiuron – Jackie Maxwell, RemTech 2022, October 12-14, 2022 – https://esaa.org/wp-content/uploads/2022/11/RT22Maxwell.pdf

Field-scale Research Trial to Demonstrate Ex Situ Remediation of Bromacil in Soil – Sarah Thacker, RemTech 2022, October 12-14, 2022 – https://esaa.org/wp-content/uploads/2022/11/RT22Thacker.pdf

The SSP was also mentioned in the following presentation:

Soil Sterilant Remediation at Utility Sites – Monica Brightwell and Jason Pentland, RemTech 2022, October 12-14, 2022 – https://esaa.org/wp-content/uploads/2022/11/RT22Pentland.pdf

1.4 Knowledge Synthesis

This report is a compilation of the final technical reports from the research projects, plus the associated fact sheets and presentations from annual knowledge sharing events. Each of the following sections includes the report citation, and the executive summary to provide a general overview of the project objectives and findings. Note that some of the projects produced more than one report.

The full reports and the presentations from the 2024 Final Annual Sharing Event are in Appendices A and B, respectively. Some projects produced Fact Sheets which are also provided in this document.

A separate report provides a synthesis of the information gathered during the Soil Sterilants Program – Drozdowski, B. and C.B. Powter, 2024. Soil Sterilants Program: Knowledge Synthesis, Recommended

Practices and Gaps. Report SSP-14B prepared by InnoTech Alberta and Enviro Q&A Services for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta.

1.5 Soil and Groundwater Remediation Guidelines

Most of the SSP reports referred to the 2019 Alberta Tier 1 Guidelines and Alberta Tier 2 Guidelines for bromacil and tebuthiuron guideline values. The citations for those documents are provided below. These guidelines were updated in 2022, however none of the bromacil or tebuthiuron guideline values changed; the 2022 citations are provided here for reference.

2019 Tier 1 Guidelines

Alberta Environment and Parks, 2019. Alberta Tier 1 Soil and Groundwater Remediation Guidelines. Alberta Environment and Parks, Land Policy Branch, Policy and Planning Division. AEP, Land Policy, 2019, No. 1. 198 pp. https://open.alberta.ca/dataset/842becf6-dc0c-4cc7-8b29-e3f383133ddc/resource/a5cd84a6-5675-4e5b-94b8-0a36887c588b/download/albertatier1guidelines-jan10-2019.pdf

2019 Tier 2 Guidelines

Alberta Environment and Parks, 2019. Alberta Tier 2 Soil and Groundwater Remediation Guidelines. Alberta Environment and Parks, Land Policy Branch, Policy and Planning Division. AEP, Land Policy, 2019, No. 2. 150 pp. https://open.alberta.ca/dataset/aa212afe-2916-4be9-8094-42708c950313/resource/157bf66c-370e-4e19-854a-3206991cc3d2/download/albertatier2guidelines-jan10-2019.pdf

2022 Tier 1 Guidelines

Alberta Environment and Parks, 2022. Alberta Tier 1 Soil and Groundwater Remediation Guidelines. Alberta Environment and Parks, Land Policy Branch, Policy and Planning Division. AEP, Land Policy, 2022, No. 4. 189 pp. https://open.alberta.ca/dataset/842becf6-dc0c-4cc7-8b29-e3f383133ddc/resource/018c0139-ae40-4537-af72-23458c8c58c7/download/aep-albertatier1guidelines-aug24-2022.pdf

2022 Tier 2 Guidelines

Alberta Environment and Parks, 2022. Alberta Tier 2 Soil and Groundwater Remediation Guidelines. Alberta Environment and Parks, Land Policy Branch, Policy and Planning Division. AEP, Land Policy, 2022, No. 5. 129 pp. https://open.alberta.ca/dataset/aa212afe-2916-4be9-8094-42708c950313/resource/157bf66c-370e-4e19-854a-3206991cc3d2/download/albertatier2guidelines-jan10-2019.pdf

1.6 How to Navigate This Document

The best way to navigate through this large document is to use the bookmarks embedded in the document. There you will find the sections in the body of the report, plus each of the Appendices. Using the bookmarks you can easily move between the body of the report and the individual Appendices.

2.0 SAMPLING BEST MANAGEMENT PRACTICES

2.1 Report Summary

Hemsley, T., K. Bessie and A. Shaikh, 2021. Sterilant Sampling Best Management Practices. Report SSP-2 prepared by TetraTech Canada Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 41 pp.

Soil sterilants are non-selective residual herbicides that were developed in the 1960s to late 1990s to provide long-term vegetation control on industrial sites along highways, railroad rights-of-way, and industrial areas. Sterilants tend to be persistent in the environment and are not selective as all plants will be affected by these chemicals. The most commonly used sterilants were atrazine, bromacil, diuron, DCPMU, linuron, simazine and tebuthiuron. These sterilants have different physical-chemical properties, modes of action on plants, fate and exposure and toxicological properties. Of these seven sterilants, bromacil and tebuthiuron were the most commonly found sterilants on industrial sites in Alberta.

InnoTech Alberta's Reclamation Team initiated the current Soil Sterilant Program focusing on bromacil and tebuthiuron after a literature review and workshop facilitated by InnoTech in 2017. The industry steering committee decided to focus additional research on three key knowledge gaps (1) Identification and Delineation, (2) Risk Assessment and Management, and (3) Remediation.

The purpose of the Sterilant Sampling Best Management Practices (BMP) is to provide specific sampling guidance for low level (≤0.2 mg/kg) concentrations of bromacil and tebuthiuron in soil and groundwater in Alberta. This BMP is intended for use for anyone engaged in environmental site assessment, remediation, and reclamation activities in respect to soil sterilant contamination. The document provides guidance in respect to regulatory considerations, site evaluations, soil and groundwater characterization guidance (e.g., soil sampling, groundwater sampling), data evaluation and interpretation.

When developing a sampling program, the following should be considered:

- Objectives of the site investigation. Is it an initial assessment; or a supplemental (detailed) assessment; or for delineation?
- The fate and transport (volatilization, absorption/desorption, mobility/leaching, soil pH and salinity) of the sterilants.
- Site historical information, date(s), and characteristics (e.g., low-lying areas, slopes, soil classification, hydraulic characteristics).
- High potential for cross contamination when sampling.
- The spatial variability of both soils, and sterilants as high concentrations of sterilants may be found at the surface or at depth within 'hot spots' but they may diminish to below laboratory detection limits within a short distance.

Due to the high potential for cross contamination when sampling for sterilants, there are special sampling techniques that should be used when assessing low concentrations (parts per billion [ppb] and parts per trillion [ppt]) of bromacil and tebuthiuron. These special sampling techniques include collection using a minimum of 3" diameter direct push drill rig with sleeves or a hollow stem auger, an 18" split barrel spoon with 6" x 2.5" stainless steel sleeves every 1.0 m down to a depth of 7.5 m or until bedrock. Each soil-filled sleeve should be sealed with Teflon tape and plastic caps and be submitted directly to the laboratory for analytical analysis. For groundwater, discrete monitoring points should be

established within different water bearing lithological units to avoid mixing of groundwater during drilling and sampling. Low flow purging and sampling is suggested as it can provide more accurate and reproducible samples of the formation water quality than using high flow/high volume purging and sampling methods.

In addition, a Triple Rinse Method should be completed on all field sampling equipment before each use, during use and after being used due to the high potential for cross contamination and low-level guidelines.

2.2 Project Report

The Report is available in Appendix A1

2.3 Project Fact Sheet

Sterilant Sampling - Recommended Best Management Practices

Challenges

- Sterilants are mobile in soil and highly soluble in water.
- Accurate delineation challenges:
  - Guideline values require low detection limits (ppb/ppt).
  - High potential for cross contamination during sampling.
- Based on application patterns and mobility, high spatial variability for sterilants, often with 'hot spots'.

Site-Specific Considerations

- Site activities and infrastructure.
- Sterilant application distribution, history and remedial strategies (e.g., activated carbon).
- Soil type(s) and hydrogeological considerations.
- Site topography and potential for offsite migration in soil or water (e.g., ephemeral drainage channels) .

Equipment Considerations

Soil Sampling (see p.3)

- Shovel (undisturbed or minimally disturbed soils) and Backhoe (disturbed soils or "test pit"), collected directly from the wall with gloved hand or stainless steel trowel or spatula.
- Drill truck - Direct Push with minimum 3" barrel or Hollow Stem with split spoon lined with sleeves (e.g. California Split Spoon).
- Sleeves- Stainless steel, Teflon™, Brass, or PVC.

Groundwater well installation

- Standard operating for installing groundwater wells and selecting screen intervals for most situations.
- Change sampling equipment between well development, purging and sampling
- Low-flow purging and sampling for shallow depths recommended.
- Deep groundwater wells >10 m standard procedures (bailer or Wattera tubing) material can be used.

Confirmatory Sampling

- Either of these two methods can be used:
  1. Core sampler equipped with a sleeve driven into excavation walls/base with the sleeve being sent directly to the laboratory; or
  2. Clean initial 0.05 m from the walls/base before collecting a soil sample and packing into glass jars.
- Use new gloves each time and clean all equipment.

Site Characterization Steps

Identify Potential for Sterilant Use

- Phase 1 ESA: historical site activities, topography and potential receptors, vegetation and surface assessment (see p.2 for more info).

Preliminary Phase 2 ESA

- Soil characterization and sampling by stratigraphic unit (Fig. 1) via solid stem auger unless otherwise specified.
- Collect samples in jars with Teflon™-lined lids.
- Sterilant screen analysis in case various types used.

Sterilant Delineation/Confirmatory Sampling

- Low contaminant (ppb or ppt range) sampling techniques (e.g. core sampling; scrape samples prior to placing in jars; isolate suspected high concentration from low concentration samples).
- Special care must be taken to prevent cross-contamination.
- Follow QA/QC protocols (see p.3).
- Increase sampling frequency for delineation (vertical and horizontal) and confirmatory sampling.
- Equipment decontamination via Triple Rinse Method recommended (see p.3)
- Analyze individual relevant sterilants.
- Install groundwater monitoring wells where potential for impacts and delineation in groundwater.

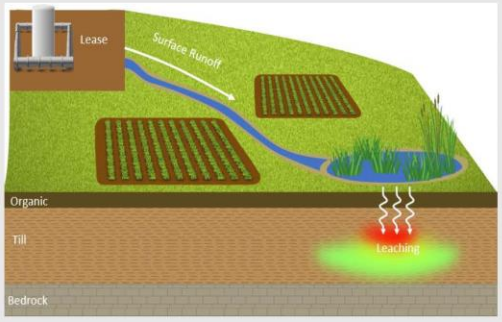
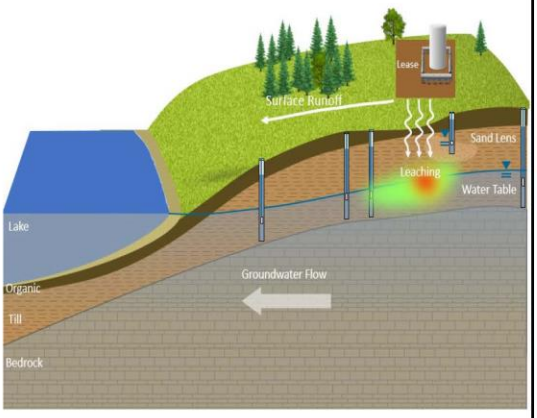
0 m

- Classify soils using *Canadian Soil Classification System* (CSSC) for undisturbed soils and/or information for equivalent capability or reclamation planning.
- Shovel is the best method to view soil profiles.
- Collect discrete samples by soil horizons (A, B and C) first and by depths second.
- Increments as small as 5 cm may be needed in some instances (e.g. fresh applications to berms)

1.0 m

- Classify soils using a modified Unified Soil Classification System utilizing ASTM D2488.
- Sample by soil stratigraphy first and foremost over depth increments.
- Discrete soil samples should be collected in <0.5 m intervals (where possible) and at changes in soil stratigraphy.

Fig. 1. Recommended soil sampling by stratigraphic unit and classification system

Typical Alberta Sterilant Impacted Scenarios	Reference Figures
Flare Pit Berms or Tank Berms ▪ Small volume. ▪ Typically not much depth penetration initially due to slopes on berms. ▪ Fill material. ▪ Age 1960s to 1990s for bromacil and tebuthiuron (30-60 years old), a variety of sterilants and herbicides used for control over time. Since 1990 quite common to use glyphosate. ▪ Due to small volume, soil is usually landfilled off-site if impacted.	 Left - Flare pit berm. Right - Propane Tank Berm.
Perimeter Berms ▪ Same scenario as above but higher potential to extend off-site. ▪ Off-site could be agricultural land use (cultivated or pastureland) and the area impacted is usually long and narrow (e.g., 5 m x 40 m). ▪ Off-site portion was commonly treated with activated charcoal and/or manure from mid-1980s to current day.	 Activated charcoal tilled into topsoil.
Off-Site Run-off onto Agricultural Fields in Ephemeral Drainage Channels ▪ Moderate volume. ▪ Infiltration is usually less on steeper slopes, but over time can move into subsoil (<1 mbgs, typically) – see Landsburg and Dwyer (1995). ▪ Often multiple applications and run-off events so can be re-contaminated. ▪ Sterilants can accumulate in wetland areas (low areas) penetrating deeper plus impact surface water. ▪ Some sites treated with activated charcoal and/or manure in mid-1980s to current.	
Full Site Area ▪ Large volume, areas typically 100 m x 100 m or larger and level. ▪ Typically has gravel over fill or subsoil (topsoil removed during site construction and saved for reclamation since 1980s) ▪ Multiple applications to entire site, often with various sterilants and herbicides. ▪ Impacted area also overlaps with other sources (spills, flarepits, etc.) that may have co-contaminant impacts (hydrocarbons, salts, metals). ▪ Level area and multiple applications over time and old sites (60 years or more) can have soil impacts as deep as 4.5 m in fine textured soils and 6 m in coarse textured soils. ▪ Shallow groundwater is often impacted but in fine texture till, or the discontinuous sand lenses within the till, the water is often not considered an aquifer due to discontinuous, low hydraulic conductivities, yield and sometimes chemistry.	

Delineation Sampling Devices

Manual

Shovel

Manual Soil Core

Mechanical

Hollow Stem Auger

18" (45.72 cm) split barrel with
6" (15.24 cm) stainless steel liners

Direct Push with 3" diameter barrel

Triple Rinse Method

Equipment

- Liquinox and distilled water
- Four 5-gallon pails
- Nitrile gloves
- One scrub brush (long handle and proper size for equipment)

Triple rinse cleaning method setup

Procedure

1. Clean all 5-gallon pails with distilled water and liquinox before use.
2. Partially fill a 5-gallon pail with distilled water, add liquinox and mix
3. Set up another three 5-gallon pails and partially fill each with distilled water (enough water to submerge sampling equipment)
4. Immerse sampling equipment in liquinox/water mixture (first 5-gallon pail), scrub equipment thoroughly and shake off excess moisture
5. Then rinse the equipment in each of the remaining three 5-gallon pails.
6. Rinsing should be from most dirty to the cleanest pail.
7. Decontamination wash and rinse water should be collected and contained for appropriate disposal.

- As washing and rinsing water becomes contaminated, dispose of water as per Step 7 then repeat Steps 1 to 6.

Quality Assurance and Quality Control (QA/QC)

- Field duplicates- at least one sample per every 10 samples (10% of the samples)
- One trip blank per shipping container and one field equipment blank per day to confirm the presence or absence of cross contamination during field activities, travel, or laboratory analysis for soils and groundwater.
- Soils and groundwater trip and equipment blanks uses distilled water and is a water analysis.
- Collection and analysis of decontaminated equipment rinsate from the fourth pail should be completed to document the absence of cross contamination.
- Obtain at least two groundwater samples on different days from any monitoring well.
- Relative percent differences (RPD) for soils may be 60%, near ppm range, and 75% to 100%, near ppb range.
- RPD for groundwater may range from 20% (ppm range) to 40% (ppb range).

3.0 LABORATORY METHOD INVESTIGATION FOR DETECTION OF BROMACIL AND TEBUTHIURON IN WATER AND SOIL

3.1 Report Summary

Periera, A.D.S, E.D. Ruan and G. Knox, 2022. Laboratory Method Investigation for Detection of Bromacil and Tebuthiuron in Water and Soil. Report SSP-3 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 38 pp.

This project addressed gaps related to laboratory analytical methods for bromacil (CAS 314-40-9) and tebuthiuron (CAS 34014-18-1) in water and soil matrices. Identified gaps include detection limits very near Alberta Tier 1 soil and groundwater remediation guidelines, elevated analytical costs and a variety of analytical methods in use. InnoTech Alberta's Chemical Testing laboratory completed the project.

Development of test methods to increase the effectiveness and efficiency in laboratory analytical methodologies for detection of total bromacil and tebuthiuron focused on the following attributes:

1. High selectivity for the analyte(s) of interest.
2. Method Detection Limits at least two orders of magnitude below regulatory guidelines for soil and groundwater[1].
3. Complete recovery of the analyte(s) of concern from the matrix containing the analyte(s).
4. High degree of trueness (i.e., accuracy and precision).
5. Cost-effective (use less solvents).
6. High throughput for the sample preparation compared to liquid-liquid extraction.

The approach for this project focused on two components of the chemical measurement process: optimization of extraction approach and instrumentation. The scope of work for the project was to:

1. Review of the literature and outreach to commercial laboratories for analytical methods used for the analysis of sterilants.
2. Develop a validated analytical method for analysis of bromacil and tebuthiuron in soil samples with a method detection limit of at least 5 µg/kg.
3. Develop a validated analytical method for analysis of bromacil and tebuthiuron in water samples with a method detection limit of at least 5 ng/L.
4. Statistically compare the results from the new methods with those currently in use by InnoTech Alberta and others. This will be achieved by the comparison of the results obtained from the analysis of "blind" samples.
5. Evaluate the new methods for cost, throughput, waste production and safety.
6. Provide method details to external laboratories for potential adoption.

The literature review identified considerable differences between the analytical methods cited in the literature and those used by the commercial laboratories in Alberta. The methods in the commercial laboratories are mainly based on liquid chromatography with ultraviolet detection (LC-UV), liquid chromatography coupled to mass spectrometry (LC-MS), and gas chromatography coupled to mass

[1] Alberta Tier 1 Guidelines: Bromacil: 0.009 mg/kg (soil); 0.0002 mg/L (water) and Tebuthiuron: 0.046 mg/kg (soil); 0.00043 mg/L (water).

spectrometry (GC-MS). Most of the literature between 1984 and 2020 also used the same analytical techniques, however in recent years methods have moved from simple UV detection and low-resolution mass spectrometry to high-resolution mass spectrometry. Sample preparation has also moved from solvent extractions to solid-phase extraction (SPE) or accelerated solvent extraction (ASE) processes.

Based on the information gathered through the literature review and outreach program, InnoTech proposed the use of the Liquid Chromatography coupled to tandem mass spectrometry (LC-MS/MS) and/or high-resolution mass spectrometry (LC-Orbitrap-MS). The choices of the LC-MS/MS and/or LC-Orbitrap-MS as possible solutions to improve the effectiveness and efficiency of the analytical methods for bromacil and tebuthiuron is based on the high throughput, excellent accuracy, and better sensitivity. The methods are the ideal platforms for the quantification of compounds in complex matrixes and multiclass risk compound screening.

A new analytical method was successfully developed and validated for analysis of bromacil and tebuthiuron with detection limits between two and three orders of magnitude lower than available through commercial laboratories.

In soil samples, the bromacil detection limits in commercial laboratories are ≥ 5 µg/kg while the new method has a validated minimum detection limit of 0.013 µg/kg using the LC-MS/MS and 0.032 µg/kg using the LC-Orbitrap-MS. For tebuthiuron, the detection limits in commercial laboratories are ≥ 5 µg/kg while the new method has a validated minimum detection limit of 0.003 µg/kg using the LC-MS/MS and 0.006 µg/kg using the LC-Orbitrap-MS.

In water samples, bromacil detection limits in commercial laboratories are ≥ 0.1 µg/L while the new method presented here has a validated minimum detection limit of 0.0001 µg/L using the LC-MS/MS and 0.00006 µg/L (or 0.6 ng/L) using the LC-Orbitrap-MS. For tebuthiuron, the detection limits in commercial laboratories are ≥ 0.1 µg/L while the new method has a validated minimum detection limit of 0.000004 µg/L (or 0.04 ng/L) using the LC-MS/MS or the LC-Orbitrap-MS.

The validated limit of quantification in soils for bromacil was 0.1 µg/Kg and for tebuthiuron 0.01 µg/kg, and for water samples, the limit of quantification for bromacil was 0.0005 µg/L (or 0.5 ng/L) and for tebuthiuron 0.00005 µg/L (or 0.05 ng/L).

Water and soil samples were extracted, concentrated, and purified by using solid phase extraction (SPE) and Accelerated Solvent Extraction (ASE) procedures, respectively. A method of liquid chromatography-tandem mass spectrometry (LC-MS/MS) was developed for the determination of bromacil and tebuthiuron. Soil and water recovery rates were between ~70% and 130% (relative standard deviation (RSD)< 10 %). The optimized method with high throughput and less solvent has been safely and successfully applied for field samples with limited matrix interference, and results were comparable to current commercial laboratory results.

3.2 Project Report

The Report is available in Appendix A2

In addition to the report, the researchers prepared a Standard Operating Procedure document for use by laboratories.

3.2.1 Project Fact Sheet

Soil Sterilants Program Project #3:
Low Level Bromacil and Tebuthiuron Detection Method

Objective:
Develop and validate low-level laboratory analytical methods for bromacil and tebuthiuron in soil and groundwater with the following attributes:

- Method Detection Limits (MDL) at least two orders of magnitude below Alberta Tier 1 regulatory guidelines[1]
- High selectivity for analytes of interest
- Complete recovery of analytes of concern from soil or groundwater matrix
- Cost-effective
- High throughput

Approach:

1. Prepare a review of literature for analytical methods used for the analysis of sterilants and conduct outreach program to identify methods used by Alberta commercial laboratories
2. Develop and validate an analytical method for analysis of bromacil and tebuthiuron in soil samples with a method detection limit of **0.1 µg/Kg** or less.
3. Develop and validate an analytical method for analysis of bromacil and tebuthiuron in water samples with a method detection limit of **0.005 µg/L (5 ng/L)** or less.
4. Statistically compare the results from the new method(s) with those currently in use by InnoTech Alberta and other analytical laboratories.
5. Share the methods to external labs based on the method development for bromacil and tebuthiuron by LC-MS/MS

1. Literature review

Analytical Methods Available vs. Employed in AB	•Liquid chromatography with ultraviolet detection (LC-UV) •Liquid chromatography coupled to mass spectrometry (LC-MS) •Gas chromatography coupled to mass spectrometry (GC-MS) •*Shift to high-resolution mass spectrometry
Extraction Methods	• Solvent extractions to solid-phase extraction (SPE) or accelerated solvent extraction (ASE) processes
Analytical Equipment	

1Alberta Tier 1 Guidelines: **Bromacil**: 0.009 mg/kg (soil); 0.0002 mg/L (water) and **Tebuthiuron**: 0.046 mg/kg (soil); 0.00043 mg/L (water)

Soil Sterilants Program Project #3:

2. Industry challenges

Key challenges identified from:
- Reviewing compiled site information
- Input from community of practice
- Validated by SSP Steering Committee industry members

Key Remediation Challenges
1. Sterilants at depths greater than 50 cm bgs in unsaturated soil, thus inaccessible to treatment at surface.
2. Destruction of bromacil and tebuthiuron (versus immobilization) in soil – *in* or *ex situ*.
3. Sterilant impacts in saturated fine-grained till soils and groundwater.

3. Technology identification and evaluation

Methods:
- Identify and tabulate all technologies for potential treatment of bromacil and tebuthiuron in soil and/or water, *in*- and *ex-situ*
- Screen based on availability in Alberta, potential limitations and advantages
- Classify to evaluate potential integration into bench- and field-scale testing projects:
  1. **Proven** for treatment of sterilants – requires no further evaluation unless providers can identify explicit requirements for testing to significantly refine the process.
  2. **Impractical** for application for reasons as specified (e.g., low effectiveness and/or longevity, elevated cost, or potential residual impacts to treated media, such as incomplete remediation resulting in harmful daughter products or impact to soil quality).
  3. **Potential** to evaluate through bench-, meso-, pilot- or field-scale trials, pending additional review and prioritization.
- Evaluate applicability to key remediation challenges
- Recommend approach for bench- and field-scale SSP testing projects

Recommendations (with proposal evaluation to follow as part of subsequent SSP project development)

Technology	Applicable Sterilants	Primary Remediation Challenges Addressed by Technology	Potential Testing Stage Based on Provider Feedback*
Soil Remediation Technologies			
Chemical Oxidation (in and ex situ)	Bromacil, Tebuthiuron	2) Sterilant destruction	Stage 1
Activated Carbon Slurry	Bromacil, Tebuthiuron	1) Sterilants at depths greater than 50 cm bgs in unsaturated soil	Stage 2
Chemical Reduction (DARAMEND) in or ex situ	Bromacil	2) Sterilant destruction	Stage 1
Electrokinetic Remediation	Bromacil, Tebuthiuron (TBD)	1) Sterilants at depths greater than 50 cm bgs in unsaturated soil 2) Sterilant destruction 3) Saturated fine-grained till soils and groundwater	Stage 1
Water Remediation Technologies			
Activated Colloidal Carbon Slurry + ChemOx	Bromacil, Tebuthiuron	2) Sterilant destruction 3) Saturated fine-grained till soils and groundwater	Stage 1
Enhanced Biodegradation (*in-situ*)	Bromacil, Tebuthiuron	2) Sterilant destruction 3) Saturated fine-grained till soils and groundwater	Stage 1
Permeable Reactive Barrier (PRB) with Embedded BOS and Reductant	Bromacil, Tebuthiuron	2) Sterilant destruction 3) Saturated fine-grained till soils and groundwater	Stage 2/3 based on prior bench-scale tests
Surfactant-Enhanced Removal	Bromacil, Tebuthiuron	3) Saturated fine-grained till soils and groundwater	Stage 1

*Proposed testing stages:

Stage 1 – Preliminary bench-scale testing: Screening test for technologies or products with reasonable justification for potential effectiveness in sterilant remediation

Stage 2 – Extended bench-scale testing: Following successful Stage 1 testing or where technologies have been previously tested, further validation through a greater range of sterilants concentrations, soil types and/or water composition

Stage 3 – Meso- and/or field-scale testing: Where extended bench scale testing proves a technology to be effective, additional testing at meso- or field-scale under controlled conditions to validate field application

4.0 EXTRACTING PHYTOACCESSIBLE STERILANTS

This project was completed as part of a Masters thesis at the University of Alberta by Jacqueline Maxwell under the supervision of Dr. Sylvie Quideau. The thesis formed the report for the project and is not included in this compilation.

4.1 Report Summary

Maxwell, J.L., 2022. Development of an Extraction Method for Estimating Phytoaccessible Fractions of Bromacil and Tebuthiuron. M.Sc. Thesis. Department of Renewable Resources, University of Alberta, Edmonton, Alberta. 51 pp.

Bromacil and tebuthiuron are herbicides used from the 1960s to 1990s on industrial sites to control vegetation. Approximately 61,750 sites are considered contaminated when comparing total herbicide concentrations (estimated by 99 percent methanol extraction) against Alberta's remediation guidelines. Remediation of these sites requires treatment or removal of soil to bring herbicide concentrations below applicable guidelines. As time passes from initial application, a portion of bromacil and tebuthiuron is thought to adsorb to the soil solid phase. The total herbicide concentration in soil is then comprised of the adsorbed (solid phase) and the phytoaccessible (plant accessible) concentrations. Measuring phytoaccessible or soluble herbicide concentrations in soil would avoid unnecessary ex-situ treatment or landfilling. It is likely that adsorption to soil organic matter or mineral particles reduces phytoaccessibility and immobilization technologies could be used to increase the natural soil adsorptive capacity to manage in-situ sites with herbicide contamination.

Calcium chloride solution (0.01 M) is often used to assess soluble (phytoaccessible) concentrations of nutrients and to conduct adsorption/desorption studies of metals and organics. In this work, it was used as an extractant to estimate the phytoaccessible concentrations of bromacil and tebuthiuron in soil. A t-test for non-parametric data with homogeneous variances was used to compare calcium chloride-extractable herbicide concentrations to total concentrations (estimated by 99 percent methanol extraction of aged soil samples, or by spiking soils using a known herbicide concentration). For this study, 149 x 1 g soil samples were included containing a known concentration of bromacil (84 samples) or tebuthiuron (66 samples). Samples were extracted with 40 mL 0.01 M calcium chloride by shaking and centrifugation. The resulting 10 mL liquid extracts were sent to a commercial laboratory for analysis with High Pressure Liquid Chromatography (HPLC) using Mass Selective Detection. Estimated total concentrations were higher than calcium chloride-extractable concentrations. Median spiked and aged bromacil concentration was 0.300 mg/kg and median calcium chloride-extractable bromacil was 0.190 mg/kg ($W = 5131$, $p < 0.001$). Median spiked and aged tebuthiuron concentration was 0.273 mg/kg and median calcium chloride-extractable was 0.140 mg/kg ($W = 2694$, $p = 0.003$).

In reviewed literature, organic matter and clay contribute most to bromacil or tebuthiuron adsorption. Categorical analysis of high or low organic matter and high or low clay content against the apparently adsorbed fraction was conducted. A two-by-two Analysis of Variance (ANOVA) assessed if increasing percentage of clay and organic matter increased the apparently adsorbed fraction, which was estimated by subtracting the calcium chloride-extracted concentration from the total estimated concentration. Mean apparently adsorbed bromacil fraction was higher for high organic matter compared to low organic matter soils ($F = 8.09$, $p < 0.01$). Clay did not significantly increase apparent bromacil adsorption ($F = 2.36$, $p = 0.133$). Similarly, mean apparent adsorbed tebuthiuron fraction was significantly higher for high organic matter compared to low organic matter soils ($F = 25.89$, $p < 0.001$), but clay did not significantly increase tebuthiuron adsorption ($F = 0.03$, $p = 0.858$).

Calcium chloride-extracted concentrations of bromacil and tebuthiuron were less than the estimated total concentrations likely due to adsorption on organic matter. Where there are large areas of marginal bromacil or tebuthiuron contamination, approaches are needed to reduce risk, meet regulatory requirements, and protect soil health. Soils with low phytoaccessible concentrations could remain in place and retain nutrients, organic matter, and structure, providing resiliency against current and future challenges to soil ecosystems.

4.2 Project Report

The thesis is available in the University of Alberta's Education and Research Archive at https://doi.org/10.7939/r3-c6w5-nk49

4.2.1 Project Fact Sheet

Soil Sterilants Program Project #4: Extracting Phytoaccessible Sterilants

Challenge:

- Analyzing soil samples for total sterilant concentration (in this case, bromacil and tebuthiuron) precludes immobilization as a remedial method.
- Currently in Alberta, there is not an accepted methodology by which to immobilize contaminants and then analyze for phytoaccessible concentrations.

Research Question 1: How can the phytoaccessible portion of bromacil and tebuthiuron be estimated, i.e., that portion which is not adsorbed to activated carbon, organic matter or clay?

Methods:

- Choose an extractant that is a good-enough proxy for pore water conditions that maintains as close as possible in-situ soil characteristics.
- 0.01 M calcium chloride was chosen as it is used extensively for estimating accessibility of nutrients and metals, and in adsorption/desorption studies of herbicides
- A modified United States Environmental Protection Agency method for adsorption/desorption studies was followed with input from Garret et al (2009).
- Soil samples represented a range of Orders found in Alberta.
- These were field-impacted or spiked and aged for at least eight weeks up to one year.
- Difference between estimated total and phytoaccessible concentrations was assessed using a Wilcoxon Ranked Sum t-test.

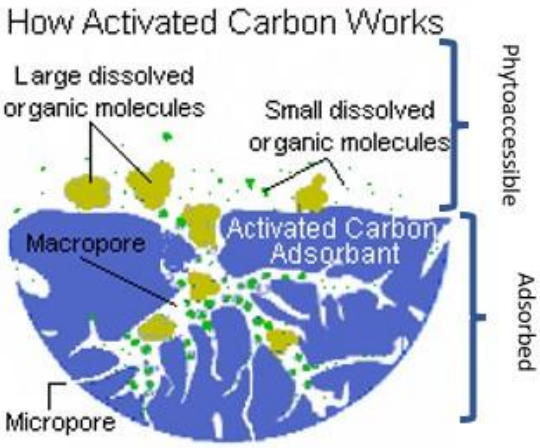


Fig. 1. Activated carbon, soil organic matter and sometimes clay can adsorb various substances. All are observed to adsorb bromacil and tebuthiuron reducing phytoaccessibility (the amount of sterilant desorbed from the solid phase and dissolved in soil pore water).
Image: Adsorption and Ion Exchange: ENGR 360 WATER IN AFRICA, TECHNOLOGY, EDUCATION AND RECIPROCITY (WATER) (jmu.edu)

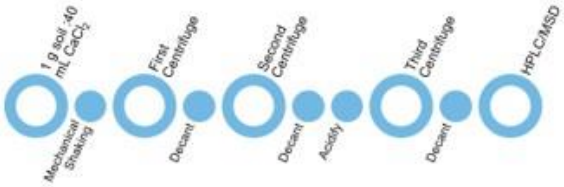


Fig. 2. Modified method from USEPA and Garrett et al (2009).
Main references: Garrett et al., "A Water-Leach Procedure for Estimating Bioaccessibility of Elements in Soils from Transects across the United States and Canada.", USEPA, "OECD GUIDELINE FOR THE TESTING OF CHEMICALS Adsorption-Desorption Using a Batch Equilibrium Method."

Phytoaccessbility Results:

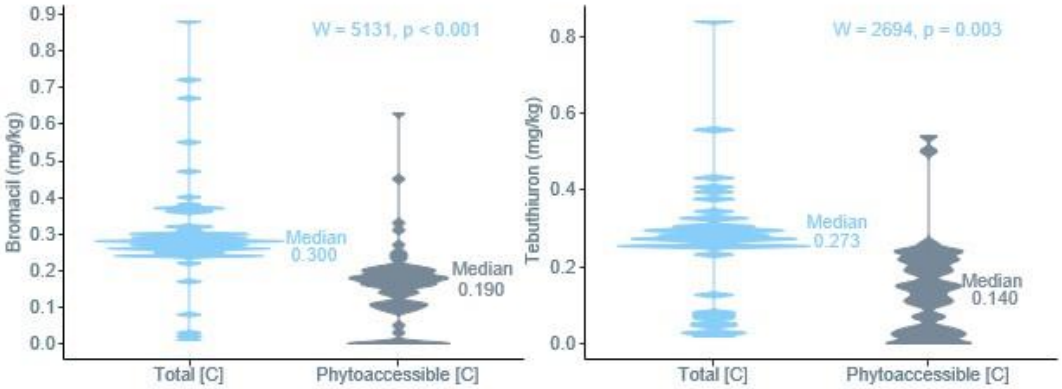


Fig. 3. The difference between the total sterilant concentration and the phytoaccessible sterilant concentration was significant for both bromacil and tebuthiuron. Extracting substances with a weakly ionic solution like 0.01 M calcium chloride is a common method to estimate phytoaccessibility.

Soil Sterilants Program Project #4: Extracting Phytoaccessible Sterilants

Challenge:

- Soil organic matter (SOM) and clay particles are naturally-occurring adsorbents that reduce phytoaccessibility. Connecting SOM and clay content to bromacil and tebuthiuron adsorption is key to understanding phytoaccessibility at a site and how much activated carbon might be needed to reduce bromacil and tebuthiuron phytoaccessibility below applicable management limits.

Research Question 2: In the absence of activated carbon, does soil organic matter and clay particles significantly increase adsorption of bromacil and tebuthiuron?

Methods:

- Categorical predictors for "high" or "low" soil organic matter or clay were compared to estimated adsorbed fraction of bromacil and tebuthiuron.
- A two-by-two Analysis of Variance (ANOVA) was selected to test if
  1) if organic matter significantly increases adsorption
  2) if clay significantly increases adsorption
  3) if there is an interactive effect between organic matter and clay in increasing adsorption of either herbicide.

The closer to the adsorbed fraction is to 1, the **less herbicide was assumed extracted by the 0.01 M calcium chloride**, and a higher herbicide concentration is assumed to be adsorbed. The closer the adsorbed fraction is to 0, the more herbicide was assumed extracted by 0.01 M calcium chloride and it is assumed that a lower herbicide concentration was adsorbed.

Adsorption Results:

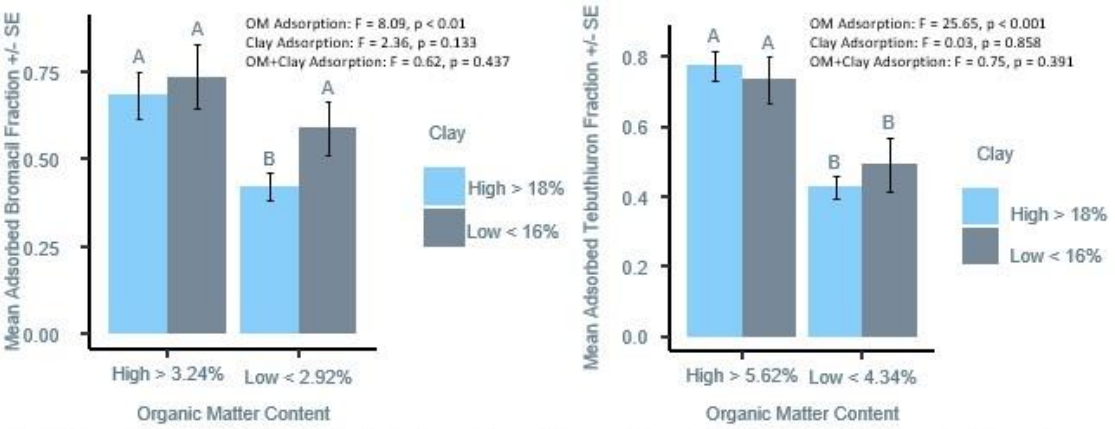


Fig. 4. For bromacil, organic matter content greater than 3.24 percent significantly increased adsorption, but not in the case of low clay content. Clay may be more reactive in adsorption compared to bromacil at a certain threshold of clay content. For tebuthiuron, organic matter content greater than 5.62 percent significantly increased adsorption regardless of clay content.

Conclusions:

- **Research Question 1:** Phytoaccessible concentrations of bromacil and tebuthiuron as estimated by 0.01 M calcium chloride extraction ***are less than*** total sterilant concentration due to adsorption on organic matter.
- **Research Question 2**: Soil organic matter is a ***significant*** naturally-occurring adsorbent of bromacil and tebuthiuron. If it does not reduce phytoaccessibility of bromacil and tebuthiuron below management limits, amending soil with activated carbon can increase adsorptive capacity to further reduce phytoaccessibility.

Site-specific conceptual models can be informed by these conclusions to manage bromacil and tebuthiuron soil impacts in-situ with activated carbon. Managing sites in this manner can reduce risk, meet regulatory requirements, and protect soil health. The next step is validation of the method for commercial availability, like what is used for barium in Alberta.

5.0 FIELD SCREENING TECHNOLOGIES FOR BROMACIL AND TEBUTHIURON

5.1 Report Summaries

This project resulted in two reports.

5.1.1 Literature Review

French, K., E. Cowan, E. Terpstra, J. Liu, Y. Li and F. He, 2021. Field Screening Technologies for Bromacil and Tebuthiuron – Literature Review. Report SSP-5A prepared by Vertex Environmental Inc. and University of Waterloo for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 28 pp. plus Appendices.

This project involved a literature review and preliminary testing on available technologies that may have the potential to be used for field screening of soil and/or groundwater samples for the presence of bromacil and tebuthiuron at sites in Alberta and elsewhere.

Based on the results of the literature review and interviews completed in relation to the potential application of existing field screening technologies for use in detecting bromacil and/or tebuthiuron in soil and groundwater at sites in Alberta, the following seven technologies showed promise:

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
- Near infrared reflectance spectroscopy (NIRS)
- X- ray fluorescence (XRF)
- Raman spectroscopy
- Laser-induced breakdown spectroscopy (LIBS)
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)

The portable gas chromatography/photoionization detector (GC/PID) technology was not promising and was eliminated from future consideration.

It is important to also note that since these seven (7) technologies are all applicable for measuring contaminants in soil and groundwater samples, it is possible that a sample preparation stage comprising extraction and concentration steps, would improve the accuracy of the detections and lower the detection limits. Such work could be completed as part of Phase 2 “optimization and validation” of the technology or technologies.

InnoTech Alberta also expressed specific interest in two biosensor technologies that have shown promise in the detection of bromacil to date: single-stranded DNA molecular recognition element (ssDNA MRE) and enzyme-linked immunosorbent assays (ELISA). Based on the results of the review, UW concluded that the ssDNA aptamer reported did not show promise in being able to be developed into a viable, field deployable, biosensor; however, the aptamer technology should still be promising provided that high quality aptamers can be obtained.

On the other hand, the ELISA technology is believed to be promising for bromacil based on the published antibody.

5.1.2 Preliminary Testing of Existing Field Screening Technologies – Phase 1 Results

French, K., E. Cowan and A. Neufeld, 2021. Preliminary Testing of Existing Field Screening Technologies for Bromacil and Tebuthiuron – Phase 1 Results. Report SSP-5B prepared by Vertex Environmental Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 33 pp. plus Appendices.

Vertex Environmental Inc. (Vertex) completed a literature review and preliminary testing on available technologies that may have the potential to be used for field screening of soil and/or groundwater samples for the presence of bromacil and tebuthiuron at sites in Alberta and elsewhere.

Results of the Phase 1 Testing (proof-of-concept) of the seven selected technologies are summarized below. Only the Raman spectroscopy method showed enough promise to be recommended for subsequent Phase 2 testing (i.e., optimization and refinement).

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
  - Overall, UVOST® was successful in detecting bromacil-based Alligare 80® at concentrations at and above approximately 1,000 mg/L in spiked water samples. Also, UVOST® was successful detecting tebuthiuron-based Spike 80® at concentrations at and above approximately 100 mg/L in spiked water samples. UVOST® was not reliable at detecting any concentrations of bromacil-based Hyvar XL® in spiked water samples.
  - Based on the results of the Phase 1 testing, the UVOST® system is not recommended to advance to Phase 2 testing. The detection limits seen in the Phase 1 testing are much higher than target detection limits, and it is considered unlikely that Phase 2 testing could optimize and refine testing protocols for soil sterilant containing samples prior to analysis by the UVOST® system to the point that several orders of magnitude of reductions in detection limits can be achieved.
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
  - Overall, the TarGOST® system was not successful at detecting any concentrations of soil sterilant in spiked soil samples. As such, at this time, the TarGOST® is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.
- Near infrared reflectance spectroscopy (NIRS)
  - Overall, the NIRS system was not successful at detecting unique responses of soil sterilant in spiked soil samples. As such, at this time, the NIRS is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.
- X-ray fluorescence (XRF)
  - Overall, the Niton® XL5 XRF system was successful in detecting bromacil-based Alligare 80® and Hyvar XL® at concentrations at and above approximately 100 mg/kg in spiked soil samples. The Niton® XL5 XRF system was also successful in detecting tebuthiuron-based Spike 80® at concentrations above approximately 1,000 mg/kg.
  - Detection limits seen in the Phase 1 testing are much higher than targeted field detection limits, and it is considered unlikely that Phase 2 testing could optimize and refine testing protocols for sterilant containing samples prior to analysis by XRF to the point that several

orders of magnitude of reductions in detection limits can be achieved. As such, XRF is not recommended to advance to Phase 2 testing.

- Raman spectroscopy
  - Overall, MISA Raman system was successful in detecting unique spectra of bromacil-based Hyvar XL® at concentrations at approximately 100 mg/L in aqueous solutions, with no preliminary extraction, and down to approximately 10 mg/L with chloroform extraction. Bromacil-based Alligare 80® and tebuthiuron-based Spike 80® were also detected in aqueous solution successfully by MISA analysis, with unique spectra acquired for each.
  - Based on the results of the Phase 1 literature review and Phase 1 testing, the MISA Raman system is recommended to advance to Phase 2 testing. While detection limits seen in Phase 1 testing are still higher than target detection limits, Phase 2 testing will look to optimize and refine testing protocols for soil sterilant containing samples prior to analysis by the MISA system. This technology is potentially applicable for detecting bromacil and tebuthiuron in soil and water samples.
- Laser-induced breakdown spectroscopy (LIBS)
  - Overall, the Hitachi Vulcan LIBS Analyzer system was not successful at detecting any concentrations of soil sterilant in spiked soil samples. As such, at this time, the LIBS is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)
  - During the Literature Review, Vertex understood that it was possible that a field-ready GC/TID device that would be capable of analyzing Phase 1 test samples could be made available. After further discussions with SRI Instruments, the supplier of Gas Chromatographs capable of enabling a GC/TID system for soil sterilant analysis, it was determined that a field-ready GC/TID was not able to be developed at this time.

Raman spectroscopy showed enough promise to be recommended for subsequent Phase 2 testing (i.e., optimization and refinement).

The objective of the Phase 2 testing would be to attempt to validate, refine and optimize the technology. Such testing could include, but may not necessarily be limited to the following tasks:

- The analysis of real-world samples of Alberta soil and groundwater contaminated with different concentrations of bromacil and tebuthiuron, if possible. Ideally, two soil types (coarse-grained and fine-grained), two groundwater or surface water sources, and at least three different concentrations of bromacil and tebuthiuron for each soil and groundwater type would be tested.
- Attempts should be made to identify the source(s) of any identified interference effects that can result in limited application for certain sites.
- Additional dilutions or diluted spiked samples of soil and groundwater should also be tested to quantify the likely lowest reliable detection limits in soil and groundwater for the technologies.
- This stage of the testing should also attempt to improve detection limits using methanol extraction (and possibly concentration) prior to testing.

- Lastly, for technologies that are demonstrated to be successful, formal protocols for their application in field screening of soil and/or groundwater samples for bromacil and/or tebuthiuron, as appropriate, should be developed (i.e., commercial implementation the technology).

5.2 Project Reports

The Reports are available in Appendix A3

Appendix A3-1: Literature Review

Appendix A3-2: Preliminary Testing of Existing Field Screening Technologies – Phase 1 Results

6.0 STERILANT-SPECIFIC MODEL INPUT DATA AND BROMACIL MOBILITY IN ALBERTA

6.1 Report Summaries

This project produced three reports.

6.1.1 Sensitivity Analysis

Marquez, G., A. Houston and T. Todoruk, 2020. Sensitivity Analysis of the Domenico and Robbins Groundwater Transport Model. Report SSP-6/8A prepared by Advisian for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 21 pp. plus Appendices.

The objective of the Project is to refine input parameters related to contaminant fate, mobility, and degradation that more realistically reflect Alberta-specific field conditions, are protective of receptors at Alberta sites, can be used to inform Tier 1 Guidelines modification, are available to site managers for Tier 2 calculations when pursuing site closure, and are acceptable to regulators.

The sensitivity analysis of the Domenico and Robbins groundwater transport model (Domenico model) used to develop Tier 1 Guidelines and Tier 2 Guidelines is the first gate, Task #1, of the Project and will be used to inform subsequent stages of the Project. The evaluation of the model sensitivity to relevant physico-chemical properties of bromacil and tebuthiuron, soil properties, geometric parameters, and flow parameters was completed to understand which parameters are sensitive in the Tier 2 Guidelines risk assessment model, and significantly influence and have meaningful impacts on guideline outcomes as defined below:

- Advisian has defined parameters that significantly influence the Tier 1 Guidelines to be parameters that result in >10-times change in the resultant soil and/or groundwater guideline. Moderate influence is defined as >5 to 10-times the guideline, and limited influence is defined as from >1 to 5-times the guideline.
- Advisian considers work that has a meaningful impact on the management of sterilant contaminated sites as work that will result in more sustainable Tier 1 Guidelines and Tier 2 Guidelines in Alberta. This would include work that results in an increase in Tier 1 Soil Guidelines protective of irrigation watering to levels that are, at minimum, above laboratory detection limits.

Sterilant half-life, water–organic carbon partition coefficient (Koc), fraction of soil organic carbon (foc), soil bulk density, and infiltration rate were manipulated in the current sensitivity analysis using the Domenico model and ranges compiled from literature or from knowledge of soils in Alberta. An additive combination scenario was also applied to approximate an increase in contaminant degradation not addressed by the Alberta Tier 1 Guidelines with an engineering scenario which limits further migration. Alberta Environment and Parks has considered that the parameters Koc and possibly half-life are directly related to Tier 1 Guideline calculations, while bulk density, organic matter content and possibly half-life could be adjusted when developing Tier 2 guidelines.

The sensitivity analysis identified the following:

- The Domenico model has higher sensitivity to half-life, foc, and infiltration rate than other parameters, especially at lower values. The sensitivity thresholds of half-life and infiltration rate are directly related to the modelled geometric and flow parameters that could vary across sites.
- The Domenico model has less sensitivity to Koc, with potential dilution increasing linearly as values increase.

- The model did not show high sensitivity to soil bulk density. However, further investigation into the relationship between site soil bulk density, porosity, and moisture content may result in a different degree of sensitivity.
- Overall, investigating site-specific or regional values for the above parameters would improve the understanding of potential transport of sterilants in the subsurface of Alberta sites and could be used to refine model input parameters.
- Soil properties, geometric parameters and flow parameters did have a meaningful impact on outcomes for tebuthiuron soil guidelines protective of irrigation water when varied independently, particularly foc (coarse- and fine-grained soil) and infiltration rate (coarse-grained soil).
- The additive combination scenario had the greatest impact on the soil irrigation guidelines estimated.

Further effects on the significance of outcomes will be associated with local site conditions such as source size, depth to groundwater and lateral distance to receptors.

6.1.2 Laboratory Experiment Design

Houston, A., T. Todoruk, B. Loescher and R. Prosser, 2020. Laboratory Experimental Design to Characterize Bromacil and Tebuthiuron Half-life and Adsorption in Alberta Soils. Report SSP-6/8B prepared by Advisian, Bureau Veritas Labs and University of Guelph for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 64 pp.

As part of InnoTech's efforts to advance the science of sterilant fate and transport in Alberta, the scope of work for the project focuses on: (1) developing refined model input parameters for the Alberta Tier 2 risk assessment models and (2) addressing some of the conservative assumptions inherent in the Alberta Tier 1 Guidelines under field conditions.

The sensitivity analysis of the Domenico and Robbins groundwater transport model (Domenico model) used to develop Tier 1 and Tier 2 guidelines identified that sterilant half-life, water–organic carbon partition coefficient (Koc), fraction of soil organic carbon (foc), soil bulk density, and infiltration rate were controlling parameters for the groundwater model. The sensitivity analysis defined parameters that significantly influence the Tier 1 Guidelines to be the parameters that result in more than a 10-times change in the resultant soil and/or groundwater guideline. Advisian considered work that has a meaningful impact on the management of sterilant contaminated sites will result in more sustainable Tier 1 Guidelines and Tier 2 Guidelines in Alberta. This would include work that could result in an increase in Tier 1 Soil Guidelines protective of irrigation watering to levels that are, at minimum, above laboratory detection limits.

Ultimately, it is expected that Tier 1 Guidelines and Tier 2 Guidelines will become less conservative with implementation of half-life and potentially with other modified input parameters. Furthermore, as these parameters would be protective at Alberta sites and acceptable to regulators, it creates more opportunities for site managers to develop Tier 2 Guidelines as a path to site closure. This effort is expected to reduce remediation and management costs at sites across Alberta. Bromacil and tebuthiuron in soil and groundwater can be widespread at relatively low concentrations, so a guideline increase could have a significant effect on the volumes of soil or groundwater requiring remediation.

The design of laboratory experiments and information matrix design is the fifth deliverable of the Project. The experiments are designed to characterize bromacil and tebuthiuron half-life and adsorption (i.e., Koc) in Alberta soils with the intention of application to Alberta Tier 1 Guidelines and Tier 2 Guidelines. The information matrix design is the preliminary framework for collating and comparing

laboratory-generated data with Alberta field data and is expected to be refined based on the results of Tasks 2 through 5.

The experiments are designed to characterize bromacil and tebuthiuron half-life and adsorption (i.e., Koc) in Alberta soils with the intention of application to Alberta Tier 1 Guidelines and Tier 2 Guidelines. The information matrix design is the preliminary framework for collating and comparing laboratory-generated data with Alberta field data. The proposed laboratory research focusses on two input parameters that can be refined in a laboratory setting and includes half-life estimation and measurement of Koc with organic carbon content (i.e., development of adsorption isotherms) for each sterilant. There are three experimental components to the proposed research design:

1. Half-life estimation using uncontaminated Alberta soil in microcosms in saturated conditions, spiked with bromacil and tebuthiuron, and measured up to 73 weeks.
2. Metabolite characterization and half-life estimation in microcosms using historically-contaminated soil from Alberta sites.
3. Development of adsorption isotherms based on the organic carbon content of uncontaminated Alberta subsoils. The measured parameters are water-organic carbon partition coefficient (Koc) and sorption distribution coefficient (Kd).

A review and summary of 40 active sites that are impacted by bromacil, or bromacil and tebuthiuron, was completed (impact is defined as a measurable concentration). No sites were identified where tebuthiuron was the only sterilant present although a member of the Soil Sterilants Program may yet have one available. Sites from this list will be used to collect weathered impacted soil and unimpacted soil for spiking experiments and also to gather information for the field measured component of the project.

The information matrix design is the preliminary framework for collating and comparing laboratory-generated data with Alberta field data and is a primary outcome for the project.

6.1.3 Metabolites Literature Review

Marquez, G., A. Houston and T. Todoruk, 2020. Literature Review to Identify Metabolites of Bromacil and Tebuthiuron. Report SSP-6/8C prepared by Advisian, Worley Group for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 18 pp.

The objective of the Project is to refine input parameters related to contaminant fate, mobility, and degradation that more realistically reflect Alberta-specific field conditions, are protective of receptors at Alberta sites, can be used to inform Alberta Tier 1 Guideline modification, are available to site managers for Tier 2 Guideline calculations when pursuing site closure, and are acceptable to regulators.

The current literature review has been completed to identify degradation processes and metabolites of bromacil and tebuthiuron in soil to support Task 4 of Project #6. Task 4 will investigate degradation rates (and presence of metabolites) of bromacil and tebuthiuron under field conditions. Bureau Veritas Laboratories will complete open scans on soil collected from the field containing weathered tebuthiuron or bromacil. The literature review focuses on supporting interpretation of the laboratory open scan results and reviews information on degradation pathways and specific metabolic products of bromacil and tebuthiuron.

Generally, the degradation of both these sterilants has been studied since the 1980s although not all processes are well understood. No chemical-specific information was found on the individual metabolites. In summary, nine bromacil degradation products were identified from laboratory studies. Eight main tebuthiuron degradation products were identified from laboratory studies. Degradation and

metabolism processes included aerobic and anaerobic biodegradation in soil and water, hydrolysis, photodegradation in soil and water, mammalian metabolism, and plant metabolism. In general, bromacil and tebuthiuron were characterized as having low adsorption; low volatility; low susceptibility to decomposition by sunlight in soil; low susceptibility to chemical degradation; and low susceptibility to microbial decomposition. Photodegradation in waters; however, has been reported as a potential target for remediation efforts as reported half-lives for bromacil and tebuthiuron were 5 to 7 days and 103 days, respectively.

6.2 Project Reports

The Reports are available in Appendix A4

Appendix A4-1: Sensitivity Analysis

Appendix A4-2: Laboratory Experiment Design

Appendix A4-3: Literature Review to Identify Metabolites of Bromacil and Tebuthiuron

7.0 DETERMINATION OF SOIL – WATER AND ORGANIC CARBON – WATER PARTITIONING COEFFICIENTS FOR BROMACIL AND TEBUTHIURON

7.1 Report Summaries

Three reports were prepared for this project.

7.1.1 Irrigation Water and Freshwater Aquatic Life Guidelines

Litalien, A., Kartz, C., Mitchell, I., Millennium EMS Solutions Ltd. 2020. Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life. Report SSP-7A. Prepared by Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 66 pp.

The Tier 1 soil guidelines for bromacil and tebuthiuron were developed using a highly conservative approach. The conservative approach has resulted in Tier 1 soil guidelines for the Freshwater Aquatic Life (FAL) and Irrigation Watering (IW) pathways for these two soil sterilants at or below laboratory detection limits, which present a challenge to site reclamation.

A literature review was conducted to determine the most recent and defensible "chemical-specific" parameters of particular relevance for bromacil and tebuthiuron Tier 1 guideline development and assess how these parameters may influence Tier 1 soil quality guidelines for the IW and FAL pathways. In addition to "chemical-specific parameters", ecotoxicological data was also reviewed to assess the surface water quality guidelines from which the soil quality guidelines are derived.

In general, most chemical specific literature data available pre-dated the development of the current Tier 1 guidelines. Further, most studies were conducted either under standard lab conditions or in tropical or semi-tropical climates. This suggests that there is a need for more studies relevant to Albertan conditions. Despite this gap, ecotoxicological findings aligned with the current Alberta surface water quality guidelines.

The organic carbon partition coefficient (Koc) for bromacil listed in the Tier 1 guidelines was within the range of commonly cited values in the literature reviewed. Conversely, the Koc value used for tebuthiuron Tier 1 guideline development was much lower than commonly reported in the literature. While half-lives were not used for either soil sterilant in their Alberta Tier 1 guideline development, most literature sources reported half lives of 0.5 to 0.75 years and 1 to 2 years for bromacil and tebuthiuron, respectively.

With the inclusion of scientifically defensible and appropriate "chemical-specific" parameters, particularly half-life, the potential for more achievable soil quality remedial guidelines for these soil sterilants, which maintain protection of applicable receptors, is possible. Further field and lab studies with an Alberta context would support the defensibility of the incorporation of adjusted "chemical-specific" parameters into Tier 1 guideline development.

7.1.2 Risk Assessment Models

Litalien, A., J. Hueser, M. Tindal, C. Kartz and I. Mitchell, 2020. Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life: Review of Alternative Models. Report SSP-7B prepared by Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 26 pp. plus Appendices.

The historic use of soil sterilants at many oil and gas sites in Alberta has led to challenges for remediation and site closure. Bromacil and tebuthiuron are mobile and persistent sterilants that are toxic to terrestrial and aquatic plants at low concentrations. These factors have contributed to very low

Tier 1 guidelines for the irrigation water and freshwater aquatic life pathways. Several of the guidelines fall below the typical detection limits of the sterilants and frequently necessitate the use of a Tier 2 or a site-specific approach.

The model currently used by Alberta Environment and Parks considers partitioning of solutes, unsaturated transport, groundwater mixing and lateral transport. At Tier 2 some site-specific factors can be included but are still limited which may result in overly conservative guidelines. The second task of the SSP Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life Project was to evaluate alternative risk models that could be used to derive soil and groundwater guidelines for bromacil and tebuthiuron that would be both protective of IW and FAL pathways.

A literature review was conducted to identify scientifically robust models that could be used to assess the transport of bromacil and tebuthiuron through variably saturated media. Thirty models were reviewed and ranked based on their defensibility, applicability, availability, ease of use, and inclusion of novel features relative to the current Tier 2 model. Three models were selected for a detailed mechanistic review and model analysis based on standard Tier 1 input values and parameters derived from the literature when necessary.

BIOSCREEN is a US EPA model that could be substituted for the current saturated transport component of the Tier 2 model. It follows similar principles to the Tier 2 model but also considers source depletion and as a result, can produce less conservative soil and groundwater guidelines for the FAL pathway. PWC is also a US EPA transport model designed specifically for agrochemicals and can be used to evaluate transport to groundwater. The results of the model analysis showed that the PWC model would produce guidelines like the current Tier 2 model however PWC is more challenging to use than the Tier 2 model and requires many input parameters that may not be readily available for all sites. However, its more detailed approach could be of benefit on a site-specific basis. PEARL is a European agrochemical transport model that can model transport through both the unsaturated zone and the flux of solutes to surface water bodies. The model proved to be challenging to employ and required values for several parameters that were not readily available but did produce a host of outputs that could be of interest on a site-specific basis. PEARL produced significantly more conservative IW guidelines as compared to the Tier 2 model, but model results suggested that lateral transport would be negligible.

None of the models reviewed could effectively replace all elements of the Tier 2 model however they could be useful supplements.

7.1.3 Soil-Water and Organic Carbon-Water Partitioning Coefficients

Bachmann, V. and M. Tindal, 2023. Determination of Soil – Water and Organic Carbon – Water Partitioning Coefficients for Bromacil and Tebuthiuron. Report SSP-7C Prepared by InnoTech Alberta and Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 15 pp.

A related project being conducted by Millennium EMS Solutions Ltd. (MEMS) will use the data generated through the experiments as model input parameters for establishing Alberta Tier 1 guidelines for bromacil and tebuthiuron for the protection of irrigation water and freshwater aquatic life. The chemical properties and interactions with soil are poorly understood for bromacil and tebuthiuron. To inform the model input parameters, more understanding of these soil interactions is required.

The objectives of this Soil Sterilants Program Project were to establish accurate adsorption coefficient (Kd and Koc) values for bromacil and tebuthiuron in soils with a range of organic carbon matter and to determine whether additional testing would be beneficial in further refining input parameters. The project used the OECD Guideline for Testing of Chemicals: Adsorption–Desorption Using a Batch Equilibrium Method. Three soils were selected from InnoTech Alberta's available stock of test soils that had a range of organic carbon.

The soils used had total organic carbon (TOC) contents of 4.96%, 1.14%, and 0.05% and had textures of silty loam, sandy loam, and sand, respectively. Tebuthiuron showed higher concentrations in soil than bromacil after the adsorption test. With both sterilants, the amount of sterilant in soil was higher with higher TOC and finer soil texture. Kd values were consistent with sterilants concentrations in the soil; finer textured and higher TOC soils had higher Kd than coarse textured and low TOC soils. On average, Kd values were 3.31 mL/g for fine soil, 1.63 mL/g for sandy loam, and 0.45 mL/g for coarse soil. The Koc values were 66.8 mL/g for fine soil, 142.8 mL/g for sandy loam, and 907.3 mL/g for coarse soil.

The chemical interactions with soil and groundwater are poorly understood for bromacil and tebuthiuron. Work to better understand these relationships are out of the scope of this project. The results produced by this project provide sufficient data to be used as model input parameters for other projects within the Soil Sterilants Program.

7.2 Project Reports

The Reports are available in Appendix A5

Appendix A5-1: Irrigation Water and Freshwater Aquatic Life Guidelines

Appendix A5-2: Risk Assessment Models

Appendix A5-3: Soil – Water and Organic Carbon – Water Partitioning Coefficients

8.0 NATIVE PLANT SPECIES TOXICITY EVALUATION

8.1 Report Summaries

Two reports were prepared for this project.

8.1.1 Sterilant Toxicity to Native Plants

Thacker, S., 2021. Toxicity of Bromacil and Tebuthiuron to Alberta Native Species. Report SSP-9A prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 49 pp.

Cost-effective strategies for managing sterilant-impacted sites are needed, but knowledge gaps exist regarding effective management practices for such sites. There is a need to better understand the sensitivity of Alberta native plant species to soil sterilants. Ecological direct contact guidelines for soil sterilants in the current Alberta Tier 1 Guidelines have largely been developed using agronomic species. Agronomic species may differ in their sensitivity to soil sterilants compared to native species. An opportunity exists to develop data for remedial endpoints in natural areas of the province where native species would be the primary receptors in surface soil. The goal of this project was to evaluate the toxicity of two common soil sterilants, bromacil and tebuthiuron, to typical Alberta native vegetation species. Information from this project is intended to be used for the development of revised direct soil eco-contact guidelines for non-agricultural areas of the province.

Definitive toxicity tests were conducted using a modified Environment Canada test method at InnoTech Alberta's greenhouse facility in Vegreville. Prior to definitive testing, a range-finding test was conducted to refine the optimal target concentration for definitive testing. Toxicity tests were conducted with various native grass species (*Agropyron dasystachyum, Bouteloua gracilis, Festuca hallii, Koeleria macrantha, Nassella viridula,* and *Pascopyrum smithii*) exposed to either bromacil or tebuthiuron in soil. Most of the seed used in the study was sourced locally, with the exception of *B. gracilis* and *K. macrantha*. The toxicity tests ran for six weeks. At the end of the test, data for biological endpoints were collected, including emergence, root and shoot length, and root and shoot biomass.

Results from the toxicity tests were used to generate regression models and inhibition concentration (IC_p) values for each endpoint from each species/sterilant test. The IC_p values indicated that while the data tended to be variable within a species and endpoint, species-specific effects were observed. For example, *B. gracilis* was more tolerant to the sterilants than other species. Generally, the species tested tended to be more sensitive to bromacil than tebuthiuron. There was not a clear difference in toxicity between root and shoots parameters. The IC_p values for *B. gracilis* in the current study were compared to values obtained from Stantec Consulting Ltd. 2008 & 2012. Differences in toxicity were observed; these differences might be due to the growth period, type of sterilant products used, and/or soil properties.

Millennium EMS Solutions Ltd. was retained to develop species sensitivity distributions using IC_ps and to propose revised soil quality guidelines. Potential revised guidelines were generated based on native plants data from the current study, plant data (including agronomic species) from historical studies, and invertebrate data from historical studies. The revised guidelines were more stringent than the current Alberta Tier 1 guidelines for ecological direct contact surface soil quality guidelines for fine-grained soil, and were a function of new data indicating that the native species tested in the current study appeared more sensitive to bromacil and tebuthiuron than species that have been historically studied. Overall, outcomes from this project constitute a valuable resource for decision makers regarding the management of sterilant-impacted sites in Alberta.

8.1.2 Ecological Contact Guideline Development

Litalien, A. and M. Tindal, 2021. Ecological Contact Guideline Development for Bromacil and Tebuthiuron. Report SSP-9B prepared by Millennium EMS Solutions for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 16 pp. plus Appendices.

Species sensitivity distributions for bromacil and tebuthiuron were developed based on the 2006 CCME protocol for development of soil quality guidelines for the protection of the ecological direct contact pathway. Datasets included the ecotoxicological responses of invertebrates and native and/or agronomic plant species in fine-grained soils. The datasets were based on both recent data collected as part of the Soil Sterilants Program as well as historical data used in the development of Tier 1 Guidelines for bromacil and tebuthiuron.

Revised soil quality guidelines for the ecological direct contact pathway are as follows:

- Bromacil – Natural/Residential/Agricultural: 0.028 mg/kg;
- Bromacil – Commercial/Industrial: 0.21 mg/kg;
- Tebuthiuron – Natural/Residential/Agricultural: 0.018 mg/kg; and
- Tebuthiuron – Commercial/Industrial: 0.15 mg/kg tebuthiuron.

The updated guidelines are more conservative than previous guidelines based on the incorporation of new data developed as part of the Soil Sterilants Program. The native species examined appear to be more sensitive to bromacil and tebuthiuron than those species examined historically.

8.2 Project Reports

The Reports are available in Appendix A6

Appendix A6-1: Sterilant Toxicity to Native Plants

Appendix A6-2: Ecological Contact Guideline Development

9.0 INVESTIGATION OF LONG-TERM EFFECTS OF ACTIVATED CARBON

9.1 Report Summary

Thacker, S., 2022. Investigation of the Long-Term Effectiveness of Activated Carbon in Immobilization of Bromacil and Tebuthiuron. Report SSP-10 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 50 pp.

There is a need for cost-effective strategies to manage sterilant-impacted sites and achieve regulatory site closure; however, knowledge gaps exist regarding effective management practices for sites impacted by residual soil sterilants. Activated carbon (AC) has long been considered one of the most effective in-situ remediation technologies for soil sterilants, adsorbing sterilants to immobilize them, thus preventing uptake by plants or leaching through the soil. However, there is hesitation from a regulatory perspective to accept immobilization as a long-term solution for managing sterilant-impacted soils due to uncertainty regarding the longevity of immobilization. Both industry and government are seeking confirmation that AC can effectively be considered a permanent remediation technology whereby a sterilant-impacted site treated with AC could be considered for regulatory closure (i.e., receive a reclamation certificate).

This project was completed in two phases to meet the overall objective of assessing the long-term immobilization of soil sterilants by AC, to validate AC's applicability as a remediation technology. The first phase included a literature review to summarize information on the stability and potential degradation of AC over time; factors that could influence desorption from AC; and methods of conducting artificial weathering experiments.

The second part of Phase 1 included desorption experiments via modified Synthetic Precipitation Leaching Procedure (SPLP) to assess the percentage of each sterilant retained by AC. Experiments included 'low' and 'high' bromacil and tebuthiuron concentrations in coarse- and fine-grained soils. Results from Phase 1 were used to inform Phase 2, an artificial weathering experiment using multiple freeze-thaw cycles of a sterilant-spiked topsoil to assess the longevity of sterilant immobilization by AC compared with soil that was not amended with AC.

The SPLP method was used to assess leaching after weathering in Phase 2; additionally, total and phytoaccessible (i.e., the fraction available to plants) sterilant concentrations were measured pre- and post-weathering. Use of the SPLP and phytoaccessible methods was required to assess the fraction of labile sterilant (i.e., not sorbed to activated carbon), as the total concentration would represent both the labile and sorbed fractions.

Results of Phase 1 showed that AC was effective at immobilizing soil sterilants when applied at a rate of 400:1 (AC:sterilant, weight basis) with significantly lower sterilant leaching in soil amended with AC compared non-amended soil. In Phase 1, desorption, assessed via SPLP, ranged from 0 to 14% in AC-amended soil, with higher desorption in coarse-grained soil compared to fine-grained soil. In Phase 2 (topsoil), desorption ranged from 1 to 3% after weathering of AC-amended soil. AC amendment significantly lowered phytoaccessible sterilant concentrations. Based on results following artificial weathering, it is interpreted that AC effectively sorbs the majority of bromacil and tebuthiuron in the long-term.

Long-term sterilant sorption to AC may be complicated by many factors, including weathering and climactic conditions, environmental conditions, sterilant properties (i.e., propensity to solubilize), competition between the sterilant and other compounds in soil for sorption sites, and the types of bonds formed between the sterilant and AC. The data from Phases 1 and 2 indicate that majority of the

bromacil and tebuthiuron remained sorbed to AC after physical weathering. In many cases AC amendment lowered phytoaccessible sterilant concentrations below limits outlined in the Alberta Tier 1 Guidelines, indicating that the phytoaccessible laboratory method is a valuable risk assessment tool. Including AC as a remediation technology in meso- or field-scale demonstrations within the Soil Sterilants Program should be considered, along with the development of best management practices for the use of AC as an immobilization technique.

9.2 Project Report

The Report is available in Appendix A7

9.2.1 Project Fact Sheet

Soil Sterilants Program Project #10: Investigation of the Long-Term Effectiveness of Activated Carbon in Immobilization of Bromacil and Tebuthiuron

Challenge:

- Uncertainty exists regarding the longevity of sterilant immobilization by activated carbon (AC)
- There are numerous factors that may influence desorption and the potential for sterilant leaching from soil amended with AC

Research Questions:

1) What is the percent effectiveness of AC in immobilizing soil sterilants when applied to soil at ratios established in previous research (i.e., 400:1 w/w)?
2) If proven sufficiently effective in immobilizing soil sterilants, under what conditions could AC release soil sterilants, thus making them available to vegetation and/or leaching through the soil profile?

Project Phases:

1. Desorption Assessment
- Modified synthetic precipitation leaching procedure (SPLP) [non-acidified] desorption experiments with coarse- and fine-grained soils

2. Literature Review
- Could AC degrade over time?
- What factors potentially influence desorption of sterilants from AC?
- How to simulate in-soil conditions over time (artificial weathering)?

3. Artificial Weathering
- 0, 10 and 20 freeze-thaw cycles
- Assess total vs. phytoaccessible (i.e., labile) fractions

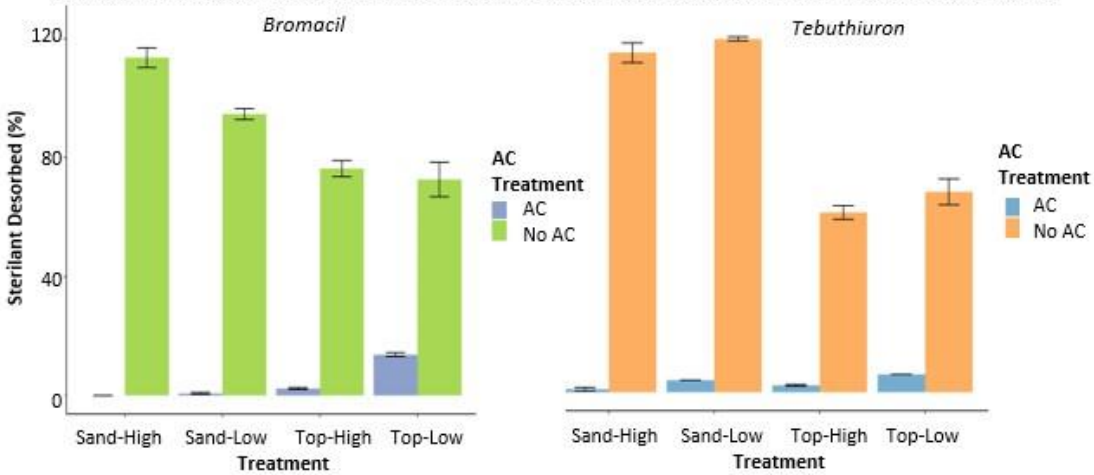
1. Desorption Assessment

Methods

- Topsoil or silica sand spiked with bromacil or tebuthiuron to high and low concentrations (target 2.4 or 0.8 mg/kg, respectively)
- AC Treatment: (1) AC at 400:1 (weight basis, AC:sterilant) or (2) no AC
- Quantify sterilant desorption from soil and AC after modified SPLP

Results

- AC was effective at immobilizing soil sterilants when applied at a rate of 400:1, with significantly lower sterilant leaching in soil amended with AC compared non-amended soil.
- Desorption ranged from 0 to 14% in AC-amended soil, with higher desorption in coarse- vs. fine-grained soil.



Desorption (%) of bromacil (left) and tebuthiuron (right) in topsoil and silica sand, either amended with activated carbon (AC), or non-amended. Bars represent means and error bars indicate the standard error (n=3). Desorption data was determined after 18-hour shaking in 0.01M $CaCl_2$. Note that in treatment names, Sand = silica sand and Top = topsoil. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

Soil Sterilants Program Project #10: Investigation of the Long-Term Effectiveness of Activated Carbon in Immobilization of Bromacil and Tebuthiuron

2. Literature Review

- Long-term sterilant sorption to AC may be complicated by many factors, including: (a) weathering and climactic conditions, (b) environmental conditions, (c) sterilant properties (i.e., propensity to solubilize), (d) competition between the sterilant and other compounds in soil for sorption sites, and (e) the types of bonds formed between the sterilant and AC.
- Evaluated artificial weathering approach to assess longevity, based on findings and regulatory consultation; chose to move forward with freeze/thaw methodology

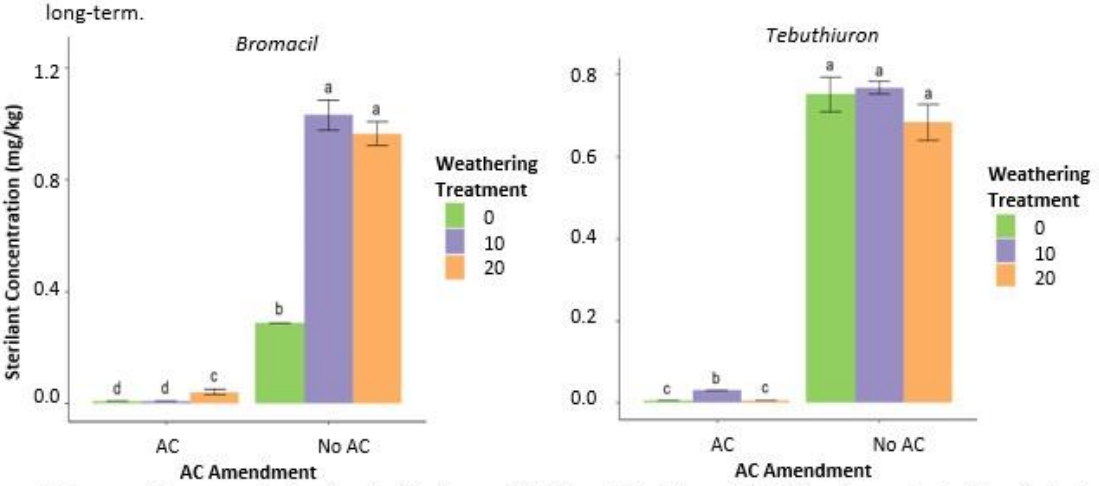
3. Artificial Weathering

Methods

- Topsoil spiked with bromacil or tebuthiuron to a single concentrations (1.95 or 1.20 mg/kg, respectively)
- AC Treatment: (1) AC at 400:1 (weight basis, AC:sterilant) or (2) no AC
- Quantify phytoaccessible sterilant fraction after weathering (using SSP#4 method); assess desorption before and post-weathering via SPLP

Results

- Desorption ranged from 1-3% after weathering of AC-amended soil.
- AC amendment significantly lowered phytoaccessible sterilant concentrations. Based on results following artificial weathering, it is interpreted that AC effectively sorbs the majority of bromacil and tebuthiuron in the long-term.



Phytoaccessible concentration (mg/kg) for bromacil (left) and tebuthiuron (right) in soil amended with activated carbon (AC) or not amended (no AC). The two AC amendment treatments were exposed to three different weathering treatments: no weathering (0), 10 freeze-thaw cycles (10), or 20 freeze-thaw cycles (20). Bars are means with error bars representing the standard error (n=3). Average values are provided above each bar. Different lowercase letters indicate significant differences among the treatments.

Conclusions:

- Data from this project indicate that majority of the bromacil and tebuthiuron remained sorbed to AC after physical weathering.
- In many cases AC amendment lowered phytoaccessible sterilant concentrations below limits outlined in the Alberta Tier 1 Soil Remediation Guidelines; it is recommended that the phytoaccessible laboratory method be adopted for use with AC-amended soils.
- Including AC as a remediation technology in meso- or field-scale demonstrations within the Soil Sterilants Program should be considered, along with the development of best management practices for the use of AC as an immobilization technique for the management of residual soil sterilants.

10.0 BENCH-SCALE TESTING OF CHEMICAL AMENDMENTS TO REMEDIATE BROMACIL AND TEBUTHIURON IN SOIL AND WATER

10.1 Report Summaries

This project produced three reports.

10.1.1 DARAMEND

Bendouz, M. and J. Paré, 2022. Bench-scale Testing of Chemical Amendments to Remediate Bromacil and Tebuthiuron in Soil. Report SSP-11A. Prepared for InnoTech Alberta, Soil Sterilants Program. 45 pp.

Bench-scale testing was conducted to evaluate chemical oxidation and reduction amendments in their ability to degrade the targeted contaminants (i.e., bromacil and tebuthiuron) in soil with and without the use of surfactants. Results show that the reductive amendment called DARAMEND was highly effective in the treatment of bromacil in the tested soil samples. Overall treatment product cost was approximately C$55/MT of impacted soil (product only) of soil using a 1 % w/w loading rate. This approach enabled a rapid, cost-effective, and long-lasting treatment.

Interesting contaminant destruction was obtained without tilling the sample after a 30-days contact time. For field deployment, this would mean that a single pass application with proper wetting could help to reach the remedial objective.

The hydrogen peroxide oxidation process using the VTX catalyst and surfactant was a little more expensive than the DARAMEND technology at C$99/MT of impacted soil (product only) for the destruction of 1.0 mg/kg contaminant concentration. For tebuthiuron, the ISCO approach with alkaline activated Klozur® persulfate has been successfully allowing a reduction of 76% of the tebuthiuron mass without adding the surfactant using a low dosage of Klozur® persulfate. This gives a treatment cost of C$5/MT of impacted soil (product only) per 1 mg/kg removal of tebuthiuron (without surfactant) compared to C$17/MT of impacted soil (with the use of surfactant). For groundwater contamination, the fact that the targeted compound is already in the water phase would facilitate its destruction via oxidative pathways.

10.1.2 Electrocoagulation

Saint-Fort, R. and S. Levy, 2022. Proof of Concept of Electrocoagulation Technology to Remediate Water Contaminated with Bromacil and Tebuthiuron. Report SSP-11B prepared by Mount Royal University and InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 7 pp. plus Appendix.

This study aimed to investigate the removal of bromacil and tebuthiuron by electrocoagulation based on two types of electrodes (Fe and Al) using a batch mode approach. The reactor was operated with four electrodes in a bipolar connection, held vertically and parallel. The gap between each electrode was 1.25 cm and each electrode had an effective area of 102 cm^2. The simulated water contained bromacil and tebuthiuron at a concentration of 4 mg/L (4,000 µg/L), respectively. The ionic strength was adjusted with the addition of 20 g of NaCl. The simulated water solution had a pH of 5.92, TDS of 2,850 mg/L, EC of 3.04 mS, and turbidity 0.55 NTU.

Overall, the removal efficiency by the electrocoagulation process for bromacil ranged from 0 to 23.40%, while for tebuthiuron it was from 0 to 16%. Both removal processes involving the Fe electrodes system and Al electrodes system were relatively low. Comparatively, removal of the pesticides was generally higher with the Fe electrodes with the highest value being 23.40% while for the Al electrodes the maximum value was 16%. The low removal from the systems could be attributed to a lack of significant

oxidative destruction and chemical transformation mechanisms under the applied electrocoagulation treatments. It also appears that there was no significant formation of a stable complexation mechanism that could have led to the removal of bromacil and tebuthiuron.

The following recommendations for further testing are made considering the low removal efficiency according to the study findings:

1. *The effectiveness of a four-cell Fe-graphite electrodes system and a four-cell Al-graphite electrodes system, respectively*. Both electrode systems will be configured in a bipolar arrangement. The removal efficiency of each electrode system will be tested using Treatment (T4) (i.e., 30 volts and 90 sec). In both electrode arrangement systems, graphite will be the non-sacrificial electrode. The rationale for this recommendation is the potential synergistic effect of hydroxyl radicals (*OH) and hypochlorous acid (HOCl) generation in the reactor during treatment. This has the potential to result in significant degradation and removal of the hydrophilic pesticides.
2. *The effect of increasing the surface area of the electrodes (cm^2) to volume (L) ratio, (S/V)*. Higher S/V ratio increases the surface area available for electrolytic reactions to occur in the reactor, which in return can have an integral effect on the pesticide removal efficiency.
3. *The effect of varying the inter electrode distance*. As an operational factor, the process efficiency can be improved by varying the distance between the electrodes. At minimum inter electrode distance, the resistance for current flow in the reactor is lowered. In this case, removal efficiency may occur due to higher current reaching the electrodes and lower resistivity in the solution to the electrical current. Optimal distance is highly characteristic of the solution matrix to be treated.
4. *The effect of voltage increase*. An increase in the voltage causes higher current to pass through the reactor. Concurrently, current density (A/m^2), which is current delivered to the electrode (A) divided by the electrode's area (m^2), also goes up. Increase in applied voltage or current density has the effect of increasing the rate of reactions in the reactor. However, voltage increase leads to higher energy consumption; economic considerations may render this approach less attractive.

10.1.3 Trap & Treat® and Zero Valent Iron

French, K., E. Cowan and A. Neufeld, 2023. Bench-scale Treatability Study using Trap & Treat® and Zero Valent Iron for Bromacil and Tebuthiuron in Alberta Soils. Report SSP-11C prepared by Vertex Environmental Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 20 pp. plus lab data.

Vertex Environmental Inc. (Vertex Environmental) was retained by InnoTech Alberta to undertake bench-scale treatability studies evaluating in-situ treatment of bromacil and tebuthiuron using samples of impacted soil from Alberta. Currently, no in-situ destructive technologies are known for bromacil and tebuthiuron and therefore the current study aims to assess the performance, efficiency and degradation rates of newly developed treatment media Trap & Treat® BOS 200+®and Trap & Treat® CAT 100. Micro-scale zero valent iron (ZVI) is also evaluated for the same parameters, with and without pH control. Trap & Treat® BOS 200+®'s treatment approach utilizes bio stimulation and inoculation, Trap & Treat® CAT 100's treatment approach utilizes chemical reduction, bio stimulation and inoculation and ZVI's treatment approach utilizes chemical reduction alone. Trap & Treat® BOS 200+®and Trap & Treat® CAT 100 also contain activated carbon which is designed to trap the contaminants, increasing the contact time between the treatment media and the contaminants to further promote biodegradation and/or chemical reduction. To isolate treatment from adsorption to the activated carbon, the current study compares the full formulations of the treatment media with simulated formulations, where the

components of the treatment media are used in the absence of activated carbon. The impact of surfactant is also investigated.

The methodology included assembling static batch reactors filled with the bromacil or tebuthiuron impacted soils mixed with remedial amendments. The reactors were kept under dark and anoxic conditions for four months. The following test reactors were assembled for each contaminant:

- Test Reactor #1 contained only the contaminated soil with no added reagents or amendments.
- Test Reactor #2 contained 1.2% by weight Trap & Treat® BOS 200+®.
- Test Reactor #3 contained 0.7% by weight Trap & Treat® CAT 100.
- Test Reactor #4 contained the components of Trap & Treat® BOS 200+® at the same weight percentage as test reactor #2 but without any activated carbon component. The mass of each component was equal to that used in the Trap & Treat® BOS 200+® reactor.
- Test Reactor #5 contained the components of Trap & Treat® CAT 100 at the same weight percentage as test reactor #3 but without any activated carbon component and with ZVI substituting for the iron component in the Trap & Treat® CAT 100.
- Test Reactor #6 contained 5% by weight ZVI.
- Test Reactor #7 contained 5% by weight ZVI with 3.5% by weight aluminum sulphate.
- Test Reactor #8 contained 1.2% by weight Trap & Treat® BOS 200+® with 0.2% by weight Tween 80 surfactant.
- Test reactor #9 contained 0.7% by weight Trap & Treat® CAT 100 with 0.2% by weight Tween 80 surfactant.
- Test reactor #10 contained 0.2% by weight Tween 80 surfactant with the components of Trap & Treat® BOS 200+® at the same weight percentage as test reactor #2, but without any activated carbon component. The mass of each component was equal to that used in the Trap & Treat® BOS 200+® reactor.
- Test reactor #11 contained 0.2% by weight Tween 80 surfactant with the components of Trap & Treat® CAT 100 at the same weight percentage as test reactor #3, but without any activated carbon component and with ZVI substituting for the iron component in the Trap & Treat® CAT 100.

During testing, bromacil treatment reactors were monitored for bromacil concentration, pH, Heterotrophic Plate Count (HPC) and bromide concentration at four sampling times: two weeks, one month, two months and four months from test start. During testing, tebuthiuron treatment reactors were monitored for tebuthiuron concentration, pH and HPC at four sampling times: two weeks, one month, two months and four months from test start. The target treatment for both bromacil and tebuthiuron was to reduce measured concentrations in the soil samples to below 0.009 mg/kg.

For bromacil, Trap & Treat® CAT 100, Trap & Treat® BOS 200+ and ZVI were all able to destructively remove bromacil from the soil, dropping concentrations to within the target withing the four-month testing period. The reactor with surfactant added to the simulated Trap & Treat® CAT 100 had the fastest degradation rate for bromacil. However, if treatment is required in the form of a permeable reactive barrier, immobilization via activated carbon and no surfactant is beneficial. Under these requirements, Trap & Treat® BOS 200+® was the best performing media.

For tebuthiuron, only Trap & Treat® BOS 200+® was successful at destructively removing tebuthiuron from the soil at a rate fast enough to reach the target within the 4-month testing period. Surfactant slowed the degradation for both Trap & Treat® reagents.

Based on the bench-scale treatability testing, both bromacil and tebuthiuron are susceptible to adsorption and degradation by Trap & Treat® BOS 200+®. Further mesocosm studies or pilot or field scale trials are recommended to confirm the suitability for treating both soil sterilants using Trap & Treat® BOS 200+®.

10.2 Project Reports

The Reports are available in Appendix A8

Appendix A8-1: DARAMEND

Appendix A8-2: Electrocoagulation Technology

Appendix A8-3: Trap & Treat® and Zero Valent Iron

11.0 EX-SITU FIELD DEMONSTRATION FOR THE REMEDIATION OF BROMACIL IN SOIL

11.1 Report Summaries

This project produced two reports.

11.1.1 Ex-situ Field Demonstration

Bachmann, V. and R.J. Thiessen, 2023. Ex-situ Field Demonstration for the Remediation of Bromacil in Soil. Report SSP-12A prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 23 pp.

Bromacil and tebuthiuron are persistent, non-selective, broad-spectrum soil sterilants used for vegetation control on industrial land. In Alberta, they were introduced in the 1960s and were used on a variety of industrial sites until their use was halted in the 1990s. Decades after ceasing treatment, bromacil and tebuthiuron impacts persist in soil and water at sites in Alberta.

A 12-week, mesoscale experiment at InnoTech Alberta's Vegreville Research Facility focused on bromacil degradation and immobilization in soil obtained from a bromacil-impacted site in Alberta. Based on previous work done by the Soil Sterilants Program (SSP), the following remediation technologies were tested: (1) chemical oxidation with a surfactant using hydrogen peroxide, VTX® catalyst, and Tween®-80 surfactant; (2) adsorption using ChemCarb PAC 800 activated carbon; and (3) chemical and biological reduction using Daramend®. The primary objectives were to evaluate the ability of these technologies to reduce total bromacil concentrations to meet the Alberta Tier 1 soil remediation guideline of 0.009 mg/kg and assess the operational application and safety of the treatment technologies.

Two of the technologies were effective in reducing total bromacil concentrations: activated carbon and Daramend®. Activated carbon reduced total bromacil concentration by 74%. Daramend® reduced total bromacil concentrations by 58%. However, final concentrations for activated carbon- and Daramend®-treated soils were an order of magnitude greater than Tier 1 soil remediation guideline for bromacil. Daramend® can actively remediate soil for up to five years and this 12-week study does not evaluate the long-term performance of Daramend®.

Phytoaccessible bromacil in activated carbon-treated soil was below the detection limit of 0.008 mg/kg two weeks after treatment. The detection limit is below the Alberta Tier 1 guideline for bromacil. Activated carbon can be effective as a risk management tool at bromacil-impacted sites.

Chemical oxidation with hydrogen peroxide, VTX® catalyst, and Tween®-80 was not effective in reducing bromacil concentration. In this experiment, the components of the chemical oxidant were not applied according to supplier recommended practices. No conclusions or recommendations on the use of this technology can be made based on the results of this experiment.

Based on the results of this experiment, the following actions are recommended:

1. Further testing of activated carbon to extend the findings in this report and work completed in SSP #10 (Thacker, 2022). The objective would be to determine the long-term efficacy of immobilizing bromacil in a field study.
2. Perform a similar mesoscale experiment to refine the application of Daramend® and evaluate its performance over multiple seasons. A corresponding lab component would confirm the degradation of bromacil and evaluate if lab-scale optimization is related to field performance. The objective would be to optimize the application of Daramend®, determine its long-term

effectiveness in reducing bromacil concentrations, and confirm whether bromacil is being degraded or adsorbed by Daramend®.

11.1.2 Optimization of Daramend®

Bachmann, V., 2024. Optimization of Daramend® for the Remediation of Bromacil in Soil. Report SSP-12B prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 27 pp.

Bromacil and tebuthiuron are non-selective, broad-spectrum soil sterilants used for vegetation control on industrial land. In Alberta, they were introduced in the 1960s and were used on a variety of industrial sites until their use was halted in the 1990s due to their ability to migrate offsite and their extreme persistence. Decades after ceasing treatment with sterilant products, impacts can persist in soil and water. These sterilants are unique and challenging contaminants to manage. To address several knowledge gaps related to the assessment, remediation, and risk management of sites impacted by these sterilants, the Soil Sterilants Program (SSP) was designed as a 5-year joint industry program that was initiated in 2019.

A year-long, mesoscale study at InnoTech Alberta's Vegreville Research Facility was executed to optimize the use of Daramend® for the remediation of bromacil in soil obtained from a contaminated site in Alberta. A parallel lab-scale experiment was performed to assess the use of bench-scale scale studies for Daramend® optimization for field planning. Daramend® was applied at 2 dosages, 0.5% and 2% by dry soil weight, with control treatments (0% Daramend®). Additionally, two application practices were compared, (1) single application of Daramend® and water (Moisture Regime 1), and (2) two applications of Daramend® and three applications of water (Moisture Regime 2). The primary objective was to determine the optimum Daramend® dosage and management practice to maximize bromacil reduction to achieve the Alberta Tier 1 soil remediation guideline of 0.009 mg/kg and minimize remediation costs.

None of the treatments in the mesoscale study were able to reach the Alberta Tier 1 target of 0.009 mg/kg. Control treatments in Moisture Regime 2 had an increase in bromacil concentrations. By the end of the treatment, Daramend® treatments did not have statistically significant different bromacil concentrations from the initial concentrations. In Moisture Regime 2, the final bromacil concentrations for both 0.5% and 2% Daramend® were significantly lower than the final bromacil concentration for the control treatment. At week 38, the first sampling event after the winter season, there was an increase in bromacil concentrations from the previous measurement for all treatments; the control treatment in Moisture Regime 2 increased to more than double the initial concentration. The week 38 increase was less for all Daramend® treatments. Bromide concentrations increased for all Daramend® treatments in Moisture Regime 2, and 2% Daramend® treatments in Moisture Regime 1, indicating that bromacil was being destructively remediated in those treatments. There appeared to be an interaction between bromides and the soil. All increases in bromides were in the surface samples; bromide concentrations in the centre of the treatments did not change over the course of the experiment, even after mixing of Moisture Regime 2 treatments.

The bromacil concentration for all treatments in the lab study decreased to within 0.003 mg/kg of the minimum detection limit (0.008 mg/kg) by week 37 and were not significantly different from each other. Bromacil concentration in the control treatment did not start decreasing until 12 weeks after treatment. In Daramend® treatments, bromacil concentrations started decreasing 2 weeks after treatment. Increases in bromacil concentration were seen at week 8 for control treatment, but the increase was not statistically significant. Bromide concentrations increased for all treatments indicating destructive remediation of bromacil. Daramend® treatments had higher bromide concentrations than controls.

There were decreases in bromide concentrations at week 4 for some treatments and at week 12 for 2% Daramend® treatments showing that bromides were interacting with soil.

For this soil, it appears that the limiting factor for bromacil degradation was moisture content and Daramend® was able to enhance degradation. The addition of water seems to release more bromacil from the soil phase and the application of Daramend® buffers this release by degrading the released bromacil. Bromacil is degraded via reductive debromination, an anaerobic process. Achieving and maintaining the required moisture content on fine-textured surface soil in in-situ applications of Daramend® is logistically unfeasible. Daramend® and other anaerobic technologies maybe better suited for application in ex-situ reactors where the prolonged saturation of the impacted soil can be achieved and maintained.

11.2 Project Reports

The Reports is available in

Appendix A9-1 – Ex-situ Demonstration

Appendix A9-2 – Optimization of Daramend®

12.0 EVALUATION AND COMPARISON OF REMEDIATION TECHNOLOGIES

12.1 Report Summary

Levy, S., X. Mo and V. Bachmann, 2021. Evaluation and Comparison of Soil Sterilant Remediation Technologies. Report SSP-13 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 30 pp.

This project was undertaken to complement previous reviews conducted on the remediation of soil sterilants. Based on input from the community of practice, additional review was needed to identify cost-effective and efficient technologies specific to remediation of bromacil and tebuthiuron. In addition, to align with the needs of the Soil Sterilants Program, potential technologies were evaluated to determine their applicability to Alberta conditions and specific site challenges, while also considering cost, logistics of application, and sustainability.

The scope of this project was expanded to include a review of applicable site types and industry challenges, and to identify high-potential technologies that could be evaluated at bench- and meso-scale to first de-risk through a series of testing stages, then potentially deploy at field scale.

Methods included review of historical SSP documentation, review of bromacil and tebuthiuron characteristics, and identification of high priority concerns in sterilant management. Three key challenges were defined for the purpose of evaluating and testing remediation technologies, including:

1. Sterilants at depths greater than 50 cm below ground surface in unsaturated soil, thus inaccessible to treatment at surface. Ideally the technologies to address deeper sterilants would function in situ to minimize excavation of overlying soil.
2. Soil treatment requirements where sterilant destruction is required, and immobilization is not considered an acceptable option, are challenging to implement. Technologies for this application could be in situ or ex situ.
3. Saturated fine-grained till soils and groundwater impacted by sterilants. In situ technologies and/or combinations thereof to avoid remedial excavation and disposal of >5,000 to 10,000 tonnes of soil and underlying groundwater, generally where sterilants are widely dispersed, would be beneficial.

A review of literature and interviews conducted with subject matter experts from the consulting industry and technology providers were used to gather more information and develop a list of potential technologies. All identified technologies were evaluated to determine if they were proven for treatment of sterilants, impractical to meet objectives of the research and testing program, or potential technologies for inclusion in the program.

Recommendations were made for staged bench-, meso- and field-scale testing and demonstration to test and potentially prove out technologies for use at the field scale. A proposed technology testing program was developed, which will be used to guide Project Service Providers in other Soil Sterilants Program remediation projects, namely projects #11 and #12, for testing remediation technologies and running a field demonstration project, respectively.

12.2 Project Report

The Report is available in Appendix A10

13.0 REFERENCES

Drozdowski, B., C.B. Powter and S. Levy, 2018a. *Management of Sterilant Impacted Lands: Literature Synthesis*. InnoTech Alberta, Edmonton, Alberta. 49 pp. https://www.cclmportal.ca/resource/management-sterilant-impacted-sites-literature-synthesis

Drozdowski, B., S. Levy and C.B. Powter, 2018b. *Remediating Soil Sterilant-Affected Lands: Summary of Stakeholder Discussions*. InnoTech Alberta, Edmonton, Alberta. 42 pp. https://www.cclmportal.ca/resource/remediating-soil-sterilant-affected-lands-summary-stakeholder-discussions

14.0 LIST OF APPENDICES

APPENDIX A: Technical Reports

APPENDIX A1: Hemsley, T., K. Bessie and A. Shaikh, 2021. Sterilant Sampling Best Management Practices. Report SSP-2 prepared by TetraTech Canada Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 41 pp.

APPENDIX A2: Periera, A.D.S, E.D. Ruan and G. Knox, 2022. Laboratory Method Investigation for Detection of Bromacil and Tebuthiuron in Water and Soil. Report SSP-3 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 38 pp.

APPENDIX A3-1: French, K., E. Cowan, E. Terpstra, J. Liu, Y. Li and F. He, 2021. Field Screening Technologies for Bromacil and Tebuthiuron – Literature Review. Report SSP-5A prepared by Vertex Environmental Inc. and University of Waterloo for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 28 pp. plus Appendices.

APPENDIX A3-2: French, K., E. Cowan and A. Neufeld, 2021. Preliminary Testing of Existing Field Screening Technologies for Bromacil and Tebuthiuron – Phase 1 Results. Report SSP-5B prepared by Vertex Environmental Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 33 pp. plus Appendices.

APPENDIX A4-1: Marquez, G., A. Houston and T. Todoruk, 2020. Sensitivity Analysis of the Domenico and Robbins Groundwater Transport Model. Report SSP-6/8A prepared by Advisian for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 21 pp. plus Appendices.

APPENDIX A4-2: Houston, A., T. Todoruk, B. Loescher and R. Prosser, 2020. Laboratory Experimental Design to Characterize Bromacil and Tebuthiuron Half-life and Adsorption in Alberta Soils. Report SSP-6/8B prepared by Advisian, Bureau Veritas Labs and University of Guelph for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 64 pp.

APPENDIX A4-3: Marquez, G., A. Houston and T. Todoruk, 2020. Literature Review to Identify Metabolites of Bromacil and Tebuthiuron. Report SSP-6/8C prepared by Advisian, Worley Group for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 18 pp.

APPENDIX A5-1: Litalien, A., C. Kartz, and I. Mitchell, 2020. Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life. Report SSP-7A. Prepared by Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 54 pp.

APPENDIX A5-2: Litalien, A., J. Hueser, M. Tindal, C. Kartz and I. Mitchell, 2020. Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life: Review of Alternative Models. Report SSP-7B prepared by Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 26 pp. plus Appendices.

APPENDIX A5-3: Bachmann, V. and M. Tindal, 2023. Determination of Soil-Water and Organic Carbon-Water Partitioning Coefficients for Bromacil and Tebuthiuron. Report SSP-7C Prepared by InnoTech Alberta and Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 15 pp.

APPENDIX A6-1: Thacker, S., 2021. Toxicity of Bromacil and Tebuthiuron to Alberta Native Plant Species. Report SSP-9A prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 49 pp.

APPENDIX A6-2: Litalien, A. and M. Tindal, 2021. Ecological Contact Guideline Development for Bromacil and Tebuthiuron. Report SSP-9B prepared by Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 16 pp. plus Appendices

APPENDIX A7: Thacker, S., 2022. Investigation of Long-Term Effectiveness of Activated Carbon in Immobilization of Bromacil and Tebuthiuron. Report SSP-10 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 50 pp.

APPENDIX A8-1: Bendouz, M. and J. Paré, 2022. Bench-scale Testing of Chemical Amendments to Remediate Bromacil and Tebuthiuron in Soil. Report SSP-11A. Prepared for InnoTech Alberta, Soil Sterilants Program. 45 pp.

APPENDIX A8-2: Saint-Fort, R. and S. Levy, 2022. Proof of Concept of Electrocoagulation Technology to Remediate Water Contaminated with Bromacil and Tebuthiuron. Report SSP-11B prepared by Mount Royal University and InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 7 pp. plus Appendix.

APPENDIX A8-3: French, K., E. Cowan and A. Neufeld, 2023. Bench-scale Treatability Study using Trap & Treat® and Zero Valent Iron for Bromacil and Tebuthiuron in Alberta Soils. Report SSP-11C prepared by Vertex Environmental Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 20 pp. plus lab data.

APPENDIX A9-1: Bachmann, V. and R.J. Thiessen, 2024. Ex-situ Field Demonstration for the Remediation of Bromacil in Soil. Report SSP-12A prepared by InnoTech Alberta for Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 23 pp.

APPENDIX A9-2: Bachmann, V., 2024. Optimization of Daramend® for the Remediation of Bromacil in Soil. Report SSP-12B prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 27 pp.

APPENDIX A10: Levy, S., X. Mo and V. Bachmann, 2021. Evaluation and Comparison of Soil Sterilant Remediation Technologies. Report SSP-13 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 30 pp.

APPENDIX B: 2024 Annual Sharing Event Presentations

APPENDIX B1: Introduction to the 2024 Sharing Event

APPENDIX B2: Summary of the 2024 Sharing Event

APPENDIX B3: Sterilant Sampling Best Management Practices

APPENDIX B4: Laboratory Method Investigation for Detection of Bromacil and Tebuthiuron in Water and Soil

APPENDIX B5: Development of an Extraction Method for Estimating Phytoaccessibility of Bromacil and Tebuthiuron

APPENDIX B6: Field Screening Technologies for Bromacil and Tebuthiuron

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Hemsley, T., K. Bessie and A. Shaikh, 2021. Sterilant Sampling Best Management Practices. Report SSP-2 prepared by TetraTech Canada Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 41 pp.

Sterilant Sampling Best Management Practices

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EXECUTIVE SUMMARY

Soil sterilants are non-selective residual herbicides that were developed in the 1960s to late 1990s to provide long-term vegetation control on industrial sites along highways, railroad rights-of-way, and industrial areas. Sterilants tend to be persistent in the environment and are not selective as all plants will be affected by these chemicals. The most commonly used sterilants were atrazine, bromacil, diuron, DCPMU, linuron, simazine and tebuthiuron. These sterilants have different physical-chemical properties, modes of action on plants, fate and exposure and toxicological properties. Of these seven sterilants, bromacil and tebuthiuron were the most commonly found sterilants on industrial sites in Alberta.

InnoTech Alberta's Reclamation Team initiated the current Soil Sterilant Program focussing on bromacil and tebuthiuron after a literature review and workshop facilitated by InnoTech in 2017. The industry steering committee decided to focus additional research on three key knowledge gaps (1) Identification and Delineation, (2) Risk Assessment and Management, and (3) Remediation.

The purpose of the *Sterilant Sampling Best Management Practices* (BMP) is to provide specific sampling guidance for low level (≤0.2 mg/kg) concentrations of bromacil and tebuthiuron in soil and groundwater in Alberta. This BMP is intended for use for anyone engaged in environmental site assessment, remediation, and reclamation activities in respect to soil sterilant contamination. The document provides guidance in respect to regulatory considerations, site evaluations, soil and groundwater characterization guidance (e.g., soil sampling, groundwater sampling), data evaluation and interpretation.

When developing a sampling program, the following should be considered:

- Objectives of the site investigation. Is it an initial assessment; or a supplemental (detailed) assessment; or for delineation?
- The fate and transport (volatilization, absorption/desorption, mobility/leaching, soil pH and salinity) of the sterilants.
- Site historical information, date(s), and characteristics (e.g., low-lying areas, slopes, soil classification, hydraulic characteristics).
- High potential for cross contamination when sampling.
- The spatial variability of both soils, and sterilants as high concentrations of sterilants may be found at the surface or at depth within 'hot spots' but they may diminish to below laboratory detection limits within a short distance.

Due to the high potential for cross contamination when sampling for sterilants, there are special sampling techniques that should be used when assessing low concentrations (parts per billion [ppb] and parts per trillion [ppt]) of bromacil and tebuthiuron. These special sampling techniques include collection using a minimum of 3" diameter direct push drill rig with sleeves or a hollow stem auger, an 18" split barrel spoon with 6" x 2.5" stainless steel sleeves every 1.0 m down to a depth of 7.5 m or until bedrock. Each soil-filled sleeve should be sealed with Teflon tape and plastic caps and be submitted directly to the laboratory for analytical analysis. For groundwater, discrete monitoring points should be established within different water bearing lithological units to avoid mixing of groundwater during drilling and sampling. Low flow purging and sampling is suggested as it can provide more accurate and reproducible samples of the formation water quality than using high flow/high volume purging and sampling methods.

In addition, a Triple Rinse Method should be completed on all field sampling equipment before each use, during use and after being used due to the high potential for cross contamination and low-level guidelines.

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ACRONYMS

AEP	Alberta Environment and Parks
AESRD	Alberta Environment Sustainable Resource Development
APEC	Areas of Potential Environmental Concern
ASTM	American Society for Testing and Materials
BC MOE	British Columbia Ministry of Environment
BDL	Below Analytical Detection Limit
BMP	Best Management Practices
CCME	Canadian Council of Ministers of the Environment
COC	Chain of Custody
CSM	Conceptual Site Model
CSSC	Canadian Soil Classification System
DCPMU	3-(3,4-dichlorophenyl)-1,1-dimethylurea
ELISA	Enzyme-linked Immunosorbent Assay
EPEA	*Environmental Protection and Enhancement Act*
ESA	Environmental Site Assessment
FCSAP	Federal Contaminated Sites Action Plan
Ha	Hectare
IVMAA	Industrial Vegetation Management Association of Alberta
mbgs	Metres Below Ground Surface
OM	Organic Matter
ppb	Parts per Billion
ppt	Parts per Trillion
PVC	Polyvinyl Chloride
QA/QC	Quality Assurance/Quality Control
RPD	Relative Percent Differences
SSP	Soil Sterilants Program
USEPA	United States Environmental Protection Agency

1.0 INTRODUCTION

Tetra Tech Canada Inc. (Tetra Tech) was retained by InnoTech Alberta (InnoTech) to assist with the Soil Sterilants Program (SSP) for Sterilant-Sampling Best Management Practices, Project #2 (the Project). Soil sampling procedures for sterilants were outlined in 1995 in the *Field Manual for Rehabilitating Soils Affected by Residual Herbicides* (IVMAA, 1995). Since then, there have been changes in environmental regulations, guidance documents, sampling, and analytical procedures. As our understanding of sterilants has evolved with time, there is a need for technical guidance for soil and groundwater investigations due to challenges with low guidelines requiring low detection limits, and potential for cross contamination when sampling for sterilants.

1.1 Sterilants in Alberta

Soil sterilants are non-selective residual herbicides that were developed in the 1960s to late 1990s to provide long-term vegetation control on industrial sites along highways, railroad rights-of-ways, and industrial areas. Sterilants tend to be persistent in the environment and are non-selective, as all plants will be affected by these chemicals. In Alberta, they have historically been used to control vegetation on oil and gas sites, gas processing plants, rights-of-way, railways, sawmills, pulp mills and electrical substations. It was estimated that there were 61,750 oil and gas sites in Alberta with soil sterilant residues (Cotton and Sharma, 1993). Due to soil sterilant contamination there are numerous sites in Alberta undergoing decommissioning that are waiting for remediation, resulting in an inability for industry to achieve site closure.

Sterilant contamination tends to be non-uniform, as sterilants were applied by hand in granular or pellet form to the surface, resulting in varying concentrations in the soils. Industry practice was to maintain bare soil through repeated application of sterilants, thus resulting in an accumulation of soil sterilants to the surface. Since sterilants were applied to the surface, there tends to be migration of sterilants from these sites to adjacent lands and waterbodies and groundwater via runoff, wind erosion and leaching. The most commonly used sterilants were atrazine, bromacil, diuron, DCPMU, linuron, simazine and tebuthiuron. These sterilants have different physico-chemical properties, modes of action on plants, fate and exposure and toxicological properties. Of these seven sterilants, bromacil and tebuthiuron (Appendix A) were found to be the most common sterilants on industrial sites in Alberta (Drozdowski et al., 2018a, b).

1.2 Soil Sterilant Program

InnoTech Alberta's Reclamation Team initiated the current soil sterilant program after a literature review and workshop facilitated by InnoTech in 2017. The soil sterilant program focuses on bromacil and tebuthiuron as they were the most commonly found sterilants on industrial sites in Alberta. The industry steering committee decided to focus additional research on bromacil and tebuthiuron for three key knowledge gaps (1) Identification and Delineation, (2) Risk Assessment and Management, and (3) Remediation. The objective of the soil sterilants program is to establish proven, technical, and cost-effective strategies and best management practices for effective management of sites impacted by residual soil sterilants, with the goal of achieving regulatory site closure. During the 2017 workshop, one common theme that arose was the need to standardize sampling methodology to ensure sterilant impacts are being accurately characterized and delineated. Specifically, that sampling methods suitable for trace concentrations in the parts per billion (ppb) range are necessary. (Drozdowski et al., 2018a). This led to the development of the *Sterilant Sampling Best Management Practices* (BMP).

1.3 Purpose of the Manual

The purpose of the *Sterilant Sampling Best Management Practices* (BMP) is to provide specific sampling guidance for low level (ppb and ppt) concentrations of bromacil and tebuthiuron in soil and groundwater in Alberta. Although there are multiple standards of practices for soils (CCME, 2012, 2016a; Environment Canada, 2012; IVMAA, 1995; Mason, 1992; USEPA, 2020) and groundwater investigations (ASTM, 2010, 2018a, 2019; CCME, 2016a; USEPA, 2008), there is a lack of guidance on appropriate field sampling procedures for low level concentrations of bromacil and tebuthiuron.

This BMP supersedes the *Field Manual for Rehabilitating Soils Affected by Residual Herbicides* (IVMAA, 1995). The BMP is not a stand-alone document and should be utilized in combination with Alberta Environment and Parks' (AEP) *Alberta Environmental Site Assessment Standard* (AEP, 2016a), and the Canadian Council of Ministers of the Environment's (CCME) *Guidance Manuals for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment*, *Volume 1 to 4* (CCME, 2016), where applicable. Furthermore, to minimize repetition with other standard procedures this document will focus specifically on information pertinent to investigations for low level concentrations of bromacil and tebuthiuron.

1.4 How to Use this Manual

The BMP is intended for use for Soil Scientists, Hydrogeologists, Environmental Scientists, and Environmental Engineers, who may be involved in environmental site assessments (ESA) or redamation and reclamation activities with sterilant contamination. The document provides guidance in respect to regulatory considerations, site evaluations, soil, and groundwater characterization guidance (e.g., soil sampling, groundwater sampling), and data evaluation and interpretation specific to sterilants, bromacil and tebuthiuron.

2.0 REGULATORY CONSIDERATIONS

Alberta's existing regulatory framework is outlined within the *Environmental Protection and Enhancement Act* (EPEA; Government of Alberta, 2000) and Regulations. This BMP is meant to be used in conjunction with Alberta's existing framework. The management of contaminated sites is guided through the *Contaminated Sites Policy Framework* (AESRD, 2014) with the support from the *Alberta Environmental Site Assessment Standard* (AEP, 2016a), *Alberta Tier 1 Soil and Groundwater Remediation Guidelines* (Alberta Tier 1) (AEP, 2019a, as amended), *Alberta Tier 2 Soil and Groundwater Remediation Guidelines* (Alberta Tier 2) (AEP, 2019b, as amended), and the *Alberta Exposure Control Guide* (AEP, 2016b).

2.1 Alberta Government Documents

The *Alberta Environmental Site Assessment Standard* (AEP, 2016a) provides a minimum set of requirements for ESA site characterization of contaminated or potentially contaminated sites (Phase 1 and 2 ESA[1]), delineation, confirmatory sampling, and development of conceptual site models (CSM). The document states that sampling of soil and groundwater must be carried out using proper field methods, and analytical procedures. Sampling designs must be tailored to specific objectives and site conditions with enough sampling points to clearly delineate contaminants of concern. A quality assurance/quality control (QA/QC) program must be included, which may include field-duplicate samples for high quality sampling programs.

In Alberta, delineation and confirmatory samples are considered complete when the measured concentrations are less than the *Alberta Tier 1 Soil and Groundwater Remediation Guidelines* (Alberta Tier 1) (AEP, 2019a, as

[1] NOTE: Phase 1 and 2 are commonly used in Alberta regulatory guidelines; Phase I and II are used in federal guidelines.

amended) or *Alberta Tier 2 Soil and Groundwater Remediation Guidelines* (Alberta Tier 2) (AEP, 2019b, as amended). The Alberta Tier 1 guideline values for Bromacil and Tebuthiuron (Tables 1 and 2) are very low and in some cases are less than the current laboratory detection limits, as is illustrated below for agricultural land use.

Table 1: Alberta Tier 1 Soil Guidelines for Bromacil and Tebuthiuron.

Soil Sterilant	Alberta Tier 1 Guidelines (Agriculture Land Use)[1]											
	Soil (Coarse-grained; mg/kg)						Soil (Fine-grained; mg/kg)					
	Human		Ecological				Human		Ecological			
	Direct Soil Contact	Protection of Domestic Use Aquifer	Direct Soil Contact	Protection of Freshwater Aquatic Life	Irrigation Water	Protection of Livestock Water	Direct Soil Contact	Protection of Domestic Use Aquifer	Direct Soil Contact	Protection of Freshwater Aquatic Life	Irrigation Water	Protection of Livestock Water
Bromacil	2,000	7.0	0.2	**0.009**	BDL	2.0	2,000	10	0.12	**0.009**	BDL	2.0
Tebuthiuron	1,600	2.5	**0.046**	BDL	BDL	0.12	1,600	3.7	**0.046**	BDL	BDL	0.11

Notes:
[1]2019 Alberta Tier 1 Soil and Remediation Guideline
BDL – below detection limit; groundwater assessment and comparison to groundwater remediation guidelines necessary.
Bold – lowest applicable guidleine.
Current laboratory detection limits varies for various labs but is about 0.005 mg/kg.
Refer to the Tier 1 guidelines for other land uses (natural area, commercial and industrial).

Table 2: Alberta Tier 1 Groundwater Guidelines for Bromacil and Tebuthiuron.

Soil Sterilant	Alberta Tier 1 Guidelines (Agriculture Land Use)[1]											
	Groundwater (Coarse-grained; mg/L)						Groundwater (Fine-grained; mg/L)					
	Human		Ecological				Human		Ecological			
	Potable	Vapour Inhalation	Direct Soil Contact	Protection of Freshwater Aquatic Life	Irrigation Water	Protection of Livestock Water	Potable	Vapour Inhalation	Direct Soil Contact	Protection of Freshwater Aquatic Life	Irrigation Water	Protection of Livestock Water
Bromacil	0.95	-	0.44	0.005	**0.0002**	1.1	0.95	-	0.30	0.005	**0.0002**	1.1
Tebuthiuron	0.66	-	0.20	0.0016	**0.00043**	0.13	0.66	-	0.25	0.0016	**0.00043**	0.13

Notes:
[1]2019 Alberta Tier 1 Soil and Groundwater Remediation Guideline.
BDL – below detection limit; groundwater assessment and comparison to groundwater remediation guidelines necessary.
Bold – lowest applicable guidleine.
Current laboratory detection limits for groundwater is 0.0001 mg/L.
Refer to the Tier 1 guidelines for other land uses (natural area, commercial and industrial).

2.2 CCME and Environment Canada Guidance Documents

In 1993, the CCME developed sampling guidance manuals Volume I, Site Characterization (CCME, 1993a) and Volume II, Analytical (CCME, 1993b), which were updated in 2016 to the *Guidance Manuals for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment*, *Volume 1 to 4* (CCME, 2016a). Volume 1 and Volume 4 were reviewed in development of this BMP for soil and groundwater characterization,

and QA/QC procedures. In 2020, CCME developed an *Ecological Risk Assessment Guidance Document* (CCME, 2020), which provides detailed information on development of CSMs.

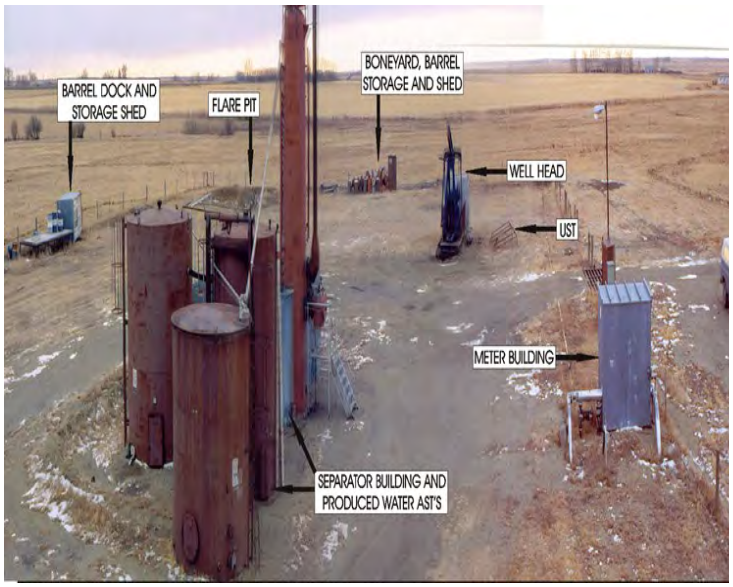
In 2012, Environment Canada developed a *Guidance Document on the Sampling and Preparation of Contaminated Soil for Use in Biological Testing* (Environment Canada, 2012), which may be used for guidance of soil sampling off-site.

3.0 SITE EVALUATIONS

3.1 Historical Guidance Review

Historically in Alberta, vegetation management was required under legislation on aboveground facilities such as substations, meters, and compressor stations. On electrical substations vegetation growth can increase the risk of electrical faults, lightning strikes and/or fires, while on oil and gas facilities vegetation can increase the potential for fires. Furthermore, the use of electric or gas power mowers may result in sparks, thus industry accomplished vegetation control through application of non-selective, residual soil sterilants (Landsburg and Dwyer, 1995).

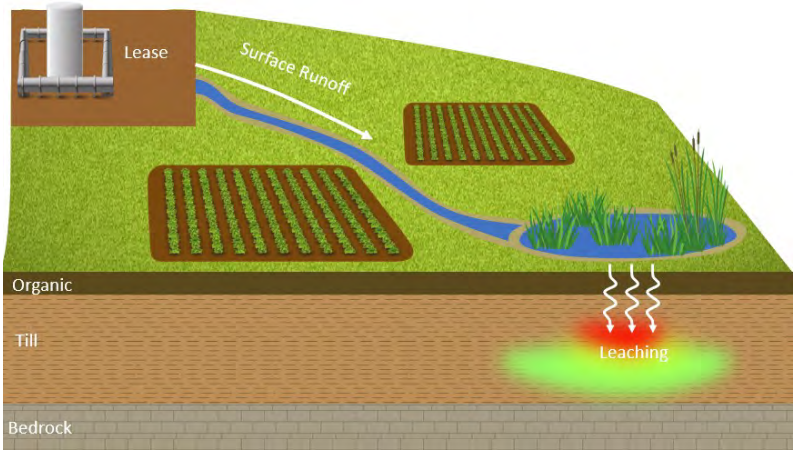
Some industrial operators responded to the legislation by using chemicals for total vegetation control within fence lines of compressor, meter, and off-line sale stations, maintenance yards and storage facilities prior to 1987. Bromacil application rates were up to 27 kg of active ingredient (a.i.) per hectare (ha) (Landsburg and Fedkenheuer, 1990). Sterilants were also applied around fence lines, infrastructure (e.g., buildings, pump jacks, storage tanks, etc.), flare pits and berms.

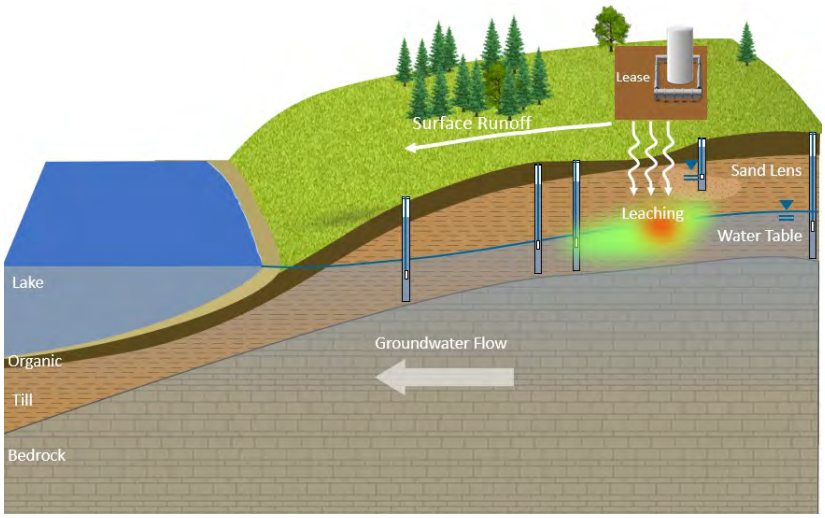


Typical infrastructure on an Oil and Gas Lease. (Photo credit Tetra Tech)

Although sterilants were applied on site, migration may have occurred off-site. Sterilant migration may have occurred due to surface runoff after heavy rainfalls or wind deposition from a high wind event (Landsburg and Dwyer, 1995). Surface runoff of sterilants typical follows ephemeral drainage channels towards low lying areas where it ponds. The steeper the slope, usually the less penetration of sterilant, limiting impact to the topsoil initially. Over time, these persistent compounds can migrate into underlying subsoil layers (B and C soil horizons). Crops can emerge and grow but as soon as the roots extend to the subsoil, the crops become affected. Where water ponds, the depth of impact may extend below the rooting zone (defined by AEP as 1.5 m; AEP (2019b)) and into groundwater. Sites with level to nearly level topography (≤2% slopes), like industrial sites, may have minimal surface runoff. On these sites, there is more potential for downward migration deeper into the subsoil (>1.0 m below ground surface [mbgs]) and groundwater via water infiltration. High concentrations and multiple applications of sterilants increase the risk of impact to subsoil and groundwater. Time is an important factor for sterilant migration. Older sites (e.g., >60 years old) have higher potential for deeper impacts to up 4.5 m in fine textured soils or even 6.0 m into the subsoil and groundwater. While newer sites (e.g., <30 years) or off-lease sloped sites treated with activated charcoal may only have sterilants within the plant rooting zone (0 metres to 1.5 metres). Table 3 illustrates typical Alberta scenarios for sterilant impacts.

Table 3: Typical Scenarios for Sterilant Impacts in Alberta.

Scenario	Reference Figures
Flare Pit Berms or Tank Berms ▪ Small volume. ▪ Typically not much depth penetration initially due to slopes on berms. ▪ Fill material. ▪ Age 1960s to 1990s for bromacil and tebuthiuron (30 to 60 years old), a variety of sterilants and herbicides used for control over time. Quite common since 1990 to use glyphosate. ▪ Due to small volume, during remediation/reclamation is usually landfilled off-site if impacted.	 Left – Flare pit berm (Photo credit Tetra Tech). Right – Propane Tank Berm (Photo credit Tetra Tech).
Perimeter Berms ▪ Same scenario as above but higher potential to extend off-site. ▪ Off-site could be agricultural land use (cultivated or pastureland) and the area impacted is usually long and narrow (e.g., 5 m x 40 m). ▪ Off-site portion was commonly treated with activated charcoal and/or manure from mid 1980s to current day.	 Activated charcoal tilled into topsoil (Photo credit Tetra Tech).
Off-site Run-off onto Agricultural Fields in Ephemeral Drainage Channels ▪ Moderate volume. ▪ Infiltration is usually less on steeper slopes, but over time can move into subsoil (<1 mbgs, typically) – see Landsburg and Dwyer (1995). ▪ Often multiple applications and run-off events so can be re-contaminated. ▪ Sterilants can accumulate in wetland areas (low areas) penetrating deeper plus impact surface water. ▪ Some sites treated with activated charcoal and/or manure in mid-1980s to current.	

Scenario	Reference Figures
Full Site Area ▪ Large volume, areas typically 100 m x 100 m or larger and level. ▪ Typically has gravel over fill or subsoil (topsoil removed during site construction and saved for reclamation since 1970s) ▪ Multiple applications to entire site, often with various sterilants and herbicides. ▪ Impacted area also overlaps with other sources (spills, flarepits, etc.) that may have co-contaminant impacts (hydrocarbons, salts, metals). ▪ Level area and multiple applications over time and old sites (60 years or more) can have soil impacts as deep as 4.5 m in fine-textured soils and 6 m in coarse-textured soils. ▪ Shallow groundwater is often impacted but in fine texture till, or the discontinuous sand lenses within the till, the water is often not considered an aquifer due to discontinuous, low hydraulic conductivities, yield and sometimes chemistry.	

Remediation of sterilants within topsoil or upper subsoil using activated carbon and other amendment was researched in Alberta field and greenhouse studies in the 1980s to 1990s (Cotton and Sharma, 1993; Landsburg and Fedkenheuer, 1990; Sharma, 1989). Activated charcoal was added to topsoil on one site and the upper 30 cm of subsoil on another site (Cotton and Sharma, 1993) to immobilize the sterilants in the soil. The intent was to prevent plants from taking up the sterilant (IVMAA, 1995) and prevent migration downwards in the soil. Monitoring of select sites to evaluate the long-term effects of activated charcoal application and determine the bioaccessible fraction of the contaminant over time is currently being investigated (Drozdowski et al., 2018b) as the current laboratory method yields “total” values. Laboratory detection limits in soils for sterilants have improved from 0.01 mg/kg in 1998.

Laboratory detection limits in soils for sterilants have improved since 1998 from 0.01 mg/kg to 0.005 mg/kg in 2008 (Bessie, 2009). Prior to 1998, plant bioassays were sometimes used to detect sterilants since impacts to plants occur at less than historical laboratory detection limit (IVMAA, 1995). Laboratory detection limits in water are commonly 0.0001 mg/L (0.1 µg/L or ppb).

There were no provincial remediation guidelines for bromacil or tebuthiuron prior to 2007. Guidelines were first introduced in the 2007 Alberta Tier 1 Guidelines (Alberta Environment, 2007) based on Health Canada inclusion of pesticides guidelines but only for water pathways. In 2010, the Alberta Tier 1 Guidelines (Alberta Environment, 2010) included the protection of aquatic life guideline for bromacil, but not for tebuthiuron. In 2014, the Ecological Direct Contact guideline for bromacil and tebuthiuron was added to the 2014 Alberta Tier 1 Guidelines (AESRD, 2014a). The 2019 Alberta Tier 1 Guidelines for protection of aquatic life for tebuthiuron and protection of irrigation for bromacil and tebuthiuron have guideline values that are below the analytical detection limit (BDL). Understanding of the changes in detection limits and guidelines is important to understand the historical information available for site assessments and interpretation.

A recent review of 40 active sites impacted by bromacil or bromacil and tebuthiuron across Alberta was completed. Information on the depth of known contamination, vertical separation, groundwater contamination and range of concentrations in surface soil (≤1 metre below ground surface [mbgs]) and subsurface soils (>1 mbgs), both in fine and coarse textured soils was collected (Houston et al., 2020.). Table 4 summarizes the information from this review. Overall, bromacil and tebuthiuron concentrations were greater at depths greater than 1 mbgs.

Table 4: Summary of Bromacil and Tebuthiuron Impacts within Coarse and Fine Textured Soils.

Description	Bromacil[1]	Tebuthiuron[1]
Depth of known impacts	0 mbgs to 6 mbgs	0.15 mbgs to 4.5 mbgs
Surface soil (≤1 mbgs) concentration range	0.0085 mg/kg to 2.4 mg/kg	0.000146 mg/kg to 0.0208 mg/kg
Subsurface soil (>1 mbgs) concentration range	0.019 mg/kg to 3.0 mg/kg	0.48 mg/kg to 1.81 mg/kg
Vertical separation between impacted soil and measured groundwater depth – 0 m (Groundwater Impacted)	18 sites (15 of 18 sites)	6 sites (2 of 6 sites)
Vertical separation between impacted soil and measured groundwater depth – 1 m to 5 m (Groundwater Impacted)	8 sites (3 of 8 sites)	1 site (None)
Vertical separation between impacted soil and measured groundwater depth – >5 m to 10 m (Groundwater Impacted)	4 sites (1 of 3 sites)	None

Notes:
[1]Information obtained from Houston et al. (2020).

3.2 Environmental Site Assessments

3.2.1 Phase 1 Environmental Site Assessments

The objective of a Phase 1 ESA is to gather pertinent information about the site such as the history, current settings, site characteristics, potential exposure pathways and receptors, and desktop soils and groundwater information to identify potential sources of contamination and impacts. The following information may help in assessing potential contamination from sterilants:

- Sterilant application records obtained in forms or from client and operator(s) interview.
- Landowner interview of any off-site runoff, spill issues or off-site damages.
- Description of on-and off-site damages.
- Description of on and off-site damage from records (physical, chemical, and biological).
- Records of previous assessments and remedial activities.
- Details of other site activities.
- Records of spills.
- Details of construction activities.
- Air photos- looking for flare pits, areas of bare soil on-site and off-site.
- Site visit including stressed vegetation notes.

3.2.2 Vegetation Assessments

A vegetation assessment should be completed during the Phase 1 ESA site visit to investigate/collect information on potential sterilants impacted areas. Preliminary assessments include bare areas and stressed vegetation symptoms (poor growth). Detailed vegetation assessments conducted as part of a Phase 2 ESA would consist of examining and describing symptoms of vegetation stress, growth stages, health, density, and plant cover and identifying the source of the poor growth (no topsoil, poor growth medium like gravel or fill, other contaminants like hydrocarbons or salts or chemical vegetation control). Vegetation assessments should be completed when annual plants are typically nearing maturity. For sterilant impact delineation on or off lease, an alternative to using natural vegetation would be to plant a cover quick germinating crop (e.g., oats) on the site to delineate potential areas of impacts.

Bare soil on site due to sterilant contamination (Burk and Bessie 2009).

Fragile straw stalks during late stage growth (Burk and Bessie 2009)

Pesticide application to farmland (Agriculture and Agri-Food Canada, 2004).

Abrupt margins between impacted and non-impacted areas is typically indicative of sterilants. Discrete patches of bare ground or severely reduced plant growth, where no presence of salt crusting, often indicates the presence of sterilants. Areas with no vegetation suggest severe contamination, while areas with plants having stunted growth, chlorosis (yellowing of the leaf tissue), or rusting of leaf tissue suggest a lower dose of sterilants (IVMAA, 1995). Plants also respond differently to different herbicides (Alberta Agriculture, 1987; Government of Alberta, 2001), thus the assessment should consider different species of plants on the site.

The different plant growth stages should be included as on-site vegetation may be used in in-situ bioassays (a laboratory method that uses sensitive plants to determine sterilant concentrations; see Government of Alberta (2001)). Impacts from sterilants at different growth stages, seedling, juvenile and mature plants, may indicate the depth at which the plants interacted with the sterilant. Seedlings have shallow roots, thus if they are being affected the sterilant is most likely in the upper surface soils, whereas annual plants that show signs of stress at juvenile or maturity or perennial plants such as alfalfa (can be affected several years later) may indicate sterilants at deeper depths (IVMAA, 1995).

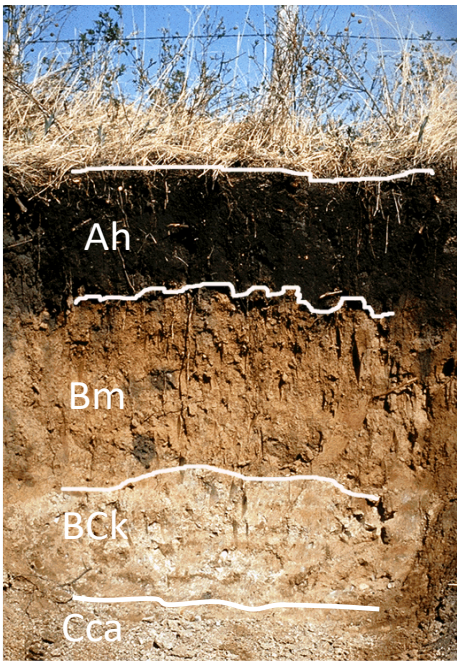
3.2.3 Phase 2 Environmental Site Assessment

Information from the Phase 1 ESA and vegetation assessment should be compiled into a figure identifying potential areas of concern on-site and off-site prior to initiating a Phase 2 ESA. The purpose of the Phase 2 ESA is to verify and determine the location, vertical and horizontal extent, degree, significance, and volume of the contamination. The Phase 2 ESA may be staged with a “preliminary assessment” that focuses on identifying if impacts have occurred in areas of potential environmental concern (APEC) and a “detailed” assessment” that delineates areas. During Phase 2 ESA, soils and groundwater samples should be collected for laboratory analysis

to confirm sterilant presence and concentrations. See Section 4.0 Soil Characterization Guidance and Section 5.0 Groundwater Characterization Guidance for specific guidance for assessing bromacil and tebuthiuron.

3.3 Background Samples

Soil background samples, sometimes called controls, are important for reclamation planning and contaminated site assessments. The objective of soil controls is to classify and compare soils to available soil surveys, collect background soil quality (e.g., soil texture, pH, organic matter (OM), salinity). Soil controls are also used to assess if there are any potential off-site herbicides (e.g., 2, 4-D) that may influence on-site vegetation observations due to spray drift or water erosion. When selecting off-site soil conditions, the investigator should review available soil surveys to select representative background soil controls (AEP, 2016a; Environment Canada, 2012; IVMAA, 1995). Representative soil controls should have similar soil series (e.g., Dunvargan), soil classification (e.g., Orthic Black Chernozem), parent material, topography, comparable sample depths, hydrologic regime, and biological activity. In addition, areas located downslope or downwind from the site should be avoided (IVMAA, 1995). Background soil data are also used to set soil reaction (pH) and salinity guidelines (Alberta Environment, 2001). Soil classification using the Canadian Soil Classification System (CSSC) (Soil Classification Working Group, 1998) is required in undisturbed soils to differentiate soil horizons and identify what might be causing effects on plant growth (e.g., lack of topsoil, natural salinity and sodicity or sterilants). Canadian Soil Classification System applies to the top metre of soil in mineral soils and 1.6 m in organic soils. Orthic Black Chernozem soil profile (Dudas and Abley, 1996).



Orthic Black Chernozem soil profile (Dudas and Abley, 1996).

Groundwater background controls are important for contaminated site assessments, as they may be used to characterize specific groundwater zones. Background conditions should be selected based on similar geographical, physical, and chemical characteristics, hydrology and sampling depths and time and not influenced by site activities. Background locations for groundwater must be located up-gradient (AESRD, 2014b).

The number of background samples required depends on the study objectives, data quality objectives, the desired level of certainty and the site-specific considerations (FCSAP, 2020). In Alberta, there is no guideline for the number of background locations required for soils and groundwater contamination assessments. The United States Environmental Protection Agency (USEPA) suggests a minimum of 10 background soil observations (USEPA, 2015). The British Columbia Ministry of Environment (BC MOE) suggests a minimum number of three groundwater monitoring wells sampled measures in at least two events (e.g., seasonal high and low water table) to characterize background groundwater conditions (BC MOE, 2021a).

3.4 Sterilant Specific Considerations

Preliminary assessments often use standard tools off-site, like a shovel and Dutch soil auger, and a drill rig equipped with a solid stem auger for on-site. These methods allow assessments to be completed with one or two people, with continually observations of the lithology. Preliminary assessments answer “yes” or “no” to the question "Are there any contaminant impacts in the potential worst-case areas based on site history and site

conditions? These assessments take less time and cost less, compared to delineation assessments. Similar strategies may be used during preliminary assessments for bromacil and tebuthiuron since the objective is to determine presence or absence of bromacil and/or tebuthiuron at a site. Table 5 outlines a few specific site-specific considerations, such as the age of the site, historical application, and previous remediation with activated charcoal. Where activated charcoal was added to topsoil or subsoil for remediation treatment it is important to also assess total organic carbon, organic matter (OM), soil pH and soluble salts. Some of the site-specific considerations may not be applicable during the preliminary assessment but should be investigated during further assessments where applicable.

Table 5: Site Specific Considerations for Bromacil and Tebuthiuron.

Site History	Soils	Groundwater	Surface Water
▪ Historical application ▪ Time of application, (start and duration) ▪ Site infrastructure ▪ Climate, precipitation ▪ Previous remedial activities (e.g., activated charcoal) ▪ Surrounding vegetation and land use (e.g., agricultural or forestry)	▪ Soil classification (e.g., Chernozems have high OM in A horizon [topsoil]) ▪ Calcareous soils (elevated soil pH) ▪ Soil stratigraphy, soil horizons ▪ Soil organic matter ▪ Soil texture, particularly clay content ▪ Soil structure, compaction[1] ▪ Topography, slope direction ▪ Soil moisture content, gleyed soils, low lying areas ▪ Bare soil, and lack of vegetation	▪ Surficial geology ▪ Sand lens ▪ Multiple water bearing zones in till ▪ Depth to bedrock ▪ Depth to groundwater ▪ Horizontal and vertical gradients ▪ Hydraulic conductivity ▪ Groundwater flow direction and velocity ▪ Sustained yield	▪ Nearest surface waterbody type (e.g., wetland, lake, river)

Notes:
[1]Arias-Estévez et al. (2008)

In addition to these site-specific considerations, there are specific physical and chemical parameters related to the fate and transport (volatilization, absorption/desorption, mobility/leaching, soil pH and salinity) that are important to consider when developing sampling plans. Table 6 summarizes these physical and chemical characteristics (Drozdowski et al., 2018b; Marquez et al., 2020).

Table 6: Summary of Environmental Fate of Bromacil and Tebuthiuron.

Parameters	Bromacil		Tebuthiuron	
	Information	**Consideration in Sampling Plan**	**Information**	**Consideration in Sampling Plan**
Volatilization	▪ Low volatilization.[1]	▪ **Low** importance.	▪ Low volatilization.[1]	▪ **Low** importance.
Adsorption/ Desorption	▪ Low sorption compared to other herbicides[2]. ▪ Clay content and organic matter (OM) increase sorption[3]. ▪ Not expected to partition to suspended particles or sediments in aquatic systems. Will remain dissolved in the water column[4].	▪ **High** importance. ▪ Sampling soil horizons (upper 1 m) and stratigraphy differences	▪ Relatively, poor soil sorption[5]. ▪ Sorption is highest in soils high in OM then by clay content[5]. ▪ <1% sorption in soil with 0.3% OM and 40% sorption in soil with 4.8% OM[5].	▪ **High** importance. ▪ Sampling soil horizons (upper 1 m) and stratigraphy differences
Mobility and Leaching Potential	▪ High mobility in soils with low OM and moderate mobility in soils high in OM and clay content[6]. ▪ Movement related to soil water. Moves laterally on surface and vertically in soil profile[3]. ▪ High leaching potential[6,7]. ▪ High water table may reduce leaching[3].	▪ **High** importance. ▪ Highly mobile compared to other sterilants; concentrations observed up to 6 mbgs into soil profile.	▪ Soil texture and OM influence mobility (high in sandy soils and soils low in OM; low in clay loams or highly organic soils)[6]. ▪ High solubility in water, weak adsorption to soil and persistent[5]. ▪ Medium to high leaching potential[5,7].	▪ **High** importance. ▪ Medium to highly mobile in soils; concentrations observed up to 4.5 mbgs into soil profile.
Soil pH	▪ Soil pH affects the structure of bromacil and may affect bioavailability, solubility, and mobility ion soils. High soil pH increases solubility in water[1].	▪ **Medium** Importance. ▪ Most soils in Alberta are neutral to slightly acidic except for calcareous till deposits.	▪ Adsorption varies inversely with soil pH; higher pH = low adsorption[8].	▪ **Medium** Importance. ▪ Most soils in Alberta are neutral to slightly acidic except for calcareous till deposits.
Salinity	▪ Soluble salts may affect sterilant solubility as they are significantly correlated with residue persistence and increased soil depth[1].	▪ **Medium** Importance. ▪ Soluble salts (chloride) co-contaminant in soils or groundwater[1].	▪ Soluble salts may affect sterilant solubility as they are significantly correlated with residue persistence and increased soil depth[1].	▪ **Medium** Importance ▪ Soluble salts (chloride) co-contaminant in soils or groundwater[1].

Notes:

[1]Houston et al. (2020).
[2]Landsburg and Fedkenheuer (1990).
[3]Landsburg and Dwyer (1995).
[4]EBA Engineering (2007).
[5]Stantec Consulting Ltd. (2011).
[6]Drozdowski et al. (2018b).
[7]Cotton and Sharma (1993)
[8]Cotton and Sharma (1992).

3.5 Conceptual Site Model

A CSM brings together the key information regarding contaminant sources, fate and transport pathways, exposure pathways, valued ecosystem components and receptors of concern (CCME, 2020). They can be a graphical representation (Figure 1 and Figure 2) and/or narrative description of the contaminant sources and physical, chemical, and biological processes occurring, or that have occurred, at a contaminated site. The CSM serves as a guide to the sampling program design, interpreting existing data, and helping to identify data gaps (AEP, 2016a; CCME, 2016a).

When developing a CSM, it is important to identify all sources of soil and groundwater contamination, inferred distribution of the contaminants and mechanisms to assess potential exposure pathways (CCME, 2016a).

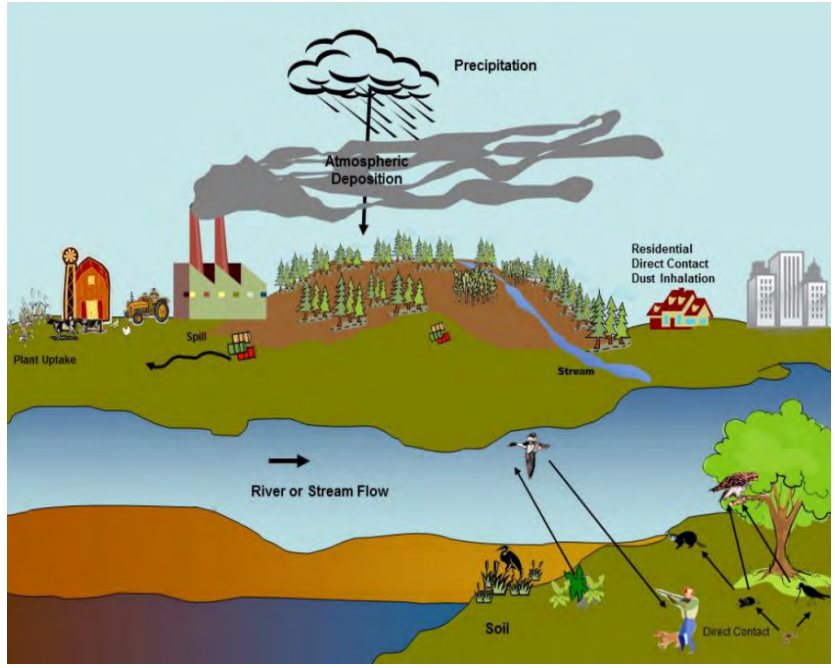


Figure 1: Generic Soil Conceptual Site Model (CCME, 2016a).

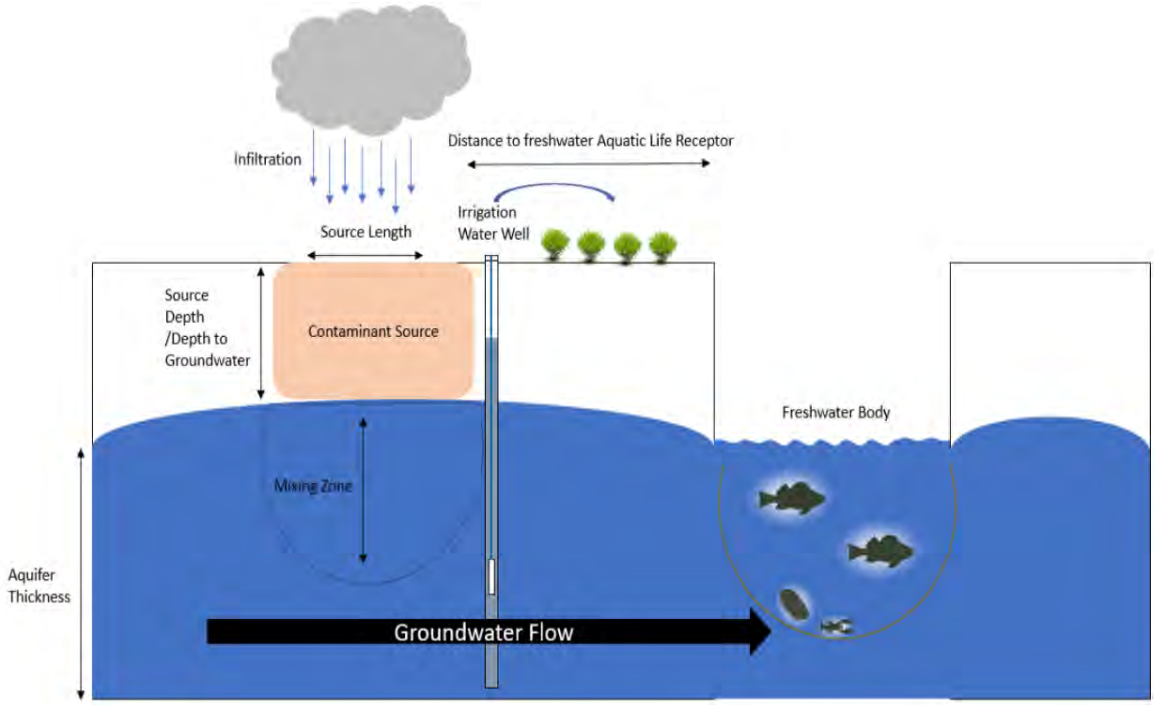


Figure 2: Generic Groundwater Conceptual Site Model based on Tier 1 and Tier 2 Guideline Models (Litalien et al., 2020).

4.0 SOIL CHARACTERIZATION GUIDANCE

Soil is the main medium within which bromacil and tebuthiuron may reside. From here it may migrate into the groundwater or surface waterbodies. Understanding the presence, extent, and characteristics of the contaminant within soil is critical in understanding the fate and potential impact to both human and ecological receptors (CCME, 2016a). Sterilant contamination in soils is often highly variable over relatively small distances, discontinuous and may be dispersed. There is a high potential for cross contamination or contaminant dilution when sampling for sterilants. This potential, plus the low-detection levels required by the guidelines, results in a greater risk of sampling error resulting in inaccurate data. Inaccurate data could affect the outcome of the decommissioning and reclamation of a site. Therefore, it is essential to obtain accurate data on the location, depth and concentrations of sterilants when designing and implementing management programs.

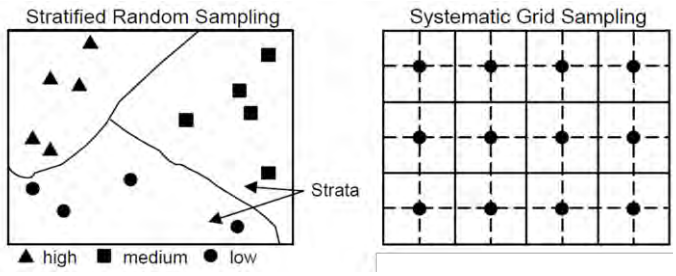
4.1 Sampling Strategies

The purpose of this section is to provide suggestions on how to develop sampling programs specific to bromacil and tebuthiuron based on the scenarios illustrated in Section 3.1, Table 3. Each scenario might consist of a preliminary assessment, delineation sampling and confirmatory sampling. When developing a soil sterilant sampling program, there are several factors that should be considered, in addition to the specific site considerations listed in Table 6. Each of the following factors should be taken into consideration when developing a site-specific sampling design:

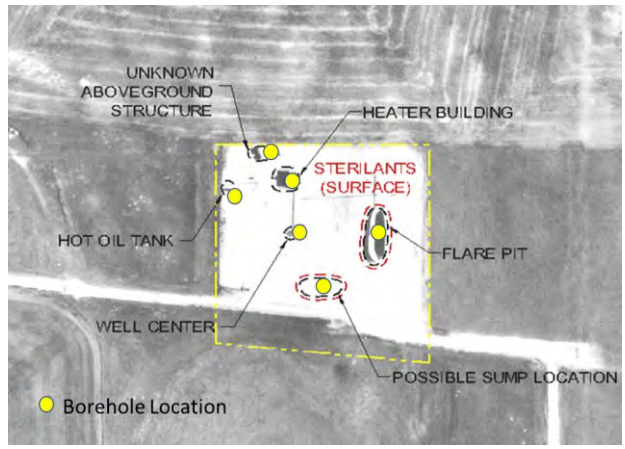
- Age of the site and time frame for sterilant application;
- Previous remedial strategies, like activated charcoal (e.g., sterilants adsorbed within upper surface soils);
- How the sterilants were applied, as sterilant application may have been to the entire site or selected areas based on the site objectives for controlling vegetation (e.g., 'hot' spots compared to entire site); and
- Was there any surficial runoff due to water erosion (e.g., ephemeral drainage channels may help sterilants migrate off-site).

In some cases, the use of statistical methods for developing your sampling design and sampling numbers may be required to increase the precision and confidence to meet the specific project objectives. Further information for developing statistical methods for sampling design can be found within the *Guidance Manuals for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment, Volume 1* (CCME, 2016a), *Guidance Document on the Sampling and Preparation of Contaminated Soil for Use in Biological Testing* (Environmental Canada, 2012) and the USEPA *ProUCL Version 5.1 Technical Guide* (USEPA, 2015).

4.1.1 Preliminary Assessment



Other potential sampling designs (USEPA, 2002).



Site diagram illustrating judgmental sampling (Photo credit Tetra Tech).

The objective of a preliminary assessment (Section 3.2.2 and 3.2.3) is to determine presence or absence and the maximum concentrations of sterilants at a site. The initial sample design is usually judgemental sampling within and outside of potential source areas identified during the Phase 1 ESA. For areas without history a stratified random sampling or stratified systemic grid sampling might be used (Carter and Gregorich, 2008; CCME, 2016a). Each of these designs have advantages and disadvantages which need to be considered depending on the specific site characteristics and study objectives. During the preliminary assessment the spacing between sample points may be larger compared to delineation sampling. Furthermore, all background samples should be collected first before initiating sampling of any potential impacted areas to minimize cross contamination.

Sampling during the preliminary assessment might only be within the rooting zone (0 mbgs to 1.0 mbgs) as sterilants were applied directly to the surface. Sampling this depth interval might capture sterilant impacts on sites that newer (e.g., <30 years old) or previously been remediated with activated charcoal. Whereas on older sites (e.g., >60 years old), sterilants may have migrated below the rooting zone and into the groundwater. Vegetation might be growing on the latter sites as the sterilant is below the rooting zone. Soil samples during this assessment should be analyzed for soil moisture, pH, texture (clay content), organic matter and salinity (electrical conductivity and sodium adsorption ratio) as these parameters may influence bromacil and tebuthiuron mobility.

When conducting off-site sampling, particularly in low areas or ephemeral drainages the spacing between sample points may need to be less than 1 m apart. This can be determined based on visual vegetation impacts, location and size of low areas and the length/width of the ephemeral drainage.

The number of samples required depends on the size of site, level of contamination and distribution of contamination. There needs to be enough samples to appropriately represent the site and characterize the concentrations of sterilants at the site. Sampling representative can be improved sample design and careful field observations (CCME, 2016a).

4.1.2 Delineation Assessment

The objective of delineation sampling is to build on the preliminary assessment to determine the horizontal and vertical extents of the contamination, used for reclamation planning and might be used to set Alberta Tier 2 guidelines. Delineation sampling should be completed using discrete samples at depths to capture the extent of the soil sterilants as they can be highly mobile (up to 6 mbgs). Due to the spatial variability of both soils, and sterilants, step outs from known impacts could range from 1 m to 5 m spacing intervals. Previous experience has shown that high concentrations of sterilants may be found at the surface or at depth within 'hot' spots, but they may diminish to below laboratory detection limits in one or so meters away (IVMAA, 1995).

4.1.3 Confirmatory Sampling

Confirmatory sampling is to verify the satisfactory completion of the remediation within the soils and/or groundwater for the accepted land use. The purpose of confirmatory sampling is to ensure that potential human health and ecological endpoints have been successfully met. In Alberta there are specific requirements for confirmatory sampling that must be followed (AEP, 2016a) following remedial activities which must be followed. The following is a list of minimum requirements for confirmatory sampling:

- Discrete samples only from excavation face and base;
- Remove the initial 5 cm of soil from the excavation surface, then collect your soil sample up to 20 cm from the excavation surface;
- One discrete sample within a grid-based on 10 m increments (5 m increments for hazardous waste);
- More close confirmatory samples are required when thin soil layers that are suspected to be contaminated; and
- Sampling techniques must minimize the loss of contaminants.

Confirmatory sampling within an excavation (Photo credit Tetra Tech).

Due to the low detection levels for Alberta Tier 1 Soil Guidelines, and potential of cross contamination, the use of 6” metal cores (similar to California split spoon) driven directly into the faces and bases of the excavation should be completed. These samples would follow the same cleaning and sampling handling procedures as the low-level delineation samples. Typically, a field screening tool is used to help select samples to be analyzed, however there currently is no reliable and effective method at this time. Therefore, all samples identified as having potential for sterilants by the sampling plan should be submitted for laboratory analysis. For cost reductions, the analysis could be staged as more information is obtained for the site.

4.1.4 Berms

Berm sampling (see Scenarios in Table 3) may be used to characterize sterilant concentrations around small berms associated with flare pits or tanks. Berms tend to be small, between 0.50 m and 1 m high, and might have other contaminants, therefore, composite sampling of the berm material may be completed. Composite sampling might consist of collecting equal portions of soil of the upper 0 to 0.15 m every 0.5 m for each wall (4 composite samples composed of at least 3 equal aliquots). These can be grab samples, where the field personnel use new nitrile gloves per composite sample, rather than cleaning equipment between each composite sample.

In addition to collecting of samples within the berms, discrete samples should be collected below the berms, downslope of the berms or in areas next to the berms that appear to have impacted vegetation as you would for surface soil investigations.

4.1.5 Stockpiles

Stockpile sampling may be used to characterize sterilant concentrations in stored topsoil/subsoil stockpiles or perimeter berm material from historical activities. Unlike berm material around tanks or flare pits this material may be used for reclamation purposes. Therefore, sampling should be conducted like a surface soil investigation with a shovel or backhoe with the exception that a combination of composites and discrete samples should be utilized. Sample depths will depend on the size of the stockpile. For small stockpiles/berms ranging from 10 m^3 to

50 m^3, one discrete sample collected per cell (2 m^3 to 10 m^3) and a composite created from a five equal portions of those discrete samples should be created. For large stockpile/berms (50 m^3 to 250 m^3) a similar method should be completed with a discrete sample representing 10 m^3 to 50 m^3 depending on the size to the pile. In addition to collecting of samples within the stockpiles, discrete samples should be collected below the stockpiles, downslope of the stockpiles or in areas adjacent to the stockpile that appear to have impacted vegetation. Table 8 summarizes the sampling and suggested number of samples to be analyzed for stockpiles.

Table 8: Guidance for Stockpile Material Characterization.
Adjusted from CCME (2016a).

Scenario	Stockpile Size	Sampling	Number of Samples Analyzed
Small Volume Stockpile	<2 m^3 to 50 m^3	1 discrete sample per cell (cell sample to represent 2 m^3 to 10 m^3) for a total of 5 discrete samples 1 composite sample combined from equal portions of the 5 discrete samples	At least one discrete sample inferred to have highest contamination and one composite sample
Large Volume Stockpile	50 m^3 to 250 m^3	1 discrete sample per cell (cell sample to represent 10 m^3 to 50 m^3) for a total of 5 discrete samples 1 composite sample combined from equal portions of the 5 discrete samples	At least two discrete samples inferred to have highest contamination and one composite sample

4.2 Soil Sampling Considerations

The following precautions should be considered when collecting any soil sample for trace level of contaminants (USEPA, 2020):

- Special care must be taken to not cross-contaminate samples.
- A clean pair of new, non-powdered, nitrile disposable gloves will be worn each time a different sample is collected. Gloves must be donned prior to sampling.
- If possible, two field personnel should be used to minimize cross contamination; one to help with cleaning field tools, taking notes, photographs, filling out labels and tags while the other collects the samples.
- Use new sample containers recently acquired from the laboratory for sampling. Glass jars with Teflon™ lids are preferred over plastic bags, as plastic bags provide less protection during transport, some chemicals can pass through the material, and potential for contamination from external sources may occur (CCME, 2016a; IVMAA, 1995).
- For delineation and confirmatory sampling, where sleeves (e.g., stainless steel, Teflon™, brass or PVC) are used within a sampler (e.g., split spoon), the sleeves should be submitted directly to the laboratory and the sampler must be cleaned following the triple rinse method.
- Soils must be scraped (dressed) to remove smeared soil prior to placing into sampling containers, unless collected directly into metal containers and sent directly to the laboratory (e.g., California split spoon). This means that all outside edges must be cleaned off to minimize the effects of cross contamination interferences due to smearing of soil from various sample depths or sampling tools.
- Sample containers with samples suspected of containing high concentrations of contaminants shall be handled and stored separately.
- All background samples will be stored separately from other samples collected at site.

4.3 Soil Sampling Methods

Soil sample methods used are planned using knowledge of site conditions (disturbed or undisturbed soils), objective of assessment, type of soil series and geological parent material and tools most suited for sampling them, costs of sampling method proposed compared to quality of sample required, and professional judgment. In Alberta, standard soil sampling methods are shovel and "Dutch" (Eikelkamp) soil auger for undisturbed soils ≤1.0 mbgs and solid stem auger >1.0 mbgs for Alberta predominant geological soil material consisting of fine-textured till. To install groundwater wells and in saturated sands, hollow stem auger is sometimes used. Wet or loose sands and gravelly materials may require specialized equipment.

There are two methods for in situ soil sampling investigations – excavations of test pits (e.g., shovel, excavator) and boreholes (e.g., Dutch ssoil auger and drilling). In practice, manual tools are usually limited to 1.0 m depth, with mechanical equipment used below. In contrast, for soil surveys, reclamation, and salinity guidelines (Alberta Environment, 2001), “topsoil” refers to the A horizon and “subsoil” refers to the B and C horizons within 1.0 mbgs for mineral soils. Within this document surface soils are defined as soils within the uppermost 1.0 m of the surface, while subsurface soils are soils greater than 1.0 mbgs. The following subsections provide suggestions for completing surface soils (≤1.0 mbgs) and subsurface soils (>1.0 mbgs) investigations to minimize cross contamination and improve accurate data collection of sterilants. Standard Alberta soil sampling methods and equipment may be suitable during the preliminary assessment stage (See Section 4.1.1), but a higher standard is required for delineation assessments (See Section 4.1.2) and confirmatory sampling (See Section 4.1.3).

4.3.1 Surface Soils (≤1.5 mbgs)

Soil investigations within the upper 1.0 m of the surface (surface soils) are important for preliminary assessment, delineation assessment, and reclamation planning. These soils could be collected and sampled for sterilants manually (e.g., a shovel and hand auger, core sampler) or mechanically (e.g., excavator, 3’ long agricultural core barrel, or split spoon). The best view of soil layers is from faces of excavations (shovel or test pit) with the second best being a continuous core. Regardless of the method used, all tools must be cleaned (See Section 6.0 – Triple Rinse) between each soil sample to reduce the potential for cross contamination among depths. Environment Canada (2012; Appendix G) and CCME (2016a; Table 5-1) provide detailed descriptions, and evaluations of various soil sampling equipment. Environment Canada (2012) also references soil sampling equipment compared to various geological materials and site conditions. The following information provides guidance specific to low level soil sampling for bromacil and tebuthiuron.

Manual Surface Soil Sampling

Manual surface soil sampling with a shovel and Dutch soil auger are used primarily to collect surface soils off-site (minimal disturbance off-site) and on-site in areas where manually digging is possible. This method is relatively inexpensive, can provide detailed soil classification and sampling by shovel only can be used for preliminary, delineation assessment and confirmatory sampling. The standard method of using a Dutch soil auger should only be used for preliminary assessments as it is not suitable for low level contaminant sampling (CCME, 2016a).

However, a modification to the standard Dutch soil auger method that can be done for low level contaminant sampling is summarized below:

- Ensure that all sampling equipment (shovel and knife) is washed with Liquinox and triple rinsed (See Section 6.0) between samples (wash and triple rinse before you start, collect a sample, wash, and triple rinse, collect a sample, wash, and triple rinse, etc.)
- Dig a hole to the desired depth with a shovel. This may be to the upper portion of the C horizon or to at least 0.60 mbgs.

- Prior to collecting soil samples, obtain a thorough field description of the soils to be sampled. These soils should be classified by soil scientist or other experienced personnel at a minimum to the Subgroup level using the Canadian Soil Classification System (CSSC) (Soil Classification Working Group, 1998). The reasons for using the CSSC classification method are:
  - CSSC classification is used for reclamation purposes for the upper soils.
  - Specific soils (e.g., Chernozems, Gleysols) are known to have specific characteristics such as higher OM content or moisture content that may influence sterilant mobility.
  - The CSSC method includes soil structure related to soil horizons (e.g., a clay Bt horizon with moderate medium, prismatic structure) unlike the Unified Soil Classification System (ASTM, 2017). Soil structure is known to influence the rate and magnitude of transport of sterilants to the groundwater (Arias-Estévez et al., 2008).

Classifying Orthic Black Chernozem with a shovel (photo credit Tetra Tech).

- Wash and triple rinse the shovel and then carefully clean off the face (sides) of the hole. You may need to wash and triple rinse the shovel more than once to ensure that potentially impacted material from the top is not clinging to the surface further down. This is to reduce the potential of cross contamination from digging.
- Collect samples by soil horizons (A, B and C) first and by depths second. The primary mineral horizons are defined as A, B, and C. The primary organic horizons are L, F, and H (forest floor or grassland litter), or O (Organic typically associated with muskegs, and bogs).
- At the base of the shovel hole use an AMS sliding hammer and cleaned core barrel lined with a sleeve to collect a soil sample. Each soil-filled sleeve should be sealed with Teflon™ tape or aluminum foil, plastic caps and labelled. The orientation (top and bottom) of the sleeve should be noted as well.
- Then use a Dutch soil auger to clean out hole and auger down to next depth. Use a cleaned (Triple Rinse) AMS sampler, core barrel and new sleeve to collect the next sample.
- Soils samples should be collected at ≤ 0.5 m intervals or at changes in soil stratigraphy to the depth of 1.0 mbgs.

Manual core sampler (photo credit AMS Samplers, 2020).

- Place samples directly into a laboratory-provided glass jar with Teflon™ lid or leave in the sleeve. Cool the samples to <4°C and transport them as soon as possible to an accredited laboratory after collection (CCME, 2016b).

Mechanical Surface Soil Sampling

Mechanical surface soil sampling maybe used off-site (minimize disturbance where possible) or on-site. There is different mechanical equipment such as a backhoe, or a drill rig with a 3” agriculture core barrel, split spoon or 3“ direct push rig that might be applicable depending on the objective of the investigation. Although each piece of equipment is different, the methodology described for manual soil sampling (e.g., triple rinse, soil classification,

sampling horizons first, laboratory containers) still applies. There are some considerations that should be examined before using mechanical surface soil sampling:

- A backhoe should only be used for preliminary assessments on-site due to the high potential for cross contamination and the high disturbance to natural soils.
  - This method is relatively less expensive compared to a drill rig.
  - Samples may be obtained from the excavation wall, only if the excavation meets applicable safety standards, or directly from the bucket at the surface.
  - When taking samples from the bucket at the surface, some precision with respect to depth and location of the soil samples may be lost, and it is hard to sample thin layers of contamination.
  - All edges of the sample should be scraped prior to placing the sample into a laboratory container.

Use of an excavator to collect soil samples (Photo credit Tetra Tech)

- A drill rig with an agriculture core barrel, split spoon or 3” direct push rig may be used for surface soils for investigations off-site and on-site.
  - An agriculture core barrel and typical split spoon should be used for preliminary assessments only.
  - Agriculture core barrels are typically 3’ long, 2” or 3” diameter stainless steel tubes. These barrels are like Shelby tubes used for unsaturated hydraulic conductivity testing except that the soil sample is pushed out of the barrel in the field to be logged and sampled. This increases the potential for cross contamination.
  - Typical split spoons may come in different lengths (e.g., 18”, 24” or 36”) and different diameters (e.g., 1¾”, 2” or 3”). There is less potential for cross-contamination with the thicker diameter samplers as there is more external soil that can be cleaned off (“dressed”). To collect a sample from the split spoon, the spoon must be opened to view the soil sample
  - These methods are typically used with a hollow stem auger. Hollow stem augers only provide a ‘snapshot’ of the soil lithology when a core or short length split spoon is used, unlike a solid stem auger that shows the lithology continuously.
  - The top few inches of material from the upper portion of an agriculture barrel or typical split spoon should be removed before collecting a sample as material tends to slough in from the borehole. The only exception would be the first sample taken at the surface, where no sloughing has occurred.

Soil sample from agriculture core barrel (Photo credit Tetra Tech).

  - Due to the potential for cross contamination from soil smearing, the outside of the soil needs to be scraped clean before a sample is collected.
  - For delineation and confirmatory sampling with a drill rig, the California split spoon or a direct push with a 3” diameter or larger core barrel, described in the following section should be used.

- Drilling is the most expensive method for collecting surface soils, however the rigs can be used off-site and on-site. Furthermore, the drill rigs can also be used for subsoil investigations as described in the following section.

4.3.2 Subsurface Soils (>1.0 mbgs)

Bromacil and tebuthiuron are mobile in the soil, thus on older sites (e.g., >60 years old) a subsurface soil investigation may be required. Subsurface investigations may be completed using different drill rigs and methods. Air rotary drills are not appropriate for sterilant sampling as there is a high degree of cross contamination occurring. Table 7 summarizes possible methods of sampling with a drill rig, depending on the objectives of the ESA.

Table 7: Subsurface Investigation Methods for Sterilant Sampling.
From (CCME, 2016a; USEPA, 2020)

Sampling Method	Description	Sampling Strategy	Considerations	Photos
Auger	Obtain samples directly from auger flights	Preliminary assessment	▪ **High** chance of cross contamination due to smearing and sloughing. ▪ Quick, but poor method for environmental sampling. ▪ Sample depth somewhat inaccurate. ▪ Sample recovery may be low in sands and gravels.	 Photo credit Tyrel Hemsley
Split Spoon (without sleeves)	Hollow stem augers with a split spoon sampler driven into the soil	Preliminary assessment	▪ **Moderate** chance of cross contamination. ▪ Common sampling technique. ▪ Discard the top portion of split spoon as it is typically sloughed material. ▪ Moderately disturbed soil sample. ▪ Sample recovery may be low in sands and gravels.	 Photo credit Brendan Guest

Sampling Method	Description	Sampling Strategy	Considerations	Photos
Split Spoon or Modified California Split Spoon equipped with sleeves	Hollow stem augers with a California split spoon sampler driven into the soil	Delineation assessment Confirmatory sampling	▪ **Low** chance of cross contamination ▪ Produces very-good quality, slightly disturbed samples. ▪ Air space above the split barrel compared to standard split-spoons. ▪ Multiple metal sleeves placed inside the split spoon. ▪ Each metal sleeve can be capped and sent directly to the laboratory. ▪ More time and additional personnel when drilling. ▪ Saturated sands and silts can be collected.	 Photo credit Kathryn Bessie
Direct Push (3" or larger)	Advances a hollow core into the soil using the weight of the rig combined with a hydraulic hammer	Preliminary assessment Delineation assessment	▪ **Low** chance of cross contamination. ▪ Continual soil core possible. ▪ Soil samples can be collected in PVC, Teflon, or stainless-steel liners that can be capped and sent directly to the laboratory. ▪ Potential for cross contamination due to smearing. ▪ Limitations due to depth and sample material. ▪ Sample recovery may be low in sands and gravels.	 Photo credit Ernco Environmental Drilling and Coring Inc.

Sampling Method	Description	Sampling Strategy	Considerations	Photos
Shelby Tube/ 3' Long Agriculture Core Barrel	Thin-walled tube with a tapered cutting head pushed into soil	Preliminary assessment	▪ **Moderate** chance of cross contamination. ▪ Cross contamination may occur when removing sample from tube. ▪ Slight to moderately disturbed soil sample. ▪ Soil typically is pushed from the tube to classify and sample. ▪ Only applicable in soft soils. ▪ Sample recovery may be low in sands and gravels. ▪ Discard the top portion of tube as soil typically is sloughed material. ▪ Agriculture core barrel is similar to a Shelby tube.	 Photo credit Tetra Tech

For preliminary assessments, there are more suggested methods available (Table 7) than for delineation and confirmatory sampling for soils below 1.0 mbgs. When conducting subsurface soil investigations, soils should be classified using a hybrid of geotechnical classifications described in the *Canadian Foundation Engineering Manual* (Canadian Geotechnical Society, 2006) and environmental descriptors (e.g., moisture content, colour, mottles, soil composition, odour) (CCME, 2016a) as they are outside of the rooting zone and are not for reclamation planning. Drilling should be started in areas least likely to be contaminated to prevent cross contamination. Discrete soil samples should be collected in 0.5 m intervals (where possible) or changes in soil stratigraphy. The change in soil stratigraphy is always first over the depths. The same equipment cleaning procedures (See Section 6.0 Triple Rinse) and soil cleaning procedures (Section 4.1) should be completed prior to placing the sample into the sampling container.

Backfill the lower portion (up to the top of perceived water table) of the borehole with bentonite chips so that cross contamination will not occur. Ensure that there is no bentonite used within 1 m of the surface. Use cuttings to backfill the upper portion of the borehole and replace the topsoil, if any.

Due to the high potential for cross contamination and low detection limits for bromacil and tebuthiuron, there are special sampling techniques that should be used when collecting delineation samples. These special sampling techniques are:

An example of a hollow stem drill rig (Photo credit Kathryn Bessie).

Hollow Stem with California Split Spoon

- Samples should be collected using a hollow stem auger, in conjunction with an 18" split barrel spoon containing three 6" x 2.5" stainless steel or brass sleeves every 1.0 m down to a depth of 7.5 m or until bedrock.
- When using a hollow stem auger, determining the soil lithology can be difficult as the California split spoon sampler is not continuous like a solid

stem auger. Therefore, additional split spoons between sampling intervals may be required to help classify the soils while drilling. Once a sample has been collected, the field personnel can visually verify the soil lithology within the 6" metal sleeve via the opening at the top and bottom of the sleeve without disturbing the soil core.

- Each soil-filled sleeve should be sealed with Teflon™ tape or aluminum foil, plastic caps and labelled. The orientation (top and bottom) of the sleeve should be noted as well. These will be sent directly to the laboratory on a chain of custody (COC) for analysis.
- Between each sample, clean the split barrel sampler using the triple rinse method outlined in Section 6.0.

Direct Push Drill Rig with ≥3" Diameter Core Barrel

- Samples should be collected using a ≥3" diameter core barrel with PVC, Teflon™, brass or stainless-steel sleeves.
- Direct push drill rig provides a continuous soil core, thus making it easier than hollow stem drilling to view the lithology. The sleeves with soil samples could be cut, sealed with Teflon™ tape or aluminum foil, plastic caps, labelled and shipped directly to the laboratory. Another method is to open the sleeves in the field, scrape the outer portions of the soil core, collect a soil sample and place into a glass jar.
- Consideration when using this method is that the sleeves are kept clean prior to use. Any debris or soil may contaminate the soils collected within the sleeve.

An example of a 3" soil core
(Photo credit Ernco Environmental Drilling and Coring Inc)

Further information for soil characterization, and sampling can be obtained from other standard operation procedures (ASTM in Appendix B; CCME, 2016a). Specialized sampling equipment could be obtained from AMS Inc. (e.g., stainless steel, brass and PVC sleeves) or Hoskin Scientific Ltd. (e.g., Dutch soil augers, split tube sampler) depending on the equipment required.

4.4 Quality Assurance and Quality Control

The purpose of quality assurance and quality control (QA/QC) is to limit errors and bias in sampling and analysis through implementation of management, assessment and control measures (CCME 2016a). General guidance for developing QA/QC programs for sampling can be found within the *Guidance Manuals for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment, Volume 1* (CCME, 2016a). The purpose of this section is to highlight areas specific for assessing precision and accuracy of the data collected for sterilants through relative percent differences (RPD) and field duplicates.

Field duplicates should be collected for soils, such that at least 1 sample per every 10 samples (10% of the samples) is collected. The samples selected as duplicates should have relatively high levels of contamination, when possible, so that there is an ability to check for precision (CCME, 2016a). Collection and analysis of decontaminated equipment rinsate should be completed to document the absence of cross contamination (CCME, 2016a).

The RPD values are used as a measurement of precision of the data collected. RPDs should be interpreted as a quantification of field variability of parameter concentrations on a micro-scale for homogenized samples Laboratory RPDs are typically lower than field RPDs due to the added variability introduced in the matrix variability, sampling, and handling (CCME, 2016a). Soils tend to be more variable than water thus an RPD of 60%

may be suitable when sterilant concentrations for the samples is in the parts per million (ppm) range. Near the detection limit (parts per billion), the acceptance criteria can be relaxed (CCME, 2016a) resulting in an RPD of 75% to 100%. The purpose of these RPDs is to highlight possible parameters with poor precision.

Quality assurance and quality control procedures for the soil sampling program should also include the following per field sampling trip:

- One water trip blank, prepared by the laboratory per shipping container;
- One field blank, using distilled water and an amber glass jar to confirm the presence or absence of cross contamination during field activities;
- One equipment blank to confirm the presence or absence of cross contamination during sampling. This equipment blank is completed by pouring distilled water over the cleaned sample equipment and collecting the water into an amber glass jar for analysis; and
- Collect a rinse water sample from the 5th (last) gallon pail to demonstrate the effectiveness of the cleaning procedure.

5.0 GROUNDWATER CHARACTERIZATION GUIDANCE

Groundwater investigation programs are required when migration of contaminants to the groundwater cannot be clearly ruled out or if contaminants exceed Alberta Tier 1 Guidelines for any of the groundwater or surface water pathways (AEP, 2016a). Bromacil and tebuthiuron are highly mobile and have shown to migrate into the groundwater on level to nearly level sites. Furthermore, if the irrigation pathway for bromacil and tebuthiuron or the protection of aquatic life for tebuthiuron is applicable then a groundwater investigation is required as per Alberta Tier 1 Guidelines.

This section builds on information provided in Section 4.0 Soil Characterization Guidance and adds specific information related to groundwater characterization for bromacil and tebuthiuron. Further information for groundwater characterization, sampling, and well installation can be obtained from other standard operation procedures (Appendix B – American Society for Testing and Materials Standards; CCME, 2016a).

5.1 Sample Design Strategies

Groundwater investigations require properly designed monitoring wells to measure groundwater levels and collect groundwater samples that accurately represent in situ groundwater conditions at the point of sampling. Monitoring wells may also be used to test hydraulic properties of formations in which they are completed. To successfully meet the objectives of a groundwater monitoring program, proper monitoring well design is required, and the development of a preliminary hydrogeological CSM that identifies potential flow paths and target monitoring zones, is recommended during the initial assessment. The CSM will then be updated and/or revised with additional soil and hydrogeological data collected during the supplemental and delineation assessments.

5.1.1 Preliminary Assessment

During the preliminary assessment, the objective of the groundwater characterization program is to determine the depth to groundwater, groundwater flow direction, hydraulic gradient (both horizontal and vertical), velocity and groundwater quality. A minimum of four groundwater monitoring wells should be installed and the number of monitoring wells should be increased depending on the size of the site.

5.1.2 Delineation Assessment

A more detailed groundwater investigation maybe warranted, depending on the site-specific groundwater characteristics and contaminate concentrations in both soil and groundwater. This assessment should address spatial, and temporal characterization of the groundwater flow conditions and quality, and delineation of groundwater contamination. High-quality samples yielding reliable, precise, and accurate chemistry data should be collected at this time by establishing discrete sampling points in different lithological units containing water and using the low-flow sampling procedure (ASTM, 2018b; CCME, 2016a).

5.1.3 Confirmatory Sampling

After remediation, if groundwater contamination was identified in the previous assessments or if required due to the presence of the aquatic life pathway (tebuthiuron) or irrigation pathway (bromacil and tebuthiuron) then confirmatory sampling in the groundwater is required (AEP, 2016a). In Alberta, the following are specific requirements when conducting confirmatory sampling for groundwater:

- Groundwater monitoring and sampling to confirm the contaminants meet Alberta Tier 1 and Alberta Tier 2 objectives post-remediation;
- To confirm if groundwater contaminants meet these applicable criteria, three groundwater monitoring events that at least span two years and reflect seasonal differences must be completed; and
- The frequency may be reduced if contaminant concentrations decrease, until the applicable criteria are met.

5.2 Groundwater Sampling Considerations

For groundwater sampling, the same precautions for minimizing sample cross contamination, and cleaning procedures for all equipment outlined under Section 4.2 should be used, where applicable to groundwater. The following precautions are added from Section 4.2 specific to collecting groundwater samples for sterilants:

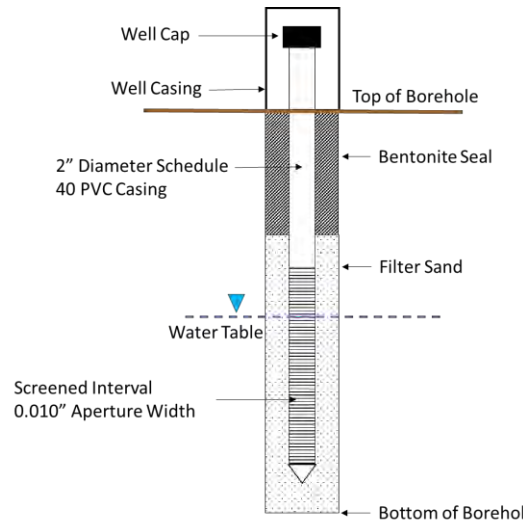
- When sampling groundwater, samples must be placed in an amber glass bottle with Teflon ™ lined lids bottles supplied from the laboratory. Water samples should be placed into a cooler and cooled to <4°C and transported as soon as possible to an accredited laboratory after collection (CCME, 2016b).
- Whenever possible, samples should be collected facing downwind to minimize introduction of contamination (USEPA, 1995).
- Only open the container when you will be adding the groundwater, and close promptly once filled.

5.3 Investigation Groundwater Methods

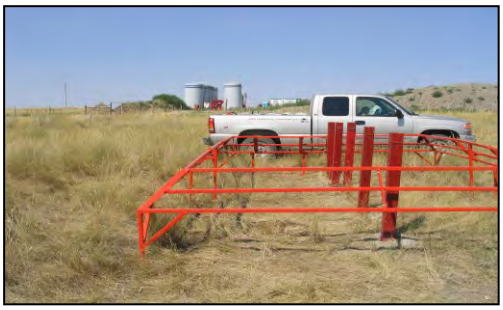
Information on the soil sampling methods while installing groundwater monitoring wells can be found within Section 4.0. The following subsections describe specific features for installing wells, screen selection, purging, and sampling of wells that should be used when investigating for sterilants.

5.3.1 Monitoring Well Installation and Screen Selection

Groundwater monitoring wells should be constructed and installed using methods and materials that minimize the effects of the chemical, biological, and physical properties of the groundwater samples as well as for accurate measurement and collection of hydraulic properties of the formations in which they are completed. Groundwater monitoring wells on contaminated sites should be drilled and installed with extra care to minimize the potential for cross contamination. Wherever feasible, the drilling equipment should be washed and decontaminated between each drilling location. Monitoring wells must be designed and constructed to minimize the potential for fluids to flow into or between distinct permeable formations for the expected life, and following decommissioning, of the monitoring well.



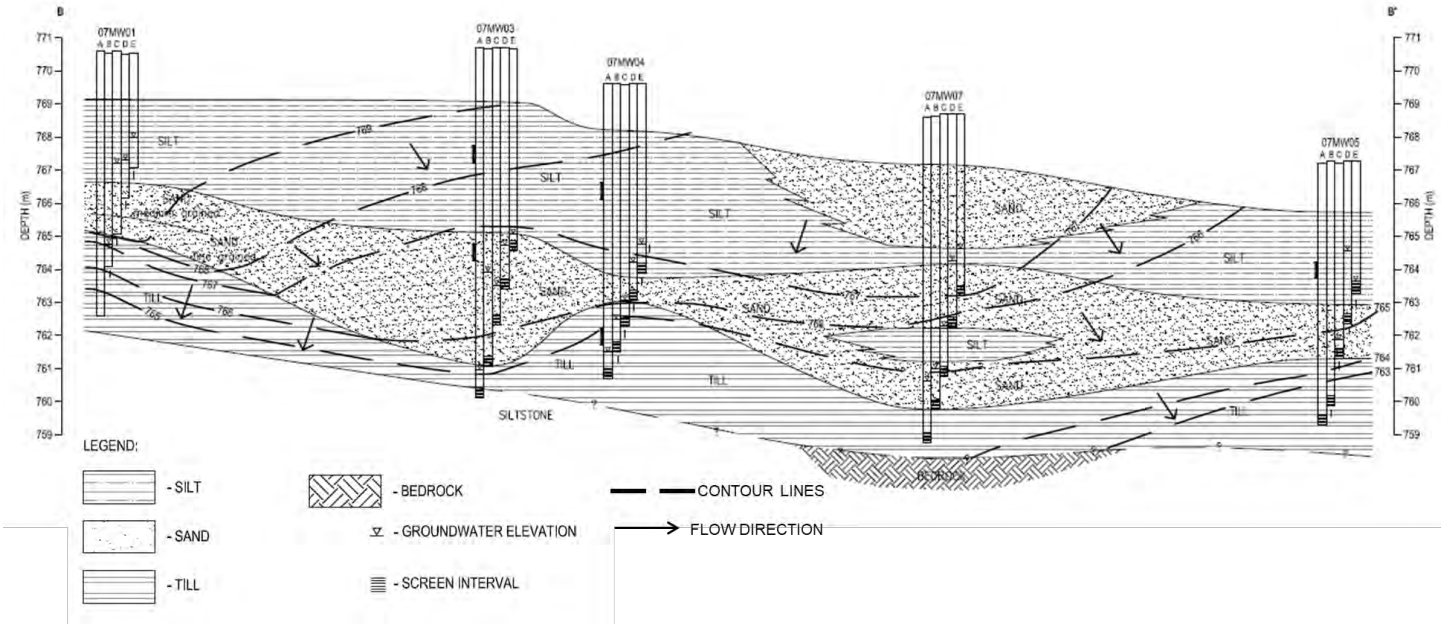
Basic well installation (Photo credit Tetra Tech).



Five nested monitoring wells in layered sediments (EBA, 2009a, b).

Stainless Steel Points (0.3 m long) (EBA, 2009a, b).

Standard operating procedures should be followed when installing groundwater wells and selecting screen intervals for most situations. In unconsolidated material where multiple lithological units containing water are present, screening each discrete unit should be considered for sampling. There may be times when site specific characteristics, such as sand lens with variable thickness may also require special considerations for discrete sampling with depth and therefore installation of multi-screen monitoring points. For example, to assess the vertical groundwater flow system and vertical profile of sterilant concentration leaching from surface into a variable thickness silt and sand layers at an LL & E "B" Pool Battery, five monitoring wells were constructed of a 0.3 m long section of stainless-steel screen approximately 0.25 m in diameter. The monitoring wells were placed at regular depth intervals extending from the water table to the top of the underlying bedrock. To select the depths for placement of the monitoring points initially a borehole was drilled using solid stem augers to the target depth. All monitoring points were placed in individual boreholes and pushed in place beneath the augers to ensure the monitoring point is in direct contact with the soil zone to be monitored (EBA Engineering, 2009a, b).



Example of lithology with five nested monitoring wells layered in sediments (EBA, 2009).

5.3.2 Well Development

In general, well development should not introduce water into the well, or disturb annular well seals. It is good practice to allow a stabilization period after well construction to allow groundwater levels to equilibrate and sealants to cure/hydrate (ASTM, 2010). Development using only bailing (pumping) moves water one way through the well screen and is generally less effective at removing fine materials or stabilizing sand filter packs and formations. The use of a Waterra Pump with a surge blocker may be more effective; development is achieved by moving water alternatively in both directions through the well screen (ASTM, 2005).

It is important to use new nitrile gloves and material (e.g., Watterra tubing and surge blocker with foot valve) for each well and to dispose of the material after well development in an appropriate manner to minimize cross contamination. Water from well development should be placed into a storage container, removed from site, and disposed of in an appropriate manner.

5.3.3 Monitoring, Purging and Sampling

When conducting groundwater monitoring, purging and sampling all equipment used in the well must be cleaned following the Triple Rinse procedure outlined in Section 6.0 before the liquids have dried on the surfaces and new nitrile gloves worn for each well and each new task (e.g., monitoring, purging, sampling).

During the preliminary assessment use of a bailer would be appropriate in determining presence and absence of sterilants in the groundwater. However, when conducting a delineation and confirmatory sampling, low flow purging and sampling is suggested for sterilants. Low flow purging and sampling can provide more accurate and reproducible samples of the formation water quality than using high flow/high volume purging and sampling methods. Low flow purging, and sampling allows for the obtaining groundwater samples with minimal sampling-induced turbidity which is important in silt, clay and silt-clay formations. Low flow sampling can reduce

the volume of purge water reducing the issue for disposal or contamination of surface soils. Additional information on use of low flow purging and sampling can be found in ASTM (2018b).

When sampling deep groundwater (> 10 m) a low flow sampling system may not be effective. In these situations, a new clean bailer or Waterra tubing may be used to collect a groundwater sample.

5.4 Quality Assurance and Quality Control

The purpose of quality assurance and quality control (QA/QC) is to limit errors and bias in sampling and analysis through implementation of management, assessment, and control measures (CCME, 2016a). General guidance for developing QA/QC programs for sampling can be found within the *Guidance Manuals for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment, Volume 1* (CCME, 2016a). The purpose of this section is to highlight areas specific to assessing precession of data collected for sterilants through relative percent differences (RPD) and number of filed duplicates.

Quality assurance and quality control procedures for the groundwater sampling program should include the following:

- One trip blank per shipping container and one field equipment blank per day to confirm the presence or absence of cross contamination during field activities, travel, or laboratory analysis;
- Collect a rinse water sample from the 5th (last) gallon pail to demonstrate the effectiveness of the cleaning procedure;
- One field duplicate for every 10 samples (10% of the samples); and
- Obtain at least two groundwater samples on different days from any monitoring well prior to making decisions based on the chemistry data as groundwater chemistry may change over time (CCME, 2016a).

The RPD values are used as a measurement of precision on the data collected. In groundwater, the RPDs for sterilants could range from 20% (CCME, 2016a) to 40% depending on if the samples are in the ppm range (20%) or ppb range (40%).

6.0 SAMPLING EQUIPMENT CLEANING METHODOLOGY

There is a high potential for cross contamination when sampling for sterilants. Care must be taken to thoroughly clean sampling equipment before the collection of each sample. An alternative mechanical method that might be available on site for cleaning equipment is the use of a water truck with a high-pressure wand or a steam truck. All washing of equipment with this method must be completed within a containment container. The water then must be tested before being released to meet applicable guidelines or disposed of off-site.

Although the above mechanical method may be used, the suggested method of cleaning sampling equipment is to use the Triple Rinse method (ASTM, 2020) outlined below. The following is a list of equipment and methods for completing the Triple Rinse method.

Triple rinse cleaning method setup (Photo credit Tyrel Hemsley).

Equipment

- Liquinox and distilled water
- Four 5-gallon pails
- Nitrile gloves
- One scrub brush (long handle and proper size for equipment)

Triple Rinse Method

1. Clean all 5-gallon pails with distilled water and Liquinox before use.
2. Partially fill a 5-gallon pail with distilled water, add Liquinox and mix.
3. Set up another three 5-gallon pails and partially fill each with distilled water (enough water to submerge sampling equipment).
4. Immerse sampling equipment in Liquinox/water mixture (first 5-gallon pail), scrub equipment thoroughly and shake off excess moisture.
5. Then rinse the equipment in each of the remaining three 5-gallon pails.
6. Rinsing should be from most dirty to the cleanest pail.
7. Decontamination wash and rinse water should be collected and contained for appropriate disposal.

As washing and rinsing water becomes contaminated, dispose of the water as per Step 7 then repeat Steps 1 to 6. Water should be changed regularly to minimize the potential for cross contamination.

7.0 FIELD SCREENING, SAMPLING PACKAGING AND LABELING, AND ANALYTICAL

7.1 Field Screening Tools

Currently there are no reliable and practical field screening methods for bromacil and tebuthiuron. An antibody-based enzyme-linked immunosorbent assay (ELISA) test was developed for bromacil detection in the 1990s but was not cost effective and had production issues (Drozdowski et al., 2018b). Field screening methods are being further investigated as part of the SSP (French et al., 2021a, b).

7.2 Sample Packaging and Labelling

Samples should be placed into a cooler and kept cool at <4°C. Each sample container (soils or groundwater) should be labeled with a waterproof black marker prior to commencing sample collection or pre-made labels. The following are suggestions for information to be included on labels, where applicable:

- The legal land location of the field sampled: Quarter – Section – Township – Range – West of Meridian;

- Project name and number;
- The test pit, borehole or monitoring well location;
- The soil sample depth interval;
- The name or initials of the sampler(s);
- The date and time of sample collection;
- Company conducting the sampling.

All samples should be documented with a chain of custody when being submitted to a laboratory.

When submitting labelled sleeves directly to the laboratory, special instructions should be given to the labs. These instructions would be that this is an undisturbed core, in which the labs subsample for analysis should be collected directly from the interior of the sleeve after removing the cap and scraping off outer soil. After this, the sample might be extruded and prepared or used for other soil analysis like salinity and particle size analysis.

7.3 Bromacil and Tebuthiuron Analysis

Analytical labs in Alberta typically use method for water (USEPA, 2018; Gas Chromatography/Mass Spectrometry) or for soils (USEPA, 2007; High Performance Liquid Chromatography/Mass Spectrometry) to analyze for sterilants. Methods are modified depending on the lab conducting the analysis, thus resulting in different detection limits (Drozdowski et al., 2018b). For example, the bromacil detection limit in soils at one laboratory may be 0.0045 mg/kg, while at another it may be 0.008 mg/kg. Knowing the detection limits of the laboratory is especially important with low level guidelines. The Alberta Tier 1 Guideline for bromacil is 0.009 mg/kg, thus if we used the laboratory with the 0.008 mg/kg detection limit there is an increased likelihood of making a Type I Error (missing a problem that is present). Laboratory method improvements have been developed as part of the SSP (Pereira et al., 2022).

Where activated charcoal was added to topsoil or subsoil for remediation treatment, the current laboratory methods use strong solvents that provide “total” concentrations of bromacil and tebuthiuron. This leads to detection of the compounds even though they may be adsorbed onto the activated charcoal. The SSP program has developed a less rigorous extraction method for quantification of “bioaccessible” fraction of the contaminant (Maxwell, 2022). Any soils that had activated charcoal and/or other organic amendments added to them should be analyzed for total organic carbon and organic matter as well as routine analysis (pH and soluble salts) to aid in interpretation of the results. Particle size analysis is also recommended.

8.0 DATA ASSESSMENT AND INTERPRETATION

Data assessment and interpretation is continuous during the soil and groundwater characterization. As new information becomes available it should be added to the CSM to aid in its development and understanding of the contaminant at the site (CCME, 2016a). Data should be evaluated against the current Alberta Tier 1, Tier 2, or Site-Specific Guidelines to assess the potential concern to receptors and if those concerns have been remediated or managed through a risk assessment and/or administrative control.

To help in evaluating and interpreting data, figures or drawings should be used as they help tell the story. Figures should include the following (CCME, 2016a):

- a scaled regional location plan and site plan, showing relevant hydrological, topographical, and physiographic features;
- a contour plan of piezometric heads in each aquifer of interest and monitoring periods, with data points posted at measurement locations on each drawing;
- stratigraphic cross sections that are longitudinal and transverse with respect to the known or estimated hydraulic gradients, and groundwater flow direction, and that include physical conditions (e.g., stratigraphy, water table, piezometric surface elevations, groundwater flow velocity, etc.);
- contours, in plan and cross section, of chemical concentrations that show the specific lateral and vertical distribution of each contaminant of concern in on-site and off-site soil and groundwater;
- sample locations with corresponding analytical results used to develop each figure, that are shown on the figure and in tabular form with reference to applicable criteria; and
- well completion details should be summarized and presented in a table.

Another tool is to use descriptive statistics and graphs (e.g., box plots with concentrations per 'hot' spot), as they may be useful in summarizing the data and providing visual representations of temporal and spatial distribution of sterilants at the site. These can be used to guide and refine further sampling efforts. With the collection of more data, statistics can be used to evaluate the population characteristics of the data. For example, percentiles can be calculated to help identify elevated concentrations (e.g., hot spots), which may not have been otherwise detected (CCME, 2016a). Further information in using statistics can be found within the *Guidance Manuals for Environmental Site Characterization in Support of Environmental and Human Health Risk Assessment, Volume 1* (CCME, 2016a) and the USEPA *ProUCL Version 5.1 Technical Guide* (USEPA, 2015).

Overall, no two sites are identical, and it is up to the qualified practitioner(s) to use professional judgement in interpretation of the data and select the most appropriate way to present, interpret and report the data.

9.0 ACKNOWLEDGEMENTS

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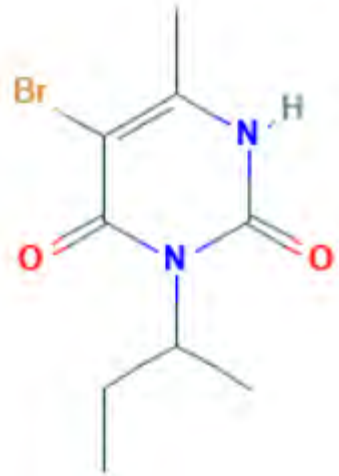
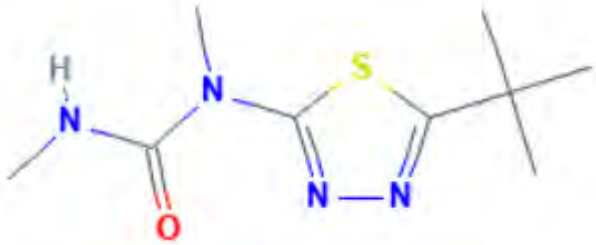
APPENDIX A: PROPERTIES OF BROMACIL AND TEBUTHIURON

Consult Marquez et al. (2020) for more details on the original sources for the information in the table.

Parameter	Bromacil[1]	Tebuthiuron[2]
Chemical Name	5-bromo-3-(butan-2-yl)-6-methylpyrimidine-2,4(1H,3H)-dione	1-(5-tert-Butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea
Physical and Chemical Characteristics	• Molecular Formula: $C_9H_{13}BrN_2O_2$ • Molecular weight: 261.12 g/mol • Melting point: 158 to 160 °C • Solubility in water: 815 mg/L at 25 °C; Solubility increases under both low and high pH conditions • Vapour pressure: 3.1×10^{-7} mm Hg • Koc of 66.6 mL/g (this value is used in Alberta Tier 1 guidelines). Koc: ranges from 2.3 to 289 mL/g in sand to peat soils	• Molecular Formula: $C_9H_{16}N_4OS$ • Molecular weight: 228.32 g/mol • Melting point: 161.5 to 164 °C • Solubility in water: 2,500 mg/L at 25 °C • Vapour pressure: 2.0×10^{-6} mm Hg at 25 °C • Koc of 23 mL/g (this value is used in Alberta Tier 1 guidelines although Oak Ridge National Laboratory now lists Koc as 42.2 mL/g. Koc: ranges from 4 to 620 mL/g
Structure		
Adsorption/Desorption	• Sorption lower than other herbicides • In soil, sorption increases with clay and organic matter (OM) content and decreased pH • Does not partition to suspended particles or sediments in aquatic systems, remaining dissolved in water column	• Relatively poorly sorbed to soil • In soil, sorption is higher in soils high in organic matter content followed by clay content which is the case for most chemicals • <1% at soil organic matter of 0.3% and 40% with soil OM of 4.8%

Parameter	Bromacil[1]	Tebuthiuron[2]
Degradation	• Microbial degradation was not considered important for bromacil. However, other studies have shown microbial degradation to have a relatively short half-life (less than one year). One study indicated bromacil at 8 parts per million (ppm) had a half-life of about 6 months in aerobic loam soil. Another study, however, identified that only 10% of bromacil applied at 3 parts per million (ppm) had degraded to carbon dioxide (CO_2) after 330 days in an aerobic sandy loam soil. Under anaerobic conditions, the study calculated a half-life of 145 days in sandy loam soil under saturated conditions. In a second test in the same study, only approximately 53% of added bromacil was still present as the parent compound after 115 days. Sterilized samples in these tests showed no signs of degradation, indicating that the degradation was microbial. • Stable to photolysis in soil and water at low pH but may be photolyzed in water under alkaline conditions. • Degradation in natural waters may occur through microbial and photo-sensitized degradation • Aerobic and anaerobic metabolites have been identified.	• Rates and relative importance of microbial degradation are variable. Microbial degradation of up to 67% was reported. • Tebuthiuron anaerobic and aerobic degradation is very slow with a calculated half-life of 35.4 months. While one author considered tebuthiuron was stable to degradation in soil, other studies show when conditions are optimized, tebuthiuron degradation is occurring. • Photodegradation occurs, although it may be of limited importance especially in soils. • One study discussed degradation pathways and investigated heterotrophic microbes in soil with the ability to degrade tebuthiuron. • Co-metabolism (non-specific microbial degradation) is important. • Aerobic and anaerobic metabolites have been identified.

Parameter	Bromacil[1]	Tebuthiuron[2]
Half-life	• Field derived soil dissipation half-life is 349 days (average from the literature). • Soil dissipation half-life is 132 days (average from the literature (aerobic). Under anaerobic conditions, bromacil appeared to degrade a half-life of approximately one month based on an aquatic study, though this study had several major deficiencies that call into question the validity of this information. Under anaerobic conditions, the study calculated a half-life of 145 days in sandy loam soil under saturated conditions. • Measured or estimated half-life values from the literature range from 12 to 46,200 days, with most measurements between 100 and 350 days. • Varies with the number of applications in a season and over time (4 to 6 months with a single application).	• Highly persistent in soils; soil half-life increases in arid and semi-arid environments with low annual precipitation and in soils high in organic matter. Soils high in organic matter, however, are likely to have lower bioavailability. • Soil half-life: 12 to 15 months in areas receiving high annual rainfall (takes longer in areas receiving less rainfall) and in soils high in organic matter. • Measured or estimated half-life values from the literature range from 20 to 1,050 days, with the majority of measurements between 100 and 400 days.

APPENDIX B: ASTM (AMERICAN SOCIETY FOR TESTING AND MATERIALS) STANDARDS

General

ASTM D5088. Standard Practice for Decontamination of Field Equipment Used at Waste Sites.

Soils

D2487 Standard Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System).

D2488. Standard Practice for Description and Identification of Soils (Visual-Manual Procedure).

D1452 Standard Practice for Soil Exploration and Sampling by Auger Borings.

D1586 Standard Test Method for Standard Penetration Test (SPT) and Split-Barrel Sampling of Soils.

D3550 Standard Practice for Thick Wall, Ring-Lined, Split Barrel, Drive Sampling of Soils.

D4220 Standard Practices for Preserving and Transporting Soil Samples.

D4700 Guide for Soil Sampling from the Vadose Zone.

D5784 Standard Guide for Use of Hollow-Stem Augers for Geoenvironmental Exploration and the Installation of Subsurface Water-Quality Monitoring Devices.

D6001 Standard Guide for Direct-Push Groundwater Sampling for Environmental Site Characterization.

Groundwater

D2466 Standard Specification for Poly (Vinyl Chloride) (PVC) Plastic Pipe Fittings, Schedule 40.

D2467 Standard Specification for Poly (Viny Chloride) (PVC) Plastic Pipe Fittings, Schedule 80.

D4044/D4044M-15. Standard Test Method for (Field Procedure) for Instantaneous Change in Head (Slug) Tests for Determining Hydraulic Properties of Aquifers.

D4050 Standard Test Method for Withdrawal and Injection Well Tests for Determining Hydraulic Properties of Aquifer Systems.

D4106 Standard Test Method for Determining Transmissivity and Storage Coefficient of Nonleaky Confined Aquifers by the Theis Nonequilibrium Method.

D4448 Standard Guide for Sampling Ground-Water Monitoring Wells.

D4630 Standard Test Method for Determining Transmissivity and Storage Coefficient of Low-Permeability Rocks by In Situ Measurements Using the Constant Head Injection Test.

D4696 Guide for Pore-Liquid Sampling from the Vadose Zone.

D4750. Standard Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation Well).

D5092 Standard Practice for Design and Installation of Ground Water Monitoring Wells.

D5521/D5521M-18. Standard Guide for Development of Ground-Water Monitoring Wells in Granular Aquifers.

D6089 Standard Guide for Documenting a Groundwater Sampling Event.

D6452 Standard Guide for Purging Methods for Wells Used for Groundwater Quality Investigations.

D6634/D6634M-14 Standard Guide for the Selection of Purging and Sampling Devices for Groundwater Monitoring Wells.

D6699 Standard Practice for Sampling Liquids using Bailers.

D6771 Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations.

D7929 Standard Guide for Selection of Passive Techniques for Sampling Groundwater Monitoring Wells.

APPENDIX A2: LABORATORY METHOD INVESTIGATION FOR DETECTION OF BROMACIL AND TEBUTHIURON IN WATER AND SOIL

Periera, A.D.S, E.D. Ruan and G. Knox, 2022. Laboratory Method Investigation for Detection of Bromacil and Tebuthiuron in Water and Soil. Report SSP-3 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 38 pp.

Laboratory Method Investigation for Detection of Bromacil and Tebuthiuron in Water and Soil

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EXECUTIVE SUMMARY

Soil sterilants are non-selective broad-spectrum herbicides that were used historically at industrial facilities in Alberta. Bromacil and tebuthiuron were those most used in Alberta and despite halting application in the 1990s, they continue to be found at concentrations exceeding regulatory guidelines in soils and groundwater. Bromacil and tebuthiuron are unique and challenging to manage as contaminants of concern, especially at sites destined for regulatory closure. To address multiple challenges associated with these parameters, the Soil Sterilants Program (SSP) was designed as a suite of applied research projects to address various challenges in the assessment, risk management and remediation of soil sterilants.

This project was designed to address gaps related to laboratory analytical methods for bromacil (CAS 314-40-9) and tebuthiuron (CAS 34014-18-1) in water and soil matrices. Gaps identified include detection limits very near Alberta Tier 1 soil and groundwater remediation guidelines, elevated analytical costs and a variety of analytical methods in use. The project was carried out by InnoTech Alberta's Chemical Testing laboratory.

Development of test methods to increase the effectiveness and efficiency in laboratory analytical methodologies for detection of total bromacil and tebuthiuron focused the following attributes:

1. High selectivity for the analyte(s) of interest
2. Method Detection Limits at least two orders of magnitude below Alberta Tier 1 Guidelines for soil and groundwater
3. Complete recovery, for analysis, of the analyte(s) of concern from the matrix containing the analyte(s)
4. High degree of Trueness (i.e., accuracy and precision)
5. Cost-effective (use less solvents)
6. High throughput for the sample preparation compared to liquid-liquid extraction

The approach for this project focused on two components of the chemical measurement process: optimization of extraction approach and instrumentation.

The literature review identified considerable differences between the analytical methods cited in the literature and those used by the commercial laboratories in Alberta. The methods in the commercial laboratories are mainly based on liquid chromatography with ultraviolet detection (LC-UV), liquid chromatography coupled to mass spectrometry (LC-MS), and gas chromatography coupled to mass spectrometry (GC-MS). Most of the literature between 1984 and 2020 also uses the same analytical techniques, however in the last years methods have moved from simple UV detection and low-resolution mass spectrometry to high-resolution mass spectrometry. Sample preparation has also moved from solvent extractions to solid-phase extraction (SPE) or accelerated solvent extraction (ASE) processes.

Based on the information gathered through the review of literature and outreach program, InnoTech proposed the use of the Liquid Chromatography coupled to tandem mass spectrometry (LC-MS/MS) and/or high-resolution mass spectrometry (LC-HRMS) using an Orbitrap mass spectrometer. The choices of the LC-MS/MS and/or LC-HRMS as possible solutions to improve the effectiveness and efficiency of the analytical methods for bromacil and tebuthiuron is based on the high throughput, excellent accuracy, and

better sensitivity. The methods are the ideal platforms for the quantification of compounds in complex matrices and multiclass risk compound screening.

A new analytical method was successfully developed and validated for analysis of bromacil and tebuthiuron with detection limits between two and three orders of magnitude lower than available through commercial laboratories.

In soil samples, the bromacil detection limits in commercial laboratories are ≥ 5 µg/kg where the new method presented here has a validated minimum detection limit of 0.013 µg/kg using the LC-MS/MS and 0.032 µg/kg using the LC-Orbitrap-MS. For tebuthiuron, the detection limits in commercial laboratories are ≥ 5 µg/kg where the new method presented here has a validated minimum detection limit of 0.003 µg/kg using the LC-MS/MS and 0.006 µg/kg using the LC-Orbitrap-MS.

In water samples, bromacil detection limits in commercial laboratories are ≥ 0.1 µg/L where the new method presented here has a validated minimum detection limit of 0.0001 µg/L using the LC-MS/MS and 0.00006 µg/L (or 0.6 ng/L) using the LC-Orbitrap-MS. For tebuthiuron, the detection limits in commercial laboratories are ≥ 0.1 µg/L where the new method presented here has a validated minimum detection limit of 0.000004 µg/L (or 0.04 ng/L) using the LC-MS/MS or using the LC-Orbitrap-MS.

The validated limit of quantification in soils for bromacil was 0.1 µg/kg and for tebuthiuron 0.01 µg/kg, and for water samples, the limit of quantification for bromacil was 0.0005 µg/L (or 0.5 ng/L) and for tebuthiuron 0.00005 µg/L (or 0.05 ng/L).

Water and soil samples were extracted, concentrated, and purified by using solid phase extraction (SPE) and Accelerated Solvent Extraction (ASE) procedures, respectively. A method of liquid chromatography-tandem mass spectrometry (LC-MS/MS) was developed for the determination of bromacil and tebuthiuron. Soil and water recovery rates were between ~70 and 130% (RSD < 10 %). The optimized method with high throughput and less solvent has been safely and successfully applied for field samples with limited matrix interference, and results were comparable to current commercial laboratory results.

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1.0 INTRODUCTION

Soil sterilants are non-selective broad-spectrum herbicides used primarily for vegetation control at industrial sites. In Alberta, the use of these compounds for vegetation control began in the 1960s and continued for more than three decades before being halted in the late 1990s. As a result, soils treated with sterilants for many decades may act as a continuous source of contamination (Schwarzenbach et al., 2003).

Despite decades of residence time, two main sterilants (bromacil and tebuthiuron) have been found impacting soil and groundwater on or near industrial sites in Alberta, where they were initially applied to surface soil (Drozdowski et al., 2018). The two compounds have low sorption coefficients (Koc and Kd) and are highly soluble in water and are therefore very mobile in the environment. In many cases, they have become highly dispersed in soil, and can also be found in groundwater – for bromacil the primary routes of dissipation appear to be photolysis in water under alkaline conditions and microbial degradation in anaerobic soil (USEPA, 1996). Soils with residual sterilants may act as a continuous source of contamination to industrial sites and their surroundings (Humburg et al., 1989).

Regulatory guidelines for bromacil and tebuthiuron are conservative, with very low permissible concentrations based on their potential impact on vegetation and aquatic vegetative species. Alberta Tier 1 guidelines for bromacil and tebuthiuron are as follows:

- Bromacil: 0.009 mg/kg (soil); 0.0002 mg/L (water)
- Tebuthiuron: 0.046 mg/kg (soil); 0.00043 mg/L (water)

Bromacil and tebuthiuron are unique and challenging to manage as contaminants of concern, especially at sites destined for regulatory closure. To address multiple challenges associated with these parameters, the Soil Sterilants Program (SSP) was designed as a suite of applied research projects to address various challenges in the assessment, risk management and remediation of soil sterilants.

This project was designed to address gaps related to laboratory analytical methods for bromacil (CAS 314-40-9) and tebuthiuron (CAS 34014-18-1) in water and soil matrices. Gaps identified include detection limits very near Alberta Tier 1 soil and groundwater remediation guidelines, elevated analytical costs and a variety of analytical methods in use. The project was carried out by InnoTech Alberta (InnoTech)'s Chemical Testing laboratory.

To address these problems, InnoTech proposed the use of the Liquid Chromatography coupled to tandem mass spectrometry (LC-MS/MS) and/or high-resolution mass spectrometry (LC-HRMS) as Orbitrap mass spectrometer. The choices of the LC-MS/MS and/or LC-HRMS as possible solutions to improve the effectiveness and efficiency of the analytical methods for bromacil and tebuthiuron is based on the high throughput, excellent accuracy, and better sensitivity. The methods are the ideal platforms for the quantification of compounds in complex matrices (Wang et al., 2019) and multiclass risk compound screening (Kong et al., 2018).

The scope of work for the Project was as follows:

1. To complete a review of literature for analytical methods used for the analysis of soil sterilants.

2. To develop a validated analytical method for analysis of bromacil and tebuthiuron in soil samples with a method detection limit of 100 ng/kg or less.
3. To develop a validated analytical method for analysis of bromacil and tebuthiuron in water samples with a method detection limit of 5 ng/L or less.
4. Statistically compare the results from the new methods with those currently in use by InnoTech Alberta and others. This will be achieved by the comparison of the results obtained from the analysis of "blind" samples.
5. Evaluate the new method for cost, throughput, waste production and safety.
6. Provide method details to external laboratories for potential adoption.

2.0 LITERATURE REVIEW

The review is divided in three sections, including extraction methods; chromatographic methods; and mass spectrometric techniques. A total of 59 publications were found using the Scopus and Web of Science databases: bromacil (34 publications); tebuthiuron (25 publications); and both compounds (4 publications). Distribution of the publication dates is shown in Figure 1.

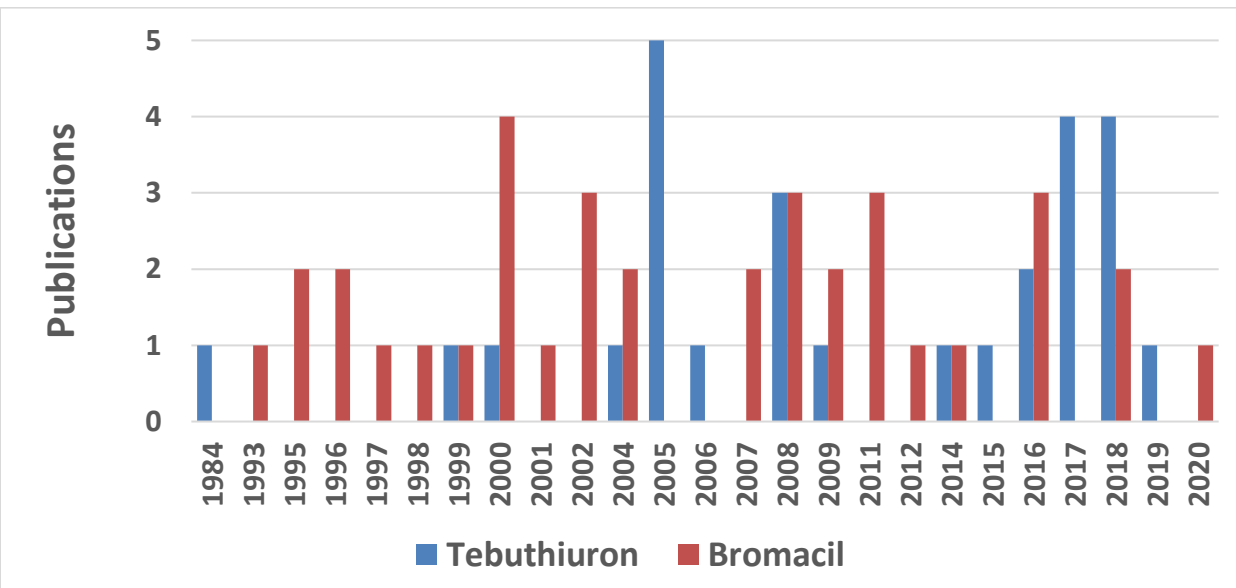

Figure 1. Distribution of the publication dates found in the Scopus and/or Web of Science databases.

2.1 Extraction Technique

In the past decades great advancement has been made in achieving highly efficient separation of sterilants from a sample matrix with high selectivity and sensitivity. Different extraction methods are employed, including solvent extraction from soils and liquid-liquid extraction from water. Poor sample treatment or roughly prepared extracts will invalidate a total analysis and will make it impossible to gain a valid result even by use of the most powerful separation method. So, correct sample preparation can be economically valuable as well as analytically important. The distribution of the different extraction procedures used for bromacil and/or tebuthiuron by year from these publications is shown in Figure 2.

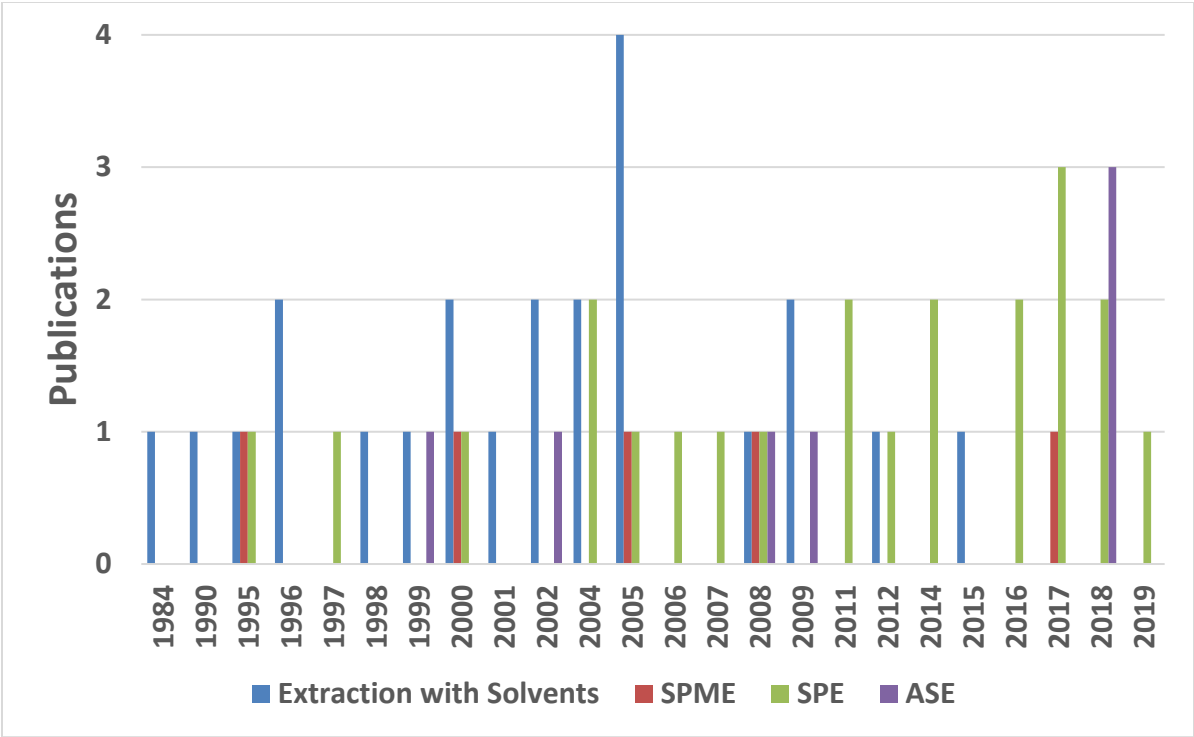

Figure 2. Distribution of the publication dates of different extraction procedures used for bromacil and/or tebuthiuron in the literature.

2.1.1 Solvent Extractions

Since analysis of sterilants in soil samples is difficult due to the analyte's low concentrations and the presence of interfering compounds in the matrix, sample pre-treatment comprising sieving, grinding and drying is often necessary to obtain homogeneous samples and reliable results. In this review 23 papers using solvent for extraction (e.g., Liquid-Liquid, Soxhlet, etc.)(Baranowska and Pieszko, 2002; Bonato et al., 1999; Brondi and Lanças, 2004; Cerdeira et al., 2005; Close et al., 2008; De Barreda et al., 1996; Ferracini et al., 2005; Furtula and Kuo, 2004; Graber et al., 2001; Ibáñez et al., 2011; Indelman et al., 1998; James and Lauren, 1995; Kudo et al., 2012; Linde et al., 1996; Macur et al., 2000; Matallo et al., 2005; Matos et al., 2015; Ogiyama et al., 2002; Saraji and Tansazan, 2009; Sarmah et al., 2009; Smith et al., 1984; Toiber-Yasur et al., 1999; Zhu et al., 2000) were found. Solvent extraction (SE) methods have some drawbacks such as: laboriousness, expense; requirements for evaporation of large volumes of toxic eluent; and time to complete. However, these methods are accepted and popular for sample preparation due to their relative simplicity (Table 1).

2.1.1.1 Solid-liquid extraction

Solid-liquid extraction is the separation of a solid solute from a mixture of solids by dissolving it in a liquid phase. There are three components in leaching: solid solute, insoluble solids, and solvent. In most cases, the diffusion of intra-particle soluble component(s) controls the extraction rate. Therefore the process is often called diffusion extraction. These conventional extractions have been used for many years, although they have many drawbacks: they require the use of high quantities of expensive and pure solvents since during the process they consume a high amount; they have a low selectivity of extraction, and they are generally characterized by long extraction times and by the thermal decomposition of thermolabile

compounds. To overcome all these limitations, new and promising solid-liquid extraction techniques, which are defined as less conventional, such as ultrasound-assisted extraction (UAE).

Table 1. Comparison of solvent extraction methods.

Technique	**Characteristics**	**Advantages**	**Disadvantages**
Soil Samples			
Solid-Liquid	Time: 30 min to 18 h. Sample: 1 to 30 g. Solvent Volume: 100 to 300 mL. Mechanical and ultrasonic shaking.	Performed at room temperature to avoid degradation of some pesticides.	Large consumption of solvent. Filtration or centrifugation is required. Clean-up required.
Soxhlet	Time: 3 to 48 h. Sample: 1 to 30 g. Solvent Volume: 100 to 500 mL.	No filtration required after extraction. Well-known procedure.	Long extraction time. Large consumption of solvent. Clean-up required.
Water Samples			
Liquid-Liquid	Time: 30 min to 4 h. Sample: 0.1 to 1 L. Solvent Volume: 100 to 300 mL. Manual, mechanical and ultrasonic shaking.	Performed at room temperature to avoid degradation of some pesticides.	Large consumption of solvent.

UAE uses ultrasonic energy (> 20 kHz) for extraction using either an ultrasonic bath and/or an ultrasonic probe. It works on the principle of making cavitation bubbles that collapse and produce higher shear, which results in complete extraction. Ultrasound accelerates the mixing of the components and facilitates contact between the extracted material and fresh solvent, as well as continuous removal of the stagnant layer barrier. Also, ultrasound contributes to the fragmentation of the extracted material and thus to the enhancement of its exposure to the solvent. It also enlarges the cell pores so that the cells are penetrated by the solvent faster. All the above processes result in an accelerated mass exchange between the material and the solvent, resulting in increased extraction yields.

2.1.1.2 Soxhlet extraction

The Soxhlet extractor, designed in 1879 by Franz von Soxhlet, consists of a round bottom flask, siphon tube, distillation path, expansion adapter, condenser, cooling water inlet, cooling water outlet, heat source, and thimble. In this method, a powdered sample is enclosed in a porous bag or "thimble" made from a strong filter paper or cellulose, which is placed, is in the thimble chamber of the Soxhlet apparatus. The extraction solvent is placed in the round bottom flask and heated by using a heating source like a heating mantle. The heating temperature is based on the solvent employed to extract. Due to heat, the solvent in the bottom flask vaporizes into the condenser and then drips back to the sample thimble. When liquid content reaches the siphon arm, the liquid contents are emptied into the bottom flask again and the end of the process is indicated by a clear solution in the siphon tube. The benefit of this system is that instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled. This method is not suitable for thermolabile compounds as extended heating may lead to the degradation of compounds. This method maintains a relatively high extraction temperature with heat from the distillation flask, and the high recovery is achieved by the displacement of transfer equilibrium by frequently carrying fresh solvent into contact with the solid matrix.

2.1.1.3 Liquid-liquid extraction (LLE)

Liquid/liquid extraction or solvent extraction is a method to separate compounds based on their relative solubility within two different immiscible liquids. The mechanism of this process is selective transfer of a substance from one phase toward the other. Without any amphiphilic molecules, and under usual conditions (room temperature and atmospheric pressure), a hydrophobic organic solvent and water form two phases in equilibrium. Therefore, for a given solute, the polarity will be determined by its solubility in one phase. The more polar solutes dissolve preferentially in the more polar solvent and the less polar solutes in the less polar solvent.

LLE is a simple technique commonly used in water samples, approved by the US Environmental Protection Agency (EPA). However, despite routine applications of LLE as the official method of choice of the EPA, there are some limitations associated with this technique. One of the larger criticisms of the method is directed towards its lack of 'greenness'; LLE needs large amounts of organic solvents, which in addition to being expensive and hazardous, increase potential environmental pollution.

During the last few decades, modern techniques, (e.g., sorption methods such as solid-phase extraction (SPE)) have been proposed to reduce sample handling and toxic waste, maximize the recovery of the analytes and minimize the accompanying interferences by use of appropriate extraction procedures. Figure 2 clearly shows the trend, mainly in the last 10 years, of replacing the use of solvent extraction techniques with Sorption Methods and Accelerated Solvent Extraction (ASE).

2.1.1.4 Accelerated solvent extraction (ASE)

Accelerated solvent extraction (ASE) employs conventional organic solvents at elevated temperatures above their atmospheric boiling points. A restriction or backpressure valve ensures that the solvent remains as a liquid but has enhanced solvation power and lower viscosity and hence a higher diffusion rate. By employing this method, the extraction procedure can be carried out in minutes on a smaller sample, considerably speeding up the sample pre-treatment. It requires a small fraction (20% to 30%) of previous solvent volumes. An essential feature of this system is the ability to carry out multiple extractions and so move towards automation. The extracts are usually much more concentrated than those obtained by conventional extractions. They can be analyzed directly, or the solvent can be cooled, and the analyte

trapped on glass beads or a cartridge and subsequently extracted into a smaller solvent volume. Raising the temperature causes an increase in the extraction rate because the viscosity and the tension of the solvent are decreased, increasing the rate of diffusion into the analyte.

The use of ASE in comparison to classical solvent extraction methods (e.g., Soxhlet extraction), reduces extraction time and solvent consumption, resulting in a greener sample preparation method and previously was successfully applied for the sample preparation for the sterilant analysis (Alavi et al., 2008; Pinto and Lanças, 2009; Rimayi et al., 2018; Su et al., 2018; Zhu and Li, 2002).

2.1.2 Solid-phase Extraction (SPE)

Solid-phase extraction is accepted as an alternative extraction-clean up which involves the use of disposable cartridges to trap the analyte and separate it from the bulk of the matrix. The adsorbent materials in the SPE procedure play a significant role in achieving greater enrichment efficiency and lower cost of organic solvents.

A wide range of phases means that polarity, hydrophobicity, or ionization can be used as trapping mechanisms and the sample matrix may now be non-polar or aqueous. Once trapped, the analyte can be released into a small volume of an extraction solvent by altering the polarity or pH.

James and Lauren (1995) successfully used C_{18} SPE columns for the analysis of bromacil in groundwater, with an estimated detection limit of 0.01 µg/L. Additionally, at least 19 other publications successfully used SPE for the preparation of water samples for analysis of bromacil and/or tebuthiuron (Brondi and Lanças, 2004, 2005; Casado et al., 2018; Cotton et al., 2016; De Souza et al., 2019; Duarte et al., 2018; Gomes et al., 2006; Hernandez et al., 2000; Hernández et al., 2004; Hu and Chen, 2016; Li et al., 2007; Nurmi and Pellinen, 2011; Pitarch et al., 2016; Prete et al., 2017; Scott, 1993; Tagert et al., 2014; Tarley et al., 2016; Troiano et al., 1997; Wilson and Boman, 2011; Zhang et al., 2014).

SPE is now a widely used sample preparation method and is included in US EPA reference methods, such as method 527 for the analysis of pesticides (including bromacil) in drinking water (Price et al., 2005).

2.1.3 Solid-Phase Microextraction (SPME)

In solid-phase extraction, it is still necessary to extract the sample from the column, usually using an organic solvent, before it can be analyzed. This last step, and the requirement of an organic solvent, were eliminated in the SPME method where a fibre coated with a stationary phase is used as the extraction medium. After carrying out extraction from a sample solution, the fibre can be placed in the injection port of a gas chromatograph, and the analytes can be thermally desorbed directly into the carrier gas stream. SPME also has been interfaced with High-Performance Liquid Chromatography (HPLC) and Liquid Chromatography coupled to Mass Spectrometry (LC-MS) to analyze compounds that are non-volatile and thermally unstable. In this system, an SPME-HPLC interface equipped with a specific desorption chamber is used before LC separation instead of thermal desorption in the injection port of the GC. SPME was used successfully and applied to the analysis of bromacil and tebuthiuron in several studies at concentration levels of 0.1 µg/L or lower (Boyd-Boland and Pawliszyn, 1995; Brondi et al., 2005; Hernandez et al., 2000, 2008; Scheel and Tarley, 2017).

2.2 Chromatographic Methods

Chromatographic methods include high-performance liquid chromatography (HPLC), gas chromatography (GC), thin-layer chromatography, and supercritical fluid chromatography. LC and GC are the cornerstones of the methods that have been published for the determination of bromacil and tebuthiuron in soil and water samples (Figure 3).

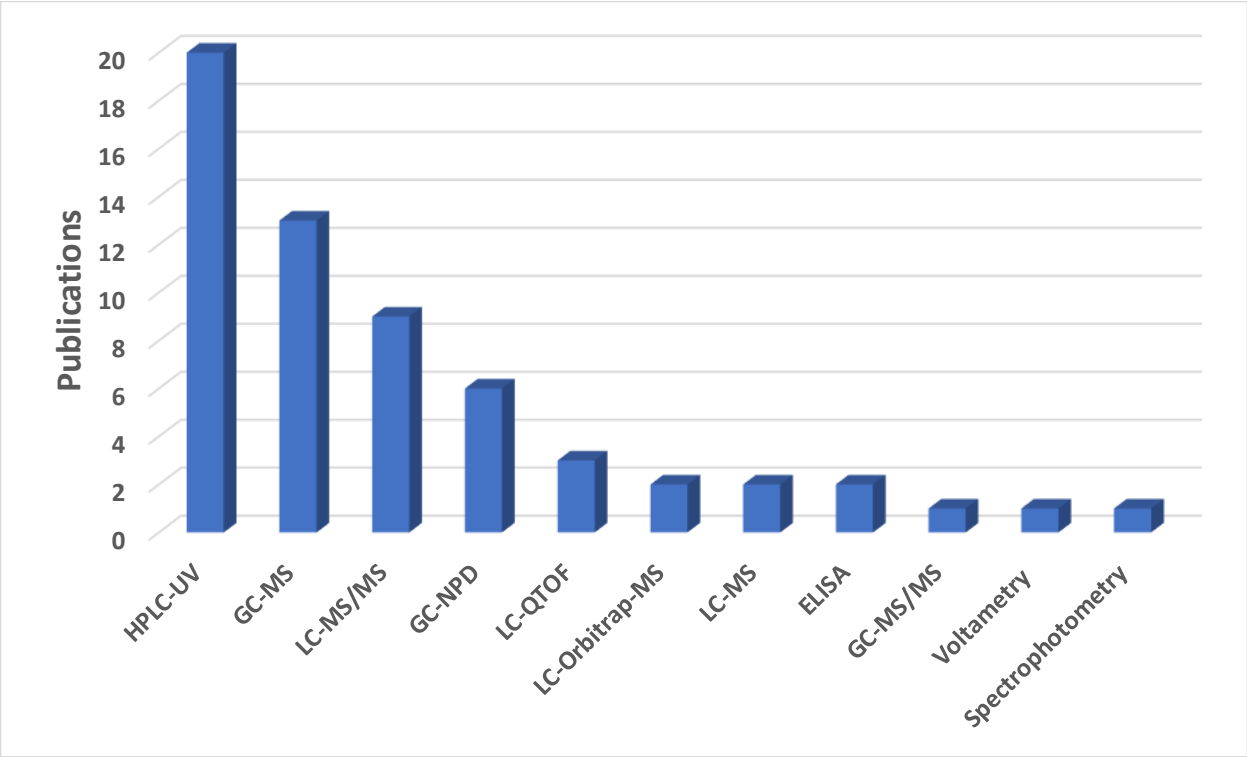

Figure 3. Frequency of use of the analytical methods used for bromacil and/or tebuthiuron in the literature.
HPLC-UV = High Performance Liquid Chromatography coupled to Ultra Violet Detector; GC-MS = Gas Chromatography coupled to Mass Spectrometer; LC-MS/MS = Liquid Chromatography coupled to Tandem Mass Spectrometer; GC-NPD = Gas Chromatography coupled to Nitrogen and Phosphorus Detector; LC-QTOF = Liquid Chromatography coupled to Quadrupole Time-of-Flight Mass Spectrometer; LC-Orbitrap-MS = Liquid Chromatography coupled to Orbitrap Mass Spectrometer; LC-MS = Liquid Chromatography coupled to Mass Spectrometer; ELISA = Enzyme-linked Immunosorbent Assay; GC-MS/MS = Gas Chromatography coupled to Tandem Mass Spectrometer.

2.2.1 High-performance Liquid Chromatography (HPLC)

Reverse-phase (RP) HPLC and ultraviolet (UV) detection have been extensively used for the separation and determination of pesticide residues, including bromacil and tebuthiuron. In reverse-phase HPLC, the separation technique is characterized by hydrophobic interactions from the analyte with the stationary phase and hydrophilic interactions from the analyte with the mobile phase depending on the proportion of organic solvent in the mobile phase.

Smith et al. (1984) used reverse-phase LC with UV detection at 254 nm and reported a quantification limit for tebuthiuron of around 0.1 µg/g (for a 25 g soil sample). James & Lauren (1995) used UV at 280 nm and reported a detection limit for bromacil of 0.01 µg/g (for a 50 g soil sample).

The main advantage of the LC-UV analytical method is its applicability to virtually any organic compound, regardless of its volatility or thermal stability, and it is also a simple and robust analytical technique. However, during recent years, a significant decline in reports of LC-UV for the analysis of pesticides in environmental samples was observed, mainly due to the lack of selectivity and the possibility of matrix interferences.

2.2.2 Gas Chromatography (GC)

Since the early 1970s, most routine pesticide residue analysis has been conducted using gas chromatography (GC) in combination with either an electron capture detector (ECD), a nitrogen-phosphorous detector (NPD), and/or a flame photometric detector (FPD). The GC-NPD method has been used for the determination of bromacil in water with a detection limit of 0.4 µg/L (Boyd-Boland and Pawliszyn, 1995). GC-NPD was used to support field studies of transport and leaching of bromacil in soil (De Barreda et al., 1996; Graber et al., 2001; Indelman et al., 1998; Toiber-Yasur et al., 1999). For GC analysis, the samples were injected to the system using split, splitless, on-column, or PTV (programmed temperature vaporization) injectors, mainly in cold splitless or in solvent vent mode.

Nowadays, GC still plays an important role, however, regulatory compliance requires that the analytical results be of guaranteed quality. Consequently, the identity of the analyte must be firmly established to avoid false-positive results. For this reason, the NPD and UV detectors have been replaced by mass spectrometry detectors. This can be seen in Figure 4 which shows the distribution of the analytical methods reported in the literature from 2011 to 2020. However, scientifically valid methods for analysis at trace levels are currently still often very close to the method's limits of detection (LODs).

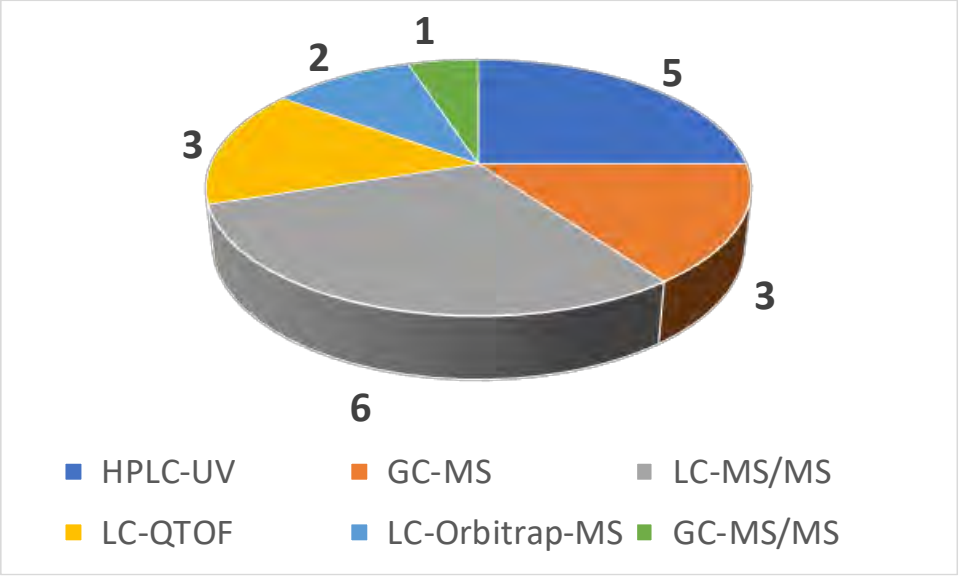

Figure 4. Frequency of the methods used for the analysis of bromacil and/or tebuthiuron reported in the literature.

2.3 Mass Spectrometry (MS)

2.3.1 Electron Ionization (EI)

The choice of mass spectrometric ionization technique is largely dependent on the introduction technique. Each has its own advantages and disadvantages. Several ionization techniques have been used in GC-MS over time; electron ionization (EI) is the most popular and widely used. EI provides valuable information on the molecular structure (from fragment ions and, in some cases, molecular ions). It is a robust and universal ionization source that generates highly reproducible spectra that can be searched in available commercial spectral libraries for the identification of non-target compounds. It is the most widely used means of ionization for pesticide residues analysis employed following GC separation and has been successfully applied for the analysis of bromacil and/or tebuthiuron (Alavi et al., 2008; Bonato et al., 1999; Boyd-Boland and Pawliszyn, 1995; Cerdeira et al., 2005; Close et al., 2008; Hernandez et al., 2000; Li et al., 2007; Ogiyama et al., 2002; Tagert et al., 2014; Wilson and Boman, 2011; Zhu and Li, 2002; Zhu et al., 2000). For example, Boyd-Boland and Pawliszyn (1995) found GC-MS reduced the detection limit (based on the signal to noise) for bromacil to 0.1 ng/L (based on the standard solution at 10 ng/L) from 400 ng/L (based in the standard solution at 10 µg/L) using the GC-NPD.

The determination of GC-amenable pesticides in water and soil samples by using tandem MS with a triple quadrupole (QqQ orTQMS) analyzer has emerged in the last decade as a valuable approach. This method allows higher selectivity and sensitivity and minimizes or eliminates most chromatographic interferences. GC using the tandem mass spectrometry (MS/MS) operation mode is the ideal analytical technique because it allows the certainty of identification of each detected compound. Chang et al. (2016) successfully validated a method based on the GC-MS/MS with a LOQ of 5 ng/g in shellfish.

2.3.2 Electrospray Ionization (ESI)

The combination of liquid chromatography and mass spectrometry occupies a prominent place in environmental organic analyses and surpasses GC-MS mainly in the analyses of polar pesticides and herbicides. Compared to traditional detectors, electrospray (ESI) mass spectrometry instruments have increased the sensitivity of LC detection by several orders of magnitude. Using ESI ionization, it is possible to obtain the protonated or deprotonated molecule with very rare fragment ions. This is an advantage as the MS-fragmentation pattern is a powerful tool, which gives confidence in identifying a parent compound. MS fragmentation can be achieved using a single quadrupole by increasing the pre-analyzer extraction (skimmer cone) voltage. However, by using tandem MS (MS/MS) detection, more selective fragmentation of the protonated or deprotonated molecule is achieved by collision-induced dissociation (CID). In addition, both sensitivity and selectivity in trace analysis are also increased with the technique. The utilities of the MS/MS and GC-MS/MS techniques derive from:

1. Selection the characteristic ion for each pesticide;

2. Obtaining qualitative structural information about the sample from the product ion spectrum; and

3. Increasing the signal-to-noise ratio by eliminating interfering matrix ions in the product ion spectrum during isolation. In fact, this technique is particularly useful for the analysis of complex mixtures, as it allows the separation and identification of pesticides at trace levels in the presence of many interfering compounds even with widely different concentration levels.

Troiano et al. (1997) used LC-MS/MS to successfully evaluate the contamination of 11 pesticides in groundwater in California, where the detection limit of the method for bromacil was 0.05 µg/L. Zhang et al. (2014) used a single solid-phase extraction and LC–MS/MS detection to develop a method for determining 5 sulfonylurea, 8 phenoxy acid, 12 triazine and 6 other selected herbicides in a range of environmental waters in Australia; this included bromacil with a LOD of 5 ng/L. Using SPE with 3 mL/500 mg C-18 cartridges and LC-MS/MS, De Souza et al. (2019) quantified 14 pesticides including tebuthiuron (LOD of 6 ng/L) in source water samples and drinking water samples from the city of Londrina, Paraná State, Brazil.

2.3.3 High Resolution Mass Spectrometry (HRMS)

The most common approach to the determination of organic compounds in environmental samples is targeted analysis using mass spectrometry (MS) focusing on known or suspected compounds.

Optimised extraction methods are used to isolate and concentrate the target analytes with subsequent analysis involving gas chromatography (GC) or liquid chromatography (LC) linked to MS. The obvious limitation of targeted analysis is that it requires a predetermined list of known compounds. Targeted analysis will only determine the selected compounds and exclude other compounds originating from a point source or the environment.

LC-triple quadrupole tandem MS (LC/MS/MS) enables highly selective and sensitive quantification and confirmation of hundreds of target pesticides in a single run, but this approach requires extensive compound-dependent parameter optimization and cannot be used to screen for untargeted pesticides.

Full scan approaches using high performance time-of-flight (TOF) or Orbitrap mass spectrometers coupled to ultra-high-performance LC's (U-HPLC) facilitate rapid and sensitive screening and detection of LC-amenable pesticide residues present in a sample. The use of electrospray ionisation (ESI) and high-resolution mass spectrometry (HRMS) has revolutionised the analysis of complex mixtures allowing the exact masses of individual molecules to be determined. The ionisation of intact molecules and their mass analysis using instruments with high resolving power and high mass accuracy mean that each ion in a spectrum potentially corresponds to a unique compound, considering adducts and isotopes, in addition to the commonly observed protonated molecules, sodium, potassium, and ammonium adducts are often encountered.

Time of flight mass spectrometry (TOF-MS)

LC coupled to time-of-flight mass spectrometer (TOF-MS) has resolving power that enables mass-measurement accuracy for small molecules, charge-state identification of multiply-charged ions, and greater differentiation of isobaric species (two different compounds with the same integer mass but different elemental compositions and therefore, different exact masses). The TOF-MS instrument represents a powerful tool for identifying nontarget compounds in complex environmental matrices because of three important characteristics:

1. The ability to collect data across a wide range of different analytes without a decrease in sensitivity;

2. The possibility of resolving interferences away from signals of interest with high resolving power; and,

3. The achievement of mass-measurement accuracy adequate for the estimation of elemental composition.

The Q-TOF-MS combines the simplicity of a quadrupole MS with ultra-high efficiency of a TOF analyzer. The TOF side always achieves simultaneous detection of ions across the full scan mass range (sensitivity). The Q-TOF-MS configuration is considered a high-resolving power instrument capable of 20,000 to 80,000 of resolution power (Full Width at Half Maximum; FWHM), and mass accuracy less than 2 ppm. Product-ion spectra can be obtained with either data dependent acquisition or data independent acquisition modes, where the instrument automatically switches after a full-scan mode acquisition to a product-ion scan mode as the second scan event in the scan cycles.

Nurmi and Pellinen (2011) developed a multiresidue method for screening emerging contaminants in aquatic environments based on SPE for sample preparation and analysis with an ultra-performance liquid chromatograph time-of-flight mass spectrometer (UPLC/TOF-MS) where the detection limit reported for bromacil was 6.5 ng/L. Ibáñez et al. (2011) used UPLC–TOF-MS for the discovery and proposal of structures for transformation products of bromacil in water subjected to chlorination.

Orbitrap high resolution mass spectrometry

An ion trap/Orbitrap (LTQ Orbitrap) instrument is a combination of two different mass spectrometer types. It has excellent detection and identification ability for compounds with a range of molecular weights from 50 to 2000 Da, even in complex matrices, where endogenous matrix components of similar mass may be co-eluted. High resolution and high mass accuracy are the keys in these applications, limiting the risk of false identifications. The Orbitrap high-resolution MS (HRMS)/MS is superior to the traditionally used low-resolution MS methods, allowing the quantification and confirmation of a theoretically unlimited number of analytes in a single analytical run. Additionally, isobaric compounds that differ in elemental composition can be distinguished even in the most complex matrices. Along with quantitative analysis and target screening, it also allows the identification of nontarget compounds and retrospective data evaluation.

Apart from mass accuracy provided by Orbitrap Fourier transform MS technology, the confirmation of positive findings was also based on MS/MS fragmentation and isotope abundance, used to reduce the number of possible formulas for a given mass (Zubarev and Makarov, 2013).

The resolving power of the Orbitrap Elite analyzer at InnoTech Alberta has been increased almost 10-fold to 240,000 at m/z 400 compared to the Q-TOF.

Using the Orbitrap Q-Exactive instrument, Cotton et al. (2016), developed a method that enables the simultaneous semi-quantitative analysis of 539 compounds (pesticides and drug residues), in 36 min with only 5 mL of water. Method validation was achieved through studies of repeatability, selectivity, linearity, and matrix effect, with LODs of 5 ng/L for bromacil and 1 ng/L for tebuthiuron. Also using an Orbitrap Q-Exactive, Casado et al. (2018) developed and validated a quantitative targeted screening method for determination of residues of a broad group of more than 250 pesticides in surface water samples. Substances were isolated from the sample matrix by SPE using hydrophilic-lipophilic balanced polymeric sorbents (HLB) and analyzed by reverse-phase LC-Orbitrap-MS. Compounds were quantified in full scan acquisition mode, while accurate data-dependent (MS^2 - which in turn separates the fragments by their m/z ratio and detects then) analysis was simultaneously triggered for the unambiguous identification of the targeted substances. This method has validated LOQs of 10 ng/L for bromacil and 1 ng/L for tebuthiuron.

3.0 INTERVIEWS/SURVEY WITH COMMERCIAL ANALYTICAL LABORATORIES

Commercial analytical laboratories in Alberta were contacted and asked to fill in a questionnaire (shown in Appendix A). As shown in Table 2, the commercial analytical laboratories use LC-MSD, LC-UV and GC-MS. Sample preparation includes liquid-liquid extraction (LLE) and solid phase extraction (SPE) based on US EPA reference methods, in some cases 25 years old.

Table 2. Extraction and analysis methods information received from Alberta commercial analytical laboratories.

Laboratory	**Water**	**Soil**
Element	Liquid-liquid extraction with dichloromethane; centrifuged, filtered, and concentrated for analysis using LC-MSD (for more information see Appendix B). Report Limit: bromacil and tebuthiuron 0.1 µg/L.	Extraction performed with shaker using methanol; centrifuged, filtered, and concentrated for analysis using LC-MSD (for more information see Appendix B). Report Limit: bromacil 8 ng/g and tebuthiuron 5 ng/g.
AGAT Laboratories	120 mL samples extracted by SPE, and concentrated for analysis using LC-UV, based on EPA 8321B*. Report Limit: bromacil 0.1 µg/L and tebuthiuron 0.2 µg/L.	5 g wet samples extracted with acetonitrile by shaking for 30 to 45 min, filtered, and concentrated for analysis using LC-UV, based on EPA 8321B*. Report Limit: bromacil 8 ng/g and tebuthiuron 41 ng/g.
CARO Analytical Services	Analysis performed with GC-MS following EPA 8270B**. Report Limit: bromacil 0.1 µg/L and tebuthiuron 0.2 µg/L.	Analysis performed with GC-MS following EPA 8270B**. Report Limit: bromacil 5 ng/g and tebuthiuron 20 ng/g.
Bureau Veritas Laboratories	Analysis performed with GC-MS. No Information received for the report limits.	Analysis performed with GC-MS. No Information received for the report limits.
Vogon Lab	No information received.	No information received.
ALS	No information received.	No information received.

*EPA 8321B details: https://www.epa.gov/hw-sw846/sw-846-test-method-8321b-solvent-extractable-nonvolatile-compounds-high-performance-liquid.

**EPA 8270B details: http://legismex.mty.itesm.mx/secc_inter/SW-846/8270b.pdf

The report limits (RL) from the commercial laboratories interviewed are at least 10 to 20 times higher than is needed to properly determine the environmental fate of bromacil and tebuthiuron and the effectiveness of the treatment technologies for the removal and/or degradation of sterilants, including the duration of effectiveness and the best materials and rate of application required to achieve optimal remediation.

4.0 EXTRACTION METHOD DEVELOPMENT

4.1 Soil and sediments samples

Accelerated solvent extraction (ASE) was used for the soil and sediment method extraction step. The ASE utilizes high temperature and pressure conditions to improve the extraction of the analyte from the solid sample. These conditions allow for the facilitated diffusion of the extraction solvent throughout the sample matrix and result in more complete dissolution and recovery of the analyte. The sample to be extracted is placed in a sealed metal cell that is then placed into the autosampler and in the sequence is then placed in a heated oven chamber and filled with the extraction solvent, as shown in the extraction process scheme in Figure 5. The extraction cell is then pressurized, allowing for an increase in the boiling point of the extraction solvent, and for the solubilization of the analyte at a temperature higher than would be possible at atmospheric pressure. The sample is then extracted and collected by the automated filling and voiding of the cell through repeated static cycles.

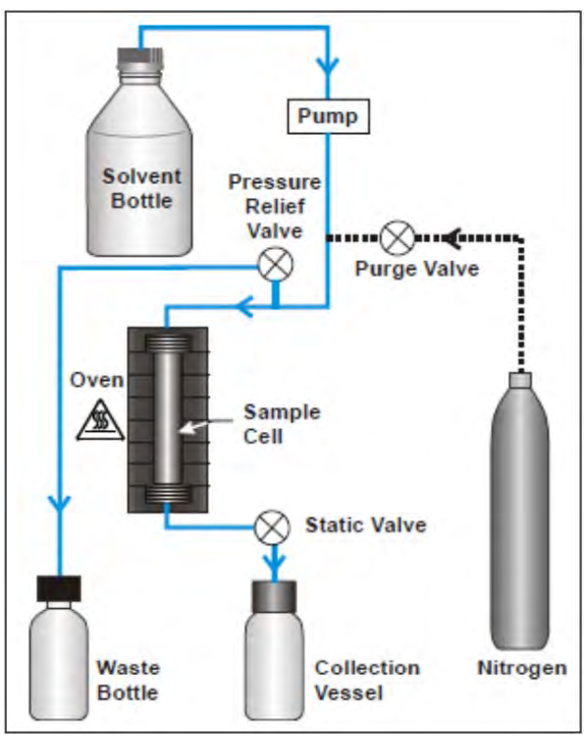

Figure 5. Schematic of ASE process.

ASE allows for the automated extraction and recovery of an analyte through repeated static extraction cycles at high temperature and pressure, to facilitate the diffusion of the extraction solvent throughout the sample matrix and allow more complete dissolution and recovery of the analyte. As the sample cell is pressurized, the solvent remains in a liquid state even above its boiling point. Thus, the volume of

solvent required for ASE extraction is relatively small (about 90% less than Soxhlet extraction). This pressurized fluid extraction method takes less time to recover the maximum extractable analyte due to (1) the solubility and mass transfer effect, and (2) disruption of surface equilibria. It is difficult to obtain the relationship between the temperature and the diffusion rate for a multicomponent analyte, but in general, the diffusion rate increases with the temperature. The introduction of fresh solvent during the static extraction increases the concentration gradient and hence enhances the mass transfer (Fick's first law of diffusion).

The use of dichloromethane as a solvent was initially tested, where the recovery of bromacil was satisfactory at 111 ± 16% for 10 samples spiked with 5 µg/kg and equilibrated during 24 h. However, the recovery of tebuthiuron for 10 samples spiked at 0.5 µg/kg was only 56 ± 26%. For this reason, despite the advantages of ASE, additional tests with different solvents were performed and the best results were achieved with a mixture of hexane and acetone at an 80/20 (v/v) ratio. The recovery of bromacil was 92 ± 10% for 10 samples spiked with 5 µg/kg and equilibrated for 24 h, and the recovery of tebuthiuron for 10 samples spiked at 0.5 µg/kg was 116 ± 7%.

4.2 Water samples

The extraction efficiency of solid-phase extraction (SPE) is influenced by many factors, such as the pH and volume of the sample, the eluent type, and flow rate, as well as the physicochemical properties of the stationary phase. Despite these factors, the development of the sample preparation step for the water samples was more straightforward as the laboratory is accredited by CALA to analyze pesticides including bromacil in water with SPE since the extraction method using the Autotrace 280 SPE instrument automatically performs all four steps of an SPE method: (1) conditioning; (2) loading; (3) rinsing and (4) eluting.

The selected stationary phase was the Oasis HLB (Hydrophilic-Lipophilic Balance) sorbent (Figure 6) that delivers high, reproducible recoveries especially suited to LC-MS/MS analysis by providing the required selectivity and sensitivity.

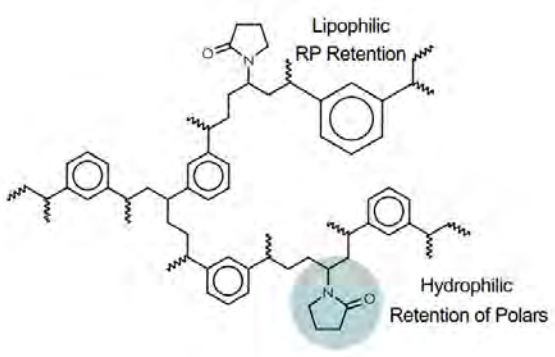

Figure 6. Structure of the OASIS HLB stationary phase.

To achieve the highest possible sensitivity, a water sample volume of 1 L was selected, where the recovery of bromacil was 116 ± 2% for 10 samples spiked at 25 ng/L, and the recovery of tebuthiuron for samples spiked at 2.5 ng/L was 122 ± 12%.

5.0 SAMPLE PREPARATION

5.1 Matrix Preparation

5.1.1 Soil and Sediment Samples

For soil and sediment samples, approximately 5 g of sample is weighed out into an Accelerated Solvent Extraction (ASE) cell and filled with diatomaceous earth or glass beads to fill any remaining cell space. Internal standard (Bromacil-D_3 and Diuron-D_6) is added before the extraction, to monitor losses that can occur through sample handling and to minimize the possibility of false-negative results. The sample is then extracted with the automated ASE, evaporated down, and analyzed using LC-Orbitrap-MS or the LC-MS/MS.

5.1.2 Water Samples

For water samples, 1 litre of sample is extracted with organic solvent using a Solid-Phase Extraction (SPE) procedure. Internal standard (Bromacil-D_3 and Diuron-D_6) is added before the extraction, to monitor losses that can occur through sample handling and to minimize the possibility of false-negative results. Compound characterization and quantification are performed using LC-Orbitrap-MS or the LC-MS/MS.

5.2 Recommended Sample Collection

5.2.1 Soil Samples

Soil samples should be collected in amber glass wide-mouth bottles, kept cool (around 4°C), and out of direct sunlight during transportation. Ideally, the sample sizes should be around 50 to 100g.

5.2.2 Water Samples

Water samples should be collected in one-liter amber glass bottles and filled so there is no headspace. Samples should be kept cool (around 4°C) and out of direct sunlight during transportation.

5.3 Recommended Sample Handling and Preservation

Samples requiring organic analysis should be placed in the appropriate containers and the cooling begun as soon as possible after sampling. Sufficient ice or other coolant should be added to produce a temperature less than or equal to (≤) 10°C in transit (but not frozen). Note that samples arriving at the laboratory on the day of sampling may not have had time to achieve a temperature of ≤ 10°C. This is acceptable as long as the cooling process has begun.

5.4 Sample Preparation

5.4.1 Soil/Sediment Samples

Make sure that the Dionex™ extraction cell filter (Fisher Scientific, Mississauga, ON, Canada) is added to the bottom of the cell before weighing out your sample. Add 5 g of sample into a 66 mL stainless steel cell and spike each sample with 10 µL of the internal standard solution (see section 4.2.2). Always include

a blank sample (5 g of sand spiked with the internal standard solution). Fill the remaining space in the cell with cleaned diatomaceous earth or glass beads. If using diatomaceous earth, add another glass fiber filter on top before screwing the lid on.

Set up samples to be extracted on the Thermo Scientific Dionex™ ASE 300 (Thermo Fisher, Mississauga, ON, Canada), using the method as described in Table 3.

Table 3. Dionex™ ASE 300 method parameters.

Temp: 110°C	Solvent A: 0
Static Time: 10 min	Solvent B: 1 (20% Acetone)
Purge time: 300 sec	Solvent C: 4 (80% Hexane)
Cycles: 6	

Transfer all the content (extract) from each ASE bottle into a large glass TurboVap tube and transfer the tubes to the TurboVap LV bath (Biotage, Salem, MA, USA) at 35°C and evaporate down to 1 to 2 mL. Transfer all volume (1 to 2 mL) into another small glass TurboVap tube and evaporate at 35°C until dry. Add 100 µL of Methanol LC-MS grade/Water LC-MS grade (1:1, v/v); vortex and transfer the sample into a small Eppendorf tube and centrifuge for 5 min @ 10,000 rpm. Transfer the sample into a 2 mL screw cap vial with a conical glass insert and analyze on the LC-Orbitrap-MS or by the Waters LC-MS/MS system.

5.4.2 Water Samples

Spike 1 L of each sample with 10 µL of the internal standard solution (see section 4.2.2). If necessary, filter the sample using a Buchner funnel and a Whatman 4 (150 mm) paper filter.

The Dionex™ AutoTrace™ 280 solid-phase extraction instrument (Thermo Fisher, Mississauga, ON, Canada) automates all four steps of SPE (conditioning, loading, rinsing, and eluting), reducing solvent consumption and improving recovery and reproducibility compared with the manual procedure. Extract the samples using the 6 mL SPE cartridges OASIS HLB 200 mg and follow extraction method #3 described in section 4.1.3.

6.0 MATERIALS AND INSTRUMENTATION

6.1 Experimental Method

6.1.1 Chemicals and Reagents

Chemicals used for the sample preparation and chemical analysis, methanol LC-MS grade (MeOH), water LC-MS grade, hexane optima grade, acetone optima grade, and ammonium acetate LC-MS grade were purchased from Fisher Scientific (Mississauga, ON, Canada), and acetic acid 99.99%, diatomaceous earth, and glass beads were purchased from Sigma-Aldrich (Oakville, ON, Canada). Oasis® HLB 2000 mg SPE cartridges 6 mL were purchased from Waters Ltd. (Mississauga, ON, Canada).

6.1.2 Standards

The standards, bromacil (98%) and tebuthiuron (99%), were purchased from Sigma-Aldrich (Oakville, ON, Canada), bromacil-D_3 (98%) was purchased from LGC (Manchester, MH, USA), and diuron-D_6 (99%) was purchased from CDN Isotopes (Pointe Claire, QC, Canada).

Experimental standard solutions preparation

Bromacil: 5 mg of bromacil was added into a 5 mL vol flask (about 1 mg/mL) and methanol LC-MS grade was added as the solvent. Intermediate working solutions of 10 µg/mL and 1 µg/mL were prepared from this stock solution.

Tebuthiuron: 5 mg of tebuthiuron was added into a 5 mL vol flask (about 1 mg/mL) and methanol LC-MS grade was added as the solvent. Intermediate working solutions of 1 µg/mL, and 0.1 µg/mL were prepared from this stock solution.

Working calibration curve standards were prepared according to Table 4. These solutions were stored at 4°C ± 3°C and are valid for 3 months.

Table 4. Preparing the working calibration solutions.

Solution	Concentration of Standard Solution	Bromacil 10 µg/mL	Tebuthiuron 1 µg/mL	MeOH (LCMS grade)
1	0.5 µg/mL bromacil, 0.05 µg/mL tebuthiuron	100 µL	100 µL	1,800 µL
2	0.2 µg/mL bromacil, 0.02 µg/mL tebuthiuron	40 µL	40 µL	1,920 µL
3	0.1 µg/mL bromacil, 0.01 µg/mL tebuthiuron	20 µL	20 µL	1,960 µL
		Bromacil 1 µg/mL	**Tebuthiuron 0.1 µg/mL**	
4	0.05 µg/mL bromacil, 0.005 µg/mL tebuthiuron	100 µL	100 µL	1,800 µL
5	0.02 µg/mL bromacil, 0.005 µg/mL tebuthiuron	40 µL	40 µL	1,920 µL
6	0.01 µg/mL bromacil, 0.001 µg/mL tebuthiuron	20 µL	20 µL	1,960 µL

Internal standards solutions preparation

An initial Diuron-D_6[1] solution was made at 1 mg/mL and diluted to a concentration of 50 µg/mL with LC-MS grade methanol. This stock concentration was stored in a sealed vial at less than -10°C and is valid for 1 year from the preparation date.

[1] Labeled tebuthiuron is not commercially available, therefore Diuron-D_6 is used as a substitute.

The Bromacil-D_3 comes from LGC as a solution in acetonitrile at 100 µg/mL and was diluted to 50 µg/mL with LC-MS grade methanol.

The working internal solution was prepared by mixing 1:1 the 50 µg/mL Diuron-D_6 and 50 µg/mL Bromacil-D_3, resulting in a solution of 25 µg/mL of each. The solution was stored in a sealed vial at 4°C and is valid for 6 months from the preparation date.

6.1.3 Calibration Curve Preparation

To prepare the calibration curve, 50 µL at each concentration level described in Table 5 was placed into a 2 mL vial with 300 µL insert, and 140 µL of mobile phase (1:1 LC-MS grade MeOH:LC-MS water) and 10 µL of the internal standard was added. The vial was then vortexed and added to the autosampler.

After the extraction in the AutoTrace 280, transfer the eluate samples) from the 40 mL vial into a small TurboVap tube, and transfer the tubes into the TurboVap LV bath (Biotage, Salem, MH, USA) at 35°C and evaporate until dryness. Add 100 µL of Methanol LC-MS grade/Water LC-MS grade (1:1, v/v); vortex and transfer the sample into a 2 mL screw cap vial with a conical glass insert and analyze on the LC-Orbitrap-MS or by the Waters LC-MS/MS system.LC-Orbitrap-MS Conditions.

Table 5. AutoTrace 280 method #3.

Step	Description
1	Condition cartridge with 10.0 mL of MeOH
2	Condition cartridge with 5.0 mL of pH 2.8 water
3	Load 1,000 mL of sample onto the cartridge
4	Dry cartridge with gas for 30 min
5	Wash syringe with 10.0 mL of MeOH
6	Collect 5.0 mL fraction into a sample tube using MeOH as elution solvent
7	Wash syringe with 10.0 mL of Dichloromethane (DCM)
8	Collect 5.0 mL fraction into a sample tube using DCM as elution solvent
9	Pause and Alert operator, resume when CONT is pressed
10	Clean each sample path with 50.0 mL of Millipore water into the aqueous waste

6.1.4 HPLC Conditions

Reversed-phase liquid chromatography was paired with a linear ion trap-Orbitrap mass spectrometer (Orbitrap Elite, Thermo Fisher Scientific, San Jose, CA, USA). The chromatographic separation was performed using an HPLC Ultimate 3000 (Thermo Fisher Scientific, San Jose, CA), consisting of a degasser, a 1,200 bar quaternary pump, and a column oven, with an HTS PAL autosampler (Thermo Fisher Scientific, San Jose, CA, USA).

The separation was performed on a Cosmosil C18 MS-II column (100 × 3.0 mm, 2.5 µm particle size, (Nacalai USA, San Diego, CA, USA) at 40 °C. A flow rate of 0.5 mL/min and an injection volume of 20 µL was used in all analyses. Additional operating conditions are shown in Table 6.

Table 6. HPLC conditions.

Solvent C	Water/methanol, 9:1 v/v with 0.1% acetic acid
Solvent D	MeOH with 0.1% Acetic Acid
Degasser	Continuous
Autosampler Temperature	12°C
Gradient	Time 0 min 90% of solvent C and 10% of Solvent D Time 2 min 20% of solvent C and 80% of Solvent D Time 12 min 100% of Solvent D Time 13 min 100% of Solvent D Time 14 min 90% of solvent C and 10% Solvent D
Total run time	17 minutes

6.1.5 Orbitrap Conditions

The Orbitrap was operated with an electrospray ionization (ESI) source operating in either positive or negative mode; separate injections of the samples were made for each mode. Needle voltage was set at 3.5 kV, while the sheath, aux, and sweep gas flows were set to 30 (arbitrary unit), 10 (arbitrary unit), and 5 (arbitrary unit), respectively. The capillary temperature was 350 °C. The acquisition was performed in scan mode from m/z 100 to m/z 300, with m/z resolving power set to a nominal value of 120,000.

Mass calibration and tuning were done externally by direct infusion of Pierce LTQ Velos ESI Positive Ion Calibration Solution (Thermo Fisher Scientific, Rockford, IL, USA). The positive ion mode calibration solution covers a mass range from m/z 74 to m/z 1,822, and both allow good m/z accuracy (<3 ppm) between m/z 100 and 2,000. All data acquisition and analysis was performed with Thermo Xcalibur software.

6.2 LC-MS/MS Conditions

6.2.1 HPLC Conditions

Reversed-phase liquid chromatography was paired with a triple quadrupole mass spectrometer (XEVO-TQS, Waters Corp., Milford, MA, USA). The chromatographic separation was performed using an Acquity UPLC I-Class Plus System (Waters Corp., Milford, MA, USA).

The separation was performed on an Acquity UPLC BEH C18 column (100 × 2.1 mm, 1.7 µm particle size, Waters Corp., Milford, MA, USA) with a VanGuard pre-column Acquity UPLC BEH C18 column (5 × 2.1 mm, 1.7 µm particle size, Waters Corp., Milford, MA, USA) at 45 °C. A flow rate of 0.45 mL/min and an injection volume of 2 µL was used in all analyses. Additional operating conditions are shown in Table 7.

Table 7. HPLC conditions.

HPLC Pump/Oven	
Alpha Pump A1 mobile phase	Water with 10 mM ammonium acetate, 0.1% acetic acid
Alpha Pump B1 mobile phase	MeOH with 10 mM ammonium acetate, 0.1% acetic acid

Gradient	Time 0 min 99% of solvent A and 1% of Solvent B Time 0.5 min 99% of solvent A and 1% of Solvent B Time 12.25 min 1% of solvent A and 99% of Solvent B Time 13 min 1% of solvent A and 99% of Solvent B Time 13.1 min 99% of solvent A and 1% of Solvent B Time 14 min 99% of solvent A and 1% of Solvent B
Seal wash	5 minutes
Run time	17 minutes
Min pressure	1,000 psi
Max pressure	1,800 psi
Column position	Position 2
Autosampler	
Wash solvent	50:50 MeOH: water mobile phase
Purge solvent	Methanol
Pre-inject wash	6 seconds
Post inject wash	6 seconds
Sample temp	12 ±5°C

6.2.2 MS/MS Conditions

A tandem quadrupole mass spectrometer, XEVO TQS was used for the analysis. Drying gas as well as nebulizing gas was nitrogen, the cone gas, and desolvation gas flows were optimized at 50 L/h flow and 1,100 L/h, respectively. For operation in MS/MS mode, collision gas was argon 99.995%. Positive ionization mode was performed using a capillary voltage of 3 kV. Interface temperature and source temperature were optimized at 550°C and 150°C, respectively. The transitions used for quantification for each compound and the transitions used as qualifiers are listed in Table 8. All compounds are quantitated off Bromacil-D_3.

Table 8. Multiple reaction monitoring (MRM) transitions.

Compound	Type	Precursor (m/z)	Product(m/z)	Cone (V)	Collision Energy (eV)
Bromacil	Quantifier	261	204.9	13	14
Bromacil	Qualifier	261	187.9	13	28
Tebuthiuron	Quantifier	229	172	5	15
Tebuthiuron	Qualifier	229	116	5	25
Bromacil-D_3	Internal Standard	264	207.9	13	14
Diuron-D_6	Internal Standard	239	78	20	19

7.0 METHOD VALIDATION PARAMETERS

7.1 Determination of the Method Detection Limit

The method validation for the Method Detection Limit (MDL) was performed according to the United States Code of Federal Regulations (CFR 40), and the procedure consists of the following steps:

(a) Select a spiking level, typically 2 to 10 times the estimated MDL (e.g., the concentration value that corresponds to an instrument signal-to-noise ratio in the range of 3 to 5).

(b) Process 10 spiked samples and 10 method blank samples through all steps of the method. The samples used for the MDL must be prepared in at least three batches on three separate calendar dates and analyzed on three separate calendar dates.

Calculate the MDLs as follows:

$$\text{MDL} = t_{(n-1,\ 1-\propto=0.99)}S$$

where: MDL = the method detection limit based on spiked samples;
$t_{(n-1,\ 1-\alpha\ =\ 0.99)}$ = the Student's t-value appropriate for a single-tailed 99th percentile t statistic and a standard deviation estimate with n-1 degrees of freedom.
S = sample standard deviation of the replicate spiked sample analyses.

7.2 Estimation of the Method Uncertainty

Generally, the most significant contributions for the method uncertainty are associated with the random error characterized by within-lab reproducibility, from the uncertainty of the standard preparation, from the uncertainty of reference compounds, and the inaccuracy associated with the measuring piece of equipment, such as pipettes, volumetric flasks, injector, detectors, etc. The uncertainty of the method was estimated by the following steps:

1. Prepare, analyze, and tabulate the results of 30 from each standard at low, medium, and high concentrations.
2. Determine the standard deviation, $SD_{standards}$, for each of the three different standard concentrations (low, medium, and high).
3. Determine the relative standard deviation (RSD), for each standard range.

   $RSD = SD_{standards}$/Concentration of the standard
4. To obtain the most conservative value select the highest RSD as $RSD_{standards}$.
5. Uncertainty is defined as:

   Uncertainty = k x $RSD_{standards}$

   Where:

   "k" is the Student`s factor, and for 30 or more data points, K = 2.

6. The analytical results should therefore be reported as:

   $C \pm (2 \times C \times RSD_{standards})$.

   Where C = Concentration of analyte determined by the analytical method.

8.0 METHOD PERFORMANCE

8.1 Method Performance

Performance characteristics of the method were determined by evaluating specificity, linearity, accuracy, and minimum detection limit.

8.1.1 Selectivity/Specificity

Selectivity is the degree to which a method can quantify the analyte accurately in the presence of interferences under the stated conditions of the assay for the sample matrix being studied. As it is impracticable to consider every potential interference, the absolute absence of interference effects can be taken as ''specificity'', so specificity = 100% selectivity.

Most of the current LC-MS analyses rely on the high sensitivity and selectivity of the selected reaction-monitoring (SRM) mode of QqQ-MS. The introduction of UHPLC and fast-switching QqQ-MS instruments significantly increased the number of analytes that can be detected in one run. Indeed, modern instruments produce high signal-to-noise (S/N) ratios, even when relying on short SRM dwell times. LC-MS/MS and LC-HRMS provide high mass accuracy resulting in both high selectivity and sensitivity in complex sample matrices.

The specificity of the method was tested by the analysis of blank samples of water or sand and soil. No chromatographic interference was observed at the retention time for both target compounds and internal standards of the blank samples showed no interfering peaks, indicating good specificity.

8.1.2 Linearity

The calibration curves for bromacil and tebuthiuron for the analysis performed on the LC-Orbitrap-MS and for the LC-MS/MS were prepared using the same six different concentrations as described in the Experimental Section.

The same calibration curve also was used for the analysis of the water and soil sediment samples, as shown in Table 9. Typical calibration curves for bromacil and tebuthiuron obtained by the analysis on the LC-Orbitrap-MS and for the LC-MS/MS are shown in Figure 7. The correlation coefficients (r^2) for both compounds were above 0.99, showing that the methods are linear in the specified concentration ranges, in both setups using the two different types of mass spectrometers.

Table 9. Calibration curve concentrations for soil and water.

Calibration Point	Bromacil Concentrations			Tebuthiuron Concentrations		
	Solution	Soil	Water	Solution	Soil	Water
1	0.5 µg/mL	5 µg/kg	25 ng/L	0.05 µg/mL	0.5 µg/kg	2.5 ng/L
2	0.2 µg/mL	2 µg/kg	10 ng/L	0.02 µg/mL	0.2 µg/kg	1 ng/L
3	0.1 µg/mL	1 µg/kg	5 ng/L	0.01 µg/mL	0.1 µg/kg	0.5 ng/L
4	0.05 µg/mL	0.5 µg/kg	2.5 ng/L	0.005 µg/mL	0.05 µg/kg	0.25 ng/L
5	0.02 µg/mL	0.2 µg/kg	1 ng/L	0.002 µg/mL	0.02 µg/kg	0.1 ng/L
6	0.01 µg/mL	0.1 µg/kg	0.5 ng/L	0.001 µg/mL	0.01 µg/kg	0.05 ng/L

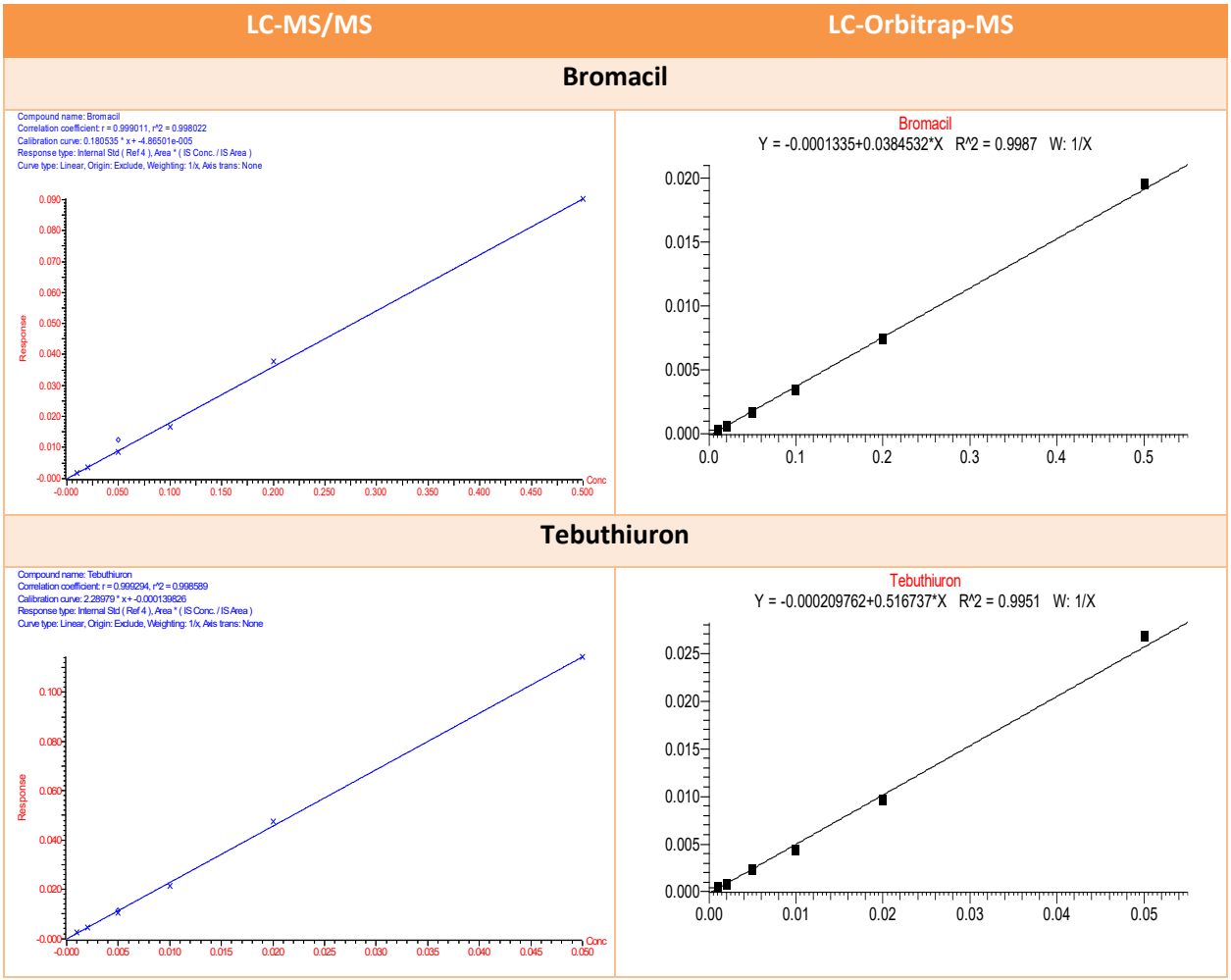

Figure 7. Typical calibration curves for bromacil and tebuthiuron.

8.1.3 Accuracy and Precision

Accuracy is a parameter that covers trueness (recovery) and certainty (repeatability and reproducibility). The method precision can have different meanings, depending on what level of variability is included. In this report, precision expresses the closeness of the results obtained with the analysis of a set of samples by the same technologist using the same equipment.

The repeatability studies were performed with 10 samples at 2 different concentrations (lower and higher) each:

a) Tebuthiuron Soil: 0.01 µg/Kg and 0.5 µg/Kg;
b) Tebuthiuron Water: 0.05 ng/L and 2.5 ng/L;
c) Bromacil Soil: 0.1 µg/Kg and 5 µg/Kg and
d) Bromacil Water: 0.5 ng/L and 25 ng/L.

The accuracy of the analytical method for bromacil in soil samples was between 92.4% and 113.5%, and precision between 1.9% and 10.1%; accuracy for tebuthiuron in soil samples was between 114% and 124.1%, and precision between 3.2% and 11.3% (Table 10).

Table 10. Accuracy and precision for soil samples spiked at low and high concentrations (results in µg/kg).

	Bromacil				**Tebuthiuron**			
	LC-MS/MS		**LC-Orbitrap-MS**		**LC-MS/MS**		**LC-Orbitrap-MS**	
	Low	High	Low	High	Low	High	Low	High
	0.111	4.201	0.105	5.154	0.011	0.526	0.015	0.485
	0.117	5.648	0.095	5.048	0.011	0.721	0.009	0.565
	0.113	5.196	0.123	5.11	0.011	0.683	0.012	0.590
	0.118	5.555	0.098	5.085	0.011	0.676	0.013	0.625
	0.116	4.343	0.130	5.393	0.011	0.573	0.012	0.586
	0.113	4.487	0.115	5.057	0.011	0.585	0.015	0.526
	0.110	3.728	0.109	4.921	0.012	0.696	0.014	0.686
	0.116	4.124	0.112	5.104	0.012	0.561	0.011	0.541
	0.110	4.135	0.099	4.955	0.012	0.563	0.011	0.572
	0.111	4.800	0.120	4.885	0.012	0.620	0.011	0.605
Average	0.113	4.622	0.111	5.071	0.011	0.620	0.012	0.578
Accuracy	113.5%	92.4%	110.6%	101.4%	114.0%	124.1%	123.0%	115.6%
Precision	1.91%	10.1%	7.50%	2.02%	3.24%	7.88%	11.3%	6.87%

Accuracy for bromacil in water samples was between 104% and 115.6%, and precision between 1.5% and 5.2%; accuracy for tebuthiuron in water samples was between 103.8% and 121.9%, and precision between 5.6% and 17.4% (Table 11).

Table 11. Accuracy and precision for water samples spiked at low and high concentrations (results in ng/L).

	Bromacil				Tebuthiuron			
	LC-MS/MS		LC-Orbitrap-MS		LC-MS/MS		LC-Orbitrap-MS	
	Low	High	Low	High	Low	High	Low	High
	0.480	11.49	0.520	10.99	0.062	1.070	0.085	1.120
	0.475	11.21	0.485	9.95	0.057	1.060	0.055	0.980
	0.505	11.68	0.490	12.54	0.052	1.130	0.048	1.250
	0.490	11.38	0.510	10.84	0.065	1.110	0.045	1.118
	0.520	11.60	0.489	11.35	0.065	1.115	0.043	1.085
	0.520	11.61	0.501	11.48	0.061	1.675	0.058	1.585
	0.515	11.24	0.520	10.95	0.058	1.485	0.042	1.504
	0.555	11.79	0.510	10.50	0.057	1.090	0.048	1.105
	0.600	11.99	0.560	10.85	0.065	1.240	0.049	1.135
	0.540	11.61	0.525	11.25	0.067	1.210	0.046	1.149
Average	0.520	11.56	0.511	11.07	0.061	1.219	0.052	1.203
Accuracy	104.0%	115.6%	102.2%	110.7%	121.8%	121.9%	103.8%	120.3%
Precision	5.2%	1.5%	3.1%	4.4%	5.63%	12.0%	17.4%	11.5%

Despite the tebuthiuron spike concentrations being 10 times lower than the bromacil spike concentrations the method accuracy and precision were similar and in the acceptable recovery limits (70% to 130%).

8.1.4 Method Detection Limit (MDL) and Uncertainty

The method detection limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte (bromacil or tebuthiuron) concentration is greater than zero. MDL is determined from the analysis of a sample in a given matrix containing the analyte and should not be confused with instrument detection limits or instrument sensitivity. The MDL results are shown in Tables 12 and 13. The determinations were performed on three different days (sets 1, 2 and 3) and the highest results were selected for the method MDLs.

For bromacil in soil samples, the MDLs were 0.013 µg/kg for the LC-MS/MS method and 0.034 µg/kg for the LC-Orbitrap-MS method. For tebuthiuron, the MDLs were 0.003 µg/kg for the LC-MS/MS method and 0.006 µg/kg for the LC-Orbitrap-MS method.

For water samples, the MDL for bromacil was 0.106 ng/L for the LC-MS/MS method and 0.063 ng/L for the LC-Orbitrap-MS method. For tebuthiuron, the MDLs were 0.045 ng/L for the LC-MS/MS method and 0.036 ng/L for the LC-Orbitrap-MS method.

Table 12. Minimum detection limit (MDL) of bromacil and tebuthiuron in soil samples (results in µg/kg).

	Bromacil						**Tebuthiuron**					
	LC-MS/MS			**LC-Orbitrap-MS**			**LC-MS/MS**			**LC-Orbitrap-MS**		
	Set 1	Set 2	Set 3	Set 1	Set 2	Set 3	Set 1	Set 2	Set 3	Set 1	Set 2	Set 3
	0.111	0.097	0.103	0.105	0.107	0.099	0.013	0.011	0.012	0.015	0.010	0.013
	0.117	0.099	0.109	0.095	0.095	0.105	0.010	0.011	0.012	0.009	0.011	0.012
	0.113	0.095	0.106	0.123	0.099	0.102	0.013	0.011	0.011	0.012	0.011	0.012
	0.118	0.097	0.110	0.098	0.102	0.097	0.014	0.011	0.013	0.013	0.010	0.011
	0.116	0.097	0.109	0.130	0.090	0.110	0.014	0.011	0.011	0.012	0.012	0.012
	0.113	0.098	0.108	0.115	0.110	0.098	0.013	0.011	0.012	0.015	0.011	0.014
	0.110	0.111	0.111	0.109	0.121	0.121	0.013	0.012	0.014	0.014	0.011	0.010
	0.116	0.097	0.102	0.112	0.099	0.099	0.014	0.012	0.013	0.011	0.012	0.014
	0.110	0.101	0.103	0.099	0.120	0.108	0.013	0.012	0.012	0.011	0.012	0.012
	0.111	0.095	0.107	0.120	0.125	0.112	0.013	0.012	0.012	0.011	0.013	0.012
Avg.	0.113	0.099	0.107	0.111	0.107	0.105	0.012	0.011	0.012	0.012	0.011	0.013
STD	0.003	0.005	0.003	0.012	0.012	0.008	0.001	0.001	0.001	0.002	0.001	0.012
MDL	**0.009**	**0.013**	**0.009**	**0.033**	**0.034**	**0.022**	**0.003**	**0.002**	**0.003**	**0.006**	**0.003**	**0.004**

Table 13. Minimum detection limit (MDL) of bromacil and tebuthiuron in water samples (results in ng/L).

	Bromacil						**Tebuthiuron**					
	LC-MS/MS			**LC-Orbitrap-MS**			**LC-MS/MS**			**LC-Orbitrap-MS**		
	Set 1	Set 2	Set 3	Set 1	Set 2	Set 3	Set 1	Set 2	Set 3	Set 1	Set 2	Set 3
	0.480	0.545	0.560	0.520	0.575	0.502	0.060	0.062	0.035	0.085	0.058	0.041
	0.475	0.565	0.510	0.485	0.529	0.515	0.040	0.057	0.035	0.055	0.052	0.039
	0.505	0.520	0.560	0.490	0.535	0.485	0.045	0.052	0.045	0.048	0.055	0.052
	0.490	0.515	0.525	0.510	0.520	0.535	0.045	0.065	0.035	0.045	0.068	0.048
	0.520	0.515	0.515	0.489	0.535	0.525	0.040	0.065	0.055	0.043	0.070	0.056
	0.520	0.540	0.515	0.501	0.520	0.528	0.090	0.061	0.035	0.058	0.058	0.050
	0.515	0.505	0.540	0.520	0.525	0.535	0.045	0.058	0.035	0.042	0.055	0.048
	0.555	0.535	0.500	0.510	0.538	0.525	0.045	0.057	0.038	0.048	0.069	0.061
	0.600	0.495	0.530	0.560	0.512	0.540	0.045	0.065	0.045	0.049	0.068	0.047
	0.540	0.530	0.525	0.525	0.520	0.550	0.035	0.067	0.048	0.046	0.065	0.042
Avg.	0.520	0.527	0.528	0.511	0.531	0.524	0.049	0.061	0.041	0.052	0.062	0.048

STD	0.038	0.021	0.020	0.023	0.018	0.019	0.016	0.005	0.007	0.013	0.007	0.007
MDL	**0.106**	**0.058**	**0.057**	**0.063**	**0.050**	**0.054**	**0.045**	**0.014**	**0.020**	**0.036**	**0.019**	**0.019**

Uncertainty is defined as the interval around the result of a measurement that contains the true value with a high probability; the estimation of uncertainty is essential in the interpretation of results and, in particular, their comparison with regulatory limits. Hence, since 2001 ISO 17025 requires testing laboratories to apply procedures for estimating uncertainty and to be associated with the analytical results. The uncertainty results for the LC-orbitrap-MS were 32% for bromacil and 18% for tebuthiuron; the uncertainty for the LC-MS/MS analysis was 21% for bromacil and 30% for tebuthiuron.

8.1.5 Limit of quantification (LOQ)

The limit of quantification (LOQ) is the lowest concentration at which the analyte can not only be reliably detected but at which some predefined goals for bias and imprecision are met. A common method for estimating quantification limit is the signal-to-noise determination (by using the signal-to-noise method, the peak-to-peak noise around the analyte retention time is measured; a signal-to-noise ratio (S/N) of 10 is generally accepted for estimating LOQ) however, as this approach does not conform to the ISO and IUPAC definitions (Zubarev and Makarov, 2013) the Precision-based approach was used, where decreasing analyte concentrations are analyzed repeatedly and the relative standard deviation is plotted against the corresponding concentration (precision function). If a predefined limit is exceeded (such as 20%), the corresponding concentration is established as the quantification limit. However, in practice, due to the high variability of standard deviations, the true precision function is much more difficult to draw unless many concentrations are included. Based on the precision of the 30 water samples and 30 soil samples (see Table 10 and 11), the limit of quantification in soils for bromacil was 0.1 µg/kg, and for tebuthiuron 0.01 µg/kg. For water samples, the limit of quantification for bromacil was 0.5 ng/L and for tebuthiuron 0.05 ng/L. Typical chromatograms at the LOQ level are shown in Figures 8 and 9.

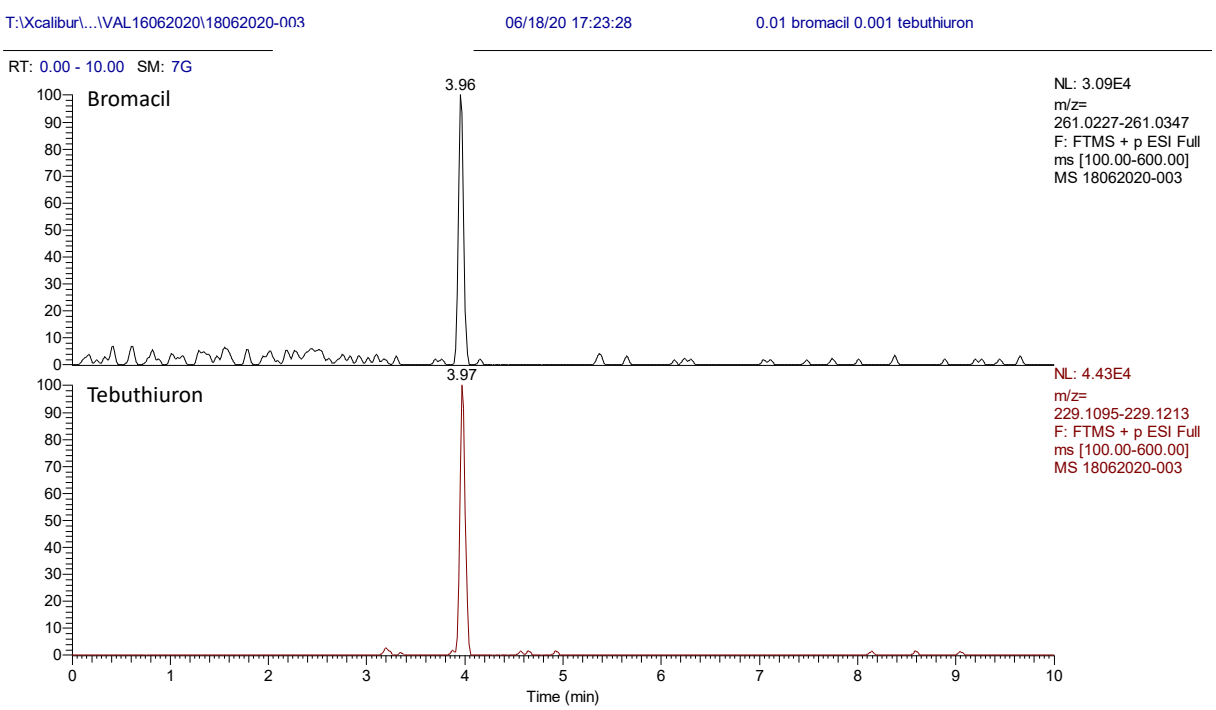

Figure 8. Typical LC-Orbitrap-MS chromatograms at LOQ concentration for bromacil and tebuthiuron.

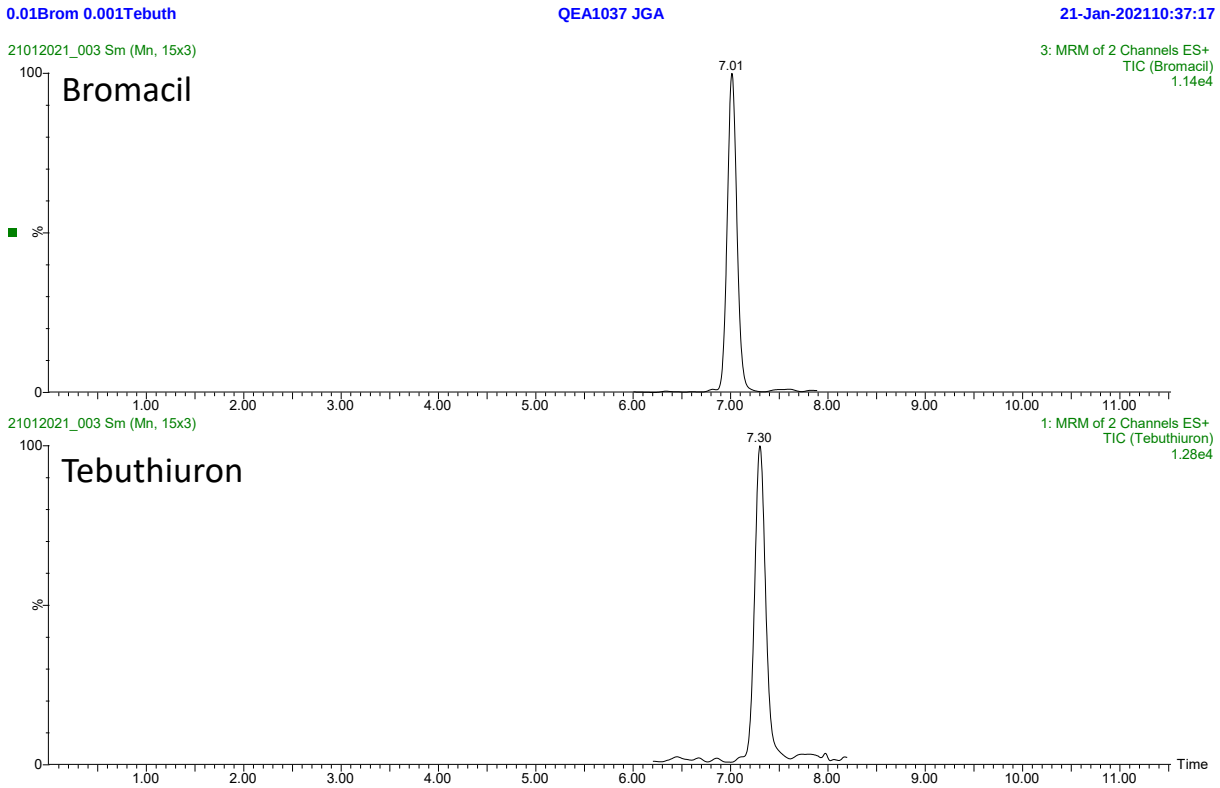

Figure 9. Typical LC-MS/MS chromatograms at LOQ concentration for bromacil and tebuthiuron.

8.2 Evaluation of matrix interference for the soil sample analytical method

The effect of the matrix on the performance of the method for analysis of soil samples was examined by analyzing four different soil samples (soil characteristics are shown in Table 14). Each soil sample was spiked with 5 µg/kg for bromacil or 0.5 µg/kg tebuthiuron. After spiking, the samples were homogenized and equilibrated for 24 h before extraction and analysis in duplicates for all samples. The recovery results for the duplicate samples are shown in Table 15.

Table 14. Characteristics for soil samples used for the matrix interference evaluation. Missing information was not available.

Parameter	Units	Soil 1	Soil 2	Soil 3	Soil 4
Sand	%	46	41	41.7	-
Silt	%	35	35	48	-
Clay	%	18	24	10.1	-
Organic Matter	%	3.44	6.49	5.02	-
Organic Carbon	%	1.73	3.24	10.2	-
pH		7.60	7.56	-	7.65
Electrical Conductivity	dS/m	1.40	0.95	-	0.51
Calcium	mg/kg	49.0	73.49	-	33.1
Magnesium	mg/kg	13.0	18.35	-	7.1

Parameter	Units	Soil 1	Soil 2	Soil 3	Soil 4
Sodium	mg/kg	85.0	20.88	-	7
Potassium	mg/kg	13.7	9.63	1.17	4
Chloride	mg/kg	18.3	34.25	-	8
Sulfate (SO_4)	mg/kg	130	122.50	-	21
Sulfate-S	mg/kg	43.3	40.83	25	0.96

Table 15. Recovery results (%) for bromacil at 5 µg/kg and tebuthiuron at 0.5 µg/kg in different soil samples and bromacil at 5 ng/L and tebuthiuron at 0.5 ng/L in water.

Parameter	Sample	Soil 1	Soil 2	Soil 3	Soil 4	Water 1
Bromacil	1st	113.9	120.8	120.2	124.5	100.0
	2nd	119.5	121.8	116.9	123.3	102.4
Tebuthiuron	1st	96.4	115.6	100.7	97.5	70.0
	2nd	103.7	101.6	98.0	97.8	72.0

8.3 Evaluation of LC-MS/MS method with blind samples

The optimized methods were used for analysis of the blind samples, which were prepared by a third party. The information of the triplicate samples and results are shown in Table 16. Recovery rates are considered acceptable and the method is therefore approved.

Table 16. Results of blind test for water and soil samples in different labs.

Labs	Matrix	Blind spike [1]		Reported Results [1]		Recovery	
		Bromacil	Tebuthiuron	Bromacil	Tebuthiuron	Bromacil	Tebuthiuron
EAS	Water	10.6	11.4	9.34	7.63	82%	67%
EAS	Water	10.6	11.4	10.1	8.37	89%	73%
EAS	Water	10.6	11.4	9.99	7.6	88%	67%
EAS	Soil	0.89	0.84	0.888	0.632	106%	75%
EAS	Soil	0.89	0.84	0.664	0.583	79%	69%
EAS	Soil	0.89	0.84	0.658	0.547	78%	65%
Commercial	Water	10.6	11.4	8.1	10.7	76%	94%
Commercial	Water	10.6	11.4	7.6	9.8	72%	86%
Commercial	Water	10.6	11.4	11	13.5	104%	118%
Commercial	Soil	0.89	0.84	0.634	0.647	75%	77%
Commercial	Soil	0.89	0.84	0.534	0.566	64%	67%
Commercial	Soil	0.89	0.84	0.559	0.514	67%	61%

[1] Blind spike and reported soil results are in mg/kg and water results are in µg/L.

8.4 Application of LC-MS/MS methods for field samples

The optimized methods were successfully applied to real water and soil samples. The soil samples were collected in different locations in Alberta. The results are shown in Table 17.

Table 17. Results of test for real water soil samples.

Sample ID	Sample Info	Reported Results	
		Bromacil	Tebuthiuron
17010077-119	17SWC80105	< 0.1 ng/L	< 0.01 ng/L
17010077-120	17SWC80105	0.08 ng/L	< 0.05 ng/L
21070322-002	M21-32 2.5 Jar 2 of 2	0.81 µg/kg	27.71 µg/kg
21070322-003	M21-33 0.50 Jar 2 of 2	< 0.1 µg/kg	0.17 µg/kg
21070322-004	M21-33 2.5 Jar 1 of 2	2.1 µg/kg	3.79 µg/kg
21070322-005	M21-34 0.5 Jar 1 of 2	0.19 µg/kg	0.55 µg/kg
21070322-006	M21-34 2.5 Jar 1 of 2	3.33 µg/kg	16.61 µg/kg
21070322-007	M21-34 3.5 Jar 1 of 2	86.75 µg/kg	ND
21070322-008	M21-34 4.8 Jar 1 of 2	4.93 µg/kg	ND

ND: Not Detected.

9.0 CONCLUSIONS

New analytical methods were successfully developed and validated for analysis of bromacil and tebuthiuron with detection limits around 1,000 times lower than available in commercial laboratories.

In soil samples, the bromacil detection limits in commercial laboratories are ≥ 5 µg/kg where the new method presented here has a validated minimum detection limit of 0.013 µg/kg using the LC-MS/MS and 0.032 µg/kg using the LC-Orbitrap-MS. For tebuthiuron, the detection limits in commercial laboratories are ≥ 5 µg/kg where the new method presented here has a validated minimum detection limit of 0.003 µg/kg using the LC-MS/MS and 0.006 µg/kg using the LC-Orbitrap-MS.

In water samples, the bromacil detection limits in commercial laboratories are ≥ 0.1 µg/L whereas the new method has a validated minimum detection limit of 0.0001 µg/L using the LC-MS/MS and 0.00006 µg/L (or 0.6 ng/L) using the LC-Orbitrap-MS. For tebuthiuron, the detection limits in commercial laboratories are ≥ 0.1 µg/L where the new method presented here has a validated minimum detection limit of 0.000004 µg/L (or 0.04 ng/L) using the LC-MS/MS or using the LC-Orbitrap-MS.

The validated limit of quantification in soils for bromacil was 0.1 µg/kg and for tebuthiuron 0.01 µg/kg, and for water samples, the limit of quantification for bromacil was 0.0005 µg/L (or 0.5 ng/L) and for tebuthiuron 0.00005 µg/L (or 0.05 ng/L).

The optimized methods passed blind tests and were successfully applied to real samples. The new methods are ready to be used in commercial laboratories for bromacil and tebuthiuron analysis.

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11.0 ACKNOWLEDGEMENTS

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APPENDIX A: QUESTIONNAIRE SENT TO COMMERCIAL LABORATORIES

Questionnaire submitted to the commercial labs.

Please provide information as accurately as possible. Elaborate where possible, and if you do not have the information, please indicate: no information available. Information will be treated confidentially and used for supporting the monitoring of sterilants in Alberta.

General information

(1) Does your laboratory currently have the capacity to analysis of sterilants in soil?

(2) Does your laboratory currently have the capacity to analysis of sterilants in water?

(3) The analytical method for sterilants in soil and/or in water includes Bromacil and tebuthiuron?

Sample preparation

(4) Which sample preparation technique is used for the water samples? Please give details as possible.

(5) Which sample preparation technique is used for the soil samples? Please give details as possible.

Analytical methods

(6) The analytical methodology is used for the water samples? HPLC or GC? Please give details as possible.

(7) The analytical methodology is used for the soil samples? HPLC or GC? Please give details as possible.

Additional information

(8) If possible give details about the analytical methods: detection limits, linearity range, etc..

element

STERILANT SCAN BY HPLC/MSD
METHOD SUMMARY

1. **METHOD**
   1.1 **Reference Method**
   Soil
   1.1.1 Cotterill, Edward G., "The *Efficiency of Methanol for the Extraction of Some Herbicide Residues from Soil*", Agricultural Research Council Weed Research Organization, Begbroke Hill, Yarnton, Oxford, September 22, 1979. **Modified**
   1.1.2 US Environmental Protection Agency. EPA 8321B Solvent-Extractable Nonvolatile Compounds by High-Performance Liquid Chromatography/Thermospray/Mass Spectrometry (HPLC/TS/MS) or Ultraviolet (UV) Detection. Revision 2. February 2007. **Modified**.
   Water
   1.1.3 Alberta Environmental Center, "*Methods Manual for the Chemical Analysis of Trace Organics and Pesticides in Environmental Samples*", Method A119.0 Tebuthiuron, Monuron, Diuron and Linuron in Water. January 1988. **Modified**
   1.1.4 Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory *Determination of Pesticides in Water by Graphitized Carbon- Based Solid-Phase Extraction and High-Performance Liquid Chromatography/Mass Spectrometry 2001*. **Modified**

   1.2 **Modifications**
   The following lists all modifications to the reference methods.
   1.2.1 Soil sample is extracted with methanol using a wrist action shaker or paint shaker technique. The extract is concentrated, filtered and then analyzed on HPLC/MSD.
   1.2.2 The water sample extraction procedure is an internally developed method rather than the separatory funnel method in AENV A119.
   1.2.3 The sample concentration procedure section was modified from the USGS method.
   1.2.4 Sample is analyzed on HPLC/MSD rather than UV detection as specified in the reference method.

2. **SIGNIFICANCE AND SCOPE**

Sterilants are a group of triazine herbicides applied to soils to selectively control germinating broadleaf and grassy weeds. They may be used in the pre-plant, pre-emergence or post-emergence treatment of soils. Sterilants are most readily absorbed through root systems, less through foliage and stems, acting as a photosynthetic inhibitor. Adsorption in soil increases as clay content and/or organic matter content of soil increases. Microbes in the soil utilize these herbicides as a source of energy and nitrogen and thus are the primary factor in the disappearance of sterilants from soils. It is important to be able to detect these compounds at low levels in soil prior to planting of broadleaf or grassy crops that may be susceptible to residual sterilants.

This method is applicable to the following sterilants in soil/solid or water/liquid.

Method Performance Characteristics

	Soil	Water	
Analyte	Reporting Limit (µg/g dry)	Reporting Limit (µg/L)	Analytical Range (ng)
Atrazine	0.005	0.1	0 – 5.0
Bromacil	0.008	0.1	0 – 5.0
Chlorotoluron	0.02	0.1	0 – 5.0
Cyanazine	0.02	0.1	0 – 5.0
Diuron	0.02	0.1	0 – 5.0
Fenuron	0.02	0.1	0 – 5.0
Isoproturon	0.02	0.1	0 – 5.0
Linuron	0.02	0.1	0 – 5.0
Metoxuron	0.02	0.1	0 – 5.0
Monolinuron	0.02	0.1	0 – 5.0

STERILANT SCAN BY HPLC/MSD

METHOD SUMMARY

Simazine	0.02	0.1	0 – 5.0
Tebuthiuron	0.005	0.1	0 – 5.0
Propanil**	N/A	0.1	0 – 5.0
Deethylatrazine*	N/A	0.1	0 – 5.0
Deisopropylatrazine*	N/A	0.1	0 – 5.0
Didealkylatrazine*	N/A	0.1	0 – 5.0

* Analytes are extracted by the procedures specified in method TM PEST 006-50. MDL based on acid herbicide extraction method for waters.
** Propanil is not a part of the sterilant scan however can be quantified using this method.

2.1 The reporting detection limits for the pesticides may vary depending on the nature of interferences in the sample matrix. The list shows MDLs as determined for clean samples with no interferences.

Associated LIMS methods:
- Sterilant - Soil
- Sterilant - Water
- HCLCMS Pesticides - Water

3. PRINCIPLE

This method involves extraction of various sterilant herbicides with organic solvents from solid and liquid matrices by wrist action shaker / paint shaker and bottle method techniques respectively.
For the atrazine metabolites, the sample is extracted with organic solvents by SPE method.
The extract from either extraction methods is concentrated, filtered and analyzed by reverse phase high performance liquid chromatography (HPLC) using mass selective (MSD) detection.

4. INTERFERENCES

4.1 Glassware
- 4.1.1 All glassware must be clean and free of potentially interfering contaminants (refer to SOP GEN 009-50 for cleaning instructions).
- 4.1.2 Clean dry glassware must be stored in a clean, dry place.

4.2 Solvents, Reagents, and other laboratory hardware
- 4.2.1 Solvents must be 'HPLC Grade' or equivalent.
- 4.2.2 Reagents must be kept free of contamination.
- 4.2.3 Other hardware including syringes, extract concentrators, sampling equipment, and transferring apparatus must be free of contamination as determined by method blanks.

4.3 Sample Co-extractive Interferences
- 4.3.1 Interferences co-extracted from samples will vary from sample to sample.
- 4.3.2 The use of high purity reagents and solvents helps to minimize interference problems.
- 4.3.3 Additional cleanup procedures may be necessary. Acceptable methods of cleanup include filtration through glass wool, sodium sulfate, high speed centrifugation or overnight settling (samples are allowed to sit overnight without agitation to allow particulates to settle). Salt may also be added to break up any emulsions.

APPENDIX A3: FIELD SCREENING TECHNOLOGIES FOR BROMACIL AND TEBUTHIURON

This project produced two reports.

Appendix A3-1: Literature Review

French, K., E. Cowan, E. Terpstra, J. Liu, Y. Li and F. He. 2021. Field Screening Technologies for Bromacil and Tebuthiuron: Literature Review. Report SSP-5A prepared by Vertex Environmental Inc. and Bionanotechnology & Interfaces Laboratory, University of Waterloo for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 28 pp. plus Appendices.

Field Screening Technologies for Bromacil and Tebuthiuron: Literature Review

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DISCLAIMER

This report was prepared as an account of work conducted by Vertex Environmental Inc. ("Vertex") and the Bionanotechnology & Interfaces Laboratory of the University of Waterloo ("UW") on behalf of InnoTech Alberta Inc. ("InnoTech Alberta") for the Sterilants Research Program ("Sterilants Program"). All reasonable efforts were made to ensure that the work conforms to accepted scientific, engineering and environmental practices, but Vertex and UW make no other representation and gives no other warranty with respect to the reliability, accuracy, validity or fitness of the information, analysis and conclusions contained in the report. Any and all implied or statutory warranties of merchantability or fitness for any purpose are expressly excluded. Reference herein to any specified commercial product, process or service by trade-name, trademark, manufacturer or otherwise does not constitute or imply an endorsement or recommendation by Vertex or UW.

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French, K., E. Cowan, E. Terpstra, J. Liu, Y. Li and F. He. 2021. Field Screening Technologies for Bromacil and Tebuthiuron: Literature Review. Report SSP-5A prepared by Vertex Environmental Inc. and Bionanotechnology & Interfaces Laboratory, University of Waterloo for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 28 pp. plus Appendices.

EXECUTIVE SUMMARY

Vertex Environmental Inc. (Vertex) and the Bionanotechnology & Interfaces Laboratory at the University of Waterloo (UW) were retained by InnoTech Alberta to undertake literature reviews and preliminary testing on available technologies that may have the potential to be used for field screening of soil and/or groundwater samples for the presence of bromacil and tebuthiuron at sites in Alberta and elsewhere.

Based on the results of the literature review and interviews completed in relation to the potential application of existing field screening technologies for use in detecting bromacil and/or tebuthiuron in soil and groundwater at sites in Alberta, Vertex concluded that the following seven technologies showed promise and are recommended for carrying forward to the next Task of proof-of concept testing:

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
- Near infrared reflectance spectroscopy (NIRS)
- X-ray fluorescence (XRF)
- Raman spectroscopy
- Laser-induced breakdown spectroscopy (LIBS)
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)

The portable gas chromatography/photoionization detector (GC/PID) technology was not promising and was eliminated from future consideration.

It is important to also note that since these seven (7) technologies are all applicable for measuring contaminants in soil and groundwater samples, it is possible that a sample preparation stage comprising extraction and concentration steps, would improve the accuracy of the detections and lower the detection limits. Such work could be completed as part of Phase 2 “optimization and validation” of the technology or technologies.

InnoTech Alberta also expressed specific interest in two biosensor technologies that have shown promise in the detection of bromacil to date: single-stranded DNA molecular recognition element (ssDNA MRE) and enzyme-linked immunosorbent assays (ELISA). Based on the results of the review, UW concluded that the ssDNA aptamer reported did not show promise in being able to be developed into a viable, field deployable, biosensor; however, the aptamer technology should still be promising provided that high quality aptamers can be obtained.

On the other hand, the ELISA technology is believed to be promising for bromacil based on the published antibody.

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1.0 INTRODUCTION

Vertex Environmental Inc. (Vertex) and the Bionanotechnology & Interfaces Laboratory at the University of Waterloo (UW) were retained by InnoTech Alberta (InnoTech) to undertake literature reviews and preliminary testing on available technologies that may have the potential to be used for field screening of soil and/or groundwater samples for the presence of bromacil and tebuthiuron at sites in Alberta and elsewhere.

This report represents Deliverables #1 and #3, as follows:

- Deliverable #1: Literature Review of Existing Field Screening Technologies
- Deliverable #3: Literature Review of ssDNA MRE and ELISA Technologies

Details of the work completed under these Tasks and the results of the various literature review activities are provided in the following sections.

2.0 PROJECT OBJECTIVES

2.1 BACKGROUND AND OBJECTIVE

Soil sterilants were commonly used from the 1960s to late 1990s for non-selective vegetation control on industrial sites in Alberta. Soils treated with sterilants often become a source of contamination to adjacent lands and waterbodies. The Soil Sterilants Program (SSP) was formed to establish proven, technical, and cost-effective strategies and best management practices sites impacted by residual soil sterilants, with the goal of achieving regulatory site closure in a timely and efficient manner.

One of the key knowledge gaps previously identified by InnoTech related to the current ability, or lack thereof, to identify and delineate bromacil and tebuthiuron impacts in soil and/or groundwater in the field. Analytical laboratories typically use Gas Chromatography/Mass Spectrometry (GC/MS) or High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS) to analyze for sterilants, with methanol typically used as the extractant to remove the sterilants from soil during sample preparation. However, analysis by these approaches is expensive, time-consuming, and not practical for use in the field. In addition, soil and groundwater guidelines for bromacil and tebuthiuron are extremely low and in some cases are below current detection limits (Drozdowski et al., 2018; Table 1), making their detection challenging.

Currently, therefore, there are no field-ready technologies that are available to achieve the goal of on-site detection, identification, quantification, and delineation, as there are for other contaminants such as petroleum hydrocarbons (PHCs) or salinity, for example. This results in high costs and long timelines for site investigation and/or remedial excavation since sample collection and laboratory analysis must be relied upon.

Table 1. Alberta Tier 1 Soil Guidelines for Bromacil and Tebuthiuron (Agriculture Land Use).

Soil Sterilant	Alberta Tier 1 Guidelines (Agriculture Land Use)[1]											
	Soil (Coarse-grained; mg/kg)						Soil (Fine-grained; mg/kg)					
	Human		Ecological				Human		Ecological			
	Direct Soil Contact	Protection of Domestic	Direct Soil Contact	Protection of Freshwater Aquatic Life	Irrigation Water	Protection of Livestock	Direct Soil Contact	Protection of Domestic	Direct Soil Contact	Protection of Freshwater Aquatic Life	Irrigation Water	Protection of Livestock
Bromacil	2,000	7.0	0.2	**0.009**	BDL	2.0	2,000	10	0.12	**0.009**	BDL	2.0
Tebuthiuron	1,600	2.5	**0.046**	BDL	BDL	0.12	1,600	3.7	**0.046**	BDL	BDL	0.11

[1] 2022 Alberta Tier 1 soil remediation guideline; BDL – below detection limit; groundwater assessment and comparison to groundwater remediation guidelines necessary; **Bold** – lowest applicable guideline.

The objective of this Project was *to develop detection/field screening or proxy laboratory analytical methods to minimize the costs associated with identification, quantification and delineation of bromacil and/or tebuthiuron in soil and/or water at impacted sites.*

The Project was designed to be completed in two Phases with Phase 1 being "proof-of-concept" and Phase 2 being "optimization and validation" of the technology or technologies. More specifically, the workplan being completed under this Project is designed to address Phase 1 and will endeavor to identify a technology or technologies that:

- Can accurately and consistently detect bromacil and/or tebuthiuron in soil and/or groundwater.
- Is practical and safe to use in the field.
- Costs a fraction of the cost of current laboratory analytical methods.
- Can be completed on-site in under four hours.

Based on the results of the literature review and preliminary testing of existing technology, promising technologies will be recommended for advancement to Phase 2 of the Project.

3.0 PROJECT METHODOLOGY

3.1 LITERATURE REVIEW OF EXISTING FIELD SCREENING TECHNOLOGIES

As part of the proposal stage Vertex completed preliminary research into technologies that are field-ready and intended (or adaptable) for use in detecting specific physical, chemical, optical, or other properties of compounds. Based on the known properties of bromacil and tebuthiuron and information on the various field screening tools currently available, an initial list of technologies to be targeted for more detailed review in terms of their potential facility towards this application was developed. All of the identified technologies were commercially available and can be accessed for proof-of-concept testing.

As part of this work, more thorough research into these and other technologies was completed. This included, but was not necessarily be limited to, the following tasks:

- A more detailed internet search.
- Further discussions with instrumentation manufacturers and suppliers.

- Obtaining and reviewing technical papers and/or user manuals to establish how the instruments work.
- Confirmation that the instruments are suitable (or adaptable) for use in the field, including an analysis of portability, temperature/weather resistance, ruggedness, etc.

The results of the literature review and interviews are documented in detail in Section 4.1, with references and supporting documentation provided (as applicable). Each technology was evaluated regarding its potential ability to detect bromacil and/or tebuthiuron. Any unacceptable or improbable technologies were eliminated from further consideration, with justification. Only those technologies that show potential were recommended for carrying forward to the next Task of proof-of-concept testing.

3.2 LITERATURE REVIEW OF SSDNA MRE AND ELISA TECHNOLOGIES

InnoTech expressed specific interest in two biosensor technologies that have shown promise in the detection of bromacil to date: single-stranded DNA molecular recognition element (ssDNA MRE) and enzyme-linked immunosorbent assays (ELISA). As such, Vertex partnered with Dr. Liu and his team at UW to complete a detailed, technical literature review of the technologies discussed in the following two papers.

1. *In Vitro Selection of a Single-Stranded DNA Molecular Recognition Element Specific for Bromacil*, by R.M. Williams, A.R. Kulick, S. Yedlapalli, L. Battistella, C.J. Hajiran and L.J. Sooter, Journal of Nucleic Acids, 2014.

2. *Regulatory Application of ELISA: Compliance Monitoring of Bromacil in Soil*, by C.D. Linde, S.J. Gee, K.S. Goh, J.C. Hsu, B.D. Hammock, T.A. Barry and D.J. Weaver, Bulletin of Environmental Contamination and Toxicology, 1996.

Dr. Liu and his team from UW examined the reported results from the perspectives of reliability, possible problems and field applicability, and provided their expert recommendation on potentially using the reported results from the technologies for developing viable, field deployable, biosensors. The results of the review are documented in detail in Section 4.2.

4.0 RESULTS AND DISCUSSION

4.1 LITERATURE REVIEW OF EXISTING FIELD SCREENING TECHNOLOGIES

For any instrument or technology to have the potential applicability to be used as a field screening tool for the detection of bromacil and/or tebuthiuron, it must be able to detect and measure one or more of the physical, chemical, optical, or other properties of the sterilant. A summary of common physical and chemical characteristics for bromacil and tebuthiuron is presented in Table 2 (Drozdowski et al., 2018).

Table 2. Common Physical and Chemical Characteristics of Bromacil and Tebuthiuron.

Soil Sterilant	Relevant Physical and Chemical Characteristics
Bromacil Chemical name: 5-bromo-3- (butan-2-yl)-6-methylpyrimidine-2,4(1H,3H)- dione Substituted uracil herbicide Commonly used product names: bromacil, 317-40-9; Bromazil, Uragan, Hyvar X (spray), Calmix (combined with 2,4-D as pellets), Krovar (combined with diuron) Typically available as wettable powder, soluble concentrate, or granular	Appearance: Colourless to white crystalline solid Molecular Formula: $C_9H_{13}BrN_2O_2$ Molecular weight: 261.119 g/mol Melting point: 158-160°C Solubility in water: 815 mg/L @25°C Vapour pressure: negligible @25°C
Tebuthiuron Chemical name: 1-(5-tert- Butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea Commonly used product names: Spike, 34014-18-1, Graslan, Perflan, Brulan; Herbec 20P Typically available in the form of granules or pellets	Appearance: Colourless crystals Non corrosive Molecular Formula: $C_9H_{16}N_4OS$ Molecular weight: 228.314 g/mol Melting point: 164°C Solubility in water: 2,500 mg/L @25°C Vapour pressure: 2.0×10^{-6} mm Hg @25°C

Many of the common field screening tools for soil and groundwater measure what are known as "collective descriptor" parameters such as pH, electrical conductivity, oxidation/reduction potential (ORP), etc. However, being non-specific, they react with many different soil and groundwater constituents in addition to contaminants and will not be able to distinguish between a response from the compound of interest and the response from everything else in the sample. As such, instruments that measure only these properties are of little use for this application and do not warrant further consideration.

Other properties measured using some of the more sophisticated field screening technologies include how the compound responds when exposed to various wavelengths of light/energy: emitted light spectrum, radiation, florescence, etc. Although details on such optical characteristics for bromacil and tebuthiuron are not available (or are not fully known at this time), there is a potential that sterilants may be detectable via such means.

As discussed in Section 3.1, Vertex's preliminary list of potentially useful technologies included the following:

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
- Near infrared reflectance spectroscopy (NIRS)
- X-ray fluorescence (XRF)
- Portable gas chromatography/photoionization detector (GC/PID)
- Raman spectroscopy
- Laser-induced breakdown spectroscopy (LIBS)

As a result of the literature review completed, Gas Chromatography/Thermionic Ionization Detector (GC/TID) was identified as having the potential to detect bromacil and/or tebuthiuron and, as such, was also included in the detailed literature review.

All of these technologies are commercially available, with the exception of the GC/TID, and can be accessed for the proof-of-concept testing to be completed in the next phase of work.

The results of the literature review and interviews are documented in detail in the following sub-sections.

4.1.1 Ultraviolet Laser Induced Fluorescence (UVOST® or OIP®) and Visible Light Laser Induced Fluorescence (TarGOST® or OIP-G®)

There are a variety of different forms of laser induced fluorescence (LIF) that are used in the field, and although there are some variations in their application the overarching theory behind this non-destructive technology is consistent. In general, LIF utilizes the unique emitted spectra of aromatic molecules to determine relative concentrations of contaminants within the system (United States Environmental Protection Agency, 2018). Depending on the type of LIF, a different wavelength range of light is used to excite the molecules within compounds such as non-aqueous phase liquids (NAPLs), which naturally have a fluorescence (Dakota Technologies, n.d.(b)). When a molecule interacts with a high energy light pulse, energy can be absorbed and released. Fluorescence occurs when the emitted wavelength is longer than the incident wavelength (Herman et al., 2015). LIF can also be used to determine the type of contaminant present, through not only the colour of fluorescence but also the time delay between pulse of the laser and the observance of fluorescence (Dakota Technologies, n.d.(b)).

Ultraviolet laser induced fluorescence (UV-LIF) uses ultraviolet light to excite the molecules of the compound or contaminant of interest to achieve the fluorescence required for analysis. UV-LIF technology, such as the UVOST® system being considered by Vertex, is mainly oriented towards PHC NAPLs and typically requires a direct-push platform where readings are recorded as the probe descends through soils and groundwater in the subsurface (Figure 1; Dakota Technologies, n.d.(a)). The UVOST® system also allows for modeling to be performed with the collected data, as required (Dakota Technologies, n.d.(a)). This technology, if deployed into the subsurface via direct-push technology, precludes the need of collecting soil and/or groundwater samples and can record data at a density of approximately 2.5 cm intervals, with a production rate of approximately 90 to 150 metres per day being covered (Dakota Technologies, n.d.(a)).

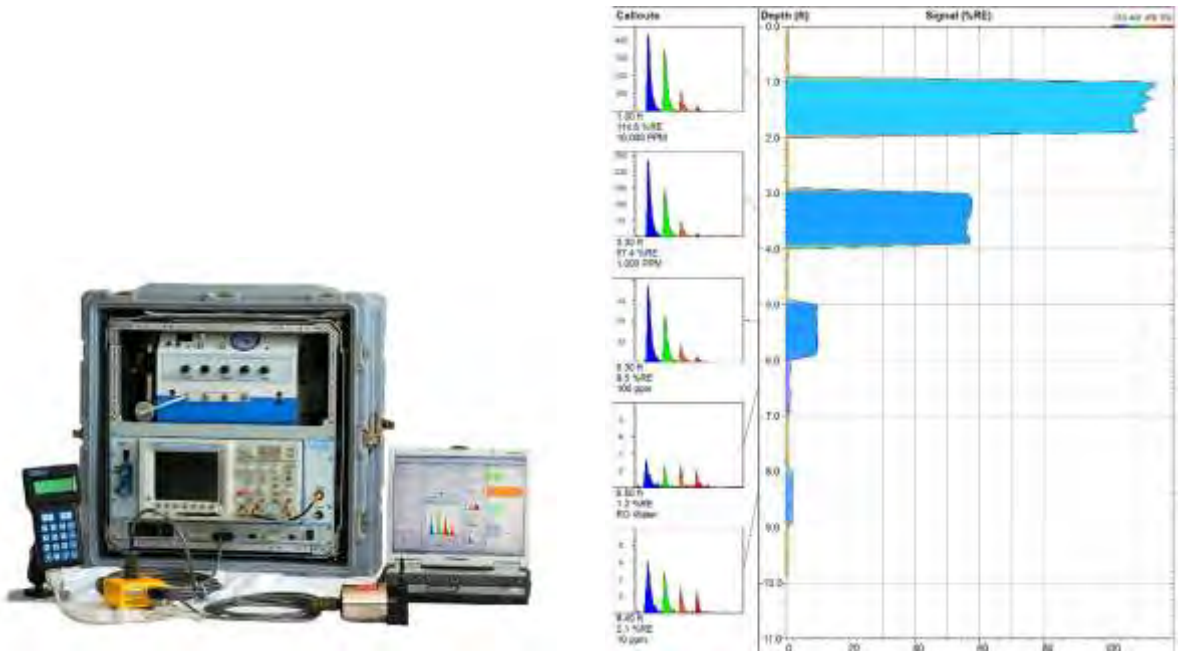

Figure 1. The UVOST® System (left) and Example Output (right).

TarGOST® (Tar-specific Green Optical Screening Tool) uses the same theory and technology as UV-LIF, but instead utilizes the visible (i.e., green) range of wavelengths to achieve fluorescence (Figure 2). Both TarGOST® and UVOST® technologies use a direct-push platform, do not require sampling, and allow for the collection of real-time data (Dakota Technologies, n.d.(a)). Furthermore, they have comparable measurement density capabilities (Dakota Technologies, n.d.(a)). The main difference between the two systems is the type of compounds that the equipment can detect. Specifically, TarGOST® technology will not identify any dissolved-phase contaminants as it is specifically blind to them (Dakota Technologies, n.d.(a)). TarGOST® is specifically designed for higher molecular weight contaminants including coal tar and heavy crudes, while UVOST® detects lower molecular weight contaminants such as diesel and gasoline. The challenge that can be anticipated from this technology is based on this selective identification, as both bromacil and tebuthiuron are highly soluble and LIF based technologies typically only detect non-aqueous phase liquids.

A general drawback for these technologies is that while they are clearly well suited for in-situ testing, they are the only type of system that requires access to a direct-push drilling platform such as a Geoprobe®. Therefore, the use of the LIF equipment in the field will also include rental fees for the drilling platforms. However, this only applies to the application of the technologies in-situ. Soil and groundwater samples can also be tested ex-situ. Therefore, as with all other technologies described here, sample collection for ex-situ testing is a separate issue.

The main advantages of the LIF technologies are the extensiveness of the analysis that can be performed. Because these technologies can involve probes accessing the subsurface in-situ and at depth, they can allow for a 3D understanding of the extent and degree of a contaminant plume.

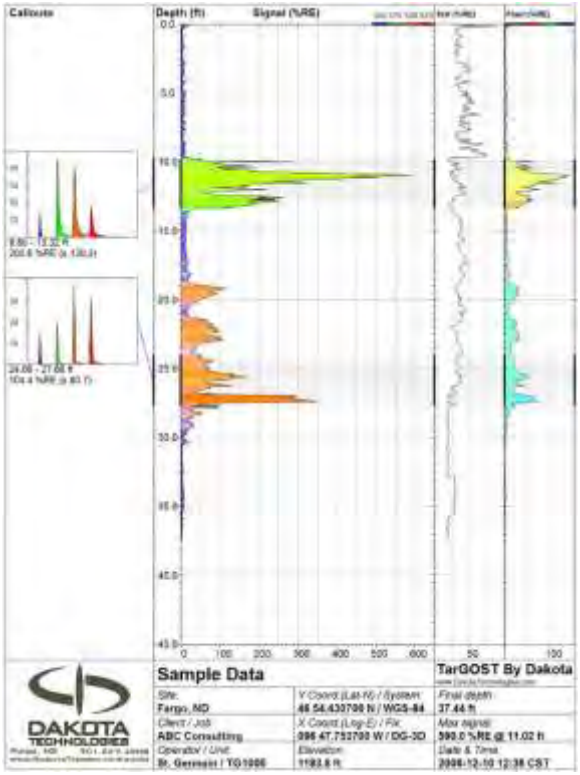

Figure 2. Field Deployment of the TarGOST® System (left) and Example Output (right).

Neither UVOST® nor TarGOST® have a history of being used to screen for or measure the concentration of herbicides such as bromacil or tebuthiuron. This does not preclude LIF technologies from being used to identify these two herbicides, although it may present more challenges to applying these two methods because typically these technologies are deployed to detect NAPLs (high concentration) and not dissolved-phased (low concentration) contaminants. Therefore, elevated detection limits may be an issue.

4.1.2 Near Infrared Reflectance Spectroscopy (NIRS)

Near-infrared reflectance spectrometry is a method by which light within the near-infrared range is scattered and absorbed by a sample (Font et al., 2007). The scatter and absorption behaviors are unique to certain molecules due to how they vibrate when interacting with electromagnetic radiation, and therefore the compound can be identified by analysis of this scatter (Font et al., 2007). NIRS is a non-destructive technique that has been used in many industries including agriculture and geology (Figure 3; Font et al., 2007).

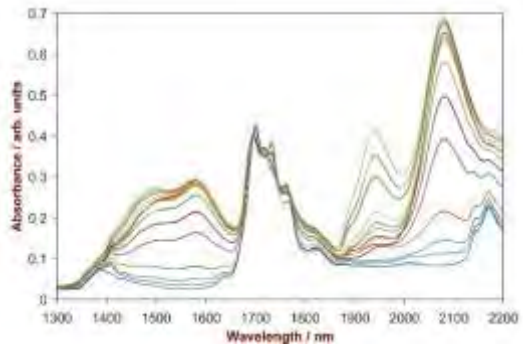

Figure 3. Field Deployment of an NIRS System (left) and Example Output (right).

One of the advantages of NIRS is that is that it less susceptible to background UV interference than other technologies (Swamy et al., 1997). NIRS devices are also portable and lightweight allowing it to easily be used on-site. The detection limit of NIRS technology can be as low as parts per billion (ppb), though this varies greatly on the application and environment (Christesen et al., 2014).

NIRS also has a history in environmental investigations and bromacil has been identified using NIRS technology in previous research into the applicability of the technology for environmental analysis (Swamy et al., 1997). In clinical experiments urea was able to be identified using NIRS technology, furthermore it was found that urea showed a unique spectrum that allowed for it to be differentiated from the other species of interest (Hall and Pollard, 1993). Tebuthiuron is a herbicide of the urea group, therefore there is the potential that if urea was able to be identified using NIRS technology so too could tebuthiuron.

One of the major drawbacks of the NIRS technology is that it can only be used to screen certain types of soil samples. Very high water content soils (such as saturated peats) cause too much interference with the signal capture. Conversely, water samples can (theoretically) be directly tested using the technology.

4.1.3 X-Ray Fluorescence (XRF)

X-ray fluorescence technology employs the understanding of spectrometry and the x-ray range of light. When this light interacts with a sample it is both scattered and absorbed, the degree to which either occurs is dependent on the chemical properties of the sample (Wirth and Barth, n.d.). This behaviour is due to the x-ray exciting the electrons within the sample, allowing them to jump to a higher energy level (Wirth and Barth, n.d.). Eventually energy is released, and these emitted rays have characteristic wavelengths dependent on the element (Wirth and Barth, n.d.). Since samples are not of one element the XRF instrumentation takes the complete wavelength emitted and resolves it into the relative amounts of elements within the sample (Wirth and Barth, n.d.).

The Innov-X device that is being considered by Vertex for testing, is focused on the identification of elements between, and including, phosphorus and uranium (Figure 4; Innov-X Systems, Inc., 2005). This is because the main focus of the Innov-X when it comes to soil analysis is the identification of contaminant metals (Olympus, n.d.). Potential challenges stem from the fact that the soil sterilants are predominantly made up of elements with atomic numbers below 15. As such, bromine in bromacil (35) and sulphur (16) in tebuthiuron are the only elements that are within the detection range for the technology.

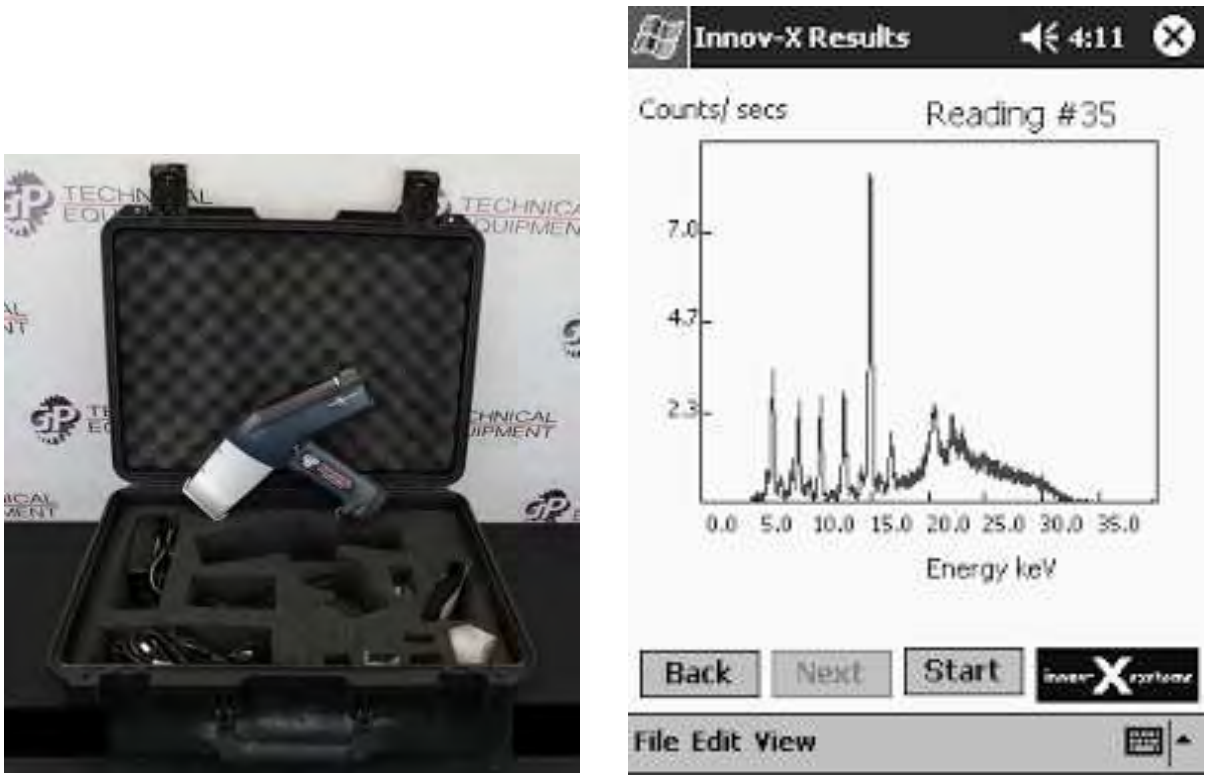

Figure 4. The Innov-X System (left) and Example output (right).

The current detection level of the Innov-X is at the parts per million (ppm) level, which is higher than hoped for the detection of bromacil and tebuthiuron. XRF, in general, does not have extremely low detection limits. In many cases elements are not able to be identified in trace concentrations as low as desired for this application (Zhang and Cresswell, 2016). The main challenge is that the detection limit for XRF is even higher for elements with a low atomic number. Elements up to and including sodium (11), have a fluorescence that is of such a low energy that they are often reabsorbed or will not reach the detector (Portable Spectral Services, n.d.). Portable Spectral Services (n.d.) reports that detection limits for such elements is as high as 3% by weight when using handheld XRF devices. This may present challenges in the identification of bromacil and tebuthiuron as both herbicides are predominantly made up of these lighter elements not easily detected by XRF. The question is whether a methodology can be identified with respect to the bromine (in bromacil) and sulfur (in tebuthiuron) within the herbicides such that they can be distinguished from other elements within the soil.

XRF technology also comes with certain advantages. The Innov-X is very portable and relatively lightweight, which will facilitate easier use in the field (Innov-X Systems, Inc., 2005). Innov-X also does

not require extensive sample preparation and can analyze samples in place or in the laboratory (Olympus, n.d.). The Innov-X can also be used on soil or liquids and is therefore well suited to soil and groundwater investigations (Olympus, n.d.).

There does not appear to be a precedent for studying or identifying bromacil or tebuthiuron, or related substances, using XRF technology. However, XRF technology has been used to study foliar applied herbicides – those being herbicides that are applied to the plant near the ground. This was found to be possible with herbicides that have atoms with atomic numbers of 11 or higher (Hess et al., 2017). There were some noted limits to this analysis though: two examples of these are the concentration of the herbicide in surface soils needed to be above 1.12 kg/ha if the substance only contained one atom above sodium (like bromacil and tebuthiuron), and if there were other substances in the soil that contained these same detectable atoms inaccuracy was reported (Hess et al., 2017).

As such, XRF technology appears to have the potential to detect bromacil and tebuthiuron in soil and groundwater samples; however, it is likely that it will prove to be more effective for bromacil since bromine (35) has a much higher atomic number than sulphur (16) and since natural background concentration of sulphur in soil and groundwater samples, as the fifth most common element on Earth (Wikipedia, n.d.), is expected to result in high levels of interference with the technology.

4.1.4 Portable Gas Chromatography / Photo-Ionization Detector (GC/PID)

Gas chromatography is the separation of gases allowing the relative amounts to be determined (Poole, 2012). In terms of this report the interest is whether volatilized bromacil and tebuthiuron can be detected within ambient air.

Photoionization detectors (PIDs) are commonly used in the environmental industry to detect trace levels of volatile and semi-volatile organic compounds. They are relatively simple to use, compact, and offer a non-destructive method of analysis and identification (Poole, 2012). The PID uses electrical impulses to determine the concentration of these compounds within ambient air (Poole, 2012). A light source within the PID uses high energy photons to ionize molecules (Poole, 2012). When the ionized molecules come in contact with the internal cathode they lose their charge, which is measured and reported by the PID to the user as a concentration (Poole, 2012). The more ions that are ionized, the higher the electrical impulse and therefore the higher the reported concentration (Poole, 2012). The range of compounds detectable by a PID is dependent on the power of the lamp. A PID will only detect elements whose ionization energies are lower than the noble gas used within the lamp, and therefore the lamp used will vary depending on the compounds of interest (Poole, 2012). It is preferable to have as large of a difference between the ionization energy of the noble gas and the molecule as possible such that ionization is more likely (Poole, 2012).

Vertex evaluated using the FROG-4000 as a potential method of identifying bromacil and tebuthiuron in soil and groundwater samples (Figure 5). The FROG-4000 is marketed as a detection tool for volatile organic compounds (VOCs) in the field (Defiant Technologies, n.d.). It is portable and can detect VOCs at concentrations in the ppb range (Defiant Technologies, n.d.). The main foreseeable challenge is that the soil sterilants are not noted as compounds that the FROG-4000 can identify and do not easily volatilize at ambient temperatures (Pine Environmental, n.d.).

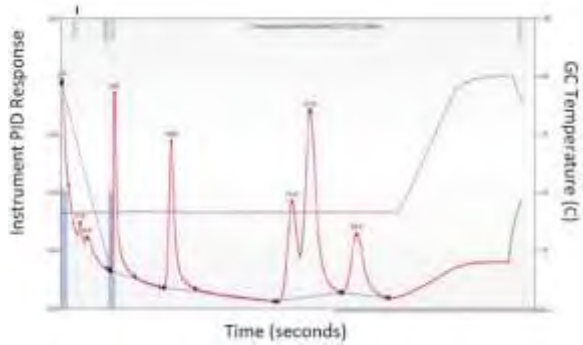

Figure 5. Field Deployment of the FROG-4000 (left) and Example Output (right).

There is evidence that GC has successfully identified both bromacil and tebuthiuron. Bromacil was detected within filtered wastewater and natural water at levels as low as 0.1 ppb (National Center for Biotechnology Information, n.d.(a)), and bromacil has been extracted for measurement through gas chromatography in a laboratory (Pease, 1966). Tebuthiuron has also been detected in groundwater using a nitrogen-phosphorus detector at levels as low as 0.58 ppb and when using select-ion monitoring levels as low as 0.015 ppb were detected in natural water (National Center for Biotechnology Information, n.d.(b)). However, both of these detection setups were more involved than typical field-ready technology, such as the FROG-4000.

There are different detectors that can be used in tandem with a GC that may offer field screening capabilities for bromacil and/or tebuthiuron (i.e., TID – see Section 4.1.7 below) which Vertex has evaluated as a potentially suitable technology for the next stage of testing.

4.1.5 Raman Spectroscopy

Raman spectroscopy is based on laser light scattering in response to its interaction with molecules (Horiba, n.d.). Raman spectroscopy uses specifically the light that is scattered at different wavelengths than the incident ray (Raman Scatter), and though this is a small percentage of the overall scatter, Raman Scatter can provide information on the chemical structure and even the phase of the compound of interest (Horiba, n.d.). The characteristics of the Raman Scatter can be attributed to a particular molecular bond or group of bonds and therefore enables the user to do a compound analysis instead of elemental (Horiba, n.d.).

The handheld Raman spectrometer being considered by Vertex is the NanoRam, which offers an analysis method that is non-destructive (Figure 6). The device is designed for both laboratory and field use and the “point and shoot” method can be used directly on soils or to analyze a groundwater sample through a clear container (B&W Tek, n.d.). The handheld Raman spectrometer is designed to be portable and easy to use on site (B&W Tek, n.d.). The NanoRam does not have specified detection limits (B&W Tek, n.d.).

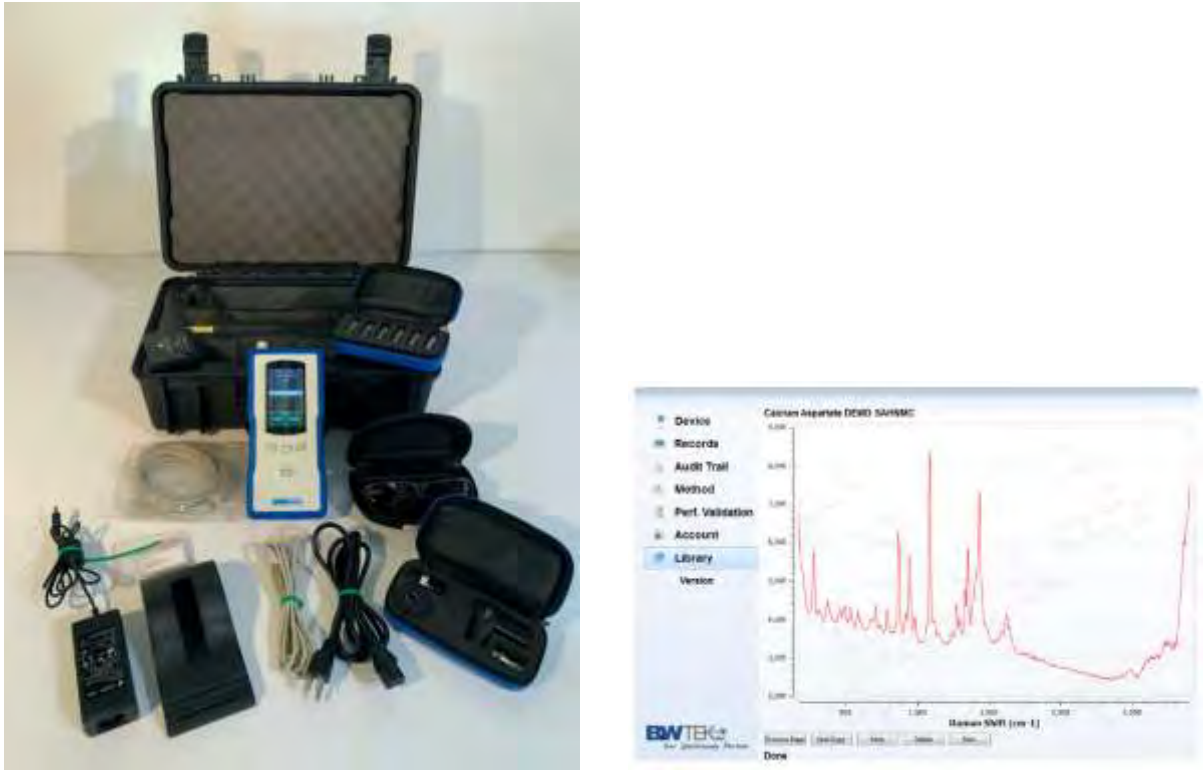

Figure 6. The NanoRam System (left) and Example Output (right).

Raman spectroscopy has been employed to characterize the degradation of bromacil in soil (Roselló-Márquez et al., 2019). While there are no references to using Raman spectroscopy to identify the presence of tebuthiuron that the authors could find, there are references to this technology being used for urea: in the quantifying of its concentration in milk (Kahn et al., 2015).

4.1.6 Laser-Induced Breakdown Spectroscopy (LIBS)

Laser-induced breakdown spectroscopy (LIBS) uses a high energy laser pulse to ionize and excite the atoms within a sample (Shah et al., 2019). This interaction between the atoms and the laser causes some evaporation of the sample which results in the production of plasma (Shah et al., 2019). The plasma gives off light whose spectra can be analyzed to determine the chemical components of the sample (Shah et al., 2019). The wavelength therefore indicates the atoms present, and the relative intensity allows for a measurement of concentration (Shah et al., 2019). This process is non-destructive, and the samples require very little or no preparation before analysis (Shah et al., 2019).

LIBS has been used to analyze a variety of materials including soils, solutions, and insecticides (Shah et al., 2019). Furthermore, LIBS has been used for different environmental applications, mainly for the identification of trace metals and crude oil and fuel residues (Shah et al., 2019). Dual pulse LIBS has also been used to determine trace contaminants within organic fertilizers (Nicolodelli et al., 2016), which suggests that it could be used to detect other organic compounds such as the soil sterilants of interest. LIBS has also been used for soil analysis in agriculture, specifically when there is concern about heavy metal contamination or in the detection of select nutrients (Peng et al., 2016).

Vertex is considering the EOS handheld LIBS analyzer for proof-of-concept testing (Figure 7). The EOS is focused on alloy composition determination and therefore determining if it can be calibrated to identify

the soil sterilants appears to be the main foreseeable challenge for this technology (BRUKER, n.d.). It does appear that the EOS's range of identification should include the elements within the soil sterilants as LIBS technology is well suited to the identification of elements with lower atomic numbers (BRUKER, n.d.). There are no specified detection limits for the devices considered; it is dependent on the application (BRUKER, n.d.). Some advantages of the EOS are its size and weight such that it is easily portable within the field. The EOS is also relatively robust, and LIBS is faster than handheld XRF analysis (BRUKER, n.d.).

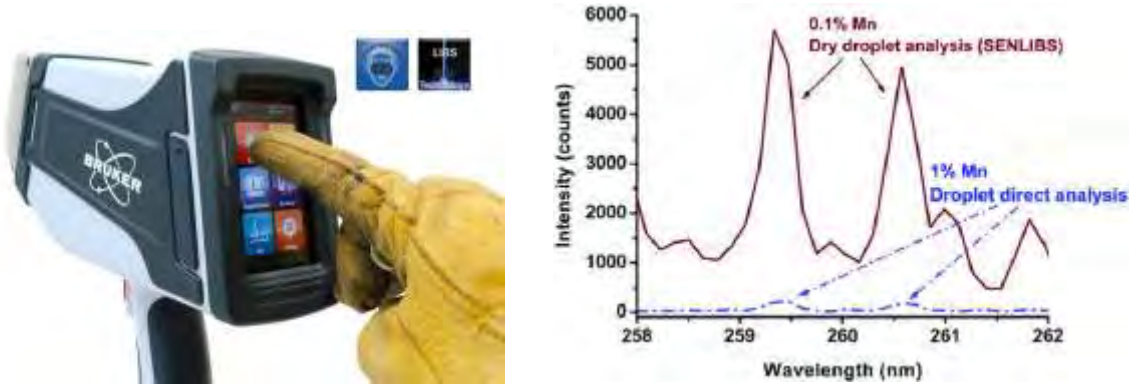

Figure 7. The EOS Handheld LIBS System (left) and Example Output (right).

There does not appear to be any precedence for identifying or screening for bromacil or tebuthiuron or either of their general families of herbicides using LIBS. This does not preclude this method as a viable option, but there is the potential that it will be more challenging to interpret the results of the screening using LIBS with no previous research done in this area.

4.1.7 Gas Chromatography / Thermionic Ionization Detector (GC/TID)

Thermionic ionization detectors (TIDs), occasionally referred to as nitrogen-phosphorous detectors, use the theory of gas chromatography as discussed previously in Section 3.1.4 above. The TID contains a thermionic ionization detector bead which heats up and when the substance of interest comes in contact with the bead a chemical reaction can occur (SRI, n.d.). The reaction occurs within the plasma that coats the surface of the TID bead and results in the substance being ionized (SRI, n.d.). These ions are measured by the electrode within the system and the resulting are reported to the user as a concentration (SRI, n.d.). The molecule type determines whether this ionization reaction occurs. Specifically, molecules containing the NO_2 functional group are the main substances that are observed by TID technology (SRI, n.d.).

TIDs, unlike many other devices used in environmental investigations, will not detect aromatic or aliphatic hydrocarbons (SRI, n.d.). The SRI TID device that it being considered by Vertex (Figure 8) has detection limits within the ppb range, which is low enough to meet the goals of the project (Quadrex Corporation, n.d.). TID devices require air to run property, and the device is listed as being able to run on ambient air in the field (Quadrex Corporation, n.d.).

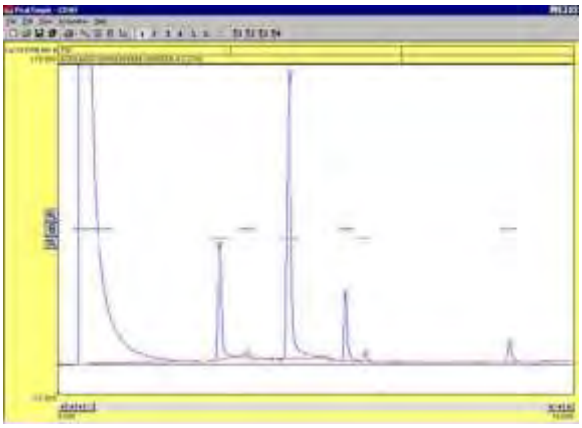

Figure 8. The SRI TID System (left) and Example Output (right).

TID technology is currently not commercially available as handheld or field-deployable devices. To employ this method in the field a TID device would need to be installed on an existing vehicle designed for gas chromatographic investigations. It is likely possible to do with existing technology available to Vertex with some further research and development work to determine the necessary modifications required.

There is an established precedence for using gas or liquid chromatography methods to screen for and study herbicides and pesticides. Bromacil was one of the compounds that was studied using TID technology as a part of larger pesticide column experiments performed within the laboratory (Draper, 1995). Bromacil was observed as a co-elute along with tetrachlorvinphos and, in a separate experiment, alachlor (Draper, 1995). In the same report tebuthiuron is also mentioned as being detectable, though there were some limitations in its detection (Draper, 1995). It was noted that tebuthiuron was not detectable in the presence of certain substances containing nitrogen, and both bromacil and tebuthiuron detection was greatly impacted by the condition of the columns used, and in some cases were not detectable if the column was not cleaned adequately or was not of the right specifications (Draper, 1995). These stipulations on the detectability of tebuthiuron but also bromacil could indicate that applying TID in the field may be a challenge due to the limited control of the environmental conditions compared to that of the laboratory.

4.1.8 Summary

Vertex evaluated a total of eight different technologies that were identified on a preliminary basis as having the potential to be directly used or adapted for use to detect bromacil and/or tebuthiuron in soil and/or groundwater samples at sites in Alberta. Seven of these technologies are proposed to be carried

forward for the next stage or work to attempt to detect and quantify both bromacil and tebuthiuron in soil or groundwater samples:

- UV-LIF (UVOST®)
- Visible-LIF (TarGOST®)
- NRIS
- XRF
- Raman spectroscopy
- LIBS
- GC/TID

Except for the LIF and GC/TID technologies, all are in the form of handheld devices. Both UV-LIF and Visible-LIF require a direct push platform (such as a Geoprobe® drill) to use in the field for in-situ detections. However, samples can be tested ex-situ by placing them directly in front of the probe. The GC/TID is currently not available as a portable or field ready device. However, as this technology shows promise for this application, it will be tested using laboratory technology in the next stage of work.

The main challenges for the technologies discussed is precedence, as they are not designed for herbicide screening, although some have been used for similar applications others. The LIF and LIBS technology do not appear to have ever been used for such an application. In theory these technologies should be able to identify bromacil and tebuthiuron given sufficient testing and calibration. It should also be noted that the detection limits of handheld devices are significantly higher than (typically) larger pieces of laboratory-grade equipment and this is a relatively consistent challenge for all the technologies evaluated so far.

Technologies like XRF and LIBS analyze samples on an elemental basis, and they tend to be better at detecting heavier elements than those below the first 15 or so elements. It is predicted therefore that if using elemental analysis, the baselines will need to be determined to a high degree of accuracy to identify the presence of bromacil or tebuthiuron since each of these herbicides are predominantly composed of lighter elements. It is possible that the other technologies that use molecular or compound-based analysis, like Raman spectroscopy, may avoid this challenge.

The next step is to complete proof-of-concept testing on these technologies using soil and groundwater samples containing known concentrations of bromacil and tebuthiuron to confirm whether they are able to reliably detect and quantify these parameters.

4.2 LITERATURE REVIEW OF SSDNA MRE AND ELISA TECHNOLOGIES

This section presents the results of the review completed on the papers on the ssDNA MRE and ELISA technologies by Dr. Liu and his team at UW.

4.2.1 SSDNA MRE

4.2.1.1 Introduction

Research documented in the Williams et al. (2014) paper identified a single-stranded DNA molecular recognition element (ssDNA MRE or aptamer) that showed a high affinity and specificity for bromacil. The ssDNA MRE developed was also tested against two competing molecules of bromacil (6-amino-3-ethyl methyl uracil and 1-methyl uracil) with negative results, thus claiming the specificity of the identified MRE. Williams et al. (2014) hypothesized that the identified MRE may be useful as the sensing element in a field deployed screening device, which could save time and expense compared to existing bromacil detection

methods (i.e., chromatography, mass spectrometry, etc.). Similar testing on tebuthiuron was not discussed.

Aptamers are the nucleic acid version of antibodies. DNA aptamers are chemically synthesized and thus can be mass produced with a good consistency. In addition, DNA aptamers can be designed into various types of biosensors for detecting a broad range of small molecular targets. However, not all reported aptamers are legitimate, and many nonspecific sequences have been reported. The review of the Williams et al. (2014) paper indicates that the legitimacy of the identified aptamer has not been convincingly established for the following reasons.

4.2.1.2 Detailed analysis

Characterization of the Secondary Structure of the MRE

This is a critical step to apply the selected aptamer for reliable sensing applications. Herein, the structures of the selected aptamers were critically analyzed based on the information presented in Willaims et al. (2014). First, the length of 80 nucleotides is considered a bit long for practical use (approximately 50 or less would be possible based on its structure).

From the secondary structure analysis, the two sequences researched by the authors are shown in Figure 9 (from Figure 3 of Williams et al. (2014)). In their Table 2, Williams et al. highlighted the conserved nucleotides, and these are highlighted in yellow below. The positions of these conserved nucleotides are mainly in duplex regions, and it is considered very unlikely they can be responsible for binding. Normally, important nucleotides should be in loops. By looking at the loops near these highlighted nucleotides, there is no sequence conservation. By also looking at other sequences, the selected library was found to be poorly aligned, suggesting nonspecific binding was selected. Therefore, it does not appear that their proposed conserved nucleotides are important for binding, and by examining the sequences, it does not appear that they can bind. To confirm this argument, truncation and mutation studies could be performed. For example, some of the nucleotides could be changed and tested for their binding ability.

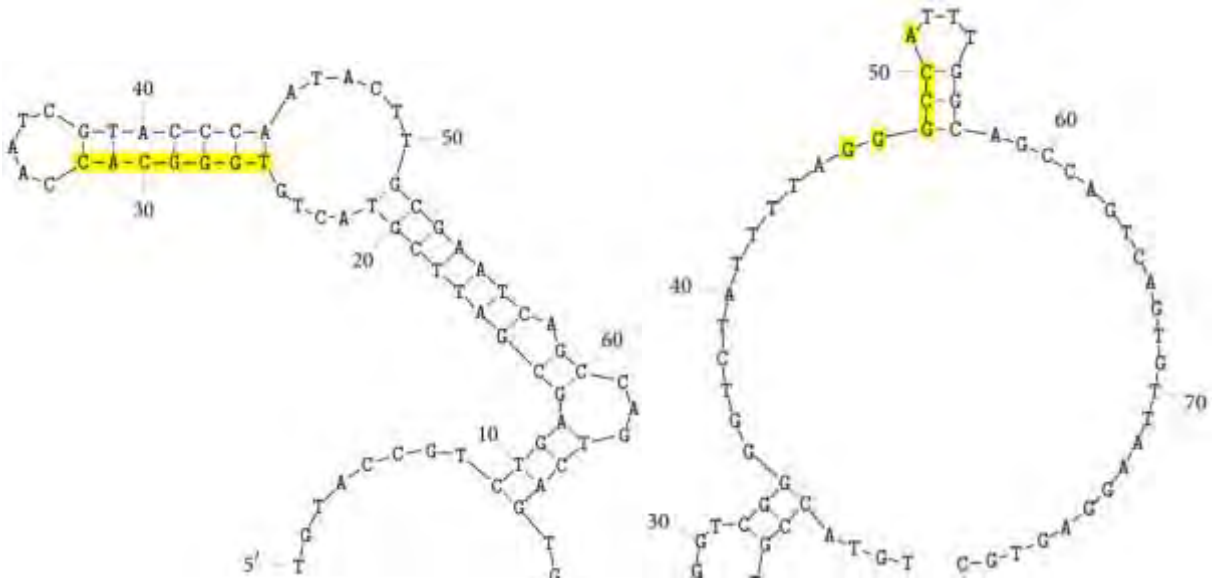

Figure 9. The Secondary Structures of the MREs.
Taken from Figure 3 of the paper. The conserved nucleotides are highlighted in yellow.

The Experiments for Evaluating the K_d were Poorly Designed and Performed

Williams et al. (2014) immobilized bromacil on magnetic beads and used a fluorophore-labeled aptamer for evaluating binding. Instead of varying the concentration of target molecules, the authors varied the aptamer concentration. Although washing was performed, non-specific binding cannot be ruled out, and it is not surprising that the more aptamer added, the more aptamer remained on the beads. In Figure 4 of Willaims et al. (2014), it was apparent that the first two concentrations of MRE (i.e., 0 and 250 pM) did not bring any fluorescence change, however the third concentration of 50 nM had already reached saturation. The difference between 250 pM and 50 nM was 200-fold. Generally, a gradually changed titration is expected for a binding curve to evaluate the K_d value. Furthermore, the data were too scattered, and the statistical quality of the data cannot be judged without error bars. Finally, there was no control experiment (e.g., the use of a random DNA or even better, a mutant to count for non-specific binding). Thus, it does not appear that the reported K_d is reliable. To obtain a more reasonable K_d, more data points between 250 and 500 pM should be added. The authors claimed a K_d of 9.6 nM, and most aptamers for small molecules cannot reach this. For a molecule like bromacil, a K_d of 1,000 nM (1 µM) would be quite good already, and the reported 9.6 nM is another indication of non-specific binding being measured.

More importantly, another independent binding assay is needed to avoid the non-specific binding problem. For example, isothermal titration calorimetry (ITC) is a reliable instrument to evaluate the aptamer's binding properties. If the aptamer really has an nM K_d, strong binding evidence can be observed from the ITC. Based on this evaluation, the binding assay is not reliable.

The Specificity of the MRE Needs to be Re-evaluated

From the cross-reactivity data (in Table 3, taken from Williams et al. (2014)), the average fluorescence of bromacil was only about one-fold higher than its analogues, and this was just from an endpoint measurement. Considering the standard deviation, the data for bromacil and other molecules are overlapping. The quality of the endpoint data is insufficient to conclude that the MRE has high specificity. To obtain more convincible data, additional control experiments need to be completed. For example, the titrations of analogues (using the same fluorescence assays) can be carried out, and then their K_d values could be fitted and used to compare with that of bromacil.

Table 3. Cross-reactivity Data of R21.2 ssDNA MRE.

Eluent	Average fluorescence (RFU)	Standard deviation	*P* value
Bromacil	0.51	0.16	—
NT-1	0.22	0.20	0.06
NT-2	0.28	0.09	0.05
BSA	0.19	0.08	0.02
Atrazine	0.22	0.15	0.04
Malathion	0.10	0.15	0.02
0.01% MeOH	−0.0045	0.12	0.006

4.2.1.3 Conclusions

Based on the critical evaluation of the Williams et al. (2014) paper, the presented data does not appear to support the claimed high affinity aptamer. Furthermore, it does not appear that the claimed aptamers are actually aptamers capable of specific binding of bromacil.

4.2.1.4 Some other related papers and discussion

To provide more information for reference, a literature search was completed for other aptamers for soil contaminants and several practical sensing strategies. Although no other reports were specific for bromacil or tebuthiuron, a review paper was found (Liu et al., 2019) that summarized twelve SELEX-derived aptamers for pesticides. For example, an iprobenfos aptamer was selected by Kwon et al. (2015), having a K_d of 1.67 µM. Its secondary structure was characterized, and its binding performance was evaluated based on both colorimetric assays (using gold nanoparticles) and ITC, showing consistent results. In addition, another aptamer was selected by Eissa et al. for detecting carbendazim (Eissa and Zourob, 2017), which exhibited a K_d of 65 nM. It showed about 8-fold selectivity over other commonly used pesticides, such as fenamiphos, isoproturon, and atrazine. Therefore, the aptamer technology for detecting bromacil and tebuthiuron should be technically viable as long as high-quality aptamers can be obtained.

To develop selected aptamers in sensors for real applications, another review (Nguyen et al., 2017) summarized some important strategies. Three sensing platforms were mentioned in this paper that might be adopted due to their sensitivity, easy operation and low cost. Firstly, a duplex region can be extended on the aptamer (Figure 1A in Nguyen et al. (2017)), with one end labeled by a fluorophore and the other by a quencher. The initial fluorescence would be quenched, whereas adding target molecules can greatly enhance the signal. Only a small UV light is required to use this sensor outdoors. Alternatively, graphene oxide can be used to induce fluorescence changes in the absence and in the presence of testing molecules (Figure 1C in Nguyen et al. (2017)). In this case, a fluorophore can be directly modified on the aptamer. Finally, a colorimetric sensor is also outdoor-friendly. A horseradish peroxidase (HRP) mimicking DNAzyme sequence can be employed and extended on the aptamer strand (Figure 1F in Nguyen et al. (2017)). For the sample containing target molecules, the subsequent addition of hemin and TMB (3,3´,5,5´-tetramethylbenzidine) will produce blue color. This can be observed directly by the naked eye and does not need any equipment.

4.2.2 ELISA

4.2.2.1 Introduction

Antibody-based enzyme-linked immunosorbent assay (ELISA) has been found to be a simple and cost-effective alternative to laboratory analysis for many environmental contaminants including total petroleum hydrocarbons (TPH), as well as pesticides and herbicides such as 2,4-dichlorophenoxyacetic acid (2,4-D), toxaphene, chlordane, etc. As such, they have a broad application for on-site analysis in the future. But the key to improving the assay is to acquire high quality and sensitive antibodies. The polyclonal antibody was produced in the 1990s (Szurdoki et al., 1992 cited in Linde et al. (1996)), and no further studies were performed on new antibody production. The reason may be that as new types of herbicides keep emerging, the application of the old and less environmental-friendly ones is reduced sharply or replaced. The problem of polyclonal antibodies is batch-to-batch variation since they were extracted from the blood of animals. In addition, the transduction of a specific antibody to a small molecule target such as bromacil is more challenging.

In Linde et al. (1996), this polyclonal antibody displayed high titers and inhibitions towards bromacil. No cross-reactivity was found with other related compounds, which demonstrated the antibody was sensitive and specific. That means the antibody could still work with good performance for now. Besides, the leading author, Prof. Bruce D. Hammock in UC Davis had worked for decades on developing immunoassays for pesticides, pesticide metabolites and environmental contaminants; the technology has been successfully transferred to government agencies, academic and commercial research laboratories domestically and internationally. Although UW cannot perform the detailed molecular analysis of the antibody as was done for the aptamer, the success of antibodies for binding similar compounds and the reputation of this research group can give confidence on this method.

4.2.2.2 Detailed Analysis

Detection Based on this Antibody

Based on this antibody, the established ELISA method reached a detection range of 0.05 to 15 µg/L with an IC_{50} of 0.247 ppb (µg/L) as the MDL for the soil assay was 0.01 µg/mL (Linde et al., 1996). There was a class-specific antibody towards benzoylphenylurea herbicides including tebuthiuron and the IC_{50} was 7.4 ppb. The assay was reproducible, and the results obtained so far had demonstrated the potential usefulness of the antibody for selective quantitative detection of bromacil at the very low levels commonly found in environmental samples. For the modified method, methanol was identified as the extractant of choice since it was easier to use and resulted in lower detection limits than sodium hydroxide, which ensured quick treatment for sample processing. Similar testing on tebuthiuron was not discussed.

A typical ELISA process is shown in Figure 10. As can be seen, it contains multiple incubation and washing steps taking around 4 hours in a typical assay. Therefore, although it is quite sensitive, it is not considered applicable for field applications for environmental samples where a relatively fast analytical time coupled with fewer sample preparation and analytical testing steps would be more desirable. Thus, further methodology improvements are needed. An ideal analytical method should be rapid and sensitive that can finish determination in a few minutes with minimal sample preparation.

Figure 10. The ELISA protocol.
Molecular Devices (n.d.).

4.2.2.3 Recommendations

Immunochromatographic assays with nanomaterials have exhibited excellent characteristics and have been developed as an inexpensive and portable monitoring tool for diagnostic purposes and small molecular detection (Kong et al., 2016). A representative example is the pregnancy test strips. Thus, a rapid, convenient, and sensitive gold (Au) nanoparticle-based immunochromatographic strip is recommended due to the high affinity antibody. Au nanoparticles are used as a colour label.

The strip not only can achieve qualitative detection by the naked eye but also quantitative calculation by strip digital reader to establish a standard curve. Under the optimized conditions, the analyte is added to sample pad on strip for chromatographing 10 min (Figure 11). A negative result is observed when the C line and T line are similar in colour, and T/C ratio is around 1.0. A lighter T line than the C line means a weak positive result, and a completely colourless T line indicates a strong positive result. The strip is invalid when C line is colourless no matter whether the T line is colourless or not. The T/C values of different concentrations of drugs was given by the digital reader to draw a standard curve by Origin 8.5. The concentration of drugs was set as x-axis and B/B_0 as y-axis (B_0 was the T/C value without any drug, B was the T/C value). The limit of detection (IC_{20}, B/B_0 =0.2), IC50 (B/B_0 =0.5), and the detection range (B/B_0 = 0.2 to 0.8) could be acquired from standard curve and the cut-off value could also obtained by naked eye.

Normally, the limit of detection would achieve 1 µg/L with an analysis rate of 10 min per assay (Byzova et al., 2014). The strip would be highly specific and can discriminate against structurally related molecules, such as other related herbicides. The detection results could be obtained visually for semi-quantitative determination and by the hand-held immunochromatography reader for more accurate quantitative determination. All results obtained from the ELISA scan would correlate well with data from the HPLC/MS chromatographic method (Huang et al., 2015). According to Huang et al. (2015), this proposed method could be successfully applied for screening herbicides in real samples and shows great promise for environmental monitoring owing to its simplicity, rapidness, and high selectivity.

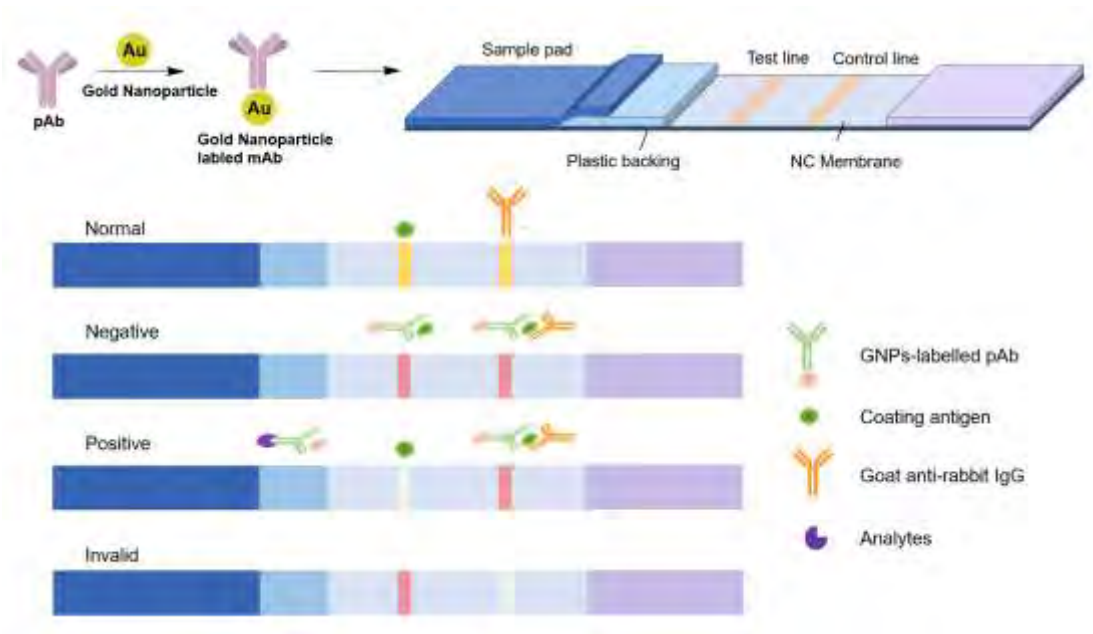

Figure 11. Illustration of the Immunochromatographic Strip: Assembly and Mechanism.

5.0 SUMMARY AND CONCLUSIONS

5.1 LITERATURE REVIEW OF EXISTING FIELD SCREENING TECHNOLOGIES

Based on the results of the literature review and interviews completed in relation to the potential application of existing field screening technologies for use in detecting bromacil and/or tebuthiuron in soil and groundwater at sites in Alberta, Vertex concluded that the following seven technologies showed promise:

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
- Near infrared reflectance spectroscopy (NIRS)
- X-ray fluorescence (XRF)
- Raman spectroscopy
- Laser-induced breakdown spectroscopy (LIBS)
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)

As a result of the literature review and interviews completed, the portable gas chromatography/photoionization detector (GC/PID) technology was identified as not showing promise and was eliminated from future consideration.

A brief discussion of the results of the review for each technology follows.

Ultraviolet laser induced fluorescence (UVOST® or OIP®) and Visible light laser induced fluorescence (TarGOST® or OIP-G®)

- LIF technology is the process of using a specific range of light to excite molecules within target compounds which naturally have a fluorescence. Certain molecules interact with high energy light pulse by emitting measurable fluorescence which then can be used to measure relative concentrations of targeted molecules.

- LIF has been successfully used in the field by Vertex and there is a proven track record for utilizing UV-LIF as a method for detecting PHC NAPLs in-situ using a direct-push platform.

- Vertex has evaluated LIF (both UVOST® and TarGOST®) as an acceptable candidate for next-stage testing for both soil and groundwater samples. LIF screening of the two target herbicides does offer challenges, including limitations with detecting low concentrations of contaminants, however the wide range of molecules that can theoretically induce fluorescence from high energy light pulses offers promise in herbicide detection.

Near infrared reflectance spectroscopy (NIRS)

- NIRS uses the unique scatter and absorption behaviours of target molecules when exposed to electromagnetic radiation.

- NIRS has been successfully used in the field for a variety of environmental investigations, including by Vertex in a field program designed to detect real-time relative concentrations of PHCs in soil.

- Vertex has evaluated the NIRS technology as an acceptable candidate for the next stage of testing for both soil and groundwater samples. NIRS is not only a proven field-ready screening device, but there is also historical precedence for the detection of bromacil.

X-ray fluorescence (XRF)

- X-ray fluorescence technology combines spectrometry and the x-ray range of light. When this light interacts with a sample it is both scattered and absorbed; the degree to which either occurs is dependent on the chemical properties of the sample.

- The Innov-X device being considered by Vertex is very portable and relatively lightweight, which will facilitate easier use in the field.

- Vertex has evaluated the XRF technology as an acceptable candidate for the next stage of testing for both soil and groundwater samples. While there does not appear to be a precedent for identifying bromacil or tebuthiuron using XRF technology, there is precedent for other herbicides being studied using XRF. It is expected that it will be more applicable to bromacil as compared to tebuthiuron due to interference effects associated with naturally-occurring sulphur in the environment.

Raman spectroscopy

- Raman spectroscopy is a non-destructive chemical analysis technique whereby a molecule scatters light from a high intensity laser light source. Depending on the chemical structure of the analyte, a small amount of light is scattered at different wavelengths which correspond to specific molecular bonds of the analyte.

- Handheld Raman spectrometers have been used successfully in a variety of field-applicable industries and is designed for non-contact analysis.

- Vertex has evaluated the Raman spectroscopy technology, specifically B&W Tek's NanoRam, as an acceptable candidate for the next stage of testing for both soil and groundwater samples. However, there does not appear to be a precedent for identifying bromacil or tebuthiuron using Raman technology.

Laser-induced breakdown spectroscopy (LIBS)

- LIBS uses a high energy laser pulse to ionize and excite the atoms within a sample. This interaction between the atoms and the laser causes some evaporation of the sample which results in the production of plasma. The plasma gives off light whose spectra can be analyzed to determine the chemical components of the sample. The wavelength therefore indicates the atoms present, and the relative intensity allows for a measurement of concentration.

- Vertex has evaluated the LIBS technology, specifically the EOS Handheld LIBS analyzer as it is a proven field-ready device and easily portable, as an acceptable candidate for the next stage of testing for both soil and groundwater samples. While there does not seem to be a precedent for detection of the sterilants, LIBS has been historically used for soil analysis and it does appear that the EOS's range of identification should include the elements within the targeted herbicides as LIBS technology is well suited to the identification of elements with lower atomic numbers.

Gas Chromatography/Thermionic Ionization Detector (GC/TID)

- The TID contains a thermionic ionization detector bead which heats up and when the substance of interest encounters the bead a chemical reaction can occur. The reaction occurs within the plasma that coats the surface of the TID bead and results in the substance being ionized. These ions are measured by the electrode within the system and the results are reported to the user as a concentration (SRI, n.d.). The molecule type determines whether this ionization reaction occurs. Specifically, molecules containing the NO_2 functional group are the main substances observed by TID technology.

- While the TID does not have a history of field use, Vertex has used a field GC with a similar detector, the Flame Ionization Detector (FID), which can be replaced with the TID. Theoretically, a field GC with a TID installed could be used for field screening and detection of both bromacil and tebuthiuron. However, further research and development work would be needed to determine the necessary modifications required to adapt this technology for a field application.

- Vertex has evaluated the TID technology as an acceptable candidate for the next stage of testing for both soil and groundwater samples. While there does not seem to be a precedent for field detection of the sterilants, the TID has been successfully used for lab analysis of both bromacil and tebuthiuron. There are hurdles to overcome to design and test the TID for field use, as it is currently not field-ready, but the technology itself is promising and will be tested using laboratory technology in the next stage of work.

Portable gas chromatography/photoionization detector (GC/PID)

- Gas chromatography is the separation of gases allowing the relative amounts to be determined, using specific detectors like the PID. The PID uses electrical impulses to determine the concentration of these aromatic compounds within ambient air. A light source within the PID uses high energy photons to ionize molecules.

- PIDs have been successfully used in the field to measure the concentrations of volatile gases such as VOCs and some PHCs. GCs in tandem with detectors such as PIDs have also been used in the field in technologies such as Membrane Interface Probe (MIP) and mobile laboratories.

- Vertex has evaluated the portable GC-PID technology, specifically the FROG-4000, as an unacceptable technology for the next round of testing. The chemical and physical properties of the target herbicides are not suitable for detection by the FROG-4000 as they are not easily volatilized under ambient conditions.

The technologies identified as showing promise for use in detecting bromacil and/or tebuthiuron in soil and groundwater at sites in Alberta are recommended for carrying forward to the next Task of proof-of concept testing.

It is important to also note that since these seven technologies are all applicable for measuring contaminants in soil and groundwater samples, it is possible that a sample preparation stage comprising extraction and concentration steps, would improve the accuracy of the detections and lower the detection limits. Such work could be completed as part of Phase 2 “optimization and validation” of the technology or technologies.

5.2 LITERATURE REVIEW OF SSDNA MRE AND ELISA TECHNOLOGIES

InnoTech Alberta expressed specific interest in two biosensor technologies that have shown promise in the detection of bromacil to date: ssDNA MRE and ELISA. Based on the results of the review, UW concluded that the ssDNA aptamer reported did not show promise in being able to be developed into a viable, field deployable, biosensor; however, the aptamer technology should still be promising provided that high quality aptamers can be obtained. On the other hand, the ELISA technology is believed to be promising based on the published antibody.

A brief discussion of the results of the review for each technology follows:

ssDNA MRE

- The literature-reported aptamer for bromacil is not considered to be reliable. It does not appear that the proposed conserved nucleotides in the described aptamer are important for binding, and by examining the sequences, it does not appear that they can bind to bromacil.

- No literature exists regarding a potential aptamer for tebuthiuron.

- It appears possible that the aptamer approach can work for these two sterilants, as demonstrated by Kwon et. al. (2015) and Eissa and Zourob (2017) with similar target molecules, but entirely new aptamer selection experiments would need to be completed.

ELISA

- The literature reported antibody for bromacil is considered to be reliable. However, the ELISA assay using the antibody process requires multiple incubation and washing steps taking around 4 hours in a typical assay. Therefore, although it is quite sensitive, it is not considered applicable for field applications for environmental samples where a relatively fast analytical time coupled with fewer sample preparation and analytical testing steps would be more desirable.

- No literature exists regarding a potential antibody for tebuthiuron.

- As an alternative, immunochromatographic assays with nanomaterials have exhibited excellent characteristics and have been developed as an inexpensive and portable monitoring tool for diagnostic purposes and small molecular detection (Kong et al., 2016). Therefore, it is recommended that consideration be given to developing an Au nanoparticle-based immunochromatographic.

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APPENDIX A: USERS MANUAL - UVOST® LIF

User Manual

UVOST®

UltraViolet Optical Screening Tool

DAKOTA TECHNOLOGIES

Version 2.12.05

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Laser Safety

The UVOST is a Class IIIb laser system. Appropriate safety procedures should be followed.

Table 1. Laser Safety Related Specifications

Manufacturer	Dakota Technologies, Inc.	**Brand name - model**	UVOST - 1000
Classification	Class IIIb	**Wavelength**	308 nm
Max Pulse Energy	0.05 mJ	**Max Rep Rate**	100 pps
Max Average Power	3 mW	**Pulse Duration**	5 ns

Eye protection: When the probe is not in the ground and the laser is on, suitable UV safety eye goggles must be worn to avoid damage from direct or scattered radiation.

The recommended optical density of the eye wear is in the range of 7-15 at 308nm.

Skin protection: Avoid skin exposure to both direct and scattered laser radiation. Skin damage can result from exposure to UV laser radiation.

Laser Labels

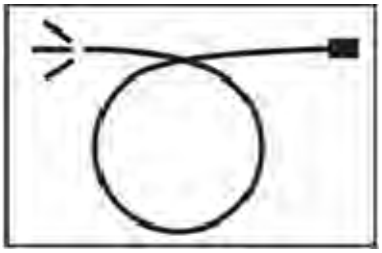
CAUTION – Use of controls or adjustments or performance of procedures other than those specified herein may result in hazardous radiation exposure.

This equipment conforms
to provisions of
US 21 CFR 1040.10
and 1040.11

DANGER
INVISIBLE LASER RADIATION WHEN OPEN
AVOID DIRECT EXPOSURE TO BEAM

Aperture Label (both labels are located adjacent to the Fiber I/O ports since the soil deteriorates the labels when placed on the probe):

AVOID EXPOSURE
INVISIBLE LASER RADIATION
IS EMITTED FROM THIS APERTURE



Introduction

The **UVOST** system is a complicated instrument and requires proper training prior to operation. If you have not been trained and/or certified please contact Dakota Technologies prior to operation. Operation without proper training:

- May cause damage to the **UVOST**
- Most likely will produce inferior or misleading data
- Will void the warranty.

Please read this document in its entirety prior to using the UVOST

System Basics

The **UVOST** system has these basic specifications.

Table 2. System Specifications

Parameter	**Value- U.S. Customary Units**	**Value- International System of Units**
Power	120V AC 60 Hz 600 W	120V AC 60 Hz 600 W
Dimensions	25 x 24 x 26 in. with covers	63.5 x 60.9 x 66.04 cm with covers
Weight/Mass	~ 120 lbs (cased instrument)	~ 54.43 Kg (cased instrument)
Operating Temp	32 - 100 °F	0 - 37.8 ºC
Storage Temp	0 - 120 °F	-17.8 - 48.9 ºC
Reference Emitter	Proprietary NAPL mixture	
Cuvette	Internal, 10mm x 10mm	
LOD	<= 100 ppm fuel on wet sand	
Dynamic Range	Three orders of magnitude (minimum)	
Excitation	308nm XeCl Laser (64Hz)	
Emission (1)	350nm (40nm bandpass)	
Emission (2)	400nm (40nm bandpass)	
Emission (3)	450nm (40nm bandpass)	
Emission (4)	500nm (40nm bandpass)	

Standard Parts

The following figure shows the standard parts for the **UVOST**. Prior to using the **UVOST**, these parts or accepted substitutions should be on hand or readily available.

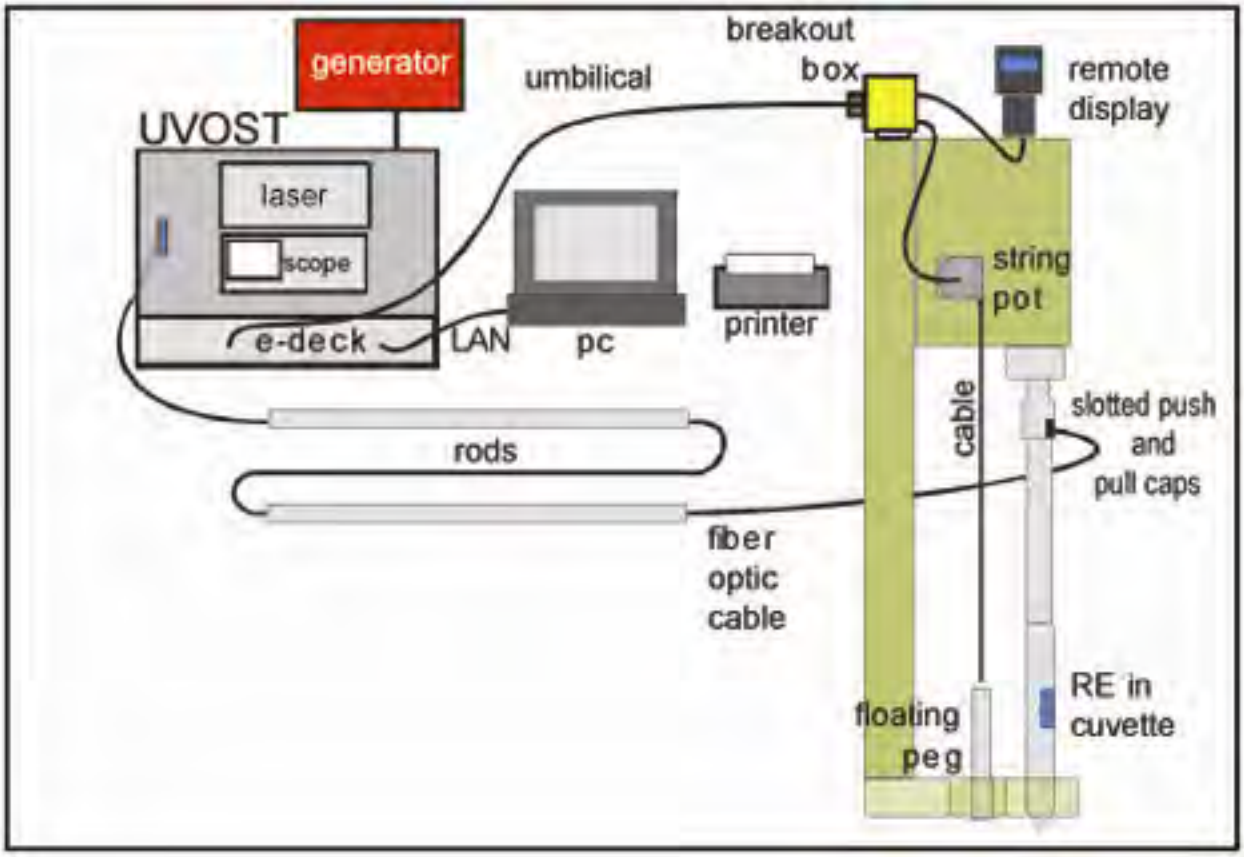


Figure 1. Standard UVOST parts

General Operating Procedures

Set Up

Prior to operation, all the sub-systems require proper connections/cabling and power. Table 3 summarizes the proper connections/cabling.

Table 3. Cabling/Connections

Primary Connections [Connection labels in blue]		
Device 1	**Device 2**	**Cable/Fiber**
Power/Generator	e-deck (front) [PWR IN]	Standard Modular AC Line Plug
e-deck (front) [NET]	Control PC	LAN (standard CAT 5)
e-deck (front) [UMBILICAL]	Breakout Box [no label]	Umbilical Cable (Amphenol to DB15)
e-deck (front) [PWR OUT]	Control PC	120V AC Line converter
Breakout Box [DEPTH]	String Pot [no label]	Depth Cable (DB9 to Amphenol)
Breakout Box [DISLAY]	Remote Display [no label]	Remote Display Cable (DB9 to DB9)
UVOST Fiber I/O [LAUNCH FIBER]	SPOC	Fiber Optic Cable (2 SMA to Special Terminator)
UVOST Fiber I/O [RETURN FIBER]	SPOC	Fiber Optic Cable (2 SMA to Special Terminator)
Secondary Connections		
e-deck (front) [GPS]	GPS NMEA GGA Output	DB9 RS-232 (Serial – usually integral to GPS)
e-deck (front) [AUX COM]	AD4 Quadrature	DB9 RS-232 (Serial)
e-deck (front) [12V AUX]	Generic 12V Accessory	Power Plug 0.1” (Switchcraft 761K)
Breakout Box [AUX]	NA (future use)	DB15 to (to be determined)

Permanent Connections		
Device 1	**Device 2**	**Cable/Fiber**
UVOST Fiber I/O (lower backside)	Detection Module (FIBER RETURN)	Single Fiber Optic (SMA-SMA)
UVOST Fiber I/O (upper backside)	Laser Launch Optics	Single Fiber Optic (High Power SMA-SMA) (standard fiber can be used as backup)
Trigger Photodiode	Oscilloscope [Ch1]	Coaxial Cable (SMA-BNC)
Emission Module [SIGNAL OUT]	Oscilloscope [Ch2]	Shielded Coax (PMT-BNC)
Trigger Photodiode	Laser back window	Single Fiber Optic (SMA-SMA)
UVOST e-deck (rear) [NET SCP]	Oscilloscope	LAN (CrossOver CAT 5)
UVOST e-deck (rear) [12V PMT]	Detection Module [12V IN PMT]	12V supply (SMA-SMA)
AC Line (external)	NA	Standard Modular AC Line Plug
e-deck (rear left-most) [PWR OUT]	Vacuum Pump (switch at front of e-deck)	Standard Modular AC Line Plug
e-deck (rear) [PWR OUT]	Laser	Standard Modular AC Line Plug
e-deck (rear) [PWR OUT]	Oscilloscope	Standard Modular AC Line Plug
e-deck (rear) [Cond.]	Conductivity Module [Cond. Out]	12V Signal Cable (switchcraft TA3FLX)

Power Up/Down

To power up the UVOST, use the power switch on the front of the UVOST's e-deck. All peripheral devices are powered through the cabling. The laser takes several minutes to warm-up, the LED lights to indicate that the system is ready. Push the ON button to activate lasing. Lasing LED should light and there should be a small rectangular yellow glow on the yellow glass indicator at front of launch optics assembly. The oscilloscope should display Trig'd – if laser has sufficient output (not in need of recharge).

Set laser rep rate to between 63-65 Hz. If powering up from cold conditions (overnight, etc.), make sure you have laser running at least 10-15 minutes prior to attempting your first RE calibration. We recommend running heaters overnight in sub-freezing conditions to minimize warm-up times in the morning. Extremely high or low temperatures negatively affect laser power. If used in extreme conditions you should attempt to house/store the UVOST system in a warmer/cooler environment to assure proper operation. There are no hard/fast rules for this – since case temperatures/heaters can assist but a lot depends on wind, ventilation, direct sun, and other conditions.

To power down the UVOST, first STOP the laser pulsing, then switch OFF the power button.

Boot PC and Check Software Function

Always makes sure the UVOST is on first then turn on the PC. Check that either there is a floppy disk in your oscilloscope, or a USB stick sticking out of the front of the scope (depending on model).

The UVOST will function without these memory devices in the oscilloscope, but you will not get the reference white lines when taking RE or Background. Once the PC has loaded, make sure all drivers are loaded and ready. Start the OST system software. Indicators in the software will assist in alerting you to connection problems and general status of the components (Hardware Tab). See software manual for specifics on OST software.

Proper System Function

Once the software is functioning you can proceed to check the depth encoding and associated peripheral functions. Actuating the probe (or hand advancing the string pot) should show Current Depth changing on the OST software **DEPTH TAB**. The Remote Display should be functioning and indicate status. Select the **INFO TAB** and make sure your job information is updated for storage with each LIF log.

SPOC or CPT LIF Sub Setup

The detailed discussion is found under SPOC Assembly on page 13 or on page 22 for CPT LIF sub setup.

RE Calibration

Calibration should be done prior to each **UVOST** logging event. Wait to calibrate until the direct push rig is ready. Pre-push with a dummy tip if obstructions are likely or getting a "straight hole" going is difficult. Place RE holder on window (making sure window is very clean). Acquire RE with Acq RE command. Extended exposure to laser light can form excimers and photodegradation – causing a morph in waveform shape/intensity. If you have changed fiber optic lengths the software may correct the delay time to achieve proper position in window. Make sure the RE signal level exceeds a 9,000 pVs minimum but does not exceed 20,000 pVs with 11,000-13,000 pVs being about optimum. Try to be consistent (± 1000 pVs) – especially for the same project/site. Make sure the RE waveform shape "looks right". Compare it to the reference waveform displayed on the scope during the RE acquisition. Extremely noisy/jagged REs, misshapen REs, and missing/low channel contributions indicate damaged or loose fiber optics/filters/detector.

Background

Wipe window clean and acquire a Background (blank) waveform with the Acq BckG command. A perfect system would yield no waveform at all – only white noise. There is always trace fluorescence from mirror/window, fiber-generated Raman, and contamination. Try to achieve <2mV peak signal in any one channel. You simply want it as small as you can get it. A severely jagged/noisy background indicates possible pickup of the large laser EMF (electromagnetic field) into the trigger and signal coax cables. This problem can be caused by grounding issues, loose connections, misrouting of cables, etc. If the first channel (350nm) is considerably larger than the other three, there is a chance that you have excessive backscatter of laser light into the system (350nm filter is near laser wavelength) or the laser rejection filter (inside I/O block) may be damaged or malfunctioning. Channels 3 and 4 being high/narrow is a classic lint signature. A background waveform that looks like your current contaminant of interest suggests leakage and contamination of the internal **SPOC** mirror/window OR simply a dirty window. Clean with methanol or solvent if soap/water doesn't work.

Logging

Steps to acquire a **UVOST** log:

Step 1. With proper RE and background acquired, pertinent log information recorded, and probe in position (window just below (~1 inch) ground surface), activate the **RECORD** command.

Step 2. Acquire RE. The OST software will alert you if you failed to acquire a recent RE (at least one log event old). You can "rescue" an RE if it's needed (i.e. an accidentally aborted log and you want to continue logging, the probe is still under ground or under water during a barge project). DO NOT purposefully continue logging without a new RE for each log. If there is a problem acquiring new REs **FIX** the problem, acquire a good RE, and then proceed. Failure to acquire a new RE for each log will generate inaccurate data.

Step 3. Choose a directory and name for your log. **UVOST** auto-suggests the name sequentially in an attempt to reduce typing. Take care to not overwrite any older data. You will get a standard 'are you sure' windows prompt if you attempt to overwrite a previous file.

Step 4. Once the name is chosen you are asked to choose whether or not to "zero" the depth. For normal logs you always choose **YES** and zero out depth. If you're continuing an aborted log (accidental termination), choose **NO**. The log should continue at depth where it was aborted.

Step 5. As the log progresses, you must make sure the system is operating properly. Observe the oscilloscope or OST display to watch for:

A. The probe advancing at approximately 0.75 inch/sec or 1.9 cm/sec. Your company may choose a slower rate. We do not recommend a faster rate.

B. Strange background drifts after several feet indicate possible fogging of the window.

C. Jumps in depth or a loss of depth increase even though the operator is advancing the probe indicates a broken string pot, string pot cable, umbilical cable or a poor connection.

D. Incorrect depths indicates a possible rod length or string pot calibration factor mismatch.

E. Sudden loss of waveform (flatline) indicates possible fiber optic break due to a broken probe.

F. Depth is advancing, but new waveform updates aren't showing up indicates poor triggering. Check to see if Trig'd is showing up on oscilloscope every second or so. If not, hit Trigger 50% button on the scope. Accidentally hitting the **STOP** button on the laser will could also cause this to happen.

Step 6. Once refusal is reached, or target depth is reached, activate the **END** command. All pertinent data is stored and the oscilloscope scale is automatically returned to the default 50mV/div scale in preparation for next RE.

Step 7. Inspect the probe, window, and all equipment for leaks, breaks, and loose parts in preparation for next the next logging/push event.

Printing/Exporting LIF Logs

Once the push is complete the log can be viewed. A log can be also opened from the file and viewed with the OST software. It is necessary to print the log to paper or export it as an electronic image (JPG file). Prior to print/export it is a good practice to select callout waveforms. Select single waveforms by clicking the log at any depth, which creates a stats bar. Transfer single logs by dragging/dropping the stats bar or with the < bar next to each callout box. Select the average of a region of waveforms along a log by clicking the log, holding down, then releasing at a second depth along the log. Transfer average zone waveforms by dragging/dropping the bottom stats bar or with the < bar next to each callout box. Reasons to select certain depths/regions include:

- Bracketing what appear to be continually affected zones. This helps the client/consultant "summarize" the general NAPL zones and easily identify depths for future validation sampling, project design or providing the site owner useful/valuable information.

- Bracketing large zones of homogenous NAPL. Do not span different products.
- Highlighting unusual signatures. This may indicate the need for sampling there or may identify things the client needs to investigate or discount.
- Highlighting a background periodically reminds reviewers what "clean" looks like
- Bracketing potential "false positives" such as mineral/plant/urban background/highly degraded NAPL. The different waveform will help the client recognize that it's not a concern.
- Use caution when highlighting single waveforms from the rising edge of NAPL hits. The waveforms in this area are usually saturated because the oscilloscope scaling wasn't able to fully respond. They are morphed and ugly and cause unnecessary confusion and alarm.
- Callouts can be chosen at any point. The appearance is more organized and easily understood if a callout is straight across from the waveform.
- Avoid identifying the depths of multiple callouts on a log with indicator lines that cross each other as this makes it confusing to read and use.

It is best to have the **UVOST** operator and client discuss depth/RE scales, depths of interest, etc. ahead of time to try and avoid multiple reprints.

Annotate the callout text boxes under each waveform to inform and guide the client. Products that are unusual, significant, or out of the ordinary, require a brief description. A product that is repeated frequently could be left blank after initially being identified.

Settings are saved each time you print/export in a lif.plt (plot) file so that the same callouts and depths are available later. The OST software and Dakota suggests that the first print/export log filed be saved with the label 'field'. This guarantees you to know what the client received originally. Subsequent print schemes are saved as well. When opening a file various scheme choices are listed for opening it.

SPOC Assembly

Figure 2. Parts and tools for SPOC assembly

Figure 2 shows all the necessary parts to properly assemble a **SPOC**. Prior to assembling the **SPOC** make sure you have the fibers properly threaded through all the rods, and that the adapter and lead rod are in place! If necessary you can sometimes thread the fiber cable through the rods "backwards" with the SMA ends leading (make sure the SMAs are capped and protected).

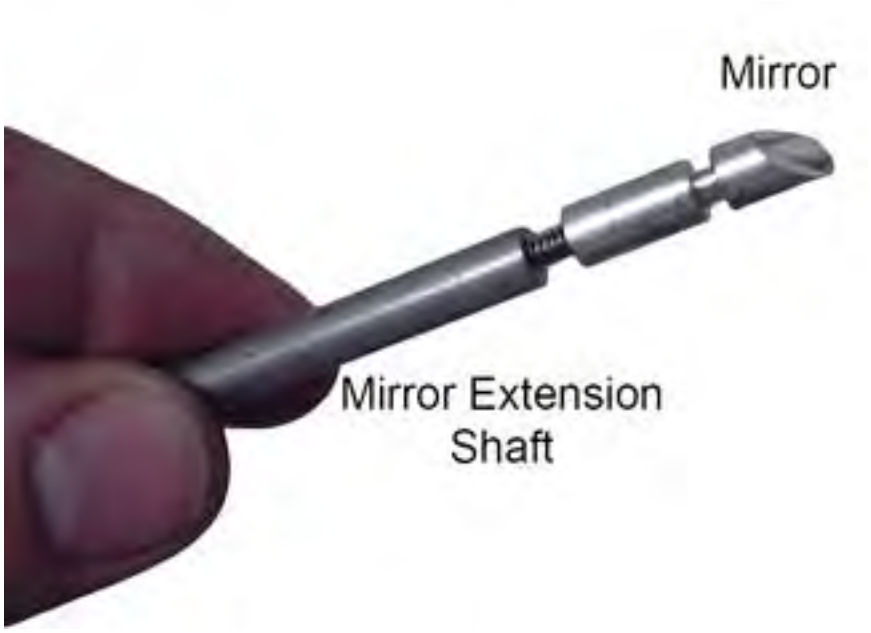


Figure 3. Attaching mirror to mirror extension shaft

First, securely fasten the mirror to the mirror extension shaft **without touching the mirror surface**. Tighten securely with pliers. Do not gouge or scar shafts.

close up of o-ring application tool

Figure 4. O-ring placement on mirror

Lubricate o-ring very sparingly with supplied silicone grease. The objective is to fill any micro-voids and use just enough grease to leave a light sheen/glistening appearance. Slide the o-ring into groove on the mirror **FROM THE BACK** of the extension shaft (or o-ring application tool) so that the mirror does not get greasy. If the mirror is contaminated with dust, lint, or debris; clean it by blowing canned air (**ALWAYS** hold can upright – liquid refrigerant will haze/ruin it!) at the mirror at a glancing angle. The mirror surface is delicate, any damage is permanent. To clean use a cotton swab and dilute Alconox soap with water. **GENTLY** swab the mirror and rinse **THOROUGHLY** with water. Blow dry using canned air that does not contain a bittering agent, which may leave deposits on the mirror. Methanol could be used for the final rinse or used to dissolve non-water-soluble stains.

Figure 5. Swage nut and nylon ferrule

Figure 6. Properly constructed SPOC mirror assembly

The ferrules and Swage fittings are attached to each **SPOC** when delivered. Remove them and slide onto mirror shaft, then insert mirror onto the end. For proper orientation of the ferrules, look at the figure above.

Temporarily arrange the mirrored surface to be in center of window hole and aligned with the window – centered side-to-side and tip-top of mirror just a tad down from the uphole edge of the brass hole (opposite end that mirror is inserted into) as shown in Figure 14. Tighten lightly with the wrenches. **CAUTION: THE BRASS "GUTS" OF THE SPOC CAN TURN INDEPENDENTLY OF THE EXTERIOR PIPE, WHICH RUINS THE SHOCK ABSORBING RUBBER SEAL OF THE SPOC**. To prevent this, **NEVER** hold the outer pipe of the **SPOC** when you tighten or loosen the Swage fittings. The wrenches are designed to allow you to tighten or loosen the Swage with shorter (6pt) wrench while holding the Swage that is permanently attached to **SPOC** with the longer (12 pt) wrench. See photo below. **ALWAYS** use the provided wrenches to isolate the outer **SPOC** from any torque being applied to the Swage fittings. Lay the **SPOC** on a flat surface (allowing it to freely rotate) and tighten or loosen while holding **ONLY** the two wrenches. Tighten the Swage on the mirror lightly, just enough to hold the mirror at center of hole and aligned to send light out the center of the brass hole and so adjustments can be made as needed. Keep in mind you will need to rotate the Swage nut to align

with the **BOTTOM/ INNER** Swage fitting's nut - so that the inner wrench can be removed. There are two distinct orientations of the Swage nut at which the inner wrench can slip past it since it is a 12 point wrench.

Figure 7. Proper wrench technique

This photo shows a technician **LIGHTLY** holding a **SPOC** and preparing to tighten a mirror by turning the top wrench, pressure on the **SPOC DOES NOT** increase when applying torque to the either wrench.

Figure 8. Holding the mirror shaft with pick tool to rotate (or hold) mirror

The mirror will want to rotate when tightening. Use the 90 degree pick tool or a 1/4" nut driver to hold the mirror and prevent rotation. This is especially important when final tightening occurs later in the process.

Figure 9. Properly assembled fiber terminator

With mirror temporarily positioned, remove the Swage from the other end of the **SPOC** and install onto the fiber terminator. **VERY CAREFULLY** slide a new silicone grease conditioned o-ring over the fiber tip and into the groove. Make sure no silicone grease or other contamination gets on the fiber faces. Insert the fiber terminator into the SPOC as far as reasonable force allows. Positioning will be close to optimal, but a little too far. Final adjustment will be made a little later in the process.

Figure 10. Inspect and prepare window

Make sure that the window, mirror, and internal cavity are free from dirt, moisture, lint, etc. Examine window **VERY** carefully. Any fluorescent contamination will create unacceptably high background. Condition an o-ring and install onto a window assembly. Now, lightly, continuously spray canned air into the mirror/window hole. (**ALWAYS HOLD CAN UPRIGHT. NEVER ALLOW COLD LIQUID REFRIGERANT FROM THE CAN TO TOUCH THE MIRROR.**) Insert the window and tighten with the window tool. Make sure the pins line up and that you do not slip the tool, which will mar the holes and/or bend the window tool pins. Tighten the window very securely, perhaps even tapping the top of window tool lightly while torquing to gently impact the window for a secure fit. This is important to prevent loosening during hammering.

Figure 11. Carefully engage window with window tool.

Figure 12. Fully seat tool's pins into window's holes

The mirror and fibers must be secured tightly into place to hold them in-place during violent hammering and seal the parts from water/mud/contaminate entry. The mirror must be adjusted to the optimum position described in the figures below. With mirror rotated to center the beam side-to-side, make sure that the laser beam is not being clipped by the brass tube (too close to the tip-end of **SPOC**) and yet is not imaging the epoxy of the window (even upon reflection from the outer surface of the sapphire window). Use the clear **UVOST** mirror-alignment card (Part #100061) as your general guide. Push/pull the mirror (possibly rotating to get it to move) to get it right and align the beam with the

smaller circle on the clear **UVOST** mirror-alignment card. Tighten mirror securely holding mirror in position with the 90 degree pick or ¼" nut driver.

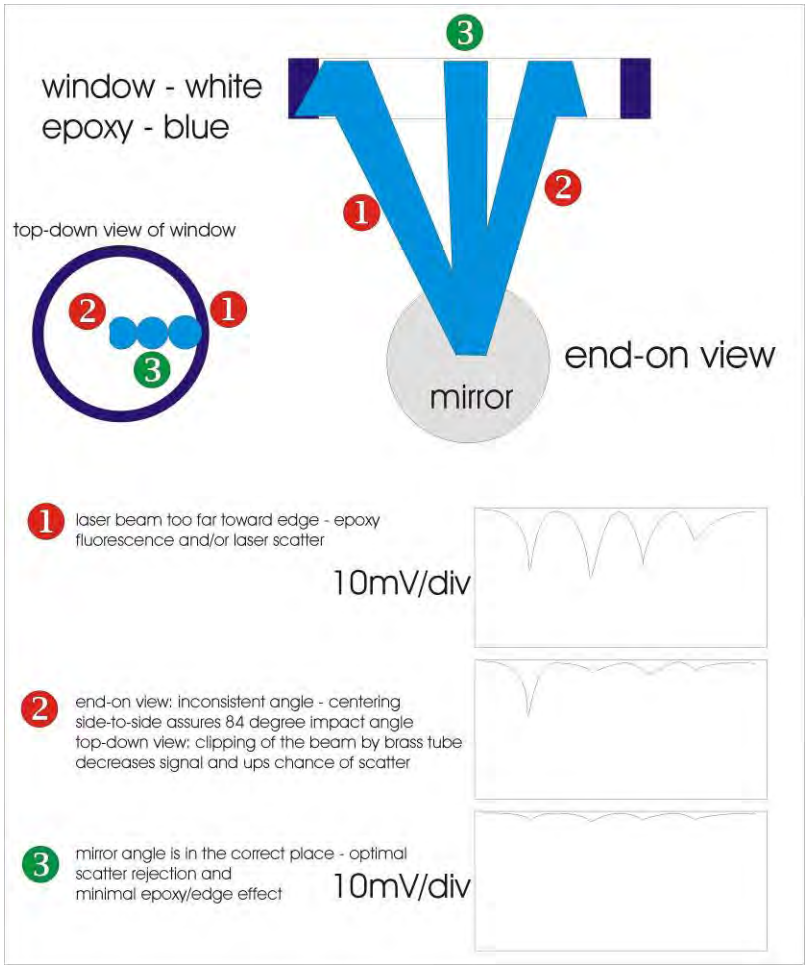


Figure 13. Optimal mirror position – view 1

The mirror is now in correct position and secure, but the beam likely needs to be collimated. With the laser ON and enough laser light emitted to readily see on a **UVOST** yellow fluorescent card (Part #100060)(or similarly fluorescing material) adjust the fiber terminator in/out until you get the sharpest round laser image possible on the fluorescent card held about 2 feet or 60 cm from the **SPOC**. Tighten the Swage fitting on the fiber terminator securely. Do a final check for proper mirror alignment with clear **UVOST** mirror alignment card.

Periodically check the **SPOC** for moisture with an ice cube, look for condensation. A tiny amount of condensation is okay because ice is much colder than the ground. If the ice cube test yields fogging you'll need to remove window, re-dry the interior of the **SPOC** chamber, then flush the optics portion with canned air while screwing in window. Chronic fogging and repeated drying likely means a leak in the **SPOC** seals or o-ring.

If you ever "flood" a **SPOC** due to a shattered window, it's best to replace with a clean, dry **SPOC**. Thoroughly clean and dry the flooded **SPOC** with soapy water, thoroughly rinse, and dry for a long time in a hot oven, on a motel room heater, or some other methid. Do not let the **SPOC**, the mirror or the internal brass cavity dry with dirty water or fuel in/on them. The dry stains/deposits are very difficult if not impossible to remove. The reflectivity of the mirror will be reduced causing the background to be too high. Also, dried debris inside the **SPOC** may be pounded to a fine dust with

percussion hammering, and the dust then coats the fiber faces, mirror, and window, negatively affecting the LIF spectroscopy.

Place the Reference Emitter (RE) on the window and adjust the energy (knob on the fiber I/O block) to achieve 3/4 scale response at 50mV/div. The reason for this is to get "in the ballpark" with the laser energy.

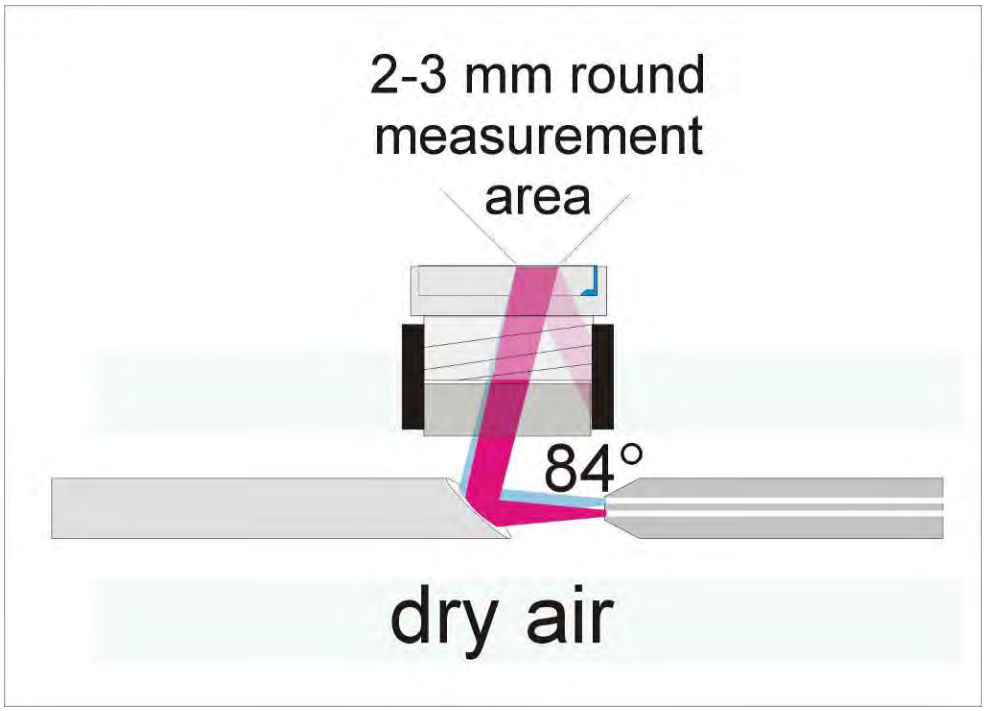


Figure 14. Optimal mirror placement – view 2

Finally, clean the window thoroughly. Place the RE on the window again and acquire a RE waveform. Remove RE from the window, clean window again. Acquire a **BACKGROUND** with OST, observing the background waveform on the oscilloscope. The blank, or background should be < 5mV maximum peak voltage (<200 pVs or <.5% RE). This may not always be possible, even the mirrors and windows vary in fluorescence, but **NEVER** exceed 10mV peaks (400 pVs or 1.0%RE). If it exceeds the recommended background you **MUST CORRECT** prior to logging! High backgrounds are especially vexing when the background waveform looks like contaminant.

Once you're certain the mirror/fiber/window system is achieving proper results you can tighten the Swage securely. Use **ONLY** the supplied wrenches. Tightening is done properly by laying the **SPOC** down and using the wrenches. Use the mirror pick/hook tool or a ¼" nut driver to hold the mirror firmly in place during tightening to prevent rotation. Make sure the laser beam stays centered in the window (side to side) and 1/3 down from the top of the window.

NOTE: direct daylight or bright sunlight will cause "photon noise" due to constant bombardment of the PMT with photons that have nothing to do with the laser excitation. Shield/darken the window area if necessary. However, be aware that the mirror can collect fluorescence from items several feet from the window – so your shielding method (cloth, etc.) needs to be non-fluorescent for a representative Background reading. When bright daylight or similar conditions allow "Constant Wave photon noise" to elevate/overwhelm the baseline, Dakota recommends the use of Liquitex® Value Series Acrylic Color Mars Black or similar flat black water-soluble paint that contains no fluorescent dyes. Flat black water soluble paint acts as perfect "black soil" – allowing only the light generated internally by the entire system to make it back to the detector.

With experience, you may want to test window/mirror cleanliness using RE and the background technique before going through entire assembly. These assembly instructions assume a clean fiber terminator, window, and mirror. Discovering a piece of lint, fuel, or other contaminant after assembly is frustrating and unnecessary. Again, **ALWAYS RESIST** the temptation to hold the outer **SPOC** during torque procedures, make sure the wrenches hold against torque!

With window/mirror/fiber terminator all secured, proceed with attaching drive tip, adapter, extension rod, and tighten extremely well with 2 pipe wrenches or pipe wrench and vice. Teflon tape helps reduce loosening due to rattling/vibration.

CPT LIF Sub Assembly

Figure 15. All the necessary parts to assemble a CPT LIF sub

Cable Make Up

Prior to assembling the CPT LIF sub make sure you have the optical fiber cable and CPT wire properly aligned and sheathed. In an open area 200' long and free of traffic (one car driving over the fiber can cost you > $4000) layout the optical fiber cable and the CPT cable parallel to each other. It is critical that the offset lengths of the CPT wire and fiber termination are set and fixed prior to applying the sheath material. Figure 16 below shows the proper way to determine the offset distance.

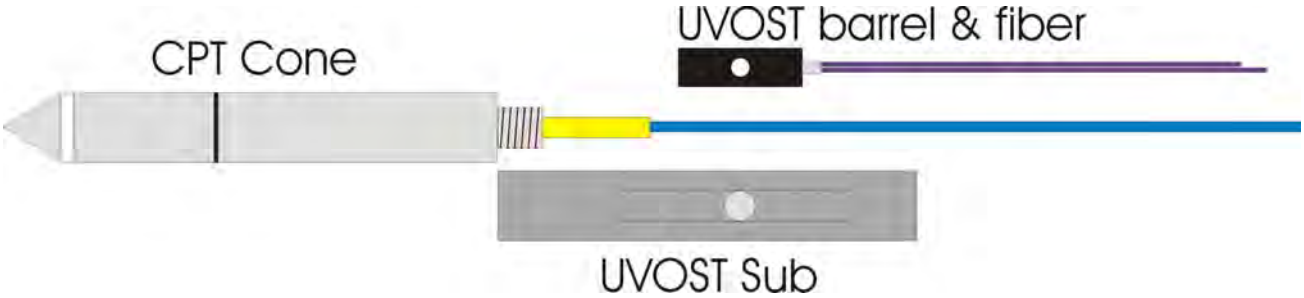


Figure 16. Determine CPT cable and fiber offset

Tape the fibers and CPT cable together with electrical tape in a couple of locations within the first two feet. Make sure the fiber faces are protected with end caps, then wrap additional tape over fiber terminator and CPT connector and begin the application of the protective sheath. The sheath material is a very durable expandable woven tube that when axially compressed, increases in diameter. The sheath should be worked onto and down the cable. This activity requires 2 people, one to push the sheath over the CPT connector and fiber end and also anchor the cable and another person to work the sheathing down the cable. Gloves are a good idea, as the sheath material is quite abrasive to skin.

About 10’ at a time can be worked down the cable. Sheathing should be stopped about one foot above the downhole fiber terminator and taped securely.

Using the downhole end as the lead, the cable assembly can now be strung through the rods starting at the bottom of the rack and working to the top. The suggested short term bend radius of the optical fiber is 2.3” so you will need to leave bigger loops than you would for just CPT wire. Long term bend radius is 3.7” if you won’t be using the cable for > 1 week but want to leave the cable in the rods. Consider the extra length used up with loops and the working length from the rod rack to the rams when deciding how many rods to string up. Making your working length too short will surely result in a broken fiber. If necessary you can sometimes thread the fiber cable through the rods backwards with the SMA ends leading (make sure the SMAs are capped and protected).

Connection to Cone

Now that the cable is strung through all the rods and you have plenty of working length between the rack and the rams the cable can be connected to the cone. Make sure any adapters to convert from the CPT LIF sub to rods are put over the cable at this time. If the CPT LIF sub you are using for your particular cone has an uphole end that is less than 1 inch, the sub needs to be slid over the cable before you proceed with the barrel and mirror alignment. If your CPT LIF sub has an uphole end that is 1 inch, then the sub can be put on after the barrel is installed and aligned.

Unwrap any tape that may be remaining on the fiber terminator and CPT connector. Place the cable end on a nice flat work surface for installation of the sub barrel. Have someone hold the cable if necessary or temporarily tape the cable down to the work surface. Take off the fiber cap and ensure that it is dust and contamination free. If you need a new o-ring on the fiber terminator, this is the time to install it. Lightly lube a new 006 o-ring with silicone grease and stretch it over the end of the terminator. It is very important that you do not get grease on the fiber face as it will give a high background signal. Make sure the ¼” bore of the sub barrel is clean by blowing it out with canned air. Insert the fiber terminator into one end until you can see the fiber face in the central window hole. Now insert a mirror (with a lubed o-ring) into the other end until it is visible in the central window hole. You can use the o-ring application tool or a long 6-32 bolt as a handle on the mirror.

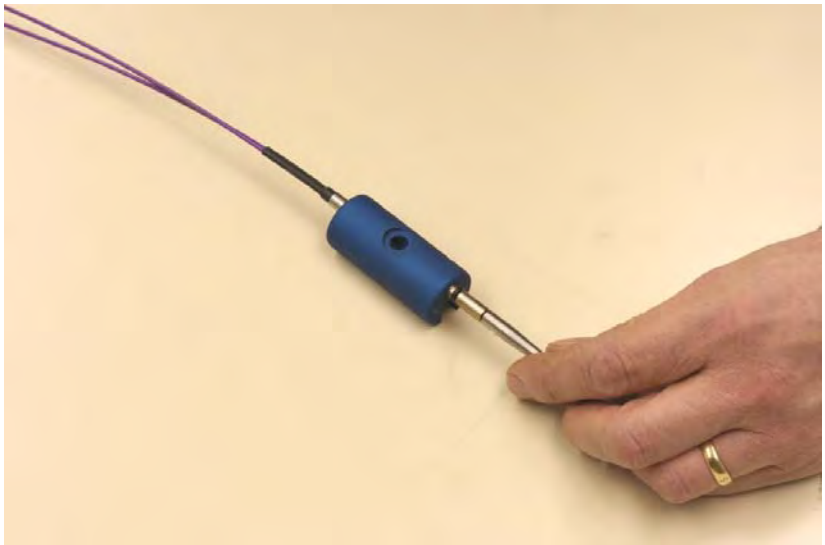


Figure 17. CPT mirror insertion

At this point the SMA ends of the fiber cable should be connected to the UVOST and the system started. Make sure the laptop is running with the OST software, as you will need to check RE and

background. Light should now be emitted from the barrel. Take care so that you do not look directly into the light without some sort of safety eyewear. Place a CPT window onto the barrel so that it is positioned exactly as it would be if it were in the sub. Using the clear UVOST alignment card (Part #100061) provided in your kit, place the card on the window (this is a bit of a balancing trick and may require another person's help) in the correct orientation.

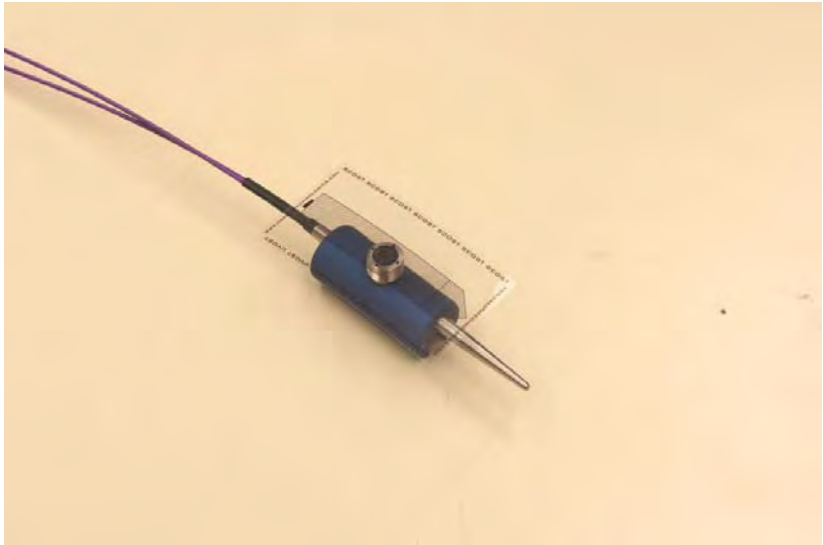


Figure 18. CPT alignment

You may need to open the I/O thumb screw to allow maximum light to be emitted at the sub barrel. This task should not be done in the direct sunlight as it will make it very difficult to see fluorescence of the transparent card. Rotate and push/pull the mirror so that light is directed to the target spot on the card. Now the fiber should be pushed or pulled to bring the light to a collimated beam. Tighten the setscrews on the side of the barrel to secure the position of the mirror and fiber.

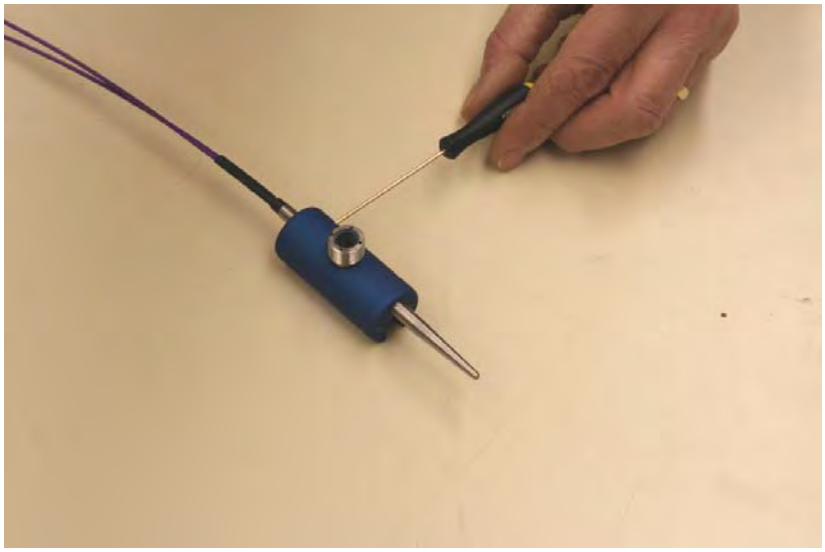


Figure 19. CPT alignment

Recheck to see that the beam didn't move too much after tightening setscrew. Now you are ready to check the RE and background. Reduce the amount of light by threading in the I/O thumbscrew. Set the RE on the window (this can be tricky) and acquire RE on the OST software.

Figure 20. CPT RE test

Adjust the I/O thumb screw so that the RE value is acceptable. Remove the RE from the window and acquire background. If background is not acceptable look for potential contamination on inside of the sapphire window, fingerprints on window surface, dust on the mirror, grease on the fibers or misalignment that is catching the edge of the window holder. Once a good clean background is acquired, snug up those set screws, check RE and background again and shut off light by closing shutter. Remove the window that is sitting on the barrel and place a self adhesive foil dot (part number 100485) over the hole this prevents dust and contamination from entering the barrel while you are threading the cone and sub together.

There are 2 threaded rods (CPT barrel insertion tool, part 100084) in the UVOST tool kit the should be threaded into the uphole end of the barrel, these will prevent the barrel from rotating while the CPT LIF sub is threaded to the cone.

Figure 21. CPT LIF sub insertion

The sub with the 1” uphole opening now needs to be slid over the cable and over the sub barrel. The CPT wires should be connected to the cone and the sub can be threaded onto the cone while holding the barrel stationary. It is important that the fibers and CPT cable don’t get all twisted up. Now look

into the window hole of the sub and rotate the barrel (should be less than ½ turn left or right) until it is directly below the hole. Here is where you find out if your cable length was accurately determined. There is not much give or take that can be done with the fibers and wire at this time.

Carefully remove the foil dot, set the square cross-section o-ring down in the hole, use a little canned air to flush the void of ambient air and thread the window into the sub. It is a good idea for you to ensure that the window is seated properly by tugging on the threaded rod tools as you thread in the window. When completed, the window surface should be flush or smooth with the CPT LIF sub. Open the shutter on the laser and check RE and background again. If acceptable the threaded rod tools can now be removed. Thread on any additional adapters or the first rod and make hole! Remember to set the cone/window offset in the software.

Figure 22. CPT RE test with sub

Some handling considerations: We have seen way too many CPT helpers pick up rods or lay down rods using the cable as a handle. If a fiber happens to be at the sharp edge of a rod and the helper lifts a little aggressively it is possible for a $4000 mistake to happen. **Never** use the cable for lifting rods! Do not step on the cable that is lying on the cone truck floor. A sharp rock or a metal edge under a big boot can result in a $4000 mistake. Keep all non-essential personnel (the client) away from the rods and cable.

Laser Recharge/Maintenance

See Appendix A for detailed instructions on recharging your PSX-100 laser.

General Laser Information

The XeCl laser is the most important component of the system. Repair or replacement involve considerable time and expense. Any **UVOST** work will be put on hold for at least a few days to possibly weeks if the laser is inoperable. Read and understand the laser manual for additional information. Proper recharging is paramount for continual laser operation. An improper recharge will often damage the vessel, and then it requires service. It is important to know that factors outside of our control, such as unresponsive 3rd party companies and shipping through customs can increase the delay. The bottom line is that your laser deserves the absolute best care and maintenance you can provide.

General information, hints, and tips:

- The incorporated laser is an air-cooled XeCl gas excimer laser, Class IIIB
- The incorporated laser outputs up to 1 mJ/pulse (0.3mJ typical) into launch fiber
- ~5ns typical pulse width
- Up to 50 µJ/pulse exit the launch block (harmless **IF** exposure is short)
- Typically 5-20 µJ/pulse exit the **SPOC** window (harmless **IF** exposure is short)
- Semi-collimated beam is reflected off the **SPOC** mirror
- Thyratron failure and vessel contamination (during recharge) are often the cause of failure
- Do not use XeCl premix below 200 PSI, remaining gas is often poor quality and may contain contaminants or particulate.
- Do not use He gas below 100 PSI, remaining gas is poor quality
- Laser doesn't like high humidity – causes arcing of HV across other components rather than electrodes
- Excessive dust on the HV capacitors exacerbate the arcing problem
- Laser needs to warm up for a period – depending on cold/conditions
- Laser energy also gets low with extremely high temps – cool with moderate temperature air flow
- Dakota can specify energy meters necessary to quantify accurately if desired

Laser Safety

- Do not service the incorporated laser
- The incorporated laser has **VERY HIGH VOLTAGE** inside – do not open
- Use any Class IV laser like you'd use a knife – carefully
- Laser outputs up to 2 mJ/pulse into the launch optics tube, which is dangerous!
- 308 nm wavelength – causes "sunburn" on skin and **CAN/WILL** cause eye damage
- Read and understand laser manual (on supplied CD)
- Observe and obey all labels and placards
- Never defeat blocks/filters/interlocks
- Do not work on any laser/optics unless trained or authorized to do so

- Corneal/skin damage (but not retinal) is **ALWAYS** a risk
- Never look directly into the laser, Launch Tube Assembly, **SPOC** window, fibers, or Fiber I/O block
- The revised ANSI Z136.1 (2007) provides guidance for the safe use of lasers and laser systems by defining control measures for each of the four laser classes
- Consult with a laser hygienist for legal opinion of client exposure risk, etc.
- HCl gas is poisonous/dangerous – handle with caution and in open air environment (even though it's dilute and there's a HCl scrubber on the vacuum pump)

Always wear safety glasses that "block 99.9% of UV" (polycarbonate). For instance, Uvex® brand are made to block UV. From UVEX web site: "In fact, Uvex stands for Ultra Violet Excluded. All Uvex SCT protective lenses employ this technology, filtering 99.9% of the UV radiation from 200 to 400nm." With the XeCl laser at 308 nm, this makes Uvex very effective at blocking the XeCl UV.

Purchasing Laser Recharge Gas

The excimer laser that comes with your **UVOST** system requires two specialty gases (xenon and hydrogen chloride mixture and research grade helium) that you will need to order before your **UVOST** system arrives at your facility. The laser manufacturer recommends purchasing the specialty gases from either Linde Electronics & Specialty Gases or Nova Gases (see contact information below). You will need to purchase at least one cylinder of each; we estimate that under normal use they should last 6-9 months.

If you have any questions please call Roxane Meidinger at (701) 237-4908

Nova Part No.	Linde Part No.	Item Description	Volume	Valve
HCX035HE-07-1000	24087450	XeCl Premix: ~0.07% hydrogen chloride, ~0.35% xenon, balance helium	1000 L	330
HE60-03-350 (may wish to get bigger tank)	24089126 (for 350L, may wish to get bigger tank)	Helium, research grade Order tank size of choice	? L	580

Table 4. Laser gas descriptions

Nova Gas Technologies, Inc.
2781 Three Lakes Road
Charleston, SC 29418 USA
Phone: (800) 221-0830
Fax: (843) 747-0958

Linde Electronics & Specialty Gases
One Greenwich Street, Ste 100
Stewartsville, NJ 08886
Phone: (800) 932-0624
Fax: (908) 329-9740

Data Files

The **UVOST** system generates various files. Here are the definitions of the various files.

"Raw" file with extension: lif.raw.bin

This is **UVOST**'s native file format, a proprietary file that contains numerous details about the **UVOST** log including Start/Stop times/dates, Notes, Info, Stats, GPS information, reference and background waveforms, and all of the individual "raw" waveforms from the oscilloscope in their compact binary form. These files are typically not to be shared with the client. Export data or give summary files instead.

"Data" file with extension: .lif.dat.txt

These are the client's data files if they need them for 3D imaging or other processes. These files can be exported from OST automatically after each push, or in singles or batches later. They contain tab-separated data in the following format:

Depth » Signal(%RE) » CH1(%RE) » CH2(%RE) » CH3(%RE) » CH4%(RE) » Rate

"PLOT" file with extension: .lif.plt

This file stores a running log of the various plotting schemes used to create JPGs or paper prints. Each time the user plots/exports the time/date, callout depths/ranges, and descriptions are saved – along with a name for each PLOT scheme (if supplied). This helps prevent confusion and saves work/time. If you're careful and preserve formatting, you can use the PLOT file to automatically create plots according to your edits. You can also delete PLOT files or move them to another directory to allow you to start fresh. Note that this file does not include scaling information.

"JPEG" data file with extension: .lif.jpg

The electronic printout of the OST LIF logs may be saved as standard jpeg images, which can be readily distributed, incorporated into reports, placed on the web or catalogued by image handling programs. Image handling programs, such as Google's Picassa can also generate contact sheets and overlays.

"Summary" data file with extension: .lif.sum.txt

The summary file contains pertinent information from a number of logs. This is a tab-separated text file. Information includes: file name, date/time, latitude, longitude, final depth, max signal, and max signal depth.

Peripheral Devices

Remote Display

The Remote Display is a simple device that allows those controlling the direct push probe to monitor and control a few basic functions of the **UVOST**. Main functions of the Remote Display include:

Boot-Up

On successful power up and communication, the display lets the user know that **UVOST** "sees" the Remote Display.

Button Function:

None

Display:

COMM ESTABLISHED_

Pre-Log

Once the **UVOST** has been calibrated with RE, the file name is chosen, and the **UVOST** system is essentially "ready to push", the Remote Display alerts the probe operator that **UVOST** is ready and displays file name and current system time. Logging can be activated by the probe operator for increased efficiency.

Button Function:

Pushing down button indicates you want to start logging.

Display:

READY-PUSH DWNARRW

UVOST_001

Logging

During a logging event the **UVOST** sends a stream of information to guide the probe operator's speed, knowledge of current depth, LIF intensity, and at what depth the maximum LIF response occurred. This provides a client with an alternative for watching the main **UVOST** display and is useful when the client wants to take notes.

Button Function:

Pushing the UP arrow button ends the log. ***Hint*:** think "it's time to pull up".

Display:

RATE 0.0 IN/S

SIGNAL 0.0 %

DEPTH 0.01 FT

MAX 126@3.6 8:00

Post-Log

Once the log has been terminated the **UVOST** sends useful information to the Remote Display. This includes notice that push is complete, final depth, maximum response and depth at which it occurred, and time.

Button Function:

None

Display:

```
PUSH COMPLETE
UVOST_001
DEPTH          32.00 FT
MAX 126@3.6   8:00
```

Depth String Pot

The **UVOST** system uses a resistive potentiometer (string pot) to measure depth. It is typically mounted on the probing machine so that as the rod is advanced into the ground the string pot wire is retracted into the device. The mounting location must be unencumbered and the anchor point must be directly above or below the cable exit. Some probe manufacturers have brackets available as well as ground pegs (e.g. Geoprobe®'s part #16791, 11751 and SC112). The string pot used with **UVOST** has 100 inches or 254 cm of cable so it can accommodate all common rod lengths. Exceeding 100"/254cm or snapping the wire will damage the device. Replacement wires are available from Dakota. The entire string pot can be sent to the manufacturer for repair and recalibration if needed. The label on the string pot indicates the sensitivity for that particular device in mV/V/inch, typically 9.92 mV/V/inch. This number needs to be input to the OST software on the depth tab, so that depth is calculated correctly. The rod length must be set in this tab also. String pot communication cables should be run in such a manner that they can be left on the machine and that the cables are not pinched or pulled during normal probe operation.

GPS

GPS logging is an unsupported (no technical support or warranty) feature of **UVOST**. The **UVOST** expects a **National Marine Electronics Association (NMEA) compliant** GGA data string. Set up your GPS to export **only the GGA data string** to its RS-232 compliant serial port. Many web sites and your GPS manuals provide information on GPS function. Set up your GPS's output serial port to export GGA data at: CAUTION: Some serial ports (A/B, etc.) have 12 volts on the ninth pin, etc.! This can damage **UVOST** serial port adapters. Use only the NMEA compliant serial port.

- 4800 b/s (bit per second rate) baud rate
- 8 bits of data
- No parity
- One stop bit

[All units that support NMEA should support this speed]

Connect serial port to GPS input of the e-deck. You can monitor success of GGA import by looking at the GPS tab of the **UVOST** OST software. The OST system passively monitors and displays the

current data it is receiving. This also allows you to monitor the quality of the data being acquired (antenna position, whether data is 2D or 3D, etc). The OST software displays much of the following information:

GGA - essential fix data which provide 3D location and accuracy data.

$GPGGA,123519,4807.038,N,01131.000,E,1,08,0.9,545.4,M,46.9,M,,*47

Where:

GGA Global Positioning System Fix Data
123519 Fix taken at 12:35:19 UTC
4807.038,N Latitude 48 deg 07.038' N
01131.000,E Longitude 11 deg 31.000' E
1 Fix quality: 0 = invalid
1 = GPS fix (SPS)
2 = DGPS fix
3 = PPS fix
4 = Real Time Kinematic
5 = Float RTK
6 = estimated (dead reckoning) (2.3 feature)
7 = Manual input mode
8 = Simulation mode
08 Number of satellites being tracked
0.9 Horizontal dilution of position
545.4,M Altitude, Meters, above mean sea level
46.9,M Height of geoid (mean sea level) above WGS84 ellipsoid
(empty field) time in seconds since last DGPS update
(empty field) DGPS station ID number
*47 the checksum data, always begins with *

Sub-meter (Differential GPS or DGPS) requires a subscription service such Omnistar or "free" WAAS. Dakota has relied on Omnistar for many years. See vendors such as www.omnistar.com for information on setting up your DGPS.

OST Daq Software

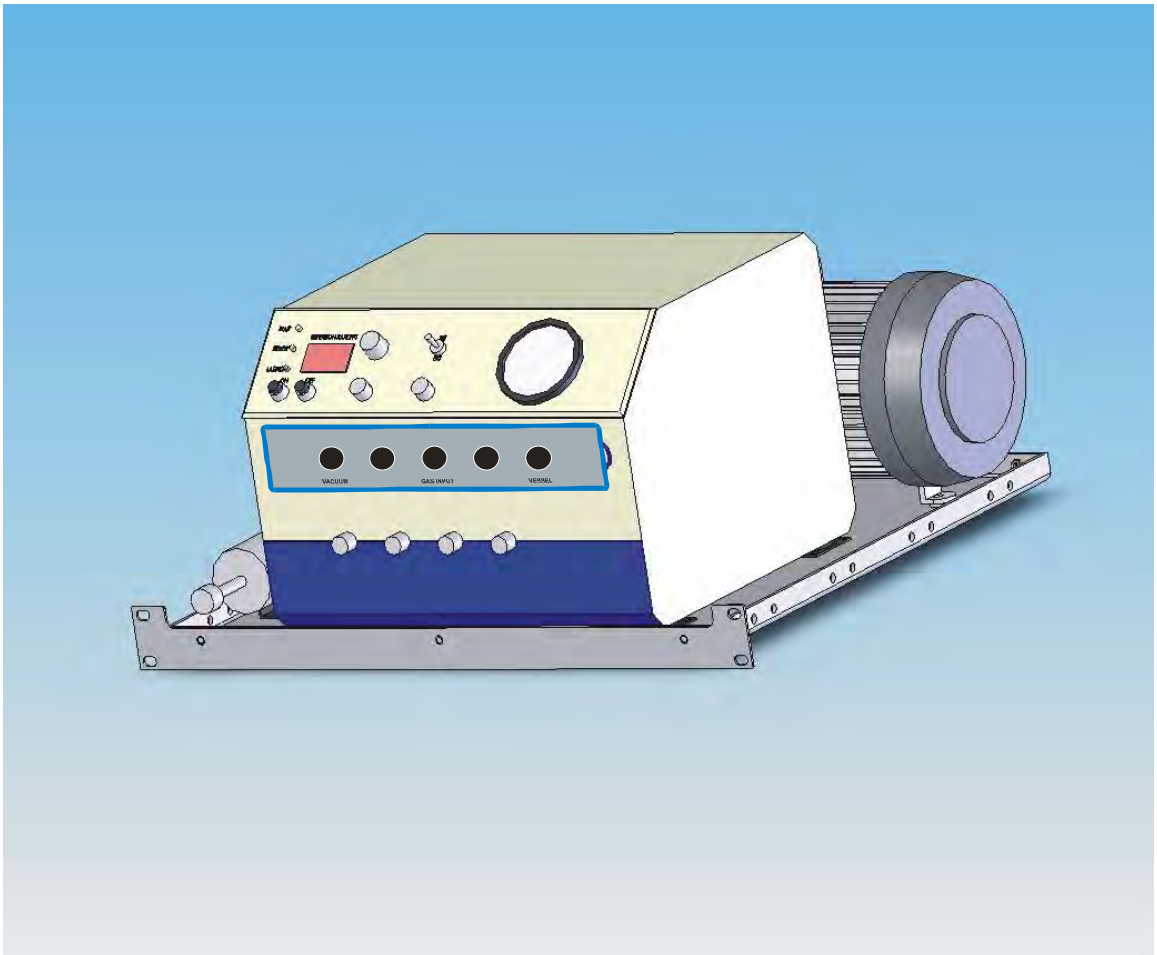
See separate OST DAQ software documentation.

Technical Support

All technical questions should be referred back to Dakota Technologies. Technical Support is available Monday through Friday 8 am to 5 pm (CDT) by calling 701-237-4908. Dakota Technologies suggests being properly set up for Window Remote Assistance http://support.microsoft.com/kb/300546 prior to system/software specific troubleshooting. You can also contact Technical Support through email at: info@dakotatechnologies.com

Appendix A - Laser Recharge

UVOST
PSX-100 Excimer Laser Recharge Procedure



Before you begin…

Read instructions and make sure you completely understand each step before you attempt it. It cannot be stressed enough that an improper recharge can seriously damage the laser - resulting in costly repairs that can only be performed by the manufacturer.

Use common sense and practice safety when transporting and setting up gas cylinders. Never transport cylinders without valve covers in place! Always secure cylinders and support cross purge assembly during recharge.

Pre-mix gas is toxic – do not release into the air unless it is passing through the Halogen filter. Recharge in a well-ventilated area.

- Do not use XeCl premix below 200 PSI, remaining gas is often of poor quality and may contain contaminants or particulate.
- Do not use He gas below 100 PSI, remaining gas is of poor quality
- It is recommended that you reorder gases when your cylinders reach 700 to 500 PSI, as it will take weeks to get new cylinders.

Always keep the cross purge assembly under a positive pressure of Helium while making connections and never let atmospheric air into lines, cross purge assembly, manifold or laser vessel. The moisture in air mixes with HCl gas, creating HCl acid which is a corrosive compound. HCl is fairly inert in the absence of H_2O. The corrosive nature of the pre-mix gas combining with the atmosphere is what damages the cross purge assembly and lines, as well as contaminating the manifold and vessel of the laser. While you can't completely prevent air from entering all the lines, valves, etc. you need to be thinking "keep the air out", "displace the air", "flush with He", the entire time you're handling the gases and hardware.

Gas fittings on the laser are **METRIC** **DO NOT** replace caps or attempt to hook up fractional fittings.

The laser manifold valves are o-ring based. You need only finger-tighten the valves. Over-tightening can damage the threads or destroy the valve. **DO NOT** over-tighten.

Supplies Needed For Recharge Procedure:

- Cross Purge Assembly
- Helium transfer line –**orange poly tubing**
- Helium regulator
- Helium cylinder
- Pre-mix cylinder
- 3 adjustable wrenches **– 2 capable of opening to 1 1/8 inches, a third smaller adjustable wrench is recommended for tightening the smaller gas fittings [Metric fittings are 14mm]**
- 3/8" hex headed wrench – **used for plug on Helium cylinder**

While following these instructions DO NOT make any connections, DO NOT remove any caps, etc. ahead of time (in other words - do not pre-assemble the equipment as shown in the figures – wait to be specifically instructed to do so).

Note for UVOST systems operated outside the United States

Companies operating **UVOST** systems outside the United States will need to purchase their gases and gas handling systems through regional vendors. Linde is an example of an international company capable of providing recharge gases and handling equipment. Linde can and will provide contact information to purchase gases within your country/region. Sizes and measurements of tools/hardware will be unique to each country/region and vendors there will provide the specifications.

Final Setup Images

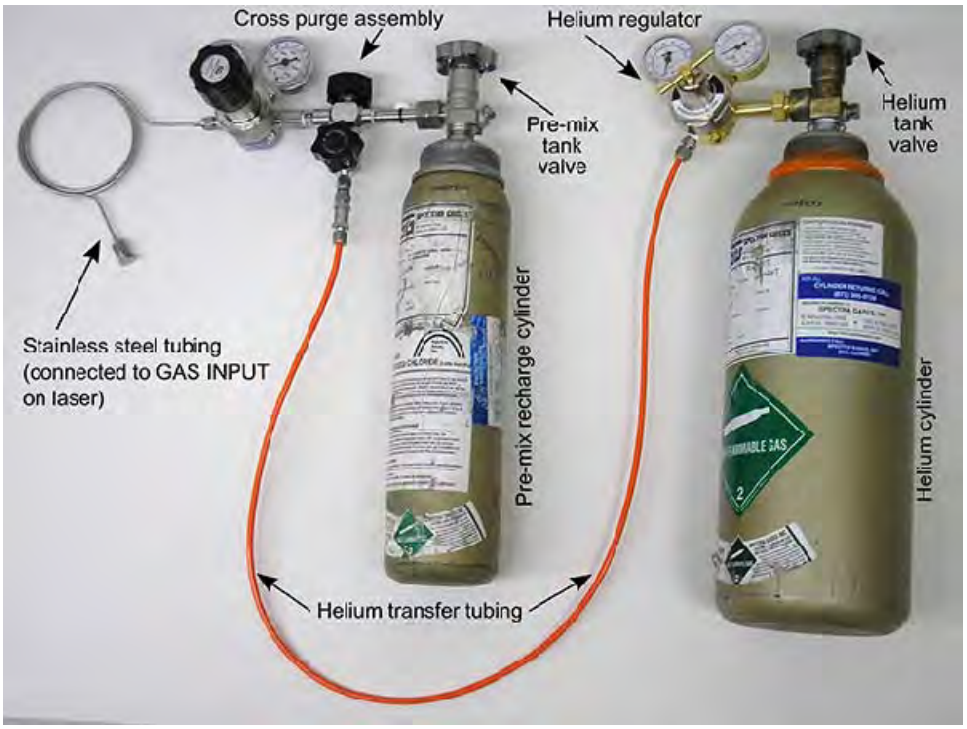


Figure A-1. Recharge tanks and cross-purge assembled

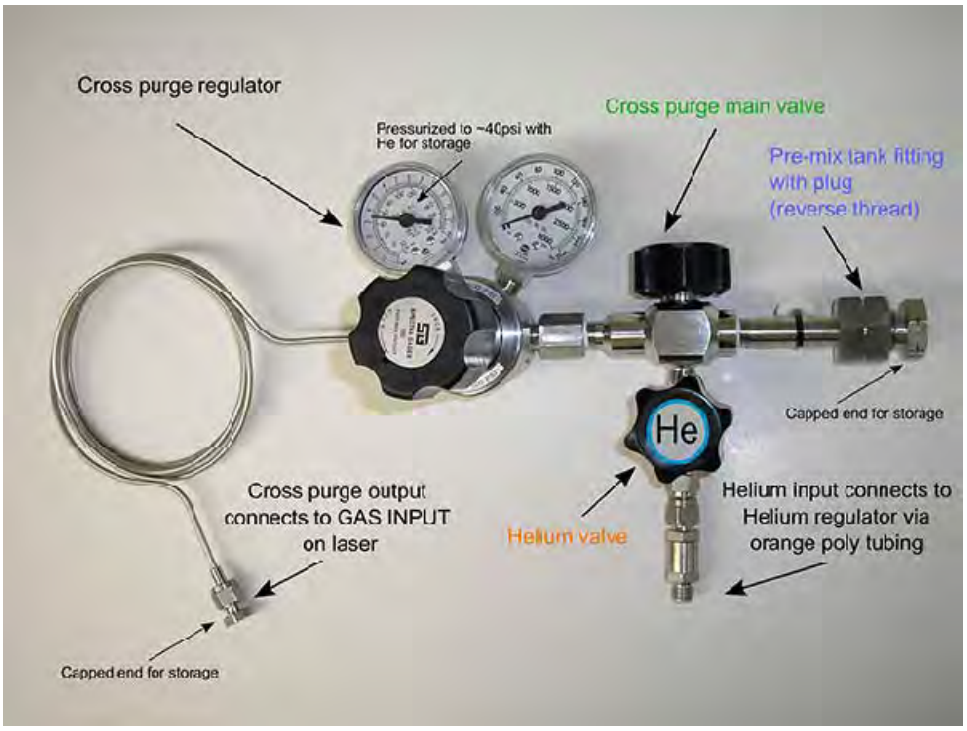


Figure A-2. Cross-purge

Recharge Procedure

Step 1. Evacuate scrubber filter and vacuum lines

A. Push the 'off' button on the face of the laser

B. Assure that **GAS INPUT** and **VESSEL** valves on the laser are closed

C. Turn on vacuum pump switch located in the lower right corner of the e-deck of the **UVOST** system.

D. Allow pump to evacuate the vacuum lines/filter for ~15 seconds

E. Turn off the vacuum pump

Step 2. Install Helium regulator on Helium tank and connect to cross purge assembly.

A. Verify that all valves on the cross purge assembly are in closed position.

B. Remove protective cylinder cap and threaded tank plug on He cylinder

C. Connect He regulator to He tank

D. Connect orange poly Helium transfer tubing between He regulator and He input on cross purge assembly (see Figure A-1)

E. Open main He cylinder valve

F. Adjust He regulator pressure to ~ 20 psi. *[you can control He flow by adjusting pressure]*

G. Open the cross purge assembly He valve (Figure A-2).

Step 3. Connecting pre-mix tank to cross purge assembly

A. Remove pre-mix cylinder cap and the **REVERSE** threaded tank cap on pre-mix cylinder in preparation of connecting the cross purge assembly.

B. In the next step, helium gas will be vented. To avoid waste of helium gas, quickly check to make certain the Teflon gasket is still present (Figure A-3) after removing plug in next step.

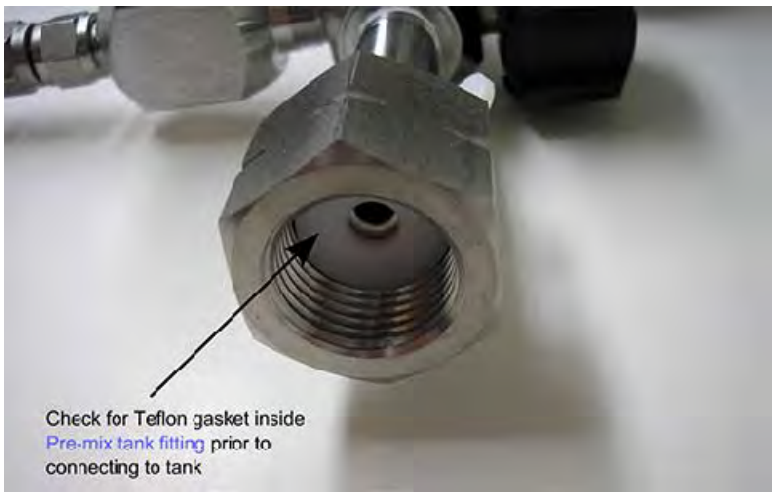


Figure A-3. Teflon gasket seal

C. On cross purge assembly, slowly remove **REVERSE** threaded **pre-mix tank fitting** plug (Figure A-2) with larger adjustable wrenches.

D. Helium should now be hissing out of tank fitting- **this is essential – the cross purge needs to be kept under positive pressure He**. You can throttle back the pressure by closing down the **He valve** some on the cross purge to conserve helium as long as you can hear hissing and you do not close the valve completely. [***NOTE:*** ***cross purge main valve*** *in* ***closed*** *position*

*will still allow He to flow out to pre-mix tank fitting (Figure A-4). Leave in **closed** position. **DO NOT** open pre-mix cylinder valve yet.]*

E. **REVERSE** thread the cross purge assembly onto pre-mix cylinder

F. Tighten connection with large adjustable wrench.

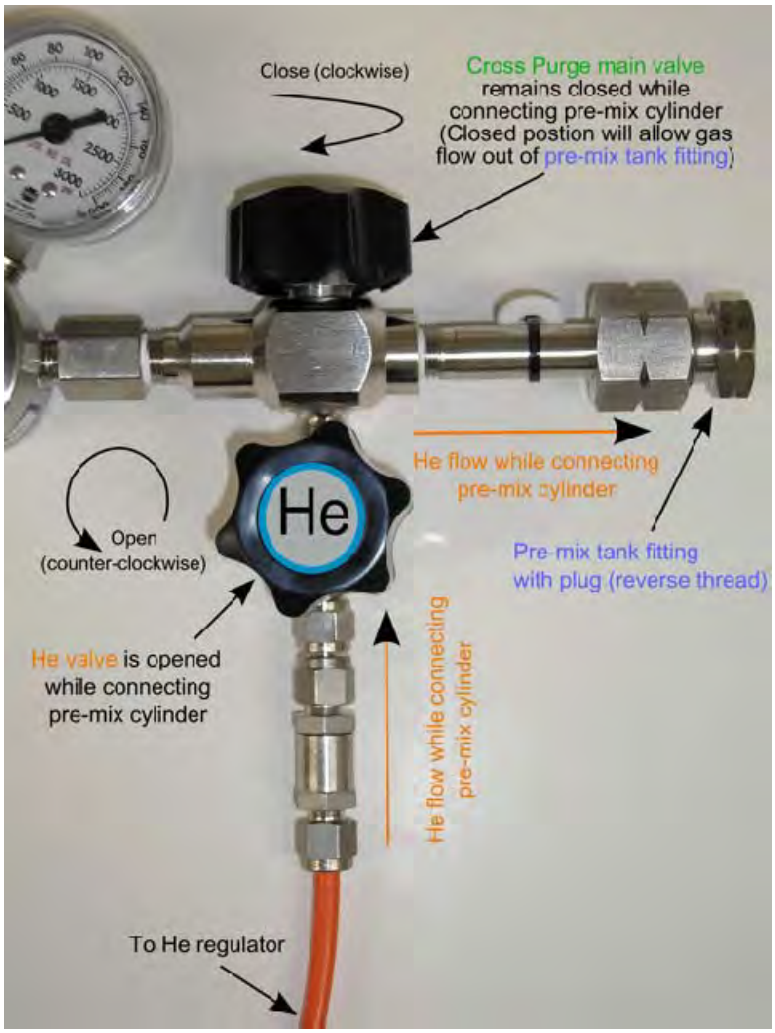


Figure A-4. Cross-purge valves and gas flow

Assembly should now look similar to Figure A-1

Step 4. Pressurize entire cross purge assembly

A. When cylinders are connected as above (Figure A-1), **open** the **main valve** on cross purge assembly. The entire cross purge assembly is now under positive He pressure, including the stainless steel transfer line.

Step 5. Connecting the cross purge assembly to the laser

A. Verify the He valve on cross purge is open and there is a pressure reading on the cross purge regulator.

B. Remove Swage fitting cap below the knob labeled **GAS INPUT** on laser *[Note: this is a metric fitting do not replace with a fractional cap.]*

C. Loosen the plug on the end of the stainless steel line attached to the cross purge assembly. Helium should be hissing out of stainless steel line- this is essential – the cross purge and lines needs to be kept under positive pressure He.

D. Positioning the stainless steel tubing near the laser, remove Swage cap from stainless steel tubing and quickly connect to the **GAS INPUT** Swage fitting.

[Note: The cross purge assembly and lines should hold the He pressure when fitting is tightened down. You should not hear any hissing from leaks.]

Step 6. Evacuate He from SS line, laser manifold, and cross purge assembly

A. **Close** the **He valve** on the cross purge assembly – but leave the **main valve** **open**.

B. Start the vacuum pump and slowly open the **VACUUM** valve on the laser manifold. *[Note: Do not open too far – only 3 turns needed!]*

C. Slowly open the **GAS INPUT** valve on laser manifold using it to control the rate at which the He is evacuated. Do this slowly as not to overwhelm the vacuum pump with a "quick slug" of gas.

D. Observe the pressure gauge on cross purge regulator. Evacuate until the pressure gauge reads –1 bar. At this point, the laser pressure gauge should read zero.

E. Close the **GAS INPUT** valve

F. Close the **VACUUM** valve on the laser

G. Turn off the vacuum pump

Step 7. Conditioning the cross purge assembly with pre-mix gas

A. Open the pre-mix tank valve (the cross purge regulator should be set to 100 psig) allowing it to fill the cross purge and SS line (**main valve** on cross purge should be **open**). The cross purge assembly and SS line should now be under positive pressure with pre-mix gas.

Step 8. Evacuating the laser vessel of old gas

A. Make sure all laser manifold valves are closed

B. Open the **VESSEL** valve on the laser (2 full turns). The Pressure gauge on the laser should shoot up to near 6 bar.

C. Turn on vacuum pump

D. Slowly open the **VACUUM** valve on the laser manifold, using it to regulate the amount of gas being drawn out of the vessel in a controlled and even fashion (~ 1 bar every 5 seconds). **CAUTION: Fully opening the vacuum valve or allowing the vessel to expel its gas quickly can overwhelm the pump.**

E. Continue evacuating until the laser is pumped down to 1 bar

F. Open the **VACUUM** valve all the way and allow the vacuum pump to completely evacuate the **VESSEL** of old gas for approximately 10 seconds. **WARNING: DO NOT LET PUMP DRAW VACUUM ON EMPTY VESSEL FOR LONGER THAN 45 SECONDS. EXTENED PERIODS OF VACUUM CAN DAMAGE VESSEL AND SEALS!!!**

G. Close **VESSEL** valve on laser manifold

H. Close **VACUUM** valve on laser manifold

I. Turn off vacuum pump

Step 9. Evacuate premix from cross purge and SS line

A. Because the pre-mix gas has sat for more than 1 minute in the SS lines or cross purge assembly it should be evacuated before filling the laser vessel. This assures you have the purest gas in the vessel and flushes any impurities out of the SS lines.

B. **Close** the **main valve** on the cross purge assembly

C. Turn on the vacuum pump

D. Open the **VACUUM** valve on the laser manifold (3 full turns). Slowly open the **GAS INPUT** valve using it to control the flow of gas (monitor the pressure dropping on the cross purge regulator).

E. Allow the vacuum pump to evacuate the SS line and the cross purge assembly

F. Once pumped down to -1 bar, close the **GAS INPUT** valve and the **VACUUM** valve on the laser manifold.

G. Turn vacuum pump off

Step 10. First fill of laser vessel with premix

A. **Open** the **main valve** on the cross purge assembly to fill the SS line and cross purge assembly with pre-mix gas again.

B. Open the **VESSEL** valve on the laser manifold

C. Slowly open the **GAS INPUT** valve using it to control the rate of pre-mix gas allowed to enter the vessel. **DO NOT FILL VESSEL TOO QUICKLY** At the proper rate the pressure should increase 1 bar every 4-5 seconds (monitor pressure increase on laser pressure gauge).

D. Fill the vessel to ~ 4 bar. *[Note that this first fill of the **VESSEL** is to rid it of any remaining contamination. This fill will be purged before the final fill.]*

E. Close the **GAS INPUT** and **VESSEL** valves on the laser manifold

Leave this first fill of pre-mix gas in the vessel for 5 minutes. This will allow it to absorb contaminants in the vessel.

Step 11. Evacuating the first fill of pre-mix gas from the laser vessel

A. Make sure all laser manifold valves are closed

B. Open the **VESSEL** valve on the laser. The Pressure gauge on the laser should read ~ 4 bar

C. Turn on vacuum pump

D. Slowly open the **VACUUM** valve on the laser manifold, using it to regulate the amount of gas being drawn out of the vessel in a controlled and even fashion (~ 1 bar every 5 seconds). **CAUTION: Fully opening the vacuum valve or allowing the vessel to expel its gas quickly can overwhelm the pump.**

E. Continue evacuating until the laser is pumped down to 1 bar

F. Open the **VACUUM** valve all the way and allow pump to completely evacuate the vessel of old gas for approximately 10 seconds. **WARNING: DO NOT LET PUMP DRAW VACUUM ON EMPTY VESSEL FOR LONGER THAN 45 SECONDS. EXTENED PERIODS OF VACUUM CAN DAMAGE VESSEL AND SEALS!!!**

G. Close **VESSEL** valve on laser manifold

H. Close **VACUUM** valve on laser manifold

I. Turn off vacuum pump

Step 12. Evacuate premix from cross purge and SS line again

A. **Close** the **main valve** on the cross purge assembly

B. Turn on the vacuum pump

C. Open the **VACUUM** valve on the laser manifold. Slowly open the **GAS INPUT** valve using it to control the flow of gas (monitor the pressure dropping on the cross purge regulator)

D. Allow the vacuum pump to evacuate the SS line and the cross purge assembly

E. Once pumped down to -1 bar, close the **GAS INPUT** valve and the **VACUUM** valve on the laser manifold

F. Turn vacuum pump off

Step 13. Final fill of laser vessel with premix

A. **Open** the **main valve** on the cross purge assembly to fill the SS line and cross purge assembly with pre-mix gas again.

B. Open the **VESSEL** valve on the laser manifold

C. Slowly open the **GAS INPUT** valve using it to control the rate of pre-mix gas allowed to enter the vessel. **DO NOT FILL VESSEL TOO QUICKLY** At the proper rate the pressure should increase 1 bar every 4-5 seconds (monitor pressure increase on laser pressure gauge).

D. **Fill the VESSEL to 6 bar.** *[NOTE: For proper laser operation is it critical that the pressure in the VESSEL be exactly 6 bar. More or less pressure will result in poor or no laser output.]*

E. Close the **GAS INPUT** and **VESSEL** valves on the laser manifold.

Step 14. Check laser energy

A. Start laser pulsing. Confirm that laser energy level is sufficient (yellow laser energy indicator, business card, RE, etc.).

Failed Laser Recharge

If laser energy is nominal/low, let it run for perhaps 10-15 minutes. Sometime it takes a while to achieve full laser energy.

If laser energy is low/non-existent, a repeated evacuation and refill is required (starting at **Step 11**).

Common causes for failed recharge include:

- Old/weak pre-mix gas

  Do not use XeCl premix below 200 PSI, remaining gas is often of poor quality and may contain contaminants or particulate.

  Do not use He gas below 100 PSI, remaining gas may be of poor quality
- Contaminated **VESSEL** (see **Suspected Laser Vessel Contamination**) below
- Laser malfunction
- Damaged/worn laser vessel electrodes

Recharge Dismantle Procedure

When/if recharge is successful and energy is sufficient, the recharge apparatus must be dismantled in specific order so as not to contaminate lines or cross purge assembly. You do not want to store the assembly/lines with pre-mix. It needs to be flushed out and stored with helium.

Step 1. Evacuating pre-mix from cross purge assembly and lines

A. Turn off laser
B. Close main pre-mix cylinder valve
C. Turn on the vacuum pump
D. Open the **VACUUM** valve on the laser manifold. Slowly open the **GAS INPUT** valve using it to control the flow of gas (monitor the pressure dropping on the cross purge regulator).
E. Allow the vacuum pump to evacuate the SS line and the cross purge assembly.
F. Once pumped down to -1 bar, the **VACUUM** valve on the laser manifold can be closed.
G. Close **GAS INPUT** valve on laser manifold
H. Turn vacuum pump off

Step 2. Pressurize all systems with Helium

A. **Open** the **He valve** on cross purge assembly, allowing cross purge and SS line to fill with He
B. Slowly open the **GAS INPUT** valve on laser using it to control the He gas flow
C. Watch the laser manifold pressure gauge and fill to between 2 and 3 bar with He. This will fill the laser manifold with He (**NOT THE VESSEL**) keeping it under positive pressure between recharges - preventing any atmospheric gas entry by small leaks.
D. Close the **GAS INPUT** valve, helium will be trapped in the manifold

Step 3. Disconnect SS line from laser

A. Make sure all valves from the He tank up to the laser **GAS INPUT** valve are still **OPEN** (**GAS INPUT** valve remains closed)
B. Make sure all valves on the laser are **CLOSED**
C. Disconnect SS line from the laser. When you loosen the fitting on the SS line at the laser He should be hissing out of SS tube.
D. Quickly replace cap on the **GAS INPUT** fitting of the laser (cap is metric do not replace with fractional cap)
E. Quickly cap SS line with Swage plug
F. C**lose** the **main valve** on the cross purge assembly. At this point, the cross purge assembly should be holding the He pressure (about 20 psi).

Step 4. Disconnect pre-mix cylinder

A. Ensure that main pre-mix cylinder valve is closed
B. With the **He valve** **open** on the cross purge assembly (**main valve** **closed**) disconnect the pre-mix tank from the cross purge with larger adjustable wrenches.
C. Helium should be hissing out through the reverse threaded fitting. Quickly install **REVERSE** thread plug to stop He discharge. Tighten plug with wrenches.

D. Cross purge should be pressurized to at least 20 psi. **Close He valve** on cross purge to hold pressure. Leave both valves on cross purge in **closed** position for storage between recharges.
E. Replace cap on pre-mix valve and protective cap on cylinder

Step 5. Close He tank valve and disconnect tubing

A. Close the main He tank valve
B. Disconnect the orange poly He line from the cross purge assembly
C. Disconnect the He regulator from the He cylinder and replace proper cap
D. Replace protective He cylinder cap

If everything is done correctly and in the proper order, the main regulator should show ~20 psi of pressure and be holding that pressure.

Suspected Laser Vessel Contamination

Notes from laser manufacture:

You can save the laser by filling and purging the chamber 2 or 3 times with pure Helium (it is much less expensive than using the XeCl premix) and it helps to clean the laser chamber. When filling a laser with pure Helium (99.999%), the discharge is established much more easily inside the chamber and if you look inside **donning appropriate eye protection** look into back-reflection side - **not laser output side.** You will notice that the discharge has a much bigger cross section than with a halogen mixture.

If you do not have time to purge with helium 2 or 3 times do not let it sit with contaminated gas in it. Purge at least once with helium ASAP.

Fill the laser at the same operating pressure (6 bar) with pure Helium, start the laser and let it pulse until the chamber gets warm. Start at lower repetition rates (10Hz) as long as you do not hear any "dzzz" instabilities in the discharge (if you hear instabilities while running the laser with helium, Stop running the laser and purge 2 or 3 more times without running the laser. If you cannot get stable operation by purging with helium it means that the chamber will need to be opened for cleaning.) Allow the laser to run (at low rep.) for about 30 min. The gas will slowly warm up and outgas some of the contaminants from the inner surface of the laser chamber. Purge the Helium in the chamber, refill with Helium and run the laser for 30 min. again. Repeat this process for a maximum of 3-4 hours of run time on Helium. It should then be filled again with the premix gas.

After refilling with XeCl mix try laser again but be careful and monitor the beam shape while you are running the laser. A nice big beam is OK but if it gets too small and concentrated in the middle, there is a chance of damaging the electrodes.

When your beam is just a small line in the middle, it means that the level of "outgased" contaminants is too high in the chamber and only the portion of the electrodes that are close enough (they have a rounded profile) can succeed to discharge. DO NOT LET THE LASER OPERATE for too long on a bad beam (If the discharge gets too concentrated in a small portion of the electrodes, it will damage them faster, and you will no longer be able to get a good beam profile.

To alleviate this do some more Helium fills and then put a diluted mixture of 1 bar of helium and 5 bar of your premix in the chamber to slowly recover the passivation.

The gas fill lifetime strongly depends on the purity of the gas, change it more often and it will finally get back its passivation. Successive refills and running the laser will slowly increase passivation.

Also, remember to always flush the old gas that was sitting in the lines (with the vessel valve closed) so you are never introducing old gas into the chamber.

The key thing is to make sure no air or almost none is introduced in the gas line when connecting it, and before filling the laser, flush the gas (and air) that was left in the line through the manifold with the vessel valve closed, and fill the line and manifold with 6 bar of XeCl premix. Let it sit there for one hour and flush again before filling the laser chamber. The inner walls of the gas line have to be passivated as well.

Every time you disconnect the gas line, please fill it to just above atmospheric pressure (~1.2 bar) with Helium and once disconnected, quickly install a Swage plug at the end of the line (two of these plugs must have been shipped along with the line), also cap the input Swage port on the laserhead. HCl is tremendously corrosive when exposed to air; it will end up making a "rusted" crust of all exposed parts.

Appendix B. UVOST Glossary

Absorbance: the phenomenon of molecules or substances capturing energy that attempts to pass through them – in **UVOST** the PAHs absorb certain frequencies of light – including the 308nm XeCl excimer laser

AD4: a quadrature to RS232 adapter made by U.S. Digital – used to encode pulsed or quadrature depth peripherals such as those used in CPT systems

Background: the signal observed without RE and with a very clean window – with **UVOST** you strive for highest RE/Background to minimize LOD – note that even a new mirror/window will generate some background due to laser scatter, Raman scattering, filter fluorescence, etc. - aka "blank"

Bandpass: the portion of spectrum between limiting frequencies – in **UVOST**'s case the approximately 40nm wide regions of light centered at 350nm, 400nm, 450nm, and 500nm

Baseline: the "clean" portion of a log that is flat/straight - where signal levels are consistent and assumed to be the natural "background" of the system/native soil combined – note that even the most non-fluorescent soils "look" like they are generating signal due to window/mirror/filter fluorescence, Raman, and other "system-generated" signal – baseline usually should be below 1%RE

BGS: Below Ground Surface

Breakout box: Dakota's electronic hookup box that connects the **UVOST**'s umbilical cable to the direct push platform peripherals via a single connecter - makes frequent attachment more convenient and lessens cabling trip hazards

BTEX: Benzene, Toluene, Ethylbenzene, and Xylenes – **UVOST** does not excite, and therefore detect, these molecules sufficiently so as to allow direct detection

Callouts: waveforms of interest highlighted for display in the OST software and prints

Canned air: Dakota's slang for any inert/dry gas used for electronics/cleaning – consisting of liquified difluoroethane, trifluoroethane, or tetrafluoroethane in a spray can. Try to avoid the canned air with the odorant, it tends to leave a film on mirrors and windows.

Coal Tar: a by-product of Manufactured Gas Plants (MGP) – often found in/around former MGPs - contains high PAH content

CPT: Cone Penetration Test – typically conducted with large/heavy trucks and tip/sleeve sensors on a rod string (SCAPS, ARA/Vertek, ConeTec, Hogentogler, A.P. van den Berg)

Creosote: name used for a variety of products: wood creosote, coal tar creosote, coal tar, coal tar pitch, and coal tar pitch volatiles – contains high PAH content

CSM: (Conceptual Site Model) – the catch phrase for the "big picture" of where the contamination is (combined with GIS info) at a contaminated site – increasingly popular with 3D modeling becoming available on standard PCs – highly promoted by TRIAD and other regulatory agencies

DeviceMaster RTS: the LAN-attached solid-state, embedded device server that enables OST software to communicate with A/D (string pot), remote display, and GPS. The DeviceMaster driver must be installed and configured correctly in order for OST to "see" those devices.

Direct Push: general term for CPT trucks and Geoprobe-class machines – no drilling

Emission: the photons that are emitted by molecules after absorbance of excitation light - in **UVOST** we use that term for the fluorescence, the fiber that delivers it back to the detection system, etc.

EULA: End Users License Agreement – the written agreement that protects Dakota's IP by preventing reverse engineering, transfer, or unauthorized sharing/selling of the OST software

Excimer: (short for excited dimer) is a short-lived dimeric or heterodimeric molecule formed from two species, at least one of which is in an electronic excited state

Excitation: the absorbance of energy by molecules – in **UVOST** we use that term for the laser light, the fiber that delivers it, etc.

Factory RE: the RE waveform recorded when the **UVOST** was manufactured and tested – this waveform can be used to track/identify system (or RE) drift/degradation over time and to check the general quality of the RE that is acquired for each log – "odd-shaped" RE's (identified by comparison with Master RE) will indicate either an improperly acquired RE, a severely degraded/contaminated RE, or damage to the integrity of the emission module

FFD: Fuel Fluorescence Detector – Vertek's mercury-lamp and filter system where the windowed sub is mounted just above CPT cone – generally single channel fluorescence data converted to voltage

Fiber I/O: the metallic blue device that houses launch coupling optics, launch attenuator, laser-blocking filter, and emission coupling optics – the design is "contactless" to prevent fiber polish damage - aka "launch block or fiber block"

Fiber Optic: the continuous fused silica filament ("light pipe") that carries excitation and emission light to/from the laser, SPOC, and emission detector

Fluorescence: a luminescence that is mostly found as an optical phenomenon in cold bodies, in which the molecular absorption of a photon triggers the eventual emission of another photon with a longer wavelength

Fugro: A large Dutch company with offices in the U.S. – provides ROST CPT - Fugro bought the ROST systems from the TRIAD group in 1996 and still operates them today.

GGA: essential fix data which provide 3D location and accuracy data – this is the string required for **UVOST** automatic capture of latitude and longitude

GPS: Global Positioning System – satellite positioning system used to locate **UVOST** logging locations – **UVOST** is capable of logging GPS [this feature is not yet officially supported]

Hardigg: the brand of **UVOST**'s shock-mounted case

in-situ: Latin phrase meaning "in the place" – common in environmental field as measuring an analyte while it's in its natural matrix (soil, water, etc.) instead of sampling or extracting the analyte/sample

Joule: SI unit of energy (J) – the PSX-100 excimer puts out 1-2 milliJoules (mJ) per pulse – SPOC emits 5-20 microJoules (μJ) per pulse

LAN: Local Area Network – the common CAT5 office network hardware and protocol used for data acquisition from PC to **UVOST**

LASER: Light Amplification by Stimulated Emission of Radiation – an ideal light source for fluorescence since it generates little if any of the same light as the analyte – there pulsed lasers like **UVOST**'s or CW (continuous wave) that are "always on"

Lead rod: The short (typically 2 foot) rod that attaches to the SPOC. Using a full size rod makes the fully assembled SPOC section too long to fit in some probes and a hassle to handle in general.

LIF: Laser-Induced Fluorescence – common term used to describe just what it says – in the environmental site investigation field it's used to describe any sapphire-window based screening probes that employ laser including Navy/Army nitrogen laser driven system (SCAPS), ROST, **UVOST**, and TarGOST. Note that FFD by Vertek is not LIF.

LOD: **Limit-of-Detection** – is the lowest quantity of a substance that can be distinguished from the absence of that substance (background/blank value) within a stated confidence limit (generally 1%) – the amount of substance needed to cause a signal 3.290 times the standard deviation of the background – note that background stability has a huge influence on LOD

MIP: **Membrane Interface Probe** – Geoprobe's chemically sensitive logging tool mainly for dissolved phase delineation – can have difficulty with NAPL "loading" making it difficult to see the "bottom" of NAPL layers

NAPL: **Non-Aqueous Phase Liquid** – exists as LNAPL or DNAPL – most LNAPLs and some DNAPLs "glow" due to PAH content – note that coal tars and creosotes are often either/both

NMEA: **National Marine Electronics Association** – is the unifying force behind the entire marine electronics industry – they set the standard for GPS data strings/protocol

ns: nanosecond – one billionth of a second – **UVOST** waveform is 300 billionths of a second long

Oscilloscope: is a piece of electronic test equipment that allows signal voltages to be viewed vs. time – **UVOST** employs a high-end digital storage oscilloscope fast enough to capture the short pulses of LIF

OST: **Optical Screening Tool** – most commonly seen on its own in the software banner, exe's, and associated generic terms – the OST in **UVOST** and TarGOST

PAH: **Polycyclic Aromatic Hydrocarbon** – the multi-ring aromatic molecules know to fluoresce and their ubiquitous presence in petroleum, coal tars, creosotes – aka PolyNuclear Aromatic hydrocarbons (PNA)

Parabolic mirror: a mirror with a curved surface that both reflects and focuses light – **UVOST**'s parabolic reflects and collimates the laser light cone emitted from the excitation fiber – it also collects and focuses the collimated emission light back into the emission fiber

Phosphorescence: like fluorescence but the decay time is measured in microseconds to seconds rather than nanoseconds (due to intersystem crossing)

PMT: **PhotoMultiplier Tube** – the transducer that converts photons to electrons and then magnifies those electrons for easier detection on the oscilloscope's CH2 (signal)

POL: **Petroleums, Oils, and Lubricants** – common DoD phrase for fuels, oils, greases, etc.

Push: Dakota term for an individual logging event – as in "did you get an RE so we can start the push?" – Aka "boring" or "sounding"

pVs: pico-Volt-seconds - the area of a waveform – the oscilloscope data dimensions are Volts and Time – 1/1000 of a nanosecond is a picosecond – so area is picoseconds x Volts or pico-Volt-seconds – note that this is in absolute area units (pVs)

RE: Reference Emitter- the standard NAPL housed in a fused silica or quartz cuvette used to calibrate **UVOST** – also the quantitative units of fluorescence as in %RE or RE% - all data is displayed/reported relative to (normalized by) RE

Red-shift: fairly common phenomenon describing NAPL fluorescence shifting from blue toward red (longer wavelengths) – typical with weathering

RGB: color model or standard that is an additive model in which red, green, and blue (often used in additive light models) are combined in various ways to reproduce other colors – in **UVOST** these colors represent a "shorthand" way of seeing waveforms

ROST: **Rapid Optical Screening Tool** – **UVOST**'s grandfather – built by Dakota in mid-late 1990s - trademark and systems operated by Fugro Consulting, Inc. (formerly Fugro Geosciences, Inc.) in Houston, TX

ROY G. BIV: is a popular mnemonic device used for memorizing the traditional optical spectrum: Red, Orange, Yellow, Green, Blue, Indigo, and Violet

RS-232: (Recommended Standard 232) is a standard for serial binary data signals connecting between a DTE (Data terminal equipment) and a DCE (Data Circuit-terminating Equipment).

Sapphire: single-crystal form of aluminum oxide (Al2O3) - a mineral known as corundum - it is the extremely hard - second only to silicon carbide and diamond – **UVOST**'s windows are made from synthetic sapphire

Sapphire window: the sapphire window potted into the metal fitting that allows it to be threaded into the SPOC or CPT LIF sub

SMA: **SubMiniature version A** – the style of connector used for the fiber optics and the PMT power (12V) connector ¼ - 32 TPI

Spectrum: a plot of phenomenon vs. wavelength that describes a molecule's or substance's behavior vs. light energy – note that more than one spectrum is spectra

Split caps: Push and pull versions of Geoprobe rod caps – contains a groove that allows cables to remain in place while pushing/pulling rods

SPOC: **Shock Protected Optics Compartment** – the special hardware that allows the mirror and fibers to survive percussion delivery

SPOC seal: (Discontinued, only relevant to old SPOCs) Short section of silicone tubing that seals active optic portion from inner SPOC chamber – helps prevent dust/moisture from collecting on window/mirror/fiber terminator – works by "joining" outside/bottom of window holder to the brass nipple inside SPOC

String Pot: (potentiometer) - The device that changes its resistance with distance of spring wound steel cable pulled from it – standard depth-encoding device for Geoprobe

Swage: the style of seals/nuts used in **UVOST** gas handling and in the SPOC – named after a privately-held international company, focusing on the manufacture and sale of gas and fluid systems components

TekVISA: an implementation of the industry-standard Virtual Instrument Software Architecture (VISA) API for communication between OST and the Tektronix® oscilloscope. The TekVISA driver must be installed and configured properly in order for the OST software to "see" the oscilloscope.

Umbilical: the cable that connects the **UVOST** to the direct push peripheral devices (remote display and string pot)

Waveform: the time vs. response of a pulsed phenomenon – in our case the time resolved measurement of photons arriving at the PMT and creating an electrical current vs. time representing the four bandpasses of fluorescent light we're interested in

Wavelength: (λ lambda) - the distance between repeating units of a propagating wave of a given frequency – used to describe light involved in **UVOST** – usually in nanometers (nm) which is one billionth of a meter

WTM: **wavelength-time-matrix** – a 3-dimensional data set of fluorescence spectra and time vs. voltage

Appendix C – Geoprobe® Parts Reference

Table of the common parts required for UVOST. The parts can be ordered directly from Geoprobe.

Item	Geoprobe® Part #
Stringpot Bottom Bracket for 6600 to 7700 models	11751
Stringpot Mounting Bracket for 6600 to 7700 models	16791
Stingpot Bottom Bracket for 7822 model	41993
Stringpot Mounting Bracket for 7822 model	41932
Stringpot Bottom Clamp for 5400 model	SC111
Stringpot Mounting Bracket for 5400 model	SC110
Hexagonal Piston Weight for all models	SC112
Probe Rod Wiper for 5400	AT1255
Rod Wiper Plate for 5410, 66, 77 and 78 Series models	23633
Rod Wiper Rubber for 5410, 66, 77 and 78 Series models	23852
Slotted Pull Cap for 1.5 inch probe rods	15164
Slotted Drive Cap for 1.5 inch probe rods	15607
Slotted Pull Cap for 1.25 inch probe rods	AT1203
Slotted Drive Cap for 1.25 inch probe rods	AT1202
Solid Drive Point for 1.25 inch probe rods	AT1245
Solid Drive Point for 1.5 inch probe rods	15219
Dampener System for 6600, 7700 and 7800 models	23321
Open ended rod rack for 18 rods (other racks available)	18625

Table 5. Common Geoprobe parts

The following are currently available through Dakota only.

Item	Dakota Part #
Adapter – SPOC to 1.25” Geoprobe style rods	100491
Adapter – SPOC to 1.5” Geoprobe style rods	100490

Table 6. Dakota Geoprobe parts

Dakota Technologies, Inc.
2201-A 12th St. N.
Fargo, ND 58102

Phone: 701-237-4908
Fax: 701-237-4926

www.dakotatechnologies.com
info@dakotatechnologies.com

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APPENDIX B: USERS MANUAL - MAAPERA® NIRS ANALYZER

Data Collection

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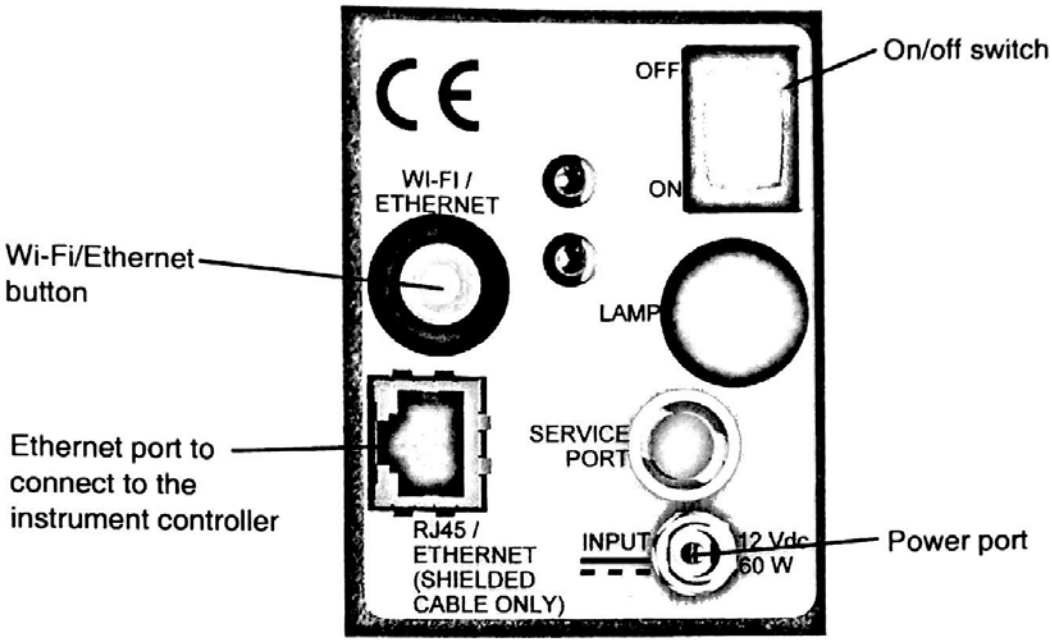
1. Introduction

This document is intended to provide instructions on how to set up the spectroradiometer and collect data.

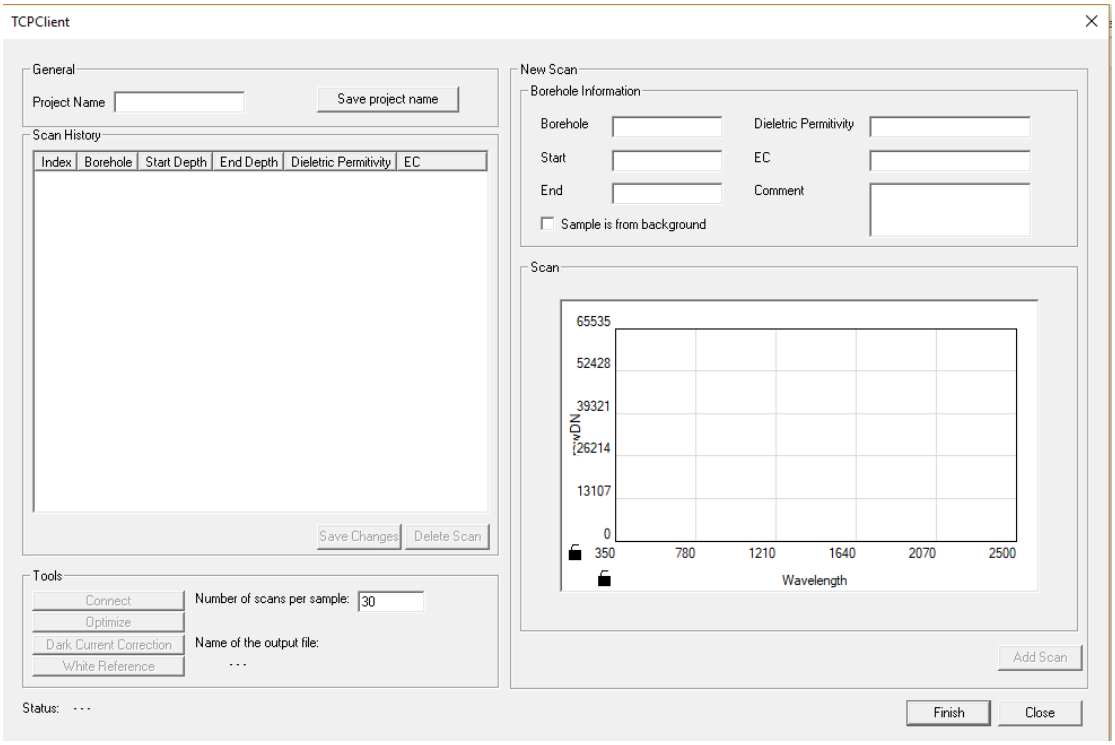
2. Spectroradiometer Set Up

1. Connect the power cable to the scanner.
    a. The power cable connects to a co-axial cable-like connection (threaded) at the back of the scanner.
2. Connect the laptop to an electrical outlet.
3. Connect the Ethernet cable to the port in the back of the scanner and to the laptop.
4. Connect the power cable to the contact probe.
    a. The power cable is a three pin connector. Insert the plugin careful, the pins are FRAGILE and can bend easily.
5. Connect the fiber optic cable into the contact probe.
    a. The fiber optic cable is FRAGILE. Do not coil the cable into loops less than 5” in diameter.
    b. Unthread the screw cap from the fiber optic port on the contact probe.
    c. Remove the safety cap from the end of the fiber optic probe.
    d. Gently insert the fiber optic probe through the screw cap and the rubber insert in the fiber optic port under you feel resistance.
    e. Thread the screw cap back on finger tight and test to see if the probe is well seated in the contact probe. It should resist movement from gentle tugging.
6. Turn on the power to the scanner and laptop.
7. Let the scanner warm up for at least 30 minutes before scanning samples.

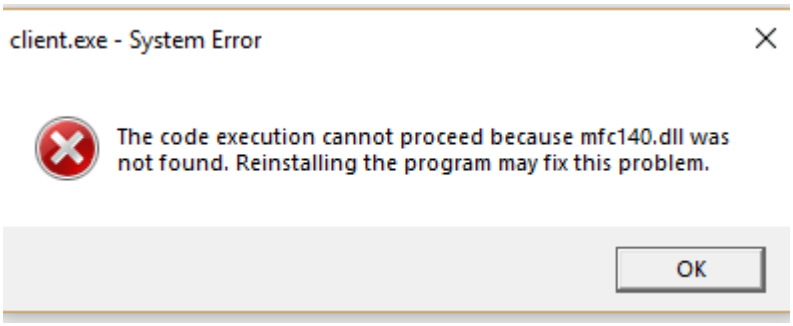


3. Sample Logging

1. Double-click the 'Client.exe' executable file and wait for the program to load.

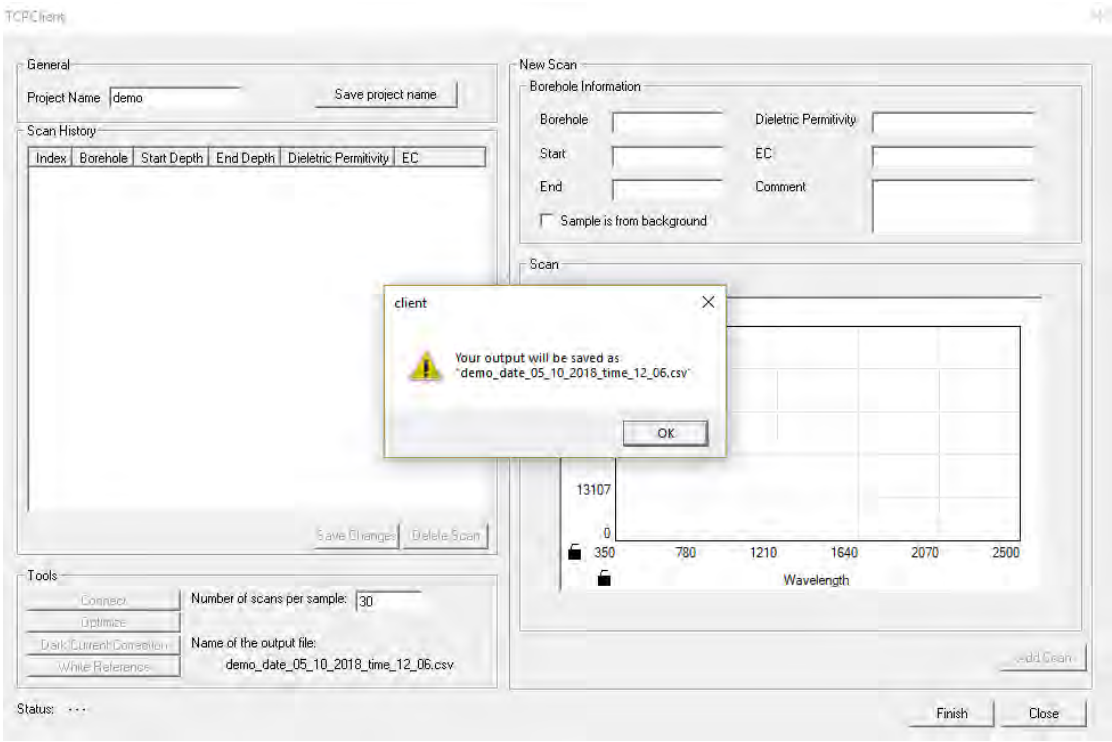
2. 

3. If the software does not load and you get the following error:

4. 

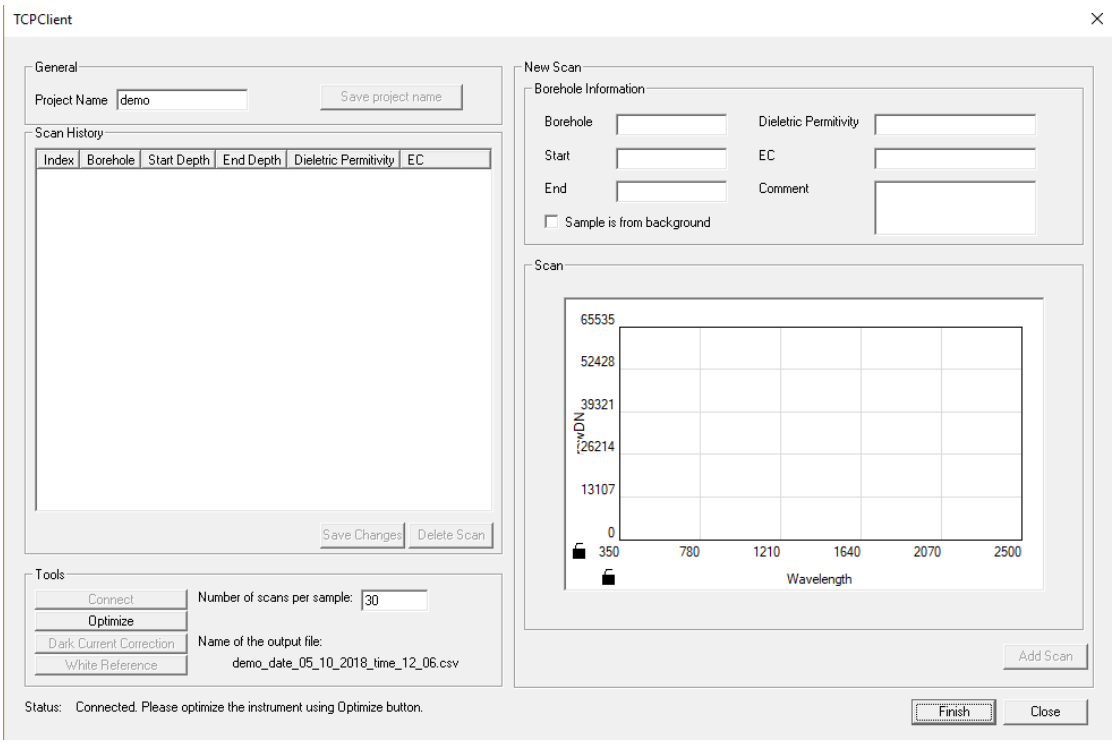
5. Then you need to install visual studio available here: https://support.microsoft.com/en-ca/help/2977003/the-latest-supported-visual-c-downloads

6. Enter a project name and click save project name
   i. Do not include slashes (back or forward slashes) in the file name

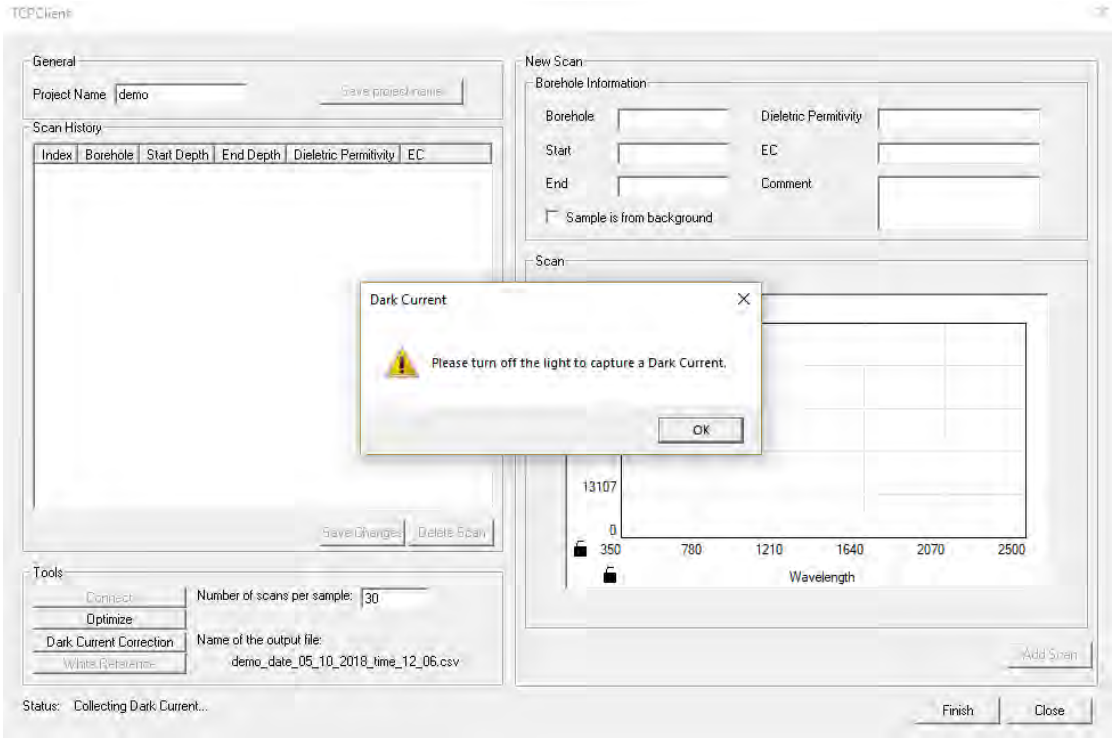
7. 

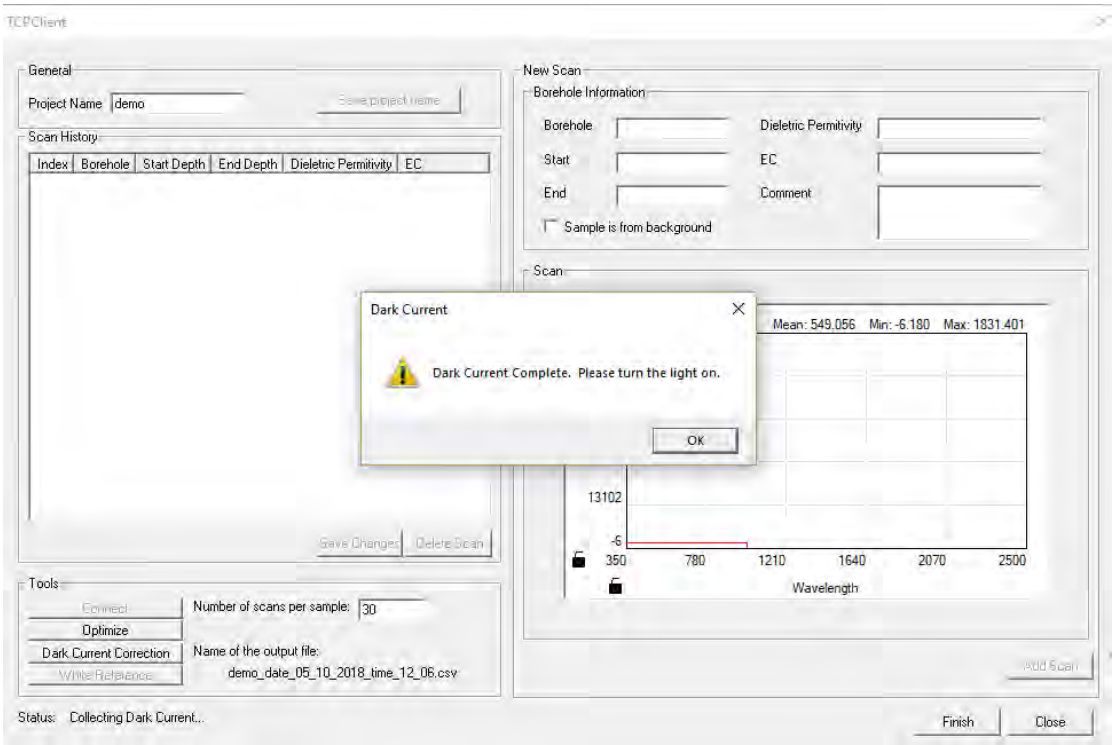
8. Project name will be saved in the outputs folder with the name you selected plus a time stamp
9. Click connect
10. After instrument has connected. Turn on contact probe light and place on Spectralon. Then click optimize

11.

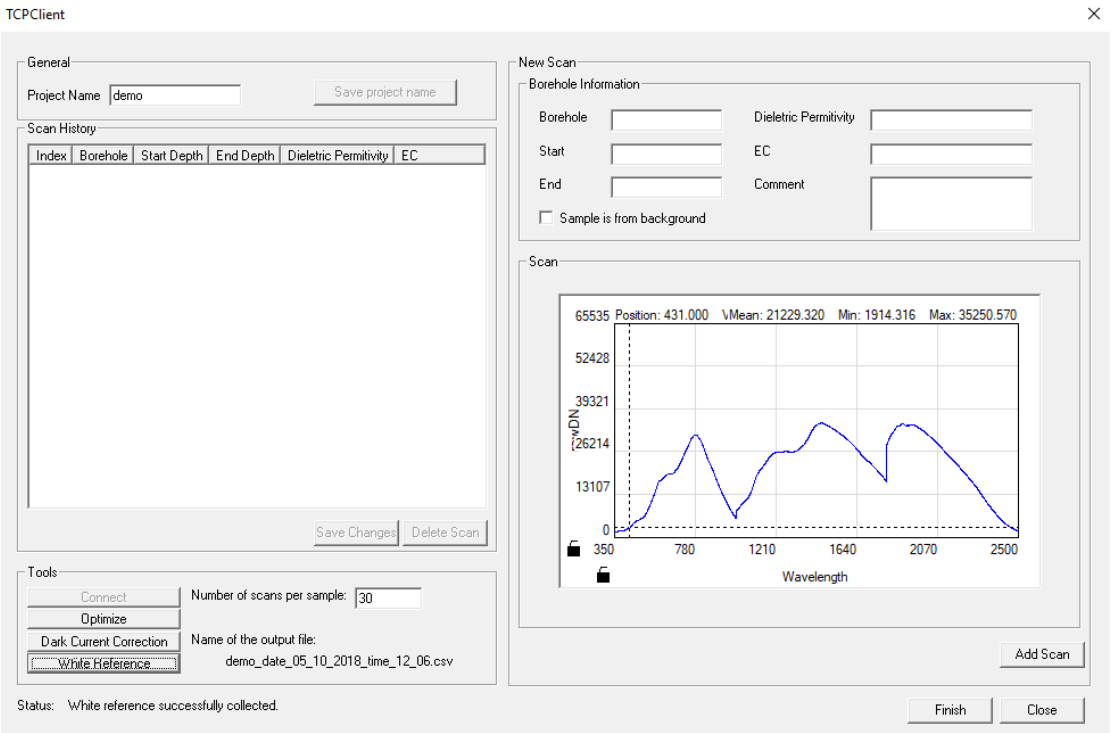
12. 

13. Once optimization is complete, then select dark current. Turn off the light as instructed on the contact probe, and then turn on the light as instructed.

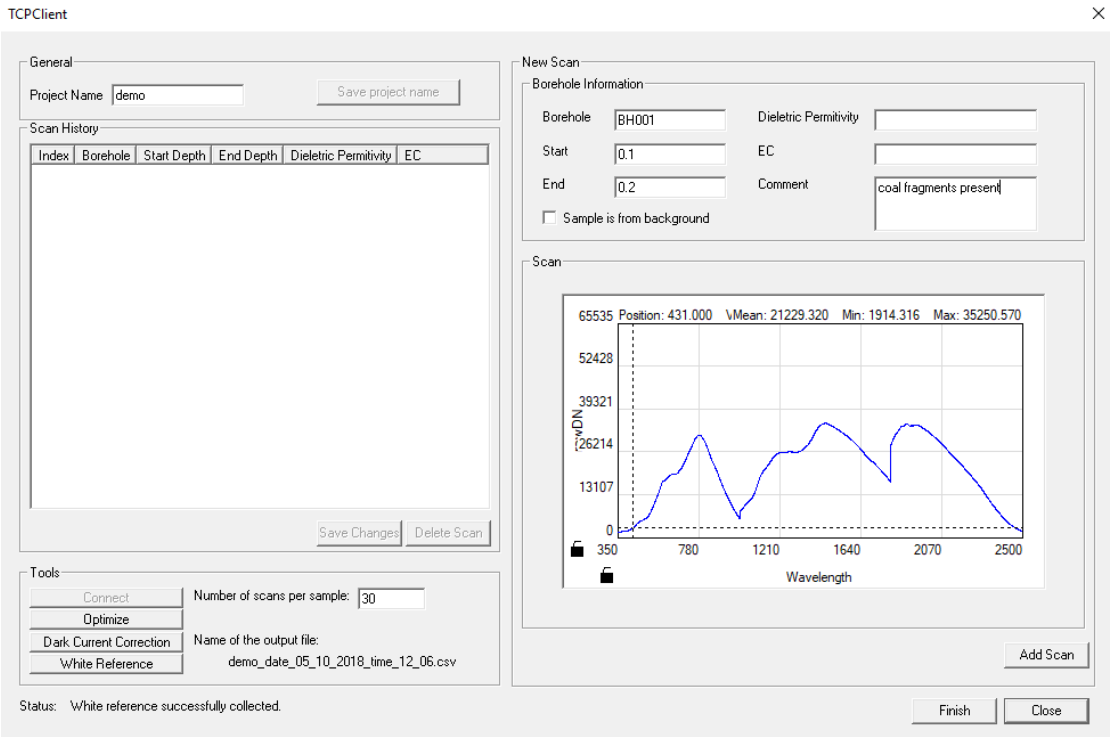
14. 

15. 

16. Once the dark current collection is complete. Then click on white reference with the light on and the contact probe set to take a reading from the Spectralon. If done correctly a curve with the following general shape should be visible

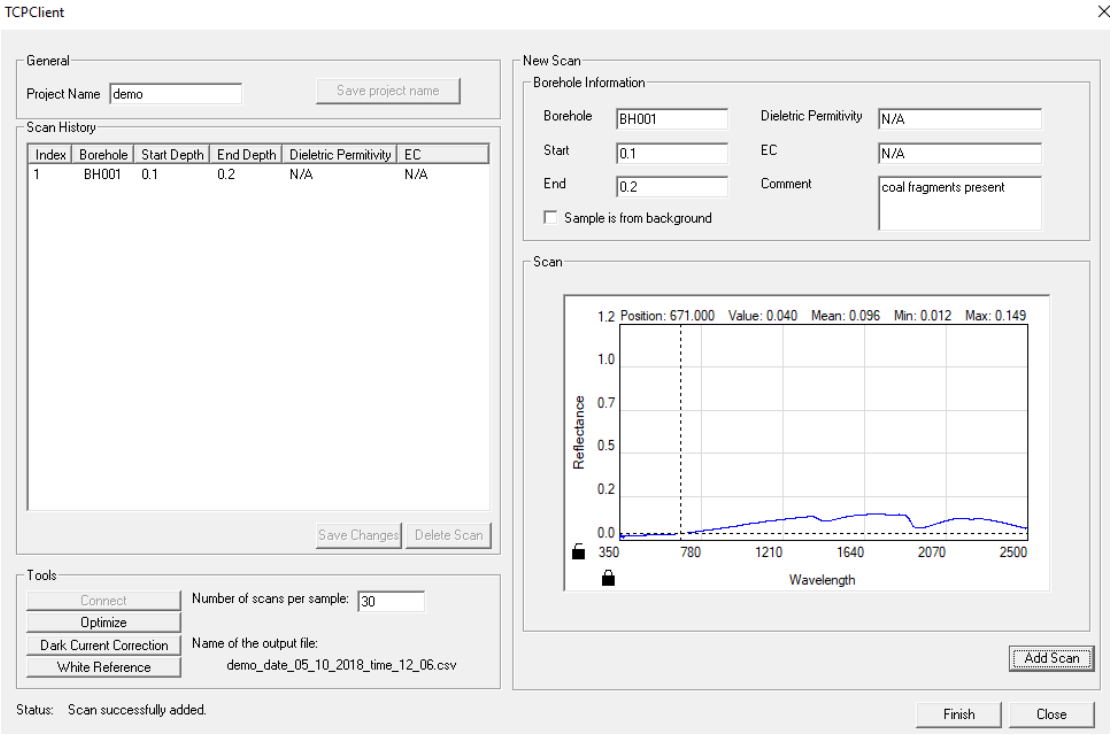
17. 

18. Next enter borehole, start and end depths for the sample. Dielectric permittivity and EC can be left blank.
19. Enter any comments in the comments field. Do not use commas in the comment field

20. 

21. Set the contact probe up to the sample. Then click add scan to collect a spectra

22.

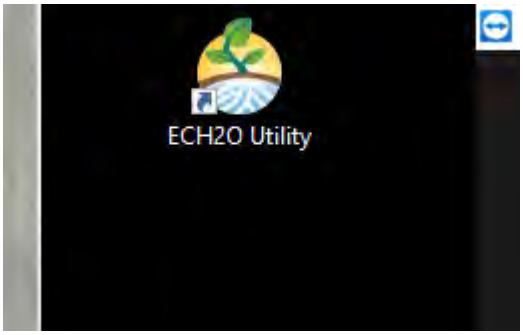
23. 

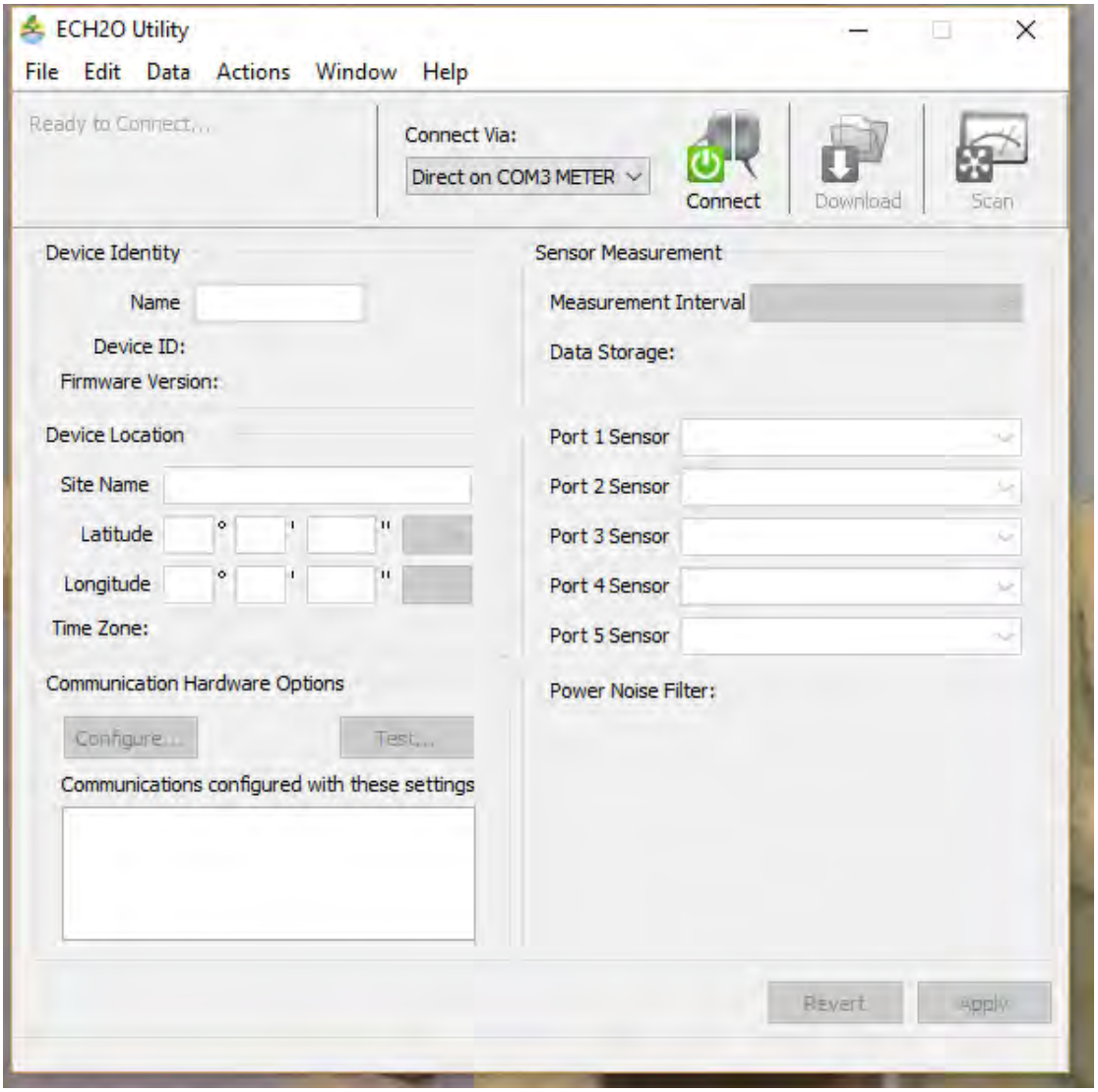
24. The spectra will then be saved and written to the .csv file in the outputs folder

25. Continue collecting spectra

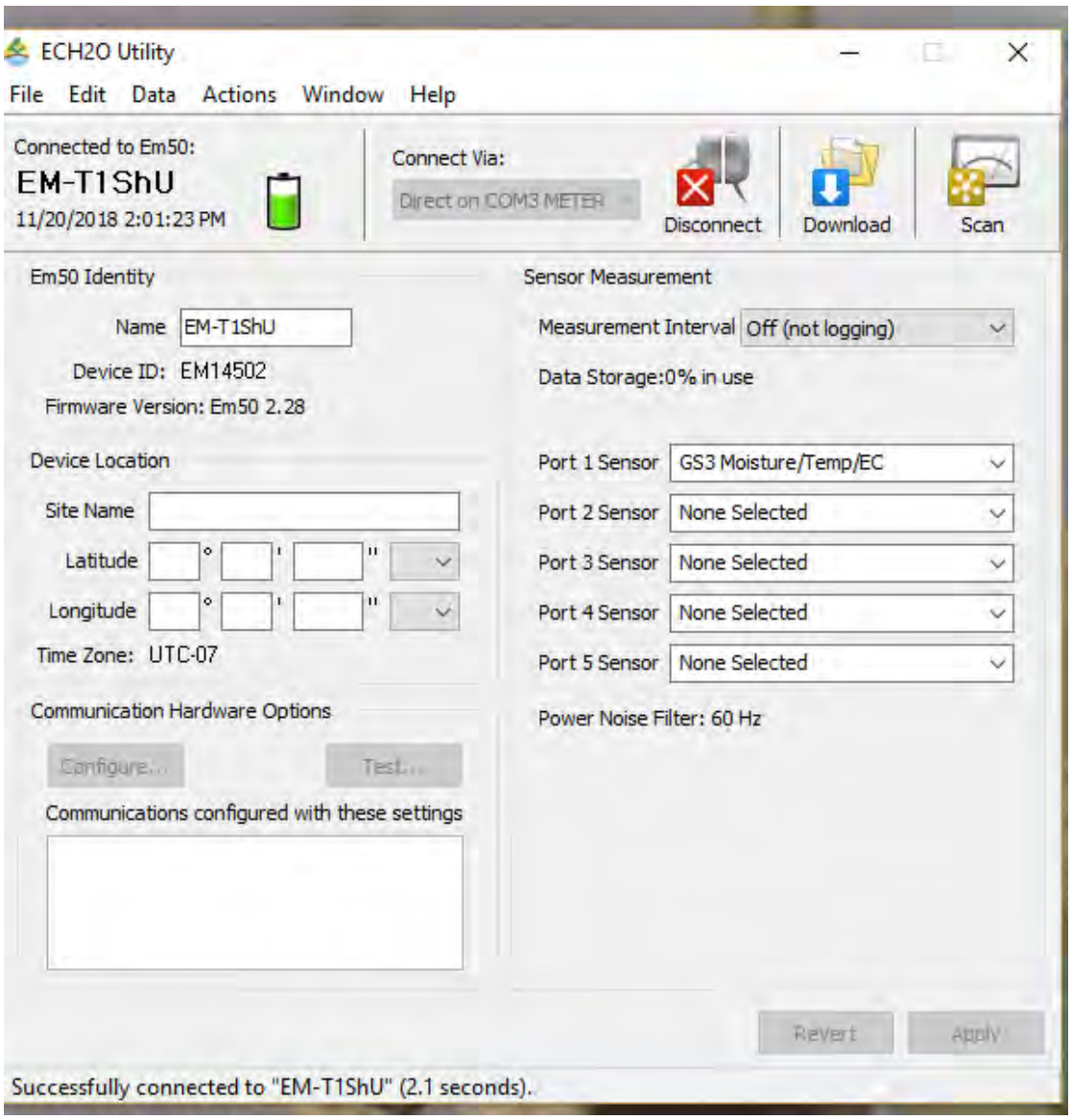
26. Repeat the optimization and reference readings every 30 minutes. After 30 minutes the program will automatically require optimization and reference readings. The user does not need to keep track.

4. EC Probe Data Collection

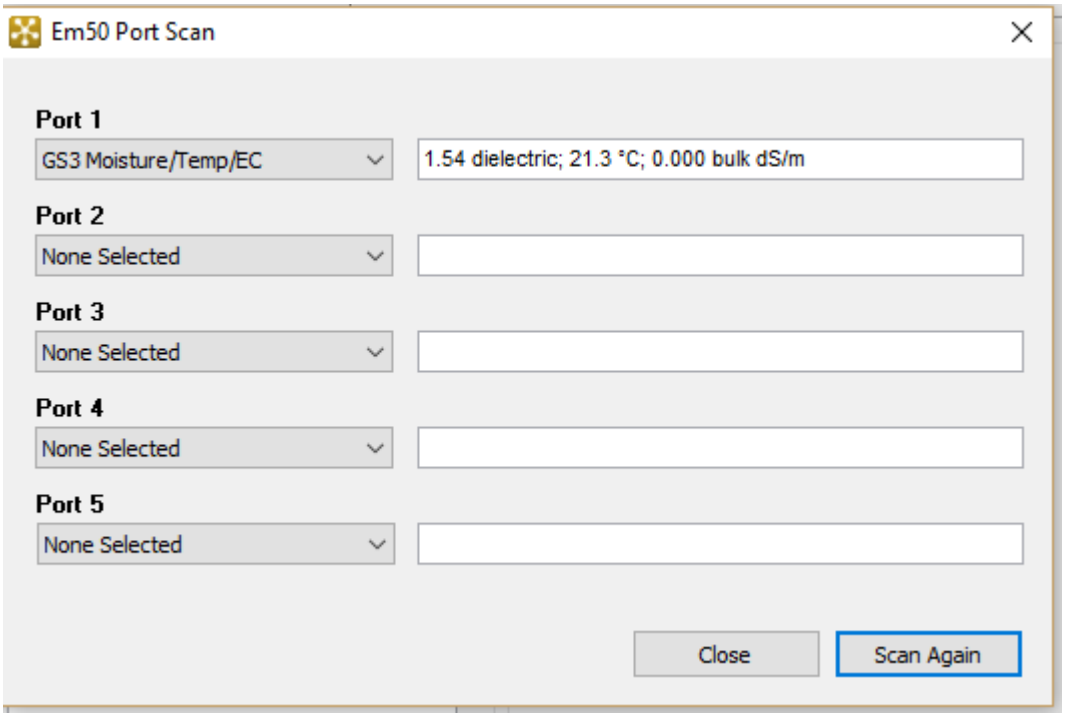
1. Double check that both plugs are firmly in place on the data logger
2. Plug the USB from the data logger into the laptop
3. Open the program ECH20 Utility
4. 

5. The following should appear
6. 

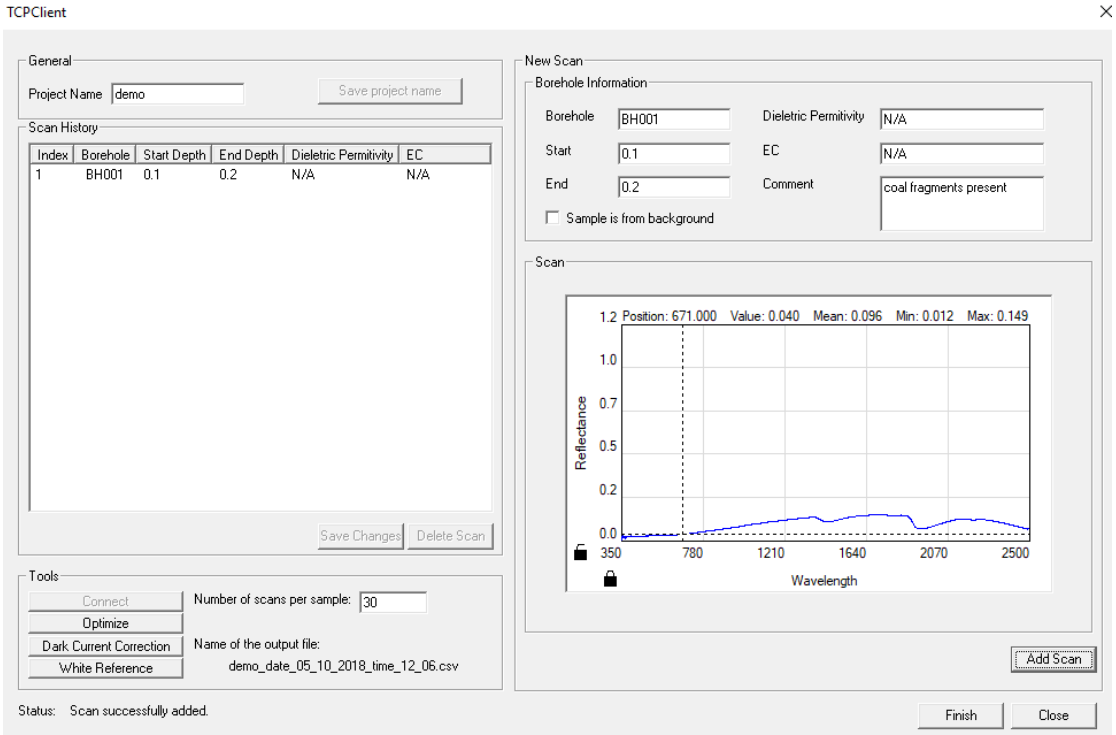
7. Click the connect button with the green power symbol

8. 

9. The above image should appear
10. Click the scan button in the top right corner

11. 

12. The port scan window above will appear.
13. Insert the probe into a soil sample. Make sure the metal probes are completely covered in soil and that the soil is well packed around the probe.
14. Click the scan again button
15. Record the first number in the dielectric permittivity field on the spectrometer software.
16. Record the third number in the EC field

17. 

5. Spectroradiometer Shut Down

1. Close the software and power down the laptop.
2. Turn the power switch on the scanner to the 'Off' position.
3. Disconnect the remote trigger from the contact probe and stow in the storage case.
4. Disconnect the fiber optic cable from the contact probe.
    a. Fully unthread the screw cap on the contact probe to remove the fiber optic cable.
    b. Gently pull the fiber optic cable from the port.
    c. The rubber insert may come away with the cable. Remove the insert from the cable and re-insert it into the port.
    d. Replace the safety cap on the end of the fiber optic probe.
    e. Thread the screw cap back onto the contact probe finger tight.
    f. LOOSELY coil the fiber optic cable (one or two loops) and stow it in the elastic mesh on the side of the scanner.
5. Disconnect the power cable to the contact probe.
    a. Grip the connector NOT the cable. Press the small black button on the connector and gently pull the cable from the contact probe.
    b. PRESS THE RELEASE BUTTON beneath the plugin on the scanner and gently pull the cable from the scanner.
6. Unthread the power cable to the scanner and disconnect the Ethernet cables from the laptop and scanner. Coil the cables and place them in the storage case.
7. Replace the scanner in its case with all cable and accessories.

APPENDIX C: USERS MANUAL - INNOV-X® ANALYZER

INSTRUCTION MANUAL

INNOV-X SYSTEMS
ALPHA SERIES™
X-RAY FLUORESCENCE
SPECTROMETERS

August 2005
Version 2.1

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Woburn, MA 01801

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Technical Specifications
Certificate of Conformity—CE
Innov-X Standard Warranty

Chapter 1 Introduction

1.0 INSPECTING YOUR INNOV-X ANALYZER

Upon receipt:

1. Locate and remove the shipping papers and documentation from under the lid's foam padding.
2. Remove the Innov-X Analyzer and all of the components from the protective carrying case and identify each on the enclosed shipping list.
3. Connect the battery charger to an 110V-240V AC power source. Place one Li-ion battery on the charger and charge it for at least 2 hours. Charge the second battery.
4. Charge the HP iPAQ using the attached AC adaptor for at least ½ hour.
5. Read and review the "Quick Start" section of the User's Manual. Innov-X recommends that you read the entire manual.
6. Install the fully charged battery into the analyzer.
7. Press the ON/OFF button on the back of the analyzer and the power button on the iPAQ.
8. Select Innov-X from the start menu located in the upper left hand corner of iPAQ screen.
9. Select the desired analysis mode (i.e., Analytical, FastID, Pass/Fail or Soil). The instrument will undergo a one minute hardware initialization period.
10. Standardize the instrument with the 316 Stainless Steel mask. Standardize the instrument every 4 hours or as directed by the display.
11. Release the software trigger lock and analyze a sample of known composition, in order to verify the correct operation of the analyzer.
12. Analyze samples of unknown composition.

1.1 COMPONENTS INCLUDED WITH THE ANALYZER

Shown here are the various items which are included with the Innov-X portable XRF analyzer. Unless otherwise noted, all items are standard accessories.

Analyzer, with iPAQ attached.

Two, Li-ion batteries (one shown).

Battery charger and an AC adaptor. Battery shown mounted in charging system.

Standardization cap and weld mask (optional)

The standard standardization cap has no weld slit.

iPAQ cradle and AC adaptor. The cradle is used to connect the iPAQ to a PC for downloading data and reports.

Testing stand. This is the benchtop docking station for the analyzer. It is an optional accessory

1.2 QUICK START INSTRUCTIONS

The following section provides a quick overview to using the Innov-X portable XRF analyzer. This is intended to provide the basic startup and operational instruction needed to perform simple analyses. It is highly recommended that the user read the sections on Radiation Safety (Chapter 3) and the detailed description on operation (Chapter 4). The following Quick Start information is also provided as a separate, bound, laminated publication for quick reference.

1. Place a battery in the analyzer.
2. Power on the Analyzer (On/Off switch located on back of analyzer)
3. Power on the iPAQ (Button located in upper right hand corner of iPAQ)
4. Select Innov-X from the start menu located in the upper left hand corner of iPAQ screen.
5. Read the radiation safety notice and acknowledge that you are a certified user by pressing Start.
6. Select Desired Mode.
7. The analyzer will undergo a 60 second hardware initialization.
8. Place a standardization clip on the nose of the analyzer. Tap the button on the screen to standardize. ***(Manual section 4.4 Standardization)***
9. When standardization is complete, remove the standardization clip.

10. Release the software trigger lock by tapping the locked icon on the iPAQ screen and tapping yes in response to the software prompt.
11. Test standard to verify instrument performance.
12. Results will display on screen. Subsequent tests may be started from either the Results or Analysis screens.

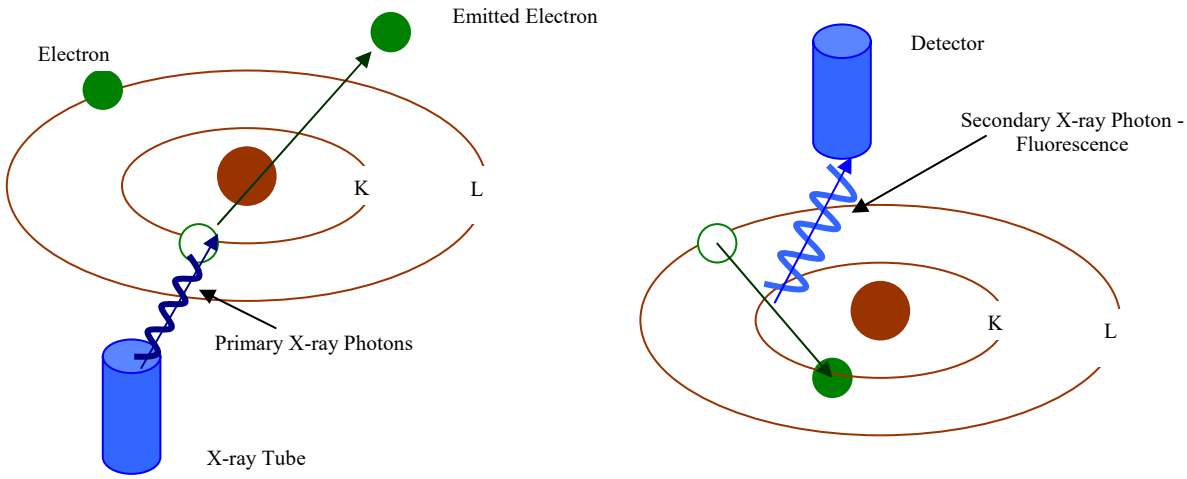
1.3 INTRODUCTION TO XRF: X-RAY FLUORESCENCE SPECTROMETRY OVERVIEW

Basic Theory

Although most commonly known for diagnostic use in the medical field, the use of x-rays forms the basis of many powerful analytical measurement techniques, including X-ray Fluorescence (XRF) Spectrometry.

XRF Spectrometry is used to identify elements in a substance and quantify the amount of those elements present. An element is identified by its characteristic X-ray emission wavelength (λ) or energy (E). The amount of an element present is quantified by measuring the intensity of its characteristic line. XRF Spectrometry ultimately determines the elemental composition of a material.

All atoms have a fixed number of electrons (negatively charged particles) arranged in orbitals around the nucleus. The number of electrons in a given atom is equal to the number of protons (positively charged particles) in the nucleus; and, the number of protons is indicated by the Atomic Number in the Periodic Table of Elements. Each Atomic Number is assigned an elemental name, such as Iron (Fe), with Atomic Number 26. Energy Dispersive (ED) XRF and Wavelength Dispersive (WD) XRF Spectrometry typically utilize activity in the first three electron orbitals, the K, L, and M lines, where K is closest to the nucleus. Each electron orbital corresponds to a specific and different energy level for a given element.



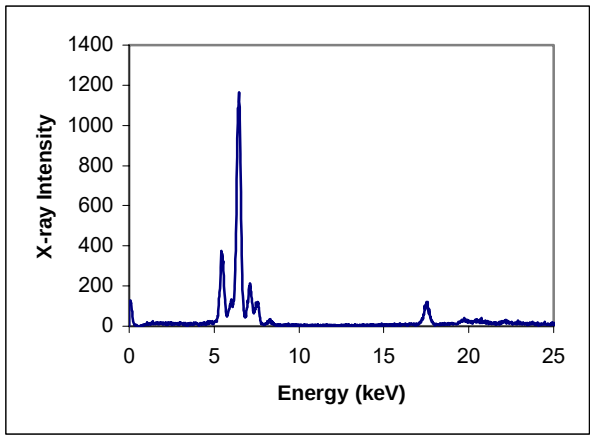
In XRF Spectrometry, high-energy primary X-ray photons are emitted from a source (X-ray tube) and strike the sample. The primary photons from the X-ray tube have enough energy to knock electrons out of the innermost, K or L, orbitals. When this occurs, the atoms become ions, which are unstable. Electrons seek stability; therefore, an electron from an outer orbital, L or M, will move into the newly vacant space at the inner orbital. As the electron from the outer orbital moves into the inner orbital space, it emits an energy known as a secondary X-ray photon. This phenomenon is called fluorescence. The secondary X-ray produced is characteristic of a specific element. The energy (E) of the emitted fluorescent X-ray photon is determined by the difference in energies between the initial and final orbitals of the individual transitions.

This is described by the formula

$$E=hc/\lambda$$

where h is Planck's constant; c is the velocity of light; and λ is the characteristic wavelength of the photon.

Wavelengths are inversely proportional to the energies; they are characteristic for each element. For example the Kα energy for Iron (Fe) is about 6.4keV. The number of element-specific characteristic X-rays produced in a sample over a given period of time, or the intensity, can be measured to determine the quantity of a given element in a sample. Typical spectra for EDXRF Spectrometry appear as a plot of Energy (E) versus the Intensity (I).



History

Wilhelm Roentgen discovered X-rays in 1895. Methods for identifying and quantifying elements using XRF were first published by Henry Moseley in 1913. Much research and development of XRF continued after Moseley's pioneering work, especially during WWII when rapid developments in the aircraft, automotive, steel and other metals industries heightened the need to identify alloys quickly and reliably. However, the first commercial XRF Spectrometers weren't available until the early 1950's. Those systems were based on WDXRF technology and measured the characteristic wavelength of an element, one element at a time. Although the use of these systems was critical for elemental analyses, they were large, expensive, and required highly skilled operators to use and maintain them.

In the late 1960's, EDXRF technology, which measures the characteristic energy of an element, began to rival the use of WDXRF due to the development of Si (Li) solid state detectors, which offered better energy resolution of the signal. EDXRF systems offered the potential of collecting and displaying information on all of the elements in a sample at the same time, as opposed to one at a time with typical WDXRF systems. Many of the early EDXRF systems used radioisotopes for excitation instead of X-ray tubes, which could require changing sources to determine all the elements of interest. Some of those early EDXRF systems did not easily resolve multiple elements in a single analytical run.

As can be imagined, the equipment and applications of XRF Spectrometers have developed tremendously since the 1960's. Advancements in technology, electronics, computers, software and the use and modification of them for XRF Spectrometers by instrument manufacturers, research scientists & engineers, and industrial users alike have led to the current state of the art in XRF Spectrometers. Now a mature technology, XRF Spectrometry is routinely used for R&D, QC and analytical services in support of production.

Elemental Analysis

XRF Spectrometry is the choice of many analysts for elemental analysis when compared to the other techniques available. Wet chemistry instrument techniques for elemental analysis require destructive and time-consuming specimen preparation, often using concentrated acids or other hazardous materials. Not only is the sample destroyed, waste streams are generated during the analytical process that need to be disposed of, many of which are hazardous. These wet chemistry elemental analysis techniques often take twenty minutes to several hours for specimen preparation and analysis time. All of these factors lead to a relatively high cost per sample. However, if PPB and lower elemental concentrations are the primary measurement need, wet chemistry instrument elemental analysis techniques are necessary.

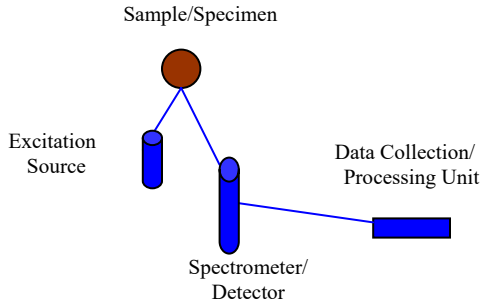
XRF Spectrometry easily and quickly identifies and quantifies elements over a wide dynamic concentration range, from PPM levels up to virtually 100% by weight. XRF Spectrometry does not destroy the sample and requires little, if any, specimen preparation. It has a very fast overall sample turnaround time. These factors lead to a significant reduction in the per sample analytical cost when compared to other elemental analysis techniques.

All elemental analysis techniques experience interferences, both chemical and physical in nature, and must be corrected or compensated for in order to achieve adequate analytical results. Most wet chemistry instrument techniques for elemental analysis suffer from interferences that are corrected for by both extensive and complex specimen preparation techniques, instrumentation advancements, and by mathematical corrections in the system's software. In XRF Spectrometry, the primary interference is from other specific elements in a substance that can influence (matrix effects) the analysis of the element(s) of interest. However, these interferences are well known and documented; and, instrumentation advancements and mathematical corrections in the system's software easily and quickly correct for them. In certain cases, the geometry of the sample can effect XRF analysis, but this is easily compensated for by grinding or polishing the sample, or by pressing a pellet or making glass beads.

Quantitative analysis for XRF Spectrometry is typically performed using Empirical Methods (calibration curves using standards similar in property to the unknown) or Fundamental Parameters (FP). FP is frequently preferred because it allows elemental analysis to be performed with no standards or calibration curves. This enables the analyst to use the system immediately, without having to spend additional time setting up individual calibration curves for the various elements and materials of interest. The capabilities of modern computers allow the use of this no-standard mathematical analysis, FP, accompanied by stored libraries of known materials, to determine not only the elemental composition of an unknown material quickly and easily, but even to identify the unknown material itself.

EDXRF Spectrometers

EDXRF Spectrometer systems are mechanically very simple; essentially there are no moving parts. An EDXRF system typically has three major components: an excitation source, a spectrometer/detector, and a data collection/processing unit. The ease of use, rapid analysis time, lower initial purchase price and substantially lower long-term maintenance costs of EDXRF Spectrometers have led to having more systems in use today worldwide than WDXRF Spectrometer systems.



EDXRF has been found most useful for scrap alloy sorting, forensic science, environmental analysis, archaeometry and a myriad of other elemental field-oriented analyses.

Handheld EDXRF Spectrometers for Field Analyses

It is clear that a future trend for elemental analysis is in rapid site investigation using techniques that are fast, inexpensive, reliable, and long-term cost effective. There is a need for immediate decisions to be made during the delivery of materials, industrial processing, and in the field for positive materials identification or environmental site assessment and remediation. It is also clear that EDXRF Spectrometry is the most suitable elemental analysis technique available for field analysis due to its simplicity, speed, precision, accuracy, reliability, and overall cost effectiveness.

Recent technological developments in cell phones, pocket PC's and other portable consumer electronics have led to the advancement of many high-performance, miniature components. X-ray equipment manufacturers began to take advantage of these developments in the late 1990's and developed Handheld EDXRF systems. An obvious advantage of Handheld EDXRF systems is that the analyzer is taken to the sample as opposed to bringing the sample to the analyzer and configuring it to fit in an analysis chamber. In addition to the per sample analytical cost savings, a key factor in using non-destructive EDXRF analysis, especially in the field, is the overall project cost savings due to improved and more timely decision making. The use of EDXRF for immediate positive materials identification or to guide an environmental site characterization will generally reduce the overall time required in the field due to the quick turnaround for the sample analysis; this invariably reduces the overall costs of analytical field work.

Of course, Handheld EDXRF technology has continued to evolve in concert with portable consumer electronic developments. Just like the early Benchtop EDXRF systems, early Handheld EDXRF systems used radioisotopes for excitation. There are several practical problems with the use of radioactive isotopes for handheld systems. The source decays and loses its testing speed over time. In addition to the loss in analytical capabilities, the sources have to be replaced incurring a cost. The use of radioactive isotopes also requires licensing (state-to-state in the US) and a radioactive materials control program; they are difficult to ship and transport, as they require hazardous materials declarations and/or permits. Consequently, the newest and most exciting development in Handheld EDXRF technology is the use of battery operated, miniature X-ray tubes, which was pioneered by the staff at Innov-X Systems.

Innov-X Systems Handheld EDXRF Spectrometers

Innov-X Systems specializes in Handheld EDXRF technology with the most advanced miniature components available for X-ray Tube sources, detectors, and PC 's. Innov-X Systems Handheld EDXRF Spectrometers are ideally suited for field analysis of alloys, lead-based paint, environmental soils, filters, dust wipes, forensics, archaeometry, and a variety of other elemental analyses in the field or around the plant. Innov-X Systems EDXRF Spectrometers are affordable, easy to use, reliable, and overall cost effective. The Innov-X Systems Handheld EDXRF units incorporate state-of the art components including a battery operated miniature X-ray tube, a high-resolution silicon pin detector, high speed data acquisition circuitry, and a Compaq IPAQ Pocket PC® handheld computer for calculations, results and operator interface.

Innov-X Systems EDXRF Spectrometers offer the following invaluable features:

- Portable
- Battery operated, rechargeable
- X-ray Tube-based (Ag or W anode, 10-40kV, 10-100uA)
- Si PiN diode detector.
- Integrated pocket PC
- Pistol-shaped design for difficult testing locations and welds
- Auto-compensation for irregular or small samples
- Fundamental Parameters for no-standard analyses
- Stored Grade Libraries for rapid Grade ID's
- Stored Fingerprint Libraries for rapid material ID's

- Docking station available for use as standard benchtop unit
- Results shown after a few seconds of testing time.

For more information on how to utilize your Innov-X Systems Handheld EDXRF Spectrometer optimally, please review this Instruction Manual or contact us directly.

Chapter 2. Usage and Assembly of Accessories

2.0 ACCESSORIES

This chapter describes the various accessories that are provided with an Innov-X XRF analysis system. Included are:

- Batteries
- Battery Charger
- iPAQ cradle and charger
- Testing Stand Assembly (not standard with all units)
- Standardization Clip or Standardization Clip/Welding mask.

2.1 ANALYZER BATTERY

The Innov-X Systems XRF Analyzer is powered by a replaceable, rechargeable Lithium ion battery. In addition, the iPAQ has its own internal battery.

Innov-X Systems Main Battery

The Innov-X Analyzer uses a rechargeable Lithium Ion Smart Battery. A picture of the battery is shown in Fig. 2.1. Two batteries are included with each analyzer. The batteries are charged an external battery charger. Batteries typically function for 4 to 8 hours, depending on usage patterns. Heavier duty cycles deplete the battery more quickly. Therefore, users who do longer and more frequent tests will need to replace their batteries more often than users who take shorter or fewer tests.

Figure 2.1. Li-ion Battery for analyzer

Replacement batteries can be purchased directly by calling Innov-X Systems at 781-938-5005. (P/N A003)

Battery power indicators:

There are two ways of determining the charge remaining on a battery: the LED indicator on the battery and the battery status icon on the analyzer screen. The battery icon, when tapped, will indicate the percent charge remaining on a battery inside the analyzer. Additionally, the battery icon will change from green to yellow when the battery gets low, indicating it has about 15 minutes left of charge.

To use the battery LED, push the button below the indicator. The lighting will indicate the % of charge. If possible, try to use batteries with at least 50% of their full charge, according to the indicator.

2.2 CHANGING A BATTERY

To change a battery, perform the following steps:

1. Hold the instrument by the handle, upside down, so the bottom of the instrument base is pointing upward. Please refer to Fig. 2.2.
2. Hold the instrument so that the nose is pointing away from the operator.
3. Open the battery door on the bottom of the handle. The batteries have a small tab attached for ease of removal.

4. Pull out the existing battery, and replace with a new battery.
5. Insert the charged battery into the analyzer such that the connectors on the top of the battery are facing to the right. Note that the battery slot is keyed so that the battery can only be inserted one way.

Figure 2.2a. Instrument handle. Pull the rubber latch and lift door. Reach into opening and remove battery.

Figure 2.2b Insert new battery into opening.

2.3 BATTERY CHARGER

The battery charger is shown in Fig. 2.3. It takes about 2 hours to completely charge a battery. The status of the charger is shown by two lights on the power adaptor. Table 2.1 lists the information conveyed by the lights.

Figure 2.3. Battery charger.

Left Light	Right light	Status
On	Off	Battery is charging
On	On	Battery is 80% charged
Off	On	Battery is completely charged
Blink	Blink	Error. Remove battery and replace on charger. If error persists, call Innov-X Systems Technical support.
Off	Off	No battery is on charger

Table 2.1 Battery charger status lights

2.4 HP IPAQ POCKET PC BATTERY

The iPAQ has an internal rechargeable battery, which can be recharged by using the power adaptor that is included with the unit. This adaptor can be connected either to the iPAQ itself, or to the cradle. If it is connected to the cradle, and plugged in, the iPAQ will recharge whenever it is placed in the cradle. In addition, the iPAQ Battery will recharge whenever the iPAQ is mounted in an Innov-X analyzer which is powered, but not actively taking a test. The amber light on the top of the iPAQ will blink whenever the battery is charging. It will remain solid when the battery is completely charged.

Since the iPAQ will be recharged whenever the Innov-X Systems Analyzer is in use, it may never be necessary to use the iPAQ power adaptor. However, care should be taken when the analyzer is not used for a period of several days, as the iPAQ uses some power even when it is powered off. It is therefore possible to completely discharge the battery simply by not using the iPAQ for several days, or by using it for several hours without recharging it.

If you do not use your Innov-X Analyzer on a daily basis, or if you will have a down period of more than several days, it is recommended that you remove the iPAQ from the Analyzer when it is not in use and plug in the iPAQ to a power outlet to recharge it. This will ensure that your iPAQ is always charged and ready for use. You should also always plug in the power cord whenever the iPAQ is removed from the analyzer for data transfer.

If you do allow the iPAQ battery to discharge significantly, either by allowing it to sit too long unused, or by using it for a period of time without it being connected to a power source, it may not be possible to operate your analyzer. If this happens, the Innov-X software will provide an error message indicating that the iPAQ battery is too low. Recharge the iPAQ for at least a half an hour before attempting another measurement.

If the iPAQ battery is completely discharged, it will not be possible to turn on the iPAQ until it is recharged. A complete power failure will erase anything that is stored in the Main Memory of the iPAQ. All Innov-X program and data files are stored on the storage card, rather than in Main Memory, so you will not lose any data or have to reinstall the Innov-X software.

1. If the battery on the iPAQ is completely discharged, charge it for at least one half hour.
2. You will be required to follow the prompts on the iPAQ screen before you can use the iPAQ. This procedure involves realigning the screen by tapping in several spots, and going through a quick tutorial.
3. The iPAQ will reinitialize the Innov-X Systems software. A message will appear indicating that this is going to happen. You must tap ok to initialize.
4. The software will open automatically; a message will appear indicating that several registries have been restored. Tap ok to dismiss this message.
5. Set the clock to the current time. **Note, this is very important,** as your data is indexed by date. If the date in the iPAQ is incorrect, you may not be able to locate your results. The instrument will not allow you to take a reading until the date has been changed.
    a. From the Start Menu, tap Settings.
    b. Select the System tab, and tap clock.
    c. Set the proper date. Further details about this procedure can be found in the HP iPAQ user's manual.

2.5 REMOVING THE IPAQ FROM THE ANALYZER

It is very important to properly remove the iPAQ Pocket PC from the analyzer to avoid damaging the connector on the back of the iPAQ.

In order to remove the iPAQ, push the iPAQ retainer shown in Fig. 2.4 towards the front of the analyzer. Holding the retainer forward, grab the iPAQ from the sides, slide the iPAQ forward until it is clear of its

connector, then tilt the front end up enough so it clears the front holder allowing the iPAQ to be lifted out of the instrument.

Note: Never grab the iPAQ and twist it side-to-side to remove it from the analyzer. Always move the iPAQ retainer forward as instructed above, slide the iPAQ forward and remove from the analyzer.

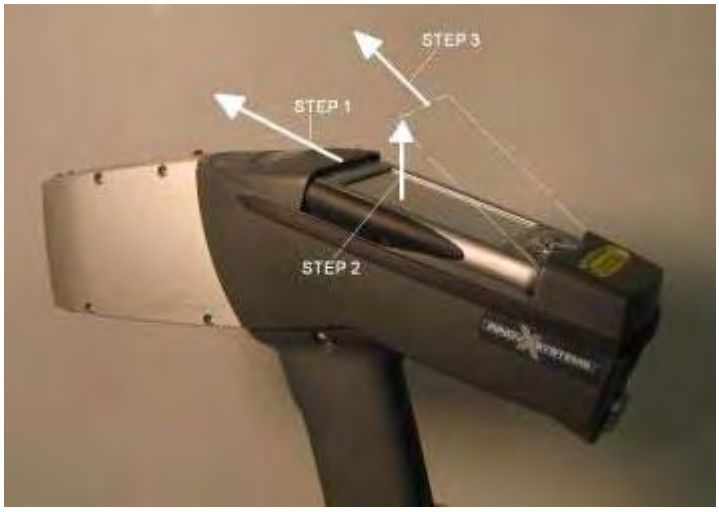


Figure 2.4. Removing the iPAQ from the analyzer.

2.6 STANDARDIZATION CAP and/or WELD TESTING MASK

All analyzers are supplied with either a standardization cap or a combination standardization cap welding mask. The standardization mask is the standard accessory. Welding masks can be purchased as an additional accessory, or in lieu of the standardization mask.

Standardization Cap

The cap clips on the front end of the analyzer and is used to standardize the system as described in Chapter 4. To attach the cap, snap it onto the nose of the analyzer over the Kapton window.

Combination Standardization Cap/Welding Mask

The standardization/welding mask is shown in Fig. 2.5. The cap clips onto the front end of the analyzer and is used to standardize the system as described in Chapter 4. To attach the cap, snap it onto the nose of the analyzer over the Kapton window. Be sure that when attaching the cap, that the solid end (as opposed to the end with the ¼" wide slit) is covering the window. To remove the mask, slide it off to either side.

The opposite end of the standardization cap serves as a welding mask. This mask is used to shield the base metal from analysis, when analyzing a weld. It is important to use this mask since failure to do so will produce an alloy chemistry that is a mixture of the base metal and the actual weld. For best results:

a. Use the welding mask only for welds that are larger than the opening in the mask;
b. Make solid contact between the surface of the mask and the material to test;
c. Use the mask only in the Analytical Mode – not with the standard Fast ID library;
d. Consider using longer test periods to compensate for the smaller testing area – especially with more difficult separations.

If it is desirable to use the welding mask in FastID mode, a user can create a special "Welding Mask Library." Teach all relevant alloys with the welding mask is in position. Make sure these fingerprints are

saved in library that contains ONLY fingerprints taught with a welding mask. When measuring a weld, make sure the "Weld" library is the only one selected. By creating a special finger print library using the welding mask, a user can get good results in the Fast ID Mode as well.

Figure 2.5 Standardization cap and welding mask. (Optional accessory)
The standard standardization cap does not have the welding slit.

2.7 TESTING STAND (optional accessory)

The testing stand is designed as a docking station for the handheld analyzer. It can be used as a bench-top system, or to test small samples. A list of components and an assembled stand is shown in Figure 2.6:

Figure 2.6. Assembled Testing Stand

Components of the testing stand:

1 Three (3) short legs
2. Three (3) long legs
3. Lower Stand
4. Upper Stand
5. Four (4) knobs for top plate
6. Test stand cradle
7. Clip for cradle.
8. Adaptor cable (connects serial connector on iPAQ cradle to auxiliary port on analyzer)

Assembly of Testing Stand

1. Insert the three Short Legs through the holes in the Lower Stand by inserting the threaded screw through the holes. This will balance the Lower Stand on the table top. (Fig. 2.7).

Figure 2.7. Mounting Lower Stand onto Short Legs.

2. Mount the three Long Legs onto the Lower Stand by inserting the threaded screws from the Short Legs into the holes on the Long Legs and turning until snug. Remove iPAQ from analyzer by following the instructions in Figure 2.4. Place the analyzer into the gap in the Lower Stand as shown. (Fig. 2.8).

Figure 2.8. Mounting Long Legs onto Lower Stand and inserting analyzer.

3. Mount the Upper Stand onto the Long Legs. The Upper Stand has holes for the screws at the end of each of the Long Legs. The Upper Stand will also fit snugly over the front end of the analyzer. Be sure that the Upper Stand is mounted so that all three screws are inserted through the holes, and the front end of the analyzer is flush with the top surface of the upper stand. (Fig. 2.9).

Figure 2.9. Mounting Upper Stand onto Testing Stand.

5. Put three knobs to secure testing stand onto analyzer. The iPAQ clip can be secured with any of the knobs. This clip grabs the base of the iPAQ cradle to hold the iPAQ securely in place.

6. Place the iPAQ in the cradle and connect it to the Auxiliary Port on the analyzer using the serial cable adaptor.

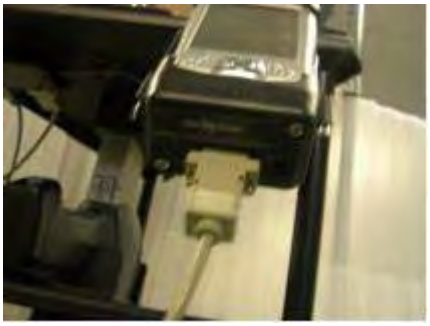


Figure 2.10. Connecting iPAQ to Auxiliary Port on analyzer.

Chapter 3 Safety Information

3.0 IMPORTANT SAFETY INFORMATION

THE XRF SHOULD NOT BE POINTED AT ANYONE OR ANY BODY PART, ENERGIZED OR DE-ENERGIZED! The safe and proper operation of the Innov-X XRF instruments is the highest priority. These instruments produce ionizing radiation and should **ONLY** be operated by individuals, who have been trained by Innov-X Systems, Inc. and received a manufacturer's training certificate. Innov-X recommends that operators and companies implement a written Radiation Safety Program, with safety components specific to the site and application of use of the instrument. The Radiation Safety Program should be reviewed annually and revised appropriately by a competent individual.

Innov-X analyzers must be used by trained operators, according to the instructions presented in this manual. Improper usage may circumvent safety protections and could potentially cause harm to the user. Pay attention to all warning labels and messages.

Important Notice for all Canadian Users:

Canadian Federal Regulations (Radiation Emitting Devices Act) require that all Canadian users must be certified according to NRC Standard CAN/CGSB-48.97/2-2000 in order to use this device.

For this certification contact: Natural Resources Canada, Manager Nondestructive Testing Certification, CANMET, 568 Booth St., Ottawa, ON, K1A 0G1; Tele: (613) 943-0583; Fax(613) 943-8297.

Users are advised to contact their appropriate federal/provincial./territorial radiation protection agency for applicable rules of operation.

The Innov-X analyzer is a very safe instrument when used according to manufacturer's recommended safety procedures as detailed in this chapter.

Radiation levels during testing are < 0.1 mR/hr on all surfaces of the analyzer except at or near the exit port for the radiation. This means that if an operator follows standard operating procedures, they will not obtain any detectable radiation dose above naturally occurring background radiation, on their hand while holding the analyzer, or on any area of their body.

This chapter details specifics of the radiation levels. It covers both standard (safe) and un-safe methods of operation, it provides radiation emission information, and also provides dose estimates for unsafe operations.

3.1 GENERAL SAFETY PRECAUTIONS AND INFORMATION:

Retain and follow all product safety and operating instructions. Observe all warnings on the product and in the operating instructions. To reduce the risk of bodily injury, electric shock, fire and damage to the equipment, observe the following precautions:

Heed service markings. Except as explained in this documentation, do not service any Innov-X product yourself. Opening or removing covers may expose you to electric shock. Service needed on components inside these compartments should be done only by Innov-X Systems, INC.

Damage requiring service:

- The power cord, plug or battery contacts for the battery charger are damaged.

- Liquid has been spilled or an object has fallen onto the instrument.
- The instrument has been exposed to rain or water.
- The instrument has been dropped or damaged.
- There are noticeable signs of overheating.
- The instrument does not operate normally when you follow operating instructions.

Safety Precautions:

Use the correct external power source: Ensure that the voltage is appropriate (100V-240 V/ 50-60 Hz) for charging the battery packs. Do not overload an electrical outlet, power strip, or convenience receptacle. The overall load should not exceed 80% of the branch circuit rating.

Use cables and power cords properly:
Plug the battery charger into a grounded electrical outlet that is easily accessible at all times. Do not pull on cords and cables. When unplugging the cord form the electrical outlet, grasp and pull the cord by the plug.

Handle battery packs properly; do not: disassemble, crush, puncture, short external contacts, dispose of in fire or water, or expose a battery pack to temperatures higher than 60 ^{o}C (140 ^{o}F).Do not attempt to open or service a battery pack.

WARNING: Danger of explosion if battery is incorrectly substituted. Replace only with Innov-X specified batteries. Used batteries may be returned to Innov-X Systems for disposal.

3.2 INNOV-X SYSTEMS – RECOMMENDED RADIATION SAFETY TRAINING COMPONENTS

Individual Companies and States have specific regulations and guidelines for the use of X-ray tube generated ionizing radiation. The purpose of the recommendations below is to provide generic guidance for an ALARA - best practice - approach to radiation safety. These recommendations do not replace the requirement to understand and comply with the specific policies of any state or organization.

1. **Proper Usage.** Never point the instrument at another person. Never point the instrument into the air and perform a test. Never hold a sample in your hand and test that part of the sample.
2. **Establish Controlled Areas.** The location of storage and use should be of restricted access to limit potential exposure to ionizing radiation. In use, the target should not be hand held and the area at least three paces beyond the target should be unoccupied.
3. **Specific Controls.** The instrument should be stored, in a locked case, or locked cabinets when not in use. When in use, it must remain in the direct control of a factory trained, certified operator.
4. **Time - Distance - Shielding Policies**. Operators should minimize the time around the energized instrument, maximize the distance from the instrument window, and shoot into high density materials whenever possible. Under no circumstances should the operator point the instrument at themselves or others.
5. **Prevent Exposure to Ionizing Radiation**. - All reasonable measures, including labeling, operator training and certification, and the concepts of time, distance, & shielding, should be implemented to limit radiation exposure to ***as low as reasonably achievable*** (ALARA).
6. **Personal Monitoring.** Radiation control regulations may require implementation of a radiation monitoring program, where each instrument operator wears a film badge or TLD detector for an initial period of 1 year to establish a baseline exposure record. Continuing radiation monitoring after this

period is recommended, but may be discontinued if accepted by radiation control regulators. Please refer to Sect. 3.10 for a list of providers of film badges.

3.3 INNOV-X SAFETY FEATURES

The Innov-X analyzer is very safe when used correctly, however the analyzer does emit radiation through the analyzer window, and all precautions must be taken to reduce exposure to this radiation. In order to minimize the possibility of accidental exposure, the following safety features are standard in all Innov-X analyzers.

1. "Deadman" trigger. The trigger must be held for the duration of the test. This requires that the user consciously depress the trigger whenever x-rays are emitted, and ensures that the analyzer is attended at all times while x-rays are emitted.

   Upon completion of safety training, an INNOV-X certified trainer may deactivate this feature upon request. The deactivation of the trigger is recommended only if long tests are required (such as for soil mode) and if the unit is used primarily by only 1 or 2 users who utilize it frequently, in a very controlled environment. In situations where multiple users are sharing the unit, it is recommended that the deadman trigger remain active.

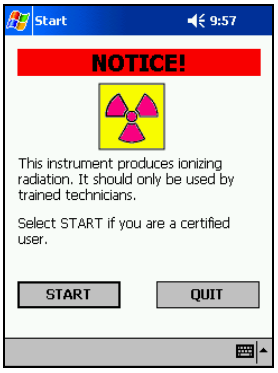
   Note: Canadian Regulations <u>require</u> that the deadman trigger be used at all times. This feature will not be disabled for usage in Canada.

2. Software Trigger lock. Before using the trigger, the user must tap on a lock icon located in the lower right hand corner of the iPAQ screen. The user must then confirm that they wish to unlock the trigger. If the instrument is used continuously, the software trigger lock will remain off. If five minutes elapse between tests, the trigger will lock automatically.

3. Software Proximity sensor. The software requires that a sample be present in front of the analyzing window. This prevents the accidental exposure of bystanders to an open beam. If the analyzer detects that a sample is not present, it will abort the test and shut off x-rays two seconds after the test is started.

3.4 PERFORMING A TEST FOLLOWING APPROPRIATE RADIATION SAFETY PROCEDURES

Starting the Analyzer:



When an operator opens the Innov-X software on the iPAQ, he or she will be presented with one of the displays shown to the right. Provided an operator has received training from an authorized Innov-X trainer, he/she should tap the START button to begin using the analyzer.

In Canada, INNOV-X ANALYZERS MUST BE OPERATED BY CERTIFIED USERS ONLY!

From this point the operator is presented with the main menu of the analyzer to choose an operating mode and begin testing (described in Chapter 4). The remainder of this section is dedicated to operational and safety aspects that pertain to safe use and storage of the analyzer.

Starting a test using the trigger.

When the trigger is depressed, the analyzer supplies power to the x-ray tube and opens the shutter to emit x-rays.

If deadman trigger is enabled, the trigger must be depressed for the duration of the test. Releasing the trigger will close the shutter and immediately end the test. If deadman trigger is disabled, pulling the trigger once will start a test, pulling it again will stop it.

Figure 3.1 Handle of analyzer. Trigger is located at top of handle.

Starting a Test Using the "Start" Icon on the iPAQ Screen

This feature is disabled in all units shipped. It will become active only if the "deadman" trigger is disabled.

An operator may also begin a test by pressing the **Start** button on the touch screen, as shown at the right. The **Start** button, rather than the trigger, is generally used when the analyzer is docked into the testing stand.

This Feature is not available in Canada. All tests must be started via the trigger.

3.5 CORRECT AND INCORRECT INSTRUMENT USAGE:

The Innov-X XRF analyzer can be used in several different testing configurations. Safety guidelines are described for each configuration.

Configuration 1: Usage as a Handheld Alloy Analyzer:

In this configuration the analyzer is held in the hand, placed on various types of samples and a test is performed. Samples include pipes, valves, large pieces of scrap metal, basically any sample large enough to be tested in place, rather than held in the operator's hand. Point the instrument at a metal sample such that no part of your body including hands and/or fingers is near the aperture of the analyzer where x-rays are emitted.

Using the analyzer in this manner assures that the operator will not obtain a radiation dose to any body part or extremity in excess of naturally occurring background radiation. The radiation at any surface of the analyzer is < 0.1 mR/hr except at the exit port and the immediate area around the exit port.

The user should take care that personnel are not located within 3' (1 m) of the front end of the analyzer during testing, in the direction of the x-ray beam. Provided the analysis window is completely covered, there is virtually no radiation being emitted around the area of the sample. However, if a small component or curved surface is being analyzed, some radiation will be detectable.

Configuration 2: Usage in the Testing Stand

Innov-X strongly recommends that testing small pieces or small samples (rod, fasteners, turnings, XRF sample cups, bagged samples, etc.) be analyzed using the Innov-X Testing Stand. This allows the sample to be placed onto the analysis window of the analyzer without requiring the sample to be held by the operator. See figure below titled "Testing Stand Operation."

Note for Canadian Usage: The testing stand is not available for use in Canada at this time because it has not received regulatory approval yet. When an interlocked version of the testing stand has received regulatory approval, it will be available for sale into Canada. Please contact Innov-X Systems for an update on this process at 781-938-5005.

Figure 3.2 Testing Stand Operation. Please refer to **Section 2.7: Testing Stand** for assembly instructions.

Warning: Innov-X strongly recommends that operators do NOT hold samples in their hand for testing. Never hold a small sample in your hand, and test that sample, such that your hand is exposed to the x-ray beam being emitted from the analyzer. This type of testing produces a small but non-negligible radiation dose to the operator's hand. Please see **Section 3.7: Radiation Doses for Several Scenarios** for dose levels. Also, see **Figure 3.4** for an example of incorrect usage.

Figure 3.2.

Testing of Small Components:

Operators often are required to test small components, particularly in the field of alloy analysis. Examples of small samples include turnings, weld rod, wires, fasteners, nuts and/or bolts.

There are specific procedures to test small components. These procedures should be followed at all times. **Never hold a small part with your fingers or in the palm of your hand and perform a test. Doing so may deliver a significant dose of radiation to your fingers or hand.** Please refer to the Examples of Mis-use below.

Method 1: Testing a sample lying on a flat surface.

Figures 3.2.: Performing a testing for a sample lying on the surface of a table. This is a good way to test small samples, rather than holding them in your hand.

To analyzer small sample:

- Place the sample onto a flat surface.
- Place the window of the analyzer onto the sample and begin the test.

Safety Precautions:

Do not test samples in this manner at a desk or table where the operator is sitting. If the desk is made of wood or another non-metallic material, some radiation will penetrate the desk and may provide exposure to legs or feet if the operator is sitting at the desk or table.

Analytical Precautions:

If the sample does not completely cover the window, be sure the surface used does not contain metals or even trace levels of metals, as this may affect the accuracy of the XRF result. The XRF may report the presence of additional metals in the surface material. For this type of testing, it is good to place the sample onto a piece of 1100series aluminum alloy and perform the analysis. The operator should disable the aluminum analysis capability (See Section 8.3.3 in the manual for instructions).

Method 2: Use the testing stand as described above (see also Fig. 3.2).

Examples of Incorrect and Possible Unsafe Operation:

Improper Operation, DO NOT TEST SAMPLES LIKE THIS:

Exposure to the operator's hand/fingers will likely be minimal for this type of a testing, because the operator's hands and fingers are not in the primary beam. However, Innov-X believes that this type of the analyzer sets a poor safety precedent in that any operation where the operator places their fingers or hands near the window should not be permitted.

Figure 3.3. Incorrect Usage. While the dose to the operator's fingers/hand is negligible, testing this way sets a poor safety example for other operators, possibly encouraging other unsafe usage. Innov-X strongly recommends against this type of testing.

DO NOT TEST SAMPLES LIKE THIS:
Never hold a sample in your hand such that any part of your body or appendages are exposed to the x-ray beam. Testing samples in this way may generate significant radiation exposure (up to 27 R/hr) to the operator's fingers.

Figure 4.4 Extreme example of incorrect usage. An operator should NEVER hold small samples by hand

3.6 RADIATION WARNING LIGHTS AND LABELING:

3.6.1 Main Power switch and Indicator Light:

The main power switch is found on the rear of the unit and is shown in the figure to the left. Pressing the switch for several seconds will turn on the main power. A green LED indicates the main power is on. The main power must be turned on in order to operate the unit however, this switch DOES NOT turn on the x-ray tube. No power will be supplied to the x-ray tube unit the Innov-X software is started.

3.6.2 Probe Light and Probe Label:

The Innov-X analyzer is equipped with warning lights that alert the operator when the tube is receiving power, and when x-rays are being emitted from the analyzer. Please see Fig. 3.5.

When the red light on the front nose of the analyzer is ON continuously (not blinking), this indicates the x-ray tube is receiving a low level of electrical power and the shutter is closed. The system is producing a low level of x-rays internally in this condition, but the shutter is providing adequate shielding to keep x-ray levels below levels of detection. The instrument is safe to be carried around or set down in this configuration.

When the red light is blinking, this indicates the tube is powered, the shutter is open and the analyzer is emitting x-ray radiation out of the analysis window. The analyzer should only be pointed at a sample, or be in the testing stand with a sample resting on the window, in this configuration.

3.6.3 Display on Back of Analyzer:

The display on the back of the analyzer, shown in Fig. 3.6, provides a "testing" message to indicate that the x-ray tube is energized and the shutter is open. This display is for testing conditions (i.e. overhead) where the operator cannot see the Probe Light or the iPAQ display.

3.6.4 Label Behind iPAQ:

The analyzer also has a label just below the iPAQ indicating, as shown in Figure 3.7:

CAUTION: Radiation. This Equipment Produces Radiation When Energized.

This label is required by most regulatory agencies. The term "When Energized" refers to the condition where the tube is fully energized and the shutter is open. This condition is also indicated by the red blinking light on the probe.

Figure 3.5. Probe light and labeling. When the light is on continuously, the x-ray tube is receiving minimal power and it is producing a minimum level of x-rays. The shutter is also closed so there is no radiation exposure to the operator or bystanders.

Figure 3.6. Back light on analyzer.

Figure 3.7. Label behind iPAQ. Top version is used in Canada

3.7 RADIATION LEVELS FROM ANALYZER

Two pictures of the analyzer are shown below. In the first picture, all the relevant components referenced in this radiation safety section are displayed and labeled. The second picture shows a close-up of the front end of the window. The four sides A, B, C and D are indicated on this picture because they are referenced in terms of radiation levels output by the analyzer. The measured radiation levels for standard operating conditions are shown in the figures and tables below. Standard operating conditions are tube voltage operating at 35 kV, tube current of 5 uA, and 2 mm aluminum filtration.

Figure 3.8 Innov-X Analyzer, Side View

Figure 3.9 Innov-X Analyzer, Front View

Radiation Levels (mrem/hr) for Alloy Analysis, Standard Beam Conditions: 35kV, 5 uA, 2mm aluminum filtering:

Sample at Window	Trigger	Location A (Top)	Location B (Right Side)	Location C (Bottom)	Location D (Left Side)
Blank (Air)	<0.1	<0.1	<0.1	<0.1	<0.1
Metal	<0.1	<0.1	<0.1	<0.1	<0.1

Table 3.1. Dose rates (units of mrem/hr) at various locations with a metal sample covering the window and with no sample present. For "no sample" the analyzer is shooting the x-ray beam into air.

As shown in the Table 3-1, the dose to the operator's hand is negligible. The radiation levels at the side surfaces of the instrument snout (aluminum housing) are all <0.1 mrem/hour. Despite these low levels of radiation, there is no reason for any body part to be in the locations denoted A, B, C and D!

Table 3-2 shows the radiation levels directly in the x-ray beam that is emitted from the analyzer. Radiation levels at the exit aperture (or "port") are substantial. There is no reason for the operator or any personnel to be exposed by the direct beam. Operators should never hold samples in their fingers or cupped in their hands, as this may generate a significant radiation exposure.

Operations should never point the analyzer at another person and start a test, as this may also provide significant exposure to the person if they are within a few inches of the port of the instrument.

Radiation Levels in the Primary Beam Versus Distance from Port:
For Alloy Analysis, Standard Beam Conditions: 35kV, 5 uA, 2mm aluminum filtering:

Tube Conditions	At Trigger, or any part of operator's body.	At Window	4 inches	12 inches	36 inches	48 inches
35 kV, 5 uA, 2 mm Al filtering	<0.05	28,160	2,080	186	24	14
15 kV, 25 uA, thinner filter material	< 0.05	27,780	1,620	145	19	11

Table 3.2. Dose rates (units of mrem/hr) in the direct x-ray beam being emitted from the analyzer

3.8 RADIATION DOSES FOR SEVERAL SCENARIOS

In this section we provide data, concrete examples of use and misuse of the analyzer and common questions and answers we encounter when training personnel on the safe use of the Innov-X analyzer. The goal is to explain scenarios of safe versus improper usage of the analyzer.

The table below presents radiation doses for normal operating conditions and also for examples of misuse of the analyzer and even extreme misuse. Innov-X provides installation training that includes detailed radiation safety training and documentation designed to prevent misuse of the analyzer

Example of Instrument Usage	Radiation Exposure and Comments
Normal Operation - Dose to Hand: User analyzes samples according to standard operating procedures described in this manual. Assumption: Operator using system with x-ray tube ON for 8 hours/day, 5 days/week, 50 weeks/year. (Practically constant usage).	Maximum exposure is to operator's hand, at the trigger. Exposure is < 0.1 mrem/hr. Annual exposure to hand is then < 200 mrem (2mSv). US: Maximum exposure under OSHA regulations is 50,000 mrem annually. Thus continuous operation provides a dose that is at least 250 times lower than maximum allowed by OSHA. Canada: Maximum exposure under ICRP regulations is 500 mSv for radiation workers and 50 mSv for the general public. Thus continuous operation provides a dosage 250 times lower for a radiation worker and and 25 times lower for the general public.
Normal Operation – Dose to Torso: Analyzer is used under the same operating conditions described above.	Exposure to Torso is so low it cannot be measured. To be conservative we use the same figure as the trigger, <0.1 mrem hr. Annual exposure using operating conditions above is < 40 mrem. (0.4 mSv) Maximum allowed is 5,000 mrem under OSHA and 20 mSv under ICRP for radiation workers (1 mSv for general public).

For the x-ray energy emitted by portable XRF analyzers (10-60 keV region), the bone in the fingers will absorb radiation about 3-5 times more than soft tissue, so the bone would be at an elevated radiation risk compared to soft tissue. For this reason no person shall hold a test specimen in front of the window with the fingers in the direct beam, or direct the beam at any part of the human body. Reference: Health Physics 66(4):463-471;1994.

Misuse Example 1: Operator holds samples in front of window with fingers, such that fingers are directly in the primary beam. Do not do this!.	For fingers at the port, in the primary beam, the maximum dose to the fingers is 28,160 mrem/hr. Assume an operator performs a 10 sec test (typical). The dose to the operator's fingers or hand is 28,160 x (10/3600) = 78 mrem. If the operator did this 641 times/year they would exceed the allowable annual dose of 50,000 mrem to an extremity. In Canada, the maximum allowed dose is 500 mSv/year (Canada ICRP radiation worker) or 50 mSv/year (Canada ICRP general public). If the test time was 30 seconds instead of 10 seconds, the operator would receive a dose of 234 mrem for each exposure, and thus would exceed the annual safe limit of 50,000 mrem after 213 tests. Even though it is unlikely to make this mistake so many times in a year, do not even do it once. Take the extra time to test a sample on a surface or use a testing stand. **Note: If the operator takes an average of only two shortcuts per week and places his/her fingers within the primary x-ray beam at the window, they will exceed the annual dose rate.**

Misuse Example 2:
Operator places analyzer against body and pulls the trigger to start a test. Analyzer tests to preset testing time (usually 10 seconds) unless operator pulls trigger again to stop test. This applies to analyzer being in contact with operator or with bystander.

Dose at exit of sampling window is 28,160 mrem/hr.

Dose for a 10 second exposure with analyzer in contact with Torso: 78 mrem (.78 mSv).
US: If an operator did this act 64 times in a year, the operator would exceed the annual safe dosage to the torso of 5,000 mrem/year. The maximum dose of 5,000 mrem/year is a whole body limit, which does not truly apply in this case because the x-ray beam size is small (about 2 cm^2 area – 1.5 cm x 1 .3 cm – at the port). Applying correction factors for the beam size is complex and beyond the scope of this manual. The important point is that for proper operation there is no reason to ever exposure any part of the human body directly to the x-ray source. This example serves to provide estimated exposure in the event this occurs.

If the testing time was 30 seconds instead of 10 seconds, thus the operator placed the port against his body or that of a bystander and performed a 30 second test, the dose would be 234 mrem. This is about the same as a mammogram. Repeating this gross mis-use 22 times would exceed the annual allowable limits.

Canada: Radiation worker would have to repeat this example (234 mrem exposure) of gross misuse 8 times to achieve the ICRP level of 20 mSv. (general public 1.3 times to achieve limit of 1mSv)

Misuse Example 3:
Operator manages to initiate a test for 10 seconds and exposes a bystander that is standing 12" away from analyzer port. What is exposure to bystander?

Note: The proximity sensor would automatically shut down the x-ray tube after 2 seconds, so this is an extremely improbable occurrence.

Note 2: Equations to scale these to other scenarios involving longer or shorter tests, and bystander being at distances other than 12" are provided at right.

Dose to bystander at 1 foot is 350 mrem/hr. For a 10 second exposure dose is 1 mrem. This is 5,000 times lower than the allowable dose to a worker in a year. This would have to happen 5,000 times to for that worker or bystander to obtain the maximum allowable dose.

Formula for calculating other scenarios:

$$Dose = 1\,mrem\left(\frac{13.25}{D+1.25}\right)^2 x\left(\frac{t}{10}\right)$$

D = distance from port in inches
T = testing time

Example: Bystander is 3' away from port for a 30 second test. In this case the dose is calculated as:

$$Dose = 1\,mr\left(\frac{13.25}{36+1.25}\right)^2 x\left(\frac{30}{10}\right) = 0.38\,mrem$$

US OSHA: Maximum allowable level is 5,000 mrem assuming bystander's torso is exposed. Thus, this misuse would have to occur 12,500 times in a year to the same bystander before that bystander achieved his maximum allowed dose.
ICRP: 5000 times for rad worker, 250 for general public

Comparative: Radiation Doses from Typical Exposures to Ionizing Radiation

Common medical and/or dental x-rays:	20-30 mrem each.
Mammogram:	100-200 mrem
Flying in a commercial jet coast to coast (6 hrs.):	1-2 mrem.
Daily exposure from background radiation: * depends on geographic location	0.3 to 0.5 mrem/day

Table 3.3 Radiation Doses from Typical Exposures to Ionizing Radiation

From the above table, a single case of analyzer misuse, thus producing a one-time exposure of 70-250 mrem, is comparable with single-event common medical x-ray procedures such as an annual chest x-ray or mammogram, or 25-50 airline flights in a year, and thus is not considered harmful. Regular misuse, such as taking safety shortcuts twice weekly, produces radiation exposure that greatly exceeds these typical levels and should be avoided entirely.

3.9 COMMON QUESTIONS AND ANSWERS REGARDING RADIATION SAFETY

Question: When I'm shooting a piece of pipe or valve on a rack or on a table top, is there any exposure to people standing in other locations, or standing several feet away from the analyzer?

> Answer: Even a thin amount of metal sample (1-2 mm thickness) is enough to completely attenuate the x-ray beam emitted from the Innov-X analyzer. Shooting a piece of material that covers the sampling window on the analyzer will completely shield any bystanders from radiation exposure. However, good practice recommends that the area for at least 4-5 feet in front of the analyzer is clear of people.

Question: If I forgot to switch the safety on the trigger to "ON", I pick up the analyzer and accidentally pull the trigger, is that dangerous to nearby personnel?

> Answer: No, this example of misuse is not dangerous, but it may produce a non-negligible radiation exposure to nearby personnel. For an exposure to occur, the following things must happen. First, you must be holding the analyzer so that a bystander is actually standing in the x-ray beam being emitted. Just being near the analyzer is totally safe otherwise. Second, the bystander must be within 1-3 feet from the nose of the analyzer in addition to being in the beam path, to receive any appreciable dose. If all of these conditions are true, the dose received by a bystander is still extremely low. It ranges between 0.1 to 0.5 mrem depending on the exact location of the bystander. This dose is 10,000 to 50,000 times less than the allowed dose. Please see Misuse Example 4 in the table above.

Question: Do I need to create restricted areas where I am using the analyzer?

> Answer: No, provided you are following normal operating procedures there is no reason to restrict access to an area where the analyzer is in use. The operator should take precautions to keep any personnel more than 3 feet away from the sampling window of the analyzer in the event of accidental misuse as detailed above. Should the operator also elect to test small components like weld rod as shown in Figure 3.3, the operator should also be sure that no personnel are standing within about 4-5 feet of the sampling window.

Question: How does the x-ray tube in the Innov-X system compare to a radiography system used for taking images of metal parts.

Answer: The x-ray tube used in the Innov-X system produces between 1,000 and 10,000 times lower power than most radiography systems (0.5-1 watt for Innov-X versus kW for radiography systems). This is because a portable XRF is designed to perform surface analysis of alloys and other samples, whereas radiography systems are designed to shoot x-rays entirely through metal components in order to obtain an image on the other side of the object being bombarded with x-rays. For example, many tube-based radiography systems use a 300-400 kV tube and currents in the tens or hundreds of milliamps (mA). The Innov-X analyzer uses a tube operating at 35 kV and 5-30 micro-amps. The radiation levels produced are therefore thousands or tens of thousands times lower with the Innov-X system.

Question: Should we use dosimeter badges with the Innov-X analyzer.

Answer: Dosimeter badges are required by some states, and optional by other states. Innov-X recommends that operators wear badges, at least for the first year of operation, as a general precaution to flag any misuse of the analyzer. Dosimeter badges are available for the torso (generally worn on the belt loop or shirt pocket) and are available as "ring" badges. The best single badge to obtain is a ring badge that is worn on a finger, on the opposite hand used to hold the analyzer. This will record accidental exposure for the most likely case – an operator grabbing a small sample and holding it in one hand while analyzing it. Note: these badges generally have a threshold of 10 mrem, and are renewed monthly. So it will take several cases of misuse even to obtain a reading on a typical badge. When purchasing a badge, obtain the type used for x-ray and low energy gamma ray radiation.

3.10 SAFE GUARDS AND EMERGENCY RESPONSE

The main safeguards to use as an owner of an Innov-X portable XRF are really intended to restrict access to properly trained operators:. **Note: Canadian regulations require certified personnel to use the device, refer to section 3.0 in this chapter.**

1. Keep the system in a controlled location, where only authorized users are likely to have access to the analyzer at any given time.
2. Make a simple sign that is kept with the analyzer indicating that an operator must have completed a training class provided by your company or must have attended an Innov-X training course in order to use the analyzer. Note that when the Innov-X system is turned on, the screen displays a message indicating that the system should only be used by authorized personnel.

Emergency Response:

Because the Innov-X system is a battery operated, x-ray tube based analyzer, the emergency response plan is very simple. If the operator believes the analyzer is locked up in an "OPEN" position, they should do two things:

1. Press the On/Off switch on the base to power the analyzer off. The green LED indicator will turn off, indicating system power is off. At this point it is not possible for the analyzer to be producing x-rays.
2. As an additional precaution, the operator may remove the battery trap door at the bottom of the analyzer (have the nose pointing away from personnel), and pull out the battery. Even if the operator has failed to properly power the system off in Step #1, removing the battery guarantees that no x-rays can be produced. There is no electrical power being provided to the x-ray tube.

Note: It would be highly unusual for an operator to somehow lock up the analyzer with the x-ray tube powered on. This would require the operator to crash the iPAQ during an analysis. If this happens the analyzer will shut off the x-ray tube 10 seconds after the last communication with the iPAQ. However, if at any time the operator believes the x-ray tube is on and no test is in progress, powering off the analyzer and

restarting will automatically shut down the x-ray tube and close the shutter. It will no longer be possible to produce x-rays at this point.

3.11 DOSIMETER BADGES

Dosimeter badges are provided as a monthly service by several companies, listed in this section (see below). The badges are generally provided monthly, and the operator returns the previous month badges to the company for analysis. The operator receives a monthly report showing any personnel with readings higher than typical background radiation.

Dosimeter badges are required by some states, and optional by other states. Innov-X recommends that operators wear badges, at least for the first year of operation, as a general precaution to flag any misuse of the analyzer. Dosimeter badges are available for the torso (generally worn on the belt loop or shirt pocket) and are available as "ring" badges. The best single badge to obtain is a ring badge that is worn on a finger, on the opposite hand used to hold the analyzer. This will record accidental exposure for the most likely case – an operator grabbing a small sample and holding it in one hand while analyzing it. Note: these badges generally have a threshold of 10 mrem, and are renewed monthly. So it will take several cases of misuse even to obtain a reading on a typical badge. When purchasing a badge, obtain the type used for x-ray and low energy gamma ray radiation.

Dosimeter Companies:

Here are two companies that provide badges as a regular service. There are certainly many more.

Landauer Inc.	AEIL
Glenwood, IL	Houston, TX
708-755-7000	713-790-9719

3.12 TYPICAL REGISTRATION REQUIREMENTS

Innov-X maintains a database of the registration requirements for every state, including sample registration forms. Most states require some form of registration, and generally they require the registration to be received within 30 days of receipt of the instrument. Some states require no registration, while a few require notification in advance. Please contact Innov-X for specific questions regarding the state where the instrument will be used, or for copies of registration forms.

In general a company will have to provide the following information regarding the device:

1. Purpose of device. Generally this is "Analytical" or "Industrial." Be sure to inform the state registration office that the device will NOT be used for radiography or for medical uses.
2. Radiation Safety Officer – Monitors training, safe use, and controls access to the instrument.
3. Authorized Users – Trained by Innov-X Factory Authorized Representatives in the safe and proper use of the XRF.
4. Operating parameters of the analyzer – 35 kV, 5-30 micro-amps.
5. Type of system, either fixed, mobile or portable. Generally the correct choice is "Portable."
6. User Training Specified – Indicate that only individuals receiving manufacturer training, documented by a manufacturer's training certificate will operate the instrument.
7. Personal Monitoring. This may be required by radiation control authorities. Many registration forms will ask that you indicate whether or not you intend to perform dosimeter monitoring.
8. Copy of Registration & Manual at the Job Site

If you have any questions regarding the type of registration form or filling out the form, please contact Innov-X Systems. Many states may confuse a portable XRF system that uses a tube with medical or

industrial radiography systems. This is because of the relative newness of portable tube-based systems. In all likelihood, Innov-X personnel have experience providing the necessary documentation to the state in question, and can readily assist the customer in this process.

Chapter 4 Operation

4.0 OPERATION - GENERAL

Power to the instrument is controlled by the ON/OFF button located at the rear of the analyzer. The green LED next to this button will illuminate when the analyzer power is on. The iPAQ operates on the Microsoft Windows CE ® operating system and is activated separately by the power button on the right top face, just over the display. The trigger is locked via the software.

4.1 WORKING WITH THE HP iPAQ Pocket PC®

The Microsoft Windows CE ® operating system and Innov-X software provided on the iPAQ handheld computer are operated by user input through the touch screen. For comprehensive details on the iPAQ's operation, please refer to the iPAQ reference materials included with your unit.

General tips

- The Start Menu is found in the upper left corner of the iPAQ screen. This is used to launch all applications, including the Innov-X Systems Analyzer software.
- The instrument is designed as a "point and shoot" system that requires little, if any, entry of information for most operations. In the event the user modifies the grade library, enters testing information data, or performs other functions, it will be necessary to enter data via the virtual keyboard, which can be accessed by tapping the keyboard icon in the lower right corner. The iPAQ also includes character recognition software. This can be selected from the drop-down menu to the right of the keyboard icon.
- The File toolbar which will be used to Change Functions, Screens and Options is located at the bottom of the screen.
- It is possible to cut, copy, rename and delete files from within Windows File Explorer by selecting the file to be modified and holding the stylus on the screen for 2 seconds.
- Pressing buttons on the bottom of the iPAQ will perform various functions that are described in the iPAQ documentation. The button on the right hand size of the analyzer is the iPAQ task manager. Pressing this button will show all programs that are currently open. Open files can be closed from this menu. Simply hold the stylus on the file for a few seconds. The option to close the file will appear.

4.2 OPERATION - MAIN SOFTWARE SCREENS

The Innov-X Software consists of three main screens:

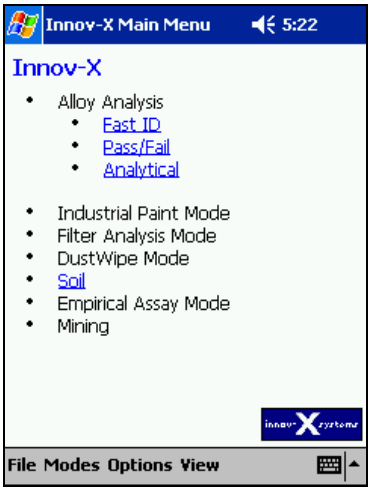
- **Main Menu screen:** Used to select the analysis mode, open the results screen, and change the administrator password.
- **Analysis Screen:** Used to change settings, edit libraries, and perform tests.
- **Results Screen:** Displays results from current reading, allows scrolling back to previous test results. Allows recorded data to be exported to a comma delimited file which is directly compatible with Microsoft Excel.

4.2.1 Innov-X Main Menu

The main menu below appears upon startup. The Main Menu allows you to choose an analysis mode, as well as perform certain administrative functions such as changing your login password. The modes which

are available on the analyzer are shown in blue. For information on adding additional analysis modes to an analyzer, please contact the Innov-X Sales Department at 781-938-5005.

- **Use the Main Menu to select the desired analysis mode.** The analysis mode can be selected by either tapping on the name of the method (shown in blue) or by selecting the appropriate mode from the Modes menu.
- The administrative password can be changed by selecting ***Options → Change Password.***
- It is possible to go directly to the Results Screen by selecting ***View→Results***. If the results screen is opened in this manner, it is possible to view results when the iPAQ is not connected to the analyzer.



4.2.2 The Analysis Screen

Selecting a mode opens the analysis window for that mode. All data acquisition and analyzer control are done from this window. This window allows the user to start or stop an analysis, change testing parameters, and modify the fingerprint and grade libraries (Alloy Analysis only).

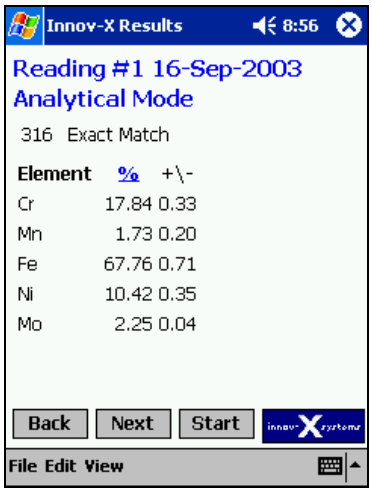
The analysis screen runs continually while during normal instrument operation. From the results menu, it is always possible to go back to the Analysis screen by selecting ***File→Exit*** or by tapping the X in the upper right hand corner of the screen.

The analysis screen for Analytical mode is shown to the right. Screens from other modes are similar and will be described in later in this manual. The analysis screen shows the name of the mode that is currently active, a start/stop button (which is inactive in most cases), an info button that is used to enter descriptive information for any given test, a trigger lock and a battery indicator. In addition, a message appears directly below the name of the mode which will indicate the current state of the analyzer. Typically it reads "Ready to Test," but also provides other information in certain circumstances. Any mode specific information will be displayed at the bottom of the screen above the menu choices.

4.2.3 The Results Screen

The Results screen displays the current reading and old data. All data handling functions such as exporting and deleting readings are carried out from this screen. Once the Results Screen is open, the user may start new tests without going back to the analysis screen by pulling and holding the trigger. Tapping the X in the upper right hand corner will return the user to the analysis screen without starting a test. If no analysis mode is running, an Exit button will appear which will close the Results screen.

The Results screen is automatically shown at the completion of any analysis. It can also be accessed from the analysis screen for any mode or the **Main Menu**, by selecting ***View→Results***. Once the Results screen has been opened, the information which is displayed can be changed by selecting options from the View menu. The various viewing options will be described in detail in later chapters.



4.3 PASSWORDS - ABOUT PASSWORD PROTECTION

Certain functions such as adding and deleting fingerprints from the libraries, and Pass/Fail setup have been specified as Administrative Level Functions. These functions are described in detail in later sections of the manual. In order to use these functions, a password must be entered. The default password is set as the lowercase letter "z". This password can be entered whenever the system prompts for a password.

Changing the Administrator Password.

The Administrator password may be changed at any time from the **Innov-X Main Menu** by choosing ***Options→Change Password***. When the change password option is selected, this screen will appear.

If you are changing the password for the first time, enter the letter "z"; otherwise enter the current system password. Then, choose a password and enter it twice, once in the "New Password" box and again in the "Confirm Password" box. Passwords may be any combination of letters or numbers.

4.4 STANDARDIZATION

4.4.1 Standardization Procedure

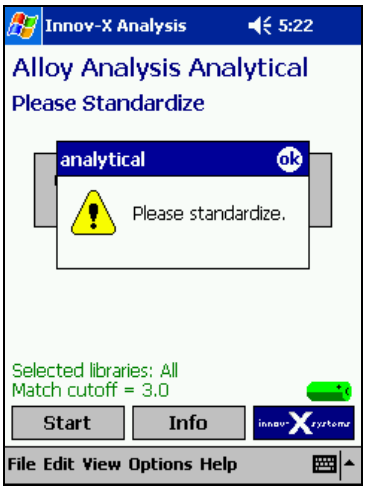
Before performing tests, it is necessary to standardize the instrument. This automated procedure involves collecting a spectrum on a known standard (Alloy 316) and comparing a variety of parameters to values stored when the instrument was calibrated at the factory. If there are any problems with the instrument, they will be indicated by an error message.

The standardization procedure takes about 1 minute. Standardization must be done any time the analyzer hardware is initiated or restarted and must be repeated if the instrument is operating for more than 4 hours.

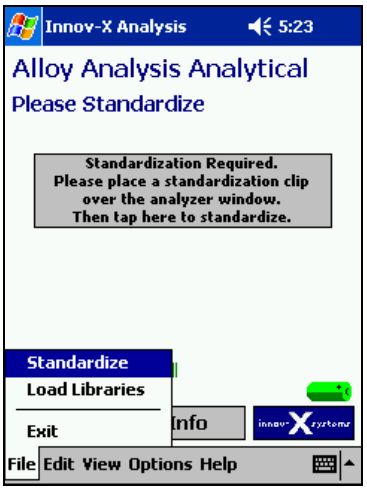
It is possible to re-standardize the instrument at any point while the software is running. Standardization is always initiated from the Analysis Screen of any Mode.

If the analyzer is restarted, you will be required to standardize the instrument before performing any measurements. This is indicated by the message "**Standardization Required. Please place a standardization clip over the analyzer window. Then tap here to standardize.**" on the analysis screen

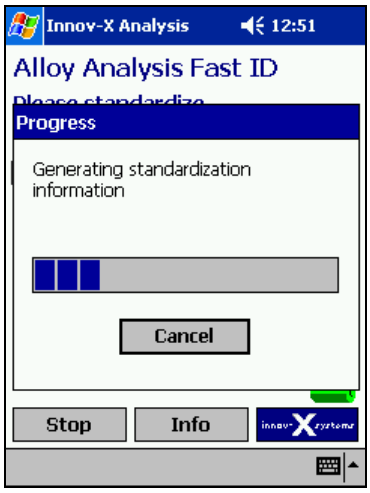
It is not possible to start a test before standardization. If the trigger is pulled before the standardization procedure is completed, a message box will appear. Press **ok** to acknowledge and clear the message.



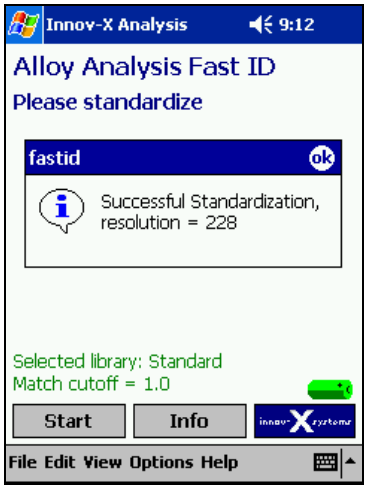
To initiate the standardization procedure, snap the standardization piece on the front of the instrument. Verify that it completely covers the analyzer window. When using a standardization mask with a weld collimator, be sure that the solid portion of the mask covers the analyzer window. Tap the grey box in the center of the screen or select ***File→Standardize*** to begin.



When standardization is in progress, the red light on the top of the instrument will blink, indicating that the X-ray tube is energized and the shutter is open. In addition, a status bar will appear, tracking the progress of the measurement.

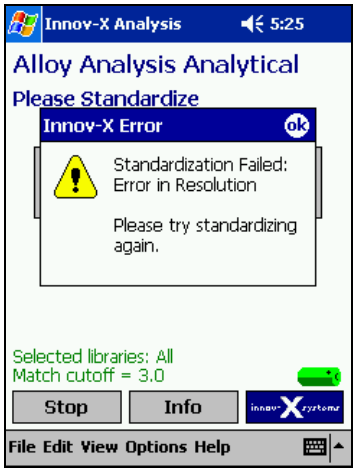


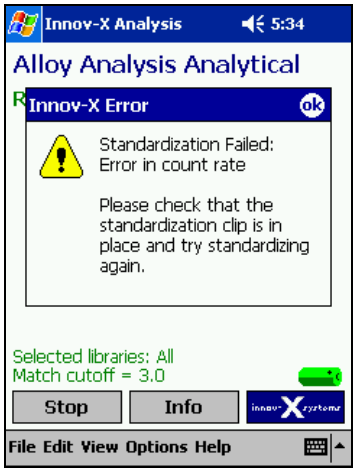
When standardization is complete, the message "Successful Standardization" will appear, along with the resolution of the instrument. Tap **ok** to acknowledge and clear the message. The instrument is ready for testing.



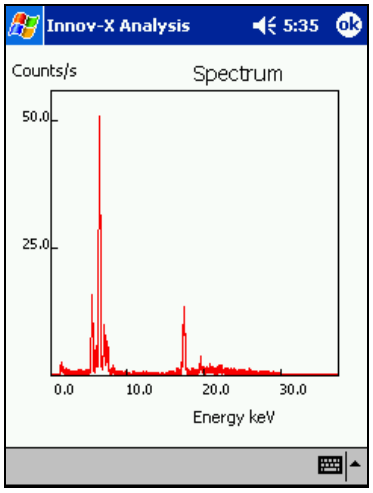
4.4.2 Standardization Errors

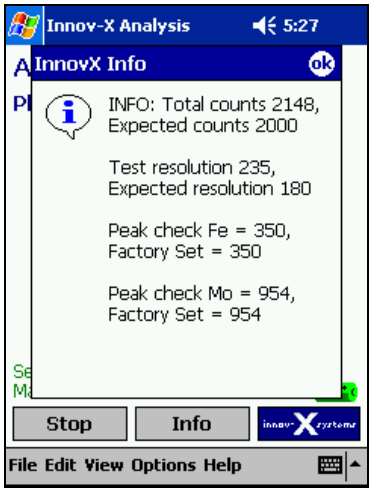
The analyzer performs several diagnostic checks during the standardization process. If the standardization fails, the instrument will prompt the user regarding the next step. Several errors could occur while standardizing: "Wrong Standardization Material," "Error in Resolution" or "Error in Count Rate"





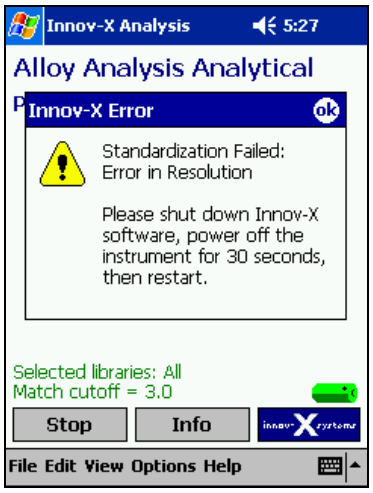
After closing the Standardization Failed message, two additional screens will appear. The first is a picture of the spectrum generated during the standardization. The second is a summary comparing factory set values for resolution, count rate, and peak positions to values calculated during the standardization.

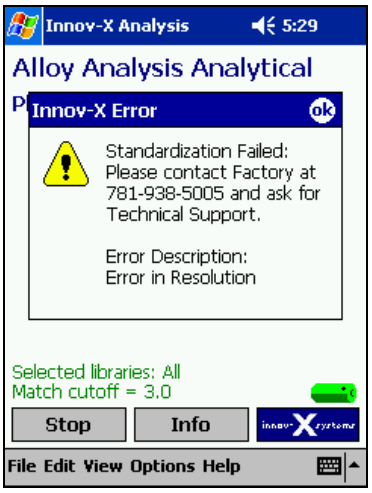




When standardization fails, verify that the standardization mask is in place, and attempt standardization again. To restandardize after a failure, tap the grey box in the center of the display, or choose ***File→Standardize***. If you are using a weld collimator, make sure that the solid part of the mask is covering the window.

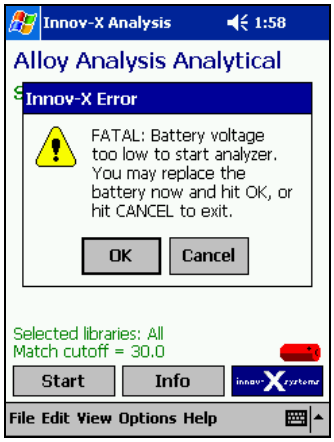
If standardization fails again, exit the analysis screen and power off the instrument. Restart and restandardize. If the standardization fails a 3rd time, you will be prompted to perform a soft reset of the iPAQ. Selecting Yes on this screen will automatically soft reset the IPAQ. You should also power cycle the instrument. Restart and restandardize. If the standardization fails again, replace the battery in the instrument and attempt another standardization. If this fails, please contact the Innov-X Systems service center at **781-938-5005.**





4.4.3 Battery Replacement and Initialization/Standardization

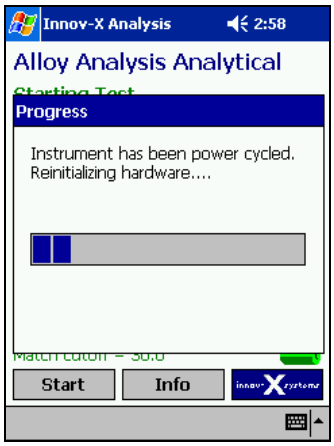
When the battery is too low to take a measurement, an error message will appear:



In order to continue testing, replace the battery immediately, and then tap "OK." The analysis screen will remain open, and the instrument will reinitialize. This process will take 1 minute. It is not necessary to re-standardize, provided that less than 4 hours has elapsed since the last standardization and the battery swap is completed within 10 minutes.

After re-initialization is completed, testing can continue.

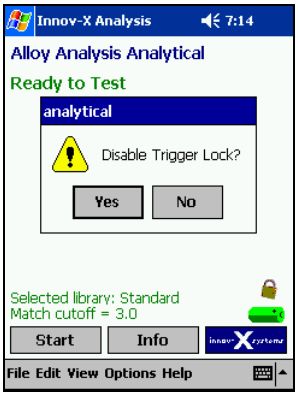
If the battery is not replaced, and cancel is selected, the Analysis screen will close. When the software is restarted, the instrument will go through a complete 1 minute initialization and will require standardization.



4.5 THE SOFTWARE TRIGGER LOCK

Innov-X analyzers are equipped with a software trigger lock which prevents the trigger from being actuated unintentionally. The lock is released by tapping an icon on the iPAQ screen. Once the lock is released, it will remain unlocked for subsequent tests, until more than five minutes has elapsed between tests. At that point, the trigger lock will be activated and will need to be disabled before additional testing can commence.

Tap the lock icon located directly above the battery indicator.



Select yes to disable the trigger lock

The open lock icon indicates when the trigger is disabled.

4.6 TEST INFORMATION - LABEL INPUT

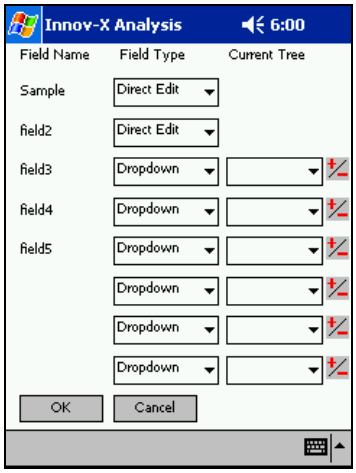
Information such as sample name, and identifying characteristics can be stored with each measurement. This is done from the test information (Test Info) screen which can be accessed from the **Analysis Screen** of any mode by tapping the **Info** button, or selecting ***Edit→Edit Test Information***.

The **Test Info** screen consists of eight fields. The name and format of each field can be changed by using the **Modify Test Info Template** feature described in section ***4.6.1* Modifying the Test Info Template**. The process of entering test information prior to each analysis is described in section **4.6.2 Entering Test Information**. Finally, the process of entering or changing test information after the analysis has been completed is described in section **4.6.3 Editing Test Info from the Results Screen**.

4.6.1 Modifying the Test Info Template

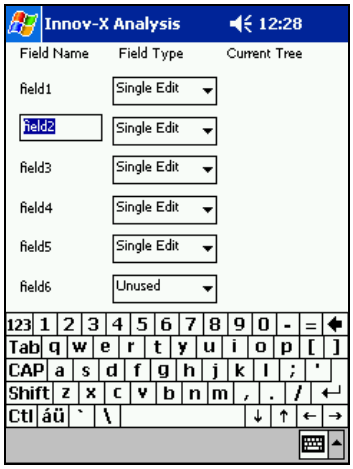
Test Info fields are modified via the Modify Test Info Template option found in the edit menu on the analysis screen in every software mode. Each field can be designated to be Direct Entry, Drop-down, or Tree. Direct entry fields allow users to enter characters directly from the virtual keyboard, or a bar code reader. Drop down menus provide a list of options to choose from. Trees are more complicated drop-downs; which allow users to subdivide large numbers of choices for ease in quickly locating the correct label. For example, a user may set up a tree with several parts for a main assembly. Subassemblies for the parts can be linked to their parent parts.

To make any changes to the Test Info format, select ***Edit ⟶Modify Test Info Template*** from the analysis screen of any Mode. Modifications of Test Info screens are specific to each mode, and will need to be made to each mode if more than one is used.



4.6.1a Changing Field Names

Field names can be edited by tapping on the current name. This will open an editable text box. A new name can be entered with the virtual keyboard. Selecting another cell or tapping **ok** will save this info.

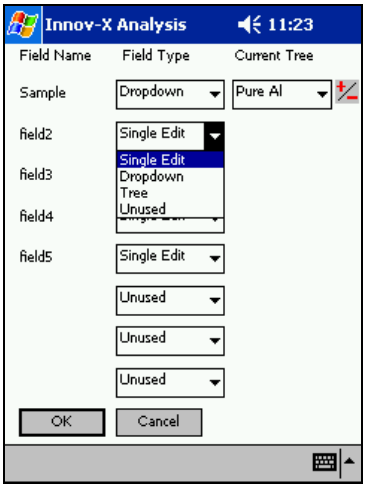


4.6.1b Selecting Field Type

From the Modify Test Info screen, the type of field can be selected from a drop-down menu. Simply tap the arrow in the Field Type box for the field being modified.

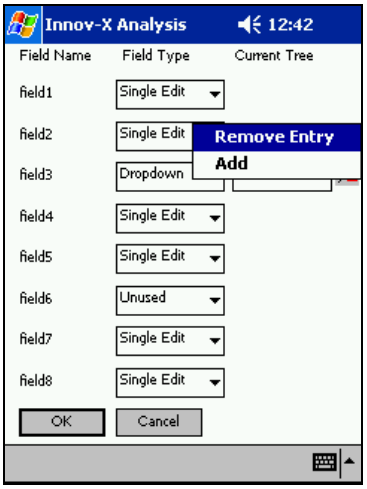
- Select **Direct Edit** for a text field which will accept data from the virtual keyboard, or a bar code scanner.
- Select **Drop-down** for a drop-down list
- Select **Tree** for a Drop-down menu with many choices, some of which may be grouped into categories and subcategories.

Select **Unused** to eliminate the field from the Test Info screen.

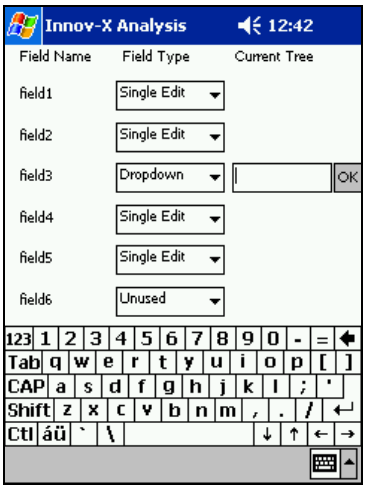


4.6.1c Changing Drop-down Menu Entries

Once a field has been designated a drop-down menu, entries can be added or deleted by clicking the +/- symbol to the right of the field. Two choices will appear; **Remove Entry** and **Add**.
To delete a drop-down entry, first select the label to be deleted, then press +/- and tap **Remove Entry**.

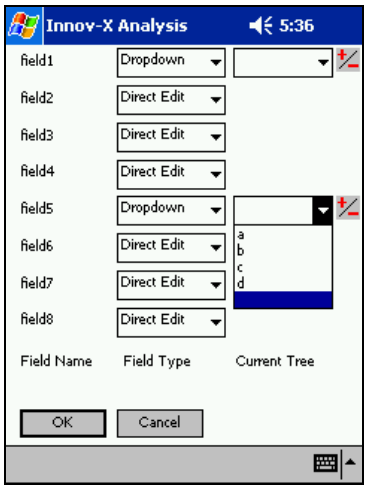


To add an entry from a drop-down list, tap the +/- symbol next to appropriate field, and select **Add**. Type the new info into the blank text box that appears. Select **OK** and the entry will be added to the drop-down menu.



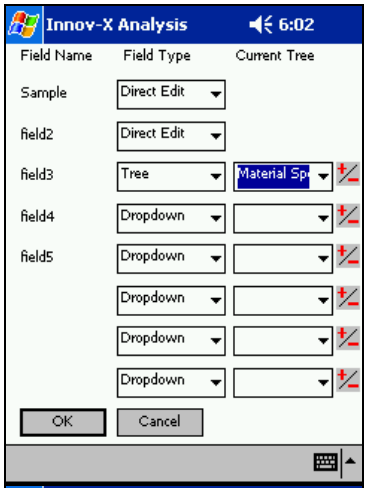
Repeat the process above to complete the complete drop-down list.

If it is anticipated that a drop-down field will not be used for all samples, enter an empty field as a choice so you can choose to leave the field blank.



4.6.1d Changing Tree lists.

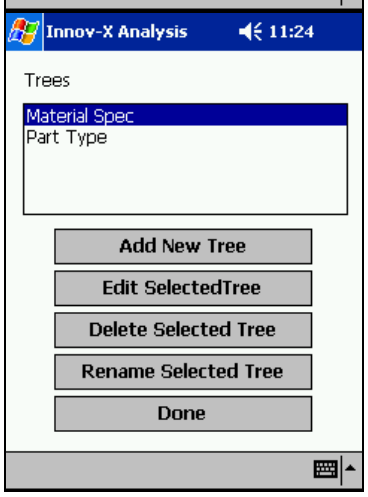
Once a field has been designated a tree, modifications to the contents of the tree can be made by tapping the +/- symbol to the right of the tree.



All modifications to trees are made from the menu shown on the right.

It is possible to add, edit, delete or rename trees. Select the appropriate choice from the menu to perform any of these functions.

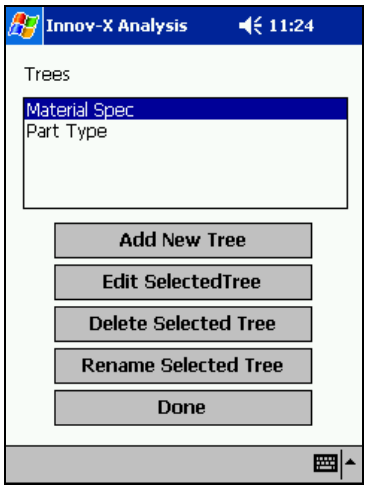
When you have finished creating/editing your tree, highlight it and select **Done.**



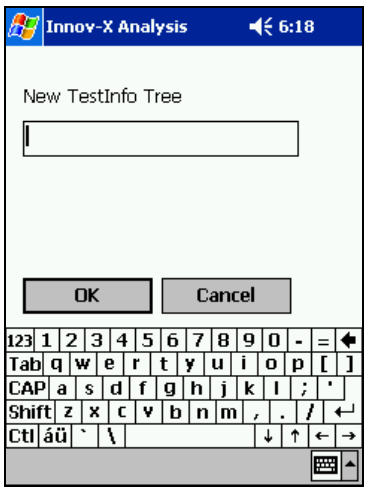
The following is an example of how a user might create a tree: A manufacturer of tubes and valves tests all parts to ensure that they're made of the proper material. The company's QC procedure involves labeling each test with the part number of the item. Rather than forcing operators to look through a long list of part numbers, a tree is created in order to subdivide the parts number into groups based on part type.

The procedure for creating the tree is as follows:

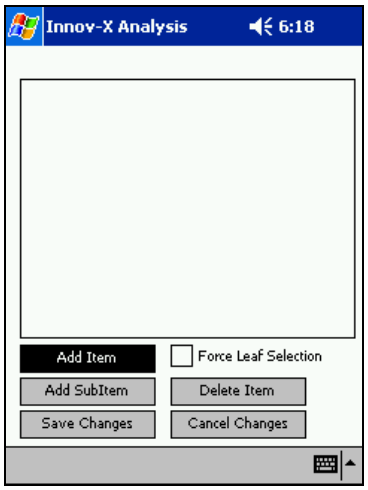
Select: Add New Tree:



Enter the Name of the Tree in the text box and select OK.



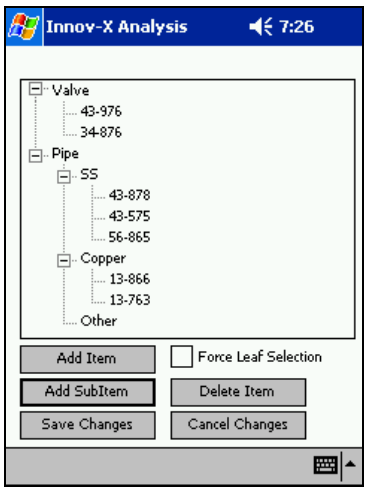
Tap Add to add the first item



Enter the name of the item

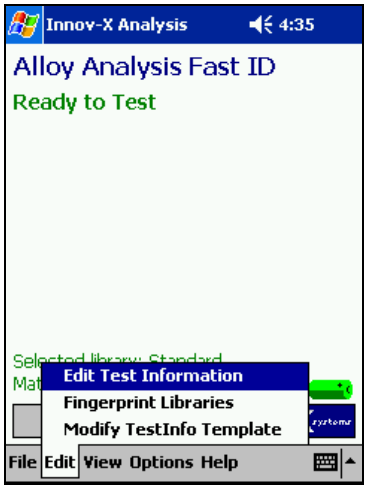
Once the tree is started, continue to Tap Add Item to add a top level menu item, or select an item and tap Add SubItem to link a subcategory to the item. Continue until all items have been added.

In this example, the part numbers for pipes and valves are separated into categories. The pipes are further subdivided by material type.

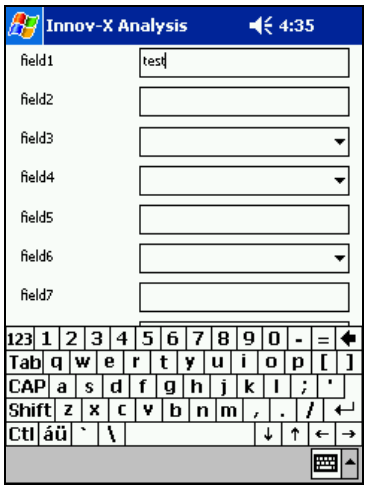


4.6.2 Entering Test Information

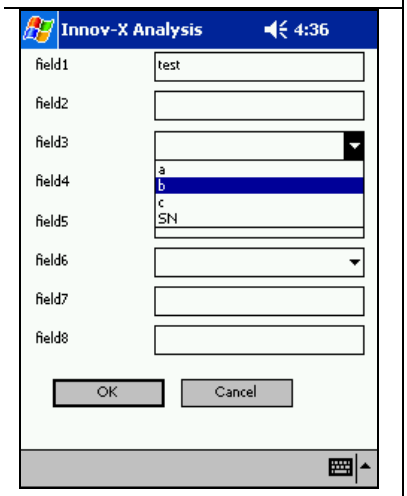
1. To enter the Test Info screen, you must be in the Analysis Screen. If the Results Screen is open, tap the ⊗ in the upper right hand corner to return to the Analysis Screen. From the Analysis Screen, select ***Edit→Edit Test Information,*** or tap the **Info** icon.



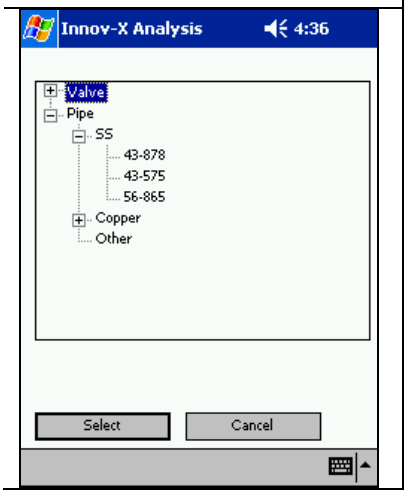
2. To enter a unique sample name or number, select a direct entry field by tapping anywhere within the field. Use the virtual keyboard to enter the information.



3. To select information from one of the drop-down menus, tap the arrow to the right of the box. Select the desired entry.



4. Some drop-down fields are formatted as trees. To select information from these fields, tap the arrow to the right of the box. A screen will appear showing options. The plus (+) symbol will appear before some choices indicating the presence of sub-items. Tap on the + symbol to expand the menu. Tap on any item or sub-item to select it, then press **Select**.

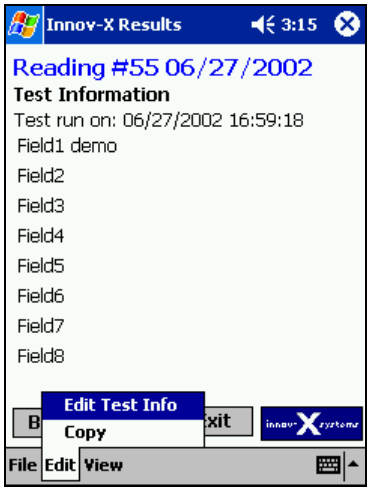


5. When all the necessary data have been entered. select OK
6. The information entered in the test info screen will be saved with each reading until the test info screen is modified again.

4.6.3 Editing Test Info from the results screen

Test information can be edited, or added to a test after its completion.

- From the results screen, scroll to the reading to be modified.
- Select ***View →Test Info*** to see in the information which is already stored.
- Select ***Edit → Edit Test Info*** to bring up the editing menu.



You will then be presented with the same test information screen described in **Section 4.5.2: Entering Test Information.**

4.7 EXPORTING AND ERASING DATA

Because the memory of the iPAQ is limited, you should periodically backup the data on your analyzer, and erase the memory. Depending on test volume, it is recommended that all data is erased on a weekly or monthly basis.

4.7.1 Installing ActiveSync

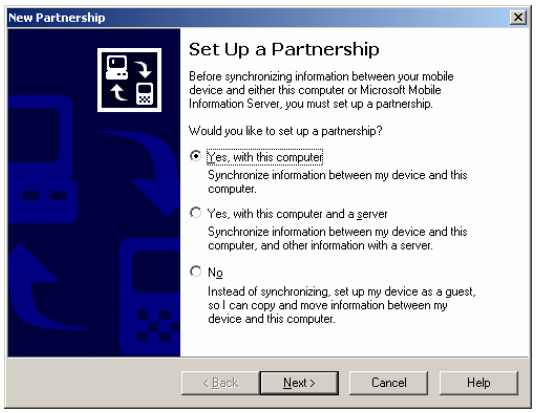
In order to copy files between the iPAQ and a desktop PC, Microsoft Active Sync Software must be installed on the desktop PC. Innov-X strongly recommends that you download the latest version of ActiveSync from the internet. ActiveSync v3.7 may be downloaded from http://www.microsoft.com/windowsmobile/resources/downloads/pocketpc/activesync37.mspx

If it is not possible to download the latest version, an ActiveSync CD (v3.5) was shipped with your analyzer. Check behind the foam in the instrument case.

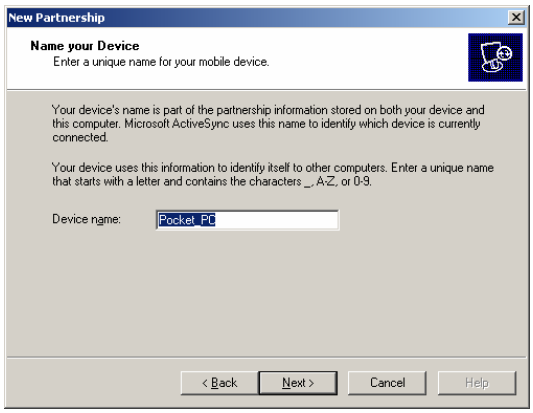
The iPAQ cradle should be hooked up to the USB port on the desktop computer before installing software.

The Procedure for installing and setting up ActiveSync is as follows:

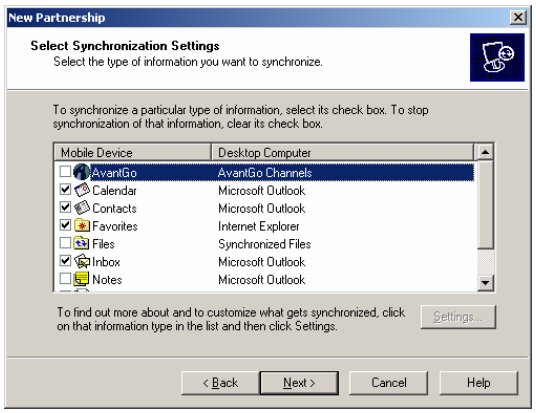
1. Insert the ActiveSync CD in your CD Drive. It will start automatically. The CD contains information about Getting Started with Your Pocket PC. This changes periodically, so it's difficult to describe exactly what the screens will look like. Step through the screens until you see the option "Install ActiveSync." Select this to start the installation process.
2. Follow the prompts on the screen. When given the choice, select "Run this program from its current location" and click OK.
3. Complete the install process. You will be required to restart your computer in order to complete the installation.
4. After restarting your computer, dock the iPAQ in the cradle. The iPAQ should automatically communicate with your computer. If it doesn't, check the connections and try removing the iPAQ and reseating it. If that doesn't work, try doing a soft reset on the iPAQ
5. When the computer communicates, you will be prompted to "Set Up a Partnership." Select "Yes, with this computer"



6. Enter a name for your iPAQ and click next.



7. You will be prompted to "Select Synchronization Settings." **Select "Files" only**. ***It is important to make sure that* Files *is the only item checked. Otherwise, the files such as address books and emails will be copied from the desktop computer to the iPAQ.***



8. Step through the rest of the process.

9. A folder will automatically be created on the PC's desktop with the name of the device entered in step 8 above. Results files saved on the iPAQ will automatically be synched and will be stored in this folder. Opening this folder and clicking on the name of the file will open the file in Excel.

10. After ActiveSync is set up correctly, copying results to a desktop computer will consist of

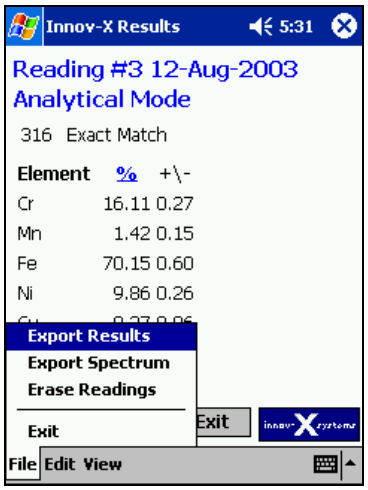
a. Exporting results on the iPAQ. (described in section 4.6.2)
b. Synching the iPAQ to the computer
c. Opening the results in Excel for viewing, or printing.

4.7.2 Exporting Results

All data from your Innov-X Systems analyzer can be exported as a comma delimited text file (csv). This format allows the data to be easily exported to spreadsheet programs. It is possible to export all data from a single day, or to export all data saved in the iPAQ. Results and spectra are exported separately.

To export or erase data, you must be in the Results Screen. This is automatically opened when a reading is taken, or can be accessed by choosing ***View→Results*** from any analysis screen.

From the results screen, select ***File→Export Results***

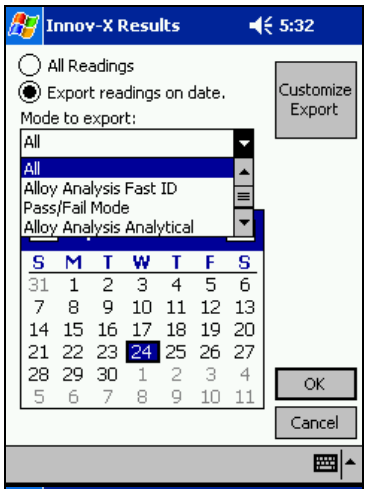


You can choose to export All Readings or just Readings on a specific date. Choosing **All Readings**: will export all readings saved in memory and is a good choice if you want to backup all data stored on the instrument before deleting. If a large number of readings stored, this option will take several minutes.

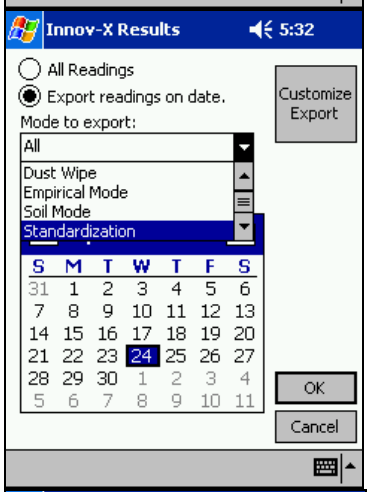
Choosing **Export Readings on date** requires that you pick a date from the calendar below. It is strongly recommended that you use this option and export data on a daily basis.

The customize export option allows users with administrative password privileges to customize the format in which data is exported. This is described in **Section 4.7.3: Customizing Results Export**.

After choosing which readings to export, you may choose to export all data, or just data from a specific mode. Selecting the arrow to the right of the mode to export will open a drop-down menu. Select the mode for which you want to export data.

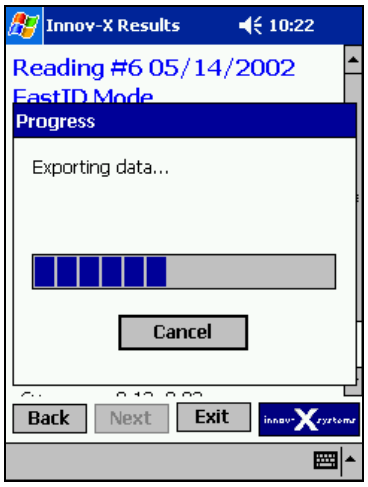


All standardization data are stored as results files. These data are automatically included in exported results files when the selected "Mode to export" is **All.** Additionally, it is possible to export only the standardization data by selecting **Standardization** as the "Mode to export."

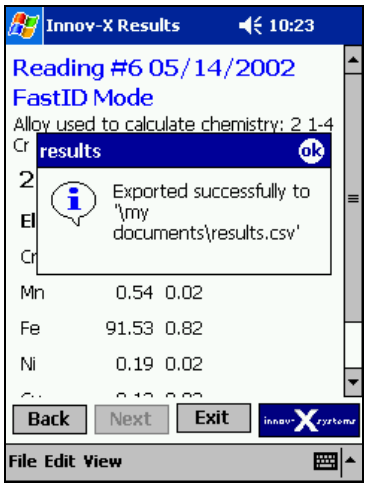


When the proper selections have been made, select **OK**. A **Save A**s box will appear. Select the folder in which you want to save the data, and name the file. The file Type will always be **Comma Separated Values**. The recommended Location is Main memory and Folder is **None.** This will export files into the "My Documents" folder in the main Memory of the iPAQ.
If you select a File Name which already exists, you will be asked if you want to replace the existing file. If you do, select **Yes**. Otherwise select **No** and choose another file name.

A status bar will indicate the progress of the export. It may take several minutes to export many readings. Daily downloading and weekly erasing of data simplifies and shortens this procedure.



When all readings are exported, a message will appear confirming the export. Tap **ok** to acknowledge and clear the reading.



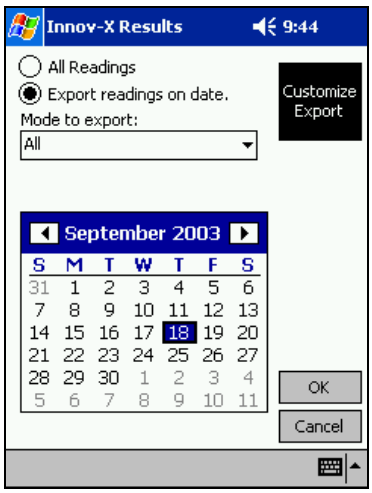
4.7.3 Customizing Results Export

All units come with a standard results export format which reports a variety of information relevant to a test. Users can select which fields are exported as well as modify the order.

To modify exported results files, select **File ⟶Export Readings** from the Results screen.

Tap the **Customize Export** box.

Enter the administrative level password when prompted.



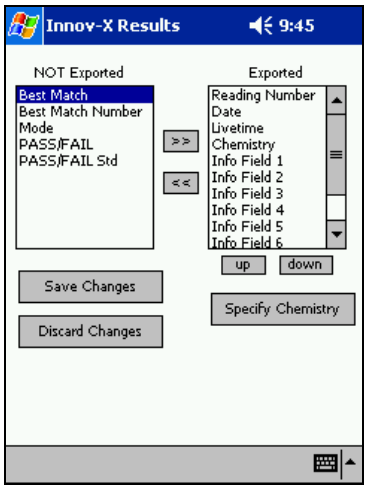
Two columns appear on the screen; the column on the left lists fields which will NOT be exported, and the right-hand column lists fields which will be exported.

Fields can be moved from one column to another via the >> and << buttons located in the center of the screen

Exported field order can be changed by using the **Up/Down** buttons. Select a field and move it up or down as desired

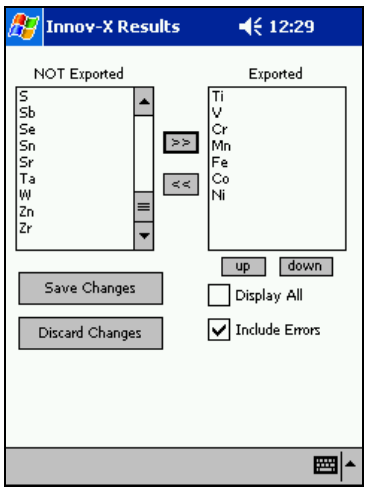
Once all changes have been made, choose **Specify Chemistry** if changes need to be made to the list of exported elements.

In chemistry is not edited, select **Save Changes** to keep the modified settings, or **Discard Changes** to ignore any changes.



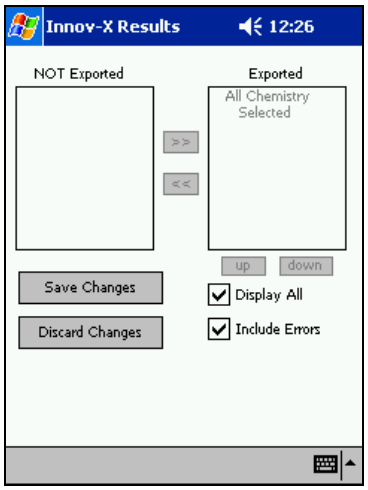
The Specify Chemistry screen resembles the previous screen. Move elements to the appropriate column, depending on whether or not an element should appear in exported files.

Select **Include Errors** to export the error associated with each measurement.



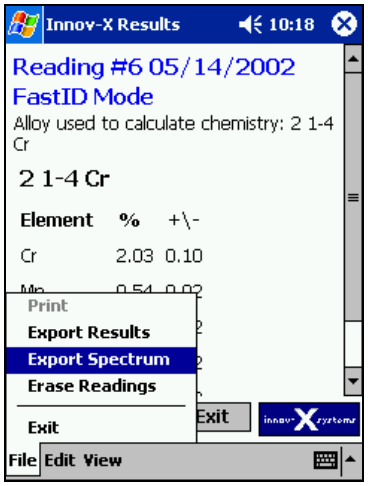
Select **Display All** to include all measured elements. *This setting is recommended, as it will ensure that all data measured with the instrument is exported.*

When all changes have been made, tap **Save Changes** or **Discard changes,** depending on whether the changes should be saved.



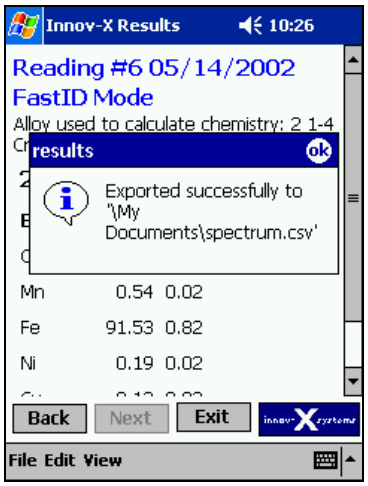
4.7.4 Exporting spectra

Only one spectrum may be exported at a time. In the results screen, scroll to the reading for which you wish to export the spectrum, and ***Select File→Export Spectrum***.



Choose the File name, and make sure that **Comma Separated Values** and **Main Memory** are selected. This will save the spectrum to the My Documents folder in the Main Memory of the iPAQ.

A message will appear indicating a successful export. Tap **ok** to acknowledge and clear the window.



4.7.5 Erasing readings

It is possible to erase a single reading, a range of readings, all readings from a specific data, or all readings before a specific date.

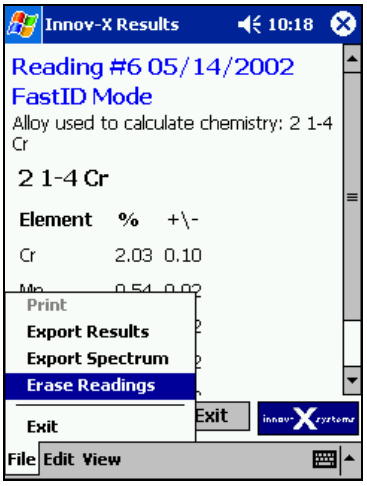
In order to erase a single reading, the reading to be erased must displayed on the screen before selecting delete. If necessary scroll to the reading you wish to delete.

In order to select a range of readings, you must have a reading open from the date you wish to delete the readings. If a reading from the desired date is not open, you may select ***View→Go to date***, and select the appropriate date.

The reading displayed in the results screen is not relevant if you want to delete all readings from a specific date, or all readings before a specific date .

From the results screen, select ***File→Erase Readings.***

A message box will appear prompting you to enter your password. Enter your administrative level password and select **OK**.

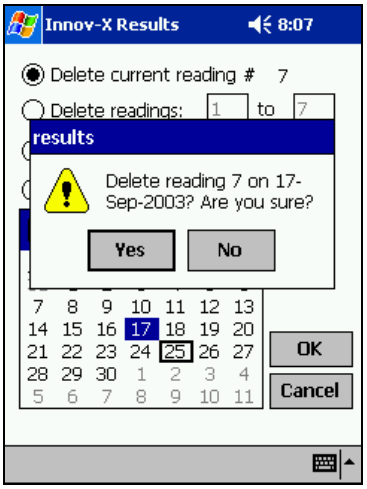


A dialogue box will appear allowing a choice of which results to delete. Select the appropriate choice:

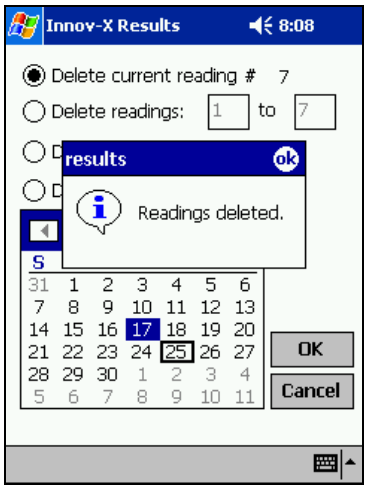
- Selecting **Delete current reading** will delete the reading that is currently open.
- Choosing **Delete readings XX to XX** will delete a range of readings from the date of the reading that is currently open.
- **Delete all readings on date** deletes all readings from a specific day.
- **Delete readings before date** deletes all readings taken prior to a specific day.

If you select **Delete all readings on date** or **Delete readings before date**, you must specify a date from the calendar. The default date is the current date.

When you've selected the readings to delete, Click **OK**. You will be asked if you're sure you want to proceed. If you want to proceed with the data erase, select **Yes**. Otherwise, click **No.**



A message will indicate the readings were successfully deleted. Tap **ok** to acknowledge and clear the message window.



Chapter 5 Soil Analysis

The Innov-X analyzer can be used to analyze in situ (directly on the ground), bagged or prepared soil samples. A guide to Soil analysis using field portable X-ray fluorescence is found in the appendix. This document summarizes EPA Method 6200 which is the standard protocol for field screening. It also provides information on prepared sample testing.

5.0 CHECK STANDARDS

It is recommended that a check standard is measured after each standardization, and periodically throughout the day. Innov-X provides several NIST certified standards for verification. The certified values for these samples are provided in the appendix. At least one standard should be measured for a minimum of 1 minute. Elemental concentrations for elements of interest plus or minus the error on the reading should be within 20% of the standard value. The Field screening guide in the appendix describes in more detail recommended quality assurance considerations.

The standards provided with the XRF analyzer are contained in XRF sample cups with a Mylar window (through which the soil can be viewed) on one side, and a solid cap on the other side. Samples should be measured in the sample cup, through the Mylar window. The best way to measure a prepared sample is using the test stand. If this is not available, the sample may be placed on the ground, and the analyzer may be pointed downwards in full contact with the soil cup. Do not hold the soil cup in your hand while measuring.

5.1 SAMPLE PRESENTATION

In situ testing:

In situ testing is performed by pointing the analyzer at the ground. Any grass or large rocks should be cleared away and the analyzer should be held such that the front of the probe head is held flush to the ground.

Since dirt can accumulate on the analyzer window, it is recommended that the window is wiped clean after each analysis. The window should also be checked to ensure it is not ripped or punctured. Instructions for replacing the window are found in the appendix.

Bagged or prepared sample testing:

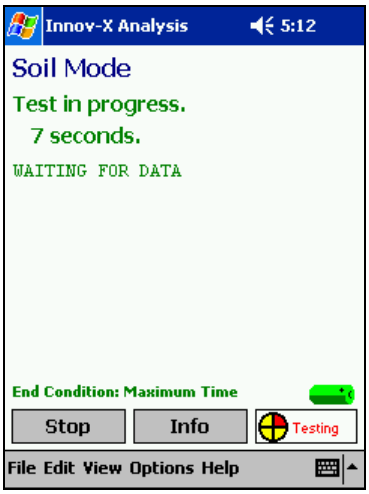
It is strongly recommended that all prepared samples be analyzed in the testing stand. Samples should be placed on top of the testing stand, completely covering the window. **Never hold prepared or bagged samples while testing,** as this could expose the operator to the x-ray beam.

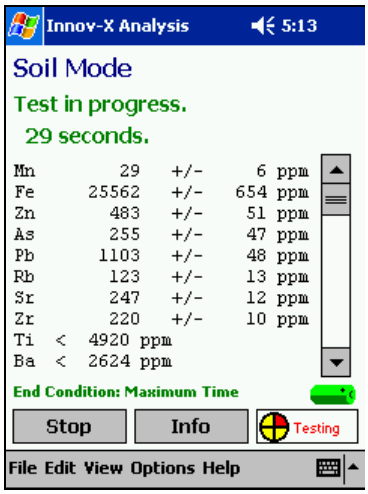
Avoid measuring very thin samples, as this can affect results. Prepare samples cups to contain at least 0.5 inches of packed samples. When analyzing bagged samples, make sure that sufficient sample exists in the bag to completely cover the window with a sample thickness of a minimum of 0.5 inches.

5.2 TESTING IN SOIL MODE

After the instrument has been standardized, testing can begin. Simply pull the trigger or press **Start** on the iPAQ screen to begin the test. The red warning light on the top of the instrument will blink, indicating X-rays are being emitted. The screen will display the words “Test in progress” and the time elapsed. The word “Testing” will blink on and off in the low right hand corner of the screen.

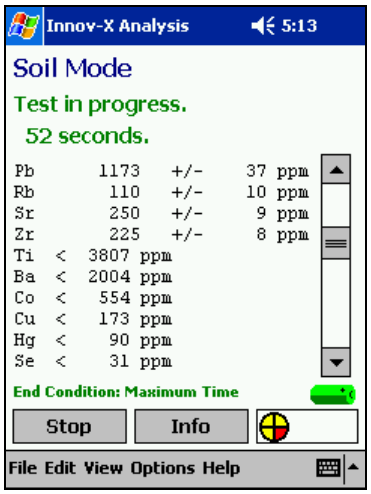
After a minimum time has elapsed, intermediate results will be displayed on the screen. Until this minimum time has elapsed, the words "WAITING FOR DATA" will appear instead. This minimum time can be set by the user by selecting ***Options→Set Testing Times***, which is described in **Section 5.4: Soil Mode Options.** Each line of the results display shows the name of an element, its calculated concentration and the error on the measurement. This error is the 1 sigma error on the counting statistics of the measurement. The error will decrease with increased testing time.





Too many elements are measured in soil mode to display them at one time. However, is possible to use the scroll bar located to the right of the chemistry display to view other elements. The complete display shows detected elements first, listed in order of emission line energy, from lowest to highest. Following the detected elements are the elements which are below the detection limit of the instrument. These elements are shown as less than a calculated LOD. This LOD is defined as three times the error on the counting statistics of the measurement.

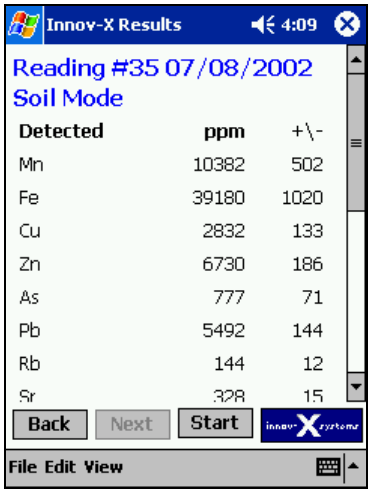
When the measurement is complete the results screen will open, displaying the final results of the measurement.

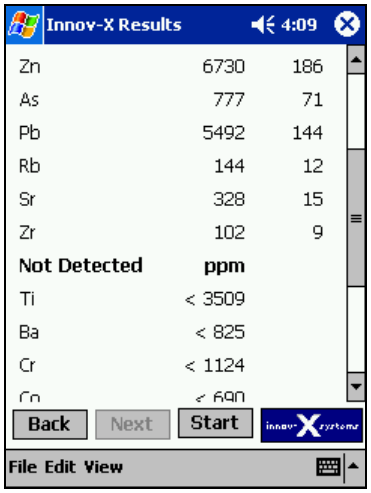


5.3 SOIL RESULTS SCREEN

5.3.1 Results View Menu

The standard Soil Mode results screen displays the concentration (in ppm) and error in measurement for detected elements, followed by the list of non-detected elements with the calculated limit of detection for each element for that test. If the display does not show soil chemistry results, change the display by selecting ***View→Results***.



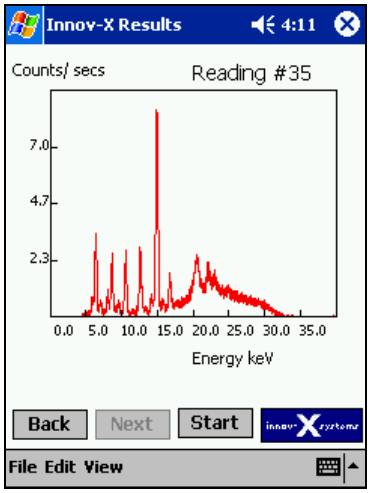


The standard soil chemistry display can be modified by using the View Menu. As with all Innov-X analytical modes, it is possible to view spectra and Test Information.

5.3.2 Spectrum Screen

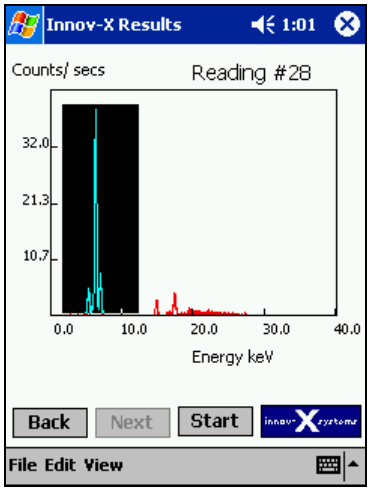
This screen displays a plot of the x-ray fluorescence spectrum for an individual test, plotting the intensity on the y-axis versus the energy of the fluorescence x-rays on the x-axis.

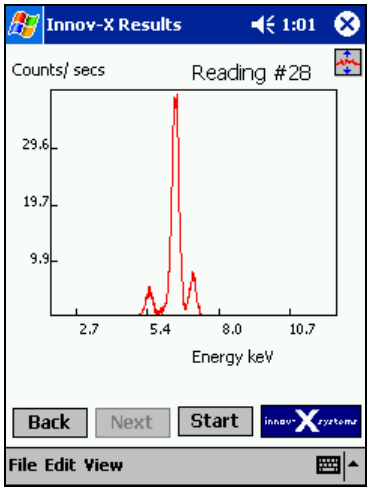
Tapping on the spectra will show the energy scale and counts rate at the selected point



It is possible to zoom in on certain areas of the graph by selecting one corner and drawing out the region

Tapping the symbol in the upper right hand corner beneath the X will restore the graph to full scale.





5.3.3 Test Info Screen

The test information screen shows any test information that was entered prior to the start of the test. Changes to that test information can be made by selecting **Edit→Test Information.**

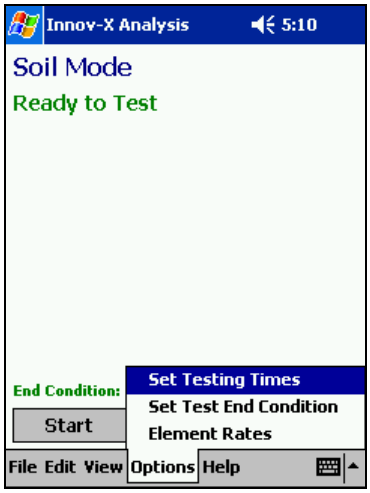
5.4 SOIL MODE OPTIONS

The length of tests in Soil Mode is user settable. Users may select a minimum testing time, and as well as choose from a variety of test end conditions.

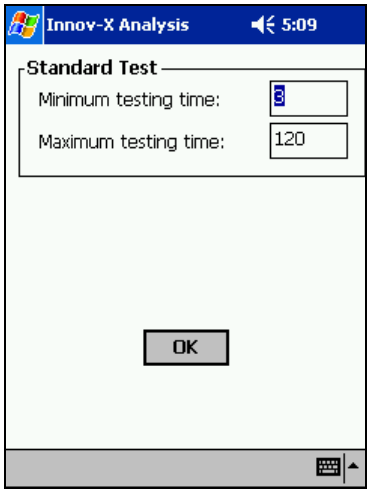
The options related to test time are contained in two menus: ***Options→Set Testing Times***, and ***Options→Set Test End Condition. Set Testing Times*** contains minimum and maximum testing time information, while ***Set Test End Condition*** allows the user to select test end conditions.

5.4.1 Set Testing Times

To set the minimum and maximum test lengths, select **Options→Set Testing Times**



A screen appears prompting you to enter a Minimum and Maximum Testing times. Instruments equipped with the optional LEAP package will be able to set Light Element Testing times in this screen, as well.



The minimum testing time is the required time that must elapse before results can be calculated. Live Update results will not be displayed on the screen until the minimum has elapsed, likewise a test must complete the minimum time before any test end condition can be used. If a test is stopped before the minimum testing time has elapsed, the test will be aborted, and no results will be calculated.

Maximum testing time is relevant only if "Maximum Testing Time" is selected from **Set Test End Condition**. This will automatically end the test at a preset testing time. Typically, the maximum testing time will be in excess of 30 seconds, and may be 1 or 2 minutes, depending on detection limits and desired precision.

It should be noted, that all testing times in this section refer to "Real Time," the time the measurement takes when timed on a normal clock. The time stored with each analytical result (accessible by selecting **View→Test Information** from the Results screen), refers to the test's "Live Time". This is the amount of time that the analyzer hardware was collecting spectra. Since there is some detector dead time associated with a measurement, the live time of a test will be slightly shorter than the preset "Real time".

5.4.2 Soil Mode Test End Condition

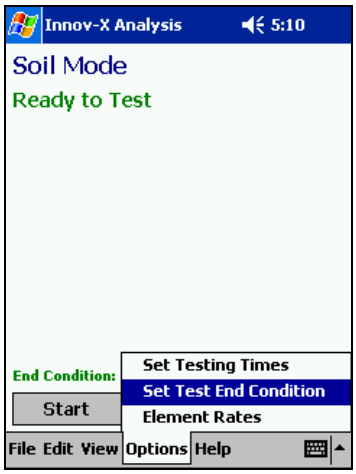
Four options exist for the test end criteria in soil mode. Depending on your application, you may choose to end the test manually, at a preset testing time, or when the uncertainty in the measurement is within a

specified relative standard deviation of the reading. Additionally, you can set up an action level for a single element. As soon as the measuring statistics are good enough to ensure that that the reading is above, below or at the action level, the test will end automatically. This allows for very rapid tests for elements that are well above or below an action level.

In all modes, pressing Stop, or pulling the trigger will end the test. If the minimum testing time has elapsed, results will be calculated. Otherwise the test will be aborted without calculating results.

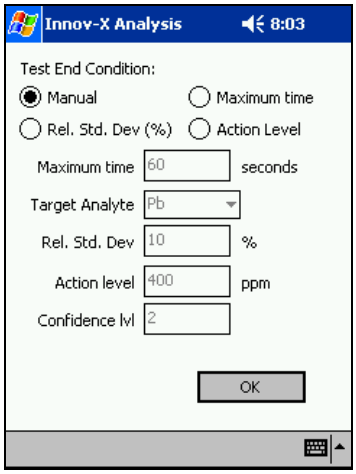
Changes to the test end condition are made by selecting ***Options→Set Test End Condition***

The currently selected end condition will be displayed at the bottom of the screen above the Start button on the Ready To Test screen.



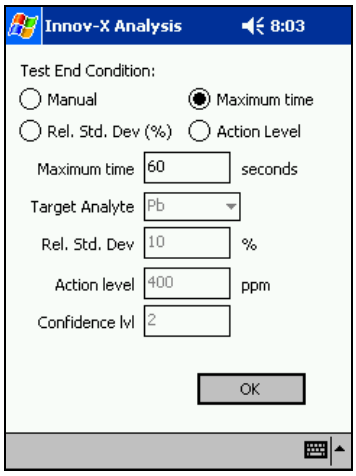
Manual: This option allows you to look at the results which are being continually updated on the screen and determine when the results look satisfactory. The test will continue until the trigger is pulled, or **Stop** is tapped on the iPAQ screen. Results will be calculated if the testing time has exceeded the Minimum Test time which is set up in ***Options→Set Testing Times***. In order to preserve battery life, the software will stop if the testing time exceeds 300 seconds, since there is little to no advantage to continuing a test beyond 300 seconds.

To use Manual Test End Condition, simply choose ***Options→Set Test End Condition*** and select **Manual**. Press **OK** to return to the analysis screen.



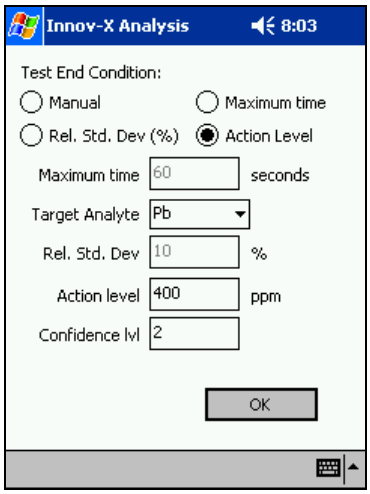
Maximum Time: If Maximum Time is selected, the test will continue until the preset time is reached. This is useful if you wish to do a set of measurements with the same testing time.

To choose to end test based on a maximum time, select ***Options→Set Test End Condition*** and select **Maximum Time**. Enter the desired testing time in the appropriate box. Tap OK to save your selections.



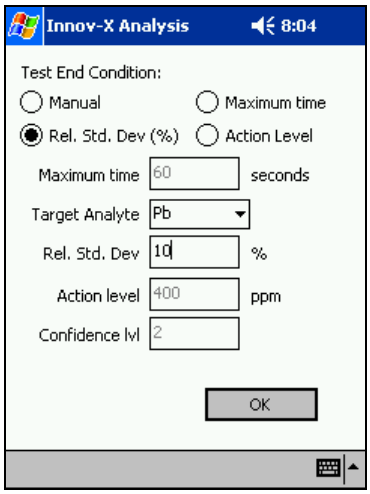
Action Level: System ends test when result for target analyte including chosen precision level is above or below pre-set action level.

To choose to end a test based on an Action Level, select ***Options→Set Test End Condition*** and select **Action Level**. Select a target analyte, specify an action level in ppm, and a confidence level. This confidence level refers to the number of sigma required for the precision. This should typically be set to 2. Tap **OK** to save your selections.



Relative Standard Deviation (RSD): When RSD is selected as a test end criteria, the system will end a test when the relative standard deviation on a target analyte reaches a pre-set level. This standard deviation is specified as a percentage of the reading. For example, if the measured value for an analyte was 1000 ppm, and the RSD was set to 10, the reading would stop when the error reached 100 ppm, or 10% of 1000.

To choose to end a test based on a Relative Standard Deviation, select ***Options→Set Test End Condition*** and select **Rel. Std. Dev (%).** Select a target analyte and the desired Relative Standard Deviation. Tap **OK** to save your selections.



5.5 LEAP Mode (Light Element Analysis Program):

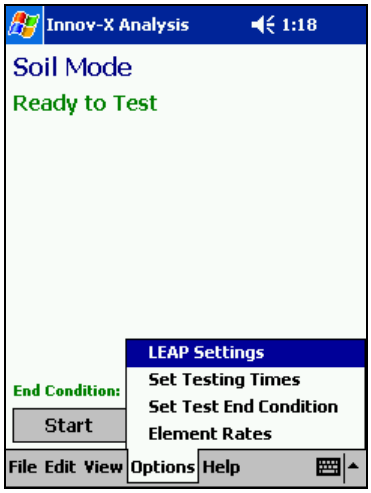
This is a factory installed optional module. Instruments can be upgraded to LEAP capabilities. Please contact the Innov-X Systems Sales department for information and pricing.

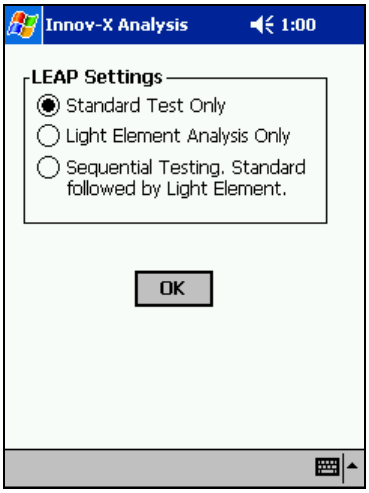
The LEAP module provides the lowest possible detection limits for elements lighter than iron. The standard LEAP package includes the elements Ti, Ba and Cr. Elements as low as Phosphorus can be detected with the Advanced LEAP package which includes a thin window detector.

The standard x-ray beam conditions used by Innov-X environmental analyzers are designed to provide good excitation for a wide range of detected elements. However it is not possible to select one beam condition which provides the absolute best excitation conditions for all elements of interest. Elements such as Chromium produce lower energy x-rays then other elements analyzed. These lower energy x-rays are not as effectively excited by the standard conditions. LEAP works by changing the X-ray tube beam conditions to settings which are optimized for the detection of elements lighter than iron. Instruments are factory calibrated with the LEAP beam conditions for all applicable elements.

5.5.1 LEAP Settings

To activate LEAP, select ***Options→LEAP Settings*** from the Soil analysis screen. This brings up the menu shown below on the right.



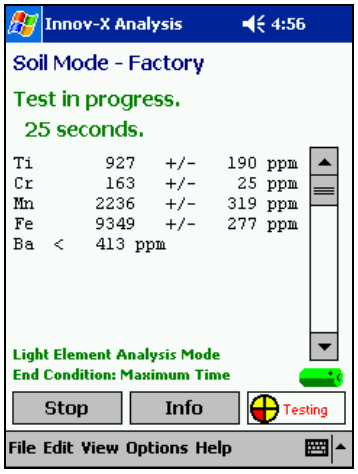


Standard Test Only: The analyzer will provide analysis for the standard suite of elements.

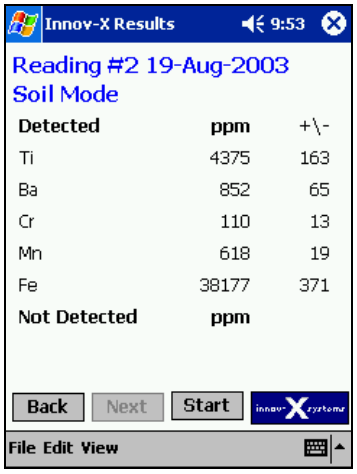
Light Element Analysis Only: The analyzer will provide analysis for elements in the LEAP suite (Typically Ti, Ba and Cr)

Sequential Testing: When sequential testing is selected, all tests will start with an analysis of elements in the standard suite. If that test ends due to reaching the selected end condition of Maximum Test Time, Action Level, or RSD, then the analyzer will immediately begin a second test analyzing the LEAP suite of elements. At the conclusion of this test, the Results screen will open with two new entries. The first summarizes the standard test results, while the second summarizes the LEAP results. For safety reasons, the second test will not begin if the test ends due to user intervention (pulling the trigger or hitting Stop). In this case, the Results screen will open with only one reading.

If Light Element Analysis Only is activated, the words "Light Element Analysis Mode" will appear above the currently selected End Condition. Instrument operation in this mode is identical to Standard (Non-LEAP) analysis. Tests can be started or stopped either by pulling the trigger, or by tapping the Start/Stop button on the iPAQ screen. The results screen for a test will show results for all elements analyzed with the LEAP mode.

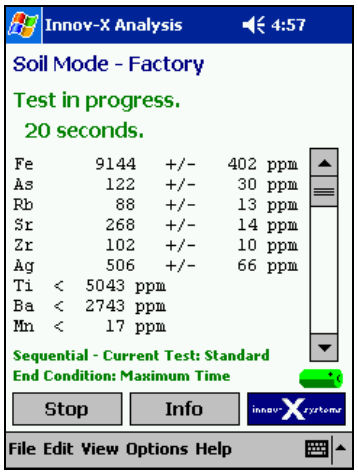


Test in progress screen, LEAP Only, Live Updates on

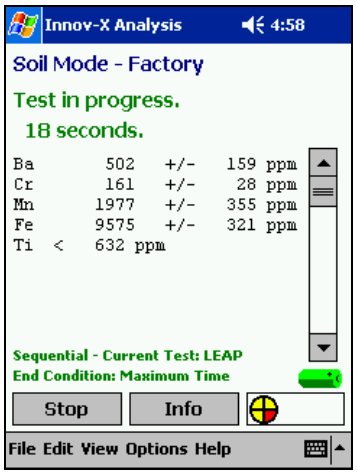


Results Screen Showing LEAP results

If Sequential testing is selected, the words “Sequential – Current Test: Standard” will appear above the currently selected End Condition. When a test is started, the instrument will appear to operate in the same manner as a Standard test. However, if the test ends according to the specified end condition (excluding Manual), the results screen will not open. Instead, the timer will reset to 0, and the description of the current test will change from “Standard” to “LEAP”. The live update screen will begin to show analysis for all LEAP elements.



Test in progress screen, Sequential.
First Test – Standard Analysis.

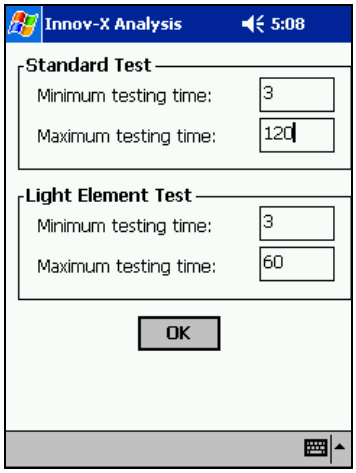


Test in progress screen, Sequential.
Second Test – LEAP Analysis

5.5.2 Testing Times

To set the minimum and maximum test lengths for LEAP analysis, select **Options→Set Testing Times.**

The testing time screen includes an extra section labeled “Light Element Test” that is not found on non-LEAP systems. These are the minimum and maximum test lengths for any LEAP tests.



As with standard tests, the minimum testing time is the required time that must elapse before results can be calculated. Live Update results will not be displayed on the screen until the minimum has elapsed, likewise a test must complete the minimum time before any test end condition can be used. If a test is stopped before the minimum testing time has elapsed, the test will be aborted, and no results will be calculated.

Appendix 1: Troubleshooting Guide—Soil Analysis

Problem	Possible Solutions
Software won't start: Software will not start when the Innov-X Systems Icon is tapped.	The flash card or the iPAQ may not be correctly seated in the black external sleeve. Remove the flash card and press it firmly into its holder. Press the iPAQ down into the black sleeve.
Software won't start: Software doesn't start when the Innov-X System icon is tapped; instead, the following error message occurs: "Cannot find 'startup' (or one of its components). Make sure the path and filename are correct and all the required libraries are available"	The flash card or the iPAQ may not be correctly seated in the black external sleeve. Remove the flash card and press it firmly into its holder. Press the iPAQ down into the black sleeve.
IPAQ locks up: iPAQ screen "locks up" and doesn't respond when screen is tapped or buttons are pressed	Remove the iPAQ from the analyzer and perform a soft reset by pressing the tip of the stylus into the small indentation found on the bottom of the iPAQ. If the iPAQ is lying flat on a table with the screen facing upwards, the reset button is found to the extreme right of the side containing the power plug and connector. See Page 4 of the Compaq "Getting Started" manual for an illustration showing the location of the reset button.

Analyzer will not standardize	Try again. Choose File -> Standardize to attempt a new standardization. Also be sure the standardization cap is on correctly, and that the solid half is in front of the window. It is OK to try this 2-3 times in the event of a failure. If a repeat attempt fails: Change the battery. In some cases the battery may be too low to provide enough power for tube startup. Follow this procedure: Reset the iPAQ; Turn off the analyzer and remove the battery. Verify that the battery is completely charged. If it is not, replace it with a fresh battery. Even if the battery has been recently recharged, remove it, and replace it in the analyzer. Restart the analyzer and software. Wait several minutes after the software has initialized before attempting standardization.
Results screen doesn't show new readings after a test is completed	Check the date on the iPAQ. The Innov-X Systems software indexes stored results by date. If the date is incorrect, results may not be displayed in the correct order.
Serial Communication Error Message: Serial Communication error occurs because iPAQ has been removed from instrument or cradle, with the software open and the instrument standardized.	This error reflects the temporary loss in communications when the iPAQ was removed. To avoid this problem, always use the **File / Exit** command to exit the software properly. Try simply removing and reseating the iPAQ to solve this problem. If that fails, see steps 1 – 4 below.
Serial communication error on startup, or while testing.	1. If the analysis screen is still open, attempt another test. 2. Verify that the iPAQ is correctly seated in the analyzer by removing and replacing it. 3. Remove the iPAQ and perform a soft reset. Replace iPAQ and restart software. 4. Turn the analyzer off and restart it.

Results take a very long time to display on the first test of the day.	There may be too many readings stored in memory. Erase readings from the results screen by selecting ***File → Delete Readings***.
Trigger will not start test.	Verify that the trigger lock is off. Reset the instrument. If this fails, call Innov-X Systems Technical Support at 781-938-5005.
Broken Kapton Window	The window is designed as a barrier to dust and dirt. If it is damaged, it should be replaced. To change the window: Turn off the analyzer Remove the screws holding the front plate in place. Remove the old kapton and adhesive, replace with new kapton and replace front plate. **Important Note:** It is very important to avoid getting dirt and sharp objects within the probe, due to the close proximity of the detector. Do not use the analyzer without a kapton window for any length of time. Also, be very careful when removing/replacing screws in face plate so as to not accidentally damage the detector. If the detector is damaged, the instrument will require factory service.
Results screen shows message "Error in calculation: No Results"	The soil mode calculation is only valid for "soil-like" samples which contain primarily light elements such as carbon, oxygen and silicon. If a dense, highly metallic sample is analyzed, the calculation fails. Make sure the sample being analyzed is a soil sample, if it is and this message occurs repeatedly; call Innov-X technical support.

Appendix 2:

Metals in Soil Analysis Using Field Portable X-ray Fluorescence

A guideline to using portable XRF according to EPA Method 6200, basic overview of the technique of x-ray fluorescence (XRF), appropriate data quality assurance protocols and sample preparation steps for operators analyzing prepared soil samples.

Prepared by:

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January, 2003

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Section 1: Regulatory Status for Field Portable XRF

EPA Reference Method 6200 has been incorporated into SW486 under RCRA, and is now available for field portable XRF analysis of soils and sediments. Please call or email Innov-X Systems for a copy of Method 6200.

Method 6200: Field Portable XRF Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.

Features of this method:

1. It is a field screening method, for analysis of *in-situ* or bagged samples.
2. The method provides basic quality assurance methods, including calibration verification, determination of instrument precision, accuracy and limit of detection.
3. The method recognizes the some XRF instruments do not require site-specific calibrations by the operator, that is, the factory calibration provides appropriate data quality.
4. The method recommends that a minimum of 5-10% of samples tested by XRF be confirmed by an outside laboratory using a total-digestion EPA analytical reference method.

The purpose of EPA Method 6200 is NOT to replace laboratory analysis. There are two primary sources of error in assessing a site for metal concentration: **Analytical error** and **Sampling error**. Analytical error is the error in the analysis of any one sample by whatever technique is used, for example XRF, ICP, or AA. Sampling error arises when too few samples are collected and tested. In this case an incomplete picture of the extent of metals contamination may be obtained. Although any one sample may be analyzed with very high analytical accuracy, measuring too few samples may result in contamination plumes being mis-judged in size, or depth into the soil. In extreme cases contamination may missed entirely.

EPA Method 6200 was developed to reduce Sampling Errors by increasing the number of samples measured. In general, a large number of screening-level measurements provide a better characterization of contamination than a small number of measurements produced by sample removal and analytical analysis. Portable XRF is an ideal tool to make a large quantity of measurements in a short period of time. A large number of in-situ samples provides detailed data on contamination profiles, depth (provided surface soil is moved aside), and approximate contamination levels. Portable XRF also can provide results with a high degree of analytical accuracy on any given sample. Please see Section 2 “Overview of Field Usage” for this discussion.

Section 2: Overview of Field Usage:

Field portable XRF is generally used in three ways to test for metals in soil:

- **In-situ soil testing:** The XRF is placed directly onto the ground for soil testing. Operators remove any plant growth and foreign objects so that the analyzer probe is flush to the soil.
- **Bagged soil sample testing.** A soil sample is collected in a thin plastic bag (i.e. a "Baggie") and testing directly through the Baggie. Except for a few elements – namely Cr, V and Ba – testing through the thin plastic used for a plastic bag has little effect on the test result. Results for Cr, V and Ba will be lower by 20-30%.
- **Prepared soil sample testing.** Prepared sample testing assures the operator of the maximum possible accuracy. Prepared sample tests require a sample to be collected, dried if necessary, sieved and ground into a powder. The prepared sample is then placed into a baggie or XRF cup for analysis. **A complete Soil Preparation Guide is provided in Appendix 1.**

All analytical methods require a uniform, homogenous sample for the best results. **XRF is no different!** The methods described in EPA Method 6200, namely In-situ and bagged sample testing, are considered *field-screening methods*. Although a field-screening method, in-situ testing is a valuable technique because it generates a great deal of data very quickly. Prepared soil samples generally offer the best accuracy, albeit with several minutes of sample preparation required per sample.

Figure 1. Use of a field portable XRF for in-situ soil testing.

Subsection 2-A: Data Quality Objectives.

The objectives of the testing generally determine the mixture of in-situ versus prepared sample testing. It is important to understand your data quality objectives (DQO) in order to determine the appropriate mix of field screening and prepared sample testing.

In-situ testing usually provides only screening-level data quality. This is because analytical testing always requires a uniform, homogeneous sample matrix. A laboratory achieves this by digesting the sample into a hot acid before analysis. Testing directly on the ground does not ensure uniformity is met. Preparing a sample provides a uniform sample and likely better analytical data quality, although several minutes of testing time is required.

Most portable XRF operators use a mixture of in-situ and prepared sample testing. Several examples are described below. The exact mixture of in-situ and prepared sample testing depends upon the goals of the soil testing. The examples below serve as guidelines. Please contact Innov-X (1-866-4 Innov-X or 866-446-6689) to discuss your specific testing requirements.

Example 1: Initial site investigation to provide detailed contamination data with efficient use of laboratory analysis costs.

Problem: Site needs to be assessed for metals contamination. Little information is available about what metals are present, likely contamination levels or geographic profile of contamination.

The goal of testing is to determine what metals are present at what levels, both in area and in depth into soil. Additionally, testing will locate possible contamination plumes and/or possible sources of contamination.

Recommended Testing Plan: This example uses predominately in-situ testing. The analyst will perform in-situ testing, and gather samples into plastic bags for XRF analysis. A testing grid should be established in two or three dimensions, every several feet. XRF tests can be taken at each location or bagged samples can be collected from each location for later analysis. The in-situ data for each element analyzed may be plotted in a 2-dimensional grid (X, Y coordinates versus elemental concentration) to profile a site. These concentration profiles are ideal for showing contamination patterns, boundaries and plumes. Combining this data with historical use data from the site often allows the operator to deduce sources of contamination. Obtaining this level of geographic data with purely laboratory analysis would produce excessive analytical costs.

Prepared sample analysis should also be done to confirm the regions where in-situ data indicates low or non-detected levels of metal contaminant. There is little need to prepare areas where in-situ testing indicates high concentration levels. Innov-X recommends the same procedure as EPA Method 6200. For locations where in-situ tested indicate low or non-detected concentrations, calculate the total number of in-situ tests, collect 5% of this number of tests from the various locations, and prepare these samples according to Appendix 1. Use these prepared samples to confirm the findings of the in-situ testing. Send a subset of these prepared samples to a laboratory for confirmatory results.

Cost Justification. To adequately characterize a site may require 100-200 samples/acre to be sure the contaminated areas are firmly established. This work may be done with in-situ testing to generate laboratory savings of $5,000 - $10,000/acre depending upon the number of elements being analyzed. The cost reduction in off-site analysis often justifies the price of the XRF.

Example 2: Monitor remediation efforts and assure site meets clearance levels before contractors leave the site.

Goal: Minimize remediation costs by only treating contaminated soil, and obtain immediate verification that various site locations meet clearance objectives.

Recommended Testing Plan: This type of project uses a lot of both in-situ and prepared sample testing. Use in-situ testing to thoroughly delineate contamination regions in both area and depth. To determine depth profiles, test surface soil, remove at least 1-2 inches, and retest. Repeat this step as necessary to profile contamination depth to guide remediation activities. (XRF is a surface technique and only analysis the first few mm of soil sample). As part of clearance, collect several samples from "cleared" area. Prepare samples according to Appendix 1 and test with portable XRF.

If XRF indicates that concentration levels are in excess of clearance requirements, then continue remediation efforts.

If XRF indicates that concentration levels are below clearance requirements, then discontinue remediation efforts, and send a subset of the samples to an analytical laboratory to confirm results. Most operators safely assume that the cleanup requirements have been met for the elements in question, but await final analysis from the laboratory.

If XRF lists concentration levels as non-detected, but the detection level reported exceeds clearance requirements, send samples to a laboratory for final results.

Cost Justification: In-situ results are used to guide remediation efforts, in order to obtain maximum efficiency. Efficiency is produced because contamination boundaries are firmly established, thus avoiding remediation efforts with "clean" soil. Prepared sample testing is used to assure that clearance requirements are met on-site in near real-time (pending laboratory confirmation). Costs savings are generated by avoiding clearance failures. The contractors can leave the site earlier and will not be called back to the site for additional cleanup.

Important Note: Never clear a site based solely on in-situ testing. Always use well-prepared samples to make a clearance decision.

Example 3: Minimize volume of hazardous waste for treatment or disposal.

Goal: For some cleanup projects, the cost of soil disposal in a hazardous waste landfill is much greater than disposal in a standard landfill. Testing soil samples with XRF may minimize the amount of "clean" soil that is inadvertently shipped to a hazardous-waste landfill.

Recommended Testing Plan: This example is almost entirely prepared sample testing. Representative samples are removed from the soil being hauled to landfill. Obtaining an accurate analysis of the samples is crucial for making a hazardous versus non-hazardous determination. For this reason, prepared sample testing is strongly recommended.

Important Note: These types of samples are subject to TCLP procedures for the landfill determination. In general, 20 times the XRF result should be less than the allowable limit for the metal in question. Please contact Innov-X Systems for more details on testing samples versus TCLP regulatory requirements.

Section 3: Quality Assurance.

Quality assurance is detailed for both the proper use of the analyzer (which is also provided in Method 6200) and for verifying the data quality of in-situ testing. All operators should perform the QC procedure, regardless of their data quality objectives. Method 6200 has strict requirements about quality assurance. Additionally, Innov-X recommends that operators verify the data quality of in-situ test results, if they are using in-situ data to guide their reporting or remediation decisions. Procedures are listed below:

3.1: Proper verification of instrument operation

These procedures are taken from EPA Method 6200 and updated to be specific to the Innov-X analyzer. Quality assurance here consists of testing known standards to verify calibration, as well as testing blank standards to determine limits of detection and to check for sample cross-contamination or instrument contamination. EPA Method 6200 provides a detailed procedure, which is provided here in abbreviated form.

Components of instrument QC:

1. An energy calibration check sample at least twice daily
2. An instrument blank for every 20 environmental samples
3. A method blank for every 20 prepared samples
4. A calibration verification check sample for every 20 samples
5. A precision sample at least one per day.
6. A confirmatory sample for every 10 environmental samples

Energy Calibration Check: The Innov-X analyzer performs this automatically; this is the purpose of the standardization check when the analyzer is started. The software does not allow the analyzer to be used if the standardization is not completed.

Instrument Blank: The operator should use the SiO_2 (silicon dioxide) blank provided with the analyzer. The purpose of this test is to verify there is no contamination on the analyzer window or other component that is "seen" by the x-rays. Method 6200 recommends an instrument blank at least once per day, preferably every 20 samples. For either in-situ or prepared-sample testing, the operator should just test the SiO_2 blank to be sure there are no reported contaminant metals.

Method Blank: The purpose of the method blank is to verify that cross-contamination is not introduced into samples during the sample preparation process. Method 6200 recommends following the sample preparation procedures with clean SiO_2 once very 20 prepared samples. This QC step is not required if the operator is not preparing samples.

Calibration Verification: Innov-X provides NIST standard reference samples for calibration check by operator. The operator should perform a 2-minute test on a NIST standard. The difference between the XRF result for an element and the value of the standard should be 20% or less. Calibration Verification should be performed upon instrument startup and periodically during testing. Note: Innov-X recommends a calibration check every 4 hours. EPA Method 6200 recommends a calibration check every 20 samples NIST reference standards are generally applicable for Pb, As, Cr, Cu, Zn. Innov-X provides additional reference standards for other RCRA or Priority Pollutant metals including Cd, Se, Ag, Hg, Ag, Ba, Sn, Sb, and Ni.

Precision Verification: Quoting from EPA "A minimum of one precision sample should be run per day by conducting from 7 to 10 replicate measurements of the sample. The precision is assessed by calculating a relative standard deviation (RSD) of the replicate measurements for the analyte. The RSD values should be less than 20 percent for most analytes, except chromium, for which the value should be less than 30 percent.

Confirmatory Sample: It is recommended that one confirmatory sample is run for every 10 samples collected. According to EPA Method 6200: "Confirmatory samples are collected from the same sample material that is analyzed on site, but are sent to an off-site laboratory for formal analysis. The purpose of a confirmatory sample is to judge the accuracy of the data obtained by analysis on site and to allow corrections, if necessary."

Important Notes about confirmatory samples:

Innov-X always recommends that customers compare prepared-sample results to laboratory results. To do this, collect and prepare a sample following the protocols of Appendix 1. Take a subsample and submit to the laboratory for analysis. The single largest error in XRF analysis is lack of sample preparation. For the best comparison, always use prepared samples.

3.2: Determining data quality of in-situ testing:

For operators relying extensively on in-situ testing, it is important to determine the data quality of this testing at a given site. *This protocol is not intended for every sample, but rather for a small percentage of samples considered representative of the site.* If the operator can demonstrate that quantitative data is achieved with little or no sample preparation, then the site characterization will be completed much more quickly but correctly.

For example, an operator may be able to demonstrate that the XRF result changes considerably when samples are passed through a 2 mm sieve, but that XRF results do NOT change appreciably upon finer sieving. In this case the operator can conclude that good XRF data is achievable with only 2 mm sieving. Sieving only to this level requires far less time than a more robust sample preparation. A protocol to determine the appropriate level of sample preparation is the following:

1. Delineate a region of soil approximately 4" x 4".
2. Perform several in-situ tests in this area, or collect the top (approximately) quarter inch of soil from this region, bag the soil, test through the bag. In either case, average the results.
3. If you did not bag the in-situ test sample, collect the top (approximately) quarter inch of soil from this region and sieve through the 2 mm sieve provided. Otherwise sieve the bagged sample used for the in-situ test. Thoroughly mix the sieved sample, and place some of the sieved material into an XRF cup, and perform a test of this sample.
4. If the results of this prepared sample differ less than 20% with the average in-situ result, this indicates the soil in this region is reasonably homogeneous. The data quality in this case is probably at the semi-quantitative level, rather than just screening data.
5. If the results differ by more than 20%, this indicates the soil is not very homogeneous, and there are serious particle size effects affecting your in-situ measurements.
6. In this case, sieve the sample through the 250 ~m sieve. Mix this sample and place a sub-sample into an XRF cup for testing. If this result differs from the previous by less than 20% then this indicates that at a minimum the 2mm sieving is necessary to achieve higher data quality.

7. If this result differs by more than 20% from the sample sieved through 2 mm, then particle size effects are still affecting the XRF result. In this case samples should be sieved through 125 µm to assure data quality at the quantitative level.

Section 4: Calibration for Innov-X Portable XRF

The Innov-X analyzer may run three different calibration methods, described below. In nearly all cases, customers use the Compton Normalization method. This method (recognized in EPA 6200) offers speed, ease of use, and generally good accuracy for concentration ranges from the ppm level up to 2-3% concentrations. As most field-testing is seeking to remediate or locate environmental contaminants, the upper limit of the calibration (2-3%) is generally not a limitation. If customers do require a calibration up to 100% concentration (i.e. a pure element) then Innov-X recommends they also include the Fundamental Parameters (FP) software module with the analyzer. The FP module may be added at time of purchase or as an upgrade at any later date.

Note: In general customers do not need to calibrate the Innov-X analyzer for soil testing. The analyzer is delivered with a factory calibration, generally based upon the Compton Normalization (CN) method. The CN method has been proven over the past several years to provide a robust calibration generally independent of site-specific soil matrix chemistry. The operator may calibrate the Innov-X system if desired, but calibration is not required to use the analyzer effectively. All customers should follow the QC procedure described in Section 3, which includes a check of the calibration.

The final model is the empirical calibration. In this case, customers run standards to generate calibration curves for various elements in specific soil matrices. Provided the sample is well-prepared, the empirical method generally yields the most accurate result. In our experience, the accuracy gains going from Compton Normalization to Empirical Mode are small and not worth the extra effort in setting up calibration curves. (The greatest source of error for in-field XRF analysis of soil is lack of adequate sample preparation, thus there is little gained in developing a sophisticated empirical calibration if the operator does to grind and homogenize the all measured samples). The empirical calibration module is an optional software package, available for an upgrade fee at the time of purchase, or as an upgrade at any later date.

Calibration Requirements:

The concentration of an element in a soil sample is well-described by the formula:

$$w_i = \frac{k_i}{M(Z,i)} I_i$$

k_i = calibration constant for element "i"

ω_i = concentration of element "i" – the quantity being measured.

I_i = measured x-ray intensity from element "i"

M(Z,I) = Soil matrix value

The factory calibration determines the value of the calibration constants k_i for each element, and a typical value M(Z,I). The calibration method – either CN, fundamental parameters, or empirical – performs the necessary corrections to the value M(Z,I) that are important for the site-specific soil chemistry. The XRF analyzer uses the measured intensity of each element's fluorescence from the sample, and the calibration data, to produce elemental concentrations.

Compton Normalization:

The Compton Normalization method calibration consists of the analysis of a single, well-characterized standard, such as an SRM or SSCS. The standard data are normalized to the Compton peak. The Compton peak is produced from incoherent backscattering of X-ray radiation from the excitation source and is present in the spectrum of every sample. The matrix affects the way in which source radiation is scattered off the samples. This scatter is directly related to the intensity of the Compton peak. For that reason, normalizing to the Compton peak can reduce problems with matrix effects that vary among samples. Compton normalization is similar to the use of internal standards in analysis for organic analytes.

Fundamental Parameters Calibration:

The fundamental parameters (FP) calibration is a "standardless" calibration. Rather than establishing a unit's calibration curve by measuring its response to standards that contain analytes of known concentrations, FP calibration relies on the known physics of the spectrometer's response to pure elements to set the calibration. Built-in mathematical algorithms are used to adjust the calibration for analysis of soil samples and to compensate for the effects of the soil matrix. The FP calibration is performed by the manufacturer, but the analyst can adjust the calibration curves (slope and y-intercept) on the bases of results of analyses of check samples, such as SRMs which are analyzed in the field.

Empirical Calibration:

The empirical calibration method requires that a number of site-specific calibration standards (SSCS) are used to establish calibration parameters. The instrument response to known analytes is measured and used to create calibration curves. Empirical calibration is effective because the samples used closely match the sample matrix. SSCSs are well-prepared samples collected from the site of interest in which the concentrations of analytes have been determined by inductively coupled plasma (ICP), atomic absorption (AA), or other methods approved by the US Environmental Protection Agency (EPA). The standards should contain all the analytes of interest and interfering analytes. Manufacturers recommend that 10 to 20 calibration samples be used to generate a calibration curve. The empirical method is the least desirable calibration method as it requires that new standards and curves are generated for each site that is analyzed.

Section 5: Effects of Moisture on XRF Results:

Sample moisture has two effects on XRF results:

- It alters the soil chemistry, since water is another chemical compound that comprises the soil matrix.
- Moisture impedes the ability to properly prepare samples.

- Laboratory results are provided on a "dry weight" basis.

Effect on Soil Chemistry:

While the presence of significant moisture does impact the soil chemistry, modern XRF analyzers all perform automatic corrections for variations in soil chemistry from site to site. Indeed, such variations are expected, and that is the reason analyzers use Compton Normalization or fundamental parameters, in order to correct for moisture content changes as well as other differences in soil geochemistry.

EPA Method 6200 states "Moisture content above 20 percent may cause problems, since moisture alters the soil matrix for which the FPXRF has been calibrated." However, the Compton Normalization or fundamental parameters methods are implemented in order to automatically correct results for changes to the soil matrix. Thus, we believe that soil moisture is not a significant effect on accuracy due to effects of soil matrix, except for the "dilution" effect that can cause discrepancies with laboratory results which is described below.

Sample preparation issues:

The inability to adequately prepare a wet sample is, we believe, the single biggest contributor to errors when testing wet samples. It is very difficult to grind or sieve a wet sample. The highest quality XRF results are generally obtained from prepared samples. If the operator is unwilling to dry the sample to prepare it, comparisons to the laboratory may yield poorer correlation since the samples are not homogeneous.

Laboratory Tests on Dry-Weigh Basis:

Laboratories always dry samples prior to analysis. They report percent weight content based upon a dry sample basis. Portable XRF may often be used to analyze wet samples in the field, and results are thus reported that include the moisture content. Thus, with all other factors the same, the laboratory will report results higher than portable XRF. The results will be higher by the amount of moisture content in the sample. For example laboratory results will be 10% higher compared to XRF results, if the sample contained 10% by weight water when it was tested with XRF. Recall, this applies to samples where other possible sources of error are the same or negligible.

Section 6: Comparing XRF Results to Laboratory Results:

Innov-X strongly recommends that operators compare prepared sample results to laboratory results. This is because prepared-sample results yield the best possible accuracy with portable XRF. Moreover, the most common source of error is due to non-uniform samples. The XRF technique, nor can any analytical technique, properly account for non-uniform sample types.

To perform a comparison between XRF results and laboratory:

1. Collect a sample and prepare it according to the sample preparation guide in Appendix 1.

2. Take a sub-sample (5-10 grams) of the fully-prepared sample, place it into an XRF cup and perform at least a one-minute test on that sample.

3. Send the same sample to the laboratory for wet chemistry analysis.

4. Require the laboratory to use a total-digestion method. If the laboratory does not use a total digestion method, they may not extract all of the elemental metal from the sample. In this case, the lab result will be lower than the XRF result. Incomplete sample digestion is one of the most commons sources of laboratory error, thus it is very important to request a total digestion method.

Example of Error: The operator collects a bag of sample, performs XRF analysis on one part of the bag, and sends the bag, or part of the bag of sample to a laboratory for analysis. The laboratory reports a very different value than the operator obtained with the XRF.

Problem: Since the sample is very non-homogeneous, the operator did not obtain a result that was representative of the entire bag of sample. The lab analyzed a different part of the sample and obtained a very different result due to the non-uniformity of the sample. The solution to this problem is, at a minimum, to test several locations in the bag of sample and report the average value. Also note the differences between the tests, as this is indicative of the non-uniformity of the sample. Operator should send entire bag of sample to the lab, and instruct lab to prepare the sample before removing sub-sample for lab analysis.

Best Practice: The operator should homogenize and prepare the entire bag of sample, and then collect a sub sample for XRF testing. After testing, the same sample should be sent to the lab.

Section 7: Common Interferences:

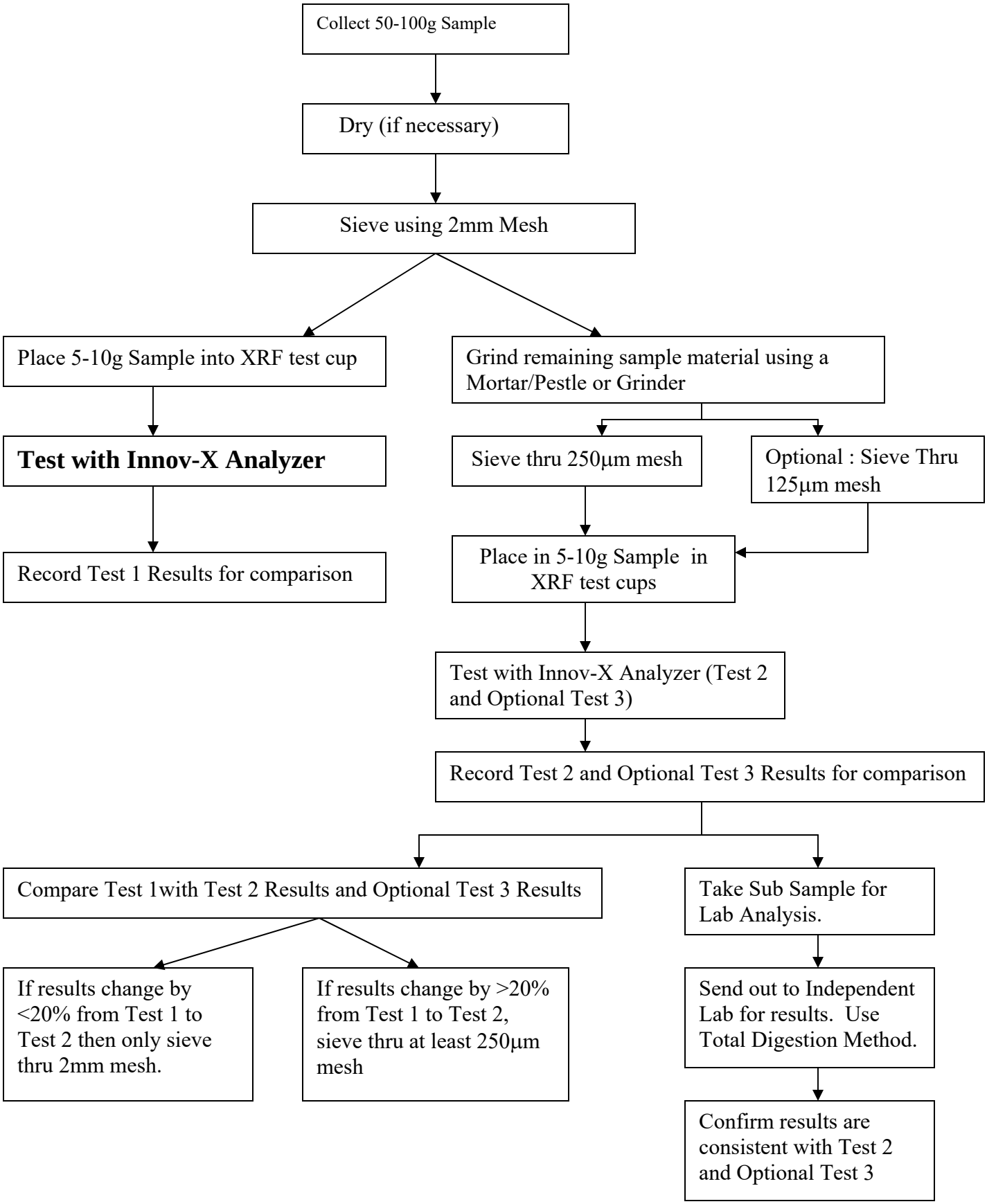
An interference occurs when the spectral peak from one element overlaps either partially or completely with the spectral peak of another. If the XRF is calibrated for both elements (CASE 1) i.e. the one causing the interference and the one being interfered with, it is generally capable of correctly handling the interference. In this case, the element being interfered with may be measured with a poorer detection limit or poorer precision, but the analytical results should still be acceptable for field-portable XRF. If the XRF is not calibrated for the element causing the interference (CASE 2), then the XRF may report the presence of elements not in the sample, or greatly elevated concentrations of elements in or not in the sample.

Example CASE 1: Lead and arsenic. Most XRFs are calibrated for lead and arsenic. Lead interferes with arsenic (not vice-versa though). The net effect is a worsened detection limit for arsenic, and poorer precision. The XRF handles the correction automatically, but the precision is affected. The loss of precision is also reported by the XRF. (Please refer to Innov-X Applications Sheet: *In-field Analysis of Lead and Arsenic in Soil Using Portable XRF* for more detail).

Example CASE 2: Bromine in the sample, but XRF is not calibrated for bromine. Bromine, as a fire retardant, is being seen more and more in soil and other sample types. For this reason, Innov-X analyzers include Br in the calibration data. If Br is not calibrated, but is present in the sample, the analyzer will report highly elevated levels of Pb, Hg and As. The levels will depend upon the concentration of Br in the sample.

Interferences between elements can be broadly categorized into a) Z, Z-1, Z+1 interferences, and b) K/L interferences. Interference type "a" occurs when high levels of an element of atomic number Z are present. This can cause elevated levels of elements with atomic number Z-1 or Z+1. Generally, portable XRFs have good correction methods, so this interference only causes problems with very high levels of the element in question. Example: High concentrations of Fe (Z=26) in excess of 10% may cause elevated levels of Mn or Co (Z=25 or Z=27 respectively).

The type "b" interference occurs when the L-shell line of one element overlaps with the K-shell spectral line of another element. The most common example is the lead/arsenic interference where the L-alpha line of lead is in nearly the exact same location as the K-alpha line of arsenic.


Collect 50-100g Sample
Dry (if necessary)
Sieve using 2mm Mesh
Place 5-10g Sample into XRF test cup
Test with Innov-X Analyzer
Record Test 1 Results for comparison
Grind remaining sample material using a Mortar/Pestle or Grinder
Sieve thru 250µm mesh
Optional : Sieve Thru 125µm mesh
Place in 5-10g Sample in XRF test cups
Test with Innov-X Analyzer (Test 2 and Optional Test 3)
Record Test 2 and Optional Test 3 Results for comparison
Compare Test 1with Test 2 Results and Optional Test 3 Results
If results change by <20% from Test 1 to Test 2 then only sieve thru 2mm mesh.
If results change by >20% from Test 1 to Test 2, sieve thru at least 250µm mesh
Take Sub Sample for Lab Analysis.
Send out to Independent Lab for results. Use Total Digestion Method.
Confirm results are consistent with Test 2 and Optional Test 3

Appendix 3: Guide to Product Registration

Generally, the Innov-X portable XRF system must be registered in the state of usage. Registration requirements are somewhat state dependent, but there are many similarities. You may contact Innov-X at 866-4-Innov-X (781-938-5005) to receive specific registration information. Innov-X also maintains sample registrations for every state that we can forward to you.

Common Registration Features:

Most states require the following for registering an x-ray emitting device that does NOT use radioactive sources:

1. Registration within 30 days of receipt of the analyzer.
2. Annual fee ranging from $25 to $100, depending upon the state.
3. Basic registration form with main information described below.

Common information required on Registration Form, and responses:

Company name, address, phone/fax numbers.

Name of responsible person:	Generally the person designated as the Radiation Safety Officer (RSO).
Name of the manufacturer:	Innov-X Systems, Inc., Woburn, MA
Model of Analyzer:	Alpha XXXX
Tube Operating Parameters:	40 kV, 20 uA current.
Type of Analysis:	Choose Analytical or Industrial
	(as opposed to radiography, medical, dental, veterinarian, etc.)
Utilization Mode:	Portable or Mobile assuming you will carry system to different locations.
	Fixed or stationary ONLY if you will always use the analyzer in the docking station

General Appendix 1

Technical Specifications

Description:

Innov-X Systems analyzers are hand-held, battery operated energy dispersive x-ray fluorescence analyzers. They are utilized for the detection and quantification of elements ranging from phosphorus (atomic number 15) though uranium (atomic number 92). Measurable concentrations of elements range from ppm to 100%.

Weight:	2.625 lbs (Base wt.) 3.375 lbs (1.6 kg) with batteries
Excitation Source:	X-ray tube, Ag or W anode, 10-40 kV, 5-50 uA, 5 filter positions
Detector:	Si PiN diode, thermoelectrically cooled, resolution < 280 eV.
Power:	Li-ion batteries, or AC power with Testing Stand
Battery Life:	4-8 hours, depending on duty cycle.
Display:	Color, high-resolution touch screen with variable backlighting on analyzer. Software available for PC/laptop operation also.
Data Storage:	10,000 tests with spectra minimum, expandable to 100,000+ with 1 Gb flash card.
Computer:	HP iPAQ with Intel processor, 64 Mb minimum memory, Windows CE operating system (unless operated from PC).
Optional Accessories:	Bluetooth wireless printing and data transfer, integrated bar-code reader, wireless LAN, other standard PDA accessories.

Operating Conditions

Temp 0 – 40° C
Humidity 10 – 90 % RH, no condensation
Altitude rating 2000 meters

Innov-X Analyzer Limited Warranty

General Terms

EXCEPT AS EXPRESSLY SET FORTH IN THIS LIMITED WARRANTY, INNOV-X SYSTEMS, INC. (INNOV-X) MAKES NO OTHER WARRANTIES OR CONDITIONS, EXPRESSED OR IMPLIED, INCLUDING ANY IMPLIED WARRANTIES OF MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE. INNOV-X EXPRESSLY DISCLAIMS ALL WARRANTIES AND CONDITIONS NOT STATED IN THIS LIMITED WARRANTY. ANY IMPLIED WARRANTIES THAT MAY BE IMPOSED BY LAW ARE LIMITED IN DURATION TO THE LIMITED WARRANTY PERIOD.

This Limited Warranty applies to Innov-X analyzers sold or leased from Innov-X its affiliates, authorized resellers, or country distributors (collectively referred to in this Limited Warranty as (“Innov-X”)).

Innov-X warrants that the analyzer and all its internal components that you have purchased are free from defects in materials or workmanship under normal use during the Limited Warranty Period. The Limited Warranty Period starts on the date of shipment by Innov-X. You may be required to provide proof of purchase or lease as a condition of receiving warranty service. You are entitled to warranty service according to the terms and conditions of this document if a repair to your Innov-X analyzer is required within the Limited Warranty Period.

During the Limited Warranty Period, Innov-X will repair or replace the defective component parts. All component parts removed under this Limited Warranty become the property of Innov-X. In the unlikely event that your Innov-X analyzer has a recurring failure, Innov-X, at its discretion, may elect to provide you with a replacement unit of Innov-X’s choosing that is at least equivalent to your Innov-X analyzer. This is your exclusive remedy for defective products. The repaired or replacement analyzer is warranted for the remainder of the limited Warranty Period.

YOU SHOULD MAKE PERIODIC BACKUP COPIES OF THE DATA STORED ON YOUR ANALYZER AS A PRECAUTION AGAINST POSSIBLE FAILURES, ALTERATION, OR LOSS OF THE DATA. BEFORE RETURNING ANY UNIT FOR SERVICE, BE SURE TO BACK UP DATA AND REMOVE ANY CONFIDENTIAL, PROPRIETARY, OR PERSONAL INFORMATION. INNOV-X IS NOT RESPONSIBLE FOR DAMAGE TO OR LOSS OF ANY PROGRAMS, OR DATA. INNOV-X IS NOT RESPONSIBLE FOR THE RESTORATION OR REINSTALLATION OF ANY PROGRAMS OR DATA OTHER THAN SOFTWARE INSTALLED BY INNOV-X WHEN THE ANALYZER IS MANUFACTURED.

Innov-X does not warrant that the operation of this analyzer will be uninterrupted or error-free. Innov-X is not responsible for damage that occurs as a result of your failure to follow the instructions that came with the Innov-X analyzer.

This Limited Warranty does not apply to expendable parts. This Limited Warranty does not extend to any analyzer from which the serial number has been removed or that has been damaged or rendered defective (A) as a result of accident, misuse, abuse, or other external causes; (b) by operation outside the usage parameters stated in user documentation that shipped with the product; (c) by modification or service by anyone other than (i) Innov-X, or(ii) a Innov-X authorized service provider, (d) installation of software not approved by Innov-X.

These terms and conditions constitute the complete and exclusive warranty agreement between you and Innov-X regarding the Innov-X analyzer you have purchased or leased. These terms and conditions supersede any prior agreements or representations --- including representations made in Innov-X sales literature or advice given to you by Innov-X or any agent or employee of Innov-X --- that may have been made in connection with your purchase or lease of the Innov-X analyzer. No change to the conditions of this Limited Warranty is valid unless it is made in writing and signed by an authorized representative of Innov-X.

Limitation of Liability

IF YOUR INNOV-X ANALYZER FAILS TO WORK AS WARRANTED ABOVE, YOUR SOLE AND EXCLUSIVE REMEDY SHALL BE REPAIR OR REPLACEMENT. INNOV-X'S MAXIMUM LIABILITY UNDER THIS LIMITED WARRANTY IS EXPRESSLY LIMITED TO THE LESSER OF THE PRICE YOU HAVE PAID FOR THE ANALYZER OR THE COST OF REPAIR OR REPLACEMENT OF ANY COMPONENTS THAT MALFUNCTION IN CONDITION OF NORMAL USE.

INNOV-X IS NOT LIABLE FOR ANY DAMAGE CAUSED BY THE PRODUCT OR THE FAILURE OF THE PRODUCT TO PERFORM INCLUDING ANY LOST PROFITS OR SAVINGS OR SPECIAL, INCIDENTAL, OR CONSEQUENTIAL DAMAGES. INNOV-X IS NOT LIABLE FOR ANY CLAIM MADE BY A THIRD PARTY OR MADE BY YOU FOR A THIRD PARTY.

THIS LIMITATION OF LIABILITY APPLIES WHETHER DAMAGE ARE SOUGHT, OR A CLAIM MADE, UNDER THIS LIMITED WARRATNY OR AS A TORT CLAIM (INCLUDING NEGLIGENCE AND STRICT PRODUCT LIABILITY), A CONTRACT CLAIM, OR ANY OTHER CLAIM. THIS LIMITATION OF LIABILITY CANNOT BE WAIVED OR AMENDED BY ANY PERSON. THIS LIMITATION OF LIABILITY WILL BE EFFECTIVE EVEN IF YOU HAVE ADVISED INNOV-X OR AN AUTHORIZED REPRESENTATIVE OF INNOV-X OF THE POSSIBILITY OF ANY SUCH DAMAGES.

Software

This Limited Warranty does not warrant software products. The Innov-X software installed on your analyzer is covered by the Innov-X Software License.

Warranty Period

The warranty period for a Model XT-245 or Model XT-260 Innov-X analyzer is two years or four thousand hours of use, whichever occurs first. The warranty for all other analyzers is one year or two thousands hours of use whichever occurs first. This warranty does not extend to expendable parts. Extended warranties are available from Innov-X.

Warranty Returns

A Return Material Authorization (RMA) Number must be obtained from the INNOV-X Service Department before any items can be shipped to the factory. Returned goods will not be accepted without an RMA Number. Customer will bear all shipping charges for warranty repairs. All goods returned to the factory for warranty repair should be properly packed to avoid damage and clearly marked with the RMA Number.

Warranty Repairs

Warranty repairs will be done either at the customer's site or at the INNOV-X plant, at our option. All service rendered by INNOV-X will be performed in a professional manner by qualified personnel.

Contacting Innov-X

Be sure to have the following information available before you call Innov-X:

- Analyzer serial number, model name, and model number
- Applicable error messages
- Description of problem
- Detailed questions

Methods of Contact

- Phone: 781-635-5005
- Fax 781-938-0128
- Email service@Innov-Xsys.com
- Mail & Shipping Address: Innov-X Systems, Inc. 10 Gill Street, Suite Q. Woburn MA 01801

APPENDIX D: USERS MANUAL - FROG-4000® – HANDHELD GC/PID

FROG-4000™

Chemical Analysis System

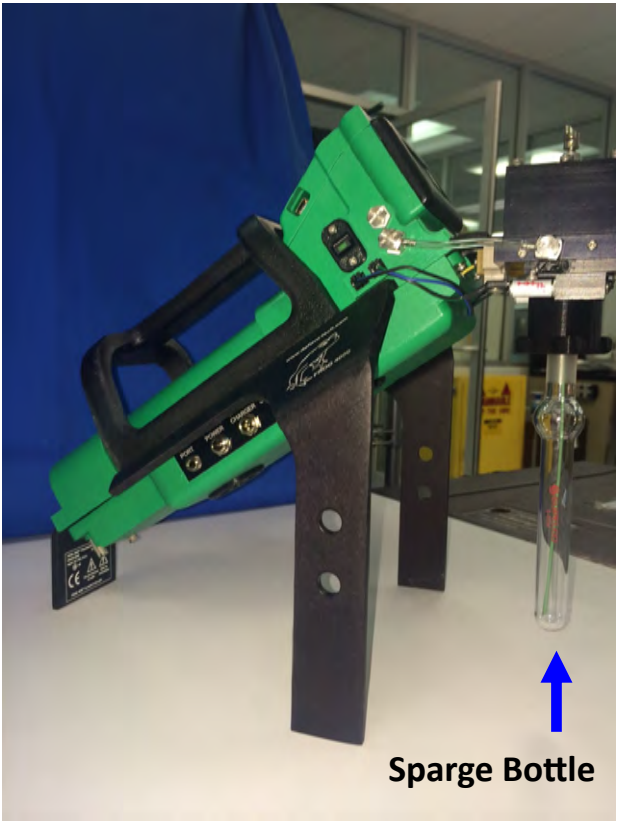
User's Manual

Defiant Technologies, Inc.

2015 Vol.5

FROG-4000™
Chemical Analysis System
User's Manual

Defiant Technologies, Inc.
2015 Vol.5
www.defiant-tech.com


Sparge Bottle

HANDLING INSTRUCTIONS

FROG-4000™ is a robust, portable instrument, which can be operated in a lab setting or out in the field. The internal components of this instrument can be damaged if the unit is abused. The following precautions are given to ensure correct handling of the instrument.

PRECAUTIONS

- **DO NOT** invert with water in the sparge bottle.

  System can NOT analyze a water or soil sample when inverted!

  Permanent damage to instrument is possible!

  (If this does occur, the system may require maintenance. Refer to Section 8, Trouble Shooting)
- **DO NOT** handle or carry system when sample is being analyzed. For the best results, limit movement to before or after sample analysis.
- **DO NOT** transport or store the instrument with liquid in the sparge bottle.

Do NOT invert 90° Angle

Do NOT invert 180° Angle

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COMMONLY USED ACRONYMS

PC: Preconcentrator

PID: Photo Ionization Detector

GC: Gas Chromatograph

VOCs: Volatile Organic Compounds

BTEX: Benzene, Toluene, Ethylbenzene, Xylenes

Ellvin: Defiant's Chromatography Software

FROG-4000™

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SECTION 1: GETTING TO KNOW THE FROG-4000™

1.1 MANUAL OVERVIEW

The FROG-4000™ uses a practical approach to instrument set-up and operations. This manual includes the following:

- An overview of the FROG-4000™ operational systems, components, and features.
- Diagrams illustrating the flow of a sample during loading, sparge, collection and analysis.
- Instructions for using the chromatography software (Ellvin).
- Detailed procedures for using the FROG-4000™.
- Instructions for calibrating the instrument.
- Routine maintenance information.
- Troubleshooting information.

1.2 OPERATIONS OVERVIEW

The FROG-4000™ instrument analyzes air, water or soil to identify volatile organic chemicals (VOCs) present in a sample and determines their concentrations.

The instrument is designed to operate either in the field or in a laboratory, and either connected or not connected to a computer running the Ellvin Software. Data is stored on the user's hard drive when the FROG is attached to a computer. Data is also stored on the FROG's internal memory card and can be imported to a computer later.

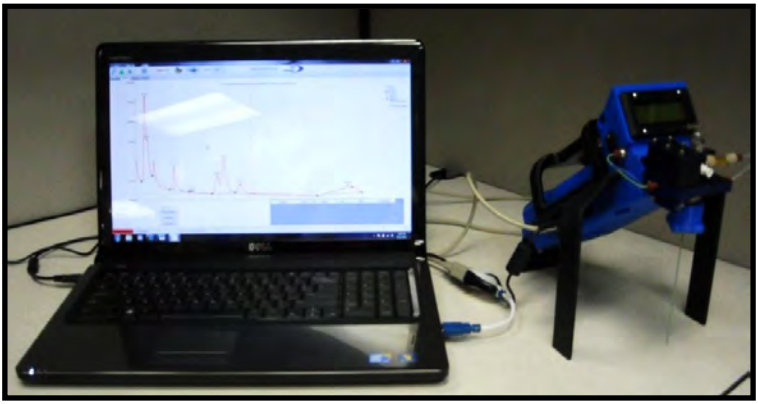
The FROG-4000™ has a 5 mL sample sparger that can be used for water or solid samples. It is good practice to keep the total volume in the sparger at a constant 5 mL. For instance, if the user wishes to dilute a water sample 10 to 1, a sample volume of 0.5 mL would be diluted with 4.5 mL of clean water, resulting in total volume of 5 mL.
If analyzing soil samples, the user must add water to the sparger to ensure that the sample is appropriately agitated.

The basic steps for operating the system are:

1. Adjust/apply the settings as needed.
2. Ensure that the instrument displays a clean baseline.
3. Load a 5 mL sample.
4. Run an analysis, either connected or not connected to Ellvin.
5. If not connected to Ellvin during the analysis cycle, read analysis data using Ellvin at a later time.

NOTE: A working knowledge of Ellvin is necessary to correctly operate the instrument. Users should be familiar with the software before attempting analyses.

The FROG-4000™ is designed for use in the field.



The FROG-4000™ is designed for use in the laboratory. Connect to Ellvin Software for more detailed analysis results.

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SECTION 2: COMPENENTS AND SYSTEMS

The FROG-4000™ instrument has two main operational systems:

The Purge System

This system manages the loading of a sample, sparging the sample, if liquid, to release VOCs, and the introduction of gas phase compounds to the Gas Phase Analysis System. All components of the Purge System are visible on the instrument exterior.

The Gas Phase Analysis System

The Gas Phase Analysis System receives the VOCs from the Purge System and carries them through all stages of sample analysis, Collection → Injection → Separation → Detection

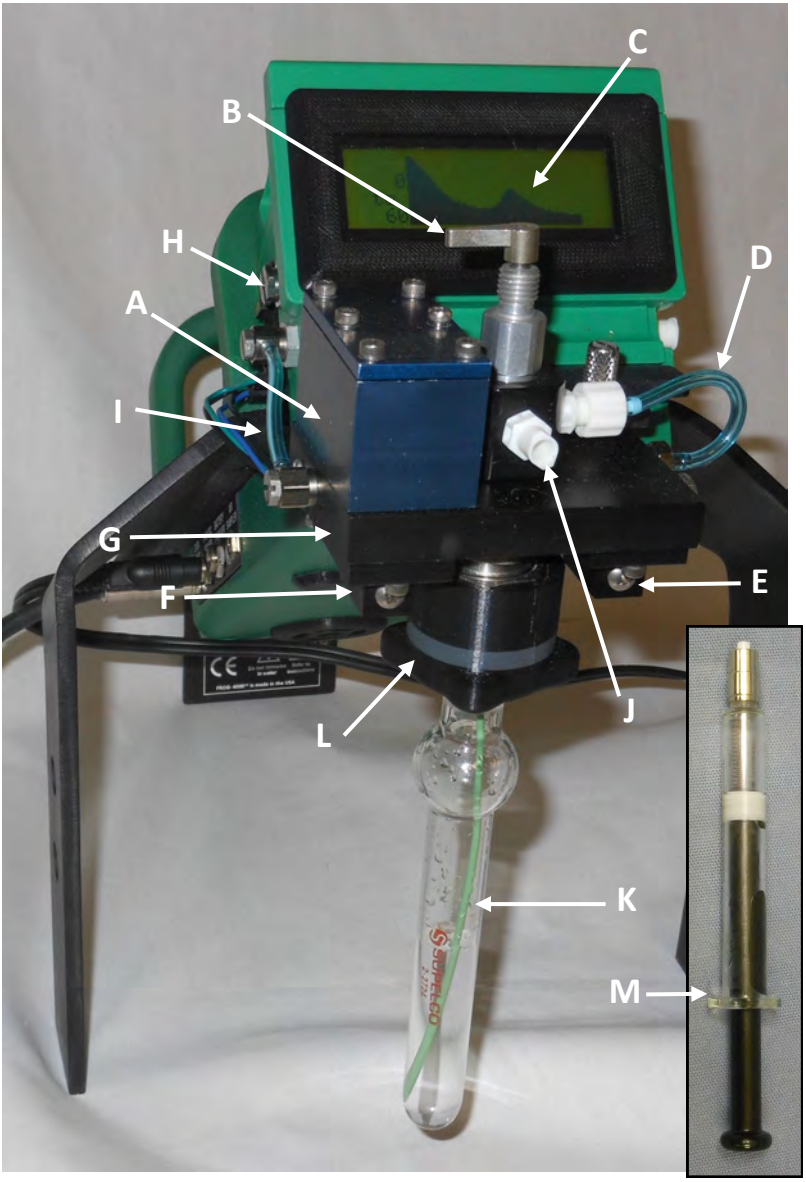
The instrument's components are briefly described on the following pages.

Section 2: Components and Systems Continued

2.1. INSTRUMENT COMPONENTS

Components Reference for FROG-4000™:

A. Scrubber
B. Load/Analyze Valve
C. Display Screen
D. Sparge-Air Line
E. Sparge-Valve
F. Flow Selection-Valve
G. Sparge Manifold
H. Pump Vent Orifice
I. Pump Air Supply Line
J. Sample Inlet
K. Sparge Bottle with PEEK Tube
L. Sparge Bottle Nut
M. 5 mL Syringe to load sample


C
B
H
D
A
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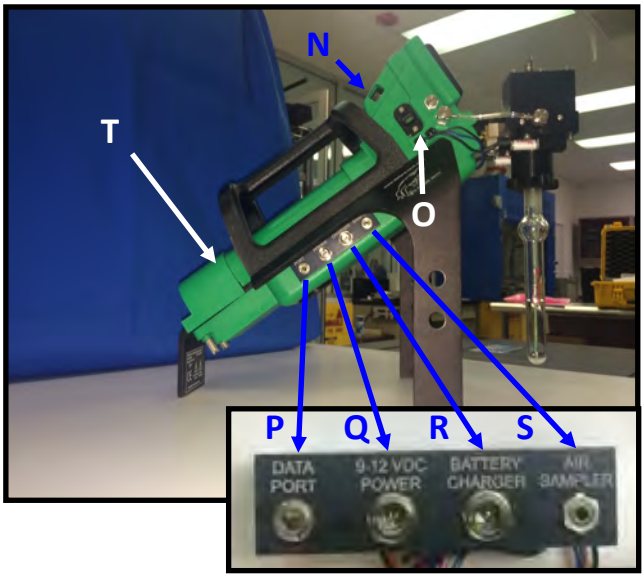
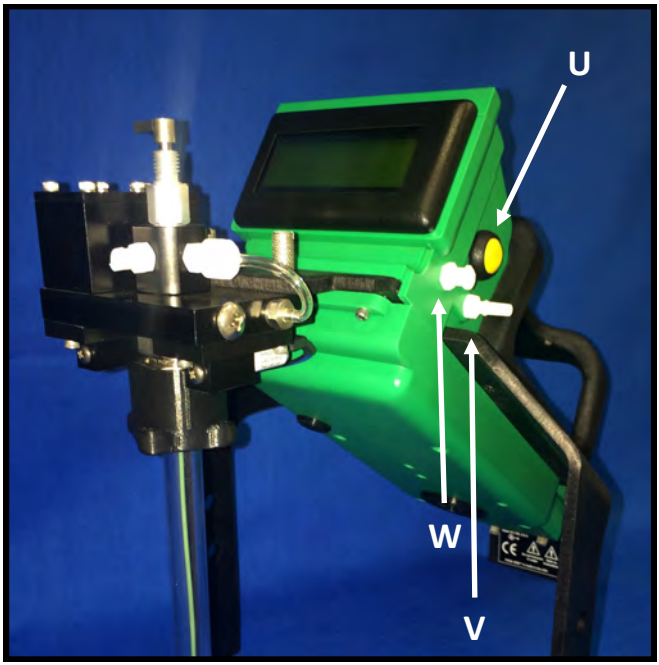
J
L
K
M

2.1. Instrument Components Continued

N. USB Port for stored chromatograms
O. Power Switch
P. Port for Serial Data Plug
Q. Port for 9V Power Plug
R. Port for Battery Charge Plug
S. Port for Air Sampler Plug
T. Battery
U. Start Button
V. Pump Inlet for Carrier/Sparge Gas
W. Exhaust from Gas Analysis Module


N
T
O
P
Q
R
S
DATA PORT
9-12 VDC POWER
BATTERY CHARGER
AIR SAMPLER


U
W
V

Section 2: Systems and Components Continued

2.2. PURGE SYSTEM

Purge System Components and their Functions
Figures 2.2-1 and 2.2-2.

A) **Scrubber:** Activated Carbon and Molecular Sieves
Function: Cleans the ambient air to prevent external VOCs from interfering in analyses.
*See NOTE on following pages for replacement supplies.

B) Load/Analyze Valve:
Function: Opens and closes the sample inlet for sample loading. The valve has two positions, LOAD and ANALYZE. (See Section 2.2.1 for operating instructions)

E) Sparge-Valve:
Function: Prevents liquid from entering air scrubber system.

G) Sparge Manifold:
Function: Routes gas to the proper ports for sparging and analysis functions.

J) Sample Inlet:
Function: Attachment for syringe to load a sample.

K) Sparge Bottle with PEEK Tube: Needle type sparge bottle, 0.5" x 5mL.
Function: Holds sample to purge VOCs. The Sparge bottle has two positions, UP and DOWN.
(See Section 2.2.2 for operating instructions)

L) Sparge Bottle Nut:
Function: Holds Sparge bottle in place and provides gas tight seal.

M) Syringe: 5mL, with Luer Lock.
Function: Loads a fixed sample volume to the sparger. Attaches to sample inlet (J).

Figure 2.2-1: Purge and Trap System

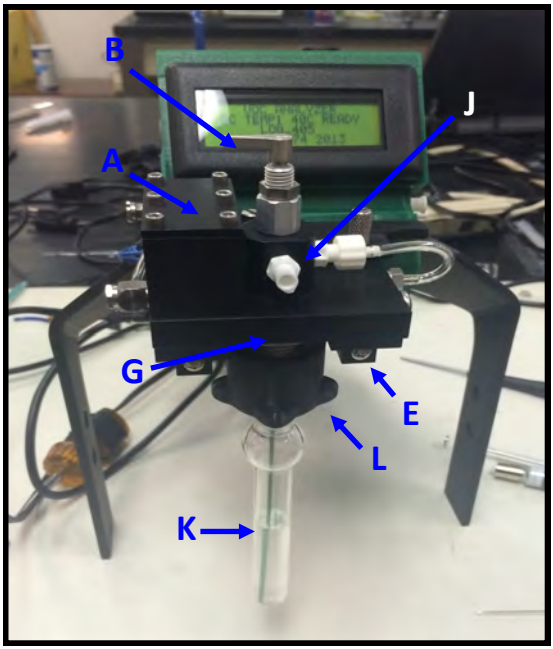
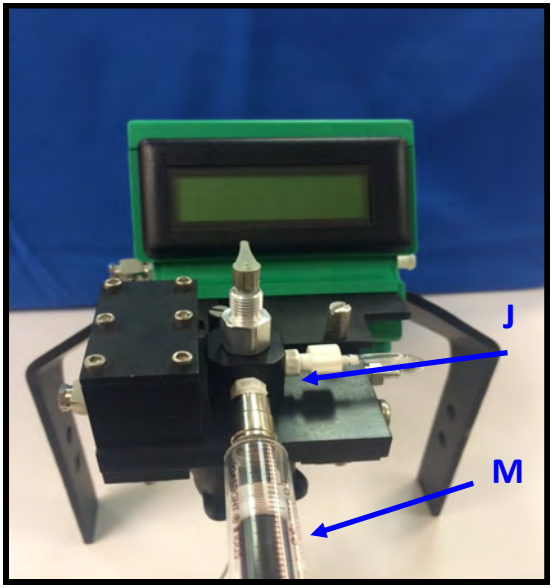


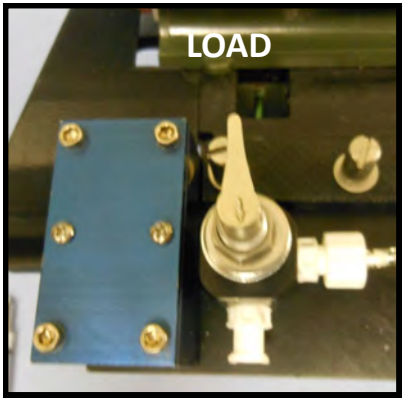
Figure 2.2-2: Purge System



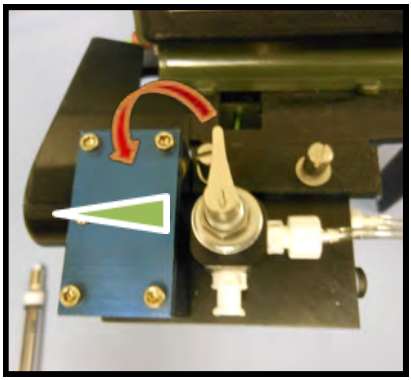
2.2 Purge and Trap System Continued

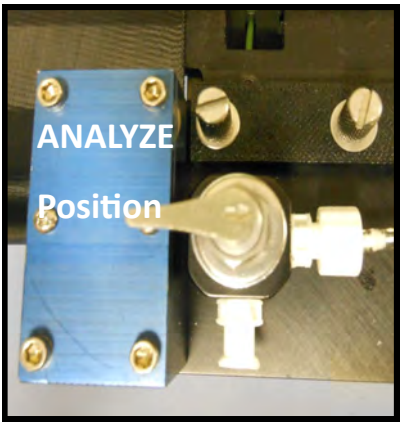
2.2.1. LOAD/ANALYZE VALVE

- Turn the load/analyze valve to the LOAD position to load a sample.



- After loading a sample, turn the handle counter clockwise to the ANALYZE position before starting an analysis cycle.

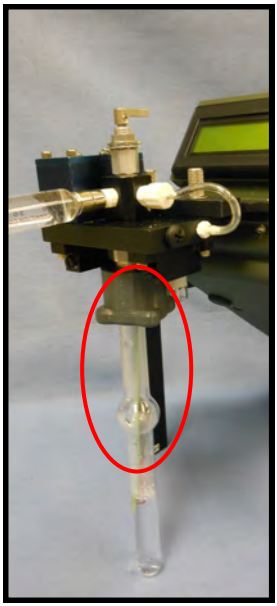




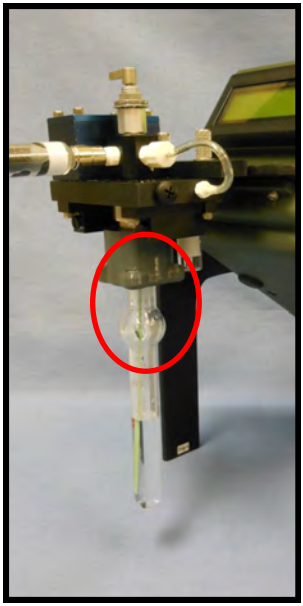
2.2.2. SPARGE BOTTLE POSITIONS

The sparge bottle moves UP and DOWN and is secured with a sparge bottle nut.

- The bottle must be in the DOWN position to rinse the instrument or to remove the sparge bottle.
- The bottle must be in the UP position to analyze a sample.
- The bottle may be in the UP or DOWN position for sample loading. We will present the DOWN position for consistency in this manual.



Sparge bottle
in the DOWN position.



Sparge bottle
in the UP position.

NOTE: When the sparge bottle is fully UP, the sparge tube is near the bottom of the sparge bottle. A partially lowered sparge bottle will cause analyte peaks to shift right.

Section 2: Components and Systems Continued

2.3. GAS PHASE ANALYSIS SYSTEM

Gas Phase Analysis System Components and their Functions
Figures 2.3-1 and 2.3-2:

A-Internal) Pump: Diaphragm pump
Function: Circulates carrier gas through system.

B-Internal) Preconcentrator (PC):
Function: Collects and injects VOCs into GC column.

C-Internal) Micro Gas Chromatography Column: (GC)
Function: Separates VOCs.

D-Internal) Photo Ionization Detector (PID): 10.6eV lamp
Function: Detects VOCs.

E) Sparge-Valve:
Function: Directs pump flow into sparge bottle to purge VOCs from sample.

F) Flow Selection Valve:
Function: Determines where the flow will be directed during Sparge or Analysis Mode.

G-Internal) Bypass-Valve:
Function: Allows the VOCs to pass over the PC and bypass the GC and PID.

H) Pump Vent Orifice:
Function: Provides a small leak in pump flow for improved flow control.

X-Internal) Injection Split:
Function: Provides a small leak to prevent rebound injection.

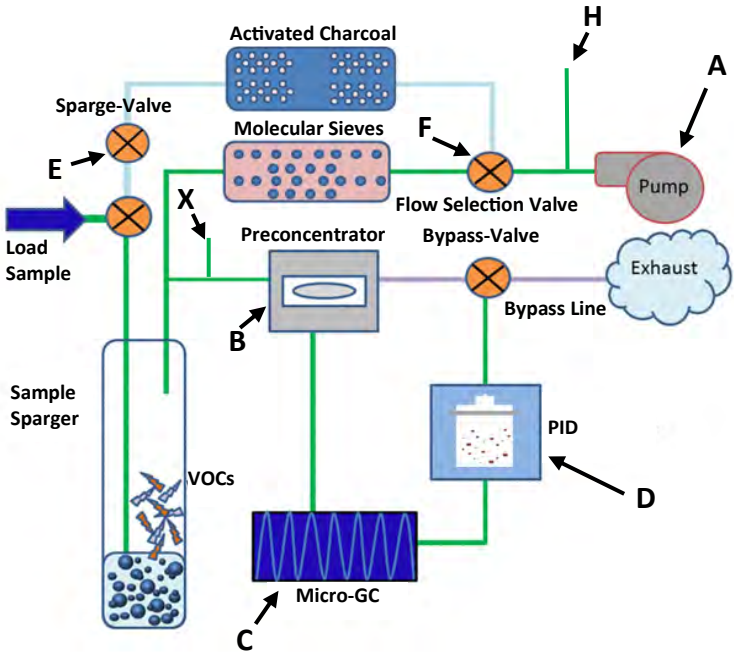


Figure 2.3-1 Gas Phase Analysis System components.

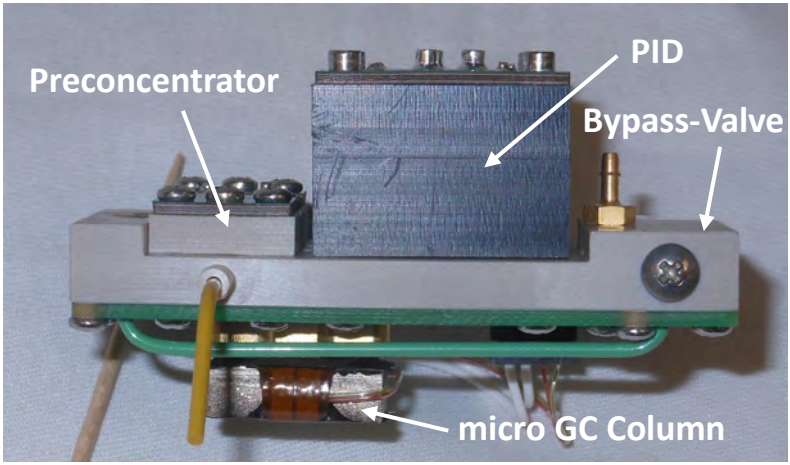


Figure 2.3-2 Gas Phase Analysis System internal components.

2.3. Gas Phase Analysis System Continued

Gas Phase Analysis System Components and their Functions
Figure 2.3-3

C) Display Screen:

Function: Shows the user which stage of analysis is being performed and displays an estimate of analysis results.

U) Start Button:

Function: Initiates the analysis cycle (can also be initiated through Ellvin).

V) Pump Inlet:

Function: Carrier gas intake for pump.

W) Exhaust:

Function: System flow exits.

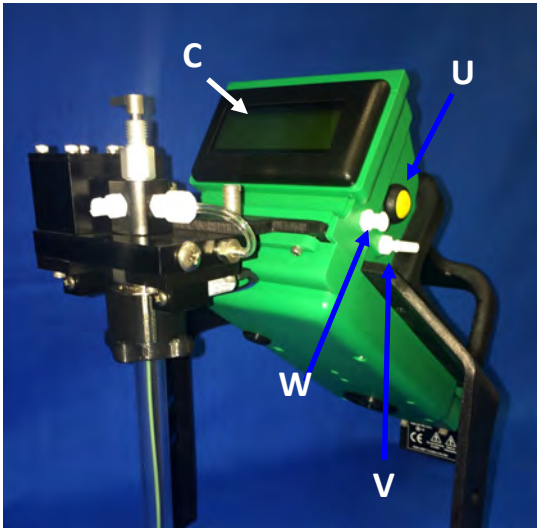


Figure 2.3-3 Gas Phase Analysis System external components

Section 2: Systems and Components Continued

2.4. GAS FLOW DIAGRAMS

This section describes and illustrates the flow of a sample from loading through the components of the Gas Phase Analysis System (Section 2.2).

2.4.1. SAMPLE LOADING

(Diagram 2.4-1) The sparge bottle is in the DOWN position for loading a liquid sample. The load/analyze valve is in the LOAD position. A sample is loaded into the sample inlet with a 5mL syringe.

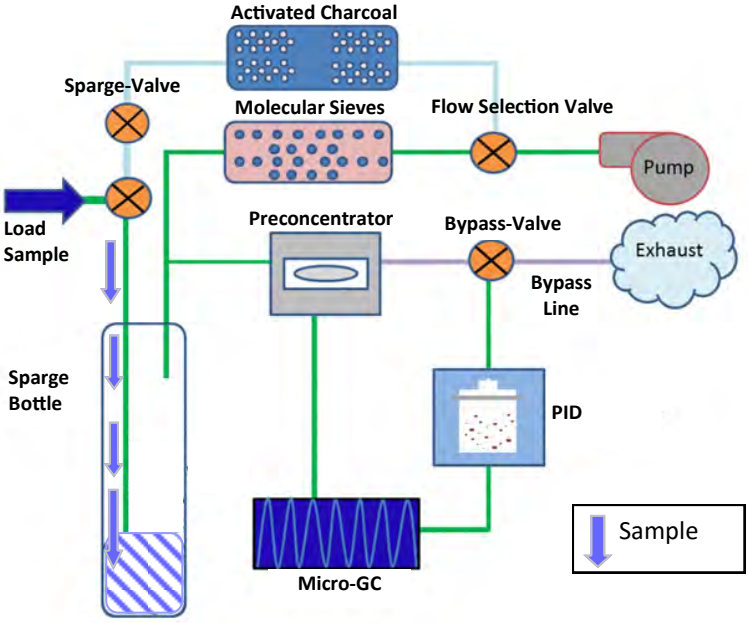


Diagram 2.4-1: Sample Loading

2.4. Gas Flow Diagram Continued

2.4.2. SPARGE AND COLLECTION

(Diagram 2.4-2) After the sample has been loaded, the load/ analyze-valve is placed in the ANALYZE position and the sparge bottle is moved into the UP position The start button is pressed and the pump flow starts. The carrier gas moves through: 1) the flow selection valve 2) activated charcoal, and 3) the sparge-valve. Air sparges the liquid (if a liquid sample) to release the VOCs into the headspace of the sparge bottle and onto the preconcentrator (PC).

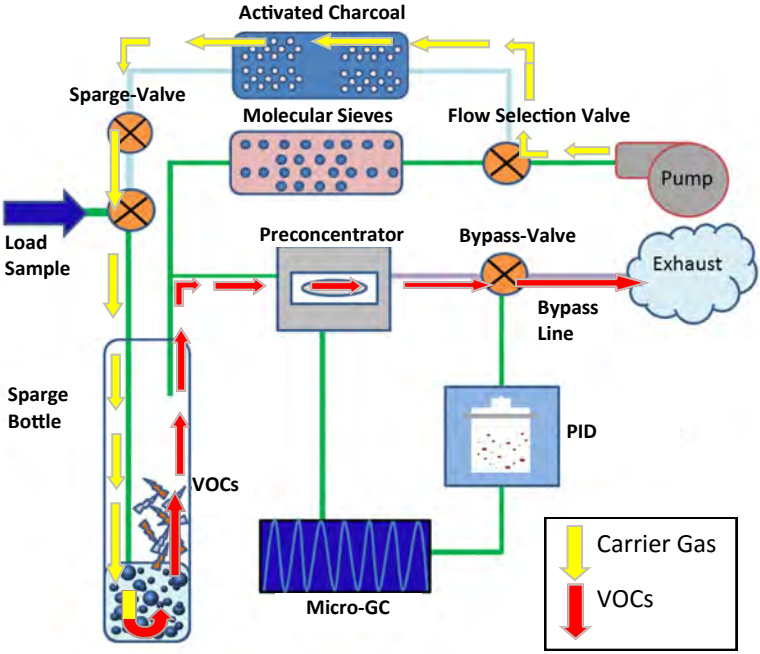


Diagram 2.3-2: Sparge and Collection

2.4.3. INJECTION (RELEASE), SEPARATION, AND ANALYSIS

(Diagram 2.4-3) Once the VOCs are collected onto the PC, the PC is heated to release the VOCs and inject them into the Micro-Gas Chromatograph Column (GC). The VOCs separate through the column and then continue to the Photo Ionization Detector (PID). The PID signal is analyzed and displayed through the software. The sample then exits through the exhaust.

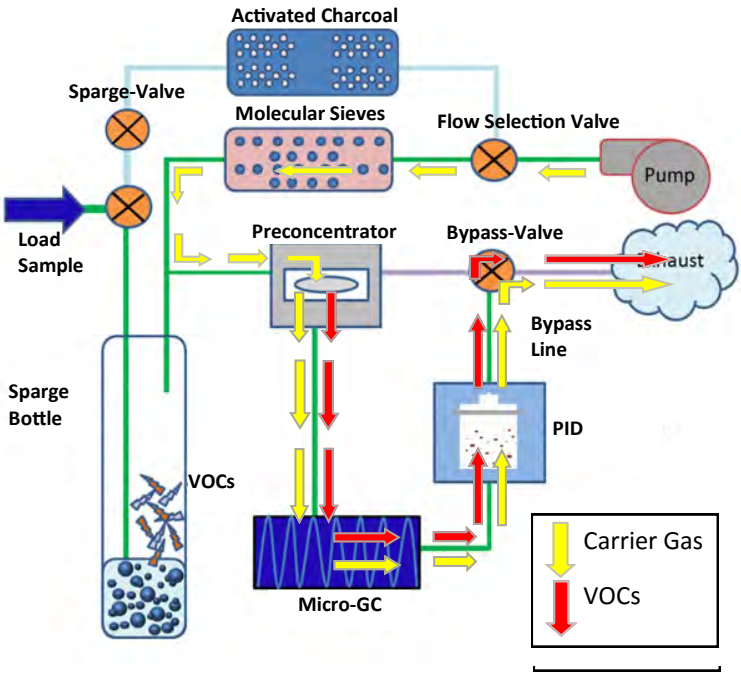


Diagram 2.4-3: Injection, Separation and Analysis

Section 2: Systems and Components Continued

2.5. GAS FLOW DIAGRAMS THROUGH AIR SAMPLER

This section describes and illustrates the flow of a sample from loading through the components of the Gas Phase Analysis System through the air sampler (Section 2.2).

2.5.1. SAMPLE COLLECTION

(Diagram 2.5-1) The air sampler is connected to the Frog-4000. The start button is pressed and the sample collection starts. The sample gas moves through: 1) an inert valve in the air sampler 2) over the preconcentrator, and 3) out of the gas module. A pump in the air sample adapter provides vacuum for pulling the air sample over the preconcentrator.

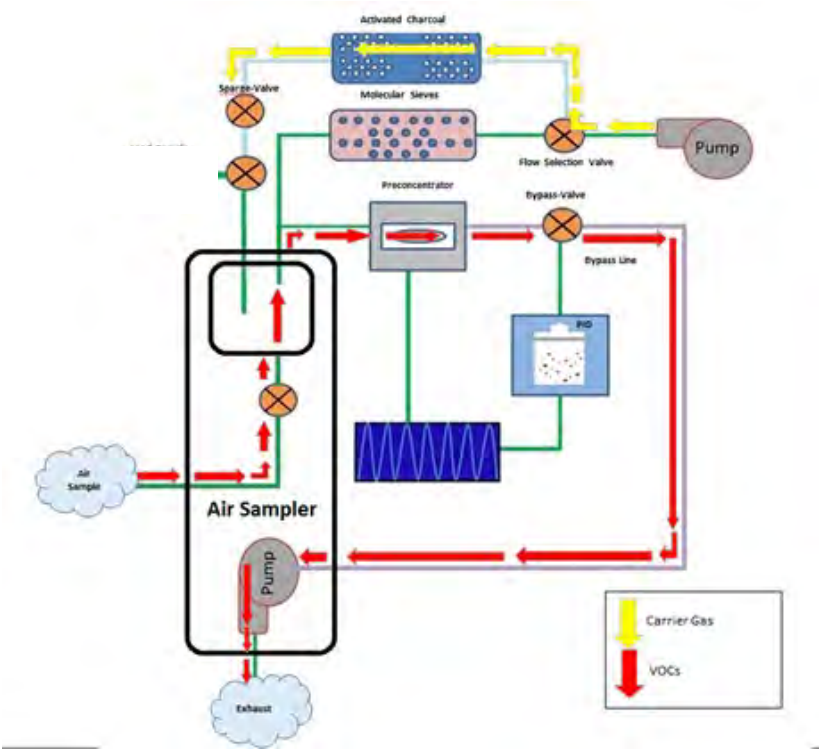


Diagram 2.5-1: Sample Collection

2.5. Gas Flow Diagram Continued

2.5.2. INJECTION (RELEASE), SEPARATION, AND ANALYSIS

(Diagram 2.5-2) Once the VOCs are collected onto the PC, the PC is heated to release the VOCs and inject them into the Micro -Gas Chromatograph Column (GC). The VOCs separate through the column and then continue to the Photo Ionization Detector (PID). The PID signal is measured and displayed through the software. The sample exits through the exhaust.

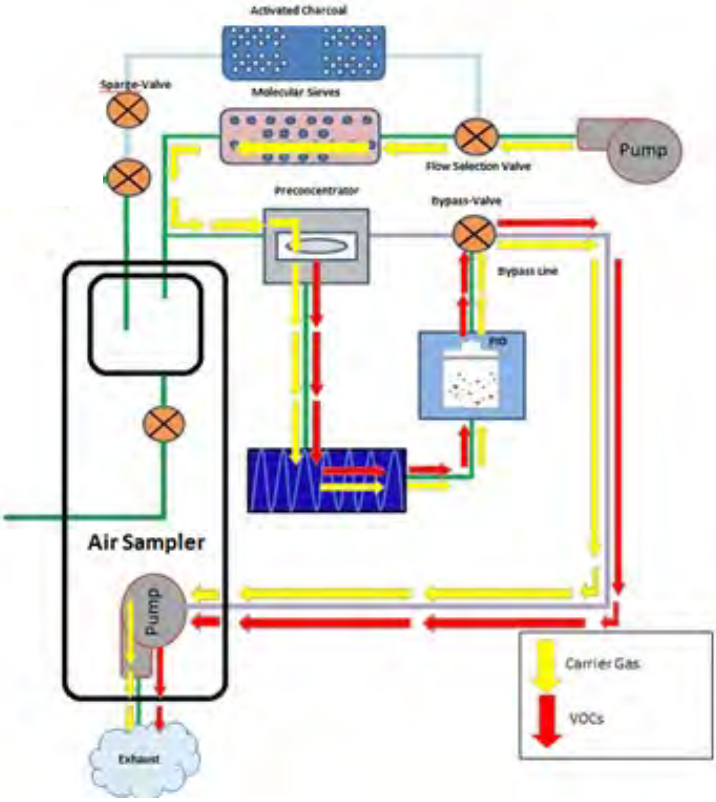
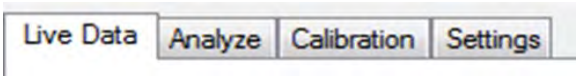


Diagram 2.5-2: Injection, Separation and Analysis

SECTION 3: OVERVIEW OF ELLVIN SOFTWARE

The Ellvin Software has four windows that are accessed with tabs when the software is open.



Window Tabs in Ellvin

- **Live Data Window**: This is the default window for Ellvin. In Live Data Window, Ellvin creates a chromatogram from sample analysis data. The data source may be:

    a. From a sample loaded and simultaneously analyzed by Ellvin.
    b. From sample data previously recorded on the instrument's SD card, then imported to Ellvin.

- **Analyze Window:** As in Live Data Window, Ellvin creates a chromatogram from sample analysis data. In this window, Ellvin retrieves analysis data that was previously stored on a computer. In Analyze Window the user can examine chromatograms closely, integrate chromatogram peaks, and export data to Excel.

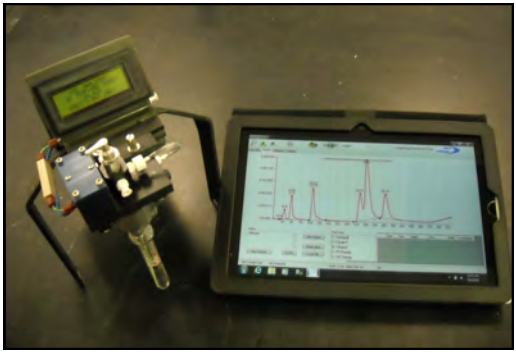
- **Calibration Window:** In this window, Ellvin uses analysis data from chemical standards to calibrate the FROG.

- **Settings Window:** In this window, Ellvin manages the settings for operation of the FROG. The settings define temperature and duration parameters for various phases of the instrument's collection and analysis cycle.

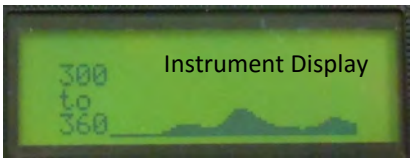
There are several general features of Ellvin as well as a few features specific to Analyze Window that are described in Section 5. The user should be familiar with all the features before starting a sample analysis.

SECTION 4: FIELD AND LAB ANALYSIS PROCEDURES

The simplest way to use the FROG is to load samples and run analyses while the instrument is connected to a computer and Ellvin. The software analyzes sample data and displays a live chromatogram during analyses. The cycle takes about five minutes. Data is stored both on the FROG's internal SD card and on the computer.



The FROG can also analyze samples when not connected to Ellvin. An analysis cycle takes the same amount of time (five minutes) and an estimate of the results are displayed on the instrument's screen. Data is stored on the FROG's internal SD card and can be imported to Ellvin and analyzed at a later time if desired. Section 4.7. gives instructions for importing data from the FROG.



Continued next page.

Section 4: Field and Lab Analysis Procedures Continued

This section provides detailed instruction for various procedures that are essential to operating the FROG-4000™.

Procedures include:

4.1: Powering On/Charging Battery

Description of components and connections.

4.2: Connecting to Computer/Ellvin

Instructions/description for components and connections.

4.3: Instrument Settings

Set parameters to optimize instrument function.

4.4: Instrument Preparation

Remove interfering contaminants/ensure a clean instrument.

4.5: Loading a Sample

Air, liquid, and soil sample preparation and loading instructions.

4.6: Running A Sample

Instructions/description for an analysis cycle.

4.7: Importing Data to Ellvin

Import stored data from FROG to Ellvin for analysis.

Complete the following procedures to run an analysis.

NOTE: The user should be familiar with Ellvin before loading and running a sample.

1. 4.1: Powering On/Charging Battery

2. 4.4: Instrument Preparation

3. 4.5: Loading a Sample

4. 4.6: Running A Sample

If not connected to Ellvin,

5. 4.7: Importing Data to Ellvin

6. Clean the instrument when all samples have been completed by repeating Step 2.

4.4: Instrument Preparation

Exception: Samples of the same, known analyte may be run consecutively from low concentration to high without rinsing the instrument and creating a clean baseline.

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Section 4: Field and Lab Analysis Procedures Continued

4.1: Powering On/Charging Battery

Powering On

- Connect power cable to power port (R) 9V POWER, or use battery power. (Figure 4.1-1)
- Turn power switch (O) to ON (fully up) position. The instrument display screen will be visible.

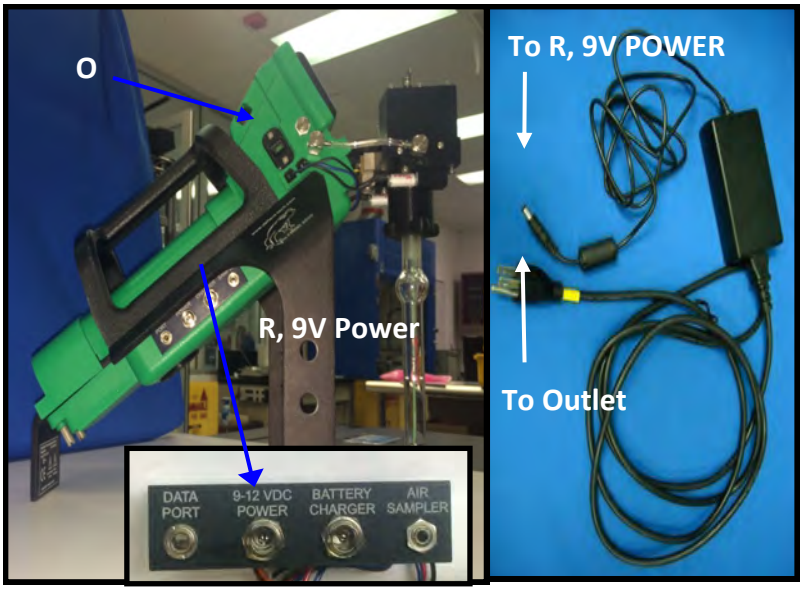
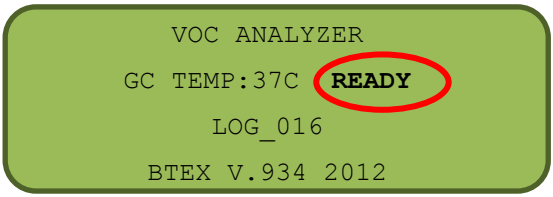


Figure 4.1-1: Power port, power cable and power switch.

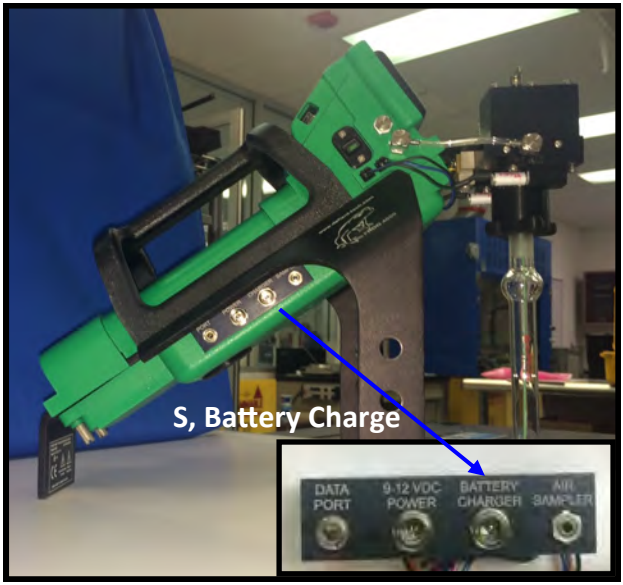
- When the FROG-4000™ display screen shows **READY,** the instrument is ready to load a sample.

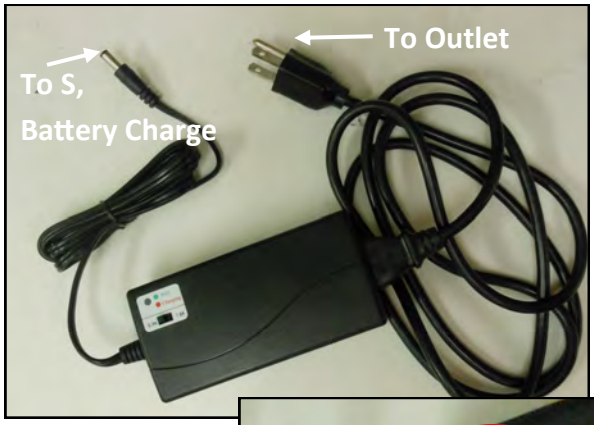


4.1. Powering On/Charging Battery Continued

Charging the Battery

1. Plug battery charger into Battery charge port (S) and outlet source.
2. Place battery charger switch to 1.8A.
3. While the battery is charging, the light on the charger switch will appear red.
4. When the battery is completely charged, the light on the charger switch will appear green.
5. It is highly recommended that the battery be fully charged before the instrument is used in a remote setting.


S, Battery Charge
DATA PORT
9-12 VDC POWER
BATTERY CHARGER
AIR SAMPLER


To Outlet
To S,
Battery Charge

Full
Charging
0.9A
1.8A

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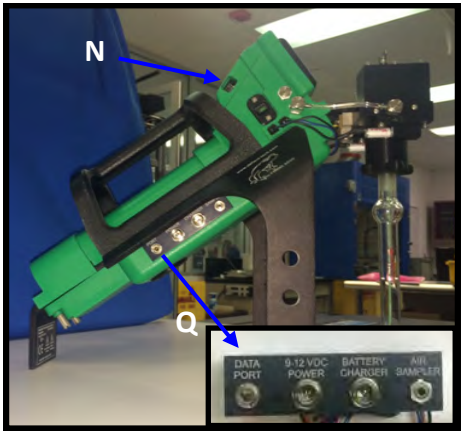
4.2: Connecting to Computer/Ellvin

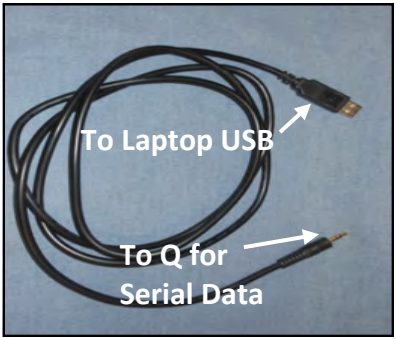
There are two possible connections between the FROG and a computer.

To receive live data and communicate with the FROG using Ellvin, connect a computer to the serial data port (Q) on the FROG with the USB to Serial Data-Cable.

To import data from the instrument's internal SD card to Ellvin, connect a computer to Port N on the FROG with the USB-Cable.

NOTE: Detailed instructions for exporting data with the USB cable are given in Section 4.7.





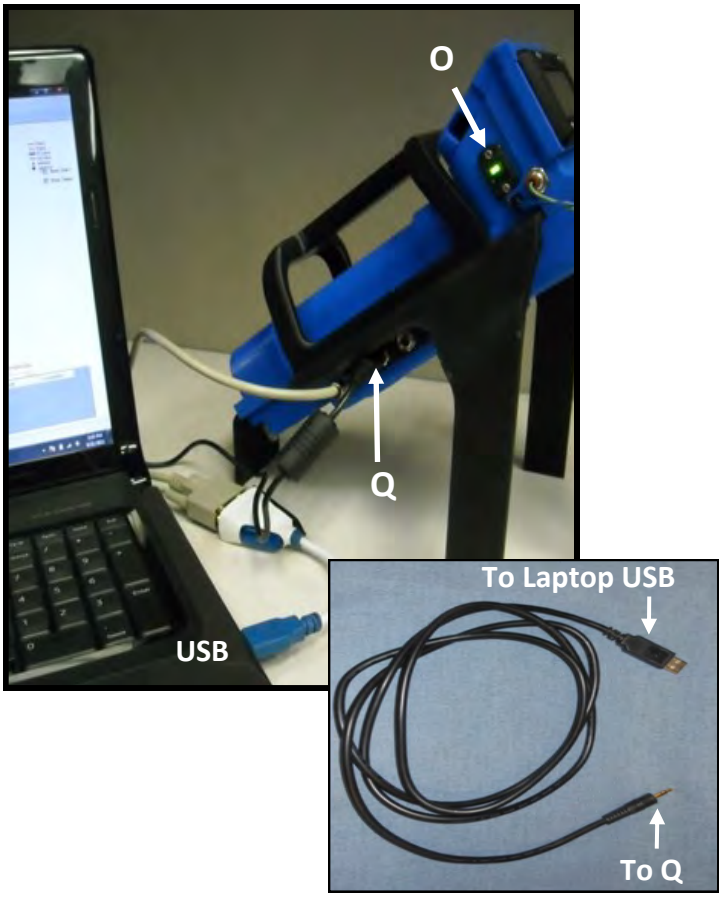
USB to Serial Data-Cable

USB-Cable

4.2. Connecting to Computer/Ellvin Continued

Serial data-cable Connection

1. Connect the serial data-cable from the FROG's serial data port (Q) to a USB port on a computer.
2. Set the instrument power switch (O) to the ON position.
3. If necessary, install Ellvin onto laptop or PC.
4. Open Ellvin by double clicking on the Ellvin icon.



Serial Data-Cable

After Ellvin has opened, the default screen that appears is the chromatogram display screen in Live Data Window.
(Figure 4.2-1)

Figure 4.2-2 shows details of the display screen

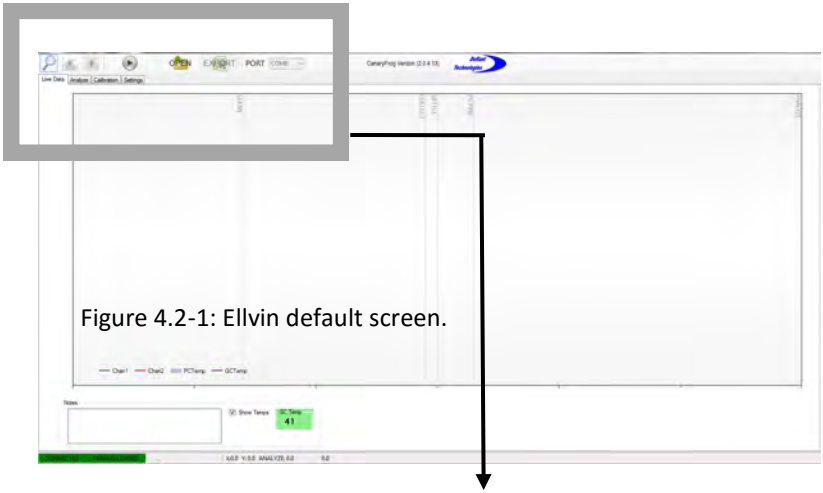


Figure 4.2-1: Ellvin default screen.

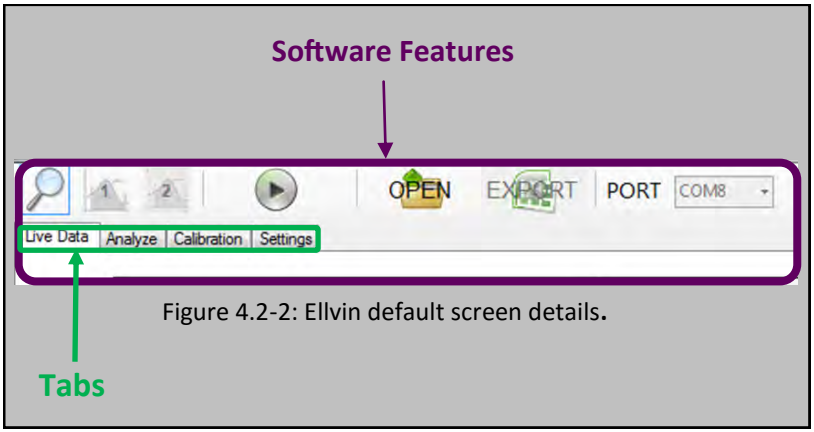
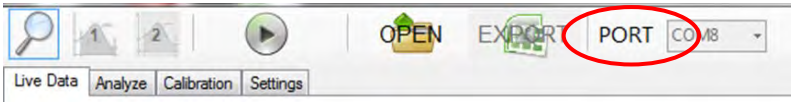


Figure 4.2-2: Ellvin default screen details.

4.2. Connecting to Computer/Ellvin Continued

5. Click "Port" on the display screen, then select a COM#.



6. The connection status indicator in the lower left corner should now read CONNECTED indicating that the FROG and Ellvin are connected. The user may now manage settings and run analyses from Ellvin.

Section 4: Field and Lab Analysis Procedures Continued

4.3: Instrument Settings

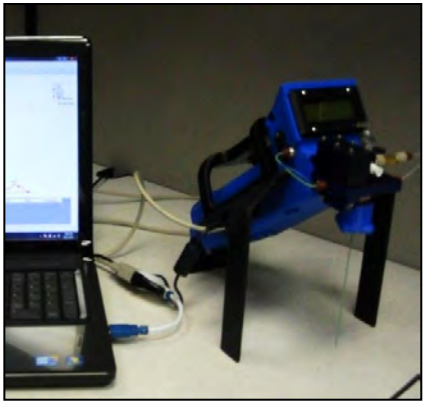
The FROG-4000™ comes with general default setting for VOCs, which are shown in Figure 4.3-2 on the following page.

The settings determine the duration of different analysis phases, as well as the desired temperature of the GC column. The settings are defined and loaded to the instrument using Ellvin. Table 4.3-1 on the following page describes the various settings.

The FROG-4000™ default settings are best for the analysis of Benzene, Toluene, Ethylbenzene and Xylenes (BTEX), but the settings can be altered for analyzing a wide variety of compounds and concentrations.
(See Appendix I for a list of detectable chemicals).

The current operational settings are stored in the FROG-4000™ memory and do not revert to the default settings when the instrument is disconnected from the software or power. They are retrieved and displayed under the Settings Window when the instrument is connected to a computer through Ellvin.

Instructions for adjusting the settings begin on the following pages.



Connect to Ellvin to manage the settings.

4.3. Instrument Settings Continued

Table 4.3.1 Description of Settings	
Settings	**Description**
T_a	Hold time at lower GC temperature (seconds)
T_b	Ramp time from GC cold to GC hot temperature (°C)
T_c	Hold time at hot GC temperature (°C)
C_t	Initial cold GC temperature (°C) **NOTE:** If used outdoors, the user must consider ambient conditions.
H_t	Final hot GC temperature (°C)
COLLECT	Collection time of VOCs onto PC (seconds) This corresponds to the sparge time.
CLEAN	Time cleaning PC by heating (seconds)
PRESETTLE	Time PC cools after cleaning (seconds)
SETTLE	Time allowed for pressure to stabilize before PC FIRE (seconds) for GC analysis
FIRE	Time PC is Heated to Release VOCs (seconds)

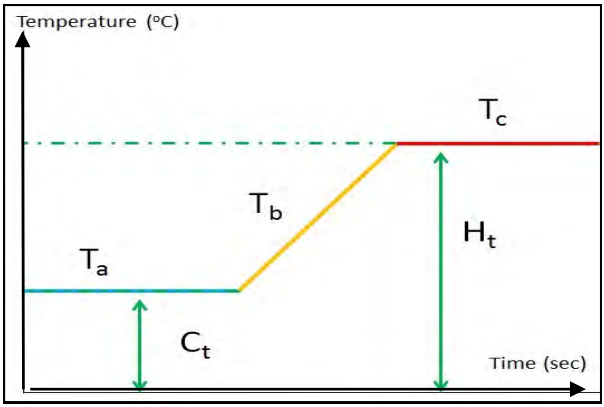


Figure 4.3-1: Description of GC Temperature Settings.

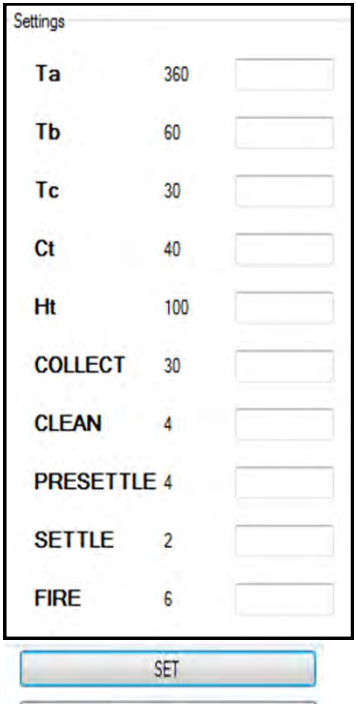
Defining and applying the settings.

1. Connect to Ellvin. Refer to:

4.2: Connecting to Computer/Ellvin

2. Click on the Ellvin Settings Tab.

3. Type in a non-zero integer then click SET to apply the settings to the instrument. Changes to the settings are stored on the instrument. Settings **DO NOT** revert to the default parameters when power is removed or computer is disconnected.
The minimum and maximum values are listed next to the Figure 4.3-2.



Settings	Min	Max
Ta	2	900
Tb	2	900
Tc	2	900
Ct	25	95
Ht	30	149
Collect	10	900
Clean	2	20
Presettle	4	20
Settle	2	20
Fire	4	20

Figure 4.3-2: Setting Window showing Default Settings

Section 4: Field and Lab Analysis Procedures Continued

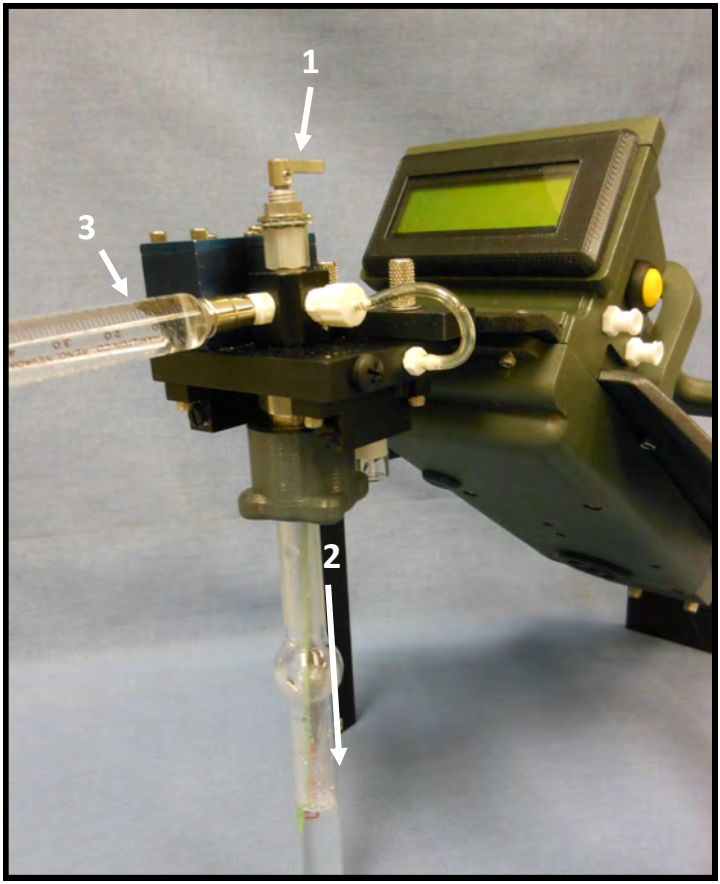


Figure 4.4-1 Rinsing the Instrument Steps 1-3

4.4: Instrument Preparation

Before running analyses, the instrument should be rinsed and display a clean baseline.

4.4.1. RINSING THE INSTRUMENT

1. Place the load/analyze valve in the LOAD position.
(See Section 2.2.1)

2. Place sparge bottle in the DOWN Position.
(See Section 2.2.2)

3. Attach syringe with 5 mL deionized water to FROG-4000™.
(Figure 4.4-1, opposite page)

Figure 4.4-2: Load/ Analyze Valve

4. Load deionized water into FROG-4000™.

5. Remove sparge bottle and empty the water into waste container.

6. Repeat steps 3-5 twice, for a total of three rinses.

7. Remove and rinse sparge bottle with deionized water.

8. Replace the sparge bottle in the DOWN position.

Proceed to demonstrate a clean baseline (following pages).

4.4. Instrument Preparation Continued

4.4.2. CREATING A CLEAN BASELINE

A Clean Baseline should be achieved before analyzing a sample. This procedure ensures that there are no contaminants in the instrument that could effect the analysis results.

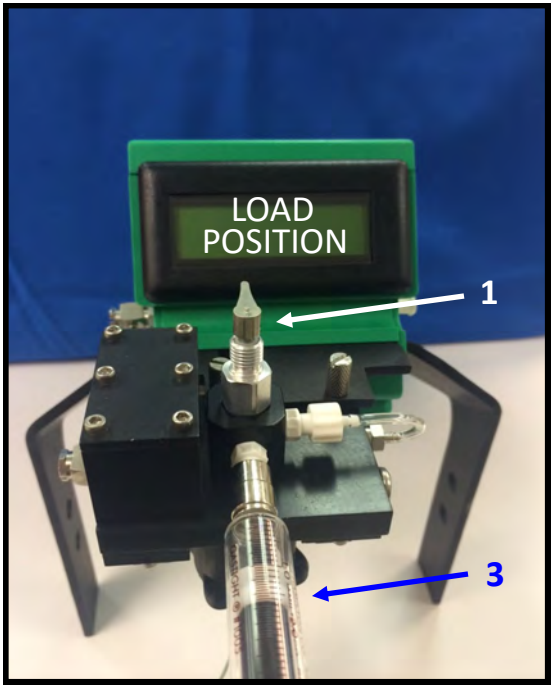
If the instrument is connected to a computer and Ellvin, the start button and display screen are in the software. If the instrument is not connected to Ellvin, the start button and display screen are on the instrument.

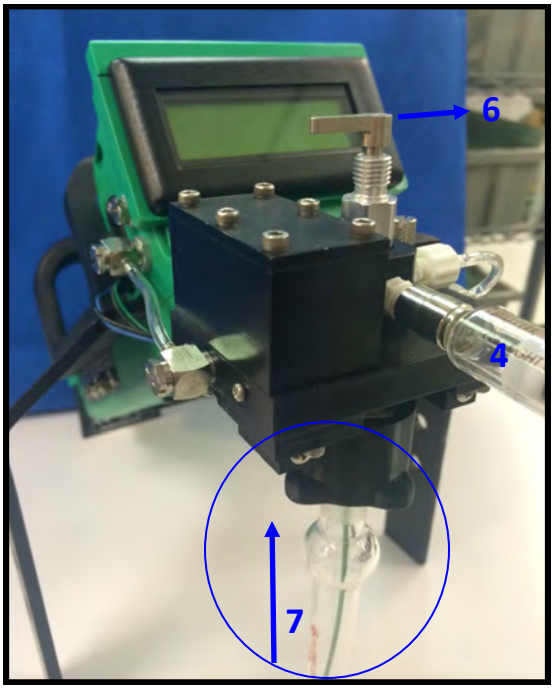
Rinse the instrument as described in Section 4.4.1 before attempting to achieve a clean baseline

Procedure:

1. Place load/analyze valve in the LOAD position.
   (See Section 2.2.1)
2. Place rinsed sparge bottle in the DOWN position.
   (See Section 2.2.2)
3. Attach syringe with 5 mL deionized water to FROG-4000™.
4. Load deionized water into FROG-4000™
5. Remove the empty syringe
6. Place the load/analyze valve in the ANALYZE position.
7. Move the sparge bottle to the fully UP position and tighten the sparge nut in the clockwise direction until lightly snug.

Continued following pages.


LOAD
POSITION
1
3


6
4
7

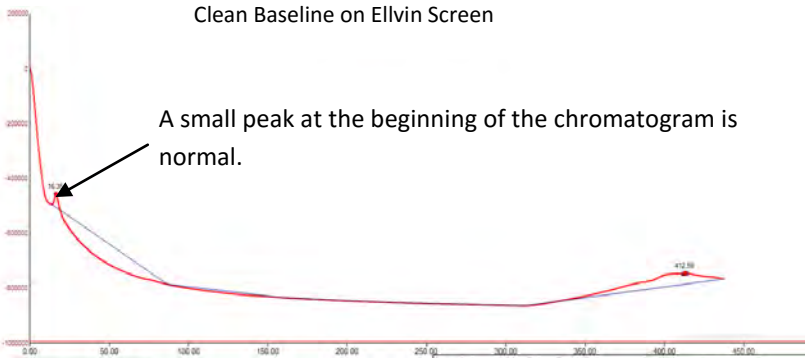
4.4.2. CREATING A CLEAN BASELINE CONTINUED

7. Begin an analysis cycle using deionized water. If connected to Ellvin, click the start button in the software. If not connected to Ellvin, press the yellow start button on the instrument.

Start Button in Ellvin

When the analysis is finished, a clean baseline should appear. A clean baseline is basically smooth with no significant peaks. A small peak at the beginning of the chromatogram and small waves in the clean baseline are acceptable.

Clean Baseline on Ellvin Screen

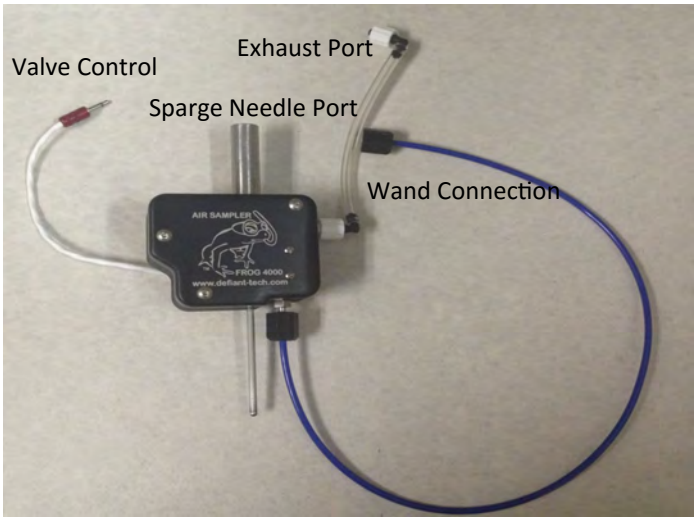


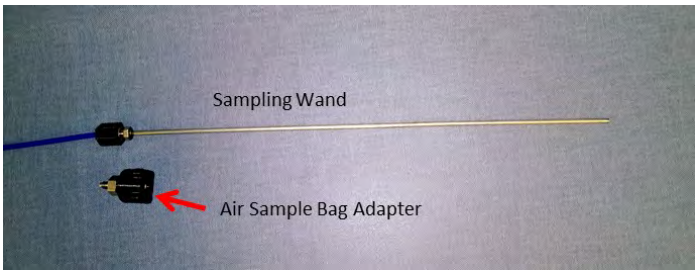
If Peaks **do** appear, repeat the instrument preparation procedures (4.4.1, Rinsing the Instrument and 4.4.2, Creating a Clean Baseline) until a clean baseline is achieved.

4.4. Instrument Preparation Continued

4.4.3. CONNECTING THE AIR SAMPLE ADAPTOR

If analyzing air sample, the user must first connect the air sample adaptor to the FROG.



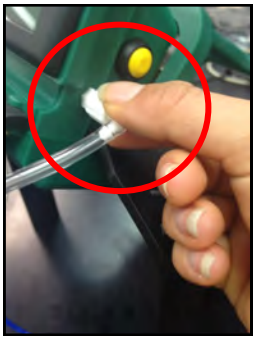


The air sample kit includes a sample wand and an air sample bag adapter. The air sample bag adapter enables direct connection to an air sample bag.

4.4.3. CONNECTING THE AIR SAMPLE ADAPTOR CONTINUED

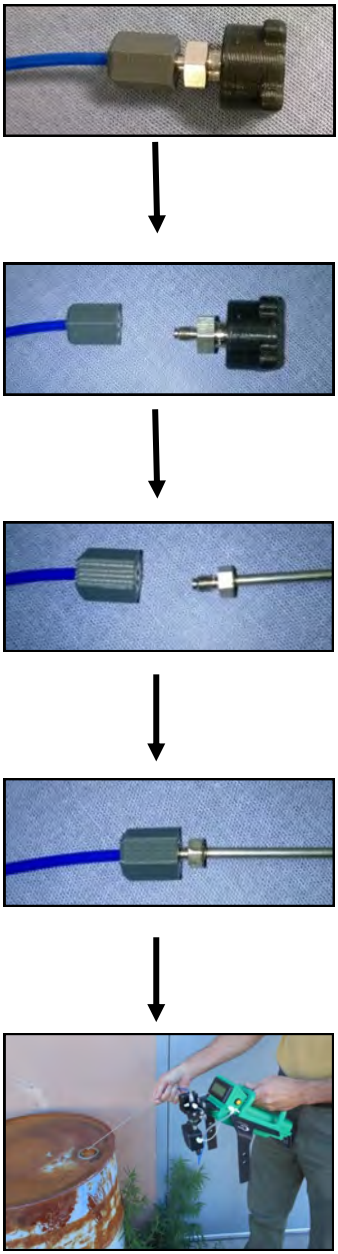
1. Attach the air sampler to the FROG sparge needle. Be sure the valve is pointed to the right.

2. Connect the air sampler's valve connector to the FROG valve connection. This connection supplies power to the air sampler.



3. Attach the exhaust connector to the FROG exhaust with a twisting motion.

6. Connect the air sample wand to the air sampler.



Section 4: Field and Lab Analysis Procedures Continued

4.5: Loading a Sample

NOTE: The instrument should have a clean baseline to begin sample loading and analysis. Refer to:

4.4: Instrument Preparation

To ensure optimal sample analysis, adhere to the following sampling and cleaning procedures :

⇒ **Liquid Sample**:

a. Pull 5mL of the sample liquid into a syringe.

b. Transfer sample liquid to the sparge bottle.

c. Rinse sparge bottle and syringe between test runs.

⇒ **Soil Sample:**

a. Remove the sparge bottle from the instrument.

b. Add 1 g of soil to the sparge bottle with then add 5 mL of clean water. (See our website for an application note on methanol extraction.)

c. Rinse the sparge bottle thoroughly between samples.

⇒ **Air Sample**: Connect the air sampler adaptor and wand to the FROG (Section 4.4.3).

When running an analysis (Section 4.6), hold the wand in the area desired for sample collection.

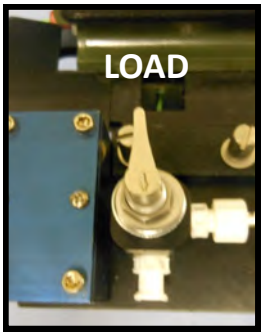
If heavy concentrations are detected, run a sample of clean air to clear the system.

Detailed instruction begin on the following page.

4.5. Loading a Sample Continued

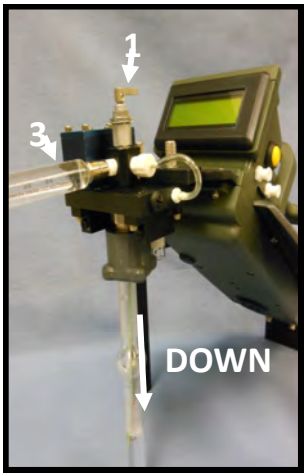
- If concentrations are known, during calibration for example, a series of samples of the **same** analyte may be run consecutively without rinsing the instrument. They must be run in order from low to high concentrations to prevent cross contamination.

Procedure:

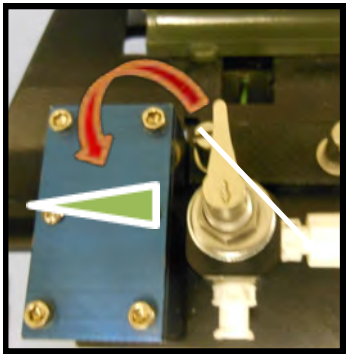


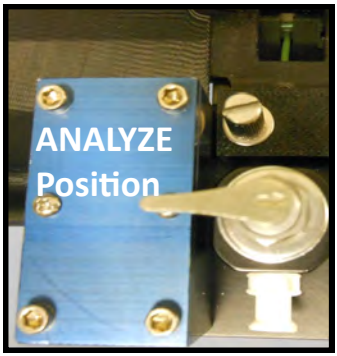
1. Place load/analyze valve in the LOAD position (open). (See Section 2.2.1)

2. Load sample into sparge bottle
   - ⇒ Liquid Samples: Place sparge bottle in DOWN position. Load 5 mL of sample through Sample Inlet
   - ⇒ Silty Liquid Samples: Load 5 mL of sample directly into the top of the sparge bottle. Place sparge bottle in DOWN position.
   - ⇒ Soil: Load 1 g sample directly into the top of the sparge bottle. Fill 5mL syringe with deionized water. Transfer the 5mL of deionized water into the sparge bottle while rinsing soil to the bottom. Place sparge bottle in DOWN position.



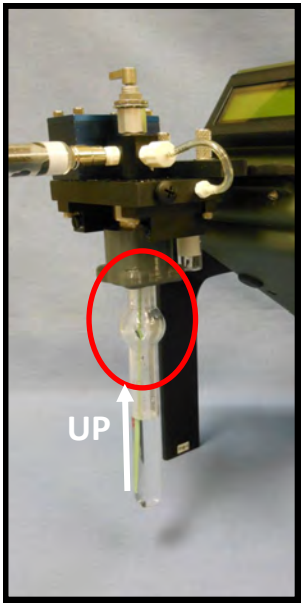
3. Immediately place the load/analyze-valve in the ANALYZE position (closed). The syringe may now be removed.





4. Return sparge bottle to the UP position. Rotate the sparge bottle nut counter clockwise until finger tight to secure the sparge bottle. The sparge bottle should not spin in the sparge bottle nut.

NOTE: When the sparge bottle is fully UP, the sparge tube is near the bottom of the sparge bottle. A partially lowered sparge bottle will cause analyte peaks to shift right.



Sparge bottle
in the UP position.

4.5. Loading a Sample Continued

The instrument display screen shows **READY** throughout Steps 1-4 of Loading a Sample. The Log # is automatically generated and assigned to the data file produced by the current analysis cycle.

```
VOC ANALYZER
GC TEMP:37C READY
LOG_016
BTEX V.934 2012
```

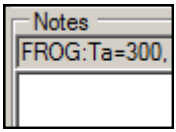
4.6: Running A Sample

This section describes the procedure for running an analysis and the instrument's stages during an analysis cycle.

Procedure:

Record notes for future reference:

- If not connected to Ellvin, the user should record the LOG#s and other relevant information for future reference. The instrument records this number in the file name on the internal SD card.
- If connected to Ellvin, the user can record relevant information for sample identification in Ellvin's Notes window. Ellvin automatically stores the analysis data file in a folder labeled with the date. The file itself is labeled with the time it was created.



After the sample loading is complete (Section 4.5), the user may begin sample analysis by pressing the start button. If connected to Ellvin, click the start button in the software. If not connected to Ellvin, press the yellow start button on the instrument.

Start Button in Ellvin

Start Button on the Frog

Continued next page.

4.6. Running a Sample Continued

During an analysis cycle, the FROG screen displays the analysis steps in sequence as illustrated below and on the following pages. This information is only visible on the instrument screen (not the Ellvin screen).

Each sequence has a clock counting down the duration of the current analysis step. The duration of the analysis step is determined by the instrument settings.

(See Section 4.3)

The GC TEMP may vary slightly from the set point.

Analysis Sequence

1. Cleaning Prior to Sparging:
The PC is heated to drive off contaminants (analytes from previous runs).

CLEANING 4

2. Settle:
The PC cools before sparge begins.

SETTLE 4

3. Sparge and Collect:
VOCs are sparged and collected on the PC.

COLLECT 30
SPARGE ON

Continued next page.

4. Release and Analyze, Settle:
The sample flow is switched to the analysis channel. The pressure is allowed to stabilize before the PC fires.

RELEASE AND ANALYZE
SETTLE 2

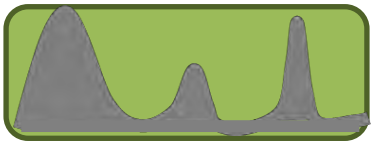
5. PC Fire:
The PC is heated and analytes are injected (released) into the GC column and continue through to the PID.

RELEASE AND ANALYZE
SPARGE OFF
PC 6

6. Analyzing:
The PID measures analytes as they emerge sequentially from the GC.

RELEASE AND ANALYZE
SPARGE OFF
ANALYZING 180

7. Chromatogram:
The analysis concludes with a chromatogram of the analytes detected.
NOTE: the chromatogram does not appear on the display if the FROG run is initiated through Ellvin.



Continued next page.

4.6. Running a Sample Continued

Analysis Sequence Continued

8. Instrument Estimation:

When the instrument is not connected to Ellvin, it makes an estimate of the analytes' concentrations based on calibration data.

BENZE 33PPB 48.33S

Estimate #1

Click the Start Button to see the next analyte estimate.

Click the yellow start button to scroll through analytes. The two estimates shown in this example are 33ppb Benzene and 63ppb Toluene. The GC retention time for Benzene is displayed as 48.33 seconds.

TOL U 63PPB 68.72S

Estimate #2

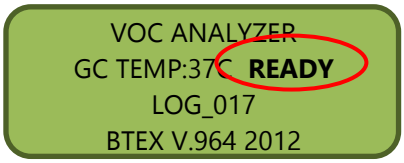
NOTE: The instrument estimates are only available immediately after the corresponding analysis. They are NOT stored on the instrument's SD card. Complete analysis chromatogram data *are* stored on the SD card and can be imported to Ellvin for further analysis.

9. Log File/WAIT:

The screen returns to the original display and shows the Log File # for the NEXT analysis. WAIT indicates that the GC temperature is above the lower GC set point.

VOC ANALYZER
GC TEMP:37C **WAIT**
LOG_017
BTEX V.964 2012

The FROG is ready for another sample loading and analysis once the GC Temperature indicator appears green and READY is displayed on the FROG screen.



Samples of the same analyte may be run consecutively from low concentration to high without rinsing the instrument and creating a clean baseline.

NOTE: If the user has run a high-concentration sample, it is advisable to complete the following procedures:

⇒ Liquid or Air Sample, perform:

4.4: Instrument Preparation

⇒ Soil Sample: Remove sparge bottle from instrument and fill it with deionized water. Rinse it thoroughly to remove all dirt from bottle. Then, perform:

4.4: Instrument Preparation

Continued next page.

Final Step: If desired, use Ellvin for detailed results analysis after completing the analysis run.

- If the sample was run while connected to Ellvin, open the data file in Analyze Window and use Integrator 2.
  (See Sections 5.2.1 and 5.2.3)
- If the sample was *not* run while connected to Ellvin, import the data to Ellvin (Section 4.7), then open the file in Analyze Window and use Integrator 2.

Section 4: Field and Lab Analysis Procedures Continued

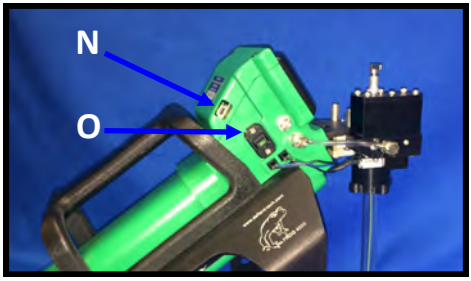
4.7. Importing Data to Ellvin

Ellvin allows the user to view live results, change operating parameters, re-plot stored data and overlay data for comparison. It also has tools for integrating peak areas, measuring retention times , and calibrating the instrument.

The FROG-4000™ stores data from every analysis on an internal SD card. The following steps describe the process for extracting data from FROG-4000™ for analysis with Ellvin.

1. Connect Port N on the FROG-4000™ to a computer using the USB-Cable.

USB-Cable



2. Turn the instrument on. (O)

Continued next page.

4.7. Importing Data Continued

3. The computer screen will display an option to "Open folder and view files". Open the folder.

4. The computer screen now displays a list of sequential files named "LOG_XXX". The file names are created and assigned by the instrument. They appear on the instrument screen at the *beginning* of each analysis cycle as shown in Figure 4.7-1.

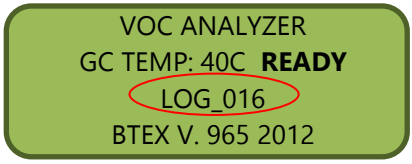


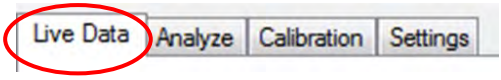
Figure 4.7-1: FROG-4000™ display screen at the beginning of a sample run.

NOTE: If the instrument is NOT connected to Ellvin when running analyses, the user must record the LOG file numbers of sample runs intended for future analysis. The LOG file numbers, as well as the instrument's screen at the time the sample is run.

5. Select the LOG file of interest and drag/copy it to the computer desktop or other location of user's choice.

6. Open Ellvin.

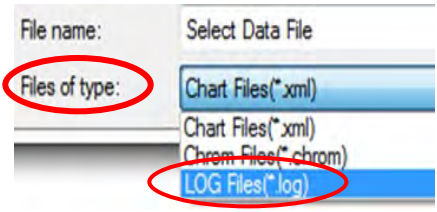
7. Open Live Data Window.



8. Click on the OPEN button.

9. Browse to the location where the LOG file of interest was dragged/copied.

10. At the bottom of the "Select Data File" window, change "Files of Type" to LOG Files.



11. Select the LOG file of interest and open it.

12. The computer screen now displays a chromatogram of the file data as it is imported into Ellvin. At this time, Ellvin also converts the data to an XML format and stores it. The location path of the stored data is displayed at the top of the chromatogram in the Live Data Window (Figure 4.7-2). The data can now be opened in the Analyze Window.

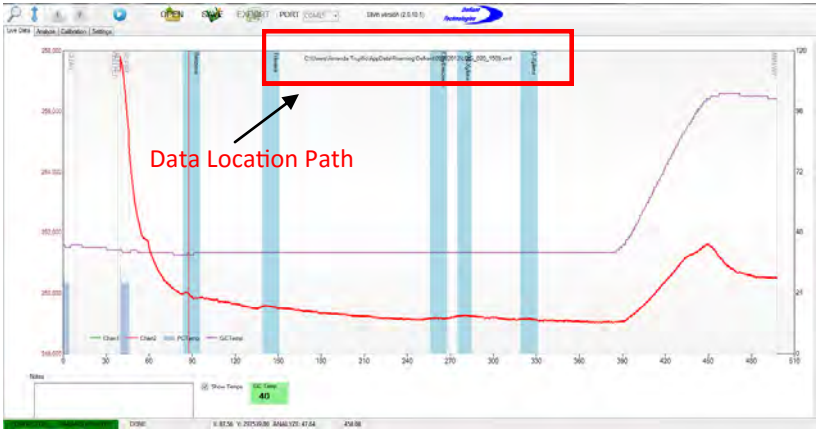


Figure 4.7-2: Live Data Window with chromatogram and data location path.

4.7. Exporting Data Continued

12. Click on the OPEN icon.

13. Follow the location path displayed in the Live Data Window to the folder that contains the data file of indicated.

14. Location Path Example:

C\Users\.....\.....\ 20140930\1716_LOG_xxx.xml

The highlighted numbers correspond to the *date* the storage folder and data file were created by Ellvin. In this example, September 30, 2014.

The folder contains a list of files. The file names are derived from the *time* Ellvin converted the data. In the example in Figure 4.7-3, the file named "1716" was converted at 5:16 PM on 9/30/2014.

15. Open the folder with the location path *date.*

16. The Select the file of interest.

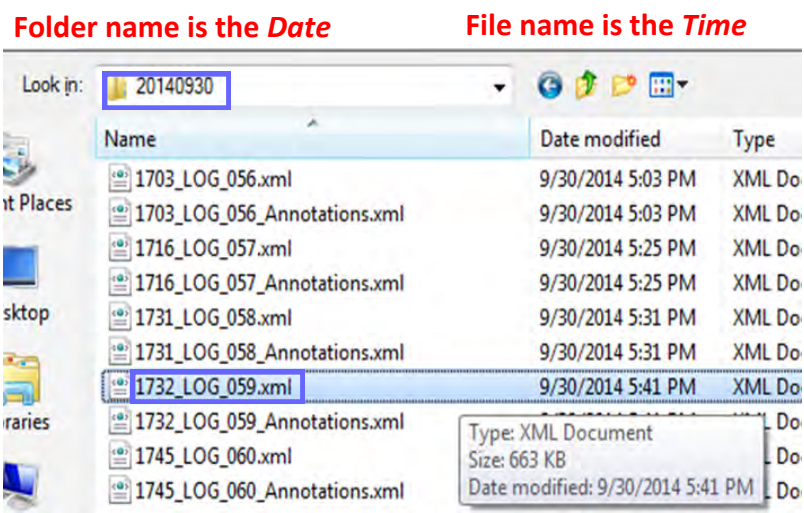


Figure 4.7-3: Data files named and stored by Ellvin.

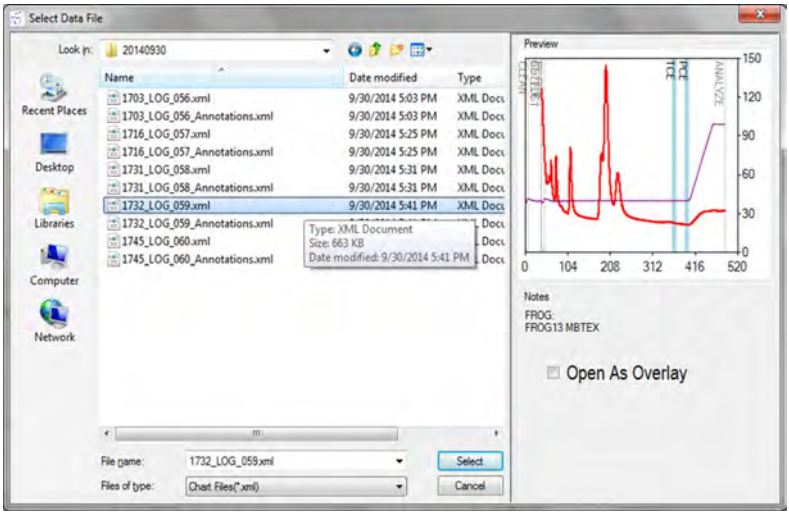


Figure 4.7-4: File Selection Screen

17. A preview chromatogram of the selected file appears to the right of the file list (Figure 4.7-4).

18. Click "Select" to open the file of interest. *Ellvin will automatically transfer to the Analyze tab and display the data.* Proceed to analyze the data with Ellvin Integrator 1 or 2. (See Section 5.2.3)

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SECTION 5: ELLVIN SOFTWARE

The chromatogram software, Ellvin™, is primarily used to perform detailed analyses of sample data. Ellvin uses calibration data to:

- Assign analytes to chromatogram peaks based on GC retention times.
- Report the analytes' concentrations based on peak heights and integrated peak areas.

Ellvin also manages the instrument settings and loads calibrations to the instrument.

Several general features of Ellvin, as well as a few features specific to Analyze Window, are described in the following pages. The user should be familiar with all the features before starting a sample analysis.

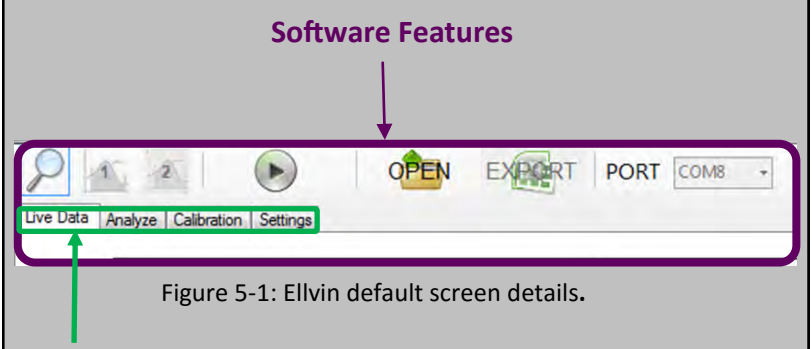


Figure 5-1: Ellvin default screen details.

To start using Ellvin, refer to:

4.2: Connecting to Computer/Ellvin

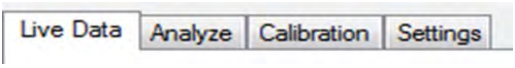
Continued next page.

Section 5. Ellvin Software Continued

5.1. FEATURES OF ELLVIN

WINDOWS

The Ellvin Software has four windows that are accessed with tabs when the software is open.



Window Tabs in Ellvin

- **Live Data Window**: This is the default window for Ellvin. In Live Data Window, Ellvin creates a chromatogram from sample analysis data. The data source may be:
    a. From a sample run on the FROG while connected to Ellvin and simultaneously imported to Ellvin.
    b. From sample data previously recorded on the instruments SD card, then imported to Ellvin.
- **Analyze Window:** As in Live Data Window, Ellvin creates a chromatogram from sample analysis data. In this window, Ellvin retrieves analysis data that was previously stored on a computer. In Analyze Window the user can examine chromatograms closely, integrate chromatogram peaks, and export data to Excel.
- **Calibration Window:** In this window, Ellvin uses analysis data from chemical standards to calibrate the FROG.
- **Settings Window:** In this window, Ellvin manages the settings for the FROG. The settings define temperature and duration parameters for various phases of the instrument's analysis cycle. Refer to:

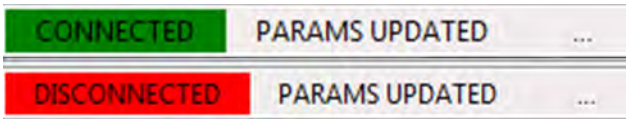
4.3: Instrument Settings

PORT

Use this feature to select the correct data port connection from the FROG-4000™. The user selects a COM# to connect to the FROG.

Connection Port

Based on the selection of COM, the Connection Port will notify the user if the FROG is CONNECTED or DISCONNECTED, and if the parameters have been updated. (Bottom left corner of the software display screen).



GC Column Temperature Indicator

This feature monitors and displays the GC temperature.

The icon is **GREEN** when instrument is ready for Loading.

It turns **RED** during sample analysis.

5.1. Features of Ellvin Continued

Start/Stop Button

Clicking on this button causes the FROG-4000™ to start an analysis cycle. Once the analysis has begun, clicking the button will stop the analysis, but will NOT save the chromatogram.

OPEN Button

Click on this button to open saved files. The files can be from data stored on a computer or on the instrument's internal SD card.

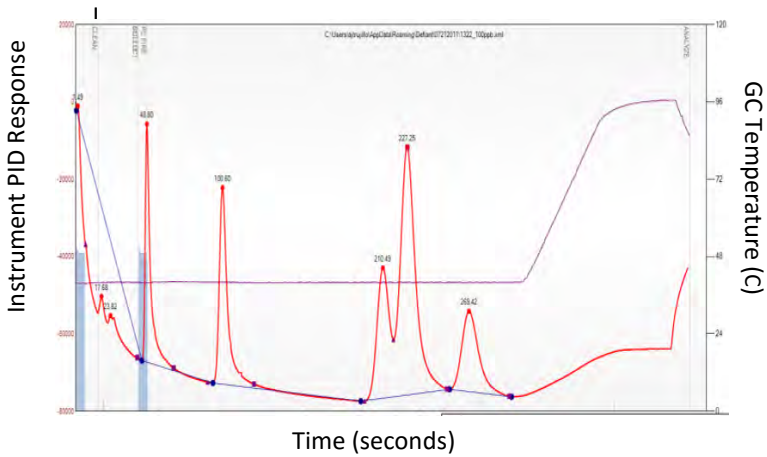
EXPORT

Export only works when Ellvin is in Analyze Window. The user can export an opened file into Microsoft Excel program for further analysis.

Chromatogram Display Screen

The software display screen shows sample analysis data.

- The X-axis is time in seconds.
- The Y-axis shows the instrument's PID response and GC temperature (°C).
- The peaks correspond to separated analytes.



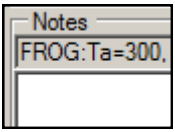
Key

The Key explains colored lines that are shown on display screen.

5.1. Features of Ellvin Continued

Notes

This tool allows the user to records notes about samples while in Live Data or Analyze Window. The notes are saved when the sample analysis is completed. It is important to record the date and time that data files are created in order to locate and retrieve them for further analysis.



Magnifying Glass

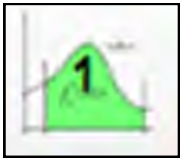
Use this tool to zoom into a chromatogram while data is being collected in Live Data Window, or while in Analyze Window to help with integration.

Detailed instructions for using Magnifying Glass follow in Section 5.2.2.

MOVE

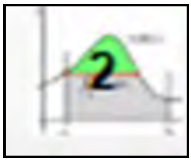
Use this tool to move the chromatogram up and down the Y-axis.

Integrator 1



This feature only operates while in Analyze Window. The user creates a baseline and integrates peaks, then calculates the peak height and area. The baseline integration limits are set by clicking the left mouse button.

Integrator 2



This feature only operates while in Analyze Window. Ellvin creates a baseline by snapping vertically from the left mouse click position to the data line. Ellvin then calculates the peak height and area. Integrator 2 is recommended for the most consistent analysis results. Detailed instructions for using Integrator 2 follow in Section 5.2.3.

Data Grid

Use with Integrator 1 and 2. The Data Grid shows:

- Analyte (Toluene) *Based on calibration retention times.*
- Peak Reference Number (1)
- Retention Time (106.157)
- Peak Height (40291)
- Peak Area (430363)
- Calculated concentration (87.31) *Based on calibration concentrations.*

Analyte	Peak	Time	Height	Area	Width	Concentration
Toluene	1	106.157	40291	430363	0	87.31

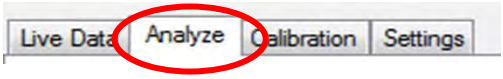
Section 5: Ellvin Software Continued

5.2. APPLYING ELLVIN FEATURES

5.2.1. OPEN BUTTON

To open stored files in Analyze Window:

- Click on the Analyze Tab.



- Click the OPEN button.

- A file selection screen appears. (Figures 5.2.1-1 and 5.2.1-2)

NOTE: Ellvin automatically labels folders and files as they are created.

⇒ Folders of data files are labeled by the *DATE* they were created.

⇒ Data files are labeled by the *TIME* they were created and the LOG number.

In the example shown in Figure 5.2.1-1, the data file was created at 5:16 PM on September 30, 2014.

- To locate the data file of interest, browse to the folder labeled with the *date* the sample was run, or the *date* the data file was imported from the FROG to Ellvin. Double click to open the folder.
- Click on a data file of interest. A preview of the data chromatogram appears to the right of the list.
- Click "Select" to open the file for analysis with Integrator 2.

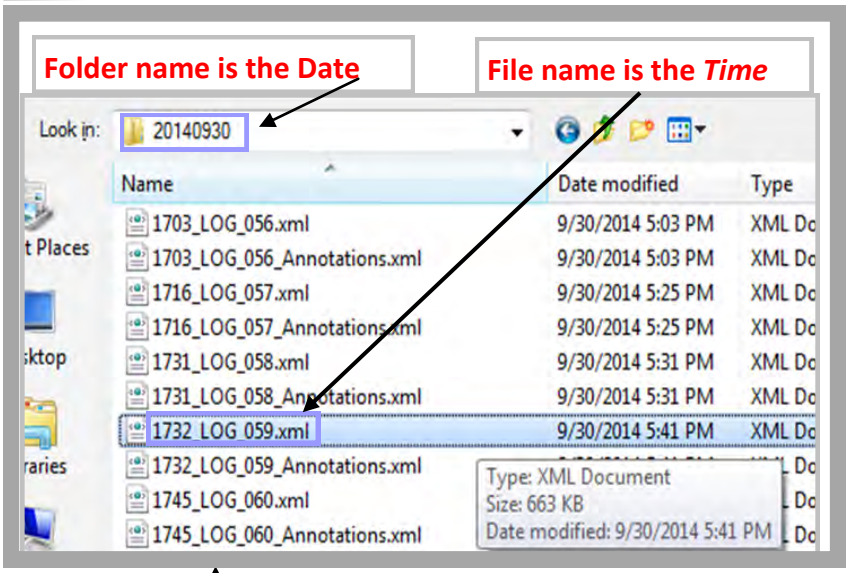


Figure 5.2.1-1 Data files

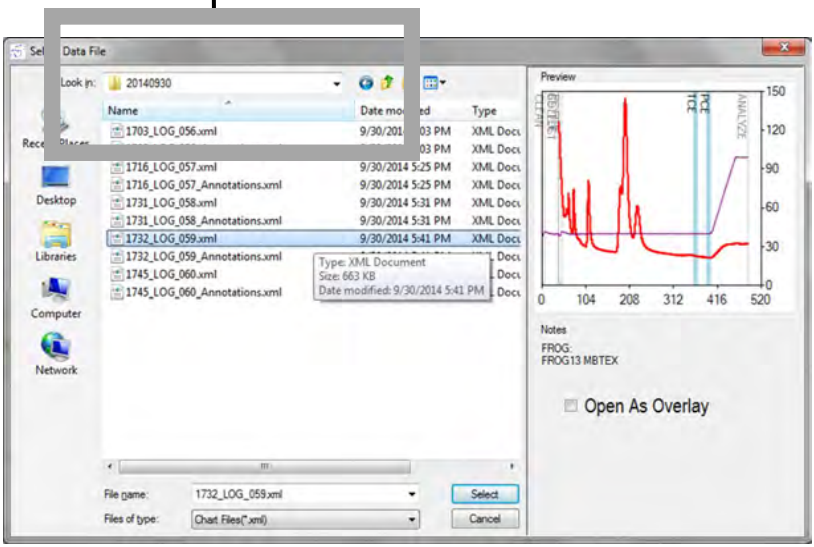
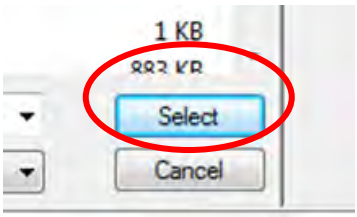


Figure 5.2.1-2: File Selection Screen



5.2. Applying Ellvin Features Continued

5.2.2. MAGNIFYING GLASS

The Magnifying Class can be used in Live Data Window during data import, or while in Analyze Window.

Click on the magnifying glass icon to start.

To Magnify:

- Left click and hold
- Drag mouse over desired magnified area. (Figure 5.2.2-1)
- Release the mouse button.
- The area being magnified is highlighted light blue.
- The display screen then readjusts to show the magnified area. (Figure 5.2.2-2).

To De-Magnify:

- Click the circle on the scroll bars.
- OR double click the magnifying glass icon.

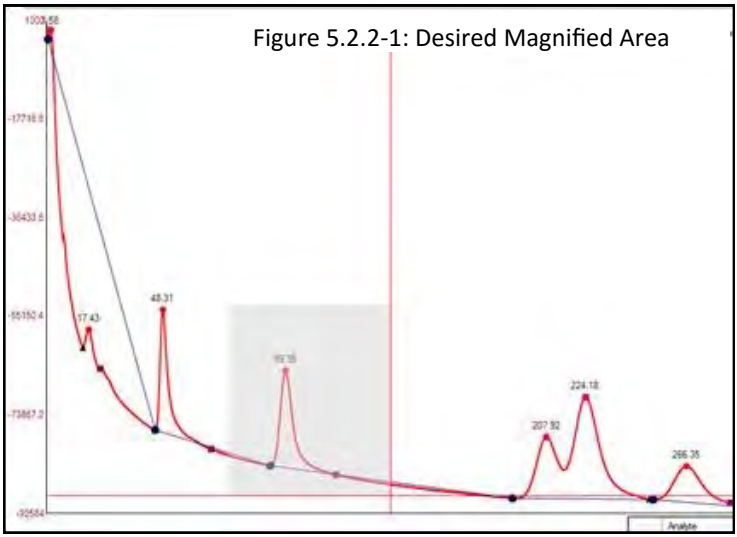


Figure 5.2.2-1: Desired Magnified Area

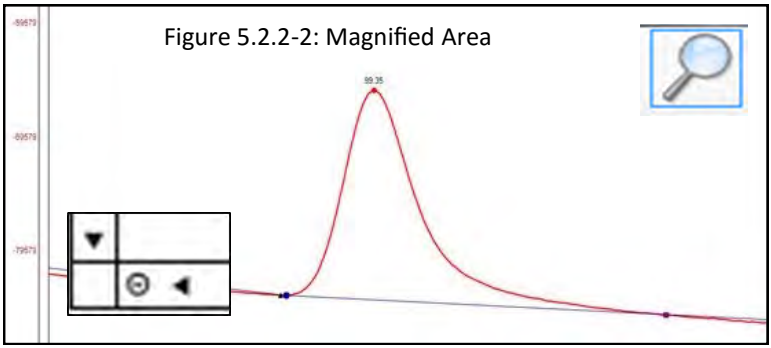
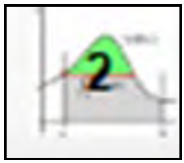


Figure 5.2.2-2: Magnified Area

5.2.3. INTEGRATOR 2

Integrator 2 can be used only in Analyze Window. This tool calculates the area under a peak and the peak height. The area or peak height helps determine the concentration of the analyte.

Click on the Integrator 2 button to start.



Technique to Integrate:

(Refer to Diagrams 5.2.3-1 and 5.2.3-2)

- Begin at the lowest point, Valley 1.
- Drag the mouse to draw an integration line, past the peak, to the second lowest point, Valley 2.
- The integration line should NOT cross the data line. Avoiding this ensures the correct calculation for the peak area.

  (Figure 5.2.3-2).

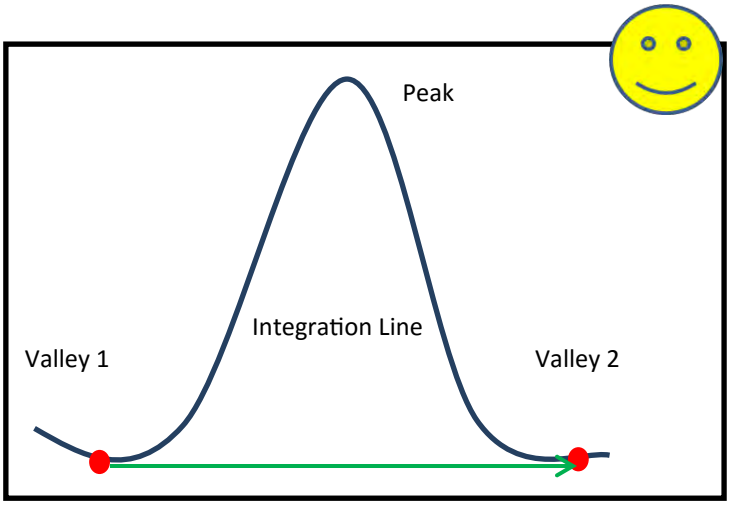


Diagram 5.2.3-1: Valleys and Peaks

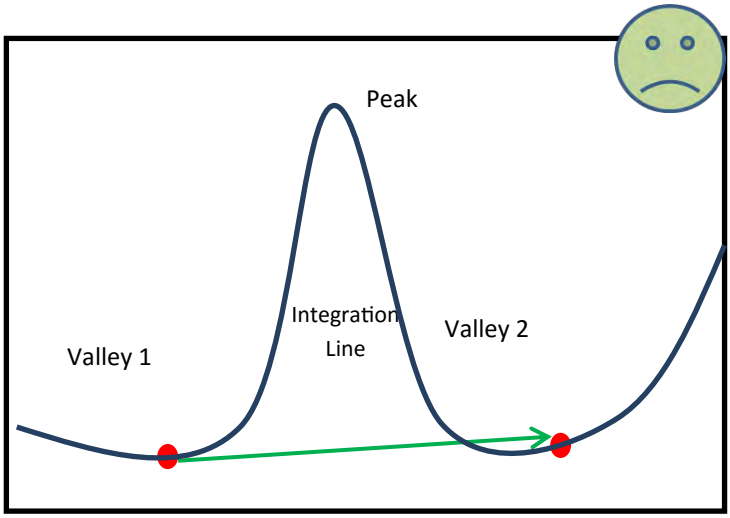


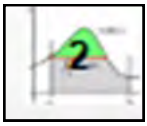
Diagram 5.2.3-2: Crossing Data Line

5.2.3. Integrator 2 Continued

Integrating a Single Peak

Using the correct technique illustrated on the previous page, select the desired peak for integration.

- Select Integrator 2.



- Left click the mouse and hold at Valley 1.
- Drag to Valley 2 and release.
- The Integrator 2 tool uses the software to select the baseline on which the integration line is drawn.
- The gray shadowed area in Ellvin will show which area is being integrated. (Figure 5.2.3-3)
- The integration is complete when a solid black line appears.
- The Data Grid shows the data that corresponds to the related peak. The user can continue integrating peaks.

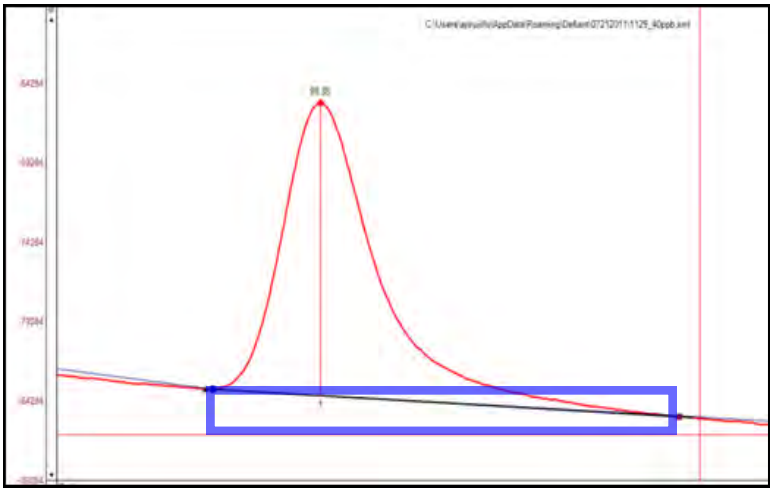


Figure 5.2.3-3: Desired Peak Integrated Area

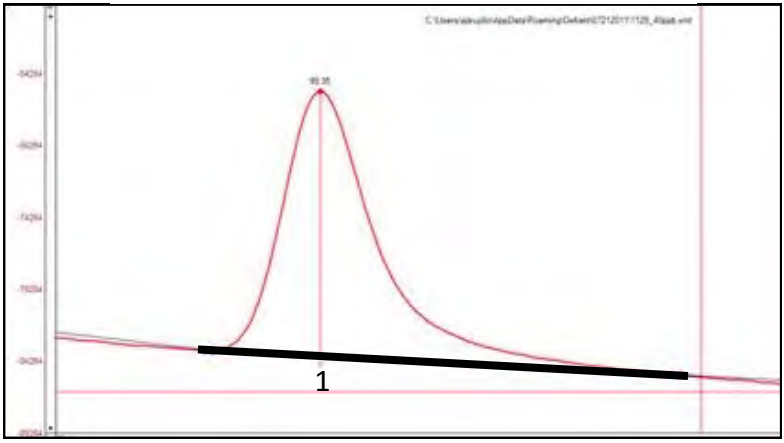


Figure 5.2.3-4: Integration Line

	Analyte	Peak	Time	Height	Area	Width	Concentration
▶	Toluene	1	106.157	40291	430363	0	87.31

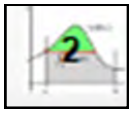
Data Grid

5.2.3. Integrator 2 Continued

Integrating Multiple Peaks

To integrate multiple peaks, follow the same procedures for integrating a single peak using Integrator 2.

Click on the Integrator 2 button to start.



- Right click and hold the mouse at Valley 1.
- Drag to Valley 3 and release.
- The integrator uses Ellvin to select the baseline on which the integration line is drawn.
- The integration is complete when a solid black line appears. The result shows the integration line and the splits placed between joined peaks.
  (Figure 5.2.3-5)
- To integrate the remaining peak (in Figure 5.2.3-5, Peak 3). Click and hold at Valley 3 and drag to Valley 4.
- The Data Grid shows the data that corresponds to the related peak. The user can continue integrating peaks.

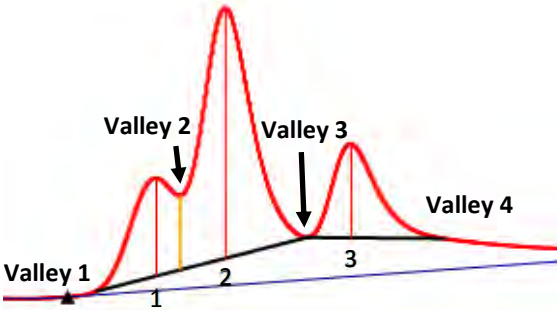


Figure 5.2.3-5: Integration of multiple peaks complete.

Results

Analyte	Peak	Time	Height	Area	Concentration	x Dilution
Ethylbenzene	1	327	288504	2415377	6.30891	6.30891
PM-Xylene	2	338.67	738267	7386991	11.5795	11.5795
o-Xylene	3	359.83	276341	2417951	7.85937	7.85937

Data Grid

When integrating multiple peaks it is necessary to follow the baseline as closely as possible. It is recommended that each peak be carefully assessed before integration. It is usually best to integrate each peak separately unless the valley between the peaks does not reach the baseline as in the case of peaks 3 and 4 in the figures below (Figure 5.2.3-6 and Figure 5.2.3-7).

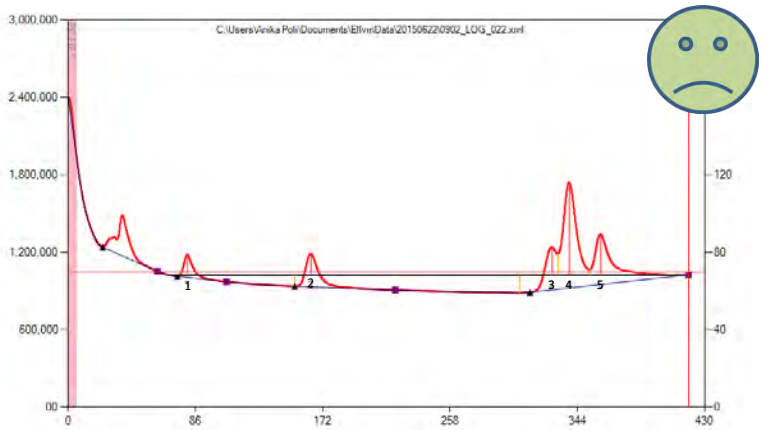


Figure 5.2.3-6: Improper integration of Multiple Peaks

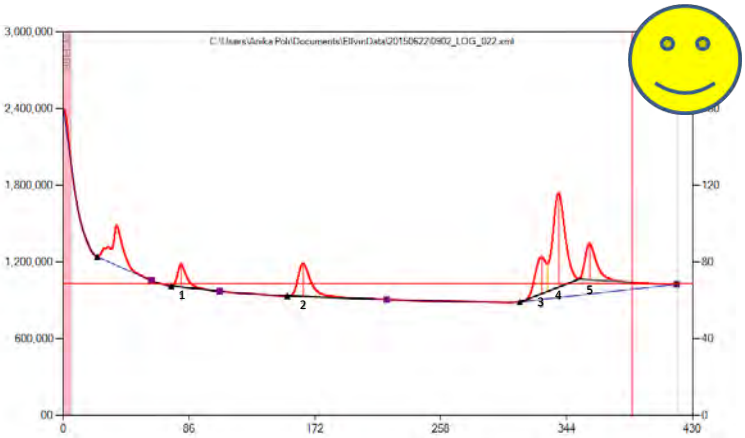


Figure 5.2.3-7: Proper integration of Multiple Peaks

SECTION 6: CALIBRATION

This section provides detailed instructions for calibrating the instrument.

The system is calibrated by testing a series of analytes at varying, known concentrations. As with all GC work, these analytes are selected from an established list of chemicals that are of foremost interest in the environment under investigation.

- Before beginning a calibration, it is recommended that the user become familiar with Ellvin. Refer to Section 5.
- The user should also be familiar with analytical techniques for GC calibration.
- The preparation and use of standards for calibrating the instrument differs for air, liquid, and soil samples. Section 6.1 introduces the procedure for preparing standards.
- Section 6.2 provides detailed instruction for using the features found in Calibration Window.
- Section 6.3 provides detailed instructions for calibrating the instrument.

Section 6: Calibration Continued

6.1. CALIBRATION STANDARDS

NOTE: The instruction in Sections 6.1.1 and 6.1.2 correspond to Step B-3 in Section 6.3.

6.1.1. STANDARDS FOR LIQUID OR SOIL SAMPLES

Run at least four calibration samples from low to high concentrations.

Preparation:

1. Calculate the dilutions for the intended calibration samples.

Traditionally, a ppb concentrations of analytes in water are expressed in micrograms of analyte per liter of water (1 Kg water). Standards typically come pre-diluted in methanol, which cannot be ionized (and therefore not detected) by the instrument's PID.

The following page provides examples for calculating dilutions.

µg/mL =mg/L =ppm (mass) µg /L = ppb (mass)

BTEX = Benzene, Toluene, Ethylbenzene, p/m-Xylene, o-Xylene

MEOH = methanol (GC/MS grade)

Diluting from a Standard

Let C_A = original concentration of an analyte in a solvent, and F = desired dilution factor so $C_B = C_A / F$. Find S = volume of mix C_A that must be added to a solvent volume D to achieve concentration C_B.

The mass of analyte in volume S is $M_A = S * C_A$

$C_B = C_A / F = M_A / (D + S * (1-C_A))$

$= S * C_A / (D + S)$ (approx. for small C_A)

Solving for S yields $S = D / (F-1)$

Example: Using C_A = 2000 µg/mL BTEX in MEOH standard to make a C_B = 200 µg/mL BTEX in MEOH standard (that is F = 10), you must add 500 µL of C_A mix to 4.5 mL MEOH.

Diluting 5mL Water with Standard

Convert mL to µL. 5mL water filled syringe into 5000µL

$$\frac{1000\ \mu L}{1\ mL} * \frac{5\ mL}{1} = 5000\ \mu L$$

Spiking the 5000µL water filled syringe

You have a 200ppm BTEX standard. What is the resulting concentration from injecting 2µL of the 200ppm BTEX standard into the 5000µL water filled syringe?

$$\frac{2\ \mu L * 200ppm(m)BTEX}{5000\ \mu L\ Water} = \frac{400\ ppm(m)}{5000\ \mu L\ Water} =$$

$$: 0.080ppm(m) * \frac{1000mL}{L} = 80ppb(m)$$

6.1.1. Standards for Liquid and Soil Samples Continued

Preparation Continued:

2. Fill a syringe with 5mL deionized water.
3. Load a known volume, as calculated on the previous pages, of a liquid standard into the syringe.
4. Connect to Ellvin and follow the sample loading instructions in Section 4.5.

4.5: Loading a Sample

6.1.2. STANDARDS FOR AIR SAMPLES

Gas calibration standards are available from several sources and we recommend searching the internet with the term "Calibration Gas Standards." The standard typically comes in a pressurized cylinder with a mixture of analytes in nitrogen to achieve the proper dilution. A typical mix for calibration would be 100 ppbv BTEX in N2. Concentrations are typically in parts per billion by volume.

A regulator on the bottle controls the flow and pressure at the exhaust. Because sample will be collected directly from the atmosphere, we suggest connecting the FROG's sample tube to the bottle with a Tee. One port on the tube should vent to the atmosphere and flow of the sample gas should exceed the collection flowrate of the Frog (~60 mL/min).

The FROG permits the creation of a single point calibration, and this is adequate for many applications. Results will be good near the calibration gas concentration, but less reliable further from that concentration. Multiple point calibrations are preferred.

6.1.2. STANDARDS FOR AIR SAMPLES (CONTINUED)

Run at least four calibration standards from low to high concentrations. Defiant Technologies sells a portable gas diluter accessory to be used with the FROG for air calibrations.

Tools Needed:

- Portable Gas Diluter
- Calibration Gas
- Air Sampler

Gas Diluter attached to Calibration gas and FROG

Instrument Preparation:

- Connect Air Sampler to instrument and then connect air sampler to the gas diluter. Place load/analyze-valve in the load position (open). (See Section 4.4.3 Connecting the Air Sample Adapter).
- Connect the calibration gas to the gas diluter.

Continued next page.

6.1.2. Standards for Air Samples Continued.

Standard Preparation and Loading:

1. Use the spreadsheet provided with the Gas Diluter. This will allow for the calculation of sample concentration using the starting concentration of the calibration gas.
2. Adjust the flow rates on the gas diluter until stable at the desired rates.
3. Press the start button and run sample.

   Refer to:

   4.6: Running A Sample

4. Repeat for other sample concentrations.

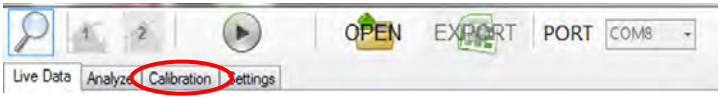
For more detail on the air calibration procedure using the Gas Diluter please refer to the Gas Diluter User's Manual.

Another method to perform multiple point calibrations is to buy multiple compressed standards or, alternatively, to prepare multiple concentrations in Tedlar ™ gas sample bags. We will not go into details on these procedures. We will point out, however, that it can be difficult to achieve accurate concentrations much below 20 ppbv. Low concentration samples tend to degrade in compressed cylinders, and sample bags often have contaminants that appear as large peaks in the chromatography. It is still possible to achieve reasonable results and a Frog user is welcome to call Defiant Technologies for further discussions.

Section 6: Calibration Continued

6.2. ELLVIN CALIBRATION WINDOW FEATURES

- To start using Calibration Window, open Ellvin and click on the Calibration Tab.



6.2.1. LIST OF ANALYTES

This feature allows the user to create a List of Analytes that may be used to calibrate the instrument. The analyte names in the List of Analytes will later be associated with analyte peaks from calibration standard runs.
(See Figure 6.2.1)

The Retention Time, Peak Height, and Peak Area in Figure 6.2.1 are generated from previous analyses of standard solutions with known concentrations.

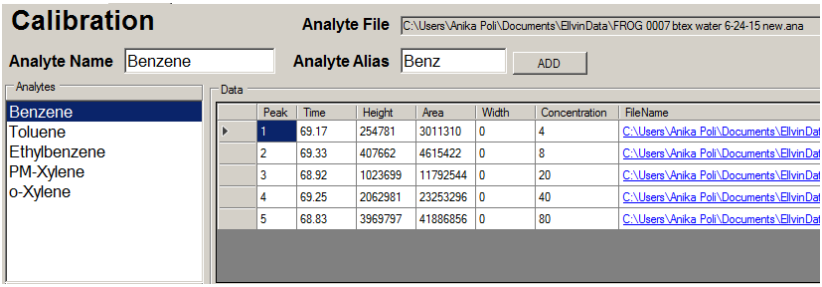
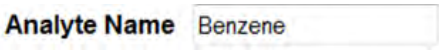


Figure 6.2.1: List of Analytes

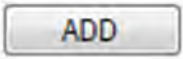
Create the List of Analytes

- Enter the name of the desired calibration analyte in the "Analyte Name" window.

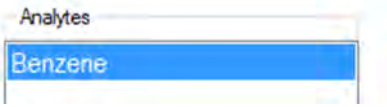


- Create and enter an abbreviated name for the analyte in the "Analyte Alias" (maximum of 5 Characters). The Analyte Alias will be displayed on instrument screen.

- To make an addition to the List of Analytes, click the ADD button.



- To delete an analyte from the list, click on the analyte in the List of Analytes. The desired analyte will be highlighted blue when selected. Click Delete on keyboard to delete the analytes from the list.



6.2. Calibration Window Features Continued

6.2.2. CORRELATION CHART AND EQUATIONS

This feature in the Calibration Window displays the degree of correlation between analyte standards of varying concentrations and the instrument's response to them.
(See Figure 6.2.2)

The correlation is calculated as both a linear equation and a 2nd order quadratic equation.

The user may choose to view the equations and a chart for either Peak Area correlation or for Peak Height correlation.

This correlation is important because Ellvin uses these parameters to calculate concentrations for future samples.

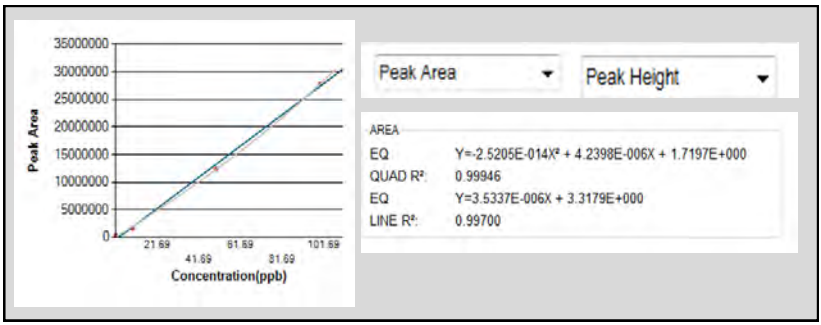


Figure 6.2.2: Correlation Equations and Chart

Section 6: Calibration Continued

6.3. CALIBRATION PROCEDURE

The Calibration Procedure consists of running a series of analysis cycles with standards of varying concentrations for a given analyte. Ellvin then uses the analysis data for the standard solutions to calibrate the instrument.

Before beginning a calibration, the user should be familiar with:

4.3: Instrument Settings

4.4: Instrument Preparation

4.5: Loading a Sample

4.6: Running A Sample

And, Using Ellvin.
(Section 5)

It is recommended to run a minimum of four standards, from low to high concentration, to create data points for calibrating the instrument.

The concentration range for calibration standards depends on the analyte and its unique retention time.

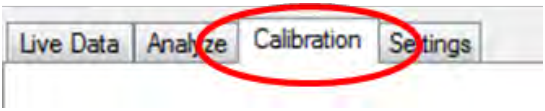
Example standard concentrations for a calibration: 2, 10, 50, 100ppb.

Calibration Procedure Steps

A. Add the Calibration Analytes to the List of Analytes.
(See Section 6.2.1)

The steps in this section prepare the software to calibrate using selected analytes.

A-1 Open the Calibration Window.



A-2 Begin by adding each of the analytes chosen for calibration, one at a time, to the Analyte List.
(See Section 6.2.1)

- No data will be displayed and the chart display area will be blank. Disregard any equations displayed.

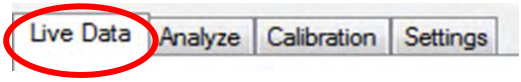
Continued next page.

6.3. Calibration Procedure Continued

B. Run the Calibration Standards

In this section the calibration samples are loaded and instrument response data is stored.

Open the Live Data Window



B-1. Create a clean baseline before running any calibration samples. Refer to:

4.4: Instrument Preparation

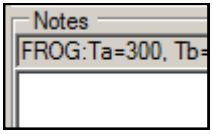
B-2. To begin the calibration, load and run a sample containing only deionized water. Refer to:

4.5: Loading a Sample

4.6: Running A Sample

B-3. Load and run a minimum of four calibration standards of the selected analytes. The samples should be of varying concentrations and should be run in order from low to high concentrations. See Section 6.1 for sample preparation.

B-4. For each of the calibration standards, record the concentrations in the Notes window. This will help identify the files during analysis and calibration.

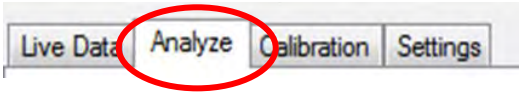


After the instrument has completed running the four (or more) calibration standards, go to the Analyze Window in Ellvin to analyze the instrument response data.

C. Analyze the Data

In this window Ellvin analyzes the stored instrument response data to create the information needed for calibration.

Open the Analyze Window



C-1. Click on the OPEN button to access a list of previously run sample files.
(Figure 6.3-1)
(See Section 5.2.1 for details)

C-2. Select the calibration sample file desired for data analysis. The files are labeled by the *time* they were created and the LOG number.

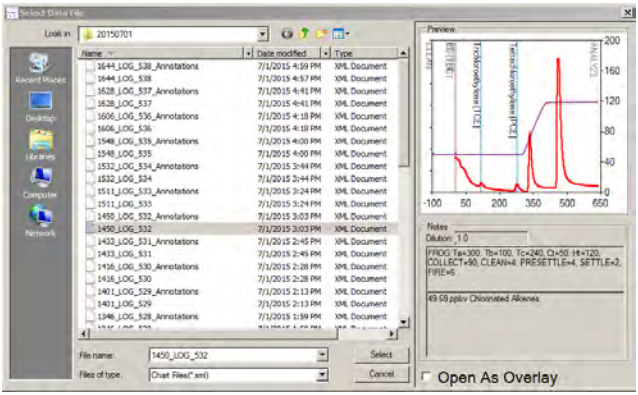


Figure 6.3-1: Open Sample Files

6.3. Calibration Procedure Continued

C-3. In the Analyze Window, click on the Integrator 2 button to integrate the sample peaks in the chromatogram. (Refer to Section 5.2.3 for detailed instructions on using the Integrator 2)

The results of the data analysis are displayed on the chromatogram and in the Data Grid.
(Figure 6.3-2)

The example shown in Figure 6.3-2 is for a sample of BTEX.

Analytes may be run one at a time to determine or confirm retention times.

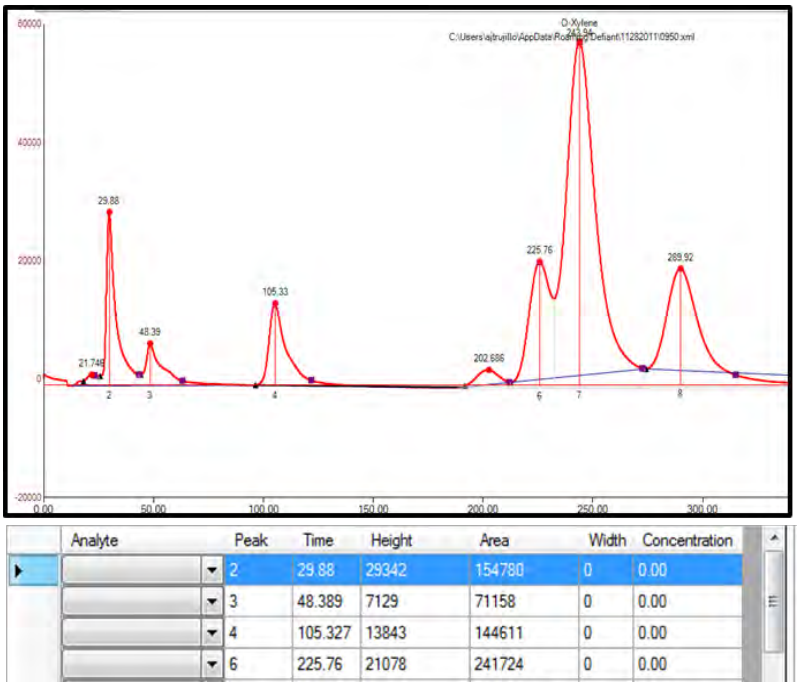


Figure 6.3-2: Analysis Chromatogram and Data Grid

D. Calibrate the Instrument

In this section, the data analyzed in Section C is transferred to the Calibration Window. Ellvin uses the data to calibrate the instrument for each analyte.

D-1. To transfer data to the Calibration Window:

Right click the Data Grid. The List of Analytes previously recorded in the Section A of the Calibration Procedures appears.

D-2. Use the Analyte drop down list to select the analyte that corresponds to each peak based on retention time. Match all the peaks with an analyte.

In the example shown in Figures 6.3-3 and 6.3-4, benzene is selected for Peak #1 because in previous single-analyte tests, benzene had a retention time of 52 seconds.

NOTE: Retention times are dependent on instrument and temperature profile, and will vary from instrument to instrument.

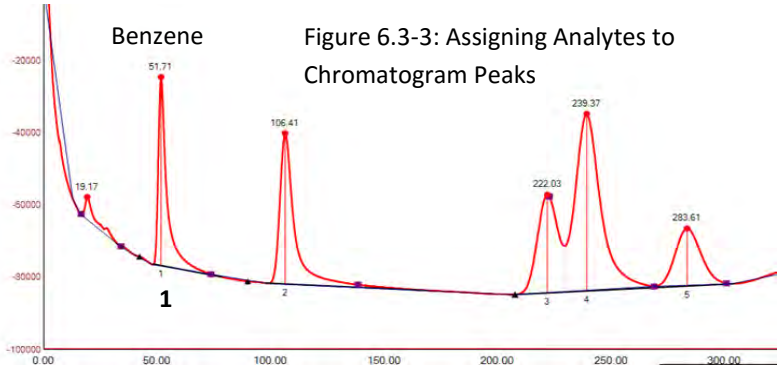


Figure 6.3-3: Assigning Analytes to Chromatogram Peaks

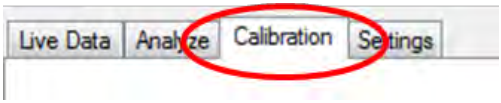
Analyte	Peak	Time	Height	Area	Width
	1	51.709	52205	288173	0
	2	106.406	41757	400032	0
	3	222.025	27246	297169	0
	4	239.372	49086	683288	0
	5	283.611	15982	232827	0

Delete Row
MTBE
Benzene
Toluene
Ethylbenzene
P/M-Xylene

Figure 6.3-4: Benzene is Selected for Peak #1.

6.3. Calibration Procedure Continued

D-3. To view the imported data, open the Calibration Window, click on List of Analytes, and select the desired analyte. The imported data for this analyte will be displayed



In the example in Figure 6.3-5, Benzene has been selected.

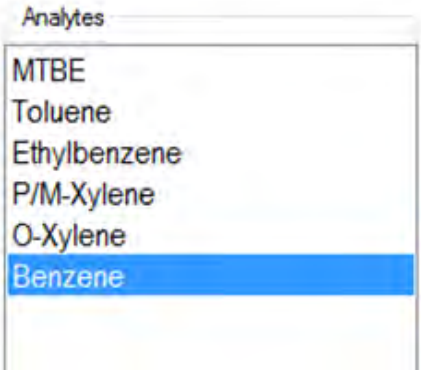


Figure 6.3-5: Select the Desired Analyte from the List of Analytes

D-4. In the Calibration Window, enter in the corresponding concentration for the calibration standard in the column titled "Concentration".

Standard concentrations were recorded in the Notes window in Section B of the Calibration Procedures.

(See B-4)

Peak	Time	Height	Area	Width	Concentration
2	29.88	29342	154780	0	0.00
3	48.389	7129	71158	0	0.00

Repeat Steps C-1 through D-4 of the Calibration Procedures to import and enter all the standard data to the Calibration Window.

The Correlation Chart and Equations (Section 6.2.2) will appear after the first point is imported into the Calibration Window. The single linear point fit will be automatically forced through zero.

As data points are added, correlation equations are generated by the Ellvin. A graph of the data points and the curve fit will be displayed in the calibration window, the user can now inspect the fit equation.

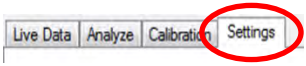
Downloading the Calibration to the Instrument

Connect the instrument to Ellvin with the USB cable. Refer to:

4.2: Connecting to Computer/Ellvin

1. All analytes listed in the calibration should show a R^2 correlation close to 1.0. The closer the R^2 value is to 1.0, then the better the software can calculate the concentration of an unknown sample.

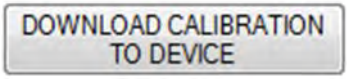
2. Open the Settings Window.



Continued next page.

6.3. Calibration Procedure Continued

3. Click on 'Download Calibration to Device'



4. This will allow the instrument to estimate the concentration of analytes uploaded into the calibration using the peak height linear function.

NOTE: The Ellvin software can compute concentrations using either peak height or area under the peak. However, when the instrument is running independently, its processing power is more limited, so peak height and a linear data fit are used in calculating concentrations.

SECTION 7: MAINTENANCE

7.1. ROUTINE CLEANING

It is important to clean the FROG-4000™ after analyzing samples in order to prevent cross-sample contamination.

The FROG-4000™ **does** need to be cleaned if:

- **More than one type of analyte** is being tested. The user must clean the instrument between sets of the different analytes.
- **A high concentration is introduced.** If the user observes large peaks in the chromatogram, the instrument should be cleaned prior to analyzing a sample.

The FROG-4000™ **does NOT** need to be cleaned immediately if:

- **Same analyte** is being tested. The user can run a set of samples of the same analyte from a LOW concentration to a HIGH concentration consecutively. The user cleans the instrument at the end of the set.
- Rinsing the sparge bottle and syringe between uses is always recommended.
- **The baseline is clear.** If no peaks are observed in the chromatogram, no cleaning is necessary.

To clean the instrument, perform the following procedures:

4.4: Instrument Preparation

The instrument is clean when a clean baseline has been achieved.

Section 7: Maintenance Continued

7.2. ANNUAL CLEANING

It is recommended to have the FROG-4000™ cleaned yearly by an authorized representative.

Please contact Defiant Technologies for support.
Email: info@defiant-tech.com
Phone: 505-999-5880

7.3. CLEANING THE SCRUBBER

It is recommended to clean the carrier gas scrubber every three months, or as needed to create a clean baseline.

Tools needed to clean the scrubber include:

1. *Clean Molecular Sieves
2. *Clean Activated Carbon
3. 3/32" allen wrench

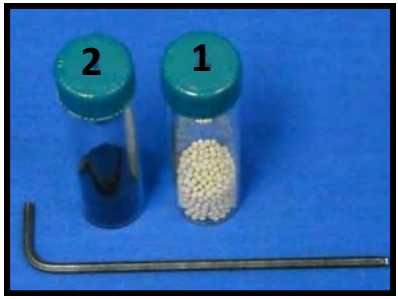


Figure 7.3-1: Tools needed.

***NOTE:** Replacement activated carbon and molecular sieves may be purchased, premeasured and cleaned, through Defiant Technologies, Inc.

Activated Carbon, Part # DT-FG4K-AC-1
Molecular Sieves, Part # DT-FG4K-MS-1

1. Remove the four corner 4-40 screws with the 3/32" allen wrench.
2. Lightly pull scrubber off FROG; place any O-rings back in place if they come out.

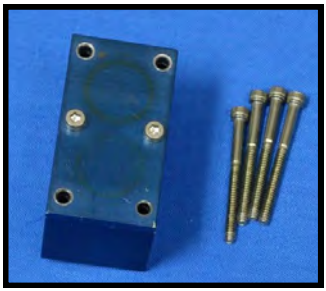


Figure 7.3-2: Four corner screws removed and scrubber removed from FROG

3. Turn the scrubber block upside down.
   - Position 1 has widely spaced ports. This chamber holds the molecular sieves.
   - Position 2 has narrowly spaced ports. This chamber holds the activated carbon.

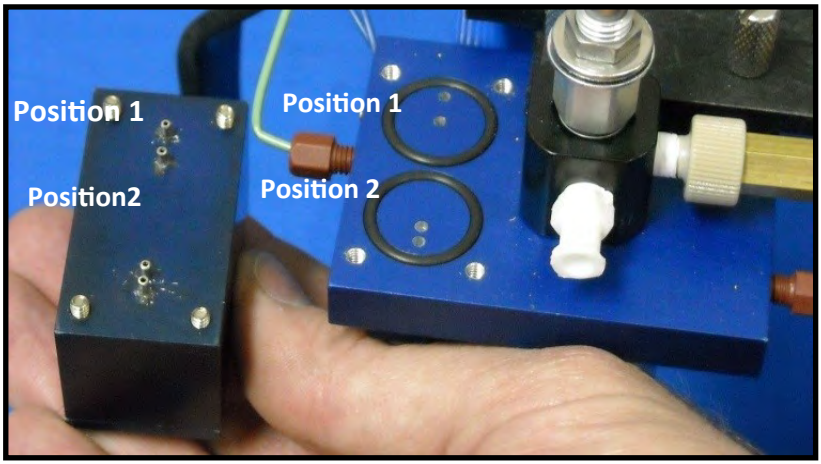


Figure 7.3-3: Upside down scrubber with ports visible.

7.3. Cleaning the Scrubber Continued

4. Turn the scrubber right-side up and remove the two, center position, 4-40 screws with the 3/32" allen wrench.

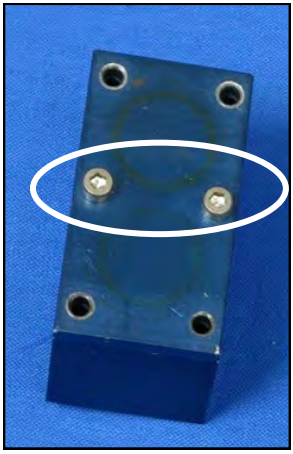


Figure 7.3-4: Two Center Screws.

5. Remove the scrubber lid; put any O-rings back in place if they come out.

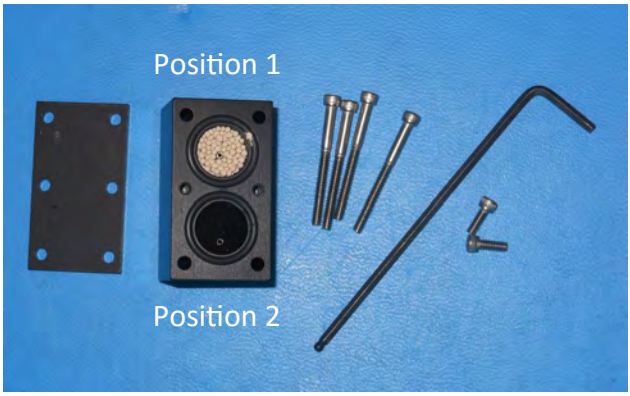


Figure 7.3-5 Open scrubber

6. Dispose of dirty activated carbon and molecular sieves.
7. Use a paper funnel to put new activated carbon into Position 1.
8. Use a paper funnel to put new molecular sieves into Position 2.
9. Replace the lid.
10. Tightly replace the two, center position, 4-40 screws with the 3/32" allen wrench.
11. Place the scrubber back onto FROG (make sure Position 1 is in correct spot).
12. Snuggly replace the four corner 4-40 screws with the 3/32" allen wrench.
13. There should be NO space in between the scrubber holder on the instrument body and the scrubber block! (Figures 7.3-6 and 7.3-7)
14. To fix space in between, remove the block and make sure O-rings are in the proper position.

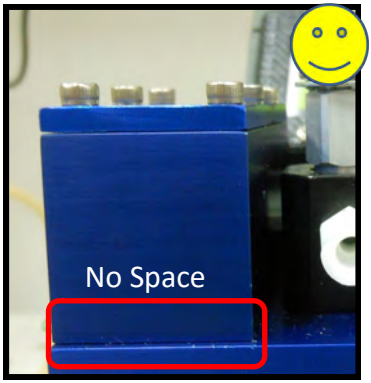


Figure 7.3-6:
Correct scrubber position.

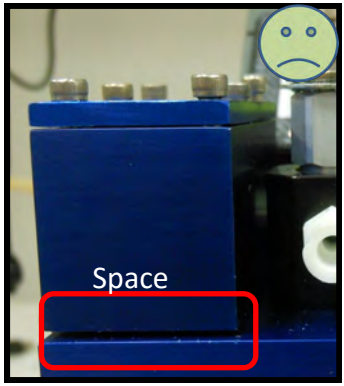


Figure 7.3-7:
Incorrect scrubber position.

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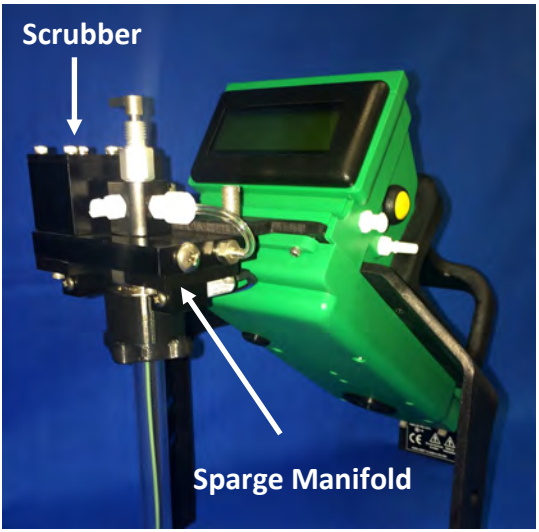
SECTION 8: TROUBLE SHOOTING

8.1. INVERTING THE FROG WITH WATER IN THE SPARGE BOTTLE

If the FROG has been inverted with water in the sparge bottle, it is likely that water will enter the sparge manifold.



The steps on the following pages can be used to remove the water.

8.1. Inverting the FROG Continued

1. Remove the scrubber. Look for liquid in Position 1 or Position 2 on the sparge manifold.

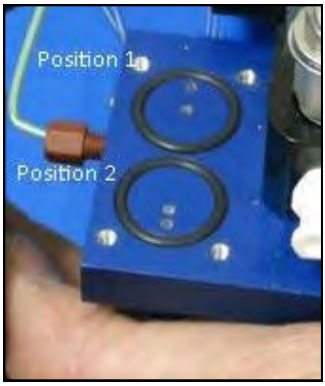


Figure 8.1-2: Look for liquid.

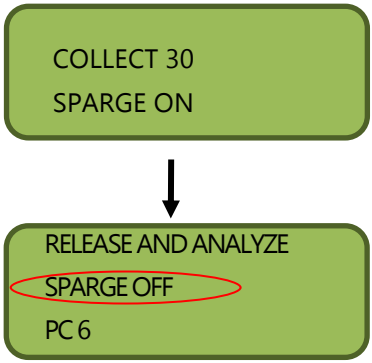
2. Turn the load/analyze valve to the ANALYZE position.

Figure 8.1-3: Close the valve to the ANALYZE position

3. With the scrubber removed, install an empty sparge bottle.

4. Press the start button on the FROG and allow the system to run through the sparge stage of the analysis cycle (a sparge cycle).

   Turn the FROG off when the screen displays SPARGE OFF.



Refer to:

4.6: Running A Sample

5. After the sparge cycle, power the unit down and look for water where the scrubber mounts on the sparge manifold (Figure 8.1-2, Positions 1 and 2).

Repeat Steps 2 through 5 until water no longer emerges from the sparge manifold.

8.1. Inverting the FROG Continued

6. Replace the activated carbon and molecular sieves in the scrubber, then reinstall the scrubber block.
   (See Section 8.1.3, Cleaning the Scrubber for procedure details)
7. Load a blank sample (deionized water) and run a third Sparge Cycle.

Look for bubbles in the sparge bottle.

- If bubbles appear, the liquid was successfully removed from the sparge manifold.

- If bubbles do not appear, then contact Defiant Technologies for consultation.

  Email: info@defiant-tech.com
  Phone: 505-999-5880

Figure 8.1-4: Look for Bubbles in the sparge bottle.

Section 8: Troubleshooting Continued

8.2. DEGRADING CHROMATOGRAPHY : SCRUBBER IS NOT SECURED PROPERLY

If the Chromatography is degrading over time:

Check the scrubber block.

The scrubber block may NOT be sealed correctly.

There should be no space in between the scrubber block and the scrubber holder.
(Figures 8.2-1 and 8.2-2)
(Refer to Section 8.1.3, Cleaning the Scrubber)

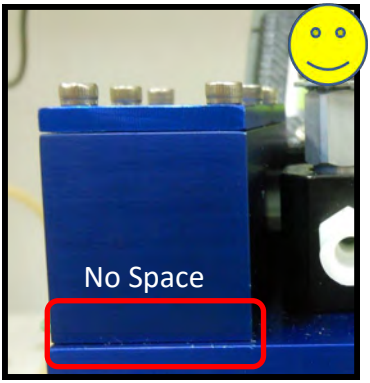


Figure 8.2-1:
Correct scrubber position.

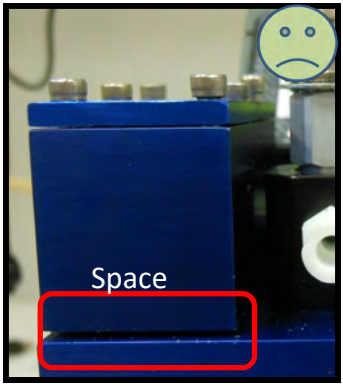


Figure 8.2-2:
Incorrect scrubber position.

Performance can also be affected by high concentrations of analytes, or high background concentrations in the surrounding environment (See next section).

Section 8: Troubleshooting Continued

8.3. CANNOT ACHIEVE A CLEAN BASELINE

If a clean baseline cannot be achieved after **repeatedly** following the procedures in Sections 4.4.1 and 4.4.2 (Rinsing the Instrument and Creating a Clean Baseline), contamination problems may stem from having loaded a sample with a high concentration of analyte, or from the presence of airborne contaminants.

NOTE: A small peak at the beginning of the chromatogram is normal for a clean baseline.

Complete the following procedures to eliminate contamination interfering with a clean baseline.

Perform procedure 4.4 while *connected to Ellvin* and using *warm* deionized water. Refer to:

4.4: Instrument Preparation

Repeat this procedure up to three times if necessary to achieve a clean baseline.

Airborne Contaminants

If it is still NOT possible to achieve a clean baseline, there may be airborne contaminants present in the ambient air. An airborne contaminant can enter the sparge bottle when it is lowered. This volume of air cannot be scrubbed and will be collected by the PC.

Airborne contaminants can also enter through the pump with the sparge and carrier gas though these are largely removed by the scrubbers.

Solutions:

1. Either circulate air in the testing environment, or move to a new location, then perform:

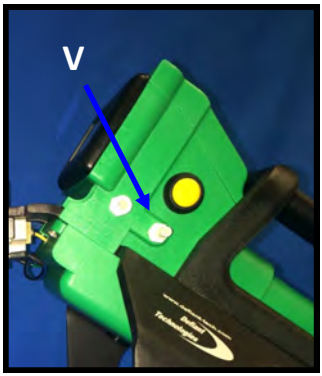
4.4: Instrument Preparation

If, a clean baseline is still not achievable,

2. Clean the scrubber.
   (See Section 7.3)

If, a clean baseline is still not achievable,

3. Provide an activated charcoal trap at the pump inlet (V).



Section 8: Troubleshooting Continued

8.4. BLACK INSTRUMENT SCREEN

Periodically, the instrument display screen will appear black. However, it should reset to appear normal at the end of an analysis run.
If the display screen on the FROG remains black, it can be a sign that the instrument is overheating.

Take the following steps to cool the FROG:

1. Place instrument in the shade or indoors to help cool the GC Temp to READY status.
2. Increase the initial cold GC temperature, Ct, to a maximum of 50 °C.
   a. Go to Settings Window. Refer to:

   4.3: Instrument Settings

   b. Change GC initial cold temperature (C_t) to the following range:
   minimum of 40°C
   maximum of 50°C
   (Figure 8.3-1)

   c. Click "SET" to save changes.

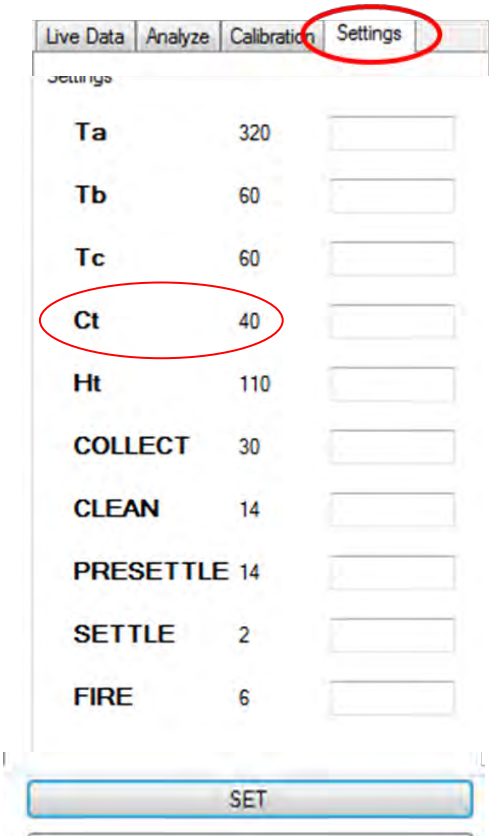


Figure 8.3-1: Change the GC Settings.

NOTE: Increasing GC Temp will affect retention times.

The instrument will operate within temperature and relative humidity conditions of 0-55°C and 0 to 90% respectively; however, an environment comfortable for human habitation (reasonable constant temperature and humidity conditions) is recommended for optimum performance.

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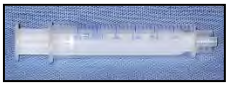
APPENDIX I: AVAILABLE ACCESSORIES/SPARE PARTS

Item	Defiant Part #	Description
FROG-4000 Warranty and Service Contract	DT-FG4K-SERV-1	One year service contract / maintenance program.
Activated Carbon	DT-FG4K-AC-1	Replacement Activated Carbon for FROG 4000 air scrubber. Pre-measured and pre-cleaned.
Molecular Sieves	DT-FG4K-MS-1	Replacement Molecular Sieves for FROG 4000 air scrubber. Pre-measured and pre-cleaned.
Sparge Bottle	DT-FG4K-SBGN-1	Sparge Bottle with globe neck.
Sparge Bottle Nut	DT-FG4K-SBN-1	Nut to connect Sparge Bottle to instrument.
5 mL Glass Syringe	DT-FG4K-SYGG-1	5mL glass syringe with Luer Lock tip.

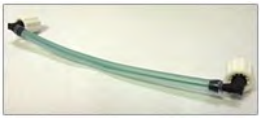
APPENDIX I: AVAILABLE ACCESSORIES/SPARE PARTS

Item	Defiant Part #	Description
5mL Plastic Syringe 	DT-FG4K-SYGP-1	5mL plastic syringe with Luer Lock tip.
60mL Rinsing Syringe	DT-FG4K-SYGN-1	60mL syringe with Luer Lock tip for rinsing Sparge Needle.
Luer Lock Inlet	DT-FG4K-LL-1	Attachment for syringe.
PID Assembly	DT-FG4K-PID-1 DT-FG4K-PID-2 DT-FG4K-PID-3	PID Assembly for normal sensitivity (1) low sensitivity (2) high sensitivity (3)
Tool Kit	DT-FG4K-TK-1	Assorted tools for maintenance of FROG-4000.
Sparge Tube Cover Guard	DT-FG4K-GUARD-1	Sparge Tube Guard for covering Sparge tube in shipping container

APPENDIX I: AVAILABLE ACCESSORIES/SPARE PARTS

Item	Defiant Part #	Description
Ferrules for Sparge Bottle Nut	DT-FG4K-SBNF-1	Replacement ferrules for the Sparge Bottle Nut, 1/2" ferrule set.
Ferrules for Air Sample Bag Adapter for FROG Air Sampler	DT-FG4K-SBNF-2	Replacement ferrules for the Air Sample bag adapter for the FROG's air sampler, 3/16" ferrule set, teflon.
Sparge Line	DT-FG4KSL-1	Sparge Line with Connectors.
Valve Assembly	DT-FG4K-VLV-1	Replacement valve assembly for FROG-4000.
Air Sampler Wand	DT-FG4K-AS-WAND	Replacement air sampler wand.
1/16-3/16 Adapter	DT-AS-316-ADAPTER	Replacement 1/16-3/16 adapter for connecting the air sampler transfer line to a Tedlar bag.

APPENDIX I: AVAILABLE ACCESSORIES/SPARE PARTS

Item	Defiant Part #	Description
Air Sample Transfer Line	DT-AS-TRAS-LINE	Replacement transfer line for connecting air sampler.
Air Sampler Coupler Line 	DT-AS-COUP	Replacement couple line for connecting the air sampler box to the Frog.
Battery	DT-BT-NIMH9V5K-1	Rechargeable NiMH Battery 9V, 5000 mAhr.
Serial Data Cable	DT-DC-1	Ellvin (software) communication cable.
USB Cable	DT-USB-1	Cable USB A / MINI B ASSY. Stored data transfer cable.
Power Supply	DT-PS9V3A-1	Power Supply, 9V 3A.

APPENDIX I: AVAILABLE ACCESSORIES/SPARE PARTS

Item	Defiant Part #	Description
Battery Charger	DT-BTCHG-1	Nickel-Metal Hydride Battery Charger.
Pump	DT-PU-1	Replacement air pump.

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APPENDIX II: DETECTABLE CHEMICALS

Common Chemicals Detectable by FROG 4000	CAS Number	IE (eV)
1,1-Dichloroethene	75-35-4	10.0
1,2,4-Trichlorobenzene	120-82-1	9.0
1,2-Dibromoethane	106-93-4	10.4
1,2-Dichlorobenzene	95-50-1	9.1
1,3-Dichlorobenzene	541-73-1	9.1
1,4-Dichlorobenzene	106-46-7	9.0
1,4-Dioxane	123-91-1	9.2
1-Propanol	71-23-8	10.2
2-Butanone (MEK)	78-93-3	9.5
2-Chloroethanol	107-07-3	10.5
2-Hexanone	591-78-6	9.4
2-Pentanone	107-87-9	9.4
2-Picoline	109-06-8	9.4
2-Propanol	67-63-0	10.2
4-Methyl-2-pentanone	108-10-1	9.3
Acetone	67-64-1	9.7
Acrolein	107-02-8	10.1
Allyl alcohol	107-18-6	9.6
Allyl chloride	107-05-1	10.1
Benzene	71-43-2	9.2
Benzyl chloride	100-44-7	9.1
Bromoacetone	598-31-2	9.7
Bromodichloromethane	75-27-4	10.6
Bromoform	75-25-2	10.5
Bromomethane	74-83-9	10.5
Carbon disulfide	75-15-0	10.1
Chlorobenzene	108-90-7	9.1
Chlorodibromomethane	124-48-1	10.6
Chloroethane	75-00-3	10.0
Chloroprene	126-99-8	8.8

APPENDIX II: DETECTABLE CHEMICALS CONTINUED

Common Chemicals Detectable by FROG 4000	CAS Number	IE (eV)
Crotonaldehyde	4170-30-3	9.7
Dibromomethane	74-95-3	10.5
Diethyl ether	60-29-7	9.5
Diisopropyl ether (DIPE)	108-20-3	9.2
Epichlorohydrin	106-89-8	10.6
Ethanol	64-17-5	10.6
Ethyl acetate	141-78-6	10.0
Ethyl tert butyl ether	637-92-3	9.4
Ethylbenzene	100-41-4	8.8
Ethylene oxide	75-21-8	10.6
Iodomethane	74-88-4	9.5
Isobutyl alcohol	78-83-1	10.1
Isopropylbenzene	98-82-8	8.8
Methacrylonitrile	126-98-7	10.3
Methyl methacrylate	80-62-6	9.7
Methyl tert-butyl ether	1634-04-4	9.2
m-Xylene	108-38-3	8.6
Naphthalene	91-20-3	8.1
n-Butanol	71-36-3	10.0
Nitrobenzene	98-95-3	9.9
n-Propylamine	107-10-8	8.8
o-Toluidine	95-53-4	7.4
o-Xylene	95-47-6	8.6
Propargyl alcohol	107-19-7	10.5
p-Xylene	106-42-3	8.5
Pyridine	110-86-1	9.3
Styrene	100-42-5	8.4
t-Butyl alcohol	75-65-0	10.3
Tetrachloroethene	127-18-4	9.3
Toluene	108-88-3	8.8

APPENDIX II: DETECTABLE CHEMICALS CONTINUED

Common Chemicals Detectable by FROG 4000	CAS Number	IE (eV)
trans-1,2-Dichloroethene	156-60-5	9.7
Trichloroethene	79-01-6	9.5
Vinyl acetate	108-05-4	9.2
Vinyl chloride	75-01-4	10.0
β-Propiolactone	57-57-8	9.7

NOTE: This list is by no means exhaustive. The FROG-4000™ uses a 10.6eV lamp, so many analytes with activation energies below 10.6eV may be detectable with the instrument.

APPENDIX E: USERS MANUAL - NANORAM® RAMAN SPECTROMETER

NanoRam® 2nd Generation Handheld Raman System User Manual

19 Shea Way, Newark, DE 19713 • Tel: (302) 368-7824 • Fax: (302) 368-7830 • Web: www.bwtek.com

290020250-I (09/14/2015)

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1. NanoRam Overview

The NanoRam is a handheld Raman instrument designed for rapid identification of sample material based on their Raman spectrum. The instrument has a touch screen operation with intuitive software for easy operation by specialists and non-specialists alike. Identification and Investigation modes of analysis are available based on qualitative analysis of sample spectra that are compared to method and/or library spectra to provide Pass/Fail and Match/No Match results. The operating software (NOS) has different user access levels, and includes a complete audit trail of measurements. Data reporting, management and account management are done by synchronizing the instrument data with the NanoRam data/library/user/report management software NID, loaded onto a PC. Library and method transfer are supported between different NanoRam units. The instrument is housed in an IP64-rated case that provides protection from ingress of dust, and water splashing on it from any direction.

1.1. Safety Warning and Cautions

The NanoRam system contains one Class 3B laser light source. The product complies with 21 CFR 1040.10, Laser products. Please read through this user manual before operating the system.

1.2. Laser Emission Aperture and Beam Shutter

Located at the laser emission aperture, the laser emission label indicates that the laser energy emission occurs at the corresponding port.

The unit comes equipped with CDRH-compliant laser safety measures including soft key switch, remote interlock, and emergency laser stop key button.

The laser hazard zone is within 30cm (11.8 inches) to the tip of the point-and-shoot adaptor.

CAUTION: The unit should be powered down when the lensed shaft is removed to accommodate any of the optional accessories that use a different shaft.

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1.3. Remote Interlock

The remote interlock is located at the bottom of the unit next to the Ethernet port. The remote interlock facilitates the laser 'on' and 'off' remote control function. When the laser stop key is inserted into the slot, the interlock is closed and laser emission is enabled. When the key is pulled out, the interlock is open and the laser does not emit and cannot be turned on.

1.4. Laser Warning Label

The laser warning label is located on the rear panel of the system. The label displays the laser safety class, wavelength and power of the laser source.

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1.5. Precautions

- **Never point the unit directly at a person.**
- **Never look directly into the laser beam path or scattered laser light from any reflective surface.**
- **Never look directly into the laser source.**
- **Maintain low beam level when performing experimental setup to prevent inadvertent beam-eye contact.**
- **As a precaution against accidental exposures to the laser beam or its reflection, user should always wear laser safety glasses (provided) with sufficient attenuation for the laser.**

Sources for additional information and assistance on laser safety:

CDRH-Radiological Health Program
Office of Communication, Education and Radiation Programs
Center for Devices and Radiological Health
Food and Drug Administration
10903 New Hampshire Avenue W066-4613
Silver Spring, MD 20993 USA
Tel: 1-800-638-2041
Fax: 1-301-847-8149
dsmica@fda.hhs.gov

Laser Institute of America
13501 Ingenuity Drive, Suite 128
Orlando, FL 32826 USA
Toll Free: 1-800-345-2737
Tel: 1-407-380-1553
Fax: 1-407-380-5588
www.lia.org

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2. Diagrams of the NanoRam

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Warranty Seal Label

The warranty seal labels are positioned on both sides of the system under the blue jacket. Any attempt to open the panel(s) of this device will break these seals and void the warranty.

Manufacturer's Identification Label

The manufacturer's general identification label located on the rear panel of the system includes warning information and also displays the manufacturer name, address, model number, serial number, and the manufacturing date.

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3. System Contents

The system should include the following items:

ITEM	PART NO.	IMAGE
One NanoRam unit	840000341 (BWS456)	
One lithium-ion battery	840000290	
One point-and-shoot adaptor	840000343	
One liquid vial holder adaptor	840000344	
One bottle adaptor	840000345	
One calibration cap with built-in polystyrene	840000348	
One accessory pouch to hold all standard accessories	840000354	
Six 15mm-diameter vials in a pouch	840000329 840000344	
One protection cap	840000353	
One 12 VDC power & adaptors for UK, EU, Australia	840000301	
One LAN cable	840000352	
One pair of laser safety goggles	840000291	
One USB memory drive with NID™ software	840000305	
One stylus for NanoRam touch screen	840000296	
NanoRam 2 O-ring replacement kit Kit includes: O-Rings 1.0, ID 9.00 mm x15 O-Rings 1.0, ID 10.00 mm x15 O-Rings 1.0, ID 13.00 mm x10	840000433	

<u>Note:</u> O-Rings 1.0(ID 13mm) are used in most standard accessories. For O-Rings 1.0 (9mm and 10mm) location, please refer to following two diagrams.

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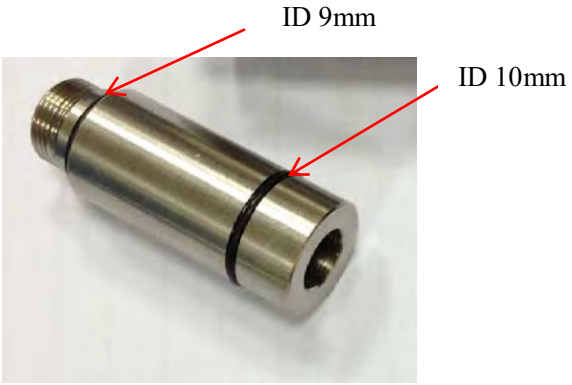
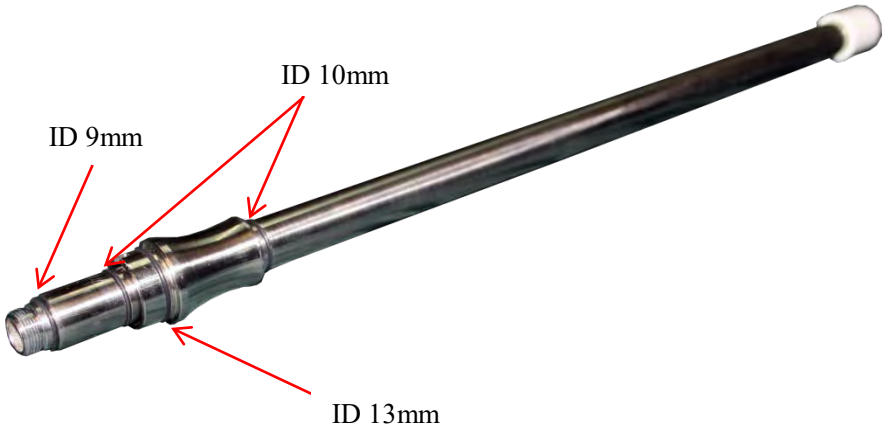
1) O-Rings on Probe Shaft:



2) O-Rings on Immersion Probe:



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4. Knowing Your NanoRam

4.1. Power Supply

The NanoRam should be operated on battery power, which lasts for approximately five hours with continuous use. A rechargeable Li-ion battery is included with the unit. Customer may order a spare battery (840000290) and battery charging cradle (840000294) to extend the operation time of a NanoRam. Before using the NanoRam with battery, make sure that the battery is fully charged. The battery status can be found on the top right corner of the screen, or the center of the screen when NanoRam is in charging only mode.

Note: It is recommended to charge the battery only when the unit is not in use.

4.2. Battery Installation

Locate and identify the battery cover at the bottom end of the NanoRam unit.
Note: there are two versions of battery door design: version A and B. To identify: version A does not have any sign on the bottom cover while version B has an unlock sign near the ring. Turn counterclockwise to unlock if you have version A and turn clockwise to unlock if you have version B.

Version A

Version B

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Version A:
Hold the ring and turn it counterclockwise 1/8th turn to unlock.

Carefully pull out the battery cover and set aside.

Insert the provided NanoRam Lithium Ion battery pack into the battery compartment as shown. Battery contacts should be facing down (towards the back of the unit) and to the right. The strap attached to the battery pack can be used for battery insertion as well as removal. Assure that the battery is fully inserted.

Install the battery cover back in the same position as removed. Use thumbs and/or fingers to firmly press the cover into place to assure correct positioning and to establish a tight seal.

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Turn the ring clockwise 1/8th turn till the ring is in a vertical position.

The cover is now locked.

Version B:
Hold the ring. Turn it clockwise 1/8th turn to unlock.

Turn it counterclockwise 1/8th turn till the ring is in a vertical position to lock.

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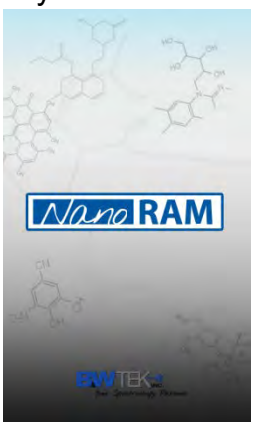
Note: The battery can be charged either through the supplied external power adaptor or using the optional charging cradle.

4.3. NanoRam Cleaning

The NanoRam requires minimal maintenance and care. In order to clean the NanoRam touchscreen, wipe it with a soft cloth dampened with ethanol or isopropanol. The main body of the unit may be wiped down with water, and plastic surfaces may be cleaned with soap and water. Use ethanol to clean the emission shaft. The rubber jacket may be cleaned with any of the above. A mild bleach solution may be used to wipe down the unit. Note: Do not use other chlorinated cleaning products or solvents for any part of the unit.

4.4. Power On/Off the NanoRam

To power on the system, press and hold the **Power On/Off** key for at least 3 seconds. An initial screen will display, followed by a NanoRam OS (NanoRam Operating System) screen indicating that the system initialization is in process with a count up in percentage of completion. After the initialization of the system is completed, the user login screen will be displayed. The unit is now operational.



The first time the unit is turned on, the user type must be the duly assigned *Administrator*. A default user name and password are provided for the first time login (refer to section 4.5 for first-time login).

There are two ways to turn the system off.

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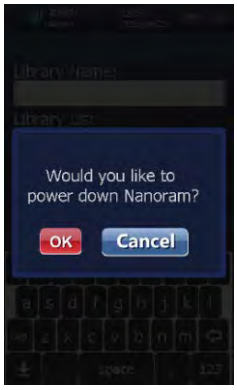
Soft power down: press the **Power On/Off** key for about one second. A message appears confirming the shutdown request. Press **OK** to confirm the operation and the system will turn off. Press **Cancel** to cancel the request and return to the previous menu.



Hard power down: press and hold the **Power On/Off** key for about 3 seconds.

Note: The instrument cannot be hard powered down when it is being charged. Avoid hard power down unless necessary.

4.5. First Time User Login

PLEASE READ THIS SECTION CAREFULLY BEFORE LOGGING IN TO THE NanoRam UNIT FOR THE FIRST TIME

4.5.1. First Time Login

When first time the NanoRam is turned on, a factory preset administrative user "ADMIN" will be used for the first time login. Below is the first time login info, all case sensitive:

User Name: ADMIN
Password: 999999

A screen will prompt for user to reset the ADMIN password. Enter and then confirm the new password. The new password should contain 6-20 characters with a combination of letters, numbers, as well as special characters. Once the password is

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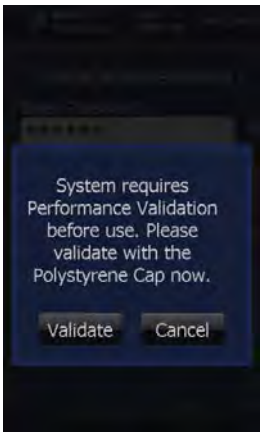
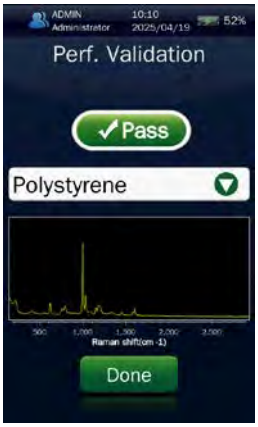
reset, the password “999999” will become invalid and cannot be used again. Passwords that contain a combination of letters, numbers and special characters are stronger passwords.

4.5.2. First Time Performance Validation

After resetting the ADMIN password, a message on performing the first time validation of the factory set calibration will be displayed along with the function key for performing the validation. Make sure the calibration cap with polystyrene is installed at the sampling port (refer to section 5.3). Press Validate to perform the validation.





After the first time validation is passed, press **Done**. Press the **Home** key to return to the Home screen.

The Home screen for the NanoRam is displayed here for an Administrator. The same home screen is displayed for an Operator-level user.

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4.6. Home Key

Pressing the **Home** key one time on the front panel will:

- return user to the previous screen
- log out and return to the login screen if the user is in the Home screen
- cancel the current operation (for example: an acquisition with laser in emission) and return to the Home screen

Pressing the **Home** key twice at any stage of the operation will return the user to the login screen.

4.7. Using the Sampling Accessories

The NanoRam unit standard package comes with three types of sampling accessories which will facilitate easy and fast sampling. Depending on the type and form of the materials to be measured, the appropriate sampling accessory can be selected. The sample can be placed directly against the adaptor.

User instructions for available adaptors that are not included in the standard package are provided with the adaptors on delivery. They are included in the Appendix of the user manual as well.

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Point-and-shoot adaptor	
Liquid vial holder adaptor that holds a 15mm(diameter)x 45mm(height) vial	
Bottle adaptor for measurement through a container	
Calibration cap with built-in polystyrene	
Right angle adaptor (optional)	
Tablet holder adaptor (optional)	
Immersion probe adaptor (optional)	

The user needs to ensure that the sampling adaptor is installed properly before using the NanoRam. Before installing any accessories the NanoRam should be at the log in screen, and laser turned off to ensure safety. No operations are permitted without an adaptor properly installed.

For installation of the right angle adaptor, tablet holder or immersion probe please read the guidelines for safe installation and use provided with the accessory.

Never remove the lensed shaft when the instrument is on.

The following steps will guide the user to successful installation of the sampling accessory: Make sure the correct shaft is installed onto the laser emission aperture.

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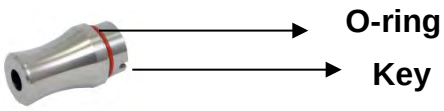
Locate the alignment key on the adaptor and the Set Pin position at the laser emission aperture.



Push the adaptor onto the shaft until the O-ring just reaches the instrument surface.

Gently turn the adaptor clockwise until a click is felt or the sound of a click is heard, which indicates that the key on the adaptor is set to the Set Pin at the laser emission aperture. Once the alignment is reached, stop turning the adaptor.

Push the adaptor further in until the O-ring is fully inside the emission port. At this point the adaptor should be positioned firmly into its position.

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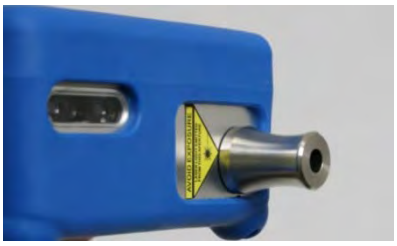

Precaution: to avoid accidental exposure to the laser beam do not look directly into laser emission aperture. Never point the laser at a person.

Using the Point-and-Shoot Adaptor

The point-and-shoot adaptor can be used for powder, solid or liquid sample measurements through a thin and transparent container. With the point-and-shoot adaptor in place, hold the NanoRam unit so that the adaptor is against the sample container surface.

Note: We do not recommend that the adaptor touch powder samples directly, as they may contaminate the lens on the sampling adaptor. The use of a protective transparent plastic film is recommended. Practice caution in measuring dark samples as they may heat up and potentially burn. Lower laser power settings are recommended for dark materials.

Point-and-Shoot Adaptor

Using the Liquid Vial Holder Adaptor

The liquid vial holder can be used for liquid, gel, or powder samples. The liquid vial holder holds a 15mm (diameter) X 45mm (height) vial. The vial holder should be used with the dark cover in place to minimize any interference from light on the measurement.

Liquid Vial Holder Adaptor

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Using the Bottle Adaptor

The bottle adaptor can be used for the measurement of samples through transparent containers of less than 5mm in thickness, such as liquid samples inside bottles, or containers. The bottle or container can be placed directly against this adaptor. The measurement beam will then be ideally focused into the sample over 5mm away from the surface of the adapter.

Bottle Adaptor

4.8. Barcode Scanner Key

The barcode scanner only functions in the appropriate display screens when the system is in **Identification**, **Investigation**, or **Method Building modes.** The scanner is capable of scanning 1-D and 2-D barcodes.

To scan the barcode, place the object in front of the barcode scanner at a distance of ~40 -245 mm, depending on the type of barcode . Press the **Barcode Scanner** key for at least 1 second to scan the barcode.

The barcode types that are supported are listed below:

1D: Code128, EAN-13, EAN-8, Code39, UPC-A, UPC-E, Codabar, Interleaved 2 of 5, ISBN, Code 93, UCC/EAN-128, GS1 Databar
2D: supports ASCII and UTF8 encoding formats for English and Chinese 2-D barcodes.

4.9. Laser Switch /Acquisition Key

To turn on the laser, press the **Laser Switch** key.

The laser can be turned on only when the system is in **Identification mode**, **Investigation mode,** or **Library and Method Building modes**.

In case of emergency, the laser can be turned off any time by pressing the Laser Switch Key or Home Key.

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5. Administrator & Developer User Operation

The following content is provided under the premise that the Administrator has completed the first time login to the NanoRam unit and a new password has been successfully set by the Administrator.

5.1. Instrument Set up

5.1.1. NOS Version

Press the **Set Up** icon on the Home screen, then **General** on the Set Up menu. Press **About**. The version of the NOS, the device SN and the name/version of purchased library will be displayed.

5.1.2. Set System Clock

Press the **Set Up** icon on the Home screen, then press **General** on the Set Up menu. Press on **System Clock**. Set the date and time according to local time zone. Press Save to save.

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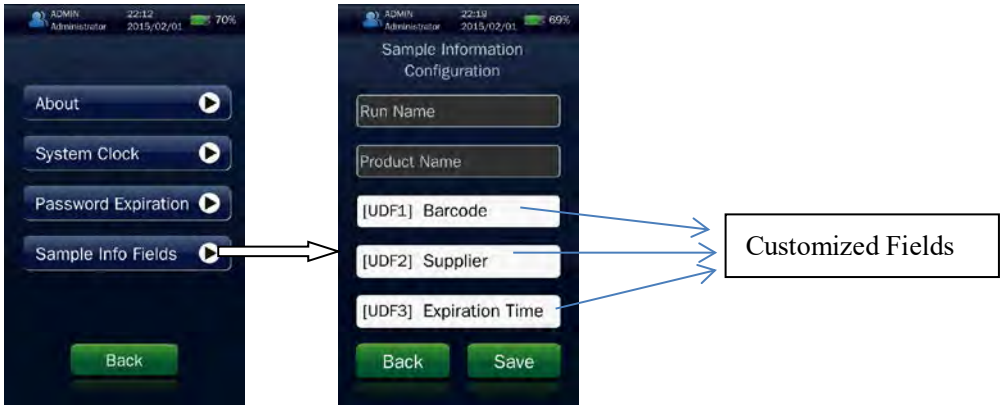
5.1.3. Set Password Expiration

Press the **Set Up** icon on the Home screen, then **General** on the Set Up menu. Press on **Password Expiration**. Set the time duration for password expiration. The default time for password expiration is 6 months. There will be a warning to the user as the password expiration is approaching. Press **Finish** to save.

5.1.4. Set Sample Info Fields Configuration

Press the **Set Up** icon on the Home screen, then **General** on the Set Up menu. Press on **Sample Info Fields** to configure the sample info structure. “Run Name” and “Product Name” are two required fields. There are three user-defined fields available (UDF1, UDF2, UDF3) for a user to define according to user company practice. The names of the UDF field can be customized to user’s need. Press **Save** to save the configuration. The saved configuration will be applied to every measurement in the Identification as well as Investigation test. Only the defined UDF will appear at the sample info input screen for Identification or Investigation test.



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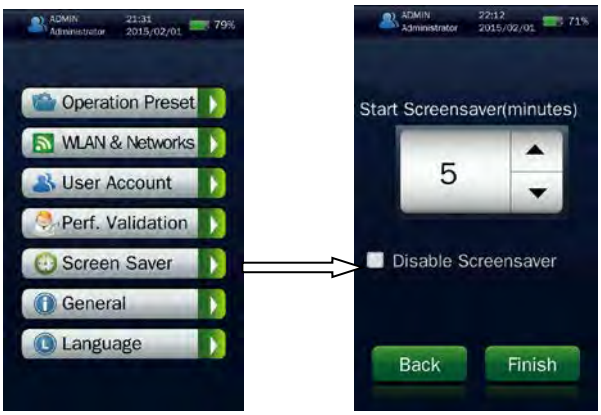
5.1.5. Set Auto Lockout Time

Press **Set Up** on the home screen. Press **Screen Saver** to set time limit (in minutes) of idle activity before the screensaver initiates and auto lockout occurs. Press **Finish** to save the setting and **Back** to return to the previous screen.



5.1.6. Set Language

Press **Set Up** then **Language**. The language of the NOS can be selected. Tap on the language area, a scroll bar will appear on the right. Five languages are available in display: English, Simplified Chinese, Traditional Chinese, Japanese and Spanish. For keyboards input, English or Simplified Chinese (pinyin) can be selected.

5.2. Manage User Account

There are three user types that determine the level of access to NOS functions:

- Operator
- Developer

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- Administrator

The user privileges are listed in the following table:

User Type	User Type Symbol	User Privileges
Operator		• Select Method • Perform Identification Test • Perform Investigation Test • Select Operation Preset • Perform Instrument Validation Test • Data Transfer
Developer		All of the above, plus: • Create /Modify/Transfer Method • Create/Modify Operation Preset • Create/Modify/Transfer Data Library • Set Screen Saver • Set Language
Administrator		All of the above, plus: • Add New User Account • Reset User Account Password; Disable Users • Create Calibration File • Set System Clock • Set Password Expiration • Set Sample Info Fields

5.2.1. Add User Account(Administrator only)

Press the **Set Up** icon on the Home screen, then press **User Account** on the Set Up menu, followed by pressing **Create**.

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Enter a new user name and password. Then confirm the password. The user name can be a combination of letters and numbers up to 28 characters with a combination of letters, numbers and spaces, but no special characters. The password allows 6-20 characters with a combination of letters, numbers, as well as special characters.

Press the arrow next to Administrator box to select the user type: Administrator, Developer**,** or Operator.

Press **Add** to create the new user account. A flashing message "*Add Operation Completed*" will be displayed at the bottom of the screen.
Repeat the procedures to add another account, or press **Back** to the previous screen.

Note: Password configuration policy and access to the password shall be controlled by the user's company policies through external measures.

5.2.2. Disable User/Enable User(Administrator only)

Press the **Set Up** icon on the Home screen, then press **User Account** on the Set Up menu, followed by pressing **View**. A list of the existing user accounts will be displayed. Press on the account that needs to be enabled or disabled. A check mark will show next to the account. Press **View** on the bottom of the screen. The account details will be displayed. Check "Enable User" box to enable the user account; or uncheck the box to disable the account.

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5.2.3. Reset User Password

Press the **Set Up** icon on the Home screen, then press **User Account** on the Set Up menu, followed by pressing **View**. A list of the existing user accounts will be displayed. Press on the account that needs to be reset. A check mark will show next to the account. Press **View** on the bottom of the screen. The account details will be displayed. Place the curser at the end of the "******" by pressing at the end of the "******". Use the backspace key on the onscreen keyboard to remove all * and enter the new password. Press **Finish**. A message "Modified Successfully" appears to confirm the completion of password reset.

5.2.4. User Login

At the user login screen, enter the user name and password and then press **Login**. The user name and user type will be displayed on the upper left of the Home screen. The user can select **Remember User Name** to remember the user name. Only the last user name can be remembered. The password is always needed for login attempts.

When the wrong user account information is entered, the system will allow three trials before the system locks out the user. After the system is locked out, the user will be prompted to turn off the system and try again with the correct account information.

"You are not authorized to access this device. The device has been temporarily locked. Please verify your login info and try again at the next power up."

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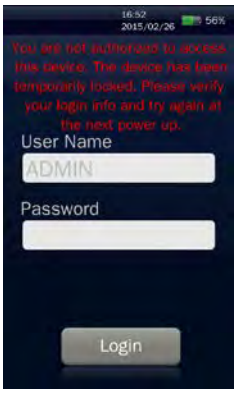
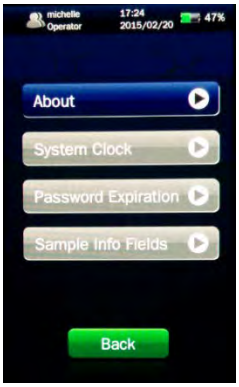


Sections that Operator/Developer cannot access are greyed out. For example, in General setting, an operator can only see following window.



5.3. Instrument Performance Validation

Instrument performance validation can be conducted using the Performance Validation functions. The validation is to validate the accuracy of the instrument in terms of the Raman shift position and peak intensity within a spectral range against a standard material. Polystyrene is used as the standard calibration material for NanoRam. A calibration cap with built-in standard polystyrene is provided. The frequency of performing the validation test should be determined by the user depending on the requirement of the applications.

Before conducting a performance validation, a spectrum of the standard material should already be created. (For polystyrene the calibration file is factory set). Place the calibration

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cap onto the laser emission aperture. The standard polystyrene material will be at the focal point of the laser beam.

Calibration cap with built-in polystyrene

5.3.1. Create Calibration File

Press **Setup** on the **Home** screen, and then press **Perf. Validation**. The Calibration screen will be displayed.

Press **Create Cal. File.** A menu screen for calibration creation will be displayed. Press the arrow ▼ next to Polystyrene. A list of the existing calibration files will be displayed. Press on **Add New** to add a new calibration reference spectrum. Enter the name for the new spectrum. Make sure that the material for new calibration is properly positioned to the NanoRam. Press on **Create** to start acquiring data for the new spectrum. The scan can be canceled anytime during the process by pressing **Cancel**. After the spectrum acquisition is done, press **Done** to save and to select the spectrum as the standard spectrum for validation and return to the previous screen.

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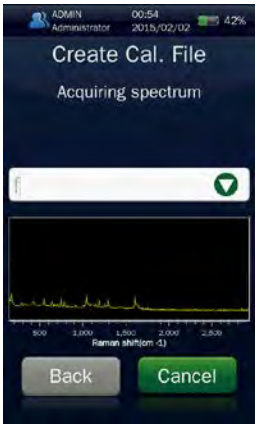

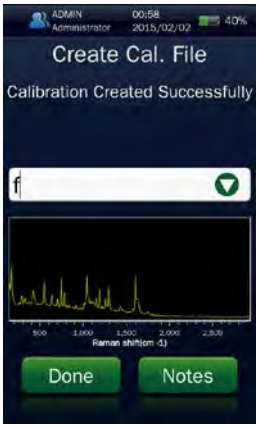

Note: The factory set calibration file "Polystyrene" cannot be overwritten by another polystyrene file created by user. A different name will be needed when user creates another calibration file using polystyrene calibration cap.

5.3.2. Performance Validation

Press **Setup** on the Home screen, and then press **Perf. Validation**. The Calibration screen will be displayed. Press **Validate.** A menu screen for validating the calibration will be displayed. Make sure the calibration cap is installed properly. Press **Validate** to start generating a new standard spectrum. The scan can be canceled anytime during the process by pressing **Cancel**.

The "Pass" result of performance validation is based on two criteria: 1) The HQI calculated between the acquired spectrum and the calibration spectrum is set at HQI ≥ 80; 2) the highest peak intensity ratio between the acquired and the calibration spectrum is within ± 50%. The performance validation will fail if the result failed either of these two criteria.

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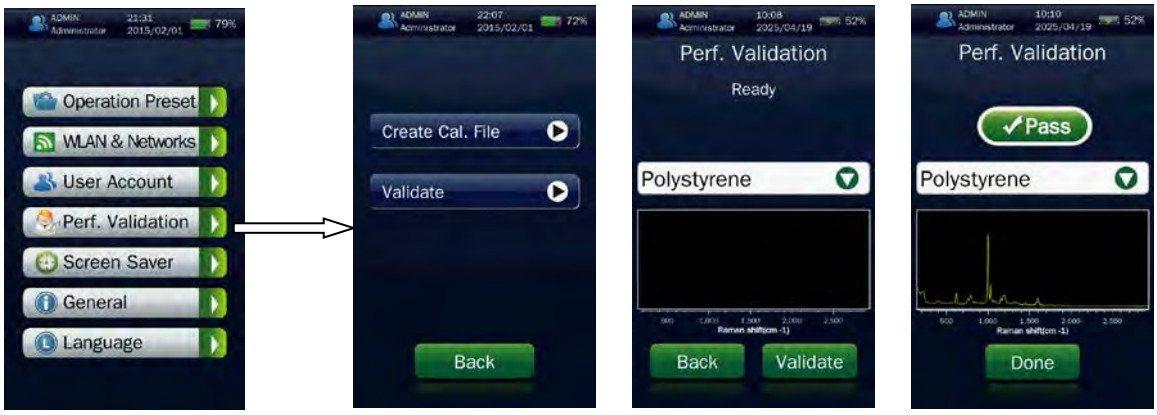
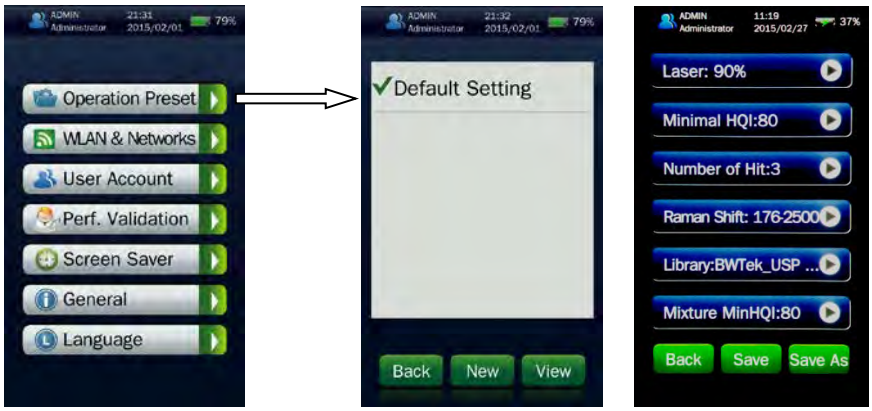


5.4. Operation Preset

Press the **Set Up** icon on the Home screen.

Press **Operation Preset** to display a list of existing operation presets. Operation preset configurations include: Laser Power; Minimal HQI; Number of Hits; Raman Shift Search Range; Libraries to be used for spectrum search and Mixture MinHQI. A default Operation Preset is already created.



To create new Preset, press **New** at bottom of the screen. The Preset with default setting will be displayed. Click on ▶ next to the configurations to change the setting to the desired value. To view an existing preset, press **View**. After preset configurations are all set, press **Save** to save the change, or press **Save As** to save the setting under a new name. Press **Finish** to finish or **Back** to return to the previous screen.

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5.4.1. Laser Power

From the operation preset screen, press **Laser.** The laser power screen will be displayed. Press ▲ or ▼ to set the required laser power as a percentage of the full laser power (300mW). Changes to the laser power are in 10% increments. Press **Back** to save and return to the previous screen.

5.4.2. Minimal HQI

The criterion for Match/No Match can be set via minimal HQI (Hit Quality Index) value. Refer to section 5.6 for details on HQI.

From the operation preset screen, press **Minimal HQI** and the minimal HQI screen will be displayed. Change minimal HQI value by pressing ▲ or ▼. The default setting for minimal HQI is 80, which means measurement with HQI≥80 would result as “Match” while measurement with HQI<80 would be “No Match”. Press **Back** to save the setting and return to the previous screen.

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5.4.3. Number of Hits

From the operation preset screen, press **Number of Hit**. The number of hit screen will be displayed. Change the number of hits by pressing ▲ or ▼. The default setting is 3, which means the top three materials with the highest HQI above the threshold will be displayed. Press **Back** to save the setting and return to the previous screen.

5.4.4. Search Range

The range of the Raman spectrum against which the matching is performed can be set via Raman shift. The default is 176-2500cm^{-1}.

From the operation preset screen, press **Raman Shift**. The Raman shift range screen will be displayed. The range starts at 176cm^{-1}, which is fixed and cannot be modified. The ending of the spectral range can be set between 1800cm^{-1} and 2900cm^{-1}. Change the ending range to the desired value. Press **Back** to save the setting and return to the previous screen.

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5.4.5 Library

The libraries against which the search and match is performed can be modified. From the operation preset screen, press **Library.** A list of the available libraries will be displayed. Select/unselect the desired library from the list by tapping on the name. A selected library is marked by✔. Multiple libraries can be selected.
The methods can also be searched to establish a match of materials using an HQI against every method that is on the system by selecting "Method Library" at the bottom of the page, press **Back** to save and return to the previous screen.

Note: The number of libraries and the number of elements in the selected library may impact the time of response in obtaining a result. We recommend dividing the different libraries by segments and enable or disable as required.

5.4.6 Mixture MinHQI

Mixture analysis settings include Mixture MinHQI and Mixture Number of Hit. The

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default setting for MinHQI is 80; and the number of hit is 3. Refer to section 5.6.4 for details on mixture analysis.

5.5. Material Identification and Method

A method is a multivariate model set up for material identification purpose for a specific material. Each type of raw material needs to have a method created specifically for the material. When properly set up, each method contains Raman spectroscopic information that defines the material. The method is comprised of at least 20 Raman spectral scans and therefore can be developed to include possible variations associated with sample uniformity such as uniformity within a drum, within a batch, or among different batches or suppliers.

The procedure for creating a new method includes collecting a minimum of 20 Raman spectral scans. When sample uniformity needs to be considered as a factor, it is best that these 20 scans are taken on the samples that reflect the various ranges of the sample batches, or on different sample spots for the same sample to reflect the uniformity within one sample.

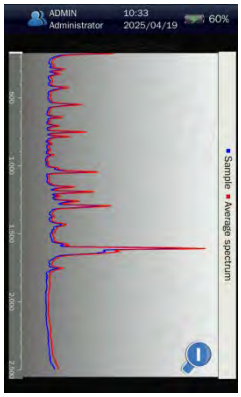
The existing method can be modified by an administrative or developer-level user by adding additional scans if needed.

5.5.1. Create New Method

Press the **Method** icon on the main menu. The method screen will display the list of available methods.
Press **New** to create a new method. Enter the method name or scan a barcode for the

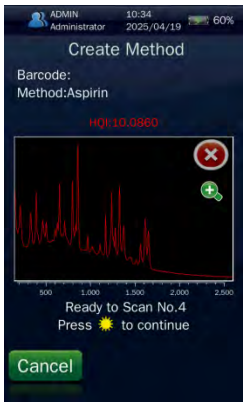
material for which the method is created. Press **Next**. Press Save to confirm the entry.

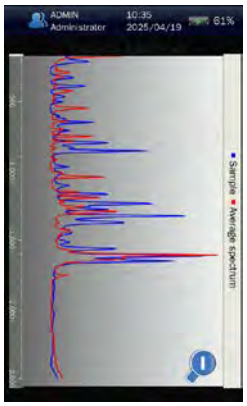
A screen for “Create Method” will be displayed along with message: “Ready to Scan No.1”. It indicates that the instrument is ready to start collecting data for a method.
Press the **Laser Switch/Acquisition** key to acquire the first scan.
After the first scan is done, the spectrum will be displayed, along with message “Ready to scan No.X”. Tap on the screen to view the spectrum. Tap to return to the method building screen. If the spectrum is acceptable, move the sampling adaptor to a different sample spot (or a different sample) and press the **Laser Switch/Acquisition** key to acquire the next scan.



HQI will be calculated for each spectrum between No. 2 to No. 20 to assist in the evaluation of the spectrum. For a spectrum with HQI lower than 85, the HQI value will be displayed on the screen in red, which indicates low level of similarity of the spectrum with others in the method. It is recommended not to include scans with HQI lower than 85 during the method building as they may be outliers. For an unacceptable spectrum press on the screen. A delete button will show on the screen. Press **Delete** to delete the current scan so that it will not be included in the

method.





After 20 scans are completed, the spectrum of the final scan will be displayed along with the message “Press Finish to accept”. Press Finish. The method name page will appear, allowing the user to modify the name. Press **Save** to save the method. A message “Please wait for the method to be saved” will be displayed while the method is being saved. After the method is saved, the message “Add operation completed” will be displayed. Press **OK** to complete.

5.5.2. Modify Existing Method

Press the **Method** icon on the home menu. The method screen appears with the list of available methods displayed. Press **Edit** on the top right corner. . Press the method to be modified, the name will be marked with ✔. Press **Modify** to modify the method.

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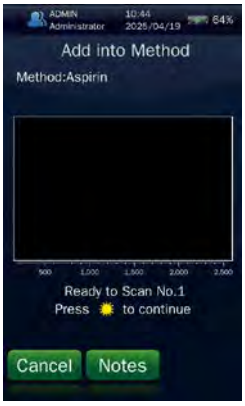
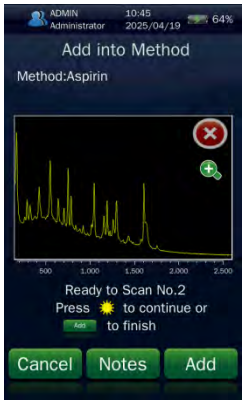
Press "**Add scans to Method**" to add additional scans to the method.

The method will be loaded and a note must be entered and saved prior to adding scans. Press the laser emission key to start the first additional scan. After the scan is completed, press the laser emission key for another scan or press **Add** to save the modification to the method.





Press "**Set significance level**" to set the p-value threshold for the Pass/Fail reading of the identification. The default is set to 0.05 if no modification is made to the setting. A note needs to be entered and saved prior to proceeding with the operation. Modify the value for significance level and press "Notes" to add notes. Press **Finish** to save the change.

Increasing the significance level will decrease the confidence interval for pass criterion (significance level= 0.05; 95% confidence level; significance level = 0.10; 90% confidence level). An increase in the significance level value will impact the number of false negatives one may get during identification; while a decrease in significance level value will impact the number of false positive results, and may be considered for

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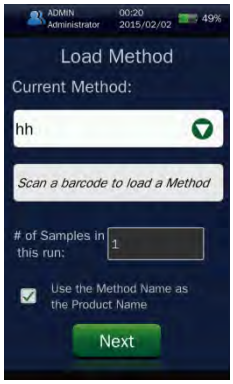
materials with very similar Raman spectra.

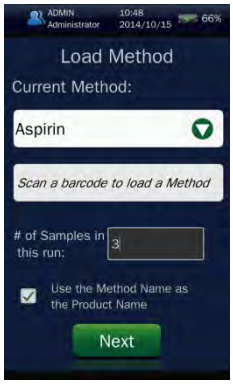
5.5.3. Perform Identification

Press the **Identification** icon on the home screen. Load Method screen will be displayed. Load the method by either scanning barcode or manual selection of the method name from the method list. Enter the number of samples to be tested. When the number of samples is more than one, the identification will be performed in a batch fashion where the samples within the same Run will carry the same Product name with a suffix of increment of one, starting from #1 (ProductName#1), as the measurement moves to the next sample.

Check the option if user chooses to “Use the Method Name as the Product Name”. Press **Next** for the page to enter **Run Name**, **Product Name**, and **Sample Info Fields** pre-defined by user (refer to section 5.1.4). When running more than one sample in a batch manner, users are required to enter a Run Name.

Press the **Laser Switch/Acquisition** key to start acquiring the Raman spectrum. Keep the sample in place until the dark scan is also completed.





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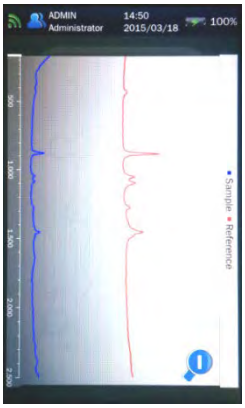
In summary, the Identification test is performed in the following order:

1) Load the Method.
2) Enter product information.
3) Acquire a Raman spectrum of the material to be identified.
4) A p-value will be calculated by comparing the spectrum acquired from the sample to the method.
5) A “Pass” or “Fail” result will be declared based on a significance level, which is set in the Method. Therefore, for a p-value greater than or equal to the set value, for example 0.05, the result of “Pass” will be declared; for a p-value less than 0.05, the result of “Fail” will be declared.

For “Pass” results, verified material information and the p-value will be displayed. Press to view the acquired spectrum and the spectrum associated with the method. Press to close the spectral overlay screen and return to the previous screen. For “Fail” results, the probable match suggestion against the library, if available, will be displayed with the corresponding HQI. Press to display the acquired spectrum and the spectrum associated with the probable match.



<u>Single Sample</u>: For identification run with a single sample, the result shows the final result.

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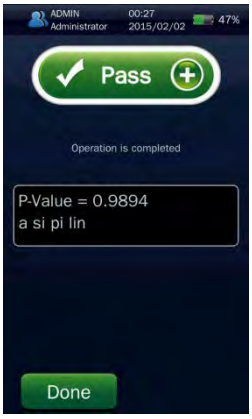
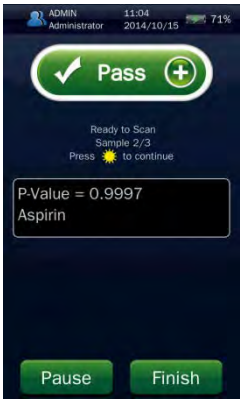
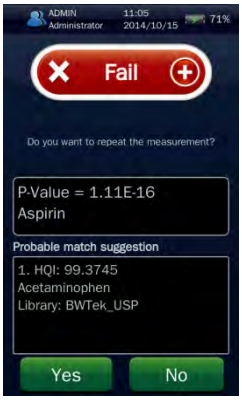


Batch Samples: For identification run with more than one sample, the result shows for each of the samples. When any sample(s) within the run **Fail** the Identification test, the user will be asked whether to run another sample. If user chooses **Yes**, a note must be entered before the repeating test. If user chooses **No**, the retesting of the sample will be skipped and the test will proceed to the next sample number. The user can choose **Pause** to stop the current run and the run will be considered as an "unfinished run". The user will be reminded of the unfinished run(s) upon loading the method associated with it again. User can press **Cancel** to continue loading the method, or press on the name of the unfinished run to resume and finish the unfinished run.





5.6. Material Investigation and Library

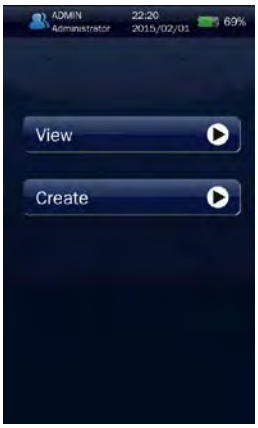
A user-defined library is created by following two steps:

1) Create a new library name

2) Add spectrum to a specified library

5.6.1. Create New Library Name

Press the **Library** icon on the Home screen. Press **Create**. Enter the new library name. Press **Create New Lib** to create a new library. The new library name will be added to the library list.



Additional new library names can be created by repeating the above procedure.

5.6.2. Add Spectrum to User-Defined Library

Press on the library name for which a new spectrum is to be added. A green check mark will be displayed next to the specified library and the **Add New Sample** function key will be available at the bottom of the screen. Press **Add New Sample**. The screen for adding a new sample will be displayed. Enter the sample name. Make sure the appropriate sampling adaptor is installed and the sample is properly placed. Press the **Acquire** button to start the spectrum collection.

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After the acquisition is finished, the spectrum will be displayed on the screen. Press **Add** to add the spectrum to the library. The message “Add operation completed” will be displayed. Press **OK**. Enter a sample name and press the **Acquire** button to continue collecting spectra to the current library, or press **Back** to return to the previous screen.
The newly created or modified library needs to be loaded to the library list in the operation presets to be put into use.

Note: The scan time for collecting a new library spectrum is longer than a regular identification scan due to the setting used for collecting a library spectrum.

5.6.3. View Spectrum Name For User-Defined Library

On the Home screen, press the **Library** icon. Press **View**, a list of the existing libraries will be displayed. Press on the library name to be viewed. A green check mark will be displayed next to the library.
Press **View** at the bottom of the screen. A list of the sample names inside the library will be displayed.

Note: The library list spectra can be viewed in NID. Spectrum names can be modified in NID and synchronized back to NOS. See section 6.5.10 Library Management for details.

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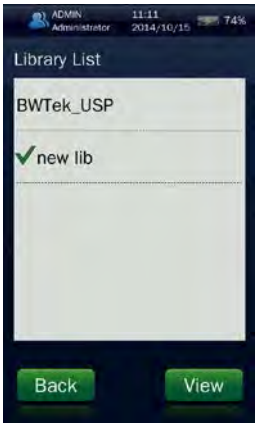
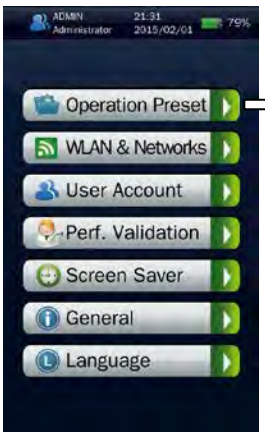
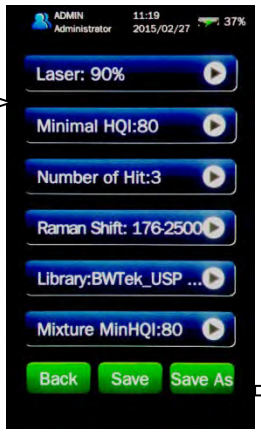


5.6.4. Perform Material Investigation

Before investigation for unknown materials, the corresponding operation preset needs to be selected. Press the **Set Up** icon on the home page, and then press **Operation Preset**. The list of the existing operation presets will be displayed. Select the desired operation preset by tapping on the name. The selected preset will be marked by a check mark. Press on **View** to view the setting or **Back** to return to the previous screen.





An Operator is only able to *view* the parameters. If a parameter is changed unintentionally, the change will not be saved, thus the preset remains intact.
Make sure the appropriate sampling adaptor is properly installed. Place sample correctly using the sampling adaptor.

Press the **Investigation** icon, and the “ready to scan” page will be displayed. A

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screen for sample information will be displayed. Enter the necessary information already set in the “Sample Info Field”. Press the **Laser Switch /Acquisition** key to start acquiring data.

As a safety warning, the NanoRam will emit 3 intermittent acoustic signals and flash a laser warning symbol on the screen before starting the acquisition. During the warning period, no laser emission is generated from the instrument.

The system will assign a default initial integration time for the first scan. The integration time will be automatically optimized. A dark scan will follow.

Note: While the dark scan is being collected, the sample needs to remain at the same position until the dark scan is completed.

After the spectrum is collected, the search for a matching spectrum in the spectral library will start automatically. The investigation result of either “**Match**” or “**No Match**” will be displayed.

For a “Match” result, possible matching compound information and their HQI (Hit Quality Index) will be displayed. Press , to display the aquired spectrum matched with the spectrum of the library. Press to close the screen and return to the previous screen. For a “No Match” result, a message will be displayed stating that there are no samples in the library with a correlation above the threshold value. Press , to display the acquired spectrum. Press to close the screen and return to the previous screen.
If the number of hits is >1, and more than one library has an HQI greater than the threshold, the other spectral matches will be displayed in descending order of HQI.

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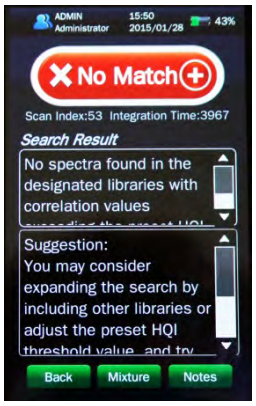

Note: When message “sample matches with an HQI lower than 93, a “mixture analysis is recommended” message shows up, user can press the OK button to ignore it or do a mixture analysis in next step.

Mixture Analysis

Upon receiving “No Match” result or matched HQI is lower than 93, user can press the **Mixture** button on the result page and the system will run mixture analysis on the given signature to determine possible substance components. The laser does not emit during the mixture analysis. A mixture result will follow.

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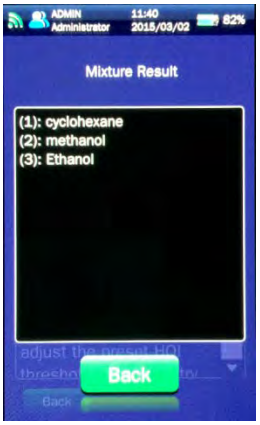

Note: HQI is a measure of the level of correlation of the sample spectrum against a spectrum from the library by use of a predetermined algorithm. HQI=100 indicates a 100% correlation score between the sample spectrum and the spectrum in the library. HQI=0 indicates a 0% correlation score between the sample spectrum and the particular spectrum in the library. While the default setting for minimal HQI is 80, the criteria for "Match" can be set by the user with Administrator or Developer level privileges.

5.7. Data Transfer

NanoRam data reporting and management and account management are done by synchronizing the instrument data with the identification (NID) software, loaded onto a PC. The synchronized data includes testing results for identification as well as investigation, method data, user account data, and audit trail data.

Two steps are needed to perform data transfer:

- Establish connection between the NanoRam unit and PC
- Enable data transfer on NOS

5.7.1. Establish Connection between NanoRam and PC

Press the **Set Up** icon on the home screen, then **WLAN & Networks**. Press **Ethernet** for connection via Ethernet, or press **Wi-Fi** for connection via wireless.

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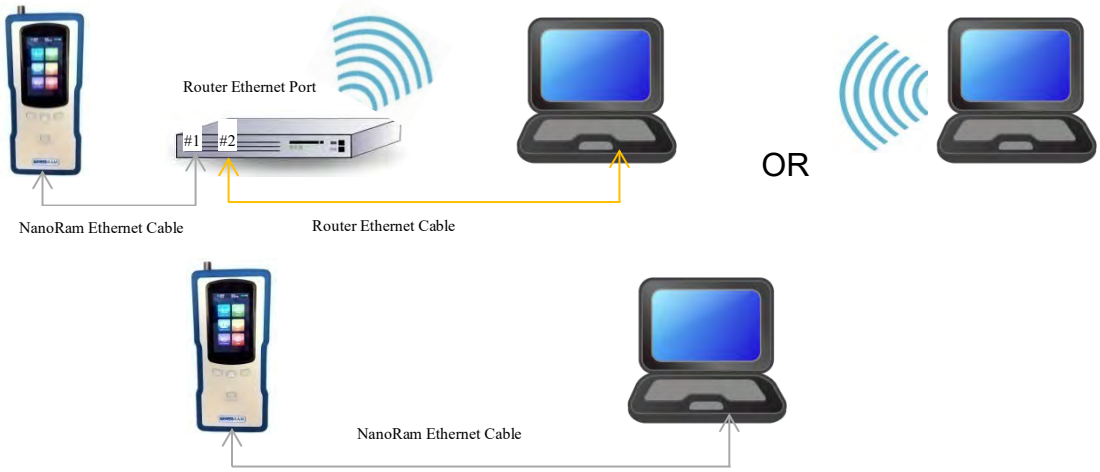
Establish Ethernet Connection

The Ethernet connection can be established using either a user assigned Static IP address or a dynamic auto assigned DHCP. There are a variety of configurations for connection and this guide will cover the most common.

Note: If this type of connection is to be used, the Wi-Fi connection of the PC needs to be disabled.

5.7.1.1. Ethernet using Static IP

NanoRam is connected directly to the PC or Router by configuring the local area connection on PC or Router to have the same NetMask, Gateway, and DNS with a unique Static IP address on the NanoRam. This is an example where the same computer could be both Client and Server.



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Note: It is important to setup the PC or router Static IP first and then connect the NanoRam. The local area connection must be established before the NanoRam will connect.

When the Static IP mode is selected, the message regarding disable Wi-Fi will be prompted. Press OK to continue.

On a Windows 7 computer, use the following path for setting the local area connection: Control panel=>Network and Internet=>View Network and Status=>Local Area Connection=>Properties (note: the path maybe different for different systems). Choose the highlighted "**Internet Protocol Version 4 (TCP/IPv4)**" by double clicking on it. Or select it and click the **Properties** button.

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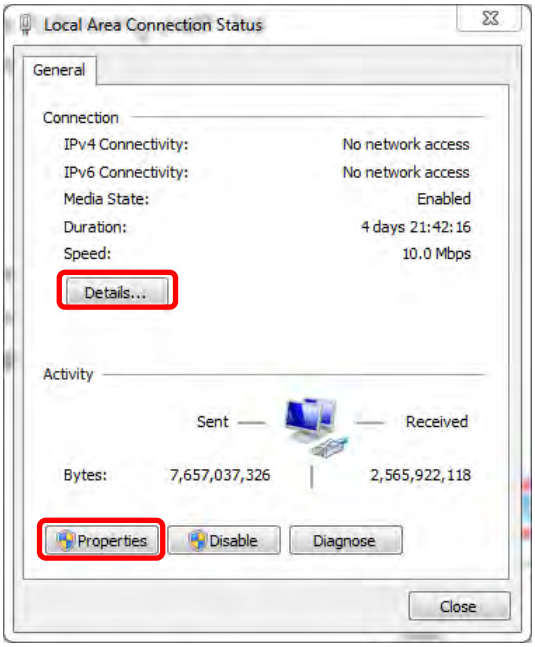
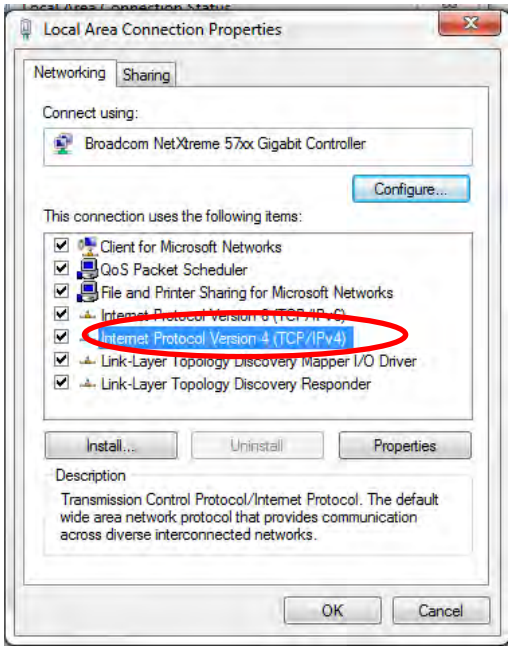
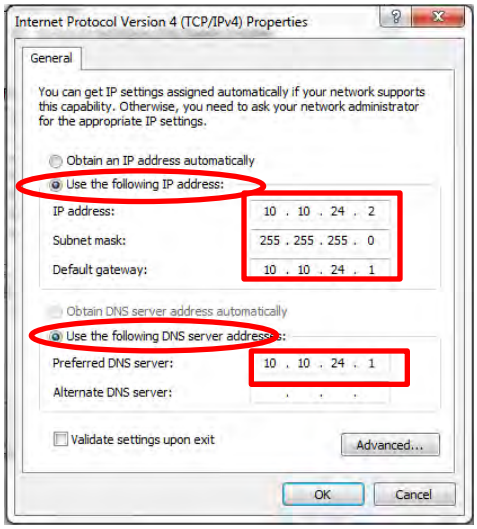




Choose “Use the following IP address” and “Use the following DNS server addresses”, and enter the desired IP address, you may use the image as an example. You may need to contact your network administrator or IT professional for your network connection specifics. Click on **OK** to save the local area connection setting.



Settings can be viewed by clicking on **Details** in the Local Area Connection Properties window.

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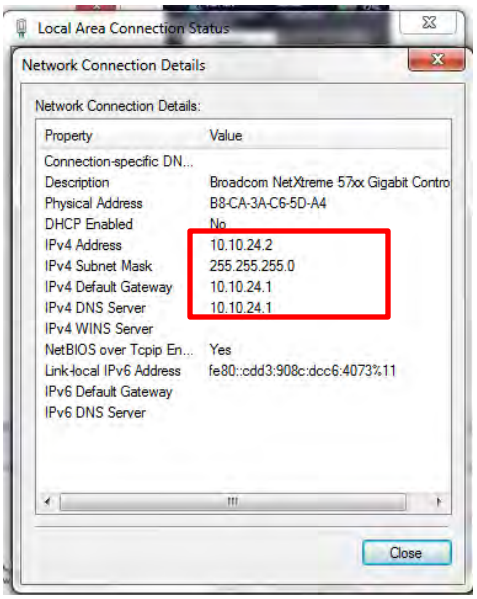

On the NanoRam unit, press the **Set Up** icon on the home screen, then **WLAN & Networks**. Tap **Ethernet**, tap on the **Static** tab to enter the Static IP settings. Check the PC or Router for established IP address settings in the previous step. Match the NanoRam Static IP settings with those in the PC with the exception of the last number in the “IP address”, shown in the screenshot below. This last number must be unique to establish a connection. Press **Connect** to finish.

<u>Note</u>: When the data synchronization is finished, restore the computer local area connection to “Obtain an IP Address Automatically”, if needed.

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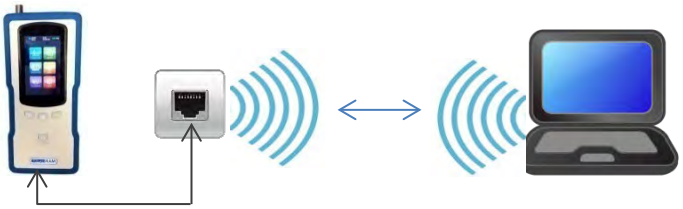
5.7.1.2. Ethernet using DHCP

The NanoRam is connected with the Ethernet cable plugged directly into the network port or router, while the PC is connected to the same Local Area Network. Ensure that your router or network switch is configured for DHCP.

NanoRam is connected to the PC through a network port with DHCP. The PC can be connected wirelessly to the same network.



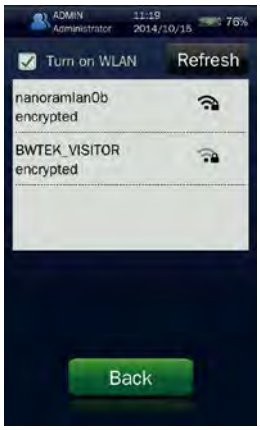
NanoRam is connected to the PC through an internet router or network switch with DHCP.

On the NanoRam unit, press the **Set Up** icon on the home screen, then **WLAN & Networks**. Tap **Ethernet**, and tap on the **DHCP** tab. Press **Connect** to finish.

For both of the above connections, the IP address details will be seen on the Ethernet detail screen under DHCP tab as shown below:

Establish Wi-Fi Connection

Press **Set Up** icon on the Home screen, and then press **Wi-Fi** on the set up menu. The Wi-Fi set up screen will be displayed. A list of available WLAN (Wireless Local Area Network) networks will be displayed. Press **Refresh** to update the available WLAN networks if needed. Scroll down the list and select the appropriate WLAN. Enter the password. Press **Join** to connect to the network. Wait until a checkmark appears next to the network name. The connection is now established.



Press on white arrow icon ▶ next to the connected network to display detailed information for the network. Press **Back** to return to the previous screen.

5.7.2 Enable Data Transfer

Press **Data Transfer** icon on the Home screen. The data transfer screen will be displayed with two options available: Ethernet and Wi-Fi.

To enable Ethernet connection, press the **Ethernet** button. Once the check mark turns

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green the data transfer via Ethernet connection is enabled.
To enable Wi-Fi connection, press the **Wi-Fi** button. Once the check mark turns green the data transfer via Wi-Fi connection is enabled.

6. NID Software

6.1. About NID

NanoRam ID (NID) is a software package included with the NanoRam Handheld Raman unit and is used for management and reporting of data collected with the NanoRam. There are two services designed in the NID software to function on the client's PC and server, respectively:

• NID Client – for client PC
• NID Server – for server PC

Separate installations are necessary for NID Server and NID Client. They can both be installed on the same computer. They can also be installed on multiple computers, and the computers with NID Server installed will act as data servers. The NID Server program must be running in the background so that the NID Client can detect an active server and access its data.

NID Client is to be installed on a PC for users to access the NanoRam device and NID Server. NID Client supports the following functions:

- Synchronization of data

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- User account management
- Library management for user-defined library including library data export, and library transfer from one NanoRam unit to another
- Method library management including method data export, method name change, method delete, and method transfer from one NanoRam unit to another.
- Test record management including test data export, generating and printing test reports, and test data export into LIMS-compatible report format
- Generating report of performance validation
- Generating an audit trail report and printing the Audit Trail Report
- Upgrade of NOS Software on a NanoRam unit

NID Server can be installed either on a server computer or on the same computer as the installed NID Client. It is recommended to install NID Server **on the user company server that is intended for secure data storage.**

Together, NID Client and NID Server are collectively referred to as NID.

The connection between the NanoRam device and the PC can be either through Ethernet cable or Wi-Fi network. Multiple NanoRam devices (up to 8) can be connected to one PC.

When the data on a NanoRam device (user account info, test result, library, method, audit trail data) is synchronized onto a server using NID Client, the data will be stored on the Server.

6.2. Operating Systems Supported

Windows XP (32 bit)
Windows Vista (32 bit & 64 bit)
Windows 7 (32 bit & 64 bit)
Windows 8 / 8.1 (32 bit & 64 bit)
Windows Server 2008 R2

6.3. NID and NOS Installation and Software Upgrades

Install and launch NID software before proceeding. Please refer to the accompanying document **"NanoRam NID V5.12 Installation Guide"**. This document provides the detailed instructions on software installation on the client server and PCs.

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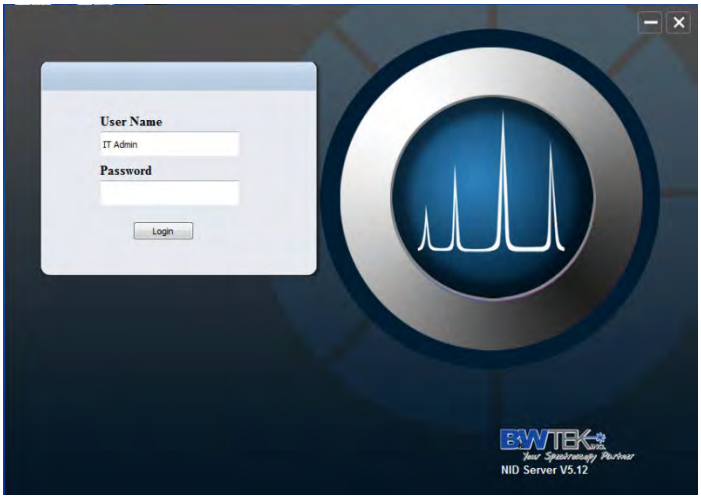
6.4. Changing NID Admin Password

An existing password can be reset in NID Server by the IT Administrator:

Click on the **NID Server** icon to start NID Server. The will be added to the taskbar at the right bottom corner of the computer.

Click on , the login screen for IT Admin will be displayed. Login NID Server as "IT Admin" with the password set in the NID installation process.



The screen for "Change NID Admin Password" will be displayed. Enter the new password and click on **OK** to reset the password. It can be **6-20 characters** with a combination of letters, numbers, as well as special characters (first and last character cannot be space).

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6.5. Working with NID

6.5.1. Login NID

Click on the NID Client icon on the desktop to start NID Client program. At the same time NID Server will open automatically, running in the background.

Login NID using the following info (case sentitive):

User Name: NID Admin

Password: 999999 (factory set default password)

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NID Home screen after login:

Click on EN in the upper right corner. Five languages are available in display: English, Simplified Chinese, Traditional Chinese, Japanese and Spanish. Once a different display language is selected, user needs to close the NID Client and restart it manually.

6.5.2. Device Connection on NID

Make sure the NanoRam unit is connected to NID via either Ethernet or Wi-Fi, and

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the connection is enabled in the **Data Transfer** menu on NanoRam unit. Once the connection between the NanoRam and NID is established, the NID screen will display the NanoRam that is connected to the PC with the serial number displayed.

Click on the NanoRam icon. Enter the login info for the NanoRam. Click on **Login**. The message "Successfully logged in" will appear. The NanoRam can now be accessed from the NID software. The appearance of ⛔ next to the NanoRam icon indicates that the NanoRam is busy.

Note: As a data security measure, the Ethernet or Wi-Fi connection will be disconnected automatically under two scenarios: 1) if the NanoRam is out of the data transfer screen; 2) after screen saver is turned on or the connection has been idle

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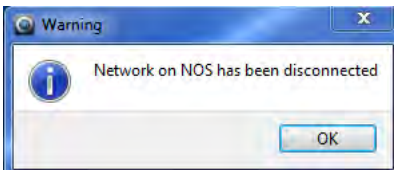
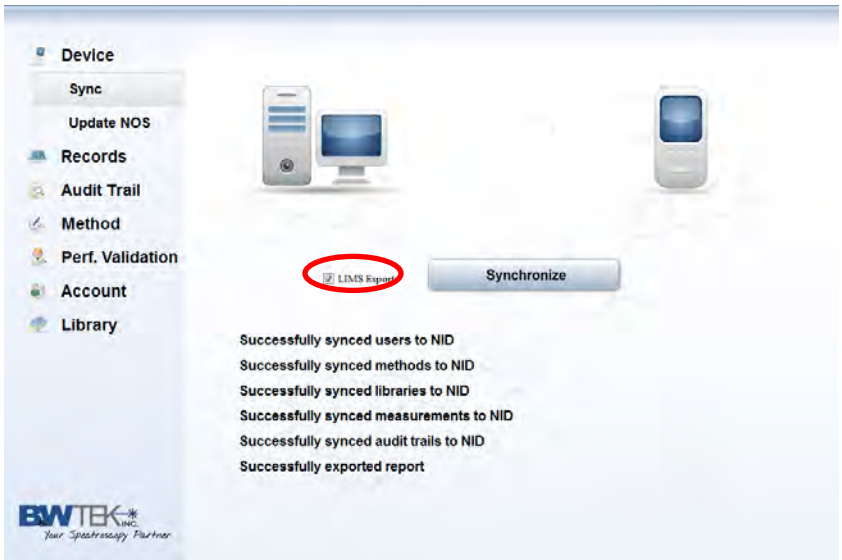
(without any data transfer actions) for 15 minutes. A warning message will appear on the screen. Data could be lost if data is being synchronized at the moment.



6.5.3. Data Synchronization

Data synchronization is to transfer data from the NanoRam's memory to the server. At this point, the user can choose whether or not to turn on LIMS Export function. By checking the "LIMS Export" box, the LIMS-compatible report will be generated for each of the Identification and Investigation tests and stored in a csv format compatible with LIMS on the Server at **C:\BWTEK\NID\DataBase\NID Report.**

Click on **Device** then **Sync** on the left menu bar of the screen. Click **Synchronize** to start the synchronization. Confirmation messages appear after synchronization is completed.



6.5.4. Update NOS

NOS software can be updated via NID software when the connection between NanoRam and NID is established (Ethernet or Wi-Fi).

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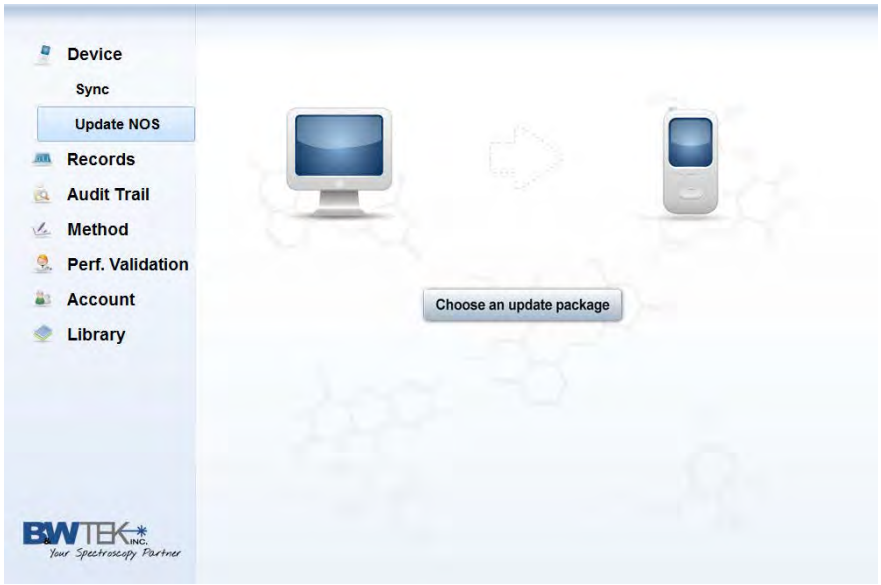
Press **Update NOS**, and then press **Choose an update package**. Choose software zipped folder and click **Open** to start the NOS upgrade.

Note: WinCE NR2 cannot be updated with NOS for Linux NR2. User need to send the unit back to B&W Tek or authorized distributor for service in order to convert from WinCE NR2 to Linux NR2. Contact B&W Tek or your distributor for this service request. Users are strongly advised to synchronize all data to their NID prior to the return.



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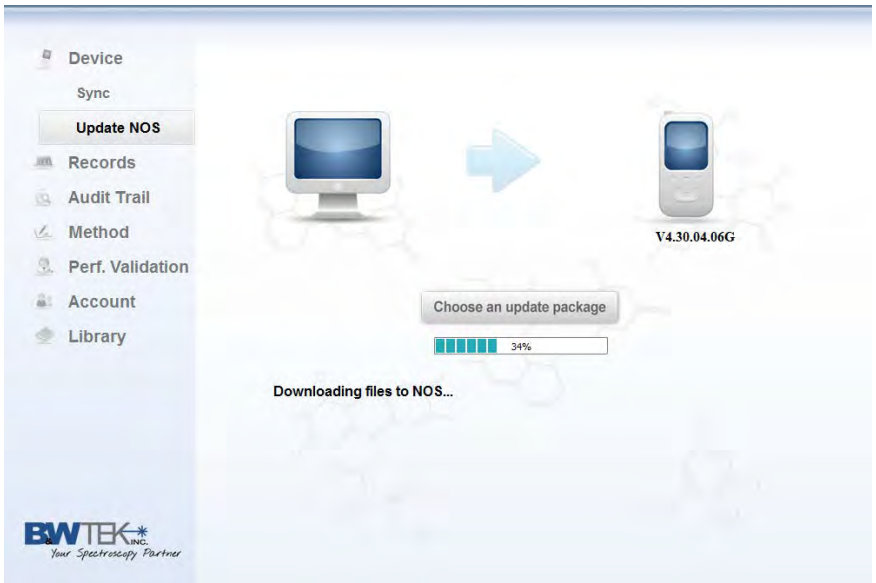


In general, the upgrade takes a few minutes. DO NOT power down during the reboot process. After the upgrade is completed, the user will be prompted to reboot the NanoRam device. The user should turn off the NanoRam, then turn on the NanoRam to verify the update has been successful by checking the version of the NOS via **Setup\General\About**.

Note: Make sure the NanoRam is not being charged and the charging cable is not connected to NanoRam unit when rebooting the NanoRam.

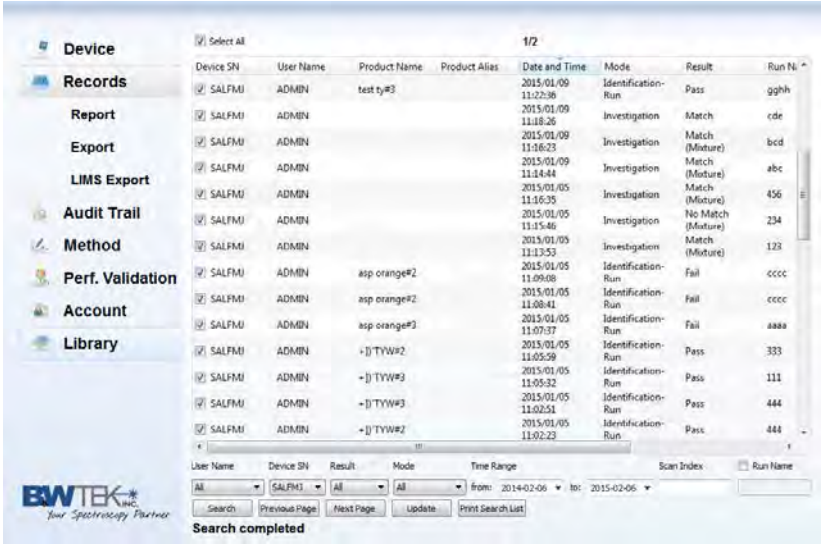
6.5.5. Test Records Management

Click on **Records** on the left menu bar. Choose the Device SN and necessary filters if needed. Press **Search**. A list of the tests will be displayed. Select the desired records by checking the boxes next to the records. Test records can be managed via NID for:

- Generate individual test report and summary report;
- Print report;
- Export raw data;
- Report in LIMS compatible format

Generate Report:

Select the desired records by checking the boxes next to those records. Click on **Report** under "Records". The thumbnail image for selected reports will be shown.



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Click on a specific report to display the report. The report includes the unique scan index for the measurement and the version of NID. The report header contains the details of the measurement, the method used, the user name, operation preset, any entries made in the user defined fields and notes, and information of the last performance validation. The report results are displayed with the sample spectrum and reference spectrum of the Method overlaid. The signature and date of the approval of the report can be entered at the bottom of the report.

Custom customer/company info and notes can be entered. The format can be saved by clicking **Apply**. The same format will apply to all the selected reports.

Note: an additional of mixture report will show below the spectra overlays if a mixture analysis was carried out during investigation.

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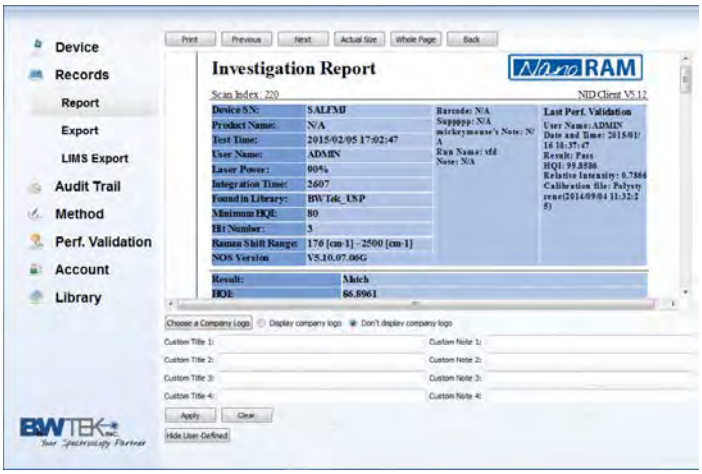

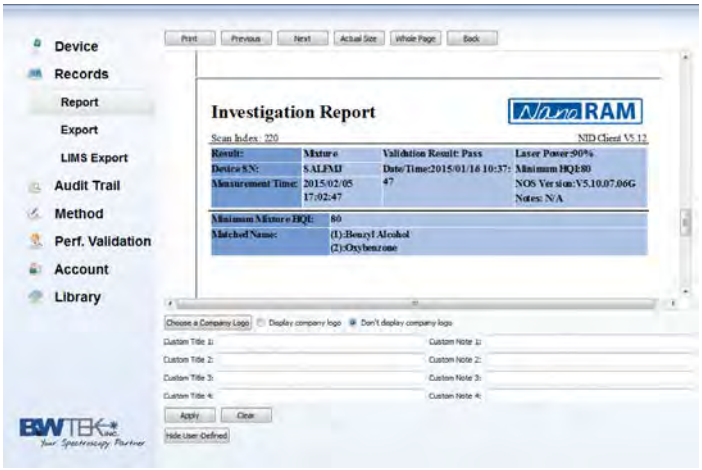

<u>Print Report</u>:
Click **Print** to print the selected report. See Appendix-1 for an example of NanoRam Identification Test Report.

Click on **View Sum Report** on the selected report screen. A summary report of the selected records can be generated which includes the sample index, sample name and the summary results for each scan.

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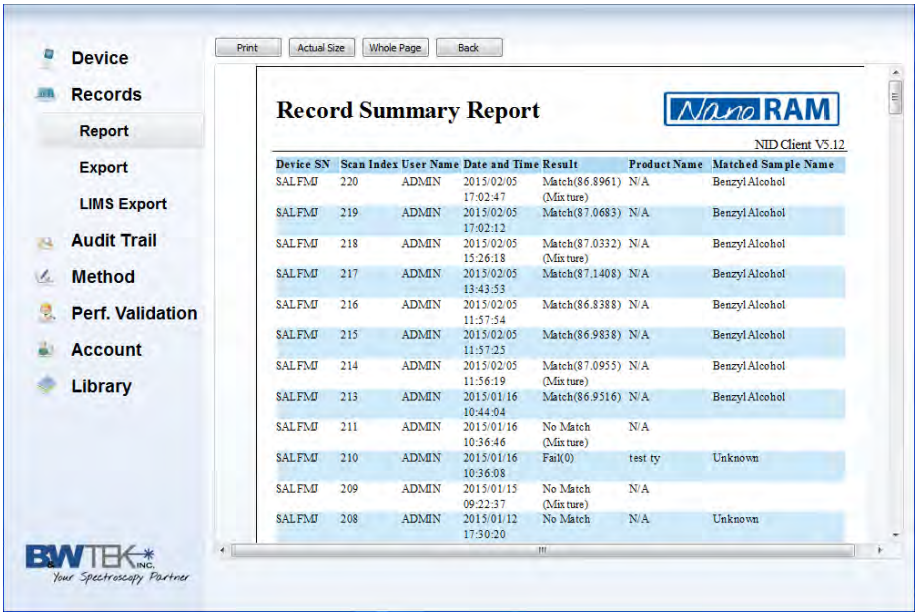
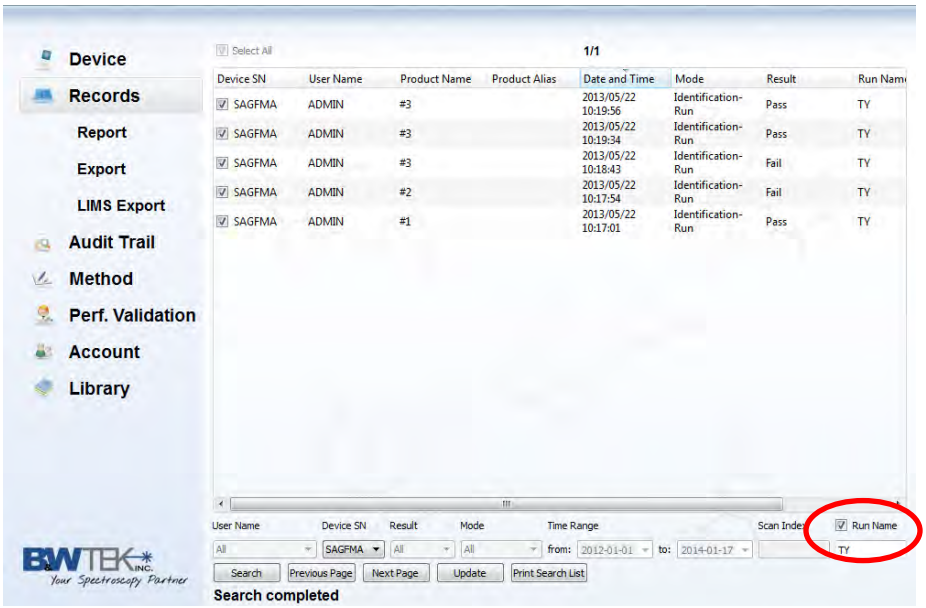


For batch sample run, after the Run Name is searched and selected, press **Report** under the Records, each of the individual reports for the batch sample run will be displayed. Click on a report icon to see the entire report.

Click on **View Sum Report**, the Run Summary Report, along with the spectra overlay for each test in the run, will be generated.



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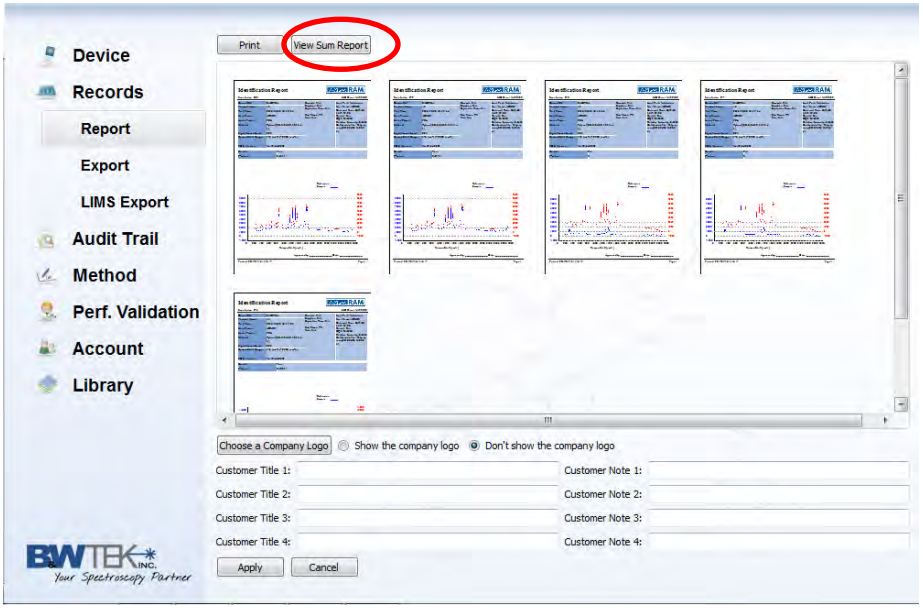
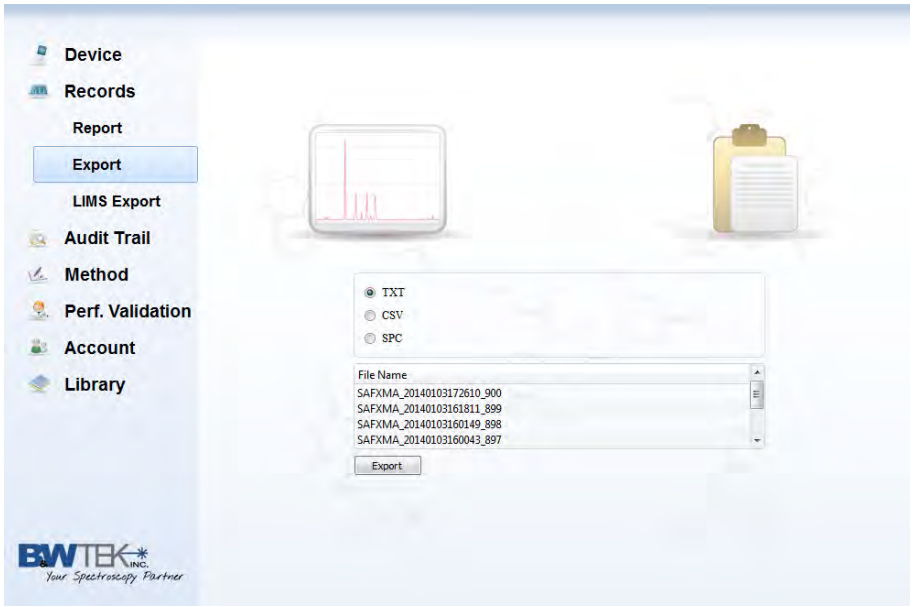


Spectral Data Export:

Click on **Export** under "Records" to export the Raman spectral data into 3 formats: TXT, CSV, SPC. Select the measurement report from the list. Click on **Export** in the center of the screen to export the data to a user-designated folder.



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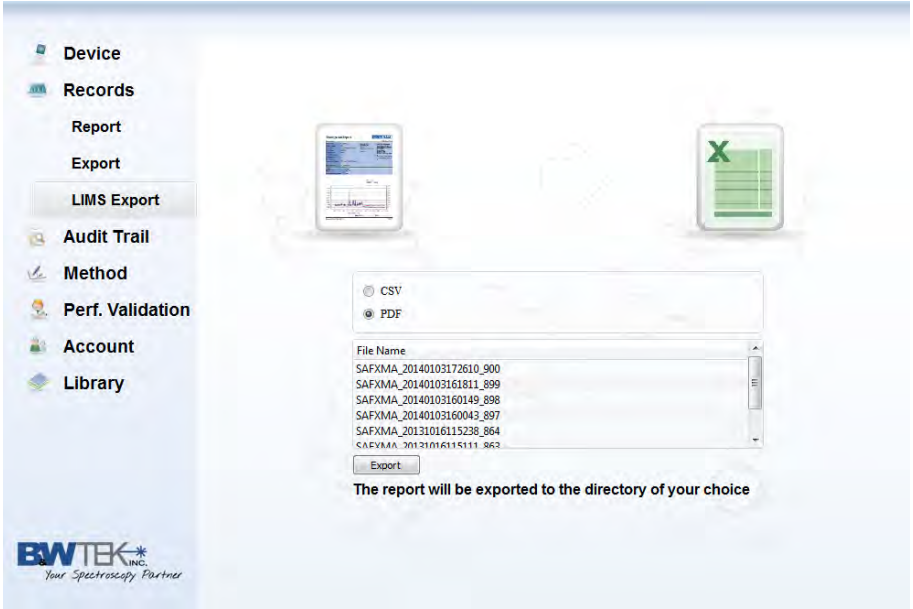
LIMS Export:

In addition to the automatic LIMS export, the LIMS export can also be performed at a later time with any data in the database. Click on **LIMS Export** under “Records” to export the data into a LIMS report. Click on **Export** in the center of the screen. The data will be exported into the Server at **C:\BWTEK\NID\DataBase\NID Report.**



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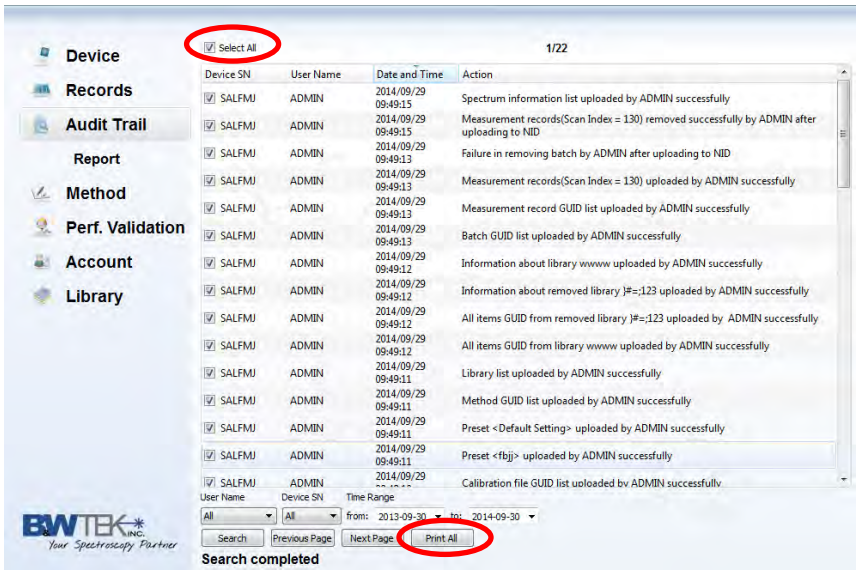
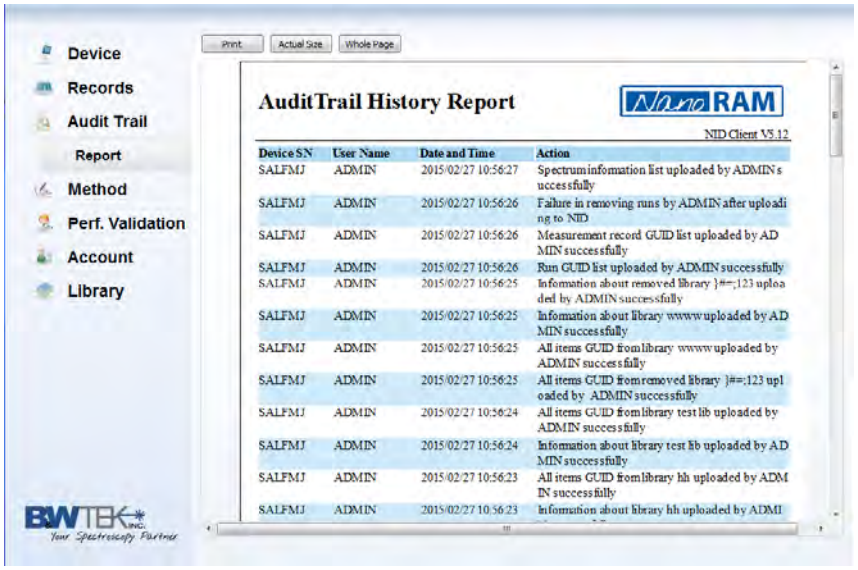
6.5.6. Audit Trail

Click on **Audit Trail** on the left side of the screen. Click on **Select All** to select all events or the audit trail can be searched by user name, device or time. User can select the events and click on **Report** to generate the report for the selected events, or select the entire audit trail to print out or be saved into a PDF file.





6.5.7. Method Management

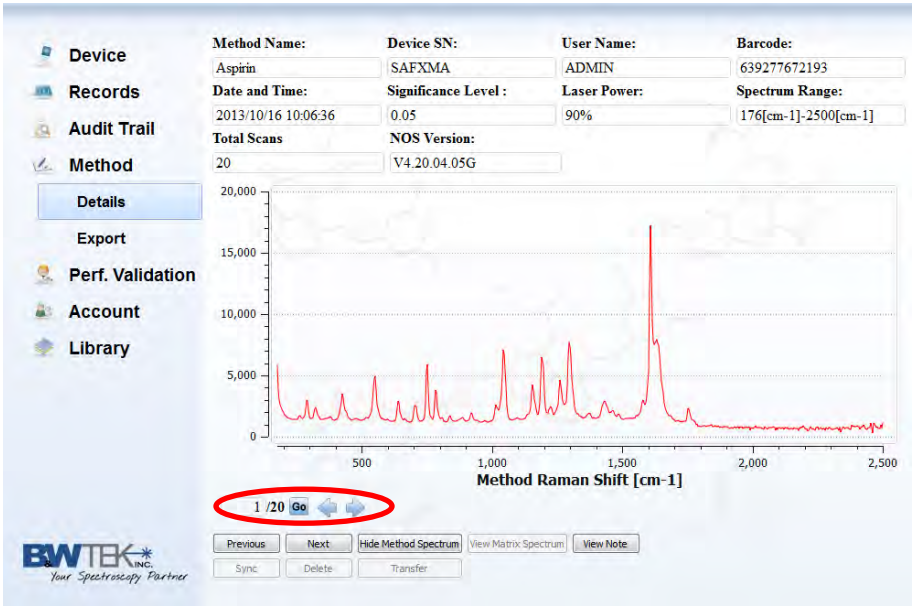
Click on **Method** on the left menu bar. Apply filters if needed. Click on **Search**. A list of existing methods will be displayed. Methods can be managed via NID to:

- View method details;
- Modify method name;
- Delete method;
- Export method spectral data;
- Transfer method from one NanoRam unit to another NanoRam unit

Changes cannot be made to methods by an operator-level user in NID or in NOS.

<u>View Method Details</u>:
Click on **Method** on the left menu bar. Apply filters if needed. Click on **Search**. A list of existing methods will be displayed. Select the method by checking the box. Click on **Details**. The details of the method will be displayed.
Toggle through the arrow keys on the bottom of the screen

to view each of the spectra included in the method.



<u>Modify Method Name</u>:
A method name can be modified in NID when NanoRam is connected to PC and the

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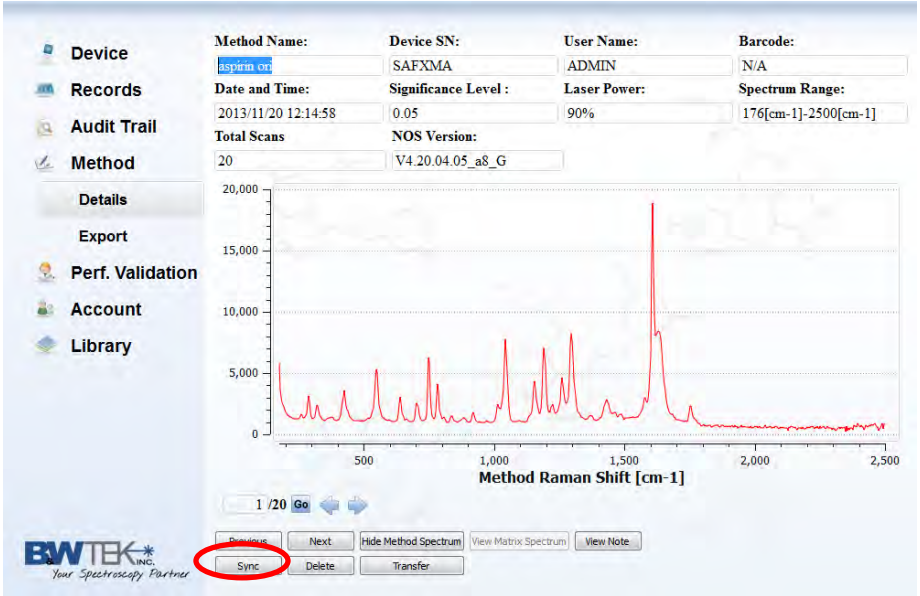
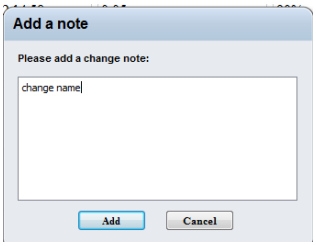
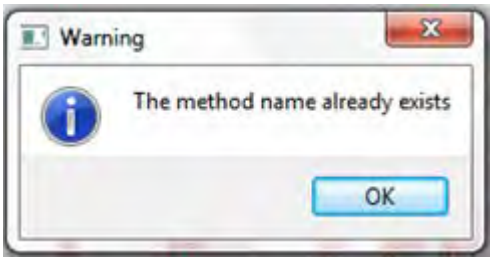
modified method can be synchronized back to NOS. Change the name in the "Method Name" field. Click on **Sync**. The name will be updated in NOS.



Click on **Sync**. User will be prompted to enter a note.



"synchronizing…" will be displaying at the bottom of the screen, indicating the name change is in process. It will take a few seconds for the name to be changed. If the new name already exists, a message will pop up:



"Updated successfully" will be displayed at the bottom of the screen after the

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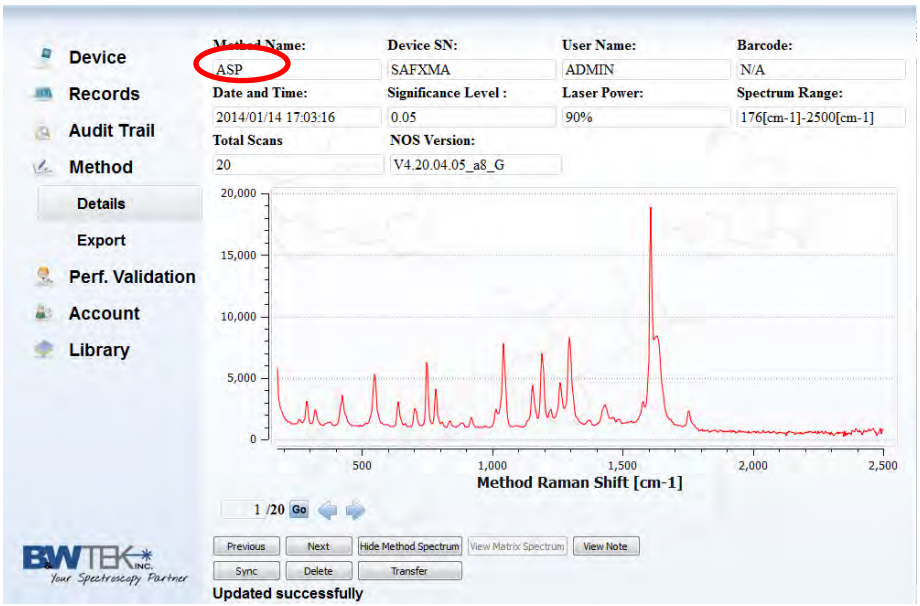
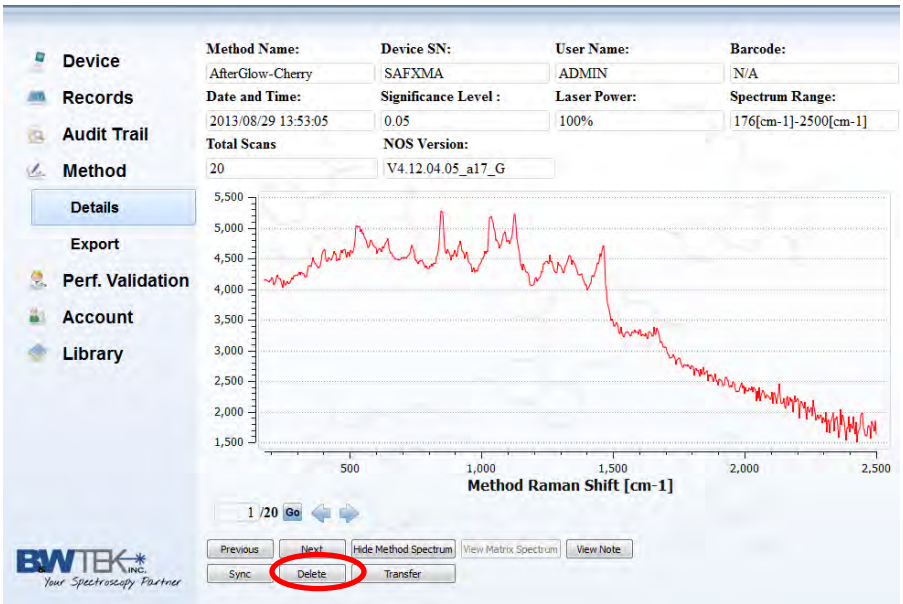
operation is completed. The new method name will be displayed.



Delete Method:

A method can be deleted via NID. Firstly, the communication needs to be established between NanoRam unit and NID, followed by synchronizing the method on NID. Select the method to be deleted and Click **Details**.



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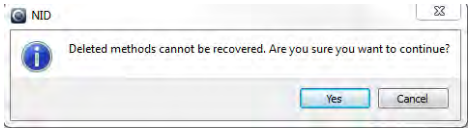
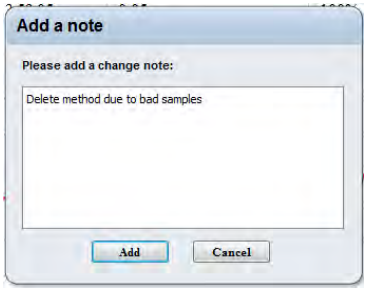
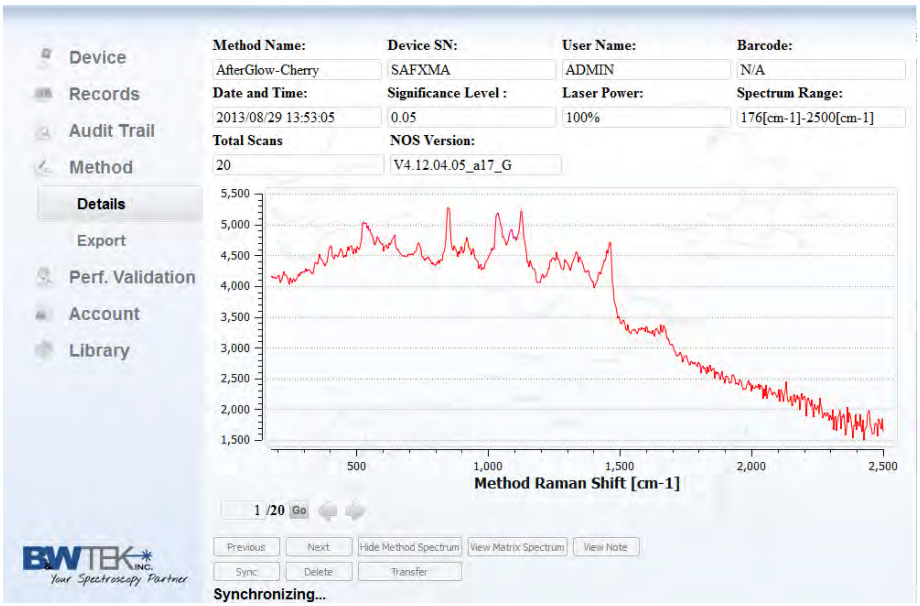
Click the **Delete** button at the bottom of the method details page. A message to confirm the delete will be displayed. Click **Yes** to continue, or **Cancel** to cancel the action.



A window will pop up for user to add a note for change.



After the note is added, "synchronizing…" will be displaying at the bottom of the screen, indicating the delete is in process. It will take a few seconds for the method deletion to be completed.



After the delete is finished, "Updated successfully" will be displayed at the bottom of the screen, while the method details will be emptied out.

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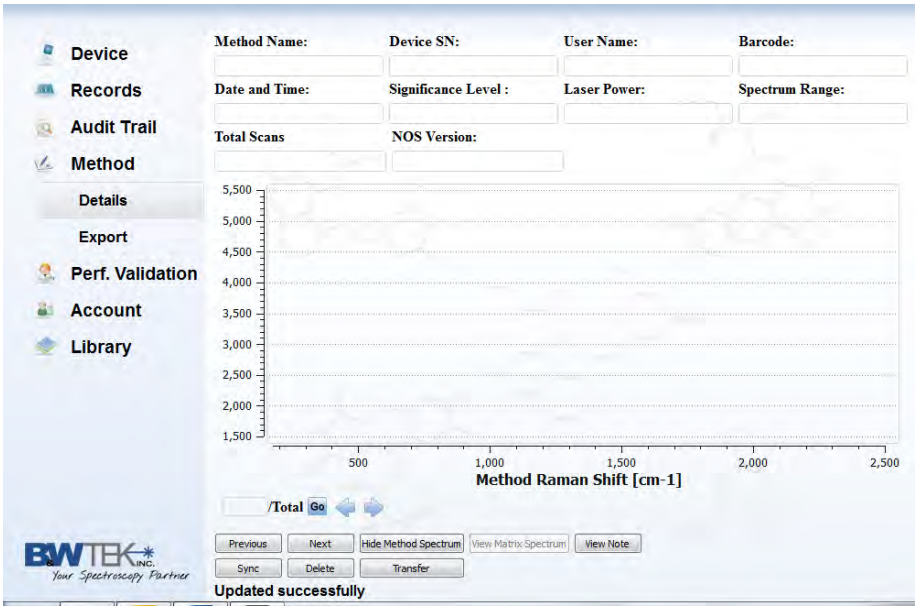
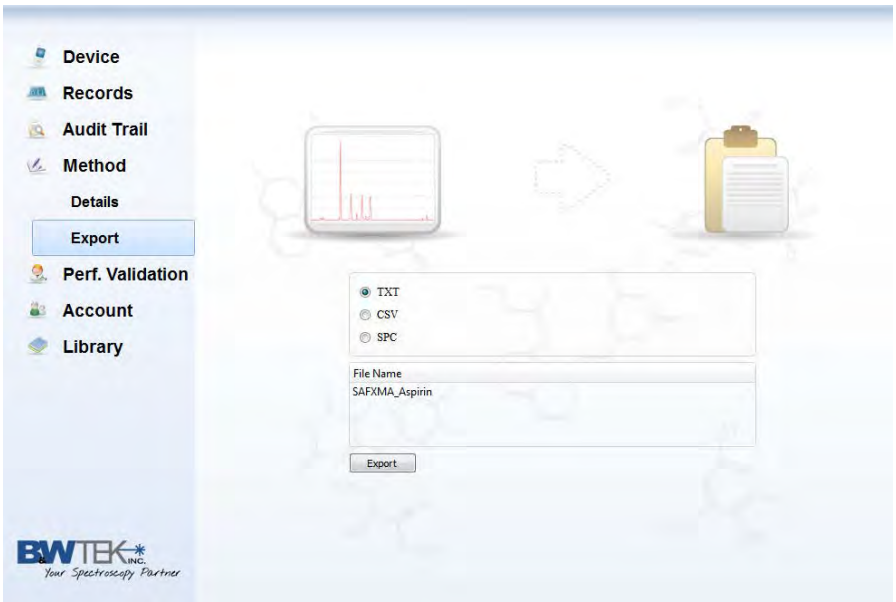


Export Method Spectral Data:

By clicking on **Export** under "Method" on the left menu bar, each individual spectrum included in method will be exported to a user-designated location in three formats: TXT, CSV, or SPC. Individual SPC files will be created for each scan, while the TXT and CSV files will include all the data for all scans in a single file.



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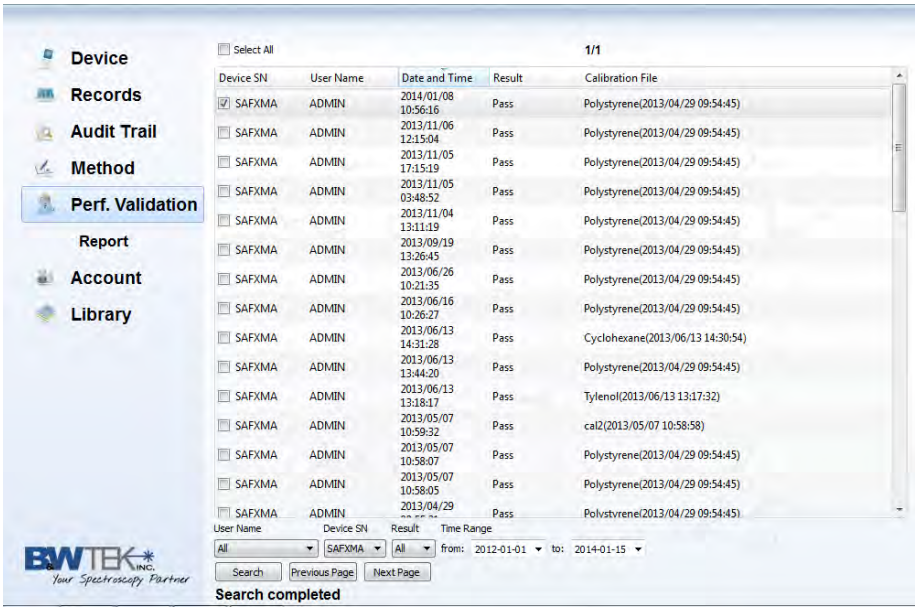
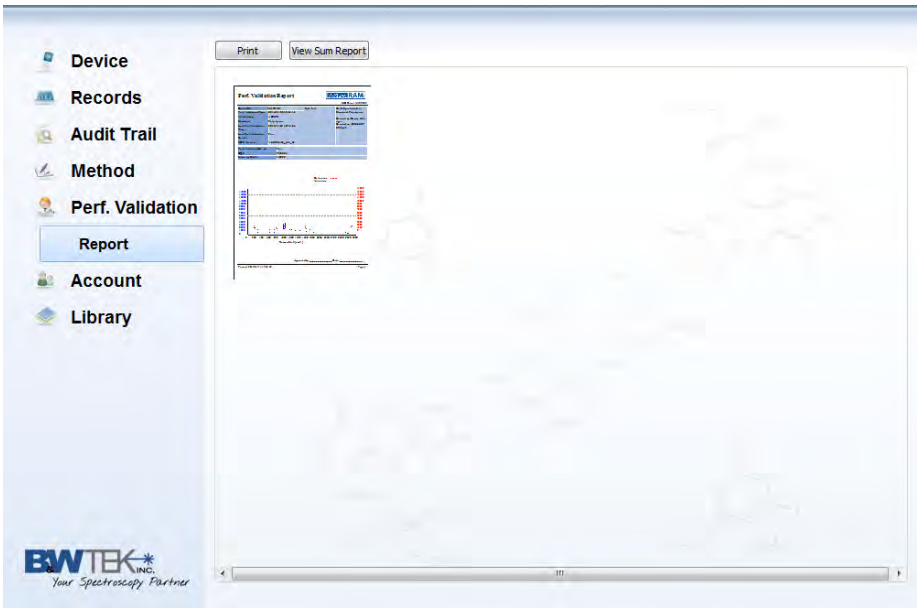
6.5.8. Performance Validation Report

Click on **Perf. Validation** on the left menu. Click on **Search** at the bottom of the screen; apply filters if needed. Select records by checking the box next to a record.



Click on **Report**. The selected performance validation reports will be displayed. Click on **Print** to print out all the reports that are in the display window. Click on **View Sum Report** to see a summary report of the performance validation records selected.



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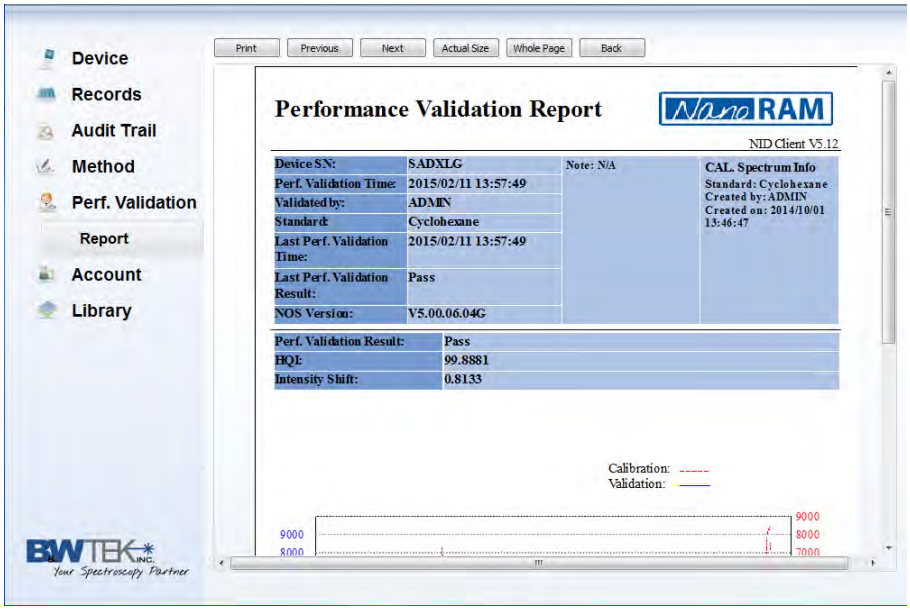
Click on the report icon to display the report. Click on **Print** to print the report.



6.5.9. User Account Management through NID (NOS Administrator only)

Click on **Account** on the left menu bar. Apply filters if needed. Click on **Search** at the bottom of the screen to display a list of the existing accounts. User account can be managed via NID for:

- Enable/disable user account;
- Resetting account password;
- Change user account type;
- Create new user account

Every user account modification needs to be synchronized back to the NanoRam unit to be effective. The synchronization must be done while NanoRam is connected to the PC. Press **Sync** on the bottom of the screen to synchronize the account back to the NanoRam. A message will appear confirming the update.

<u>Enable/Disable User Account</u>:

For a specific account, right-click on the “Enable” column, options of “Enable” and “Disable” will be displayed. Select the desired status.

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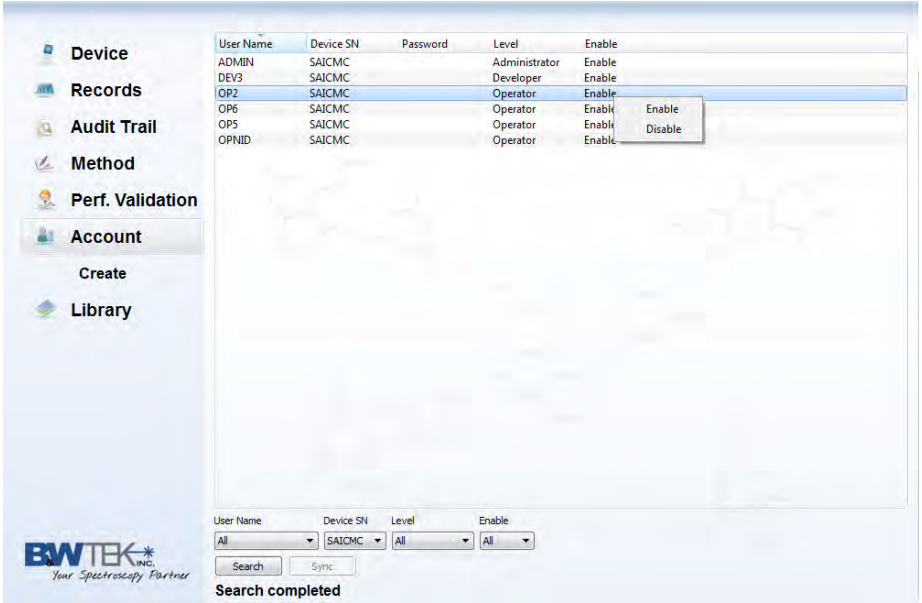
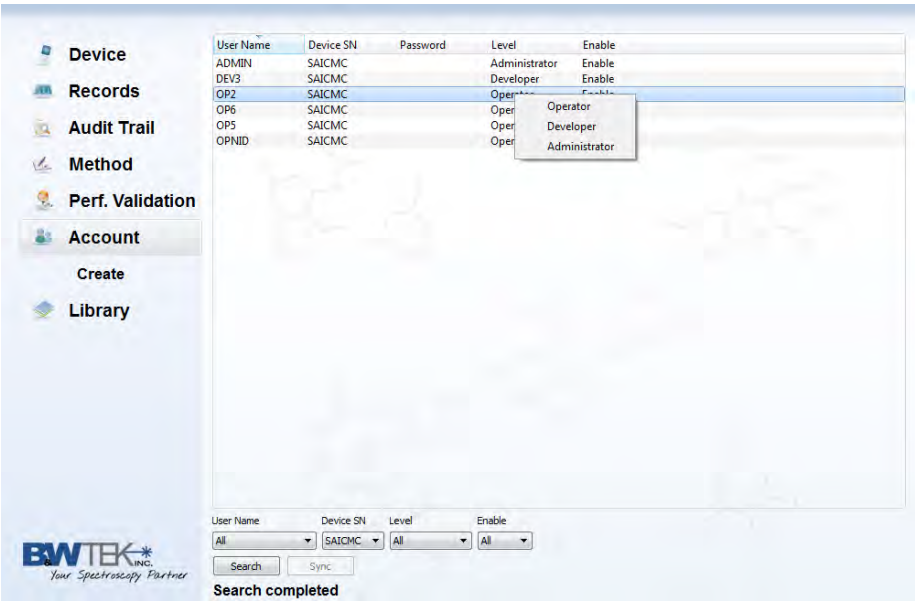


Modify User Account Type:

For a specific account, right-click on the “Level” column, options of user types will be displayed. Select the desired level.



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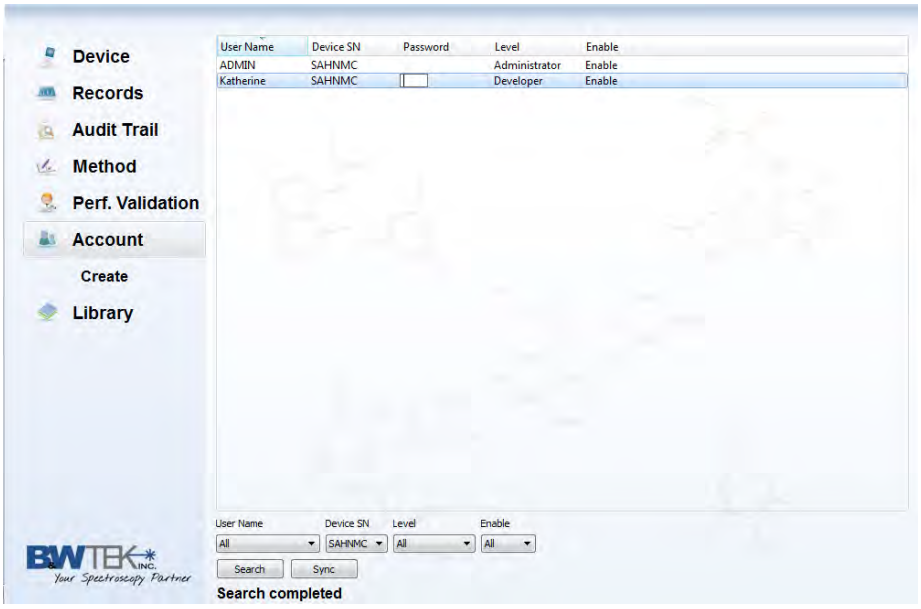
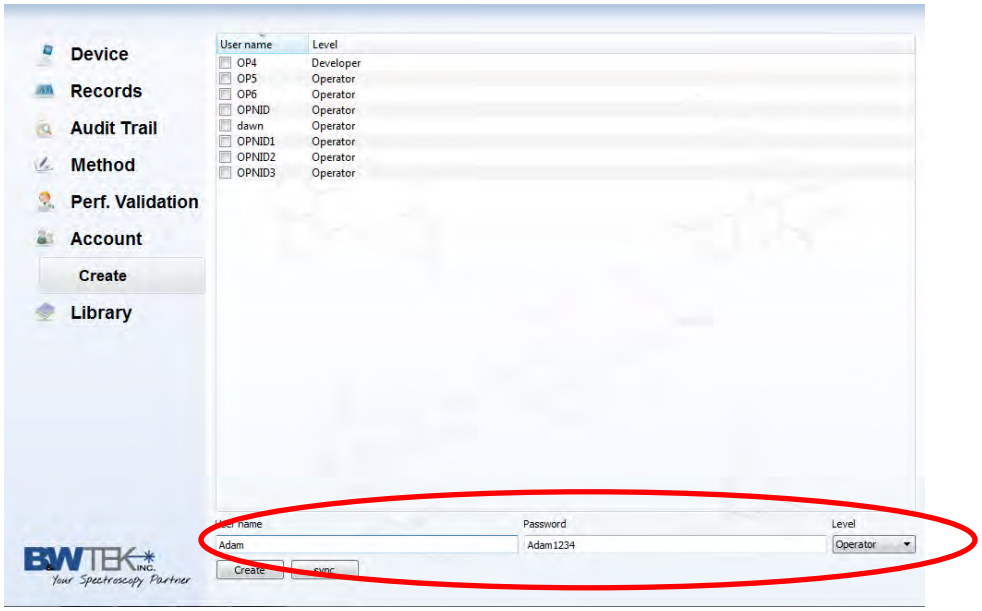
Reset Account Password:

For a specific account, double click on the “Password” column. A cursor will appear at the password space. Enter the new password as desired.



Create New Account:

A new account can be created on a PC via NID. Click on **Create**. Enter the new account info including user name, password and the user level. Press **Create**.



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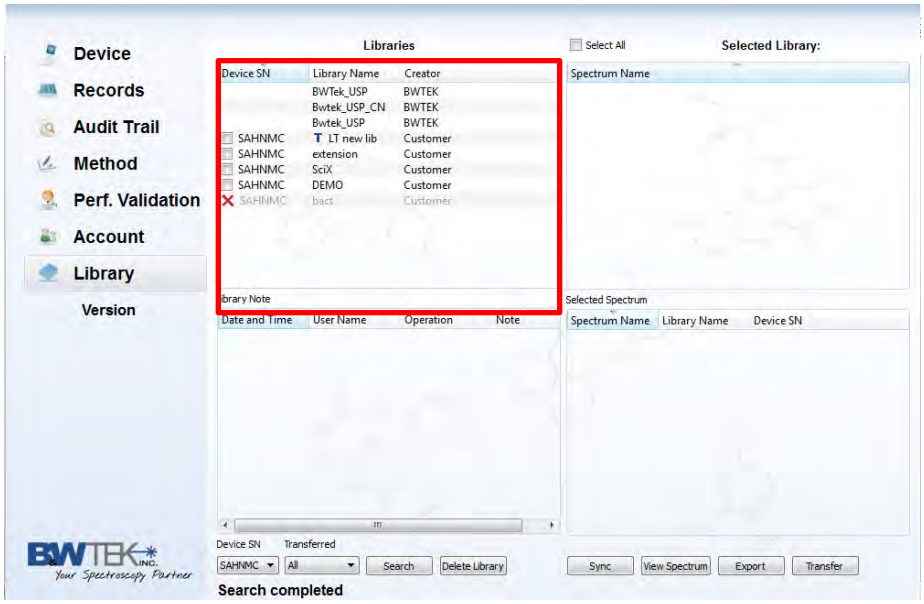
6.5.10. Library Management

Libraries can be managed via NID to:

- Modify library spectrum name;
- View Library spectrum;
- Delete library;
- Delete spectrum inside user-defined library;
- Export library spectral data for user-defined library;
- Transfer user-defined library from one NanoRam to another NanoRam unit.

Click on **Library** on the left menu bar. Click on **Search**. A list of the libraries will be displayed on the top-left "Libraries" screen. Libraries with a blue T before their name indicate a library that has been transferred from another NanoRam. The Creator name indicates who made the library. Libraries purchased from B&W Tek have BWTEK listed as creator, and are not transferrable or exportable.



Note: The "X" next to a library indicates that the library has already been deleted. These libraries can still be viewed but the spectra in them cannot be exported or transferred.

Double click on a library name, the spectra list of the library will be displayed on the top-right "Selected Library" quadrant. Any note added at the time of generating the

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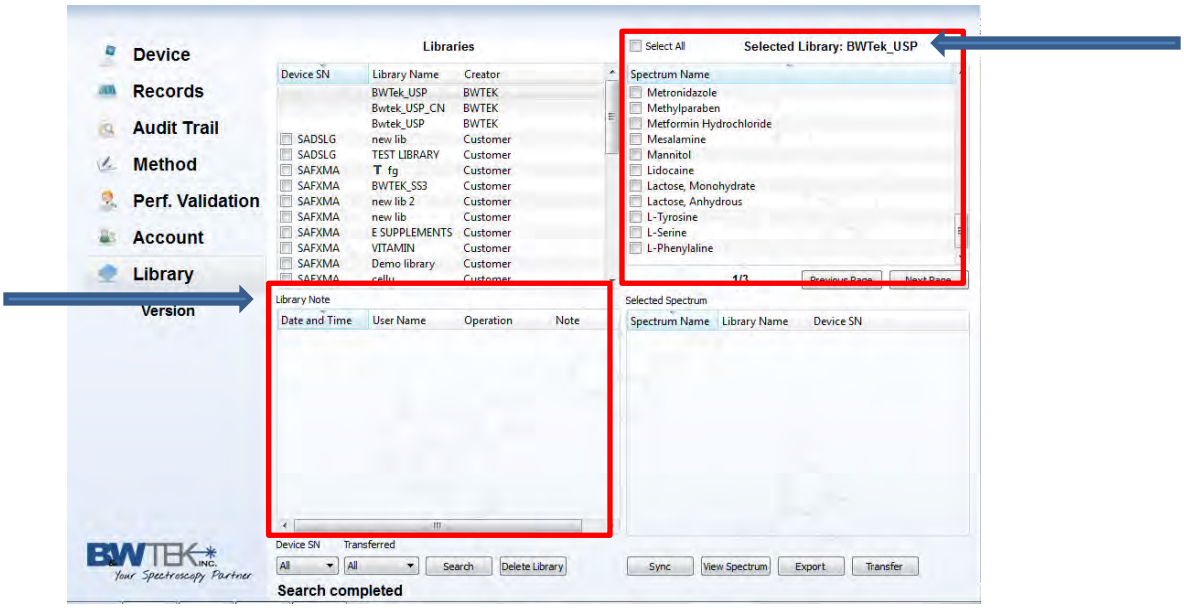
library will be displayed on the bottom-left “Library Note” quadrant.



Modify Library Spectrum Name:

The names of spectra in the library can be changed by selecting an entry, double clicking and changing. To update the name in NOS, the library must be synchronized back to the NOS using the **Sync** button on the bottom of the screen while the NanoRam is connected to the PC. Press **Sync** to synchronize the account back to the NanoRam. A message will appear confirming the update.

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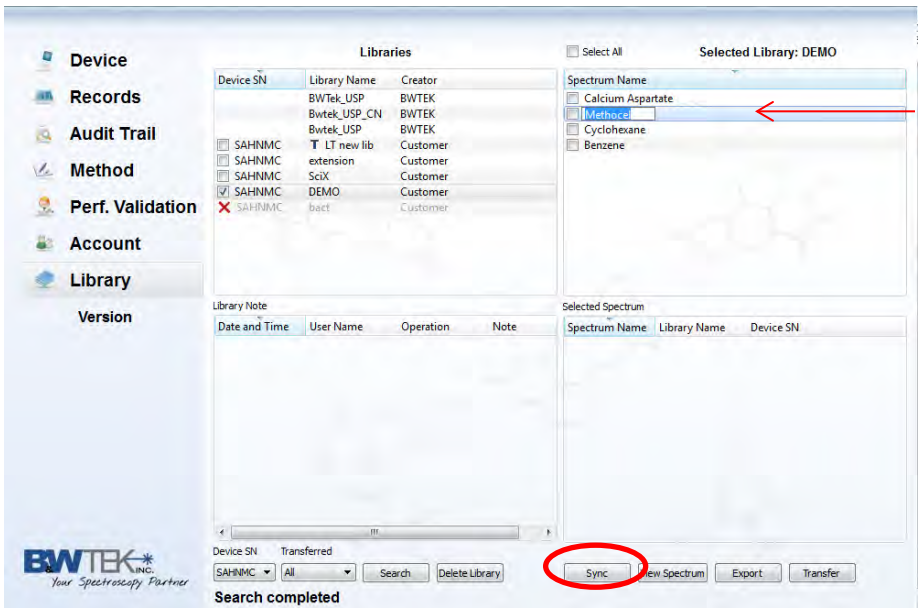
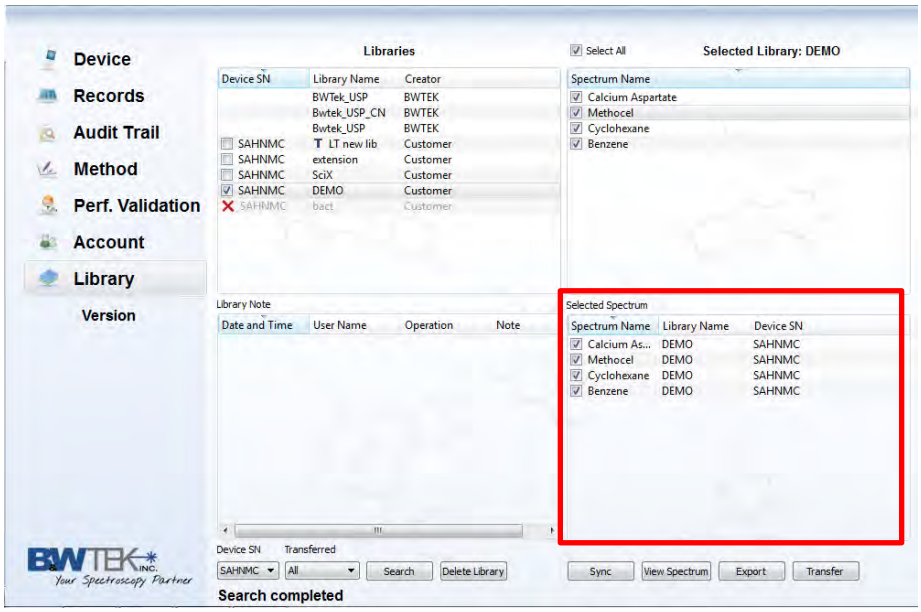


View Spectrum:

Select the spectrum by clicking on **Select All** or choose the individual spectrum by checking the box next to the spectrum in the upper right quadrant. The selected spectrum or spectra will be listed on the right-bottom "Selected Spectrum" space.



The spectra in the Selected Spectrum space can be deselected by right-clicking and

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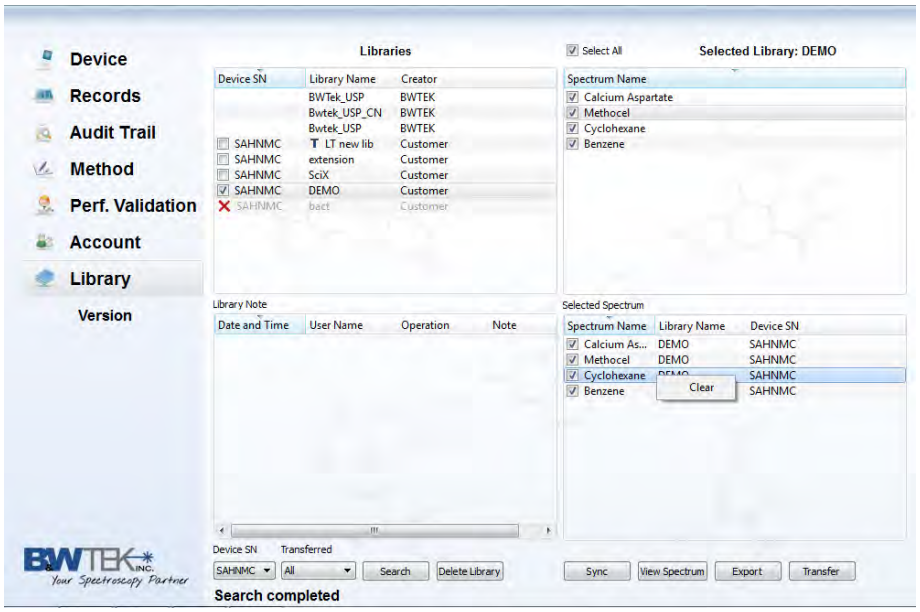
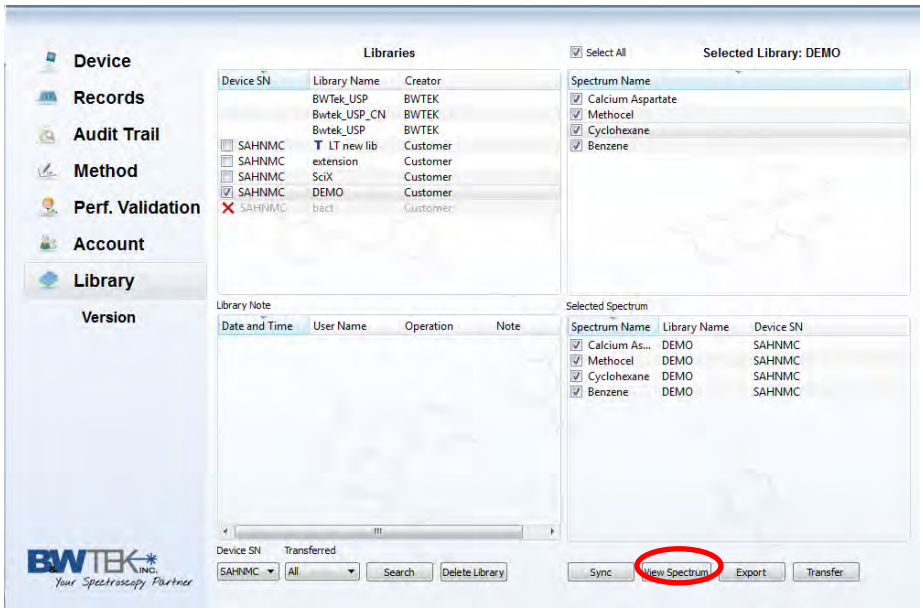
selecting **Clear**.



Once the spectrum is selected, click the **View Spectrum** button. The selected spectrum will be displayed in a new screen.



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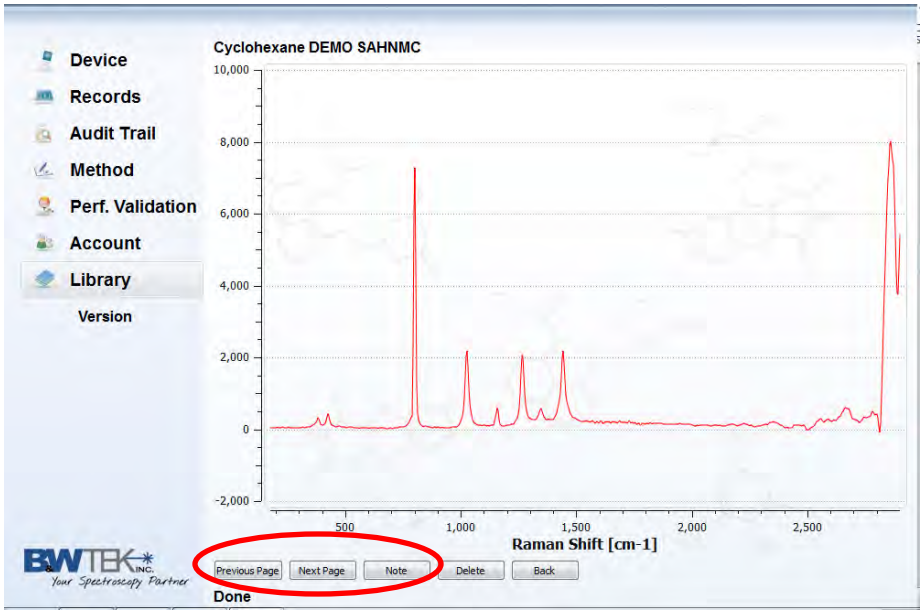
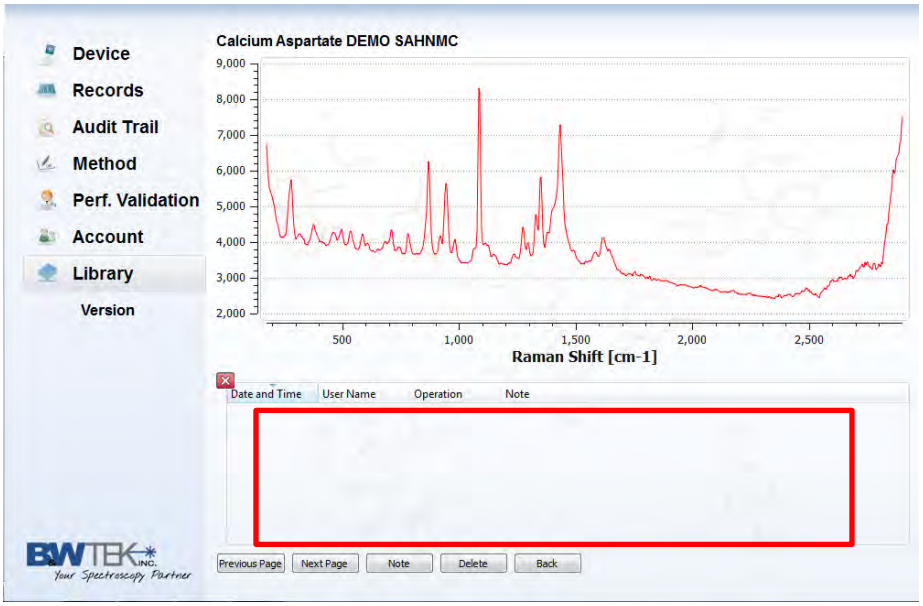


Press **Previous Page** or **Next Page** on the bottom of the screen to view the selected spectra one by one. Press **Back** to return to the Library page.

Any notes entered for a library spectrum can be viewed by selecting **Note**. This will include notes related to the transfer of a library spectrum.



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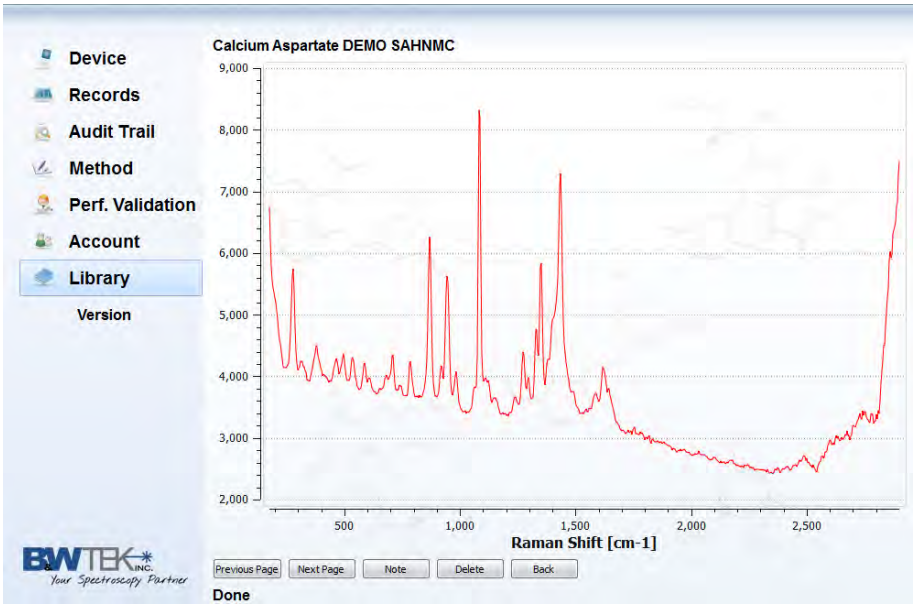
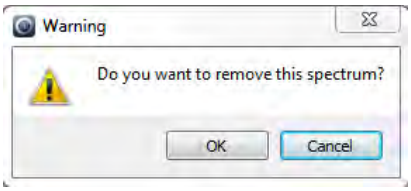
Delete Spectrum in Library:

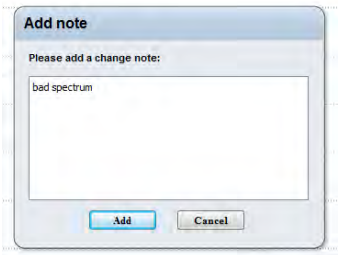
At the View Spectrum screen of a selected spectrum, press **Delete** button on the bottom of the screen.



A message to confirm the delete will be displayed. Click **Yes** to continue, or **Cancel** to cancel the action.



A window will pop up for user to add a note for change. Enter the note and press **Add**. It will take a few seconds for the spectrum to be deleted.



After the delete is finished, “Successful” will be displayed at the bottom of the screen. The spectrum will be marked with “X”.

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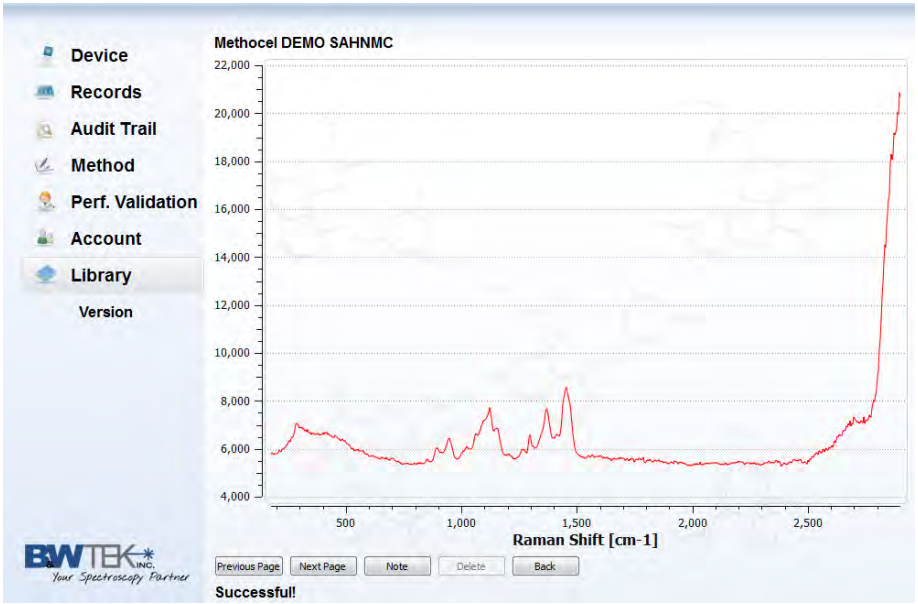
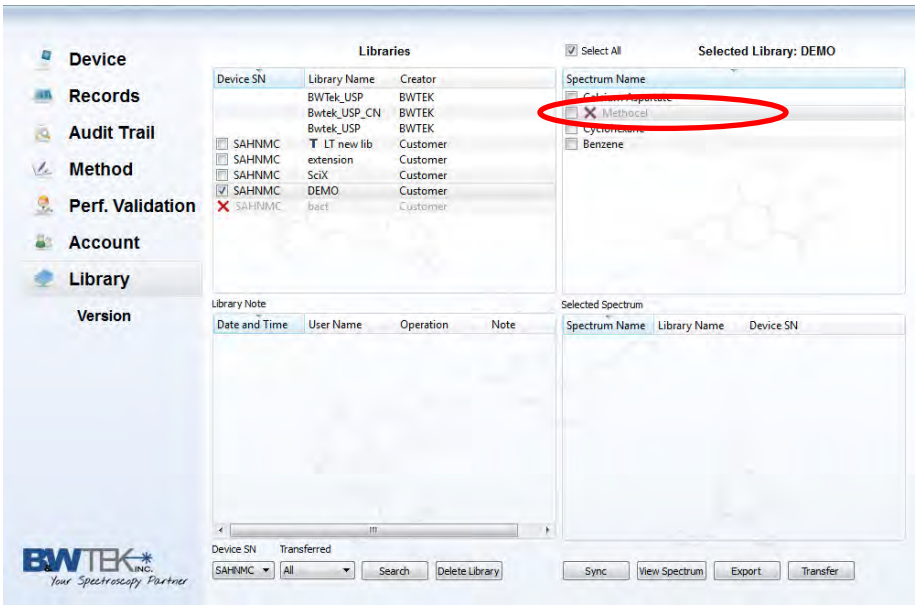


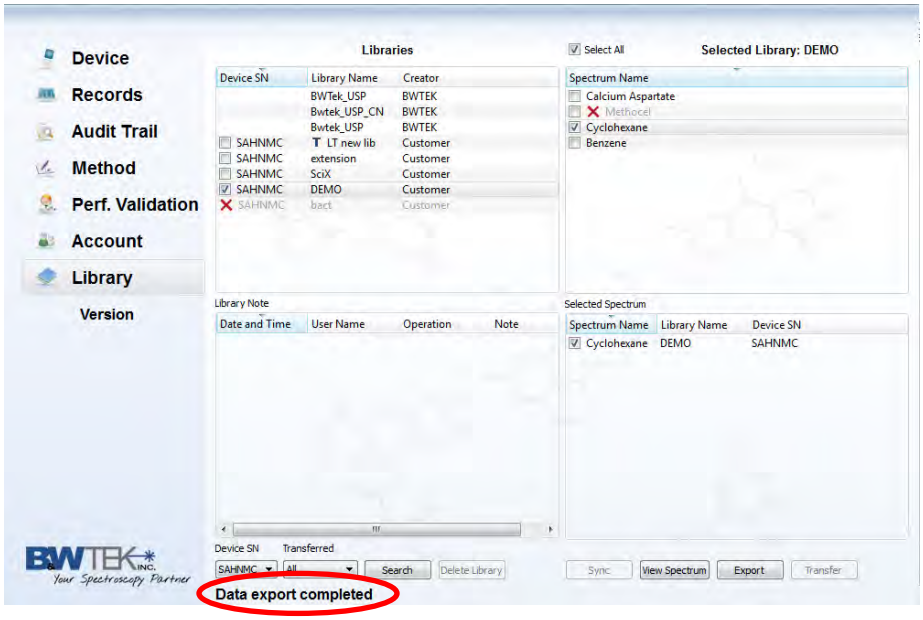
Note: Deleting a library spectrum or library itself require a live connection to a NanoRam.



Export Spectrum:

Selected spectrum can be exported on the PC. Click **Export** on the bottom of the

screen to export the library data in CSV, TXT or SPC file format to a user-designated location such as to the desktop of the user PC. The library data are displayed and exported over the spectral range from 176 – 2900cm^{-1}. A message "Data export completed" will appear to confirm the operation.



Note: Library exporting is for user-defined library files only.

Library Version:

Click **Version** under **Library**, the library version for BWTek-created will be displayed.

7. Data Transfer Between Two NanoRam Units

Spectral libraries created by users can be transferred from one NanoRam unit to another. The data must be collected from NOS version 4.00 or higher. The library transfer function does require Wi-Fi or Ethernet connectivity between NOS and NID. Methods created with NOS version 4.00 and higher can also be transferred between NanoRam units when both units are using NOS/NID software version 4.30 and higher.

7.1. Library Transfer Between Two Units

User-created spectral libraries can be transferred across different NanoRam units. The library transfer is done through NID software to where the original library from one

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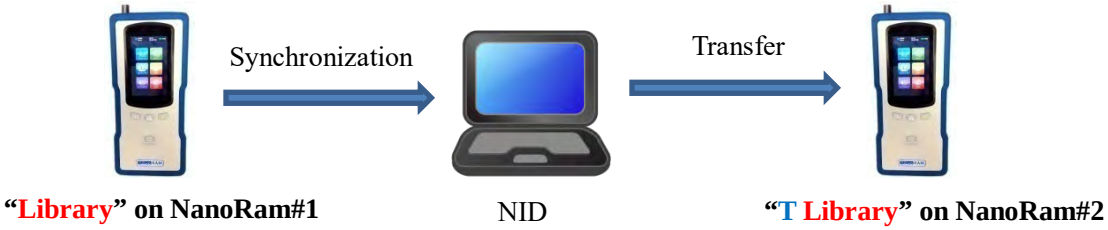
NanoRam (NanoRam#1) is firstly synchronized to NID and then transferred to another NanoRam (NanoRam#2).

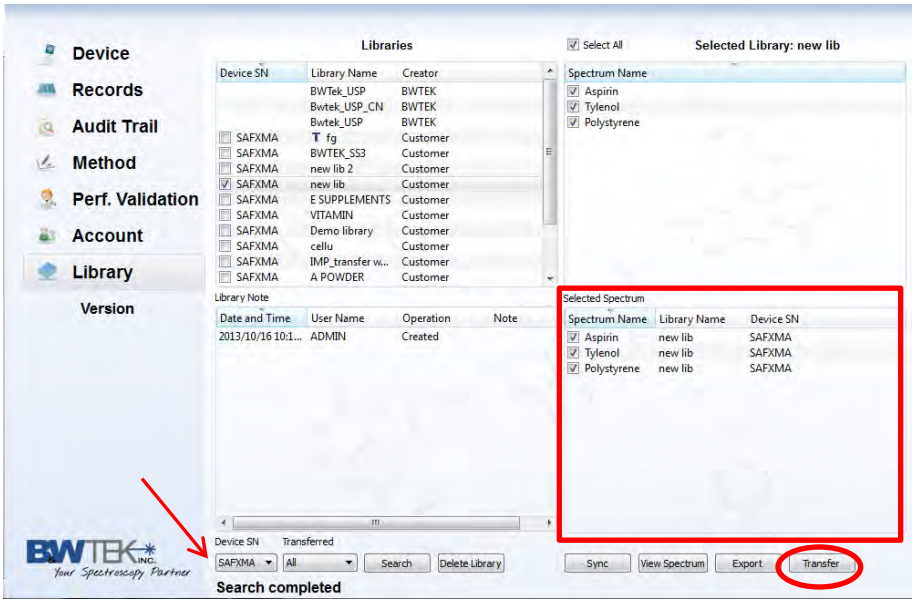


It is advisable to make the transfer from the unit on which the library was created to another unit (and not transfer a transferred library) to more easily maintain traceability of the origin of libraries).

The library transfer can be done in the following order:

1) Connect NanoRam#1 with NID software and synchronize the NanoRam#1.
2) Disconnect NanoRam#1 from NID software.
3) Connect NanoRam#2 with NID software.
4) On NID: search library on NanoRam#1 and select the library to be transferred.

Example screenshot showing Library of NanoRam#1 to be transferred:



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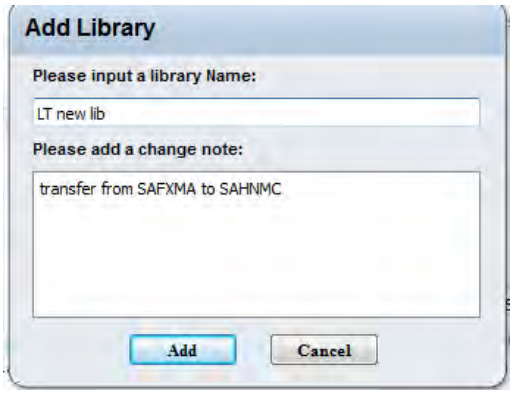
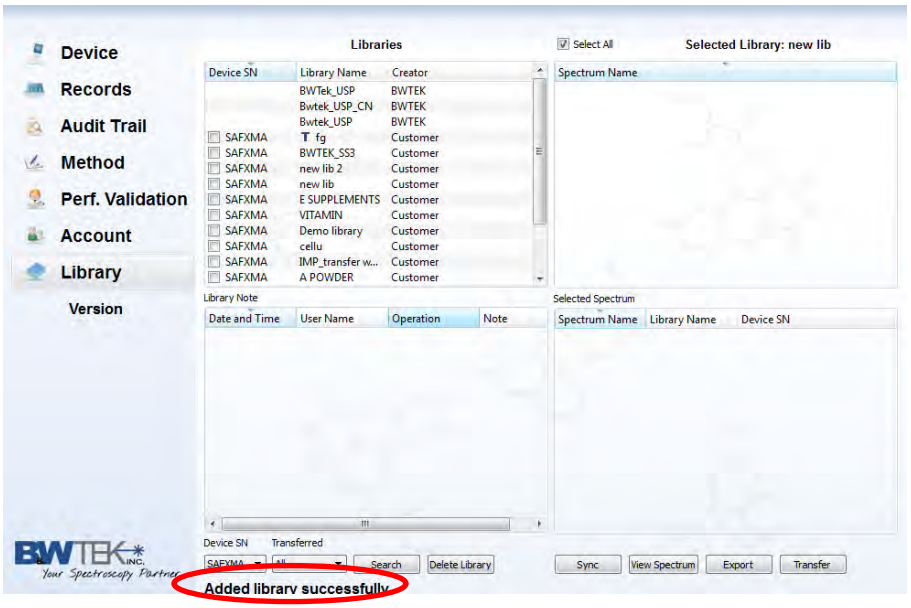
5) Transfer the libraries to NanoRam#2 by pressing **Transfer**. User will be prompted to enter the library name to be used on the NanoRam#2 and a note.



6) After the library transfer is done, a message will be displayed at the bottom of the screen: “Added library successfully”.



Search NanoRam#2 for Library via NID, the transferred library will be marked with “**T**” before the the library name. The note associated with the library transfer will be shown by clicking on **View Spectrum**, then **Note**.

Example screenshot showing transferred Library on NanoRam#2:

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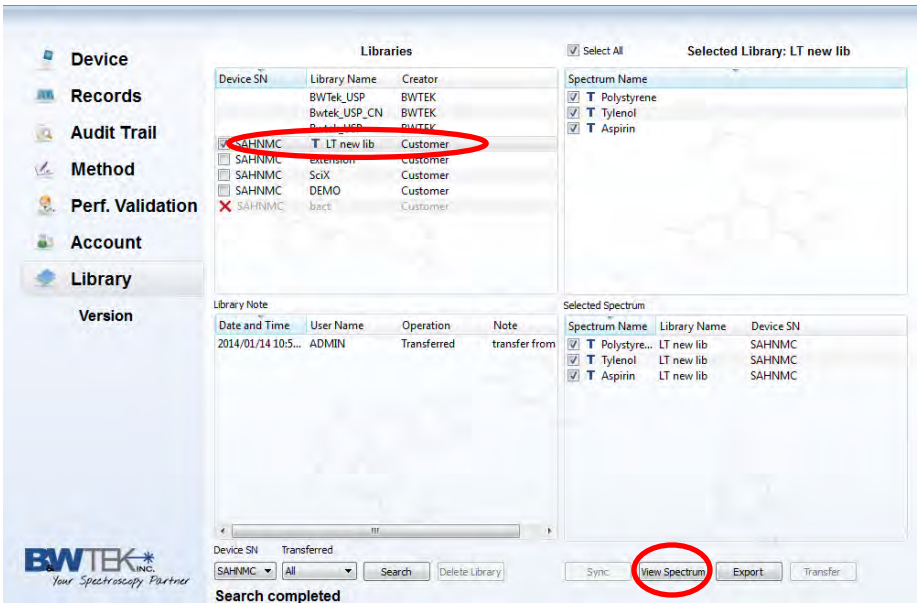
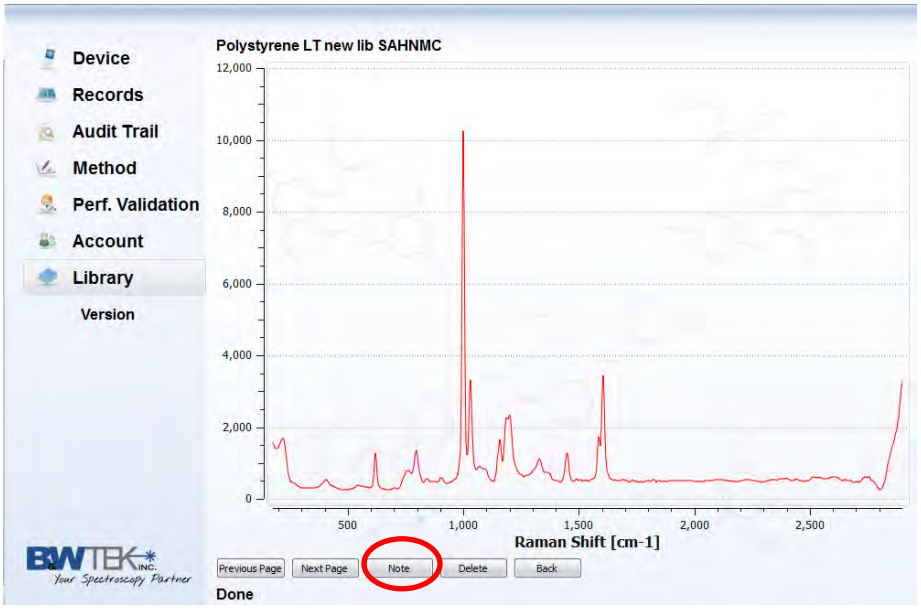
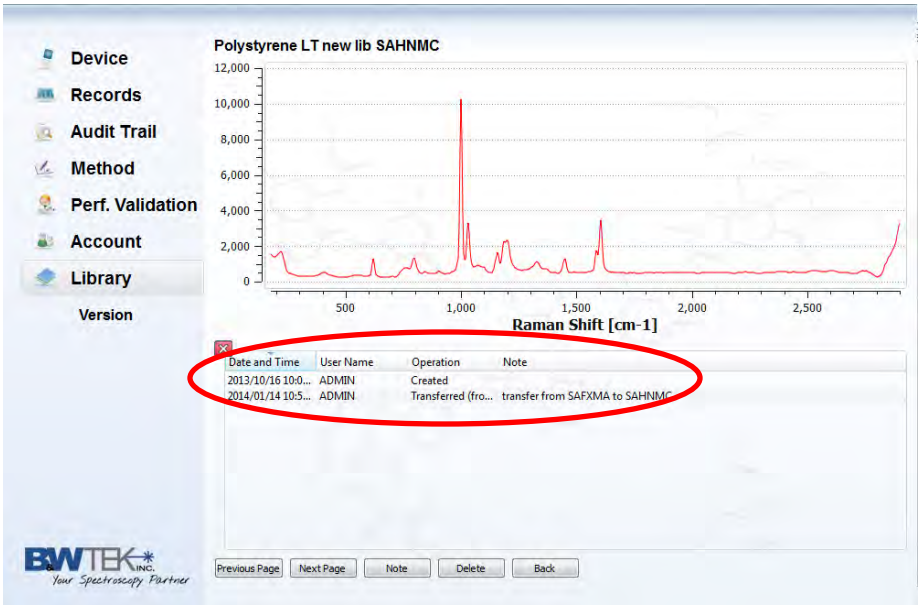
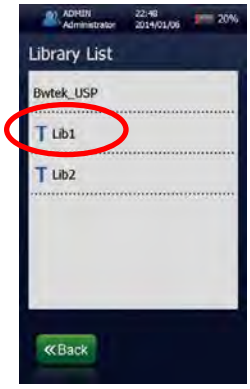

Device
Records
Audit Trail
Method
Perf. Validation
Account
Library
Version
Libraries
Select All
Selected Library: LT new lib
Device SN
Library Name
Creator
BWTek_USP
BWTEK
Bwtek_USP_CN
BWTEK
SAHNMC
LT new lib
Customer
SciX
DEMO
Spectrum Name
Polystyrene
Tylenol
Aspirin
Library Note
Selected Spectrum
Date and Time
User Name
Operation
Note
2014/01/14 10:5...
ADMIN
Transferred
transfer from
Device SN
Transferred
All
Search
Delete Library
Sync
View Spectrum
Export
Transfer
Search completed


Device
Records
Audit Trail
Method
Perf. Validation
Account
Library
Version
Polystyrene LT new lib SAHNMC
12,000
10,000
8,000
6,000
4,000
2,000
0
500
1,000
1,500
2,000
2,500
Raman Shift [cm-1]
Previous Page
Next Page
Note
Delete
Back
Done



On the NanoRam#2 unit, the transferred library will be shown in the Library List marked with "**T**".



7.2. Method Transfer Between Two Units

Methods can be transferred across different NanoRam units. Both units must be operating with the same version of NOS (version NOS 4.30 or higher), and synchronized to the NID from the latest NOS version. The method transfer is done through NID software to where the original method "Method" from one NanoRam (NanoRam#1) is firstly synchronized to NID and then transferred to another NanoRam (NanoRam#2) as "T Method". The "T Method" is then converted to the

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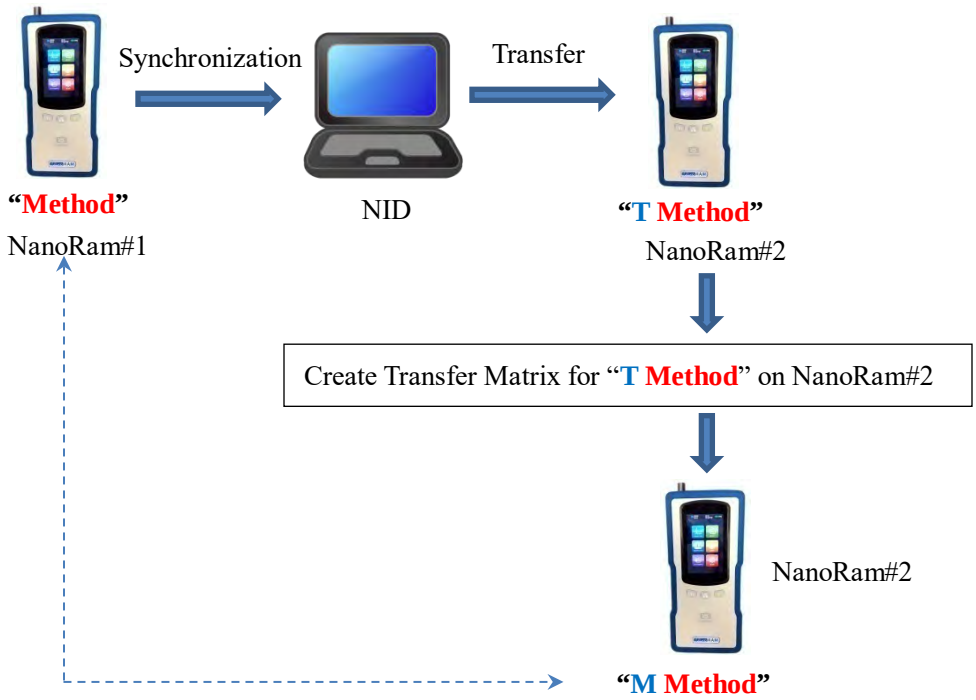
finished method, “M Method” by adding a transfer matrix on NanoRam#2 using the same samples used for the original method.



It is advisable to make the transfer from the unit on which the method was created to another unit (and not transfer a transferred method) to more easily maintain traceability of the origin of methods).

The method transfer can be done in the following order:

1) Connect NanoRam#1 with NID software and synchronize NanoRam#1.
2) Disconnect NanoRam#1 from NID software.
3) Connect NanoRam#2 with NID software.
4) On NID: Search the method on NanoRam#1. Select the method to be transferred from NanoRam#1 to NanoRam#2 and click **Details**. Click on **Transfer**.

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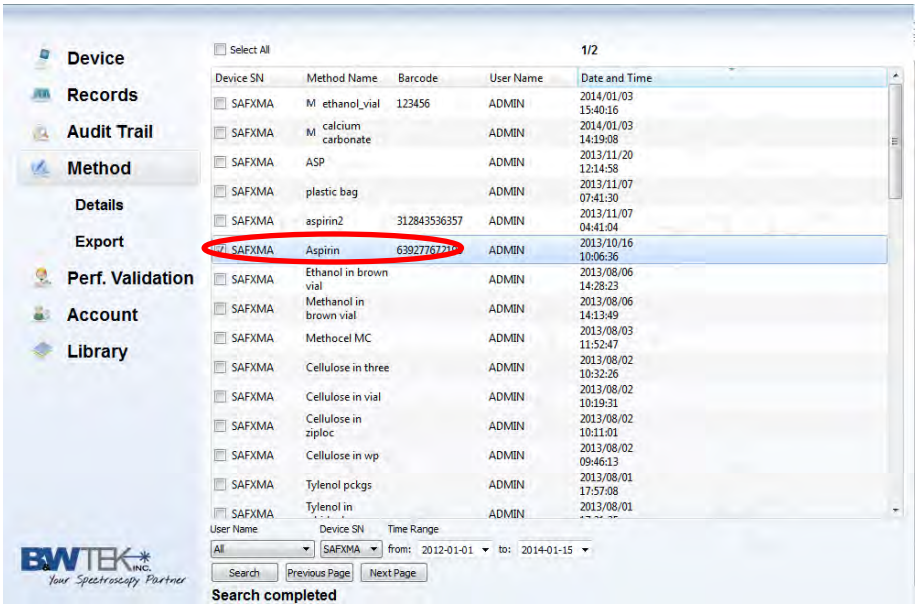

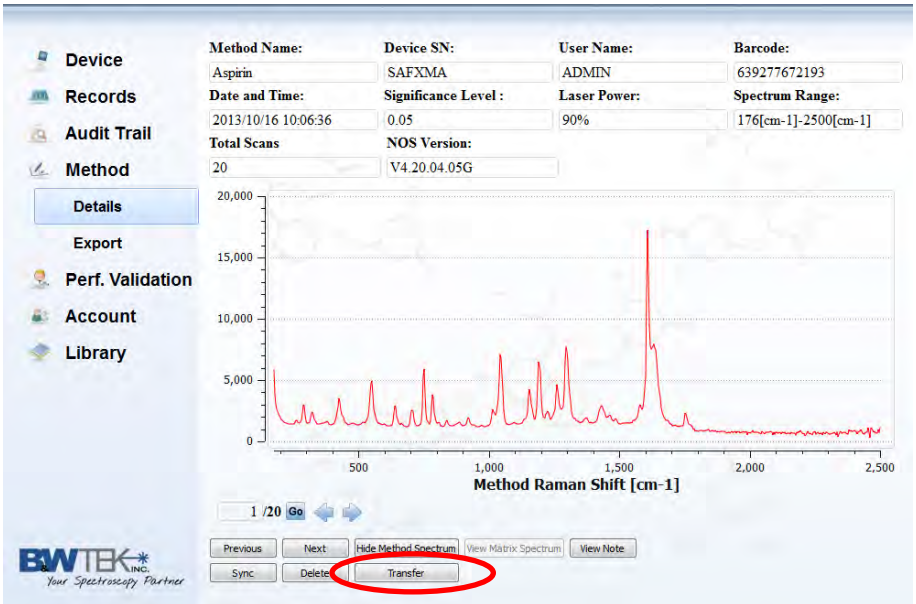

The user needs to enter a note for the method transfer.

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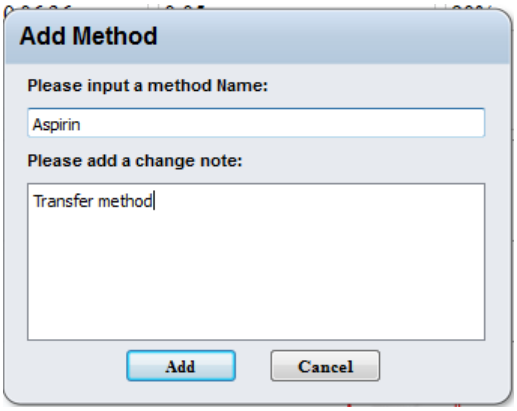
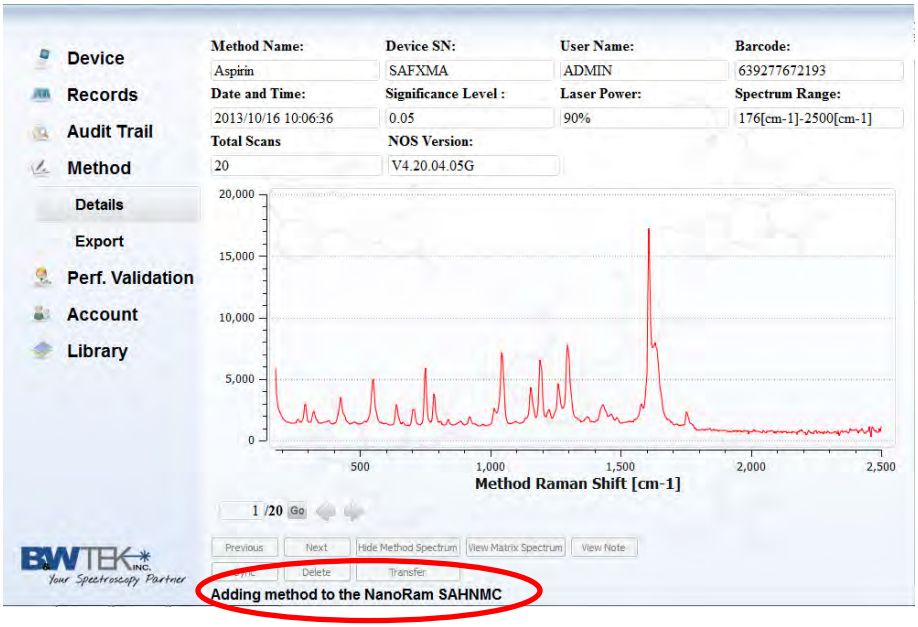


After the note is added, “Adding method the to NanoRam xxxxxx (the SN for NanoRam#2)” will be displaying at the bottom of the screen, indicating the transfer is in process. It will take a few seconds for the transfer to complete.



When the method transfer is completed, “Successfully transferred method to xxxxxx (NanoRam#2), create transfer matrix before using the method” will be displayed at the bottom of the screen.

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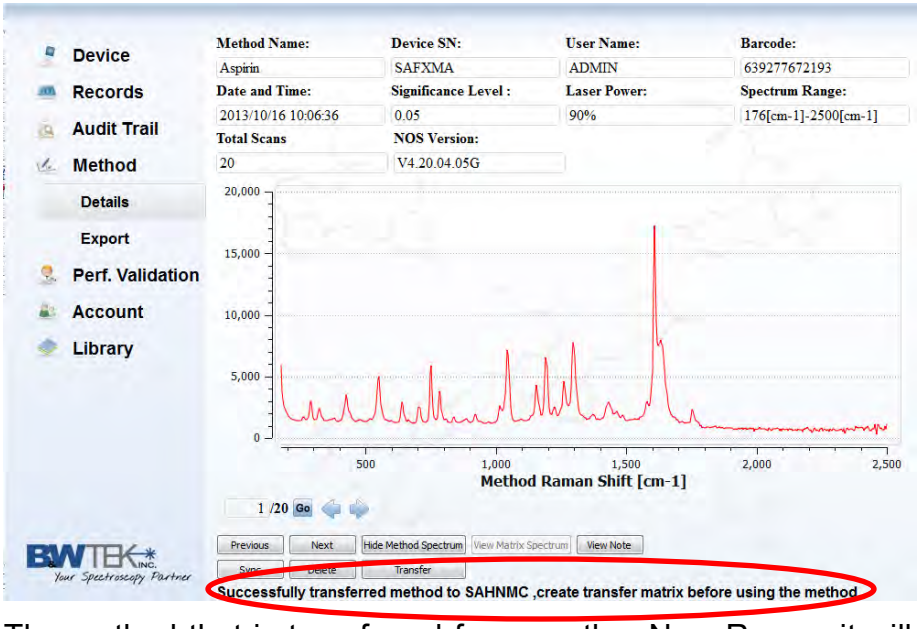
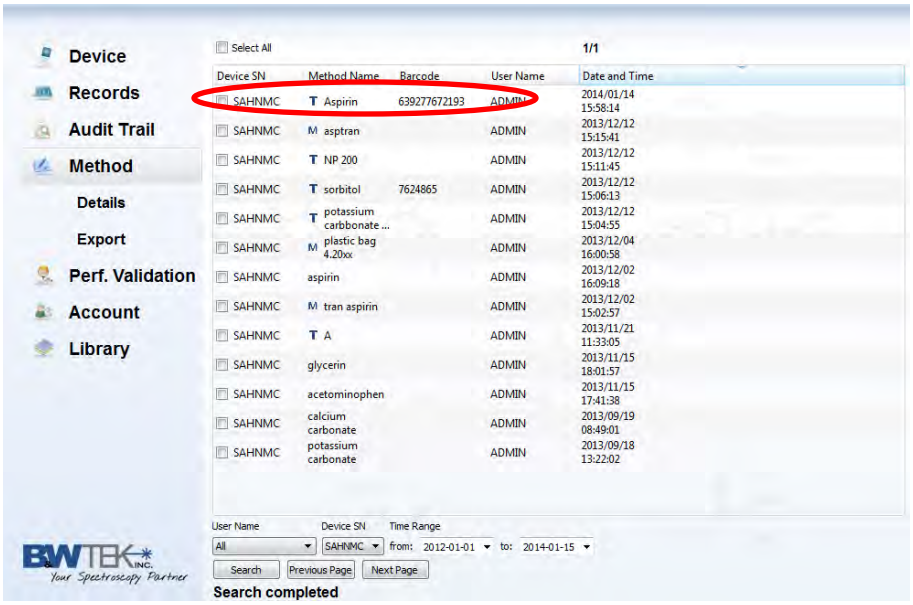


The method that is transferred from another NanoRam unit will be marked with "**T**" before the the method name.



Note: The method marked with "**T**" is not useable until a transfer matrix is created on NanoRam#2 for this method.

5) Disconnect the NanoRam#2 with NID.

6) Create transfer matrix on NanoRam#2. Press Method icon on NanoRam main menu. Locate the transferred method marked with **T**. Press **Edit**, followed by pressing the method for the transfer matrix to be created. A green check will show beside the **T** . Press **Modify**. Press **Create Transfer Matrix** to start creating the transfer matrix.

Transfer Matrix should be created by collection of five spectra of the same samples used for the original method , and collected using the same sampling conditions. A note must be entered. Press **Notes** to enter the notes.

Make sure the correct sampling adaptor is installed and the sample is properly placed. Press laser button to start collecting spectra. It is advisable to choose the five samples that can best represent the method. Press **Finish** at the end of the five scans to accept the scans and save the transfer matrix. A message "Add operation completed" will appear after the scans are saved. The "**T** method" will now be converted to "**M** method". The transferred method "**M** method" can be loaded from the Method list to use. The Method after creation of transfer matrix can only be edited to create a new transfer matrix. No other changes can be made in NOS. The Method name can be changed in NID when the NanoRam is connected to the NID.

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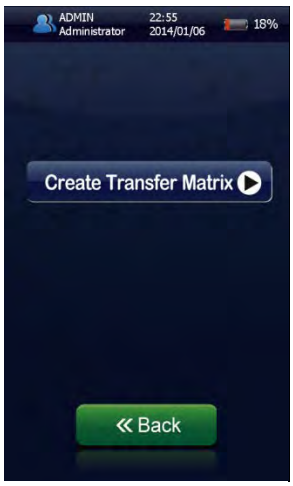
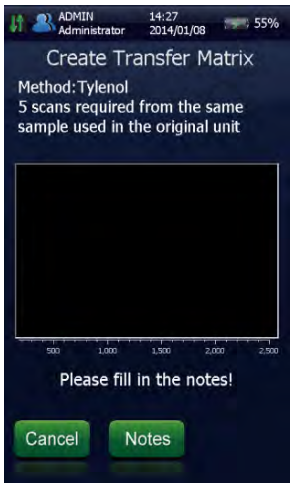
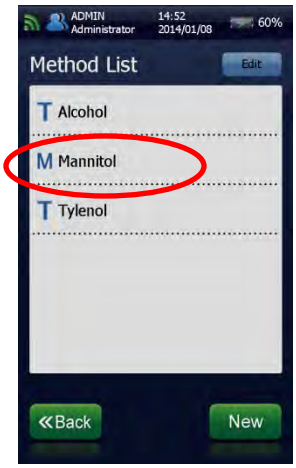
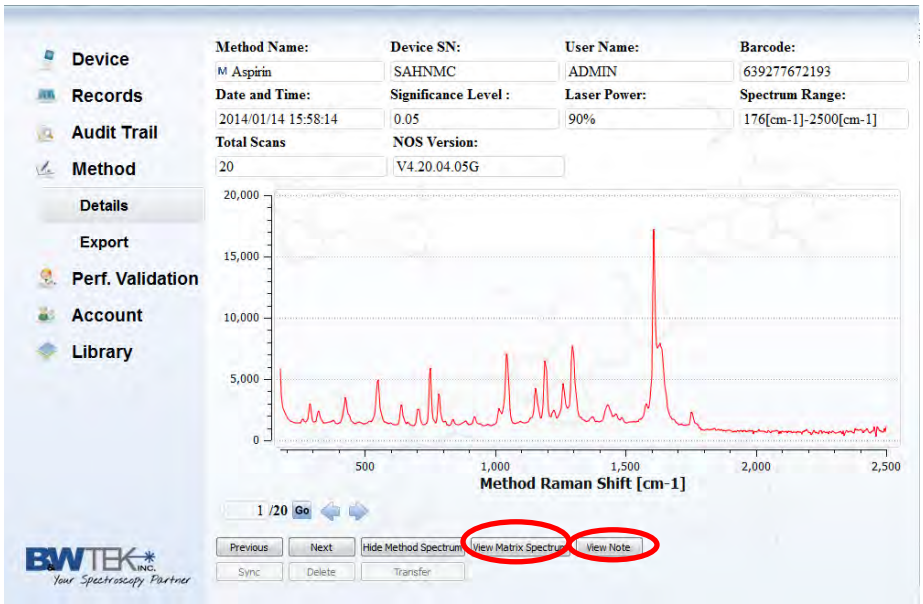






Note: Method validation is needed before use of the method.

After "**M** method" is created, synchronize NanoRam#2 to NID. The transferred method details can be viewed by clicking on **View Matrix Spectrum**. The transfer matrix spectra will be displayed in the window next to the orginal method spectra. Toggle through the arrow keys on the bottom of the screen to view each of the spectra included in the method. By clicking on **View Note**, the notes associated with the method will be displayed.



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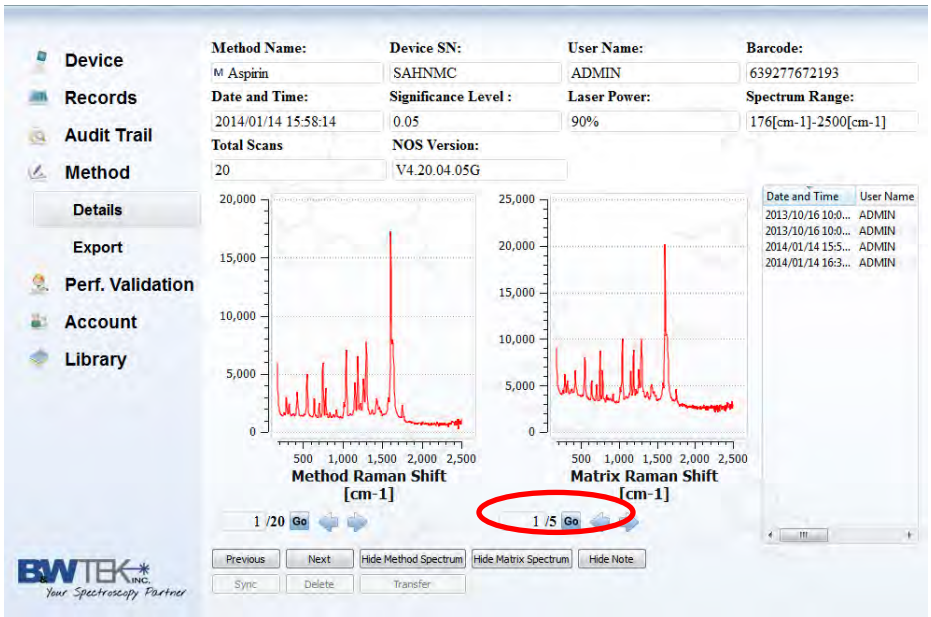

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Appendix-1 NanoRam Test Report

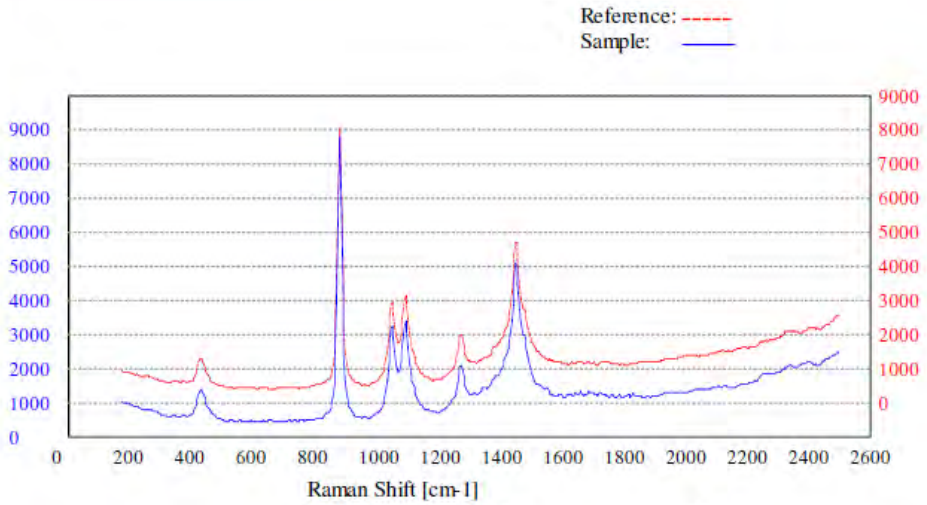
Identification Report

NanoRAM

Scan Index: 68 NID Client V5.12

Device SN:	SAOQNE	Barcode: N/A Supplier: N/A Expiration Time: N/A Note: N/A	Last Perf. Validation User Name: ADMIN Date and Time: 2015/02/07 06:42:33 Result: Pass HQI: 99.8589 Relative Intensity: 0.8788 Calibration file: Polystyrene(2015/01/06 09:33:23)
Run Name:	1		
Product Name:	ethanol#3		
Test Time:	2015/03/04 14:55:32		
User Name:	ADMIN		
Laser Power:	90%		
Integration Time:	2930		
Method:	ethanol(2015/03/04 14:54:23)		
Significance Level:	0.05		
Raman Shift Range:	176 [cm-1] - 2500 [cm-1]		
NOS Version	V5.12.07.06NM		

Result:	Pass
P-value:	0.9821
ADFSFSF	



Approved by:_____ Date:_____

Printed: 2015-03-18 14:53:05 Page 1

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Appendix-2 NanoRam Run Summary Report

Run Summary Report

NID Client V5.12

Device SN:	SAIRMH
Run Name:	ace2
NOS Version	V5.11.07.06G_b1
Last Perf. Validation Time	2014/09/19 17:27:28
Perf. Validation User Name	ADMIN
Perf. Validation Result	Pass
Calibration File	Polystyrene(2014/09/12 11:11:06)
Product Name:	ace
Method Name:	ace(2015/02/20 16:18:02)
# Of Samples In Run	3
# Of Samples Pass (First)	3
# Of Samples Fail (First)	0
Database Location:	bwtek-ts13-02-C:/BWTEK/NID/DataBase/NanoramId.dat

Product Name	Scan Index	User Name	Date and Time	Result	P-value
ace#3	137	ADMIN	2015/02/24 09:39:49	Pass	0.9951
ace#2	136	ADMIN	2015/02/24 09:39:36	Pass	0.9987
ace#1	135	ADMIN	2015/02/24 09:35:44	Pass	0.9906

Approved by:_____ Date:_____

Printed: 2015-02-27 15:33:45 1

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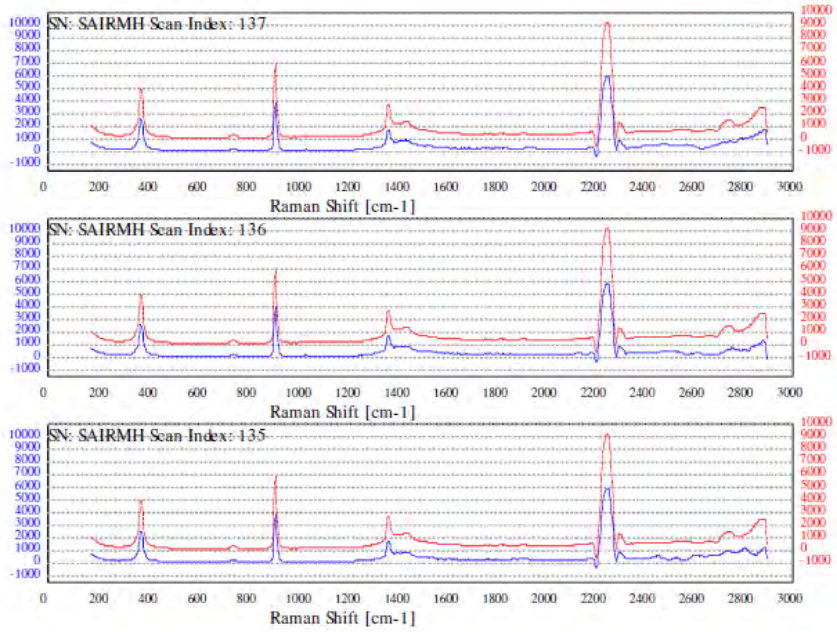
Record Summary Report

NanoRAM

----Appendix Spectrum

NID Client V5.12



Approved by:_____ Date:_____

Printed: 2015-02-27 15:33:45 1

Reference: ----------

Sample: ————

Appendix-3 NanoRam LIMS Report

Report type	Identification Report		
Scan Index	952		
NID Version	NID Client V5.0		
Device SN	SAFXMA		
Run Name	ETHANOL RUN		
Product Name	ethanol in vial#1		
Test Time	2/21/2014 17:47		
User Name	ADMIN		
Laser Power	100%		
Minimum HQI	N/A		
Significance Level	0.05		
Hit Number	N/A		
Found in Library	N/A		
Method	ethanol in vial(2013/07/31 11:17:06)		
Result	Pass		
P-value	0.9994		
HQI	N/A		
Matched Sample Name	N/A		
Raman Shift Range	176 [cm-1] - 2500 [cm-1]		
NOS Version	V4.30.04.06G		
LOT NO.	N/A		
SUPPLIER	N/A		
EXP DATE	N/A		
Note	N/A		
Last Perf. Validation Date and Time	1/8/2014 10:56		
Perf. Validation User Name	ADMIN		
Perf. Validation Result	Pass		
Perf. Validation HQI	99.8353		
Relative Intensity	1.2988		
Calibration file	Polystyrene(2013/04/29 09:54:45)		
Sample Data	582		
RamanShift	Intensity		
176	527.899		
180	489.072		
184	464.159		
188	446.953		

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Appendix-4 NanoRam LIMS Run Summary Report

Report type	Run Summary Report				
NID Version	NID Client V5.0				
Device SN	SAFXMA				
Run Name	RUN TEST				
NOS Version	V4.22.04.10_a22_G				
Last Perf. Validation Date and Ti	1/8/2014 10:56				
Calibration File	Polystyrene(2013/04/29 09:54:45)				
Product Name	ethanol in vial				
Method Name	ethanol in vial				
# Of Samples In Run	5				
# Of Samples Pass (First)	5				
# Of Samples Fail (First)	0				
# Of Samples Pass On Repeat	0				
# Of Samples Fail On Repeat	0				
LOT NO.	123				
SUPPLIER	SIGMA				
EXP DATE	2/18/2015				
Database Location	dawny-latitude-C:/BWTEK/NID/DataBase/NanoramId.dat				
Product Name	Scan Index	User Nam	Date and Time	Result	P-value
ethanol in vial#5	951	ADMIN	2/18/2014 17:35	Pass	0.5813
ethanol in vial#4	950	ADMIN	2/18/2014 17:34	Pass	0.5127
ethanol in vial#3	949	ADMIN	2/18/2014 17:34	Pass	0.5991
ethanol in vial#2	948	ADMIN	2/18/2014 17:33	Pass	0.5908
ethanol in vial#1	947	ADMIN	2/18/2014 17:33	Pass	0.4416

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Appendix-5 NanoRam Specifications

Spectral Range	176cm^{-1} to 2900cm^{-1}
Spectral Resolution	~9cm^{-1} at 912nm
Excitation Wavelength	785nm
Laser Output Power	Adjustable from 0mW to 300mW in 10% increments
Display	High brightness OLED touch screen
Bar Code Reader	Linear and 2D Standards
Software	NanoRam OS® (Embedded) NanoRam ID® (PC)
Computer Interface	Ethernet, Wi-Fi
Battery	Rechargeable Li-ion battery, >5 hours operation
External Power Supply	INPUT: AC 100-240v, 1.5A, 50-60HZ. OUTPUT: DC 12V, 2A minimum
Weight	~ 2.5 lbs (~1.2 kg)
Size	8.8in x 3.9in x 2.0in (22cm x 10cm x 5cm)
Operating Temperature	-20ºC to 40ºC
Storage Temperature	-30ºC to 60ºC

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Appendix-6 Doc#400000050: Safe Installation and User of the NanoRam Right Angle Adaptor

Description: NanoRam Right Angle Adaptor

Model Number: NR2-RAA

Part Number: 840000342

Safety Precautions:

The NanoRam Right Angle Adaptor (NR2-RAA) is an accessory designed to be used with the NanoRam Handheld Raman Spectrometer.

The installation and operation of this adapter requires proper training of the users to follow all safety precautions. Failure in strictly following these procedures may result in hazardous situations which will be the sole responsibility of the user.

The installation of the right angle adapter requires that the lensed shaft be removed from the NanoRam device and replaced with a matching lens-less shaft. The lens-less shaft cannot be used alone and cannot be misused with accessories other than what is described in this document. The NanoRam unit must be powered down when the lensed shaft is removed. The

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NanoRam must never be powered on without the lensed shaft or a fully installed accessory that uses a lens-less shaft. This constitutes improper use of the unit. The NOHD from the lens-less aperture and NanoRam without any aperture is 12 meters.

Installation Instructions:

1. Users are recommended to wear the Laser Safety goggles supplied with the NanoRam while installing the right angle adaptor. The safety precautions as given in the NanoRam User Manual should always be followed when operating the NanoRam.

2. Completely power down the NanoRam unit before installation of the right angle adaptor. Because the standard lensed shaft must be removed from the NanoRam and replaced by a lensless shaft compatible with the right angle adaptor, the NanoRam must be turned off to avoid the possibility of the laser being turned on before the installation is completed.

3. Remove any adaptor on the NanoRam by pulling it off.

4. Remove the standard lensed shaft by unthreading it from the NanoRam measurement port.

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5. Install the specified lens-less shaft by threading into the measurement port.

6. Insert the right angle adaptor onto the lens-less shaft. Situate the adaptor by sliding in all the way with the locating notch aligned with the location pin on the NanoRam measurement port. Carefully rotate as needed to align the adaptor for proper positioning. When properly situated no black O-ring from the adaptor should be seen.

Use of the NanoRam® Right Angle Adaptor:

During measurement operations place the NanoRam so that its right angle adapter port is contact with the sample surface.

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Appendix-7 Doc#400000051: Safe Installation and Use of the NanoRam Immersion Probe

Description: NanoRam Immersion Probe - 12 inch length; Immersion Probe Disposable Protective Sleeve

Model Number: NR2-IMP; NR2-IMPS

Part Number: 840000347; 840000398

Safety Precautions:

The NanoRam Immersion Probe (NR2-IMP) is an accessory designed to be used with the NanoRam Handheld Raman Spectrometer. Disposable protective sleeves can also be purchased for use with the Immersion Probe (NR2-IMPS)

The installation and operation of this Immersion probe accessory requires proper training of the users to follow all safety precautions. Failure to strictly follow these procedures may result in hazardous situations which will be the sole responsibility of the user.

The Immersion Probe accessory requires that the lensed shaft be removed from the NanoRam unit and replaced with the immersion probe. The NanoRam must be powered down when the lensed shaft is removed. The NanoRam must never be powered on without the lensed shaft or a fully installed accessory that uses a lens-less shaft. This constitutes improper use of the unit.

Note: The Nominal Ocular Hazard Distance (NOHD) from the lens-less aperture on a NanoRam without any aperture is 12 meters. When the lensed shaft or Immersion probe is installed, the NOHD is 30 cm or less.

The Immersion Probe is manufactured from 316 SS, and can be can be cleaned between use. It has Kalrez® O-rings and a quartz window. An optional disposable probe sleeve is available for use in conjunction with the Immersion Probe. The probe sleeve is made from Polyethylene Terephthalate Copolymer (PETG), and is designed for single use. Users may refer to the Chemical Compatibility Chart in Appendix A for guidance on the chemical resistance of the probe assembly with/without sleeve. Users should consult the compatibility of their materials with the

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probe and sleeve before use, and should limit exposure of the probe for any extended periods of time, especially at elevated temperatures. The chart is provided as a guide and for situations where chemical resistance may be of concern, it is recommended that users conduct testing with the specific materials under actual use conditions.

It is strongly suggested that the probe sleeve only be used once. Due to the differences in chemical compatibility, it is also recommended that the user conduct chemical resistance testing of the sleeve depending on application.

Installation Instructions:

1. Users are recommended to wear the Laser Safety goggles supplied with the NanoRam while installing the Immersion Probe. The safety precautions as given in the NanoRam User Manual should always be followed when operating the system.

2. Completely power down the NanoRam unit before installation of the immersion probe. The NanoRam must be turned off to avoid the possibility of the laser being turned on when the lensed shaft is removed as the standard lensed shaft must be removed from the NanoRam in order to install the Immersion Probe

3. Remove any adaptor on the NanoRam by pulling it off.

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4. Remove the standard lensed shaft by unthreading it (turn counter-clockwise) from the NanoRam measurement port.

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5. Install the immersion probe by threading the matching end all the way into the measurement port. Screw in the immersion probe clockwise until it is snugly in place. Hand tighten only!

6. Slide protective cap down all the way into the measurement port with the locating notch aligned with the location pin on the NanoRam port.

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The Following Steps are for the Use of the optional Immersion Probe Sleeves

7. Insert the NanoRam Immersion Probe into the sleeve

8. Push the NanoRam Immersion Probe to the end of the sleeve. At the very end, the sleeve should cover the rubber O-ring on the instrument end of the immersion probe. The probe tip should sit flush against the probe sleeve's flat sealed end.

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9. Insert immersion probe into the sample for identification measurement.

10. After each use, remove and discard the sleeve. Pinch the sleeve near the O-ring and slide the sleeve off of the probe. Exercise caution to not allow the chemicals to touch the skin. Dispose of the used sleeve following site safety guidelines.

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Use of the NanoRam® Immersion Probe:

The immersion probe is designed for contact measurements with solids and liquids. It is the responsibility of the user to ensure material compatibility of their samples with the immersion probe.

- The immersion probe should be cleaned of any sample before introducing it to a new sample. The probe can be cleaned by wiping with a soft cloth with isopropyl alcohol. An immersion probe sleeve can be used to minimize the need for probe cleaning between measurements.

- The immersion probe sleeve is designed to be used in conjunction with the Immersion probe for the NanoRam. This is a disposable one time use only protective sleeve that minimizes the need for probe cleaning between measurements. The sleeve itself is made from Polyethylene Terephthalate Copolymer (PETG), and should only be used with chemicals within a limited time frame.

Appendix A: Chemical Compatibility Chart

Compatibility Guide			
A = Suitable for use			
X = Not Recommended			
U = Unknown or Not Applicable			
F= Some effect			
	Immersion Probe without Sleeve	***Immersion Probe with Sleeve***	
		20°C	50°C
Acetic Acid	A	X	X
Acetone	A	X	X
Alcohols: Isobutyl	A	U	U
Alcohols: Isopropyl	A	U	U
Alcohols: Methyl	A	A	F
Ammonia, Anhydrous	A	U	U

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Ammonia, Liquid	A	U	U
Ammonium Hydroxide	A	X	X
Amines	F	U	U
Benzene, pure	F	X	X
Benzol, pure	U	X	X
Benzyl Alcohol, pure	U	X	X
Boric Acid	A	X	X
Butyl Acetate	A	U	U
Calcium Chloride	A	U	U
Calcium Hypochlorite	A	U	U
Carbon Tetrachloride (wet)	A	X	X
Carbonic Acid	A	U	U
Caustic Potash, 50%, concentrated	U	X	X
Caustic Soda, 1%	U	A	U
Caustic Soda, 50%, concentrated	U	X	X
Cedarwood Oil, pure	U	X	X
Chlorine Water	X	U	U
Chlorine, Anhydrous Liquid	X	U	U
Chromic Acid, 10%, 20%	U	A	U
Citric Acid, 10%	F	A	U
Citric Acid, 1M	F	A	F
Copper Sulfate, pure	U	A	U
Cyclohexane, pure	U	A	X
Cyclohexanone, pure	F	X	X
Detergents	A	U	U
Diacetone, pure	U	X	X
Diesel Fuel	A	U	U
Diethyl ether, pure	A	A	U
Dimethyl Formamide, pure	A	X	X
Dimethylsulfoxide (DMSO), pure	U	X	X
Ether, pure	U	A	U
Ethyl Acetate, pure	U	X	X
Ethyl Alcohol, (ethanol) pure, 40%, 96%	A	F	X
Ethyl Benzene, pure	A	A	U
Ethylene Chloride, pure	U	X	X

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Ethylene Glycol, pure	A	A	U
Ethylene Glycol	A	F	X
Ethylene Dichloride	A	U	U
Ethylene/ Propylene Oxide	X	A	F
Ethylene Oxide, gas, pure	U	A	F
Fatty Acids saturated/unsaturated, pure	U	A	F
Ferric Chloride	X	U	U
Fuel Oils (#1 and #2)	A	U	U
Gasoline, Unleaded	A	A	U
Glutaraldehyde, pure	U	A	U
Heptane	A	U	U
Hexane, pure	U	A	U
Hydraulic Oil (Petro)	A	U	U
Hydraulic Oil (Synthetic)	A	U	U
Hydrochloric Acid 5%	U	A	U
Hydrochloric Acid 20%	X	A	U
Hydrochloric Acid 37%	X	A	U
Hydrochloric Acid 100%	X	U	U
Hydrofluoric Acid 4%	X	F	X
Hydrofluoric Acid 48%	X	X	X
Hydrofluoric Acid 20%	X	U	U
Hydrofluoric Acid 100%	X	U	U
Hydrogen Peroxide 10%	A	A	U
Hydrogen Peroxide 30%	A	A	U
Hydrogen Peroxide 100%	A	U	U
Isopropyl Acetate	A	U	U
Kerosene	A	A	U
Ketones	A	U	U
Lacquer Thinners	A	X	X
Lacquers	A	U	U
Lactic Acid, 3%	U	F	X
Lactic Acid, 85%	U	X	X
Lye: NaOH Sodium Hydroxide	X	U	U
Magnesium Hydroxide	A	U	U
Mercuric Chloride, pure	X	X	X

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Methanol (Methyl Alcohol)	A	A	U
Methoxyethyl Oleate, pure	U	A	U
Methyl Acetate, pure	A	X	X
Methyl Ethyl Ketone (MEK)	A	A	U
Methyl Isobutyl ketone, pure (MIBK)	F	X	X
Methyl Propyl Ketone, pure	U	X	X
Methylene Chloride, pure	F	X	X
Methyl-t-Butyl Ether, pure	U	X	X
Mineral Oil	A	A	X
Mineral Spirits	U	A	U
Motor Oil	A	U	U
Nitrating Acid (>15% H2SO4)	X	U	U
Nitric Acid (5-10%)	A	A	U
Nitric Acid (50%)	A	A	U
Nitric Acid (Concentrated)	A	X	X
Nitrobenzene, pure	A	X	X
Nitromethane, pure	A	X	X
o-Dichlorobenzene, pure	U	X	X
Oils: Fuel, Mineral and Hydraulic	A	U	U
Oxidizers, Strong	F	U	U
p-Dichlorobenzene, pure	U	X	X
Phenol, 50%, 100%, Crystal, Liquid	U	X	X
Phosphoric Acid	X	U	U
Potassium Chloride	A	U	U
Potassium Hydroxide (Caustic Potash)	X	X	X
Potassium Hypochlorite	A	U	U
Propane (Liquefied)	A	U	U
Propylene Glycol	A	U	U
Silicone Oil, pure	A	X	X
Soap Solutions	A	U	U
Sodium Bicarbonate	A	U	U
Sodium Carbonate, pure	A	A	U
Sodium Chloride	A	U	U
Sodium Hydroxide (20%)	A	U	U
Sodium Hydroxide (50%)	A	X	X

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Sodium Hydroxide (80%)	A	X	X
Sodium Hypochlorite (<20%)	X	A	U
Sodium Hypochlorite (100%)	X	U	U
Sulfuric Acid (<10%)	A	A	U
Sulfuric Acid (75-100%)	X	X	X
Toluene (Toluol)	A	X	X
Tris Buffer Solution, PH 11	U	F	X
Tris Buffer Solution, PH 7.0	U	A	A
Trichloroethylene	A	U	U
Turpentine	A	A	U
Vinegar	A	U	U
Water	A	U	U
Water, Steam/Hot	F	U	U
Xylene	A	U	U

For more detailed information please refer to manufacturer's chemical compatibility charts for PETG copolymer, Dupont's Kalrez® and 316 SS.

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Appendix-8 Doc#400000052: Safe Installation and Use of the NanoRam Tablet Holder

Description: NanoRam Tablet Holder Adaptor

Model Number: NR2-TAH

Part Number: 840000346

Safety Precautions:

The NanoRam Tablet Holder (NR-TAH) is an adaptor designed to be used with the NanoRam Handheld Raman Spectrometer for analysis of tablets and other solid dosage form samples.

The installation and operation of this adapter requires proper training of the users to follow all safety precautions. Failure in strictly following these procedures may result in hazardous situations which will be the sole responsibility of the user.

The installation of the tablet holder adapter requires that the lensed shaft be removed from the device and replaced with a matching lensless shaft. The lensless shaft cannot be used alone and cannot be misused with accessories other than what is described in this document. The NanoRam unit must be powered down when the lensed shaft is removed. The NanoRam must never be powered on without the lensed shaft or a fully installed accessory that uses a lensless shaft. This constitutes improper use of the unit. The NOHD from the lensless aperture and NanoRam without any aperture is 12 meters.

Installation Instructions:

1. Users are recommended to wear the Laser Safety goggles supplied with the NanoRam while installing the Tablet Holder adaptor. The safety precautions as given in the NanoRam User Manual should always be followed when operating the NanoRam.

2. Completely power down the NanoRam unit before installation of the tablet holder adaptor. Because the standard lensed shaft must be removed from the NanoRam and replaced by a

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lensless shaft compatible with the tablet holder, the NanoRam must be turned off to avoid the possibility of the laser being turned on before the installation is completed.

3. Remove any adaptor on the NanoRam by pulling it off.

4. Remove the standard lensed shaft by unthreading it from the NanoRam measurement port.

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5. Install the specified lensless shaft by threading into the measurement port.

6. Insert the tablet holder onto the lensless shaft. Situate the holder by sliding in all the way with the locating notch aligned with the location pin on the NanoRam measurement port. Carefully rotate as needed to align the adaptor for proper positioning. When properly situated no black O-ring from the adaptor should be seen.

Use of the NanoRam® Tablet Holder

The tablet holder is designed with a flip top cover which can only be partially open while loading a tablet sample. Do not force the cover for greater opening since it may compromise the laser safety protection nature of the design. Position a tablet sample at the center of the sampling insert. Restore the cover into its closed position after loading a tablet sample before starting the measurement operations.

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APPENDIX F: USERS MANUAL - EOS® HANDHELD LIBS ANALYZER

EOS

- Handheld LIBS Analyzer for Alloy Determination

Handheld Laser Induced Breakdown Spectroscopy (HH-LIBS)

HH-LIBS technology allows for incredibly FAST analysis of alloy grade ID and chemistry; especially for light element alloys containing Li, Mg, Al or Si. Compared to handheld XRF, light element analysis with the EOS is approximately 10x faster. Over the course of a day, this can easily save you time and money. Optional calibrations are available for Iron, Nickel, Copper and Cobalt alloys.

Being fast is only part of the equation. The EOS will give you accurate and repeatable results that you can count on. In addition, user-friendly data transfer will allow you to easily create custom reports.

Benefits:

- HH-LIBS Technology
- No X-ray Regulations
- Preferred for Li, Mg, Al, Si
- Fast Grade ID & Chemistry
- Accurate & Repeatable
- Flexible Battery Design
  - 1 battery operation for reduced weight
  - 2 battery operation for 12hr run-time
  - "Hot-swap" capability

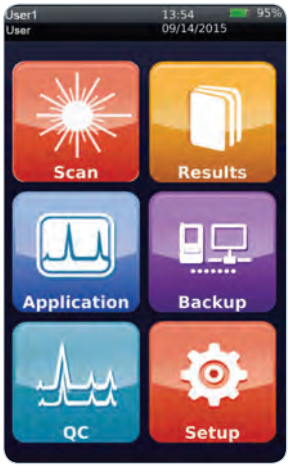
LIBS Scrap Metal Sorting

Applications Include:

- Metal sorting and valuation
- Fingerprint ID
- Positive Material Identification (PMI)
- Light element capability
- Li, Be, Mg, Al, Si

Calibrations:

- Calibrations based on traceable standards
- Accurate measurement for Al, Ti and Mg alloys
- Optional Fe, Ni, Cu and Co alloy calibration
- Automatic selection of calibrations
- Modes: Assay, Grade ID, Fingerprint ID
- Easily identify and separate Al Grades such as 356, 357, 6061, 6063 and 1000



EOS Software Features:

- Intuitive icon-based software
- Multi-Level Users login account for fleet management & user identification
- On-board instrument performance check
- On-board averaging with burst mode
- Type standardization
- Assay & grade ID mode based on advanced chemometrics algorithm
- Fingerprint spectral ID mode

Extensive Grade Library:

Bruker's EOS includes extensive grade libraries (400+ grade definitions) covering various international standards. User selectable libraries: UNS, DIN and others. The Bruker Toolbox software allows user to:

- Modify existing Alloy Grade Definition
- Add new Alloy Grades
- Upload, download and share grade libraries among instruments

Easy to use:

The EOS is an advanced portable HH-LIBS analyzer, with laboratory-grade hardware. The user interface has been designed to provide exceedingly intuitive operation and results presentation. Data management and transfer are very easy to use.

- Intuitive user interface - just point and shoot
- Requires very little operator training
- Multiple fields for sample identification
  Report generation tools
- Lightweight – only 2.4kg, including battery

EOS Hardware Features:

Air-Flow Optics Shield™:

HH-LIBS technique, like most other optical techniques, requires a small distance between the instrument nose and the sample surface in order to achieve an accurate analysis. The dust generated during the laser ablation stage is a significant source of contamination for internal optics. Over time, the dust will settle on the optics and hence reduce the light transmission. Without routine cleaning, this could result in precision and accuracy issues. Bruker's EOS has a unique "Air-Flow Optics Shield" feature which creates a continuous air shield in front of the optics in order to prevent dust build-up and allow the EOS to operate in the most demanding environments.

Rastering Scan:

The laser beam is very small and thus only gives data for a very precise spot. The EOS' rastering feature allows the laser beam to scan a larger area of the sample and therefore gives a more representative assay of the sample.

Multi-Detector (Multi-Spectrometer) Design:

Bruker's Multi-Detector design allows the EOS to cover an extended wavelength range from 170 nm to 720 nm, while maintaining outstanding resolution for a complicated metal matrix such as titanium. This broad wavelength range allows the detection of elements such as Li, Be, Si, etc.; which a single-spectrometer system could not cover. In addition, the extensive wavelength range also allows the EOS to utilize alternative measurement wavelengths and hence achieve better accuracy by avoiding spectrum overlap.

Environmental conditions:

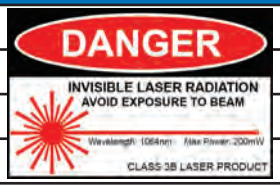
The EOS is designed to withstand field operation in nearly all environments, including humid and dusty conditions in a scrap yard.

Proprietary laser technology:

Bruker's HH-LIBS analyzer, EOS, uses a proprietary 1064 nm laser for low background laser ablation atomic emission spectroscopy. Traditional LIBS systems utilize a high energy, low frequency laser design for plasma generation. Such designs results in a high background "noise", especially in the lower end of spectrum. Bruker's 1064 nm laser generates strong atomic emission signals without creating high background emissions, hence eliminating the need for a complicated gating system. Utilizing such a design, Bruker's EOS can easily analyze the most challenging elements such as Si and Mg at <0.1% concentration levels within seconds.

LIBS Scrap Metal Sorting

Specifications	
Laser	Class 3B, 1064nm
Average Power	~ 100mW
Power Density	> 1GW/cm^2
Rep Rate	5KHz
Elemental Range / Precision / LOD	See calibration sheet for details
Calibrations	Al, Ti, Mg alloys; optional Fe, Ni, Cu, Co alloys
Dimensions	275mm x 315mm x95mm (Length x Height x Width), 2.4kg (1 battery)
Operating Environment	10-40° C
Display	High brightness OLED display with touch screen. 48 x 80mm
Battery Pack	(2x) 7.2V, 6.8Ah, Li-Ion battery pack, hot-swap capable, 12hrs operation, >4,000 shots per charge
Data Storage / Transfer	250 MB internal and 4 GB USB flash external
Analytical Modes	Assay and Grade ID, Fingerprint ID



HH-LIBS and HH-XRF:
Physics indicates that HH-LIBS and HH-XRF are naturally complementary and each technique is preferred to measure certain elements and certain types of alloys. HH-LIBS is well suited to rapidly measuring the low atomic number elements like the alkaline (Li, Na, etc.) and alkaline-earth metals (Be, Mg, etc.) but are not well suited to measuring high atomic number elements such as the refractory elements (Nb, Mo, W, etc.). HH-XRF on the other hand, is well suited to measuring high atomic number elements but not well suited at measuring low atomic number elements like Mg, Al, Si. This makes HH-LIBS the ideal technique for measuring light alloys such as Mg, Al and Ti alloys while HH-XRF is the ideal technique for measuring standard alloys like stainless steel, high temperature alloys and the like. Now is your chance; choose the right tool for the job!

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HH-XRF and HH-LIBS for alloy analysis
Choosing the Right Tool for the Right Job

By: John I.H. Patterson, Ph.D., Principal, Portable Analytical Technologies LLC

April 30, 2015

Handheld X-ray fluorescence spectrometry (HH-XRF) has been established as the gold standard method for in-situ elemental determination in metals and alloys in the last 10 years. More than 5,000 analyzers are sold yearly worldwide for scrap metals sorting and positive material identification (PMI). PMI is a quality assurance tool consisting of the identification of alloy grades in various industries using metals in order to verify compliance to specification and to avoid mixing up of the materials. Handheld laser induced breakdown spectrometry (HH-LIBS) is an emerging method which show promising capabilities for alloy analysis and may be able to complement HH-XRF in alloy analysis, especially in alloys containing low atomic number elements like Be, Li, Mg, Al and Si (e.g. light elements).

These methods are based on different principles:

HH-XRF is a method of EDXRF in which the radiation produced by a miniature X-ray tube strikes the sample surface and causes ionizations of the inner shell of the atoms constituting the sample. The resulting vacancies in the inner shell of the atom are filled by electrons from higher shells and thereby photons specific to the element are emitted and detected with a Si-detector. Since XRF involves transition within inner shells of atoms, the spectra obtained will contain a limited number of lines, typically 2 to 6 resolved lines per element in energy-dispersive XRF. For metal analysis, HH-XRF can work simultaneously for determining elements ranging from Ti to Pb within few seconds. When needed, a second beam condition is used to determine light elements resulting in longer measurements of typically 10 to 60 sec.

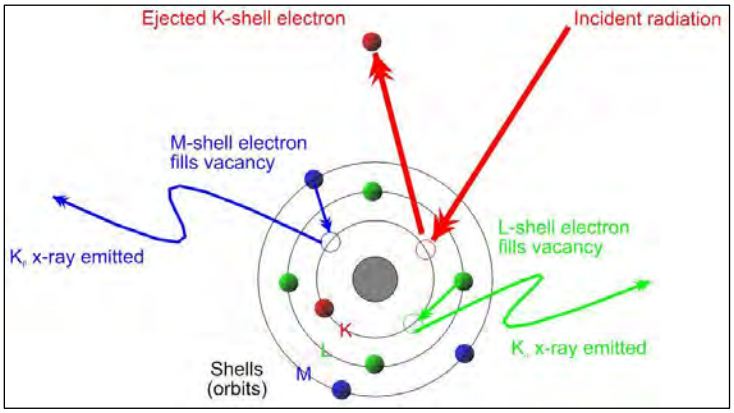

Figure 1: Characteristic X-ray production in handheld XRF

HH-LIBS is a method of optical emission spectrometry but unlike spark-OES, the emission is subsequent to the generation of a plasma induced by a laser. In HH-LIBS, a laser pulse strikes the surface of the sample and ablates an amount of material in the range of 1 ng and generates a plasma plume (partially ionized gas) in the temperature range of 5,000-20,000K. The energy of the laser is low, but is focused to a microscopic point on the sample to generate the plasma. In this plasma, the matter constituting the samples is dissociated into atoms (atomization) and partially ionized. Those atoms and ions will be excited (transition of electrons from lower to higher energy levels of valence shell) and by returning into their ground state (transition from higher to lower level of valence shell) they will emit characteristic lines for each element. The emitted light is transmitted through optical fibers and the polychromatic radiation is dispersed in one or more spectrometers by diffraction gratings and detected by CCD chips. The spectra of LIBS can contain hundreds or even thousands of lines for a single element. The sensitivity of those lines can differ by several orders of magnitude and result in extremely line rich spectra, especially when the sample contains high concentrations of transition metals as it is the case for alloys like stainless steel. In typical HH-LIBS systems, the dispersion power of the spectrometer is often limited by its size and some important analytical lines may not be fully resolved from lines emitted by the matrix. In order to cover the entire spectral range between 180 and 800 nm multiple spectrometers may be required. Moreover, wavelengths of less than 200 nm (like C 193.09 nm or S 180.73 m) are strongly absorbed by air and require an argon purge of the optical path to be detected. Almost any element generally contained in metals can be detected with HH-LIBS: the sensitivity for alkaline (Li, Na, etc.) and alkaline-earth metals (Be, Mg, etc.) is very high and the sensitivity for transition metals is good, except for refractory elements like Nb, Mo, W, or Ta which are difficult to determine [1,2]. The sensitivity for C, P and S is generally not sufficient to analyze those elements at relevant levels in alloys.

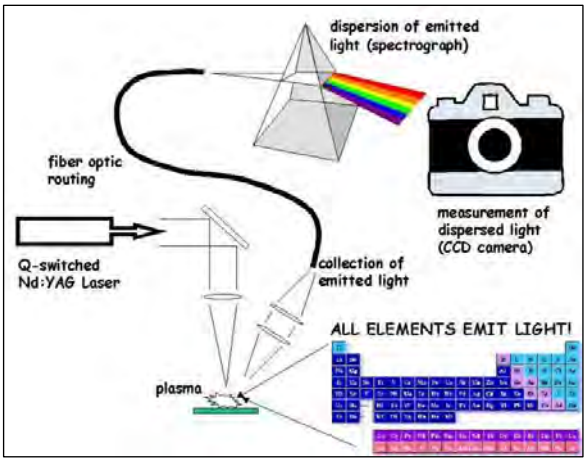

Figure 2: Schematic of LIBS (laser-induced breakdown spectroscopy) by US Army Research Laboratory - Courtesy of US Army Research Laboratory

Typical spot diameter of HH-XRF is 3 to 8mm, whereas the crater generated by the laser in HH-LIBS has a diameter of typically 50 to100 µm. Only a fraction of 15 to 20 µm in diameter of this crater will actually be analyzed. Hence HH-LIBS may be more sensitive to local heterogeneities. The laser pulse can be moved

during the analysis to correct for effects caused by heterogeneities. On the other hand, much smaller spots and very narrow weld seams can be analyzed using HH-LIBS.

The optical emission induced by the laser is a transient phenomenon, whereas the X-ray beam is constant and well controlled. Hence, it is expected that HH-XRF delivers more stable, repeatable and reproducible results than HH-LIBS. The quantitative analysis is considered as Achilles' heel of LIBS - first because of the complex laser-sample interaction process which depends upon both laser characteristics and material properties, and second, due to the plasma–particle interaction process which are time and space dependent [2].

When compared to HH-XRF, HH-LIBS offers new possibilities in terms of applications: Li can be detected in aluminum alloys used in aerospace, Be can be detected in Be-bronze and C can be detected in carbon steel and cast iron. Moreover, the sensitivity of Mg and Al is much higher in HH-LIBS than HH-XRF so that sorting of Aluminum and Titanium alloys is significantly faster (few seconds vs. 30-60s with HH-XRF). In contrast, HH-LIBS may not be able to detect low concentrations of S and P which can be quantified by HH-XRF in stainless steel (SS 303, SS 416) and in phosphorous bronzes. Generally, for scrap metal sorting, HH-LIBS is expected to be faster for aluminum alloys and more or less equivalent to HH-XRF for stainless steel. HH-LIBS may be able to sort most of the Ti-alloys faster than HH-XRF, with few exceptions like Ti Grade 11 containing around 0.15% Pd, which can be identified using HH-XRF. Sorting of stainless steel can be done within few seconds using both HH-XRF and HH-LIBS. For heavier alloys like super alloys, copper alloys (except aluminum and beryllium bronze), solders, lead alloys or precious metal alloys, HH-XRF delivers better sensitivity and accuracy for the analysis than HH-LIBS. In addition, the measurement of Tramp elements in scrap may be difficult for HH-LIBS, for example, the detection of Pb and Sn in stainless steel alloys at 100-500 ppm will be difficult using HH-LIBS.

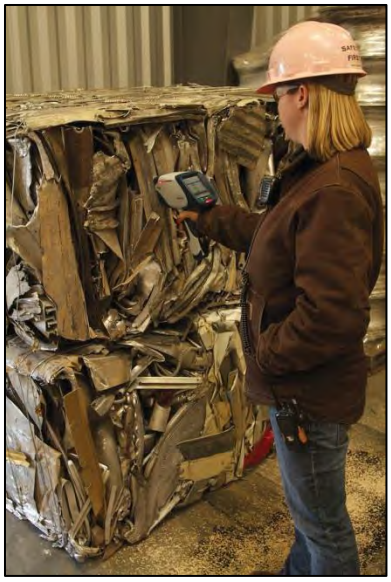

Figure 3: Metal sorting by means of handheld XRF

For fast sorting of aluminum alloys based upon light elements, HH-LIBS is clearly the best alternative as well as for separating many magnesium and titanium grades. When precision and accuracy matter more as in PMI analysis and quality control or when price figures are required in scrap trading (Ni, Mo, etc.), then HH-XRF is the still the method of choice. From a regulatory point, the use of HH-XRF requires, paperwork,

licensing and in some countries, long radiation safety training. In contrast, the utilization of lasers (class 1 or 3b) does not require any of these.

Thus, if your main application is measuring magnesium, aluminum or titanium alloys or red metals containing significant amounts of Be, Al or Si, the instrument of choice will be HH-LIBS. If your application is measuring stainless steel, high temp alloys or other heavy metal alloys, the instrument of choice will be HH-XRF. In both cases, the instrument of choice can be used to measure most alloy classes, however, there are compromises in speed, accuracy and precision which must be understood. Make sure that you evaluate the various choices on your unique set of samples and select the tool which meets your needs the best.

Pros & Cons of HH XRF and HH LIBS

HH XRF	HH LIBS
Pros • Speed of analysis for element Ti-U (2-5s) • Established technique • Robust and reliable method • Large analyzed surface (7 to 50 mm^2) • Excellent sensitivity and accuracy for metals with atomic number >22 • Good for analysis of Tramp elements • Completely non-destructive method	**Pros** • Speed of analysis (2 s) including light element • Lower LODs for light elements with low excitation potential / low ionization potential (alkaline and alkaline-earth elements) • No x-ray safety requirement • Ideal to analyze small areas like weldings • Potential to measure Li, Be, B, C
Cons • Needs compliance with local radiation safety regulation • Long measurement time when light elements required (10 s and more) • No detection of Li, Be, B, C, Na	**Cons** • Not a mature method • Not accepted by important organizations such as API • Not yet suitable for trace analysis – e.g. cannot analyze most Tramp elements • Can't quantify C at 200-300 ppm • High LODs for S, P. • Poorer accuracy due to transient nature of plasma • Small analyzed area sensitive to heterogeneities • Resolution of compact spectrometers/need of multiple spectrometers + optical fibers resulting in bulky and heavier instruments • Destructive method (small crater or pattern left on the analyzed item)

References:

[1] R.C. Wiens, S. Maurice, The Chem The ChemCam Instrument Suite on the Mars Science Laboratory Rover Curiosity: Remote Sensing by Laser-Induced Plasmas, Geochemical News 145 (June 2011).

[2] D.W. Hahn, N. Omnetto, Laser Induced breakdown spectrometry, Part 1: Diagnostics and plasma-particle interactions: still-challenging issues within the analytical plasma community, Applied Spectroscopy 12 (2010), 335A-360A.

Appendix A3-2: Preliminary Testing of Existing Field Screening Technologies – Phase 1 Results

French, K., E. Cowan and A. Neufeld, 2021. Preliminary Testing of Existing Field Screening Technologies: Phase 1 Results. Report SSP-5B prepared by Vertex Environmental Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 33 pp. plus Appendices.

Preliminary Testing of Existing Field Screening Technologies: Phase 1 Results

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EXECUTIVE SUMMARY

Vertex Environmental Inc. (Vertex) was retained by InnoTech Alberta to undertake literature reviews and preliminary testing on available technologies that may have the potential to be used for field screening of soil and/or groundwater samples for the presence of bromacil and tebuthiuron at sites in Alberta and elsewhere.

The first phases of work completed under this project have previously been presented in the report entitled *Field Screening Technologies for Bromacil and Tebuthiuron – Literature Review*, prepared by Vertex and the Bionanotechnology and Interfaces Laboratory of the University of Waterloo (UW), dated July 17, 2020.

InnoTech Alberta expressed specific interest in two biosensor technologies that have shown promise in the detection of bromacil to date: single-stranded DNA molecular recognition element (ssDNA MRE) and enzyme-linked immunosorbent assays (ELISA). Based on the results of the previously completed literature review, UW, working in partnership with Vertex, concluded that the ssDNA aptamer reported did not show promise in being able to be developed into a viable, field deployable, biosensor; however, the aptamer technology should still be promising provided that high quality aptamers can be obtained. On the other hand, the ELISA technology was believed to be promising based on the published antibody. The literature review reported antibody for bromacil was considered to be reliable, however, the ELISA assay using the antibody process requires multiple incubation and washing steps taking around 4 hours in a typical assay. Therefore, although it is quite sensitive, it was considered not applicable for on-site field applications for environmental samples. Alternate immunochromatographic assays with nanomaterials (i.e., Au nanoparticle based) have been developed as an inexpensive and portable monitoring tool for diagnostic purposes and small molecular detection. While it was recommended that consideration should be given to both aptamer and antibody screening technologies, neither technology was included in this Phase 1 Testing as field-ready devices have not yet been developed for detection of bromacil and/or tebuthiuron in soil or groundwater samples.

Based on the results of the previously completed literature review and interviews completed in relation to the potential application of existing field screening technologies for use in detecting bromacil and/or tebuthiuron in soil and groundwater at sites in Alberta, Vertex concluded that the following seven technologies showed promise and were included in this Phase 1 Testing program:

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
- Near infrared reflectance spectroscopy (NIRS)
- X-ray fluorescence (XRF)
- Raman spectroscopy
- Laser-induced breakdown spectroscopy (LIBS)
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)

Based on the results of the previously completed literature review and interviews completed in relation to the potential application of existing field screening technologies for use in detecting bromacil and/or

tebuthiuron in soil and groundwater at sites in Alberta, Vertex concluded that the following seven technologies showed promise and were included in this Phase 1 Testing program:

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- X-ray fluorescence (XRF)
- Raman spectroscopy
- Laser-induced breakdown spectroscopy (LIBS)
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)

Results of the Phase 1 Testing (proof-of-concept) of the above technologies are summarized below:

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
    - Overall, UVOST® was successful in detecting bromacil-based Alligare 80® at concentrations at and above approximately 1,000 mg/L in spiked water samples. Also, UVOST® was successful in detecting tebuthiuron-based Spike 80® at concentrations at and above approximately 100 mg/L in spiked water samples. UVOST® was not reliable at detecting any concentrations of bromacil-based Hyvar XL® in spiked water samples.
    - Based on the results of the Phase 1 testing, the UVOST® system is not recommended to advance to Phase 2 testing. The detection limits seen in the Phase 1 testing are much higher than target detection limits, and it is considered unlikely that Phase 2 testing could optimize and refine testing protocols for soil sterilant containing samples prior to analysis by the UVOST® system to the point that several orders of magnitude of reductions in detection limits can be achieved.

- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
    - Overall, the TarGOST® system was not successful at detecting any concentrations of soil sterilant in spiked soil samples. As such, at this time, the TarGOST® is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.

- Near infrared reflectance spectroscopy (NIRS)
    - Overall, the NIRS system was not successful at detecting unique responses of soil sterilant in spiked soil samples. As such, at this time, the NIRS is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.

- X-ray fluorescence (XRF)
    - Overall, Niton® XL5 XRF system was successful in detecting bromacil-based Alligare 80® and Hyvar XL® at concentrations at and above approximately 100 mg/kg in spiked soil

samples. The Niton® XL5 XRF system was also successful in detecting tebuthiuron-based Spike 80® at concentrations above approximately 1,000 mg/kg.

  - Detection limits seen in the Phase 1 testing are much higher than targeted field detection limits, and it is considered unlikely that Phase 2 testing could optimize and refine testing protocols for sterilant-containing samples prior to analysis by the XRF to the point that several orders of magnitude of reductions in detection limits can be achieved. As such, XRF is not recommended to advance to Phase 2 testing.

- Raman spectroscopy
  - Overall, MISA Raman system was successful in detecting unique spectra of bromacil-based Hyvar XL® at concentrations at approximately 100 mg/L in aqueous solutions, with no preliminary extraction, and down to approximately 10 mg/L with chloroform extraction. Bromacil-based Alligare 80® and tebuthiuron-based Spike 80® were also detected in aqueous solution successfully by MISA analysis, with unique spectra acquired for each.
  - Based on the results of the Phase 1 literature review and Phase 1 testing, the MISA Raman system is recommended to advance to Phase 2 testing. While detection limits seen in Phase 1 testing are still higher than target detection limits, Phase 2 testing will look to optimize and refine testing protocols for soil sterilant containing samples prior to analysis by the MISA system. This technology is potentially applicable for detecting bromacil and tebuthiuron in soil and water samples.

- Laser-induced breakdown spectroscopy (LIBS)
  - Overall, the Hitachi Vulcan LIBS Analyzer system was not successful at detecting any concentrations of soil sterilant in spiked soil samples. As such, at this time, the LIBS is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.

- Gas Chromatography/Thermionic Ionization Detector (GC/TID)
  - During the Literature Review portion of the project, Vertex understood that it was possible that a field-ready GC/TID device would be capable of analyzing Phase 1 test samples. After further discussions with SRI Instruments, the supplier of Gas Chromatographs capable of enabling a GC/TID system for soil sterilant analysis, it was determined that a field-ready GC/TID was not able to be developed at this time.

Raman spectroscopy showed enough promise to be recommended for subsequent Phase 2 testing (i.e., optimization and refinement).

The objective of the Phase 2 testing would be to attempt to validate, refine and optimize the technologies. Such testing could include, but may not necessarily be limited to the following tasks:

- The analysis of real-world samples of Alberta soil and groundwater contaminated with different concentrations of bromacil and tebuthiuron1, if possible. Ideally, two soil types (coarse-grained and fine-grained), two groundwater or surface water sources, and at least three different concentrations of bromacil and tebuthiuron for each soil and groundwater type would be tested.
- Attempts should be made to identify the source(s) of any identified interference effects that can result in limited application for certain sites.
- Additional dilutions or diluted spiked samples of soil and groundwater should also be tested to quantify the likely lowest reliable detection limits in soil and groundwater for the technologies.
- This stage of the testing should also attempt to improve detection limits using methanol extraction (and possibly concentration) prior to testing.
- Lastly, for technologies that are demonstrated to be successful, formal protocols for their application in field screening of soil and/or groundwater samples for bromacil and/or tebuthiuron, as appropriate, should be developed (i.e., commercial implementation the technology).

[1] Several real-world samples of Alberta soil and groundwater contaminated with different concentrations of bromacil and tebuthiuron have been provided to Vertex and the analysis of these samples by the promising technologies noted above is currently underway with results pending.

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1.0 INTRODUCTION

Vertex Environmental Inc. (Vertex) was retained by InnoTech Alberta (InnoTech) to undertake "proof of concept" testing of various technologies that may have the potential to be used for field screening of soil and/or groundwater samples for the presence of bromacil and tebuthiuron at sites in Alberta and elsewhere.

Details of the work completed under these Tasks and the results of the various literature review activities are provided in the following sections.

Based on the results of the Phase 1 literature review (French et al., 2021) and interviews completed in relation to the potential application of existing field screening technologies for use in detecting bromacil and/or tebuthiuron in soil and groundwater at sites in Alberta, Vertex concluded that the following seven technologies showed promise:

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
- Near infrared reflectance spectroscopy (NIRS)
- X-ray fluorescence (XRF)
- Raman spectroscopy
- Laser-induced breakdown spectroscopy (LIBS)
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)

The technologies at focus have been used in similar practices providing successful and reliable results. The seven listed technologies were all considered to have the potential to detect as least one physical and/or one chemical characteristic and can differentiate between responses from the compound of interest and the response from everything else in the sample. The Phase 1 testing results of the seven technologies listed above will be further discussed in this report.

2.0 PROJECT OBJECTIVES

2.1 Background and Objective

Soil sterilants were commonly used from the 1960s to late 1990s for non-selective vegetation control on industrial sites in Alberta. Soils treated with sterilants often become a source of contamination to adjacent lands and waterbodies. The Alberta Soil Sterilants Program was recently formed to establish proven, technical, and cost-effective strategies and best management practices sites impacted by residual soil sterilants, with the goal of achieving regulatory site closure in a timely and efficient manner.

Currently, therefore, there are no field-ready technologies that are available to achieve the goal of on-site detection, identification, quantification, and delineation, as there are for other contaminants such as petroleum hydrocarbons (PHCs) or salinity, for example. This results in high costs and long timelines for site investigation and/or remedial excavation since sample collection and laboratory analysis must be relied upon.

Accordingly, the objective of this Project was *to develop detection/field screening or proxy laboratory analytical methods to minimize the costs associated with identification, quantification and delineation of bromacil and/or tebuthiuron in soil and/or water at impacted sites.*

The Project was designed to be completed in two Phases with Phase 1 being "proof-of-concept" and Phase 2 being "optimization and validation" of the technology or technologies. More specifically, the workplan being completed under this overall Project was designed to address Phase 1 and will endeavor to identify a technology or technologies that:

- Can accurately and consistently detect bromacil and/or tebuthiuron in soil and/or groundwater.
- Is practical and safe to use in the field.
- Costs a fraction of the cost of current laboratory analytical methods.
- Can be completed on-site in under four hours.

Based on the results of the Phase 1 literature review (French et al., 2021) and preliminary testing of existing technology (the subject of this report), promising technologies will be recommended for advancement to Phase 2 of the Project. More specifically, Phase 2 of the Project will encapsulate a more refined and advanced test protocol for the technologies that are recommended to proceed from Phase 1. The more refined test protocols could include more advanced preliminary sample alterations including advanced extraction methodology. Note that Phase 2 testing of these technologies is not included in the scope of work for this Project.

3.0 PROJECT METHODOLOGY

3.1 Phase 1 Testing – Technology Suppliers

Based on the results of the Phase 1 literature review (French et al., 2021), seven (7) existing field screening technologies showed promise for use in detecting Bromacil and/or Tebuthiuron in soil and groundwater at impacted sites. Local suppliers for the various instruments were approached to supply and train Vertex personnel (if necessary) on their use. Arrangements were made for access to the instruments on a rental basis or outsourced to the supplier's own in-house laboratory for the testing to be completed. Below is a list of the technologies that were tested and the specific suppliers of the field-ready instruments:

- Ultraviolet laser induced fluorescence (UVOST®)
  - Vertex supplied UVOST® unit
  - Samples analyzed in Vertex's in-house laboratory
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
  - Dakota Technologies Inc. (Dakota) TarGOST® unit, 2201-A 12th St N, Fargo, North Dakota, United States, 58102
  - Samples sent to Dakota's in-house laboratory for analysis
- Near infrared reflectance spectroscopy (NIRS)
  - Maapera Analytics Inc., PO Box 22682, Southbrook, Edmonton, AB, Canada, T6W0C3
  - Samples sent to Maapera's in-house laboratory for analysis

- X-ray fluorescence (XRF)
  - Elemental Controls Limited (ECL), 3230 Wharton Way, Mississauga, ON L4X 2C1
  - Samples sent to ECL's in-house laboratory for analysis
- Raman spectroscopy
  - Metrohm Canada, 4160 Sladeview Crescent, Mississauga, ON L5L 0A1
  - Samples sent to Metrohm's in-house laboratory for analysis
- Laser-induced breakdown spectroscopy (LIBS)
  - Non-Destructive Testing Products Ltd. (NDT), 113 Cushman Rd unit 21-23, St. Catharines, ON L2M 6S9
  - NDT supplied Vertex with rental Hitachi Vulcan LIBS Analyzer to analyze samples in Vertex's in-house laboratory
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)
  - No field-ready technology was available for testing

Each supplier of the field-ready technologies either made arrangements for access to the specific instrument for use by Vertex (i.e., rental) or were able to complete in-house testing of sterilant samples with their own instruments. In the case of UVOST® and LIBS, Vertex was able to complete testing with Vertex-owned equipment (UVOST®) or rental (LIBS). For the remaining field-ready instruments, Vertex prepared samples containing various sterilant concentrations and sent them to specific technology suppliers for in-house testing (TarGOST®, NIRS, XRF, and Raman). Each technology and field-ready instrument has limitations (i.e., sample type) and requires specific sample preparation (e.g., soil drying). The specific limitations and sample preparation protocols for each technology are discussed in Section 4.0 of this report. Section 3.2, below, discusses the sample preparation completed by Vertex prior to test execution completed by suppliers and/or Vertex.

3.2 Phase 1 Testing – Experimental Design

The Phase 1 testing included the following steps for each technology:

- Samples of commercially available bromacil and tebuthiuron-containing products were obtained by Vertex or supplied by or on behalf of InnoTech to Vertex. The following commercially available products were obtained and used for Phase 1 testing:
  - Alligare 80® - Bromacil
  - Hyvar XL® - Bromacil
  - Spike 80® - Tebuthiuron
    - Safety Data Sheets (SDS) for each commercially available herbicide listed above attached in Appendix A
- A sample of clean, washed, fine-grained silica sand was obtained to replicate a neutral soil matrix
  - Safety Data Sheet (SDS) for the fine-grained sand listed above attached in Appendix A

- The following test product samples were prepared:
  - Spiked samples of silica sand containing the following concentrations of each sterilant[2]:
    - 10,000 mg/kg
    - 1,000 mg/kg
    - 100 mg/kg
    - 10 mg/kg
    - 1 mg/kg
    - 0 mg/kg (sand only)
  - Each of these spiked sand samples was saturated (i.e., approximate water content of 25%) using distilled water.
  - Spiked samples of distilled water containing the following concentrations of each sterilant (subject to the amount of the different sterilant products obtained):
    - 10,000 mg/L
    - 1,000 mg/L
    - 100 mg/L
    - 10 mg/L
    - 1 mg/L
    - 0 mg/L (distilled water only)
  - Laboratory analysis for bromacil and/or tebuthiuron were *not* completed on any of these samples.[3]
- Each instrument that incorporates non-destructive testing was used to scan/measure/detect the above spiked test samples. Separate samples or aliquots of the above were used for instruments that are destructive in nature. Replicate tests were run on each of the samples for each technology to determine repeatability.

Results of the technology testing and evaluation is documented in detail in sections below, with methodology, results and analysis/interpretation provided for each technology and test completed. Readings/measurements/outputs from each of the instruments was examined and evaluated in an attempt to identify whether:

- The sterilant of focus appears to have been detected in one or more of the samples.
- Whether the pattern of detection appears to be unique.

---

[2] Since this Phase 1 of the testing is designed to be proof-of-concept only it focuses on the ability of the technologies to detect bromacil and tebuthiuron and not necessarily at the levels required to meet soil or groundwater cleanup standards. It is understood that calibrating and/or improving the detection limits of the technologies would be part of the focus of Phase 2 of the work, not included in this Project.

[3] Only products known to contain bromacil or tebuthiuron will be used during this Phase of the work. Since Phase 1 is designed to be proof-of-concept only it is not considered necessary to validate or correlate the instrument responses to actual concentrations of bromacil or tebuthiuron in the samples. That task would be part of the focus of Phase 2 of the work, not included in this Project.

- Whether the response appears to vary in relation to sample concentration.
- It is possible that the results may need to be provided to the instrument manufacturers and suppliers, or some other third party to assist in this interpretation.

Preliminary conclusions were drawn regarding the potential ability for each technology to detect bromacil and/or tebuthiuron. Unacceptable, unreliable, or inconclusive technologies were eliminated from further consideration, with justification. This interim report will comment on each of these targets for each technology tested. Only those technologies that show promise will warrant carrying forward to Phase 2 of the project.

4.0 RESULTS AND DISCUSSION

4.1 Ultraviolet Laser Induced Fluorescence (UVOST®) and Visible Light Laser Induced Fluorescence (TarGOST® or OIP-G®)

There are a variety of different forms of Laser Induced Fluorescence (LIF) that are used in the field, and although there are some variations in their application the overarching theory behind this non-destructive technology is consistent. In general, LIF utilizes the unique emitted spectra of aromatic molecules to determine relative concentrations of contaminants within the system (United States Environmental Protection Agency, 2018). Depending on the type of LIF, a different wavelength range of light is used to excite the molecules within compounds such as non-aqueous phase liquids (NAPLs), which naturally have a fluorescence (Dakota Technologies, n.d.(b)). When a molecule interacts with a high energy light pulse, energy can be absorbed and released. Fluorescence occurs when the emitted wavelength is longer than the incident wavelength (Herman et al., 2015). LIF can also be used to determine the type of contaminant present, through not only the colour of fluorescence but also the time delay between pulse of the laser and the observance of fluorescence (Dakota Technologies, n.d.(b)).

4.1.1 Ultraviolet Laser Induced Fluorescence

4.1.1.1 Technology Background

Ultraviolet laser induced fluorescence (UV-LIF) uses ultraviolet light to excite the molecules of the compound or contaminant of interest to achieve the fluorescence required for analysis. UV-LIF technology, such as the UVOST® system owned by Vertex (Figure 1), is mainly oriented towards PHC NAPLs and typically requires a direct-push platform where readings are recorded as the probe descends through soils and groundwater in the subsurface (Dakota Technologies, n.d.(a)). The UVOST® system also allows for modeling to be performed with the collected data, as required (Dakota Technologies, n.d.(a)). This technology, if deployed into the subsurface via direct-push technology, precludes the need for collecting soil and/or groundwater samples and can record data at a density of approximately 2.5 cm intervals, with a production rate of approximately 90 to 150 metres per day (Dakota Technologies, n.d.(a)).

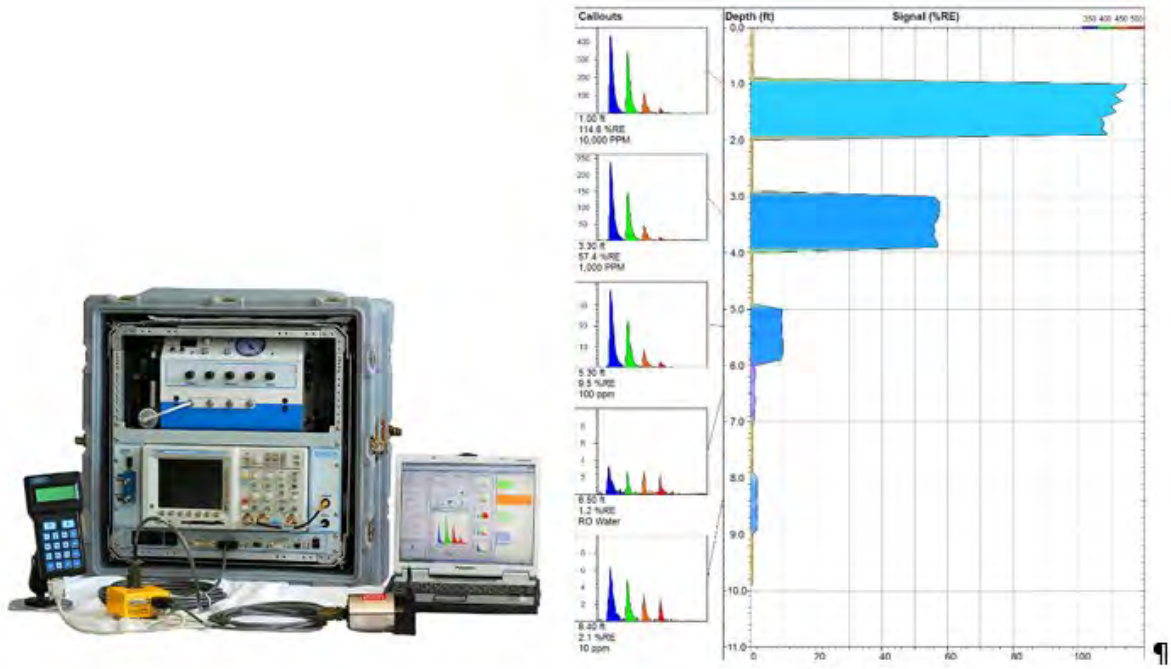


Figure 1. The UVOST® system (left) and example output (right).

4.1.1.2 Sample Preparation and Test Execution

The UVOST® system used by Vertex for Phase 1 testing can be used for semi-quantitative analysis of both soil and groundwater samples with no pre-analysis sample preparation (i.e., extraction and/or drying). While the UVOST® system typically is deployed via a direct-push drilling platform such as a Geoprobe®, the software enabled by UVOST® allows for "above-ground" analysis of samples via an "emulator" software setting that scans samples for analysis collection in a laboratory setting. Vertex used this "emulator" setting to scan the following 'spiked' sample sets:

- Spiked samples of distilled water containing the following concentrations of each sterilant (subject to the amount of the different sterilant products obtained):
    - 10,000 mg/L
    - 1,000 mg/L
    - 100 mg/L
    - 10 mg/L
    - 1 mg/L

No preliminary extractions or alterations were made to these samples prior to analysis via Vertex's UVOST(s) system. Each sample was scanned independently, and results were logged on a UVOST® software log output, with each sample tracked as a depth interval on the y-axis.

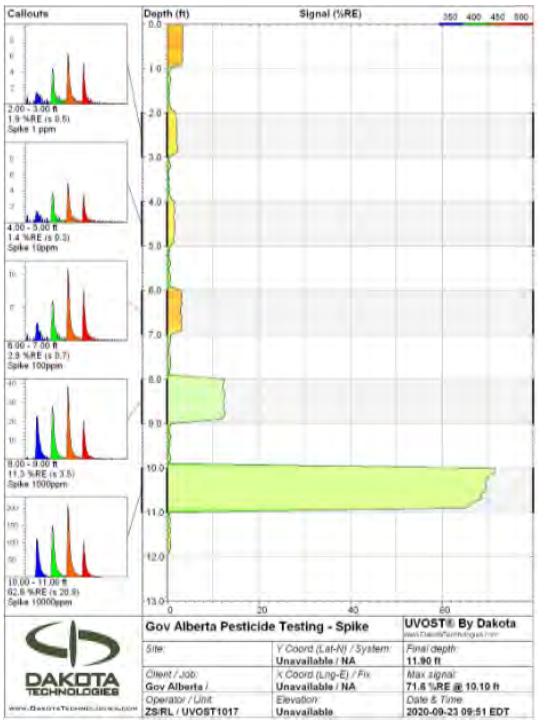
4.1.1.3 Results

Three (3) different water-based sterilant sample sets (with concentrations ranging from 1 mg/L to 10,000 mg/L) were tested using Vertex's UVOST® system:

- Alligare 80® - Bromacil
- Hyvar XL® - Bromacil
- Spike 80® - Tebuthiuron

Each sample set was scanned from lowest concentration (1 mg/L) to highest concentration (10,000 mg/L), preceded by a "blank" sample of distilled water only (0 mg/L).

The UVOST® software outputted results for the analysis of 'spiked' water-based samples are shown in Figure 2.



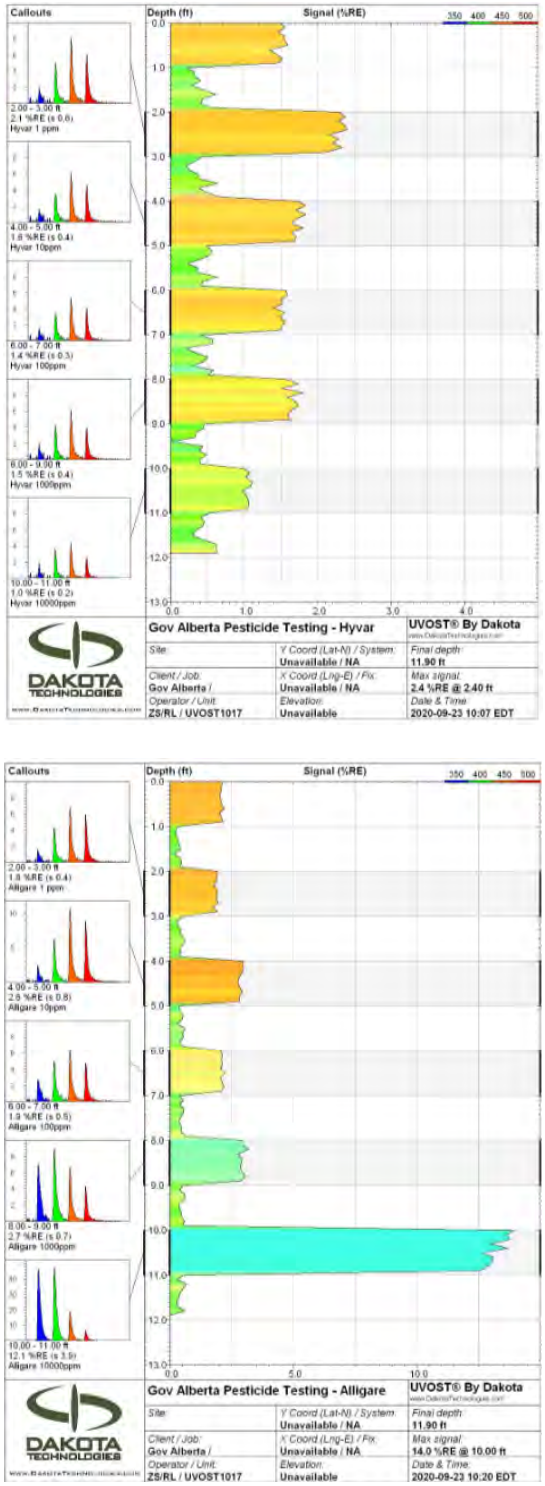


Figure 2. UVOST® results.
"Spiked" Spike 80® (top), "spiked" Hyvar XL ® (middle), and "spiked" Alligare 80® (bottom) water samples.

Figure 2 shows UVOST® result logs of each set of "spiked" set of water-based sterilant samples made by Vertex. Signal (total fluorescence) is measured on the x-axis and in units of response (%RE) relative to a

baseline reference emitter (a set amount of fluorescent material provided by Dakota Technologies). Depth is listed on the y-axis, however within the "emulator" software mode utilized for Phase 1 testing – depth only symbolizes discrete sample at 1' intervals. Each test sample is paired with a "call-out" which highlights the waveform created by the fluorescent response from the sample. A waveform is a coloured depiction of the intensity of each wavelength channel (350, 400, 450, 500 nm) of fluorescence outputted by the sample, with the tail on each peak showing the time over which the fluorescence signal decays. These bars are coloured based on the ratio of the intensity of the different wavelengths of fluorescence. Each sample will have a unique "fingerprint" due to the relative amplitude of the four wavelength channels and/or broadening of one or more channels. The combination of channel amplitude and total signal fluorescence (%RE) gives a distinct picture of the unique fluorescence released by each sample.

Figure 2 (top) depicts the UVOST® results of the tebuthiuron-based Spike 80® sterilant water samples. Consistency is seen in waveform outputs of the 100, 1,000, and 10,000 mg/L mixtures and there is a clear increasing trend in total fluorescence (signal intensity) as the concentrations increase. Dakota Technologies recommends a minimum signal response percentage of 1% to confirm presence of fluorescent material, above background levels. The results indicated that UVOST® can detect Spike 80® in water down to a detection limit of approximately 10 ppm where signal response percentage is greater than 1% and there is evidence of a distinct waveform fingerprint.

Figure 2 (middle) depicts the UVOST® results of the bromacil-based Hyvar XL® sterilant water samples. The results indicated that UVOST® cannot detect Hyvar XL® in water reliably, even to concentrations up to 10,000 mg/L. Signal intensity (%RE) is inexplicably highest at lowest concentrations (1 mg/L) and decreases as the concentration of Hyvar XL® increases. This likely indicates background fluorescence is more impactful than the Hyvar XL® constituents and, therefore, UVOST® is likely unable to differentiate between bromacil-based Hyvar XL®-induced fluorescence and background interference.

Figure 2 (bottom) depicts the UVOST® results of the bromacil-based Alligare 80® sterilant water samples. Consistency is seen in waveform outputs of the 1,000, and 10,000 mg/L mixtures and there is a clear increasing trend in total fluorescence (signal intensity) as the concentrations increase. The results indicated that UVOST® can detect Alligare 80® in water down to a detection limit of approximately 1,000 mg/L where signal response percentage is greater than 1% and there is evidence of a distinct waveform fingerprint. At lower concentrations, there is no clear trend in intensity as a function of concentration and the waveform differs from that of the high concentration standard.

Overall, UVOST® was successful in detecting bromacil-based Alligare 80® at concentrations at and above approximately 1,000 mg/L in spiked water samples. Also, UVOST® was successful in detecting tebuthiuron-based Spike 80® at concentrations at and above approximately 100 mg/L in spiked water samples. UVOST® was not reliable at detecting any concentrations of bromacil-based Hyvar XL® in spiked water samples. Based on the results of the Phase 1 literature review and Phase 1 testing, the UVOST® system is not recommended to advance to Phase 2 testing. The detection limits seen in the Phase 1 testing are much higher than target detection limits, and it is considered unlikely that Phase 2 testing could optimize and refine testing protocols for soil sterilant containing samples prior to analysis by the UVOST® system to the point that several orders of magnitude of reductions in detection limits can be achieved.

Vertex has been working with Dakota Technologies to develop new field analysis techniques and protocols to expand the detection limits of the UVOST® system. Currently, UVOST® is typically limited to, and designed for, detecting Non-Aqueous Phase Liquids which contain fluorescent PAH compounds within their substrate. Recently however, Dakota Technologies has experimented with various extraction

techniques to lower detection limits of targeted contaminants of concern that contain fluorescent compounds in the dissolved phase. During Phase 1 testing, Vertex saw some success with detecting fluorescent materials in dissolved phase dilutions of bromacil-based Alligare 80® and tebuthiuron-based Spike 80®. However, the detection limits of the UVOST® system for these dissolved phase compounds were much higher than target detection limits. As such, Vertex and Dakota Technologies are continuing to experiment with extraction methods, including methanol extractions of soil/groundwater samples containing contaminants of concern, to lower the expected detection limits of the UVOST® system. Also, Dakota Technologies has expanded the capabilities of the UVOST® system's field applicability by developing a hand-held screening tool that utilizes UV-LIF technology. This alleviates the restriction of past UVOST® systems to only direct-push drilling platforms for detecting contaminants of concern in the subsurface and opens the possibility for field-screening with UVOST® at surface or in laboratory settings.

4.1.2 TarGOST® (Tar-specific Green Optical Screening Tool)

4.1.2.1 Technology background

TarGOST® (Tar-specific Green Optical Screening Tool) uses the same theory and technology as UVOST, but instead utilizes the visible (i.e., green) range of wavelengths to achieve fluorescence (Figure 3). However, TarGOST® technology is unable to detect dissolved phase contaminants (Dakota Technologies, n.d.(a)) and is specifically designed for higher molecular weight contamination including coal tar and heavy crudes. Furthermore, they have comparable measurement density capabilities (Dakota Technologies, n.d.(a)). The main difference between the two systems is the type of compounds that the equipment can detect. Specifically, TarGOST® technology will not identify any dissolved-phase contaminants as it is specifically blind to them (Dakota Technologies, n.d.(a)). TarGOST® is specifically designed for higher molecular weight contamination including coal tar and heavy crudes, while UVOST® detects lower molecular weight contaminants such as diesel and gasoline.

Figure 3. Field deployment of the TarGOST® (left) and green-light emanating from TarGOST® probe (right).

4.1.2.2 Sample Preparation and Test Execution

The TarGOST® system tested by Dakota Technologies can be used for semi-quantitative analysis of both soil and groundwater samples with no pre-analysis sample preparation (i.e., extraction and/or drying). While the TarGOST® system typically is deployed via a direct-push drilling platform such as a Geoprobe®, the software enabled by TarGOST® allows for "above-ground" analysis of samples via an "emulator"

software setting that scans samples for analysis collection in a laboratory setting. Dakota Technologies utilized this "emulator" setting to scan the following "spiked" sample sets:

- Spiked samples of silica sand containing the following concentrations of each sterilant:
  - 10,000 mg/kg
  - 1,000 mg/kg
  - 100 mg/kg
  - 10 mg/kg
  - 1 mg/kg
  - 0 mg/kg (sand only)
- Each of these spiked sand samples was saturated (i.e., approximate water content of 25%)

No preliminary extractions or alterations were made to these samples prior to analysis via Dakota's TarGOST® system. Each sample is scanned independently, and results are logged on a TarGOST® software log output, with each sample tracked as a depth interval on the y-axis.

4.1.2.3 Results

Three (3) different soil-based sterilant sample sets (with concentrations ranging from 0 mg/kg to 10,000 mg/kg) were tested using Dakota's TarGOST® system:

- Alligare 80® - Bromacil
- Hyvar XL® - Bromacil
- Spike 80® - Tebuthiuron

Each sample set was scanned from lowest concentration (1 mg/kg) to highest concentration (10,000 mg/kg), preceded by a "blank" sample of silica sand only. TarGOST® software outputted results for the analysis of "spiked" soil-based samples are shown in Figure 4.

Figure 4 depicts the TarGOST® results for scans completed on "spiked" soil samples of tebuthiuron-based Spike 80®, bromacil-based Hyvar XL®, and bromacil-based Alligare 80® soil samples created by Vertex and sent to Dakota's in-house lab for analysis. Similar to the UVOST® logs, signal (total fluorescence) is measured on the x-axis and in units of response (%RE) relative to a baseline reference emitter (a set amount of fluorescent material provided by Dakota Technologies). Depth is listed on the y-axis, however within the "emulator" software mode utilized for Phase 1 testing – depth only symbolizes discrete sample at 1' intervals. Each test sample is paired with a "call-out" which highlights the waveform created by the fluorescent response from the sample. A waveform is a coloured depiction of the intensity of each wavelength channel (350, 400, 450, 500 nm) of fluorescence outputted by the sample, with the tail on each peak showing the time over which the fluorescence signal decays. These bars are coloured based on the ratio of the intensity of the different wavelengths of fluorescence. Each sample will have a unique "fingerprint" due the relative amplitude of the four wavelength channels and/or broadening of one or more channels. The combination of channel amplitude and total signal fluorescence (%RE) gives a distinct picture of the unique fluorescence released by each sample.

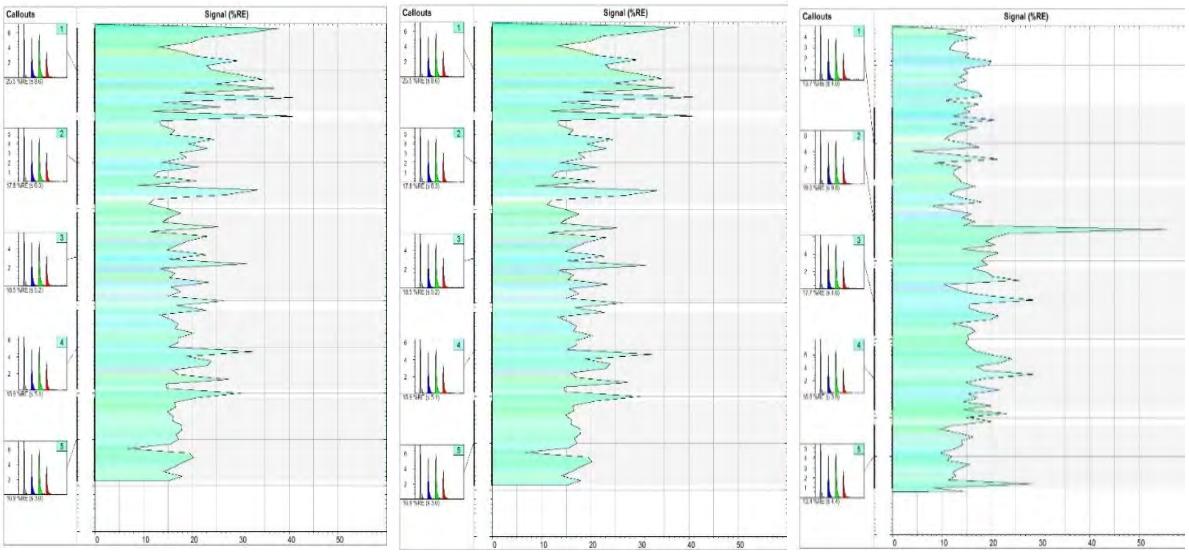


Figure 4. TarGOST® results.
"Spiked" Spike 80® (left), Hyvar XL® (centre), and Alligare 80® (right) soil samples.

Figure 4 indicates there were no discernable trends of TarGOST® reflectance as concentrations of any soil sterilants increased. The waveforms and signal intensity seen in Figure 4 appear to be nothing more than background noise from the sand material the soil sterilants were mixed with. Again, Dakota Technologies recommends a minimum signal response percentage of 1% to confirm presence of fluorescent material, above background levels. While these results indicate the green optical reflectance utilized by the TarGOST® system is detecting responses above 1% RE, there is no distinguishable pattern of response between soil sterilant type or increasing concentration. Therefore, Vertex concludes that the TarGOST® system is incapable of detecting any of the soil sterilants in question, even at exceedingly high concentrations, at the time of testing.

Overall, the TarGOST® system was not successful at detecting any concentrations of soil sterilant in spiked soil samples prepared by Vertex. As such, at this time, the TarGOST® is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.

4.2 Near infrared reflectance spectroscopy (NIRS)

4.2.1 Technology Background

Near-infrared reflectance spectrometry is a method by which light within the near-infrared range is scattered and absorbed by a sample (Font et al., 2007). The scatter and absorption behaviors are unique to certain molecules due to how they vibrate when interacting with electromagnetic radiation, and therefore the compound can be identified by analysis of this scatter (Font et al., 2007). NIRS is a non-destructive technique that has been used in many industries including agriculture and geology (Font et al., 2007).

One of the advantages of NIRS is that it is less susceptible to background UV interference than other technologies (Swamy et al., 1997). NIRS devices are also portable and lightweight allowing it to easily be

used on-site (Figure 5). The detection limit of NIRS technology can be as low as parts per billion (ppb), though this varies greatly on the application and environment (Christesen et al., 2014).

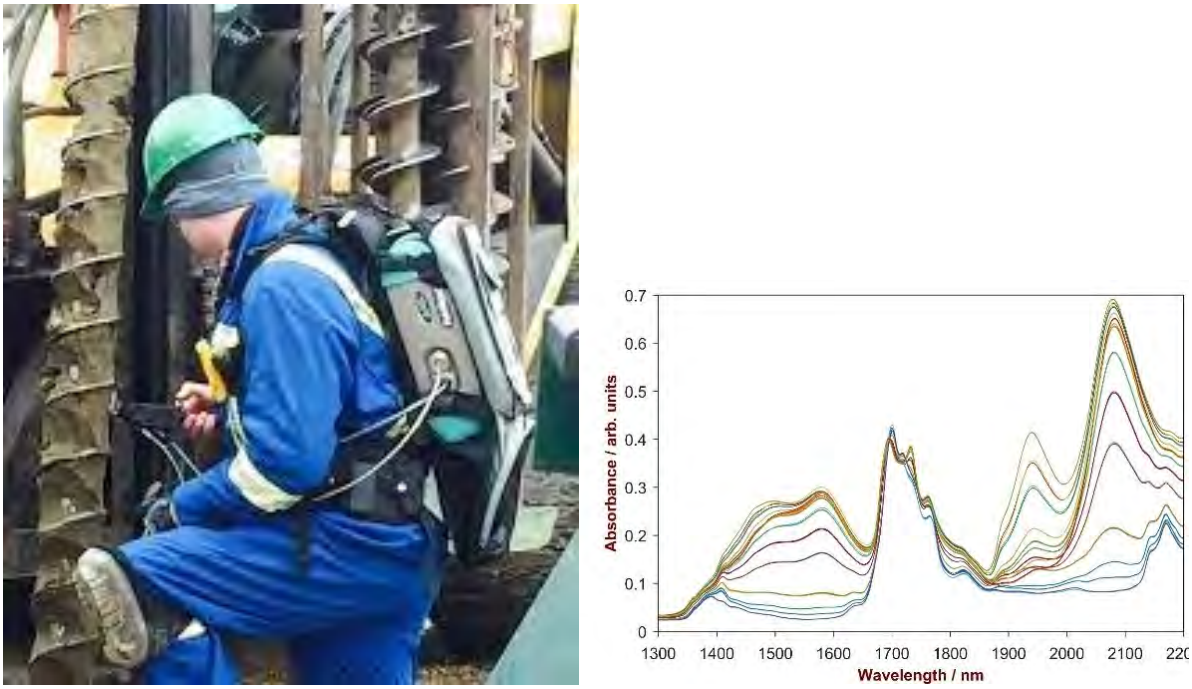


Figure 5. Field deployment of an NIRS System (left) and example output (right).

One of the major drawbacks of the NIRS technology is that it can only be used to screen certain types of soil samples. Very high water content soils (such as saturated peats) cause too much interference with the signal capture. Conversely, water samples can (theoretically) be directly tested using the technology.

4.2.2 Sample Preparation and Test Execution

No preliminary alterations were made to samples prior to analysis by NIRS field-ready device conducted by Maapera Analytics Inc. However, NIRS technology is currently limited to low moisture content (below saturation) soil samples only. Increased moisture content and, similarly, water only samples, are not able to be scanned by NIRS field-ready devices as moisture causes too much reflectance interference, as mentioned above. Therefore, spiked soil samples were sent to Maapera with lower water content than other technologies' spiked sample sets.

Below is a summary of sample delivery to Maapera for NIRS analysis:

- Spiked samples of silica sand containing the following concentrations of each sterilant:
    - 10,000 mg/kg
    - 1,000 mg/kg
    - 100 mg/kg
    - 10 mg/kg
    - 1 mg/kg
    - 0 mg/kg (sand only)

- Each of these spiked sand samples had water added (i.e., approximate water content of 20%)

Maapera's NIRS device is a simple handheld unit that scan up to 12 samples per minute and delivers real-time spectral results. Prior to scanning the spiked soil samples provided by Vertex, Maapera would have scanned a white "blank", also known as the "Spectralon" (Figure 6) to calibrate the NIRS to a baseline reflectance for each round of scans. Once "Spectralon" optimization is complete, a secondary optimization test is completed with the NIRS device light turned off, enabling an optimization process named "dark-current" optimization of the device. Following these two optimization processes, the probe is then placed back on the "Spectralon" and a white reference spectral curve is collected to ensure proper spectral analysis is completed prior to sample analysis.

4.2.3 Results

Three (3) different soil sterilant sample sets (with concentrations ranging from 0 mg/kg to 10,000 mg/kg) were tested using Maapera's NIRS system:

- Alligare 80® - Bromacil
- Hyvar XL® - Bromacil
- Spike 80® - Tebuthiuron

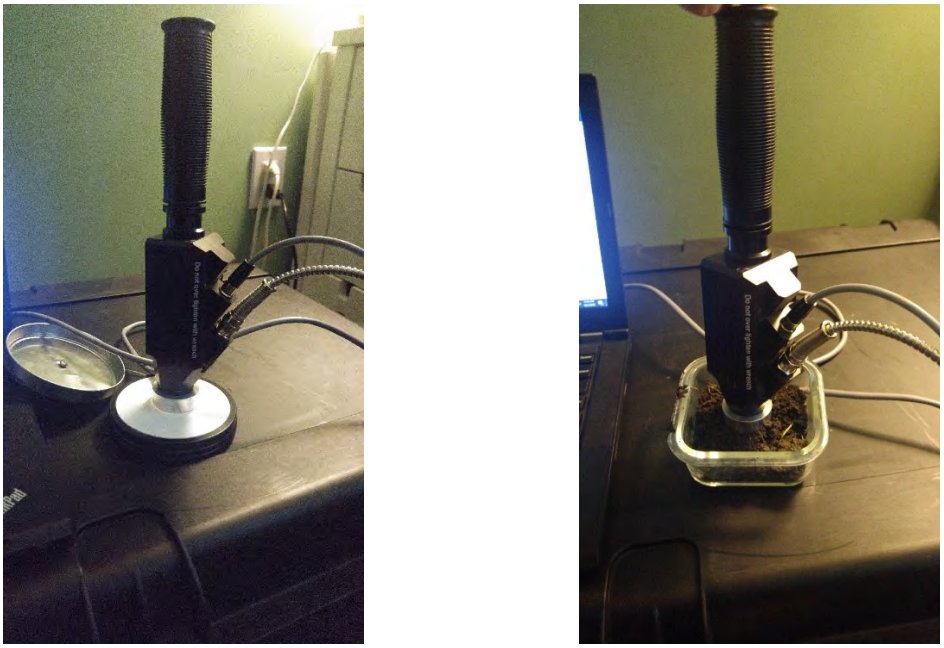
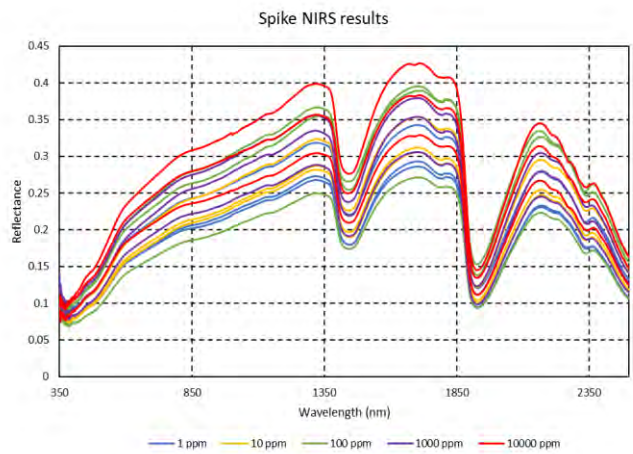


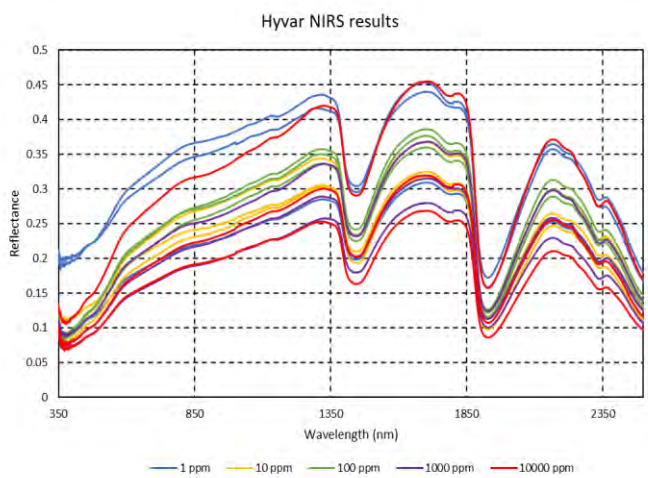
Figure 6. NIRS Spectralon optimization (left) and NIRS soil scan operation (right).

Each sample set was scanned from lowest concentration (1 mg/kg) to highest concentration (10,000 mg/kg).

Figure 7 depicts the raw spectral results of the NIRS scans of each soil sterilant provided to Maapera by Vertex. The raw spectral data is plotted as reflectance as a function of wavelength. NIRS was reportedly able to detect the herbicides in all the standards, though there is a not a clear concentration dependence

on the signal strength. There are two main features seen in the spectra for all the herbicides, one at approximately 1,450 nm and one at approximately 1,950 nm. Based on communications with Maapera, these features are likely from the reflectance of the N-H functional group and/or the C=O functional group present in both herbicides. There is also a small feature at approximately 2,300 nm which is likely due to CH_2 bonds. Because NIRS is detecting these general functional groups, interference with other compounds, including non-contaminants and natural soil constituents, is a concern. For example, if there are hydrocarbons present, NIRS will not be able to distinguish between the CH_2 groups of the hydrocarbons versus the CH_2 groups of the herbicides. It is also clear that the spectra for tebuthiuron and bromacil are very similar and would thus be difficult to distinguish in field samples.





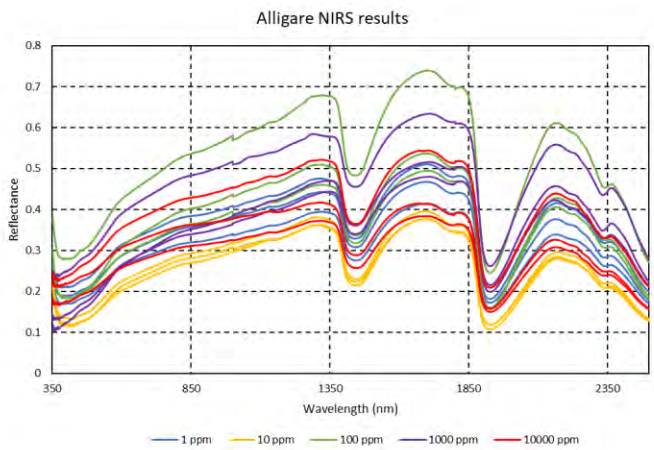


Figure 7. NIRS spectral results.
"Spiked" Spike 80® (top), Hyvar XL® (middle), and Alligare 80® (bottom) soil samples.

Overall, the Maapera NIRS system was not successful at detecting unique responses of soil sterilant in spiked soil samples prepared by Vertex. As such, at this time, the NIRS is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.

However, if this technology is chosen in the future for further study, Maapera has developed a Standard Operation Procedure (SOP) to create a model for screening for new contaminants of concern, such as the soil sterilants of focus in this report. Briefly, this would require 100 samples at a range of concentrations and 25 samples of the same concentration to train a data model. Following this, at least 250 samples would be necessary to complete a proof of concept and model evaluation. If successful, this would develop a model to identify and quantify these target species. While the model SOP for new contaminants is developed by Maapera, Phase 1 test results were not promising, and Vertex recommends to not include NIRS in Phase 2 testing as the SOP described is outside the scope of proposed testing in Phase 2.

4.3 X-Ray Fluorescence (XRF)

4.3.1 Technology Background

X-ray fluorescence technology employs the understanding of spectrometry and the x-ray range of light. When this light interacts with a sample it is both scattered and absorbed, the degree to which either occurs is dependent on the chemical properties of the sample (Wirth and Barth, n.d.). This behaviour is due to the x-ray exciting the electrons within the sample, allowing them to jump to a higher energy level (Wirth and Barth, n.d.). Eventually energy is released, and these emitted rays have characteristic wavelengths dependent on the element (Wirth and Barth, n.d.). Since samples are not of one element the XRF instrumentation takes the complete wavelength emitted and resolves it into the relative amounts of elements within the sample (Wirth and Barth, n.d.).

4.3.2 Sample Preparation and Test Execution

Spiked soil samples were created by Vertex and supplied to Elemental Controls Limited for XRF analysis via their Niton™ XL5 XRF Analyzer (Figure 8). Prior to XRF analysis, the following preliminary alterations were conducted on the supplied samples:

- Samples were oven-dried for 1 hour.
- Following oven-drying, samples were then crushed with a mortar and pestle.
- Dried, crushed samples were then loaded into 32 mm XRF sample cups using polypropylene XRF film.
- Approximately 10 g of sample was used per sample.
- Analysis time was approximately 120 seconds per sample.

Figure 8. Niton™ XL5 XRF Analyzer (left) and overview of XRF technology (right).

Below is a summary of sample delivery to Elemental Controls for XRF analysis:

- Spiked samples of silica sand containing the following concentrations of each sterilant:
  - 10,000 mg/kg
  - 1,000 mg/kg
  - 100 mg/kg
  - 10 mg/kg
  - 1 mg/kg
  - 0 mg/kg (sand only)

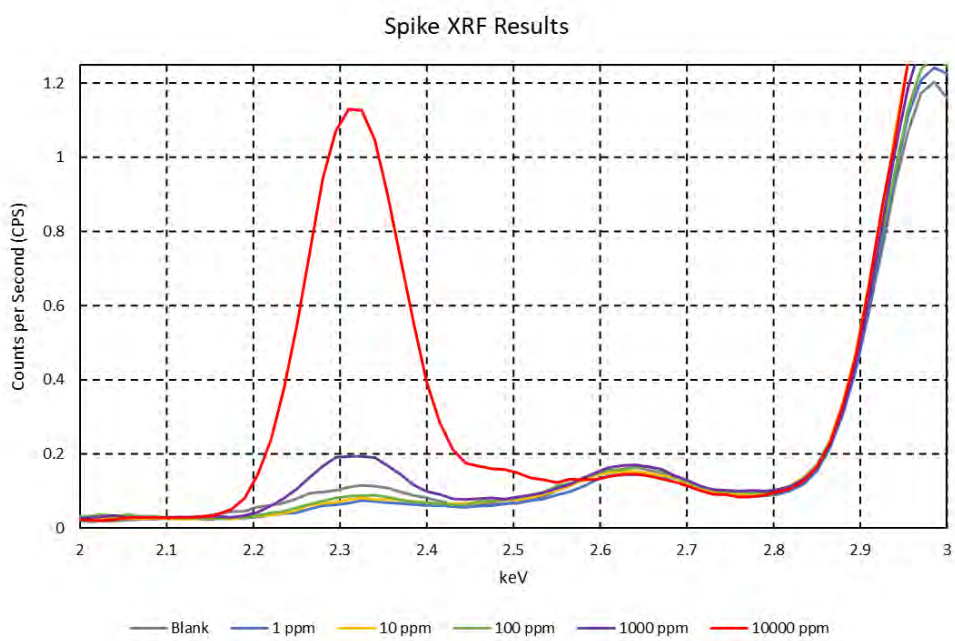
4.3.3 Results

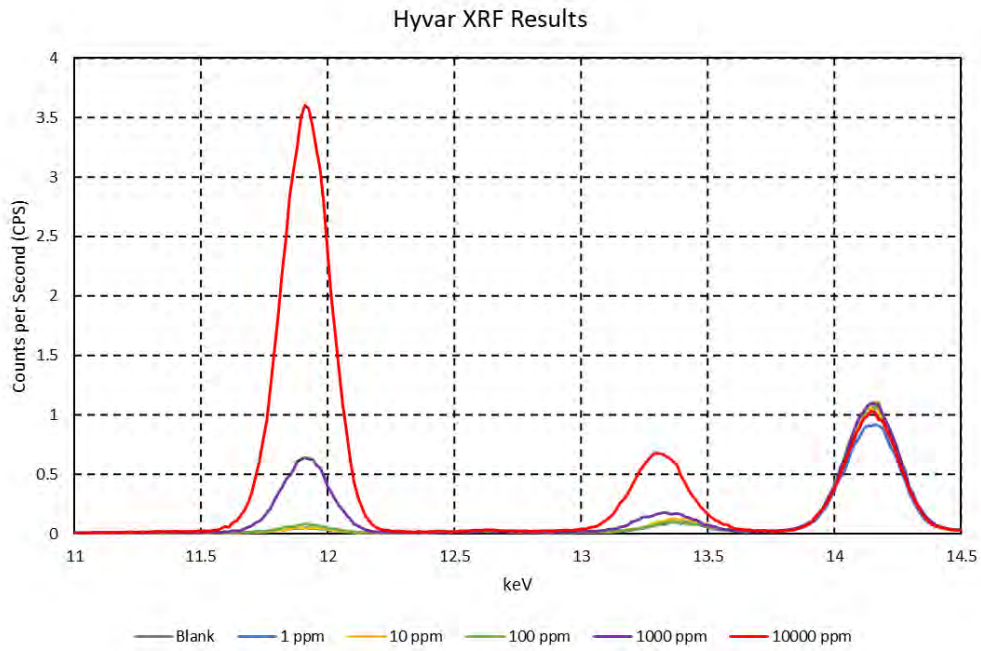
Three (3) different soil sterilant sample sets (with concentrations ranging from 0 mg/kg to 10,000 mg/kg) were tested using Elemental Controls' Niton® XL5 XRF system:

- Alligare 80® Bromacil
- Hyvar XL® Bromacil
- Spike 80® Tebuthiuron

Each sample set was scanned from lowest concentration (1 mg/kg) to highest concentration (10,000 mg/kg).

The XRF instrumentation takes the wavelengths emitted and resolves them into the relative amounts of elements within the sample (Wirth and Barth, n.d.). In the case of bromacil (Alligare 80® and Hyvar XL®), XRF is used to detect bromine. In the case of tebuthiuron, XRF is used to detect sulphur. Figure 9 shows counts per second (signal strength) as a function of keV energy level. Bromine spectral peaks occur at 11.92 and 13.92 keV while sulphur spectral peaks occur at 2.32 keV. The Niton® XL5 XRF system was set to Mining/Soils calibration mode which includes a calibrated reference library for sulphur and thus these raw spectra could be used to quantify the amount of Sulphur in the samples (Table 1). However, this was not the case for bromine as there was no prior reference library in the Niton® XL5 XRF system for that element. As such, only the raw spectra were available at this time for bromine analysis. It would be possible to calibrate the system to allow for Bromine quantification for future analysis.





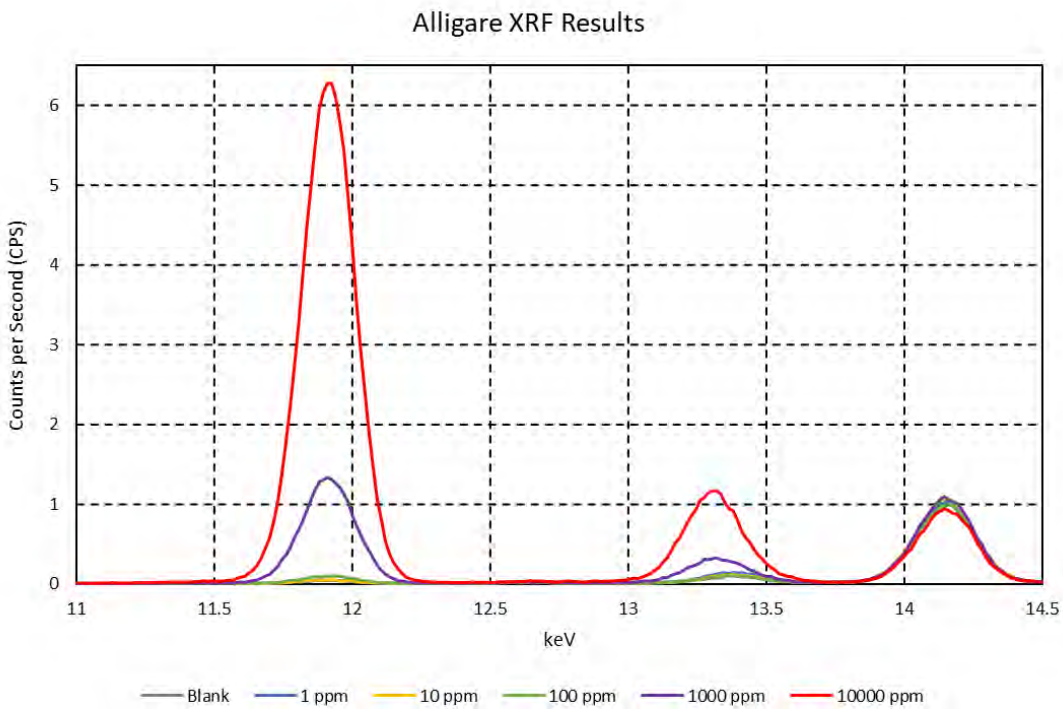


Figure 9. XRF spectral results.
"Spiked" Spike 80® (top), Hyvar XL® (middle), and Alligare 80® (bottom) soil samples.

Table 1. Sulphur content (weight %) calculated in each sample via XRF analysis.

Sample	Sulfur (weight %)	Standard Deviation
Blank	0.1505	0.0056
1 ppm Spike	0.0571	0.0044
10 ppm Spike	0.0734	0.0045
100 ppm Spike	0.0953	0.0048
1000 ppm Spike	0.3558	0.0072
10000 ppm Spike	2.5744	0.0161
1 ppm Hyvar	0.0605	0.0044
10 ppm Hyvar	0.0537	0.0043
100 ppm Hyvar	0.0624	0.0045
1000 ppm Hyvar	0.0744	0.0045
10000 ppm Hyvar	0.0993	0.0047
1 ppm Alligare	0.1727	0.0056
10 ppm Alligare	0.0701	0.0046
100 ppm Alligare	0.0576	0.0044
1000 ppm Alligare	0.071	0.0048
10000 ppm Alligare	0.0758	0.0047

In summary, the Niton® XL5 XRF system was able to detect unique responses of bromacil-based soil sterilants – Hyvar XL® and Alligare 80®. A pattern of detection, which appears to be unique at discrete KeV energy levels, also indicated a relation between response intensity and sample concentration. For both bromacil-based samples, the raw spectra results indicate that the XRF system can detect elemental bromine in bromacil-based samples down to approximately 100 mg/kg in spiked soil samples.

Similarly, the Niton® XL5 XRF system was able to detect unique responses of the tebuthiuron-based soil sterilant – Spike 80®. Furthermore, because of the existing calibrated reference library within the Niton® XL5 XRF system, the raw spectra results were quantified in weight percentage of sulphur within the samples (Table 1). The weight percentage of sulphur calculated from XRF system generally correlates with the concentration of herbicide in each sample. However, the amount of sulphur in the 1 mg/kg, 10 mg/kg and 100 mg/kg samples are indistinguishable from the bromacil- based Hyvar XL® and Alligare 80® samples which were not expected to contain detectable amounts of sulphur. This highlights the lack of specificity of this method and therefore the challenges of distinguishing sulphur from tebuthiuron from background sulphur in the soil sample.

Overall, the Niton® XL5 XRF system was successful in detecting bromacil-based Alligare 80® and Hyvar XL® at concentrations at and above approximately 100 mg/kg in spiked soil samples. The Niton® XL5 XRF system was also successful in detecting tebuthiuron-based Spike 80® at concentrations above approximately 1,000 mg/kg. However, the detection limits seen in the Phase 1 testing are much higher than targeted field detection limits, and it is considered unlikely that Phase 2 testing could optimize and refine testing protocols for sterilant containing samples prior to analysis by the XRF to the point that several orders of magnitude of reductions in detection limits can be achieved. As such, at this time, XRF is not recommended to advance to Phase 2 testing.

4.4 Raman spectroscopy

4.4.1 Technology Background

Raman spectroscopy is based on a laser light scattering in response to its interaction with molecules (Horiba, n.d.). Raman spectroscopy uses specifically the light that is scattered at different wavelengths than the incident ray (Raman Scatter), and though this is a small percentage of the overall scatter, Raman Scatter can provide information on the chemical structure and even the phase of the compound of interest (Horiba, n.d.). The characteristics of the Raman Scatter can be attributed to a particular molecular bond or group of bonds and therefore enables the user to do a compound analysis instead of elemental (Horiba, n.d.). Samples are mixed with gold or silver nanoparticles to enhance the signal strength, which typically enables detection limits of ppb to ppm levels. The acquired Raman spectra are compared to reference spectra to identify and quantify specific compounds. For this technology to be effective, the analyte of interest must have diagnostic peak regions that are sufficiently robust, that they do not match with false results.

Specifically, Vertex used the Metrohm Instant SERS Analyzer (MISA), supplied by Metrohm Canada Inc. for Phase 1 testing (Figure 10). MISA is a new product similar to existing Raman field-screening devices used largely in pharmaceutical and chemical manufacturing industries. MISA features a high-efficiency spectrograph equipped with Orbital-Raster-Scan (ORS) technology. It has a minimal footprint and extended battery life, perfect for on-site testing or mobile laboratory applications, and operation is available through BlueTooth or USB connectivity. The uses SERS (Surface Enhanced Raman Spectroscopy) techniques to amplify signals. A small amount of sample is added to a colloidal suspension of gold or silver nanoparticles in solution (water) and subsequent Raman analysis enables significantly improved signal response, allowing detection of substances in ng/mL (ppb or lower) quantities.

Figure 10. Metrohm Instant SERS Analyzer.

4.4.2 Sample Preparation and Test Execution

Spiked soil samples were created by Vertex and supplied to Metrohm Canada Inc. for Raman spectral analysis via their MISA analyzer. Prior to sample analysis, some preliminary alterations needed to be completed to successfully analyze samples via MISA. Figure 11 shows the general workflow of the MISA.

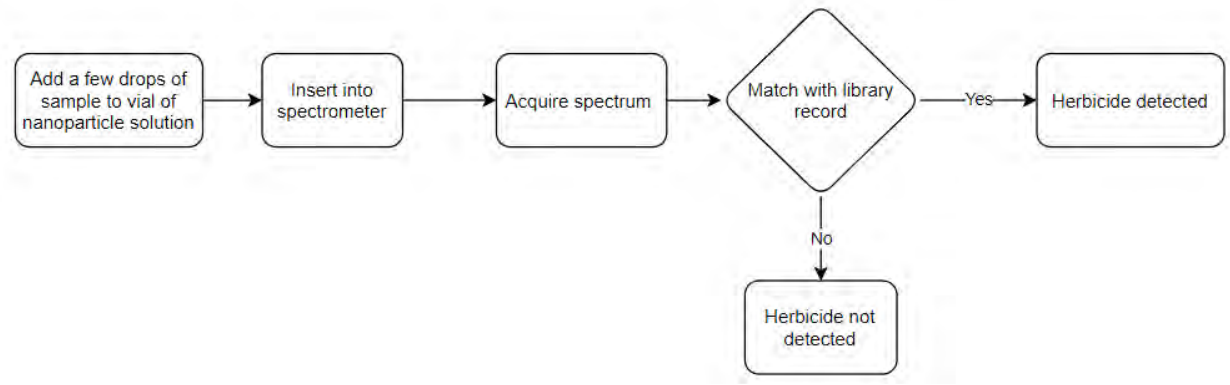


Figure 11. General MISA workflow.

Prior to sample analysis, various extraction techniques were utilized by Metrohm to enhance the Raman spectra observed in these samples. Inherent to the MISA device, however, is a technique using gold (Au) nanoparticle solution. Prior to analysis by the MISA device, test samples are added to the Au nanoparticle solution, a specialized test strip is dipped into the mixed solution and then placed into the MISA spectrometer for analysis. More detail on preliminary sample alterations for MISA analysis will be discussed below alongside their results.

Below is a summary of sample delivery to Metrohm Canada for Raman Spectral analysis:

- Spiked samples of distilled water containing the following concentrations of each sterilant (subject to the amount of the different sterilant products obtained):
    - 10,000 mg/L
    - 1,000 mg/L
    - 100 mg/L
    - 10 mg/L
    - 1 mg/L
    - 0 mg/L (distilled water only)

4.4.3 Results

The first step of the MISA test for tebuthiuron and bromacil detection was to acquire reference spectra from 10,000 mg/L aqueous mixtures of Spike 80®, Alligare 80® and Hyvar XL®. These samples were mixed with an Au nanoparticle solution and an NaCl solution.

Figure 12 shows the spectra acquired for Spike 80® (blue), Hyvar XL® (yellow) and Alligare 80®(red). Each sample showed a unique spectrum, with some overlapping peaks. The peak location and shape are dependent on the sample matrix (i.e., salt content, pH, temperature, etc.) and, as such, the spectra shown in Figure 12, while indicating promise for detecting active herbicide peaks, is likely matrix interference which inhibits use as a reference spectra.

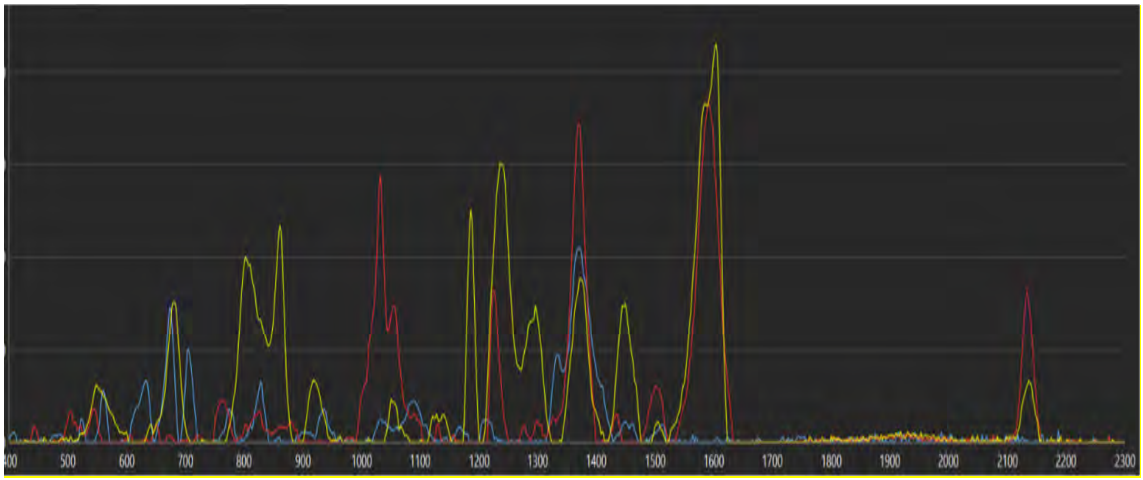


Figure 12. Overlaid spectra of Alligare 80® (red), Hyvar XL® (yellow) and Spike 80® (blue).

Following the preparation and analysis of 10,000 mg/L reference samples above, it was decided to attempt a serial dilution of the 10,000 mg/L Hyvar XL® sample to create 100, 50, and 10 mg/L samples. Each diluted sample was created by adding 100 uL of undiluted sample (10,000 mg/L) with 100 uL NaCl (500 mmol) which was then added to 800 uL Au nanoparticle solution prior to analysis.

Figures 13 and 14 show a stacked plot of 100 (blue) 50 (red) and 10 (yellow) ppm Hyvar XL® spectra. The zoomed region indicates diagnostic peak regions at 1,250 and 1,500 cm^{-1}, where wavenumbers are decreasing in magnitude with lowered concentration. Note that due to the signals becoming comparable to the baseline noise at less than approximately 100 ppm, MISA software auto-baseline correction algorithm skews their line shape.

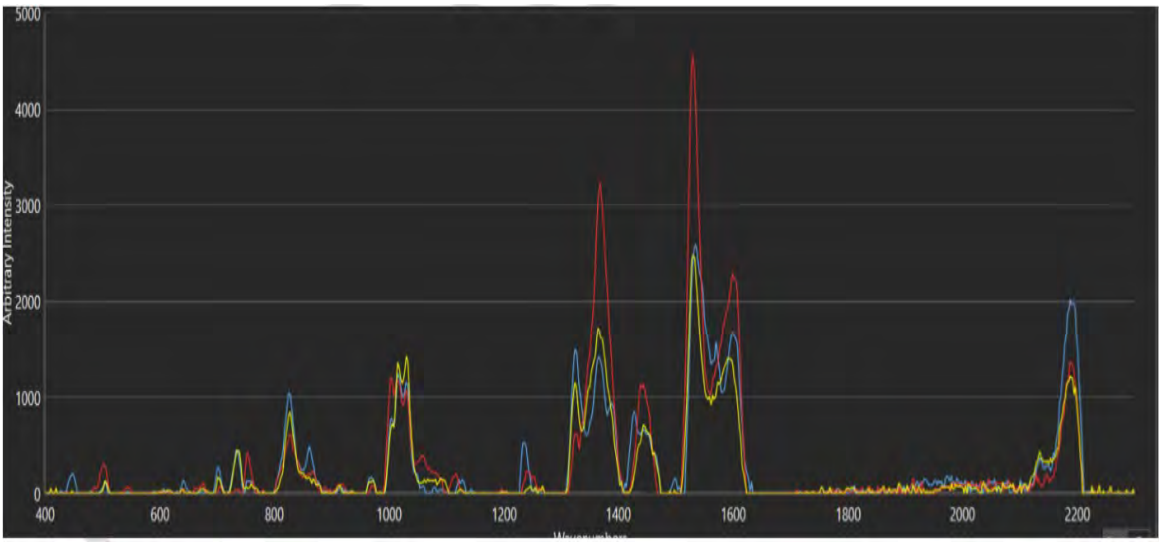


Figure 13. Stacked plot of 100 (blue), 50 (red), and 10 (yellow) ppm Hyvar XL® spectra.

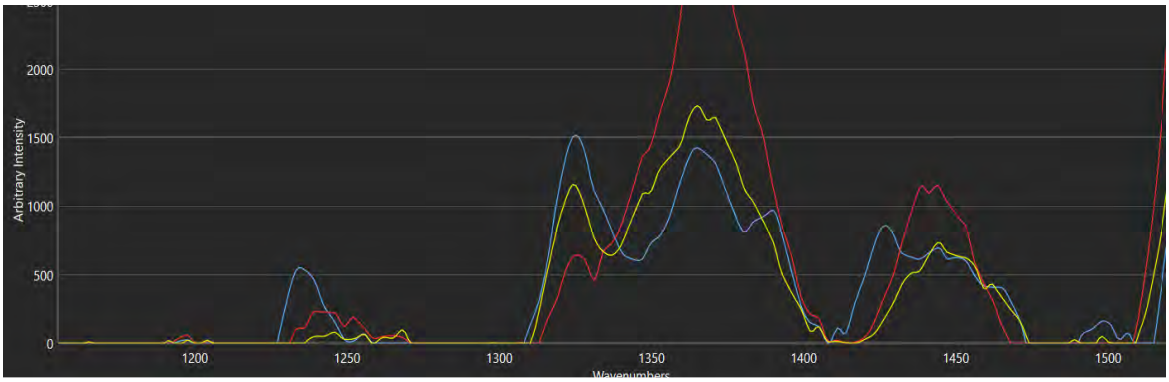


Figure 14. Zoomed stack plot 100 (blue), 50 (red), and 10 (yellow) ppm Hyvar XL® spectra

Handheld Raman devices such as the MISA are best suited for qualitative analysis rather than providing results such as % composition. With this is in mind, an attempt to improve detection limits was completed via micro-extraction into chloroform to concentrate the herbicides in solution. Following the reference spectra and serial dilution analysis above, chloroform micro-extractions were attempted for proof-of-concept detection of soil sterilants and lower detection limits.

200 uL of chloroform was added to 2 mL of non-diluted Hyvar XL® aqueous solution. After agitation, the mixed solution was allowed to settle, and the bottom layer of chloroform was removed via pipette and placed in a vial. Following removal, the chloroform layer was placed on a hotplate and the solvent was boiled off. Following boiling, 100 uL of NaCl solution (500 mmol) and 500 uL Au nanoparticle solution was added. Serially diluted samples of Hyvar XL® which underwent the above chloroform extraction enabled spectral diagnostic matching down to approximately 10 mg/L, an order of magnitude improvement compared to straightforward aqueous sample.

Overall, MISA Raman system was successful in detecting unique spectra of bromacil-based Hyvar XL® at concentrations at approximately 100 mg/L in aqueous solutions, with no preliminary extraction, and down to approximately 10 mg/L with chloroform extraction. Bromacil-based Alligare 80® and tebuthiuron-based Spike 80® were also detected in aqueous solution successfully by MISA analysis, with unique spectra acquired for each. Following the reference spectra, serial dilution, and chloroform extraction analysis techniques conducted by Metrohm, it was decided to pause testing to await more representative soil/water/herbicide samples which are more thoroughly characterized in advance. This would enable the creation of more robust library spectra and spectral regions so more reliable matches can be made in the future. Based on the results of the Phase 1 literature review and Phase 1 testing, the MISA Raman system is recommended to advance to Phase 2 testing. While detection limits seen in Phase 1 testing are still higher than target detection limits, Phase 2 testing will look to optimize and refine testing protocols for soil sterilant containing samples prior to analysis by the MISA system. This technology is potentially applicable for detecting bromacil and tebuthiuron in soil and water samples.

4.5 Laser-induced Breakdown Spectroscopy (LIBS)

4.5.1 Technology Background

Laser-induced breakdown spectroscopy (LIBS) uses a high energy laser pulse to ionize and excite the atoms within a sample (Shah et al., 2019). This interaction between the atoms and the laser causes some evaporation of the sample which results in the production of plasma (Shah et al., 2019). The plasma gives

off light whose spectra can be analyzed to determine the chemical components of the sample (Shah et al., 2019). The wavelength indicates the atoms present, and the relative intensity allows for a measurement of concentration (Shah et al., 2019). This process is overall non-destructive, and the samples require very little or no preparation before analysis (Shah et al., 2019). LIBS is best suited for metal analysis.

LIBS has been used to analyze a variety of materials including soils, solutions, and insecticides (Shah et al., 2019). Furthermore, LIBS has been used for different environmental applications, mainly for the identification of trace metals and crude oil and fuel residues (Shah et al., 2019). Dual pulse LIBS has also been used to determine trace contaminants within organic fertilizers (Nicolodelli et al., 2016), which suggests that it could be used to detect other organic compounds such as the soil sterilants of interest. LIBS has also been used for soil analysis in agriculture, specifically when there is concern about heavy metal contamination or in the detection of select nutrients (Peng et al., 2016).

4.5.2 Sample Preparation and Test Execution

Spiked soil samples were created and tested by Vertex with the Hitachi Vulcan LIBS Analyzer (Figure 15). Non-Destructive Testing Products Limited provided Vertex with the rental Hitachi Vulcan LIBS Analyzer for Phase 1 testing. The Hitachi Vulcan is a hand-held LIBS analyzer typically used for metal analyses and works on a point-and-shoot methodology. No preliminary alterations were conducted on the spiked soil samples prior to analysis by the Hitachi Vulcan. The Hitachi Vulcan typically uses a reference library to match samples to reference spectral results, however, since Vertex was using the Vulcan to detect soil sterilants without a reference library available within the Vulcan database, each sample was scanned in manual mode, collecting raw spectral data.

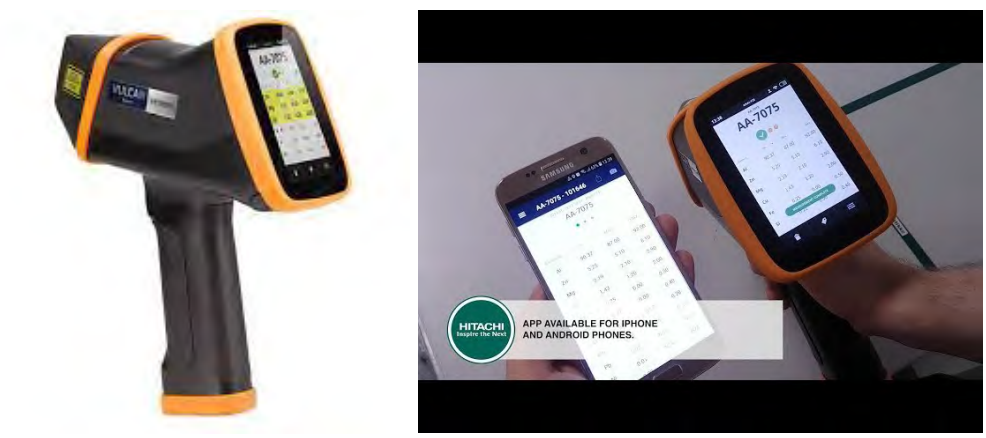


Figure 15. Hitachi Vulcan LIBS Analyzer (left) and example output (right).

Spiked samples of silica sand containing the following concentrations of each sterilant:

- 10,000 mg/kg
- 1,000 mg/kg
- 100 mg/kg
- 10 mg/kg
- 1 mg/kg
- 0 mg/kg (sand only)

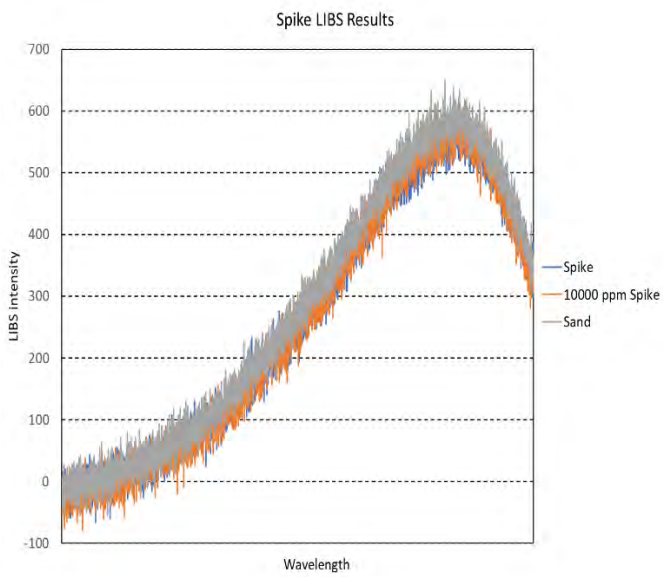
4.5.3 Results

Three (3) different soil sterilant sample sets (with concentrations ranging from 0 mg/kg to 10,000 mg/kg) were tested using Hitachi's Vulcan LIBS Analyzer system:

- Alligare 80® Bromacil
- Hyvar XL® Bromacil
- Spike 80® Tebuthiuron

Each sample set was scanned from lowest concentration (1 mg/kg) to highest concentration (10,000 mg/kg), Hitachi Vulcan spectral results were plotted, wavelength on the x-axis versus LIBS intensity on the y-axis, for the analysis of "spiked" soil-based samples.

Figure 16 indicates there were no discernable trends of LIBS intensity as concentrations of any soil sterilant increased. The LIBS signal intensities are nothing more than background noise from the sand material the soil sterilants were mixed with. There is no distinguishable pattern of response between soil sterilant type or increasing concentration. Therefore, Vertex concludes that the Hitachi Vulcan LIBS Analyzer system incapable of detecting any of the soil sterilants in question, even at exceedingly high concentrations, at this time of testing.



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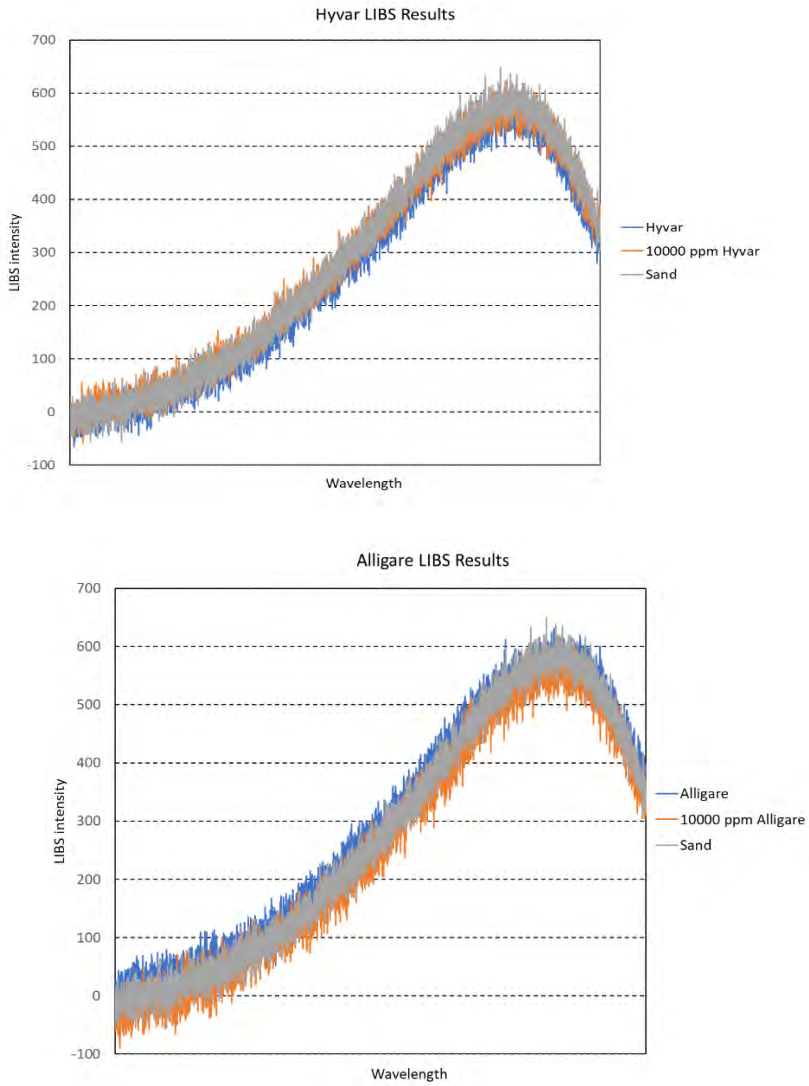

Figure 16. Hitachi Vulcan LIBS Analyzer spectral results.
"Spiked" Spike 80® (top), Hyvar XL® (middle) and Alligare 80® (bottom) soil samples.

Overall, the Hitachi Vulcan LIBS Analyzer system was not successful at detecting any concentrations of soil sterilant in spiked soil samples prepared by Vertex. As such, at this time, the LIBS is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.

4.6 Gas Chromatography/Thermionic Ionization Detector (GC/TID)

4.6.1 Technology Background

Thermionic ionization detectors (TIDs), occasionally referred to as nitrogen-phosphorous detectors, use the theory of gas chromatography as discussed previously in Section 3.1.4. The TID contains a thermionic ionization detector bead which heats up and when the substance of interest comes in contact with the bead a chemical reaction can occur (Figure 17; SRI, n.d.). The reaction occurs within the plasma that coats the surface of the TID bead and results in the substance being ionized (SRI, n.d.). These ions are measured

by the electrode within the system and the resulting are reported to the user as a concentration (SRI, n.d.). The molecule type determines whether this ionization reaction occurs. Specifically, molecules containing the NO_2 functional group are the main substances that are observed by TID technology (SRI, n.d.).

TIDs, unlike many other devices used in environmental investigations, will not detect aromatic or aliphatic hydrocarbons (SRI, n.d.). The SRI TID device that was being considered by Vertex has detection limits within the ppb range, which is low enough to meet the goals of the project (Quadrex Corporation, n.d.). TID devices require air to run properly, and the device is listed as being able to run on ambient air in the field (Quadrex Corporation, n.d.).

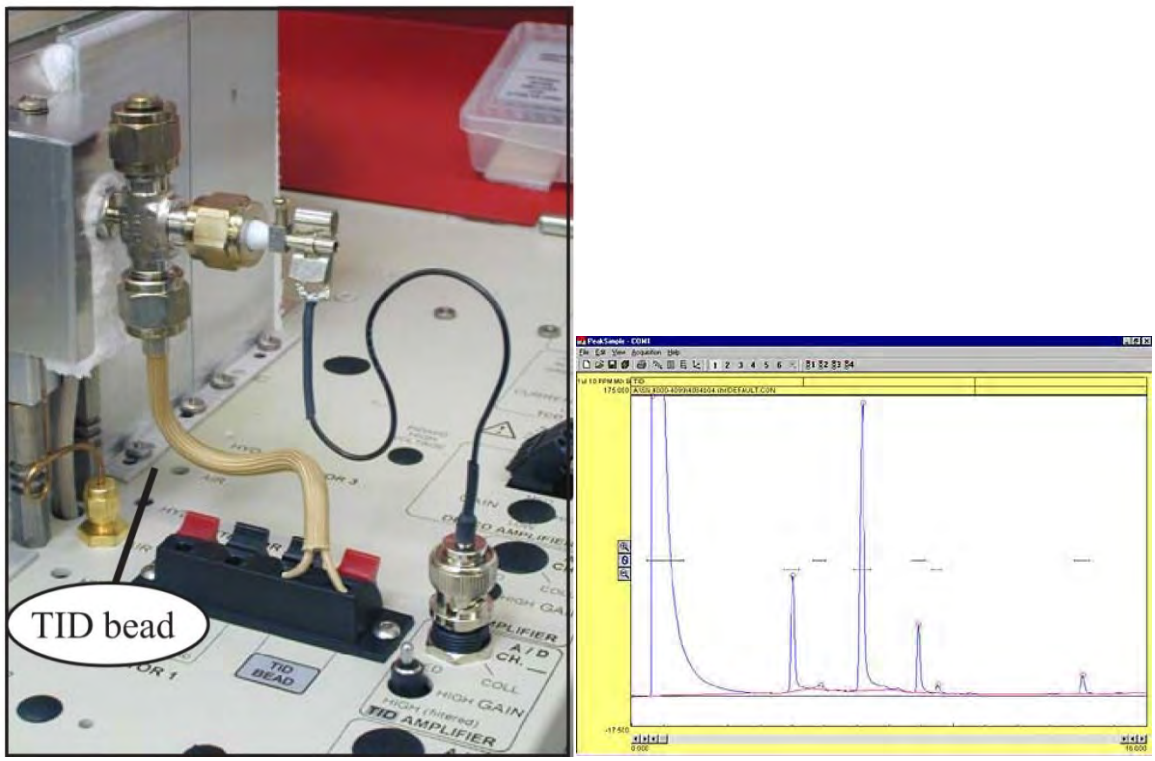

Figure 17. SRI TID system (left) and example output (right).

4.6.2 Results

Following the literature review, it was determined that a GC/TID was not currently available as a hand-held or field-deployable device that would be capable of analyzing Phase 1 test samples as was done for the other six (6) other Phase 1 technologies. There is an established precedent for using gas chromatography methods to screen for and study herbicides and pesticides. Bromacil was one of the compounds that was studied using TID technology as a part of larger pesticide column experiments performed within the laboratory (Draper, 1995).

After further discussions with SRI Instruments, the supplier of Gas Chromatographs capable of enabling a GC/TID system for soil sterilant analysis, it was determined that a field-ready GC/TID was not able to be developed at this time. It was estimated that it would cost approximately $15,000 to build a field prototype. Due to the high cost and expected challenges with the lack of volatility of the herbicides in

question, Vertex decided to not proceed with the development of a prototype at this time. This technology was not investigated further.

5.0 SUMMARY AND CONCLUSIONS

Based on the results of the previously completed literature review and interviews completed in relation to the potential application of existing field screening technologies for use in detecting bromacil and/or tebuthiuron in soil and groundwater at sites in Alberta, Vertex concluded that the following seven technologies showed promise and were included in this Phase 1 Testing program:

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
- Visible light laser induced fluorescence (TarGOST® or OIP-G®)
- Near infrared reflectance spectroscopy (NIRS)
- X-ray fluorescence (XRF)
- Raman spectroscopy
- Laser-induced breakdown spectroscopy (LIBS)
- Gas Chromatography/Thermionic Ionization Detector (GC/TID)

Results of the Phase 1 Testing (proof-of-concept) of the above technologies are summarized below:

- *Ultraviolet laser induced fluorescence (UVOST® or OIP®)*
    - Overall, UVOST® was successful in detecting bromacil-based Alligare 80® at concentrations at and above approximately 1,000 mg/L in spiked water samples. Also, UVOST® was successful detecting tebuthiuron-based Spike 80® at concentrations at and above approximately 100 mg/L in spiked water samples. UVOST® was not reliable at detecting any concentrations of bromacil-based Hyvar XL® in spiked water samples.
    - Based on the results of the Phase 1 testing, the UVOST® system is not recommended to advance to Phase 2 testing. The detection limits seen in the Phase 1 testing are much higher than target detection limits, and it is considered unlikely that Phase 2 testing could optimize and refine testing protocols for soil sterilant containing samples prior to analysis by the UVOST® system to the point that several orders of magnitude of reductions in detection limits can be achieved.
- *Visible light laser induced fluorescence (TarGOST® or OIP-G®)*
    - Overall, the TarGOST® system was not successful at detecting any concentrations of soil sterilant in spiked soil samples. As such, at this time, the TarGOST® is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.

- *Near infrared reflectance spectroscopy (NIRS)*
    - Overall, the NIRS system was not successful at detecting unique responses of soil sterilant in spiked soil samples. As such, at this time, the NIRS is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.
- *X-ray fluorescence (XRF)*
    - Overall, the Niton® XL5 XRF system was successful in detecting bromacil-based Alligare 80® and Hyvar XL® at concentrations at and above approximately 100 mg/kg in spiked soil samples. The Niton® XL5 XRF system was also successful in detecting tebuthiuron-based Spike 80® at concentrations above approximately 1,000 mg/kg.
    - Detection limits seen in the Phase 1 testing are much higher than targeted field detection limits, and it is considered unlikely that Phase 2 testing could optimize and refine testing protocols for sterilant containing samples prior to analysis by the XRF to the point that several orders of magnitude of reductions in detection limits can be achieved. As such, at this time, XRF is not recommended to advance to Phase 2 testing.
- *Raman spectroscopy*
    - Overall, the MISA Raman system was successful in detecting unique spectra of bromacil-based Hyvar XL® at concentrations of approximately 100 mg/L in aqueous solutions, with no preliminary extraction, and down to approximately 10 mg/L with chloroform extraction. Bromacil-based Alligare 80® and tebuthiuron-based Spike 80® were also detected in aqueous solution successfully by MISA analysis, with unique spectra acquired for each.
    - Based on the results of the Phase 1 literature review and Phase 1 testing, the MISA Raman system is recommended to advance to Phase 2 testing. While detection limits seen in Phase 1 testing are still higher than target detection limits, Phase 2 testing will look to optimize and refine testing protocols for soil sterilant containing samples prior to analysis by the MISA system. This technology is potentially applicable for detected bromacil and tebuthiuron in soil and water samples.
- *Laser-induced breakdown spectroscopy (LIBS)*
    - Overall, the Hitachi Vulcan LIBS Analyzer system was not successful at detecting any concentrations of soil sterilant in spiked soil samples. As such, at this time, the LIBS is not recommended to advance to Phase 2 testing as Phase 1 testing failed to indicate consistent detection of the sterilant(s) of focus. No pattern of detection appears to be unique, and there was no relation between response intensity and sample concentration.
- *Gas Chromatography/Thermionic Ionization Detector (GC/TID)*
    - During the Literature Review portion of the project, Vertex understood that it was possible that a field-ready GC/TID device that would be capable of analyzing Phase 1 test samples. After further discussions with SRI Instruments, the supplier of gas chromatographs capable of enabling a GC/TID system for soil sterilant analysis, it was determined that a field-ready GC/TID was not able to be developed at this time.

A summary of the existing, field-ready technologies that showed enough promise to be recommended for subsequent Phase 2 testing (i.e., optimization and refinement) therefore includes the following:

- X-ray fluorescence (XRF): potentially for bromacil in soil samples
- Raman spectroscopy: potentially for bromacil and tebuthiuron in soil and water samples

The objective of the Phase 2 testing would be to attempt to validate, refine, and optimize the technologies. Such testing could include, but may not necessarily be limited to, the following tasks:

- The analysis of real-world samples of Alberta soil and groundwater contaminated with different concentrations of bromacil and tebuthiuron[4], if possible. Ideally, two soil types (coarse-grained and fine-grained), two groundwater or surface water sources, and at least three different concentrations of bromacil and tebuthiuron for each soil and groundwater type would be tested.
- Attempts should be made to identify the source(s) of any identified interference effects that can result in limited application for certain sites.
- Additional dilutions or diluted spiked samples of soil and groundwater should also be tested to quantify the likely lowest reliable detection limits in soil and groundwater for the technologies.
- This stage of the testing should also attempt to improve detection limits using methanol extraction (and possibly concentration) prior to testing.
- Lastly, for technologies that are demonstrated to be successful, formal protocols for their application in field screening of soil and/or groundwater samples for bromacil and/or tebuthiuron, as appropriate, should be developed (i.e., commercial implementation the technology).

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[4] Several real-world samples of Alberta soil and groundwater contaminated with different concentrations of bromacil and tebuthiuron have been provided to Vertex and the analysis of these samples by the promising technologies noted above is currently underway with results pending.

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7.0 ACKNOWLEDGEMENTS

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8.0 LIST OF APPENDICES

Appendix A – Safety Data Sheets

Appendix B – Updated Technology Brochures

Appendix C – Addendum Technology Reports

APPENDIX A: SAFETY DATA SHEETS

SAFETY DATA SHEET
DOW AGROSCIENCES LLC

Product name: SPIKE™ 80DF Herbicide

Issue Date: 05/15/2015
Print Date: 05/26/2015

DOW AGROSCIENCES LLC encourages and expects you to read and understand the entire (M)SDS, as there is important information throughout the document. We expect you to follow the precautions identified in this document unless your use conditions would necessitate other appropriate methods or actions.

1. IDENTIFICATION

Product name: SPIKE™ 80DF Herbicide

Recommended use of the chemical and restrictions on use
Identified uses: End use herbicide product

COMPANY IDENTIFICATION
DOW AGROSCIENCES LLC
9330 ZIONSVILLE RD
INDIANAPOLIS IN 46268-1053
UNITED STATES

Customer Information Number: 800-992-5994
info@dow.com

EMERGENCY TELEPHONE NUMBER
24-Hour Emergency Contact: 800-992-5994
Local Emergency Contact: 352-323-3500

2. HAZARDS IDENTIFICATION

Hazard classification
This material is hazardous under the criteria of the Federal OSHA Hazard Communication Standard 29CFR 1910.1200.
Acute toxicity - Category 4 - Oral
Eye irritation - Category 2A
Carcinogenicity - Category 2
Specific target organ toxicity - repeated exposure - Category 2 - Oral

Label elements
Hazard pictograms

Signal word: **WARNING!**

Hazards
Harmful if swallowed.
Causes serious eye irritation.
Suspected of causing cancer.
May cause damage to organs (Pancreas) through prolonged or repeated exposure if swallowed.

Precautionary statements

Prevention
Obtain special instructions before use.
Do not handle until all safety precautions have been read and understood.
Do not breathe dust/ fume/ gas/ mist/ vapours/ spray.
Wash skin thoroughly after handling.
Do not eat, drink or smoke when using this product.
Wear eye protection/ face protection.
Use personal protective equipment as required.

Response
IF SWALLOWED: Call a POISON CENTER or doctor/ physician if you feel unwell. Rinse mouth.
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
IF exposed or concerned: Get medical advice/ attention.
If eye irritation persists: Get medical advice/ attention.

Storage
Store locked up.

Disposal
Dispose of contents/ container to an approved waste disposal plant.

Other hazards
no data available

3. COMPOSITION/INFORMATION ON INGREDIENTS

This product is a mixture.

Component	CASRN	Concentration
Tebuthiuron	34014-18-1	80.0%
Silica gel, precipitated, crystalline-free	112926-00-8	3.0%
Kaolin	1332-58-7	>= 0.3 - <= 6.9 %
Titanium dioxide	13463-67-7	0.1%
Balance	Not available	>= 10.0 - <= 16.6 %

4. FIRST AID MEASURES

Description of first aid measures
Inhalation: Move person to fresh air. If person is not breathing, call an emergency responder or ambulance, then give artificial respiration; if by mouth to mouth use rescuer protection (pocket mask etc). Call a poison control center or doctor for treatment advice.

Skin contact: Take off contaminated clothing. Rinse skin immediately with plenty of water for 15-20 minutes. Call a poison control center or doctor for treatment advice.

Eye contact: Hold eyes open and rinse slowly and gently with water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eyes. Call a poison control center or doctor for treatment advice.

Ingestion: Call a poison control center or doctor immediately for treatment advice. Have person sip a glass of water if able to swallow. Do not induce vomiting unless told to do so by the poison control center or doctor. Never give anything by mouth to an unconscious person.

Most important symptoms and effects, both acute and delayed: Aside from the information found under Description of first aid measures (above) and Indication of immediate medical attention and special treatment needed (below), any additional important symptoms and effects are described in Section 11: Toxicology Information.

Indication of any immediate medical attention and special treatment needed
Notes to physician: No specific antidote. Treatment of exposure should be directed at the control of symptoms and the clinical condition of the patient.

5. FIREFIGHTING MEASURES

Suitable extinguishing media: Water. Dry chemical fire extinguishers. Carbon dioxide fire extinguishers.

Unsuitable extinguishing media: no data available

Special hazards arising from the substance or mixture
Hazardous combustion products: During a fire, smoke may contain the original material in addition to combustion products of varying composition which may be toxic and/or irritating. Combustion products may include and are not limited to: Nitrogen oxides. Carbon dioxide.

Unusual Fire and Explosion Hazards: Pneumatic conveying and other mechanical handling operations can generate combustible dust. To reduce the potential for dust explosions, do not permit dust to accumulate.

Advice for firefighters
Fire Fighting Procedures: Keep people away. Isolate fire and deny unnecessary entry. Soak thoroughly with water to cool and prevent re-ignition. Cool surroundings with water to localize fire zone. Hand held dry chemical or carbon dioxide extinguishers may be used for small fires. Contain fire water run-off if possible. Fire water run-off, if not contained, may cause environmental damage. Review the “Accidental Release Measures” and the “Ecological Information” sections of this (M)SDS.

Special protective equipment for firefighters: Wear positive-pressure self-contained breathing apparatus (SCBA) and protective fire fighting clothing (includes fire fighting helmet, coat, trousers, boots, and gloves). If protective equipment is not available or not used, fight fire from a protected location or safe distance.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions, protective equipment and emergency procedures: Isolate area. Keep upwind of spill. Spilled material may cause a slipping hazard. Ventilate area of leak or spill. Use appropriate safety equipment. For additional information, refer to Section 8, Exposure Controls and Personal Protection.

Environmental precautions: Prevent from entering into soil, ditches, sewers, waterways and/or groundwater. See Section 12, Ecological Information.

Methods and materials for containment and cleaning up: Contain spilled material if possible. Small spills: Sweep up. Collect in suitable and properly labeled containers. Large spills: Contact Dow AgroSciences for clean-up assistance.

7. HANDLING AND STORAGE

Precautions for safe handling: Keep out of reach of children. Do not swallow. Avoid breathing dust or mist. Avoid contact with eyes, skin, and clothing. Use with adequate ventilation. Wash thoroughly after handling. Keep container closed. Good housekeeping and controlling of dusts are necessary for safe handling of product. See Section 8, EXPOSURE CONTROLS AND PERSONAL PROTECTION.

Conditions for safe storage: Store in a dry place. Store in original container. Do not store near food, foodstuffs, drugs or potable water supplies.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Control parameters

Exposure limits are listed below, if they exist.

Component	Regulation	Type of listing	Value/Notation
Silica gel, precipitated, crystalline-free	OSHA Z-3	TWA Dust	20 Million particles per cubic foot, Silica
	OSHA Z-3	TWA Dust	80 mg/m3 / %SiO2, Silica
Kaolin	ACGIH	TWA Respirable fraction	2 mg/m3
	OSHA Z-1	TWA total dust	15 mg/m3
	OSHA Z-1	TWA respirable fraction	5 mg/m3
Titanium dioxide	OSHA Z-1	TWA total dust	15 mg/m3
	ACGIH	TWA	10 mg/m3 , Titanium dioxide

RECOMMENDATIONS IN THIS SECTION ARE FOR MANUFACTURING, COMMERCIAL BLENDING AND PACKAGING WORKERS. APPLICATORS AND HANDLERS SHOULD SEE THE PRODUCT LABEL FOR PROPER PERSONAL PROTECTIVE EQUIPMENT AND CLOTHING.

Exposure controls
Engineering controls: Use engineering controls to maintain airborne level below exposure limit requirements or guidelines. If there are no applicable exposure limit requirements or guidelines, use only with adequate ventilation. Local exhaust ventilation may be necessary for some operations.

Individual protection measures

Eye/face protection: Use safety glasses (with side shields). If there is a potential for exposure to particles which could cause eye discomfort, wear chemical goggles.

Skin protection

Hand protection: Chemical protective gloves should not be needed when handling this material. Consistent with general hygienic practice for any material, skin contact should be minimized.

Other protection: No precautions other than clean body-covering clothing should be needed.

Respiratory protection: Respiratory protection should be worn when there is a potential to exceed the exposure limit requirements or guidelines. If there are no applicable exposure limit requirements or guidelines, use an approved respirator. Selection of air-purifying or positive-pressure supplied-air will depend on the specific operation and the potential airborne concentration of the material. For emergency conditions, use an approved positive-pressure self-contained breathing apparatus.
The following should be effective types of air-purifying respirators: Organic vapor cartridge with a particulate pre-filter.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance	
Physical state	Granules.
Color	Brown
Odor	Musty
Odor Threshold	No test data available
pH	6.09 1% *pH Electrode*
Melting point/range	No test data available
Freezing point	Not applicable
Boiling point (760 mmHg)	Not applicable
Flash point	**closed cup** Not applicable
Evaporation Rate (Butyl Acetate = 1)	Not applicable
Flammability (solid, gas)	no data available
Lower explosion limit	Not applicable
Upper explosion limit	Not applicable
Vapor Pressure	Not applicable
Relative Vapor Density (air = 1)	Not applicable
Relative Density (water = 1)	Not applicable
Water solubility	No test data available
Partition coefficient: n-octanol/water	no data available
Auto-ignition temperature	Not applicable

Decomposition temperature	No test data available
Dynamic Viscosity	Not applicable
Kinematic Viscosity	no data available
Explosive properties	no data available
Oxidizing properties	no data available
Bulk density	60 g/cm3
Molecular weight	no data available

NOTE: The physical data presented above are typical values and should not be construed as a specification.

10. STABILITY AND REACTIVITY

Reactivity: no data available

Chemical stability: Thermally stable at recommended temperatures and pressures.

Possibility of hazardous reactions: Polymerization will not occur.

Conditions to avoid: Exposure to elevated temperatures can cause product to decompose.

Incompatible materials: no data available

Hazardous decomposition products: Decomposition products depend upon temperature, air supply and the presence of other materials. Decomposition products can include and are not limited to: Nitrogen oxides. Sulfur oxides.

11. TOXICOLOGICAL INFORMATION

Toxicological information appears in this section when such data is available.

Acute toxicity

Acute oral toxicity
Moderate toxicity if swallowed. Small amounts swallowed incidentally as a result of normal handling operations are not likely to cause injury; however, swallowing larger amounts may cause injury.

Single dose oral LD50 has not been determined.
LD50, Rat, > 400 mg/kg Estimated.

Acute dermal toxicity
Prolonged skin contact is unlikely to result in absorption of harmful amounts.

The dermal LD50 has not been determined.
LD50, Rabbit, > 5,000 mg/kg Estimated.

Acute inhalation toxicity
Prolonged excessive exposure to dust may cause adverse effects.

The LC50 has not been determined.
LC50, Rat, 4 Hour, Dust, > 3 mg/l Estimated.

Skin corrosion/irritation
Prolonged exposure not likely to cause significant skin irritation.

Serious eye damage/eye irritation
Solid or dust may cause irritation or corneal injury due to mechanical action.
May cause slight temporary eye irritation.

Sensitization
For the active ingredient(s):
Did not cause allergic skin reactions when tested in guinea pigs.

For respiratory sensitization:
No relevant data found.

Specific Target Organ Systemic Toxicity (Single Exposure)
Evaluation of available data suggests that this material is not an STOT-SE toxicant.

Specific Target Organ Systemic Toxicity (Repeated Exposure)
For the active ingredient(s):
In animals, effects have been reported on the following organs:
Pancreas.
For the minor component(s)
Diatomaceous earth or amorphous silica is considered a nuisance dust and does not cause the lung injury associated with crystalline silica. However, repeated excessive exposures to dust of amorphous silica (which is the main component in this product) may cause potentially reversible lung effects.

Carcinogenicity
For the active ingredient(s): Did not cause cancer in laboratory animals.

Teratogenicity
For the active ingredient(s): Did not cause birth defects or other effects in the fetus even at doses which caused toxic effects in the mother.

Reproductive toxicity
For the active ingredient(s): In animal studies, did not interfere with reproduction.

Mutagenicity
For the active ingredient(s): In vitro genetic toxicity studies were negative in some cases and positive in other cases. Animal genetic toxicity studies were negative.

Aspiration Hazard
Based on physical properties, not likely to be an aspiration hazard.

Carcinogenicity

Component	List	Classification
Titanium dioxide	IARC	Group 2B: Possibly carcinogenic to humans

12. ECOLOGICAL INFORMATION

Ecotoxicological information appears in this section when such data is available.

Toxicity

Tebuthiuron

Acute toxicity to fish
Material is very highly toxic to aquatic organisms on an acute basis (LC50/EC50 <0.1 mg/L in the most sensitive species).
Material is very toxic to aquatic organisms (LC50/EC50/IC50 below 1 mg/L in the most sensitive species).
LC50, Lepomis macrochirus (Bluegill sunfish), static test, 96 Hour, 106 mg/l
LC50, Danio rerio (zebra fish), 96 Hour, 31.07 mg/l

Acute toxicity to aquatic invertebrates
EC50, Daphnia magna (Water flea), semi-static test, 48 Hour, > 100 mg/l
EC50, pink shrimp (Penaeus duorarum), static test, 48 Hour, 62 mg/l

Acute toxicity to algae/aquatic plants
ErC50, Pseudokirchneriella subcapitata (green algae), 72 Hour, > 0.1 mg/l
EC50, diatom Navicula sp., 7 d, 0.213 mg/l
EC50, Skeletonema costatum, 7 d, 0.01 mg/l
EC50, Lemna gibba, 14 Hour, 0.235 mg/l

Chronic toxicity to fish
NOEC, Pimephales promelas (fathead minnow), flow-through test, 33 d, growth, 9.3 mg/l
NOEC, Oncorhynchus mykiss (rainbow trout), flow-through test, 45 d, survival, 26 mg/l

Chronic toxicity to aquatic invertebrates
Daphnia magna (Water flea), semi-static test, 21 d, number of offspring, 21.8 mg/l

Toxicity to Above Ground Organisms
Material is slightly toxic to birds on a dietary basis (LC50 between 1001 and 5000 ppm).
Material is practically non-toxic to birds on an acute basis (LD50 > 2000 mg/kg).
dietary LC50, Anas platyrhynchos (Mallard duck), 8 d, > 5093mg/kg diet.
oral LD50, Anas platyrhynchos (Mallard duck), > 2000mg/kg bodyweight.
dietary LC50, Taeniopygia guttata (Zebra Finch), 8 d, 1636mg/kg diet.
oral LD50, Apis mellifera (bees), > 100µg/bee
contact LD50, Apis mellifera (bees), 48 Hour, > 100µg/bee

Silica gel, precipitated, crystalline-free

Acute toxicity to fish
Material is practically non-toxic to aquatic organisms on an acute basis (LC50/EC50/EL50/LL50 >100 mg/L in the most sensitive species tested).
LC50, Danio rerio (zebra fish), Static, 96 Hour, 5,000 - 10,000 mg/l

Acute toxicity to aquatic invertebrates
EC50, Daphnia magna (Water flea), Static, 24 Hour, > 10,000 mg/l, OECD Test Guideline 202

Acute toxicity to algae/aquatic plants
EC50, Pseudokirchneriella subcapitata (green algae), 72 Hour, Biomass, 440 mg/l

Kaolin

Acute toxicity to fish
Not expected to be acutely toxic to aquatic organisms.

Titanium dioxide

Acute toxicity to fish
Material is practically non-toxic to aquatic organisms on an acute basis
(LC50/EC50/EL50/LL50 >100 mg/L in the most sensitive species tested).
NOEC mortality, Leuciscus idus (Golden orfe), static test, 48 Hour, > 1,000 mg/l

Acute toxicity to aquatic invertebrates
EC50, Daphnia magna (Water flea), static test, 48 Hour, > 1,000 mg/l

Balance

Acute toxicity to fish
No relevant data found.

Persistence and degradability

Tebuthiuron

Biodegradability: Material is not readily biodegradable according to OECD/EEC guidelines.

Theoretical Oxygen Demand: 2.66 mg/mg

Stability in Water (1/2-life)
, > 64 d, pH 3 - 9

Photodegradation
Test Type: Half-life (indirect photolysis)
Sensitizer: OH radicals
Atmospheric half-life: 3.225 d
Method: Estimated.

Silica gel, precipitated, crystalline-free

Biodegradability: Biodegradation is not applicable.

Kaolin

Biodegradability: Biodegradation is not applicable.

Titanium dioxide

Biodegradability: Biodegradation is not applicable.

Balance

Biodegradability: No relevant data found.

Bioaccumulative potential

Tebuthiuron

Bioaccumulation: Bioconcentration potential is low (BCF < 100 or Log Pow < 3).
Partition coefficient: n-octanol/water(log Pow): 1.83 Measured
Bioconcentration factor (BCF): 1.98 - 3.4 Lepomis macrochirus (Bluegill sunfish) Measured

Silica gel, precipitated, crystalline-free

Bioaccumulation: Partitioning from water to n-octanol is not applicable.

Kaolin

Bioaccumulation: Partitioning from water to n-octanol is not applicable.

Titanium dioxide

Bioaccumulation: Partitioning from water to n-octanol is not applicable.

Balance

Bioaccumulation: No relevant data found.

Mobility in soil

Tebuthiuron

Potential for mobility in soil is very high (Koc between 0 and 50).
Partition coefficient(Koc): 27

Silica gel, precipitated, crystalline-free

No relevant data found.

Kaolin

No relevant data found.

Titanium dioxide

No data available.

Balance

No relevant data found.

13. DISPOSAL CONSIDERATIONS

Disposal methods: If wastes and/or containers cannot be disposed of according to the product label directions, disposal of this material must be in accordance with your local or area regulatory authorities. This information presented below only applies to the material as supplied. The identification based on characteristic(s) or listing may not apply if the material has been used or otherwise contaminated. It is the responsibility of the waste generator to determine the toxicity and physical properties of the material generated to determine the proper waste identification and disposal methods in compliance with applicable regulations. If the material as supplied becomes a waste, follow all applicable regional, national and local laws.

14. TRANSPORT INFORMATION

DOT

Not regulated for transport

Classification for SEA transport (IMO-IMDG):

Proper shipping name	ENVIRONMENTALLY HAZARDOUS SUBSTANCE, SOLID, N.O.S.(Tebuthiuron)
UN number	UN 3077

Class	9
Packing group	III
Marine pollutant	Tebuthiuron
Transport in bulk according to Annex I or II of MARPOL 73/78 and the IBC or IGC Code	Consult IMO regulations before transporting ocean bulk

Classification for AIR transport (IATA/ICAO):

Proper shipping name	Environmentally hazardous substance, solid, n.o.s.(Tebuthiuron)
UN number	UN 3077
Class	9
Packing group	III

This information is not intended to convey all specific regulatory or operational requirements/information relating to this product. Transportation classifications may vary by container volume and may be influenced by regional or country variations in regulations. Additional transportation system information can be obtained through an authorized sales or customer service representative. It is the responsibility of the transporting organization to follow all applicable laws, regulations and rules relating to the transportation of the material.

15. REGULATORY INFORMATION

OSHA Hazard Communication Standard
This product is a “Hazardous Chemical” as defined by the OSHA Hazard Communication Standard, 29 CFR 1910.1200.

Superfund Amendments and Reauthorization Act of 1986 Title III (Emergency Planning and Community Right-to-Know Act of 1986) Sections 311 and 312
Acute Health Hazard
Chronic Health Hazard

Superfund Amendments and Reauthorization Act of 1986 Title III (Emergency Planning and Community Right-to-Know Act of 1986) Section 313

Components	**CASRN**
Tebuthiuron	34014-18-1

Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) Section 103
To the best of our knowledge, this product does not contain chemicals at levels which require reporting under this statute.

California Proposition 65 (Safe Drinking Water and Toxic Enforcement Act of 1986)
This product contains no listed substances known to the State of California to cause cancer, birth defects or other reproductive harm, at levels which would require a warning under the statute.

Pennsylvania (Worker and Community Right-To-KnowAct): Pennsylvania Hazardous Substances List and/or Pennsylvania Environmental Hazardous Substance List:

The following product components are cited in the Pennsylvania Hazardous Substance List and/or the Pennsylvania Environmental Substance List, and are present at levels which require reporting.

Components	**CASRN**
Silica gel, precipitated, crystalline-free	112926-00-8
Kaolin	1332-58-7

Pennsylvania (Worker and Community Right-To-KnowAct): Pennsylvania Special Hazardous Substances List:
To the best of our knowledge, this product does not contain chemicals at levels which require reporting under this statute.

United States TSCA Inventory (TSCA)
This product contains chemical substance(s) exempt from U.S. EPA TSCA Inventory requirements. It is regulated as a pesticide subject to Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) requirements.

Federal Insecticide, Fungicide and Rodenticide Act
EPA Registration Number: 62719-107
This chemical is a pesticide product registered by the Environmental Protection Agency and is subject to certain labeling requirements under federal pesticide law. These requirements differ from the classification criteria and hazard information required for safety data sheets, and for workplace labels of non-pesticide chemicals. Following is the hazard information as required on the pesticide label:

CAUTION

Harmful if swallowed, inhaled or absorbed through the skin.
Causes eye irritation.

16. OTHER INFORMATION

Hazard Rating System
NFPA

Health	Fire	Reactivity
2	0	0

Revision
Identification Number: 101202930 / A211 / Issue Date: 05/15/2015 / Version: 3.0
DAS Code: NAF-508
Most recent revision(s) are noted by the bold, double bars in left-hand margin throughout this document.

Legend

ACGIH	USA. ACGIH Threshold Limit Values (TLV)
OSHA Z-1	USA. Occupational Exposure Limits (OSHA) - Table Z-1 Limits for Air Contaminants
OSHA Z-3	USA. Occupational Exposure Limits (OSHA) - Table Z-3 Mineral Dusts
TWA	8-hour, time-weighted average

Information Source and References

This SDS is prepared by Product Regulatory Services and Hazard Communications Groups from information supplied by internal references within our company.

DOW AGROSCIENCES LLC urges each customer or recipient of this (M)SDS to study it carefully and consult appropriate expertise, as necessary or appropriate, to become aware of and understand the data contained in this (M)SDS and any hazards associated with the product. The information herein is provided in good faith and believed to be accurate as of the effective date shown above. However, no warranty, express or implied, is given. Regulatory requirements are subject to change and may differ between various locations. It is the buyer's/user's responsibility to ensure that his activities comply with all federal, state, provincial or local laws. The information presented here pertains only to the product as shipped. Since conditions for use of the product are not under the control of the manufacturer, it is the buyer's/user's duty to determine the conditions necessary for the safe use of this product. Due to the proliferation of sources for information such as manufacturer-specific (M)SDSs, we are not and cannot be responsible for (M)SDSs obtained from any source other than ourselves. If you have obtained an (M)SDS from another source or if you are not sure that the (M)SDS you have is current, please contact us for the most current version.

Safety Data Sheet

DuPont™ Hyvar® X-L Herbicide

Version 2.0

Revision Date 07/14/2015 Ref. 130000023989

This SDS adheres to the standards and regulatory requirements of the United States and may not meet the regulatory requirements in other countries.

SECTION 1. PRODUCT AND COMPANY IDENTIFICATION

Product name	:	DuPont™ Hyvar® X-L Herbicide
Tradename/Synonym	:	HYVAR® XL Bromacil: (5-bromo-3-sec-butyl-6-methyluracil) Lithium Salt of Bromacil: 5-Bromo-3-sec-butyl-6-methylpyrimidine-2,4(1H,3H)-dione, lithium salt
Product Use	:	Herbicide
Restrictions on use	:	Do not use product for anything outside of the above specified uses
Manufacturer/Supplier	:	DuPont 4417 Lancaster Pike Wilmington, DE 19805, USA
Product Information	:	1-800-441-7515 (outside the U.S. 1-302-774-1000)
Medical Emergency	:	1-800-441-3637 (outside the U.S. 1-302-774-1139)
Transport Emergency	:	CHEMTREC: +1-800-424-9300 (outside the U.S. +1-703-527-3887)

SECTION 2. HAZARDS IDENTIFICATION

Product hazard category

Flammable liquids	Category 3
Acute toxicity (Oral)	Category 4
Acute toxicity (Inhalation)	Category 4
Serious eye damage/eye irritation	Category 2B
Specific target organ toxicity - single exposure	Category 1
Specific target organ toxicity - single exposure	Category 3
Specific target organ toxicity - repeated exposure	Category 2

Label content

Pictogram :

Signal word : Danger

Hazardous warnings : Flammable liquid and vapour.
Harmful if swallowed or if inhaled
Causes eye irritation.
May cause respiratory irritation.
May cause drowsiness or dizziness.
Causes damage to organs. (Central nervous system, Eyes)
May cause damage to organs through prolonged or repeated exposure. (Kidney)

Hazardous prevention measures : Keep away from heat/sparks/open flames/hot surfaces. No smoking.
Keep container tightly closed.
Ground/bond container and receiving equipment.
Use explosion-proof electrical/ ventilating/ lighting/ equipment.
Use only non-sparking tools.
Take precautionary measures against static discharge.
Do not breathe dust/ fume/ gas/ mist/ vapours/ spray.
Wash skin thoroughly after handling.
Do not eat, drink or smoke when using this product.
Use only outdoors or in a well-ventilated area.
Wear protective gloves/ eye protection/ face protection.
IF SWALLOWED: Call a POISON CENTER or doctor/ physician if you feel unwell.
IF ON SKIN (or hair): Remove/ Take off immediately all contaminated clothing. Rinse skin with water/ shower.
IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
IF exposed: Call a POISON CENTER or doctor/ physician.
Rinse mouth.
If eye irritation persists: Get medical advice/ attention.
In case of fire: Use dry sand, dry chemical or alcohol-resistant foam for extinction.
Store in a well-ventilated place. Keep container tightly closed.
Store in a well-ventilated place. Keep cool.
Store locked up.
Dispose of contents/ container to an approved waste disposal plant.

Other hazards
No applicable data available.

SECTION 3. COMPOSITION/INFORMATION ON INGREDIENTS

Component	CAS-No.	Concentration

Bromacil lithium salt	53404-19-6	21.9 %
Ethane-1,2-diol	107-21-1	30 - 35 %
Methanol	67-56-1	1 - 5 %
Hydroxide Salt		1 - 5 %
Ethanol	64-17-5	5 - 10 %
Other Ingredients		23.1 - 41.1 %

Acid Equivalent

Bromacil	314-40-9	21.4 %

The specific chemical identity and/or exact percentage (concentration) of composition has been withheld as a trade secret.

SECTION 4. FIRST AID MEASURES

General advice : Have the product container or label with you when calling a poison control center or doctor, or going for treatment. For medical emergencies involving this product, call toll free 1-800-441-3637. See Label for Additional Precautions and Directions for Use.

Inhalation : Move to fresh air. If person is not breathing, call 911 or an ambulance, then give artificial respiration, preferably mouth-to-mouth, if possible. Call a poison control center or doctor for treatment advice.

Skin contact	:	Take off all contaminated clothing immediately. Rinse skin immediately with plenty of water for 15-20 minutes. Call a poison control center or doctor for treatment advice.
Eye contact	:	Hold eye open and rinse slowly and gently with water for 15-20 minutes. Remove contact lenses, if present, after the first 5 minutes, then continue rinsing eye. Call a poison control center or doctor for treatment advice.
Ingestion	:	Call a poison control center or doctor for treatment advice. Have person sip a glass of water if able to swallow. DO NOT induce vomiting unless directed to do so by a physician or poison control center. Do not give anything by mouth to an unconscious person.
Most important symptoms/effects, acute and delayed	:	No applicable data available.
Protection of first-aiders	:	No applicable data available.
Notes to physician	:	No applicable data available.

SECTION 5. FIREFIGHTING MEASURES

Suitable extinguishing media	:	Water spray, Dry chemical, Foam, Carbon dioxide (CO2)
Unsuitable extinguishing media	:	No applicable data available.
Specific hazards	:	No applicable data available.
Special protective equipment for firefighters	:	Wear full protective clothing and self-contained breathing apparatus.
Further information	:	Do not allow run-off from fire fighting to enter drains or water courses. Runoff from fire control may be a pollution hazard. Control Runoff. (on small fires) If area is heavily exposed to fire and if conditions permit, let fire burn itself out since water may increase the area contaminated. Cool containers/tanks with water spray.

SECTION 6. ACCIDENTAL RELEASE MEASURES

NOTE: Review FIRE FIGHTING MEASURES and HANDLING (PERSONNEL) sections before proceeding with clean-up. Use appropriate PERSONAL PROTECTIVE EQUIPMENT during clean-up.

Safeguards (Personnel)	:	Evacuate personnel, thoroughly ventilate area, use self-contained breathing apparatus. Use personal protective equipment.
Environmental precautions	:	Prevent material from entering sewers, waterways, or low areas.
Spill Cleanup	:	Dike spill. If spill area is on ground near valuable plants or trees, remove top 2 inches of soil after initial cleanup. Sweep up and shovel into suitable containers for disposal.
Accidental Release Measures	:	Never return spills in original containers for re-use. Dispose of in accordance with local regulations.

SECTION 7. HANDLING AND STORAGE

Handling (Personnel)	:	Do not use or store near heat or open flame. Wash hands thoroughly with soap and water after handling and before eating, drinking, chewing gum, using tobacco, or using the toilet. Remove clothing/PPE immediately if material gets inside. Wash thoroughly and put on clean clothing. Wash the outside of gloves before removing. As soon as possible, wash thoroughly and change into clean clothing.
Handling (Physical Aspects)	:	Combustible Keep away from heat and sources of ignition.
Dust explosion class	:	No applicable data available.
Storage	:	Store in original container. Do not contaminate water, other pesticides, fertilizer, food or feed in storage. Keep containers tightly closed in a dry, cool and well-ventilated place. Keep out of the reach of children.
Storage period	:	No applicable data available.
Storage temperature	:	No applicable data available.

SECTION 8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls : Use only with adequate ventilation. Keep container tightly closed. When handlers use closed systems, enclosed cabs, or aircraft in a manner that meets the requirements listed in the Worker Protection Standard (WPS) for agricultural pesticides [40 CFR 170.240 (d)(4-6)], the handler PPE requirements may be reduced or modified as specified in the WPS.

Personal protective equipment

Skin and body protection : Applicators and other handlers must wear:
Long sleeved shirt and long pants
Shoes plus socks
Chemical-resistant gloves

Protective measures : Discard clothing and other absorbent materials that have been drenched or heavily contaminated with this product. Do not reuse them. Follow manufacturer's instructions for cleaning/maintaining PPE. If no such instructions for washables exist, use detergent and hot water. Keep and wash PPE separately from other laundry.

Exposure Guidelines

Exposure Limit Values

Bromacil

TLV	(ACGIH)	10 mg/m3	TWA
AEL *	(DUPONT)	10 mg/m3	8 & 12 hr. TWA

Ethane-1,2-diol

TLV	(ACGIH)	100 mg/m3	TLV-C	Aerosol.
AEL *	(DUPONT)	10 mg/m3	8 & 12 hr. TWA	Particulate.
AEL *	(DUPONT)	50 ppm	8 & 12 hr. TWA	Vapor.

Methanol

Permissible exposure limit:	(OSHA)	200 ppm	260 mg/m3	8 hr. TWA
TLV	(ACGIH)	200 ppm	TWA	
TLV	(ACGIH)	250 ppm	STEL	
AEL *	(DUPONT)	200 ppm	8 & 12 hr. TWA, Skin	

Hydroxide Salt

AEL *	(DUPONT)	1 mg/m3	8 & 12 hr. TWA Lithium

Ethanol

Permissible exposure limit:	(OSHA)	1,000 ppm	1,900 mg/m3	8 hr. TWA
TLV	(ACGIH)	1,000 ppm	STEL	
AEL *	(DUPONT)	1,000 ppm	8 & 12 hr. TWA	

Bromacil lithium salt

No applicable data available.

Other Ingredients

No applicable data available.

Biological Exposure Indices

Methanol

BEI	(ACGIH)	15 mg/l Methanol/Urine Sampling time: End of shift.

* AEL is DuPont's Acceptable Exposure Limit. Where governmentally imposed occupational exposure limits which are lower than the AEL are in effect, such limits shall take precedence.

SECTION 9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance		
Physical state	:	liquid
Form	:	liquid
Color	:	amber
Odor	:	alcohol-like
Odor threshold	:	No applicable data available.
pH	:	11.2 - 12.2
Melting point/range	:	No applicable data available.

Boiling point/boiling range	:	No applicable data available.
Flash point	:	44 °C Method: Setaflash closed cup - SCC
Evaporation rate	:	No applicable data available.
Flammability (solid, gas)	:	No applicable data available.
Upper explosion limit	:	No applicable data available.
Lower explosion limit	:	No applicable data available.
Vapour Pressure	:	No applicable data available.
Vapour density	:	No applicable data available.
Specific gravity (Relative density)	:	No applicable data available.
Water solubility	:	soluble
Solubility(ies)	:	No applicable data available.
Partition coefficient: n-octanol/water	:	No applicable data available.
Auto-ignition temperature	:	410 °C
Decomposition temperature	:	No applicable data available.
Viscosity, kinematic	:	No applicable data available.
Viscosity, dynamic	:	No applicable data available.

SECTION 10. STABILITY AND REACTIVITY

Reactivity	:	No applicable data available.
Chemical stability	:	Stable at normal temperatures and storage conditions.
Possibility of hazardous reactions	:	Heating can release vapours which can be ignited. Polymerization will not occur.
Conditions to avoid	:	Heat, flames and sparks.

Incompatible materials	:	Incompatible with acids. Amines
Hazardous decomposition products	:	Carbon oxides, Decomposes with heat.

SECTION 11. TOXICOLOGICAL INFORMATION

DuPont™ Hyvar® X-L Herbicide

Inhalation 4 h LC50	:	> 2.0 mg/l , Rat
Dermal LD50	:	> 5,000 mg/kg , Rat
Oral LD50	:	3,927 mg/kg , male, Rat
Oral LD50	:	1,414 mg/kg , female, Rat
Skin irritation	:	No skin irritation, Rabbit Minimal effects that do not meet the threshold for classification.
Eye irritation	:	Mild eye irritation, Rabbit
Sensitisation	:	Did not cause sensitisation on laboratory animals., Guinea pig

Ethane-1,2-diol

Repeated dose toxicity	:	Oral Rat - Target Organs: Kidney Kidney damage
Carcinogenicity	:	Not classifiable as a human carcinogen. Animal testing did not show any carcinogenic effects.
Mutagenicity	:	Animal testing did not show any mutagenic effects. Tests on bacterial or mammalian cell cultures did not show mutagenic effects.
Reproductive toxicity	:	No toxicity to reproduction No effects on or via lactation Animal testing showed no reproductive toxicity.
Teratogenicity	:	Evidence suggests the substance is not a developmental toxin in animals.

Methanol

Carcinogenicity	:	Not classifiable as a human carcinogen. Overall weight of evidence indicates that the substance is not carcinogenic.
Mutagenicity	:	Animal testing did not show any mutagenic effects. Tests on bacterial or mammalian cell cultures did not show mutagenic effects. Overall weight of evidence indicates that the substance is not mutagenic. Did not cause genetic damage in animals. Genetic damage in cultured mammalian cells was observed in some laboratory tests but not in others. Genetic damage in cultured bacterial cells was observed in some laboratory tests but not in others.
Reproductive toxicity	:	No toxicity to reproduction Evidence suggests the substance is not a reproductive toxin in animals.
Teratogenicity	:	Evidence suggests the substance is not a developmental toxin in animals.

Ethanol

Repeated dose toxicity	:	Oral Rat - No toxicologically significant effects were found. Inhalation Rat - No toxicologically significant effects were found.
Carcinogenicity	:	Not classifiable as a human carcinogen. Overall weight of evidence indicates that the substance is not carcinogenic.
Mutagenicity	:	Animal testing did not show any mutagenic effects. Tests on bacterial or mammalian cell cultures did not show mutagenic effects.
Reproductive toxicity	:	No toxicity to reproduction

Animal testing showed effects on reproduction at levels equal to or above those causing parental toxicity.

Teratogenicity : Animal testing showed effects on embryo-fetal development at levels equal to or above those causing maternal toxicity.

Bromacil

Repeated dose toxicity :

The following effects occurred at levels of exposure that significantly exceed those expected under labeled usage conditions.

Oral
Rat
-
Liver effects, Organ weight changes, Thyroid effects, Reduced body weight gain

Inhalation
Rat
-
Increased liver weight, altered blood chemistry

Carcinogenicity : Not classifiable as a human carcinogen.
The following effects occurred at levels of exposure that significantly exceed those expected under labeled usage conditions.
An increased incidence of tumours was observed in laboratory animals.

Mutagenicity : Weight of evidence does not support classification as a germ cell mutagen.

Reproductive toxicity : No toxicity to reproduction
Animal testing showed no reproductive toxicity.

Teratogenicity : Animal testing showed effects on embryo-fetal development at levels equal to or above those causing maternal toxicity.

Carcinogenicity

The carcinogenicity classifications for this product and/or its ingredients have been determined according to HazCom 2012, Appendix A.6. The classifications may differ from those listed in the National Toxicology Program (NTP) Report on Carcinogens (latest edition) or those found to be a potential carcinogen in the International Agency for Research on Cancer (IARC) Monographs (latest edition).

None of the components present in this material at concentrations equal to or greater than 0.1% are listed by IARC, NTP, or OSHA, as a carcinogen.

SECTION 12. ECOLOGICAL INFORMATION

Aquatic Toxicity

Ethane-1,2-diol

96 h LC50	:	Pimephales promelas (fathead minnow) 72,860 mg/l
96 h ErC50	:	Pseudokirchneriella subcapitata (green algae) 6,500 mg/l
48 h EC50	:	Daphnia magna (Water flea) > 100 mg/l OECD Test Guideline 202

Methanol

96 h LC50	:	Pimephales promelas (fathead minnow) 28,100 mg/l
96 h LC50	:	Selenastrum capricornutum (green algae) 22,000 mg/l
48 h EC50	:	Daphnia (water flea) > 10,000 mg/l

Ethanol

96 h LC50	:	Pimephales promelas (fathead minnow) 14,200 mg/l
96 h ErC50	:	Pseudokirchneriella subcapitata (green algae) 675 mg/l OECD Test Guideline 201
48 h EC50	:	Daphnia magna (Water flea) 5,012 mg/l
30 d	:	NOEC Fish (unspecified species) 245 mg/l

Bromacil

96 h LC50	:	Lepomis macrochirus (Bluegill sunfish) 127 mg/l
96 h LC50	:	Oncorhynchus mykiss (rainbow trout) 36 mg/l
72 h ErC50	:	Pseudokirchneriella subcapitata (green algae) 0.017 mg/l
NOEC	:	Algae 0.001 mg/l
48 h EC50	:	Daphnia magna (Water flea) 119 mg/l

Environmental Fate

Ethane-1,2-diol

Biodegradability	:	Readily biodegradable 90 - 100 % OECD Test Guideline 301
Bioaccumulation	:	Bioaccumulation is unlikely.

Methanol

Biodegradability	:	Readily biodegradable
Bioaccumulation	:	Bioaccumulation is unlikely.
Additional ecological information	:	Do not apply directly to water, or to areas where surface water is present, or to intertidal areas below the mean high water mark. Do not contaminate water when cleaning equipment or disposing of equipment washwaters or rinsate.

SECTION 13. DISPOSAL CONSIDERATIONS

Waste disposal methods - Product	:	Do not contaminate water, food or feed by disposal. Wastes resulting from the use of this product must be disposed of on site or at an approved waste disposal facility.
Waste disposal methods - Container	:	Container Refilling and Disposal: Refer to the product label for instructions. Do not transport if this container is damaged or leaking. In the event of a major spill, fire or other emergency, call 1-800-441-3637 day or night.
Contaminated packaging	:	No applicable data available.

SECTION 14. TRANSPORT INFORMATION

DOT	UN number	:	1993
	Proper shipping name	:	Flammable liquids, n.o.s. (Ethanol, Methanol)
	Class	:	3
	Packing group	:	III
	Labelling No.	:	3
IATA_C	UN number	:	1993

	Proper shipping name	:	Flammable liquid, n.o.s. (Ethanol, Methanol)
	Class	:	3
	Packing group	:	III
	Labelling No.	:	3
IMDG	UN number	:	1993
	Proper shipping name	:	FLAMMABLE LIQUID, N.O.S. (Ethanol, Methanol)
	Class	:	3
	Packing group	:	III
	Labelling No.	:	3
	Marine pollutant	:	yes (Bromacil)

Note: Shipper may use the DOT provision found in 49 CFR, 173.120(b)(2) and transport as "Not Transport Regulated" by DOT for U.S. domestic transportation in non-bulk packages.

SECTION 15. REGULATORY INFORMATION

Other regulations	:	This Safety Data Sheet is for a pesticide product registered by the US Environmental Protection Agency (USEPA) and is therefore also subject to certain labeling requirements under US pesticide law (FIFRA). These requirements differ from the classification criteria and hazard information required by OSHA for safety data sheets, and for workplace labels of non-pesticide chemicals. The following is the mandatory hazard information required by USEPA on the pesticide label: CAUTION! Harmful if swallowed or absorbed through the skin . Causes moderate eye irritation. Avoid contact with skin, eyes and clothing.
SARA 313 Regulated Chemical(s)	:	Bromacil, Methanol , Ethylene Glycol
PA Right to Know Regulated Chemical(s)	:	Substances on the Pennsylvania Hazardous Substances List present at a concentration of 1% or more (0.01% for Special Hazardous Substances): Bromacil, Ethanol, Methanol, Ethylene Glycol
Title III hazard classification	:	Acute Health Hazard: Yes Chronic Health Hazard: Yes

Fire: Yes
Reactivity/Physical hazard: Yes
Pressure: Yes

EPA Reg. No. : 352-346
In the United States this product is regulated by the US Environmental Protection Agency (EPA) under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). It is a violation of Federal law to use this product in a manner inconsistent with its labeling. Read and follow all label directions. This product is excluded from listing requirements under EPA/TSCA.

California Prop. 65 : Developmental toxin.Male reproductive toxin.Bromacil lithium salt

SECTION 16. OTHER INFORMATION

		NFPA
Health	:	1
Flammability	:	2
Reactivity/Physical hazard	:	0

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Revision Date : 07/14/2015

Contact person : DuPont Crop Protection, Wilmington, DE, 19898, Phone: 1-888-638-7668

The information provided in this Safety Data Sheet is correct to the best of our knowledge, information and belief at the date of its publication. The information given is designed only as a guidance for safe handling, use, processing, storage, transportation, disposal and release and is not to be considered a warranty or quality specification. The information relates only to the specific material designated and may not be valid for such material used in combination with any other materials or in any process, unless specified in the text.

Significant change from previous version is denoted with a double bar.

SAFETY DATA SHEET

EMERGENCY CALL: 1-800-424-9300 (CHEMTREC)

1. IDENTIFICATION

PRODUCT NAME: Bromacil 80
DESCRIPTION: A granular herbicide.
EPA Reg. No.: 81927-4

COMPANY IDENTIFICATION:
Alligare, LLC
13 N. 8th Street
Opelika, AL 36801

2. HAZARD IDENTIFICATION

WARNING

Harmful if swallowed (H302)

Causes eye irritation (H320)

May be harmful in contact with skin (H313)

Very toxic to aquatic life with long lasting effects (H410)

HAZARD CLASSIFICATION

Health Hazard	Category
Eye Damage / Irritation	2B
Acute Toxicity, Oral	4
Acute Toxicity, Dermal	5

Physical Hazards	Category
None	

Environmental Hazards	Category
Hazardous to the aquatic environment, chronic	1

PRECAUTIONARY STATEMENTS

Wash hands thoroughly after handling. Do not eat, drink or smoke when using this product. (P264+P270)

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. If eye irritation persists: Get medical advice/attention. (P305+P351+P338+P337+P313)

IF SWALLOWED: Call a poison control center or doctor if you feel unwell. Rinse mouth. (P301+P312+P330)

IF ON SKIN: Call a Poison Control Center or doctor if you feel unwell. (P302+P312)

Avoid release to the environment. Collect spillage. (P273 +P391)

Dispose of contents / container in accordance with local regulations. Refer to the product label for specific disposal instructions. (P501)

3. COMPOSITION / INFORMATION ON INGREDIENTS

Common Name	Chemical Name	CAS #	Composition
Bromacil	5-bromo-3-*sec*-butyl-6-methyluracil	314-40-9	80.0%

4. FIRST AID MEASURES

Have the product container or label with you when calling a poison control center or doctor or going for treatment. You may also contact CHEMTREC at 1-800-424-9300 for emergency medical information.

IF SWALLOWED: Immediately call a poison control center or doctor. Rinse mouth and have person sip a glass of water if able to swallow. Do not induce vomiting unless told to do so by a poison control center or doctor. Do not give anything by mouth to an unconscious person.

IF ON SKIN OR CLOTHING: Take off contaminated clothing and wash before reuse. Rinse skin immediately with plenty of water. If skin irritation or rash occurs: call a poison control center or doctor for treatment advice.

IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. If eye irritation persists, get medical advice/attention.

5. FIREFIGHTING MEASURES

Flash Point (PMCC): Not flammable

Flammable Limits (LFL-UFL): Not Determined

Fire and Explosion Hazards: Thermal decomposition will release irritating gases and fumes (see Section 10).

Extinguishing Medium: Foam, CO_2, dry chemical or water mist. To avoid environmental contamination do not use high pressure water jet and, if conditions permit, allow fire to burn itself out.

Fire Fighting Equipment: Firefighters should be equipped with self-contained positive pressure breathing apparatus and full bunker gear.

Fire Fighting Instructions: Evacuate area of all unnecessary personnel and fight fire from a safe distance upwind. Contain contaminated water / firefighting water; do not allow to enter drains or waterways. Foam or dry chemical fire extinguishing systems are preferred to prevent environmental damage from excessive water runoff.

NFPA Ratings: Health – 1 / Flammability – 1 / Reactivity - 0

6. ACCIDENTAL RELEASE MEASURES

Clean up spills immediately observing the precautions in Section 8 of this SDS. Isolate the hazard area and keep unnecessary and unprotected personnel from entering. In case of spill on floor or paved surfaces, shovel or sweep up and remove to chemical waste storage area until proper disposal can be made if product cannot be used according to label. Prevent material from contaminating soil or from entering sewage and drainage systems and bodies of water. If spill area is on ground near valuable plants or trees, remove the top two inches of soil after initial cleanup.

7. HANDLING AND STORAGE

Avoid contact with skin, eyes or clothing. In case of contact, immediately remove contaminated clothing and shoes. Wash contaminated clothing with soap and hot water before re-use. Wash thoroughly with soap and water after handling and before eating, drinking, chewing gum, using tobacco or using the toilet.

Do not apply directly to water, or to areas where surface water is present, or to intertidal areas below the mean high water mark. Do not contaminate water when cleaning equipment or disposing of equipment washwaters.

Store out of direct sunlight in original container only. Do not store near food or feed.

8. EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering Controls: Facilities storing or utilizing this material should be equipped with an eyewash station and a safety shower.

Protective Clothing: Applicators and other handlers must wear long-sleeved shirt and long pants, chemical resistant gloves made of any waterproof material such as polyethylene or polyvinylchloride (PVC), and shoes plus socks. In addition to the above, mixers and loaders must wear a non-powered air purifying respirator equipped with an N, R, P or HE series filter (NIOSH approved number prefix 84A). Some materials that are chemical resistant to this product are made of any waterproof material. If you want more options, follow the instructions for category A on an EPA chemical resistance category selection chart.

General: Discard clothing or other absorbent materials that have been drenched or heavily contaminated with this product's concentrate. Do not reuse them. Follow manufacturer's instructions for cleaning/maintaining PPE. If no such instructions for washables exist, use detergent and hot water. Keep and wash PPE separately from other laundry.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance:	Brown granules	**pH:**	7.0-10.0
Odor:	Faint	**Kinematic viscosity:**	not available
Melting/freezing point:	not available	**Solubility:**	in water, miscible
Boiling point/Boiling range:	not available	**Partition coefficient:**	not available
Flammability:	not available	**Vapor pressure:**	not available
Flammability limits (upper/lower):	not available	**Density:**	0.53 g/cm^3
Flash point:	not flammable	**Relative vapor density:**	not available
Auto-ignition temperature:	not available	**Particle characteristics:**	not available
Decomposition temperature:	not available		

10. STABILITY AND REACTIVITY

CONDITIONS TO AVOID: None known.

CHEMICAL STABILITY: Stable under all normal use and storage conditions.

HAZARDOUS DECOMPOSITION PRODUCTS: None when stored and handled as prescribed. Thermal decomposition may release oxides of carbon and nitrogen as well as bromine compounds.

INCOMPATIBILITY WITH OTHER MATERIALS: Oxidizers, strong acids and bases.

POLYMERIZATION: Will not occur.

11. TOXICOLOGICAL INFORMATION

ORAL TOXICITY (rat LD_{50}): 1,723 mg/kg

DERMAL TOXICITY (rat LD_{50}): > 2,000 mg/kg

INHALATION TOXICITY (rat LC_{50}): > 5.09 mg/L (4-hour)

EYE IRRITATION: Mildly irritating

SKIN IRRITATION: Mildly irritating

SKIN SENSITIZATION: Not a contact sensitizer

CARCINOGENICITY:

EPA:	Not Listed		
ACGIH:	Not Listed	**NTP:**	Not Listed
IARC:	Not Listed	**OSHA:**	Not Listed

MUTAGENIC TOXICITY: No evidence of mutagenic effects during *in vivo* and *in vitro* assays.

REPRODUCTIVE TOXICITY: No evidence in animal studies.

12. ECOLOGICAL INFORMATION

Bromacil is known to leach through soil and has been found in ground water as a result of normal field use. Users are advised not to apply in areas where soils are permeable, particularly where ground water is used for drinking water. Consult with the pesticide state lead agency for information regarding soil permeability and aquifer vulnerability in your area.

The following is for the active ingredient, Bromacil:

AQUATIC TOXICITY
Rainbow Trout (96-hr LC_{50}): 38 ppm

13. DISPOSAL CONSIDERATIONS

PESTICIDE DISPOSAL: Wastes resulting from the use of this product may be disposed of on-site or at an approved waste disposal facility

CONTAINER DISPOSAL: Nonrefillable container. Do not reuse or refill this container. Refer to the product label for specific container handling instructions.

14. TRANSPORT INFORMATION

UN Number:	UN3077
Proper Shipping Name:	Environmentally hazardous substance, solid, N.O.S. (contains bromacil)
Transport Hazard Class:	9
Packing Group:	III
Hazard Zone:	A
Marine Pollutant:	Yes[1]
Hazardous Substance RQ:	None
Labels / Placards:	US-DOT: Class 9 Environmentally Hazardous Substance[2] IMDG, IATA: Class 9 Environmentally Hazardous Substance[3]
Emergency Guide:	171 (NAERG – North American Emergency Response Guide)
[1] **Marine Pollutant Note:**	Ground-only shipments are excluded from Marine Pollutant labeling requires as per 49CFR172.101 Appendix B (4). For any shipments involving all or part of the transport by vessel, the shipment must be classified as a Marine Pollutant unless a limited quantity exemption applies (see note 3 below).
[2] **US-DOT Note:**	Not regulated for “ground only” shipments.
[3] **IMDG / IATA Note:**	Not regulated when shipped in single or inner packaging ≤1.32 gal. (5 L).

This information is not intended to convey all specific regulatory or operational requirements/information relating to this product. Transportation classifications may vary by container volume and may be influenced by regional or country variations in regulations. Additional transportation system information can be obtained through an authorized sales or customer service representative. It is the responsibility of the transporting organization to follow all applicable laws, regulations and rules relating to the transportation of the material.

15. REGULATORY INFORMATION

FIFRA –

This chemical is a pesticide product registered by the Environmental Protection Agency and is subject to certain labeling requirements under federal pesticide law. These requirements differ from the classification criteria and hazard information required for safety data sheets, and for workplace labels of non-pesticide chemicals. The following is the hazard information as required on the pesticide label:

PRECAUTIONARY STATEMENTS

HAZARDS TO HUMANS AND DOMESTIC ANIMALS

CAUTION: Harmful if absorbed through skin or swallowed. Causes moderate eye irritation. Avoid contact with skin, eyes, or clothing.

See inside label booklet for additional Precautionary Statements and Directions for Use including Storage and Disposal instructions.

ENVIRONMENTAL HAZARDS

Bromacil is known to leach through soil and has been found in ground water as a result of normal field use. Users are advised not to apply in areas where soils are permeable, particularly where ground water is used for drinking water. Consult with the pesticide state lead agency for information regarding soil permeability and aquifer vulnerability in your area. DO NOT apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high water mark. DO NOT contaminate water when disposing of equipment washwater or rinsate.

15. REGULATORY INFORMATION (CONT.)

All pesticides are governed under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). The regulatory information presented below is pertinent only when this product is handled outside of the normal use and application as a pesticide. This product is excluded from listing requirements under EPA/TSCA.

SARA Title III – Section 302 Extremely Hazardous Substances
Not listed

SARA Title III – Section 311/312 Hazard Categories
Immediate, Delayed

SARA Title III – Section 312 Threshold Planning Quantity
N/A

SARA Title III – Section 313 Reportable Ingredients
Bromacil (CAS No. 314-40-9): 80.0%

CERCLA –
Not listed

CALIFORNIA PROP 65 STATUS –
This product does not contain any chemicals known to the state of California to cause cancer or reproductive toxicity.

CANADA –
This product has been classified in accordance with the hazard criteria of the Controlled Products Regulations (CPR) and the SDS contains all of the information required by CPR.

16. OTHER INFORMATION

THIS INFORMATION IN THIS SDS IS BASED ON DATA AVAILABLE AS OF THE REVISION DATE GIVEN HEREIN, AND BELIEVED TO BE CORRECT. CONTACT ALLIGARE, LLC TO CONFIRM IF YOU HAVE THE MOST CURRENT MSDS. JUDGMENTS AS TO THE SUITABILITY OF THE INFORMATION HEREIN FOR THE INDIVIDUAL'S OWN USE OR PURPOSES IS NECESSARILY THE INDIVIDUAL'S OWN RESPONSIBILITY. ALTHOUGH REASONABLE CARE HAS BEEN TAKEN IN THE PREPARATION OF SUCH INFORMATION, ALLIGARE, LLC EXTENDS NO WARRANTIES, MAKES NO REPRESENTATIONS, AND ASSUMES NO RESPONSIBILITY AS TO THE ACCURACY OR SUITABILITY OF SUCH INFORMATION FOR APPLICATION TO THE INDIVIDUAL'S PURPOSES OR THE CONSEQUENCES OF ITS USE.

This Safety Data Sheet (SDS) serves different purposes than and DOES NOT REPLACE OR MODIFY THE EPA APPROVED PRODUCT LABELING (attached to and accompanying the product container). This SDS provides important health, safety, and environmental information for employers, employees, emergency responders and others handling large quantities of the product in activities generally other than product use, while the labeling provides that information specifically for product use in the ordinary course.

SDS Version: 3.0 Effective Date: 04/18/2018

K&E Sand and Gravel
Safety Data Sheet

1. *IDENTIFICATION*

Product Identifier: Silica Sand or Ground Silica; crystalline silica (quartz)

Product Name/Trade Names:
K&E 32, K&E 4.0, K&E 3.0, F-70, Locomotive sand, BodyShot, Pool Filtration Sand, All Purpose, Frac Sand, Dike Sand, Well Pack #1, #0, #00N, #2, #3, Traction Sand,
3/8" & 3/16" Peastone, Salt and Pepper

Chemical Name or Synonym:
Crystalline Silica (Quartz), Sand, Silica Sand, Ground Silica, Fine Ground Silica, Flint

Recommended use of the chemical and restrictions on use: (non-exhaustive list): brick, ceramics, foundry castings, glass, grout, hydraulic fracturing sand, frac sand, proppant, mortar, paint and coatings, silicate chemistry, silicone rubber, thermoset plastics.

Manufacturer:
K&E Sand and Gravel
4359 London Line
Wyoming, ON N0N 1T0
Canada

Phone: 519-845-3396
Fax: 519-845-3398

2. *HAZARD(S) IDENTIFICATION*

Classification:

Physical	Health
Not hazardous	Carcinogen Category 1A Specific Target Organ Toxicity - Repeated Exposure Category 1

DANGER
May cause cancer by inhalation.
Causes damage to lungs through prolonged or repeated exposure by inhalation.
Response:
If exposed or concerned: Get medical advice.
Disposal:
Dispose of contents/containers in accordance With local regulation.

PREVENTION
Obtain special instructions before use.
Do not handle until all safety precautions have been read and understood.
Do not breathe dust.
Do not eat, drink or smoke when using this product.
Wear protective gloves and safety glasses or goggles.
In case of inadequate ventilation ear respiratory protection.

3. *COMPOSITION/INFORMATION OF INGREDIENTS*

Component	CAS No.	Percent
Crystalline Silica (quartz)	14808-60-7	95-99.9

4. FIRST-AID MEASURES

Inhalation: First aid is not generally required. If irritation develops from breathing dust, move the person from the overexposure and seek medical attention if needed.
Skin contact: First aid is not required.
Eye contact: Wash immediately with plenty of water. Do not rub eyes. If irritation persists, seek medical attention.
Ingestion: First aid is not required.
Most important symptoms/effects, acute and delayed: Particulates may cause abrasive eye injury. Inhalation of dust may cause respiratory tract irritation. Symptoms of exposure may include cough, sore throat, nasal congestion, sneezing, wheezing and shortness of breath. Prolonged inhalation of respirable crystalline silica above certain concentrations may cause lung diseases, including silicosis and lung cancer.
Indication of immediate medical attention and special treatment, if necessary: Immediate medical attention is not required.

5. FIRE-FIGHTING MEASURES

Suitable (and unsuitable) extinguishing media: Use extinguishing media appropriate for surrounding fire.
Specific hazards arising from the chemical: Product is not flammable, combustible or explosive.
Special protective equipment and precautions for fire-fighters: None required.

6. ACCIDENTAL RELEASE MEASURES

Personal precautions, protective equipment, and emergency procedures: Wear appropriate protective clothing and respiratory protection (see Section 8). Avoid generating airborne dust during cleanup.
Environmental precautions: No specific precautions. Report releases to regulatory authorities if required by local, state and federal regulations.
Methods and materials for containment and cleaning up: Avoid dry sweeping. Do not use compressed air to clean spilled sand or ground silica. Use water spraying/flushing or ventilated or HEPA filtered vacuum cleaning system, or wet before sweeping. Dispose of in closed containers.

7. HANDLING AND STORAGE

Precautions for safe handling:
Avoid generating dust. Do not breathe dust. DO not rely on your sight to determine if dust is in the air. Respirable crystalline silica dust may be in the air without a visible dust cloud. Use adequate exhaust ventilation and dust collection to reduce respirable crystalline silica dust levels to below the permissible exposure limit ("PEL"). Maintain and test ventilation and dust collection equipment. Use all available work practices to control dust exposure, such as water sprays. Practice good housekeeping. Do not permit dust to collect on walls, floors, sills, ledges, machinery, or equipment. Keep airborne dust concentrations below permissible exposure limits.

Where necessary to reduce exposures below the PEL or other applicable limit (if lower than the PEL), wear a respirator approved for silica containing dust when using, handling, storing or disposing of this product or bag. See Section 8, for further information on respirators. Do not alter the respirator. Do not wear a tight-fitting respirator with facial hair such as a beard or moustache that prevents a good face to face piece seal between the respirator and face. Maintain, clean, and fit test respirators in accordance with applicable standards. Wash or vacuum clothing that has become dusty.

Participate in training, exposure monitoring, and health surveillance programs to monitor any potential adverse health effects that may be caused by breathing respirable crystalline silica. The OSHA hazard Communication Standard, 29 CFR Sections 1910.1200, 1915.1200, 1917.28, 1918.90, 1926.59 and 1928.21, and state and local worker or community "right-to-know" laws regulations should be strictly followed.

Conditions for safe storage, including any incompatibilities: Use dust collection to trap dust produced during loading and unloading. Keep containers closed and store bags to avoid accidental tearing, breaking, or bursting.

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Exposure guidelines:

Component	OSHA PEL	ACGIH TLV	NIOSH REL
Crystalline silica (quartz)	10 mg/m3 % SiO_2 + 2 TWA (respirable dust) 30 mg/m3 %SiO2 + 2 TWA (total dust)	0.025 mg/m3 TWA (respirable dust)	0.05 mg/m3 TWA (respirable dust)

If crystalline silica (quartz) is heated to more than 870°C, quartz can change to a form of crystalline silica known as tridymite; if crystalline silica (quartz) is heated to more than 1470°C, quartz can change to a form of crystalline silica known as cristobalite. The OSHA PEL for crystalline silica as tridymite or cristobalite is one-half of the OSHA PEL for crystalline silica (quartz).

Appropriate engineering controls: Use adequate general or local exhaust ventilation to maintain concentrations in the workplace below the applicable exposure limits listed above.

Respiratory protection: If it is not possible to reduce airborne exposure level to below the OSHA PEL or other applicable limit with ventilation, us the table below to assist you in selecting respirators that will reduce personal exposures to below the OSHA PEL. This table is part of the NIOSH Respirator Selection Logic, 2004, Chapter III, Table 1, "Particulate Respirators". The full document can be found at www.cdc.gov/niosh/npptl/topics/respirators; the user of this MSDS is directed to that site for information concerning respirator selection and use. The assigned protection factor (APF) is the maximum anticipated level of protection provided by each type of respirator worn in accordance with an adequate respiratory protection program. For example, an APF of 10 means that the respirator should reduce the airborne concentration of a particulate by a factor of 10, so that if the workplace concentration of a particulate was 150 ug/m3, then a respirator with an APF of 10 should reduce the concentration of particulate to 15 ug/m3. In using, chemical cartridges, consideration must be given to selection of the correct cartridge for the chemical exposure and the maximum use concentration for the cartridge. In additional a cartridge change-out schedule must be developed based on the concentrations in the workplace.

Assigned Protection factor[1]	**Type of Respirator** (Use only NIOSH-certified respirators)
10	Any air purifying elastomeric half-mask respirator equipped with appropriate type of particulate filter.[2] Appropriate filtering facepiece respirator.[2,3] Any air-purifying full facepiece respirator equipped with appropriate type of particulate filter.[2] Any negative pressure (demand) supplied-air respirator equipped with a half-mask.
25	Any powered air-purifying respirator equipped with a hood or helmet and a high efficiency (HEPA) filter. Any continuous flow supplied-air respirator equipped with a hood or helmet.
50	Any air-purifying full facepiece respirator equipped with N-100, R-100, or P-100 filter(s). Any powered air-purifying respirator equipped with a tight-fitting facepiece (half or full facepiece) and a high-efficiency filter. Any negative pressure (demand) supplied-air respirator equipped with a full facepiece.

	Any continuous flow supplied-air respirator equipped with a tight-fitting facepiece (half or full facepiece). Any negative pressure (demand) self-contained respirator equipped with a full facepiece.
1,000	Pressure-demand supplied-air respirator equipped with a full facepiece.

1. The protection offered by a given respirator is contingent upon (1) the respirator user adhering to complete program requirements (such as the ones required by OSHA in 29CFR1910.134), (2) the use of NIOSH-certified respirators in their approved configuration, and (3) individual fit testing to rule out those respirators that cannot achieve a good fit on individual workers.
2. Appropriate means that the filter medium will provide protection against the particulate in question.
3. An APF of 10 can only be achieved if the respirator is qualitatively or quantitatively fit tested on individual workers.

Skin protection: Maintain good industrial hygiene. Protection recommended for workers suffering from dermatitis or sensitive skin.

Eye protection: Safety glasses with side shield or goggles recommended if eye contact is anticipated.

Other: None known.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance (physical state, color, etc.): White or tan sand: granular, crushed or ground to a powder.
Odor: None.

Odor threshold: Not determined	pH: 6-8
Melting point/freezing point: 31100F/17100C	Boiling point/range: 40460F/22300C
Flash point: Not applicable	Evaporation rate: Not applicable
Flammable limits: LEL: Not applicable	UEL: Not applicable
Vapor pressure: Not applicable	Vapor density: Not applicable
Relative density: 2.65	Solubility(ies): Insoluble in water
Partition coefficient: n-octanol/water: Not applicable	Auto-ignition temperature: Not determined
Decomposition temperature: Not determined	Viscosity: Not applicable
Flammability (solid, gas): Not applicable	

10. STABILITY AND REACTIVITY

Reactivity: Not reactive under normal conditions of use.
Chemical stability: Stable
Possibility of hazardous reactions: Contact with powerful oxidizing agents, such as fluorine, chlorine, trifluoride and oxygen difluoride, may cause fires.
Conditions to avoid: Avoid generation of dust in handling and use.
Incompatible materials: Powerful oxidizers such as fluorine, chlorine trifluoride, and oxygen difluoride and hydrofluoric acid.
Hazardous decomposition products: Silica will dissolve in hydrofluoric acid and produce a corrosive gas, silicon tetrafluoride.

11. TOXICOLOGICAL INFORMATION

Acute effects of exposure:
Inhalation: Inhalation of dust may cause respiratory tract irritation. Symptoms of exposure may include cough, sore throat, nasal congestion, sneezing, wheezing and shortness of breath.
Ingestion: Ingestion in an unlikely route of exposure. If dust is swallowed, it may irritate the mouth and throat.
Skin contact: No adverse effects are expected.
Eye contact: Particulates may cause abrasive injury.

Chronic effects: Prolonged inhalation of respirable crystalline silica may cause lung disease, silicosis, lung cancer and other effects as indicated below.

The method of exposure that can lead to the adverse health effects described below is inhalation.

A. SILICOSIS

Silicosis can exist in several forms, chronic (or ordinary), accelerated, or acute.

Chronic or Ordinary Silicosis is the most common form of silicosis, and can occur after many years (10 to 20 or more) of prolonged repeated inhalation of relatively low levels of airborne respirable crystalline silica dust. It is further defined as either simple or complicated silicosis. Simple silicosis is characterized by lung lesions (shown as radiographic opacities) less than 1 centimeter in diameter, primarily in the upper lung zones. Often, simple silicosis is not associated with symptoms, detectable changes in lung function or disability. Simple silicosis may be progressive and may develop into complicated silicosis or progressive massive fibrosis (PMF). Complicated silicosis or PMF is characterized by lung lesions (shown as radiographic opacities) greater than 1 centimeter in diameter. Complicated silicosis or PMF symptoms, if present, are shortness of breath and cough. Complicated silicosis of PMF may be associated with decreased lung function and may be disabling. Advanced complicated silicosis or PMF may lead to death. Advanced complicated silicosis of PMF can result in heart disease secondary to the lung disease (cor pumonale).

Accelerated Silicosis can occur with prolonged repeated inhalation of high concentrations of respirable crystalline silica over a relatively short period; the lung lesions can appear within five (5) years of initial exposure. Progression can be rapid. Accelerated silicosis is similar to chronic or ordinary silicosis, except that lung lesions appear earlier and progression is more rapid.

Acute Silicosis can occur after the repeated inhalation of very high concentrations of respirable crystalline silica over a short time period, sometimes as short as a few months. The symptoms of acute silicosis include progressive shortness of breath, fever, cough, weakness and weight loss. Acute silicosis is fatal.

B. CANCER

IARC – The International Agency for Research on Cancer ("IARC") concluded that "crystalline silica in the form of quartz or cristobalite dust is carcinogenic to humans (Group 1)". For further information on the IARC evaluation, see IARC Monographs on the Evaluation of Carcinogenic Risks to Humans, Volume 100C,"A Review of Human Carcinogens: Arsenic, Metals, Fibres and Dusts" (2011).

NTP classifies "Silica, Crystalline (respirable size)" as Known to be human carcinogen.

C. AUTOIMMUNE DISEASES

Several studies have reported excess cases of several autoimmune disorders – scleroderma, systemic lupus erythematosus, and rheumatoid arthritis – among silica-exposed workers.

D. TUBERCULOSIS

Individuals with silicosis are at increased risk to develop pulmonary tuberculosis, if exposed to tuberculosis bacteria. Individuals with chronic silicosis have a three-fold higher risk of contracting tuberculosis than similar individuals without silicosis.

E. KIDNEY DISEASE

Several studies have reported excess cases of kidney diseases, including end stage renal disease, among silica-exposed workers. For additional information on the subject, the following may be consulted: Kidney Disease and Silicosis", Nephron, Volume 85, pp. 14-19 (2000).

F. NON-MALIGNANT RESPIRATORY DISEASES

The reader is referred to Section 3.5 of the NIOSH Special Hazard Review cited below for information concerning the association between exposure to crystalline silica and chronic bronchitis, emphysema and small airways disease. There are studies that disclose an association between dusts found in various mining occupations and non-malignant respiratory diseases, particularly among smokers. It is unclear whether the observed associations exist only with underlying silicosis, only among smokers, or result from exposure to

mineral dusts generally (independent of the presence or absence of crystalline silica, or the level of crystalline silica in the dust).

Sources of information:
The NIOSH Hazard Review - Occupational Effects of Occupational Exposure to Respirable Crystalline Silica published in April 2002 summarizes and discusses the medical and epidemiological literature on the health risks and diseases associated with occupational exposures to respirable crystalline silica. The NIOSH Hazard Review is available from NIOSH web site, *www.cdc.gov/niosh/topics/silica*, and then click on the link "NIOSH Hazard Review: Health Effects of Occupational Exposure to Respirable Crystalline Silica".

For a more recent review of the health effects of respirable crystalline silica, the reader may consult Fishman's Pulmonary Diseases and Disorders, Fourth Edition, Chapter 57. "Coal Workers' Lung Diseases and Silicosis".

Finally, the US Occupational Safety and Health Administration (OSHA) published a summary of respirable crystalline silica health effects in connection with OSHA's Proposed Rule regarding occupational exposure to respirable crystalline silica. The summary was published in the September 12, 2013 Federal Register, which can be found at *www.federalregister.gov/articles/2013/09/12/2013-20997/occupational-exposure-to-respirable-crystalline-silica.*

Numerical measures of toxicity:
Crystalline Silica (quartz): LD50 oral rat>22,500 mg/kg.

12. ECOLOGICAL INFORMATION

Ecotoxicity: Crystalline silica (quartz) is not known to be ecotoxic.
Persistence and degradability: Silica is not degradable.
Bioaccumulative potential: Silica is not bioaccumulative.
Mobility in soil: Silica is not mobile in soil.
Other adverse effects: No data available.

13. DISPOSAL CONTAINERS

Discard any product, residue, disposable container or line in full compliance with national regulations.

14. TRANSPORT INFORMATION

UN number: None
UN proper shipping name: Not regulated
Transport hazard classes(es): None
Packing group, if applicable: None
Environmental hazards: None

Transport in bulk (according to Annex II of MARPOL 73/78 and the IBC Code): Not determined
Special precautions: None known

15. REGULATORY INFORMATION

UNITED STATES (FEDERAL AND STATE)

TSCA Status: Crystalline silica (quartz) appears on the EPA TSCA inventory under the CAS No. 14808-60-7.

RCRA: This product is nor classified as a hazardous waste under the Resource Conservation and Recovery Act, or its regulations, 40 CFR §261 et seq.

CERCLA: Crystalline silica (quartz) is not classified as a hazardous substance under regulations of the Comprehensive Environmental Response Compensation and Liability Act (CERCLA), 40 CFR §302.

Emergency Planning and Community Right to Know Act (SARA Title III): This product contains the following chemicals subject to SARA 302 or SARA 313 reporting: None above the de minimus concentrations.

Clean Air Act: Crystalline silica (quartz) mined and processed by K&E Sand and Gravel is not processed with or does not contain any Class 1 or Class II ozone depleting substances.

FDA: Silica is included in the list of substances that may be included in coatings used in food contact surfaces, 21 CFR §175.300(b) (3) (xxvi).

California Proposition 65: Crystalline silica (airborne particles of respirable size) is classified as a substance known to the state of California to be a carcinogen.

California Inhalation Reference Exposure Level (REL): California established a chronic non-cancer effect REL of 3 ug for silica (crystalline, respirable). A chronic REL is an airborne level of a substance at or below which no non-cancer health effects are anticipated in individuals indefinitely exposed to the substance at that level.

Massachusetts Toxic Use Reduction Act: Silica, crystalline (respirable size, <10 microns) is "toxic" for purposes of the Massachusetts Toxic Use Reduction Act.

Pennsylvania Worker and Community Right to Know Act: Quartz is a hazardous substance under the Act, but it is not a special hazardous substance or an environmental hazardous substance.

Texas Commission on Environmental Quality: The Texas CEQ has established chronic and acute Reference Values and short term and long term Effects Screening Levels for crystalline silica (quartz). The information can be accessed through *www.tceq.texas.gov*.

CANADA

Domestic Substances List: K&E Sand and Gravel products, as naturally occurring substances, are on the Canadian DSL.

WHMIS Classification: D2A

OTHER NATIONAL INVENTORIES

Australian Inventory of Chemical Substances (AICS): All of the components of this product are listed on the AICS inventory or exempt form notification requirements.

China: Silica is listed on the IECSC inventory or exempt form notification requirements.

Japan Ministry of International Trade and Industry (MITI): All of the components of this product are existing chemical substances as defined in the Chemical Substance Control Law Registry Number 1-548.

Korea Existing Chemicals Inventory (KECI) (set up under the Toxic Chemical Control Law): Listed on the ECL with the registry number 9212-5667.

New Zealand: Silica is listed on the HSNO inventory or exempt from notification requirements.

Philippines Inventory of Chemicals and Chemical Substances (PICCS): Listed for PICCS.

Taiwan: Silica is listed on the CSNN inventory or exempt from notification requirements.

16. OTHER INFORMATION

Date of preparation/revision: November 14, 2018
Hazardous Material Information System (HMIS):
Health*

Flammability 0
Physical Hazard 0
Protective Equipment E
*For further information on health effects, see Sections 2, 8 and 11 of this MSDS.

National Fire Protection Association (NFPA):
Health 0
Flammability 0
Instability 0

Web Sites with Information about Effects of Crystalline Silica Exposure:

The U.S. National Institute for Occupational Safety and Health (NIOSH) and Occupational Safety and Health Administration (OSHA) maintain sites with information about crystalline silica and its potential health effects. For NIOSH, *http://www.cdc.gov/niosh/topics/silica*; for OSHA, *http://www.osha.gov/dsg/topics/silicacrystalline/index.*

The IARC Monograph that includes crystalline silica, Volume 100C, can be accessed in PDF form at the IARC web site, *http://monographs.iarc.fr/ENG/Monographs/PDFs/index.php.*

K&E Sand and Gravel Disclaimer

Disclaimer: The information provided in this Safety Data Sheet relates only to the specific material designated herein and does not relate to use in combination with any other material or in any process. The information set forth herein is based on technical data that K&E Sand and Gravel believes to be reliable. It is intended for use by persons having technical skill and at their own discretion and risk. Since the conditions of use are outside the control of K&E Sand and Gravel, no warranties, expressed or implied, are made and no liability is assumed in connection with any use of this information. Any use of this data and information must be determined by the user to be in accordance with provincial, federal, state and local laws and regulations.

K & E Sand and Gravel shall not be liable for any damages arising out of the use of the Safety Data Sheet howsoever caused, if the product is not employed in a normal or reasonable foreseeable use or circumstance.

APPENDIX B: UPDATED TECHNOLOGY BROCHURES

Small size, big power

Fast, accurate, versatile XRF analysis

When versatility, low limits of detection (LODs) and high sample throughput are critical, industrial businesses rely on the Thermo Scientific™ Niton™ XL5 Plus handheld XRF analyzer. Providing customers with solutions designed to meet their most demanding applications, the Niton XL5 Plus maximizes performance and productivity.

Applications

- Verification of metals and alloys in manufacturing operations
- Non-destructive field inspections for positive material identification
- Point-and-shoot sorting at scrap recycling operations
- Measurement of single or multi-layer coat weight and coating thickness in surface treatment control
- Precious metal assay of bullion and jewelry
- Real-time geochemical analysis for mining exploration
- On-site heavy metal screening of polluted soils
- Screening for hazardous substances in consumer goods
- Custom applications on demand

Analytical performance

Designed to return lab quality results, the Niton XL5 Plus' low limits of detection allow operators to scan a broad range of materials for diverse applications. Identify pure metals and alloys, obtain geochemical data, screen for heavy metals or determine plating and coating thickness. From metals to mining, and everything in between, the Niton XL5 Plus is ready to work.

Rapid results

Powered by a 5W x-ray tube, the Niton XL5 Plus generates fast and accurate results. An upgraded graphene window ensures optimum sensitivity for each measurement - even light elements. Results are displayed in real time, enabling you to make faster decisions. And with a standard system health check designed to verify operating parameters, your device will operate smoothly.

Size and weight

Make light work of heavy industrial tasks utilizing the Niton XL5 Plus. Weighing an industry leading 2.8 pounds (1.3 kilograms), the Niton XL5 Plus is the lightest handheld XRF analyzer available for elemental determination and alloy identification.[1] It's small footprint and featherweight design reduce operator fatigue while increasing productivity.

Design

Tight spots are no match for the Niton XL5 Plus. Discover expanded field use with improved compact geometry and ergonomics. Reaching tight welds, corners and joints, are no longer defined as awkward test spots for the Niton XL5 Plus. Standard Detector ProGuard protection also reduces risk when measuring sharp items.

The Niton XL5 Plus in use, analyzing a tight weld in an oil refinery.

Functionality

Vivid new icons and an application interface ease navigation and configuration. Utilize swipe and touchscreen functionality, even with a gloved hand. Optional directional keys provide added usability. A hot swap battery keeps you up and running when it's time to replace a low battery. Micro and macro cameras enable precise sample positioning and collect images for better record keeping. Finally, WiFi accessibility automatically transmits data from your device to PC.

Product Specifications

Weight	2.8 lbs with battery (1.3 kg)
Dimensions	9.54 x 8.19 x 2.67 in (242.56 x 208.17 x 67.90 mm)
X-Ray Source	X-Ray Tube: Ag anode (6-50kV, 0-500uA, 5W max) Filter: Six (6) position filter wheel for enhanced spectral range coverage Current: Dynamically adjustable current for optimal sensitivity on every analysis
Detector	High count rate, high resolution, extra large area silicon drift detector (1µm graphene window) Detector ProGuard protection included
Spot Size	Standard: 8mm collimation Optional: 3mm small-spot collimation
Analytical Range	Mg-U (ultra low light element detection), Na (spectrum based detection)
Calibration Modes	General Metals, Precious Metals, Coatings, Mining, Soils, Electronic Alloys, Plastics, Industrial Lead in Paint, Spectral Fingerprint, TestAll™
Libraries	Default alloy libraries based on SAE, AISI, ASTM, AA,DIN, GB standards Users may create, clone and edit libraries
System Check	Built-in standardization and health check verifies system integrity and operating conditions
IP Rating	IP54 (splash and dust proof)
Operating Environment	Temperature: 0°C to 50°C (external fan recommended when ambient temperature is greater than 33°C) Humidity: 10% to 90% relative humidity non-condensing
Display	Tilting, color, resistive touchscreen display
Power	12V lithium-ion battery, or 12V DC, 3A, 3.6W power supply Hot swap functionality keeps analyzer powered during battery replacements
Macro Camera	Integrated CCD macro camera for capturing overview images of parts and tagging measurement locations
Micro Camera	Integrated CCD micro camera for locating and recording measurement positions
Global Positioning System	Internal GPS and optional external GPS (via Bluetooth) GPS data included with sample information
Bluetooth	Supports print functionality, external GPS connectivity and barcode reader
Memory / Data Storage	512 MB internal system memory / 16 GB industrial grade storage Stores approximately 130,000 readings with spectra (fewer if macro and micro images are saved)
Data Entry	Touchscreen keyboard User customizable data entry Optional wireless remote barcode reader
Data Transfer	WiFi, USB-c
Operating System	Linux
Support Software	NitonConnect PC software
Security	Password-protected user security
Languages	English, Chinese, Spanish, Portuguese, Russian, Japanese, German, Korean, French, Turkish, Italian
Standard Accessories	Locking shielded carrying case Two (2) lithium-ion battery packs One (1) 110/220 VAC battery charger/ AC adaptor Check samples Safety lanyard PC connection cable (USB)
Optional Accessories	Thermo Scientific™ portable test stand Thermo Scientific™ mini test stand Thermo Scientific™ backscatter shield Thermo Scientific™ hotwork stand off Thermo Scientific™ soil guard Thermo Scientific™ belt holster Bluetooth printer
Compliance	Compliance CE, RoHS, FCC, Industry Canada, Safety to IEC 61010-1:2010
Licensing / Registration	Varies by region. Contact your local distributor.

1. The Thermo Scientific™ Niton™ XL5 Plus handheld XRF analyzer weighs 2.8lbs (1.3 kg). The Niton XL5 Plus is the smallest and lightest handheld XRF analyzer leveraging x-ray tube technology.

Learn more at **thermofisher.com/NitonXL5Plus**

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Protecting consumers with the latest in food testing technology

PEOPLE
YOU
CAN
TRUST

Metrohm

Prepare to fight against food fraud

Food fraud is more common than most people think. Misa puts the latest food testing technology in your hands to help you detect and combat this scourge. With this portable tool, you can instantly identify substances most commonly found in adulterated food.

Take the laboratory to the problem – for fast and easy analysis

- Compact, portable design
- Intuitive guided workflows for straightforward operation
- No chemical know-how required
- Complete trace detection solution

FRUITS AND VEGETABLES

Pesticides

MEAT

Antibiotics and growth hormones

PROCESSED FOODS

Illegal additives

SPICES

Artificial dyes

For a comprehensive list of applications visit
→ **metrohm.com/misa**

Simple, Efficient, and Green!

Misa is a highly sensitive laboratory at your fingertips. A simple guided workflow gives you immediate answers when every minute counts. Let Misa do the work for you – rely on fully automated analyses to quickly and accurately identify trace contaminants, even within complex food samples.*

*Misa combines nanotechnology with Raman spectroscopy to generate a fingerprint spectrum. The resulting Surface-Enhanced Raman Scattering (SERS) spectrum provides for unambiguous identification of food contaminants.

Anyone can use Misa

You do not need to be a chemist to use Misa. All you need to do is …

1

Prepare the sample

Follow simple, step-by-step target-specific methods to prepare the sample for analysis.

2

Apply the sample

Apply the processed sample to dedicated SERS test materials from Metrohm.

3

Acquire a signal

Start the measurement with a single click on the instrument or mobile app.

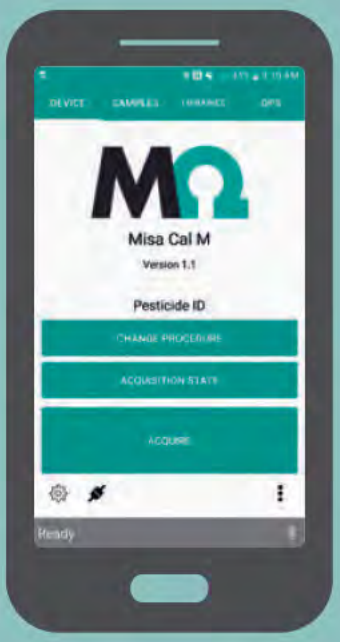
4

Read and share the result immediately

Only seconds later you can read the result and take immediate action.

Hazard detected? Sound the alarm and save lives!

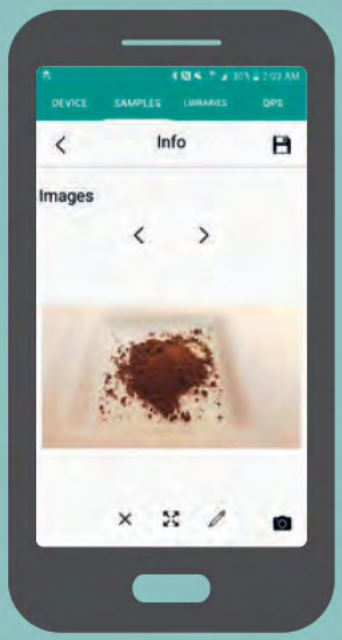
Misa can travel anywhere with you to quickly gather and share crucial data when tainted food is found. The Misa Cal M app is a powerful mobile platform that provides critical information about potentially dangerous substances. With Misa, you can take immediate action, helping you save lives.



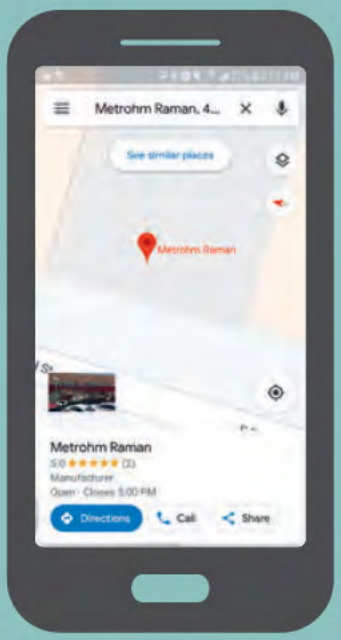
Simple testing

Quality results

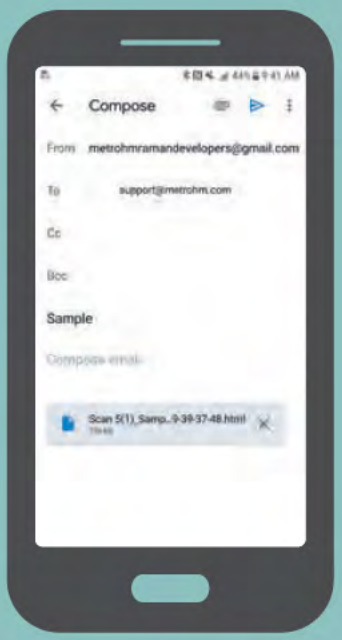
Clear warnings



Visual evidence



Geo-tagging



Share alerts

ORDERING INFORMATION

Instrument Packages	
2.950.0010	Misa Basic (Contains Misa instrument and Misa Vial Attachment)
2.950.0020	Misa Advanced (Contains Misa instrument and all optional accessories)
Optional Accessories	
6.07501.010	ASTM Calibration Standard
6.07505.030	P-SERS Attachment
6.07505.040	Misa Vial Attachment
6.02707.030	Misa Ruggedized Carrying Case
Consumables	
6.07506.400	ID Kit – Illicit Drugs
6.07506.440	ID Kit – Au NP
6.07506.450	ID Kit – Ag NP
6.07506.460	ID Kit – Au P-SERS
6.07506.470	ID Kit – Ag P-SERS
SERS Libraries	
6.6071.670	SERS Library – Illicit Materials
6.6071.672	SERS Library – Food Additives
6.6071.674	SERS Library – Dyes
6.6071.676	SERS Library – Pesticides

Visit www.metrohm.com/misa for more accessories and consumables options

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VULCAN

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Read the metal. Reveal the quality.

QAQC

This is Vulcan.

It's one of the fastest metals analyzers in the world. It will help you to quality control and check large inventories and avoid material mix ups that can have serious consequences. It's an ideal tool to carry out 100% PMI.

Vulcan allows you to identify and analyze a wide range of alloys. It gives results on all common alloys, including aluminum, magnesium, titanium, cobalt, chromium, nickel, and copper alloys as well as stainless steels, tool steels, low alloy steels and more.

It's a light (1.5 kg) and ergonomic laser analyzer, so even when used for long periods it will feel comfortable and easy to operate.

Why is Vulcan the perfect tool for your business?

SIMPLE TO USE

'Point and shoot' operation and intuitive user interface hugely reduces if not almost completely eliminates user error. It's ready to go straight out of the box.

BUILT TO LAST

Its measurement optics are protected by sapphire glass, one of the toughest materials available. It's also splash water and dust proof (IP54 certified, NEMA 3 equivalent), and complies with the MIL-STD-810G military grade standard for ruggedness.

INCREASED PRODUCTIVITY

Vulcan gives results in one second, regardless of the alloy type. A couple of seconds difference in speed can have a huge impact to your operations. When measuring aluminum alloys, Vulcan can be even 10 times faster than XRF analyzers.

FULL DAY OPERATION

Vulcan's 8–10 hour battery life ensures that there will be no interruptions in your work routine.

LATEST TECHNOLOGY

Share and store your results securely, and generate reports with our cloud-based service, EXTOPE Connect. You can also connect Vulcan directly to your mobile phone to add pictures and to share results instantly.

LOW COST OF OWNERSHIP

A much lower cost of ownership than an XRF analyzer, which requires expensive licenses and time consuming radiation safety training classes.

WORKS ALMOST INVISIBLY

Less than one billionth of a gram of material is consumed during a typical analysis leaving an almost invisible burn mark on the surface of the metal.

An option to suit your needs

We offer three different models to provide you with an instrument for your needs, all with a one second measurement time.

Features	Vulcan Smart+	Vulcan Optimum+	Vulcan Expert+
Grade identification and full chemistry	●	●	●
Stainless steels, low alloy steels, tool steels, Ni, Co, Cu, Pb, Sn, Ti and Zn alloys.	●	Cu, Ti	●
Al and Mg alloys	N/A	●	●
Li in Al alloys	N/A	●	N/A
Built-in camera	Optional	Optional	Optional
WiFi	●	●	●
Pre-burn to clean the sample surface	●	●	●
IP54 (NEMA 3 equivalent) dust and splash water protected	●	●	●
MIL-STD-810G compliant	●	●	●
Full day operation with one battery*	●	●	●

***Based on analyzing one sample every five seconds for eight hours.**

The instrument comes with up to 1500 pre-installed grades. AISI, DIN, JIS and GB libraries are included as standard. You can also easily modify the existing libraries, as well as add your own custom libraries.

Our Service

Our global network of service hubs can offer a full range of technical support to keep you up and running:

- Annual calibration checks and recertification services.
- Rental instruments so you can keep working if your analyzer isn't.
- A range of consumables and accessories from spare batteries to window cleaners.
- Extended warranties to give you peace of mind and avoid unplanned costs.
- Training to help you get the most from your analyzer and all its features.
- Telephone help desks to guarantee a fast response to any problem.
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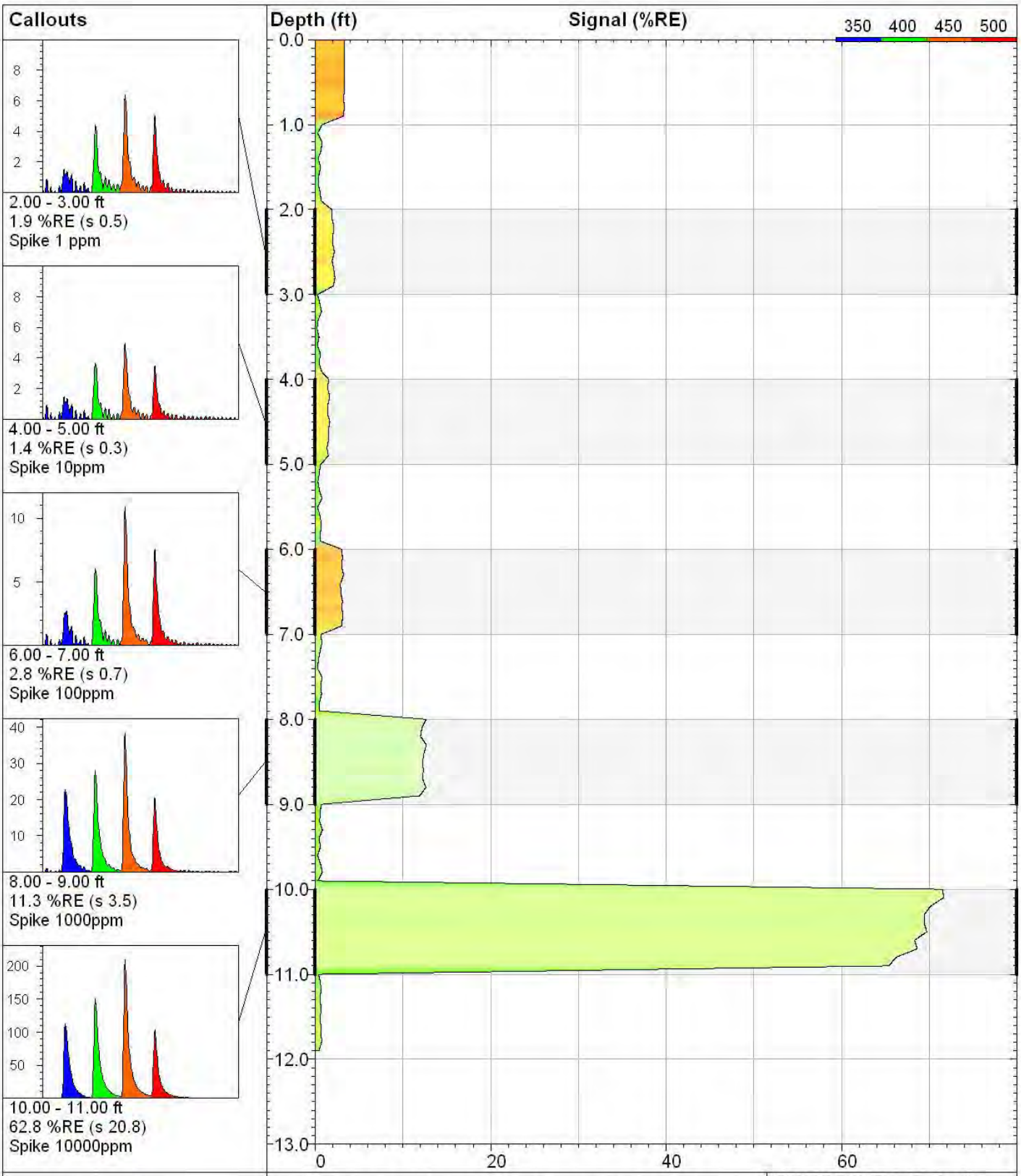
APPENDIX C: ADDENDUM TECHNOLOGY REPORTS

Technology Reports – UVOST®



DAKOTA TECHNOLOGIES

www.DakotaTechnologies.com

Gov Alberta Pesticide Testing - Spike		UVOST® By Dakota www.DakotaTechnologies.com
Site:	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **11.90 ft**
Client / Job: **Gov Alberta /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **71.6 %RE @ 10.10 ft**
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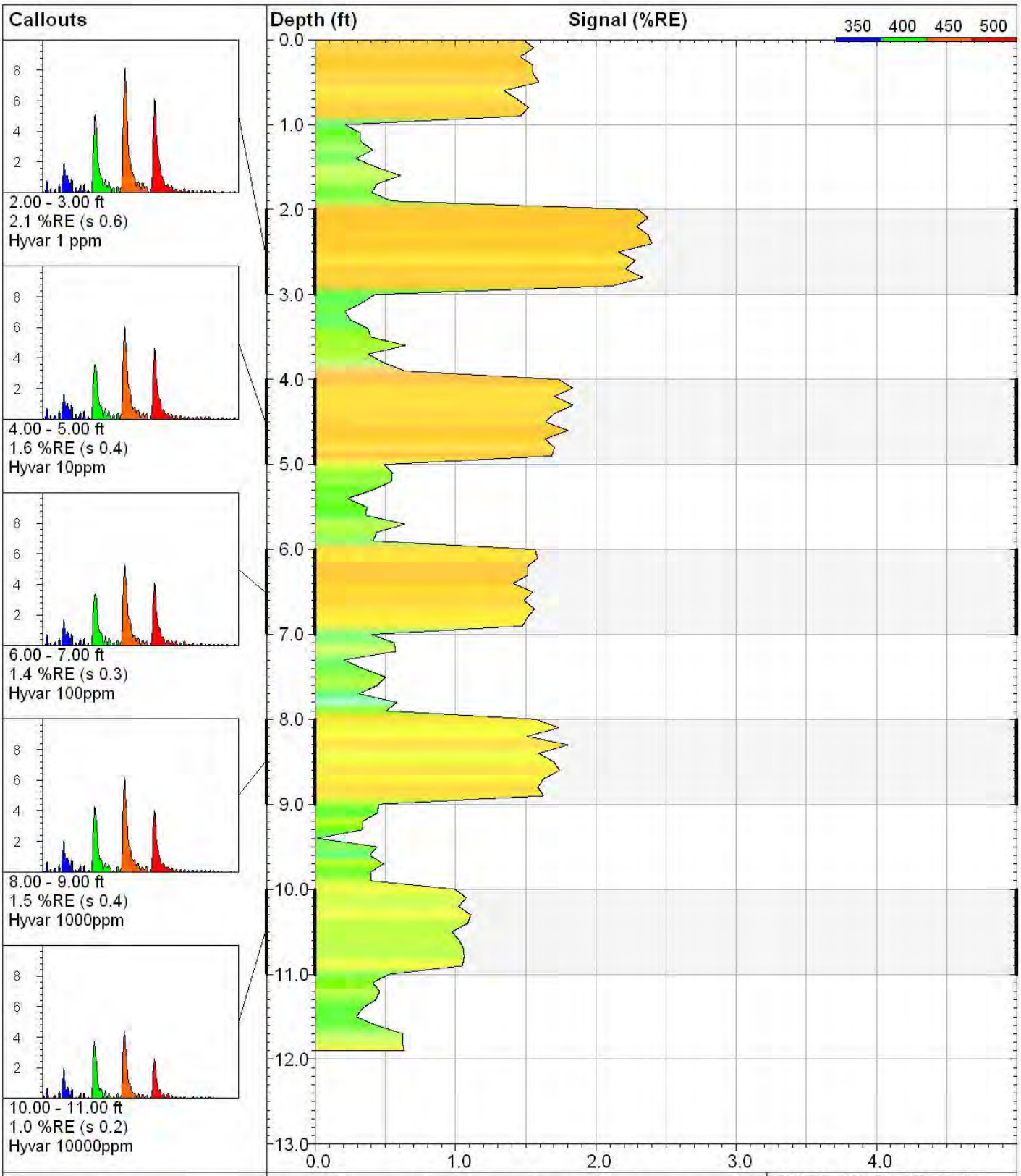

DAKOTA TECHNOLOGIES

www.DakotaTechnologies.com

Gov Alberta Pesticide Testing - Hyvar		UVOST® By Dakota www.DakotaTechnologies.com
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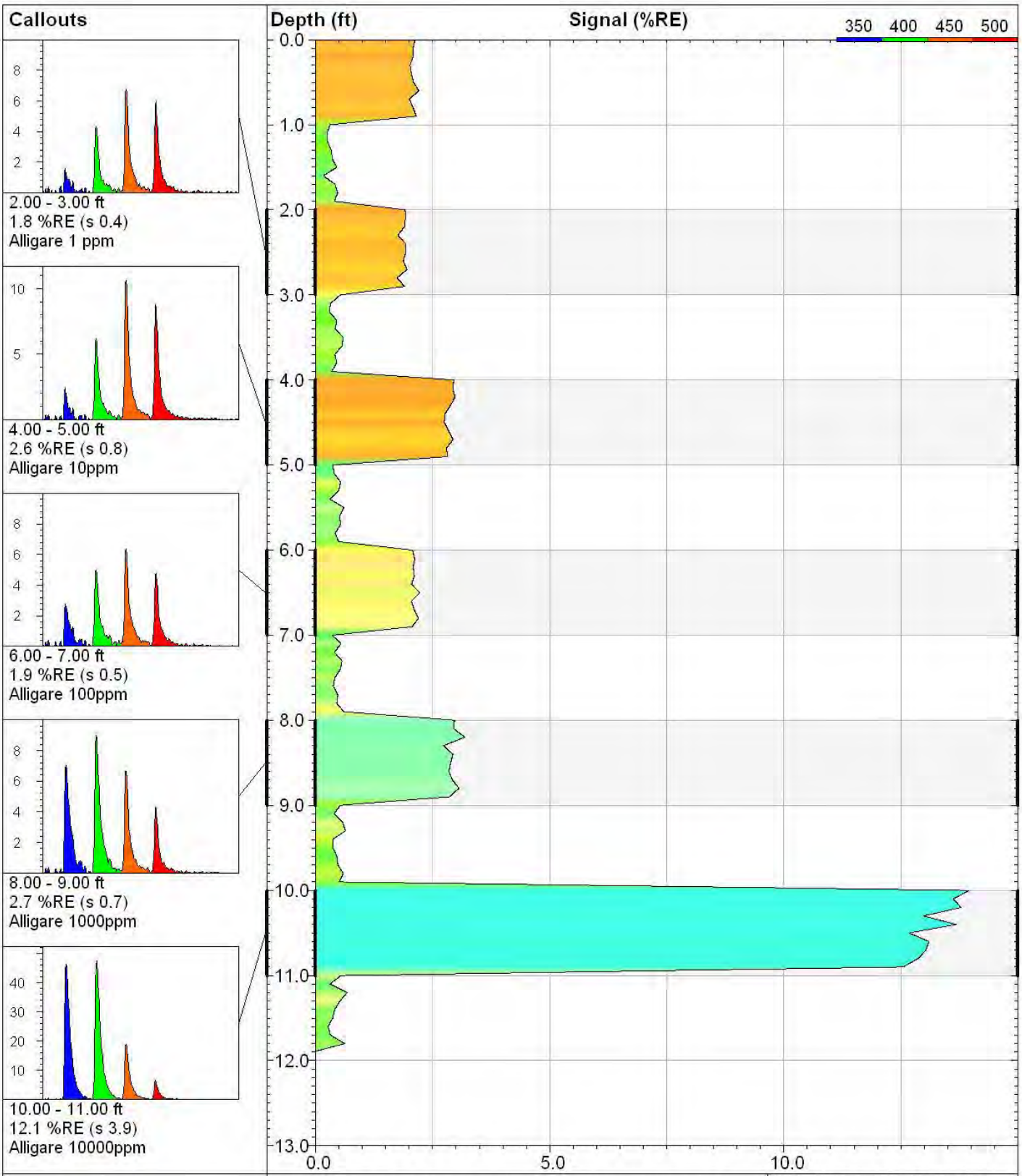

DAKOTA TECHNOLOGIES

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Gov Alberta Pesticide Testing - Alligare		UVOST® By Dakota www.DakotaTechnologies.com
Site:	*Y Coord.(Lat-N) / System:* **Unavailable / NA**	*Final depth:* **11.90 ft**
Client / Job: **Gov Alberta /**	*X Coord.(Lng-E) / Fix:* **Unavailable / NA**	*Max signal:* **14.0 %RE @ 10.00 ft**
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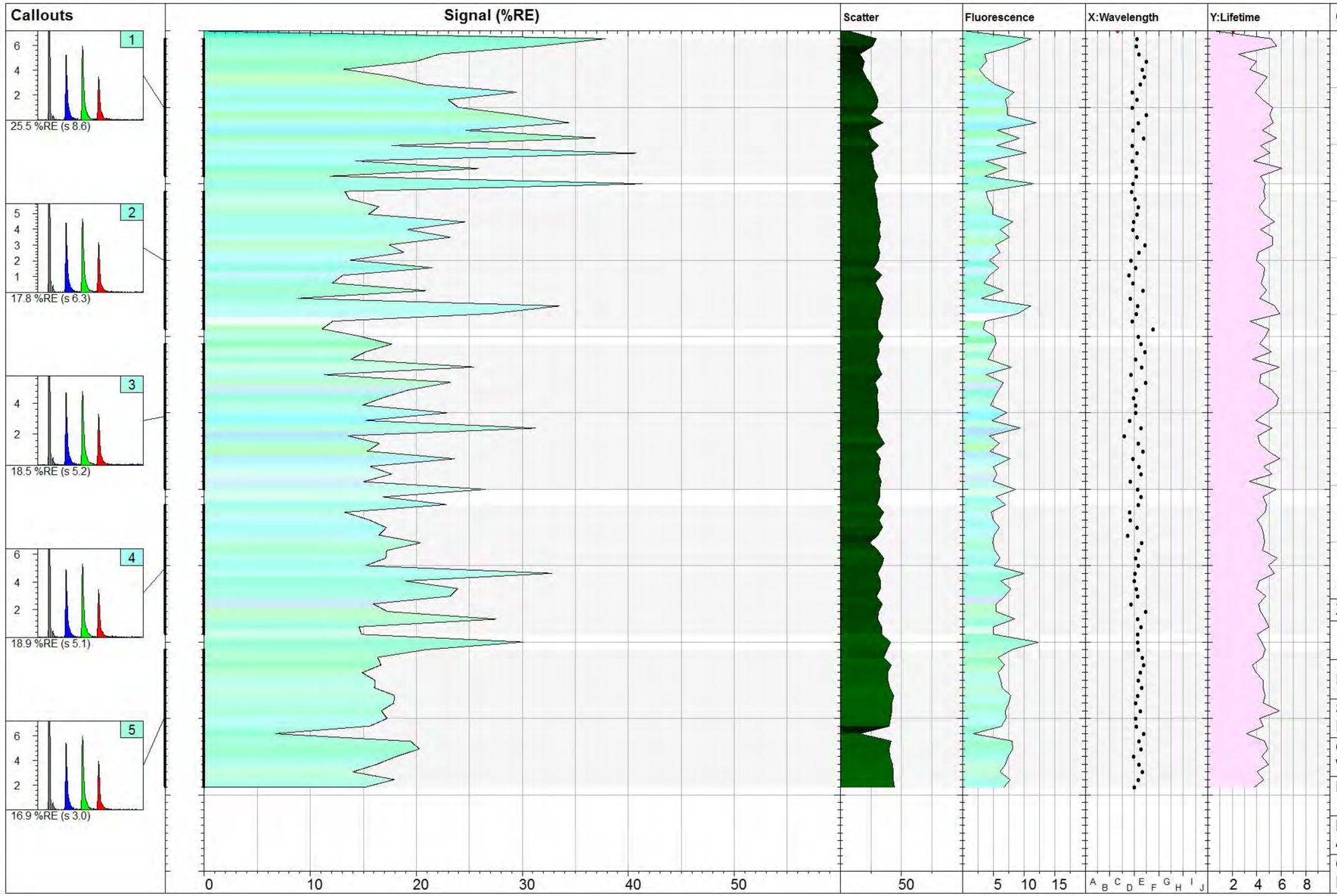
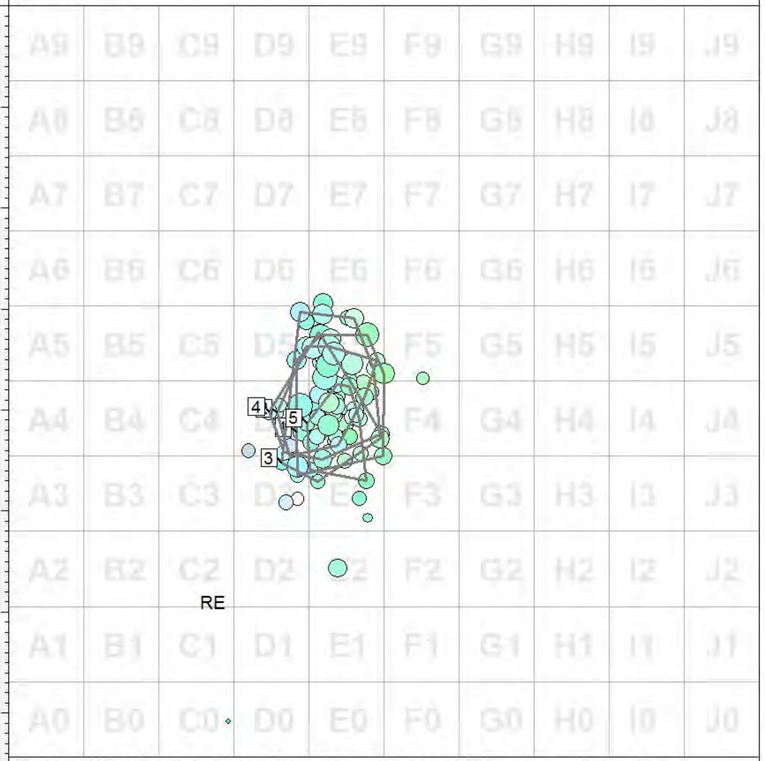
Technology Reports – TarGOST®



Cluster Plot



X-axis = Wavelength balance of waveform; Y-axis = Lifetime avg. of waveform

TarGOST® By Dakota

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Log: **SPIKE**

Site: **Lab Study**	Date & Time: **2020-10-20 14:02 CDT**
Client: **Vertex**	Job:
Final Depth:	X Coord.(Long/East): **Unavailable**
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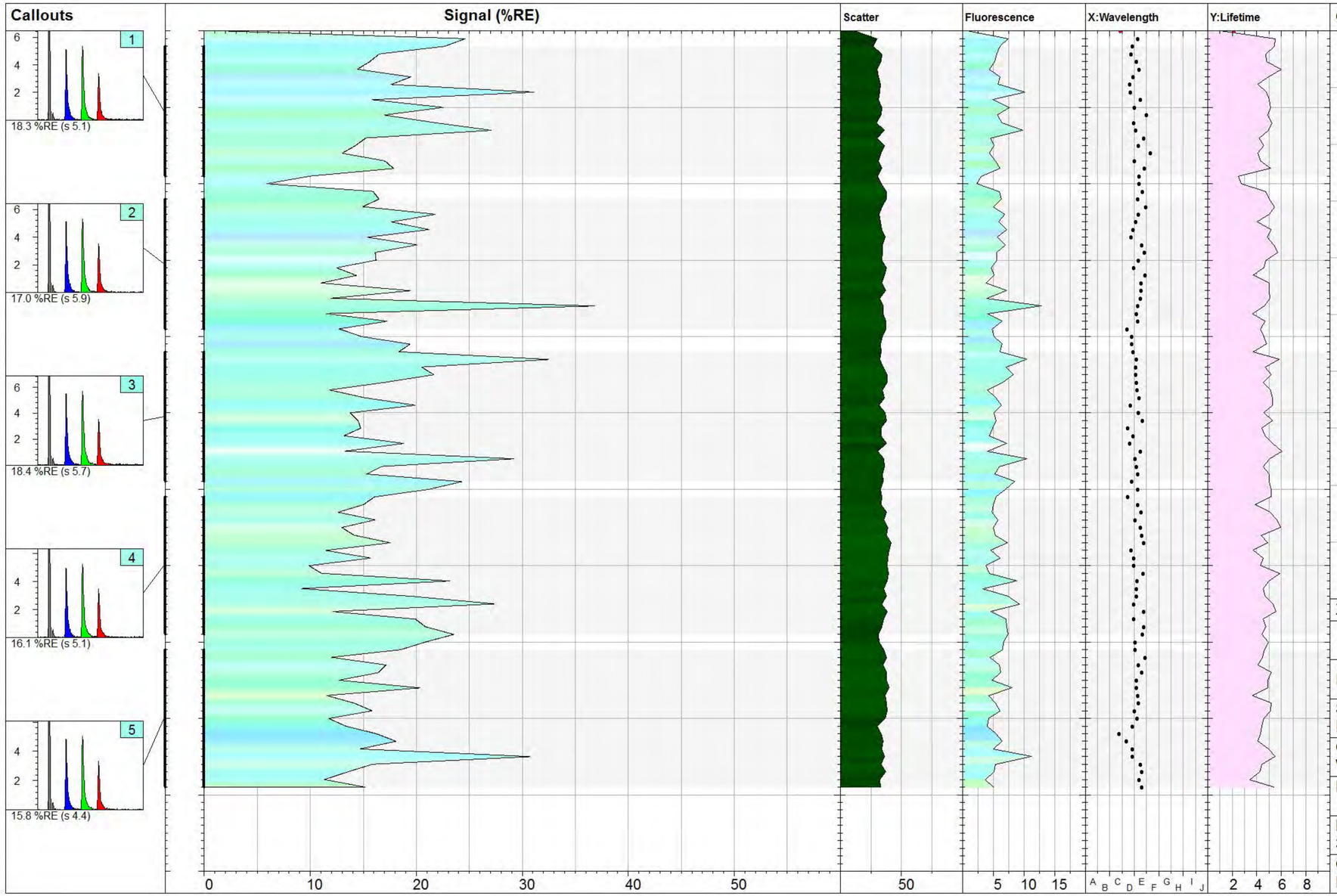

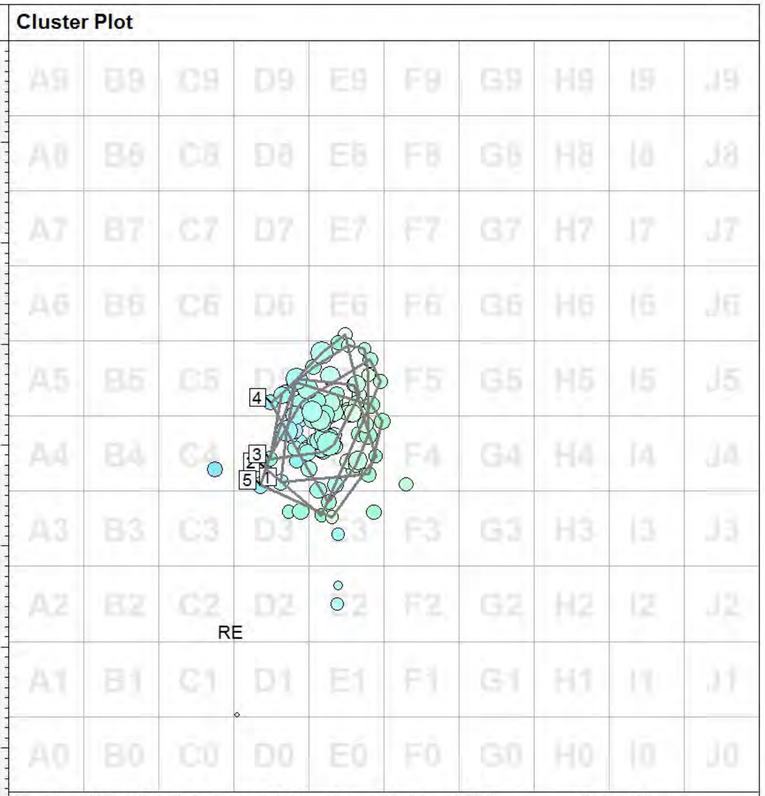

X-axis = Wavelength balance of waveform; Y-axis = Lifetime avg. of waveform

TarGOST® By Dakota

Data Presentation Format © 2020 Dakota Technologies, Inc. (v2.5.38)

Log: **HYVAR**

Site: **Lab Study**	Date & Time: **2020-10-20 14:09 CDT**
Client: **Vertex**	Job:
Final Depth:	X Coord.(Long/East): **Unavailable**
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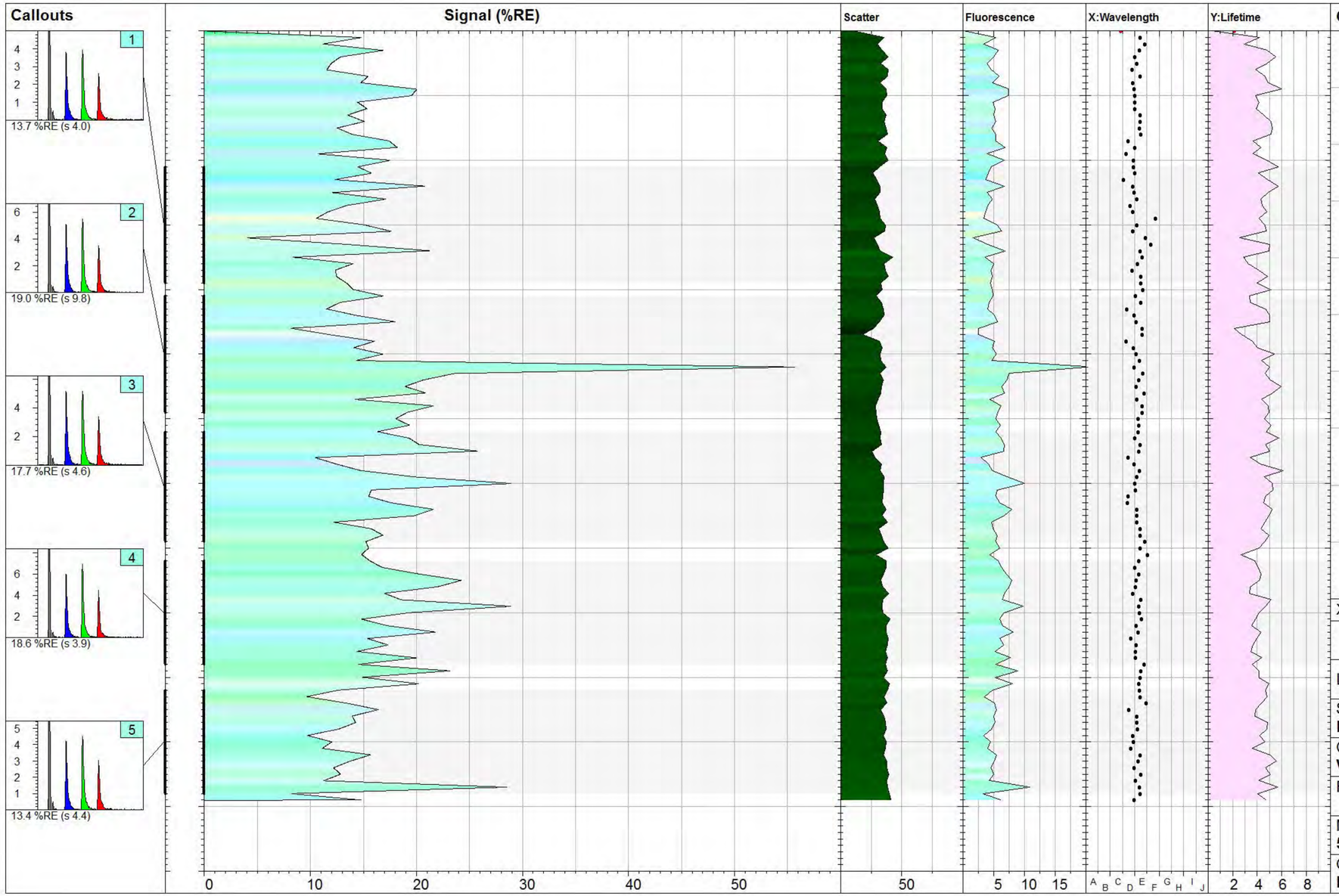

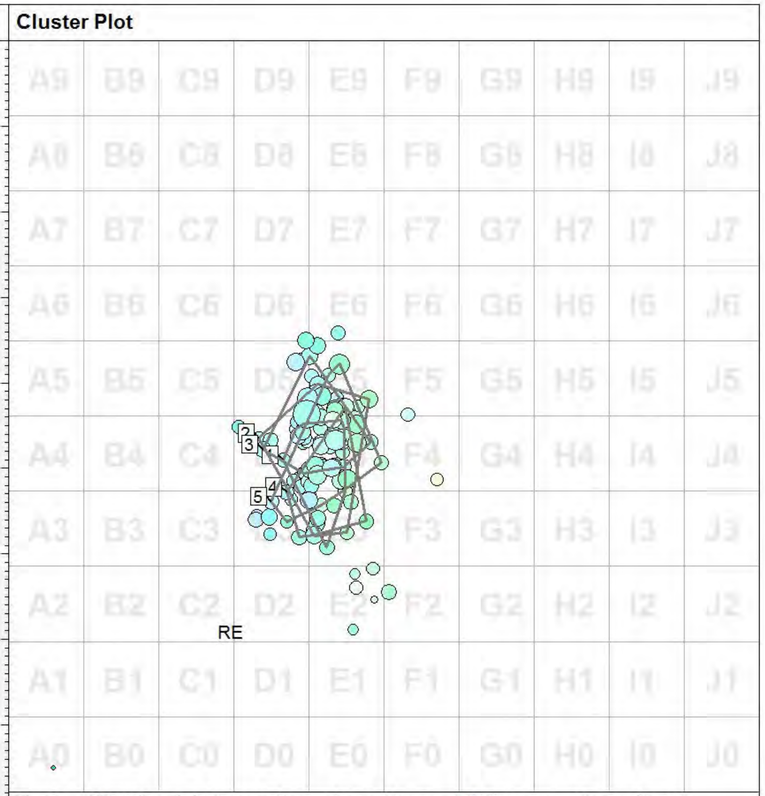

X-axis = Wavelength balance of waveform; Y-axis = Lifetime avg. of waveform

TarGOST® By Dakota

Data Presentation Format © 2020 Dakota Technologies, Inc. (v2.5.38)

Log: **ALLIGARE**

Site: **Lab Study**	Date & Time: **2020-10-20 14:14 CDT**
Client: **Vertex**	Job:
Final Depth:	X Coord.(Long/East): **Unavailable**
Max Signal: **55.7 %RE**	Y Coord.(Lat/North): **Unavailable**
Operator / Unit: **RWS / TG1099**	Elevation: **Unavailable**

Technology Reports – NIRS

Adding Additional Contaminants of Concern as Product Offerings

1. Introduction

This document provides an outline of the performance expectations for different soil contaminants with Maapera's field analysis system. This document provides the different technology development stages for Maapera's system, and the steps to determine if a contaminant can be moved to a performance level.

2. Performance Levels

Overall, there are three categories of performance.

1. **Laboratory** - Literature review has indicated that analysis for a parameter is possible and testing in the laboratory testing has taken place with a relevant number of certified samples.
2. **Semi-quantitative field screening** - Initial laboratory field testing has been completed and at least one field trial for the parameter has been completed. Quantitative data for products at this stage can be provided. Anchor data has been collected and added to Maapera's models to ensure convergence with site conditions.
3. **Quantitative Field Analysis** - Product offerings at the quantitative field analysis stage have been tested on multiple sites and shown to provide reliable quantitative data for a parameter.

3. Moving between categories

Laboratory to Semi-quantitative field screening

To move from proof of concept to semi-quantitative field screening the following steps must be undertaken:

- At least 250 samples are prepared and tested in the laboratory for training data. Model performance is evaluated with a 10-fold cross validation and a ratio of performance to deviation (RPD) greater than 2 must be obtained.
    - RPD is root mean square error (RMSE) divided by the training data standard deviation
    - RPD = RMSE/SD
- One field trial should be completed. A minimum of 10 field samples must be collected from the site and sent to an accredited lab for analysis that can be incorporated in to Maapera's data set. A leave-one-out cross validation shall be completed. If at least 50 samples are collected, a 10-fold cross validation shall be completed. An RPD of at least 2 must be obtained.

Semi-quantitative field screening to Quantitative Field Measurement

To move from semi-quantitative field screening to quantitative field measurement the following steps must be undertaken:

- A library of at least 1500 samples for the parameter must be collected.
    - This number is based on the amount of data it took to obtain adequate performance for prior contaminants, such as the heavy-end hydrocarbons.
    - At least 300 of these samples need to be real field samples
- Adequate performance must be observed on at least 10 field projects with the system being used as a semi-quantitative field screening tool
    - Performance requirements are: Less than 2% false positive and false negatives
    - 80 percent of values are within 100% of the laboratory values as per CCME guidelines (Canadian Council of Ministers of the Environment 2016)[1].
    - RPD value greater than 2 based on a 10-fold cross validation of the entire training dataset (Chang et al. 2001)[2]

References

Canadian Council of Ministers of the Environment 2016. Guidance Manual for Environmental Site Characterisation in Support of Human Health Risk Assessment: Volume 1 Guidance Manual.

Chang, C.-W., Laird, D. A., Mausbach, M. J., and Hurburgh, C. R. 2001. Near-Infrared Reflectance Spectroscopy–Principal Components Regression Analyses of Soil Properties. Soil Sci. Soc. Am. J. **65**: 480. doi:10.2136/sssaj2001.652480x.

[1] High variability in samples at small scales combined with lab variability means that the system may vary more than 50% for a single data point.

[2] RPD values cannot be accurately calculated on small samples sizes as they can be heavily affected by outliers. If a sample has less than 100 samples and has an outlier (defined as a value greater than 2 standard deviations above or below the mean), then RPD calculations will be unreliable.

Technology Reports – Raman MISA

Feasibility Study for Vertex Environmental –

Herbicide Detection with Misa

A McLachlan 9/12/20

andrew.mclachlan@metrohmca.com

1. Introduction

Vertex Environmental wishes to test the Metrohm Misa portable Raman spectrometer for low level herbicide analysis in the field. This document describes the instrument and its performance when tested with some herbicide / water samples provided. The work described here is the first external testing of the Misa. What follows is a description of work to date and suggestions for further testing.

2. What is the Misa?

The Metrohm Instant SERS Analyzer (shown in Figure 1 below) is a new product similar to handheld Raman devices used largely in the defence and security, pharmaceutical and chemical manufacturing industries for the identification of materials, using built in reference libraries. It features a high-efficiency spectrograph equipped with Orbital-Raster-Scan (ORS) technology. It has a minimal footprint and extended battery life, perfect for on-site testing or mobile laboratory applications, and operation is available through BlueTooth or USB connectivity. The Misa uses SERS (Surface Enhanced Raman Spectroscopy) techniques to amplify signals; a small amount of sample is added to a colloidal suspension of gold or silver nanoparticles in solution (water) and subsequent Raman analysis enables significantly improved signal response, allowing detection of substances in ng/mL quantities (ppm / ppb).

Figure 1. The Misa Raman spectrometer showing results in MisaCal on an Android phone.

3. Misa Operation

Figure 2 below shows the procedure for standard operation of the Misa. Preliminary work is required in order for this to be possible in that reference spectra of the analytes of interest must be acquired in advance, and diagnostic peak regions must be specified which are suitably robust in that they don't match with false results.

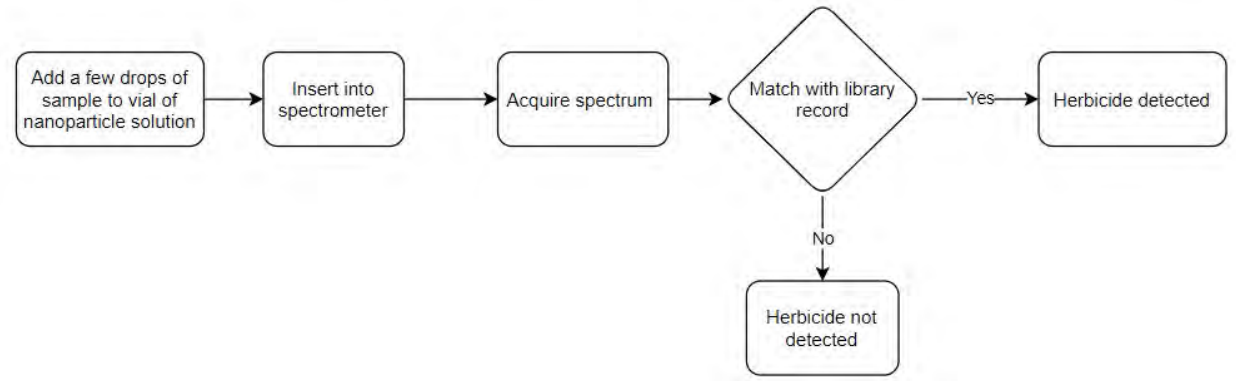

Figure 2. The Misa general use workflow.

4. Misa Setup

Can the Misa detect the herbicides at all? Initial testing begins with acquisition of reference spectra. Several samples were provided in vials for testing in the Metrohm applications lab in Mississauga; tebuthiuron and bromacil in pure form and in 10,000 ppm aqueous samples formulated from commercial pellets (spike, alligare and hyvar, respectively).

The reference samples were prepared using the provided 10,000 ppm aqueous samples which also contained some sediment. 100 µL from these was added to a 2 mL vial containing 0.5 mL Au nanoparticle solution with 100 µL 500 mmol NaCl solution. After closing the vial and some gentle shaking this was placed in the Misa vial holder and a spectrum acquired (with laser power 5, integration time 5 s, 3 averages). Figure 3 below shows three overlaid spectra with baseline correction exhibiting several overlapped and distinct peaks for hyvar (yellow), alligar (red) and spike (blue). In order to

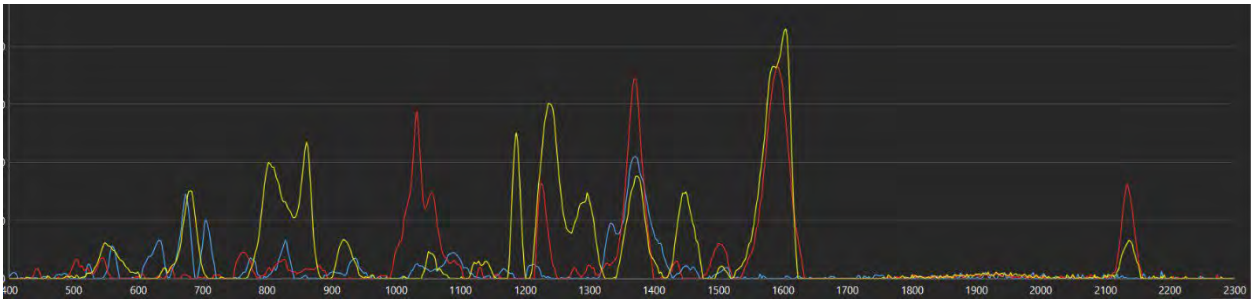

Figure 3. Overlaid spectra of hyvar(yellow), alligar (red) and spike (blue).

5. Sample investigation – qualitation.

The Raman spectra of these samples are subject to change (i.e. peak shape and wavenumber), depending on the sample matrix i.e. salt content, pH, temperature etc. Using a repeatable method for sample preparation enables a degree of consistency, but a key consideration here is that peaks in each spectrum are not only the active herbicide signals; they are from the whole sample matrix which includes additives, water impurities etc.

This makes qualitative identification subject to error if diagnostic peaks used for reference matching shift. Considering that real samples will contain variation in soil composition, robust reference spectra need to be acquired to reflect such differences.

6. Sample investigation – quantitation of aqueous samples.

Sample detection limits were tested by serial dilution of the 10,000 ppm samples, with 100 uL + 100 uL aqueous NaCl (500 mmol) added to 800 uL Au nanoparticle solution before analysis. Spectra were acquired with identical parameters and processing (auto baseline), then compared in order to identify which peaks were diagnostic. Figures 4 and 5 below shows a stacked plot of 100 (blue) 50 (red) and 10 (yellow) ppm hyvar spectra. The zoomed region shows diagnostic peak regions at ~1250 and 1500 wavenumbers decreasing in magnitude with lowered concentration. Note that due to the signals becoming comparable to the baseline noise at less than 100 ppm, the auto baseline correction algorithm skews their lineshape.

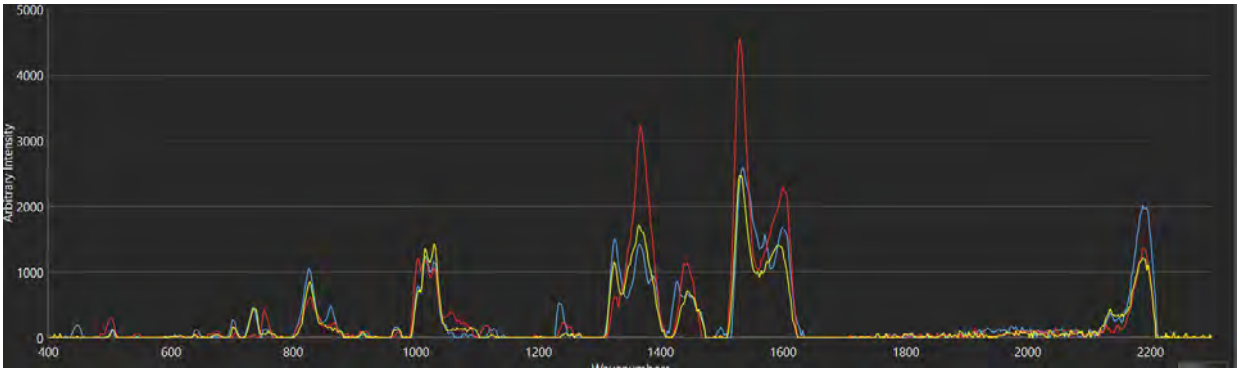

Figure 4. Stacked plot of 100 (blue) 50 (red) and 10 (yellow) ppm hyvar spectra.

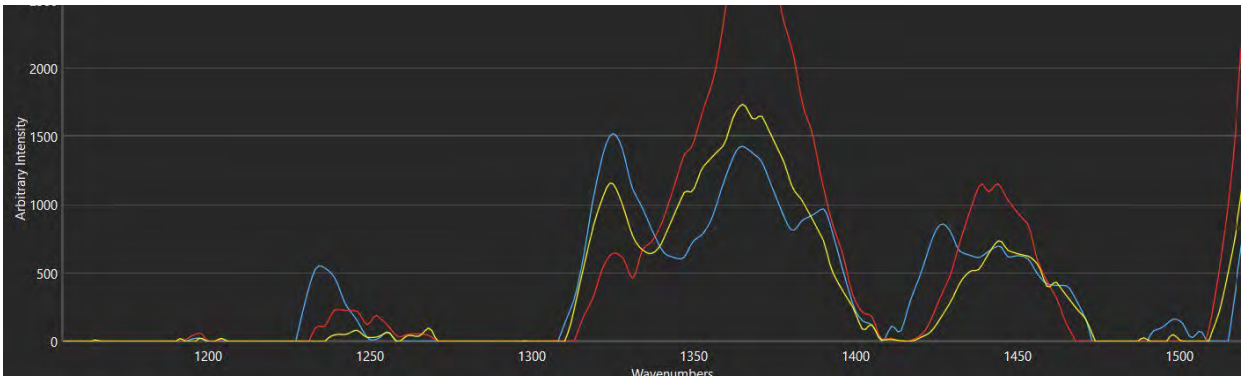

Figure 5. Zoomed stacked plot of 100 (blue) 50 (red) and 10 (yellow) ppm hyvar spectra.

7. Sample investigation – quantitation with samples extracted into chloroform.

Handheld Raman devices such as the Misa are not designed to perform quantitative measurements i.e. to provide results such as % composition. Rather, they are best suited to qualitative analysis – identify what something is based on what they have been trained to identify. With this in mind, and knowing that of the herbicides tested, an approximate 100 ppm limit could be detected with careful sample preparation, micro extractions into chloroform were performed in an attempt to concentrate the herbicides in solution.

7.1 Procedure

To 2 ml aqueous herbicide solution in a vial, add 200 uL $CHCl_3$. After shaking and settling, the bottom chloroform layer was removed by pipette and added to a clean vial. This was then placed on a warm hotplate for a few minutes while the solvent boiled off. 100 uL NaCl solution (500 mmol) was then added along with 500 uL Au nanoparticle solution.

8. Results & Discussion

Serially diluted samples which underwent chloroform, extraction enabled matching down to approx 10 ppm, an order of magnitude improvement compared to the straightforward aqueous sample. Analysis of samples with standard parameters yielded usable spectra with peaks shifted somewhat compared to those acquired in only aqueous / saline conditions.

At this point it was decided that investigation should be paused with a view to extending this work with more representative soil / water / herbicide samples which are more thoroughly characterized in advance. This would enable the creation of more robust library spectra & spectral regions so that matches can be made reliably in the field with the app, rather than the approach taken here which involved interrogating the spectra and identifying herbicide peak regions using the PC based software.

9. Recommendation

Further work is needed to study representative soil + herbicide samples, to create robust methods for sample preparation, and to further probe detection limits (with extraction & concentration) so that results can be comparable to other early studies which can detect analytes at low ppm and ppb levels. Work can also be performed to optimise the extraction process in order to concentrate aqueous analytes. Metrohm would be happy to revisit this work if Vertex Environmental can provide characterized reference (e.g. with GCMS) soil + herbicide samples.

APPENDIX A4: STERILANT-SPECIFIC MODEL INPUT DATA AND BROMACIL MOBILITY IN ALBERTA

This project produced three reports.

Appendix A4-1: Sensitivity Analysis

Marquez, G., A. Houston and T. Todoruk, 2020. Sensitivity Analysis of the Domenico and Robbins Groundwater Transport Model. Report SSP-6/8A prepared by Advisian for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 21 pp. plus Appendices.

Sensitivity Analysis of the Domenico and Robbins Groundwater Transport Model

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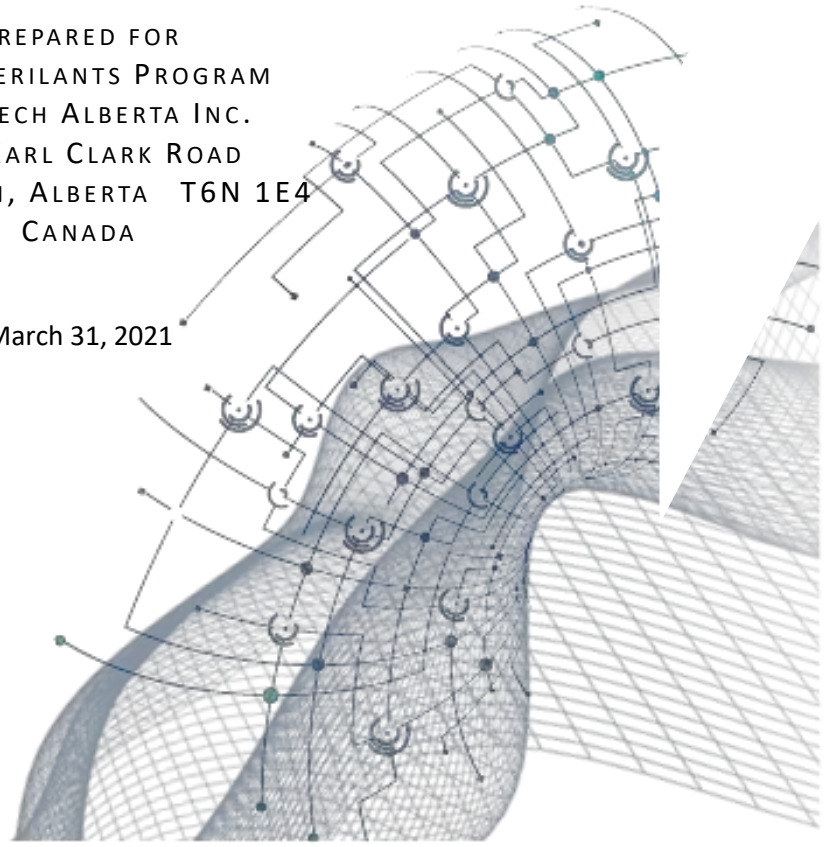
March 31, 2021



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CITATION

This report may be cited as:

Marquez, G., A. Houston and T. Todoruk, 2020. Sensitivity Analysis of the Domenico and Robbins Groundwater Transport Model. Report SSP-6/8A prepared by Advisian for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 21 pp. plus Appendices.

EXECUTIVE SUMMARY

Worley Canada Services Ltd. (Worley), operating as Advisian, was retained by InnoTech Alberta (InnoTech) to assist with the Soil Sterilants Program to develop Sterilant-Specific Model Input Data. The objective of the project is to refine input parameters related to contaminant fate, mobility, and degradation that more realistically reflect Alberta-specific field conditions, are protective of receptors at Alberta sites, can be used to inform Alberta Tier 1 Soil and Groundwater Guidelines modification, are available to site managers for Tier 2 Soil and Groundwater Guidelines calculations when pursuing site closure, and are acceptable to regulators.

The sensitivity analysis of the Domenico and Robbins groundwater transport model used to develop Tier 1 and Tier 2 guidelines is the first task of the Project and will be used to inform subsequent stages of the Project. The evaluation of the model sensitivity to relevant physico-chemical properties of bromacil and tebuthiuron, soil properties, geometric parameters, and flow parameters was completed to understand which parameters are sensitive in the AEP Tier 2 risk assessment model, and significantly influence and have meaningful impacts on guideline outcomes as defined below:

- Advisian has defined parameters that significantly influence the Tier 1 Guidelines to be parameters that result in >10-times change in the resultant soil and/or groundwater guideline. Moderate influence is defined as >5 to 10-times the guideline and limited influence is defined as from >1 to 5-times the guideline.
- Advisian considers work that has a meaningful impact on the management of sterilant contaminated sites as work that will result in more sustainable Tier 1 Guidelines and Tier 2 Guidelines in Alberta. This would include work that results in an increase in Tier 1 Soil Guidelines protective of irrigation watering to levels that are, at minimum, above laboratory detection limits.

Sterilant half-life, water-organic carbon partition coefficient (K_{oc}), fraction of soil organic carbon (f_{oc}), soil bulk density, and infiltration rate were manipulated in the current sensitivity analysis using the Domenico model and ranges compiled from literature or from knowledge of soils in Alberta. An additive combination scenario was also applied to approximate an increase in contaminant degradation not addressed by the Alberta Tier 1 Guidelines with an engineering scenario which limits further migration.

The sensitivity analysis identified the following:

- The Domenico model has higher sensitivity to half-life, f_{oc}, and infiltration rate than other parameters, especially at lower values. The sensitivity thresholds of half-life and infiltration rate are directly related to the modelled geometric and flow parameters that could vary across sites.
- The Domenico model has less sensitivity to K_{oc}, with potential dilution increasing linearly as values increase.
- The model did not show high sensitivity to soil bulk density. However, further investigation into the relationship between site soil bulk density, porosity, and moisture content may result in a different degree of sensitivity.
- Overall, investigating site-specific or regional values for the above parameters would improve the understanding of potential transport of sterilants in the subsurface of Alberta sites and could be used to refine model input parameters.

- Soil properties, geometric parameters, and flow parameters did have a meaningful impact on outcomes for tebuthiuron soil guidelines protective of irrigation water when varied independently, particularly f_{oc} (coarse- and fine-grained soil) and infiltration rate (coarse-grained soil).
- The additive combination scenario had the greatest impact on the soil irrigation guidelines estimated.

Further effects on the significance of outcomes will be associated with local site conditions such as source size, depth to groundwater and lateral distance to receptors.

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1.0 INTRODUCTION

Worley Canada Services Ltd. (Worley), operating as Advisian, was retained by InnoTech Alberta (InnoTech) to assist with the Soil Sterilants Program (SSP) for Sterilant-Specific Model Input Data (the Project).

Remedial endpoint (i.e., guideline) modification using the available Alberta Tier 2 risk assessment models from Alberta Environment and Parks ([AEP] 2019a, b) to develop Alberta Tier 2 Soil and Groundwater Remediation Guidelines (Tier 2 Guidelines; AEP, 2019b) can be an effective and relatively inexpensive approach to site management when sterilants are present. The intent of Tier 2 Guidelines is that they provide an equivalent level of protection as Tier 1 Soil and Groundwater Remediation Guidelines (Tier 1 Guidelines; AEP, 2019a). However, as the model input parameters available within the Tier 2 Guidelines are also conservative, they may not reflect actual field conditions at specific sites or Alberta sites in general.

As part of InnoTech's efforts to advance the science of sterilants in Alberta, this scope of work focuses on:

1. Developing refined model input parameters for the Tier 2 risk assessment models, and
2. Addressing some of the conservative assumptions inherent in the Tier 1 Guidelines under field conditions.

The sensitivity analysis of the groundwater transport model is the first deliverable (Task 1) of the Project.

The evaluation of the sensitivity of relevant physico-chemical properties of bromacil and tebuthiuron, soil properties, geometric parameters and flow parameters is described below. The outcomes are discussed within the framework of whether a parameter manipulation has a significant, moderate, or limited influence on calculated guidelines and could result in a meaningful impact for management of bromacil and tebuthiuron-contaminated sites.

Advisian has defined parameters that significantly influence the Tier 1 Guidelines to be the parameters that result in >10-times change in the resultant soil and/or groundwater guideline. Moderate influence is defined as >5 to 10-times the guideline and limited influence is defined as from >1 to 5-times the guideline.

Advisian considers work that has a meaningful impact on the management of sterilant contaminated sites as work that will result in more sustainable Tier 1 Guidelines and Tier 2 Guidelines in Alberta. This would include work that results in an increase in Tier 1 Soil Guidelines protective of irrigation watering to levels that are, at minimum, above laboratory detection limits.

1.1 Background

Soil sterilants were commonly used from the 1960s to late 1990s for non-selective vegetation control on industrial sites across Alberta. As these sites have moved into the decommissioning, remediation, and/or reclamation phases, it has become evident that sterilants pose unique technical challenges for site remediation and closure. In particular, bromacil and tebuthiuron have been identified as challenging sterilants due to their widespread application across sites in Alberta and their high mobility and recalcitrance in the environment, which combined has created the potential for off site migration and contamination of adjacent lands.

Residual bromacil and tebuthiuron at sites in Alberta are managed within the current Alberta framework using conservative generic Tier 1 Guidelines, Tier 2 approaches (e.g., guideline modification, exposure pathway exclusion, or site-specific risk assessment), or exposure control measures. Application of overly conservative Tier 1 Guidelines or Tier 2 Guidelines results in unnecessary remediation of soil and

groundwater when used to achieve site closure, or indefinite risk management if remediation to meet the guidelines cannot be achieved.

1.2 Objectives

The objective of the Project is to refine input parameters related to contaminant fate, mobility, and degradation that more realistically reflect Alberta-specific field conditions, are protective of receptors at Alberta sites, can be used to inform Tier 1 Guideline modification, are available to site managers for Tier 2 Guideline calculations when pursuing site closure, and are acceptable to regulators.

The Project contributes to the overall SSP objective as, ultimately, it is expected that Tier 1 Guidelines and Tier 2 Guidelines will become less conservative with modified input parameters. Furthermore, as these parameters will be protective at Alberta sites and acceptable to regulators, it creates more opportunities for site managers to develop Tier 2 Guidelines as a path to site closure. Ultimately, this is expected to reduce remediation and management costs at sites across Alberta.

2.0 DOMENICO GROUNDWATER TRANSPORT MODEL

Calculation of soil and groundwater guidelines for soil sterilants is completed in accordance with guidance from the Tier 1 and 2 Guidelines (AEP 2019a, b). The guideline calculations use the Domenico and Robbins groundwater transport model (Domenico model; Domenico, 1987; Domenico and Robbins, 1985). The Domenico model is used to calculate guidelines protective of underlying or down-gradient receptors using the surface water guidelines or toxicity values protective of receptors and the four dilution factors calculated within the model. The four dilution factors (Dilution Factors 1 through 4; DF 1 to DF4) are applied to calculate the soil guidelines although guidelines protective of groundwater uses with no lateral transport considered only use DF1 through DF3. One dilution factor (Dilution Factor 4; DF4) is applied to calculate the groundwater guidelines with a lateral transport component. Each dilution factor reflects processes that affect the concentration of bromacil or tebuthiuron from the source (in soil) to the concentrations in underlying groundwater or surface water at some distance down-gradient of the source. A summary of the four dilution factors and associated equations is presented below. Dilution equations, supporting equations and symbol abbreviations are presented below and in Appendix 1.

2.1 Dilution Factor 1 (DF1)

A linear distribution coefficient is used to describe the partitioning between the sorbed, aqueous, and gaseous phases in soils. The partitioning of non-polar chemicals is a function of the organic carbon-water partitioning coefficient (K_{oc}) of the contaminant and the amount of organic carbon in the soil (fraction of organic carbon [f_{oc}]). Dilution factor 1 (DF1) is the ratio of the concentration of a contaminant in soil to the concentration in leachate that is in contact with the soil.

DF1 Equation:

$$DF1 = K_{oc} \times f_{oc} \times \frac{\theta_w + H' \times \theta_a}{\rho_b}$$

2.2 Dilution Factor 2 (DF2)

Dilution Factor 2 is the ratio of the concentration of the chemical in leachate at the source to that in the porewater just above groundwater. DF2 should be included in the model recalculations only when contamination in soil does not extend down to the water table. Where contamination does extend to the water table, a value of 1.00 (unity) is used for DF2. DF2 was assumed to be 1 for the sensitivity analysis, consistent with the Tier 1 Guidelines.

DF2 Equation:

$$DF2 = \frac{1}{\exp\left(\frac{b}{2\delta_u} - \frac{b}{2\delta_u}(1 + \frac{4\delta_u \mathrm{L}_{us}}{v_u})^{1/2}\right)}$$

2.3 Dilution Factor 3 (DF3)

A groundwater mixing zone model is used to represent the dilution of leachate entering groundwater at the interface between the unsaturated and saturated zones. DF3 is the ratio of the concentration of a chemical in pore water just above the groundwater table, to the concentration in groundwater beneath the source.

DF3 Equation:

$$DF3 = 1 + \frac{Z_d \times V}{I \times X}$$

2.4 Dilution Factor 4 (DF4)

DF4 accounts for the processes of dispersion, sorption, and biodegradation that attenuate the concentration of a chemical compound from the concentration observed in groundwater immediately below the source zone, to the concentration at a discharge point some distance down-gradient of the source. DF4 is based on analytical solutions to the advection-dispersion equation presented by Domenico and Robbins (Domenico, 1987; Domenico and Robbins, 1985). If surface water (discharge point) is closer than 10 m from the source, DF4 takes on a value of 1.00 (unity).

DF4 Equation:

$$DF4 = \frac{4}{\exp(A) \times \mathrm{erfc}(B) \times [\mathrm{erf}(C) - \mathrm{erf}(D)]}$$

Supporting equations for the four dilution factors include:

Thickness of the unsaturated zone below the source equation:

$$b = d - z$$

Average thickness of the mixing zone equation:

$$Z_d = r + s$$

Mixing depth due to dispersion equation:

$$r = 0.01 \times X$$

Mixing depth due to infiltration rate equation:

$$s = d_a \left\{1 - exp\left(\frac{-2.178 \times X \times I}{V \times d_a}\right)\right\}$$

Dimensionless group (A) equation:

$$A = \frac{x}{2D_x}\left\{1 - \left(1 + \frac{4L_s D_x}{v}\right)^{1/2}\right\}$$

Dimensionless group (B) equation:

$$B = \frac{x - vt\left(1 + \frac{4L_s D_x}{v}\right)^{1/2}}{2(D_x vt)^{1/2}}$$

Dimensionless group (C) equation:

$$C = \frac{y + Y/2}{2\left(D_y x\right)^{1/2}}$$

Dimensionless group (D) equation:

$$D = \frac{y - Y/2}{2\left(D_y x\right)^{1/2}}$$

First-order decay of the organic compound (in the saturated zone) equation:

$$L_s = \frac{0.6931}{t_{1/2s}} \times \exp(-0.07d)$$

First-order decay of the organic compound (in the unsaturated zone) equation:

$$L_{us} = \frac{0.6931}{t_{1/2us}} \times \exp(-0.07d)$$

One-dimensional advection (or uniform groundwater flow) and physical retardation equation:

$$v = \frac{V}{\theta_t R_s}$$

Velocity equation:

$$V = K \times i$$

Retardation factor in the saturated zone (unitless) equation:

$$R_s = 1 + \frac{\rho_b K_{oc} f_{oc}}{\theta_t}$$

Retardation factor in the unsaturated zone (unitless) equation:

$$R_u = 1 + \frac{\rho_b K_{oc} f_{oc}}{\theta_w}$$

Dispersivity in the direction of groundwater flow:

$$D_x = 0.1x$$

Dispersivity perpendicular to the direction of groundwater flow:

$$D_y = 0.01x$$

Where:

H'	Henry's Law constant (dimensionless)
ρ_b	dry soil bulk density (g/cm^3)

K	aquifer hydraulic conductivity (m/year)
i	lateral hydraulic gradient in aquifer (dimensionless)
K_{oc}	organic carbon partition coefficient (mL/g)
f_{oc}	fraction organic carbon (g/g)
θ_t	total soil porosity (unitless)
θ_w	water filled porosity (unitless)
θ_a	air filled porosity (unitless)
b	thickness of the unsaturated zone below the source (m)
d	depth from surface to groundwater surface (water table depth; m)
d_a	unconfined aquifer thickness (m)
Z	depth to bottom of contaminated soil (m)
Z_d	average thickness of the mixing zone (calculated for eco pathways)
X	length of contaminated soil (m)
I	Infiltration rate (m/y)
r	mixing depth due to dispersion (m)
s	mixing depth due to infiltration rate (m)
erf	error function
erfc	complimentary error function
A	dimensionless group A
B	dimensionless group B
C	dimensionless group C
D	dimensionless group D
x	distance from source to receptor (m)
D_x	dispersivity in the direction of groundwater flow (m)
D_y	dispersivity perpendicular to the direction of groundwater flow (m)
δ_u	dispersivity in the unsaturated zone (m)
L_s	decay constant (1/year), saturated soil
L_{us}	decay constant (1/year), unsaturated soil
υ	velocity of the contaminant (m/year)
t	transport time (years)
y	distance of the receptor perpendicular to the direction of groundwater flow (m)
Y	source width (m)
$t_{1/2s}$	decay half-life of contaminant in the saturated zone of aquifer (years)
$t_{1/2us}$	decay half-life of contaminant in the unsaturated zone (years)
V	Darcy velocity in groundwater (m/year)
R_s	Retardation factor in the saturated zone (unitless)
R_u	Retardation factor in the unsaturated zone (unitless)

The sensitivity analysis included here evaluates both soil contaminants migrating vertically and laterally to groundwater, and contaminants in groundwater beneath the source migrating to a nearby surface water receiving environment. Results of the model include both potential soil quality guidelines and potential groundwater quality guidelines which have been calculated by varying model input parameters. The estimated guideline values were compared to identify the sensitivity of specific model parameters.

3.0 SOIL STERILANT GUIDELINES

Guideline recalculations for the aquatic life, irrigation water, drinking water, and livestock watering pathways were included in the sensitivity analysis. For soil sterilants, typically aquatic life and irrigation water receptors are more sensitive than human health and livestock watering. Soil sterilant toxicity to aquatic and terrestrial plants is typically high and may pose hazards to these receptors at low concentrations. The Tier 1 Guidelines for surface water used in the assessment as toxicity endpoints are summarized in Table 1. These values are also equal to the Tier 1 Guidelines for groundwater as the recalculation from surface water guidelines to groundwater guidelines assumes no attenuation for bromacil and tebuthiuron. Tier 1 soil guidelines for bromacil and tebuthiuron were estimated by AEP using the Domenico model.

Table 1. Tier 1 Bromacil and Tebuthiuron Surface Water Guidelines.

Pathway	Units	Bromacil Guidelines	Tebuthiuron Guidelines
Freshwater Aquatic Life (FAL)	mg/L	0.005	0.0016
Irrigation Water (IW)	mg/L	0.0002	0.00043
Drinking Water (DW)	mg/L	0.95	0.66
Livestock Watering (LW)	mg/L	1.1	0.13

Notes:

1. mg/L = milligrams per litre.
2. Guidelines compiled from Tier 1 Guidelines.

4.0 SENSITIVITY ANALYSIS

The Domenico model uses physico-chemical properties, soil properties, geometric parameters, and flow parameters to evaluate transport of chemical contaminants from a source in soils to groundwater to a nearby surface water body. Previous preliminary sensitivity analysis on the Domenico model for bromacil completed by Advisian identified that sterilant half-life, water–organic carbon partition coefficient (K_{oc}), fraction of organic carbon (f_{oc}), soil bulk density, and infiltration rate were controlling parameters for the model. The sensitivity of these parameters was evaluated below. Ranges of these values included in the analysis were based on information from literature and an understanding of soil conditions in Alberta.

Site scenarios associated with geometric parameters (e.g., source length and depth to groundwater table) and flow parameters vary greatly from one site to another. Ultimately, these parameters detail the size of the source and how fast contamination will migrate. A larger contaminant source and/or faster transport of the source decreases the attenuation potential from the source to nearby surface water bodies linearly. These parameters were not assessed in detail here since they are a function of local site conditions and cannot be varied. Default AEP parameters for coarse and fine soils were retained for use in the analysis. This includes the distance down-gradient to the nearby surface water body (a conservative value of 10 metres) and a transport time of 500 years, which may represent an infinite source if the geometric and flow parameters are below a threshold for the mass of the contaminant source.

The complete groundwater transport model sensitivity analysis, including guidelines calculations for each pathway, is attached as Appendix 1. Figures 1 through 4 in Appendix 2 show dilution factors for bromacil and tebuthiuron in coarse- and fine-grained soil. A summary of the analysis is presented below for each parameter identified as potentially significant to the outcome of the model. Pathway guideline recalculations use the same dilution factors and, therefore, have the same trends. For the summary below, only the freshwater aquatic life guideline recalculations are included for discussion. To better understand the significance of the sensitivity of a parameter, the dilution factors used to modify the surface water guidelines have been included with DF1 to DF3 applied to calculate soil guidelines and DF4 applied to calculate groundwater guidelines. These values are representative of the magnitude of impact that a single parameter can have on the model outputs and are discussed within the framework of significant, moderate, or limited influence on the guidelines and meaningful impact for management of bromacil and tebuthiuron-contaminated sites (as defined in Section 1.0). Additional dilution factors are also discussed if they are affected by parameter manipulation. The sensitivity analysis also includes a remedial capping scenario (where multiple parameters are manipulated) and soil irrigation guideline outcomes are also discussed.

4.1 Half-Life

Half-lives for bromacil and tebuthiuron were compiled from the U.S. National Library of Medicine (NLM) Toxicology Data Network (TOXNET; USNLM, 2010, 2012) as they were not available from AEP (2019a, b).

Half-life values reported in TOXNET for bromacil ranged from 60 days to upwards of 8 months, with a maximum value of 1,494 days (approximately four years). This half-life corresponds to the maximum reported half-life in field dissipation studies by Landsburg and Dwyer (1995 citing Gardiner et al. (1969)). This value also corresponds to the results of USEPA field dissipation studies (124 to 155 days) with an added safety factor of 10. The assumed 1,494-day (4 year) half-life was considered to be a conservative assumption and may overestimate residence time in the environment. Half-life values reported in TOXNET for tebuthiuron ranged from 12 months upwards to 35 months.

The half-life range of 0.25 to 64 years was included in the sensitivity analysis for both bromacil and tebuthiuron with the intent to determine the half-life values at which no further increase in dilution factors were observed. With the default geometric and flow parameters, a half-life of 64 years or higher resulted in no significant attenuation during simulated transport of bromacil and a half-life of 32 years or higher resulted in little to no attenuation during simulated transport for tebuthiuron. DF1, DF2, and DF3 are not affected by half-life.

Results of the half-life sensitivity analysis are included below for bromacil and tebuthiuron in coarse-grainedsoil (Table 2) and fine-grained soil (Table 3). Half-life is generally a sensitive parameter at the lower ends of the included ranges as shown, with the largest variation in dilution factors within the 0.25- to 4-year half-life range. Within this range, there is potential for a dilution factor of the surface water guideline of 13 for bromacil (significant influence) and 3 for tebuthiuron (moderate) in coarse-grained soil. Also, within this range, there is potential for a dilution factor of the surface water guideline of 1.18×10^{05} for bromacil (significant influence), and 4,630 for tebuthiuron (significant influence) in fine-grained soil. The trends observed in outcomes are similar between coarse- and fine-grained soils. Half-life is generally considered to have a significant influence on soil and groundwater guideline outcomes. With the same half-life, the estimated dilution factor for bromacil is slightly higher than the dilution factor for tebuthiuron due to bromacil's higher AEP default K_{oc} value.

Table 2. Half-Life Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Coarse-grained Soil.

Half-life (years)	Bromacil (Coarse)				Tebuthiuron (Coarse)			
	DF4	Overall DF	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF4	Overall DF	Soil Guideline (mg/kg)	GW Guideline (mg/L)
0.25	6.99	**13.1**	0.065	0.035	3.46	**2.97**	0.0047	0.0055
0.5	2.86	**5.35**	0.027	0.014	1.92	**1.65**	0.0026	0.0031
1	1.73	**3.24**	0.016	0.0087	1.40	**1.20**	0.0019	0.0022
2	1.33	**2.48**	0.012	0.0066	1.19	**1.02**	0.0016	0.0019
4	1.13	**2.11**	0.011	0.0057	1.08	**0.93**	0.0015	0.0017
8	1.08	**2.01**	0.010	0.0054	1.04	**0.90**	0.0014	0.0017
16	1.04	**1.94**	0.0097	0.0052	1.02	**0.88**	0.0014	0.0016
32	1.02	**1.90**	0.0095	0.0051	1.01	**0.87**	0.0014	0.0016
64	1.01	**1.89**	0.0094	0.0050	1.01	**0.86**	0.0014	0.0016
Default FAL Tier 1 Guideline (half-life set at 1,000,000)	1	**1.87**	0.009	0.005	1	**0.86**	0.0014	0.0016

Notes:

1. mg/L = milligrams per litre.
2. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
3. FAL guidelines compiled from Tier 1 Guidelines.

Table 3. Half-Life Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Fine-grained Soil.

Half-life (years)	Bromacil (Fine)				Tebuthiuron (Fine)			
	DF4	Overall DF	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF4	Overall DF	Soil Guideline (mg/kg)	GW Guideline (mg/L)
0.25	6.74×10^4	**1.18×10^5**	590	337	5,100	**4,630**	7.41	8.17
0.5	1,030	**1,800**	8.98	5.13	182	**165.3**	0.26	0.29
1	63.4	**111**	0.55	0.32	20.8	**18.9**	0.030	0.033
2	10.7	**18.8**	0.09	0.05	5.43	**4.93**	0.0079	0.0087
4	3.07	**5.37**	0.03	0.02	2.22	**2.01**	0.0032	0.0035
8	1.99	**3.48**	0.02	0.01	1.60	**1.46**	0.0023	0.0026
16	1.43	**2.49**	0.01	0.01	1.27	**1.16**	0.0018	0.0020
32	1.20	**2.10**	0.01	0.01	1.13	**1.03**	0.0016	0.0018
64	1.10	**1.92**	0.01	0.01	1.06	**0.97**	0.0015	0.0017
Default FAL Tier 1 Guideline (half-life set at 1,000,000)	1	**1.87**	0.0088	0.005	1	**0.86**	0.0015	0.0016

Notes:

1. mg/L = milligrams per litre.
2. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
3. FAL guidelines compiled from Tier 1 Guidelines.

4.2 Water-Organic Carbon Partition Coefficient (K_{oc})

K_{oc} values for bromacil and tebuthiuron were compiled from the U.S. National Library of Medicine (NLM) Toxicology Data Network (TOXNET; USNLM 2010, 2012) with published K_{oc} values from AEP (2019a) also included. For the analysis of K_{oc} and the other parameters below, the half-life of bromacil was assumed to be 4 years and the half-life for tebuthiuron was assumed to be 3 years based on the maximum reported half-lives as discussed above. Using a half-life allows for the sensitivity of the model to the variation of other parameters to be captured. Without the application of a half-life, no dilution through DF4 can be assumed.

K_d parameters are related directly to K_{oc}. K_d values are calculated directly by multiplying K_{oc} and f_{oc}. This relationship does not hold for soils with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME, 2006). For this analysis the default f_{oc} from the Tier 1 Guidelines was retained (i.e., 0.005). It should also be noted that the model is sensitive to the K_{oc} parameter when used in conjunction with the default AEP f_{oc} (0.005). At higher values for f_{oc}, the model is more sensitive to K_{oc}. The sensitivity analysis for f_{oc} based on Alberta soils is presented in the following section.

K_{oc} values reported in TOXNET for bromacil ranged from 12 mL/g to 126 mL/g. The default AEP value for bromacil is set at 66.6 mL/g. K_{oc} values reported in TOXNET for tebuthiuron ranged from 4 mL/g to 157 mL/g. The default AEP value for tebuthiuron is set at 23 mL/g which is relatively low compared to the value for bromacil. The K_{oc} range of 4 mL/g to 157 mL/g was included in the analysis for both sterilants with model inputs included for the upper- and lower-most reported values and the default parameters. Both DF1 and DF4 increase with K_{oc} value (Appendix 1).

Results of the K_{oc} sensitivity analysis are included below for bromacil and tebuthiuron in coarse-grained soil (Table 4) and fine-grained soil (Table 5). K_{oc} is moderately sensitive in the model with a correlated linear increase to the overall dilution factors. With the reported values, there is potential for moderate overall dilution factor of 5.1 for bromacil and for a moderate overall dilution factor of 5.6 for tebuthiuron in coarse-grained soil (Appendix 1). With the reported values, there is potential for a significant influence on overall dilution factor (i.e., 25.9) for bromacil soil quality guidelines and for a significant influence on overall dilution factor (i.e., 47.2) for tebuthiuron in fine-grained soil (Appendix 1). The trends observed in outcomes are similar between coarse- and fine-grained soils. K_{oc} is considered to generally have a significant influence on soil and groundwater guideline outcomes.

Table 4. Water-Organic Carbon Partition Coefficient (K_{oc}) Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Coarse-grained Soil.

Water-Organic Carbon Partition Coefficient (K_{oc}) (mL/g)	Bromacil (Coarse)				Tebuthiuron (Coarse)			
	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)
4	0.09	1.06	0.0022	0.0053	0.09	1.09	0.0007	0.0017
12	0.13	1.07	0.0032	0.0054	0.13	1.10	0.0011	0.0018
23*	0.19	1.09	0.0047	0.0054	0.19	1.12	0.0015	0.0018
40	0.27	1.11	0.0070	0.0056	0.27	1.16	0.0023	0.0018
66.6**	0.40	1.15	0.011	0.0058	0.40	1.21	0.0036	0.0019
80	0.47	1.17	0.013	0.0059	0.47	1.24	0.0043	0.0020
100	0.57	1.20	0.016	0.0060	0.57	1.28	0.0054	0.0020

Water-Organic Carbon Partition Coefficient (K_{oc}) (mL/g)	Bromacil (Coarse)				Tebuthiuron (Coarse)			
	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)
126	0.7	1.24	0.020	0.0062	0.70	1.34	0.0070	0.0021
157	0.86	1.29	0.026	0.0064	0.86	1.41	0.0089	0.0023

Notes:

1. mg/L = milligrams per litre.
2. DF4 = dilution factor 4. Overall DF = the combination of dilution factors 1 through 4.
3. FAL guidelines compiled from Tier 1 Guidelines.
4. Tier 1 Guidelines and a half-life of four years for bromacil and three years for tebuthiuron.

* Default Tier 1 Guideline K_{oc} value for tebuthiuron.

** Default Tier 1 Guideline K_{oc} value for bromacil.

Table 5. Water-Organic Carbon Partition Coefficient (K_{oc}) Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Fine-grained Soil.

Water-Organic Carbon Partition Coefficient (K_{oc}) (mL/g)	Bromacil (Fine)				Tebuthiuron (Fine)			
	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)
4	0.14	2.04	0.0055	0.010	0.14	2.59	0.0022	0.0041
12	0.18	2.20	0.0076	0.011	0.18	2.85	0.0032	0.0046
23*	0.24	2.43	0.011	0.012	0.24	3.25	0.0047	0.0052
40	0.32	2.83	0.018	0.014	0.32	3.97	0.0078	0.0063
66.6**	0.45	3.57	0.031	0.018	0.45	5.35	0.015	0.0086
80	0.52	4.00	0.040	0.020	0.52	6.18	0.020	0.010
100	0.62	4.72	0.057	0.024	0.62	7.64	0.029	0.012
126	0.75	5.82	0.084	0.029	0.75	9.96	0.046	0.016
157	0.91	7.41	0.13	0.037	0.905	13.5	0.076	0.022

Notes:

1. mg/L = milligrams per litre.
2. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.

3. FAL guidelines compiled from Tier 1 Guidelines.
4. Tier 1 Soil and Groundwater Remediation Guidelines and a half-life of four years for bromacil and three years for tebuthiuron.
* Default Tier 1 Guideline K_{oc} value for tebuthiuron.
** Default Tier 1 Guideline K_{oc} value for bromacil.

4.3 Fraction of Organic Carbon (f_{oc})

As discussed above, K_d values are calculated by multiplying K_{oc} and f_{oc}. For this analysis, the default Tier 1 Guideline K_{oc} was retained with bromacil set at 66.6 mL/g and tebuthiuron set at 23 mL/g.

The f_{oc} range chosen for this assessment was zero to six percent based on the Alberta potential mineral topsoil and subsoil ranges. Results of the f_{oc} sensitivity analysis are included below for bromacil and tebuthiuron for coarse-grained soil (Table 6) and fine-grained soil (Table 7). The model is sensitive to f_{oc}, with increases to the overall dilution factors across the entire range. With the reported values, there is potential for a significant influence on overall dilution factor (i.e., 51) for bromacil and tebuthiuron (i.e., 11.5) in coarse-grained soil (Appendix 1). There is the potential for a significant influence on overall dilution factor (i.e., 5,568) for bromacil and for tebuthiuron (i.e., 228) in fine-grained soil (Appendix 1). The trends observed in outcomes are similar between coarse- and fine-grained soils. Both DF1 and DF4 increase with f_{oc} value (Appendix 1). Soil f_{oc} for mineral soils (i.e., f_{oc} less than 4%), f_{oc} is considered to generally have a significant influence on soil and groundwater guideline outcomes depending on soil particle size.

Table 6. Fraction of Organic Carbon (f_{oc}) Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Coarse-grained Soil.

Fraction of Organic Carbon (f_{oc}) (unitless)	Bromacil (Coarse)				Tebuthiuron (Coarse)			
	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)
0.0	0.07	1.06	0.0017	0.0053	0.07	1.08	0.0006	0.0017
0.0025	0.24	1.10	0.0061	0.0055	0.13	1.10	0.0010	0.0018
0.005*	0.40	1.15	0.011	0.0058	0.19	1.12	0.0015	0.0018
0.0075	0.57	1.20	0.016	0.0060	0.24	1.14	0.0021	0.0018
0.01	0.74	1.25	0.021	0.0063	0.30	1.17	0.0026	0.0019
0.015	1.07	1.36	0.034	0.0068	0.42	1.21	0.0037	0.0019
0.02	1.40	1.47	0.048	0.0074	0.53	1.26	0.0050	0.0020
0.04	2.73	2.01	0.13	0.010	0.99	1.47	0.011	0.0024
0.06	4.07	2.71	0.26	0.014	1.45	1.71	0.018	0.0027

Notes:

1. mg/L = milligrams per litre.
2. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
3. FAL guidelines compiled from Tier 1 and Groundwater Remediation Guidelines (AEP 2019a).
4. Tier 1 Guidelines and a half-life of four years for bromacil and three years for tebuthiuron.

* Default Tier 1 Guideline K_{oc} value.

Table 7. Fraction of Organic Carbon (f_{oc}) Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Fine-grained Soil.

Fraction of Organic Carbon (f_{oc}) (unitless)	Bromacil (Fine)				Tebuthiuron (Fine)			
	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)
0.0	0.12	1.96	0.005	0.010	0.12	2.46	0.0018	0.0039
0.0025	0.29	2.67	0.015	0.013	0.18	2.84	0.0031	0.0045
0.005*	0.45	3.57	0.031	0.018	0.24	3.25	0.0047	0.0052
0.0075	0.62	4.72	0.056	0.024	0.29	3.72	0.0067	0.0060
0.01	0.79	6.16	0.094	0.031	0.35	4.25	0.0092	0.0068
0.015	1.12	10.2	0.22	0.051	0.47	5.49	0.016	0.0088
0.02	1.45	16.4	0.46	0.082	0.58	7.02	0.025	0.011
0.04	2.78	85.8	4.61	0.43	1.04	17.4	0.11	0.028
0.06	4.12	350	27.8	1.75	1.50	39.4	0.37	0.063

Notes:

1. mg/L = milligrams per litre.
2. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
3. FAL guidelines compiled from Tier 1 Guidelines.
4. Tier 1 Guidelines and a half-life of four years for bromacil and three years for tebuthiuron.

* Default Tier 1 Guideline K_{oc} value.

4.4 Soil Bulk Density

In the Domenico model, where site parameters are not available, soil bulk density is used to directly calculate total porosity as well as vapour-filled and moisture-filled porosity. This is done as part of the provision of default parameters rather than by the user on a typical site and there is an opportunity to adjust these parameters even if site-specific information is not available to align with literature values more closely for site-specific soil types. In the Tier 1 model, total porosity does not equate effective porosity and both vapour-filled and moisture-filled porosity may be over-estimated.

In addition, soil moisture content and particle density are modifying factors for soil bulk density and the estimated porosities. Soil moisture content and particle density may be further evaluated at sites or on a regional basis to refine the model. For the Tier 1 Guidelines, total porosity is estimated from the soil bulk density, assuming a particle density of 2.65 g/cm^3. The moisture-filled porosity is calculated as the soil bulk density multiplied by the moisture content. For this analysis, moisture content was assumed to be 0.12 for fine soils (soil bulk density at or less than 1.4 g/cm^3) and 0.07 for coarse soils (soil bulk density at or greater than 1.7 g/cm^3). This is consistent with the values used by AEP to estimate the default parameters for the Tier 1 Guidelines for fine and coarse soils (AEP, 2019a; CCME, 2006). The vapour-filled porosity is then obtained by subtracting the moisture-filled porosity from the total porosity.

Because of the interrelationship of these values, the reactiveness of the model to changes in soil bulk density may or may not show an accurate degree of sensitivity. The soil bulk density range chosen for this assessment was 1 g/cm^3 to 2 g/cm^3 based on the potential range in Alberta mineral topsoils and subsoils. Results of the sensitivity analysis are included below for bromacil and tebuthiuron in coarse-grained soil (Table 8) and fine-grained soil (Table 9). The model is relatively insensitive to variation in soil bulk density with limited significance on outcomes in coarse- and fine-grained soil. Field studies measuring the different combinations of site soil bulk density, porosity and moisture content may result in different sensitivities within the model. It should also be noted that, in the case of this assessment, the choice of soil moisture was the controlling factor regarding the overall dilution factor. The trends observed in outcomes are similar between coarse- and fine-grained soils. Both DF1 and DF4 increase slightly with bulk density value with DF1 results the same in both coarse- and fine-grained soils (Appendix 1).

Table 8. Soil Bulk Density Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Coarse-grained Soil.

Soil Bulk Density (g/cm^3)	Bromacil (Coarse)				Tebuthiuron (Coarse)			
	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)
1	0.45	1.16	0.012	0.0058	0.24	1.16	0.0020	0.0019
1.2	0.45	1.15	0.012	0.0058	0.24	1.15	0.0020	0.0018
1.4*	0.45	1.15	0.012	0.0058	0.24	1.14	0.0020	0.0018
1.7**	0.40	1.15	0.011	0.0058	0.19	1.12	0.0015	0.0018
1.9	0.40	1.15	0.011	0.0057	0.19	1.11	0.0015	0.0018
2.0	0.40	1.15	0.011	0.0057	0.19	1.10	0.0015	0.0018

Notes:

1. g/cm^3 = grams per cubic centimetre.
2. mg/L = milligrams per litre.
3. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
4. The model used the FAL guidelines compiled from Tier 1 Guidelines and a half-life of four years for bromacil and three years for tebuthiuron.

*Default Tier 1 Guideline value for fine-grained soil.

**Default Tier 1 Guideline value for coarse-grained soil.

Table 9. Soil Bulk Density Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Fine-grained Soil.

Soil Bulk Density (g/cm^3)	Bromacil (Fine)				Tebuthiuron (Fine)			
	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF1	DF4	Soil Guideline (mg/kg)	GW Guideline (mg/L)
1	0.45	3.66	0.032	0.018	0.24	3.89	0.0056	0.0062
1.2	0.45	3.62	0.032	0.018	0.24	3.56	0.0052	0.0057
1.4*	0.45	3.58	0.031	0.018	0.24	3.26	0.0047	0.0052
1.7**	0.40	3.52	0.027	0.018	0.19	2.85	0.0033	0.0046
1.9	0.40	3.48	0.027	0.017	0.19	2.60	0.0030	0.0042
2.0	0.40	3.46	0.027	0.017	0.19	2.49	0.0028	0.0040

Notes:

1. g/cm^3 = grams per cubic centimetre.
2. mg/L = milligrams per litre.
3. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
4. The model used the FAL guidelines compiled from Tier 1 Guidelines and a half-life of four years for bromacil and three years for tebuthiuron.

*Default Tier 1 Guideline value for fine-grained soil.

**Default Tier 1 Guideline value for coarse-grained soil.

4.5 Infiltration Rate

Infiltration rates can vary greatly for sites. Engineering controls such as asphalting or engineered caps can greatly decrease the infiltration across a site. Infiltration rates are related to vertical flow of the source and are therefore dependent on the other geometric and flow parameters as well as half-life. Default Tier 1 infiltration rates are set at 0.012 m/year for fine soils and 0.06 m/year for coarse soils.

The infiltration rate range chosen for this assessment was 0.001 m/year to 0.5 m/year. This range accounts for infiltration rates across several orders of magnitude but could potentially be greater in Alberta especially for soils under irrigation. Infiltration rate can be estimated from irrigation rates or rainfall rates modified for regional evapotranspiration. Results of the sensitivity analysis are included below for bromacil and tebuthiuron for coarse-grained soil (Table 10) and fine-grained soil (Table 11). The calculation for DF4 is not affected by infiltration rate. Table 10 and Table 11 show DF3 which is affected by infiltration rate and is the same for both bromacil and tebuthiuron. The model is sensitive to infiltration rate at small values (values less than 0.012 m/year) with significant influence on the overall dilution factors at low levels of infiltration. With the reported values, there is potential for an overall dilution factor of 43 for bromacil and 19.3 for tebuthiuron in coarse-grained soil. There is potential for an overall dilution factor of 19.6 for bromacil and 9.3 for tebuthiuron in fine-grained soil. The same trends are observed in the dilution factors for coarse- and fine-grained soils. Soil infiltration rate is considered to have a significant influence on soil guideline outcomes.

Table 10. Infiltration Rate Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Coarse-grained Soil.

Infiltration Rate (m/year)	Bromacil (Coarse)				Tebuthiuron (Coarse)			
	DF3	Overall DF***	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF3	Overall DF***	Soil Guideline (mg/kg)	GW Guideline (mg/L)
0.001	92.8	**43.0**	0.22	0.0058	92.8	**19.3**	0.031	0.0018
0.0025	39.0	**18.1**	0.091	0.0058	39.0	**8.10**	0.013	0.0018
0.005	21.1	**9.78**	0.050	0.0058	21.1	**4.38**	0.0070	0.0018
0.0075	15.1	**7.01**	0.035	0.0058	15.1	**3.14**	0.0050	0.0018
0.012*	10.6	**4.93**	0.025	0.0058	10.6	**2.21**	0.0035	0.0018
0.030	6.15	**2.85**	0.014	0.0058	6.15	**1.28**	0.0020	0.0018
0.060**	4.64	**2.15**	0.011	0.0058	4.64	**0.96**	0.0015	0.0018
0.100	4.02	**1.86**	0.0093	0.0058	4.02	**0.83**	0.0013	0.0018
0.500	3.11	**1.44**	0.0072	0.0058	3.11	**0.65**	0.0010	0.0018

Notes:

1. m/year = metres/year.
2. DF3 = Dilution Factor 3
3. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
4. The model used the FAL guidelines compiled from Tier 1 Guidelines and a half-life of four years for bromacil and three years for tebuthiuron.

*Default Tier 1 Guideline value for fine-grained soil.
**Default Tier 1 Guideline value for coarse-grained soil.
***DF4 for bromacil was 1.15 and for tebuthiuron was 0.0019.

Table 11. Infiltration Rate Sensitivity Analysis (Protection of Freshwater Aquatic Life) – Fine-grained Soil.

Infiltration Rate (m/year)	Bromacil (Fine)				Tebuthiuron (Fine)			
	DF3***	Overall DF	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF3***	Overall DF	Soil Guideline (mg/kg)	GW Guideline (mg/L)
0.001	12.1	**19.6**	0.098	0.018	12.13	**9.28**	0.015	0.0052
0.0025	6.75	**10.9**	0.055	0.018	6.75	**5.16**	0.0083	0.0052
0.005	4.94	**8.00**	0.040	0.018	4.94	**3.78**	0.0060	0.0052
0.0075	4.33	**7.01**	0.035	0.018	4.33	**3.31**	0.0053	0.0052
0.012*	3.86	**6.25**	0.031	0.018	3.86	**2.95**	0.0047	0.0052

Infiltration Rate (m/year)	Bromacil (Fine)				Tebuthiuron (Fine)			
	DF3***	Overall DF	Soil Guideline (mg/kg)	GW Guideline (mg/L)	DF3***	Overall DF	Soil Guideline (mg/kg)	GW Guideline (mg/L)
0.030	3.33	**5.38**	0.027	0.018	3.33	**2.54**	0.0041	0.0052
0.060*	3.04	**4.91**	0.025	0.018	3.04	**2.32**	0.0037	0.0052
0.100	2.81	**4.55**	0.023	0.018	2.81	**2.15**	0.0034	0.0052
0.500	1.84	**2.97**	0.015	0.018	1.84	**1.40**	0.0022	0.0052

Notes:

1. m/year = metres/year.
2. DF3 = Dilution Factor 3.
3. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
4. The model used the FAL guidelines compiled from Tier 1 Guidelines and a half-life of four years for bromacil and three years for tebuthiuron.

*Default Tier 1 Guideline value for fine-grained soil.
**Default Tier 1 Guideline value for coarse-grained soil.
***DF4 for bromacil was 1.15 and for tebuthiuron was 0.0019.

4.6 Additive Combination Sensitivity Analysis

A scenario was included in the analysis that combined the highest modelled K_{oc} values, the minimum modelled half-life, and a capping scenario that assumes the infiltration rate to be at the lower end of the analysis range. This scenario is relevant as it combines an increase in contaminant degradation not addressed by the Tier 1 guidelines with an engineering scenario which limits further migration of contaminants. The Tier 1 Guideline default values for the other parameters were retained. The results are detailed below for bromacil and tebuthiuron in coarse-grained soil (Table 12) and fine-grained soil (Table 13). The overall dilution factors estimated for these scenarios for coarse-grained soil were 9,735 and 780 for bromacil and tebuthiuron, respectively. The overall dilution factors estimated for these scenarios for fine-grained soil were 3.63×10^{09} and 1.46×10^{05} for bromacil and tebuthiuron, respectively. Appendix 1 provides the calculated values and individual dilution factors.

Table 12. Additive Combination Sensitivity Analysis (Freshwater Aquatic Life) – Coarse-grained Soil.

Parameter	Bromacil	Tebuthiuron
Half-life (years)	0.25	1
Water-organic Carbon Partition Coefficient (K_{oc}) (mL/g)	126	157
Fraction of Organic Carbon (f_{oc})	0.01	0.01
Soil Bulk Density	1.7	1.7
Infiltration Rate (m/year)	0.001	0.001

Parameter	Bromacil	Tebuthiuron
DF1	1.33	1.64
DF2	1.00	1.00
DF3	92.8	92.8
DF4	78.9	5.12
Overall DF	9740	780
Soil Guideline (mg/kg)	48.7	1.25
GW Guideline (mg/L)	0.39	0.0082

Notes:

1. m/year = metres/year.
2. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
3. The model used the FAL guidelines compiled from Tier 1 Guidelines.

Table 13. Additive Combination Sensitivity Analysis (Freshwater Aquatic Life) – Fine-grained Soil.

Parameter	Bromacil	Tebuthiuron
Half-life (years)	0.25	1
Water-organic Carbon Partition Coefficient (K_{oc}) (mL/g)	126	157
Fraction of Organic Carbon (f_{oc})	0.010	0.005
Soil Bulk Density	1.4	1.4
Infiltration Rate (m/year)	0.001	0.001
DF1	1.38	1.69
DF2	1.00	1.00
DF3	12.1	12.1
DF4	2.17×10^{08}	7096
Overall DF	3.63×10^{09}	1.46×10^{05}
Soil Guideline (mg/kg)	1.81×10^{07}	233
GW Guideline (mg/L)	Above solubility	11.4

Notes:

1. m/year = metres/year.
2. DF4 = Dilution Factor 4. Overall DF = the combination of dilution factors 1 through 4.
3. The model used the FAL guidelines compiled from Tier 1 Guidelines.

4.7 Soil Irrigation Guideline Outcomes

The Alberta Tier 1 soil guidelines protective of irrigation water are lower than the laboratory method detection limits for bromacil and tebuthiuron (as defined in AEP, 2019a). As defined earlier in this section, a meaningful impact on soil guidelines would at least increase the soil guideline protective of irrigation above laboratory method detection limits. For the purpose of this discussion, the method detection limit (as provided by Bureau Veritas Laboratories) is 0.009 mg/kg for bromacil and 0.001 mg/kg for tebuthiuron in soil. For the scenarios described above, the range of outcomes for soil guidelines protective of irrigation are summarized in Table 14 (coarse-grained soil) and Table 15 (fine-grained soil).

While soil properties, geometric parameters and flow parameters affect guideline outcomes, the ranges of values applied in the sensitivity analysis did not result in bromacil soil guidelines protective of irrigation water greater than laboratory method detection limits (i.e., 0.009 mg/kg) for coarse-grained soil. Tebuthiuron has a method detection limit lower than bromacil and the ranges of values applied in the sensitivity analysis resulted in tebuthiuron soil guidelines protective of irrigation greater than the laboratory method detection limit (i.e., 0.001 mg/kg) for coarse-grained soil, with the exception of half-life and bulk density which had little effect. For bromacil in fine-grained soil, trends are similar to coarse-grained soils and the ranges of values applied in the sensitivity analysis did not result in bromacil soil guidelines protective of irrigation water greater than laboratory method detection limits (i.e., 0.009 mg/kg) for fine-grained soil. For tebuthiuron in fine-grained soil, similar to the findings for coarse-grained soil, the ranges of values applied in the sensitivity analysis resulted in tebuthiuron soil guidelines protective of irrigation greater than the laboratory method detection limit (i.e., 0.001 mg/kg), with the exception of half-life and bulk density which had little effect.

The combination scenario for both soil sterilants in coarse- and fine-grained soil resulted in an increase to the soil irrigation guidelines such that they were greater than laboratory method detection limits.

Table 14. Sensitivity Analysis (Irrigation) – Coarse-grained Soil.

Parameter Manipulated	Bromacil Soil Guideline Range (Coarse)	Tebuthiuron Soil Guideline Range (Coarse)
Tier 1 Guideline for coarse-grained soil calculated using default parameters	0.00037	0.00037
Laboratory Method Detection Limits	0.009	0.001
Half-life (years)	0.00037	0.00037
Water-organic Carbon Partition Coefficient (K_{oc}) (mL/g)	0.00008 – 0.0008	0.00018 – 0.0017
Fraction of Organic Carbon (f_{oc})	0.00006 – 0.0038	0.00014 – 0.0029
Soil Bulk Density	0.00037 – 0.00042	0.00037 – 0.00047
Infiltration Rate (m/year)	0.00025 – 0.0075	0.00025 – 0.0074
Additive Combination Scenario	0.025	0.065

Notes:

1. The model used the IW Tier 1 Guidelines.

Table 15. Sensitivity Analysis (Irrigation) – Fine-grained Soil.

Parameter Manipulated	Bromacil Soil Guideline Range (Fine)	Tebuthiuron Soil Guideline Range (Fine)
Tier 1 Guideline for coarse-grained soil calculated using default parameters	0.00037	0.00037
Laboratory Method Detection Limits	0.009	0.001
Half-life (years)	0.00035	0.00039
Water-organic Carbon Partition Coefficient (K_{oc}) (mL/g)	0.00011 – 0.0007	0.00023 – 0.0015
Fraction of Organic Carbon (f_{oc})	0.00009 – 0.0032	0.00020 – 0.0025
Soil Bulk Density	0.00031 – 0.00035	0.00031 – 0.00039
Infiltration Rate (m/year)	0.00017 – 0.0011	0.00019 – 0.0012
Additive Combination Scenario	0.0034	0.0088

5.0 DISCUSSION AND CONCLUSIONS

The objective of the Project was to refine input parameters related to contaminant fate, mobility, and degradation that more realistically reflect Alberta-specific field conditions, are protective of receptors at Alberta sites, can be used to inform Tier 1 Guideline modification, are available to site managers for Tier 2 Guideline calculations when pursuing site closure, and are acceptable to regulators. The sensitivity analysis of the Domenico groundwater transport model is Task 1, of the Project. Evaluation of Domenico model sensitivity to relevant physico-chemical properties of bromacil and tebuthiuron, soil properties, geometric parameters, and flow parameters was completed to identify sensitive parameters in the Tier 2 risk assessment models that can significantly influence and have meaningful impacts on guideline outcomes. Previous preliminary sensitivity analysis for bromacil identified that sterilant half-life and K_{oc}, f_{oc}, soil bulk density, and infiltration rate were controlling parameters for the model. These parameters were manipulated in the current sensitivity analysis using the Domenico model and ranges compiled from literature or from knowledge of soils in Alberta.

The Domenico model has higher sensitivity to half-life, $f_{oc,}$ and infiltration rate than other parameters, especially at lower values. The sensitivity thresholds of half-life and infiltration rate are directly related to the modelled geometric and flow parameters that could vary across sites. The Domenico model has less sensitivity to K_{oc}, with potential dilution increasing linearly as values increase. The model did not show high sensitivity to soil bulk density. However, further investigation into the relationship between site soil bulk density, porosity, and moisture content may result in a different degree of sensitivity. Overall, investigating site-specific or regional values for the above parameters would improve the understanding of potential transport of sterilants in the subsurface of Alberta sites and used to refine model input parameters.

Soil properties, geometric parameters, and flow parameters had a meaningful impact on outcomes for tebuthiuron soil guidelines protective of irrigation water when varied independently, particularly f_{oc} (coarse- and fine-grained soil) and infiltration rate (coarse-grained soil). An additive combination scenario designed to approximate an increase in contaminant degradation not addressed by the Tier 1 guidelines with an engineering scenario which limits further migration had the greatest impact on the soil irrigation guidelines estimated.

Further effects on the significance of outcomes will be associated with local site conditions such as source size, depth to groundwater and lateral distance to receptors.

6.0 REFERENCES

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7.0 LIST OF APPENDICES

Appendix 1: Sensitivity Analysis Data

Appendix 2: Sensitivity Analysis Figures

APPENDIX 1: SENSITIVITY ANALYSIS DATA

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters							Half-life 0.25 year to 64 years (~64 years + = guideline)								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Bromacil (Fine Soil)	Default Tier 1 Parameter Values Bromacil (Coarse Soil)	Additive Combination Bromacil_upper end	Bromacil (Coarse Soil)_t1/2_0.25 years	Bromacil (Coarse Soil)_t1/2_0.5y ears	Bromacil (Coarse Soil)_t1/2_1yea rs	Bromacil (Coarse Soil)_t1/2_2yea r	Bromacil (Coarse Soil)_t1/2_4yea rs	Bromacil (Coarse Soil)_t1/2_8yea rs	Bromacil (Coarse Soil)_t1/2_16ye ars	Bromacil (Coarse Soil)_t1/2_32ye ars	Bromacil (Coarse Soil)_t1/2_64ye ars
Soil Guidelines															
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**48.6728**	**0.0654**	**0.0268**	**0.0162**	**0.0124**	**0.0106**	**0.0101**	**0.0097**	**0.0095**	**0.0094**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.02468**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**2265**	**12**	**12**	**12**	**12**	**12**	**12**	**12**	**12**	**12**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**135.73**	**2.06**	**2.06**	**2.06**	**2.06**	**2.06**	**2.06**	**2.06**	**2.06**	**2.06**
Groundwater Guidelines															
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.394**	**0.0350**	**0.0143**	**0.0087**	**0.0066**	**0.0057**	**0.0054**	**0.0052**	**0.0051**	**0.0050**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.0158**	**0.00140**	**0.00057**	**0.00035**	**0.00027**	**0.00023**	**0.00022**	**0.00021**	**0.00020**	**0.00020**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**74.95**	**6.64**	**2.72**	**1.65**	**1.26**	**1.07**	**1.02**	**0.99**	**0.97**	**0.96**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**86.78**	**7.69**	**3.15**	**1.91**	**1.46**	**1.24**	**1.18**	**1.14**	**1.12**	**1.11**
Chemical Properties							**Assumptions - distance = 10 m.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**126**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**1.26**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties															
soil bulk density	p_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.010**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters															
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.												
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**5**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters							Half-life 0.25 year to 64 years (~64 years + = guideline)								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Additive Combination Bromacil_upper end**	**Bromacil (Coarse Soil)_t1/2_0.25 years**	**Bromacil (Coarse Soil)_t1/2_0.5y ears**	**Bromacil (Coarse Soil)_t1/2_1yea rs**	**Bromacil (Coarse Soil)_t1/2_2yea r**	**Bromacil (Coarse Soil)_t1/2_4yea rs**	**Bromacil (Coarse Soil)_t1/2_8yea rs**	**Bromacil (Coarse Soil)_t1/2_16ye ars**	**Bromacil (Coarse Soil)_t1/2_32ye ars**	**Bromacil (Coarse Soil)_t1/2_64ye ars**
Flow Parameters															
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.001**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δu	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.000	0.088	0.088	0.088	0.088	0.088	0.088	0.088	0.088	0.088
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		3.8	5.8	19.0	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8
retardation factor in saturated zone	R_s	-		2.0	2.6	7.0	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
velocity of the contaminant	v	*m/year*		1.0	9.7	3.6	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7
Degradation Parameters															
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	2.5E-01	0.25	0.50	1.00	2.00	4.09	8.00	16.00	32.00	64.00
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	2.25E+00	2.25E+00	1.12E+00	5.62E-01	2.81E-01	1.19E-01	7.02E-02	3.51E-02	1.76E-02	8.78E-03
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	2.5E-01	0.25	0.50	1.00	2.00	4.09	8.00	16.00	32.00	64.00
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	2.25E+00	2.25E+00	1.12E+00	5.62E-01	2.81E-01	1.19E-01	7.02E-02	3.51E-02	1.76E-02	8.78E-03
Mixing Zone Calculation															
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.002	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144
overall mixing depth	Z_d	*m*		0.38	0.24	0.10	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Calculation of Dilution Factors															
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	1.330	0.403	0.403	0.403	0.403	0.403	0.403	0.403	0.403	0.403
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	92.78	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	1793.00	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**78.89**	**6.99**	**2.86**	**1.73**	**1.33**	**1.13**	**1.08**	**1.04**	**1.02**	**1.01**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-4.37E+00	-1.94E+00	-1.05E+00	-5.50E-01	-2.82E-01	-1.22E-01	-7.21E-02	-3.62E-02	-1.81E-02	-9.07E-03
dimensionless group	B	-		-1.07E+01	-3.47E+01	-3.95E+01	-4.82E+01	-4.20E+01	-3.85E+01	-3.67E+01	-3.56E+01	-3.52E+01	-3.50E+01	-3.48E+01	-3.48E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**9734.56**	**13.08**	**5.35**	**3.24**	**2.48**	**2.11**	**2.01**	**1.94**	**1.90**	**1.89**
Water Quality Guidelines															
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Parameters						Water - organic carbon partition coefficient 4 mL/g to 157 mL/g								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Bromacil (Fine Soil)	Default Tier 1 Parameter Values Bromacil (Coarse Soil)	Bromacil (Coarse Soil)_K_{oc}_4	Bromacil (Coarse Soil)_K_{oc}_12	Bromacil (Coarse Soil)_K_{oc}_23	Bromacil (Coarse Soil)_K_{oc}_40	Bromacil (Coarse Soil)_K_{oc}_66	Bromacil (Coarse Soil)_K_{oc}_80	Bromacil (Coarse Soil)_K_{oc}_100	Bromacil (Coarse Soil)_K_{oc}_126	Bromacil (Coarse Soil)_K_{oc}_157
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**0.0022**	**0.0032**	**0.0047**	**0.0070**	**0.0108**	**0.0128**	**0.0159**	**0.0201**	**0.0256**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00008**	**0.00012**	**0.00017**	**0.00025**	**0.00037**	**0.00044**	**0.00053**	**0.00065**	**0.00079**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**3**	**4**	**5**	**8**	**12**	**14**	**17**	**21**	**25**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**0.46**	**0.66**	**0.94**	**1.38**	**2.06**	**2.40**	**2.91**	**3.57**	**4.36**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.0053**	**0.0054**	**0.0054**	**0.0056**	**0.0058**	**0.0059**	**0.0060**	**0.0062**	**0.0064**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.00021**	**0.00021**	**0.00022**	**0.00022**	**0.00023**	**0.00023**	**0.00024**	**0.00025**	**0.00026**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**1.01**	**1.02**	**1.03**	**1.06**	**1.09**	**1.11**	**1.14**	**1.18**	**1.22**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**1.17**	**1.18**	**1.20**	**1.22**	**1.27**	**1.29**	**1.32**	**1.36**	**1.42**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 4.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	4	12	23	40	**66.6**	80	100	126	157
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**0.02**	**0.06**	**0.115**	**0.2**	**0.333**	**0.4**	**0.5**	**0.63**	**0.785**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties														
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Water - organic carbon partition coefficient 4 mL/g to 157 mL/g								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Coarse Soil)_K_{oc}_4**	**Bromacil (Coarse Soil)_K_{oc}_12**	**Bromacil (Coarse Soil)_K_{oc}_23**	**Bromacil (Coarse Soil)_K_{oc}_40**	**Bromacil (Coarse Soil)_K_{oc}_66**	**Bromacil (Coarse Soil)_K_{oc}_80**	**Bromacil (Coarse Soil)_K_{oc}_100**	**Bromacil (Coarse Soil)_K_{oc}_126**	**Bromacil (Coarse Soil)_K_{oc}_157**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.392	0.271	0.191	0.131	0.088	0.075	0.062	0.050	0.041
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		3.8	5.8	1.3	1.9	2.6	3.9	5.8	6.7	8.1	10.0	12.2
retardation factor in saturated zone	R_s	-		2.0	2.6	1.1	1.3	1.5	1.9	2.6	2.9	3.4	4.0	4.7
velocity of the contaminant	v	*m/year*		1.0	9.7	22.7	19.4	16.1	12.8	9.7	8.6	7.4	6.3	5.3
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144
overall mixing depth	Z_d	*m*		0.38	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	0.090	0.130	0.185	0.270	0.403	0.470	0.570	0.700	0.855
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.06**	**1.07**	**1.09**	**1.11**	**1.15**	**1.17**	**1.20**	**1.24**	**1.29**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-6.00E-02	-7.03E-02	-8.44E-02	-1.06E-01	-1.40E-01	-1.57E-01	-1.82E-01	-2.15E-01	-2.53E-01
dimensionless group	B	-		-1.07E+01	-3.47E+01	-5.39E+01	-4.99E+01	-4.56E+01	-4.08E+01	-3.57E+01	-3.38E+01	-3.14E+01	-2.91E+01	-2.69E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**0.44**	**0.65**	**0.93**	**1.39**	**2.15**	**2.55**	**3.17**	**4.03**	**5.11**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Fraction of organic carbon 0 % to 6 %								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Bromacil (Fine Soil)	Default Tier 1 Parameter Values Bromacil (Coarse Soil)	Bromacil (Coarse Soil)_f_{oc}_0%	Bromacil (Coarse Soil)_f_{oc}_0.25%	Bromacil (Coarse Soil)_f_{oc}_0.5%	Bromacil (Coarse Soil)_f_{oc}_0.75%	Bromacil (Coarse Soil)_f_{oc}_1%	Bromacil (Coarse Soil)_f_{oc}_1.5%	Bromacil (Coarse Soil)_f_{oc}_2%	Bromacil (Coarse Soil)_f_{oc}_4%	Bromacil (Coarse Soil)_f_{oc}_6%
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**0.0017**	**0.0061**	**0.0108**	**0.0159**	**0.0214**	**0.0337**	**0.0479**	**0.1278**	**0.2556**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00006**	**0.00022**	**0.00037**	**0.00053**	**0.00068**	**0.00099**	**0.00130**	**0.00254**	**0.00377**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**2**	**7**	**12**	**17**	**22**	**31**	**41**	**80**	**119**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**0.36**	**1.21**	**2.06**	**2.91**	**3.76**	**5.46**	**7.16**	**13.95**	**20.75**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.0053**	**0.0055**	**0.0058**	**0.0060**	**0.0063**	**0.0068**	**0.0074**	**0.0101**	**0.0135**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.00021**	**0.00022**	**0.00023**	**0.00024**	**0.00025**	**0.00027**	**0.00029**	**0.00040**	**0.00054**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**1.00**	**1.05**	**1.09**	**1.14**	**1.19**	**1.29**	**1.40**	**1.91**	**2.57**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**1.16**	**1.21**	**1.27**	**1.32**	**1.38**	**1.49**	**1.62**	**2.22**	**2.98**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 4.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**0**	**0.1665**	**0.333**	**0.4995**	**0.666**	**0.999**	**1.332**	**2.664**	**3.996**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties														
soil bulk density	p_b	*g/cm³*	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**
total porosity	q_t	*cm³/cm³*	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**
soil moisture-filled porosity	q_w	*cm³/cm³*	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**
soil air-filled porosity	q_a	*cm³/cm³*	Not sensitive. Calculated.	**0.302**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	0.000	0.0025	**0.005**	0.0075	0.010	0.015	0.020	0.040	0.060
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Fraction of organic carbon 0 % to 6 %								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Coarse Soil)_f_{oc}_0%**	**Bromacil (Coarse Soil)_f_{oc}_0.25%**	**Bromacil (Coarse Soil)_f_{oc}_0.5%**	**Bromacil (Coarse Soil)_f_{oc}_0.75%**	**Bromacil (Coarse Soil)_f_{oc}_1%**	**Bromacil (Coarse Soil)_f_{oc}_1.5%**	**Bromacil (Coarse Soil)_f_{oc}_2%**	**Bromacil (Coarse Soil)_f_{oc}_4%**	**Bromacil (Coarse Soil)_f_{oc}_6%**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δu	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.504	0.149	0.088	0.062	0.048	0.033	0.025	0.013	0.009
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		3.8	5.8	1.0	3.4	5.8	8.1	10.5	15.3	20.0	39.1	58.1
retardation factor in saturated zone	R_s	-		2.0	2.6	1.0	1.8	2.6	3.4	4.1	5.7	7.3	13.6	19.9
velocity of the contaminant	v	*m/year*		1.0	9.7	24.9	13.9	9.7	7.4	6.0	4.4	3.4	1.8	1.3
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144
overall mixing depth	Z_d	*m*		0.38	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	0.070	0.237	0.403	0.570	0.736	1.069	1.402	2.734	4.066
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.06**	**1.10**	**1.15**	**1.20**	**1.25**	**1.36**	**1.47**	**2.01**	**2.71**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-5.48E-02	-9.76E-02	-1.40E-01	-1.82E-01	-2.24E-01	-3.06E-01	-3.87E-01	-7.00E-01	-9.96E-01
dimensionless group	B	-		-1.07E+01	-3.47E+01	-5.63E+01	-4.25E+01	-3.57E+01	-3.15E+01	-2.85E+01	-2.46E+01	-2.21E+01	-1.71E+01	-1.48E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**0.34**	**1.21**	**2.15**	**3.17**	**4.27**	**6.74**	**9.58**	**25.55**	**51.12**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Parameters						Soil Bulk Density 1 g/cm^3 to 2 g/cm^3					
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Coarse Soil)_ρ_b_1.0**	**Bromacil (Coarse Soil)_ρ_b_1.2**	**Bromacil (Coarse Soil)_ρ_b_1.4**	**Bromacil (Coarse Soil)_ρ_b_1.7**	**Bromacil (Coarse Soil)_ρ_b_1.9**	**Bromacil (Coarse Soil)_ρ_b_2.0**
Soil Guidelines											
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**0.0121**	**0.0121**	**0.0121**	**0.0108**	**0.0107**	**0.0107**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00042**	**0.00042**	**0.00042**	**0.00037**	**0.00037**	**0.00037**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**13**	**13**	**13**	**12**	**12**	**12**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**2.31**	**2.31**	**2.31**	**2.06**	**2.06**	**2.06**
Groundwater Guidelines											
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.0058**	**0.0058**	**0.0058**	**0.0058**	**0.0057**	**0.0057**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.00023**	**0.00023**	**0.00023**	**0.00023**	**0.00023**	**0.00023**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**1.10**	**1.10**	**1.10**	**1.09**	**1.09**	**1.09**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**1.27**	**1.27**	**1.27**	**1.27**	**1.26**	**1.26**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 4. total porosity =1-(bulk density/2.65). Water content = 0.12 for 0-1.4 and 0.07 for 1.7+.**					
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties											
soil bulk density	ρ_b	*g/cm^3*	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1**	**1.2**	**1.4**	**1.7**	**1.9**	**2**
total porosity	q_t	*cm^3/cm^3*	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.62**	**0.55**	**0.47**	**0.36**	**0.28**	**0.25**
soil moisture-filled porosity	q_w	*cm^3/cm^3*	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.120**	**0.144**	**0.168**	**0.119**	**0.133**	**0.140**
soil air-filled porosity	q_a	*cm^3/cm^3*	Not sensitive. Calculated.	**0.302**	**0.241**	**0.503**	**0.403**	**0.304**	**0.239**	**0.150**	**0.105**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters											
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.								
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Soil Bulk Density 1 g/cm^3 to 2 g/cm^3					
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Coarse Soil)_ρ_b_1.0**	**Bromacil (Coarse Soil)_ρ_b_1.2**	**Bromacil (Coarse Soil)_ρ_b_1.4**	**Bromacil (Coarse Soil)_ρ_b_1.7**	**Bromacil (Coarse Soil)_ρ_b_1.9**	**Bromacil (Coarse Soil)_ρ_b_2.0**
Flow Parameters											
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.132	0.110	0.095	0.088	0.078	0.074
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		3.8	5.8	3.8	3.8	3.8	5.8	5.8	5.8
retardation factor in saturated zone	R_s	-		2.0	2.6	1.5	1.7	2.0	2.6	3.2	3.7
velocity of the contaminant	v	*m/year*		1.0	9.7	9.4	9.5	9.6	9.7	9.8	9.8
Degradation Parameters											
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
Mixing Zone Calculation											
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.144	0.144	0.144	0.144	0.144	0.144
overall mixing depth	Z_d	*m*		0.38	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Calculation of Dilution Factors											
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	0.453	0.453	0.453	0.403	0.403	0.403
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	4.64	4.64	4.64	4.64	4.64	4.64
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	30.87	30.87	30.87	30.87	30.87	30.87
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.156**	**1.154**	**1.153**	**1.150**	**1.149**	**1.148**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-1.44E-01	-1.43E-01	-1.42E-01	-1.40E-01	-1.38E-01	-1.38E-01
dimensionless group	B	-		-1.07E+01	-3.47E+01	-3.51E+01	-3.53E+01	-3.55E+01	-3.57E+01	-3.59E+01	-3.60E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**2.43**	**2.43**	**2.42**	**2.15**	**2.15**	**2.15**
Water Quality Guidelines											
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Infiltration Rate 0.001 m/year to 0.5 m/year								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Coarse Soil)_Infiltration_0.001**	**Bromacil (Coarse Soil)_Infiltration_0.0025**	**Bromacil (Coarse Soil)_Infiltration_0.005**	**Bromacil (Coarse Soil)_Infiltration_0.0075**	**Bromacil (Coarse Soil)_Infiltration_0.012**	**Bromacil (Coarse Soil)_Infiltration_0.03**	**Bromacil (Coarse Soil)_Infiltration_0.06**	**Bromacil (Coarse Soil)_Infiltration_0.1**	**Bromacil (Coarse Soil)_Infiltration_0.5**
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**0.2151**	**0.0905**	**0.0489**	**0.0351**	**0.0247**	**0.0143**	**0.0108**	**0.0093**	**0.0072**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00748**	**0.00314**	**0.00170**	**0.00122**	**0.00086**	**0.00050**	**0.00037**	**0.00032**	**0.00025**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**686**	**275**	**138**	**92**	**58**	**23**	**12**	**7**	**2**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**41.13**	**17.30**	**9.35**	**6.70**	**4.72**	**2.73**	**2.06**	**1.78**	**1.38**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.0058**	**0.0058**	**0.0058**	**0.0058**	**0.0058**	**0.0058**	**0.0058**	**0.0058**	**0.0058**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.00023**	**0.00023**	**0.00023**	**0.00023**	**0.00023**	**0.00023**	**0.00023**	**0.00023**	**0.00023**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**1.09**	**1.09**	**1.09**	**1.09**	**1.09**	**1.09**	**1.09**	**1.09**	**1.09**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**1.27**	**1.27**	**1.27**	**1.27**	**1.27**	**1.27**	**1.27**	**1.27**	**1.27**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 4.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties														
soil bulk density	p_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Infiltration Rate 0.001 m/year to 0.5 m/year								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Coarse Soil)_Infiltration_0.001**	**Bromacil (Coarse Soil)_Infiltration_0.0025**	**Bromacil (Coarse Soil)_Infiltration_0.005**	**Bromacil (Coarse Soil)_Infiltration_0.0075**	**Bromacil (Coarse Soil)_Infiltration_0.012**	**Bromacil (Coarse Soil)_Infiltration_0.03**	**Bromacil (Coarse Soil)_Infiltration_0.06**	**Bromacil (Coarse Soil)_Infiltration_0.1**	**Bromacil (Coarse Soil)_Infiltration_0.5**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.001**	**0.0025**	**0.005**	**0.0075**	**0.012**	**0.030**	**0.060**	**0.100**	**0.500**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δu	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.001	0.004	0.007	0.011	0.018	0.044	0.088	0.146	0.730
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		3.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8	5.8
retardation factor in saturated zone	R_s	-		2.0	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
velocity of the contaminant	v	*m/year*		1.0	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7	9.7
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.002	0.006	0.012	0.018	0.029	0.072	0.144	0.237	1.079
overall mixing depth	Z_d	*m*		0.38	0.24	0.10	0.11	0.11	0.12	0.13	0.17	0.24	0.34	1.18
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	0.403	0.403	0.403	0.403	0.403	0.403	0.403	0.403	0.403
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	92.78	39.02	21.10	15.12	10.64	6.15	4.64	4.02	3.11
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	1793.00	717.80	359.40	239.93	150.33	60.73	30.87	18.92	4.58
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.15**	**1.15**	**1.15**	**1.15**	**1.15**	**1.15**	**1.15**	**1.15**	**1.15**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-1.40E-01	-1.40E-01	-1.40E-01	-1.40E-01	-1.40E-01	-1.40E-01	-1.40E-01	-1.40E-01	-1.40E-01
dimensionless group	B	-		-1.07E+01	-3.47E+01	-3.57E+01	-3.57E+01	-3.57E+01	-3.57E+01	-3.57E+01	-3.57E+01	-3.57E+01	-3.57E+01	-3.57E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**43.02**	**18.09**	**9.78**	**7.01**	**4.93**	**2.85**	**2.15**	**1.86**	**1.44**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters							Half-life 0.25 year to 64 years (~64 years + = guideline)								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Bromacil (Fine Soil)	Default Tier 1 Parameter Values Bromacil (Coarse Soil)	Additive Combination Bromacil_upper end	Bromacil (Fine Soil)_t1/2_0.25years	Bromacil (Fine Soil)_t1/2_0.5years	Bromacil (Fine Soil)_t1/2_1years	Bromacil (Fine Soil)_t1/2_2year	Bromacil (Fine Soil)_t1/2_4years	Bromacil (Fine Soil)_t1/2_8years	Bromacil (Fine Soil)_t1/2_16years	Bromacil (Fine Soil)_t1/2_32years	Bromacil (Fine Soil)_t1/2_64years
Soil Guidelines															
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**1.81E+07**	**589.9830**	**8.9785**	**0.5545**	**0.0938**	**0.0269**	**0.0174**	**0.0125**	**0.0105**	**0.0096**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00335**	**0.00035**	**0.00035**	**0.00035**	**0.00035**	**0.00035**	**0.00035**	**0.00035**	**0.00035**	**0.00035**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**236.24**	**6.86**	**6.86**	**6.86**	**6.86**	**6.86**	**6.86**	**6.86**	**6.86**	**6.86**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**18.42**	**1.92**	**1.92**	**1.92**	**1.92**	**1.92**	**1.92**	**1.92**	**1.92**	**1.92**
Groundwater Guidelines															
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**Above Solubility**	**337.2014**	**5.1316**	**0.3169**	**0.0536**	**0.0153**	**0.0099**	**0.0071**	**0.0060**	**0.0055**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**Above Solubility**	**13.48806**	**0.20527**	**0.01268**	**0.00215**	**0.00061**	**0.00040**	**0.00029**	**0.00024**	**0.00022**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**Above Solubility**	**Above Solubility**	**Above Solubility**	**60.22**	**10.19**	**2.92**	**1.89**	**1.35**	**1.14**	**1.04**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**Above Solubility**	**Above Solubility**	**Above Solubility**	**69.73**	**11.80**	**3.38**	**2.19**	**1.57**	**1.32**	**1.21**
Chemical Properties							**Assumptions - distance = 10 m.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**126**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**1.26**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties															
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.010**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters															
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.												
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**5**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
Flow Parameters															

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters							Half-life 0.25 year to 64 years (~64 years + = guideline)								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Additive Combination Bromacil_upper end**	**Bromacil (Fine Soil)_t1/2_0.25years**	**Bromacil (Fine Soil)_t1/2_0.5years**	**Bromacil (Fine Soil)_t1/2_1years**	**Bromacil (Fine Soil)_t1/2_2year**	**Bromacil (Fine Soil)_t1/2_4years**	**Bromacil (Fine Soil)_t1/2_8years**	**Bromacil (Fine Soil)_t1/2_16years**	**Bromacil (Fine Soil)_t1/2_32years**	**Bromacil (Fine Soil)_t1/2_64years**
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.001**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δu	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.001	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019	0.019
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		3.8	5.8	11.5	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
retardation factor in saturated zone	R_s	-		2.0	2.6	4.8	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
velocity of the contaminant	v	*m/year*		1.0	9.7	0.4	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Degradation Parameters															
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	2.5E-01	0.25	0.50	1.00	2.00	4.09	8.00	16.00	32.00	64.00
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	2.25E+00	2.25E+00	1.12E+00	5.62E-01	2.81E-01	1.19E-01	7.02E-02	3.51E-02	1.76E-02	8.78E-03
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	2.5E-01	0.25	0.50	1.00	2.00	4.09	8.00	16.00	32.00	64.00
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	2.25E+00	2.25E+00	1.12E+00	5.62E-01	2.81E-01	1.19E-01	7.02E-02	3.51E-02	1.76E-02	8.78E-03
Mixing Zone Calculation															
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.024	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283
overall mixing depth	Z_d	*m*		0.38	0.24	0.12	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Calculation of Dilution Factors															
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	1.380	0.453	0.453	0.453	0.453	0.453	0.453	0.453	0.453	0.453
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	12.13	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	180.20	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**2.17E+08**	**67440.28**	**1026.33**	**63.39**	**10.73**	**3.07**	**1.99**	**1.43**	**1.20**	**1.10**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-1.92E+01	-1.11E+01	-6.93E+00	-4.15E+00	-2.37E+00	-1.12E+00	-6.87E-01	-3.54E-01	-1.80E-01	-9.09E-02
dimensionless group	B	-		-1.07E+01	-3.47E+01	-3.39E+01	-3.50E+01	-2.59E+01	-1.98E+01	-1.59E+01	-1.32E+01	-1.22E+01	-1.15E+01	-1.11E+01	-1.09E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**3.63E+09**	**1.18E+05**	**1795.71**	**110.91**	**18.77**	**5.37**	**3.48**	**2.49**	**2.10**	**1.92**
Water Quality Guidelines															
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Parameters						Water - organic carbon partition coefficient 4 mL/g to 157 mL/g								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Bromacil (Fine Soil)	Default Tier 1 Parameter Values Bromacil (Coarse Soil)	Bromacil (Fine Soil)_Koc_4	Bromacil (Fine Soil)_Koc_12	Bromacil (Fine Soil)_Koc_23	Bromacil (Fine Soil)_Koc_40	Bromacil (Fine Soil)_Koc_66	Bromacil (Fine Soil)_Koc_80	Bromacil (Fine Soil)_Koc_100	Bromacil (Fine Soil)_Koc_126	Bromacil (Fine Soil)_Koc_157
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**0.0055**	**0.0076**	**0.0110**	**0.0175**	**0.0312**	**0.0402**	**0.0565**	**0.0843**	**0.1295**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00011**	**0.00014**	**0.00018**	**0.00025**	**0.00035**	**0.00040**	**0.00048**	**0.00058**	**0.00070**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**2.12**	**2.72**	**3.56**	**4.84**	**6.86**	**7.87**	**9.38**	**11.35**	**13.70**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**0.59**	**0.76**	**1.00**	**1.36**	**1.92**	**2.21**	**2.63**	**3.19**	**3.84**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.0102**	**0.0110**	**0.0122**	**0.0142**	**0.0179**	**0.0200**	**0.0236**	**0.0291**	**0.0371**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.00041**	**0.00044**	**0.00049**	**0.00057**	**0.00071**	**0.00080**	**0.00094**	**0.00116**	**0.00148**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**1.94**	**2.09**	**2.31**	**2.69**	**3.39**	**3.80**	**4.48**	**5.53**	**7.04**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**2.24**	**2.42**	**2.67**	**3.12**	**3.93**	**4.40**	**5.19**	**6.40**	**8.15**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 4.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**4**	**12**	**23**	**40**	**66.6**	**80**	**100**	**126**	**157**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**0.02**	**0.06**	**0.115**	**0.2**	**0.333**	**0.4**	**0.5**	**0.63**	**0.785**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties														
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
Flow Parameters														

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Parameters						Water - organic carbon partition coefficient 4 mL/g to 157 mL/g								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Fine Soil)_Koc_4**	**Bromacil (Fine Soil)_Koc_12**	**Bromacil (Fine Soil)_Koc_23**	**Bromacil (Fine Soil)_Koc_40**	**Bromacil (Fine Soil)_Koc_66**	**Bromacil (Fine Soil)_Koc_80**	**Bromacil (Fine Soil)_Koc_100**	**Bromacil (Fine Soil)_Koc_126**	**Bromacil (Fine Soil)_Koc_157**
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.061	0.048	0.036	0.027	0.019	0.016	0.014	0.011	0.009
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		3.8	5.8	1.2	1.5	2.0	2.7	3.8	4.3	5.2	6.3	7.5
retardation factor in saturated zone	R_s	-		2.0	2.6	1.1	1.2	1.3	1.6	2.0	2.2	2.5	2.9	3.3
velocity of the contaminant	v	*m/year*		1.0	9.7	1.8	1.6	1.4	1.2	1.0	0.9	0.8	0.7	0.6
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283
overall mixing depth	Z_d	*m*		0.38	0.24	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	0.140	0.180	0.235	0.320	0.453	0.520	0.620	0.750	0.905
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**2.04**	**2.20**	**2.43**	**2.83**	**3.57**	**4.00**	**4.72**	**5.82**	**7.41**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-7.12E-01	-7.87E-01	-8.88E-01	-1.04E+00	-1.27E+00	-1.39E+00	-1.55E+00	-1.76E+00	-2.00E+00
dimensionless group	B	-		-1.07E+01	-3.47E+01	-1.70E+01	-1.63E+01	-1.55E+01	-1.46E+01	-1.35E+01	-1.31E+01	-1.26E+01	-1.20E+01	-1.15E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**1.10**	**1.53**	**2.21**	**3.50**	**6.25**	**8.03**	**11.30**	**16.86**	**25.90**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

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Parameters						Fraction of organic carbon 0 % to 6 %								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Bromacil (Fine Soil)	Default Tier 1 Parameter Values Bromacil (Coarse Soil)	Bromacil (Fine Soil)_foc_0%	Bromacil (Fine Soil)_foc_0.25 %	Bromacil (Fine Soil)_foc_0.5%	Bromacil (Fine Soil)_foc_0.75 %	Bromacil (Fine Soil)_foc_1%	Bromacil (Fine Soil)_foc_1.5%	Bromacil (Fine Soil)_foc_2%	Bromacil (Fine Soil)_foc_4%	Bromacil (Fine Soil)_foc_6%
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**0.0046**	**0.0148**	**0.0312**	**0.0564**	**0.0935**	**0.2206**	**0.4591**	**4.6130**	**27.8388**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00009**	**0.00022**	**0.00035**	**0.00048**	**0.00061**	**0.00086**	**0.00112**	**0.00215**	**0.00318**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**1.82**	**4.34**	**6.86**	**9.38**	**11.90**	**16.94**	**21.98**	**42.14**	**62.30**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**0.51**	**1.22**	**1.92**	**2.63**	**3.34**	**4.75**	**6.17**	**11.83**	**17.49**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.0098**	**0.0133**	**0.0179**	**0.0236**	**0.0308**	**0.0510**	**0.0819**	**0.4290**	**1.7511**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.00039**	**0.00053**	**0.00071**	**0.00094**	**0.00123**	**0.00204**	**0.00327**	**0.01716**	**0.07005**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**1.87**	**2.53**	**3.39**	**4.48**	**5.85**	**9.70**	**15.56**	**81.51**	**332.72**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**2.16**	**2.93**	**3.93**	**5.19**	**6.78**	**11.23**	**18.01**	**94.38**	**385.25**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 4.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**0**	**0.1665**	**0.333**	**0.4995**	**0.666**	**0.999**	**1.332**	**2.664**	**3.996**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties														
soil bulk density	p_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.000**	**0.0025**	**0.005**	**0.0075**	**0.010**	**0.015**	**0.020**	**0.040**	**0.060**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
Flow Parameters														

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Fraction of organic carbon 0 % to 6 %								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Fine Soil)_foc_0%**	**Bromacil (Fine Soil)_foc_0.25 %**	**Bromacil (Fine Soil)_foc_0.5%**	**Bromacil (Fine Soil)_foc_0.75 %**	**Bromacil (Fine Soil)_foc_1%**	**Bromacil (Fine Soil)_foc_1.5%**	**Bromacil (Fine Soil)_foc_2%**	**Bromacil (Fine Soil)_foc_4%**	**Bromacil (Fine Soil)_foc_6%**
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.071	0.030	0.019	0.014	0.011	0.008	0.006	0.003	0.002
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		3.8	5.8	1.0	2.4	3.8	5.2	6.6	9.3	12.1	23.2	34.3
retardation factor in saturated zone	R_s	-		2.0	2.6	1.0	1.5	2.0	2.5	3.0	4.0	5.0	8.9	12.9
velocity of the contaminant	v	*m/year*		1.0	9.7	1.9	1.3	1.0	0.8	0.6	0.5	0.4	0.2	0.1
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283
overall mixing depth	Z_d	*m*		0.38	0.24	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	0.120	0.287	0.453	0.620	0.786	1.119	1.452	2.784	4.116
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.96**	**2.67**	**3.57**	**4.72**	**6.16**	**10.21**	**16.37**	**85.80**	**350.23**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-6.74E-01	-9.81E-01	-1.27E+00	-1.55E+00	-1.82E+00	-2.32E+00	-2.80E+00	-4.45E+00	-5.86E+00
dimensionless group	B	-		-1.07E+01	-3.47E+01	-1.74E+01	-1.49E+01	-1.35E+01	-1.26E+01	-1.19E+01	-1.10E+01	-1.04E+01	-9.28E+00	-8.75E+00
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**0.91**	**2.95**	**6.25**	**11.29**	**18.70**	**44.12**	**91.83**	**922.61**	**5567.75**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Parameters						Soil Bulk Density 1 g/cm^3 to 2 g/cm^3					
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Fine Soil)_ρb_1.0**	**Bromacil (Fine Soil)_ρb_1.2**	**Bromacil (Fine Soil)_ρb_1.4**	**Bromacil (Fine Soil)_ρb_1.7**	**Bromacil (Fine Soil)_ρb_1.9**	**Bromacil (Fine Soil)_ρb_2.0**
Soil Guidelines											
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**0.0320**	**0.0316**	**0.0313**	**0.0274**	**0.0271**	**0.0270**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00035**	**0.00035**	**0.00035**	**0.00031**	**0.00031**	**0.00031**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**6.86**	**6.86**	**6.86**	**6.10**	**6.10**	**6.10**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**1.92**	**1.92**	**1.92**	**1.71**	**1.71**	**1.71**
Groundwater Guidelines											
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.0183**	**0.0181**	**0.0179**	**0.0176**	**0.0174**	**0.0173**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.00073**	**0.00072**	**0.00072**	**0.00070**	**0.00070**	**0.00069**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**3.47**	**3.44**	**3.40**	**3.34**	**3.31**	**3.29**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**4.02**	**3.98**	**3.94**	**3.87**	**3.83**	**3.81**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 4. total porosity =1-(bulk density/2.65). Water content = 0.12 for 0-1.4 and 0.07 for 1.7+.**					
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties											
soil bulk density	ρ_b	*g/cm^3*	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1**	**1.2**	**1.4**	**1.7**	**1.9**	**2**
total porosity	q_t	*cm^3/cm^3*	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.62**	**0.55**	**0.47**	**0.36**	**0.28**	**0.25**
soil moisture-filled porosity	q_w	*cm^3/cm^3*	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.120**	**0.144**	**0.168**	**0.119**	**0.133**	**0.140**
soil air-filled porosity	q_a	*cm^3/cm^3*	Not sensitive. Calculated.	**0.302**	**0.241**	**0.503**	**0.403**	**0.304**	**0.239**	**0.150**	**0.105**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters											
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.								
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
Flow Parameters											

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Soil Bulk Density 1 g/cm^3 to 2 g/cm^3					
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Fine Soil)_ρb_1.0**	**Bromacil (Fine Soil)_ρb_1.2**	**Bromacil (Fine Soil)_ρb_1.4**	**Bromacil (Fine Soil)_ρb_1.7**	**Bromacil (Fine Soil)_ρb_1.9**	**Bromacil (Fine Soil)_ρb_2.0**
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δu	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.026	0.022	0.019	0.018	0.016	0.015
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		3.8	5.8	3.8	3.8	3.8	5.8	5.8	5.8
retardation factor in saturated zone	R_s	-		2.0	2.6	1.5	1.7	2.0	2.6	3.2	3.7
velocity of the contaminant	v	*m/year*		1.0	9.7	0.9	0.9	1.0	1.0	1.0	1.0
Degradation Parameters											
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
Mixing Zone Calculation											
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.283	0.283	0.283	0.283	0.283	0.283
overall mixing depth	Z_d	*m*		0.38	0.24	0.38	0.38	0.38	0.38	0.38	0.38
Calculation of Dilution Factors											
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	0.453	0.453	0.453	0.403	0.403	0.403
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	3.86	3.86	3.86	3.86	3.86	3.86
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	15.93	15.93	15.93	15.93	15.93	15.93
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**3.656**	**3.617**	**3.578**	**3.520**	**3.482**	**3.463**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-1.30E+00	-1.29E+00	-1.27E+00	-1.26E+00	-1.25E+00	-1.24E+00
dimensionless group	B	-		-1.07E+01	-3.47E+01	-1.34E+01	-1.34E+01	-1.35E+01	-1.35E+01	-1.36E+01	-1.36E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**6.40**	**6.33**	**6.26**	**5.48**	**5.42**	**5.39**
Water Quality Guidelines											
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Infiltration Rate 0.001 m/year to 0.5 m/year								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Fine Soil)_Infiltration_0.001**	**Bromacil (Fine Soil)_Infiltration_0.0025**	**Bromacil (Fine Soil)_Infiltration_0.005**	**Bromacil (Fine Soil)_Infiltration_0.0075**	**Bromacil (Fine Soil)_Infiltration_0.012**	**Bromacil (Fine Soil)_Infiltration_0.03**	**Bromacil (Fine Soil)_Infiltration_0.06**	**Bromacil (Fine Soil)_Infiltration_0.1**	**Bromacil (Fine Soil)_Infiltration_0.5**
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters. AEP surface soil guidelines differ slightly but are generally consistent.	**0.0088**	**0.0094**	**0.0981**	**0.0546**	**0.0400**	**0.0350**	**0.0312**	**0.0269**	**0.0246**	**0.0228**	**0.0148**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00035**	**0.00037**	**0.00110**	**0.00061**	**0.00045**	**0.00039**	**0.00035**	**0.00030**	**0.00028**	**0.00025**	**0.00017**
Soil Remediation Objective - DUA		**mg/kg**		**7**	**12**	**77.55**	**31.28**	**15.85**	**10.71**	**6.86**	**3.00**	**1.72**	**1.20**	**0.58**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**1.92**	**2.06**	**6.05**	**3.36**	**2.46**	**2.16**	**1.92**	**1.66**	**1.51**	**1.40**	**0.91**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. AEP guidelines assume no dilution/degradation.	**0.005**	**0.005**	**0.0179**	**0.0179**	**0.0179**	**0.0179**	**0.0179**	**0.0179**	**0.0179**	**0.0179**	**0.0179**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.0002**	**0.0002**	**0.00071**	**0.00071**	**0.00071**	**0.00071**	**0.00071**	**0.00071**	**0.00071**	**0.00071**	**0.00071**
Soil Remediation Objective - DUA		**mg/L**		**0.95**	**0.95**	**3.39**	**3.39**	**3.39**	**3.39**	**3.39**	**3.39**	**3.39**	**3.39**	**3.39**
Soil Remediation Objective - Livestock Watering		**mg/L**		**1.10**	**1.10**	**3.93**	**3.93**	**3.93**	**3.93**	**3.93**	**3.93**	**3.93**	**3.93**	**3.93**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 4.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to K_{oc}. If released to soil, bromacil is expected to have very high to high mobility based upon a Koc range of 12 to 126 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+1522).	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**	**66.6**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**	**0.333**
solubility	S	*mg/L*	Not sensitive.	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties														
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**
Flow Parameters														

Appendix 1
Domenico and Robbins Groundwater Transport Model
Bromacil Recalculation

Parameters						Infiltration Rate 0.001 m/year to 0.5 m/year								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Bromacil (Fine Soil)**	**Default Tier 1 Parameter Values Bromacil (Coarse Soil)**	**Bromacil (Fine Soil)_Infiltration_0.001**	**Bromacil (Fine Soil)_Infiltration_0.0025**	**Bromacil (Fine Soil)_Infiltration_0.005**	**Bromacil (Fine Soil)_Infiltration_0.0075**	**Bromacil (Fine Soil)_Infiltration_0.012**	**Bromacil (Fine Soil)_Infiltration_0.03**	**Bromacil (Fine Soil)_Infiltration_0.06**	**Bromacil (Fine Soil)_Infiltration_0.1**	**Bromacil (Fine Soil)_Infiltration_0.5**
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.001**	**0.0025**	**0.005**	**0.0075**	**0.012**	**0.030**	**0.060**	**0.100**	**0.500**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.019	0.088	0.002	0.004	0.008	0.012	0.019	0.047	0.095	0.158	0.788
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		3.8	5.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
retardation factor in saturated zone	R_s	-		2.0	2.6	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
velocity of the contaminant	v	*m/year*		1.0	9.7	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between 365 days and the value used 1494 days is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 64 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution.	**1.0E+06**	**1.0E+06**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**	**4.09E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01	1.37E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.024	0.060	0.120	0.179	0.283	0.679	1.265	1.925	4.560
overall mixing depth	Z_d	*m*		0.38	0.24	0.12	0.16	0.22	0.28	0.38	0.78	1.37	2.03	4.66
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.453	0.403	0.453	0.453	0.453	0.453	0.453	0.453	0.453	0.453	0.453
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	12.13	6.75	4.94	4.33	3.86	3.33	3.04	2.81	1.84
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	180.20	72.68	36.84	24.89	15.93	6.97	3.99	2.79	1.36
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**3.57**	**3.57**	**3.57**	**3.57**	**3.57**	**3.57**	**3.57**	**3.57**	**3.57**
dimensionless group	A	-		-5.87E-06	-5.81E-07	-1.27E+00	-1.27E+00	-1.27E+00	-1.27E+00	-1.27E+00	-1.27E+00	-1.27E+00	-1.27E+00	-1.27E+00
dimensionless group	B	-		-1.07E+01	-3.47E+01	-1.35E+01	-1.35E+01	-1.35E+01	-1.35E+01	-1.35E+01	-1.35E+01	-1.35E+01	-1.35E+01	-1.35E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**1.75**	**1.87**	**19.62**	**10.92**	**8.00**	**7.01**	**6.25**	**5.38**	**4.91**	**4.55**	**2.97**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**	**0.0002**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**	**0.95**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**	**1.1**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters							Half-life 0.25 year to 64 years (~32 years + = guideline)								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)	Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)	Additive Combination Tebuthiuron_ upper end	Tebuthiuron (Coarse Soil)_t1/2s_0.25years	Tebuthiuron (Coarse Soil)_t1/2_0.5years	Tebuthiuron (Coarse Soil)_t1/2_1years	Tebuthiuron (Coarse Soil)_t1/2_2years	Tebuthiuron (Coarse Soil)_t1/2_4years	Tebuthiuron (Coarse Soil)_t1/2_8years	Tebuthiuron (Coarse Soil)_t1/2_16years	Tebuthiuron (Coarse Soil)_t1/2_32years	Tebuthiuron (Coarse Soil)_t1/2_64years
Soil Guidelines															
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**1.2464**	**0.0047**	**0.0026**	**0.0019**	**0.0016**	**0.0015**	**0.0014**	**0.0014**	**0.0014**	**0.0014**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.06543**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**	**0.00037**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.8**	**1940.74**	**3.77**	**3.77**	**3.77**	**3.77**	**3.77**	**3.77**	**3.77**	**3.77**	**3.77**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**19.78**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**	**0.11**
Groundwater Guidelines															
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0082**	**0.0055**	**0.0031**	**0.0022**	**0.0019**	**0.0017**	**0.0017**	**0.0016**	**0.0016**	**0.0016**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00220**	**0.00149**	**0.00083**	**0.00060**	**0.00051**	**0.00046**	**0.00045**	**0.00044**	**0.00043**	**0.00043**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**3.38**	**2.28**	**1.27**	**0.92**	**0.78**	**0.71**	**0.69**	**0.67**	**0.67**	**0.66**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.67**	**0.45**	**0.25**	**0.18**	**0.15**	**0.14**	**0.14**	**0.13**	**0.13**	**0.13**
Chemical Properties							**Assumptions - distance = 10 m.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	**157**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**1.57**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**
Soil Properties															
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.010**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters															
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.												
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**5**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Parameters							Half-life 0.25 year to 64 years (~32 years + = guideline)								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Additive Combination Tebuthiuron_ upper end**	**Tebuthiuron (Coarse Soil)_t1/2s_0.25years**	**Tebuthiuron (Coarse Soil)_t1/2_0.5years**	**Tebuthiuron (Coarse Soil)_t1/2_1years**	**Tebuthiuron (Coarse Soil)_t1/2_2years**	**Tebuthiuron (Coarse Soil)_t1/2_4years**	**Tebuthiuron (Coarse Soil)_t1/2_8years**	**Tebuthiuron (Coarse Soil)_t1/2_16years**	**Tebuthiuron (Coarse Soil)_t1/2_32years**	**Tebuthiuron (Coarse Soil)_t1/2_64years**
Flow Parameters															
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.001**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δu	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.000	0.191	0.191	0.191	0.191	0.191	0.191	0.191	0.191	0.191
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		2.0	2.6	23.4	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
retardation factor in saturated zone	R_s	-		1.3	1.5	8.4	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
velocity of the contaminant	v	*m/year*		1.4	16.1	3.0	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1
Degradation Parameters															
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**1.0E+00**	0.25	0.50	1.00	2.00	4.00	8.00	16.00	32.00	64.00
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	5.62E-01	2.25E+00	1.12E+00	5.62E-01	2.81E-01	1.22E-01	7.02E-02	3.51E-02	1.76E-02	8.78E-03
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**1.0E+00**	0.25	0.50	1.00	2.00	4.00	8.00	16.00	32.00	64.00
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	5.62E-01	2.25E+00	1.12E+00	5.62E-01	2.81E-01	1.22E-01	7.02E-02	3.51E-02	1.76E-02	8.78E-03
Mixing Zone Calculation															
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.002	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144
overall mixing depth	Z_d	*m*		0.38	0.24	0.10	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Calculation of Dilution Factors															
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	1.640	0.185	0.185	0.185	0.185	0.185	0.185	0.185	0.185	0.185
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	92.78	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	1793.00	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**5.12**	**3.46**	**1.92**	**1.40**	**1.19**	**1.08**	**1.04**	**1.02**	**1.01**	**1.01**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-1.63E+00	-1.24E+00	-6.54E-01	-3.37E-01	-1.71E-01	-7.51E-02	-4.34E-02	-2.17E-02	-1.09E-02	-5.44E-03
dimensionless group	B	-		-1.31E+01	-4.48E+01	-2.54E+01	-5.60E+01	-5.07E+01	-4.79E+01	-4.64E+01	-4.55E+01	-4.52E+01	-4.50E+01	-4.49E+01	-4.49E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**778.99**	**2.97**	**1.65**	**1.20**	**1.02**	**0.93**	**0.90**	**0.88**	**0.87**	**0.86**
Water Quality Guidelines															
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

Parameters						Water - organic carbon partition coefficient 4 mL/g to 157 mL/g								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Coarse Soil)_K_{oc}_4**	**Tebuthiuron (Coarse Soil)_K_{oc}_12**	**Tebuthiuron (Coarse Soil)_K_{oc}_23**	**Tebuthiuron (Coarse Soil)_K_{oc}_40**	**Tebuthiuron (Coarse Soil)_K_{oc}_66**	**Tebuthiuron (Coarse Soil)_K_{oc}_80**	**Tebuthiuron (Coarse Soil)_K_{oc}_100**	**Tebuthiuron (Coarse Soil)_K_{oc}_126**	**Tebuthiuron (Coarse Soil)_K_{oc}_157**
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**0.0007**	**0.0011**	**0.0015**	**0.0023**	**0.0036**	**0.0043**	**0.0054**	**0.0070**	**0.0089**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00018**	**0.00026**	**0.00037**	**0.00054**	**0.00080**	**0.00094**	**0.00114**	**0.00140**	**0.00171**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.8**	**1.83**	**2.65**	**3.77**	**5.50**	**8.21**	**9.57**	**11.61**	**14.26**	**17.42**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**0.05**	**0.08**	**0.11**	**0.16**	**0.24**	**0.28**	**0.34**	**0.42**	**0.52**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0017**	**0.0018**	**0.0018**	**0.0018**	**0.0019**	**0.0020**	**0.0020**	**0.0021**	**0.0023**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00047**	**0.00047**	**0.00048**	**0.00050**	**0.00052**	**0.00053**	**0.00055**	**0.00058**	**0.00061**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**0.72**	**0.73**	**0.74**	**0.76**	**0.80**	**0.82**	**0.85**	**0.88**	**0.93**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.14**	**0.14**	**0.15**	**0.15**	**0.16**	**0.16**	**0.17**	**0.17**	**0.18**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 3.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	4	12	23	40	**66.6**	80	100	126	157
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**0.02**	**0.06**	**0.115**	**0.2**	**0.333**	**0.4**	**0.5**	**0.63**	**0.785**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties														
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters						Water - organic carbon partition coefficient 4 mL/g to 157 mL/g								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Coarse Soil)_K_{oc}_4**	**Tebuthiuron (Coarse Soil)_K_{oc}_12**	**Tebuthiuron (Coarse Soil)_K_{oc}_23**	**Tebuthiuron (Coarse Soil)_K_{oc}_40**	**Tebuthiuron (Coarse Soil)_K_{oc}_66**	**Tebuthiuron (Coarse Soil)_K_{oc}_80**	**Tebuthiuron (Coarse Soil)_K_{oc}_100**	**Tebuthiuron (Coarse Soil)_K_{oc}_126**	**Tebuthiuron (Coarse Soil)_K_{oc}_157**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.392	0.271	0.191	0.131	0.088	0.075	0.062	0.050	0.041
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		2.0	2.6	1.3	1.9	2.6	3.9	5.8	6.7	8.1	10.0	12.2
retardation factor in saturated zone	R_s	-		1.3	1.5	1.1	1.3	1.5	1.9	2.6	2.9	3.4	4.0	4.7
velocity of the contaminant	v	*m/year*		1.4	16.1	22.7	19.4	16.1	12.8	9.7	8.6	7.4	6.3	5.3
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144
overall mixing depth	Z_d	*m*		0.38	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	0.090	0.130	0.185	0.270	0.403	0.470	0.570	0.700	0.855
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.09**	**1.10**	**1.12**	**1.16**	**1.21**	**1.24**	**1.28**	**1.34**	**1.41**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-8.17E-02	-9.56E-02	-1.15E-01	-1.44E-01	-1.90E-01	-2.13E-01	-2.47E-01	-2.91E-01	-3.42E-01
dimensionless group	B	-		-1.31E+01	-4.48E+01	-5.41E+01	-5.01E+01	-4.59E+01	-4.11E+01	-3.60E+01	-3.41E+01	-3.18E+01	-2.95E+01	-2.74E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**0.45**	**0.66**	**0.96**	**1.45**	**2.26**	**2.70**	**3.39**	**4.35**	**5.59**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

Parameters						Fraction of organic carbon 0 % to 6 %								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)	Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)	Tebuthiuron (Coarse Soil)_f_{oc}_0%	Tebuthiuron (Coarse Soil)_f_{oc}_0.25%	Tebuthiuron (Coarse Soil)_f_{oc}_0.5%	Tebuthiuron (Coarse Soil)_f_{oc}_0.75%	Tebuthiuron (Coarse Soil)_f_{oc}_1%	Tebuthiuron (Coarse Soil)_f_{oc}_1.5%	Tebuthiuron (Coarse Soil)_f_{oc}_2%	Tebuthiuron (Coarse Soil)_f_{oc}_4%	Tebuthiuron (Coarse Soil)_f_{oc}_6%
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**0.0006**	**0.0010**	**0.0015**	**0.0021**	**0.0026**	**0.0037**	**0.0050**	**0.0108**	**0.0184**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00014**	**0.00025**	**0.00037**	**0.00048**	**0.00060**	**0.00083**	**0.00106**	**0.00198**	**0.00289**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.8**	**1.43**	**2.60**	**3.77**	**4.94**	**6.11**	**8.45**	**10.80**	**20.17**	**29.54**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**0.04**	**0.08**	**0.11**	**0.15**	**0.18**	**0.25**	**0.32**	**0.60**	**0.87**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0017**	**0.0018**	**0.0018**	**0.0018**	**0.0019**	**0.0019**	**0.0020**	**0.0024**	**0.0027**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00046**	**0.00047**	**0.00048**	**0.00049**	**0.00050**	**0.00052**	**0.00054**	**0.00063**	**0.00074**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**0.71**	**0.73**	**0.74**	**0.76**	**0.77**	**0.80**	**0.83**	**0.97**	**1.13**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.14**	**0.14**	**0.15**	**0.15**	**0.15**	**0.16**	**0.16**	**0.19**	**0.22**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 3.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**0**	**0.0575**	**0.115**	**0.1725**	**0.23**	**0.345**	**0.46**	**0.92**	**1.38**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**
Soil Properties														
soil bulk density	p_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	0.000	0.0025	**0.005**	0.0075	0.010	0.015	0.020	0.040	0.060
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters						Fraction of organic carbon 0 % to 6 %								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Coarse Soil)_f_{oc}_0%**	**Tebuthiuron (Coarse Soil)_f_{oc}_0.25%**	**Tebuthiuron (Coarse Soil)_f_{oc}_0.5%**	**Tebuthiuron (Coarse Soil)_f_{oc}_0.75%**	**Tebuthiuron (Coarse Soil)_f_{oc}_1%**	**Tebuthiuron (Coarse Soil)_f_{oc}_1.5%**	**Tebuthiuron (Coarse Soil)_f_{oc}_2%**	**Tebuthiuron (Coarse Soil)_f_{oc}_4%**	**Tebuthiuron (Coarse Soil)_f_{oc}_6%**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.504	0.277	0.191	0.146	0.118	0.085	0.067	0.036	0.024
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		2.0	2.6	1.0	1.8	2.6	3.5	4.3	5.9	7.6	14.1	20.7
retardation factor in saturated zone	R_s	-		1.3	1.5	1.0	1.3	1.5	1.8	2.1	2.6	3.2	5.3	7.5
velocity of the contaminant	v	*m/year*		1.4	16.1	24.9	19.6	16.1	13.7	11.9	9.5	7.8	4.7	3.3
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144	0.144
overall mixing depth	Z_d	*m*		0.38	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	0.070	0.128	0.185	0.243	0.300	0.415	0.530	0.990	1.450
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64	4.64
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87	30.87
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.08**	**1.10**	**1.12**	**1.14**	**1.17**	**1.21**	**1.26**	**1.47**	**1.71**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-7.47E-02	-9.48E-02	-1.15E-01	-1.35E-01	-1.55E-01	-1.94E-01	-2.33E-01	-3.87E-01	-5.37E-01
dimensionless group	B	-		-1.31E+01	-4.48E+01	-5.66E+01	-5.04E+01	-4.59E+01	-4.25E+01	-3.97E+01	-3.57E+01	-3.27E+01	-2.59E+01	-2.24E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**0.35**	**0.65**	**0.96**	**1.29**	**1.63**	**2.34**	**3.11**	**6.77**	**11.51**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

Parameters						Soil Bulk Density 1 g/cm^3 to 2 g/cm^3					
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Coarse Soil)_ρ_b_1.0**	**Tebuthiuron (Coarse Soil)_ρ_b_1.2**	**Tebuthiuron (Coarse Soil)_ρ_b_1.4**	**Tebuthiuron (Coarse Soil)_ρ_b_1.7**	**Tebuthiuron (Coarse Soil)_ρ_b_1.9**	**Tebuthiuron (Coarse Soil)_ρ_b_2.0**
Soil Guidelines											
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**0.0020**	**0.0020**	**0.0020**	**0.0015**	**0.0015**	**0.0015**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00047**	**0.00047**	**0.00047**	**0.00037**	**0.00037**	**0.00037**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.8**	**4.79**	**4.79**	**4.79**	**3.77**	**3.77**	**3.77**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**0.14**	**0.14**	**0.14**	**0.11**	**0.11**	**0.11**
Groundwater Guidelines											
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0019**	**0.0018**	**0.0018**	**0.0018**	**0.0018**	**0.0018**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00050**	**0.00050**	**0.00049**	**0.00048**	**0.00048**	**0.00047**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**0.77**	**0.76**	**0.75**	**0.74**	**0.73**	**0.73**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.15**	**0.15**	**0.15**	**0.15**	**0.14**	**0.14**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 3. total porosity =1-(bulk density/2.65). Water content = 0.12 for 0-1.4 and 0.07 for 1.7+**					
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**
Soil Properties											
soil bulk density	ρ_b	*g/cm^3*	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1**	**1.2**	**1.4**	**1.7**	**1.9**	**2.0**
total porosity	q_t	*cm^3/cm^3*	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.62**	**0.55**	**0.47**	**0.36**	**0.28**	**0.25**
soil moisture-filled porosity	q_w	*cm^3/cm^3*	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.120**	**0.144**	**0.168**	**0.119**	**0.133**	**0.140**
soil air-filled porosity	q_a	*cm^3/cm^3*	Not sensitive. Calculated.	**0.302**	**0.241**	**0.503**	**0.403**	**0.304**	**0.239**	**0.150**	**0.105**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters											
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.								
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Parameters						Soil Bulk Density 1 g/cm^3 to 2 g/cm^3					
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Coarse Soil)_ρ_b_1.0**	**Tebuthiuron (Coarse Soil)_ρ_b_1.2**	**Tebuthiuron (Coarse Soil)_ρ_b_1.4**	**Tebuthiuron (Coarse Soil)_ρ_b_1.7**	**Tebuthiuron (Coarse Soil)_ρ_b_1.9**	**Tebuthiuron (Coarse Soil)_ρ_b_2.0**
Flow Parameters											
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**	**0.060**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.255	0.213	0.182	0.191	0.171	0.162
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		2.0	2.6	2.0	2.0	2.0	2.6	2.6	2.6
retardation factor in saturated zone	R_s	-		1.3	1.5	1.2	1.3	1.3	1.5	1.8	1.9
velocity of the contaminant	v	*m/year*		1.4	16.1	12.1	13.1	14.2	16.2	17.9	18.9
Degradation Parameters											
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Mixing Zone Calculation											
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.144	0.144	0.144	0.144	0.144	0.144
overall mixing depth	Z_d	*m*		0.38	0.24	0.24	0.24	0.24	0.24	0.24	0.24
Calculation of Dilution Factors											
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	0.235	0.235	0.235	0.185	0.185	0.185
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	4.64	4.64	4.64	4.64	4.64	4.64
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	30.87	30.87	30.87	30.87	30.87	30.87
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.16**	**1.15**	**1.14**	**1.12**	**1.11**	**1.10**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-1.52E-01	-1.41E-01	-1.31E-01	-1.14E-01	-1.04E-01	-9.84E-02
dimensionless group	B	-		-1.31E+01	-4.48E+01	-4.01E+01	-4.15E+01	-4.31E+01	-4.59E+01	-4.82E+01	-4.94E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**1.27**	**1.26**	**1.24**	**0.96**	**0.95**	**0.95**
Water Quality Guidelines											
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters						Infiltration Rate 0.001 m/year to 0.5 m/year								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)	Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)	Tebuthiuron (Coarse Soil)_Infiltration_0.001	Tebuthiuron (Coarse Soil)_Infiltration_0.0025	Tebuthiuron (Coarse Soil)_Infiltration_0.005	Tebuthiuron (Coarse Soil)_Infiltration_0.0075	Tebuthiuron (Coarse Soil)_Infiltration_0.012	Tebuthiuron (Coarse Soil)_Infiltration_0.03	Tebuthiuron (Coarse Soil)_Infiltration_0.06	Tebuthiuron (Coarse Soil)_Infiltration_0.1	Tebuthiuron (Coarse Soil)_Infiltration_0.5
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**0.0308**	**0.0130**	**0.0070**	**0.0050**	**0.0035**	**0.0020**	**0.0015**	**0.0013**	**0.0010**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00738**	**0.00310**	**0.00168**	**0.00120**	**0.00085**	**0.00049**	**0.00037**	**0.00032**	**0.00025**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.8**	**218.93**	**87.64**	**43.88**	**29.30**	**18.36**	**7.42**	**3.77**	**2.31**	**0.56**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**2.23**	**0.94**	**0.51**	**0.36**	**0.26**	**0.15**	**0.11**	**0.10**	**0.07**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0018**	**0.0018**	**0.0018**	**0.0018**	**0.0018**	**0.0018**	**0.0018**	**0.0018**	**0.0018**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00048**	**0.00048**	**0.00048**	**0.00048**	**0.00048**	**0.00048**	**0.00048**	**0.00048**	**0.00048**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**0.74**	**0.74**	**0.74**	**0.74**	**0.74**	**0.74**	**0.74**	**0.74**	**0.74**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**	**0.15**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 3.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**
Soil Properties														
soil bulk density	p_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**	**1.7**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**	**0.36**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**	**0.119**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**	**0.241**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters						Infiltration Rate 0.001 m/year to 0.5 m/year								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Coarse Soil)_Infiltration_0.001**	**Tebuthiuron (Coarse Soil)_Infiltration_0.0025**	**Tebuthiuron (Coarse Soil)_Infiltration_0.005**	**Tebuthiuron (Coarse Soil)_Infiltration_0.0075**	**Tebuthiuron (Coarse Soil)_Infiltration_0.012**	**Tebuthiuron (Coarse Soil)_Infiltration_0.03**	**Tebuthiuron (Coarse Soil)_Infiltration_0.06**	**Tebuthiuron (Coarse Soil)_Infiltration_0.1**	**Tebuthiuron (Coarse Soil)_Infiltration_0.5**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**	**320.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.001**	**0.0025**	**0.005**	**0.0075**	**0.012**	**0.030**	**0.060**	**0.100**	**0.500**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.003	0.008	0.016	0.024	0.038	0.095	0.191	0.318	1.590
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96	8.96
retardation factor in unsaturated zone	R_u	-		2.0	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6	2.6
retardation factor in saturated zone	R_s	-		1.3	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5	1.5
velocity of the contaminant	v	*m/year*		1.4	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1	16.1
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.002	0.006	0.012	0.018	0.029	0.072	0.144	0.237	1.079
overall mixing depth	Z_d	*m*		0.38	0.24	0.10	0.11	0.11	0.12	0.13	0.17	0.24	0.34	1.18
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	0.185	0.185	0.185	0.185	0.185	0.185	0.185	0.185	0.185
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	92.78	39.02	21.10	15.12	10.64	6.15	4.64	4.02	3.11
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	1793.00	717.80	359.40	239.93	150.33	60.73	30.87	18.92	4.58
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**1.12**	**1.12**	**1.12**	**1.12**	**1.12**	**1.12**	**1.12**	**1.12**	**1.12**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-1.15E-01	-1.15E-01	-1.15E-01	-1.15E-01	-1.15E-01	-1.15E-01	-1.15E-01	-1.15E-01	-1.15E-01
dimensionless group	B	-		-1.31E+01	-4.48E+01	-4.59E+01	-4.59E+01	-4.59E+01	-4.59E+01	-4.59E+01	-4.59E+01	-4.59E+01	-4.59E+01	-4.59E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**19.26**	**8.10**	**4.38**	**3.14**	**2.21**	**1.28**	**0.96**	**0.83**	**0.65**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters							Half-life 0.25 year to 64 years (~32 years + = guideline)								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)	Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)	Additive Combination Tebuthiuron_ upper end	Tebuthiuron (Fine Soil)_t1/2s_0.25years	Tebuthiuron (Fine Soil)_t1/2_0.5years	Tebuthiuron (Fine Soil)_t1/2_1years	Tebuthiuron (Fine Soil)_t1/2_25years	Tebuthiuron (Fine Soil)_t1/2_4years	Tebuthiuron (Fine Soil)_t1/2_8years	Tebuthiuron (Fine Soil)_t1/2_16years	Tebuthiuron (Fine Soil)_t1/2_32years	Tebuthiuron (Fine Soil)_t1/2_64years
Soil Guidelines															
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**232.8007**	**7.4126**	**0.2645**	**0.0302**	**0.0079**	**0.0032**	**0.0023**	**0.0018**	**0.0016**	**0.0015**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00882**	**0.00039**	**0.00039**	**0.00039**	**0.00039**	**0.00039**	**0.00039**	**0.00039**	**0.00039**	**0.00039**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.77**	**201.0**	**2.5**	**2.5**	**2.5**	**2.5**	**2.5**	**2.5**	**2.5**	**2.5**	**2.5**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**2.67**	**0.12**	**0.12**	**0.12**	**0.12**	**0.12**	**0.12**	**0.12**	**0.12**	**0.12**
Groundwater Guidelines															
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**11.3538**	**8.1667**	**0.2914**	**0.0333**	**0.0087**	**0.0035**	**0.0026**	**0.0020**	**0.0018**	**0.0017**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**3.05132**	**2.19481**	**0.07833**	**0.00895**	**0.00234**	**0.00095**	**0.00069**	**0.00055**	**0.00049**	**0.00046**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**Above Solubilit**	**Above Solubility**	**120.22**	**13.74**	**3.59**	**1.46**	**1.06**	**0.84**	**0.75**	**0.70**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**922.49**	**663.55**	**23.68**	**2.71**	**0.71**	**0.29**	**0.21**	**0.17**	**0.15**	**0.14**
Chemical Properties							**Assumptions - distance = 10 m.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	**157**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**1.57**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**
Soil Properties															
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.010**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters															
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.												
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**5**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters							Half-life 0.25 year to 64 years (~32 years + = guideline)								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Additive Combination Tebuthiuron_ upper end**	**Tebuthiuron (Fine Soil)_t1/2s_0.25years**	**Tebuthiuron (Fine Soil)_t1/2_0.5years**	**Tebuthiuron (Fine Soil)_t1/2_1years**	**Tebuthiuron (Fine Soil)_t1/2_25years**	**Tebuthiuron (Fine Soil)_t1/2_4years**	**Tebuthiuron (Fine Soil)_t1/2_8years**	**Tebuthiuron (Fine Soil)_t1/2_16years**	**Tebuthiuron (Fine Soil)_t1/2_32years**	**Tebuthiuron (Fine Soil)_t1/2_64years**
Flow Parameters															
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.001**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δu	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.000	0.036	0.036	0.036	0.036	0.036	0.036	0.036	0.036	0.036
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		2.0	2.6	14.1	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
retardation factor in saturated zone	R_s	-		1.3	1.5	5.7	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
velocity of the contaminant	v	*m/year*		1.4	16.1	0.3	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Degradation Parameters															
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**1.0E+00**	0.25	0.50	1.00	2.00	4.00	8.00	16.00	32.00	64.00
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	5.62E-01	2.25E+00	1.12E+00	5.62E-01	2.81E-01	1.22E-01	7.02E-02	3.51E-02	1.76E-02	8.78E-03
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**1.0E+00**	0.25	0.50	1.00	2.00	4.00	8.00	16.00	32.00	64.00
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	5.62E-01	2.25E+00	1.12E+00	5.62E-01	2.81E-01	1.22E-01	7.02E-02	3.51E-02	1.76E-02	8.78E-03
Mixing Zone Calculation															
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.024	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283
overall mixing depth	Z_d	*m*		0.38	0.24	0.12	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Calculation of Dilution Factors															
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	1.690	0.235	0.235	0.235	0.235	0.235	0.235	0.235	0.235	0.235
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	12.13	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	180.20	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**7096.10**	**5104.20**	**182.15**	**20.81**	**5.43**	**2.22**	**1.60**	**1.27**	**1.13**	**1.06**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-8.87E+00	-8.54E+00	-5.20E+00	-3.04E+00	-1.69E+00	-7.96E-01	-4.72E-01	-2.41E-01	-1.22E-01	-6.14E-02
dimensionless group	B	-		-1.31E+01	-4.48E+01	-1.76E+01	-3.59E+01	-2.70E+01	-2.12E+01	-1.76E+01	-1.53E+01	-1.44E+01	-1.38E+01	-1.35E+01	-1.33E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**1.46E+05**	**4632.85**	**165.33**	**18.89**	**4.93**	**2.01**	**1.46**	**1.16**	**1.03**	**0.97**
Water Quality Guidelines															
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

Parameters						Water - organic carbon partition coefficient 4 mL/g to 157 mL/g								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Fine Soil)_Koc_4**	**Tebuthiuron (Fine Soil)_Koc_12**	**Tebuthiuron (Fine Soil)_Koc_23**	**Tebuthiuron (Fine Soil)_Koc_40**	**Tebuthiuron (Fine Soil)_Koc_66**	**Tebuthiuron (Fine Soil)_Koc_80**	**Tebuthiuron (Fine Soil)_Koc_100**	**Tebuthiuron (Fine Soil)_Koc_126**	**Tebuthiuron (Fine Soil)_Koc_157**
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**0.0022**	**0.0032**	**0.0047**	**0.0078**	**0.0150**	**0.0199**	**0.0293**	**0.0461**	**0.0755**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00023**	**0.00030**	**0.00039**	**0.00053**	**0.00075**	**0.00086**	**0.00103**	**0.00125**	**0.00150**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.77**	**1.5**	**1.9**	**2.5**	**3.4**	**4.8**	**5.5**	**6.5**	**7.9**	**9.5**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**0.07**	**0.09**	**0.12**	**0.16**	**0.23**	**0.26**	**0.31**	**0.38**	**0.45**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0041**	**0.0046**	**0.0052**	**0.0063**	**0.0086**	**0.0099**	**0.0122**	**0.0159**	**0.0216**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00111**	**0.00123**	**0.00140**	**0.00171**	**0.00230**	**0.00266**	**0.00328**	**0.00428**	**0.00580**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**1.71**	**1.88**	**2.15**	**2.62**	**3.53**	**4.08**	**5.04**	**6.57**	**8.91**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.34**	**0.37**	**0.42**	**0.52**	**0.69**	**0.80**	**0.99**	**1.29**	**1.75**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 3.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	4	12	23	40	66.6	80	100	126	157
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**0.02**	**0.06**	**0.115**	**0.2**	**0.333**	**0.4**	**0.5**	**0.63**	**0.785**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**	**815**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**	**5.27E-09**
Soil Properties														
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters						Water - organic carbon partition coefficient 4 mL/g to 157 mL/g								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Fine Soil)_Koc_4**	**Tebuthiuron (Fine Soil)_Koc_12**	**Tebuthiuron (Fine Soil)_Koc_23**	**Tebuthiuron (Fine Soil)_Koc_40**	**Tebuthiuron (Fine Soil)_Koc_66**	**Tebuthiuron (Fine Soil)_Koc_80**	**Tebuthiuron (Fine Soil)_Koc_100**	**Tebuthiuron (Fine Soil)_Koc_126**	**Tebuthiuron (Fine Soil)_Koc_157**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.061	0.048	0.036	0.027	0.019	0.016	0.014	0.011	0.009
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		2.0	2.6	1.2	1.5	2.0	2.7	3.8	4.3	5.2	6.3	7.5
retardation factor in saturated zone	R_s	-		1.3	1.5	1.1	1.2	1.3	1.6	2.0	2.2	2.5	2.9	3.3
velocity of the contaminant	v	*m/year*		1.4	16.1	1.8	1.6	1.4	1.2	1.0	0.9	0.8	0.7	0.6
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283
overall mixing depth	Z_d	*m*		0.38	0.24	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	0.140	0.180	0.235	0.320	0.453	0.520	0.620	0.750	0.905
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**2.59**	**2.85**	**3.25**	**3.97**	**5.35**	**6.18**	**7.64**	**9.96**	**13.50**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-9.51E-01	-1.05E+00	-1.18E+00	-1.38E+00	-1.68E+00	-1.82E+00	-2.03E+00	-2.30E+00	-2.60E+00
dimensionless group	B	-		-1.31E+01	-4.48E+01	-1.77E+01	-1.70E+01	-1.63E+01	-1.54E+01	-1.44E+01	-1.40E+01	-1.35E+01	-1.30E+01	-1.26E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**1.40**	**1.98**	**2.95**	**4.90**	**9.35**	**12.41**	**18.28**	**28.84**	**47.18**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters						Fraction of organic carbon 0 % to 6 %								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)	Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)	Tebuthiuron (Fine Soil)_foc_0%	Tebuthiuron (Fine Soil)_foc_0.25 %	Tebuthiuron (Fine Soil)_foc_0.5%	Tebuthiuron (Fine Soil)_foc_0.75 %	Tebuthiuron (Fine Soil)_foc_1%	Tebuthiuron (Fine Soil)_foc_1.5%	Tebuthiuron (Fine Soil)_foc_2%	Tebuthiuron (Fine Soil)_foc_4%	Tebuthiuron (Fine Soil)_foc_6%
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**0.0018**	**0.0031**	**0.0047**	**0.0067**	**0.0092**	**0.0158**	**0.0252**	**0.1120**	**0.3647**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00020**	**0.00029**	**0.00039**	**0.00049**	**0.00058**	**0.00077**	**0.00096**	**0.00173**	**0.00249**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.77**	**1.3**	**1.9**	**2.5**	**3.1**	**3.7**	**4.9**	**6.1**	**10.9**	**15.8**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**0.06**	**0.09**	**0.12**	**0.15**	**0.18**	**0.23**	**0.29**	**0.52**	**0.75**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0039**	**0.0045**	**0.0052**	**0.0060**	**0.0068**	**0.0088**	**0.0112**	**0.0279**	**0.0630**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00106**	**0.00122**	**0.00140**	**0.00160**	**0.00183**	**0.00236**	**0.00302**	**0.00749**	**0.01692**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**1.63**	**1.87**	**2.15**	**2.46**	**2.80**	**3.62**	**4.63**	**11.50**	**25.97**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.32**	**0.37**	**0.42**	**0.48**	**0.55**	**0.71**	**0.91**	**2.27**	**5.12**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 3.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**0**	**0.0575**	**0.115**	**0.1725**	**0.23**	**0.345**	**0.46**	**0.92**	**1.38**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**
Soil Properties														
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	0.000	0.0025	**0.005**	0.0075	0.010	0.015	0.020	0.040	0.060
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

Parameters						Fraction of organic carbon 0 % to 6 %								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Fine Soil)_foc_0%**	**Tebuthiuron (Fine Soil)_foc_0.25 %**	**Tebuthiuron (Fine Soil)_foc_0.5%**	**Tebuthiuron (Fine Soil)_foc_0.75 %**	**Tebuthiuron (Fine Soil)_foc_1%**	**Tebuthiuron (Fine Soil)_foc_1.5%**	**Tebuthiuron (Fine Soil)_foc_2%**	**Tebuthiuron (Fine Soil)_foc_4%**	**Tebuthiuron (Fine Soil)_foc_6%**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.071	0.048	0.036	0.029	0.024	0.018	0.015	0.008	0.006
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		2.0	2.6	1.0	1.5	2.0	2.4	2.9	3.9	4.8	8.7	12.5
retardation factor in saturated zone	R_s	-		1.3	1.5	1.0	1.2	1.3	1.5	1.7	2.0	2.4	3.7	5.1
velocity of the contaminant	v	*m/year*		1.4	16.1	1.9	1.6	1.4	1.3	1.1	0.9	0.8	0.5	0.4
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283	0.283
overall mixing depth	Z_d	*m*		0.38	0.24	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38	0.38
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	0.120	0.178	0.235	0.293	0.350	0.465	0.580	1.040	1.500
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86	3.86
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93	15.93
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**2.46**	**2.84**	**3.25**	**3.72**	**4.25**	**5.49**	**7.02**	**17.43**	**39.35**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-9.01E-01	-1.04E+00	-1.18E+00	-1.31E+00	-1.45E+00	-1.70E+00	-1.95E+00	-2.86E+00	-3.67E+00
dimensionless group	B	-		-1.31E+01	-4.48E+01	-1.81E+01	-1.71E+01	-1.63E+01	-1.56E+01	-1.51E+01	-1.43E+01	-1.37E+01	-1.22E+01	-1.15E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**1.14**	**1.94**	**2.95**	**4.21**	**5.74**	**9.86**	**15.73**	**70.01**	**227.96**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

Parameters						Soil Bulk Density 1 g/cm^3 to 2 g/cm^3					
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Fine Soil)_ρb_1.0**	**Tebuthiuron (Fine Soil)_ρb_1.2**	**Tebuthiuron (Fine Soil)_ρb_1.4**	**Tebuthiuron (Fine Soil)_ρb_1.7**	**Tebuthiuron (Fine Soil)_ρb_1.9**	**Tebuthiuron (Fine Soil)_ρb_2.0**
Soil Guidelines											
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**0.0056**	**0.0052**	**0.0047**	**0.0033**	**0.0030**	**0.0028**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00039**	**0.00039**	**0.00039**	**0.00031**	**0.00031**	**0.00031**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.77**	**2.5**	**2.5**	**2.5**	**1.9**	**1.9**	**1.9**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**0.12**	**0.12**	**0.12**	**0.09**	**0.09**	**0.09**
Groundwater Guidelines											
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0062**	**0.0057**	**0.0052**	**0.0046**	**0.0042**	**0.0040**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00167**	**0.00153**	**0.00140**	**0.00123**	**0.00112**	**0.00107**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**2.57**	**2.35**	**2.15**	**1.88**	**1.72**	**1.64**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.51**	**0.46**	**0.42**	**0.37**	**0.34**	**0.32**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 3. total porosity =1-(bulk density/2.65). Water content = 0.12 for 0-1.4 and 0.07 for 1.7+**					
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**
Soil Properties											
soil bulk density	ρ_b	*g/cm^3*	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1**	**1.2**	**1.4**	**1.7**	**1.9**	**2.0**
total porosity	q_t	*cm^3/cm^3*	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.62**	**0.55**	**0.47**	**0.36**	**0.28**	**0.25**
soil moisture-filled porosity	q_w	*cm^3/cm^3*	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.120**	**0.144**	**0.168**	**0.119**	**0.133**	**0.140**
soil air-filled porosity	q_a	*cm^3/cm^3*	Not sensitive. Calculated.	**0.302**	**0.241**	**0.503**	**0.403**	**0.304**	**0.239**	**0.150**	**0.105**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters											
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.								
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

Parameters						Soil Bulk Density 1 g/cm^3 to 2 g/cm^3					
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Fine Soil)_ρb_1.0**	**Tebuthiuron (Fine Soil)_ρb_1.2**	**Tebuthiuron (Fine Soil)_ρb_1.4**	**Tebuthiuron (Fine Soil)_ρb_1.7**	**Tebuthiuron (Fine Soil)_ρb_1.9**	**Tebuthiuron (Fine Soil)_ρb_2.0**
Flow Parameters											
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**	**0.012**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.051	0.043	0.036	0.038	0.034	0.032
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		2.0	2.6	2.0	2.0	2.0	2.6	2.6	2.6
retardation factor in saturated zone	R_s	-		1.3	1.5	1.2	1.3	1.3	1.5	1.8	1.9
velocity of the contaminant	v	*m/year*		1.4	16.1	1.2	1.3	1.4	1.6	1.8	1.9
Degradation Parameters											
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Mixing Zone Calculation											
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.283	0.283	0.283	0.283	0.283	0.283
overall mixing depth	Z_d	*m*		0.38	0.24	0.38	0.38	0.38	0.38	0.38	0.38
Calculation of Dilution Factors											
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	0.235	0.235	0.235	0.185	0.185	0.185
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	3.86	3.86	3.86	3.86	3.86	3.86
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	15.93	15.93	15.93	15.93	15.93	15.93
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**3.89**	**3.56**	**3.26**	**2.85**	**2.60**	**2.49**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-1.36E+00	-1.27E+00	-1.18E+00	-1.05E+00	-9.57E-01	-9.10E-01
dimensionless group	B	-		-1.31E+01	-4.48E+01	-1.55E+01	-1.58E+01	-1.63E+01	-1.70E+01	-1.76E+01	-1.80E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**3.53**	**3.24**	**2.96**	**2.04**	**1.86**	**1.78**
Water Quality Guidelines											
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

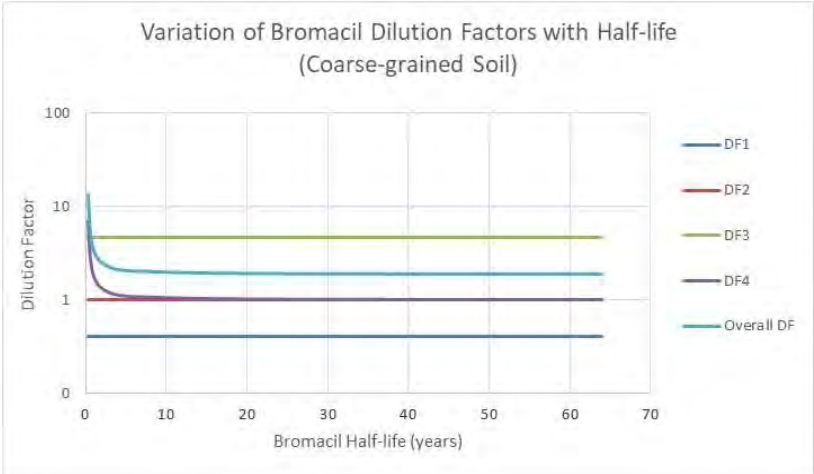
Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

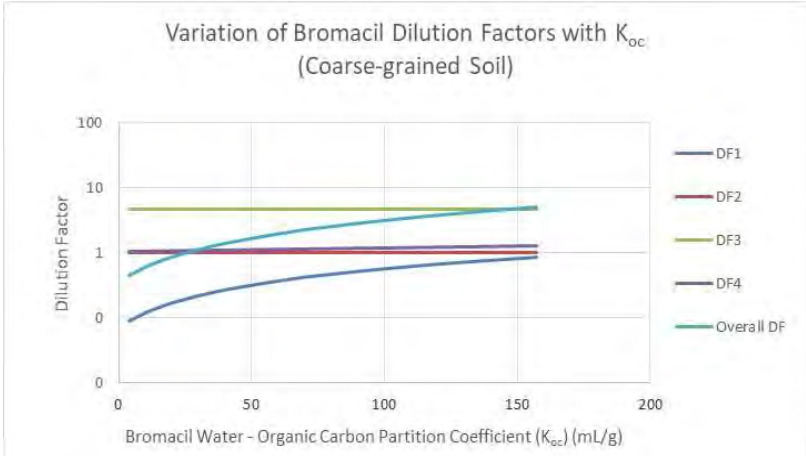
Parameters						Infiltration Rate 0.001 m/year to 0.5 m/year								
Parameters	Symbol	*Unit*	*Sensitivity Analysis / Notes*	Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)	Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)	Tebuthiuron (Fine Soil)_Infiltration_0.001	Tebuthiuron (Fine Soil)_Infiltration_0.0025	Tebuthiuron (Fine Soil)_Infiltration_0.005	Tebuthiuron (Fine Soil)_Infiltration_0.0075	Tebuthiuron (Fine Soil)_Infiltration_0.012	Tebuthiuron (Fine Soil)_Infiltration_0.03	Tebuthiuron (Fine Soil)_Infiltration_0.06	Tebuthiuron (Fine Soil)_Infiltration_0.1	Tebuthiuron (Fine Soil)_Infiltration_0.5
Soil Guidelines														
Soil Remediation Objective - Aquatic Life		**mg/kg**	Note that the default soil quality guidelines herein were calculated based on the SWQG and the default parameters.	**0.0015**	**0.0014**	**0.0148**	**0.0083**	**0.0060**	**0.0053**	**0.0047**	**0.0041**	**0.0037**	**0.0034**	**0.0022**
Soil Remediation Objective - Irrigation Water		**mg/kg**		**0.00039**	**0.00037**	**0.00123**	**0.00068**	**0.00050**	**0.00044**	**0.00039**	**0.00034**	**0.00031**	**0.00028**	**0.00019**
Soil Remediation Objective - DUA		**mg/kg**		**2.5**	**3.77**	**27.9**	**11.3**	**5.7**	**3.9**	**2.5**	**1.1**	**0.6**	**0.4**	**0.2**
Soil Remediation Objective - Livestock Watering		**mg/kg**		**0.12**	**0.11**	**0.37**	**0.21**	**0.15**	**0.13**	**0.12**	**0.10**	**0.09**	**0.09**	**0.06**
Groundwater Guidelines														
Groundwater Remediation Objective - Aquatic Life		**mg/L**	Note that the default groundwater quality guidelines herein were calculated based on the SWQG and the default parameters. Alberta Tier 1 guidelines assume no dilution/degradation.	**0.0016**	**0.0016**	**0.0052**	**0.0052**	**0.0052**	**0.0052**	**0.0052**	**0.0052**	**0.0052**	**0.0052**	**0.0052**
Groundwater Remediation Objective - Irrigation Water		**mg/L**		**0.00043**	**0.00043**	**0.00140**	**0.00140**	**0.00140**	**0.00140**	**0.00140**	**0.00140**	**0.00140**	**0.00140**	**0.00140**
Soil Remediation Objective - DUA		**mg/L**		**0.66**	**0.66**	**2.15**	**2.15**	**2.15**	**2.15**	**2.15**	**2.15**	**2.15**	**2.15**	**2.15**
Soil Remediation Objective - Livestock Watering		**mg/L**		**0.13**	**0.13**	**0.42**	**0.42**	**0.42**	**0.42**	**0.42**	**0.42**	**0.42**	**0.42**	**0.42**
Chemical Properties						**Assumptions - distance = 10 m. t1/2 = 3.**								
water - organic carbon partition coefficient	K_{oc}	*mL/g*	Model results are sensitive to this value as it is used in conjunction with the Site's fraction of organic carbon which itself is assumed to be low. At higher values for fraction of organic carbon, the model is not as sensitive to Koc. If released to soil, Tebuthiuron is expected to have very high to high mobility based upon a Koc range of 4 to 157 (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**	**23**
water-soil partition coefficient	K_d	*mL/g*	Value is calculated using Koc and fraction organic carbon. This relationship does not hold for soil with very low organic carbon, where adsorption to mineral surfaces may become significant. The organic carbon content at which this happens is dependent on both the chemical and soil properties (CCME 2006)	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**	**0.115**
solubility	S	*mg/L*	Not sensitive.	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**	**2500**
dimensionless Henry's law coefficient	H'	-	Not sensitive.	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**	**4.91E-09**
Soil Properties														
soil bulk density	ρ_b	g/cm^3	Lower bulk density results in higher dilution if the soil moisture remains constant (1-1.4 and 1.7-2.0) but increased soil bulk density had higher overall dilution due to the change in moisture content.	**1.4**	**1.7**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**	**1.4**
total porosity	q_t	cm^3/cm^3	Very sensitive. However the possible range for this value is low. Calculated.	**0.47**	**0.36**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**	**0.47**
soil moisture-filled porosity	q_w	cm^3/cm^3	Low sensitivity. Lower values result in lower dilution factors.	**0.168**	**0.119**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**	**0.168**
soil air-filled porosity	q_a	cm^3/cm^3	Not sensitive. Calculated.	**0.302**	**0.241**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**	**0.302**
fraction of organic carbon	f_{oc}	*mass/mass*	Very sensitive. The possible range for this value is low. Lower values result in lower dilution factors.	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**	**0.005**
Geometric Parameters														
source length (along groundwater flow)	X	*m*	Low sensitivity. Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source width (perpendicular to gw flow)	Y	*m*	Not sensitive except at very low values (less than approximately 10 m). Higher values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
source thickness (from surface)	Z	*m*	Low sensitivity. Effects of this parameter on dilution factors are captured with a combination of depth to surface water and the thickness of unsaturated zone.	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**
distance downgradient to water body	x	*m*	Low sensitivity. Lower values result in lower dilution factors.	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**	**10**
perpendicular distance to water body	y	*m*	Not sensitive.											
depth from surface to groundwater surface (water table depth)	d	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**	**3**
thickness of unsaturated zone below the source	b	*m*	Low sensitivity, although this value itself is related to the water table depth and the source thickness and is difficult to analyze unless assuming different Site scenarios.	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**	**0**
thickness of unconfined aquifer	d_a	*m*	Low sensitivity. A lower unconfined aquifer thickness results in higher dilution factors.	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**	**5**

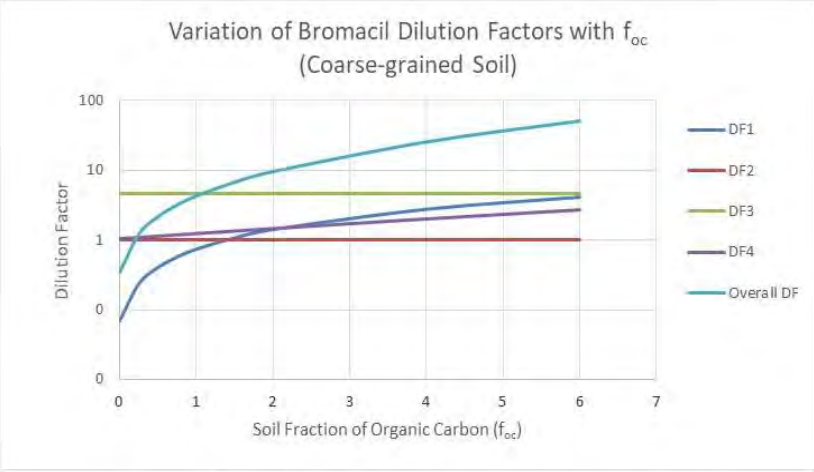
Appendix 1
Domenico and Robbins Groundwater Transport Model
Tebuthiuron Recalculation

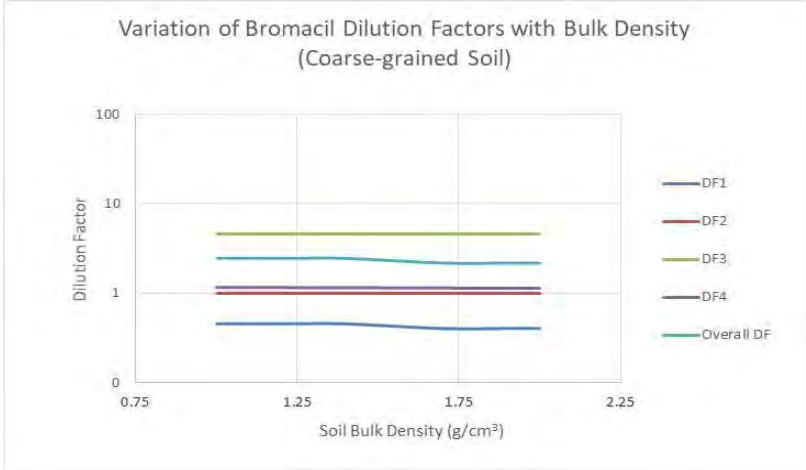
Parameters						Infiltration Rate 0.001 m/year to 0.5 m/year								
Parameters	**Symbol**	***Unit***	***Sensitivity Analysis / Notes***	**Default Tier 1 Parameter Values Tebuthiuron (Fine Soil)**	**Default Tier 1 Parameter Values Tebuthiuron (Coarse Soil)**	**Tebuthiuron (Fine Soil)_Infiltration_0.001**	**Tebuthiuron (Fine Soil)_Infiltration_0.0025**	**Tebuthiuron (Fine Soil)_Infiltration_0.005**	**Tebuthiuron (Fine Soil)_Infiltration_0.0075**	**Tebuthiuron (Fine Soil)_Infiltration_0.012**	**Tebuthiuron (Fine Soil)_Infiltration_0.03**	**Tebuthiuron (Fine Soil)_Infiltration_0.06**	**Tebuthiuron (Fine Soil)_Infiltration_0.1**	**Tebuthiuron (Fine Soil)_Infiltration_0.5**
Flow Parameters														
aquifer hydraulic conductivity	K	*m/year*	Model results are very sensitive at lower values. Sensitivity to this parameter begins to bottom out at values over approximately 40 m/year. At values above approximately 200 m/year, variability to hydraulic conductivity becomes negligible.	**32.0**	**320.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**	**32.0**
lateral hydraulic gradient in aquifer	i	-	Very sensitive at values below approximately 0.03 m/m.	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**	**0.028**
infiltration rate	I	*m/year*	Very sensitive at values below approximately 0.012 m/year.	**0.012**	**0.060**	**0.001**	**0.0025**	**0.005**	**0.0075**	**0.012**	**0.030**	**0.060**	**0.100**	**0.500**
transport time	t	*years*	Low sensitivity, although this value itself is related to size of the source, i.e. how long the scenario is applicable.	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**	**500**
longitudinal dispersivity	D_x	*m*		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
transverse dispersivity	D_y	*m*		0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
dispersivity in the unsaturated zone	δ_u	*m*		0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
average linear leachate velocity	v_u	*m/year*		0.036	0.191	0.003	0.008	0.015	0.023	0.036	0.091	0.182	0.304	1.520
Darcy velocity in groundwater	V	*m/year*		0.896	8.96	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896	0.896
retardation factor in unsaturated zone	R_u	-		2.0	2.6	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
retardation factor in saturated zone	R_s	-		1.3	1.5	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3	1.3
velocity of the contaminant	v	*m/year*		1.4	16.1	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4	1.4
Degradation Parameters														
contaminant half life (saturated)	$t_{1/2s}$	*year*	Very sensitive. The variance between the lower reported values of ~100 days and the max value reported, 35.4 months, is several magnitudes. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (saturated)	L_s	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
contaminant half life (unsaturated)	$t_{1/2US}$	*year*	Very sensitive. The variance between the lower reported values of 12 months and the max value reported, 35.4 months, is several magnitudes. 1-2 year field dissipation half-life reported for CA sites. Sensitivity to this parameter begins to bottom out at approximately 32 years (dependent on scenario) with longer half-lives resulting in lower calculated dilution (https://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6863).	**1.0E+06**	**1.0E+06**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**	**3.00E+00**
decay constant (unsaturated)	L_{US}	*1/year*		5.62E-07	5.62E-07	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01	1.87E-01
Mixing Zone Calculation														
mixing depth due to dispersion	r	*m*		0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
mixing depth due to infiltration rate	s	*m*		0.283	0.144	0.024	0.060	0.120	0.179	0.283	0.679	1.265	1.925	4.560
overall mixing depth	Z_d	*m*		0.38	0.24	0.12	0.16	0.22	0.28	0.38	0.78	1.37	2.03	4.66
Calculation of Dilution Factors														
Dilution Factor 1 ($C_{soil}/C_{leachate}$)	DF1	*L/kg*		0.235	0.185	0.235	0.235	0.235	0.235	0.235	0.235	0.235	0.235	0.235
Dilution Factor 2 ($C_{leachate}/C_{porewater}$)	DF2	-		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Dilution Factor 3 ($C_{porewater}/C_{groundwater}$)	DF3	-		3.86	4.64	12.13	6.75	4.94	4.33	3.86	3.33	3.04	2.81	1.84
Drinking Water DF3 ($C_{porewater}/C_{groundwater}$)	DF3	-		15.93	30.87	180.20	72.68	36.84	24.89	15.93	6.97	3.99	2.79	1.36
Dilution Factor 4 ($C_{groundwater}/C_{guideline}$)	**DF4**	**-**		**1.00**	**1.00**	**3.25**	**3.25**	**3.25**	**3.25**	**3.25**	**3.25**	**3.25**	**3.25**	**3.25**
dimensionless group	A	-		-3.96E-06	-3.48E-07	-1.18E+00	-1.18E+00	-1.18E+00	-1.18E+00	-1.18E+00	-1.18E+00	-1.18E+00	-1.18E+00	-1.18E+00
dimensionless group	B	-		-1.31E+01	-4.48E+01	-1.63E+01	-1.63E+01	-1.63E+01	-1.63E+01	-1.63E+01	-1.63E+01	-1.63E+01	-1.63E+01	-1.63E+01
dimensionless group	C	-		2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
dimensionless group	D	-		-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50	-2.50
Overall Dilution Factor	**DF**	***L/kg***		**0.91**	**0.86**	**9.28**	**5.16**	**3.78**	**3.31**	**2.95**	**2.54**	**2.32**	**2.15**	**1.40**
Water Quality Guidelines														
Freshwater Aquatic Life (FWAL)	**$SWQG_{AL}$**	***mg/L***		**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**	**0.0016**
Irrigation Water (IW)	**$SWQG_{IW}$**	**mg/L**		**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**	**0.00043**
Drinking Water (DW)	**$SWQG_{DW}$**	**mg/L**		**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**	**0.66**
Protection of Livestock Watering (LW)	**$SWQG_{LW}$**	**mg/L**		**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**	**0.13**

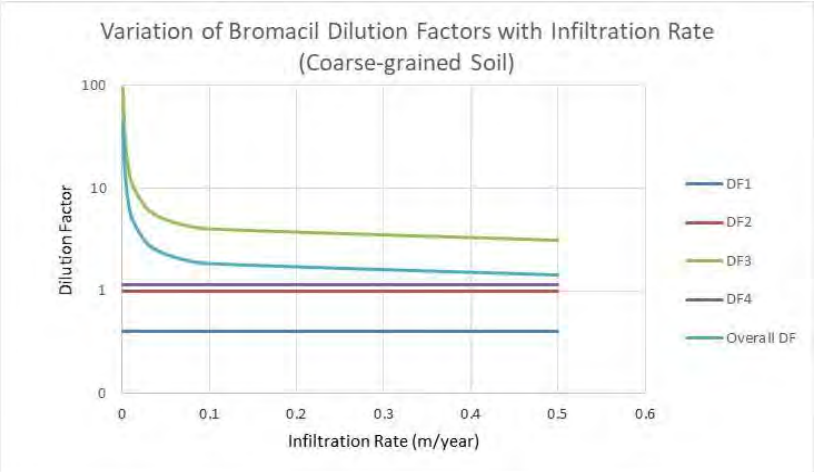
APPENDIX 2: SENSITIVITY ANALYSIS FIGURES











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Soil Sterilants Program
Sensitivity Analysis

Sensitivity Analysis Bromacil (Coarse-grained Soil)

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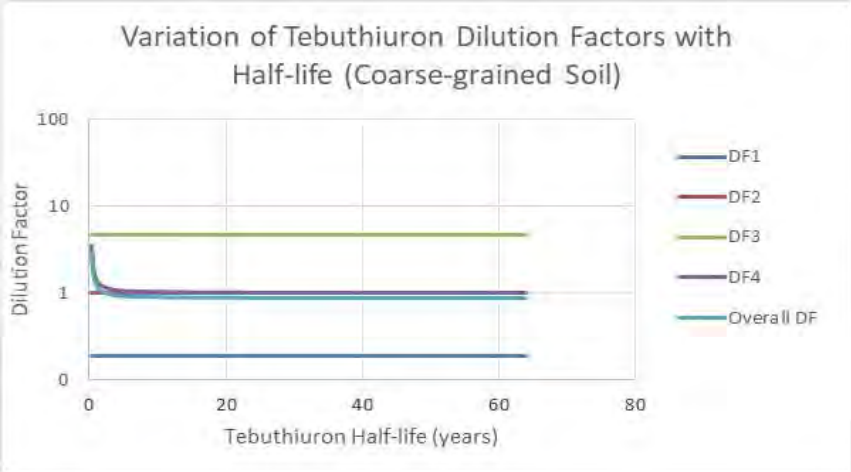

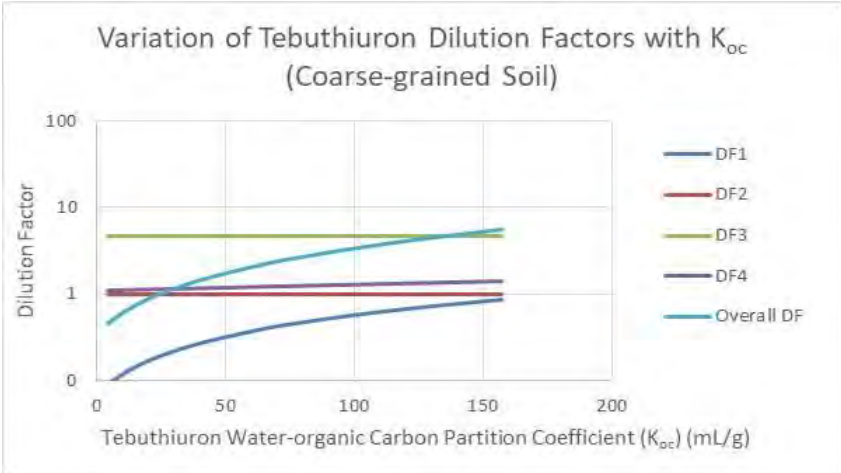

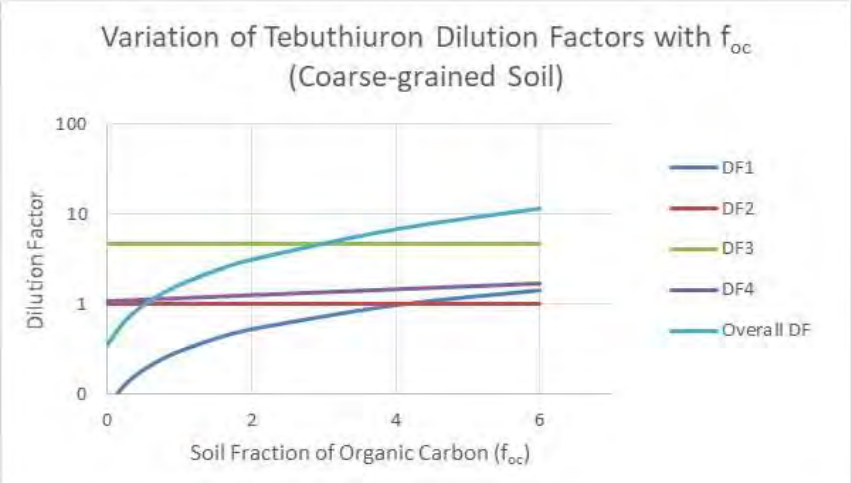

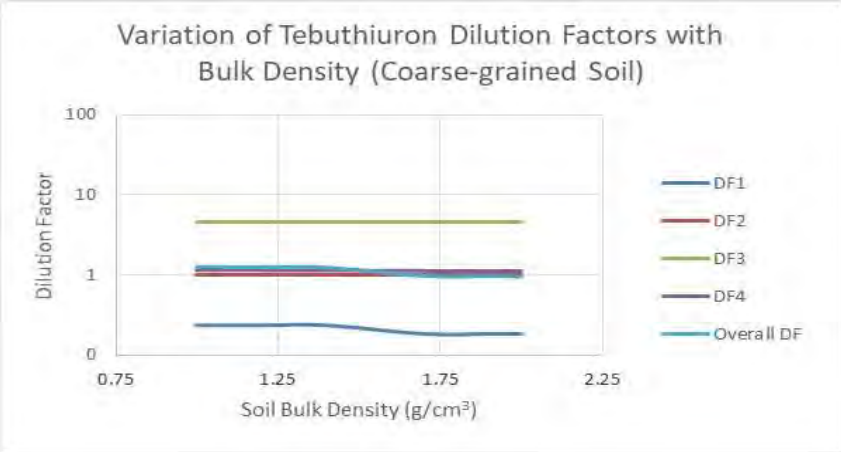

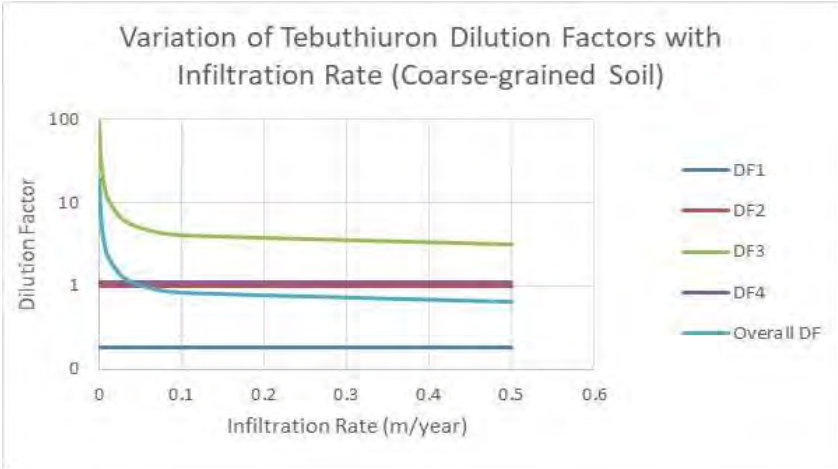

InnoTech
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Sensitivity Analysis

Sensitivity Analysis Tebuthiuron (Coarse-grained Soil)

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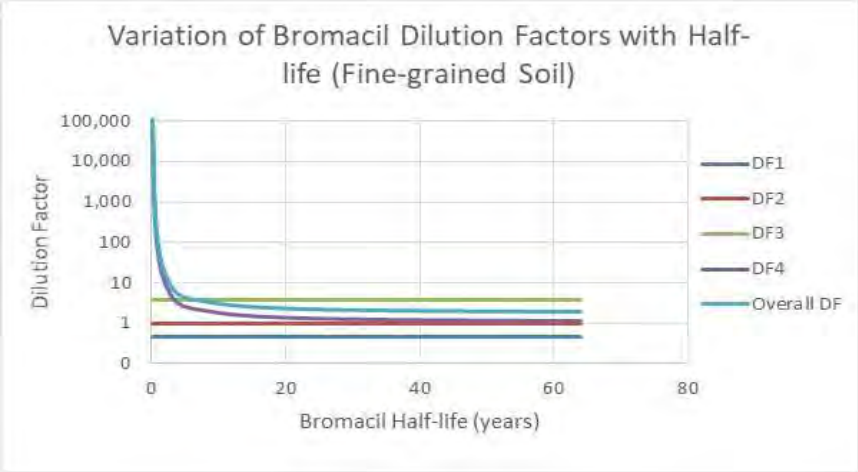

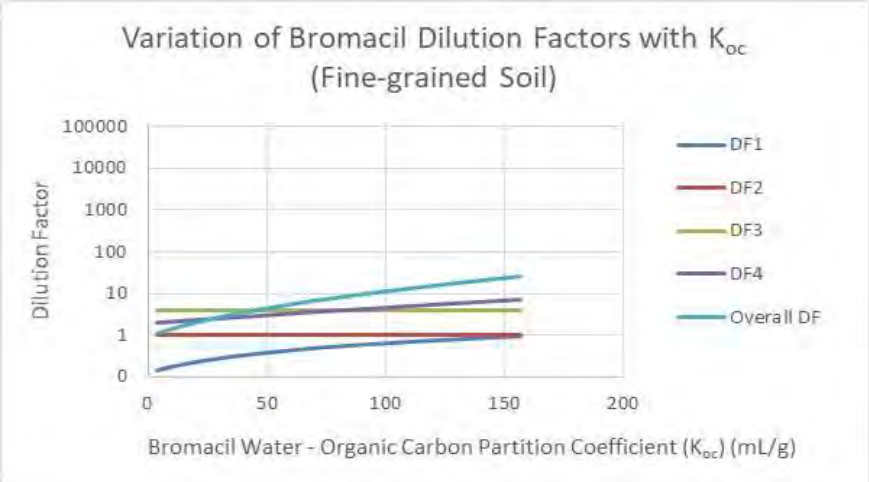

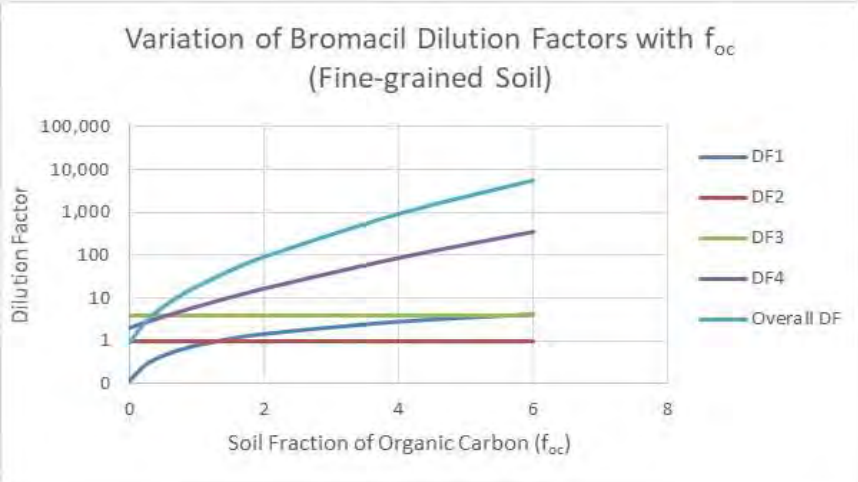

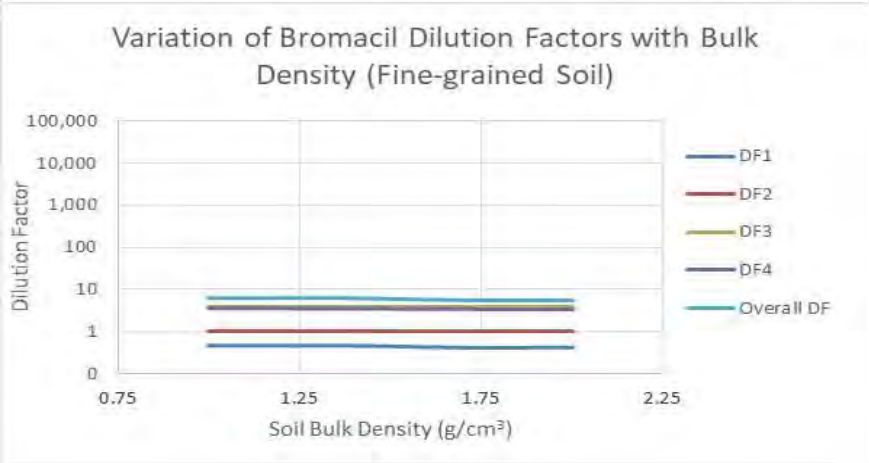

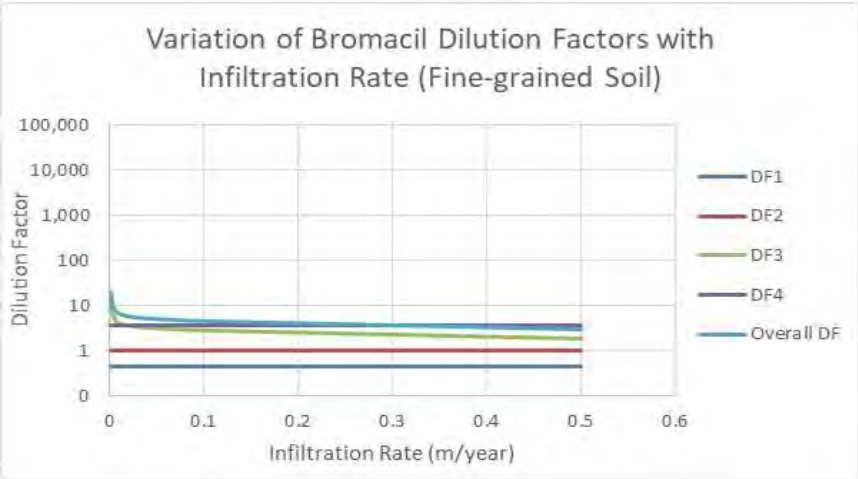

InnoTech
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Sensitivity Analysis

Sensitivity Analysis Bromacil (Fine-grained Soil)

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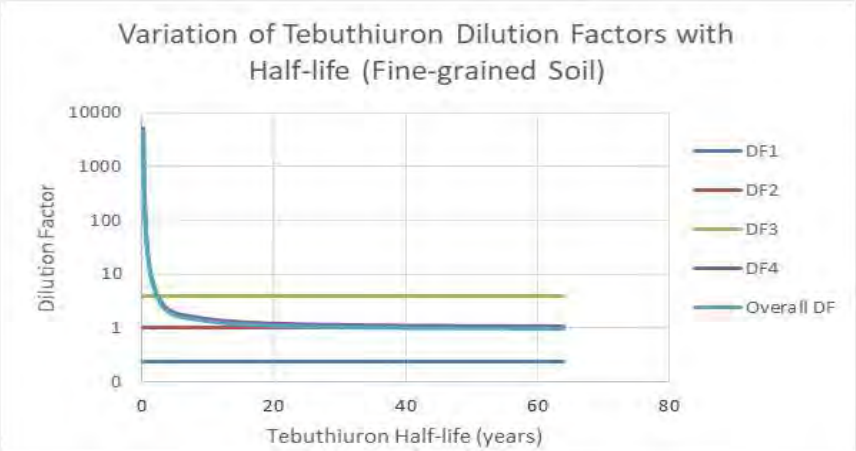

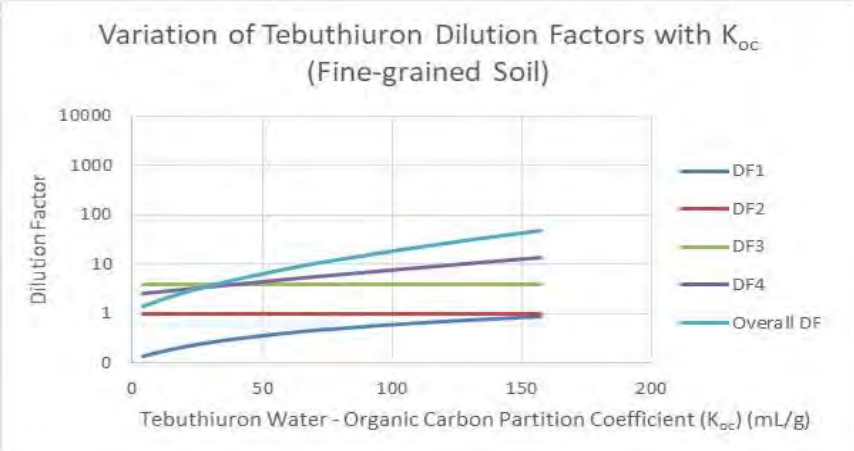

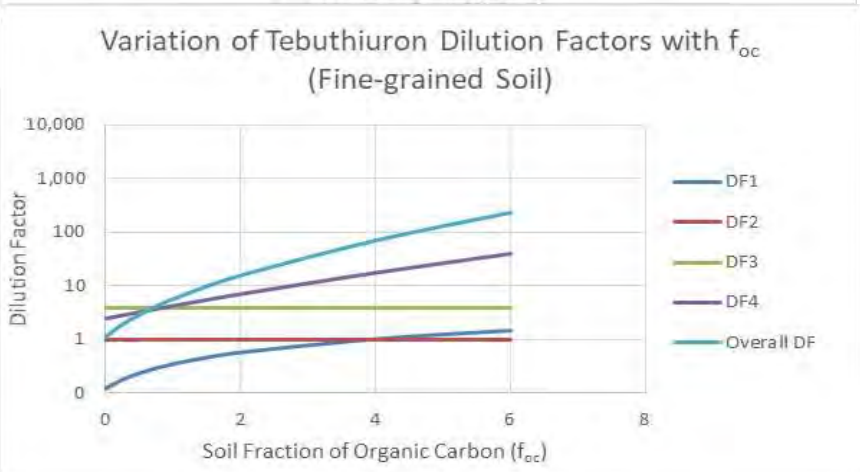

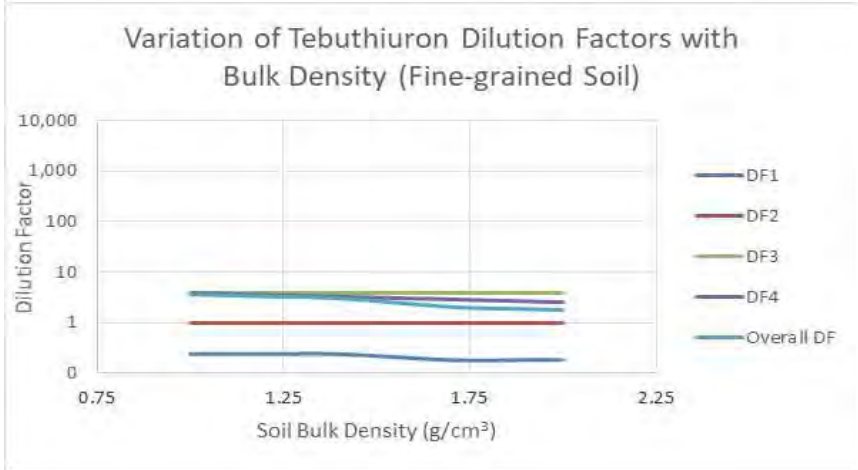

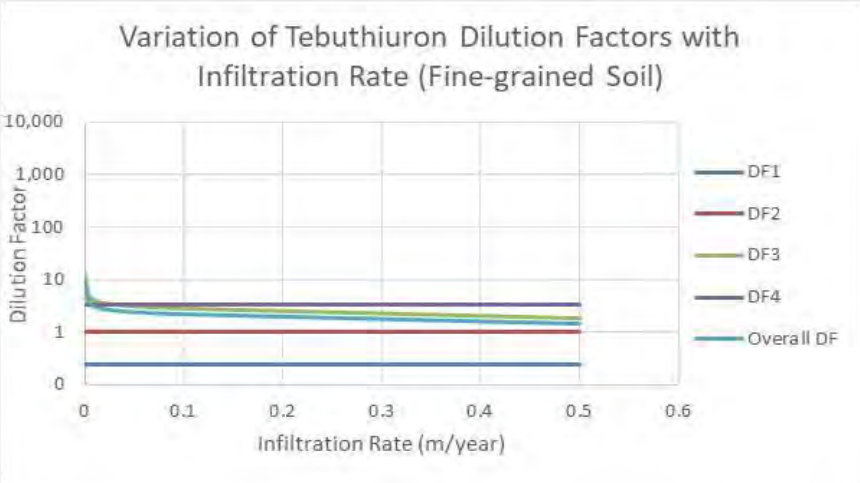

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Soil Sterilants Program
Sensitivity Analysis

Sensitivity Analysis Tebuthiuron (Fine-grained Soil)

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Appendix A4-2: Laboratory Experiment Design

Houston, A., T. Todoruk, B. Loescher and R. Prosser, 2020. Laboratory Experimental Design to Characterize Bromacil and Tebuthiuron Half-life and Adsorption in Alberta Soils. Report SSP-6/8B prepared by Advisian, Bureau Veritas Labs and University of Guelph for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 64 pp.

Laboratory Experimental Design to Characterize Bromacil and Tebuthiuron Half-life and Adsorption in Alberta Soils

Adele Houston, Tiona Todoruk, Advisian, Worley Group
Barry Loescher, Bureau Veritas Labs
and Ryan Prosser, University of Guelph

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April 24, 2020

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EXECUTIVE SUMMARY

As part of InnoTech Alberta's efforts to advance the science of sterilant fate and transport in Alberta, the scope of work for the project focused on: (1) developing refined model input parameters for the Alberta Tier 2 risk assessment models and (2) addressing some of the conservative assumptions inherent in the Alberta Tier 1 Guidelines under field conditions.

The previous sensitivity analysis of the Domenico and Robbins groundwater transport model (Domenico model) used to develop Alberta Environment and Parks (AEP) Tier 1 and Tier 2 guidelines identified that sterilant half-life, water–organic carbon partition coefficient (K_{oc}), fraction of soil organic carbon (f_{oc}), soil bulk density, and infiltration rate were controlling parameters for the groundwater model. The sensitivity analysis defined parameters that significantly influence the Tier 1 Guidelines to be the parameters that result in more than a 10-times change in the resultant soil and/or groundwater guideline. A meaningful impact on the management of sterilant contaminated sites will result in more sustainable Tier 1 Guidelines and Tier 2 Soil and Groundwater Remediation Guidelines (Tier 2 Guidelines) in Alberta. This would include work that could result in an increase in Tier 1 Soil Guidelines protective of irrigation watering to levels that are, at minimum, above laboratory detection limits.

Ultimately, it is expected that Tier 1 Guidelines and Tier 2 Guidelines will become less conservative with implementation of half-life and potentially with other modified input parameters. Furthermore, as these parameters would be protective at Alberta sites and acceptable to regulators, it creates more opportunities for site managers to develop Tier 2 Guidelines as a path to site closure. This effort is expected to reduce remediation and management costs at sites across Alberta. Bromacil and tebuthiuron in soil and groundwater can be widespread at relatively low concentrations, so a guideline increase could have a significant effect on the volumes of soil or groundwater requiring remediation.

The experiments are designed to characterize bromacil and tebuthiuron half-life and adsorption (i.e., K_{oc}) in Alberta soils with the intention of application to Alberta Tier 1 Guidelines and Tier 2 Guidelines. The information matrix design is the preliminary framework for collating and comparing laboratory-generated data with Alberta field data. The proposed laboratory research focusses on two input parameters that can be refined in a laboratory setting and includes half-life estimation and measurement of K_{oc} with organic carbon content (i.e., development of adsorption isotherms) for each sterilant. There are three experimental components to the proposed research design:

1) Half-life estimation using uncontaminated Alberta soil in microcosms in saturated conditions, spiked with bromacil and tebuthiuron, and measured up to 73 weeks.

2) Metabolite characterization and half-life estimation in microcosms using historically-contaminated soil from Alberta sites.

3) Development of adsorption isotherms based on the organic carbon content of uncontaminated Alberta subsoils. The measured parameters are water-organic carbon partition coefficient (K_{oc}) and sorption distribution coefficient (K_d).

A review and summary of 40 active sites that are impacted by bromacil, or bromacil and tebuthiuron, was completed (impact is defined as a measurable concentration). No sites were identified where tebuthiuron was the only sterilant present although a member of the Soil Sterilants Program may yet have one

available. Sites from this list will be used to collect weathered impacted soil and unimpacted soil for spiking experiments and also to gather information for the field measured component of the project.

The information matrix design is the preliminary framework for collating and comparing laboratory-generated data with Alberta field data and is a primary outcome for the project.

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1.0 INTRODUCTION

Worley Canada Services Ltd. (Worley), operating as Advisian, was retained by InnoTech Alberta (InnoTech) to assist with the Soil Sterilants Program (SSP) to develop Sterilant-Specific Model Input Data (the Project).

As part of InnoTech's efforts to advance the science of sterilant fate and transport in Alberta, the scope of work for the project focused on: (1) developing refined model input parameters for the Alberta Tier 2 risk assessment models; and (2) addressing some of the conservative assumptions inherent in the Alberta Tier 1 Guidelines under field conditions.

The draft sensitivity analysis of the Domenico and Robbins groundwater transport model (Domenico model) used to develop Alberta Environment and Parks (AEP) Tier 1 and Tier 2 guidelines (AEP, 2019a, b) was the first Task of the Project and designed to inform subsequent stages of the Project (Marquez et al., 2019a). The sensitivity analysis identified sterilant half-life, water–organic carbon partition coefficient (K_{oc}), fraction of soil organic carbon (f_{oc}), soil bulk density, and infiltration rate were controlling parameters for the groundwater model.

The design of laboratory experiments and information matrix design is the fifth deliverable of the Project. The experiments are designed to characterize bromacil and tebuthiuron half-life and adsorption (i.e., K_{oc}) in Alberta soils with the intention of application to Tier 1 and 2 Guidelines. The information matrix design is the preliminary framework for collating and comparing laboratory-generated data with Alberta field data and is expected to be refined based on the results of other Project Tasks.

This document describes the proposed experimental designs and the information matrix design.

1.1 SUMMARY OF PREVIOUS WORK

As discussed in the literature review completed by Drozdowski et al. (2018), a challenge to applying available literature to the management of sterilant-impacted sites in Alberta is that research and demonstration studies undertaken in laboratory or greenhouse settings have limited applicability to Alberta conditions.

Recent Alberta-specific studies on bromacil and tebuthiuron have focused on plant and soil ecotoxicity and biodegradation and include the following:

1) Ecotoxicity Assessment of a Soil Sterilant – Bromacil (Stantec, 2012). Coarse- and fine-textured soil from Alberta was amended with bromacil in the laboratory to achieve a range of concentrations. Ecotoxicity testing was completed using three plant species, one earthworm species (*Eisenia andrei*) and one collembola species (*Folsomia candida*). The plant species included durum wheat (*Triticum durum*), blue gramma grass (*Bouteloua gracilis*), and alfalfa (*Medicago sativa*). Point estimates (e.g., effects concentrations, lethal concentrations) were obtained. Proposed standards for ecological soil direct contact were developed for both coarse-textured (0.11 mg/kg agricultural and 0.3 mg/kg commercial/industrial) and fine-textured (0.25 mg/kg agricultural and 0.93 mg/kg commercial/industrial) soils using species sensitivity distributions.

2) Ecotoxicity Evaluation in Support of the Derivation of Tier 2 Values for Tebuthiuron (Stantec, 2008a). Ecotoxicity testing was conducted with four plant species, one earthworm

species (*Eisenia andrei*) and one collembola species (*Folsomia candida*). The plant species included durum wheat (*Triticum durum*), blue gramma grass (*Bouteloua gracilis*), western wheatgrass (*Pascopyrum smithii*), and silver sagebrush (*Artemesia cana* subsp. *cana*). Point estimates (e.g., effects concentrations, lethal concentrations) were obtained and were proposed for inclusion into a site-specific species sensitivity distribution (see 3 below).

3) Species Sensitivity Evaluation in Support of Tebuthiuron Tier 2 Benchmark Derivation (Stantec, 2008b). Species sensitivity distributions for plants and soil invertebrates were developed using data from the chronic/definitive ecotoxicity tests from Stantec (2008a). The species sensitivity distribution was used to derive a site-specific ecological direct soil contact criterion of 0.02 mg/kg.

4) Biodegradation Study for Tebuthiuron in a Sandy Clay Loam Subsoil (Stantec, 2011). This study measured the site-specific half-life of tebuthiuron in a laboratory setting under standard optimal conditions (i.e., 22°C in the dark, optimized soil moisture and either with or without amendment of nutrients) to determine if the site-specific direct soil contact criteria derived by Stantec (2008b) was attainable. Half-life estimates ranged from 114 to 403 days.

1.2 SUMMARY OF CONDITIONS AT 40 IMPACTED SITES

An initial list of 51 sites was compiled, including 16 sites submitted by the SSP steering committee members and 24 sites Advisian was working on. Upon review Advisian determined that some of the steering committee sites were duplicates of Advisian sites or were lacking bromacil and/or tebuthiuron impacts. While the original numbering of the sites was kept (i.e., 1 through 51), 11 sites from members of the steering committee (Sites 17, 34 and 36 through 44) were excluded from the following summary.

A review of the remaining 40 active sites impacted by bromacil, or bromacil and tebuthiuron, was completed (impact is defined as a measurable concentration). No sites were identified where tebuthiuron was the only sterilant present although an SSP member may yet have one available. A summary and map of locations is provided in Appendix A.

The 40 sites are located in the southeast corner of Alberta (15 sites), between Edmonton and Calgary (11 sites), east of Edmonton (6 sites), and north of Edmonton in proximity to Slave Lake and Peace River (8 sites). Sterilants were historically applied to surface. Vertical delineation does not appear to have been achieved at all sites.

The following summary is current as of the date of the current report.

1.2.1 Bromacil

At the 40 sites, bromacil-impacted soil ranged from 0 to a maximum depth of 6 metres below ground surface (mbgs; impact is defined as a measurable concentration). Table 1 summarizes bromacil distribution in soil by depth. Note, some of the sites are counted twice since the impacted soil interval spanned soils across both depth intervals. Site 15 has confirmed impacts in groundwater, but soil impacts have not yet been identified and depths of impact were not available for sites 32, 33 and 35 (Appendix A). As summarized in Table 1, concentrations in soil are generally higher at depth (>1 mbgs).

Table 1. Summary of Bromacil Distribution at Impacted Sites

Description	Details
Impacts in soil ≤1 mbgs	18 sites (2, 3, 8, 12, 13, 14, 16, 18 through 25, 27, 31, 51) Concentrations ranged from 0.0085 to 2.4 mg/kg
Impacts in soil >1 mbgs	25 sites (1, 4, 5, 6, 7, 9, 10, 11, 14, 16, 19, 20, 21, 25, 26 through 30, 45 through 50) Concentrations ranged from 0.019 to 3.0 mg/kg
Groundwater depth ≤1 mbgs	6 sites (7, 33, 46, 48, 49, 51)
Reported vertical separation distance between soil impact depth [1] and measured groundwater depth was 0 m or soil impacts were deeper than groundwater depth	18 sites (1, 4 through 7, 11, 16, 19, 21, 25, 27, 30, 45, 46, 48 through 51) 8 of the 18 sites achieved vertical delineation of impacts in soil (1, 7, 19, 27, 45, 46, 50, 51) Both coarse- and fine-grained soil were represented in these 18 sites 15 of the 18 sites yielded groundwater impacted by bromacil (1, 4 through 7, 11, 16, 21, 25, 27, 30, 48 through 51)
Reported vertical separation distance between soil impact depth and measured groundwater depth of 1 to 5 m	8 sites (Sites 2, 3, 10, 12, 14, 18, 24 47) 5 of the 8 sites achieved vertical delineation of impacts in soil (3, 10, 14, 18, 47) Only fine-grained soil was represented in these 8 sites 3 of the 8 sites yielded groundwater impacted by bromacil (10, 12, 24)
Reported vertical separation distance between soil impact depth and measured groundwater depth of >5 to 10 m	4 sites (13 ,20, 22, 23) 2 of the 4 sites achieved vertical delineation of impacts in soil (13 and 23) Both coarse- (13, 23) and fine-grained soil (20, 22) was represented at these 4 sites 1 site (23) with coarse-grained soil yielded groundwater impacted by bromacil

[1] Soil impact depth refers to the greatest depth that soil impacts were noted at the site.

There were 18 sites with no reported vertical separation between soil impact depth and measured groundwater depth (vertical separation distance). As summarized in Table 1, 14 of the sites yielded impacted groundwater. Two sites where groundwater was not impacted had fine-grained soils and two had coarse-grained soils (Site 27 had historical groundwater impacts that were not observed during the last three monitoring events).

There were eight sites with a reported vertical separation distance of 1 to 5 m as summarized in Table 1. All eight sites have fine grained soil. Three of these sites reported groundwater impacted by bromacil.

There were four sites with a reported vertical separation distance of 6.5 to 10 m as summarized in Table 1. Three of the sites were dominated by coarse-grained soils with the remaining site dominated by fine-grained soil. One of the sites, which had coarse-grained soil and a vertical separation distance of 7.7 m, had groundwater impacted by bromacil.

1.2.2 Tebuthiuron

Tebuthiuron impacts in soil co-occurred with bromacil at eight impacted sites (impact is defined as a measurable concentration; none of the 40 sites had tebuthiuron impacts alone). At the eight tebuthiuron and bromacil-impacted sites, tebuthiuron impacts in soil ranged from 0.15 mbgs to a maximum depth of 4.5 mbgs. Most of the sites (6 of 8) did not have tebuthiuron impact in the uppermost metre and like bromacil, concentrations are greater at depth (>1 mbgs).

There were six sites with a reported vertical separation distance of 0 m or soil impacts were deeper than groundwater depth. At these six sites (of which coarse- and fine-grained soils were represented), two yielded groundwater impacted by tebuthiuron (Sites 1 and 30). The six sites where groundwater was not impacted with tebuthiuron (Sites 3, 4, 11, 31, 49, 50) had both fine- and coarse-grained soil. The site where the maximum soil concentration of tebuthiuron was measured (i.e., 1.81 mg/kg; Site 49) did not yield tebuthiuron-impacted groundwater. One site (31) had an unknown groundwater depth.

There was one site with a vertical separation distance of 4 m (Site 3). This site has fine-grained soil. Groundwater at this site was not impacted by tebuthiuron.

Table 2. Summary of Tebuthiuron Distribution at Impacted Sites.

Description	**Details**
Impacts in soil ≤1 mbgs	2 sites (3 and 31) Concentrations ranged from 0.00146 to 0.0208 mg/kg
Impacts in soil >1 mbgs	6 sites (Sites 1, 4, 11, 30, 49, 50), Concentrations ranged from 0.048 to 1.81 mg/kg
Groundwater depth ≤1 mbgs	1 site (49)
Reported vertical separation distance between soil impact depth and measured groundwater depth was 0 m or soil impacts were deeper than groundwater depth	6 sites (Sites 1, 4, 11, 30, 49, 50) 2 of the 6 sites achieved vertical delineation of impacts in soil. Both coarse- and fine-grained soil were represented in these 6 sites 2 of the 6 sites yielded groundwater impacted by tebuthiuron (1, 30)
Reported vertical separation distance between soil impact depth and measured groundwater depth of 1 to 5 m	One (Site 3) (Site 31 did not have a groundwater depth available)

2.0 LABORATORY EXPERIMENT DESIGN

2.1 RESEARCH QUESTION

The proposed laboratory experiments for half-life estimation focus on physico-chemical properties of bromacil and tebuthiuron, soil properties, geometric parameters, flow parameters, and climatic characteristics in Alberta that may significantly influence Tier 1 and Tier 2 Guidelines or have a meaningful impact for management of bromacil and tebuthiuron-contaminated sites.

The sensitivity analysis (Marquez et al., 2019a) defined parameters that significantly influence the Tier 1 Guidelines to be the parameters that result in more than a 10-times change in the resultant soil and/or groundwater guideline. Marquez et al. (2019a) considered work that has a meaningful impact on the management of sterilant contaminated sites will result in more sustainable Tier 1 Guidelines and Tier 2 Guidelines in Alberta. This would include work that could result in an increase in Tier 1 Soil Guidelines protective of irrigation watering to levels that are, at minimum, above laboratory detection limits.

Ultimately, it is expected that Tier 1 Guidelines and Tier 2 Guidelines will become less conservative with implementation of half-life and potentially with other modified input parameters. Furthermore, as these parameters would be protective at Alberta sites and acceptable to regulators, it creates more opportunities for site managers to develop Tier 2 Guidelines as a path to site closure. This effort is expected to reduce remediation and management costs at sites across Alberta. Bromacil and tebuthiuron in soil and groundwater can be widespread at relatively low concentrations, so a guideline increase could have a significant effect on the volumes of soil or groundwater requiring remediation.

The proposed research focusses on two input parameters that can be refined in a laboratory setting and includes half-life estimation and measurement of K_{oc} with organic carbon content (i.e., development of adsorption isotherms) for each sterilant.

2.2 HYPOTHESIS AND EXPECTED OUTCOMES

The hypothesis of the proposed study is that development of half-life values for bromacil and tebuthiuron in saturated Alberta subsoils will significantly influence and have a meaningful impact on Alberta Tier 2 and potentially Tier 1 guideline values for groundwater pathways and that application will result in less conservative guidelines that are representative of Alberta conditions.

The outcome of K_{oc} measurement on Alberta Tier 2 and potentially Tier 1 guideline values for groundwater pathways may result in more or less conservative guidelines that are representative of Alberta conditions.

2.3 RESEARCH DESIGN

There are three experimental components to the proposed research design:

1) Half-life estimation using uncontaminated Alberta soil in microcosms in saturated conditions, spiked with bromacil and tebuthiuron, and measured up to 73 weeks.

2) Metabolite characterization and half-life estimation in microcosms using historically-contaminated soil from Alberta sites. The microcosm experiments will not be completed if it is determined that further degradation of sterilants over time is unlikely.

3) Development of adsorption isotherms based on the organic carbon content of uncontaminated Alberta subsoils. The measured parameters are water-organic carbon partition coefficient (K_{oc}) and sorption distribution coefficient (K_d).

Experiments 1 and 2 will simulate field conditions in subsoils in Alberta and relevant physico-chemical and environmental variables are considered in experimental design.

Experimental designs are presented in the following sections.

2.4 EXPERIMENT 1

Experiment 1 aims to estimate sterilant half-life in Alberta subsoils in a series of microcosms. There are several experimental conditions and parameters that could be manipulated and potentially affect half-life measurements. Advisian understands the intent of the laboratory experiment is to develop half-life values representative of Alberta conditions, as opposed to optimal degradation conditions.

Sterilant persistence in soil is influenced by degradation processes (i.e., biological, chemical, and photochemical) and transfer processes (i.e., volatilization, soil adsorption, surface runoff, leaching through soil, and uptake/exudation by plants). Physico-chemical properties (i.e., sterilant chemical structure, physical and adsorptive properties) and soil properties (i.e., temperature, moisture, composition, and microbial flora) will also generate effects. Half-life values for bromacil from the literature range from 12 to 46,200 days with most measurements ranging from 100 and 350 days (aerobic and anaerobic). Half-life values for tebuthiuron from the literature range from 13 to 1,050 days (aerobic and anaerobic) with most measurements ranging from 100 and 400 days. Values for half-life from a preliminary literature search are compiled in Appendix B.

An evaluation of environmental factors and potential application to the half-life experimental design is summarized in Table 3.

Table 3. Environmental Factors that Affect Pesticide Persistence.
Adapted from Ney (1995).

Environmental Factors	Role in Chemical Degradation	Half-life Experimental Design
Sunlight	Radiation from the sun breaks certain chemical bonds, creating break-down products	Bromacil is stable to photolysis on soil (PubChem, 2019a). Direct photolysis by sunlight is not likely to be an important environmental fate process for tebuthiuron (CCME, 1999). Field subsoil conditions will be dark. Experiment 1 will be conducted in the dark.

Environmental Factors	Role in Chemical Degradation	Half-life Experimental Design
Microorganisms	Bacteria and fungi can break down chemicals, creating biodegradation products	Bromacil degradation by microorganisms is considered important by Landsburg and Dwyer (1995) but occurs slowly (US EPA, 1996). Anaerobic processes may be important (Wolf and Martin (1974). Microbial degradation was not considered important for bromacil by PubChem (2019a cited in US EPA, 1994) based on the study by Madhun and Freed (1987). Tebuthiuron anaerobic and aerobic degradation is very slow. Although Rainey (1989a, b cited in US EPA, 1994) considered tebuthiuron as stable to degradation in soil, other studies show when conditions are optimized, tebuthiuron degradation occurs (Stantec 2011). Subsoil (greater than 1 m depth) will be used in Experiment 1. While fewer microorganisms are likely to be present at this depth, subsoil (greater than 1 m depth) is representative of impacts present under Alberta field conditions and at the 40 sites with historical impacts, concentrations appear to be greater at depth.
Plant / Animal Metabolism	Plants and animals can change chemicals into forms that dissolve better in water (metabolites); this makes removal from the body easier	Plants will not be included in Experiment 1 because subsoil, below the typical rooting zone, is the focus.
Water	Hydrolysis	Bromacil is stable to hydrolysis at environmental pHs ranging between 5 and 9 (US EPA, 1996). Tebuthiuron is stable in aqueous media between pH 5 and 9. The hydrolysis half-life at 25°C is greater than 64 days at pH 3, 6, and 9 (PubChem, 2019b). Since bromacil and tebuthiuron are stable to hydrolysis, it is not an important fate process and not evaluated in the experiment.

Environmental Factors	Role in Chemical Degradation	Half-life Experimental Design
Soil Moisture Content	Direct effects on soil microorganisms, sterilant mobility	The half-life for bromacil (Gerstl and Yaron, 1983 cited in Landsburg and Dwyer, 1995) and tebuthiuron increases with lower moisture content (Raman and Rao, 1987). The Domenico model used by AEP (2019 a, b) includes both unsaturated (Dilution Factor 2) and saturated (Dilution Factor 4) half-life values. Unsaturated half-life modification (Dilution Factor 2) will have application for Tier 2 guideline adjustment at sites where soil impacts and underlying groundwater are separated. Saturated half-life modification (Dilution Factor 4) may have application for both Tier 1 and Tier 2 guideline adjustment. Experiment 1 will be conducted under saturated soil conditions to provide the greatest application of experiment outcomes. The unsaturated soils will be collected below 1 mbgs and saturated to 100% water holding capacity in the laboratory.
Dissociation	Chemicals can break apart into smaller pieces (dissociation products)	This may occur during a half-life experiment but is considered a minor factor as the pesticides are formulated to be stable.
Sorption	Chemicals that stick tightly to particles can become inaccessible and/or move away with those particles	Adsorption of bromacil and tebuthiuron has an important role in half-life; generally increasing adsorption is associated with increasing organic matter content (Koskinen et al., 1996; Landsburg and Dwyer, 1995; Shipman, 1983 cited in PubChem, 2019a), increasing clay content (PubChem, 2019a; Raman and Rao, 1987) and decreased pH (Angemar et al., 1984; Landsburg and Dwyer, 1995). In semi-arid soils, leaching of tebuthiuron was not appreciably different in clay or loam soils (Johnsen and Morten, 1989). The solvent used in the experiment will measure total concentrations of bromacil and tebuthiuron in soil. Thus, factors that affect sorption are not relevant in Experiment 1 unless binding is irreversible, which may occur in some soils with increased organic matter content and/or at low moisture contents. K_d and K_{oc} (adsorption) are evaluated in Experiment 3.

Environmental Factors	Role in Chemical Degradation	Half-life Experimental Design
Soil Type	Cation exchange capacity, clay content, and adsorption differences affect toxicity for plants and sorption (see above)	Fine-grained soil typically yields less recovery of detectable bromacil and tebuthiuron (Chang and Stritke, 1977; Shipman, 1983 cited in PubChem, 2019a) and has greater cation exchange capacity. Johnsen and Morton (1989) did not identify tebuthiuron persistence to be markedly affected by soil type. Soil type (coarse-grained and fine-grained soils as defined by AEP, 2019a) is included as a variable in Experiment 1.
Soil pH	Potential effects on soil microorganisms	Bromacil and tebuthiuron are not expected to have large effects on soil pH. The pH of the environmental medium affects the chemical structure of bromacil and may have effects on bioavailability, solubility, and mobility in soils and thus, fate and transport. For example, solubility in water at pH 5, 7, and 9 is 807, 700, and 1,287 mg/L, respectively, at 25°C (MacBean, 2008-2010, cited in PubChem, 2019a). Available soil pH data from the 40 active sites indicated soil is typically neutral to weakly basic. Soil pH is not included as a manipulated variable in the experiment, although soil pH will be measured.
Volatilization	Degradation process	Volatilization from moist soil surfaces is not expected to be an important fate process for bromacil based upon an estimated Henry's Law constant of 5.27×10^{-9} (AEP, 2019a; PubChem, 2019a). Volatilization from moist soil surfaces is not expected to be a major fate process for tebuthiuron based on Henry's Law constant of 4.91×10^{-9} (AEP, 2019a; PubChem, 2019b). Volatilization is not considered to be an important fate process for these sterilants in the experiment.
Temperature	Can affect chemical and biological degradation	Increases in soil temperature are associated with greater bromacil and tebuthiuron degradation rates (Chang and Stritzke, 1977; Madhun and Freed, 1987; Zimdahl et al., 1970). There are five soil temperature classes in Alberta (NRCan, 1974). Subsoil temperature measured near Edmonton, central Alberta exhibited seasonal variation to depths of 6 m. For subsoil depths from 2 to 15 mbgs (regardless of seasonal variation), a temperature of approximately 5°C appears to be average (Toogood, 1976). Experiment 1 proposes suboptimal temperature representative of subsoils to be held at approximately 5°C.

Environmental Factors	Role in Chemical Degradation	Half-life Experimental Design
Sterilant Concentration	The original concentration applied may affect degradation processes	Lower initial concentrations of bromacil resulted in lower half-life measurements (Gerstl and Yaron, 1983 cited in Landsburg and Dwyer, 1995). Johnsen and Morton (1989) did not find application rate affected the speed of tebuthiuron loss from soil; however, tebuthiuron would also be expected to demonstrate a first order degradation rate. It is expected that first order degradation rates will apply to the sterilants. Two soil concentrations for each sterilant are proposed for Experiment 1: a high "fresh application rate" (recommended maximum by US EPA, 1996, 2019) and a "weathered", lower application rate (95 percentile reported from the 40 contaminated sites reviewed; available dataset includes eight sites with measurable tebuthiuron and 37 with measurable bromacil). It is noted application rates used historically at Alberta sites probably exceeded the maximum recommended rate.
Salinity	Salinity is expected to affect sterilant solubility and is potentially toxic to soil microorganisms	Soluble salt concentrations were significantly correlated with residue persistence and increased depth in four soils (Shipman, 1983 cited in PubChem, 2019a). Soluble salts (chloride) in soil or groundwater were co-contaminants at sites with bromacil and tebuthiuron in at least 13 of the 40 sites reviewed, with concentrations of chloride ranging up to 8,640 mg/kg at one location. A salinity treatment (proposed at 2,500 mg/kg) is included in the experimental design. This concentration is equivalent to the BC Environment and Climate Change Strategy direct soil contact guideline for industrial, commercial, and residential high-density sites (BC ENV, 2019) and is the same order of magnitude as chloride concentrations measured at many of the co-contaminated sites.

Experiment 1 Design Details are summarized in Table 4.

Table 4. Experiment 1 Design Details.

Description	Details
Soil Types	Two unimpacted subsoils to be collected. At the time of collection, field soil temperature will be measured. Experiments to be completed separately for coarse- and fine-grained Alberta subsoils.

Description	Details
Soil Characterization	Full characterization to be completed once at the beginning of the experiment on control soil of each soil type and includes: particle size (hydrometer) and classification as coarse- or fine-grained, soil pH, a salinity package including electrical conductivity (EC) and major ions, nutrients (ammonia, nitrate and nitrite), total Kjeldahl nitrogen, total phosphorus, total metals, sterilants, bulk density, total organic carbon, fraction of organic carbon (f_{oc}), bromide and oxidation-reduction potential (ORP). Microbial quantification analyses include a heterotrophic plate count (HPC). Partial characterization is to be completed on one soil replicate from each treatment at sampling event 1 and three other sampling events. Partial characterization includes pH, nutrients (ammonia, nitrate, and nitrite) and bromide. ORP will be measured at the sampling event after soil becomes anaerobic. Oxygen indicator packets (Intelledot [Wondersensor] Oxygen Detector) will be placed in vessels slated for characterization parameters. The paper in the packet changes colour when oxygen content drops to less than 0.1% and is expected to indicate when the system is moving from aerobic to anaerobic conditions. If the experiment does not go anaerobic, ORP will be measured at the end of the experiment. HPC will be measured at the sampling event after soil becomes anaerobic (if it does) and at the end of the experiment. The dates of partial analyses, ORP and HPC will be adjusted based on results obtained as the experiment progresses.
Treatments and Replicates	Treatments are the variables manipulated in the experiment. The replicates refer to the repetition of the experimental condition to evaluate variability. The treatments (and associated replicates) include: 1) High “fresh application rate” and low “weathered” concentrations of spiked sterilant in coarse- and fine-grained soils for each sterilant (three replicates). 2) As described in Table 1, due to the potential effects of salinity on half-life, the higher “fresh application rate” concentration of the sterilants in coarse-grained soil will also have a “salinity” treatment (three replicates). 3) To identify whether differences in degradation rates are seen with a commercial formulation as compared to laboratory standards, a “commercial formulation” treatment was added (one replicate). 4) To identify whether the mass of soil and volume of the incubation jar have an effect on degradation rates, a “bulk incubation” treatment was added. The bulk incubation set up will have the same ratio of soil volume:headspace volume as the primary experiment (one replicate). Controls (unspiked) for bromacil and tebuthiuron will also be included (one replicate each).

Description	Details
Experimental Set Up and Refinement	Approximately 5 kg of each soil type will be homogenized. 10 g of soil will be placed in dedicated vessels (60 mL glass jar), and water added to reach desired water content (saturated paste – 100% water holding capacity) and the soil spiked with bromacil or tebuthiuron. A dedicated vessel set up has been used by others with some half-life studies described in Appendix B. Dedicated vessels are expected to prevent heterogeneity issues and constant disruption of a larger sample. This experimental design has been used successfully by BV Labs for other studies of chemical stability over time. The vessels will have headspace present and although the jars are sealed, the threads are not airtight. Vessels will be incubated in the dark at 5°C and analyzed on scheduled dates (see Table 5 below). Each replicate and duplicate measurement will be conducted from a separate 60 mL jar. Partial characterizations will require approximately 120 g of saturated soil. The soil will be placed in a larger jar such that the exposed surface area will be proportional to the 10 g in 60 mL jars. The soils will be spiked with the high concentration of the analyte of interest. The full characterization data will be used to establish the final experimental design. The ORP analysis gives insight into whether soil is expected to become anaerobic over time. Anaerobic degradation of bromacil appears to be an important breakdown pathway; however, it is understood that the majority of shallow groundwater aquifers in Alberta are aerobic and so aerobic conditions are desirable for the current experiment. As described earlier, oxygen indicator packets (Intelledot [Wondersensor] Oxygen Detector) will be placed in vessels slated for characterization parameters to indicate when the system is moving from aerobic to anaerobic conditions.
Duration and Sampling Events	The experiment is scheduled to run for 512 days and include 8 sampling events on days 1, 8, 16, 32, 64, 128, 256, and 512. The duration of the experiment may be decreased if several consecutive measurements of stable concentrations are observed. The frequency of measurement will be revisited after initial measurements. Available literature (Appendix B) indicates saturated half-lives for bromacil ranged from 144 to 198 days and for tebuthiuron ranged from 83 to 403 days (depending on amendments added to soil). The current experiment will not include amendment and thus, the upper end of the half-life range is expected.
Sterilant	Laboratory-grade standards for bromacil and tebuthiuron will be used to spike soil with the exception of the treatment using commercial formulations where bromacil as HyvarXL™ and tebuthiuron as Spike™ will be used.

Description	Details
Sterilant Spiking Concentration	Two soil concentrations will be applied. High "fresh application rate" and low "weathered" concentrations are proposed as follows: • High bromacil "fresh application rate": The maximum recommended rate of HyvarXL™ (commercial bromacil formulation) is 12 pounds per acre (13.45 kg/ha; US EPA, 2019). Fresh application rate for bromacil applicable to laboratory samples is estimated as 32 mg/kg *. Other field and laboratory studies have also used 12 pounds per acre (Schneiders, 1990 cited in US EPA, 1996; US EPA, 1996; see Appendix B). • High tebuthiuron "fresh application rate": The maximum recommended rate of Spike 20P (commercial tebuthiuron formulation) is 5 pounds per acre (5.6 kg/ha; US EPA 2006). Fresh application rate for tebuthiuron applicable to laboratory samples is estimated as 13 mg/kg*. This is comparable to the upper end of reviewed studies which included a laboratory application of 20 mg/kg, and field application rates of 5.33 to 21 mg/kg (Rainey and Magnussen, 1976, 1978 cited in US EPA/ODW, 1998; Raman and Rao, 1987; see Appendix B). • Low "weathered": 95th percentile weathered concentrations of bromacil and tebuthiuron measured at the 40 active sites are 2.6 mg/kg and 1.3 mg/kg, respectively. While these concentrations are similar to those used in half-life studies by others, residual concentrations measured at several of the historical sites reviewed have lower concentrations of the sterilants present.
Duplicates	There will be one or two duplicates per sampling event (10 duplicates total). This is approximately 1 duplicate for every 29 samples (288 sterilant analyses total).
Analytical	The laboratory method detection limit is 0.009 mg/kg for bromacil and 0.001 mg/kg for tebuthiuron. Total sterilant will be measured using a methanol extraction and liquid chromatography-tandem mass spectrometry (LC/MS/MS).
Outcomes	The outcomes of this experiment are expected to be a figure showing concentration versus time for each treatment. Using appropriate fit models, the decay model will be proposed and half-life calculated for each of the 10 treatments where three replicates are available.

* Using the general conversion of 1 ha of soil to a depth of 3 cm with a bulk density of 1.4 g/cm^3 yields approximately 420,000 kg soil per ha (or 170,000 kg per acre). The bulk density used is the generic value from AEP (2019a) for fine soil which calculates a lower mass per area and resulting greater concentration than using the bulk density value for coarse soil of 1.7 g/cm^3).

The detailed design for Experiment 1 is provided in Table 5.

Table 5. Detailed Proposed Experiment 1 Design.

Soil Type	Sterilant	Sterilant Concentration	Moisture Treatment	Additional Treatment	Sampling Events for Sterilant Concentration								Sampling Events for Characterization							
					1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
					(Day of Experiment)								(Day of Experiment)							
					1	8	16	32	64	128	256	512	1	8	16	32	64	128	256	512
Coarse	None	None (control)	Saturated	None	X	X	X	X	X	X	X	X	**F**	P		P*		O, H*		P, H*
Coarse	Bromacil	High	Saturated	None	X (dup)	X	X	X	X	X	X	X	P	P		P*		O, H*		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Coarse	Bromacil	High	Saturated	2500 mg/kg chloride	X	X (dup)	X	X	X	X	X	X	P	P		P*		O, H*		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Coarse	Bromacil	High	Saturated	Commercial formulation	X	X	X	X	X	X	X	X	P	P		P*		O, H*		P, H*
Coarse	Bromacil	High	Saturated	Bulk incubation	X	X	X	X	X	X	X	X	P	P		P*		O, H*		P, H*
Coarse	Bromacil	Low	Saturated	None	X	X	X (dup)	X	X	X	X	X	P	P		P*				P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Coarse	Tebuthiuron	High	Saturated	None	X	X	X	X (dup)	X	X	X	X	P	P		P*		O, H*		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Coarse	Tebuthiuron	High	Saturated	2500 mg/kg chloride	X	X	X	X	X (dup)	X	X	X	P	P		P*		O, H		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Coarse	Tebuthiuron	High	Saturated	Commercial formulation	X	X	X	X	X	X	X	X	P	P		P*		O, H*		P, H*
Coarse	Tebuthiuron	High	Saturated	Bulk incubation	X	X	X	X	X	X	X	X	P	P		P*		O, H*		P, H*
Coarse	Tebuthiuron	Low	Saturated	None	X	X	X	X	X	X (dup)	X	X	P	P		P*		O, H*		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Fine	None	None (control)	Saturated	None	X	X	X	X	X	X	X	X	**F**	P		P*		O, H*		P, H*
Fine	Bromacil	High	Saturated	None	X	X	X	X	X	X	X (dup)	X	P	P		P*		O, H*		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Fine	Bromacil	Low	Saturated	None	X	X	X	X	X	X	X	X (dup)	P	P		P*		O, H*		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Fine	Tebuthiuron	High	Saturated	None	X (dup)	X	X	X	X	X	X	X	P	P		P*		O, H*		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								
Fine	Tebuthiuron	Low	Saturated	None	X	X (dup)	X	X	X	X	X	X	P	P		P*		O, H*		P, H*
					X	X	X	X	X	X	X	X								
					X	X	X	X	X	X	X	X								

Notes:
X: Sterilant analysis
X (dup): Sterilant analysis and a duplicate. One or two duplicates for each sampling event
F: Full characterization parameters
P: Partial characterization parameters
O: Oxidation Reduction Potential (ORP)
H: Heterotrophic plate count
* Dates may vary depending on results as experiment progresses.
Indicates additional treatment (i.e., salinity, commercial formulation or bulk incubation)

2.5 EXPERIMENT 2

Experiment 2 aims to characterize degradation products of bromacil and tebuthiuron and potentially estimate half-life in a series of microcosms using impacted Alberta subsoils.

Impacted soils will be characterized initially (as in Experiment 1) and extractions completed to quantify bromacil or tebuthiuron concentrations and identify weathering products present. Weathering products will be identified using an open scan as standards are expected to be unavailable for weathering products. To assist in open scan interpretation, a draft literature review of weathering products and metabolites in soil was prepared (Marquez et al., 2020b).

Of the 40 available sites, 37 yielded detectable bromacil concentrations (all soil depths) ranging from 0.0085 mg/kg to 3 mg/kg. The half-life studies completed by others in a laboratory setting (described in Appendix B), used initial soil concentrations ranging from 0.55 mg/kg to 36 mg/kg. Impacted, field-collected soil from available sites with bromacil concentrations greater than 0.55 mg/kg should allow generation of saturated half-life estimates.

Of the 40 available sites, 8 yielded detectable tebuthiuron concentrations (all soil depths) ranging from 0.0015 mg/kg to 1.81 mg/kg. Interestingly, detectable tebuthiuron co-occurred with bromacil at the 8 sites. The half-life studies completed by others in a laboratory setting (described in Appendix B), used initial soil tebuthiuron concentrations ranged from 0.04 mg/kg to 36 mg/kg. Stantec (2011) used historically-impacted subsoils with a weathered tebuthiuron concentration of approximately 0.04 mg/kg dry weight soil in their degradation study (treatment: 1.0x water holding capacity, no nutrient amendment and incubated at 22°C). At the conclusion of the experiment (256 days), biodegradation as described by the exponential decay regression models used and mineralization was estimated at 13.5 months. While impacted field soil collected from available sites with tebuthiuron concentrations greater than 0.04 mg/kg should allow generation of saturated half-life estimates, none of the tebuthiuron-impacted sites are currently considered appropriate for testing due to co-contamination with contaminants other than sterilants, or remediation has already occurred. *A non-company member of the SSP may have a site with tebuthiuron-only impacts; this is being verified at the time of this report and the experimental design has been completed assuming tebuthiuron-impacted soil from this site will be available.*

A final decision to proceed with half-life experiments using impacted, field-collected soil will be made following characterization and open scan analysis of collected soil. Assuming half-life experiments can be completed, the following experimental design is proposed in Table 6 and Table 7.

Table 6. Experiment 2 Design Details.

Description	Detail
Soil Types	Three impacted Alberta subsoils to be collected (coarse and fine soil contaminated with bromacil and a coarse or fine soil contaminated with tebuthiuron). At the time of collection, field soil temperature will be measured.

Description	Detail
Soil Characterization	Full characterization to be completed once at the beginning of the experiment on each soil type and is the same as for Experiment 1 and includes: particle size (hydrometer) and classification as coarse- or fine-grained, soil pH, a salinity package including electrical conductivity (EC) and major ions, nutrients (ammonia, nitrate and nitrite), total Kjeldahl nitrogen, total phosphorus, total metals, sterilants, bulk density, total organic carbon, fraction of organic carbons (f_{oc}), bromide and oxidation-reduction potential (ORP). Microbial quantification analyses include a heterotrophic plate count (HPC). Open scans will be completed at the beginning and the end of the experiment on each soil type (sampling events 1 and 5). Partial characterization is to be completed on one soil replicate from each treatment at three other sampling events. Partial characterization includes pH, nutrients (ammonia, nitrate, and nitrite) and bromide. ORP will be measured at the sampling event after soil becomes anaerobic. Oxygen indicator packets (Intelledot [Wondersensor] Oxygen Detector) will be placed in vessels slated for characterization parameters. The paper in the packet changes colour when oxygen drops to less than 0.1% and is expected to indicate when the system is moving from aerobic to anaerobic conditions. If the experiment does not go anaerobic, ORP will be measured at the end of the experiment. HPC will be measured at the sampling event after soil becomes anaerobic (if it does) and at the end of the experiment. The dates of partial analyses, ORP and HPC will be adjusted based on results obtained as the experiment progresses.
Treatments	There are no varying treatments in Experiment 2, but there are three soil/sterilant combinations included (i.e., bromacil in coarse soil, bromacil in fine soil, and tebuthiuron in coarse or fine soil).

Description	Detail
Experimental Set Up and Refinement	The experimental set up for Experiment 2 is expected to be the same as Experiment 1. Approximately 5 kg of each soil type will be homogenized. 10 g of soil will be placed in dedicated vessels (60 mL glass jar), water added to reach desired water content (saturated paste – 100% water holding capacity). Three replicates of each soil will be set up. Each replicate and duplicate measurement will be conducted from a separate 60 mL jar. Partial characterizations will require approximately 120 g of saturated soil. The soil will be placed in a larger jar such that the exposed surface area will be proportional to the 10 g in 60 mL jars. The soils will be spiked with the high concentration of the analyte of interest. The full characterization data will be used to establish the final experimental design. The ORP analysis will give insight whether soil is expected to become anaerobic over time. Anaerobic degradation of bromacil appears to be an important breakdown pathway; however, it is understood that most shallow groundwater aquifers in Alberta are aerobic and so aerobic conditions are desirable for the current experiment. As described earlier, oxygen indicator packets (Intelledot [Wondersensor] Oxygen Detector) will be placed in vessels slated for characterization parameters to indicate when the system is moving from aerobic to anaerobic conditions.
Duration	The experiment is scheduled to run for 512 days and include 8 sampling events on days 1, 8, 16, 32, 64, 128, 256, and 512. The duration of the experiment may be decreased if several consecutive measurements of stable concentrations are observed. The frequency of measurement will be revisited after initial measurements. Available literature (Appendix B) indicate saturated half-lives for bromacil ranged from 144 to 198 days and for tebuthiuron ranged from 83 to 403 days (depending on amendments added to soil). The current experiment will not include amendment and thus, the upper end of the half-life range is expected.
Sterilant	Sterilant will be present in impacted soil. Further spiking is not required.
Duplicates	There will be one duplicate every other sampling event (4 duplicates total). This is approximately 1 duplicate for every 18 samples (72 sterilant analyses total).
Analytical	The laboratory method detection limit is 0.009 mg/kg for bromacil and 0.001 mg/kg for tebuthiuron. Total sterilant will be measured using a methanol extraction and liquid chromatography-tandem mass spectrometry (LC/MS/MS). The open scan characterization for metabolites of the sterilants will be completed using gas chromatography mass spectrometry with library matching.

Description	Detail
Outcomes	The outcomes of this experiment are expected to be figures showing concentration versus time for each of the four treatments. Using appropriate fit models, the decay model will be proposed and half-life calculated for each of the four soils. The outcomes of this experiment are expected to be a figure showing concentration versus time for each of the treatments. Using appropriate fit models, the decay model will be proposed and half-life calculated for each of the three treatments where three replicates are available.

The detailed design for Experiment 2 is provided in Table 7. Further refinement of the detailed design will be performed upon receiving feedback from identified stakeholders.

Table 7. Detailed Proposed Experiment 2 Design.

Soil Type	Sterilant	Sterilant Concentration	Moisture Treatment	Sampling Events for Sterilant Concentration								Sampling Events for Open Scan								Sampling Events for Characterization							
				1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8	1	2	3	4	5	6	7	8
				(Day of Experiment)								(Day of Experiment)								(Day of Experiment)							
				1	8	16	32	64	128	256	512	1	8	16	32	64	128	256	512	1	8	16	32	64	128	256	512
Coarse	Bromacil	Weathered	Saturated	X (dup)	X	X	X	X	X	X (dup)	X	S							S	**F**	P		P		O, H*		P, H*
			Saturated	X	X	X	X	X	X	X	X																
			Saturated	X	X	X	X	X	X	X	X																
Fine	Bromacil	Weathered	Saturated	X	X	X (dup)	X	X	X	X	X	S							S	**F**	P		P		O, H*		P, H*
			Saturated	X	X	X	X	X	X	X	X																
			Saturated	X	X	X	X	X	X	X	X																
Fine or Coarse	Tebuthiuron		Saturated	X	X	X	X	X (dup)	X	X	X	S							S	**F**	P		P		O, H*		P, H*
		Weathered	Saturated	X	X	X	X	X	X	X	X																
			Saturated	X	X	X	X	X	X	X	X																

Notes

X: Sterilant analysis

X (dup): Sterilant analysis and a duplicate. Proposed three events to be duplicated (all treatments) are 1, 4, 7, which can be adjusted as experiment progresses

S: Open scan

F: Full characterization parameters

P: Partial characterization parameters

O: Oxidation Reduction Potential (ORP)

H: Heterotrophic plate count

* Dates may vary depending on results as experiment progresses.

2.6 EXPERIMENT 3

Experiment 3 aims to characterize K_{oc} in coarse- and fine-grained Alberta unimpacted subsoils for use during development of Alberta Tier 1 or 2 Guidelines. The applicability is expected to depend on the range of results measured, with any drastically different measurement between soil types requiring further study.

Using a modified version of the Organization of Economic Co-operation and Development (OECD) Test Number 106: Adsorption-Desorption Using a Batch Equilibrium Method and Tier 3 of the method (OECD, 2000), adsorption isotherms will be generated and used to study the influence of sterilant concentration on the extent of adsorption by Alberta coarse and fine-grained subsoils. Experiment 3 was completed by Dr. Prosser at the University of Guelph with sterilant analyses completed by BV Labs (Appendix C).

Table 8. Experiment 3 Design Details.

Description	**Detail**
Soil Types	Two unimpacted Alberta subsoils to be collected (coarse- and fine-grained soil). It is anticipated the same soil as Experiment 1 will be used.
Soil Characterization	Soil will be characterized for organic carbon content, texture, pH, and cation exchange capacity. These analyses will have been completed at the commencement of Experiment 1.
Treatments	While treatments are not applied, there are four soil/sterilant combinations: bromacil and tebuthiuron adsorption will be measured in coarse- and fine-grained soil.
Experimental Set Up	The experimental set up is described in OECD (2000) with modifications. Tier 3 of the OECD method will be completed and modified to investigate adsorption to determine a K_d and K_{oc} measurement for each soil/sterilant combination.
Sterilant concentrations	Five solute concentrations will be applied: • Bromacil: The five concentrations will range from 0.032 mg/kg to 32 mg/kg (the high "fresh application rate" concentration used for Experiment 1). • Tebuthiuron: The five concentrations will range from 0.013 mg/kg to 13 mg/kg (the "fresh application rate" concentration used for Experiment 1). Concentrations may be adjusted by Dr. Prosser.
Analytical	The laboratory method detection limit is 0.009 mg/kg for bromacil and 0.001 mg/kg for tebuthiuron. Total sterilant will be measured using a methanol extraction and liquid chromatography-tandem mass spectrometry (LC/MS/MS) by BV Labs.
Duplication	Sterilant analyses during the experiment will be duplicated.

Description	Detail
Outcomes	The outcomes of this experiment are expected to be an adsorption isotherm for each of the four sterilant/soil combinations. The adsorption isotherm will be used to estimate water–organic carbon partition coefficient (K_{oc}) and sorption distribution coefficient (K_d) using organic carbon content.

Table 9. Detailed Proposed Experiment 3 Design.

Soil Type	Sterilant	Sterilant Concentration	Sterilant Analyses
Coarse	Bromacil	Five concentrations ranging from 0.032 mg/kg to 32 mg/kg	10
Coarse	Tebuthiuron	Five concentrations ranging from 0.013 mg/kg to 13 mg/kg	10
Fine	Bromacil	Five concentrations ranging from 0.032 mg/kg to 32 mg/kg	10
Fine	Tebuthiuron	Five concentrations ranging from 0.013 mg/kg to 13 mg/kg	10

3.0 STATISTICAL ANALYSES FOR EXPERIMENTS 1 AND 2

While statistical analyses for Experiments 1 and 2 will be parametric if possible, non-parametric methods may be required. The following discussion assumes parametric analysis will be possible.

For each treatment, sterilant concentrations from each replicate and event will be plotted versus time, and the replicate concentrations within each event will be used to estimate the event's mean concentration and desired confidence interval (CI) (e.g., 95% CI).

Non-linear regression analysis of the time-dependent concentration data within each treatment will then be performed using a biodegradation kinetics model that fits the data. Consistent with the tebuthiuron biodegradation research completed by Stantec (2011), possible kinetics models are those applied by Sarmah and Close (2009), who investigated the degradation of six pesticides (atrazine, bromacil, diazinon, hexazinone, procymidone, and terbuthylazine), and by Kookana et al. (2010), who focused on atrazine degradation. Generally, these researchers applied variants of Michaelis and Menten (1913) and Monod (1949) first-order and second-order equations to model biodegradation. Additionally, Alexander (1999), Schmidt et al. (1985), and Simkins and Alexander (1984) have investigated and compiled lists of possible models for consideration (Boethling and Mackay, 2000).

Recognizing the large list of possible biodegradation kinetics models, candidates will be those that fit a regression curve within the mean confidence interval for sampling events within a treatment. Within the subset of candidate models, the ordinary least squares (OLS) method will be applied to identify the model or models the provide the best fit; preference will be given to the model requiring the fewest input

parameters (i.e., parsimony principle). The treatment-specific biodegradation half-life will then be estimated using the selected kinetic model.

The presence of statistically and practically significant kinetics differences across treatments will also be evaluated to understand which variables are required to more accurately estimate sterilant biodegradation rates. A familywise statistical test (i.e., across all treatments) will be performed to determine if treatment differences exist. Given the non-linear nature of concentration versus time data, analysis of variance (ANOVA) and analysis of covariance (ANCOVA) assumptions will be violated. Thus, a generalized form of these two methods, the identical-distribution test as described by Nelson (2004), will be applied. If a significant familywise difference exists, subsequent pairwise comparisons (i.e., between treatments couples), using the parameter-ratio test (Nelson, 2004), will be performed to locate those differences. Finally, practical significances among treatments will be visually established via superimposed, treatment-specific concentration versus time graphs. The fitted curves and the associated confidence interval will guide this inspection. An example of the process can be found in the dissertation by Thiessen (2018).

Given the specialized statistical analyses described above, Advisian recommends they be performed using R (https://www.r-project.org/). However, depending on InnoTech's and stakeholder expectations, other software packages may be explored.

4.0 INFORMATION MATRIX DESIGN

The information matrix design is the preliminary framework for collating and comparing lab-generated data with Alberta field data and will be used to make recommendations to inform management approaches, especially recommended model input values for Tier 1 and Tier 2 Guideline calculation. The information matrix will incorporate the following (as appropriate, given experimental and field results):

- Collate and compare lab-generated degradation data for bromacil and tebuthiuron with Alberta field data and including physico-chemical parameters and field conditions addressed in the Project.
- Laboratory-measured parameters will be validated against existing environmental field data where available.
- Recommended Alberta-specific input parameters for the Tier 1 Guidelines and Tier 2 Guidelines based on experimental and field measured outcomes.
- Risk modifiers for specific environmental conditions at bromacil and tebuthiuron-affected sites that are expected to affect whether sterilant will migrate into groundwater or surface water will be identified (e.g., depth to groundwater, distance to closest surface water body).
- Uncertainties associated with the field and laboratory measurements will be documented and recommendations to inform management approaches where sterilants are present will be provided.

The information matrix will present ranges and measures of central tendency for the data collected (as available). Ranges and measures of central tendency for both characterization and calculated parameters will be provided. Soil-specific ranges of input parameters for specified soils are recommended because stochastic approaches such as prediction ranges can be generated in model outcomes. The use of ranges

of input is recommended by U.S. Environmental Protection Agency for the Johnson and Ettinger Model (US EPA, 2017). Advisian recognizes the value this approach may have in the Tier 2 risk assessment models when a realistic range of outcomes are available to assess uncertainty in model predictions. Error bars and uncertainties will be clearly defined.

It may also be possible to estimate mass flux at the field sites using available data.

The information matrix is expected to be refined based on the results of Tasks 2 through 5.

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APPENDIX A: STERILANT IMPACTED SITES: SUMMARY OF CHARACTERISTICS AND LOCATIONS

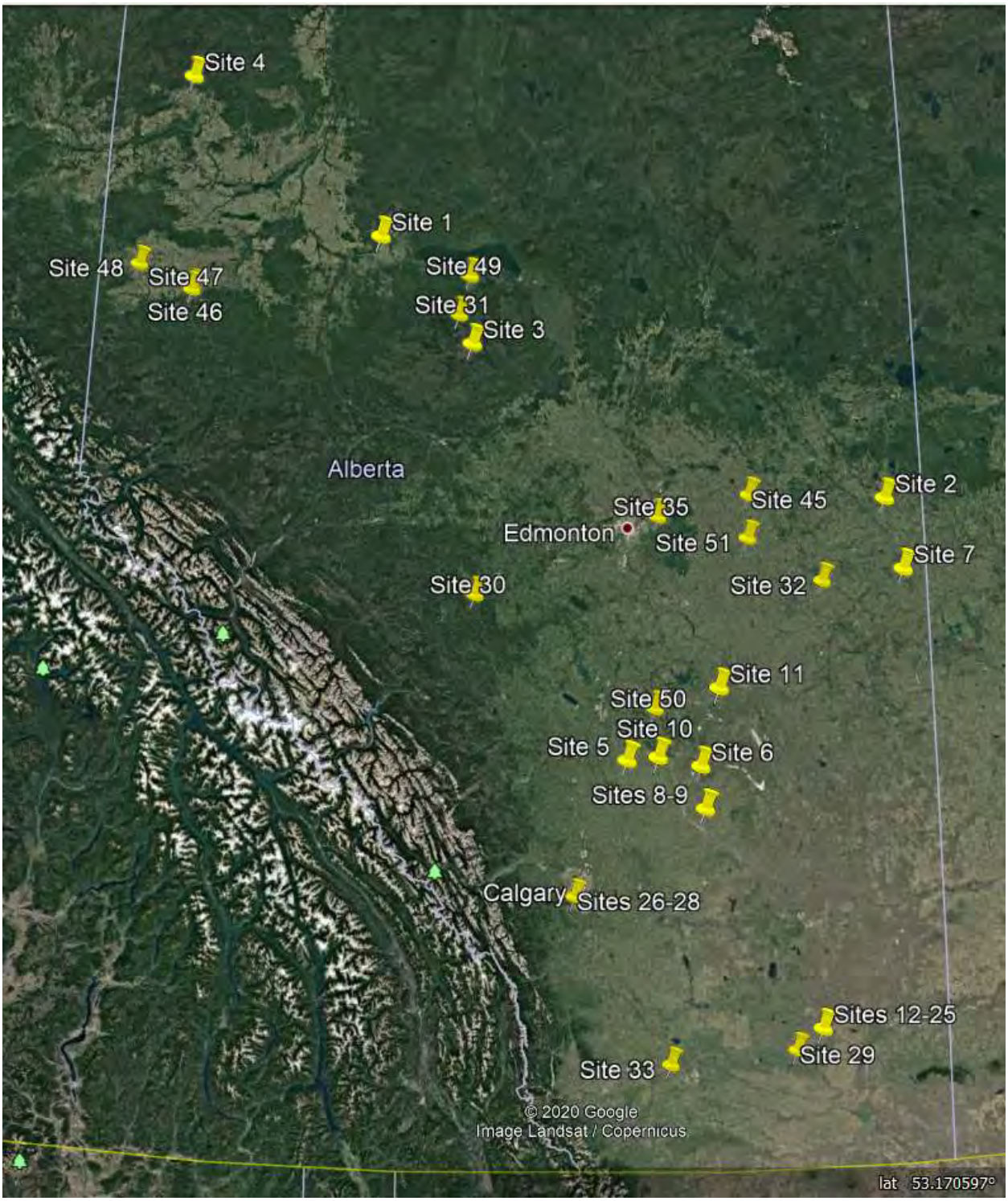

Table AppA-1 Sterilants Summary Sites

Site Number[1]	Soil Impacts	Brief Description of Lithology	Soil Type Determining Contaminant Migration (Coarse or Fine)	Has Soil been Characterized for foc, pH, salinity, bulk density?	Soil Impact Depth (m)	Soil Bromacil Maximum Concentration (mg/kg)	Soil Tebuthiuron Maximum Concentration (mg/kg)	The Years Soil Data were Collected?	Is Groundwater Data Available? (yes/no)	How many years of Groundwater Data are Available (Approximately)?	Depth to Groundwater (m below ground surface))	Hydraulic Conductivity (m/s) of the impacted groundwater bearing zone	Hydraulic Gradient (m/m)	Is Groundwater Impacted by Sterilants? (yes/no)	If Impacted, Maximum Concentration of Bromacil in Groundwater (mg/L)	If Impacted, Maximum Concentration of Tebuthiuron in Groundwater (mg/L)	The Years Sterilants were Detected?	Co-contaminants Present in Soil or Groundwater
1	Bromacil and tebuthiuron	Silty Clay over Sand	Fine/Coarse	Foc, pH, salinity, bulk density	3	1.3	0.4	2018, 2019	Yes	2	2	2.4E-05	0.004	Yes, bromacil and tebuthiuron	0.0364	0.0015	2018, 2019	Phenols, PCP
2	Bromacil	Silty Clay/Clayey Silt	Fine	pH, Salinity	0.5	0.83	Non-detect	2018	Yes	1	2	5.9E-06	—	No	—	—	—	Boron, Phenols
3	Bromacil and tebuthiuron	Silty clay	Fine	pH, Salinity	1	0.163	0.0208	2014	Yes	1	5	2.0E-09	0.15	No	—	—	—	Impacts excavated.
4	Bromacil and tebuthiuron	Sand and Gravel Fill/Silty Clay/Sand	Coarse	pH, Salinity	2	0.126	0.169	2019	Yes	1	2	1.3E-08	0.3	Yes	0.0002	—	1	PHCs, PAHs, PCBs, Phenols, TCP, cadmium, zinc
5	Bromacil	Clay to sandy clay loam with sand layers	Fine	pH, Salinity	4	2.63	Non-detect	2014	yes	4	2	4.4E-07	0.03	Yes, bromacil	0.17	—	2014, 2015, 2016	Boron, picloram
6	Bromacil	Silty clay	Fine	pH, Salinity	4	2.61	N/A	2013, 2014, 2016	Yes	6	2	1.4E-08	0.02	Yes, bromacil	0.004	—	2015, 2017, 2018, 2019	Dicambra, Boron
7	Bromacil	Silty clay with some sand pockets Sand at depth.	Fine	pH, Salinity	6	0.087	Non-detect	2016, 2018	Yes	2	1	9E-08(shallow); 3E-05(Deep)	0.07	Yes, bromacil	0.1	—	2016, 2018	None
8	Bromacil	Silt and sand	Coarse	pH, Salinity	1	2.4	Non-detect	2015, 2017, 2018	No	—	—	—	—	—	—	—	—	None
9	Bromacil	Topsoil fill over sandy clay.	Coarse	pH, Salinity	2	3	Non-detect	2015, 2016, 2019	yes	—	—	—	—	GW not tested	—	—	—	Boron, Lead, Tin, BTEX, F1, F3
10	Bromacil	Silty Clay	Fine	pH, Salinity	3	1.76	Non-detect	2019	Yes	1	6	—	—	Yes, bromacil	0.0006	—	2019	None
11	Bromacil and tebuthiuron	Silty Clay	Fine	pH, Salinity	3	0.226	0.049	2019	Yes	1	2	4.2E-08	0.0073	Yes, bromacil	0.0357	—	2019	Atrazine(soil)
12	Bromacil	Silt, Clayey silt with some sand lenses	Fine	pH, Salinity	0.0-0.3	1.3	Non-detect	2006, 2007, 2008	Yes	8	4 - >28	1.3E-07	Downward	Yes, bromacil	0.0021	—	2016	Chloride, PHCs
13	Bromacil	Silt, Sand, Gravel, Trace Clay	Coarse	pH, salinity	0.0-0.6	0.35	Non-detect	1990, 2006, 2010, 2018	Yes	6	11-16	7.6E-06	too flat to estimate	No	—	—	N/A	Chloride
14	Bromacil	Silt, clayey silt, silty sand, sand	Fine	pH, Salinity	0.0-2.0	1.69	Non-detect	1990, 2007, 2010, 2017, 2018	Yes	5	3-7	UGMZ= 8.9E-8 SGMZ= 1.5E-7	0.12	No	—	—	N/A	Chloride, metals
15	Bromacil	Silty clay with some sand	Fine	pH, Salinity	N/A	Non-detect	Non-detect	2007, 2008	Yes	1	4-8	3.5E-07	0.14	Yes, bromacil	0.0053	—	2019	Chloride
16	Bromacil	Sandy silt and sandy clay	Fine/Coarse	pH, Salinity	0.0-1.2	1.14	Non-detect	1990, 2009	Yes	10	1-3	2.8E-06	too flat to estimate	Yes, bromacil	0.3	—	2011, 2013, 2014, 2015, 2016, 2017, 2018, 2019	Chloride
18	Bromacil	Silty clay, sandy clay, some sandy silt	Fine	pH, Salinity	0.0-0.3	0.92	Non-detect	1990, 2010, 2018	Yes	5	4-7	2.1E-07	<0.01	No	—	—	N/A	Chloride
19	Bromacil	Silty clay, silty sand, sand, gravel	Coarse	Foc, pH, Salinity	0.6-2.2	0.489	Non-detect	2013, 2014, 2017, 2018	Yes	2	2-11	N/A	too flat to estimate	No	—	—	N/A	Chloride, metals
20	Bromacil	Sandy silt, sandy clay	Fine	pH, Salinity	0.0-2.5	0.82	Non-detect	1990, 2013, 2015	Yes	4	8 - >13	N/A	N/A	No	—	—	N/A	Chloride
21	Bromacil	Clayey silt, silt, or sandy silt	Fine	pH, Salinity	0.0-2.5	1.64	Non-detect	1990, 2000, 2011, 2015	Yes	8	2-11	1.3E-06	North = 0.05 South = 0.014	Yes, bromacil	0.0747	—	2013, 2014, 2015, 2016, 2017, 2018, 2019	Chloride
22	Bromacil	Clayey sandy silt	Fine	pH, Salinity	0.3-0.6	0.0398	Non-detect	2011	Yes	6	8-12	6.2E-06	too flat to estimate	No	—	—	N/A	Chloride, Calcium, EC, SAR
23	Bromacil (detected, but below guidelines)	Silt, sandy silt, sand	Coarse	pH, Salinity	0.0-0.3	0.0085	Non-detect	2011	Yes	8	8-10	3.7E-07	0.02	Yes, bromacil	0.0021	—	2013, 2014, 2015, 2016, 2018, 2019	Chloride, metals
24	Bromacil	Silt, silty clay, and sandy clay, with sand layers 0.1-0.9 m thick	Fine	pH, Salinity	0-0.6	0.8	Non-detect	2011	Yes	7	3	1.20E-06	too flat to estimate	Yes, bromacil	0.00465	—	2011, 2013, 2014, 2016, 2017, 2019	Chloride
25	Bromacil	Sandy clay, sand, sand and gravel	Fine	pH, Salinity	0.3-2.5	0.394	Non-detect	2011, 2014, 2015, 2017, 2018	Yes	10	1-5	4.10E-07	0.04	Yes, bromacil	0.008	0.000032	2015, 2016, 2017, 2018	PHCs, metals, methanol
26	Bromacil	Loam and silty clay	-	No	1.5-2.0	0.0306	---	2017	No	NA	unknown	Unknown	Unknown	Unknown	NA	NA	NA	NA
27	Bromacil	Sand underlain by clay	Coarse	pH	1.0-3.0	0.025	---	2016, 2017	Yes	3	1-3	---	---	Yes, bromacil in 2017. Not since 3 consecutive sampling events	0.00768	—	2017	---
28	Bromacil	Silt and clay with some sand and gravel	Fine	No	2.0-2.5	0.0229 (duplicate sample 0.0438)	---	2018	No	NA	Unknown	Unknown	Unknown	Unknown	NA	NA	NA	NA
29	Bromacil	Silty clay loam and clay loam	Fine	No	3.8	0.019	Non-detect	2017	No	—	—	—	—	Yes	0.038	Non-detect	2018	None

Site Number[1]	Soil Impacts	Brief Description of Lithology	Soil Type Determining Contaminant Migration (Coarse or Fine)	Has Soil been Characterized for foc, pH, salinity, bulk density?	Soil Impact Depth (m)	Soil Bromacil Maximum Concentration (mg/kg)	Soil Tebuthiuron Maximum Concentration (mg/kg)	The Years Soil Data were Collected?	Is Groundwater Data Available? (yes/no)	How many years of Groundwater Data are Available (Approximately)?	Depth to Groundwater (m below ground surface))	Hydraulic Conductivity (m/s) of the impacted groundwater bearing zone	Hydraulic Gradient (m/m)	Is Groundwater Impacted by Sterilants? (yes/no)	If Impacted, Maximum Concentration of Bromacil in Groundwater (mg/L)	If Impacted, Maximum Concentration of Tebuthiuron in Groundwater (mg/L)	The Years Sterilants were Detected?	Co-contaminants Present in Soil or Groundwater
30	Bromacil and tebuthiuron	Silty clay, sandy clay, silty sand, clay with some coarse wet sand seams.	Fine/Coarse	pH, salinity	4.5	0.075	0.085	2000, 2002, 2016, 2017, 2018	Yes	5	1-3	9.95E-08	0.029	Yes	0.0576	0.000906	2017, 2018	Hydrocarbons
31	Bromacil and tebuthiuron	Sand and gravel overlying clay	Fine	FOC	0.15-0.3	0.0209	0.00146	2016	No	NA	Unknown	Unknown	Unknown	Unknown	NA	NA	NA	NA
32	Bromacil (assumed as it is present in groundwater), impacts delineated	-	Coarse	—	—	—	—	—	Yes	4	3-6	2.48E-05	—	Yes	0.0852	-	2011, 2012, 2013, 2014, 2015	Benzene, dicamba, aluminum, arsenic, cadmium, manganese, TDS, nitrate
33	No soil information included in Phase 2 ESA	Sand and clay	Fine	pH	—	—	—	—	Yes	1	0.2-0.5	—	0.014	Yes	0.14	Non-detect	2017	Selenium, uranium, TDS, sodium, sulphate, D14-Terphenyl (groundwater)
35	Bromacil	Silt, sand, clay	Fine	pH, salinity	—	0.0368	-	2004, 2007, 2011, 2012, 2017	Yes	3	1-4	1.14E-06	0.017	Yes	0.0062	Non-detect	2017	Chloride, sodium, sulphate, TDS, manganese, nitrate, arsenic, selenium, uranium
45	Bromacil	Silt, sand, clay till	Fine	No	3.0	1.2	—	2017	Yes	2	2-3	2.50E-07	0.02	No	NA	NA	NA	No
46	Bromacil	Clay, silty clay	Fine	No	2.25	0.446	—	2018, 2019	Yes	2	1	—	—	No	NA	NA	NA	—
47	Bromacil	Silty sand, clay	Fine	No	1.5	0.499	—	2018, 2019	Yes	2	3-4	—	—	No	NA	NA	NA	—
48	Bromacil	Clay, silty clay, sand	Fine	No	2.25	0.052	—	2018	Yes	1	1	—	—	Yes	0.00041	—	2018	Yes (specific co-contaminants not available)
49	Bromacil and tebuthiuron	Clay fill, silty clay, sand	Coarse	No	4.4	0.848	1.81	2019	Yes	1	0.46	3.37E-08	-	Yes	0.072	—	2019	Yes (specific co-contaminants not available)
50	Bromacil and tebuthiuron	Silty clay	Fine	No	2.8	0.366	0.048	2014, 2015, 2016	Yes	5	2.86	2.50E-05	0.1	Yes	0.01	—	2014 to 2018	No
51	Bromacil	Silty, silty clay	Fine	No	1.0	0.668	—	2019	Yes	1	0.23	9.70E-07	0.004	Yes	0.0496	—	2019	Yes (specific co-contaminants not available)

Notes:

NA Data not applicable

— Data not available

1 Sites 17, 34, and 36 to 44 were excluded from the original working list provided by InnoTech as they were duplicates or were lacking bromacil or tebuthiuron impacts.

APPENDIX B: SUMMARY OF LITERATURE HALF-LIFE VALUES AND EXPERIMENTAL DESIGNS

Half-life measurements vary for bromacil and tebuthiuron in soil with experimental conditions affecting outcomes. A preliminary literature search was completed which included the search terms "bromacil half-life, bromacil degradation, tebuthiuron half-life, tebuthiuron degradation" in Google and Web of Science, and searching for listed references from Drozdowski et al. (2018), Stantec (2011), ARS (2001), PubChem (2019a, c), ENSR International (2005) and US EPA (1994, 1996), US EPA/ODW (1988).

APPENDIX B.1 BROMACIL

Table B-1 presents half-life values for bromacil obtained from the literature.

Table B-1. Bromacil Half-Life Values from the Literature.

Non-saturated Half-life (days)	Saturated Half-life (days)	Reference	Details
106 - 349*	-	Overcash and Davidson (1988) cited in Agricultural Research Service (ARS [2001])	Reference unavailable (book).
150 - 180*	-	Weed Society of America (1983) cited in ARS (2001)	Field study. 4 lb/acre of bromacil was applied to Butlertown silt loam. Reference unavailable (handbook for purchase).
350	-	Jury et al. (1987) cited in ARS (2001)	Mathematical model. Modelled pesticide leaching to estimate potential of pesticide to reach groundwater. Assumed steady water flow, equilibrium linear adsorption, and depth dependent first order biodegradation. Assumed soil had uniform values of water content, soil bulk density and organic carbon. Model applied to two scenarios: low and high potential groundwater contamination.
61*	-	Nofziger et al. (1988) cited in ARS (2001)	General reference. Reference not available.
349		Hornsby et al. (1996). cited in ENSR International (2005)	Average disappearance in field soil
120*	-	Dupont (1989) cited in ARS (2001)	Delaware soil, pH of 6.4 and 2.5% organic matter (OM). Reference unavailable, insufficient detail in ARS (2001) to search.
175*	-	Dupont (1989) cited in ARS (2001)	Delaware. Reference unavailable, insufficient detail in ARS (2001) to search.
350*	-	Soil and Crop Science Society of Florida (1985) cited in ARS (2001)	Presumably soil from Florida. Reference unavailable.
5,429 - 46,200		Madhun and Freed (1987)	Laboratory study, Oregon. Determined degradation rate of ^{14}C-labeled bromacil by monitoring $^{14}CO_2$ evolution at 25, 30, and 35°C. Two soil types: Adkins loamy sand and Semiahmoo mucky peat. Bromacil concentrations applied were 5 and 100 µmol/kg soil, containing a specific activity of 3.97 µCi/mg. Soil and bromacil added to 50 ml capacity flask.
-	144 – 198	Wolf and Martin (1974)	Laboratory study. Greenfield sandy loam under saturated conditions and 60% water holding capacity. Some treatments had corn stalks or lima bean straw added. Bromacil added at a rate of 2.88 ppm containing 2 µCi of activity/500 g soil. Soil and bromacil added to 1 L Erlenmeyer flasks. Moisture content maintained by passing saturated air through incubation system.
60	-	Wauchope et al. (1991) cited in PubChem (2019a)	Reference not available.
240 (8 months)	-	Leistra et al. (1975)	Field study, the Netherlands. Two apple orchards where bromacil was applied annually for 6-7 years. First orchard was on sandy loam and bromacil applied at 1.6 or 2.4 kg active ingredient/ha. Second orchard was on silty clay loam and bromacil applied at 1.2 or 2.4 kg active ingredient/ha.
150 - 180 (5 to 6 months)	-	Gardiner et al. (1969)	Field study, Butlertown. Measured half-life of 2-^{14}C labeled bromacil. Butlertown silt loam. Field plots treated with 4 lb bromacil per acre (3.69 mg [8.10 µc] of bromacil). Stainless steel tubing driven into ground (12 inches long, 4 inch diameter). ½ inch left above ground surface.

Non-saturated Half-life (days)	Saturated Half-life (days)	Reference	Details
183 (31 to 65% degraded)	-	Jolliffe et al. (1967)	Laboratory study. Six California soils ranging from sand to silt loams incubated in the laboratory for 6 months at room temperature, in covered vessels, at field capacity. Moisture maintained at field capacity. Soil analyzed at 3 days and 6 months. Spiked with 1 ppm bromacil.
122 - 152	-	Zimdahl et al. (1970)	Laboratory study. Chehalis loam soil was spiked with 8 ppm bromacil and incubated at either 13.2°C or 31.2°C. Temperatures did not have significance, they were available at the laboratory and provided a desirable range. Three kilograms of soil for each treatment was prepared and placed in jars with lids. Untreated controls were prepared. Moisture was maintained at 40% field capacity. Subsamples were collected every 30 days for six months.
155	-	United States Environmental Protection Agency (US EPA [1996])	Field study, Delaware. A single application of bromacil at 12 lb active ingredient/acre. Measured in the upper 10 cm of a bare ground plot of silty clay loam soil in Newark, Delaware.
-	155	Menzie (1978) cited in PubChem (2019a)	Book review. Soils were incubated. Flooded soil. Reference (book) not available. Cited bromacil half life from Wolf and Martin (1974)., but the value of 155 days cited did not appear to be a measured value from the study (which was available during this review).
-	198	Menzie (1978) cited in PubChem (2019a)	Book review. Soils were incubated. Flooded soil plus organic carbon source (bean straw). Reference (book) not available. Cited bromacil half life from Wolf and Martin (1974).
124	-	Schneiders (1990) cited in US EPA (1996)	Laboratory study. A single application of bromacil at 12 lb active ingredient/acre. Measured in the upper 10 cm of a bare ground plot of loam soil in Madera, California. Not available, unpublished study.
273	-	Das (1988) cited in US EPA (1996)	Laboratory study. Silty clay loam soil kept in the dark. Incubated at 25 ºC for 30 days. Ring-labeled [2-^{14}C] bromacil applied at 0.13 mg/mL (equivalent to 0.12 lb active ingredient/ha). Unpublished study, reference unavailable.
275	-	Vigon and Arthur (1988) cited in US EPA (1996)	Ring-labeled [2-^{14}C]bromacil applied at 9 ppm to silty clay loam soil to measure aerobic metabolism. Soil laboratory incubated in the dark and at 25°C and 75% field moisture for 12 months. Unpublished study, reference unavailable.
12 - 46	-	Sarmah et al. (2009)	Laboratory study. Uncontaminated topsoil (0 to 0.2 m depth) and subsoil (0.2 to 0.4 m depth) of two silt loams (Motupiko and Waikiwi) were sieved and moisture contents were measured. Soil was spiked with analytical grade bromacil to 0.55 mg/kg and five other sterilants (each soil was spiked separately) based on recommended application rates. Sterile soil, non-contaminated soil and pesticide without soil controls were used. Moisture was brought up to 60% maximum water holding capacity, incubated in the dark at 20°C and 7.5°C (to simulate average soil temperature where the soils are from).
130	-	Close et al. (2008)	Field study, New Zealand. Two silt loams (Motupiki and Waikiwi). Bromacil applied at 10 kg/ha in Motupiki soil and 11 kg/ha in Waikiwi soil. Soil samples were taken at 10 cm increments to a depth of 1 m.

Notes:

*Because reference unavailable, it is not known if saturated conditions were included. Included half-life values under column for non-saturated soil.

OM = organic matter

APPENDIX B.2 TEBUTHIURON

Table B-2 presents half-life values for bromacil obtained from the literature.

Table B-2. Tebuthiuron Half-Life values from the Literature.

Non-saturated Half-life (days)	Saturated Half-life (days)	Reference	Details
114 - 210	114 - 403	Stantec (2011)	Laboratory study. Used historically-impacted Alberta clay loam subsoil amended with organic material and three moisture regimes. Three moisture treatments (50%, 70% and 100% moisture holding capacity) with two organic matter treatments (with or without alfalfa) for six treatments. Microcosms were used. Tebuthiuron concentrations were as high as 0.06 mg/kg in soil. Four replicates were completed for each of five sampling times (1, 32, 63, 128 and 255/257 days). Experimental design was aerobic with 75 g dry weight subsoil placed in 500 mL mason jars or bags. Soil moisture was maintained gravimetrically and microcosms were incubated in the dark at 22°C. Half life was determined to be between 4 and 13.5 months, depending on organic matter amendment and the model used to describe degradation and moisture content.
360 - 450*	-	Weed Society of America (1983) cited in Agricultural Research Service (ARS [2001]) and PubChem (2019c)	From areas receiving 40 to 60 inches of rainfall annually. Half-life is greater in low rainfall areas. Reference unavailable (handbook for purchase).
13 - 100*	-	Pionke and Deangelis in Knisel (1980)	This value could not be verified. Reference unavailable.
20	-	Cerdeira et al. (2007)	Field study, Brazil. Tropical sandy soils from Brazil watershed, with and without sugarcane cover. Soil impacts not present below 0.4 m and after 180 days, no tebuthiuron remaining. Attributed to microbial activity (rapid organic matter turnover and warm temperatures). Tebuthiuron applied at rate to 1 kg active ingredient/ha.
360*	-	Day (personal communication) (1989). cited in ARS (2001)	Not available.
1050*	-	Dow Chemicals cited in ARS (2001)	Sandy loam soil, aerobic conditions. Manufacturer information. Reference not available.
1020	-	Rainey (1989a) cited in United States Environmental Protection Agency (US EPA) (1994)	Laboratory 9-month study. Thiadiazole-labeled ^{14}C tebuthiuron at 6 ppm. Sandy loam soil incubated aerobically, in the dark, at 24°C and 75% field moisture capacity. Concluded tebuthiuron stable to aerobic degradation. Unpublished study, reference not available.
	Much greater than 60 days (4.7% reduction after 60 days)	Rainey (1989b) cited in US EPA (1994)	Laboratory 30-day study. Thiadiazole-labeled ^{14}C tebuthiuron at 6 ppm. Sandy loam soil incubated anaerobically at 24°C and 75% field moisture capacity and 60 days under flooded conditions. Very little further reduction in concentrations once flooding occurred. Concluded tebuthiuron stable to anaerobic soil metabolism. Unpublished study. Reference not available.
After 21 months, 38% applied remained	-	Emmerich et at. (1984) cited in PubChem (2019c)	Field study. Arizona 0.34 ha rangeland (slope 3%, soil organic carbon about 1.05%, precipitation 586 mm) where tebuthiuron was applied at 0.84 kg active ingredient/ha active (applied as 0.32 cm diameter extruded pellets).
360	-	Flury (1996) cited in PubChem (2019c)	Literature review for field half-life with focus on leaching to groundwater. Looked at several factors that influence pesticide leaching: surface preparation, soil structure, soil water content, type of irrigation, pesticide formulation, time of application, and rainfall.
383, 806, 575*	-	Peacock et al. (1995) cited in PubChem (2019c)	Field study. Half-lives measured at sites near Live Oak, Florida; Davenport, California; and Mead, Nebraska. Reference not available.

Non-saturated Half-life (days)	Saturated Half-life (days)	Reference	Details
276 and 276	139	Raman and Rao (1987)	Laboratory study. Vertisol from Hyderabad, India (pH 8.4, 1.015% organic matter, 46.9 meq/100 g cation exchange capacity [CEC]) dried and sieved, then 2 kg spiked with tebuthiuron to achieve 20 µg/g dry soil. 10 g of treated soil in duplicate portions were placed in polythene bags and moisture was adjusted to saturation, field capacity and 50% field capacity. The bags were sealed and incubated at constant temperature. Soil was analyzed every 4 days until 40 days, 8 days until 80 days, 15 days until 125 days and 30 days until 155 days. Duplicate subsamples (40 g) from the bulk soil sample for each depth and site were analyzed on days 0, 7, 14, 45, 70 and 120.
91 and 99	83	Raman and Rao (1987)	Laboratory. Alfisol from Hyderabad, India (pH 8.3, 0.640% organic matter, 21.6 meq/100 g CEC) dried and sieved, then 2 kg spiked with tebuthiuron to achieve 20 µg/g dry soil. 10 g of treated soil in duplicate portions were placed in polythene bags and moisture was adjusted to saturation, field capacity and 50% field capacity. The bags were sealed and incubated at constant temperature. Soil was analyzed every 4 days until 40 days, 8 days until 80 days, 15 days until 125 days and 30 days until 155 days. Duplicate subsamples (40 g) from the bulk soil sample for each depth and site were analyzed on days 0, 7, 14, 45, 70 and 120.
>273	-	Rainey and Magnussen (1976 and 1978) cited in US EPA/ Office of Drinking Water (ODW) (1988)	Literature review. Cites Rainey and Magnussen (1976 and 1978). Loam soil. Thiadiazole ring-labeled ^{14}C tebuthiuron applied at 8 ppm. From US EPA/ODW; Health Advisories for 50 Pesticides (1988). Unpublished studies, reference not available.
-	>48 weeks	Berard (1977) cited in US EPA/ODW (1988) and Stantec (2011)	Laboratory. Applied at 1 ppm to loam soil at 23°C, anaerobic and dark conditions. Reference not available.
>990, 360-450, 360-450	-	Rainey and Magnussen (1976, 1978) cited in US EPA/ODW (1988)	Field plots in California. Thiadiazole ring-labeled ^{14}C tebuthiuron (loam at 8.96 kg/ha), Louisiana (clay at 2.24 kg/ha) and Indiana (loam at 8.96 kg/ha). References not available.

Notes:

*Because reference unavailable, it is not known if saturated conditions were included. Assumed available half-life values were for non-saturated soil.

APPENDIX B.3 SUMMARY OF HALF-LIFE EXPERIMENTAL DESIGN BY OTHERS

The experimental designs applied by others to determine half-life measurements for bromacil and tebuthiuron are summarized in Table B1-3.

Table B-3. Summary of Half-life Experiments by Others.

Field or Laboratory Study	Saturated Treatment (Y/N)	Description	Reference
Laboratory	Y	Tebuthiuron-impacted subsoil was collected, homogenized through sieving and characterized. Microcosms were established and residual concentrations were measured over time. Three moisture treatments (50%, 70% and 100% moisture holding capacity) with two organic matter treatments (with or without alfalfa) for six treatments. Four replicates were completed for each of five sampling times (1, 32, 63, 128 and 255/257 days). Characterization and tebuthiuron characterization was completed at the beginning and at four subsequent intervals. Experimental design was aerobic with 75 g dry weight subsoil placed in 500 mL mason jars or bags. Soil moisture was maintained gravimetrically and microcosms were incubated in the dark at 22°C. Measured degradation as tebuthiuron concentration as a direct measure of half-life. Half-life was determined to be between 4 and 13.5 months, depending in organic matter amendment, the model used to describe degradation and moisture content.	Stantec (2011)
Field	N	Site in northwestern AB (north of Town of Blueberry Mountain) where bromacil applied at unknown concentration. Agricultural humic luvic gleysol soil. Added well-decomposed cow manure and anhydrous ammonia. Soil monitored for 3 years. Soil organic matter content, electrical conductivity and pH subsequently increased. Bromacil concentrations with depth correlated with organic matter. Decreases in bromacil were related to microbial degradation within the surface 0.24 m and leaching below 0.24 m.	Landsburg and Dwyer 1995
Field	N	Sandy soil from watershed in Brazil applied at recommended rate 1 kg/ha active ingredient.	Cerdeira et al. (2007)
Laboratory	N	Two topsoils (Eufala sand and Hector loam) were incubated in double plastic bags mixed with 2 ppm of tebuthiuron. Water was added to create moisture contents of 5% and 15% by weight. Incubation at 14°C, 20°C and 30°C for 160 days. Size of soil sample not provided, but sufficient to grow corn in. Samples were analyzed at days 0, 10, 20, 40, 80 and 160. Four replicates of all treatments were made. Corn grown in the soil as a bioassay to determine incubation conditions on tebuthiuron degradation. Half-life not calculated.	Chang and Stritzke (1977)
Field	N	4 lb active ingredient/acre added to Butlertown silt loam using 4-inch diameter stainless steel tubes to isolate the soil. Radiolabelled bromacil and terbacil were added to different cylinders and watered in. Bromacil and terbacil. Cylinders were removed at 5 weeks, 14 weeks and 1 year. As well unlabelled bromacil and terbacil were applied at the same rate and the uppermost inch of soil was analyzed one year later.	Gardiner et al. (1969)
Laboratory	N	Bromacil breakdown in six California soils (ranging from sands to silt loams) was measured over six months with soil placed in Styrofoam cups, spiked with 1 ppm, covered and kept at room temperature with moisture maintained at field capacity. Soil was analyzed at 3 days and 6 months.	Jolliffe et al. 1967
Laboratory	N	Two shallow soils (from 0 to 0.2 m) from Oregon were collected (a coarse Adkins loamy sand and Semiahnoo mucky peat). Samples were dried, ground and sieved. In a 50 ml glass flask, 10 g dry soil was spiked with ^{14}C-labelled bromacil (two other pesticides were considered, but run in separate flasks) to reach 5 and 100 µmol/kg. Flasks were incubated at 25°C, 30°C and 35°C. CO_2 evolution from the flasks was measured.	Madhun and Freed (1987)
Laboratory	Y	Two soils were dried and sieved, then 2 kg of each soil was spiked with tebuthiuron to achieve 20ug/g dry soil. 10 g of treated soils in duplicate portions were placed in polythene bags and moisture was adjusted to saturation, field capacity and 50% field capacity. The bags were sealed and incubated at constant temperature. Soil was analyzed every 4 days until 40 days, 8 days until 80 days, 15 days until 125 days and 30 days until 155 days. Duplicate subsamples (40 g) from the bulk soil sample for each depth and site were analyzed on days 0, 7, 14, 45, 70 and 120.	Raman and Rao (1987)
Laboratory	N	Uncontaminated topsoil (0 to 0.2 m depth) and subsoil (0.2 to 0.4 m depth) of two silt loams were sieved and moisture contents were measured. Soil was spiked with analytical grade bromacil to 0.55 mg/kg and five other sterilants (each soil was spiked separately) based on recommended application rates. Sterile soil, non-contaminated soil and pesticide without soil controls were used. Moisture was brought up to 60% maximum water holding capacity, incubated in the dark at 20°C and 7.5°C (to simulate average soil temperature where the soils are from)	Sarmah et al. (2009)

Field or Laboratory Study	Saturated Treatment (Y/N)	Description	Reference
Laboratory	Y	Greenfield sandy loam soil (pH 7.1, organic carbon content of 1.1%) was spiked with ^{14}C-labelled bromacil. Two moisture contents – saturated (incubated for 145 days) and 60% field saturated (incubated for 600 days) at 22°C. Bromacil added at 2.88 ppm and two organic amendments were provided (lima bean straw and corn stalks). Soil was collected, dried, sieved and spiked. Also ran a sterile soil control treatment. CO_2 evolution was measured.	Wolf and Martin (1974)
Laboratory	N	Chehalis loam soil was spiked with 8 ppm bromacil and incubated at either 13.2°C or 31.2°C. Temperatures did not have significance, they were available at the laboratory and provided a desirable range. Three kilograms of soil for each treatment was prepared and placed in jars with lids. Untreated controls were prepared. Moisture was maintained at 40% field capacity. Subsamples were collected every 30 days for six months.	Zimdahl et al. (1970)

APPENDIX B.4 REFERENCES

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APPENDIX C: DETERMINATION OF SOIL – WATER AND ORGANIC CARBON – WATER PARTITION COEFFICIENTS FOR BROMACIL AND TEBUTHIURON IN TWO SOILS COLLECTED FROM ALBERTA

Determination of soil-water and organic carbon-water partition coefficients for bromacil and tebuthiuron in two soils collected from Alberta

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July 23, 2021

Objective

To determine the soil-water partition coefficient (K_d) and organic carbon-water partition coefficient (K_{OC}) for bromacil and tebuthiuron in two soils collected by Advisian in Alberta

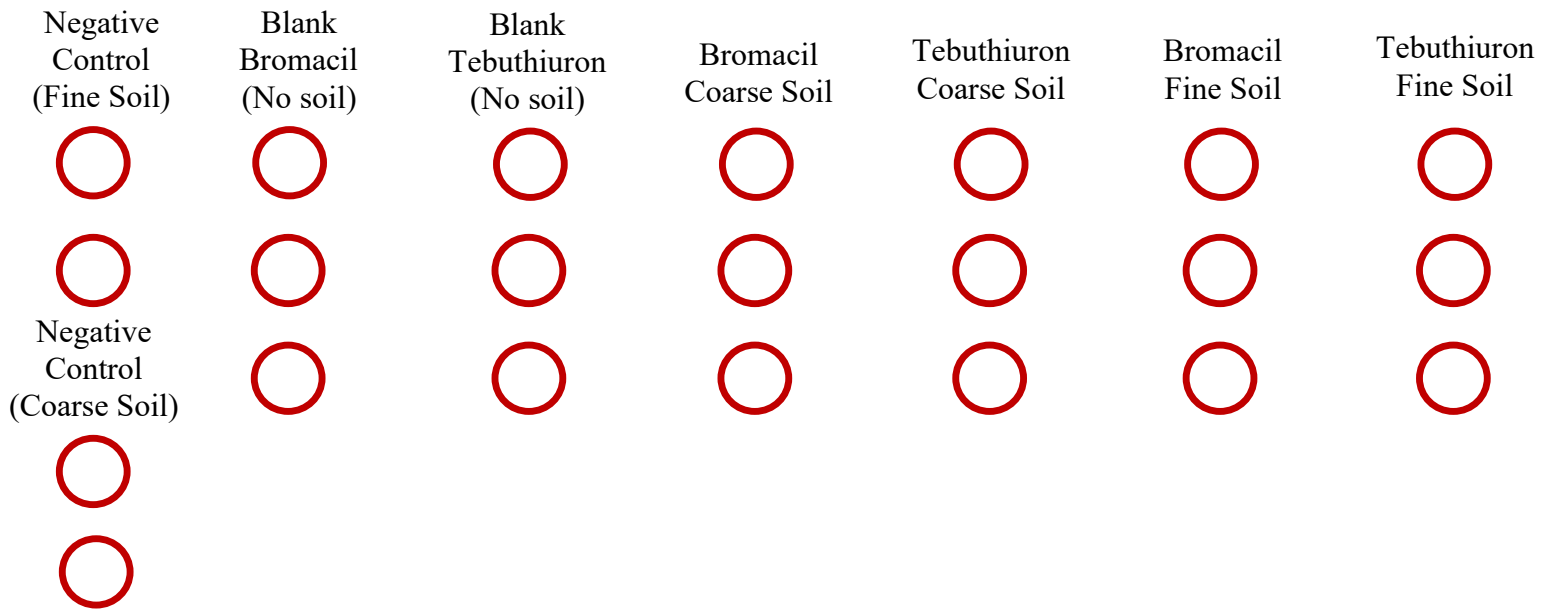
Methods

The method used in this experiment was modelled after the Adsorption-Desorption Using a Batch Equilibrium Method, which is an OECD guideline for the testing of chemicals (OECD, 2000).

Two soils were received from Bureau Veritas. The soils were labelled as "coarse clean" and "fine clean". The physicochemical properties of the soils were provided by Bureau Veritas. When the soil was received from Bureau Veritas, they were stored in the dark at 4ºC. The experiment was initiated by air drying the soils at 23ºC. A 0.01 M solution of $CaCl_2$ and 500 mg/L solutions of bromacil and tebuthiuron in distilled water were prepared for use in the partition experiment. Five grams of air-dried soil was placed in a 50-mL centrifuge tube and equilibrated by shaking with 22.5 mL of 0.01 M $CaCl_2$ for 12 h at 23ºC in the dark before the initiation of the partitioning experiment. Three replicate tubes were prepared for each soil type and sterilant combination (Fig. 1). Three replicate tubes were prepared with only 22.5 mL of 0.01 M $CaCl_2$ for each sterilant blank (i.e., same concentration of sterilant but no soil) and two replicate tubes with only 22.5 mL of 0.01 M $CaCl_2$ and 5 g of soil were prepared as a negative control for each soil type (i.e., soil with no sterilant) (Fig. 1). After 12 h of equilibration, 2.5 mL of the 500 mg/L solution of bromacil or tebuthiuron were added to their respective centrifuge

tubes. The replicate tubes for the negative control received 2.5 mL of 0.01 M $CaCl_2$. Following the addition, all tubes were shaken for 24 h at 23ºC in the dark. After being shaken or 24 h, the

Figure 1 Experimental design of partition experiment with two soils (fine and coarse) and two sterilants (bromacil and tebuthiuron). Each red circle represents a 50-mL centrifuge tube.



centrifuge tubes were centrifuged for 1 h at 3000 x g. A 15-mL aliquot of the aqueous phase was removed from each replicate tube to an amber glass bottle and stored at -20ºC. The samples of the aqueous phase were sent to Bureau Veritas to measure the concentration of bromacil and tebuthiuron.

The concentration of bromacil and tebuthiuron measured in the aqueous phase of the treatments was used to calculate soil-water partition coefficients (K_d) and organic carbon-water partition coefficients (K_{OC}) for the sterilants in each type of soil. The equations below were used to calculate K_d and K_{OC}. The difference in the mass of sterilant measure in the aqueous phase of the treatment without soil from the mass of sterilant measured in the aqueous phase of the treatment with soil was used to determine the mass of sterilant adsorbed to the soil.

$$K_d = \frac{m_s^{ads}}{m_{aq}^{ads}} \times \frac{V_0}{m_{soil}} \ (cm^3 g^{-1})$$

m_s^{ads}: mass of the sterilant adsorbed on the soil at adsorption equilibrium (µg)

m_{aq}^{ads}: mass of the sterilant in the solution at adsorption equilibrium (µg)

V_0: initial volume of the aqueous phase in contact with the soil (cm3)

m_{soil}: quantity of the soil phase, expressed in dry mass of soil (g)

$$K_{OC} = K_d \times \frac{100}{\%OC} \ (cm^3 g^{-1})$$

$\%OC$: Percent of organic carbon in soil

Results

Adsorption of bromacil and tebuthiuron on the fine and coarse soil was observed (Table 1). Neither sterilant were detected in the negative control treatments for the fine and coarse soils (Table 1). Greater adsorption occurred in the fine soil compared to the course soil, which is expected based on the fine soil having a relatively greater organic carbon content than the coarse soil (Table 1). Greater adsorption occurred with tebuthiuron compared to bromacil in both soil types. The percent of organic carbon in the coarse soil was below the detection limit of Bureau Veritas' method (i.e., < 0.05%). The absence of a measure of percent organic carbon in the soil makes calculating a K_{OC} problematic. In this report, the detection limit of 0.05% was used to calculate a K_{OC} for both sterilants in the coarse soil (Table 1).

Table 1 The concentration of sterilant measured in aqueous phase and the resulting soil-water partition coefficients (K_d) and organic carbon-water partition coefficient (K_{OC}) for bromacil and tebuthiuron in fine soil and coarse soil.

Sterilant	Soil	Replicate	Concentration in aqueous phase (µg/L)	Mean concentration in aqueous phase (µg/L)†	Water-soil partition coefficient (K_d)	Organic carbon – water partition coefficient (K_{OC})	Organic carbon content of soil (%)
Bromacil	Fine soil	1	40000	46000	1.01	507	0.20
		2	50000				
		3	48000				
	Coarse soil	1	51000	49667	0.57	1141	<0.05*
		2	50000				
		3	48000				
	No soil	1	50000	55333			
		2	59000				
		3	57000				
Tebuthiuron	Fine soil	1	27000	27667	7.05	3524	0.20
		2	30000				
		3	26000				
	Coarse soil	1	48000	50667	1.58	3158	<0.05*
		2	63000				
		3	41000				
	No soil	1	70000	66667			
		2	78000				
		3	52000				
Negative control	Fine soil	1	<0.10				
		2	<0.10				
Negative control	Coarse soil	1	<0.10				
		2	<0.10				

† mean = arithmetic mean

*Used the method detection limit of 0.05% reported by Bureau Vertias as the total organic carbon value in the calculation of Koc

Your P.O. #: 7001052050
Your Project #: 417011-00030-20100
Your C.O.C. #: 1 of 1

Attention: AARON TANGEDAL

WORLEY CANADA SERVICES LTD.
Suite 150
205 Quarry Park Blvd SE
CALGARY, AB
CANADA T2C 3E7

Report Date: 2020/09/21
Report #: R2931409
Version: 5 - Revision

CERTIFICATE OF ANALYSIS – REVISED REPORT

BV LABS JOB #: C055648
Received: 2020/08/07, 15:35

Sample Matrix: Soil
Samples Received: 6

Analyses	Quantity	Date Extracted	Date Analyzed	Laboratory Method	Analytical Method
Bulk Density (1)	2	N/A	2020/09/10	AB SOP-00050	McKeague 2nd 2.21 m
Bromide by IC (1)	2	N/A	2020/09/11	AB SOP-00052	SM 23 4110 B m
Cation/EC Ratio (1)	2	N/A	2020/09/09		Auto Calc
Chloride (Soluble) (1)	2	2020/09/09	2020/09/09	AB SOP-00033 / AB SOP-00020	SM 23-4500-Cl-E m
Hexavalent Chromium (1, 4)	1	2020/09/09	2020/09/09	AB SOP-00063	SM 23 3500-Cr B m
Hexavalent Chromium (1, 4)	1	2020/09/10	2020/09/10	AB SOP-00063	SM 23 3500-Cr B m
Conductivity @25C (Soluble) (1)	2	2020/09/09	2020/09/09	AB SOP-00033 / AB SOP-00004	SM 23 2510 B m
Fraction of Organic Carbon (1)	2	N/A	2020/09/17		Auto Calc
Elements by ICP -Soils (1)	2	2020/09/09	2020/09/11	AB SOP-00001 / AB SOP-00042	EPA 6010d R5 m
Elements by ICPMS - Soils (1)	2	2020/09/09	2020/09/10	AB SOP-00001 / AB SOP-00043	EPA 6020b R2 m
Sum of Cations, Anions (1)	2	N/A	2020/09/09		Auto Calc
ORP MEND SFE Extract (2)	2	N/A	2020/09/11	BBY0SOP-00004	SM 23 2580 B
Moisture (1)	4	N/A	2020/08/13	AB SOP-00002	CCME PHC-CWS m
Moisture (1)	2	N/A	2020/09/01	AB SOP-00002	CCME PHC-CWS m
Ammonia-N (Soluble) (1, 5)	2	2020/09/09	2020/09/09	AB SOP-00033 / AB SOP-00007	SM 23 4500 NH3 A G m
Non Routine/Non Validated Matrix Tested (1, 6)	2	N/A	2020/09/10		
Nitrite-N and Nitrate-N (soluble) (1)	2	2020/09/09	2020/09/09	AB SOP-00033 / AB SOP-00023	SM 23 4110 B m
pH @25C (1:2 Calcium Chloride Extract) (1)	2	2020/09/09	2020/09/09	AB SOP-00033 / AB SOP-00006	SM 23 4500 H+B m
Particle Size by Sieve (75 micron) (1)	4	N/A	2020/08/14		Auto Calc
Particle Size by Sieve (75 micron) (1)	2	N/A	2020/09/08		Auto Calc
Particle Size by Sieve (1)	4	N/A	2020/08/14	AB SOP-00022	ASTM D6913-17 m
Particle Size by Sieve (1)	2	N/A	2020/09/08	AB SOP-00022	ASTM D6913-17 m
Sodium Adsorption Ratio (1)	2	N/A	2020/09/09		Auto Calc
Soluble Ions (1)	2	2020/09/09	2020/09/09	AB SOP-00033 / AB SOP-00042	EPA 6010d R5 m

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Sample Matrix: Soil
Samples Received: 6

Analyses	Quantity	Date Extracted	Date Analyzed	Laboratory Method	Analytical Method
Soluble Paste (1)	2	2020/09/09	2020/09/09	AB SOP-00033	Carter 2nd ed 15.2 m
Soluble Boron Calculation (1)	2	N/A	2020/09/09		Auto Calc
Soluble Ions Calculation (1)	2	N/A	2020/09/08		Auto Calc
Total Organic Carbon LECO Method (1)	2	N/A	2020/09/17	CAL SOP-00243	LECO 203-821-498 m
Texture by Hydrometer (1)	4	N/A	2020/08/14	AB SOP-00030	Carter 2nd ed 55.3 m
Texture by Hydrometer (1)	2	N/A	2020/09/02	AB SOP-00030	Carter 2nd ed 55.3 m
Texture Class (1)	4	N/A	2020/08/14		Auto Calc
Texture Class (1)	2	N/A	2020/09/02		Auto Calc
Theoretical Gypsum Requirement (1, 7)	2	N/A	2020/09/09		Auto Calc
Total Kjeldahl Nitrogen - Soil (1)	2	2020/09/10	2020/09/12	AB SOP-00008	EPA 351.1 R1978 m
Pesticides/Sterilants in Soil by LC/MS/M (3)	4	2020/08/22	2020/08/24	CAM SOP-00333	USEPA 8321B (mod)
Pesticides/Sterilants in Soil by LC/MS/M (3)	2	2020/09/03	2020/09/04	CAM SOP-00333	USEPA 8321B (mod)

Remarks:

Bureau Veritas Laboratories are accredited to ISO/IEC 17025 for specific parameters on scopes of accreditation. Unless otherwise noted, procedures used by BV Labs are based upon recognized Provincial, Federal or US method compendia such as CCME, MELCC, EPA, APHA.

All work recorded herein has been done in accordance with procedures and practices ordinarily exercised by professionals in BV Labs profession using accepted testing methodologies, quality assurance and quality control procedures (except where otherwise agreed by the client and BV Labs in writing). All data is in statistical control and has met quality control and method performance criteria unless otherwise noted. All method blanks are reported; unless indicated otherwise, associated sample data are not blank corrected. Where applicable, unless otherwise noted, Measurement Uncertainty has not been accounted for when stating conformity to the referenced standard.

BV Labs liability is limited to the actual cost of the requested analyses, unless otherwise agreed in writing. There is no other warranty expressed or implied. BV Labs has been retained to provide analysis of samples provided by the Client using the testing methodology referenced in this report. Interpretation and use of test results are the sole responsibility of the Client and are not within the scope of services provided by BV Labs, unless otherwise agreed in writing. BV Labs is not responsible for the accuracy or any data impacts, that result from the information provided by the customer or their agent.

Solid sample results, except biota, are based on dry weight unless otherwise indicated. Organic analyses are not recovery corrected except for isotope dilution methods.
Results relate to samples tested. When sampling is not conducted by BV Labs, results relate to the supplied samples tested.
This Certificate shall not be reproduced except in full, without the written approval of the laboratory.
Reference Method suffix “m” indicates test methods incorporate validated modifications from specific reference methods to improve performance.

Your P.O. #: 7001052050
Your Project #: 417011-00030-20100
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Attention: AARON TANGEDAL

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Report Date: 2020/09/21
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CERTIFICATE OF ANALYSIS – REVISED REPORT

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Received: 2020/08/07, 15:35

* RPDs calculated using raw data. The rounding of final results may result in the apparent difference.
(1) This test was performed by BV Labs Calgary Environmental
(2) This test was performed by BV Labs Vancouver
(3) This test was performed by BV Labs Ontario (From Calgary)
(4) Some soil samples may react with the Cr(VI) spike reducing it to Cr(III). These samples are highly unlikely to contain native hexavalent chromium. Thus a failed spike recovery does not invalidate a negative result on the native sample.
(5) Soluble Ammonia > Soluble Total Kjeldahl Nitrogen Imbalance: When applicable, Soluble Ammonia and Soluble Total Kjeldahl Nitrogen results were reviewed and data quality meets acceptable levels unless otherwise noted.
(6) Sample(s) analyzed using methodologies that have not been subjected to Bureau Veritas Laboratories' standard validation process for the submitted matrix and is not an accredited method. Analysis performed with client consent, however results should be viewed with discretion.
(7) TGR calculation is based on a theoretical SAR of 4. Salt Contamination and Assessment and remediation guideline 2001 recommended SAR is ranging 4-8. TGR is reported in tonnes/ha.

Encryption Key

Ioana Stoica
Key Account Specialist
21 Sep 2020 14:19:35

Please direct all questions regarding this Certificate of Analysis to your Project Manager.
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Email: Ioana.Stoica@bvlabs.com
Phone# (403)735-2227
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BV Labs Job #: C055648
Report Date: 2020/09/21

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Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

AT1 METALS & SALINITY IN SOIL (SOIL)

BV Labs ID		YF3987				YF3990			
Sampling Date		2020/07/27				2020/07/27			
COC Number		1 of 1				1 of 1			
	UNITS	**ADVISIAN SITE #15-FINE-CLEAN #1**	**MU**	**RDL**	**QC Batch**	**ADVISIAN SITE #22-COARSE-CLEAN #1**	**MU**	**RDL**	**QC Batch**
Calculated Parameters									
Anion Sum	meq/L	0.38	N/A	N/A	9986582	0.36	N/A	N/A	9986582
Cation Sum	meq/L	2.6	N/A	N/A	9986582	2.5	N/A	N/A	9986582
Cation/EC Ratio	N/A	11	N/A	0.10	9986581	11	N/A	0.10	9986581
Calculated Calcium (Ca)	mg/kg	2.6	N/A	0.31	9986176	2.6	N/A	0.33	9986176
Calculated Magnesium (Mg)	mg/kg	3.4	N/A	0.21	9986176	3.2	N/A	0.22	9986176
Calculated Sodium (Na)	mg/kg	2.0	N/A	0.52	9986176	2.1	N/A	0.55	9986176
Calculated Potassium (K)	mg/kg	1.7	N/A	0.27	9986176	1.7	N/A	0.29	9986176
Calculated Boron (B)	mg/kg	0.033	N/A	0.021	9986017	0.026	N/A	0.022	9986017
Calculated Chloride (Cl)	mg/kg	<2.1	N/A	2.1	9986176	<2.2	N/A	2.2	9986176
Calculated Sulphate (SO4)	mg/kg	3.5	N/A	1.0	9986176	3.5	N/A	1.1	9986176
Elements									
Hex. Chromium (Cr 6+)	mg/kg	<0.080	N/A	0.080	9992240	<0.080	N/A	0.080	9993394
Soluble Parameters									
Soluble Boron (B)	mg/L	0.16	+/- 0.12	0.10	9992039	0.12	+/- 0.12	0.10	9992039
Soluble Chloride (Cl)	mg/L	<10	N/A	10	9992049	<10	N/A	10	9992049
Soluble Conductivity	dS/m	0.23	+/- 0.039	0.020	9992005	0.22	+/- 0.038	0.020	9992005
Soluble (CaCl2) pH	pH	7.85	+/- 0.233	N/A	9991344	8.07	+/- 0.239	N/A	9991344
Sodium Adsorption Ratio	N/A	0.42	N/A	0.10	9986166	0.45	N/A	0.10	9986166
Soluble Calcium (Ca)	mg/L	12	+/- 2.8	1.5	9992039	12	+/- 2.7	1.5	9992039
Soluble Magnesium (Mg)	mg/L	16	+/- 2.6	1.0	9992039	15	+/- 2.4	1.0	9992039
Soluble Sodium (Na)	mg/L	9.6	+/- 2.6	2.5	9992039	9.7	+/- 2.6	2.5	9992039
Soluble Potassium (K)	mg/L	8.1	+/- 1.3	1.3	9992039	7.8	+/- 1.3	1.3	9992039
Saturation %	%	21	+/- 1.6	N/A	9991412	22	+/- 1.7	N/A	9991412
Soluble Sulphate (SO4)	mg/L	17	+/- 6.2	5.0	9992039	16	+/- 6.1	5.0	9992039
Theoretical Gypsum Requirement	tonnes/ha	<0.20	N/A	0.20	9986585	<0.20	N/A	0.20	9986585
Elements									
Total Antimony (Sb)	mg/kg	<0.50	N/A	0.50	9993077	<0.50	N/A	0.50	9993077
Total Arsenic (As)	mg/kg	6.3	+/- 1.1	1.0	9993077	2.1	+/- <RDL	1.0	9993077
Total Barium (Ba)	mg/kg	170	+/- 26	1.0	9993077	54	+/- 7.9	1.0	9993077

RDL = Reportable Detection Limit
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

AT1 METALS & SALINITY IN SOIL (SOIL)

BV Labs ID		YF3987				YF3990			
Sampling Date		2020/07/27				2020/07/27			
COC Number		1 of 1				1 of 1			
	UNITS	**ADVISIAN SITE #15-FINE-CLEAN #1**	**MU**	**RDL**	**QC Batch**	**ADVISIAN SITE #22-COARSE-CLEAN #1**	**MU**	**RDL**	**QC Batch**
Total Beryllium (Be)	mg/kg	0.62	+/- <RDL	0.40	9993077	<0.40	N/A	0.40	9993077
Total Cadmium (Cd)	mg/kg	0.26	+/- 0.060	0.050	9993077	0.060	+/- 0.053	0.050	9993077
Total Chromium (Cr)	mg/kg	24	+/- 4.7	1.0	9993077	3.8	+/- 1.1	1.0	9993077
Total Cobalt (Co)	mg/kg	9.1	+/- 1.5	0.50	9993077	3.0	+/- <RDL	0.50	9993077
Total Copper (Cu)	mg/kg	17	+/- 2.8	1.0	9993077	2.7	+/- <RDL	1.0	9993077
Total Lead (Pb)	mg/kg	9.5	+/- 1.6	0.50	9993077	2.1	+/- <RDL	0.50	9993077
Total Mercury (Hg)	mg/kg	0.059	+/- 0.11	0.050	9993077	<0.050	N/A	0.050	9993077
Total Molybdenum (Mo)	mg/kg	2.2	+/- 0.58	0.40	9993077	<0.40	N/A	0.40	9993077
Total Nickel (Ni)	mg/kg	26	+/- 5.1	1.0	9993077	8.5	+/- 1.7	1.0	9993077
Total Selenium (Se)	mg/kg	2.2	+/- <RDL	0.50	9993077	<0.50	N/A	0.50	9993077
Total Silver (Ag)	mg/kg	<0.20	N/A	0.20	9993077	<0.20	N/A	0.20	9993077
Total Thallium (Tl)	mg/kg	0.16	+/- <RDL	0.10	9993077	<0.10	N/A	0.10	9993077
Total Tin (Sn)	mg/kg	<1.0	N/A	1.0	9993077	<1.0	N/A	1.0	9993077
Total Uranium (U)	mg/kg	2.4	+/- 0.23	0.20	9993077	0.38	+/- <RDL	0.20	9993077
Total Vanadium (V)	mg/kg	24	+/- 6.4	1.0	9993077	8.3	+/- 2.4	1.0	9993077
Total Zinc (Zn)	mg/kg	44	+/- <RDL	10	9993077	11	+/- <RDL	10	9993077

RDL = Reportable Detection Limit
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

AT1 METALS & SALINITY IN SOIL (SOIL)

BV Labs ID		YF3990			
Sampling Date		2020/07/27			
COC Number		1 of 1			
	UNITS	**ADVISIAN SITE #22-COARSE-CLEAN #1 Lab-Dup**	**MU**	**RDL**	**QC Batch**
Elements					
Hex. Chromium (Cr 6+)	mg/kg	<0.080	N/A	0.080	9993394
Soluble Parameters					
Soluble Boron (B)	mg/L	0.16	+/- 0.12	0.10	9992039
Soluble Chloride (Cl)	mg/L	<10	N/A	10	9992049
Soluble Conductivity	dS/m	0.21	+/- 0.037	0.020	9992005
Soluble (CaCl2) pH	pH	8.06	+/- 0.239	N/A	9991344
Soluble Calcium (Ca)	mg/L	12	+/- 2.6	1.5	9992039
Soluble Magnesium (Mg)	mg/L	15	+/- 2.5	1.0	9992039
Soluble Sodium (Na)	mg/L	9.4	+/- 2.6	2.5	9992039
Soluble Potassium (K)	mg/L	7.9	+/- 1.3	1.3	9992039
Saturation %	%	23	+/- 1.8	N/A	9991412
Soluble Sulphate (SO4)	mg/L	15	+/- 6.0	5.0	9992039
Elements					
Total Antimony (Sb)	mg/kg	<0.50	N/A	0.50	9993077
Total Arsenic (As)	mg/kg	2.3	+/- <RDL	1.0	9993077
Total Barium (Ba)	mg/kg	55	+/- 8.1	1.0	9993077
Total Beryllium (Be)	mg/kg	<0.40	N/A	0.40	9993077
Total Cadmium (Cd)	mg/kg	0.062	+/- 0.053	0.050	9993077
Total Chromium (Cr)	mg/kg	3.6	+/- 1.1	1.0	9993077
Total Cobalt (Co)	mg/kg	3.1	+/- 0.50	0.50	9993077
Total Copper (Cu)	mg/kg	2.9	+/- <RDL	1.0	9993077
Total Lead (Pb)	mg/kg	2.3	+/- <RDL	0.50	9993077
Total Mercury (Hg)	mg/kg	<0.050	N/A	0.050	9993077
Total Molybdenum (Mo)	mg/kg	<0.40	N/A	0.40	9993077
Total Nickel (Ni)	mg/kg	8.4	+/- 1.7	1.0	9993077
Total Selenium (Se)	mg/kg	<0.50	N/A	0.50	9993077
Total Silver (Ag)	mg/kg	<0.20	N/A	0.20	9993077

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

AT1 METALS & SALINITY IN SOIL (SOIL)

BV Labs ID		YF3990			
Sampling Date		2020/07/27			
COC Number		1 of 1			
	UNITS	**ADVISIAN SITE #22-COARSE-CLEAN #1 Lab-Dup**	**MU**	**RDL**	**QC Batch**
Total Thallium (Tl)	mg/kg	<0.10	N/A	0.10	9993077
Total Tin (Sn)	mg/kg	<1.0	N/A	1.0	9993077
Total Uranium (U)	mg/kg	0.38	+/- <RDL	0.20	9993077
Total Vanadium (V)	mg/kg	8.5	+/- 2.5	1.0	9993077
Total Zinc (Zn)	mg/kg	11	+/- <RDL	10	9993077

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

RESULTS OF CHEMICAL ANALYSES OF SOIL

BV Labs ID		YF3987		YF3987		YF3988			
Sampling Date		2020/07/27		2020/07/27		2020/07/27			
COC Number		1 of 1		1 of 1		1 of 1			
	UNITS	**ADVISIAN SITE #15-FINE-CL**	**MU**	**ADVISIAN SITE #15-FINE-CL Lab-Dup**	**MU**	**ADVISIAN SITE #16-COARSE-IMPACTED #1**	**MU**	**RDL**	**QC Batch**
Parameter									
MEND Extract ORP	mV	233	N/A	238	N/A	N/A	N/A	N/A	9998772
Misc. Inorganics									
Fraction of Organic Carbon	g/g	0.0020	N/A	N/A	N/A	N/A	N/A	0.00020	9986650
Anions									
Dissolved Bromide (Br)	mg/L	0.031	+/- <RDL	0.028	+/- <RDL	N/A	N/A	0.010	9995182
MISCELLANEOUS									
Sample Matrix	N/A	SOLID	N/A	N/A	N/A	N/A	N/A	N/A	ONSITE
Nutrients									
Soluble Ammonia (N)	mg/L	0.85	+/- <RDL	N/A	N/A	N/A	N/A	0.20	9992487
Kjeldahl Nitrogen	mg/kg	190 (1)	+/- 47	N/A	N/A	N/A	N/A	10	9993065
Pesticides & Herbicides									
Tebuthiuron	mg/kg	<0.0010	N/A	N/A	N/A	<0.0010	N/A	0.0010	9971699
Atrazine + Desethyl-atrazine	mg/kg	<0.0080	N/A	N/A	N/A	<0.0080	N/A	0.0080	9971699
Simazine	mg/kg	<0.010	N/A	N/A	N/A	<0.010	N/A	0.010	9971699
Diuron	mg/kg	<0.010	N/A	N/A	N/A	<0.010	N/A	0.010	9971699
Linuron	mg/kg	<0.0070	N/A	N/A	N/A	<0.0070	N/A	0.0070	9971699
Bromacil	mg/kg	<0.0090	N/A	N/A	N/A	0.067	N/A	0.0090	9971699
Soluble Parameters									
Soluble Nitrite (N)	mg/L	<0.20	N/A	N/A	N/A	N/A	N/A	0.20	9992209
Soluble Nitrate (N)	mg/L	0.42	+/- <RDL	N/A	N/A	N/A	N/A	0.20	9992209
Physical Properties									
Dry Bulk Density	g/cm3	1.4	N/A	N/A	N/A	N/A	N/A	0.010	9990984
Grain Size	N/A	FINE	N/A	N/A	N/A	FINE	N/A	N/A	9955433
Sieve - #10 (>2.00mm)	%	0.38	N/A	N/A	N/A	0.87	N/A	0.20	9959130
Sieve - #200 (>0.075mm)	%	29	N/A	N/A	N/A	47	N/A	0.20	9959130
Sieve - Pan	%	71	N/A	N/A	N/A	53	N/A	0.20	9959130

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty
N/A = Not Applicable
(1) Detection limits raised due to dilution to bring analyte within the calibrated range.

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

RESULTS OF CHEMICAL ANALYSES OF SOIL

BV Labs ID		YF3988			YF3989			
Sampling Date		2020/07/27			2020/07/27			
COC Number		1 of 1			1 of 1			
	UNITS	**ADVISIAN SITE #16-COARSE-IMPACTED #1 Lab-Dup**	**MU**	**QC Batch**	**ADVISIAN SITE #16-COARSE-IMPACTED #2**	**MU**	**RDL**	**QC Batch**
Pesticides & Herbicides								
Tebuthiuron	mg/kg	<0.0010	N/A	9971699	<0.0010	N/A	0.0010	9987763
Atrazine + Desethyl-atrazine	mg/kg	<0.0080	N/A	9971699	<0.0080	N/A	0.0080	9987763
Simazine	mg/kg	<0.010	N/A	9971699	<0.010	N/A	0.010	9987763
Diuron	mg/kg	<0.010	N/A	9971699	<0.010	N/A	0.010	9987763
Linuron	mg/kg	<0.0070	N/A	9971699	<0.0070	N/A	0.0070	9987763
Bromacil	mg/kg	0.070	N/A	9971699	0.076	N/A	0.0090	9987763
Physical Properties								
Grain Size	N/A	N/A	N/A	9955433	FINE	N/A	N/A	9972573
Sieve - #10 (>2.00mm)	%	N/A	N/A	9959130	4.8	N/A	0.20	9990269
Sieve - #200 (>0.075mm)	%	N/A	N/A	9959130	46	N/A	0.20	9990269
Sieve - Pan	%	N/A	N/A	9959130	54	N/A	0.20	9990269

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

RESULTS OF CHEMICAL ANALYSES OF SOIL

BV Labs ID		YF3990		YF3990			
Sampling Date		2020/07/27		2020/07/27			
COC Number		1 of 1		1 of 1			
	UNITS	**ADVISIAN SITE #22-COARSE-CLEAN#1**	**MU**	**ADVISIAN SITE #22-COARSE-CLEAN #1 Lab-Dup**	**MU**	**RDL**	**QC Batch**
Parameter							
MEND Extract ORP	mV	154	N/A	N/A	N/A	N/A	9998772
Misc. Inorganics							
Fraction of Organic Carbon	g/g	<0.00020	N/A	N/A	N/A	0.00020	9986650
Anions							
Dissolved Bromide (Br)	mg/L	<0.010	N/A	N/A	N/A	0.010	9995182
MISCELLANEOUS							
Sample Matrix	N/A	SOLID	N/A	N/A	N/A	N/A	ONSITE
Nutrients							
Soluble Ammonia (N)	mg/L	0.85	+/- <RDL	N/A	N/A	0.20	9992487
Kjeldahl Nitrogen	mg/kg	14	+/- <RDL	18	+/- <RDL	10	9993065
Pesticides & Herbicides							
Tebuthiuron	mg/kg	<0.0010	N/A	N/A	N/A	0.0010	9971699
Atrazine + Desethyl-atrazine	mg/kg	<0.0080	N/A	N/A	N/A	0.0080	9971699
Simazine	mg/kg	<0.010	N/A	N/A	N/A	0.010	9971699
Diuron	mg/kg	<0.010	N/A	N/A	N/A	0.010	9971699
Linuron	mg/kg	<0.0070	N/A	N/A	N/A	0.0070	9971699
Bromacil	mg/kg	<0.0090	N/A	N/A	N/A	0.0090	9971699
Soluble Parameters							
Soluble Nitrite (N)	mg/L	<0.20	N/A	<0.20	N/A	0.20	9992209
Soluble Nitrate (N)	mg/L	0.39	+/- <RDL	0.36	+/- <RDL	0.20	9992209
Physical Properties							
Dry Bulk Density	g/cm3	1.7	N/A	1.8	N/A	0.010	9990984
Grain Size	N/A	COARSE	N/A	N/A	N/A	N/A	9955433
Sieve - #10 (>2.00mm)	%	0.67	N/A	N/A	N/A	0.20	9959130
Sieve - #200 (>0.075mm)	%	93	N/A	N/A	N/A	0.20	9959130
Sieve - Pan	%	6.5	N/A	N/A	N/A	0.20	9959130

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

RESULTS OF CHEMICAL ANALYSES OF SOIL

BV Labs ID		YF3992		YF3992			
Sampling Date		2020/07/27		2020/07/27			
COC Number		1 of 1		1 of 1			
	UNITS	**ADVISIAN SITE #25-FINE-IMPACTED #1**	**MU**	**ADVISIAN SITE #25-FINE-IMPACTED #1 Lab-Dup**	**MU**	**RDL**	**QC Batch**
Pesticides & Herbicides							
Tebuthiuron	mg/kg	<0.0010	N/A	<0.0010	N/A	0.0010	9987763
Atrazine + Desethyl-atrazine	mg/kg	<0.0080	N/A	<0.0080	N/A	0.0080	9987763
Simazine	mg/kg	<0.010	N/A	<0.010	N/A	0.010	9987763
Diuron	mg/kg	<0.010	N/A	<0.010	N/A	0.010	9987763
Linuron	mg/kg	<0.0070	N/A	<0.0070	N/A	0.0070	9987763
Bromacil	mg/kg	<0.0090	N/A	<0.0090	N/A	0.0090	9987763
Physical Properties							
Grain Size	N/A	FINE	N/A	N/A	N/A	N/A	9972573
Sieve - #10 (>2.00mm)	%	<0.20	N/A	N/A	N/A	0.20	9990269
Sieve - #200 (>0.075mm)	%	7.8	N/A	N/A	N/A	0.20	9990269
Sieve - Pan	%	92	N/A	N/A	N/A	0.20	9990269

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

RESULTS OF CHEMICAL ANALYSES OF SOIL

BV Labs ID		YF3993			
Sampling Date		2020/07/27			
COC Number		1 of 1			
	UNITS	**ADVISIAN SITE #25-FINE-IMPACTED #2**	**MU**	**RDL**	**QC Batch**
Pesticides & Herbicides					
Tebuthiuron	mg/kg	<0.0010	N/A	0.0010	9971699
Atrazine + Desethyl-atrazine	mg/kg	<0.0080	N/A	0.0080	9971699
Simazine	mg/kg	<0.010	N/A	0.010	9971699
Diuron	mg/kg	<0.010	N/A	0.010	9971699
Linuron	mg/kg	<0.0070	N/A	0.0070	9971699
Bromacil	mg/kg	<0.0090	N/A	0.0090	9971699
Physical Properties					
Grain Size	N/A	FINE	N/A	N/A	9955433
Sieve - #10 (>2.00mm)	%	<0.20	N/A	0.20	9959130
Sieve - #200 (>0.075mm)	%	11	N/A	0.20	9959130
Sieve - Pan	%	89	N/A	0.20	9959130

RDL = Reportable Detection Limit
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

PHYSICAL TESTING (SOIL)

BV Labs ID		YF3987		YF3988			
Sampling Date		2020/07/27		2020/07/27			
COC Number		1 of 1		1 of 1			
	UNITS	**ADVISIAN SITE #15-FINE-CLEAN #1**	**MU**	**ADVISIAN SITE #16-COARSE-IMPACTED #1**	**MU**	**RDL**	**QC Batch**
Physical Properties							
% sand by hydrometer	%	40	+/- 5.4	58	+/- 7.8	2.0	9959146
% silt by hydrometer	%	21	+/- 3.4	17	+/- 2.7	2.0	9959146
Clay Content	%	39	+/- 7.9	26	+/- 5.2	2.0	9959146
Texture	N/A	CLAY LOAM	N/A	SNDY CL LO	N/A	N/A	9955873
Moisture	%	10	+/- 0.78	13	+/- 0.96	0.30	9958668

RDL = Reportable Detection Limit
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs ID		YF3989		YF3989			
Sampling Date		2020/07/27		2020/07/27			
COC Number		1 of 1		1 of 1			
	UNITS	**ADVISIAN SITE #16-COARSE-IMPACTED #2**	**MU**	**ADVISIAN SITE #16-COARSE-IMPACTED #2 Lab-Dup**	**MU**	**RDL**	**QC Batch**
Physical Properties							
% sand by hydrometer	%	54	+/- 7.3	54	+/- 7.3	2.0	9984180
% silt by hydrometer	%	18	+/- 2.9	19	+/- 3.0	2.0	9984180
Clay Content	%	28	+/- 5.6	28	+/- 5.6	2.0	9984180
Texture	N/A	SNDY CL LO	N/A	N/A	N/A	N/A	9973087
Moisture	%	14	+/- 1.0	N/A	N/A	0.30	9982124

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

PHYSICAL TESTING (SOIL)

BV Labs ID		YF3990			YF3992			
Sampling Date		2020/07/27			2020/07/27			
COC Number		1 of 1			1 of 1			
	UNITS	**ADVISIAN SITE #22-COARSE-CLEAN #1**	**MU**	**QC Batch**	**ADVISIAN SITE #25-FINE-IMPACTED #1**	**MU**	**RDL**	**QC Batch**
Physical Properties								
% sand by hydrometer	%	96	+/- 13	9959146	20	+/- 2.7	2.0	9984180
% silt by hydrometer	%	<2.0	N/A	9959146	49	+/- 7.9	2.0	9984180
Clay Content	%	3.3	+/- <RDL	9959146	31	+/- 6.3	2.0	9984180
Texture	N/A	SAND	N/A	9955873	SLTY CL LO	N/A	N/A	9973087
Moisture	%	1.0	+/- <RDL	9958668	29	+/- 2.0	0.30	9982124

RDL = Reportable Detection Limit
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs ID		YF3992			YF3993			
Sampling Date		2020/07/27			2020/07/27			
COC Number		1 of 1			1 of 1			
	UNITS	**ADVISIAN SITE #25-FINE-IMPACTED #1 Lab-Dup**	**MU**	**QC Batch**	**ADVISIAN SITE #25-FINE-IMPACTED #2**	**MU**	**RDL**	**QC Batch**
Physical Properties								
% sand by hydrometer	%	N/A	N/A	9984180	26	+/- 3.5	2.0	9959146
% silt by hydrometer	%	N/A	N/A	9984180	39	+/- 6.3	2.0	9959146
Clay Content	%	N/A	N/A	9984180	35	+/- 7.1	2.0	9959146
Texture	N/A	N/A	N/A	9973087	CLAY LOAM	N/A	N/A	9955873
Moisture	%	27	+/- 1.9	9982124	17	+/- 1.2	0.30	9958668

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

WORLEY CANADA SERVICES LTD.
Client Project #: 417011-00030-20100
Your P.O. #: 7001052050
Sampler Initials: LM

ELEMENTS BY ATOMIC SPECTROSCOPY (SOIL)

BV Labs ID		YF3987		YF3990		YF3990			
Sampling Date		2020/07/27		2020/07/27		2020/07/27			
COC Number		1 of 1		1 of 1		1 of 1			
	UNITS	**ADVISIAN SITE #15-FINE-CLEAN #1**	**MU**	**ADVISIAN SITE #22-COARSE-CLEAN #1**	**MU**	**ADVISIAN SITE #22-COARSE-CLEAN #1 Lab-Dup**	**MU**	**RDL**	**QC Batch**
Elements									
Total Phosphorus (P)	mg/kg	250	+/- 65	79	+/- 33	76	+/- 33	20	9993079

RDL = Reportable Detection Limit
Lab-Dup = Laboratory Initiated Duplicate
MU = Measurement Uncertainty

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Sampler Initials: LM

MISCELLANEOUS (SOIL)

BV Labs ID		YF3987		YF3990			
Sampling Date		2020/07/27		2020/07/27			
COC Number		1 of 1		1 of 1			
	UNITS	**ADVISIAN SITE #15-FINE-CLEAN #1**	**MU**	**ADVISIAN SITE #22-COARSE-CLEAN #1**	**MU**	**RDL**	**QC Batch**
Misc. Inorganics							
Total Organic Carbon (C)	%	0.20	+/- 0.053	<0.050	N/A	0.050	A002888

RDL = Reportable Detection Limit
MU = Measurement Uncertainty
N/A = Not Applicable

BV Labs Job #: C055648
Report Date: 2020/09/21

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GENERAL COMMENTS

Each temperature is the average of up to three cooler temperatures taken at receipt

Package 1	18.3°C
Package 2	18.0°C
Package 3	18.7°C
Package 4	16.0°C
Package 5	16.3°C
Package 6	16.7°C
Package 7	18.0°C

Version 2: Report reissued to include additional analysis on samples Advisian Site #16-Coarse-Impacted #2 and Advisian Site #25-Fine-Impacted #1 as per client request on 2020/08/25
Sieve (75micron)
Texture
Sterilant Scan

Sample YF3987 [ADVISIAN SITE #15-FINE-CLEAN #1] : Soil Sterilants: Analysis was performed past sample holding time. This may increase the variability associated with these results. Please see attachment for Heterotrophic Plate count (Soil) results.

Sample YF3988 [ADVISIAN SITE #16-COARSE-IMPACTED #1] : SNDY CL LO = SANDY CLAY LOAM Soil Sterilants: Analysis was performed past sample holding time. This may increase the variability associated with these results.

Sample YF3989 [ADVISIAN SITE #16-COARSE-IMPACTED #2] : SNDY CL LO = SANDY CLAY LOAM Soil Sterilants: Analysis was performed past sample holding time. This may increase the variability associated with these results.

Sample YF3990 [ADVISIAN SITE #22-COARSE-CLEAN #1] : Soil Sterilants: Analysis was performed past sample holding time. This may increase the variability associated with these results. Please see attachment for Heterotrophic Plate count (Soil) results.

Sample YF3992 [ADVISIAN SITE #25-FINE-IMPACTED #1] : SLTY CL LO = SILTY CLAY LOAM Soil Sterilants: Analysis was performed past sample holding time. This may increase the variability associated with these results.

Sample YF3993 [ADVISIAN SITE #25-FINE-IMPACTED #2] : Soil Sterilants: Analysis was performed past sample holding time. This may increase the variability associated with these results.

The estimate of uncertainty has been reported as an expanded uncertainty and calculated using a coverage factor of 2, which gives a level of confidence of 95%.

Results relate only to the items tested.

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QUALITY ASSURANCE REPORT

WORLEY CANADA SERVICES LTD.
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Sampler Initials: LM

			Matrix Spike		Spiked Blank		Method Blank		RPD		QC Standard	
QC Batch	Parameter	Date	% Recovery	QC Limits	% Recovery	QC Limits	Value	UNITS	Value (%)	QC Limits	% Recovery	QC Limits
9958668	Moisture	2020/08/13					<0.30	%	1.6	20		
9959130	Sieve - #10 (>2.00mm)	2020/08/14							61 (1)	30		
9959130	Sieve - #200 (>0.075mm)	2020/08/14							3.2	30	102	75 - 125
9959130	Sieve - Pan	2020/08/14							0.85	30	99	75 - 125
9959146	% sand by hydrometer	2020/08/14							0.82	30	102	87 - 113
9959146	% silt by hydrometer	2020/08/14							0.53	30	101	90 - 110
9959146	Clay Content	2020/08/14							0.83	30	95	79 - 121
9971699	Atrazine + Desethyl-atrazine	2020/08/24	106	70 - 130	98	70 - 130	<0.0080	mg/kg	NC	30		
9971699	Bromacil	2020/08/24	86	70 - 130	108	70 - 130	<0.0090	mg/kg	4.4	30		
9971699	Diuron	2020/08/24	106	70 - 130	100	70 - 130	<0.010	mg/kg	NC	30		
9971699	Linuron	2020/08/24	109	70 - 130	100	70 - 130	<0.0070	mg/kg	NC	30		
9971699	Simazine	2020/08/24	104	70 - 130	103	70 - 130	<0.010	mg/kg	NC	30		
9971699	Tebuthiuron	2020/08/24	104	70 - 130	97	70 - 130	<0.0010	mg/kg	NC	30		
9982124	Moisture	2020/09/01					<0.30	%	6.5	20		
9984180	% sand by hydrometer	2020/09/02							0.078	30	103	87 - 113
9984180	% silt by hydrometer	2020/09/02							0.79	30	100	90 - 110
9984180	Clay Content	2020/09/02							0.38	30	95	79 - 121
9987763	Atrazine + Desethyl-atrazine	2020/09/04	93	70 - 130	102	70 - 130	<0.0080	mg/kg	NC	30		
9987763	Bromacil	2020/09/04	92	70 - 130	101	70 - 130	<0.0090	mg/kg	NC	30		
9987763	Diuron	2020/09/04	98	70 - 130	109	70 - 130	<0.010	mg/kg	NC	30		
9987763	Linuron	2020/09/04	91	70 - 130	95	70 - 130	<0.0070	mg/kg	NC	30		
9987763	Simazine	2020/09/04	96	70 - 130	94	70 - 130	<0.010	mg/kg	NC	30		
9987763	Tebuthiuron	2020/09/04	101	70 - 130	104	70 - 130	<0.0010	mg/kg	NC	30		
9990269	Sieve - #10 (>2.00mm)	2020/09/08							NC	30		
9990269	Sieve - #200 (>0.075mm)	2020/09/08							150 (1)	30	100	75 - 125
9990269	Sieve - Pan	2020/09/08							1.4	30	100	75 - 125
9990984	Dry Bulk Density	2020/09/10							3.2	35		
9991344	Soluble (CaCl2) pH	2020/09/09			100	97 - 103			0.12	N/A	100	98 - 102
9991412	Saturation %	2020/09/09							4.1	12	98	75 - 125
9992005	Soluble Conductivity	2020/09/09			99	90 - 110	<0.020	dS/m	4.5	20	94	75 - 125
9992039	Soluble Boron (B)	2020/09/09	104	75 - 125	104	80 - 120	<0.10	mg/L	28	30		

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QUALITY ASSURANCE REPORT(CONT'D)

WORLEY CANADA SERVICES LTD.
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			Matrix Spike		Spiked Blank		Method Blank		RPD		QC Standard	
QC Batch	Parameter	Date	% Recovery	QC Limits	% Recovery	QC Limits	Value	UNITS	Value (%)	QC Limits	% Recovery	QC Limits
9992039	Soluble Calcium (Ca)	2020/09/09	98	75 - 125	97	80 - 120	<1.5	mg/L	2.1	30	89	75 - 125
9992039	Soluble Magnesium (Mg)	2020/09/09	97	75 - 125	96	80 - 120	<1.0	mg/L	3.3	30	89	75 - 125
9992039	Soluble Potassium (K)	2020/09/09	98	75 - 125	97	80 - 120	<1.3	mg/L	1.7	30	100	75 - 125
9992039	Soluble Sodium (Na)	2020/09/09	97	75 - 125	97	80 - 120	<2.5	mg/L	3.6	30	99	75 - 125
9992039	Soluble Sulphate (SO4)	2020/09/09					<5.0	mg/L	4.9	30	86	75 - 125
9992049	Soluble Chloride (Cl)	2020/09/09	108	75 - 125	108	80 - 120	<10	mg/L	NC	30	106	75 - 125
9992209	Soluble Nitrate (N)	2020/09/09	99	75 - 125	107	80 - 120	<0.20	mg/L	9.5	30	92	75 - 125
9992209	Soluble Nitrite (N)	2020/09/09	100	75 - 125	109	80 - 120	<0.20	mg/L	NC	30		
9992240	Hex. Chromium (Cr 6+)	2020/09/09	96	75 - 125	110	80 - 120	<0.080	mg/kg	NC	35		
9992487	Soluble Ammonia (N)	2020/09/09	101	75 - 125	102	80 - 120	<0.20	mg/L	5.2	35		
9993065	Kjeldahl Nitrogen	2020/09/12	76	75 - 125	116	75 - 125	<10	mg/kg	23	30	105	75 - 125
9993077	Total Antimony (Sb)	2020/09/10	98	75 - 125	102	80 - 120	<0.50	mg/kg	NC	30	109	15 - 182
9993077	Total Arsenic (As)	2020/09/10	102	75 - 125	107	80 - 120	<1.0	mg/kg	10	30	113	53 - 147
9993077	Total Barium (Ba)	2020/09/10	NC	75 - 125	109	80 - 120	<1.0	mg/kg	2.0	35	107	80 - 119
9993077	Total Beryllium (Be)	2020/09/10	99	75 - 125	103	80 - 120	<0.40	mg/kg	NC	30		
9993077	Total Cadmium (Cd)	2020/09/10	105	75 - 125	110	80 - 120	<0.050	mg/kg	2.8	30	118	72 - 128
9993077	Total Chromium (Cr)	2020/09/10	102	75 - 125	110	80 - 120	<1.0	mg/kg	5.0	30	105	59 - 141
9993077	Total Cobalt (Co)	2020/09/10	102	75 - 125	108	80 - 120	<0.50	mg/kg	1.0	30	106	58 - 142
9993077	Total Copper (Cu)	2020/09/10	101	75 - 125	108	80 - 120	<1.0	mg/kg	6.3	30	114	83 - 117
9993077	Total Lead (Pb)	2020/09/10	105	75 - 125	111	80 - 120	<0.50	mg/kg	6.2	35	121	79 - 121
9993077	Total Mercury (Hg)	2020/09/10	98	75 - 125	116	80 - 120	<0.050	mg/kg	NC	35		
9993077	Total Molybdenum (Mo)	2020/09/10	107	75 - 125	113	80 - 120	<0.40	mg/kg	NC	35	118	67 - 133
9993077	Total Nickel (Ni)	2020/09/10	101	75 - 125	110	80 - 120	<1.0	mg/kg	1.1	30	119	79 - 121
9993077	Total Selenium (Se)	2020/09/10	105	75 - 125	108	80 - 120	<0.50	mg/kg	NC	30		
9993077	Total Silver (Ag)	2020/09/10	105	75 - 125	110	80 - 120	<0.20	mg/kg	NC	35	119	47 - 153
9993077	Total Thallium (Tl)	2020/09/10	102	75 - 125	109	80 - 120	<0.10	mg/kg	NC	30		
9993077	Total Tin (Sn)	2020/09/10	105	75 - 125	109	80 - 120	<1.0	mg/kg	NC	35	112	67 - 133
9993077	Total Uranium (U)	2020/09/10	95	75 - 125	102	80 - 120	<0.20	mg/kg	0.23	30	104	77 - 123
9993077	Total Vanadium (V)	2020/09/10	100	75 - 125	109	80 - 120	<1.0	mg/kg	1.6	30	113	79 - 121
9993077	Total Zinc (Zn)	2020/09/10	94	75 - 125	108	80 - 120	<10	mg/kg	3.5	30	114	79 - 121
9993079	Total Phosphorus (P)	2020/09/11	103	75 - 125	93	80 - 120	<20	mg/kg	3.6	30	83	82 - 118

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QUALITY ASSURANCE REPORT(CONT'D)

WORLEY CANADA SERVICES LTD.
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Your P.O. #: 7001052050
Sampler Initials: LM

			Matrix Spike		Spiked Blank		Method Blank		RPD		QC Standard	
QC Batch	Parameter	Date	% Recovery	QC Limits	% Recovery	QC Limits	Value	UNITS	Value (%)	QC Limits	% Recovery	QC Limits
9993394	Hex. Chromium (Cr 6+)	2020/09/10	101	75 - 125	101	80 - 120	<0.080	mg/kg	NC	35		
9995182	Dissolved Bromide (Br)	2020/09/11	99	80 - 120	98	80 - 120	<0.010	mg/L	11	20		
9998772	MEND Extract ORP	2020/09/11					214	mV	2.0	20		
A002888	Total Organic Carbon (C)	2020/09/17			99	80 - 120	<0.050	%	3.7	35	101	75 - 125

N/A = Not Applicable

Duplicate: Paired analysis of a separate portion of the same sample. Used to evaluate the variance in the measurement.

Matrix Spike: A sample to which a known amount of the analyte of interest has been added. Used to evaluate sample matrix interference.

QC Standard: A sample of known concentration prepared by an external agency under stringent conditions. Used as an independent check of method accuracy.

Spiked Blank: A blank matrix sample to which a known amount of the analyte, usually from a second source, has been added. Used to evaluate method accuracy.

Method Blank: A blank matrix containing all reagents used in the analytical procedure. Used to identify laboratory contamination.

NC (Matrix Spike): The recovery in the matrix spike was not calculated. The relative difference between the concentration in the parent sample and the spike amount was too small to permit a reliable recovery calculation (matrix spike concentration was less than the native sample concentration)

NC (Duplicate RPD): The duplicate RPD was not calculated. The concentration in the sample and/or duplicate was too low to permit a reliable RPD calculation (absolute difference <= 2x RDL).

(1) Recovery or RPD for this parameter is outside control limits. The overall quality control for this analysis meets acceptability criteria.

Appendix A4-3: Literature Review to Identify Metabolites of Bromacil and Tebuthiuron

Marquez, G., A. Houston and T. Todoruk, 2020. Literature Review to Identify Metabolites of Bromacil and Tebuthiuron. Report SSP-6/8C prepared by Advisian for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 18 pp.

Literature Review to Identify Metabolites of Bromacil and Tebuthiuron

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February 13, 2020

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CITATION

This report may be cited as:

Marquez, G., A. Houston and T. Todoruk, 2020. Literature Review to Identify Metabolites of Bromacil and Tebuthiuron. Report SSP-6/8C prepared by Advisian for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 18 pp.

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EXECUTIVE SUMMARY

Worley Canada Services Ltd. (Worley), operating as Advisian, was retained by InnoTech Alberta (InnoTech) to assist with the Soil Sterilants Program to develop Sterilant-Specific Model Input Data (the Project). The objective of the Project is to refine input parameters related to contaminant fate, mobility, and degradation that more realistically reflect Alberta-specific field conditions, are protective of receptors at Alberta sites, can be used to inform Alberta Tier 1 Soil and Groundwater Guideline (Tier 1 Guidelines) modification, are available to site managers for Tier 2 Soil and Groundwater Guideline (Tier 2 Guidelines) calculations when pursuing site closure, and are acceptable to regulators.

The current literature review has been completed to identify degradation processes and metabolites of bromacil and tebuthiuron in soil to support Task 4 of the Project. Task 4 will investigate degradation rates (and presence of metabolites) of bromacil and tebuthiuron under field conditions. Bureau Veritas Laboratories will complete open scans on soil collected from the field containing weathered tebuthiuron or bromacil. The literature review focuses on supporting interpretation of the open scan results and reviews information on degradation pathways and specific metabolic products of bromacil and tebuthiuron.

Generally, the degradation of both sterilants has been studied since the 1980's although not all processes are well understood. No chemical-specific information was found on the individual metabolites. In summary, nine bromacil and eight tebuthiuron degradation products were identified from laboratory studies. Degradation and metabolism processes included aerobic and anaerobic biodegradation in soil and water, hydrolysis, photodegradation in soil and water, mammalian metabolism, and plant metabolism. In general, bromacil and tebuthiuron were characterized as having low adsorption; low volatility; low susceptibility to decomposition by sunlight in soil; low susceptibility to chemical degradation; and low susceptibility to microbial decomposition. Photodegradation in water, however, has been reported as a potential target for remediation efforts as reported half-lives for bromacil and tebuthiuron were 5 to 7 days and 103 days, respectively.

1 INTRODUCTION

Worley Canada Services Ltd. (Worley), operating as Advisian, was retained by InnoTech Alberta (InnoTech) to assist with the Soil Sterilants Program (SSP) to develop Sterilant-Specific Model Input Data (the Project). As part of InnoTech's efforts to advance the science of sterilants in Alberta, this Project focuses on: (1) developing refined model input parameters for the Alberta Tier 2 risk assessment models (Alberta Environment and Parks [AEP], 2019b) and (2) addressing some of the conservative assumptions inherent in the Alberta Tier 1 Guidelines (AEP, 2019a) under field conditions.

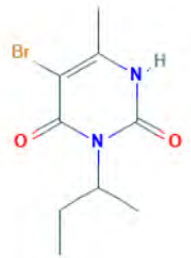
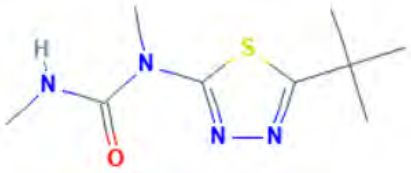
Task 4 of the Project involves investigating degradation rates and presence of metabolites for bromacil and tebuthiuron under Alberta field conditions. Bureau Veritas Laboratories (BV Labs) will complete open scans on soil collected from the field containing weathered tebuthiuron or bromacil. To assist with upcoming Task 4, the current literature review was completed to identify metabolites of bromacil and tebuthiuron, and potential degradation processes. The literature review focused on supporting interpretation of the open scan results and reviews information on degradation pathways and specific metabolic products of bromacil and tebuthiuron.

2 PROPERTIES OF BROMACIL AND TEBUTHIURON

A literature synthesis was recently prepared for InnoTech that provided a high-level summary of available information related to remediation of soil sterilants commonly found in Alberta (Drozdowski et al., 2018). The literature synthesis document provides available information on sterilant physical and chemical properties, persistence and fate in the environment, ecotoxicological information, regulatory guidelines, applicable remediation technologies, and operational challenges associated with residual sterilants. Drozdowski et al. (2018) searched through multiple resources to identify relevant references. Once collected, the references were reviewed, and a database created which identifies the type of information contained within each document (Drozdowski et al., 2018).

In general, bromacil and tebuthiuron are characterized as having low adsorption; low volatility; low susceptibility to photodegradation in soils; low susceptibility to chemical degradation; and low susceptibility to microbial decomposition. Photodegradation in waters, however, has been reported as a potential target for remediation efforts as reported half-lives for bromacil and tebuthiuron were 5 to 7 days and 103 days, respectively. Detailed information on the physical and chemical characteristics for bromacil and tebuthiuron is provided below in Table 1**Error! Reference source not found.**, taken from Drozdowski et al. (2018) except where noted.

Table 1. Properties of Bromacil and Tebuthiuron.

Parameter	Bromacil[1]	Tebuthiuron[2]
Chemical Name	5-bromo-3-(butan-2-yl)-6-methylpyrimidine-2,4(1H,3H)-dione	1-(5-tert-Butyl-1,3,4-thiadiazol-2-yl)-1,3-dimethylurea
Physical and Chemical Characteristics	• Molecular Formula: $C_9H_{13}BrN_2O_2$ • Molecular weight: 261.12 g/mol (PubChem, 2019a). • Melting point: 158 to 160 °C (PubChem, 2019a). • Solubility in water: 815 mg/L at 25 °C (PubChem, 2019a); Solubility increases under both low and high pH conditions. (MacBean, 2008-2010 cited in PubChem, 2019a). • Vapour pressure: 3.1×10^{-7} mm Hg (US EPA, 2019). • Koc of 66.6 mL/g (ORNL [Oak Ridge National Laboratory], 2005; this value is used in Alberta Tier 1 guidelines (AEP, 2019a). Koc: ranges from 2.3 to 289 mL/g in sand to peat soils (ENSR, 2005 cited in Drozdowski et al., 2018).	• Molecular Formula: $C_9H_{16}N_4OS$ • Molecular weight: 228.32 g/mol (PubChem, 2019c). • Melting point: 161.5 to 164 °C (PubChem, 2019d). • Solubility in water: 2,500 mg/L at 25 °C (PubChem, 2019d). • Vapour pressure: 2.0×10^{-6} mm Hg at 25 °C (US EPA, 2019). • K_{oc} of 23 mL/g (ORNL, 2005; this value is used in Tier 1 Guidelines, Alberta Environment and Parks [AEP], 2019a) although ORNL (2019) now lists K_{oc} as 42.2 mL/g. K_{oc}: ranges from 4 to 620 mL/g (cited in United States Department of Agriculture Agricultural Research Service [USDA ARS], 2001).
Structure		

Parameter	Bromacil[1]	Tebuthiuron[2]
Adsorption / Desorption	• Sorption lower than other herbicides (Landsburg and Fedkenheuer, 1990 cited in Drozdowski et al., 2018). • In soil, sorption increases with clay and organic matter (OM) content and decreased pH (Angemar et al., 1984; Landsburg and Dwyer, 1995 cited in Drozdowski et al., 2018). • Does not partition to suspended particles or sediments in aquatic systems, remaining dissolved in water column (EBA Engineering, 2007 cited in Drozdowski et al., 2018).	• Relatively poorly sorbed to soil (Stantec Consulting Ltd., 2011). • In soil, sorption is higher in soils high in organic matter content followed by clay content which is the case for most chemicals (Stantec Consulting Ltd., 2011). • <1% at soil organic matter of 0.3% and 40% with soil OM of 4.8% (Stantec Consulting Ltd., 2011).
Degradation	• Microbial degradation was not considered important for bromacil (PubChem, 2019a; US EPA, 1994) based on a study by Madhun and Freed (1987 cited in US EPA, 1994). However, other studies have shown microbial degradation to have a relatively short half-life (less than one year). A study by Zimdahl et al. (1970 cited in US EPA, 1988) indicated bromacil at 8 ppm had a half-life of about 6 months in aerobic loam soil. A study by Wolf and Martin (1974), however, identified that only 10% of bromacil applied at 3 ppm had degraded to carbon dioxide (CO_2) after 330 days in an aerobic sandy loam soil. Under anaerobic conditions, the study calculated a half-life of 145 days in sandy loam soil under saturated conditions. In a second test in the same study, only approximately 53% of added bromacil was still present as the parent compound after 115 days. Sterilized samples in these tests showed no signs of degradation, indicating that the degradation was microbial. • Stable to photolysis in soil (PubChem, 2019b) and water at low pH (PubChem, 2019a) but may be photolyzed in water under alkaline conditions (US EPA, 1996). • Degradation in natural waters may occur through microbial and photo-sensitized degradation (Dube et al., 2009 cited in Drozdowski et al., 2018). • Metabolites (aerobic and anaerobic) listed in US EPA (1996).	• Rates and relative importance of microbial degradation are variable as reported by Stantec Consulting Ltd. (2011). Microbial degradation of up to 67% was reported. • Tebuthiuron anaerobic and aerobic degradation is very slow with a calculated half-life of 35.4 months (Rainey, 1989a). While Rainey (1989a, b cited in US EPA, 1994) considered tebuthiuron was stable to degradation in soil, other studies show when conditions are optimized, tebuthiuron degradation is occurring (Stantec Consulting Ltd., 2011). • Photodegradation occurs, although it may be of limited importance especially in soils (CCME, 1999). • Stantec Consulting Ltd. (2011) discussed degradation pathways and investigated heterotrophic microbes in soil with the ability to degrade tebuthiuron. • Co-metabolism (non-specific microbial degradation) is important (Stantec Consulting Ltd., 2011). • Metabolites (aerobic and anaerobic) listed in US EPA (1994).

Parameter	Bromacil[1]	Tebuthiuron[2]
Half-life	• Field derived soil dissipation half-life is 349 days (average from the literature) (Drozdowski et al., 2018; ENSR, 2005 cited in Drozdowski et al., 2018). • Soil dissipation half-life is 132 days (average from the literature (aerobic) (Drozdowski et al., 2018). Under anaerobic conditions, bromacil appeared to degrade with a half-life of approximately one month based on an aquatic study, though this study had several major deficiencies that call into question the validity of this information (US EPA, 1996). Under anaerobic conditions, the study calculated a half-life of 145 days in sandy loam soil under saturated conditions. • Measured or estimated half-life values from the literature range from 12 to 46,200 days, with most measurements between 100 and 350 days (Houston et al., 2020). • Varies with the number of applications in a season and over time [4 to 6 months with a single application] (Drozdowski et al., 2018).	• Highly persistent in soils; soil half-life increases in arid and semi-arid environments with low annual precipitation and in soils high in organic matter (Drozdowski et al., 2018). Soils high in organic matter, however, are likely to have lower bioavailability. • Soil half-life: 12 to 15 months in areas receiving high annual rainfall (takes longer in areas receiving less rainfall) and in soils high in organic matter (Rakewich and Bakker, 2017 and studies cited in Drozdowski et al., 2018) • Measured or estimated half-life values from the literature range from 20 to 1,050 days, with most measurements between 100 and 400 days (Houston et al., 2020).

Notes:

Table adapted from literature synthesis (Drozdowski et al., 2018).

US EPA – US Environmental Protection Agency.

[1] Bromacil information generally adapted from the literature: Bromacil Ecological Risk Assessment (ENSR International, 2005 cited in Drozdowski et al., 2018) and the US EPA (1996) Reregistration Eligibility Decision (RED) for Bromacil.

[2] Tebuthiuron information generally adapted from the literature: Biodegradation Study for Tebuthiuron in a Sandy Clay Loam Subsoil (Stantec Consulting Ltd., 2011; table information compiled in Drozdowski et al., 2018) and the US EPA (1994) Reregistration Eligibility Decision (RED) for Tebuthiuron.

3 DEGRADATION METABOLITES

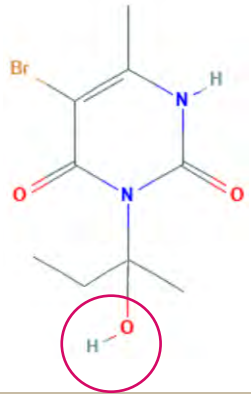
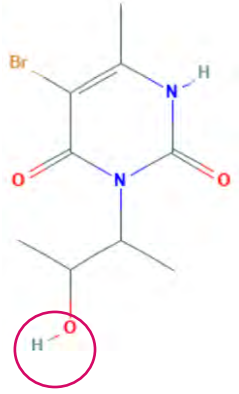
The degradation of both sterilants has been studied since the 1980's although, currently, not all processes are well understood. The US EPA previously compiled summaries of degradation processes of each of these sterilants in its Reregistration Eligibility Decision (RED) documents (US EPA, 1994, 1996). These summaries include details on environmental degradation as well as mammal and plant metabolism. Although some degradation pathway information was available, no chemical-specific information was found on the individual metabolites. Many of the studies cited in the RED documents referenced unpublished laboratory studies that were not available for primary review. The available information has been compiled below with additional studies referenced where available.

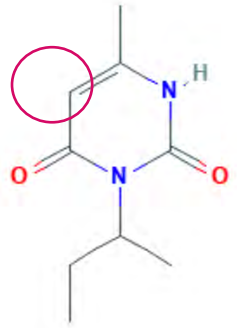
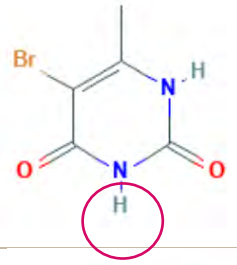
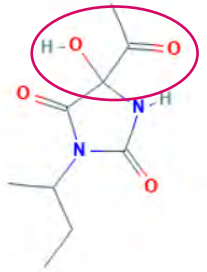
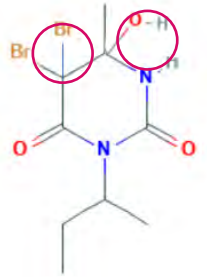
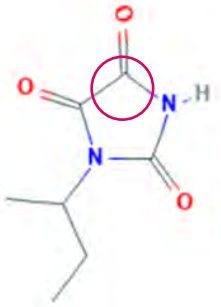
3.1 Metabolites of Bromacil

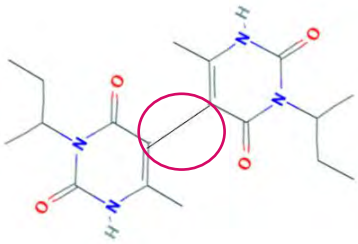
The US EPA RED document for bromacil identified five bromacil degradation products, labelled as Metabolites A, C, D, F and G from laboratory studies as shown in Table 2. Additional degradation products were identified by Archer (1994); these are also included below. Degradation and metabolism processes considered included aerobic and anaerobic biodegradation in soil and water, hydrolysis, photodegradation in soil and water, mammal metabolism, and plant metabolism. These processes are described in detail below.

Table 2. Metabolites of Bromacil.

Chemical Name	Molecular Weight (grams/mole)	Suspected Process/Mechanism	Structure
Bromacil (parent compound)	261.12	—	

Chemical Name	Molecular Weight (grams/mole)	Suspected Process/Mechanism	Structure
5-bromo-3-sec-butyl-6-hydroxymethyluracil (Metabolite A)	277.11	Biodegradation	
5-bromo-3-(alpha-hydroxymethylpropyl)-6-methyluracil (Metabolite C)	277.11	Biodegradation	
5-bromo-3-(2-hydroxy-1-methylpropyl)-6-methyluracil (Metabolite D)	277.11	Biodegradation	

Chemical Name	Molecular Weight (grams/mole)	Suspected Process/Mechanism	Structure
3-sec-butyl-6-methyluracil (Metabolite F)	182.22	Biodegradation, Debromination, Photodecomposition in aqueous solutions (Ultraviolet [UV] photolysis at 254 nm)	
5-bromo-6-methyluracil (Metabolite G)	205.01	Biodegradation	
3-sec-butyl-5-acetyl-5-hydroxyhydantoin	214.22	Ozonation, Photodegradation	
3-sec-butyl-5,5-dibromo-6-methyl-6-hydroxyuracil	358.03	Ozonation, Sensitized Sunlight Photodegradation	
3-sec-butylparabanic acid	170.17	Ozonation	

Chemical Name	Molecular Weight (grams/mole)	Suspected Process/Mechanism	Structure
Debromobromacil Radical Dimer	362.43	Sensitized Sunlight Photodegradation	

Molecular weights and structures adapted from PubChem (2019a, b).

3.1.1 Biodegradation in Soil

The RED document states that biodegradation of bromacil in aerobic soil is slow, with a reported half-life of 275 days although additional aerobic studies have also reported slightly shorter half-lives. The RED document half-life was based on a study measuring radiolabelled bromacil at 9 ppm in silty clay loam soil. The soil was incubated with microbes in the dark at 25°C and 75% of field moisture capacity for up to 12 months. Bromacil concentrations decreased from contributing to 98.5% of the applied radioactivity immediately post-treatment to 53.1% at 184 days, 48.6% at 240 days, and 38.6% at 12 months. Carbon dioxide was the major degradation product measured in this study, totalling 40.3% of the applied radioactivity at 12 months post-treatment. In extracts of sterilized silty clay loam soil, there was less degradation with bromacil comprising 87.5% of the applied radioactivity at 12 months post-treatment. Levels of bromacil metabolites measured post-treatment were found to be negligible totalling a maximum of 1.6% of applied radioactivity in the study.

Five metabolites presented in Table 2 were identified in the study (Vigon and Arthur, 1988a cited in US EPA, 1996). A study by Zimdahl et al (1970 cited in US EPA, 1988) indicated bromacil at 8 ppm had a half-life of approximately 6 months in aerobic loam soil. A study by Wolf and Martin (1974), however, identified that only 10% of bromacil applied at 3 ppm had degraded to CO_2 after 330 days in an aerobic sandy loam soil. Degradation of bromacil by a *Pseudomonas sp*., a gram-negative, aerobic, rod-shaped bacterium was studied by Chaudhry and Cortex (1988). It was found that the bacterium could use bromacil as its sole source of carbon with evidence of growth of the bacterium and reduction of bromacil in soil.

No studies on bromacil biodegradation in anaerobic soil were cited in the RED document although the document did identify microbial degradation in anaerobic soil as a primary route of dissipation. This identification may be based on the results of the aquatic biodegradation study detailed below. Studies have observed degradation in soils and water by reductive dehalogenation mechanisms and this mechanism has been targeted for remediation efforts (Sims et al., 1991). It was found that anaerobic dehalogenation reactions specifically involving reductive processes can effectively degrade a wide variety of halogenated contaminants in soil and groundwater (Kuhn and Suflita, 1989 cited in Sims et al., 1991; Vogel et al., 1987 cited in Sims et al., 1991). The bromacil degradation study by Wolf and Martin (1974) calculated a half-life of 144 days in sandy loam soil under anaerobic conditions, sterilized samples in the tests showed no signs of degradation, indicating that the degradation was microbial. This study also identified that bromacil metabolized completely at 144 days in sandy loam soil under saturated conditions

under several treatments that included tests with organic amendments to the soil. In a second test in the study, only about 53% of added bromacil was still present as the parent compound after 115 days.

3.1.2 Biodegradation in Water

No studies on aerobic biodegradation in water were identified in the RED document. However, a study on the anaerobic aquatic biodegradation was completed that measured relatively high biodegradation rates. Though the study was deemed unsatisfactory because the sampling intervals were inadequate to accurately establish the half-life of the test substance, there was more than a 50% degradation between two samplings events. Between test day 28 and day 93, the percent applied radioactivity identified as bromacil decreased from 78.1% to 1.3%. The major degradation product in this study was Metabolite F, contributing to a maximum of 80.7% of the applied radioactivity at day 304 post-treatment. Metabolite F is likely formed through reductive dehalogenation, a reaction favoured under anaerobic conditions (Vigon and Arthur, 1988b cited in US EPA, 1996). Similar results were found by Adrian and Suflita (1990) although they state that anaerobic debromination by microflora only occurs under methanogenic conditions. The study found bromacil did not degrade under denitrifying or sulphate-reducing conditions. Neither study characterized the microflora. Both studies used sample waters from anoxic habitats including sewage sludge, ponds, a methanogenic aquifer, and a sulphate-reducing aquifer. Suflita et. al (1991) continued to study bromacil degradation in additional aquifer slurries with similar results.

3.1.3 Hydrolysis

Bromacil is stable to hydrolysis at environmental pH, with testing completed from pH 5 to 9. Radiolabelled bromacil at 20 ppm was stable to hydrolysis in sterile aqueous pH 5, 7, and 9 buffer solutions that were incubated in the dark at 25 °C for 30 days. At 30 days post-treatment, bromacil comprised 94.4% to 96.4%, 94.6% to 99.0%, and 96.5% to 97.0% of the recovered radioactivity in the pH 5, 7, and 9 solutions, respectively. Metabolites in this study could not be identified. Unidentified carbon peaks from thin layer chromatography (TLC) analyses of the test solutions revealed three minor, unknown degradates, one of which reached a maximum of 3.9% of the recovered radioactivity in the pH 7 at the end of the study (Das, 1988a cited in US EPA, 1996).

3.1.4 Photodegradation

Bromacil is stable to photolysis in soil based on laboratory studies. In one study, radiolabelled bromacil at a concentration equivalent to 0.12 lb bromacil per acre, photodegraded with a calculated half-life of 166 days in silty clay loam soil that was irradiated for 12 hours per day with a xenon arc lamp for 30 days at 25°C. Based on TLC analysis of the irradiated samples, bromacil decreased to 90.4% of the applied radioactivity after 30 days. Metabolites in this study could not be identified. The two unidentified degradation products each comprised 2.5% of the applied radioactivity in the irradiated samples post-treatment (Das, 1988b cited in US EPA, 1996). Johnson (1993) implied that these two degradation products are the debromination product, Metabolite F, and 3-sec-butyl-5-acetyl-5-hydroxyhydantoin. The UV spectrum of bromacil was described completely by Johnson (1993) during a thesis investigation of photodegradation of bromacil by UV radiation. Bromacil has wavelength of maximum absorbance (λ_{max}) values of 278 and 210 nanometres (nm). The first band can be attributed to the electronic transition from a nitrogen lone pair non-bonding orbital to an empty ring π-orbital, in short to n-π* transition. The intense

band at 210 nm is attributed to a transition from the occupied π-orbital of the ring having the highest energy to the empty π-orbital of lowest energy, a π-π* transition.

The results of the Johnson (1993) study indicated that bromacil in water was stable towards sunlight but also that there was an appreciable change in concentration when irritated with UV radiation at 253.7 nm; the degradation reaction was about 90% complete in only 5 hours. It was observed that the n-π* band is the one which is affected by the photodegradation process. This is because the n-π* band is the Highest Occupied Molecular Orbital – Lowest Unoccupied Molecular Orbital (HOMO-LUMO) band. It is also observed that there is a slight shift in band maxima as bromacil gets degraded (shift towards lower wavelength). This could possibly be due to the dealkylation which takes place during the photodegradation. The two main degradation products were the debromination product, Metabolite F, and 3-sec-butyl-5-acetyl-5-hydroxyhydantoin.

Varying pH was also found to affect the photodegradation of bromacil in water. Bromacil is stable to photolysis in water at lower pH, with calculated half-lives of 326 days and 102 days at tested pHs of 5 and 7, respectively. Bromacil degrades more rapidly in water with higher pH, tested at pH 9, with a half-life of 4 to 7 days. This is because once ionized at higher pH, there is a shift in the absorption spectrum of bromacil thereby making it more susceptible to photolysis. Eight unidentified degradation products were isolated in the lower pH solution studies, each present at less than 8.1% of the recovered radioactivity. Metabolites in the pH 9 solution test were not identified. (Das, 1986 cited in US EPA, 1996).

3.1.5 Mammal Metabolism

The nature of bromacil metabolization in mammals is adequately understood based on the results of a study completed through oral dosing in rats. Metabolic studies were conducted with rats given single (low and high) and multiple (low) doses of radiolabelled bromacil. The major route of elimination was via release in urine. Bromacil was absorbed readily from the gastrointestinal tract, extensively metabolized by hydroxylation, and then excreted. The major metabolite of bromacil in the urine of rats was Metabolite A. Trace levels of bromacil and two unidentified metabolites were also found to be excreted in the urine (McCooey, 1989 cited in US EPA, 1996).

3.1.6 Plant Metabolism

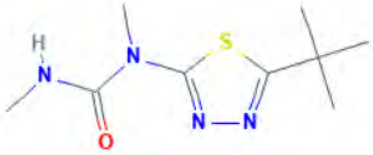
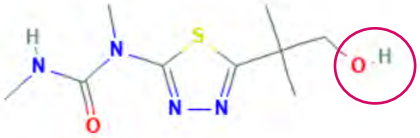
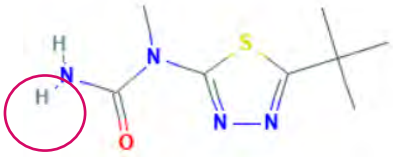
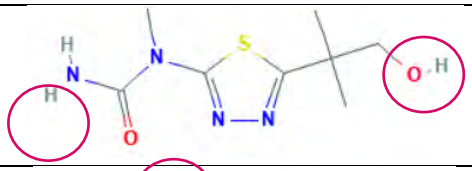
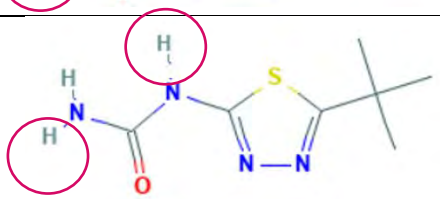
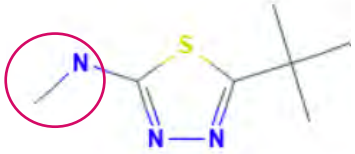
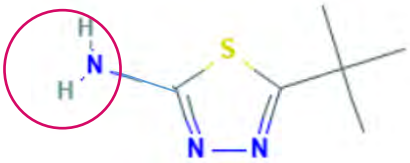
The chemical breakdown of bromacil in plants is sufficiently understood based on information from orange and pineapple metabolism studies. Results from a study of bromacil metabolism in orange plants (Schneiders and Irelan, 1993 cited in US EPA, 1996) indicate that bromacil undergoes hydroxylation at the 6-ethyl group to produce Metabolite A. The metabolite is readily conjugated with glucose and is converted to a malonyl ester of glucose conjugate of Metabolite A. In studies completed with pineapple plants, the metabolism of bromacil proceeds from hydroxylation of the sec-butyl side chain followed by conjugation of the hydroxylated metabolites (Schneiders and Irelan, 1994 cited in US EPA, 1996).

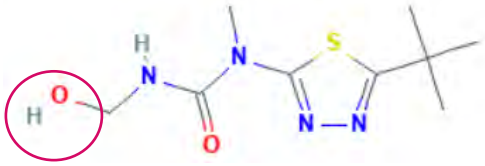
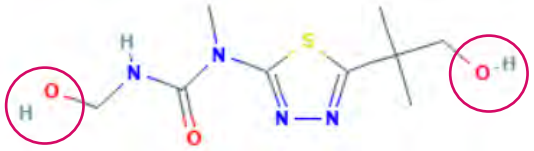
3.2 Metabolites of Tebuthiuron

Eight main tebuthiuron degradation products, labelled as Metabolites 103(OH), 104, 104(OH), 106, 107, 108, 109, and 109(OH) were identified from laboratory studies as shown in Table 3 below. Degradation and metabolism processes included aerobic and anaerobic biodegradation in soil and water, hydrolysis,

photodegradation in soil and water, mammal metabolism, and plant metabolism. These processes are described in detail below.

Table 3. Metabolites of Tebuthiuron.

Chemical Name	Molecular Weight (grams/mole)	Suspected Process/Mechanism	Structure
Tebuthiuron	228.31	—	
N-(5-(2-hydroxy-1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl)-N,N'-dimethylurea (Metabolite 103[OH])	244.32	Plant Metabolism	
N-(5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl)-N-methylurea (Metabolite 104)	214.29	Biodegradation, Mammal Metabolism, Plant Metabolism	
N-(5-(2-dimethylethyl)-1,3,4-thiadiazol-2-yl)-N-methylurea (Metabolite 104[OH])	230.29	Mammal Metabolism	
N-(5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl)urea (Metabolite 106)	200.26	Mammal Metabolism	
5-(1,1-dimethylethyl)-2-methylamino-1,3,4-thiadiazol (Metabolite 107)	171.27	Biodegradation	
2-dimethylethyl-5 amino-1,3,4-thiadiazol (Metabolite 108)	157.24	Biodegradation, Mammal Metabolism	

Chemical Name	Molecular Weight (grams/mole)	Suspected Process/Mechanism	Structure
N-(5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl)-N'-hydroxymethyl-N-methylurea (Metabolite 109)	244.32	Mammal Metabolism, Plant Metabolism	
N-(5-(2-hydroxy-1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl)-N'-hydroxymethyl-N-methylurea (Metabolite 109[OH])	260.32	Mammal Metabolism	

Molecular weights and structures adapted from PubChem (2019c, d).

3.2.1 Biodegradation in Soil

Biodegradation of tebuthiuron in aerobic soil is expected to be slow. In a 9-month study, radiolabelled tebuthiuron, at a concentration of 6 ppm in sandy loam soil incubated in darkness at 24°C and 75% field moisture capacity, degraded with a calculated half-life of 35.4 months. The degradates identified in the study were Metabolite 104, Metabolite 107, and Metabolite 108. The concentration of Metabolite 104 measured highest, accounting for 6.9% of the applied radioactivity at the end of the experiment and appeared to be increasing (Rainey, 1989a cited in US EPA, 1994).

Tebuthiuron also showed little biodegradation in anaerobic soils. Following 60-days under anaerobic flooded conditions in a sandy loam soil, the concentration of tebuthiuron decreased only 4.7%. Degradates identified were Metabolite 104 and Metabolite 109 (Rainey, 1989b cited in US EPA, 1994). Berard (1977) had similar results with tebuthiuron degrading with a half-life of greater than 48 weeks in loam soil maintained under anaerobic conditions in the dark. Metabolite 104 was found to be the major degradate.

3.2.2 Biodegradation in Water

In a 4-week study, tebuthiuron did not degrade appreciably in pond water and sediment that was incubated in darkness at 24°C under aerobic conditions. After 4 weeks of incubation, the parent tebuthiuron had decreased only 4.7%. The degradates identified were Metabolite 104, Metabolite 107, Metabolite 108, and Metabolite 109 (Rainey, 1989c cited in US EPA, 1994).

Similarly, tebuthiuron did not degrade appreciably in an anaerobic system containing pond water and sediment when testing in a one-year study. Degradates were not reported but comprised only approximately 1.4% of the applied radioactivity at the termination of the study (Kesterson and Wick, 1991 cited in US EPA, 1994).

A twelve-month degradation experiment was conducted under different light scenarios and in the presence and absence of coastal sediments (Mercurio et al., 2016). The effects of light and sediments on herbicide persistence were likely due to their influence on microbial community composition and its ability to utilise the herbicides as a carbon source. Under control conditions tebuthiuron had a calculated half-life of 1,766 days. The half-life increased to 3,330 days under the presence of light with no addition of sediment but decreased by almost half to 944 days in the presence of light with the addition of the coastal sediment.

3.2.3 Hydrolysis

Tebuthiuron is stable to hydrolysis at environmental pH, with testing completed from pH 3 to 9 (Loh et al., 1980 cited in Stantec Consulting Ltd. 2011; Moiser and Saunders, 1976). The primary literature was not available for review. It was stated that in the Moiser and Saunders experiment, radiolabelled tebuthiuron at 10 ppm and 100 ppm did not degrade during 64 days of incubation in sterile aqueous solutions at pH 3, 6, and 9.

3.2.4 Photodegradation

Various studies have reported photodegradation as an effective way to remediate for tebuthiuron at environmental pH (Batterham, 1992 cited in Stantec Consulting Ltd., 2011; Rainey and Magnussen, 1976) with a reported photodegradation half-life of tebuthiuron under full sunlight of 103 days in solution. At lower pH, tebuthiuron did not photodegrade when tested using sterile aqueous buffered (pH 5) solutions that were continuously irradiated for 33 days; tebuthiuron was the only compound identified in the irradiated and dark control solutions at each sampling interval (Saxena, 1989 cited in US EPA, 1994). Only photodegradation in water is of importance because solar radiation does not penetrate beyond the top 1 cm of surface soil.

3.2.5 Mammal Metabolism

Tebuthiuron metabolism was tested in four species: mice, rabbits, dogs, and rats. Tebuthiuron was readily absorbed, metabolized, and excreted in urine and faeces of all four species. In rats, 99% of the tebuthiuron dose was released in urine and faeces. The parent tebuthiuron accounted for 23% of the concentrations measured in urine. In rabbits, dogs, and rats, 84% to 95% of the testing dose was measured in the releases. The parent tebuthiuron accounted for less than 1% of the total measurements in the released urine. At least seven of the major metabolites in Table 3 were excreted in the urine of all species (Hoffman, 1988 cited in US EPA, 1994).

3.2.6 Plant Metabolism

The qualitative nature of the residues in plants was stated as adequately understood although no studies were referenced (US EPA, 1994). The metabolites of concern were stated to be Metabolite 103[OH], Metabolite 104, and Metabolite 109 (US EPA, 1994).

4 DISCUSSION AND CONCLUSIONS

The objective of the Project was to refine input parameters related to contaminant fate, mobility, and degradation that more realistically reflect Alberta-specific field conditions, are protective of receptors at Alberta sites, can be used to inform Tier 1 Guideline modification, are available to site managers for Tier 2 Guideline calculations when pursuing site closure, and are acceptable to regulators.

To assist with the upcoming Task 4 of the Project, a literature review to identify degradation processes and metabolites of bromacil and tebuthiuron was completed. Task 4 will investigate degradation rates (and presence of metabolites) under field conditions utilizing data provided by the SSP and field-generated data. Specifically, the literature review focused on supporting the open scan results to be completed by BV Labs which is going to be run on field soils with weathered contamination. The literature review focused on reviewing information on the degradation pathways and the specific metabolic products of bromacil and tebuthiuron.

Generally, the degradation of both sterilants has been studied since the 1980's although, currently, not all processes are well understood. The US EPA (1994, 1996) has compiled summaries of degradation processes of each of these sterilants. These summaries include details on environmental degradation as well as mammal and plant metabolism. No chemical-specific information was found on the individual metabolites. Most of the studies cited in the US EPA documents referenced unpublished laboratory studies that were not available for primary review.

In summary, nine bromacil degradation products were identified from laboratory studies. Eight main tebuthiuron degradation products were identified from laboratory studies. Degradation and metabolism processes included aerobic and anaerobic biodegradation in soil and water, hydrolysis, photodegradation in soil and water, mammalian metabolism, and plant metabolism. In general, bromacil and tebuthiuron were characterized as having low adsorption; low volatility; low susceptibility to decomposition by sunlight in soil; low susceptibility to chemical degradation; and low susceptibility to microbial decomposition. Photodegradation in waters, however, has been reported as a potential target for remediation efforts as reported half-lives for bromacil and tebuthiuron were 5 to 7 days and 103 days, respectively.

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APPENDIX A5: DETERMINATION OF SOIL-WATER AND ORGANIC CARBON-WATER PARTITIONING COEFFICIENTS FOR BROMACIL AND TEBUTHIURON

This project produced three reports.

Appendix A5-1: Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life

Litalien, A., Kartz, C., Mitchell, I., Millennium EMS Solutions Ltd., 2020. Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life. Report SSP-7A. Prepared by Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 54 pp.

Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life

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EXECUTIVE SUMMARY

Many former industrial sites throughout Alberta, now undergoing decommissioning and remediation, have historically used soil sterilants for onsite weed management. Many of these herbicides, including bromacil and tebuthiuron, now present a challenge to site closure due to their persistence and mobility in soil. The Alberta Tier 1 soil guidelines for bromacil and tebuthiuron were developed using a highly conservative approach. The conservative approach has resulted in Tier 1 soil guidelines for the Freshwater Aquatic Life (FAL) and Irrigation Watering (IW) pathways for these two soil sterilants at or below laboratory detection limits, which present a challenge to site reclamation.

A literature review was conducted to determine the most recent and defensible "chemical-specific" parameters of relevance for bromacil and tebuthiuron Tier 1 guideline development and assess how these parameters may influence Tier 1 soil quality guidelines for the IW and FAL pathways. In addition to "chemical-specific parameters", ecotoxicological data was also reviewed to assess the surface water quality guidelines from which the soil quality guidelines are derived.

In general, most chemical-specific literature data available pre-dated the development of the current Alberta Tier 1 guidelines. Further, most studies were conducted either under standard lab conditions or in tropical or semi-tropical climates. This suggests that there is a need for more studies relevant to Albertan conditions. Despite this gap, ecotoxicological findings aligned with the current Alberta surface water quality guidelines.

The organic carbon partition coefficient (Koc) for bromacil listed in the Alberta Tier 1 guidelines was within the range of commonly cited values in the literature reviewed. Conversely, the Koc value used for tebuthiuron Alberta Tier 1 guideline development was much lower than commonly reported in the literature. While half-lives were not utilized for either soil sterilant in their Alberta Tier 1 guideline development, most literature sources reported half lives of 0.5 to 0.75 years and 1 to 2 years for bromacil and tebuthiuron, respectively.

With the inclusion of scientifically defensible and appropriate "chemical-specific" parameters, particularly half-life, the potential for more achievable soil quality remedial guidelines for these soil sterilants, which maintain protection of applicable receptors, is possible. Further field and lab studies with an Alberta context would support the defensibility of the incorporation of adjusted "chemical-specific" parameters into Tier 1 guideline development.

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1 INTRODUCTION

As part of the Soil Sterilants Program, InnoTech Alberta (InnoTech) retained Millennium EMS Solutions Ltd. (MEMS) to assess and evaluate the risk model used to establish the Alberta Tier 1 guideline values for bromacil and tebuthiuron for the protection of irrigation water (IW) and freshwater aquatic life (FAL) pathways and identify alternative models and considerations for guideline development for these soil sterilants, if warranted.

The overall objective of the project, therefore, is to determine appropriate risk model(s) and model parameters to develop screening guidelines for bromacil and tebuthiuron deemed to be protective of the IW and FAL pathways which better reflect the contaminants' "real-world" fate and mobility in the subsurface under Alberta field conditions.

The work was divided into four Milestone Tasks:

1. Current Tier 1 model evaluation for IW and FAL pathways for bromacil and tebuthiuron,
2. Alternative model evaluation to adjust IW and FAL pathways for bromacil and tebuthiuron,
3. Sterilant-pathway risk matrix development, and
4. Guideline development considering source depletion and varying Alberta field conditions.

This report serves as a summary report of Milestone Task #1 described above.

1.1 BACKGROUND

Soil sterilants are a category of broad-spectrum herbicides that were historically used in agriculture (1960s to 1970s) prior to the development of targeted herbicides (Holm and Johnson, 2010). Soil sterilants have also been used extensively at oil and gas sites for weed management (Rakewich and Bakker, 2017). Soil sterilants have a non-specific phytotoxic mode of action; however, by varying the concentration and frequency of application, more sensitive species can be targeted (Landsburg and Dwyer, 1995).

Two soil sterilants of concern herein are bromacil (trade name: Hyvar) and tebuthiuron (trade name: Spike) (MEMS, 2019; Rakewich and Bakker, 2017). Both are substituted uracil herbicides which inhibit photosystem II, a protein required for oxygenic photosynthesis, effectively resulting in hindered growth and/or plant death (Gao et al., 2018; Holm and Johnson, 2010).

1.1.1 Bromacil

Bromacil is a substituted uracil containing bromo and methyl groups. It has a molecular formula of C9H13BrN2O2 and a molecular weight of 261.12 g/mol. In its pure form, bromacil is a colourless to white, odorless crystalline solid but when sold as an herbicide, can be found in both liquid and wettable powder formulations (NLM, 2020a; NIOSH, 2016). Bromacil is slightly soluble and MacBean et al. (2008) and O'Neil et al. (2006) report solubilities in water of 700 mg/L and 815 mg/L, respectively at 25 °C (NLM, 2020a). Bromacil is produced as an herbicide and has been used at many industrial sites for weed management (Rakewich and Bakker, 2017). It is stable, non-combustible and has a low vapour pressure at standard conditions. Chemical properties of bromacil determined from a review of literature are discussed further in Section 5.4.1 and summarized in Appendix C, Table C1 and C2.

1.1.2 Tebuthiuron

Tebuthiuron is a urea-based herbicide with a molecular formula of $C_9H_{16}N_4OS$ and a molecular weight of 228.32 g/mol. It is a colourless and odourless crystalline solid but when produced as a herbicide may be available as a colourless solid to gray or dark brown pellets (NLM, 2020b). Tebuthiuron is slightly soluble in water; Tomlin (2005) reported 2,500 mg/L in water at standard conditions. It is stable, non-flammable,

and has a low vapour pressure but emits toxic degradation products when heated (NLM, 2020b). Chemical properties of tebuthiuron determined from a review of literature are discussed further in Section 5.4.2 and summarized in Appendix C, Table C3 and C4.

1.2 REMEDIAL IMPLICATIONS

In Alberta, soil sterilants have been historically used at many industrials sites now undergoing decommissioning and remediation (InnoTech, 2019). Bromacil and tebuthiuron are both considered highly persistent with moderate to high mobility in soil (Rakewich and Bakker, 2017). As a result, soil sterilants have the potential to migrate to adjacent lands. Several studies have examined the residual activity of these sterilants and have found them to remain phytotoxic for several years after the initial application, depending on soil and climatic conditions (Toit et al., 2012; Zanardo et al., 2019). However, Alberta Tier 1 guidelines are based on a highly conservative approach which presents a challenge to site reclamation.

Current soil quality guidelines for the IW pathway for both bromacil and tebuthiuron as well as the FAL pathway for tebuthiuron fall below current detection limits (0.009 mg/kg and 0.001 mg/kg, respectively (Advisian, 2019)), and the soil quality guideline for the FAL pathway of bromacil is equal to the detection limit. As a result, groundwater investigations are generally required, and remediation may not be achievable.

In the current iteration of the Alberta Tier 1 guidelines, degradation of these sterilants over time is not considered despite evidence in the literature that degradation does occur (US EPA RED, 1994, 1996). Also, other chemical-specific parameters used in the development of the Alberta Tier 1 guidelines for these sterilants may not be representative of the Alberta context.

1.3 CURRENT REMEDIAL SCREENING GUIDELINE LIMITATIONS FOR BROMACIL AND TEBUTHIURON IN ALBERTA

As indicated by InnoTech (2019), soils treated with sterilants often become a source of contamination to adjacent land and waterbodies through leaching, surface runoff and wind dispersion.

The Alberta Tier 1 soil screening guidelines for soil sterilants were developed using *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* (CCME, 2006) as a starting point and adapted as necessary to reflect Alberta conditions and for developing groundwater screening guidelines.

Currently, the combination of the risk model used and assumptions within the risk model for the derivation of the Alberta Tier 1 screening guidelines for bromacil and tebuthiuron have resulted in guidelines which are often considered to be over-conservative in many cases. The parameter values used in the above risk models that calculate the Alberta Tier 1 Soil and Groundwater Remediation Guidelines fall into two main groups: (1) parameters relating to receptor exposure and properties of the site, referred to as “non-chemical-specific parameters”; and, (2) parameters that relate to the chemical properties, toxicity, or background exposure to chemicals, referred to as “chemical-specific parameters” (AEP, 2019).

The overall purpose of this project is to determine appropriate risk model(s) and model parameters to develop screening guidelines for bromacil and tebuthiuron deemed to be protective of the IW and FAL pathways and better reflect the contaminants “real-world” fate and mobility in the subsurface under Alberta field conditions.

The “chemical-specific parameters” used to calculate Tier 1 guidelines are based on the best available information for a contaminant at the time of publishing. For bromacil and tebuthiuron the available

information has been historically limited and of questionable relevance to Alberta, particularly for the inclusion of a reliable degradation rate (half-life).

2 PROJECT OBJECTIVES

The objective of Milestone Task #1 is to conduct an evaluation of the current Tier 1 model for IW and FAL pathways for bromacil and tebuthiuron. The information from Milestone Task #1 will support the overall objective of the Project.

The scope of work designed to meet the objective for Milestone Task #1 included:

- Review of the Task #1 Sterilant-Specific Model Input Data, Sensitivity Analysis document developed as part of the Soil Sterilants Program Sterilant-Specific Model Input Data (Project #6) completed by Advisian (2019).
- Completing a literature review to determine if more relevant and defensible "chemical specific" parameters for bromacil and tebuthiuron are available to better inform current Alberta Tier 1 model parameter inputs. This will include a review of new data on aquatic toxicity (freshwater life and irrigation) since the original guidelines were developed. Consideration of the effect of the Tier 1 model update with respect to "capping" transport time to a surface water body was also considered.
- Completing a re-evaluation of the FAL and IW guidelines using current Alberta Tier 1 models based on the most recent and defensible data available regarding "chemical-specific" parameters for bromacil and tebuthiuron from the literature review and Project #6, including a re-evaluation of the surface water and irrigation water guidelines based on current protocols.
- Development of a Milestone Task #1 summary report.

3 PROJECT METHODOLOGY

The scope for Milestone Task #1 included a literature review to determine if more relevant and defensible "chemical specific" parameters for bromacil and tebuthiuron are available to better inform current Alberta Tier 1 model parameter inputs. The literature review will focus on those "chemical-specific" parameters identified in Advisian (2019), including sterilant half-life and Koc. This review also includes a review of available data on ecotoxicity (freshwater aquatic life and irrigation) since the original Alberta Tier 1 guidelines were developed. While sources from all geographic areas were reviewed, an emphasis was placed on those with particular Alberta relevance.

The detailed literature search involved:

- Planning and search – Four key questions and 22 primary search terms were selected and searched in Google Scholar, Science Direct and PubMed. Articles were selected that presented "chemical-specific" parameters for bromacil and tebuthiuron, or their behaviour in the environment or on crops or freshwater aquatic species;
- Narrowing search results – primary search terms were combined to find specific articles directly related to key questions and the review focused where possible on the past 10 years of published articles and grey-literature reports;
- Document screening – A high-level review of all retrieved documents was conducted, and 170 documents identified in the literature search were thoroughly reviewed to identify information relevant to the key questions; and

- Data analysis and reporting – 94 articles were identified for inclusion in the review. Each article was briefly summarized in terms of study objectives, high level methodology, key results/trends; and conclusion/recommendations, if appropriate. These summaries are presented in Appendix A.

4 RESULTS AND DISCUSSION

4.1 REVIEW OF SENSITIVITY ANALYSIS OF STERILANT-SPECIFIC MODEL INPUT DATA

Advisian (2019) completed a sensitivity analysis of the Domenico and Robbins groundwater transport model (Domenico model). The calculation of Alberta Tier 1 soil and groundwater guidelines for the FAL and IW pathways for soil sterilants utilizes the Domenico Model.

The Domenico model comprises four dilution factors (DF) including:

- DF1, which represents partitioning of the contaminant between soil, pore water, and soil vapour. DF1 considers how a contaminant may sorb to soil organic matter and mineral soil particles.
- DF2, which represents the ratio of the concentration of the contaminant in porewater at the source to that of the porewater just above groundwater. This includes dilution due to biodegradation and dispersion as the contaminant moves down through the soil profile. At Tier 1, it is assumed that contaminated soil extends down to the groundwater table therefore DF2 is equal to 1.
- DF3, which represents the ratio of the concentration of the contaminant in porewater just above groundwater to the concentration in groundwater. DF3 includes mixing as a result of dispersion and water infiltration.
- DF4, which represents the dilution that occurs due to dispersion and biodegradation as groundwater travels downgradient from the source to a receptor. At Tier 1 it is assumed that the distance between the source and the receptor is 10 m for the FAL pathway. Dilution factor 4 is not active for the IW pathway and will be equal to 1.

The Domenico model uses “non-chemical” specific and “chemical-specific” parameters to evaluate transport of chemical contaminants from a source in soils to groundwater to a nearby surface water body.

Based on prior assessments, Advisian selected “chemical-specific” parameters including sterilant half-life and water-organic carbon partition coefficient (Koc), and “non-chemical specific” parameters including fraction of soil organic carbon (foc), soil bulk density, and infiltration rate for the sensitivity analysis.

The results of the sensitivity analysis indicated that the Domenico model has a higher sensitivity to sterilant half-life, foc and infiltration rate. The Domenico model was moderately sensitive to Koc with increasing sensitivity to Koc in conjunction with a higher foc value. MEMS’s review of the Domenico model is consistent with these conclusions.

The literature review conducted in the following section considers the results of the Advisian (2019) sensitivity analysis with respect to the relative effect of “chemical-specific” parameters on the Domenico Model. Specifically, the literature will first and foremost consider sterilant half-life and Koc. As Advisian’s preliminary study identified that H’ was not a highly sensitive parameter, this “chemical-specific” parameter was noted and considered, but not extensively reviewed.

4.2 LITERATURE SEARCH AND REVIEW – SCREENING GUIDELINES FOR BROMACIL AND TEBUTHIURON FOR THE FAL AND IW PATHWAYS

4.2.1 Jurisdictional Guideline Search

MEMS completed a jurisdictional search for existing guidelines, guidance values, or screening values related to bromacil and tebuthiuron.

In Canada, water quality guidelines exist for the protection of FAL and IW both at the federal and provincial level. Provincial guidelines for Alberta, British Columbia, Saskatchewan, and Manitoba are based on the Canadian Council of Ministers of the Environment (CCME) guidelines which are in turn derived from toxicological data.

4.2.2 Freshwater Aquatic Life

The CCME (1999a) Canadian water quality guideline for the protection of aquatic life (CWQG-PAL) for bromacil is 5.0 µg/L. The guideline was derived from the 30-day lethal concentration 50 (LC_{50}), the concentration required to kill 50% of the population, of the most sensitive aquatic species recorded, the alga *Chlamydomonas terricola* and *Haematococcus lacustris*. The LC_{50} was 0.05 mg/L and was multiplied by a safety factor of 0.1 (CCME, 1999a). The CCME (1999a) CWQG-PAL (5.0 µg/L) is currently utilized in the development of the Alberta Tier 1 surface water guideline for the FAL pathway for bromacil.

The CCME (1999b) CWQG-PAL for tebuthiuron is 1.6 µg/L. The guideline was derived from the lowest observable effect level (LOEL) for the most sensitive species, an algae *Selenastrum capricornutum*. The LOEL of 0.016 mg/L was multiplied by a safety factor of 0.1 (CCME, 1999b). The CCME (1999a) CWQG-PAL (1.6 µg/L) is currently utilized in the development of the Alberta Tier 1 surface water guideline for the FAL pathway for tebuthiuron.

Several other countries have developed drinking water guidelines associated with bromacil; however, Canada is the only one to develop specific surface water guidelines for the protection of aquatic life.

Bromacil and tebuthiuron are not listed in the National Recommended Aquatic Life Criteria table, a set of water quality guidelines in the United States (US EPA, 2020a). However, based on the United States Environmental Protection Agency (US EPA) Office of the Pesticide Program (OPP)'s aquatic life and ecological risk assessment for registered pesticides, the most sensitive group of species are non-vascular plants with an acute toxicity of 6.8 µg/L for bromacil and 50 µg/L for tebuthiuron. The US surface water guideline for bromacil is similar to the CCME CWQG-PAL, however the US EPA surface water guideline for tebuthiuron is an order of magnitude less conservative than the CCME FAL guideline (Table 1).

Table 1: US EPA/OPP Freshwater Aquatic Life Benchmarks (ug/L).

	Fish		Invertebrates		Nonvascular Plants	Vascular Plants
	Acute	chronic	Acute	Chronic	Acute	Acute
Bromacil	18,000	3,000	60,500	8,200	6.8	45
Tebuthiuron	53,000	9,300	148,500	21,800	50	130

From US EPA (2020b).

4.2.3 Irrigation Water

The CCME (1999b) Canadian water quality guideline for the protection of agricultural water uses (irrigation water) (CWQG-IW) for bromacil is 0.2 µg/L. The guideline was derived from the species maximum acceptable toxicant concentration (SMATC), the maximum concentration that will not be toxic to the test

organism, for the most sensitive species (cucumber). The SMATC is calculated as the geometric mean of the lowest observed effects level (LOEC) and the no observed effects level (NOEC). However, the SMATC for bromacil included an uncertainty factor of 100 due to its persistence in soils. Sorghum also reported a SMATC of 0.6 µg/L, and accordingly this value is also suggested for cereal crops, tame hays, and pastures. The CCME (1999b) CWQG-IW (0.2 µg/L) is currently utilized in the development of the Alberta Tier 1 surface water guideline for the IW pathway for bromacil.

The CCME (1999c) CWQG-IW for tebuthiuron is 0.27 µg/L. The guideline was derived from the SMATC of wheat (0.27 µg/L) which was the most sensitive of the cereal crops, tame hays, and pasture. It should be noted that insufficient data was available for other crops. The SMATC for tebuthiuron included an uncertainty factor of 20. Alberta Tier 1 guideline for surface water quality (0.43 µg/L) is based on the lowest SMATC value but recalculated with an irrigation rate of 750 mm per year (7.5 x 106 L/ha) vs the 1.2 x 107 L/ha used in the CCME calculation.

4.2.4 Alberta Tier 1 Guidelines for Bromacil and Tebuthiuron – FAL and IW Pathways

Alberta Tier 1 surface water and groundwater guidelines for the protection of FAL and IW pathways are identical, and closely match their respective Canadian water quality guidelines. Alberta Tier 1 soil, groundwater and surface water guidelines from AEP (2019) are shown in Table 2.

Table 2: Summary of Alberta Tier 1 Guidelines for Bromacil and Tebuthiuron.

Sterilant	Surface Water Quality Guidelines (mg/L)		Groundwater Quality Guidelines (mg/L)		Soil Quality Guidelines (mg/kg)		Laboratory Detection Limit (mg/kg)
	FAL Pathway	IW Pathway	FAL Pathway	IW Pathway	FAL Pathway	IW Pathway	
Bromacil	0.005	0.0002	0.005	0.0002	0.009	BDL	0.009
Tebuthiuron	0.0016	0.00043	0.0016	0.00043	BDL	BDL	0.001

BDL = below laboratory detection limit.

4.3 LITERATURE REVIEW RESULTS – ECOTOXICITY FOR BROMACIL AND TEBUTHIURON

4.3.1 Toxicological Data

Ecotoxicity values were reviewed for bromacil and tebuthiuron. The Government of Alberta (AEP, 2017) document titled *Guidance for Selecting Toxicity Reference Values (TRV) for Alberta Tier 1 and Tier 2 Soil and Groundwater Remediation Guidelines* was consulted to determine toxicity values from approved sources (AEP, 2017).

Published literature was reviewed and the primary reference sources, agreed upon by the Scientific Working Group on Contaminated Sites in Alberta (SWGCSA) as acceptable, included:

- Canadian Council of Ministers of the Environment (CCME);
- United States Environmental Protection Agency (US EPA) and,
- USEPA Office of Pesticide Programs (OPP).

However, secondary sources were also reviewed and included:

- US Bureau of Land management (ENSR International, 2005 a/b);
- Extension Toxicology Network (EXTOXNET, 2001 a/b);

- US National Library of Medicine-Pubchem (NLM, 2020 a/b);
- US Reregistration Eligibility Decision (RED, 1994; RED, 1996) and,
- USDA Agricultural Research Service (ARS) Pesticides Properties Database (ARS, 2001). Primary research papers were primarily consulted for more recent data (2010 to 2020).

4.3.2 Bromacil

Significant ecotoxicity data on bromacil exists within the literature; however, most information predates the development of the Canadian water quality guidelines for the protection of aquatic life and agricultural water discussed above.

In 2012, Stantec Consulting Ltd. (Stantec) published an ecotoxicity assessment of bromacil for the purpose of developing an Alberta Tier 1 soil quality guideline for the ecological direct contact exposure pathway. Other recent toxicology research on bromacil focuses mainly on species relevant to tropical regions where bromacil is still used extensively to manage weeds in citrus and pineapple fields and grazing leases (Alavi et al., 2008; de Paz et al., 2006; Dube et al., 2011; Echeverria-Saenz et al., 2018; Wilson et al., 2016). Bromacil ecotoxicity data is presented in Appendix B including ecotoxicity to freshwater species in Table B1 and ecotoxicity to terrestrial plants and crop species in Table B2. The highlighted bromacil toxicity data for aquatic species and terrestrial plants is summarized below.

4.3.2.1 Freshwater Aquatic Life

The general consensus within the literature is that bromacil is relatively non-toxic to freshwater fish and invertebrates but algae and macrophytes can be very sensitive. The lowest reported EC_{50} value was 0.0068 mg/L for *Selenastrum capricornutum*, a microalga, in the US EPA Pesticide Reregistration Eligibility Decision (1996) which is slightly above the current Alberta surface water quality guideline for bromacil. More recent studies have generally focused on more complex systems such as multiple pesticide interactions, marine systems, cyanobacterial mats, and toxicity of interstitial water in impacted sediments (Nahhal and El-Hams, 2017; Magnusson et al., 2013; Wilkinson et al., 2015).

The CCME (1999a) report on bromacil cites ecotoxicological data from several papers including Call et al. (1983, 1987), Cullimore (1975), Geiger et al. (1988), and Sherman and Kaplan (1975). Typical LC_{50} values reported by these authors for fish species (bluegill sunfish, tilapia, fathead minnow, and carp) and for invertebrates (*Daphnia magna* and *Chironomus tentans*) ranged from 10^2 to 10^3 mg/L. Plant species reported EC50 values in the order of 10^{-2} mg/L.

The US EPA pesticide ecotoxicity database (US EPA/OPP, 2020) reports ecotoxicological data for five aquatic plant species, three crustaceans, and four fish species. Fish and crustaceans are much less sensitive to bromacil than freshwater aquatic plants and report EC50 values between 1 mg/L and 180 mg/L, and a geometric mean of 32 mg/L. Aquatic plants reported EC50 values between 0.0068 mg/L and 0.07 mg/L and a geometric mean of 0.018 mg/L. US EPA Pesticide Reregistration Eligibility Decision (US EPA RED, 1996) also reported toxicological data for rainbow trout, bluegill sunfish, *Daphnia magna*, and *Selenastrum capricornutum*, the latter microalgae reported the lowest EC50 value of 0.0068 mg/L.

Wilson and Wilson (2009) studied the impact of bromacil on a common aquatic plant in North America, *Vallisneria americana* Michx. It is an important source of food and shelter to aquatic species and waterfowl and is commonly found in areas susceptible to herbicide runoff. The study reported EC_{50} values as low as 0.032 mg/L demonstrating that it is significantly less sensitive than many of the algal and diatom species previous reported by the CCME and the US EPA.

A recent study by Nahhal and El-Hams (2017) on the effects of bromacil on cyanobacterial mats collected in Israel found that these structures were not very sensitive and reported an EC_{50} of 12.36 mg/L. Wilkinson

et al. (2015) studied the acute and additive toxicity of ten different herbicides including bromacil. The study focused on the marine paddle weed species Halophila ovalis and found that it had a 24-hour EC_{50} value of 0.025 mg/L which is significantly higher than the reported sensitivity of many algal species. Magnusson et al. (2013) studied the toxicity of interstitial water from sediments contaminated with herbicides on *Navicula* diatom species native to Australia. While these samples were generally in mixtures of multiple herbicides, the sample with the highest proportion of bromacil reported an impacts concentration (IC10) of 14 ng/L, suggesting that *Navicula* diatoms may be more sensitive to mixtures of herbicides.

4.3.2.2 Irrigation Water

As bromacil was originally registered in Canada and the United States as a herbicide for agricultural purposes many of the initial studies focused on target weed species and non-target crop plants. Given the age of the herbicide, most of the studies pre-date the development of the CCME guidelines. A few studies have been conducted over the past 10 years with some species relevant to the Alberta context (Nahhal and Hamdona, 2015; Niebch, 2013; Stantec, 2012; Wilson et al., 2016). However, most of these studies present results with respect to soil concentrations (mg/kg) rather than the concentration in the watering solution (µg/L) and would thus be more relevant to the ecological direct contact pathway.

For example, Stantec (2012) assessed the toxicity of bromacil to durum wheat (*Triticum durum*), blue gramma grass (*Bouteloua gracilis*), and alfalfa (*Medicago sativa*). The reported EC_{50} values (shoot mass) for durum wheat, blue gramma grass, and alfalfa were 0.14 mg/kg, 0.24 mg/kg, and 0.16 mg/kg, respectively. Nahhal and Hamdona (2015) studied the toxicity of bromacil on melon, molokhia, and wheat and reported EC_{50} values of 4.77 mg/kg, 0.08 mg/kg, and 3.08 mg/kg, respectively. Wilson et al. (2016) and Niebch (2013) both studied the toxicity of bromacil on *Sorghum bicolor* and reported similar findings with no effects levels (NOEC) at approximately 0.1 mg/kg and a lowest effects level (LOEC) of 1 mg/kg.

Relying solely on ecotoxicological data for aqueous solutions, CCME (1999) cites two primary research papers by Hilton and Nomura (1964) and Ashton et al. (1969) which investigated sorghum and cucumber, and oat and radish respectively. Effects concentrations for these species ranged from 0.05 mg/L for cucumber to 0.26 mg/L for oats. The US EPA pesticide ecotoxicity database (US EPA/OPP, 2020) has also consolidated ecotoxicological data on 11 crop species with reported EC_{25} values ranging from 0.34 µg/L (rapeseed) to 92 µg/L (soybean) with a geometric mean of 7.5 µg/L. The reregistration eligibility decision for bromacil (RED, 1994) also reports ecotoxicological data for nine plant species with some cross-over with the EPA pesticide ecotoxicity database. The EC_{25} values ranged from 1.59 µg/L (cucumber) to 92 µg/L (soybean) with a geometric mean of 9.0 µg/L.

4.3.2.3 Summary

While a limited number of papers have been published within the last decade on the ecotoxicity of bromacil there have been many prior studies that demonstrate its toxicity to species relevant to both the FAL and IW pathways.

Research on the toxicity of bromacil to freshwater aquatic species has mainly focused on standard test species that may not be fully representative of the Alberta context. The literature clearly suggests that bromacil is relatively non-toxic to fish and invertebrates. However, further studies on the toxicity of bromacil to aquatic plants and algae prevalent in northern climates such as Alberta could be beneficial. Toxicity studies of crop species are extensive and include many of the crops grown throughout Alberta. In addition, Stantec (2012) has conducted a recent ecotoxicity study of plant species specifically relevant to Alberta.

Reported toxicity values for several algal species, are on the same order of magnitude as the current Alberta surface water quality guideline for bromacil suggesting that this is likely not overly conservative. Similarly, several crop species report adverse effect at concentrations on the same order of magnitude as the current IW surface water quality guideline suggesting that this value is also not overly conservative (Table B1 and B2, Appendix B).

4.3.3 Tebuthiuron

Like bromacil, most recent research on tebuthiuron toxicity focuses on tropical species. Tebuthiuron was identified as one of five priority herbicides entering the great barrier reef (Thornton and Elledge, 2016). It is used extensively in sugar cane fields and is also used to manage woody invasive species (Allan et al., 2017; Toit et al., 2012). However, the US forestry department uses tebuthiuron regularly to control woody invasive species and as a result, several ecological risk assessments are available that may be more comparable to the Alberta context (Durkin, 2016; ENSR, 2005b; Stavola, 2004).

Tebuthiuron ecotoxicity data is presented in Appendix B including ecotoxicity to freshwater species in Table B3 and to terrestrial plants and crop species in Table B4. Tebuthiuron toxicological data for aquatic species and terrestrial plants is summarized below.

4.3.3.1 Freshwater Aquatic Life

Primary literature published within the last decade on the aquatic toxicity of tebuthiuron has primary focused on tilapia. Tilapia farming is practiced extensively in Brazil where tebuthiuron is also used regularly in agricultural settings (Almeida et al., 2014; Cerdeira et al., 2007; Moura and Jonsson, 2016). As a result, several authors have investigated the impacts of tebuthiuron on tilapia at several life stages and have noted its high tolerance of up to 250 mg/L (Almeida et al., 2014; Moura and Jonsson, 2016). The US Office of Pesticide Programs also conducted a risk analysis for environmental exposure of tebuthiuron to endangered and threatened pacific salmon and steelhead fish (Stavola, 2004). The risk assessment determined that broadcast use of tebuthiuron does not present direct acute or chronic risk to the species investigated. LC_{50} values for freshwater fishes exposed to tebuthiuron as reported by the EFED Pesticide Ecotoxicity Database (2020) range from 98 mg/L to 180 mg/L (sheepshead minnow and fathead minnow, respectively).

There is a consensus throughout the literature that tebuthiuron poses little direct threat to fish and invertebrates but is particularly harmful to aquatic plants, algae and diatoms. As a result, Stavola (2004) also assessed if salmon and steelhead would be indirectly impacted by loss of habitat and food. Using toxicological data extracted from EFED Pesticide Ecotoxicity Database and the RED assessment for tebuthiuron, the authors determined that there was little indirect risk to these species.

The pesticide ecotoxicity database for tebuthiuron cites EC50 values for plants and algae ranging between 0.050 mg/L for freshwater green algae and 81 mg/L for blue-green algae. Toxicity data from the RED (1994) assessment determined that the most sensitive freshwater species was the algae *Selenastrum capricornutum* with an EC_{50} of 0.05 mg/L and the least sensitive aquatic plant to be duckweed with an EC_{50} of 0.135 mg/L. The CCME (1999b) reported similar results with S. capricornutum as the most sensitive species with an EC_{50} of 0.08 to 0.307 mg/L and the least sensitive aquatic plant, duckweed, reporting an EC_{50} of 0.235 mg/L.

4.3.3.2 Irrigation Water

The use of tebuthiuron in Canada and the United States is limited to non-agricultural sites; however, in tropical regions it is commonly used on sugarcane crops. Recent literature on the toxicity of tebuthiuron to crop species is extremely limited. One study by Zanardo et al. (2019) found that residues of tebuthiuron in soil from a sugarcane field was toxic to five genotypes of peanut cultivars. Rocha et al. (2019) also

investigated the impact of tebuthiuron on the biofuel crop *Jatropha curcas* and found that pre-emergent applications of 1.1 Kg/ha caused greater than 80% morbidity by 48 days post application.

The CCME and several US databases do however report toxicological results for several crop species relevant to the Alberta context. The CCME (1999c) report on tebuthiuron includes results from Baur et al. (1977) and Waldrep (1988) which reported NOEAR and LOEAR values for two native grass species and four crop species. The crops reported LOEAR values of 0.012 mg/L and the grasses reported LOEAR values of 0.147 mg/L. The US EPA toxicological database reported EC_{25} values for 13 different species including wheat, soybean and rye; EC_{25} values ranged from 0.0069 mg/L to 0.133 mg/L for carrot and corn respectively. The geometric mean of the EC_{25} values was 0.0133 mg/L.

4.3.3.3 Summary

The ecotoxicity of tebuthiuron has been well documented for several species relevant to both the FAL and IW pathways (Tables B3 and B4, Appendix B). These studies largely pre-date the development of the Alberta Tier 1 guidelines and their findings generally align with the current guidelines. Reported toxicity data for algal species is on the same order of magnitude as the FAL surface water quality guidelines. The Alberta surface water quality guideline for IW is on the same order of magnitude where adverse effect was observed for some crop plants. Thus, neither the FAL nor the IW surface water quality guidelines are likely over conservative. However, like bromacil, toxicity studies for tebuthiuron have generally focused on standard lab species and more recent research has focused on tropical species.

4.4 ALBERTA TIER 1 TRANSPORT TIME CAP

In 2019, AEP released an updated version of the Alberta Tier 1 Soil and Groundwater Remediation Guidelines (AEP, 2019). Included in the updated guidelines was the consideration of a time cap on lateral groundwater transport. Specifically, the lateral groundwater transport (DF4) component of the Domenico Model is now calculated on a time dependent basis with a 500-year travel time. This affects only the protection of the FAL pathway.

A 500-year cap on transportation time was investigated for its impact on Tier 1 soil quality guidelines for the FAL pathway for bromacil and tebuthiuron in both fine and coarse-grained soils. For the analysis all "non-chemical" and "chemical" specific parameters applied in the Domenico model utilized AEP Tier 1 default values (AEP, 2019) with the exception of the application of a 500-year time cap within DF4.

With the inclusion of a 500-year transport time cap, the bromacil and tebuthiuron soil quality guidelines for the protection of the FAL pathway, when rounded, are no different from the current Tier 1 soil quality guidelines (Table 3).

Table 3: Summary of 500-Year Time Cap Analysis.

Sterilant	Current Tier 1 Soil Quality Guidelines – FAL (mg/kg)		Soil Quality Guidelines – FAL with 500-year Cap (mg/kg)		Detection Limit (mg/kg)
	Coarse-grained	Fine-grained	Coarse-grained	Fine-grained	
Bromacil	0.009	0.009	0.0094	0.0088	0.009
Tebuthiuron	BDL	BDL	0.0014	0.0015	0.001

4.5 "CHEMICAL-SPECIFIC" PARAMETERS FOR BROMACIL AND TEBUTHIURON

While at least 50 primary research papers report on the dissipation, migration, and or half lives for either bromacil or tebuthiuron, most data pre-date the development of the Alberta Tier 1 guidelines. More recent chemical specific parameters for these sterilants come primarily from tropical regions where these products are still used extensively for weed management in citrus, pineapple, and sugar cane crops as well as the management of woody shrubs in rangelands (Alavi et al., 2008; Cerdeira et al., 2007; dePaz et al., 2006). Further, much of the chemical specific data available through US EPA databases is derived from registrant-submitted studies that are not available to the public (Durkin, 2016).

Chemical specific parameters, half-life and Koc, for bromacil and tebuthiuron, found within both databases and primary research papers are further discussed below. Sensitivity analyses of the reviewed parameters is also presented within the corresponding sections.

4.5.1 Bromacil

4.5.1.1 Bromacil Half-life Literature Review Results

The AEP Tier 1 (2019) guidance document does not indicate a half-life, or degradation rate for bromacil.

In several major databases, however, the half-life of bromacil is identified as 60 days; though this value was highly variable throughout the literature with 14 to 1494 days reported by some sources (Pubchem, 2020; UN, 1999; Wauchope et al., 1991; Gerstl and Yaron, 1983). Of the 42 sources reviewed, 30 reported half lives between 6 months and 1 year, with the most commonly cited half-lives ranging between 120 and 180 days. Ten sources reported half-lives of less than 90 days (Figure 1).

Many of the sources reviewed which reported half-lives of bromacil were based on experiments conducted under standard lab conditions, or field studies conducted in tropical regions (Gerl and Yaron, 1983; Jolliffee et al., 1967; US EPA RED, 1996; Zimdahl et al., 1970). Of the limited number of studies from temperate climates, the reported half-lives ranged from 60 to 180 days. Based on the information available, most studies were conducted on surface soil (<1.5 m bellow ground surface). A study of bromacil dissipation from the upper 10 cm of a bare ground plot of silty loam in Newark, Delaware reported a half-life of 155 days (US EPA RED, 1996). A field dissipation study in New Zealand reported a half-life of 120 to 180 days and noted that dissipation occurred more rapidly on virgin soils than those that had previous exposures to bromacil (Sarmah et al., 2009). A review of soil residual herbicides reported a half-life of 60 to 150 days in temperate soils (Helling, 2005). A field dissipation study conducted by Landsburg and Dwyer (1995) on humic luvic gleysols in northwestern Alberta reported decreasing bromacil concentrations

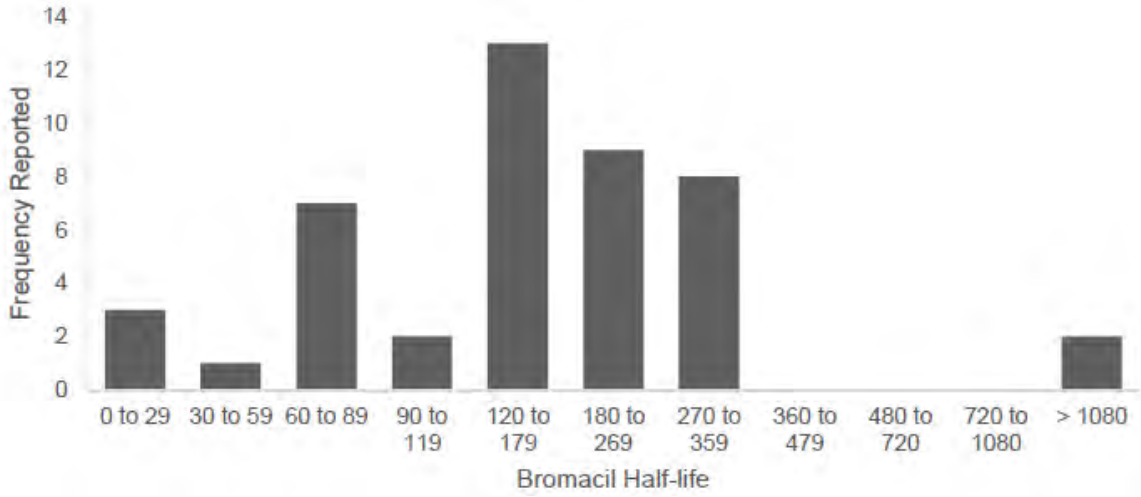

Figure 1: Distribution of bromacil half-life values reported in the literature.

through time that corresponded to a half-life of approximately 270 days (~0.75 years). While it is at the upper end of half-lives for bromacil cited in the literature, temperature, annual precipitation, and soil organic carbon content have been noted as major drivers for the half-life of bromacil. Cooler temperatures, drier climates, and high soil organic carbon resulted in longer half-lives for bromacil in several studies (US EPA RED, 1996; Wolf and Martin, 1974; Zimdahl et al., 1970). While these half-lives may approach bromacil's half-life in Alberta, the limited number of studies available suggests that there is a need for more studies from northern climates.

4.5.1.2 Bromacil Half-Life Sensitivity Analysis

A sensitivity analysis was conducted using the half-life values for bromacil reported in the literature. The values ranged from 0.033 years (12 days) to 4.0 years (1,494 days). For the sensitivity analysis all other "non-chemical" and "chemical" specific parameters applied in the Domenico model utilized AEP Tier 1 default values (AEP, 2019).

The Alberta Tier 1 soil quality guideline for the protection of the FAL pathway developed using the Domenico Model is highly sensitive to the inclusion of a bromacil half-life (Figure 2). With the inclusion of even the longest half-life reported in the literature (1,494 days), the soil quality guideline is raised above the detection limit of 0.009 mg/kg cited by Advisian (2019). Using the half-life of approximately 0.75 years reported by Landsburg and Dwyer (1995) for an Alberta soil, the soil quality guideline would be approximately 0.02 mg/kg and 1.5 mg/kg for coarse-grained and fine-grained soils respectively.

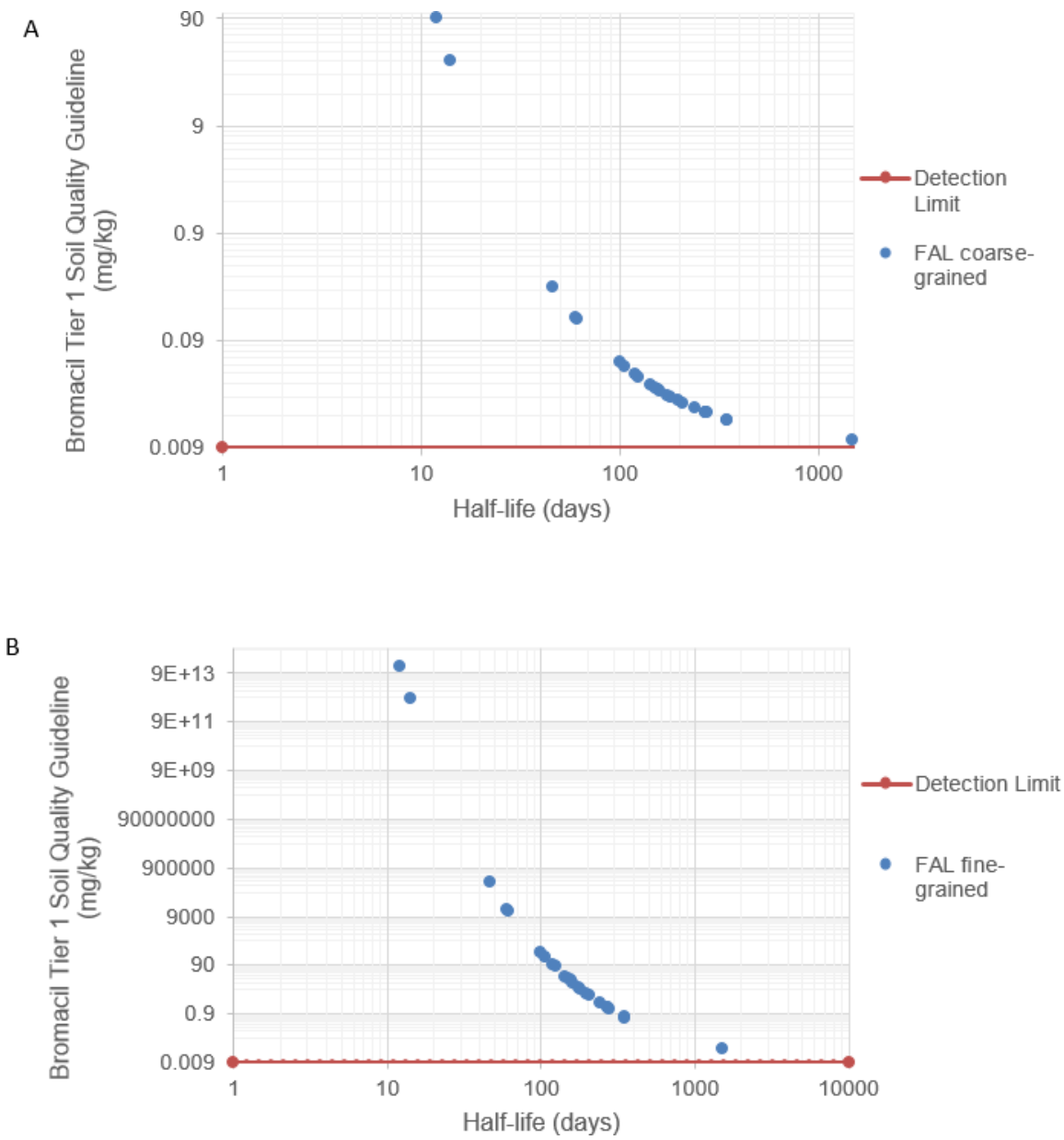

Figure 2: **Tier 1 bromacil soil quality guidelines for the protection of the FAL pathway with inclusion of literature-derived half-life values.**
(A) for coarse-grained soil, (B) for fine-grained soil.

Under a Tier 1 scenario, the inclusion of a half-life in the Domenico Model does not have an impact on the soil quality guideline for the protection of the IW pathway, as both DF2 and DF4 have a default value of 1. However, applying a simple Tier 2 approach (i.e. DF2>1) allows the for the inclusion of a half-life for bromacil to have a meaningful impact on the soil quality guideline for the IW pathway.

As an example, Tier 2 soil quality guidelines for bromacil for the protection of the IW pathway were evaluated considering the literature reported half-life values and 1 m of coarse-grained or fine-grained

separation between base of bromacil impact and the shallowest potential IW groundwater source. The inclusion of a bromacil half-life of less than 1 year increases the soil quality guideline above the detection limit.

With 1 m separation and the inclusion of Landsburg and Dwyer's (1995) half-life of approximately 0.75 years, the soil quality guideline for the protection of the IW pathway increases to 0.091 mg/kg in coarse-grained soil and 1,831 mg/kg in fine-grained soil (Figure 3).

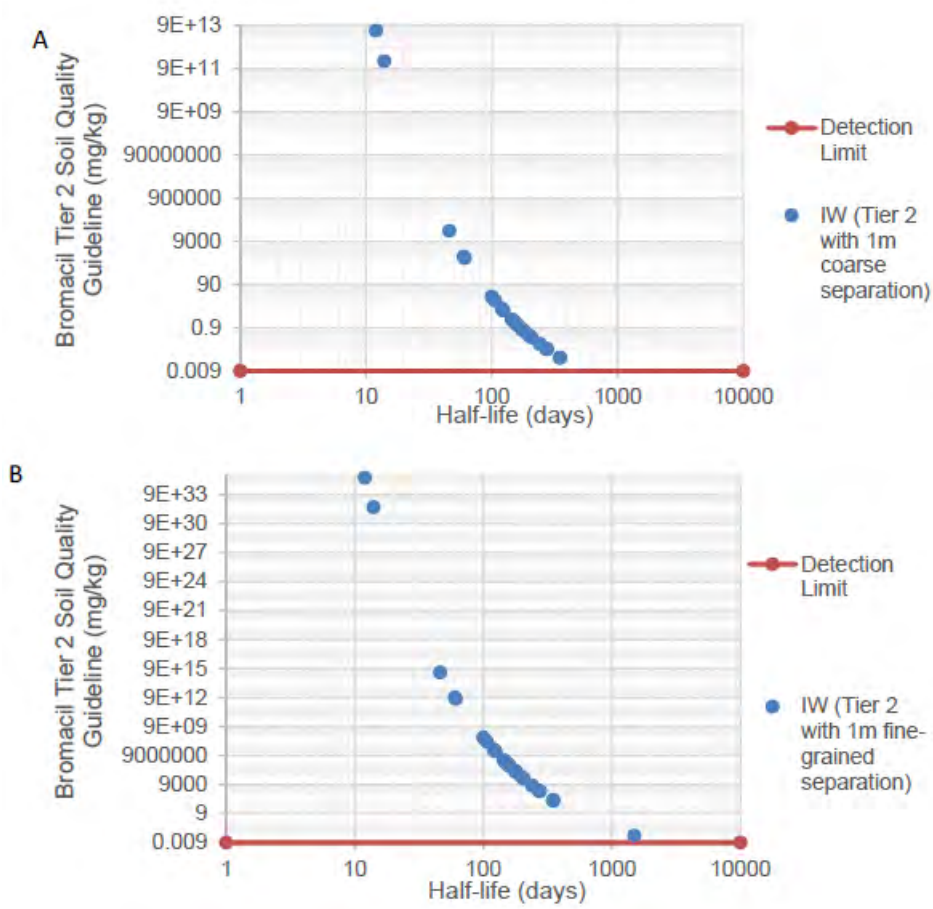

Figure 3: **Tier 2 bromacil soil quality guidelines for the protection of the IW pathway considering 1 m separation with inclusion of literature-derived half-life values.**
(A) for coarse-grained soil, (B) for fine-grained soil.

4.5.1.3 Bromacil Water-Organic Carbon Partition Coefficient (Koc) Literature Review Results

Water-organic carbon partition coefficient, Koc, a partition coefficient normalized to the soil's organic carbon content, is generally used to provide an indication of the mobility of a compound in soil. A Koc of less than 100 indicates that a compound is very mobile (Branham et al., 1995). Most reviewed studies (23 of 32) reported Koc values for bromacil of less than 100 (Figure 4). The most commonly reported Koc range for bromacil is between 30 and 40 mL/g which is cited by several major databases (ARS, 2001; ENSR, 2005a; Helling, 2005;). The Koc value (66.6 mL/g) for bromacil utilized in the development of bromacil Tier 1 screening guidelines using the Domenico model (AEP, 2019) is slightly higher than the most commonly cited value range (30 to 40 mL/g).

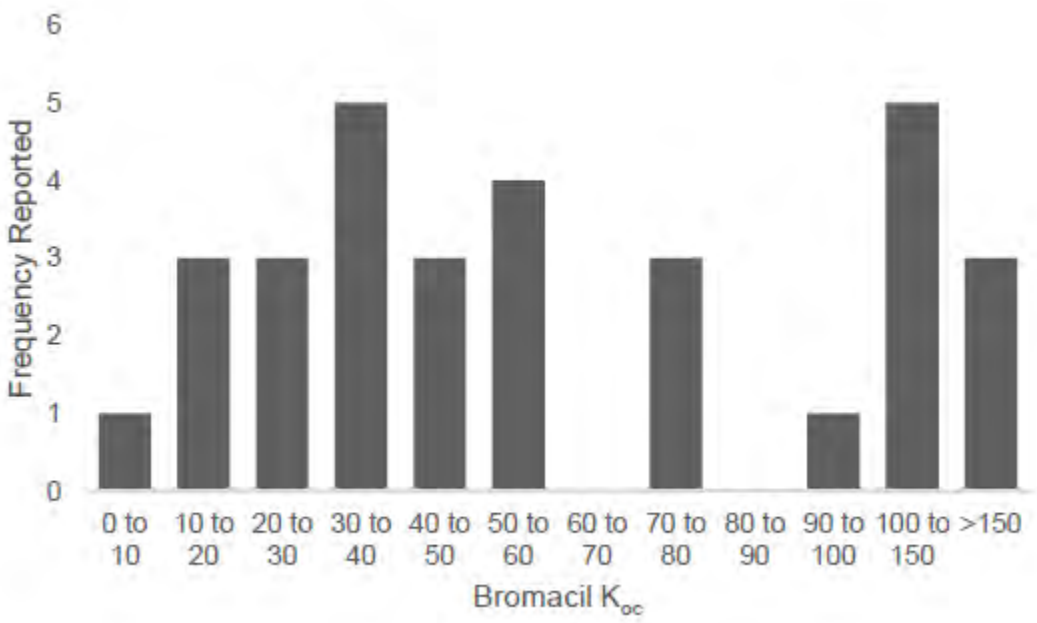

Figure 4: Distribution of Koc values for bromacil identified in the literature review.

There are a limited number of studies reporting a Koc value for bromacil, particularly from studies conducted in temperate regions. Many studies reporting Koc values for bromacil were conducted in Israel, southern United States such as California and Florida, and Spain (Angemar et al., 1984; ARS, 2001; dePaz et al., 2006; Gerstl and Yaron, 1983; Reddy et al., 1992).

A portion of the studies that reported half-lives for bromacil also reported Koc values. For example, Sarmah et al. (2009) reported that bromacil was significantly more mobile in a New Zealand topsoil than in subsoil. One subsoil sample reported a Koc value greater than 1,700 mL/g while topsoil samples reported Koc of 40 to 75 mL/g. Two registrant submitted studies cited in the ARS pesticide database reported Koc values of 2.3 and 109 mL/g for a clay loam in Maryland and a silt loam in Delaware, respectively, demonstrating the Koc of bromacil is highly variable depending on soil type and climatic conditions. Based on these few studies comparable to the Alberta context, a plausible Koc value from the literature is difficult to determine.

4.5.1.4 *Bromacil Water-Organic Carbon Partition Coefficient (Koc) Sensitivity Analysis*

A sensitivity analysis was conducted using the Koc values for bromacil reported in the literature. The values ranged from 2.3 mL/g to 1,768 mL/g, in addition to the current EPA Koc of 66.6 mL/g. For the sensitivity analysis all other "non-chemical" and "chemical" specific parameters applied in the Domenico model used EPA Tier 1 default values (AEP, 2019).

Koc had a moderate impact on the Tier 1 soil quality guideline for the protection of the FAL pathway (Figure 5). In coarse-grained soils, the threshold Koc value required to bring the soil quality guideline above the detection limit was approximately 65 mL/g, whereas in fine-grained soils it was approximately 70 mL/g. Using the current EPA value of 66.6 mL/g, the soil guideline in coarse-grained and fine-grained soils was 0.0094 mg/kg and 0.0088 mg/kg, respectively.

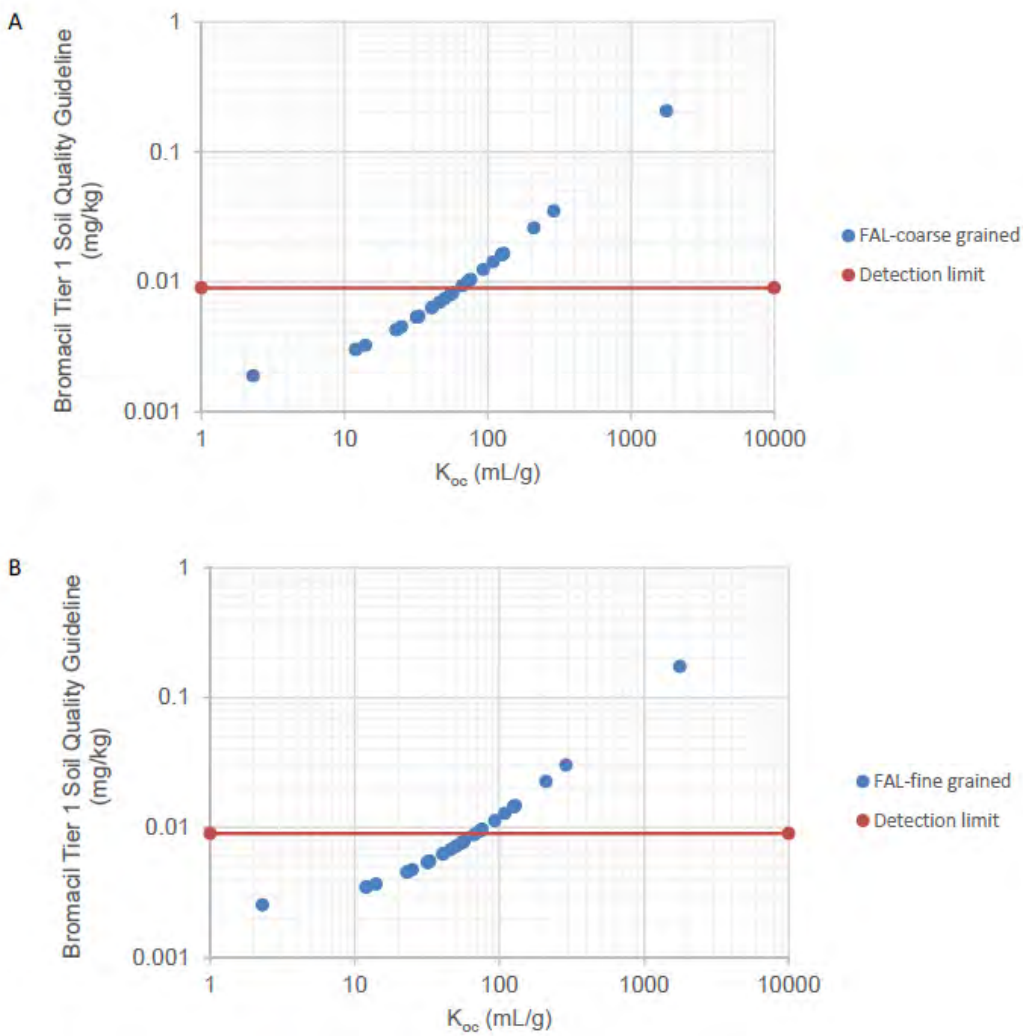

Figure 5: **Tier 1 bromacil soil quality guidelines for the protection of the FAL pathway with inclusion of literature-derived Koc values.**
(A) for coarse-grained soil, (B) for fine-grained soil.

A sensitivity analysis of the impact of Koc on the Tier 1 soil quality guideline for the protection of the IW pathway was conducted. For the sensitivity analysis all other "non-chemical" and "chemical" specific parameters applied in the Domenico model used EPA Tier 1 default values (AEP, 2019).

The irrigation water pathway was not very sensitive to Koc and using even the highest reported value still produced a guideline below detection limit in both coarse- and fine-grained soils (Figure 6).

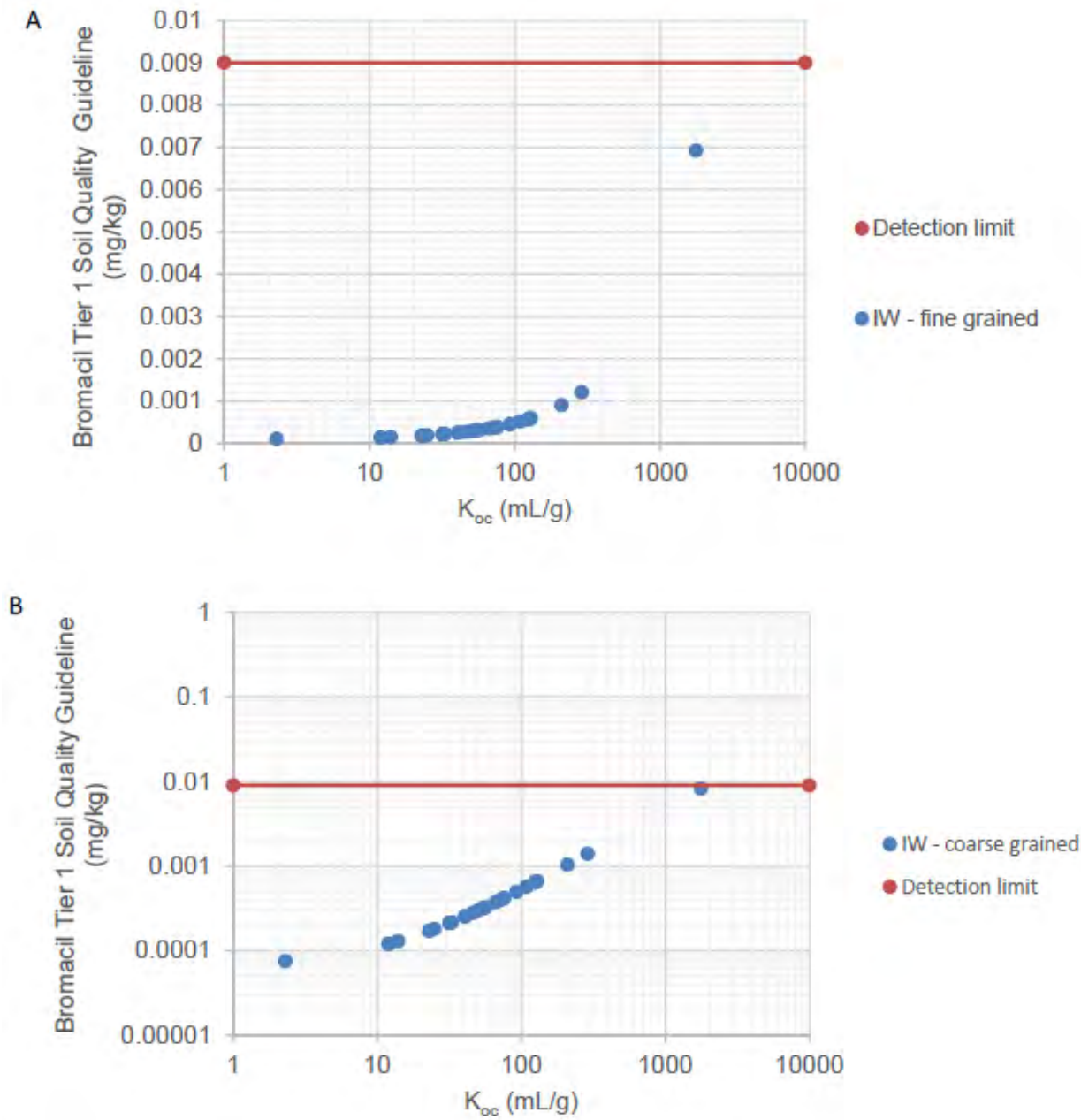

Figure 6: **Bromacil Tier 1 soil quality guidelines for the protection of the IW pathway with inclusion of literature-derived Koc values.**
(A) for coarse-grained soil, (B) for fine-grained soil.

4.5.2 Tebuthiuron

4.5.2.1 Tebuthiuron Half-Life Literature Review Results

The AEP Tier 1 (2019) guidance document does not indicate a half-life, or degradation rate for tebuthiuron.

Most databases report half lives for tebuthiuron of approximately 1 year (ARS, 2001; Beste, 1983; EXTOXNET, 2001). However, values range from 0.033 years (12 days) to 8 years (2,920 days). The most commonly (16 of 58) reported half-life for tebuthiuron is approximately 1 year, however 7 of 58 sources report half lives of less than 50 days and 6 of 58 reported half lives greater than 1,000 days (Figure 7).

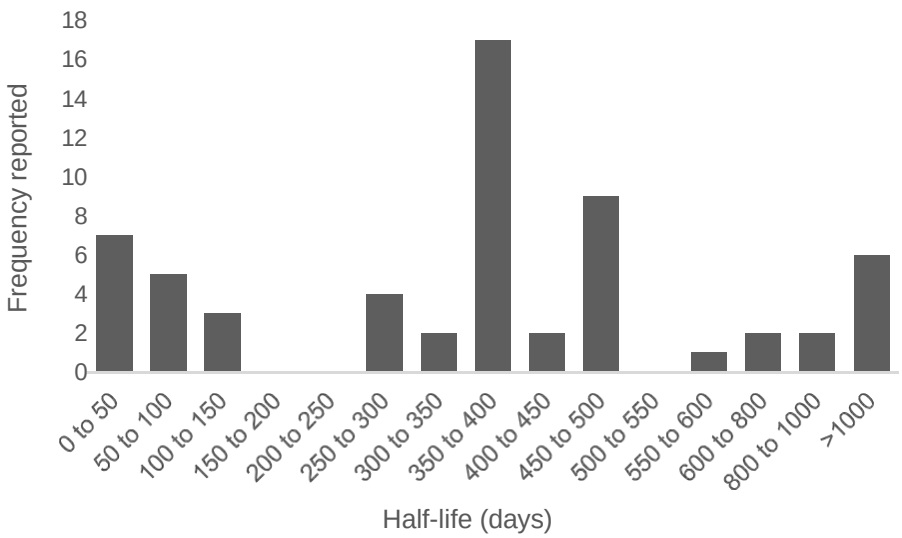

Figure 7: Distribution of half-life values for tebuthiuron reported in the literature.

Like bromacil, half-life values for tebuthiuron are primarily sourced from warmer climates such as India, southern United States including Florida and California, Brazil and South Africa (Lourencetti et al, 2012; Peacock et al, 1995; Raman et al., 1987; Toit and Sekwadi, 2012). Based on the information available, most studies were conducted on surface soil (<1.5 m below ground surface). Significantly shorter half lives are reported in flooded soils and regions that receive greater annual precipitation (Beste, 1983; ENSR, 2005b; Raman et al., 1987). Very few studies on the half-life of tebuthiuron in temperate climates are available and many of the reported values in databases are derived from registrant submitted studies that are not open to the public (ARS, 1999). One study from Greenfield, Indiana reported a field dissipation half-life of 12 to 15 months in a loam (Behl et al., 1999; ENSR, 2005). Another study by Helbert et al. (1990) in a boreal forest in Newfoundland found that tebuthiuron persisted in soils for greater than 486 days. The lack of studies available from cooler climates demonstrates a need for further field dissipation studies of tebuthiuron with Alberta relevance.

4.5.2.2 Tebuthiuron Half-Life Sensitivity Analysis

A sensitivity analysis was conducted using the half-life values reported in the literature for tebuthiuron to determine the impact of these half lives on the soil quality guideline for the protection of the FAL pathway. Half-life values used in the sensitivity analysis were between 0.033 years (12 days) and 8 years.

All other “non-chemical” and “chemical” specific parameters applied in the Domenico model utilized AEP Tier 1 default values (AEP, 2019).

With the incorporation of a half-life of approximately 1 year, the soil quality guideline is increased to 0.0005 mg/kg in coarse-grained soils and 0.008 mg/kg in fine-grained soils. The threshold half-life required to bring the soil quality guideline above the detection limit of 0.001 mg/kg reported by Advisian (2019) is approximately 100 days (0.27 years) in coarse-grained soils and 336 days (0.92 years) in fine-grained soils. This length of half-life was typically associated with saturated soils and is unlikely to be representative of a typical Albertan soil (ENSR, 2005; Koskinene et al., 1996; Qian et al., 2017).

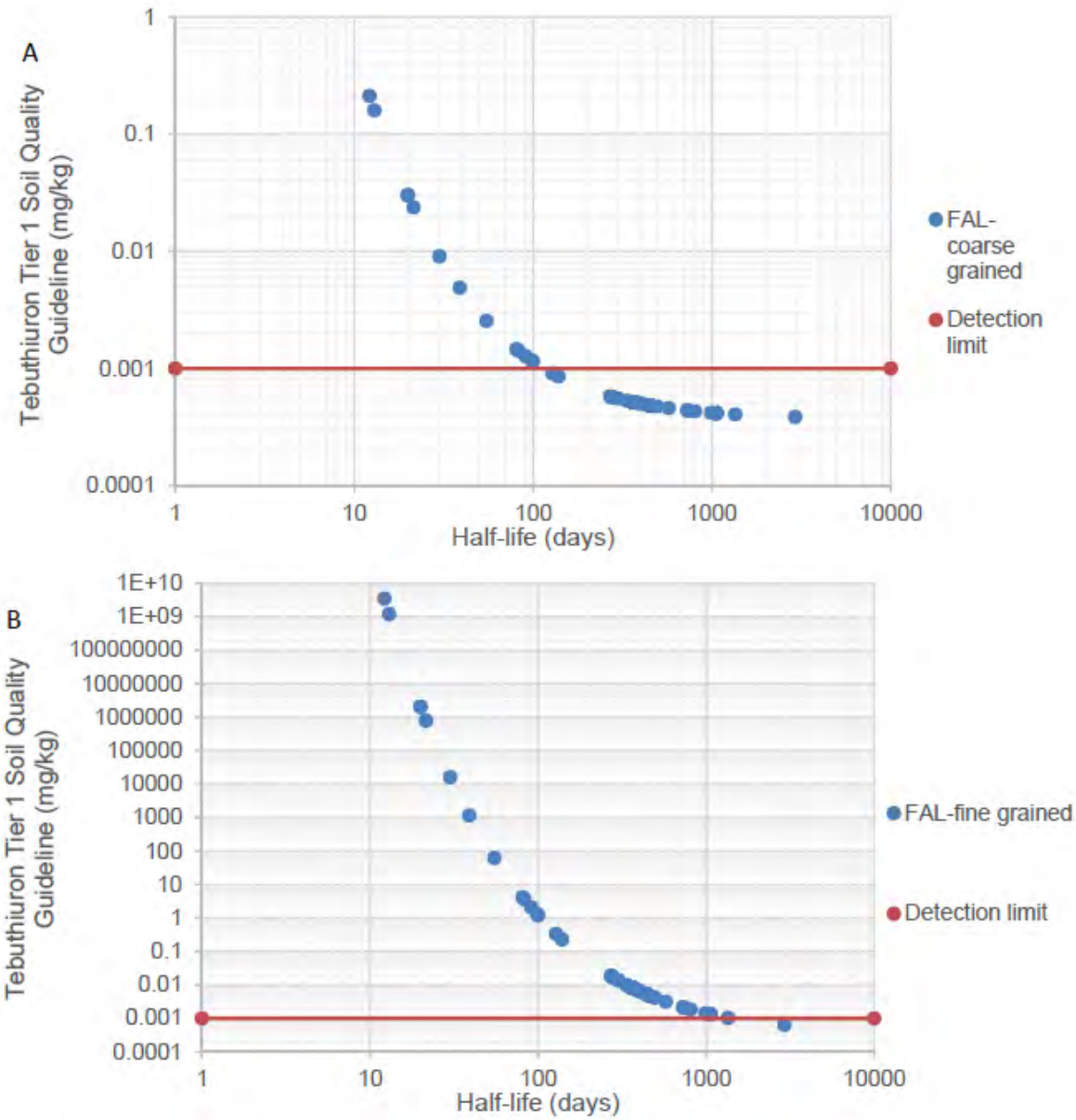

Figure 8: **Tebuthiuron Tier 1 soil quality guideline for the protection of the FAL pathway with inclusion of literature-derived half-life values.**
(A) for coarse-grained soil, (B) for fine-grained soil.

Under a Tier 1 scenario, the inclusion of a half-life into the Domenico Model does not have an impact on the soil quality guideline for the protection of the IW pathway, as both DF2 and DF4 have a default value

of 1. However, applying a simple Tier 2 approach (i.e. DF2>1) allows for the inclusion of a half-life for tebuthiuron to have a meaningful impact on the soil quality guideline for the IW pathway.

As an example, Tier 2 soil quality guidelines for tebuthiuron for the protection of the IW pathway were evaluated considering the literature reported half-life values and 1 m of coarse-grained or fine-grained separation between base of tebuthiuron impact and the shallowest potential IW groundwater source. The results indicated that with the incorporation of a realistic half-life of 1 year, the soil quality guideline increased to 0.004 mg/kg in coarse-grained soil and 1.8 mg/kg in fine-grained soil. These values are above the detection limit of 0.001 mg/kg for tebuthiuron.

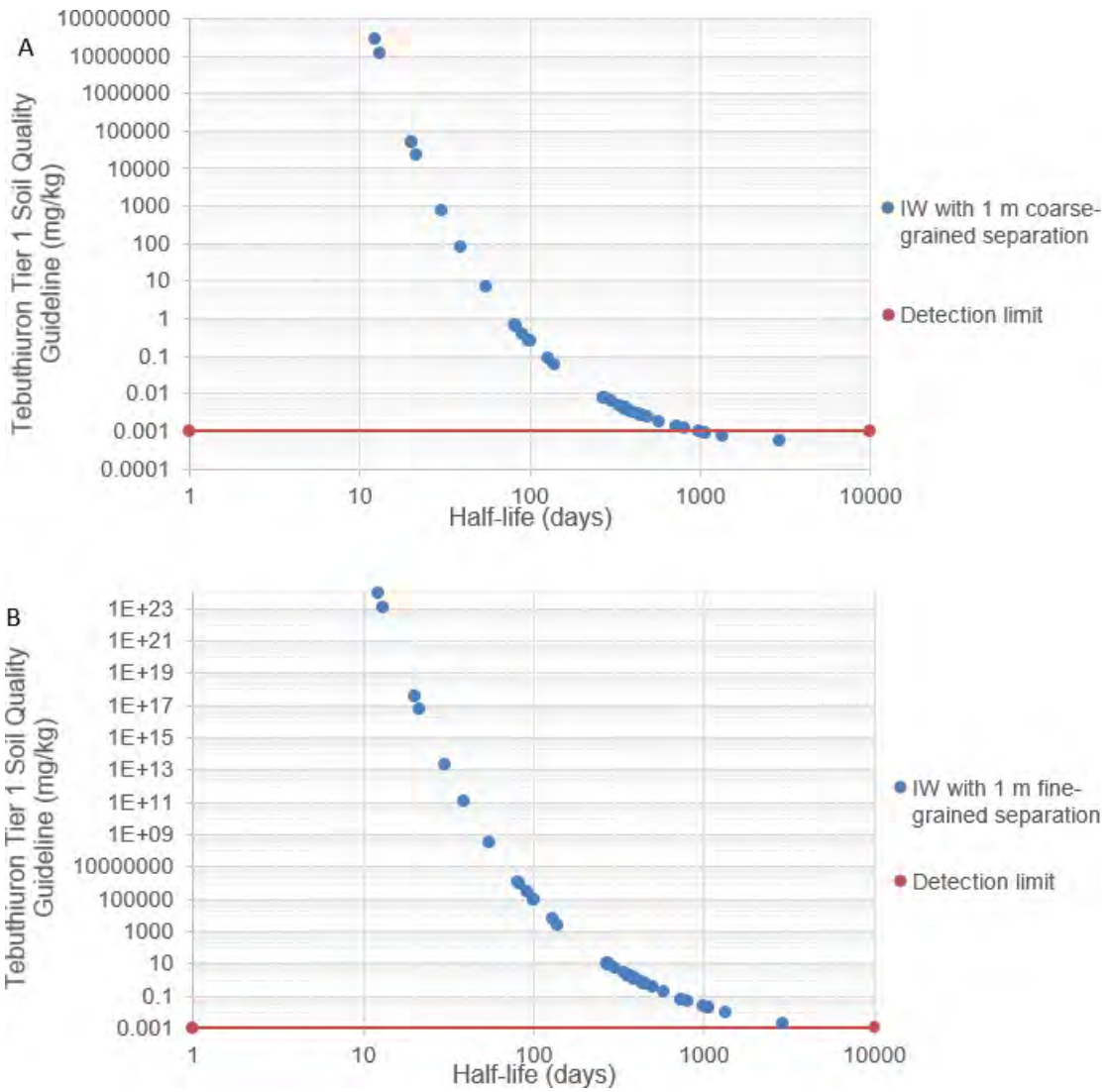

Figure 9: **Tebuthiuron Tier 2 soil quality guideline for the IW pathway and 1 m of separation with the inclusion of literature-derived half-life values.**
(A) for coarse-grained soil, (B) for fine-grained soil.

4.5.2.3 Tebuthiuron Water-Organic Carbon Partition Coefficient (Koc) Literature Review Results

The Koc value for tebuthiuron typically cited in databases was 80 mL/g. Koc values cited in the literature range from 2.7 mL/g to 620 mL/g, but 25 of 34 sources reported Koc values less than 100 mL/g demonstrating that tebuthiuron is very mobile in soils. The most commonly cited value in the literature, 80 mL/g is higher than the value 23 mL/g reported in Table C6 of the Alberta Tier 1 guidelines.

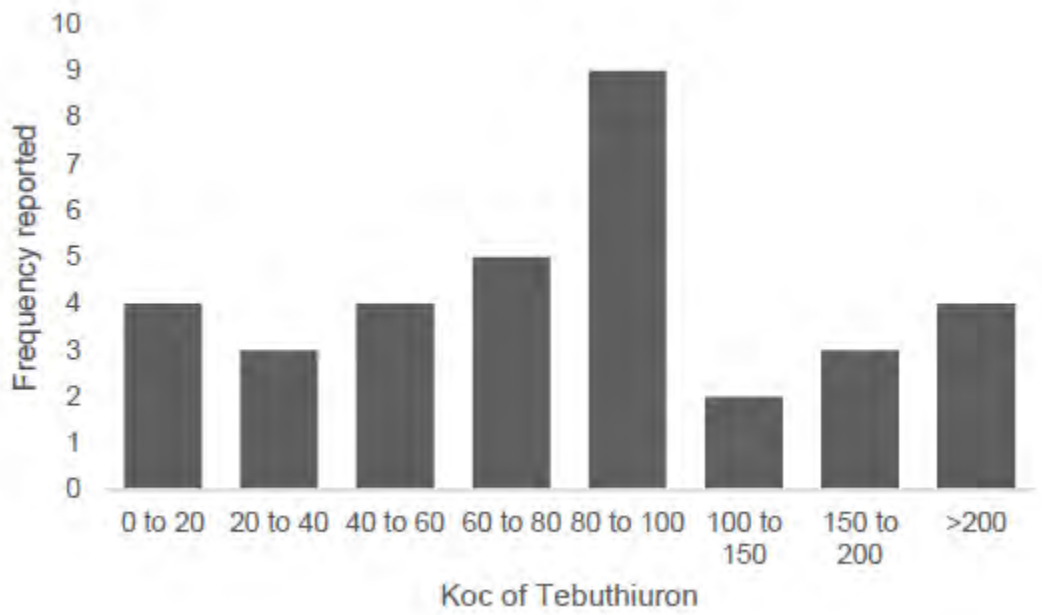

Figure 10: Distribution of Koc values for tebuthiuron reported in the literature.

The majority of the Koc values come from the ARS pesticides properties database (2001) and are derived from registrant-submitted studies. Primary research papers are typically from tropical areas such as Brazil and Australia (Lourencetti et al., 2012; Mercurio et al., 2016). In a series of studies presented in the ARS pesticides properties database (2001), Koc values typically increased with clay content in soil (38 mL/g for sand, 77 mL/g for sandy loam, 79 mL/g for loam, and 157 mL/g for clay loam). Very little data was available to support a Koc relevant to the Alberta context suggesting that further studies are necessary.

4.5.2.4 Tebuthiuron Water-Organic Carbon Partition Coefficient (Koc) Sensitivity Analysis

A sensitivity analysis was conducted using the Koc values reported in the literature for tebuthiuron to determine the impact of Koc on the soil quality guideline for the protection of the FAL pathway. Koc values between 2.7 mL/g and 620 mL/g, in addition to the current AEP value of 23 mL/g were used. For the sensitivity analysis all other “non-chemical” and “chemical” specific parameters applied in the Domenico model utilized EPA Tier 1 default values (AEP, 2019).

With the current value of 23 mL/g, the soil quality guideline is 0.00037 mg/kg and 0.00039 mg/kg in coarse-grained and fine-grained soils, respectively. Using the Koc value commonly cited in the literature, 80 mL/g, the soil quality guideline increases to 0.00094 mg/kg and 0.00086 mg/kg in coarse- and fine-grained soils, respectively, which approaches the detection limit of 0.001 mg/kg. However, a Koc value of 90 mL/g or greater is required to bring the soil quality guideline above the detection limit in coarse-grained soils and 100 mL/g in fine-grained soils.

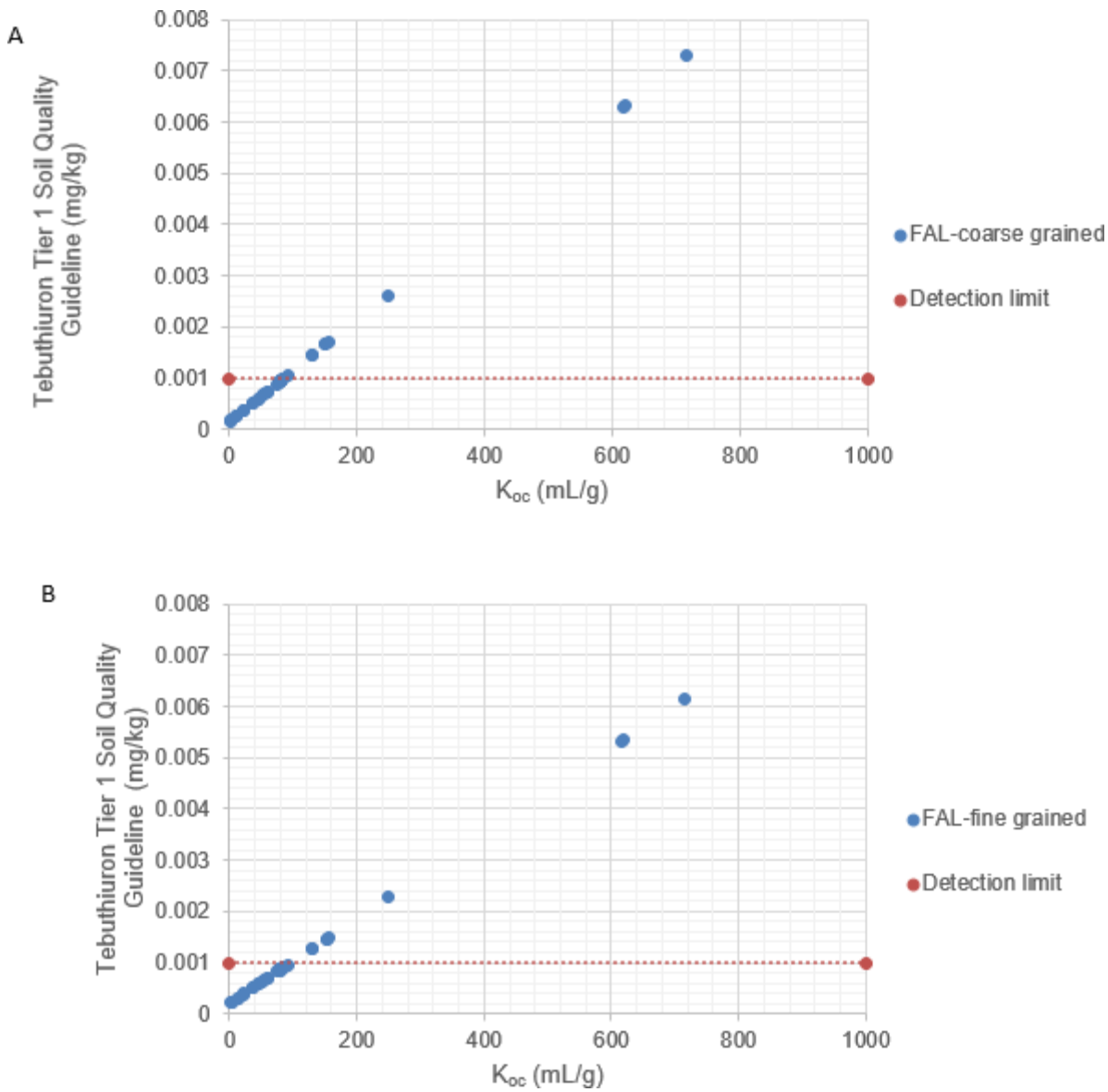

Figure 11: Tebuthiuron Tier 1 soil quality guidelines for the protection of the FAL pathway with inclusion of literature-derived Koc values.
(A) for coarse-grained soil, (B) for fine-grained soil.

Soil quality guidelines for the protection of the IW pathway were also evaluated with respect to Koc values reported in the literature. Applying the Koc value of 23 mL/g currently used in Tier 1 guideline development results in a soil quality guideline of 0.00039 mg/kg in fine-grained soils and 0.00037 mg/kg in coarse-grained soils. Applying the accepted value of 80 mL/g resulted in coarse-grained and fine-grained soil quality guidelines of 0.00094 mg/kg and 0.00086 mg/kg, respectively. Neither value raises the soil guideline above the detection limit of 0.001 mg/kg. The minimum necessary Koc value would be approximately 90 mL/g and 100 mL/g in coarse- and fine-grained soils, respectively.

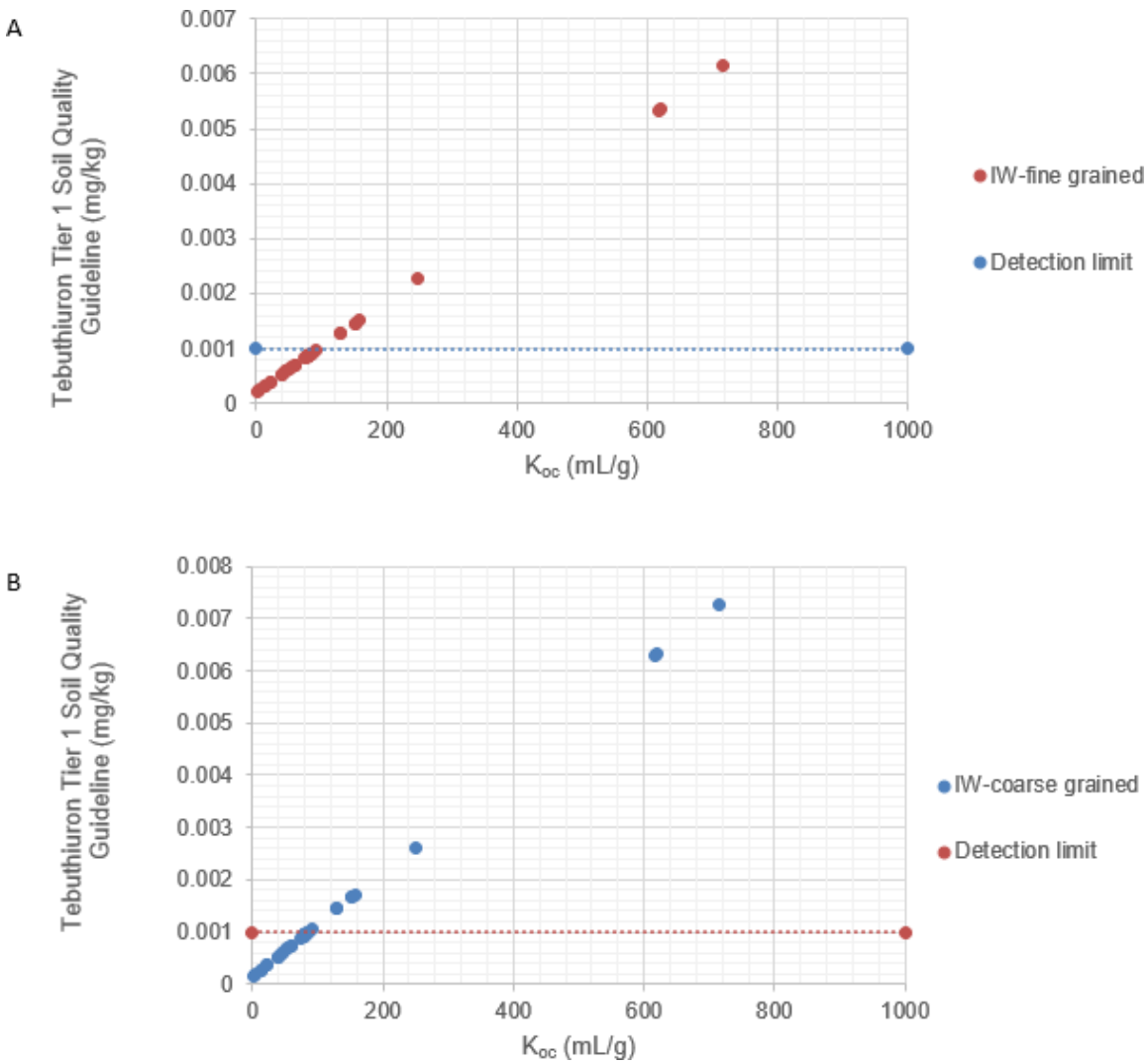

Figure 12: **Tebuthiuron Tier 1 soil quality guideline for the protection of the IW pathway with inclusion of literature-derived Koc values.**
(A) for coarse-grained soil, (B) for fine-grained soil.

5 SUMMARY AND CONCLUSIONS

Both bromacil and tebuthiuron are soil sterilants which have been used extensively in the past at upstream oil and gas sites for weed management. Current Alberta Tier 1 soil quality guidelines for the protection of the FAL and IW pathways are below, or close to laboratory detection limits for both herbicides. The Alberta Tier 1 guidelines are based on a highly conservative approach which present a challenge to site reclamation with respect to these two chemicals.

The overall objective of this project was to determine appropriate risk model(s) and model parameters to develop screening guidelines for bromacil and tebuthiuron deemed to be protective of the IW and FAL pathways which better reflect the contaminants "real-world" fate and mobility in the subsurface under Alberta field conditions. The purpose of Milestone #1 described here, was to contribute to the overall

objective of the project by conducting an evaluation of the current Alberta Tier 1 model for the IW and FAL pathways for bromacil and tebuthiuron.

First, the Sterilant-Specific Model Input Data completed by Advisian (2019) was reviewed. It was determined that the "chemical-specific" parameters to which the Domenico model was most sensitive to were half-life and Koc, consistent with MEMS conclusion. A literature review of ecotoxicity data, half-life, and Koc for both bromacil and tebuthiuron was then conducted with a focus on research published since the development of current Alberta Tier 1 guidelines.

There have been a significant number of studies published that explore the ecotoxicity of bromacil and tebuthiuron to aquatic species and terrestrial plants; however, most pre-date the development of the current Alberta Tier 1 guidelines for these two chemicals. Of historically published papers, ecotoxicological data is generally in agreement with current Alberta Tier 1 surface water quality guidelines, though more recent data is noted to generally focus on tropical species.

Similarly, many studies have examined the degradation and dissipation of bromacil and tebuthiuron both in lab and field settings, providing useful "chemical-specific" data. Half-life values for bromacil and tebuthiuron were generally reported as 0.5 to 0.75 years for bromacil and 1 to 2 years for tebuthiuron. The Koc values were generally reported at 32 mL/g for bromacil and 80 mL/g for tebuthiuron. Variations were apparent based on soil physical characteristics and regional climatic conditions.

Using "chemical-specific" parameter ranges identified in the literature review for half-life and Koc a sensitivity analysis of the FAL and IW Tier 1 soil quality guidelines using the current Alberta Tier 1 model was conducted.

It was determined that incorporation of a half-life for bromacil could increase the FAL pathway soil quality guidelines meaningfully above detection as well as provide potentially beneficial results for the IW pathway under a Tier 2 approach. Generally, literature derived Koc values for bromacil were consistent with the current value used in Alberta Tier 1 guideline development. Thus, the incorporation of bromacil Koc values reported in the literature into the Alberta Tier 1 model resulted in derived Tier 1 soil quality guidelines generally consistent with current Alberta Tier 1 guidelines.

For tebuthiuron, the incorporation of a half-life into Tier 1 guideline derivation allows for both the FAL and IW pathway guidelines to be raised above laboratory detection limits. Generally, literature derived Koc values for tebuthiuron were consistent with the current value used in Alberta Tier 1 guideline development and did not provide a meaningful difference when considered alone.

The literature review indicated the number of recent studies on the dissipation and migration of bromacil and tebuthiuron in soils are limited and generally focus on tropical climates where these soil sterilants are still used extensively in agriculture. The review indicates, at minimum, the incorporation of a defensible half-life parameter into guideline development for both bromacil and tebuthiuron would be beneficial, though additional studies with an Alberta context are likely required to ensure any adopted parameter is scientifically defensible.

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APPENDIX A: LITERATURE SEARCH TERMS AND NOTES

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
Adrian et al., 1990	Primary research paper. The dissipation of bromacil was studied under several anaerobic conditions including denitrifying, sulfate-reducing, and methanogenic. Bromacil was only degraded under methanogenic conditions suggesting that microbial degradation is primarily mediated by this pathway.		y				
AEP 2017	Government report. Provides guidance for selecting toxicity reference values for Alberta Tier 1 and Tier 2 Soil and Groundwater Remediation Values.						
Alavi et al., 2008	Primary research paper. Study of the movement of bromacil in a pineapple field in Oahu, Hawaii. Leaching of bromacil was investigated following two different application rates of 2.25 and 1.8 kg/ha. Over a period of 9 months, there was significant dissipation of bromacil in topsoil.		y				
Allan et al., 2017	Primary research paper. Determined the concentration of herbicides, including tebuthiuron, in beach sand adjacent to sugarcane crops and conducted a cell-based assay to determine the toxicity of the herbicides on sea turtle species that nest on the beach.				y		
Almeida et al., 2014	Primary research paper. Ecotoxicity study of tebuthiuron on tilapia of various ages, based on mortality and genotoxicity. A high mortality rate was observed in fish exposed to 250 mg/L tebuthiuron. Genotoxic effect were observed in small fish exposed to 125 mg/L.				y		
Angemar et al., 1984	Primary research paper. The behaviour of bromacil in soil was studied using four Israeli soils. Adsorption was determined using batch slurry experiments, phytotoxicity was studied using a bioassay with black mustard, soil leachability was determined using soil thick layer chromatography and dissipation was also determined.			y			
ARS, 2001	Database. United States Department of Agriculture (USDA) pesticides properties database as updated by 2001. Provides registrant submitted chemical specific data as well as other EPA study results, experiments, and reviews. Includes chemical specific data for bromacil and tebuthiuron including: boiling point, melting point, hydrolysis and photolysis, solubility, Kow, Kd, and Koc values, and field dissipation half-life.		y	y		y	y
Ashton et al., 1969	Primary research paper. Seeds were germinated in a solution containing bromacil in order to assess the impacts on root elongation, and development. Root elongation was inhabited with bromacil concentrations as low as 1x10^-6 M.						
Baur et al., 1977	Primary research paper. A field study of the impacts of tebuthiuron on Bermuda grass and Kleingrass was conducted in a claypan region of Texas. Application rates of 2.2 kg/ha inhibited the establishment of kleingrass but had no significant impact on Bermuda grass.				y		
Beste, 1983	Book. Herbicide handbook of the weed science society of America. Provides chemical specific information on both bromacil and tebuthiuron.	`	y			y	
Branham et al., 1995	Primary research paper. Study of groundwater contamination from golf courses using lysimeters.						
Call et al., 1983	Government report. US EPA study of the toxicity of five herbicides including bromacil on freshwater fish. Acute and chronic toxicity tests were conducted in rainbow trout, fathead minnows as well as the invertebrate *Daphnia magna* . LC50 for fathead minnows was 182 mg/L, no effects level was less than 1.0 mg/L.	y					

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
Call et al., 1987	Primary research paper. The toxicity of bromacil on freshwater fish was investigated by exposing eggs, newly hatched fry, and juvenile fish to various concentrations of bromacil for periods of 24, 48, 96, and 168 hours. Growth was impacted by concentrations as low as 1.0 mg/L.	y					
CCME, 1999a	Government report. Background on bromacil is reviewed as well as chemical characteristics and water quality guidelines for the protection of freshwater aquatic life derivation. Cited ecotoxicology demonstrates that bromacil is not very toxic to fish or invertebrates, but aquatic plants and algae are sensitive. The guideline is set to 5.0 µg/L based on protection of aquatic plants and algae's which is the product of the lowest LC50 cited by Cullimore (1975) and a safety factor of 0.1. The EC50 value for growth inhibition ranged from 0.05 mg/L for *Haematococcus lacustris* to 10 mg/L to *Chlorella vulgaris* .	y					
CCME, 1999b	Government report. Chemical characteristics and freshwater aquatic life guideline derivation are reviewed for tebuthiuron. Toxicity values are reviewed. Tebuthiuron is relatively non toxic to fish and invertebrates but EC50 values for plants and algae ranged from 0.08 mg/L to 0.307 mg/L (Meyerhof et al., 1985). The guideline of 1.6 µg/L is the product of the lowest LOEL (lowest effects level) for *Selenastrum capricornutum* and a safety factor of 0.1.						
CCME, 1999b	Government report. Bromacil is reviewed in the context of an agricultural setting. Toxicity values for several crop species are discussed. Species maximum acceptable toxicity concentration (SMATC) was generally 0.6 µg/L to 1 µg/L for cereals, and pastures, and 0.2 µg/L for other crops. The water quality guideline for bromacil of 0.2 µg/L is based on the lowest calculated SMATC for cucumbers.	y					
CCME, 1999c	Government report. Tebuthiuron is reviewed in the context of an agricultural setting. Limited toxicity data was available and the water quality guideline of 0.27 µg/L is based on the SMATC for wheat due to a lack of available studies on non-cereal crops.						
Cerdeira et al., 2007	Primary research paper. A study of leaching and degradation of tebuthiuron in a sugar cane field was conducted in Brazil. Trial plots containing sandy soil were either planted with sugar cane or not , and were exposed to tebuthiuron. Tebuthiuron did not migrate below 40 cm over the course of the experiment and the reported half-life was 20 days. Experiment duration was 300 days.				y	y	
Cohen et al., 1984	Review. Synthesis of studies conducted by state agencies, pesticide registrants and university scientists on the presence of pesticides in groundwater in the United States and their behaviour in soil.			y			
Corwin et al., 1984	Primary research paper. Study of the adsorption and desorption of bromacil and diquat to freshwater sediments. Bromacil's non-single value adsorption-desorption isotherms were well described by Freundlich equations. Koc values for Bromacil ranged from 26.3 to 289.1 mL/g with and average of 41.1+/- 12.5 mL/g (n=8). The soil reporting the highest Koc value had a low organic carbon content suggesting that mineral soil may contribute significantly to the adsorption of bromacil to soil.			y			
Cullimore, 1975	Primary research paper. Invitro sensitivity testing of 17 Chloriphycea algal strains to herbicides. Of the 14 herbicides studied bromacil was the second most toxic. Hormidium and Haematococcus were the most sensitive algal species.	y					
dePaz and Rubio, 2006	Primary research paper. A GIS-AF/RF model for herbicide leaching was developed. It involved a case study of a citrus orchard in Valencia Spain. One of the herbicides studied was bromacil, it was one of the herbicides noted for its high mobility and risk of leaching.	y		y			

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
Dube et al., 2011	Review. Study of the impact of the use of bromacil for the control of invasive acacia in South Africa. Acacia impacts the productivity of rangelands, so bromacil has been historically used to manage it. Based on concentration of application you can select for species control, broadleaved species being more susceptible. Provides background on mobility in soil, bioavailability, and persistence. Cited half lives include: 2-8 months based on Fishel, 2005 and Meister, 1998. Koc of 32 mL/g based on de Paz and Rubio, 2006 and EXTOXNET, 1993 and Gomez de Barreda et al., 1998. Based on James and Lauren, 1995, bromacil adsorbs to organic matter and is less mobile in soils with 5% or more organic carbon. It is noted that soils with high organic matter content can retain bromacil for 1 to 2 year. Soils with low organic carbon content have a half-life of 3 to 7 months (EXTOXNET, 1993, Paz and Rubio, 2006). Sander et al., 1996 report bromacil degraded within 4 to 6 months when applied only once in a season. Alavi et al., 2008 reported that bromacil persisted in the top 75 mm of soil for nearly a year. The review also discusses the economics of the use of bromacil and how	y					
Durkin, 2016	Government report. The report is a human health and ecological risk assessment. Tebuthiuron is reviewed extensively in the context of the US department o forestry's use of the sterilant to mange woody invasive species. The ecological risk assessment includes a review of ecotoxicity values for tebuthiuron, of particular interest, terrestrial plants and aquatic plants. The study notes that toxicity is reduced with higher organic carbon content. Chemical specific parameters are also reviewed in the context of modelling scenarios applied in the risk assessment.				y		y
Echeverria-Saenz et al., 2018	Primary research paper. Study of the *in situ* toxicity of pesticide runoff, including bromacil, in the riviera Madre de Dios in the Caribbean Sea on fish, *Daphnia magna* , and aquatic macroinvertebrate community structure. Only macroinvertebrate communities showed were significantly impacted by the presence of bromacil and other pesticides.	y					
EFED Pesticide Ecotoxicity Database	Database. Ecological Fate and Effects Division of the US EPA Office of Pesticides Program. Provides ecotoxicity data for tebuthiuron.				y		
Emmerich et al., 1984	Primary research paper. Field dissipation study of tebuthiuron on rangeland plots where 0.84 kg/ha was applied. After 21 months, 38% had dissipated, tebuthiuron was not detectable after 2.9 to 7.2 years following initial application.					y	
ENSR, 2005a	Government Report. Ecological risk assessment for bromacil. Provides a description of the activity of bromacil, its historical and current use. Pathways for environmental contamination are discussed and evaluated using three models: AgDRIFT, GLEAMS, and CALPUFF. Toxicological data was reviewed as well as physical-chemical properties and environmental fate (Table 3-2). Toxicological data (Table 3-1) is included for terrestrial organisms including mammals, birds, invertebrates, and plants, as well as aquatic species including fish, amphibians, invertebrates, and plants.	y	y	y			
ENSR, 2005b	Government Report. Ecological risk assessment for Tebuthiuron. Provides a description of the activity of tebuthiuron, its historical and current use. Pathways for environmental contamination are discussed and evaluated using three models: AgDRIFT, GLEAMS, and CALPUFF. Toxicological data was reviewed as well as physical-chemical properties and environmental fate (Table 3-2). Toxicological data (Table 3-1) is included for terrestrial organisms including mammals, birds, invertebrates, and plants, as well as aquatic species including fish, amphibians, invertebrates, and plants.				y	y	y

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
EXTOXNET, 1993a	Database. Extension Toxicology Network is a pesticide information project of Cornell, UC Davis and Michigan State Universities. Pesticide Information Profile for Bromacil. Provides human toxicity data, ecological toxicity parameters for birds and aquatic animals. Provides a brief description of environmental fate in soil and water and lists a half-life of 60 days, but cites that half-life may be as high as 8 months (Wauchope et al., 1992). Also sites US national library of medicine (1995) for studies of persistence in soil. Also lists several Koc values of ranging from 32 mL/g to 210 mL/g.						
EXTOXNET, 1993b	Database. Extension Toxicology Network is a pesticide information project of Cornell, UC Davis and Michigan State Universities. Pesticide Information Profile for Tebuthiuron Provides human toxicity data, ecological toxicity parameters for birds and aquatic animals. Provides a brief description of environmental fate in soil and water and lists a half-life of 360 days. Also lists a Koc value of 80 mL/g.						
Fishel, 2005	Report. Brief report on the agricultural use of bromacil, its background, and chemical specific parameters.		y				
Flury et al., 1996	Review. Review of pesticide transport in soils with a focus on leaching to groundwater. Discusses general trends as well as chemical specific observations.					y	y
Gao et al., 2018	Review. Review of the structure and function of the photosystem complexes. Discusses photosystem II which is the target of bromacil and tebuthiuron.						
Gardiner et al., 1969	Primary research paper. The dissipation of radio labelled bromacil was studied in a Butlertown silt loam. The half-life was determined to be 5 to 6 months.		y				
Geiger et al. (1988),	Book chapter. Review of acute toxicity values for organic chemicals to fathead minnows. Includes values for bromacil.	y					
Gerstl and Yaron, 1983	Primary research paper. Bromacil and Napropamide adsorption and degradation were studied in Israeli soils. Bromacil adsorption was low but correlated strongly with soil organic carbon and slightly with clay content. Use of Kow gave more accurate predictions than solubility. Degradation was studied at various soil moisture, temperature and initial concentrations. A half-life of 14 to 1494 days was determined.		y	y			
Helbert et al., 1990	Primary research paper. Study of tebuthiuron and other herbicide behaviour in boreal podzols in northeast central Newfoundland. Herbicides were applied to clear-cut plots and soil horizons were sampled 486 days following application. The concentration of herbicide residues was significantly higher in those soil horizons with higher organic carbon content. Tebuthiuron persisted in the soil for greater than 486 days.					y	
Helling, 2005	Review. The impacts of soil, weather, field management, and herbicide chemistry are explored in order to estimate the persistence of herbicides in soils from temperate regions. The objective was to be able to assess carrying of herbicides from one crop rotation to the next in order to manage plant injury.		y	y		y	y
Hilton and Nomura, 1964	Primary research paper. The toxicity of several herbicides including bromacil was investigated with respect to cucumber, sorghum, and wheat species. It was determined that sorghum was generally a less sensitive species than cucumber and wheat. Cucumber was the most sensitive and reported lethality to bromacil at 1.9 x 10^-7 M.	y					
Holm and Johnson, 2010	Review. Brief history of herbicide use in western Canada. Bromacil was used from 1963 to 1977 and is a soil sterilant acting on PSII causing photosynthesis inhibition. Tebuthiuron was used from 1965 to 1977 and is also a PSII inhibitor.						
Jollifee et al., 1967	Primary research paper. The paper describes the development of gas-liquid chromatography for the determination of bromacil concentrations in soil.		y				

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
	Crop residues were evaluated.						
Kidd and James, 1990	Book. Agrochemicals handbook. Describes chemical properties of common herbicides including tebuthiuron.						y
Knisel and Davis, 2000	Government Report. User manual for the GLEAMS driver (Groundwater Loading Effects of Agricultural Management Systems)						y
Koskinen et al., 1996	Primary research paper. The sorption of tebuthiuron and two other compounds was examined under acidic and basic conditions in sand. The reported Koc value for all soils was 39 +/- 22 L/kg. It was also noted that retardation of herbicide movement occurred primarily in the top 10 cm of soil.					y	y
Landsburg and Dwyer, 1995	Primary research paper. Study of bromacil dissipation in humic luvic gleysols in northwestern Alberta. The paper cites several authors for the half-life and environmental behaviour of bromacil. Results include the variability of organic carbon throughout the soil profile as well as bromacil concentrations immediately following the application and two years later. Half-life can be calculated.		y				
Leistra et al., 1975	Primary research paper. Study of two apple orchards that were treated with bromacil annually for 6 or 7 years. Leaching and persistence was examined. 35% of bromacil dissipated in one year. The highest concentration of bromacil was found between 10 to 20 cm bellow ground surface.		y				
Lourencetti et al., 2012	Primary research paper. The leaching and degradation of tebuthiuron and other herbicides is examined in a sugar cane field kept either bare or supplemented with sugar cane vinasse. Both sandy and clay soils were used under standard lab conditions. The addition of sugar cane vinasse significantly decreased the half-life of the herbicides.					y	y
MacBean et al., 2008	Book. Pesticide manual.						
Madhun et al., 1986	Primary research paper. Involved a lab study of bromacil degradation using C14. Half lives were determined at 25, 30, 35 Celsius and demonstrated that temperature has a significant impact on degradation rate (3x faster at 35 than 25C).			y			
Magnusson et al., 2013	Primary research paper. The acute toxicity of sediments contaminated with herbicides (including bromacil) to benthic microalgae was examined in Queensland Australia. Phytotoxicity was measured using PAM fluorometry. Herbicide toxicity was compared to diuron as a standard. Results demonstrated that microalgae are impacted by environmentally relevant concentrations.	y					
Menzie et al., 1978	Government report. Review of the metabolism of pesticides.		y				
Mercurio et al., 2016	Primary research paper. Study of the half-life of tebuthiuron (and other pesticides) in seawater. A flask experiment lasting 60 days or 365 days as well as an outdoor tank experiment was conducted. Tebuthiuron had the longest half lives of 433 to 5214 days for the flask experiment and 1766 days in the outdoor tank experiment.						y
Montgomery, 1997	Book. Agrochemicals Desk Reference						y
Moura and Jonsson, 2016	Primary research paper. Acute toxicity of tebuthiuron and other herbicides singly or in mixtures on tilapia fingerlings was examined. Tebuthiuron produced an LC50 value of 260 mg/L but mixtures resulted in a lower toxicity value.				y		
Nahhal and El-Hams, 2017	Primary research paper. Lab based ecotoxicology study of cyanobacterial mats exposed to bromacil and other herbicides/pesticides. Bromacil significantly impacted the growth of cyanobacterial mats.	y					

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
Nahhal and Hamdona, 2015	Primary research paper. Greenhouse study of phytotoxicity of alachlor, bromacil, and/or diuron singly or in mixtures, on melon, molokhia and wheat. EC50 graphs are shown. Phytotoxicity of bromacil was reported with an EC50 of 4.77 mg/kg for melon; 0.08 mg/kg for molokhia, 3.08 for wheat.	y					
Niebch, 2013	Primary research paper. Phytotoxicolgy study of sorghum in soil treated with bromacil and other herbicides used in the Florida citrus industry. The observed LOEC was 0.1 mg/kg.	y					
NIOSH, 2016	Database/Facts sheet. National Institute for Occupational Safety and Health. Lists formulation of bromacil, their characteristics, toxicity and safety measures.						
NLM, 2020a	Database. US National Library of Medicine-PubChem review of Bromacil. Chemical specific parameters are listed including physical properties, chemical properties, environmental fate, and toxicity. Koc is listed to range from 12 to 126 mL/g. half-life is listed as 60 days based on the ARS database, but studies are also referenced with half lives from 4 months to 8 months. EPA ecotoxicity data is also available for download.	y	y	y			
NLM, 2020b	Database. US National Library of Medicine-PubChem review of Tebuthiuron. Chemical specific parameters are listed including physical properties, chemical properties, environmental fate, and toxicity. Koc is listed at 67.6 L/kg but cites Koc values from 2.70 to 130 mL/g. Half-life is listed as 12 to 15 months but cites sources reporting half-lives of up to 9 years.				y	y	y
O'Neil et al., 2006	Book. The MERCK Index, provides herbicide chemical specific information by the Royal Society of Chemistry.						
Peacock et al., 1995	Primary research paper. Field study of the dissipation of tebuthiuron. The half-life of tebuthiuron in soil from Live Oak, Florida, Davenport, California, and Mead, Nebraska were determined to be 383, 806, and 575 days respectively.					y	
Qian et al., 2017	Primary research paper. A new method was developed for the environmental detection of tebuthiuron with the goal of minimizing risk to aquatic ecosystems. Field dissipation and ecotoxicity studies (earthworms) were completed in conjunction with the above goal. Tebuthiuron dissipated via a first order rate model and showed a half-life of 12.2 to 21.5 days in a sugarcane field.					y	
Rainey and Magnussen, 1976	Primary research paper. Study of the photodegradation of tebuthiuron. After 15 days, 42.5% of tebuthiuron was photodegraded.					y	
Rakewhich and Baker, 2017	Presentation. Presentation by Nichols environmental at remediation technologies symposium (2017). Provides background on environmental parameters of pesticides, lists parameters for bromacil dicamba, tebuthiuron, glyphosate. Bromacil half-life: 14-1494 days, primarily microbial degradation, tebuthiuron half-life: 12-15 months, primarily microbial degradation. Migration is typically >45 cm bgs. IW for bromacil and FAL and IW soil quality guidelines for tebuthiuron are bellow detection limit. Goes over contaminated sites framework, remediation methods and case studies. Case study used in-situ chemical oxidation did not reduce bromacil concentrations.		y	y		y	y
Raman et al., 1987	Primary research paper. The influence of soil moisture content on tebuthiuron degradation was investigated in an alfisol and vertisol from Hyderabad, India.					y	
Rao et al., 1983	Report. Report by Cornelle university pesticide safety education program (PSEP) regarding the fate and behaviour of pesticides in soil and water. Lists the persistence of bromacil in soils as greater than 100 days.		y				
Reddy et al., 1992	Primary research paper. The sorption and leaching of bromacil and another pesticide is investigated in a Florida Flatwoods soil.			y			

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
Rocha et al., 2019	Primary research paper. The phytotoxicity of tebuthiuron on physic nut (*Jatropha curcas*), a biofuel crop produced in Brazil. Relevant pre-emergent herbicide application residues resulted in severe phytotoxicity of all studied genotypes.				y		
Sanders et al., 1996	Primary research paper. Bromacil degradation was studied in two soils with different management histories in New Zealand. Bromacil applied to a virgin soil degraded within 4 to 6 months following a single application. However a soil with 10 years of prior bromacil applications had a significantly slower degradation rate. Bromacil applications resulted in significant stress to microflora found in the virgin soil.		y				
Sarmah, 2009	Primary research paper. Bromacil dissipation was studied in two New Zealand soils. The reported half-life was 12 days in topsoil and 40 days in subsoil. The impact of temperature was also evaluated, half lives were three times longer at 7.5 degrees Celsius than at 20 C in a Motupiko soil. Degradation rates were significantly lower in sterilized soils.		y	y			
Sherman and Kaplan, 1975	Primary research paper. Toxicity studies of mammals exposed to bromacil. Cited by CCME, 1999b.	y					
Stantec, 2012	Report. Ecotoxicity assessment of a soil sterilant-bromacil. Fine and coarse texted soil was amended with a range of bromacil concentrations (0 to 2000 mg/kg). Plants and soil invertebrates were then tested. Plants included: durum wheat (*Triticum durum*), blue gramma grass (*Bouteloua gracilis*), alfalfa (*Medicago sativa*), invertebrates included: earthworms (*Eisenia andrei*), springtail (*Folsomia candida*), the tests were conducted using standard environment Canada procedures.	y					
Stavola, 2004	Report. Analysis of risk of tebuthiuron on pacific salmon and steelhead. Modelling procedures are described using Tier II PRZM/EXAMS model. Background on tebuthiuron is reviewed along with chemical specific parameters, environmental behaviour, and ecotoxicity. The model results are then compared to the risk assessment conducted for the US EPA RED, 1994.				y	y	
Thornton and Elledge, 2016	Primary research paper. Environmental behaviour of tebuthiuron was examined in a field plot in Queensland Australia. Runoff and leaching was studied in a grazed vertisol and alfisol. Tebuthiuron concentrations decreased at all depths after 55 to 104 days.				y		
Toit et al., 2012	Primary research paper. Study of the emergence of oats and cabbage in soils historically (8 years prior) treated with tebuthiuron. Seedling emergence was unaffected but two weeks later phytotoxicity symptoms were evident.				y	y	
Tomlin, 2005	Book. Pesticide manual. Includes chemical specific information on Tebuthiuron. Cited by NLM, 2020b.						
United National Chemical Review, 1983	Government Report. PIC decision guidance document for a banned or severely restricted chemical-bromacil. The report outlines chemical and physical properties, effects on human health, effects on the environment including Koc and half-life. Listed Koc is 32 mL/g and half-life is listed as 60 days but 100 days is also cited. Ecotoxicology is also cited.	y	y	y			
US EPA/OPP, 2020	Database. USEPA Pesticide Ecotoxicity Database. Provides tables of ecotoxicity values for bromacil and tebuthiuron.	y			y		
US EPA /OPP, 2014	Government report. Registration review with ecological risk assessment. Includes chemical specific parameters including Koc and half-life, consistent with previous US EPA RED assessment (1994). Registrant submitted toxicity data is also presented but remains consistent with the US EPA RED assessment (1994).				y	y	y
US EPA health advisories, 1988	Government report. Health advisory for pesticides. Includes a study on the aerobic degradation of C14 labeled tebuthiuron in soil. The reported half-life was 273 days.					y	

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
US EPA RED, 1994	Government Report. Reregistration Eligibility Decision (RED) for Tebuthiuron. Environmental fate is reviewed with respect to registrant submitted studies. Photodegradation in water, aerobic soil metabolism, anaerobic soil metabolism, anaerobic aquatic metabolism, aerobic aquatic metabolism, bioaccumulation in fish, and field dissipation are reviewed. Tebuthiuron half-life is listed as 1 to 2 years based on preliminary field studies. Koc is listed as 4 mL/g. Toxicity is also reviewed with respect to humans, birds mammals, fish, invertebrates, crustaceans, and non target plants.				y	y	
US EPA RED, 1996	Government Report. Reregistration Eligibility Decision (RED) for Bromacil. Goes over toxicity to humans, terrestrials animals, aquatic animals and plants. Environmental fate is also reviewed with respect to registrant submitted studies. Hydrolysis, photodegradation in water, photodegradation in soil, aerobic soil metabolism, anaerobic aquatic metabolism, mobility, accumulation, and field dissipation are reviewed. Bromacil's half-life is listed as 124 to 155 days based on field dissipation studies.	y	y				
US EPA, 2020a	Government table. US EPA National Recommended Water Quality Criteria for Aquatic life. Provides bromacil and tebuthiuron freshwater quality guidelines for the protection of aquatic life including fish, invertebrates, nonvascular plants, and vascular plants.						
US EPA, 2020b	Government table. US EPA aquatic ecotoxicity benchmark values.						
US EPA/OPP, 2012	Government report. Registration review with ecological risk assessment for endangered species and drinking water exposure. Includes chemical specific parameters including Koc and half-life, consistent with previous US EPA RED assessment (1996). Toxicity data is also presented but remains consistent with the US EPA RED assessment (1996).	y	y	y			
Waldrep, 1988	Primary research paper. Seedling emergence and vegetative vigor was studied for 10 crops exposed to tebuthiuron. Cited by CCME 1999c.				y		
Wauchope et al., 1991	Book. Explores environmental risk assessment modelling of pesticides. Includes chemical specific parameters for bromacil.		y				
Wilkinson et al., 2015	Primary research paper. Study of toxicity of photosystem II inhibitors on the seagrass *Halophila ovalis* . The 24 hour acute toxicity D50 value for was 2 ug/L and 25 ug/L for tebuthiuron and bromacil respectively.	y					
Wilson and Wilson, 2009	Primary research paper. The toxicity of bromacil to the aquatic macrophyte *Valliseneria americana* Minchx was studied as it is an important plant species for waterfowl. NOAEC, LOAEC, and EC50 values are provided for fresh weight gain, new leaf production, and total leaf growth.	y					
Wilson et al., 2016	Primary research paper. The toxicity of bromacil to sorghum is studied to determine the potential impact soil residues of herbicides used on citrus crops can have on the potential to grow biofuel crops. Plants were grown in soil exposed to bromacil, photosynthetic capacity, plant height, biomass, and leaf colour was then monitored. Bromacil concentrations greater than 0.09 mg/kg impaired growth and development.	y					
Wolf and Martin, 1974	Primary research paper. The degradation rate of bromacil was determined using carbon-14 labelling. Sandy loam soil was spiked with the bromacil and was maintained at 60% water holding capacity. After 600 days 22.1% had degraded to CO2. Soil that had been supplemented with corn stalks and lima bean straw resulted in approximately 33% degradation after 600 days.		y				
Woodard et al., 1985	Report. Cited by EXTOXNET for Bromacil's Koc value. Study of the Sacramento-San Joaquin Delta soil and water quality. Agriculture related activities were monitored and agricultural water discharges mapped. Pesticides and herbicides, including Bromacil, were among the chemicals studied.			y			

References	Summary	Bromacil			Tebuthiuron		
		Ecotox	Half-life	Koc	Ecotox	Half-life	Koc
Zanardo et al., 2019	Primary research paper. Ecotoxicological study of Tebuthiuron and other herbicides used in sugar cane production, on five peanut cultivars. Herbicides we applied pre-emergent and phytotoxicity was accessed based on emergence. Tebuthiuron was toxic to all cultivars studied.				y		
Zimdahl et al., 1970	Primary research paper. The degradation of bromacil and other uracil based herbicides was studied in soil at 13.2 and 31.2 degrees Celsius. The degradation rate was determined to follow a first order rate law and the energy of activation was also determined.		y				
Total		23	22	15	18	20	13
Primary research papers		11	11	6	10	10	3

APPENDIX B: TOXICOLOGICAL DATA

Table B1. Bromacil Literature Review Results - Freshwater Aquatic Life Ecotoxicity

Source	Organism	Scientific Name	Common Name	Age	Study Length	Dose Type	Toxicity mg/L	Author
Recent Primary Research Papers	algae	*N/A*	cyanobacterial mats	not listed	not listed	EC50	12.36	Nahhal and El-Hams, 2017
	aquatic plant	*Halophila ovalis*	paddle weed	not listed	24 hr	EC50	0.025	Wilkinson et al., 2015
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	NOAEC	0.02	Wilson and Wilson, 2009
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	LOAED	0.036	Wilson and Wilson, 2010
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	EC50	0.032	Wilson and Wilson, 2011
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	NOAEC	0.036	Wilson and Wilson, 2012
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	LOAED	0.054	Wilson and Wilson, 2013
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	EC50	0.036	Wilson and Wilson, 2014
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	NOAEC	0.036	Wilson and Wilson, 2015
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	LOAED	0.054	Wilson and Wilson, 2016
	aquatic plant	*Vallisneria americana Michx.*	tape grass	not listed	not listed	EC50	0.043	Wilson and Wilson, 2017
	diatom	*Navicula pyriformis*	boat shaped diatom	not listed	not listed	IC10	0.021	Magnusson et al., 2014
	diatom	*Navicula sp.*	boat shaped diatom	not listed	not listed	IC10	0.014	Magnusson et al., 2013
	phytoplankton	*Daphnia magna*	phytoplankton	not listed	not listed	EC50	0.59	Nahhal and El-Hams, 2017
CCME, 1999	algae	*Chlamydomonas terricola*	algae	not listed	not listed	EC50	34	Cullimore, 1975
	algae	*Chlorella ellipsoidea*	green algae	not listed	not listed	NOEC	10	Cullimore, 1975
	algae	*Chlorella pyrenoidosa*	green algae	not listed	not listed	EC50	1	Kratky and Warren, 1971
	algae	*Chlorella vulgaris*	green algae	not listed	not listed	EC50	10	Cullimore, 1975
	algae	*Coccomyxa subellipsoidea*	green algae	not listed	not listed	NOEC	10	Cullimore, 1975
	algae	*Haematococcus lacustris*	algae	not listed	not listed	EC50	0.05	Cullimore, 1975
	fish	*Cyprinus carpio*	carp	not listed	48 hr	LC50	164	Sherman and Kaplan, 1975
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	48 hr	LC50	71	Sherman and Kaplan, 1975
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	48 hr	LC50	75	Sherman and Kaplan, 1975
	fish	*Pimephales promelas*	fathead minnows	not listed	48 hr	LC50	184	Call et al., 1987; Geiger et al., 1988
	fish	*Pimephales promelas*	fathead minnows	fry	60 day	NOEC	1.9	Call et al., 1983
	invertebrate	*Chironomus tentans*	midge	larvae	96 hr	LC50	210	Environment Canada, 1996
	crustacean	*Daphnia magna*	plankton	neonates	48 hr	EC50	313	Environment Canada, 1996
	crustacean	*Daphnia magna*	plankton	neonates	48 hr	LC50	363	Environment Canada, 1996

Source	Organism	Scientific Name	Common Name	Age	Study Length	Dose Type	Toxicity mg/L	Author
US EPA Toxicology Data	aquatic plant	*Anabaena flos-aquae*	blue-green algae	not listed	5 day	EC50	0.0699	-
	aquatic plant	*Lemna gibba*	duckweed	not listed	14 day	EC50	0.045	-
	aquatic plant	*Navicula pelliculosa*	freshwater diatom	not listed	5 day	EC50	0.000691	-
	aquatic plant	*Pseudokirchneriella subcapitata*	freshwater green algae	not listed	5 day	EC50	0.0068	-
	aquatic plant	*Skeletonema costatum*	marine diatom	not listed	5 day	EC50	0.0121	-
	crustacean	*Americamysis bahia*	mysid	<24 hr	96 hr	LC50	112.9	-
	crustacean	*Daphnia magna*	water flea	<24 hr	48 hr	EC50	121	-
	crustacean	*Daphnia magna*	water flea	lie cycle	21 day	LOEC	21	-
	crustacean	*Penaeus aztecus*	brown shrimp	juvenile	48 hr	LC50	1	-
	fish	*Cyprinodon variegatus*	sheepshead minnow	17 D	96 hr	LC50	162.8	-
	fish	*Leiostomus xanthurus*	spot	juvenile	48 hr	LC50	1	-
	fish	*Lepomis macrochirus*	bluegill sunfish	0.2 g	96 hr	LC50	127	-
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	96 hr	LC50	100	-
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	96 hr	LC50	100	-
	fish	*Lepomis macrochirus*	bluegill sunfish	0.88 g	96 hr	LC50	180	-
	fish	*Lepomis macrochirus*	bluegill sunfish	0.37 g	96 hr	LC50	3.95	-
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	96 hr	LC50	2.6	-
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	96 hr	LC50	180	-
	fish	*Oncorhynchus mykiss*	rainbow trout	0.3 g	96 hr	LC50	35.7	-
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	96 hr	LC50	180	-
	fish	*Oncorhynchus mykiss*	rainbow trout	early life	90 day	LOEC	7.2	-
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	72 hr	LC50	38	-
	mollusc	*Crassostrea virginica*	eastern oyster	embro larvae	48 hr	EC50	130	-
	mollusc	*Crassostrea virginica*	eastern oyster	juvenile	96 hr	EC50	1	-
US EPA RED, 1996	algae	*Selenastrum capricornutum*	algae	not listed	not listed	EC50	0.0068	-
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	not listed	LC50	127	Wetzel, 1986
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	not listed	LC50	36	Wetzel, 1986
	phytoplankton	*Daphnia magna*	phytoplankton	not listed	not listed	LC50	121	Hall, 1986
Extoxnet	fish	*Cyprinus carpio*	carp	not listed	48 hr	LC50	164	-
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	48 hr	LC50	71	-
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	48 hr	LC50	5675	-
	fish	*Pimephales promelas*	fathead minnow	not listed	96 hr	LC50	182	-

Notes: EC50: concentration required to produce an effect in 50% of the population; LC50: concentration lethal to 50% of the population; LOAED: lowest observed adverse effects dose; NOAED: no observed adverse effects dose; LOEC: lowest observed effects concentration; NOEC: no observed effects concentration; IC10: concentration of an inhibitor required to reduce the population by 10%

Table B2. Bromacil Literature Review Results - Irrigation Water Ecotoxicity

Source	Organism	Scientific Name	Common Name	Age	Study Length	Dose Type	Toxicity		Author
							mg/kg	mg/L	
Recent Primary Research Papers	terrestrial plant	*Corchorus olitorius*	molokhia	not listed	not listed	EC50	0.08	-	Nahhal and Hamdona, 2015
	terrestrial plant	*Cucumis melo var.*	melon	not listed	not listed	EC50	4.77	-	Nahhal and Hamdona, 2015
	terrestrial plant	*Medicago sativa*	alfalfa	not listed	not listed	EC50	0.16	-	Stantec, 2012
	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	toxicity	0.09	-	Wilson et al., 2016
	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	NOEC	0.1	-	Niebch, 2013
	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	LOEC	1	-	Niebch, 2013
	terrestrial plant	*Triticum*	wheat	not listed	not listed	EC50	3.08	-	Nahhal and Hamdona, 2015
	terrestrial plant	*Triticum durum*	durum wheat	not listed	not listed	EC50	0.14	-	Stantec, 2012
CCME,1999	terrestrial plant	*Avena sativa*	oat	not listed	not listed	EC50	-	0.26	Ashton et al., 1969
	terrestrial plant	*Avena sativa*	oat	4 weeks	not listed	NOEC	-	0.2	Sharma, 1989
	terrestrial plant	*Avena sativa*	oat	7 days	not listed	severe effects	-	2	Sharma, 1989
	terrestrial plant	*Cucumis sativus*	cucumber	not listed	not listed	LC50	-	0.05	Hilton and Nomura, 1964
	terrestrial plant	*Raphanus sativus*	radish	not listed	not listed	EC50	-	0.26	Ashton et al., 1969
	terrestrial plant	*Sorghum bicolor*	sorghum	11 days	not listed	LC50	-	0.128	Hilton and Nomura, 1964
US EPA Toxicology Data	terrestrial plant	*Allium cepa*	onion	juvenile plant	21 D	EC25	-	0.01345	-
	terrestrial plant	*Allium cepa*	onion	seedling	14 D	EC25	-	0.134502	-
	terrestrial plant	*Allium cepa*	onion	juvenile plant	21 D	EC25	-	0.110441	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	juvenile plant	21 D	EC25	-	0.138238	-
	terrestrial plant	*Brassica compestris*	rapeseed	juvenile plant	21 D	EC25	-	0.003437	-
	terrestrial plant	*Brassica compestris*	rapeseed	seedling	14 D	EC25	-	0.020325	-
	terrestrial plant	*Brassica napus*	oilseed rape	seedling	14 D	EC25	-	0.007024	-
	terrestrial plant	*Brassica napus*	oilseed rape	juvenile plant	21 D	EC25	-	0.00822	-
	terrestrial plant	*Brassica napus*	oilseed rape	juvenile plant	21 D	EC25	-	0.087875	-
	terrestrial plant	*Cucumnis sativa*	cucumber	juvenile plant	21 D	EC25	-	0.158414	-
	terrestrial plant	*Glycine max*	soybean	juvenile plant	21 D	EC25	-	0.016439	-
	terrestrial plant	*Glycine max*	soybean	seedling	14 D	EC25	-	0.923581	-
	terrestrial plant	*Glycine max*	soybean	juvenile plant	21 D	EC25	-	0.05141	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	juvenile plant	21 D	EC25	-	0.041845	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	seedling	14 D	EC25	-	0.134502	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	juvenile plant	21 D	EC25	-	0.02167	-
	terrestrial plant	*Pisum sativum*	garden pea	juvenile plant	21 D	EC25	-	0.313838	-
	terrestrial plant	*Sorghum bicolor*	sorghum	juvenile plant	21 D	EC25	-	0.312344	-
	terrestrial plant	*Sorghum bicolor*	sorghum	seedling	14 D	EC25	-	0.269004	-
	terrestrial plant	*Sorghum bicolor*	sorghum	juvenile plant	21 D	EC25	-	0.288432	-
	terrestrial plant	*Triticum aestivum*	wheat	juvenile plant	21 D	EC25	-	0.134502	-
	terrestrial plant	*Triticum aestivum*	wheat	seedling	14 D	EC25	-	0.109096	-
	terrestrial plant	*Triticum aestivum*	wheat	seedling	14 D	EC25	-	0.044834	-
	terrestrial plant	*Triticum aestivum*	wheat	juvenile plant	21 D	EC25	-	0.062768	-

	terrestrial plant	*Triticum aestivum*	wheat	juvenile plant	21 D	EC25	-	0.159908	-
	terrestrial plant	*Zea mays*	corn	juvenile plant	21 D	EC25	-	0.101325	-

Source	Organism	Scientific Name	Common Name	Age	Study Length	Dose Type	Toxicity		Author
							mg/kg	mg/L	
US EPA RED, 1996	terrestrial plant	*Allium cepa*	onion	not listed	not listed	NOEL	-	5.25E-05	-
	terrestrial plant	*Allium cepa*	onion	not listed	not listed	NOEL	-	0.00762	-
	terrestrial plant	*Allium cepa*	onion	not listed	not listed	NOEC	-	0.000105	-
	terrestrial plant	*Allium cepa*	onion	not listed	not listed	NOEC	-	0.014	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	not listed	not listed	EC25	-	4.26E-05	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	not listed	not listed	NOEC	-	2.62E-05	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	not listed	not listed	EC25	-	0.00568	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	not listed	not listed	NOEC	-	0.00349	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	not listed	not listed	EC25	-	2.39E-05	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	not listed	not listed	NOEC	-	2.62E-05	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	not listed	not listed	EC25	-	0.00318	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	not listed	not listed	NOEC	-	0.00349	-
	terrestrial plant	*Brassica napus*	canola	not listed	not listed	EC25	-	1.72E-05	-
	terrestrial plant	*Brassica napus*	canola	not listed	not listed	EC25	-	0.00229	-
	terrestrial plant	*Brassica napus*	canola	not listed	not listed	EC25	-	1.75E-05	-
	terrestrial plant	*Brassica napus*	canola	not listed	not listed	NOEC	-	1.31E-05	-
	terrestrial plant	*Brassica napus*	canola	not listed	not listed	EC25	-	0.00234	-
	terrestrial plant	*Brassica napus*	canola	not listed	not listed	NOEC	-	0.00175	-
	terrestrial plant	*Cucumis sativus*	cucumber	not listed	not listed	NOEC	-	5.25E-05	-
	terrestrial plant	*Cucumis sativus*	cucumber	not listed	not listed	NOEC	-	0.00762	-
	terrestrial plant	*Cucumis sativus*	cucumber	not listed	not listed	EC25	-	1.19E-05	-
	terrestrial plant	*Cucumis sativus*	cucumber	not listed	not listed	NOEC	-	1.31E-05	-
	terrestrial plant	*Cucumis sativus*	cucumber	not listed	not listed	EC50	-	0.00159	-
	terrestrial plant	*Cucumis sativus*	cucumber	not listed	not listed	NOEC	-	0.00174	-
	terrestrial plant	*Glycine max*	soybean	not listed	not listed	EC25	-	0.000692	-
	terrestrial plant	*Glycine max*	soybean	not listed	not listed	EC25	-	0.0923	-
	terrestrial plant	*Glycine max*	soybean	not listed	not listed	EC25	-	2.06E-05	-
	terrestrial plant	*Glycine max*	soybean	not listed	not listed	NOEC	-	1.31E-05	-
	terrestrial plant	*Glycine max*	soybean	not listed	not listed	EC25	-	0.00275	-
	terrestrial plant	*Glycine max*	soybean	not listed	not listed	NOEC	-	0.00175	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	not listed	not listed	NOEL	-	2.62E-05	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	not listed	not listed	NOEL	-	0.00349	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	not listed	not listed	EC25	-	0.000026	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	not listed	not listed	NOEC	-	2.62E-05	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	not listed	not listed	EC25	-	0.00347	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	not listed	not listed	NOEC	-	0.00349	-
	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	EC25	-	0.000207	-

	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	EC25	-	0.0276	-
	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	EC25	-	0.000318	-
	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	NOEC	-	0.000211	-
	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	EC25	-	0.0424	-

Source	Organism	Scientific Name	Common Name	Age	Study Length	Dose Type	Toxicity		Author
							mg/kg	mg/L	
US EPA RED, 1996	terrestrial plant	*Sorghum bicolor*	sorghum	not listed	not listed	NOEC	-	0.02816	-
	terrestrial plant	*Triticum*	wheat	not listed	not listed	EC25	-	8.19E-05	-
	terrestrial plant	*Triticum*	wheat	not listed	not listed	EC25	-	0.0109	-
	terrestrial plant	*Triticum*	wheat	not listed	not listed	EC25	-	7.66E-05	-
	terrestrial plant	*Triticum*	wheat	not listed	not listed	NOEC	-	5.25E-05	-
	terrestrial plant	*Triticum*	wheat	not listed	not listed	EC25	-	0.0102	-
	terrestrial plant	*Triticum*	wheat	not listed	not listed	NOEC	-	0.007	-
	terrestrial plant	*Zea mays*	corn	not listed	not listed	EC25	-	0.000194	-
	terrestrial plant	*Zea mays*	corn	not listed	not listed	NOEC	-	0.000105	-
	terrestrial plant	*Zea mays*	corn	not listed	not listed	EC25	-	0.0259	-
	terrestrial plant	*Zea mays*	corn	not listed	not listed	NOEC	-	0.014	-

Notes: * Based on an irrigation rate of 7.5 x106 L/ha (ENRS, 2014; CCME, 1999c)

EC50(25): concentration required to produce an effect in 50%(25%) of the population; NOEC: no observed effects concentration; NOEL: no observed effects level

Table B3. Tebuthiuron Literature Review Results - Freshwater Aquatic Life Ecotoxicity

Source	Organism	Scientific Name	Common Name	Age	Study Length	Dose Type	Toxicity mg/L	Author
Primary Research Papers	aquatic plant	*Halophila ovalis*	paddle weed	not listed	24 hrs	EC50	0.028	Wilkinson et al., 2015
	fish	*Oreochromis niloticus*	tilapia	not listed	not listed	high mortality	250	Almeida et al., 2014
	fish	*Oreochromis niloticus*	tilapia	not listed	not listed	genotoxic effects	125	Almeida et al., 2014
	fish	*Oreochromis niloticus*	tilapia	fingerlings	24 hrs	LC50	260.5	Moura & Jonsson, 2016
	fish	*Oreochromis niloticus*	tilapia	fingerlings	96 hrs	LC50	245.5	Moura & Jonsson, 2016
CCME, 1999	algae	*Selesnastrum capricornutum*	algae	not listed	96 hr	LOEL	0.00008 to 0.000307	Blaise and Harwood 1991
	algae	*Selesnastrum capricornutum*	algae	not listed	not listed	EC50	0.00001 to 0.00005	Meyerhoff et al. 1985
	algae	*Selesnastrum capricornutum*	algae	not listed	not listed	NOEL	0.000016 to 0.000168	Adams et al., 1985
	amphibian	*Rana catesbeiana*	bullfrog	not listed	not listed	LOEL	0.1	Todd et al., 1984
	amphibian	*Rana catesbeiana*	bullfrog	not listed	24 hr	LC50	0.398	Todd et al., 1984
	amphibian	*Rana catesbeiana*	bullfrog	not listed	72 hr	LC50	0.316	Todd et al., 1984
	aquatic plant	*Lemna gibba*	duckweed	not listed	not listed	NOEL	0.000091	Negilsky & Cocke, 1989
	aquatic plant	*Lemna gibba*	duckweed	not listed	not listed	LOEL	0.00019	Negilsky & Cocke, 1989
	aquatic plant	*Lemna gibba*	duckweed	not listed	not listed	EC50	0.000235	Negilsky & Cocke, 1989
	cyanobacteria	*Aphanizomenon flos-aquae*	cyanobacteria	not listed	not listed	LOEL	1	Negilsky & Cocke, 1989
	crustacean	*Daphnia magna*	phytoplankton	not listed	48 hr	EC50	10^2	not listed
	crustacean	*Daphnia magna*	phytoplankton	not listed	not listed	EC50	10	not listed
	diatom	*Navicula pelliculosa*	boat shaped diatom	not listed	not listed	LOEL	0.1	Negilsky & Cocke, 1990
	diatom	*Navicula pelliculosa*	boat shaped diatom	not listed	7 day	EC50	0.1	Negilsky & Cocke, 1989
	fish	*Carassius auratus*	goldfish	not listed	not listed	LOEL	10^2	Day, 1993
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	96 hr	LC50	10^2	not listed
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	96 hr	LC50	10^2	not listed
	fish	*Oncorhynchus mykiss*	tilapia	not listed	not listed	LOEL	10	not listed
	fish	*Pimephales promelas*	fathead minnow	not listed	not listed	LOEL	10	Day, 1993
US EPA Toxicology Data	aquatic plant	*Anabaena flos-aquae*	blue-green algae	not listed	7 day	EC25	81	-
	aquatic plant	*Lemna gibba*	duckweed	not listed	14 day	EC50	0.126	-
	aquatic plant	*Navicula pelliculosa*	freshwater diatom	not listed	7 day	EC50	0.09	-
	aquatic plant	*Pseudokirchneriella subcapitata*	freshwater green algae	not listed	14 day	EC50	0.05	-
	aquatic plant	*Skeletonema costatum*	marine diatom	not listed	7 day	EC50	0.05	-
	crustacean	*Daphnia magna*	water flea	<10 hr	48 hr	EC50	297	-
	crustacean	*Daphnia magna*	water flea	life cycle	21 day	LOEC	44.2	-
	crustacean	*Penaeus duorarum*	pink shrimp	not listed	96 hr	EC50	62	-
	crustacean	*Uca pugilator*	fiddler crab	not listed	96 hr	EC50	100	-
	fish	*Carassius auratus*	goldfish	2 inches	96 hr	LC50	160	-
	fish	*Cyprinodon variegatus*	sheepshead minnow	0.48 g	96 hr	LC50	98	-
	fish	*Lepomis macrochirus*	bluegill sunfish	0.8 g	96 hr	LC50	106	-
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	96 hr	LC50	143	-

Source	Organism	Scientific Name	Common Name	Age	Study Length	Dose Type	Toxicity mg/L	Author
	fish	*Oncorhynchus mykiss*	rainbow trout	early life	45 day	LOEC	52	-
	fish	*Pimephales promelas*	fathead minnow	juvenile	96 hr	LC50	180	-
	fish	*Pimephales promelas*	fathead minnow	juvenile	96 hr	LC50	180	-
	fish	*Pimephales promelas*	fathead minnow	early life	28 day	LOEC	18	-
	fish	*Pimephales promelas*	fathead minnow	juvenile	96 hr	LC50	180	-
	mollusc	*Crassostrea virginica*	eastern oyster	embryo-larvae	48 hr	EC50	320	-
	mollusc	*Crassostrea virginica*	eastern oyster	juvenile	96 hr	EC50	95	-
US EPA RED, 1994	algae	*Selenastrum capricomurum*	algae	5 days	not listed	EC50	0.05	-
	aquatic plant	*Lemna gibba*	duckweed	14 days	not listed	EC50	0.135	-
	crustaean	*Crassostrea virginica*	eastern oyster	not listed	not listed	LC50	180 to 320	-
	crustaean	*Daphnia magna*	crustacean	not listed	not listed	LC50	297	-
	crustaean	*Daphnia magna*	crustacean	not listed	not listed	MATC	21.8 to 44.2	-
	crustaean	*Pandalus borealis*	pink shrimp	not listed	not listed	LC50	62	-
	cyanobacteria	*Anabaeno flos-aquae*	cyanobacteria	5 days	not listed	EC50	4.06	-
	diatom	*Navicula pellicufosa*	diatom	5 days	not listed	EC50	0.081	-
	diatom	*Skeletonema costatum*	diatom	5 days	not listed	EC50	0.05	-
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	not listed	LC50	106	-
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	not listed	LC50	143	-
	fish	*Oncorhynchus mykiss*	rainbow trout	embryo-larvae	not listed	MATC (growth & survival)	26 to 52	-
	fish	*Pimephales promelas*	fatheah minnow	embryo-larvae	not listed	MATC (growth)	9.3 to 18	-
	fish	*Pimephales promelas*	fatheah minnow	embryo-larvae	not listed	MATC (survival)	76	-
EXTOXNET	crustacean	*Daphnia magna*	phytoplankton	not listed	48 hr	LC50	225	-
	crustacean	*Pandalus borealis*	pink shrimp	not listed	not listed	LC50	>48	-
	crustacean	*Uca*	fiddler crab	not listed	not listed	LC50	320	-
	fish	*Carassius auratus*	goldfish	not listed	96 hr	LC50	>160	-
	fish	*Lepomis macrochirus*	bluegill sunfish	not listed	96 hr	LC50	97 to 112	-
	fish	*Oncorhynchus mykiss*	rainbow trout	not listed	96 hr	LC50	87 to 144	-
	fish	*Pimephales promelas*	fathead minnow	not listed	96 hr	LC50	>160	-
Stavola, 2004	algae	*Anabaena flos-aquae*	blue-green algae	not listed	9 day	NOEC	0.31	-
	algae	*Anabaena flos-aquae*	blue-green algae	not listed	10 day	EC50	4.06	-
	algae	*Navicula pelliculosa*	freshwater diatom	not listed	5 day	NOEC	0.056	-
	algae	*Navicula pelliculosa*	freshwater diatom	not listed	6 day	EC50	0.081	-
	algae	*Selenastrum capricornutum*	green algae	not listed	96 hr	LC 50	0.307	-
	algae	*Selenastrum capricornutum*	green algae	not listed	7 day	NOEC	0.013	-
	algae	*Selenastrum capricornutum*	green algae	not listed	8 day	EC50	0.05	-
	algae	*Skeletonema costatum*	marine diatom	not listed	11 day	NOEC	0.031	-
	algae	*Skeletonema costatum*	marine diatom	not listed	12 day	EC50	0.05	-
	aqautic plant	*Lemna gibba*	duckweed	not listed	14 day	NOEC	<0.066	-
	aqautic plant	*Lemna gibba*	duckweed	not listed	14 day	EC50	0.135	-
	fish	*Anguilla japonia*	japanese eel	not listed	96 hr	LC 50	> 40	-

Notes: EC50: concentration required to produce an effect in 50% of the population; LC50: concentration lethal to 50% of the population; LOEL: lowest observed effects level; NOEL: no observed effects level;

NOEC: no observed effects concentration; MATC: maximum acceptable toxicant concentration

Table B4. Tebuthiuron Literature Review Results - Irrigation Water Ecotoxicity

Source	Organism	Scientific Name	Common Name	Age	Study Length	Dose Type	Toxicity* mg/L	Author
CCME, 1999	terrestrial plant	*Brassica oleracea var. capitata*	cabbage	not listed	not listed	NOAER	0.0060	(Waldrep, 1988)
	terrestrial plant	*Brassica oleracea var. capitata*	cabbage	not listed	not listed	LOAER	0.0120	(Waldrep, 1988)
	terrestrial plant	*Brassica oleracea var. capitata*	cabbage	not listed	not listed	EC50	0.0213	(Waldrep, 1988)
	terrestrial plant	*Cucumis sativus*	cuccumber	not listed	not listed	NOAER	0.0060	(Waldrep, 1988)
	terrestrial plant	*Cucumis sativus*	cuccumber	not listed	not listed	LOAER	0.0120	(Waldrep, 1988)
	terrestrial plant	*Panicum coloratum*	kleingrasss	not listed	not listed	NOAER	0.053333333	(Baur et al., 1977)
	terrestrial plant	*Panicum coloratum*	kleingrasss	not listed	not listed	LOAER	0.146666667	(Baur et al., 1977)
	terrestrial plant	*Raphanus sativus*	radish	not listed	not listed	NOAER	0.0060	(Waldrep, 1988)
	terrestrial plant	*Raphanus sativus*	radish	not listed	not listed	LOAER	0.0120	(Waldrep, 1988)
	terrestrial plant	*Scutch grass*	bermuda grass	not listed	not listed	NOAER	0.053333333	(Baur et al., 1977)
	terrestrial plant	*Scutch grass*	bermuda grass	not listed	not listed	LOAER	0.146666667	(Baur et al., 1977)
	terrestrial plant	*Triticum*	wheat	not listed	not listed	NOAER	0.0060	(Waldrep, 1988)
	terrestrial plant	*Triticum*	wheat	not listed	not listed	LOAER	0.0120	(Waldrep, 1988)
US EPA Toxicology Data	terrestrial plant	*Allium cepa*	onion	seedling	21 day	EC25	0.0687	-
	terrestrial plant	*Allium cepa*	onion	juvenile plant	21 day	EC25	0.0852	-
	terrestrial plant	*Avena sativa*	oat	seedling	21 day	EC25	0.0777	-
	terrestrial plant	*Avena sativa*	oat	juvenile plant	21 day	EC25	0.1390	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	seedling	21 day	EC25	0.0299	-
	terrestrial plant	*Beta vulgaris*	sugarbeet	juvenile plant	21 day	EC25	0.0239	-
	terrestrial plant	*Brassica oleracea*	cabbage	seedling	7-21 day	EC25	0.0045	-
	terrestrial plant	*Brassica oleracea*	cabbage	seedling	21 day	EC25	0.0344	-
	terrestrial plant	*Brassica oleracea*	cabbage	juvenile plant	21 day	EC25	0.0478	-
	terrestrial plant	*Cucumis sativus*	cucumber	seedling	7-21 day	EC25	0.0090	-
	terrestrial plant	*Cucumis sativus*	cucumber	seedling	21 day	EC25	0.0493	-
	terrestrial plant	*Cucumis sativus*	cucumber	juvenile plant	21 day	EC25	0.0418	-
	terrestrial plant	*Daucus carota*	carrot	seedling	21 day	EC25	0.0027	-
	terrestrial plant	*Daucus carota*	carrot	juvenile plant	21 day	EC25	0.0777	-
	terrestrial plant	*Glycine max*	soybean	seedling	21 day	EC25	0.179	-
	terrestrial plant	*Glycine max*	soybean	juvenile plant	21 day	EC25	0.043	-
	terrestrial plant	*Lolium perenne*	ryegrass	seedling	21 day	EC25	0.040	-
	terrestrial plant	*Lolium perenne*	ryegrass	juvenile plant	21 day	EC25	0.045	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	seedling	21 day	EC25	0.039	-
	terrestrial plant	*Lycopersicon esculentum*	tomato	juvenile plant	21 day	EC25	0.064	-
	terrestrial plant	*Raphanus sativus*	radish	seedling	7-21 day	EC25	0.009	-
	terrestrial plant	*Triticum aestivum*	wheat	seedling	7-21 day	EC25	0.010	-
	terrestrial plant	*Zea mays*	corn	seedling	21 day	EC25	0.463	-
	terrestrial plant	*Zea mays*	corn	juvenile plant	21 day	EC25	0.389	-

Notes: * Based on an irrigation rate of 7.5 x106 L/ha (ENRS, 2014; CCME, 1999c)

EC50(25): concentration required to produce an effect in 50%(25%) of the population; LOAER: lowest observed adverse effects rate; NOAER: no observed adverse effects rate

APPENDIX C: CHEMICAL SPECIFIC PARAMETERS

Table C1. Bromacil Literature Review Results - Half-life

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
12	Lab	Silt loam	New Zealand		2.4 to 3.9 %OC, topsoil	Sarmah	2009	Primary research paper
46	Lab	Silt loam	New Zealand		2.4 to 3.9 %OC, sub soil	Sarmah	2009	Primary research paper
60	Field	Not listed	Not listed		Not listed	ARS, 2001	2001	Database
60	Not listed	Not listed	Not listed		Not listed	UN Chem Rev	1999	Review
60 to 240	Not listed	Not listed	Not listed		Various conditions	Fishel	2005	Report
60-150	Not listed	Not listed	Temperate zone		Average half life	Helling	1968	Review
61	Field	Not listed	Not listed		Not listed	ARS, 2001	2001	Database
>100	Not listed	Not listed	Not listed		Not listed	Rao et al.	1983	Review
120	Field	Not listed	Delaware, USA		pH: 6.4, %OM: 2.8, registrant: DUPON	ARS	2001	Database
120	Field	Not listed	New Zealand		Asparagus farm, virgin soil	Sanders et al.	1996	Primary research paper
120	Lab	Loam	not listed		13.2 C, soil treated with 8 ppm bromacil	Zimdahl et al.	1970	Primary research paper
124	Field	Loam	Madera, California, USA		Upper 10 cm of bare ground plot	US EPA RED	1996	Government report
144	Lab	Sandy loam	not listed		Saturated	Wolf and Martin	1974	Primary research paper
150	Lab	Loam	not listed		31.2 C, soil treated with 8 ppm bromacil	Zimdahl et al.	1970	Primary research paper
150 to 180	Field	Not listed	not listed		Not listed	ARS	2001	Database

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
150 to 180	Field	Silt loam	Butlertown		Citing Gardiner et al., 1969; C14 labelled bromacil applied at a rate of 4 lbs per acre	Beste	1983	Review
150 to 180	Field	Silt loam	Butlertown, Maryland, USA		C14 labelled bromacil applied at a rate of 4 lbs per acre	Gardiner et al.	1969	Primary research paper
155	Field	Sandy loam	Not listed		Citing Wolf & Martin, 1974, 60% water holding capacity, with lima bean straw or corn stalks added	Menzie et al.	1978	Government report
155	Field	Silty clay loam	Newark, Delaware, USA		Upper 10 cm of bare ground plot	US EPA RED	1996	Government report
160	Lab	Not listed	Not listed		Methanogenic conditions	Adrian et al.	1990	Primary research paper
175	Field	Not listed	Delaware, USA		Registrant: DUPON	ARS	2001	Database
180	Lab	Not listed	Not listed		Standard lab conditions, six soils	Jolliffee et al.	1967	Primary research paper
180	Field	Not listed	New Zealand		Asparagus farm, soil with history of application.	Sanders et al.	1996	Primary research paper
198	Field	Sandy loam	Not listed		Citing Wolf & Martin, 1974, 60% water holding capacity, without added straw	Menzie et al.	1978	Government report
198	Lab	Sandy loam	Not listed		Saturated, bean straw added	Wolf and Martin	1974	Primary research paper
207	Not listed	Not listed	Not listed		Average half life	ARS	2001	Database
240	Field	Not listed	Not listed		Historic applications of bromacil (6 to 7 years of application)	Leistra et al.	1975	Primary research paper
270	Field	Not listed	Hawaii, USA		Pineapple field	Alavi et al.	2008	Primary research paper

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
272	Field	Humic luvic gleysol	Northwestern Alberta, CAN	0.2 to 7 ppm	Concentrations at various depths over several years at two field sites	Landsburg and Dwyer	1995	Primary research paper
273	Not listed	Not listed	Not listed	**Site 1:** ranged between 0.62 ± 0.07 ppm (0 to 4 cm) to 0.1 ± 0.07 ppm (36 to 38 cm) **Site 2:** ranged between 0.59 ± 0.12 ppm (0 to 4 cm) to 0.05 ± 0.01 ppm (36 to 38 cm)	Aerobic soil metabolism	US EPA RED	1996	Government report
275	Lab	Silty clay loam	Delaware, USA		Aerobic conditions, registrant: DUPON	ARS	2001	Database
275	Lab	Silty clay loam	Not listed		Aerobic microbial degradation, application of 9 ppm radiolabelled bromacil	US EPA RED	1996	Government report
350	Field	Not listed	Not listed		Not listed	ARS	2001	Database
350	Field	Not listed	Not listed		Not listed	ARS	2001	Database
106 to 349	Field	Not listed	Not listed		Not listed	ARS	2001	Database
14 to 1494	Lab	Not listed	Israel	16 and 4 µg/g	Varying moisture contents, varying temperatures, varying initial concentrations	Gerstl and Yaron	1983	Primary research paper
14 to 1494	Lab	Varying	Israel	16 and 4 µg/g	Citing Gerstl and Yaron, 1983, varying moisture contents, varying temperatures, varying initial concentrations	Rakewich and Baker	2017	Industry presentation

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
not listed	Field	Humic luvic gleysols	Alberta, Canada	0.1 to 16 ppm	Leaching and microbial degradation Rehabilitation of bromacil-contaminated soils by activated carbon, manure, wet-dry soil cycles, and plant seedlings	Landsburg and Fedkenheuer	1990	Primary research paper
not listed	Lab/field	Loamy sand and silt loam	Alberta, Canada	2 and 6 kg/ha active ingredient	Treatment with manure, peat, fertilizer, combination of them	Cotton and Sharma	1993	Primary research paper
140 -168	Not listed	Not listed	Not listed	not listed	Koc of 72 (Kenaga 1980), Cited WSSA (1989) for half life			Cited in literature review
60	Not listed	Not listed	Not listed	not listed	Cited various paper as listed below:	EXTOXNET	1993	A toxicological review by Pesticide Management Education Program (PMEP)
>100	Not listed	Not listed	Not listed	not listed	Cited Rao et al. (1983)			
150-180	Not listed	Silt loam	Not listed	not listed	Cited–(March 1975), office of pesticides program; VanDriesche (1985)			
Simazine: 27-126	Lab	Sandy loam	Not listed	not listed	Cited Garcia-Valcarcel and Tadeo (1999)-Simazine half life depended on the soil moisture content (4-18%)	Gunasekekara	2004	Government report
Simazine: 175 to 424	Field	Sandy/silt loam	Western Washington	top 15 cm: 400 and 2310 ug/kg; 120-180 cm depth: 15 ug/kg	Cited Cogger et al. (1998)			

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
Simazine: 91	Not listed	Sandy loam	Not listed	not listed	Cited Vencill (2002) Aerobic microbial half life of simazine at 25 °C			
Diuron : 90	Not listed	Not listed	Not listed	not listed	Cited Kidd and James (1991)	Moncada	2004	Government report
Diuron : 37	Field	Clay 12%, silt 75%, sand 13%	Gorsem, Belgium	2378 µg/kg to 11.4 µg/kg (3 kg ai/ha)	Cited Bulcke et al. (2000) - treated with the diuron for 12 years			
Diuron : 81	Field	Clay 12%, silt 75%, sand 13%	Gorsem, Belgium	2626 µg/kg to 52µg/kg (3 kg ai/ha)	Cited Bulcke et al. (2000) - treated for the first time with diuron			
not listed	Not listed	Not listed	Alberta	0.1 to 1 µg/L	Concentrations of various pesticides in surface water in Alberta differ in sampling design	Anderson	2005	Primary research paper
Pendimethalin : 47	Lab	Varying	Italy and Colorado	3.87 to 4.24 µg/g	Cited Zimdahl et al. (1984) different temperature and soil moisture	Henderson et al.	2005	Primary research paper
Pendimethalin : 98 to 407	Not listed	Not listed	Not listed	not listed	Cited Walker and Bond (1977) different temperature			
Field half-life of Atrazine: 2 to 742	Field	Not listed	Not listed	not listed	Abiotic and biotic degradation persistent in aquifers_ t1/2 in surface water : 13.9 years.	Lazorko-connon	2008	Industry presentation
Diuron:372	Not listed	Silt loam (Keyport soil)	Not listed	not listed	Aerobic soil; 25°C, 75% 0.3 bar (The half-life for the non-sterile soils was determined by first order kinetics as 372 days and for sterile control was 1920 days)	Australian government	2011	Government report

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
Diuron: 20	Not listed	Loamy sand	Not listed	not listed	Aerobic soil; 70% MWHC, 20°C			
Diuron:119	Not listed	Sand	Not listed	not listed	Aerobic soil; 70% MWHC, 20°C			
Diuron:51	Not listed	Sandy loam	Not listed	not listed	Aerobic soil; 70% MWHC, 20°C			
Diuron:143	Not listed	Sandy loam	Not listed	not listed	Aerobic soil; 70% MWHC, 10°C			
Diuron:27	Not listed	Sandy loam	Not listed	not listed	Aerobic soil; 35% MWHC, 20°C			
Diuron:112	Not listed	Sand	Not listed	not listed	Aerobic soil; 20°C, pF 2.5			
Diuron:20-119	Not listed	Not listed	Three soils from Europe	not listed	Aerobic soil metabolism; 20°C, 70 per cent MWHC			
Diuron:143	Not listed	Not listed	Three soils from Europe	not listed	10°C _low temperature increased the half-life			
Diuron:27	Not listed	Not listed	Three soils from Europe	not listed	Aerobic soil metabolism; 35 per cent of soil's maximum water holding capacity			
Diuron:186	Not listed	Sand soil	Germany	not listed	Aerobic soil metabolism; incubated in the dark with positive flow of carbon dioxide–free air for 101 days at 20°C and at field capacity			
Diuron: 60 to 365	Field	Not listed	Netherlands	not listed				
Diuron: 79 to 108	Not listed	Aerobic soil	Netherlands	not listed				
DIURON: 173		Silt loam soil		not listed	Photolysis of diuron on soil			
Diuron:No degradation during anaerobic phase/very slow	Not listed	Silt loam	Not listed	not listed	Anaerobic soil; 25°C, 75% field moisture. 30 days aerobic then anaerobic			

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
Diuron:6.5 to 250	Field	Not listed	Four field sites in the Bundaberg region, Australia	not listed	A three-year period; normal farming practices of cultivation and irrigation; Runoff of diuron was monitored (less than 0.2% of the annual application rate)			
Diuron:49	Field	Not listed	Coastal Queensland (Burnett catchment), Australia	not listed	A spray application of diuron at 1.6 kg/ha was made to a 6.3 hectare block; about 25 millimetres of irrigation applied immediately after spraying			
Diuron:73, 141 and 135 days	Field	Sand, silt loam and silty clay	Not listed (International Field)	target rate of 13.44 kg ac/ha (the applications averaged between 86 to 101 per cent of the target rate)	Sites received natural rainfall plus additional irrigation			
Diuron:134 and 102 days for Delaware and California respectively	Field	Silty clay loam (Delaware) and sandy loam (California)	Delaware and California	target rate of 13.44 kg ac/ha (achieved 30% of the target concentration at both sites)	Newark site received mainly 1659 millimetres of natural rainfall; The California site was irrigated for the first three months and was irrigated for 1–4 hours per day			
Diuron:67 to 231(for most sites); one site:533	Field	Not listed	Six sites in Germany	not listed	Sites without vegetation; applied to bare soil at 8 kg ac/ha			
Diuron:142	Field	Clay soil	California	target rate of 13.44 kg ac/ha	Dry weather			
Diuron: 800 to 4000	Lab	Mucky peat	Oregan, USA	5-100 µmol/kg soil	Cited Madhun and Freed (1987);	Environment Canada & Health	2011	Government report

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
Diuron: 200 to 1400	Lab	Sandy loam	Oregan, USA		Carbonyl- C-labelled and unlabelled analytical grade chemicals (purity > 99%) -the half life was derived from the rate of CO2 production from herbicide treated soils _used three different temperatures (25, 30, 35 °C)	Canada		
Diuron: 80.7	Not listed	Loam	Not listed	an application rate of 3 kg/ha per year	Cited Rouchaud (2000)			
Diuron: 37	Not listed	Loam	Not listed	12 years of consecutive annual applications of diuron				
Diuron: 37 to 80.7	Not listed	Not listed	Not listed	Aerobic primary biodegradation	Cited Rouchaud et al. (2000)			
not listed	Not listed	Not listed	Not listed	not listed	Main Points: The half-life is only valid for the particular conditions under which the study was conducted. Field studies required to consider many factors.	Cheng and Lehmann	1985	Review
5429+/-876	Lab	Peat	25°C	5 µmol/kg	Lab degradation rates under various conditions	Yousef and Virgil	1987	Primary research paper
6789+/-2125	Lab	Peat	35°C	5 µmol/kg				
8044+/-2517	Lab	Peat	35°C	5 µmol/kg				
46200+/-38707	Lab	Sand	25°C	5 µmol/kg				
12391+/-178	Lab	Sand	35°C	5 µmol/kg				
5856+/-3957	Lab	Sand	35°C	5 µmol/kg				

Half-Life (Days)	Field / Lab Study	Soil Type	Location	Starting Concentration	Additional Experimental Conditions	Author	Date	Type of Publication
6293+/-1000	Lab	Peat	25°C	100 µmol/kg				
5986+/-4401	Lab	Peat	35°C	100 µmol/kg				
6784+/-7543	Lab	Peat	35°C	100 µmol/kg				
18851+/-2401	Lab	Sand	25°C	100 µmol/kg				
9925+/-803	Lab	Sand	35°C	100 µmol/kg				
7588+/-4207	Lab	Sand	35°C	100 µmol/kg				

Table C2. Bromacil Literature Review Results - Water-Organic Carbon Partition Coefficient (Koc)

Koc (mL/g)	Field/Lab study	Soil Type	Location	Additional Experimental Conditions	Author	Date	Type of Publication
2.3	Not listed	Clay loam	Maryland, USA	25 C, 2.2 %OM, pH 4.2, registrant: DUPON	ARS	2001	Database
12	Not listed	Sand	Florida, USA	25 C, 1.3 %OM, pH 7.0, registrant: DUPON	ARS	2001	Database
14	Not listed	Silt loam	Delaware, USA	25C, 3.0 % OM, pH 6.2, registrant: DUPON	ARS	2001	Database
23	Not listed	Various	Not listed	average of 8 soils and 4 sediments	ENSR	2005	Database
23	Lab	Various	Israel	Not listed	Gerstl and Yaron	1983	Primary research paper
25 to 50	Not listed	Not listed	Israel	6 soils	ENSR	2005	Database
32	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
32	Not listed	Not listed	Valencia, Spain	Citrus orchard	dePaz and Rubio	2006	Primary research paper
32	Not listed	Not listed	Not listed	Not listed	ENSR	2005	Database
32	Not listed	Not listed	Not listed	Not listed	Helling	1968	Review
33	Not listed	Sandy loam	California, USA	25 C, 1.3 % OM, registrant: DUPON	ARS	2001	Database
40.56	Lab	Silt loam	Waikiwi, New Zealand	Topsoil, 2.4 to 3.9 %OC	Sarmah et al.	2009	Primary research paper
41.1	Not listed	Sediment	Not listed	8 freshwater sediments	ENSR	2005	Database
26.3 to 289.1 (41.1)	Not listed	Sediment	Not listed	8 sediments	Corwin et al.	1984	Primary research paper
46 to 93	Lab	Sand	Florida, USA	7 flatwood soils collected from citrus groves	Reddy et al.	1992	Primary research paper
55	Lab	Not listed	Newe Ya'ar, Israel	Batch slurry experiment	Angemar et al.	1984	Primary research paper
55 to 126	Not listed	Not listed	Not listed	Not listed	ENSR	2005	Database

Koc (mL/g)	Field/Lab study	Soil Type	Location	Additional Experimental Conditions	Author	Date	Type of Publication
12 to 289 (57)	Not listed	Not listed	Not listed	Not listed	ENSR	2005	Database
72	Not listed	Not listed	Not listed	Not listed	Helling	1968	Review
75.41	Lab	Silt loam	Motupiko, New Zealand	Topsoil, 2.4 to 3.9 %OC	Sarmah et al.	2009	Primary research paper
76 to 129	Not listed	Mucky peat and sandy loam	Oregon, USA	4 to 25 C	Madhun et al.	1986	Primary research paper
109	Not listed	Not listed	Not listed	Not listed	Cohen	1984	Primary research paper
126	Lab	Not listed	Hula, Israel	Batch slurry experiment	Angemar et al.	1984	Primary research paper
126	Lab	Various	Israel	Not listed	Gerstl and Yaron	1983	Primary research paper
210	Not listed	Not listed	Not listed	Not listed	Woodard et al.	1985	Primary research paper
1767.95	Lab	Silt loam	Motupiko, New Zealand	Subsoil	Sarmah et al.	2009	Primary research paper

Table C3. Tebuthiuron Literature Review Results - Half-life

Half-Life (Days)	Field/Lab Conditions	Soil Type	Location	Starting concentration	Experimental Conditions	Author	Date	Type of Publication
12.2 to 21.5	Not listed	Not listed	Southern China		Aquatic ecosystem	Qian et al.	2017	Primary research paper
13 to 100	Field	Not listed	Not listed		Not listed	ARS	2001	Database
20	Field	Sand	Brazil		Sugar cane field	Cerdeira et al.	2007	Primary research paper
30	Not listed	Not listed	Not listed		After 30 days in aerobic conditions and 60 days in flooded conditions	ENSR	2005	Government report
39	Lab	Sand	Not listed		Saturated, acid and basic conditions	Koskinen et al.	1996	Primary research paper
55	Lab	Sandy and clay soil	Brazil		Soil from a sugar cane field, supplemented with sugar cane vinasse	Lourencetti et al.	2012	Primary research paper
81	Field	Not listed	Florida, USA		registrant study ID: MRID 43318101	U.S. EPA/OPP	2014	Government report
83	Lab	Alfisol	Hyderabad, India		At saturation	Raman et al.	1987	Primary research paper
91	Lab	Alfisol	Hyderabad, India		At field capacity	Raman et al.	1987	Primary research paper
99	Lab	Alfisol	Hyderabad, India		At 50% field capacity	Raman et al.	1987	Primary research paper
128	Lab	Sandy and clay soil	Brazil		Soil from a sugar cane field	Lourencetti et al.	2012	Primary research paper
139	Lab	Vertisol	Hyderabad, India		At saturation	Raman et al.	1987	Primary research paper
270.6	Not listed	Not listed	Not listed		registrant study ID: MRID 41328001	U.S. EPA/OPP	2014	Government report

Half-Life (Days)	Field/Lab Conditions	Soil Type	Location	Starting concentration	Experimental Conditions	Author	Date	Type of Publication
273	Lab	Loam soil	Not listed		Not listed	US EPA Health Advisories	1988	Government report
276	Lab	Vertisol	Hyderabad, India		At field capacity	Raman et al.	1987	Primary research paper
276	Lab	Vertisol	Hyderabad, India		At 50% field capacity	Raman et al.	1987	Primary research paper
300	Field	Podzol	Northeast central Newfoundland, CAN		Clear cut plot of boreal forest	Helbert	1990	Primary research paper
336	Lab	Loam soil	Not listed		Anaerobic conditions at 23 C	US EPA Health Advisories	1988	Government report
360	Field	Not listed	Not listed		Not listed	ARS	1990	Database
360	Field	Not listed	Not listed		Not listed	ARS	2001	Database
360	Field	Not listed	Arizona, USA		Not listed	ENSR	2005	Government report
360	Not listed	Not listed	Not listed		Not listed	Flury et al.	1996	Review
360	Not listed	Not listed	Not listed		Not listed	Knisel and Davis	2000	Government report
360 to 400	Not listed	Not listed	Not listed		Not listed	Helling	1968	Review
360 to 450	Field	Not listed	Not listed		Not listed	ARS	2001	Database
360 to 450	Not listed	Not listed	Not listed		Average of areas receiving 40 to 60 inches of annual rainfall	Beste	1983	Book
360 to 450	Not listed	Not listed	Not listed		Persistence inversely proportional to soil moisture	ENSR	2005	Government report

Half-Life (Days)	Field/Lab Conditions	Soil Type	Location	Starting concentration	Experimental Conditions	Author	Date	Type of Publication
360 to 450	Field	Not listed	Not listed		Area receiving 40 to 60 inches of annual rainfall	ENSR	2005	Government report
360 to 450	Field	Loam	Greenfield, Indiana, USA		Not listed	ENSR	2005	Government report
360 to 450	Lab	Not listed	Not listed		Photochemical degradation study	Rainey and Magnussen	1976	Primary research paper
360 to 450	Field	Clay soil	Louisiana, USA		Not listed	ENSR	2005	Government report
365 to 730	Field	Not listed	California and Nebraska, USA		Not listed	ENSR	2005	Government report
365 to 730	Field	Not listed	California, Nebraska, Florida, USA		Not listed	Stavola	2004	Primary research paper
383	Field	Sand	Florida, USA		Not listed	Peacock et al.	1995	Primary research paper
385	Field	Not listed	Nebraska, USA		Registrant study ID: MRID 43318101	U.S. EPA/OPP	2014	Government report
433	Field	Not listed	Arizona, USA		Rangeland, 0.84 kg/ha applied	Emmerich et al.	1984	Primary research paper
450	Field	Not listed	not listed		Areas with heavy rainfall	ENSR	2005	Government report
495	Field	Not listed	California, USA		Registrant study ID: MRID 43318101	U.S. EPA/OPP	2014	Government report
575	Field	Not listed	Nebraska, USA		Not listed	Peacock et al.	1995	Primary research paper
806	Field	Not listed	California, USA		Not listed	Peacock et al.	1995	Primary research paper
990	Field	Loam soil	Fresno California, USA		Not listed	ENSR	2005	Government report

Half-Life (Days)	Field/Lab Conditions	Soil Type	Location	Starting concentration	Experimental Conditions	Author	Date	Type of Publication
1050	Field	Not listed	Not listed		Aerobic degradation conditions, registrant: DOW	ARS	2001	Database
1062	Lab	Sandy loam	Not listed		24 C and 75% field capacity	ENSR	2005	Government report
1062	Not listed	Not listed	Not listed		Registrant study ID: MRID 41328001	U.S. EPA/OPP	2014	Government report
1062	Field	Sandy loam	Not listed		75% field capacity	US EPA RED	1994	Government report
1350	Field	Not listed	Not listed		Areas with low rainfall	ENSR	2005	Government report
2920	Field	Not listed	South Africa		Semi-arid grassland	Toit & Sekwadi	2012	Primary research paper
2555	Field	Loam	Arizona	Not listed	Cited Johnsen and Morton (1989); Semiarid	Stantec Consulting Ltd	2011	Industry presentation
390	Field	Clay	Louisiana	Not listed	Cited Rainey and Magnussen (1976)			
270 to 300	Field	Silt loam	Louisiana	Not listed				
990	Field	Loam	California	Not listed				
365	Field	Loam	Indiana	Not listed				
365	Field	Loam	Indiana	Not listed	Cited Elanco (1974); Semiarid			
>330	Lab	Loam	Not listed	Not listed	Anaerobic conditions cited Berard (1977)			
270	Lab	Loam	Not listed	Not listed	Aerobic conditions cited Rainey and Magnussen (1976)			

Half-Life (Days)	Field/Lab Conditions	Soil Type	Location	Starting concentration	Experimental Conditions	Author	Date	Type of Publication
77	Lab	Nr	Simulated flood plain/tropical	Not listed	Cited Batterham (1992)			
21	Field	Sand	Paulo State, Brazil	1.0 kg/ha a.i.	cited Cerdeira et al., (2007)			

Table C4. Tebuthiuron Literature Review Results - Water-Organic Carbon Partition Coefficient (Koc)

Koc (mL/g)	Field/Lab Study	Soil Type	Location	Experimental Conditions	Author	Date	Type of Publication
1.7853	Not listed	Not listed	Not listed	25C and pH7	Kidd and James	1991	Review
4	Not listed	Not listed	Not listed	EPAO	ARS	2001	Database
13	Not listed	Not listed	Not listed	EPAO	ARS	2001	Database
38	Not listed	Sand	Not listed	OM 0.5 %, pH:7.7, registrant: DOW	ENSR	2005	Database
38	Not listed	Sand	Not listed	Not listed	U.S. EPA/OPP	2014	Government report
45.76	Lab	Clay	Brazil	Sugar cane vinasse	Lourencetti et al.	2012	Primary research paper
45.94	Lab	Sand	Brazil	Not listed	Lourencetti et al.	2012	Primary research paper
51.41	Lab	Sand	Brazil	Sugar cane vinasse	Lourencetti et al.	2012	Primary research paper
54.63	Lab	Clay	Brazil	Not listed	Lourencetti et al.	2012	Primary research paper
60	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
61	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
75	Not listed	Loam	Not listed	Not listed	U.S. EPA/OPP	2014	Government report
77	Not listed	Sandy loam	Not listed	OM 1.4%, pH:5.7, registrant: DOW	ENSR	2005	Database
79	Not listed	Loam	Not listed	OM 1.8 %, pH: 6.5, registrant: DOW	ENSR	2005	Database
80	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
80	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
80	Not listed	Not listed	Not listed	Not listed	Flury et al.	1996	Review
80	Not listed	Not listed	Not listed	Not listed	Knisel and Davis	2000	Government report
80	Field	Not listed	Australia	Not listed	Mercurio	2016	Primary research paper
85.2	Not listed	Not listed	Not listed	Not listed	U.S. EPA/OPP	2014	Government report
130	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
130	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
152	Not listed	Loam	Not listed	Not listed	U.S. EPA/OPP	2014	Government report

Koc (mL/g)	Field/Lab Study	Soil Type	Location	Experimental Conditions	Author	Date	Type of Publication
157	Not listed	Clay loam	Not listed	OM 2.0%, pH: 6.9, registrant: DOW	ENSR	2005	Database
249	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
617	Not listed	Not listed	Not listed	Not listed	Montgomery	1997	Textbook
620	Not listed	Not listed	Not listed	Not listed	ARS	2001	Database
716	Not listed	Sandy loam	Not listed	Not listed	U.S. EPA/OPP	2014	Government report
12.2 to 152	Not listed	Not listed	Not listed	Not listed	Durkin	2015	Government report
2.70 to 84.1	Lab	Sand	Not listed	Saturated, acid and basic conditions	Koskinen et al.	1996	Primary research paper
22 to 92 (80)	Not listed	Not listed	Not listed	Not listed	Helling	1968	Review

Appendix A5-2: Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life

Litalien, A., J. Hueser, M. Tindal, C. Kartz and I. Mitchell, 2020. Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life. Report SSP-7B prepared by Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 22 pp.

Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life: Review of Alternative Models

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EXECUTIVE SUMMARY

The historic use of soil sterilants at many oil and gas sites in Alberta has led to challenges for remediation and site closure. Bromacil and tebuthiuron are mobile and persistent sterilants that are toxic to terrestrial and aquatic plants at low concentrations. These factors have contributed to very low Tier 1 guidelines for the irrigation water and freshwater aquatic life pathways. Several of the guidelines fall below the typical detection limits of the sterilants and frequently necessitate the use of a Tier 2 or a site-specific approach.

The model currently used by Alberta Environment and Parks considers partitioning of solutes, unsaturated transport, groundwater mixing and lateral transport. At Tier 2 some site-specific factors can be included but are still limited which may result in overly conservative guidelines. The second task of the SSP Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life Project was to evaluate alternative risk models that could be used to derive soil and groundwater guidelines for bromacil and tebuthiuron that would be both protective of IW and FAL pathways.

A literature review was conducted to identify scientifically robust models that could be used to assess the transport of bromacil and tebuthiuron through variably saturated media. Thirty models were reviewed and ranked based on their defensibility, applicability, availability, ease of use, and inclusion of novel features relative to the current Tier 2 model. Three models were selected for a detailed mechanistic review and model analysis based on standard Tier 1 input values and parameters derived from the literature when necessary.

BIOSCREEN is a US EPA model that could be substituted for the current saturated transport component of the Tier 2 model. It follows similar principles to the Tier 2 model but also considers source depletion and as a result, can produce less conservative soil and groundwater guidelines for the FAL pathway. PWC is also a US EPA transport model designed specifically for agrochemicals and can be used to evaluate transport to groundwater. The results of the model analysis showed that the PWC model would produce guidelines similar to the current Tier 2 model however PWC is more challenging to use than the Tier 2 model and requires many input parameters that may not be readily available for all sites. However, its more detailed approach could be of benefit on a site-specific basis. PEARL is a European agrochemical transport model that can model transport through both the unsaturated zone and the flux of solutes to surface water bodies. The model proved to be challenging to employ and required values for several parameters that were not readily available but did produce a host of outputs that could be of interest on a site-specific basis. PEARL produced significantly more conservative IW guidelines as compared to the Tier 2 model but model results suggested that lateral transport would be negligible.

None of the models reviewed could effectively replace all elements of the Tier 2 model however they could be useful supplements.

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Figure 1 Conceptual Site Model on which the Tier 1 and Tier 2 guideline models are based. 5

1.0 INTRODUCTION

As part of the Soil Sterilants Program (SSP), InnoTech Alberta (InnoTech) retained Millennium EMS Solutions Ltd. (MEMS) to assess and evaluate the risk model used to derive the Alberta Tier 1 guideline values for bromacil and tebuthiuron for the protection of irrigation water (IW) and freshwater aquatic life (FAL) pathways and identify alternative models and considerations for guideline development for these soil sterilants, if warranted.

The overall objective of the SSP Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life Project was to determine appropriate risk model(s) and model parameters which can be used to develop screening guidelines for bromacil and tebuthiuron deemed to be protective of the IW and FAL pathways which better reflect the contaminants' "real-world" fate and mobility in the subsurface under Alberta field conditions.

The work was divided into four tasks:

1. Current Tier 1 model evaluation for IW and FAL pathways for bromacil and tebuthiuron
2. Alternative model evaluation to adjust IW and FAL pathways for bromacil and tebuthiuron
3. Sterilant-pathway risk matrix development
4. Guideline development considering source depletion and varying Alberta field conditions

This document serves as a summary report of Task 2.

1.1 Background

1.1.1 Soil Sterilants

Soil sterilants have been used historically for vegetation management at many upstream oil and gas facilities as well as industrial sites throughout Alberta. As these sites undergo decommissioning and remediation, sterilants such as bromacil and tebuthiuron can present a challenge due their persistence in soils and tendency to migrate off lease. Current Tier 1 soil guidelines for both sterilants fall below the detection limit for the protection of the irrigation water pathway as well as the freshwater aquatic life pathway for tebuthiuron. As a result, sites with these sterilants present may require Tier 2 approach.

1.1.2 Tier 2 Site Specific Guidelines

Under the Alberta framework for the management of contaminated sites three options exist, Tier 1, Tier 2, and Exposure Control. Where Tier 1 takes on a generalized approach, Tier 2 allows for the inclusion of site-specific conditions while providing the same level of protection to receptors as generic Tier 1 guidelines.

The Tier 1/2 model for calculating soil guidelines protective of the IW and FAL pathways is comprised of four dilution factors (DF) including:

- DF1, which represents partitioning of the contaminant between soil, pore water, and soil vapour. DF1 considers how a contaminant may sorb to soil organic matter and mineral soil particles.

- DF2, which represents the ratio of the concentration of the contaminant in porewater at the source to that of the porewater just above groundwater. This includes dilution due to biodegradation and dispersion as the contaminant moves down through the soil profile.

- DF3, which represents the ratio of the concentration of the contaminant in porewater just above groundwater to the concentration in groundwater. DF3 addresses mixing between vadose zone pore water and groundwater.

- DF4, which represents the dilution that occurs due to dispersion and biodegradation as groundwater travels downgradient from the source to a receptor.

Within the Tier 1 framework, DF2 is equal to 1 as it is assumed that the source of contamination extends down to the shallow groundwater table. At Tier 2, DF2 can be altered by confirming a separation unit between the source and shallow groundwater. Similarly, at Tier 1 DF4 is calculated based on the assumption that the distance between the source and the FAL receptor is 10 m, however the distance between the source and the nearest FAL receptor can be defined using site-specific measurements at Tier 2.

Even at Tier 2, the model uses a relatively generalized approach which allows for its simple, rapid, and cost-effective application to numerous sites. The model relies on a limited number of parameters which can be effectively measured on site, exist within the literature or can be easily estimated. Further, the model is based on algebraic equations that don't require extensive programming to apply. The Tier 2 model does however include several assumptions (CCME, 2006):

1. Soil is physically and chemically homogeneous;
2. Groundwater aquifer is unconsolidated mineral soil;
3. Soil moisture is uniform throughout the unsaturated zone;
4. Infiltration rate is uniform throughout the unsaturated zone;
5. Decay of contaminant source is not considered;
6. Flow in the unsaturated zone is assumed to be one-dimensional (vertical);
7. The contaminant is not present in the free phase;
8. The aquifer is unconfined;
9. Groundwater flow is unconfined and steady;
10. Oxidation/reduction is not considered;
11. Attenuation of the contaminant in the saturated zone is considered with respect to dispersivity in the direction of groundwater flow, partitioning, and decay;
12. There is no vertical dispersion within the saturated zone;
13. Mixing of leachate into groundwater is assumed to occur as a result of mass fluxes; and
14. Dilution of the plume by groundwater recharge downgradient is not considered.

The simplicity of the model likely results in conservative estimates as the complexity of the system is not fully addressed. Ideally some of these assumptions may be addressed using scientifically sound and easily understandable methods for which parameters are readily available and applicable to Canadian conditions. For example, well-established equations can be combined with relevant meteorological data to produce time-dependent infiltration rates. Source depletion may be considered, or non-homogeneous soil profiles may be considered.

2.0 PROJECT OBJECTIVES

Task 2 focused on evaluating alternative model usage for calculating IW and FAL guidelines for bromacil and tebuthiuron at a Tier 2/site-specific level. This task did not include any evaluation of alternative models to be used at Tier 1.

Task 2 steps included (1) completing a literature review to identify alternative groundwater contaminant flow models, and (2) completing a mechanistic review and model analysis of models identified in (1) above.

The review focused on unique model features which are not currently considered in the Tier 1 models and were ranked with respect to their defensibility and applicability in achieving "real-world" representation of sterilant transport in the subsurface.

3.0 PROJECT METHODOLOGY

3.1 Literature Review

The scope for Task 2 included a literature review to identify alternative groundwater contaminant flow models as the receptors of interest (IW and FAL) are governed by groundwater transport. The literature review focused on models with a similar conceptual basis to the Tier 2 model but that also included features that were absent from, or had the capacity to model more complex systems than, the Tier 2 model. A particular emphasis was placed on models that were suggested for use with herbicides and pesticides.

The detailed literature search involved:

- Planning and search – Three key questions and 18 primary search terms were selected and searched in Google Scholar, Science Direct and PubMed. Articles were selected that discussed the modelling of contaminants within the soil profile and groundwater;

- Narrowing search results – Primary search terms were combined to find specific articles directly related to key questions and the review focused where possible on the past 10 years of published articles and grey-literature reports;

- Document screening – A high-level review of all retrieved documents was conducted, and 105 documents identified in the literature search were thoroughly reviewed to identify information relevant to the key questions; and

- Data analysis and reporting – 60 articles were identified for inclusion in the review. Each article was briefly summarized in terms of study objectives, high level methodology, key results/trends; and conclusion/recommendations, if appropriate (Appendix A).

After conducting a high-level review of identified models, a further literature review of each model was conducted following the above procedure. This allowed the authors to achieve a better understanding of each individual model.

3.2 Mechanistic Review and Model Ranking

Upon completion of the literature review, models were examined to determine their defensibility, applicability, availability, ease of use, novel features, and relevance to the IW and FAL pathways.

Defensibility was considered based on the degree to which the model has been tested; many models created by government programs have undergone rigorous testing and evaluation and would be given a

rank of '3'. Models created by academic groups may not have undergone as much testing, or those which have not demonstrated significant validation received a rank of '1'.

The ranking for applicability was based on the semblance to the Tier 2 Conceptual Site Model (CSM); a rank of '1' was given to models that were not relevant, a rank of '2' to models that incorporated most elements of the CSM but missed some components, and a rank of '3' was given to models that have the capacity to cover all elements of the Tier 2 CSM.

Availability was ranked based on access and the ability to activate the program. A rank of '1' was given to models that have been archived or are available only from the creator. A rank of '2' was given to programs that are still available in some form but are not open to the public, models that may not be updated, models that lack some form of support, and models that may be challenging to install. A rank of '3' was given to models that were simple to find, download, and install.

Ease of use was only ranked for programs that discussed the user interface are/or were downloaded and opened. Models with a rank of '1' generally require advanced knowledge of coding or are generally difficult to use, those with a rank of '2' have a user interface but workflow may be challenging and errors are common. A rank of '3' refers to models that were simple and straightforward to run.

Novel features were used to rank models based on features they provide that would be useful to the CSM but are not included in the Tier 2 model. A rank of '1' represents models that have no or few novel features, '2' represents those with some features, and '3' represents models with many new features.

Each model was also evaluated for its ability to be used for the IW and FAL pathways. Models that included transport to groundwater were considered useful for both the IW and FAL pathways while those that allowed for transport through the saturated zone were considered useful for the FAL pathway. Models that covered both IW and FAL pathways received two points, those with one model, one point, and models with neither, zero points.

The sum of the ranks was taken (maximum 17 points) and a mechanistic review of three highly ranked models was conducted. Model components were compared to the features of the Tier 2 model to identify novel features, discrepancies, and overall similarities and differences. The Tier 2 model was broken down into its main components and the processes within new models were compared to those of the Tier 2 model. The mechanics of some of the novel features were also reviewed. Additionally, input parameters of each model were reviewed to determine if Alberta-specific inputs were available either through the Tier 1 document or literature review.

3.3 Model Analysis and CSM

An analysis of the models was conducted to determine how soil and groundwater quality guidelines would differ if each of the models was used. A CSM was established based on Tier 1 model criteria to conduct the model analysis. Where parameters required by the models were not listed in the Alberta Tier 1 tables C-2 (Soil and hydrogeological parameters), C-3 (site characteristics), and C-6 (chemical parameters), an attempt was made to best replicate typical Alberta conditions using parameters published in the literature or estimates.

The Tier 1 CSM assumed that the contaminant source is found within the unsaturated zone with the bottom in contact with the saturated zone. The pathway connecting the source to the IW receptor is transport of the contaminant from the source in the unsaturated zone into the saturated zone. The

groundwater is considered the receptor since the groundwater from any location within an aquifer may be used to irrigate crops. The pathway connecting the source to the FAL receptor is transport of the contaminant from the unsaturated source zone into the saturated groundwater zone followed by lateral transport through the saturated zone to the boundary of the freshwater body. At both Tier 1 and Tier 2, no dilution between the saturated zone and the freshwater body is considered as sensitive receptors may be present in the sediment that forms the boundary between groundwater and surface water. In the case of both bromacil and tebuthiuron, the most sensitive FAL receptors are aquatic plants, some of which are submerged and may be rooted in this boundary layer.

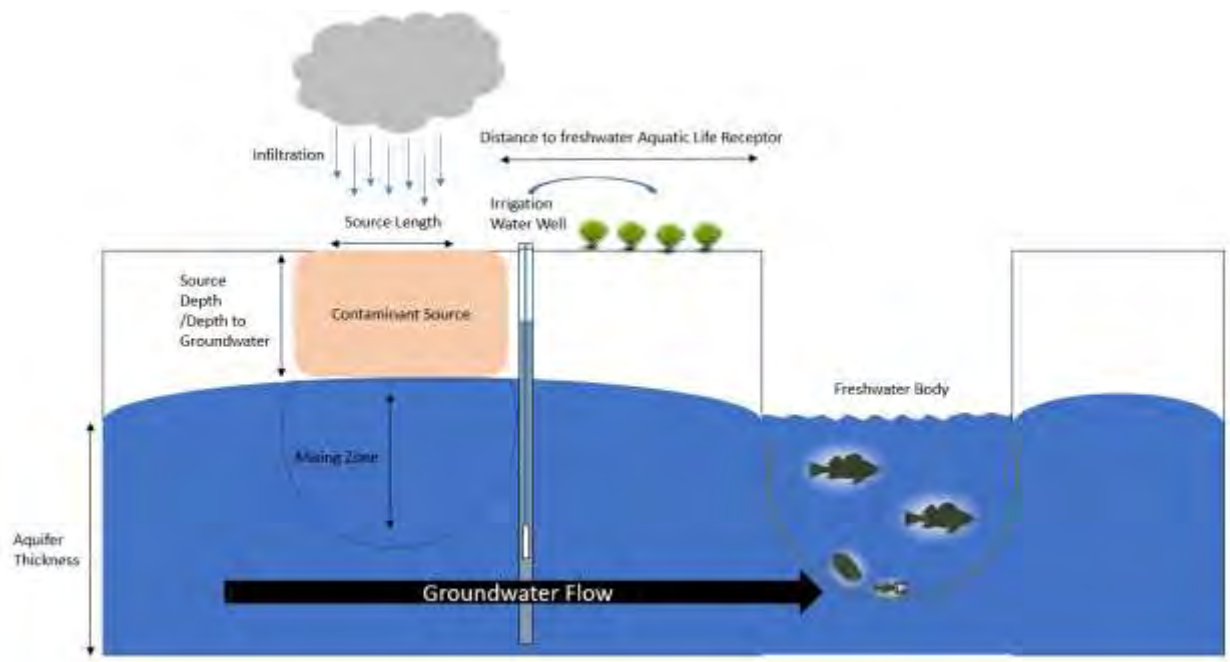

Figure 1 Conceptual Site Model on Which the Tier 1 and Tier 2 Guideline Models are Based. Modified from BC MOE (2016).

Many of the default Tier 1 model parameters are standard between sites, however soil and hydrogeological parameters may differ based on the predominant soil type found on site (Table 1). Default Tier 1 site characteristics (Table 2) are standard and chemical specific parameters are defined by the chemical.

Table 1. Default Tier 1 Soil and Hydrogeological Parameters.

Parameter	**Unit**	**Fine-grained soil**	**Coarse-grained soil**
Dry soil bulk density (ρ_b)	g/cm^3	1.4	1.7
Total soil porosity (θ_t)	vol/vol	0.47	0.36
Water filled porosity (θ_w)	vol/vol	0.168	0.119
Air filled porosity (θ_a)	vol/vol	0.302	0.241

Parameter	Unit	Fine-grained soil	Coarse-grained soil
Fraction organic carbon (f_{oc})	g/g	0.005	0.005
Saturated Hydraulic Conductivity (K)	m/y	32	320
Hydraulic Gradient (i)	m/m	0.028	0.028
Infiltration rate (I)	m/y	0.012	0.06
Soil permeability to vapour flow (kv)	cm^2	10^{-9}	$6x10^{-8}$

Table 2. Default Tier 1 values for Site Characteristics.

Parameter	Unit	Value
Contaminant Source Width Perpendicular to Groundwater Flow (Y)	m	10
Contaminant Source Length Parallel to Groundwater Flow (X)	m	10
Contaminant Source Depth (Z)	m	3
Distance to Surface Water (x)	m	10
Distance to Agricultural Water User (x)	m	0
Depth to groundwater (d)	m	3
Depth of unconfined aquifer (d_a)	m	5
Transport time (t)	yr	500
Thickness of zone below the source (b)	m	Tier 2-site specific

4.0 RESULTS AND DISCUSSION

4.1 Models Documented Within the Literature

Many models have been created to predict the movement of contaminants through soil and groundwater. Models present within the literature vary in complexity and specificity and may address one or more components of the CSM. Models were reviewed in terms of applicability to the CSM, comparability to the Tier 2 model, and specificity to herbicides such as bromacil and tebuthiuron.

4.1.1 General Contaminant Transport Models

Many contaminant transport models exist, however open-source models available from regulatory bodies were primarily reviewed. The US EPA Environmental Modeling Community of Practice (US EPA, 2020a) lists three groundwater models on their website to assess exposures including:

- 3D Finite Element Model for Groundwater/ 3D Leaching Waste (3D FEMWATER/3DLEWASTE);
- Pesticide Root Zone Model (PRZM); and

- Wellhead Analytical Element Model (WhAEM).

While WhAEM is specific to the Wellhead Protection Program in the United States, both 3D FEMWATER/3DLEWASTE and PRZM are indicated to have the capacity to model pesticide transport in soil and/or groundwater. The United States Geological Survey (USGS) also provides open-source groundwater and contaminant transport models such as MODFLOW and PHREEQC.

BIOSCREEN is another general model identified within the literature which is a natural attenuation decision support system that relies on similar parameters and equations as the Tier 2 model but allows for source depletion (Newell et al., 1996).

4.1.2 Models Used for Environmental Assessments of Herbicides and Pesticides

Previous assessments of groundwater models specific to herbicides and pesticides have been conducted at the national level. Under the North American Free Trade Agreement (NAFTA) the Health Canada Pest Management Regulatory agency (PMRA) and the US EPA Office of Pesticide Programs (US EPA/OPP) combined efforts in 2004 to harmonize groundwater modelling protocols for pesticides. A review of 19 models capable of modelling unsaturated zone transport was completed to assess the applicability, accessibility, and quality of models currently available (Baris et al., 2012). The reviewed models included:

- Chemical Movement in Layered Soils (CMLS)
- CRACK-Nitrogen and Pesticides (CRACK-NP)
- Groundwater Loading Effects of Agricultural Management Systems (GLEAMS)
- HYDRUS-1D and HYDRUS-2D
- Leaching Estimation and Chemistry Model (LEACHM) – Pesticides (LEACHP)
- MACRO
- Pesticide Emission Assessment at Regional and Local Scales (PEARL)
- Pesticide Leaching Model (PELMO)
- Pesticide Leaching and Accumulation (PESTLA)
- Pesticide Transport Assessment (PESTRAS)
- Pesticide Root Zone Model (PRZM)
- Root Zone Water Quality Model (RZWQM)
- Simultaneous Heat and Water (SHAW)
- Soil Water Assessment Tool (SWAT)
- VARLEACH
- Vadose Zone Leaching Model (VLEACH)
- Variably Saturated Two Dimensional Transport I (VS2DTI)
- Variably Saturated Two Dimensional Transport (VS2DT)
- Water and Agrochemicals in soil crop and Vadose Environment (WAVE)

A summary of the findings related to each model is included in Appendix B. The Baris et al. (2012) review included screening of the above models based on technical requirements including input data, the minimum runtime, and scope of the model, as well as user requirements including ease of use, access to technical support, public access, and the programming language. The results indicated that PRZM, PEARL, and LEACHP were the most suitable candidates to model pesticide movement to groundwater. The review considered models that predict water movement through the unsaturated zone via the Richard's equation (see Appendix C, Section 1.5.2) or a capacity type approach but did not include models that rely on a kinematic wave model.

Like the findings outlined in the above NAFTA assessment, McQueen et al. (2007) evaluated three pesticide fate models with respect to 10 pesticides commonly used in Manitoba. PRZM, LEACHP, and MACRO were used to analyze leaching risk of pesticides in Canada. All three models showed similar results however MACRO required a significantly longer run time and was only capable of analyzing two pesticides in the same time that the other two models were able to assess 10 pesticides.

4.1.3 Models Used for Environmental Assessments of Bromacil and Tebuthiuron

As part of registration process of most herbicides and pesticides environmental modelling is required. Several studies have been conducted by and on behalf of the US EPA/OPP to assess the environmental migration of bromacil and tebuthiuron.

The US Department of Forestry applies tebuthiuron for the management of woody invasive species (Durkin, 2016). The herbicide is applied to the soil as its mode of action relies on root uptake. The GLEAMS (Groundwater Loading Effects of Agricultural Management Systems) model was used to estimate peak and long-term concentrations of tebuthiuron in surface water bodies. Two EPA Tier 1 screening models were also used. The FIRST (FQPA Index Reservoir Screening Tool) model was used to estimate tebuthiuron concentrations in surface water and PRZM-GW (Pesticide Root Zone Model – Ground Water) was used to estimate tebuthiuron concentrations in groundwater. The US EPA Tier 2 model PRZM/EXAMS (PRZM/Exposure Analysis Modeling System) was also applied to estimate tebuthiuron concentrations in groundwater.

PRZM/EXAMS was also used by the US EPA/OPP for an assessment of bromacil in surface water. TerrPlant was used to assess estimated environmental concentrations for exposure of terrestrial and wetland plants. Groundwater modeling was conducted using SCIGROW (Screening Concentration in Ground Water) to estimate concentrations in shallow unconfined aquifers (US EPA/OPP/EFED, 2012). In the 1994 reregistration eligibility decision (RED) of tebuthiuron, the PRZM/EXAMS model was applied. Finally, the Department of Land Management conducted an assessment of Bromacil and Tebuthiuron and used the GLEAMS model for groundwater transport, and CALPUFF and AgDRFIT for aerial transport of soil particles containing with the herbicides (ENSR, 2005 a, b).

Several models have also been created by academic groups to study the fate and transport of bromacil and tebuthiuron. For example, dePaz and Rubio (2006) developed an attenuation factor/retardation factor model to determine how bromacil and other agrochemicals leached through the soil profile of citrus orchards. This simplistic model was tied to Arc GIS and was intended to develop risk factors related to individual agrochemicals. The model does not however predict movement below the root zone.

4.2 Considerations for Model Ranking

4.2.1 Defensibility

Most of the models reviewed have been well verified and validated. Many are from government groups and have been used and tested under various scenarios. Some models from academic origins may be valid but have not been tested and validated at as many sites. For example, de Paz and Rubio's (2006) model has been verified for a citrus orchard in Spain however it may not be appropriate for other settings.

4.2.2 Model Availability

The availability and versions of many models previously discussed has greatly evolved within the last decade. Many models have been archived, combined, updated, or altered. PRZM is the most common model mentioned through the literature to assess the movement of herbicides and pesticides throughout the soil column. It has historically been combined with EXAMS, GW, etc. but is currently only available in the pesticide in water calculator (PWC 1.52) which can be used to predict pesticide concentrations in groundwater as well as surface water (as a result of runoff). The PEARL model is still available but in an updated form, FOCUS/PEARL 4.4.4.

Several other models mentioned above have been archived and are no longer readily available such as SCIGROW, FIRST and EXPRESS. Other models such as LEACHP were not easily accessible and only available from the creator (Hutson, 2003).

4.2.3 Ease of Use

While some models may provide sophisticated predictions of contaminant transport, their complexity can pose a challenge to the end user both in the difficulty of running the program and in acquiring the necessary input parameters. For example, 3D FEMWATER is suggested by the US EPA for modelers with significant experience in numerical modelling and strong background in hydrogeology. PHREQC is also an advanced modelling tool that may be difficult for most users.

Most of the models discussed above require significantly more input parameters to run than the Tier 2 model. For example, both PWC and PEARL require weather files, detailed site information, and vegetation parameters.

4.2.4 Applicability to the CSM

While many models contain novel features that may improve the prediction of herbicide and pesticide transport in soils, some features may be overly specific and thus restrictive. Given that most models used to predict pesticide behaviour focus on agricultural systems they generally include features that don't fit the AEP Tier 2 CSM relevant to contaminated sites in Alberta. Despite having different intents and purposes some application settings may be altered to simulate the target CSM while maintaining the assumptions of the model. For example, in PWC and PEARL, the agrochemical can be applied as a ground application, a foliar application, or injected into the soil. The soil injection at a given depth scenario could be useful in mimicking the Tier 2 CSM which would place residual sterilant in the subsurface.

Very few models cover all elements of the Tier 2 model. While the Tier 2 model allows for the incorporation of vertical and lateral transport, several models such as PRZM only include vertical transport while other models focus on lateral transport such as BIOSCREEN. These models may be useful in targeting specific pathways, for example using the groundwater component of the PWC model for the IW pathway and the BIOSCREEN model for the FAL pathway. The PEARL model includes both vertical and lateral transport mechanisms.

4.2.5 Novel Features

The Tier 2 model is at its core an analytical solution of several transport equations. Analytical solutions are preferred by many regulatory bodies due to their ease of implementation and greater transparency, however, analytical solutions typically require approximation of the problem (Paladino et al., 2017; Srinivasan et al., 2007). Alternatively, other models may apply numerical solutions. For example, the PRZM

component of PWC relies on the finite-difference method of numerical analysis (Suarez, 2005). An analysis of the Domenico model, used for DF4 of the Tier 2 model, by Srinivasan et al. (2017) found that the solution was accurate when longitudinal dispersivity is zero but a study by West and Kueper (2004) found that the Domenico model could produce errors of up to 50% in the near field.

Both BIOSCREEN and the model used in the Alberta Tier 2 guidelines rely on analytical solutions formulated by Domenico. However, the Alberta Tier 2 guidelines are based on the Domenico-Robbins solution (Domenico and Robbins, 1985) which is purposed to model non-depleting contaminant plumes. BIOSCREEN is based on a solution published by Domenico (1987) which is purposed to model the 3D transport of a contaminant plume with a finite patch source (Srinivasan et al., 2007). Other models also present unique features such as weather dependent degradation and infiltration rates, plant uptake and variable soil profiles.

Further model evaluation and ranking is presented in Appendix B.

4.3 Models of Interest

Despite the great number of chemical transport models available, few contain all desired components, have the capacity to address the CSM, or are designed to handle chemicals such as bromacil and tebuthiuron. Based on the above criteria, PEARL was the highest-ranking model with 15/17 points but BIOSCREEN, PWC, 3DFEMWATER/3DLEWASTE, MODFLOW, and SWAP all received 14/17 points (Appendix B). SWAP was not pursued as it is a module contained within PEARL and was not available for download. 3DFEMWATER/3DLEWASTE and MODFLOW were considered to be more advanced models that would be more appropriate for site-specific risk assessments rather than a Tier 2 approach. The remaining three models, PEARL, PWC, and BIOSCREEN were selected for further analysis and are discussed below.

4.3.1 BIOSCREEN

BIOSCREEN is a contaminant transport model designed by the US EPA, to simulate dissolved hydrocarbon attenuation within the saturated zone. It is an Excel-based program that accounts for advection, dispersion, adsorption, decay and source depletion. It was designed as a screening tool to help manage sites impacted by petroleum fuel releases (Newell et al., 1996).

BIOSCREEN is a simple model that is very similar to the saturated zone transport component (FAL) of the Tier 2 model with the modification that is considers source zone depletion. Transport can be simulated without decay, with first order decay, or with instantaneous biodegradation. While BIOSCREEN was not originally intended to model herbicides such as bromacil and tebuthiuron, these compounds have been noted to have first order degradation rates throughout the literature (Madhum and Freed, 1987; Qian et al., 2017). BIOSCREEN has the capacity to help determine how far a contaminant plume will extend, how long the plume will persist, and at what concentration.

BIOSCREEN was selected as a model for further investigation as its similarity to the current Tier 2 model could allow for rapid integration and it includes elements not currently available in the Tier 2 model such as source depletion. It is based on analytical solutions to transport phenomena which lends well to Tier 2 guideline development.

4.3.2 PWC

The US EPA PWC model is the most recently updated version of an available model that includes the PRZM model. PWC's primary function is to determine pesticide concentrations in surface water bodies as a result of runoff. However, it also contains a groundwater module and allows for tracking of agricultural chemicals as they migrate through the soil profile to the groundwater level.

PWC is a combination of the PRZM5 (5.02) and variable volume water model (VVWM 1.02). It has the capacity to model chemicals applied to the soil, as a foliar application, or injected into the soil at a given depth. PRZM uses numerical modelling methods to determine pesticide migration through the unsaturated zone. PWC has a markedly different approach to the current Tier 2 model, however it contains many of the same basic features while incorporating other factors that influence contaminant concentrations within the unsaturated zone (see section 4.4). PWC may be useful for modelling contaminant transport relevant to the IW pathway.

PRZM (in the form of PWC) was selected as a model for further investigation as it has been previously used for modelling the transport of agricultural chemicals including bromacil and tebuthiuron. While the program is typically used for agricultural applications the "soil injection" scenario may be appropriate to the Tier 2 CSM.

4.3.3 PEARL

PEARL is a European model designed to evaluate "plant protection products" leaching to groundwater, drainage to surface water bodies and persistence in topsoil (van den Berg et al., 2016). The model integrates the Soil-Water-Atmosphere-Plant (SWAP) hydrological model to address water and solute movement through the unsaturated zone and into the saturated zone. Like PWC, PEARL is primarily intended for agricultural scenarios but allows the user to select the method of chemical application to be soil surface application, foliar application, or injected into the soil.

PEARL was selected due to both its specificity to agricultural chemicals and its ability to parallel the desired elements of the Tier 2 model. The PEARL model addresses both leaching to groundwater and leaching of contaminated groundwater to freshwater bodies, which is analogous to the IW and FAL pathways.

4.4 Mechanistic Review

The selected models were compared to the Tier 2 model based on the each of the mechanisms that drive the pathway between the source and IW and FAL receptors. The Tier 2 approach is based on a protocol derived by the CCME (2006) and considers four main processes:

1. Soil-Leachate Partitioning (DF1)
2. Transport through the unsaturated zone (DF2)
3. Groundwater Mixing (DF3)
4. Lateral transport through the saturated zone (DF4)

The method through which chemical partitioning is calculated was similar among all models reviewed. However, the Tier 2 model separates partitioning into a distinct process, while the other models incorporate partitioning into different transport components.

Contaminant transport through the unsaturated zone is not handled by BIOSCREEN and differs significantly between the Tier 2 model, PWC, and PEARL. The three models cover many of the same

features but employ different equations and methods. The Tier 2 model is solved analytically and the PWC and PEARL models are solved numerically. Of the three models evaluated, only PEARL considers mixing of the leachate into groundwater and does so using a mass-balance approach. Both the Tier 2 and BIOSCREEN models rely on solutions developed by Domenico of the three-dimensional advection-dispersion equation. However, the BIOSCREEN model is based on a slightly updated version that includes source depletion. The PWC model does not consider saturated transport. The PEARL model relies primarily on solute flux and mass balance equations combined with hydrological modelling. Both the PWC and PEARL models also take a more sophisticated approach to infiltration rates using a tipping bucket approach and Richard's equation respectively.

These processes are explored in detail for each model in Appendix C and summarized below in Table 3.

Table 3. Factors Considered by Reviewed Models.

	Tier 2	**BIOSCREEN**	**PWC**	**PEARL**
Soil-Leachate Partitioning				
Freundlich Isotherms	✓	✓	✓	✓
Henry's law	✓	✓	✓	✓
Transport through the Unsaturated Zone				
One-dimensional	✓	N/A	✓	✓
Advection	✓	N/A	✓	✓
Dispersion	✓	N/A	✓	✓
Adsorption	✓	N/A	✓	✓
Decay	✓	N/A	✓	✓
Plant uptake	X	N/A	✓	✓
Variable Infiltration	X	N/A	✓	✓
Volatilization	X	N/A	✓	✓
Analytical/Numerical	Analytical	N/A	Numerical	Numerical
Groundwater Mixing				
Mass Balance Approach	✓	N/A	X	✓
Infiltration	✓	N/A	X	X
Hydraulic gradient	✓	N/A	X	X
Based on Drainage Flux	✓	N/A	X	✓
Transport through the Saturated Zone				
Advection	✓	✓	N/A	X
Dispersion	✓	✓	N/A	X
Adsorption	✓	✓	N/A	✓
Decay	✓	✓	N/A	✓

	Tier 2	BIOSCREEN	PWC	PEARL
Dilution from Infiltration	X	X	N/A	X
Novel Features				
Can consider variable soil physical and chemical parameters	X	X	✓	✓
Soil moisture can vary between horizons	X	X	✓	✓
Can consider variable infiltration rates	X	X	✓	✓
Source depletion is considered	X	✓	X	✓
Capacity to model multidimensional flow in the unsaturated zone	X	X	X	✓
Variable Infiltration Rates	X	X	✓	✓
Preferential flow	X	X	✓	✓

4.5 Input Parameters

A critical consideration for the use of a model is the required input parameters. One of the benefits of the current Tier 2 model is the limited number of site-specific parameters that are required. To complete a model analysis, it was necessary to determine the required input parameters. Where AEP values were not available, values were determined from the literature and/or user manual and guidance documents that would be most representative of a typical Alberta site.

Parameters were classified into three groups based on the ease with which they were determined. First were parameters already available within AEP guidance documents. Second were parameters which could be easily estimated from the CSM or were readily available within the literature such as relevant chemical data on Pubchem (NLM, 2020). The third group are parameters which are not clearly defined, are highly specific and thus not easy to estimate, or required selection between a range presented in the user manual.

While most of the input parameters for the BIOSCREEN model were available within AEP guidance documents or could be estimated, numerous input parameters for both the PWC and PEARL model were challenging to acquire.

A detailed review of the input parameters is included in Appendix D and summarized below in Table 4.

Table 4. Required Model Input Parameters.

	Included in AEP Guidance Documents	**Available within Literature/ Calculated from AEP variable**	**Unique Parameters, Provided in the User Manual, or Estimated**
Tier 2	– Organic Carbon Partition Coefficient (Koc) (mL/g) – Henry's Constant – Depth to bottom of contaminated soil (m) – Depth from surface to potential DUA (m) – Thickness of zone below the source (m) – Fraction organic carbon (foc) (%) – Dry soil bulk density (ρ_b) (g/cm^3) – Water filled porosity (θ_w) (–) – Total soil porosity (θ) (–) – Air filled porosity (θ_a) (-) – Infiltration rate (I)	– Half-life (years)	
BIOSCREEN	– Hydraulic gradient (ft/ft) – Porosity – Hydraulic conductivity (cm/s) – Estimated plume length (ft) – Partition coefficient (L/kg) – Soil bulk density (kg/L) – Organic carbon fraction – Modeled area length (ft) – Modeled area width (ft) – Simulation time (yr) – Source thickness in saturated zone (ft) – Distance from source (ft)	– Solute half-life (yr) – Soluble Mass – Groundwater concentration (mg/L)	

	Included in AEP Guidance Documents	Available within Literature/ Calculated from AEP variable	Unique Parameters, Provided in the User Manual, or Estimated
PWC	– Koc – Solubility (mg/L) – Henry's la constant (dimensionless)* – Depth (cm) – Horizon thickness (cm) – Bulk density (ρ) (g/cm^3) – OC (%) – Field Area (m^2) – Groundwater Initial Depth (m) – Groundwater Max Depth (m)	– Soil Half-life (days) – Soil reference temperature (C) – Molecular Weight (g/mol) – Vapour Pressure (torr) – Number of applications – Days since emergence – Amount (kg/ha) – Application method – Application occurs every (years) – Application occurs from year – Application occurs to year – Meteorological files – Post-harvest foliage – Irrigation – Number of horizons – Number of chemical in the simulation – Simulation Type	– Heat of Henry (J/mol) – Q10 – Reservoir efficiency – Reservoir Drift – Pond efficiency – Pond drift – Custom efficiency – Custom drift – Scenario – Emergence date – Mature date – Harvest date – Root depth (cm) – Canopy cover (%) – Canopy height (cm) – Canopy holdup (cm) – Pan factor – Snowmelt factor (cm/°C/day) – Evaporation depth (cm) – Max Cap (field capacity) (cm^3/cm^3) – Min. Cap. (wilting point) (cm^3/cm^3) – N – Number of Time-Varying Factors – Curve number – USLE cover management factor – Soil erodibility – Topographic factor – Practice factor – Location of NRCS 24 hrs hyetograph – Slope of hydraulic flow path – Runoff Depth (cm) – Runoff Decline (1/cm) – Efficiency – Erosion Depth (cm) – Erosion Decline (1/cm) – Efficiency – Water body area (m^2) – Hydraulic Length (m) – Cropped Area Fraction – Base Flow (m^3/s) – Water Body Physical Parameters – Sediment Accounting

	Included in AEP Guidance Documents	Available within Literature/ Calculated from AEP variable	Unique Parameters, Provided in the User Manual, or Estimated
PEARL	– Location – F_{oc} (kg/kg) – Dry bulk density (kg/m3) – Solubility in water (mg/L) – Measured at (°C) – Kom	– Longitude – Latitude – Altitude – Number of Soil Horizons – Percent Sand – Percent Silt – Percent Clay – Meteostation source – Longitude – Latitude – Altitude – Crop – Irrigation regime – Tillage regime – Application repeat interval – Molar mass (g/mol) – Saturated vapour pressure – Measured at (°C) – Half-life (d) – Half-life on crop surface (d) – Application type – Date – Dosage (kg/ha) – Depth (m) – Initial depth and concentration – Deposition – Initial groundwater depth	– Max ponding depth (m) – Initial Soil temperature at bottom of profile (°C) – Air boundary thickness layer thickness (m) – Relative diffusion coefficient – Thickness of horizon (m) – Number of numerical components – Dispersion length (m) – pH – Theta Sat (m^3/m^3) – Theta Res (m^3/m^3) – Alpha dry (/cm) – Alpha wet (/cm) – Lambda (-) – K Sat (m/day) – n (-) – Lower boundary – Molar enthalpy of vaporization (kg/mol) – Molar enthalpy of dissolution (kg/mol) – Molar enthalpy of sorption (kJ/mol) – Reference concentration in liquid phase (mg/L) – Freundlich sorption exponent (-) – Desorption rate coefficient (/day) – Factor relating CofFreNeq and CofFreEql – Liquid content in incubation experiment (kg/kg) – Exponent for the effect of liquid (-) – Molar activation energy (kg/mol) – Reference temperature for diffusion (°C) – Reference diffusion coefficient in water (m^2/d) – Reference diffusion coefficient in air (m^2/d) – Wash-off factor – Coefficient for plant uptake (-)

4.6 Model Analysis and Comparison

An analysis of the selected models was conducted to determine the maximum concentration of bromacil or tebuthiuron in the soil and groundwater at the source that would be protective of IW and FAL at the receptor. Three scenarios were considered that would allow for comparison to groundwater quality guidelines (GWQG) and soil quality guidelines (SQG) from the Tier 2 model. The first scenario mimics current Tier 1 settings for bromacil and tebuthiuron as closely as possible and does not include a half-life or an unsaturated separation unit. The second considers half-life derived from literature sources, but no unsaturated separation unit. The third considers both a literature derived half-life and a one-metre unsaturated vertical separation unit.

A detailed analysis is presented in Appendix E. Resulting GWQGs and SQGs are summarized in Tables 5 through 8.

4.6.1 BIOSCREEN

The BIOSCREEN model is similar to the DF4 portion of the Tier 2 model but considers source depletion. The maximum allowable concentration of bromacil and tebuthiuron in groundwater at the source was determined to keep groundwater concentrations of the compound 10 m downgradient from the source within the surface water quality guidelines. The maximum concentration at the source was determined at the point in time where concentrations 10 m downgradient were maximal (Appendix E). GWQGs produced by BIOSCREEN were 2 to 3 times higher than those produced by the Tier 2 model under all scenarios evaluated (Table 5). Soil quality guidelines were determined based off the BIOSCREEN groundwater concentrations using the Tier 2 model with DF1 through DF3. SQGs were also 2 to 3 times higher than those of the Tier 2 model.

4.6.2 PWC

PWC can be used to determine the concentration of agrochemicals leached to groundwater and runoff to surface water bodies, however it does not consider groundwater transport to surface water bodies. The SQGs produced by PWC for the IW pathway for both bromacil and tebuthiuron were fairly similar to the Tier 2 SQGs but marginally more conservative. The inclusion of a half-life did not have a significant impact on the SQGs for PWC nor did the inclusion of a 1 m unsaturated separation unit. The SQGs between soil types were only marginally different.

4.6.3 PEARL

PEARL can be used to determine the leaching of agrochemicals to groundwater and can also consider transport to water bodies via lateral transport. However, under all scenarios examined, lateral transport, which the model terms 'lateral drainage', was negligible compared to leaching and degradation where scenarios included a half-life (Appendix E). While this was initially surprising, other studies have found that lateral transport of pesticides in groundwater to surface water bodies to be negligible due to slow groundwater movement, sorption, and degradation (Groenboek, 2002; Holvoet et al., 2007; Ropke et al., 2004). Therefore, GWQGs and SQGs for the FAL pathway were not presented. The SQGs produced by PEARL for the IW pathway for both bromacil and tebuthiuron were approximately twice as conservative as associated Tier 2 guidelines. The PEARL model was not sensitive to half-life or the inclusion of a separation unit but and was only marginally sensitive to soil type.

Table 5. Bromacil Freshwater Aquatic Life Guidelines.

		Tier1/Tier2		BIOSCREEN		PWC		PEARL	
	Soil Type	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**
No half-life	Fine	0.005	0.009	0.01	0.0175	N/A	N/A	***	***
	Coarse	0.005	0.009	0.011	0.021	N/A	N/A	***	***
Half-life (0.75 years)	Fine	0.879	1.537	2.94	5.14	N/A	N/A	***	***
	Coarse	0.0103	0.01923	0.02	0.037	N/A	N/A	***	***
Half-life (0.75 years) with 1 m separation	Fine	0.879	8.4×10^{6}	2.94	2.8×10^{7}	N/A	N/A	***	***
	Coarse	0.0103	4.77	0.02	9.27	N/A	N/A	***	***
Detection Limit	0.009 mg/kg								

Table 6. Bromacil Irrigation Water Guidelines.

		Tier 1/Tier2		BIOSCREEN		PWC		PEARL	
	Soil Type	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**
No half-life	Fine	$2x10^{-4}$	$3.5x10^{-4}$	N/A	N/A	$2x10^{-4}$	$3.5 x10^{-4}$	$2x10^{-4}$	$1.45x10^{-4}$
	Coarse	$2x10^{-4}$	$3.7 x10^{-4}$	N/A	N/A	$2x10^{-4}$	$4 x10^{-4}$	$2x10^{-4}$	$1.4x10^{-4}$
Half-life (0.75 years)	Fine	$2x10^{-4}$	$3.5 x10^{-4}$	N/A	N/A	$2x10^{-4}$	$3.6x10^{-4}$	$2x10^{-4}$	$1.45x10^{-4}$
	coarse	$2x10^{-4}$	$3.7 x10^{-4}$	N/A	N/A	$2x10^{-4}$	$4.1 x10^{-4}$	$2x10^{-4}$	$1.4x10^{-4}$
Half-life (0.75 years) with 1 m separation	Fine	$2x10^{-4}$	1,900	N/A	N/A	$2x10^{-4}$	$3.6 x10^{-4}$	$2x10^{-4}$	$1.45x10^{-4}$
	Coarse	$2x10^{-4}$	0.093	N/A	N/A	$2x10^{-4}$	$4.1 x10^{-4}$	$2x10^{-4}$	$1.4x10^{-4}$
Detection Limit	0.009 mg/kg								

Table 7. Tebuthiuron Freshwater Aquatic Life Guidelines.

		Tier1/Tier2		BIOSCREEN		PWC		PEARL	
	Soil Type	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**
No half-life	Fine	0.0016	0.0015	0.0032	0.0029	N/A	N/A	***	***
	Coarse	0.0016	0.0014	0.0056	0.0048	N/A	N/A	***	***
Half-life (1.5 years)	Fine	0.0141	0.0128	0.029	0.0263	N/A	N/A	***	***
	Coarse	0.0020	0.00172	0.0067	0.0058	N/A	N/A	***	***
Half-life (1.5 years) with 1 m separation	Fine	0.0141	6.94	0.029	14.3	N/A	N/A	***	***
	Coarse	0.002	0.00925	0.0067	0.03	N/A	N/A	***	***
Detection Limit	0.001 mg/kg								

***Under all scenarios examined, PEARL determined that lateral drainage was insignificant compared to leaching, and degradation (under scenarios that included a half-life)

Table 8. Tebuthiuron Irrigation Water Guidelines.

		Tier1/Tier2		BIOSCREEN		PWC		PEARL	
	Soil Type	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**	**GWQG (mg/L)**	**SQG (mg/kg)**
No half-life	Fine	$4.3x10^{-4}$	$3.9x10^{-4}$	N/A	N/A	$4.3x10^{-4}$	$4.3x10^{-4}$	$4.3x10^{-4}$	$1.67x10^{-4}$
	Coarse	$4.3x10^{-4}$	$3.7x10^{-4}$	N/A	N/A	$4.3x10^{-4}$	$4.7x10^{-4}$	$4.3x10^{-4}$	$1.25x10^{-4}$
Half-life (1.5 years)	Fine	$4.3x10^{-4}$	$3.9x10^{-4}$	N/A	N/A	$4.3x10^{-4}$	$4.5x10^{-4}$	$4.3x10^{-4}$	$1.67x10^{-4}$
	Coarse	$4.3x10^{-4}$	$3.7x10^{-4}$	N/A	N/A	$4.3x10^{-4}$	$4.8x10^{-4}$	$4.3x10^{-4}$	$1.25x10^{-4}$
Half-life (1.5 years) with 1 m separation	Fine	$4.3x10^{-4}$	0.21	N/A	N/A	$4.3x10^{-4}$	$4.5x10^{-4}$	$4.3x10^{-4}$	$1.67x10^{-4}$
	Coarse	$4.3x10^{-4}$	$2.0x10^{-3}$	N/A	N/A	$4.3x10^{-4}$	$4.8x10^{-4}$	$4.3x10^{-4}$	$1.25x10^{-4}$
Detection Limit	0.001 mg/kg								

4.6.4 Considerations

Some of the models examined rely on methods that differ significantly from the Tier 2 model methodology. They also include more site-specific flexibility than the Tier 2 model, which could lead to more accurate guidelines but could also contribute to inaccuracies within the model analysis.

BIOSCREEN considers source depletion and requires the user to input the total source mass. For the analysis, it was assumption that the entire source (10 m X 10 m X 3 m) was within the groundwater unit and the mass was derived based on the partition coefficient. This was selected for simplicity, but the

model is sensitive to the source mass. A more accurate source mass and field concentration measurements could produce vastly different GWQGs. This reflects the importance of the quality of the input parameters on the model analysis results.

Both the PWC and PEARL models are significantly more complex in their consideration of soil water movement and are much more sensitive to these site-specific soil and hydrological parameters. Both models require many input parameters that are not included in the Tier 2 model. Some of these parameters could be determined on a site-specific basis however others were not straightforward or were difficult to acquire. The user manuals provided typical ranges for several parameters, however a true sensitivity analysis of the model to the required parameters was not conducted. While every effort was made to select the most appropriate input parameters, an accurate representation of a typical Albertan site may not have been fully achieved. The selection of certain parameters was necessary to avoid some errors when running the models. In particular, PWC and PEARL were sensitive to some soil and hydrological parameters and would produce errors or irregular results when set to a value other than a specific pre-set.

Further, some unexpected results were observed, such as the lack of sensitivity to the half-life of the sterilants and to a separation unit, for both the PWC and PEARL models, which likely requires further investigation.

5.0 SUMMARY AND CONCLUSIONS

The purpose of Task 2 was to evaluate alternative models to the current Tier 2 model for the IW and FAL pathways that could be used to assess the transport of bromacil and tebuthiuron. A literature review was conducted, and several models were identified that have the capacity to model agrochemical transport through unsaturated and/or saturated media. These models were reviewed, ranked, and three potential models were selected: BIOSCREEN, PWC, and PEARL.

BIOSCREEN models solute transport through the saturated zone using principles like the lateral transport component of the Tier 2 model. It contains many of the same parameters as the Tier 2 model but also considers source depletion. As compared to the Tier 2 model, GWQGs and SQGs generated by BIOSCREEN for the FAL pathway were generally higher than those generated by the Tier 2 model and all guidelines were above detection limits. BIOSCREEN may be a suitable alterative or supplemental model that would integrate well with the current Tier 2 model. However, BIOSCREEN can only be used for the FAL pathway as unsaturated transport is not considered.

PWC is a standard model used by the US EPA for the evaluation of pesticide transport. It relies on numerical methods and varies significantly from the current Tier 2 model both in methodology and required input parameters. The SQGs for the IW pathways produced by the model were similar if slightly more conservative than those of the Tier 2 model. PWC does not consider lateral transport and thus cannot be used for the FAL pathway, however it does consider runoff to surface water bodies which may be of interest at certain sites. Given the similarity of the results to the Tier 2 model but the significant increase in complexity, the PWC model is not suggested for most scenarios. However, this model appears to be more sensitive to some soil and hydrogeological parameters and thus sites where these factors vary significantly from the typical CSM could benefit from the application of this model.

The PEARL model is a standard model applied in Europe to model agrochemical transport in variably saturated soils. It contains many useful preset scenarios however allows for the flexibility to create new site-specific scenarios. PEARL varies significantly from the Tier 2 model, is much more complex and challenging to use, requires more input parameters, but also generates many results that may be useful on a site-specific basis. SQGs for the IW pathway were approximately twice as conservative as those of the Tier 2 guidelines. PEARL, like PWC, was sensitive to some soil and hydrogeological parameters which may be available for a specific site but are not specified within Tier 2. PEARL is purported to model lateral solute flux to surface water bodies, however under the examined scenarios this pathway was insignificant which may highlight a limitation of the model for the application under consideration.

None of the three models examined in detail effectively cover all elements of the Tier 2 model. However, they may be useful in supplementing the current model. The BIOSCREEN model may be helpful when considering the FAL pathway. The PWC model may be useful for scenarios with significant surface runoff. The PEARL model may provide other useful output information such as solute tracking within the soil profile including upwards and downwards migration, solute accounting between soil, water, and gas phases, as well as advanced water balances.

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US EPA SSG. 1996b. Soil Screening Guidance: Technical Background Document. Part 3: models for detailed assessment.

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van den Berg, F., Tiktak, A., Boesten, J.J.T.I., van der Linden, A.M.A. 2016. PEARL Model for Pesticide Behaviour and Emissions in Soil-plant Systems: Description of Processes. Statutory Research Tasks Unit for Nature & the Environment, Wageningen, The Netherlands. WOt-Technical Report 61. 134 pp. https://www.pesticidemodels.eu/sites/default/files/documents/pearlthe.pdf

Vanclooster, M., Viaene, P., Christiaens, K., Ducheyne, S. 1996. WAVE, A Mathematical Model for Simulating Water and Agrochemicals in the Soil and the Vadose Environment, Reference and User's Manual, Release 2.1, Institute for Land and Water Management, Katholieke Universiteit Leuven, Belgium, 15 pp.

Walker, A. and Barnes, A. 1981. Simulation of Herbicide Persistence in Soil: A Revised Computer Model. Pest. Sci. 12, 123–132.

West, M. and B.H. Kueper. 2004. Natural attenuation of solute plumes in bedded fractured rock. In Proceedings of USEPA/NGWA Fractured Rock Conference, 388–401. Portland, Maine: National Ground Water Association.

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Yeh, G.T., Sharp-Hansen, S., Lester, B., Strobl, R., Scarbrough, J. 1992. 3DFEMWATER/3DLEWASTE: Numerical codes for delineating wellhead protection areas in agricultural regions based on the assimilative capacity criterion. Publication No. EPA/600/R-92/223.

Young, D.F. 2015. Pesticide in Water Calculator User Manual (Version 1.50) Overview.

Young, D., and Fry, M. 2014. PRZM5 A Model for Predicting Pesticide in Runoff, Erosion, and Leachate: User Manual USEPA/OPP 734F14002. June 2014, 53. https://doi.org/10.13140/2.1.1828.6408

7.0 ACKNOWLEDGEMENTS

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8.0 LIST OF APPENDICES

APPENDIX A: Literature Review

APPENDIX B: Model Summaries and Ranking

APPENDIX C: Mechanistic Review

APPENDIX D: Input Parameters

APPENDIX E: Model Analysis and Comparisons

APPENDIX A: LITERATURE REVIEW

Citation	Article Type	Summary	Reference
AEP, 2019a	Report	Alberta Tier 1 guidelines, includes site specific parameters in tables within appendix C, provides soil quality guidelines, water quality guidelines and surface water quality guidelines for IW and FAL pathways.	Alberta Environment and Parks (AEP). (2019a). *Alberta Tier 1 Soil and Groundwater Remediation Guidelines* .
AEP, 2019b	Report	Alberta Tier 2 guidelines: provides outline and equations for the calculation of Tier 1 and 2 guidelines, provides guidance on developing Tier 2 guidelines, including Iwi and FAL pathways	Alberta Environment and Parks (AEP). (2019b). Alberta Tier 2 Soil and Groundwater Remediation Guidelines. In *Land and Forestry Policy Branch, Policy Division* . https://doi.org/ISBN 978-1-4601-2695-0
Baris et al., 2012	Report	Joint US EPA/OPP and Health Canada review of pesticide models designed to assess transport to groundwater. PRZM, LEACHM, and PEARL are identified as the most suitable and reasoning behind the selection is outlined.	Baris, R. Barrett, M., Bohaty, R.F.H. Echeverria, M., Kennedy, I., Malis, G., Wolf, J., Young, D. (2012). *Identification and Evaluation of Existing Models for Estimating Environmental Pesticide Transport to Groundwater* . 1–71.
BC MOE, 2016	Report	Report reviews the CSST model, the conceptual site model, default site conditions and characteristics as well as rationale. Assumptions and equations are discussed.	BC MOE. 2016. Protocol 28 “2016 Standards Derivation Methods” Chapter 4. Derivation of Soil to Groundwater Protection Matrix Soil Quality Standards.
CCME, 2006	Report	Protocol for the development of environmental and human health soil quality guidelines, methods and equations are elaborated, origins of the method are discussed, CSM, assumptions, standard reference values etc.	CCME. (2006). *A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines* .
dePaz & Rubio (2006	Primary Research Paper	Development of a attenuation factor/retardation factor model for the transport of agrochemicals to groundwater in a citrus orchard in Valencia, Spain. Risk factors associated with groundwater contamination are developed, bromacil is included the in the assessment.	de Paz, J. M., & Rubio, J. L. (2006). Application of a GIS-AF/RF model to assess the risk of herbicide leaching in a citrus-growing area of the Valencia Community, Spain. *Science of the Total Environment* , *371* (1–3), 44–54. https://doi.org/10.1016/j.scitotenv.2006.07.018
Domenico (1987)	Primary Research Paper	Elaborates the theoretical and mathematical derivation and solution of the three dimensional advection dispersion equation. Includes decay and source depletion.	Domenico, P. A. (1987). AN ANALYTICAL MODEL FOR MULTIDIMENSIONAL TRANSPORT OF A DECAYING CONTAMINANT SPECIES. In *vfJ ENTERED Journal of Hydrology* (Vol. 91).
Domenico and Robbins (1985)	Primary Research Paper	Elaborates the theoretical and mathematical derivation and solution of the three dimensional advection dispersion equation. Includes decay.	Domenico, P. A., & Robbins, G. A. (1985). A New Method of Contaminant Plume Analysis. *Ground Water* , *23* (4), 476–485. https://doi.org/10.1111/j.1745-6584.1985.tb01497.x
Durkin 2016	Report	Human health and ecological risk assessment of tebuthiuron. The herbicide is reviewed in the context of the US department of forestry's use of the sterilant to mange woody invasive species. Several modelling efforts are made and outlined throughout the report. GLEAMS and PRZM are among the models used.	Durkin, P. R. (2016). *Tebuthiuron: Human Health and Ecological Risk Assessment FINAL REPORT* . www.sera-inc.com
ENSR, 2014a	Report	Ecological risk assessment for bromacil. Provides a description of the activity of bromacil, its historical and current use. Pathways for environmental contamination are discussed and evaluated using three models: AgDRIFT, GLEAMS, and CALPUFF.	ENSR. (2005). *Bromacil, Ecological Risk Assessment, Final Report Bromacil, Ecological Risk Assessment, Final Report ENSR International* . https://digitalcommons.usu.edu/govdocs/78
ENSR, 2014b	Report	Ecological risk assessment for Tebuthiuron. Provides a description of the activity of tebuthiuron, its historical and current use. Pathways for environmental contamination are discussed and evaluated using three models: AgDRIFT, GLEAMS, and CALPUFF.	ENSR. (2005). *Tebuthiuron Ecological Risk Assessment* . https://digitalcommons.usu.edu/govdocs/417
Golder, 2005	Report	Report reviewing the method developed by the B.C. Ministry of Environment Contaminated Sites Standards Task (CSST) Group for the development of soil and water quality guidelines. Includes the equations developed, the process through which they were derived and the theory behind each process.	Golder. 2005. Report on: Scientific Review of British Columbia CSST Soil Standards Derivation Protocol.
Kool et al (1994	Primary Research Paper	Development of a vertical transport model within the unsaturated zone. The process of derivation and theory behind the model is outlined.	Kool, J. B., Huyakorn, P. S., Sudicky, E. A., & Saleem, Z. A. (1994). A composite modeling approach for subsurface transport of degrading contaminants from land-disposal sites. *Journal of Contaminant Hydrology* , *17* (1), 69–90. https://doi.org/10.1016/0169-7722(94)90078-7

Citation	Article Type	Summary	Reference
Madhum et al., 1987	Primary Research Paper	Involved a lab study of bromacil degradation using C14. Half lives were determined at 25, 30, 35 Celsius and demonstrated that temperature has a significant impact on degradation rate (3x faster at 35 than 25C).	Madhum, Y. A., & Freed, V. H. (1987). Degradation of the herbicides bromacil, diuron and chlortoluron in soil. *Chemosphere* , *16* (5), 1003–1011. https://doi.org/10.1016/0045-6535(87)90037-3
McQueen et al. (2007)	Primary Research Paper	PRZM, LEACHP, and MACRO models were evaluated for their ability to determine the risk of leaching to groundwater of pesticides in Canada. For the assessment, Manitoba was selected as a test province and fourteen pesticides commonly used in the province were assessed. All models proved to have similar capabilities but MACRO was significantly less efficient.	McQueen, D. A. R., Farenhorst, A., Allaire, S., & Cessna, A. J. (2007). Automation and evaluation of three pesticide fate models for a national analysis of leaching risk in Canada. *Canadian Journal of Soil Science* , *87* (2 SPEC. ISS.), 203–212. https://doi.org/10.4141/s06-065
Paladino et al., 2017	Primary Research Paper	A solution to the three-dimensional advection-dispersion equation is developed including decay, first-order reactions and retardation. The solution was compared to previous analytical open and closed form solutions.	Paladino, O., Moranda, A., Massabò, M., & Robbins, G. A. (2017). *Analytical solutions of three-dimensional contaminant transport models with exponential source decay:* https://doi.org/10.1111/gwat.12564
Qian et al., 2017	Primary Research Paper	A new method was developed for the environmental detection of tebuthiuron with the goal of minimizing risk to aquatic ecosystems. Field dissipation were completed in conjunction with the above goal. Tebuthiuron dissipated via a first order rate model.	Qian, Y., Matsumoto, H., Liu, X., Li, S., Liang, X., Liu, Y., Zhu, G., & Wang, M. (2017). Dissipation, occurrence and risk assessment of a phenylurea herbicide tebuthiuron in sugarcane and aquatic ecosystems in South China. *Environmental Pollution* , *227* , 389–396. https://doi.org/10.1016/j.envpol.2017.04.082
RED 1994	Report	Reregistration Eligibility Decision (RED) for Tebuthiuron. Environmental fate is reviewed with respect to registrant submitted studies. Photodegradation in water, aerobic soil metabolism, anaerobic soil metabolism, anaerobic aquatic metabolism, aerobic aquatic metabolism, bioaccumulation in fish, and field dissipation are reviewed.	US EPA. (1994). *RED Facts Tebuthiuron* .
Srinivasan et al., 2007	Primary Research Paper	Review and critique of the Domenico solution of the three-dimensional advection-dispersion equation. A mathematic review and derivation is conducted and it was determined that the Domenico solution is true so long as longitudinal dispersity is 0, but that significant error is introduced in non-zero situations.	Srinivasan, V., Clement, T. P., & Lee, K. K. (n.d.). *Domenico Solution-Is It Valid?* https://doi.org/10.1111/j.1745-6584.2006.00281.x
US EPA SSG, 1996a	Report	Guidance document describing the methods to calculate soil quality guidelines for residential exposure pathways. The technical background and methods is provided along with assumptions and limitations.	*US EPA SSG. 1996a.Soil Screening Guidance: Technical Background Document. Part 2: DEVELOPMENT OF PATHWAY-SPECIFIC SOIL SCREENING LEVELS* .
US EPA SSG, 1996b	Report	Guidance document describing the equations and methods through which groundwater and vapour inhalation exposure is evaluated. The method described however includes conservative assumptions including an infinite source, no degradation and no adsorption. Few input parameters are however required.	*US EPA SSG. 1996b.Soil Screening Guidance: Technical Background Document. Part 3: MODELS FOR DETAILED ASSESSMENT* .
US EPA, 2020	Website	Lists models developed by the US EPA Center for Exposure Assessment Modeling to determine groundwater exposure.	US EPA. 2020. Groundwater Models to Assess Exposures. Environmental Modeling Community of Practice Available from: https://www.epa.gov/ceam/groundwater-models-assess-exposures
US EPA/OPP/EFED, 2012	Report	Environmental fate and ecological risk assessment of bromacil. Modelling efforts were conducted to support this goal, models included PRZM/EXAMS, T-REX, TerrPlant and STIR.	*US EPA/OPP/EFED. 2012. Registration Review: Preliminary Problem Formulation for Environmental Fate and Ecological Risk, Endangered Species, and Drinking Water Assessments for Bromacil and Bromacil Lithium salt (Case No. 0041)*
USGS, 2020	Website	Lists groundwater models developed by the USGS that are publicly available, provides a brief description of each model as well as links to download and access user manuals.	*USGS. 2020. Water Resources Groundwater Software. Available from:https://water.usgs.gov/software/lists/groundwater/*
West and Kueper, 2004	Primary Research Paper	Investigation of natural attenuation of solutes in fractured bedrock. Vertical dispersion in steady-state plumes was assessed using the three-dimensional analytical solution (Domenico) for solute transport in saturated porous media.	West, M., and B.H. Kueper. 2004. Natural attenuation of solute plumes in bedded fractured rock. In Proceedings of USEPA/NGWA Fractured Rock Conference, 388–401. Portland, Maine: National Ground Water Association.

Citation	Article Type	Summary	Reference
Ahuja et al., 2000	User Manual	RZWQM	Ahuja et al. Root Zone Water Quality Model, Modeling Management Effects on Water Quality & Crop Production. In L.R. Ahuja, K.W. Rojas, J.D. Hanson, M.J. Shaffer and L. Ma, Eds.; Water Resources Publications, LLC: Colorado, USA; 2000; 360 pp.
Armstrong et al., 2000	User Manual	CRACK-NP	Armstrong, A. C., Matthews, A. M., Portwood, A. M., Leeds-Harrison, P. B., & Jarvis, N. J. (2000). CRACK-NP: A pesticide leaching model for cracking clay soils. *Agricultural Water Management* , *44* (1–3), 183–199. https://doi.org/10.1016/S0378-3774(99)00091-8
Barrett et al., 2015	User Manual	PRZM-GW	Barrett, M., Bohaty, R., Corbin, M., Cowles, J., Shelby, A., Wolf, J., Young, D. 2015. Standard Operating Procedure for Using PRZM-GW to Estimate Pesticide Concentrations in Groundwater for Drinking Water Exposure Assessments
Burns, 2006	User Manual	EXAMS-PRZM	Burns, L.A. 2006. User Manual for EXPRESS, the "EXAMS-PRZM Exposure Simulation Shell". Publication No. 600/R-06/095.
de Paz and Rubio, 2006	User Manual	GIS-AF/RF	de Paz, J.M., Rubio, J.L. (2006). Application of a GIS–AF/RF model to assess the risk of herbicide leaching in a citrus-growing area of the Valencia Community, Spain. Science of the Total Environment 371 (2006) 44–54
Flerchinger, 2000	User Manual	SHAW	Flerchinger, G.N. The Simultaneous Heat and Water (SHAW) Model: User's Manual. Technical Report NWRC 2000-10. Northwest Watershed Research Center, USDA. Agricultural Research Service, Boise, ID. 2000, 23 pp.
Healy, 1990	User Manual	VS2D	Healy, R.W. Simulation of solute transport in variably saturated porous media with supplemental information on modifications to the U.S. Geological Survey's Computer Program VS2D: U.S. Geological Survey, Water-Resources Investigations Report 90-4025, 1990. 125 pp.
Hutson, 2003	User Manual	LEACHM	Hutson, J. L. Leaching Estimation and Chemistry Model (LEACHM): Model Description and User's Guide. Flinders University of South Australia, School of Chemistry, Physics, and Earth Sciences: Adelaide, SA, 2003, 142 pp
Jarvis, 1994	User Manual	MACRO	Jarvis, N.J. The MACRO Model (Version 3.1). Technical Description and Sample Simulations. Reports and Dissert. 19, Department of Soil Science, Swedish University. Agricultural Sciences, Uppsala, Sweden, 1994; 51 pp.; Jarvis, N.J.; Larsson, M. T. The MACRO Model (Version 4.1) Technical Description. Department of Soil Science, Swedish University. Agricultural Sciences, Uppsala, Sweden, 1998, 41 pp.
Klein, 1995	User Manual	PELMO	Klein, M. PELMO Pesticide Leaching Model, Version 2.01, User Manual, Fraunhofer-Institut für Umweltchemie und Okotoxikologie, Schmallenberg, Germany. 1995, 91 pp.
Kraemer and Haitjeman, 2018	User Manual	WhAEM	Kraemer, S.R., Haitjeman, H.M. (2018) Working with WhAEM. US EPA
Kroes et al., 2008	User Manual	SWAP	Kroes, J. G., Van Dam, J. C., Groenendijk, P., Hendriks, R. F. A., & Jacobs, C. M. J. (2008). *Uitloop 0 lijn rug 14 mm SWAP version 3.2 Theory description and user manual Alterra Postbus 47 6700 AA Wageningen www.alterra.wur.nl* . Retrieved April 29, 2020, from www.alterra.wur.nl

Citation	Article Type	Summary	Reference
Leistra et al., 2001	User Manual	PEARL	Leistra, M.; van der Linden, A.M.A.; Boesten, J.J.T.I.; Tiktak, A.; van den Berg, F. PEARL model for pesticide behavior and emissions in soil-plant systems. Description of Processes. FOCUS PEARL Version 1.1.1. Bilthoven, National Institute of Public Health and Environment. Wageningen, Alterra, Green World Research, RIVM report 71140009/Alterra- Report 013 Alterra, Wageningen, the Netherlands, 2001,107 pp.; Tiktak, A.; van den Berg, F.; Boesten, J.J.T.I; van Kraalingen, D; Leistra, M.; van der Linden, A.M.A. Manual of FOCUS PEARL Version 1.1.1; RIVM Report 711401008, Alterra Report 28; Alterra Green World Research, Wageningen, National Institute of Public Health and the Environment Bilthoven, Wageningen, The Netherlands, 2000, 144 pp.
Neitsch et al., 2005	User Manual	SWAT	Neitsch, S. L.; Arnold, J. G.; Kiniry, J. R.; Williams, J. R. Soil and Water Assessment Tool. Theoretical Documentation: Version 2005; U.S. Department of Agriculture, Agricultural Research Service, Grassland, Soil, and Water Research Laboratory; Blackland Research Center, Texas Agricultural Experiment Station: Temple, TX, 2005, 476 pp.
Newell et al., 1996	User Manual	BIOSCREEN	Newell, C.J., McLeod, R.K., Gonzales, J.R. 1996. BIOSCREEN Natural Attenuation Decision Support System, User's Manual, Version 1.3. Publication No. EPA/600/R-96/087.
Nofziger et al., 2005	User Manual	CMLS	Nofziger, D. L., Nofziger, D. L., & Wu, J. (2005). *CHEMICAL MOVEMENT IN LAYERED SOILS, CMLS Java Web Start Version By* . http://citeseerx.ist.psu.edu/viewdoc/summary?doi=10.1.1.544.345
Parkhurst, 2020	User Manual	PREEQC	Parkhurst D., Webb. 2020. PREEQC Version 3. USGS.
Ravi and Johnson, 1997	User Manual	VLEACH	Ravi, V.; Johnson, J. A. VLEACH: A One-Dimensional Finite Difference Vadose Zone Leaching Model. Version 2.2 for U.S. Environmental Protection Agency; U.S. Environmental Protection Agency, Office of Research and Development, Robert S. Kerr Environmental Research Laboratory, Center for Subsurface Modeling Support: Ada, OK, 1997;70 pp.
Shirmohammadi et al., 2001	User Manual	GLEAMS	Shirmohammadi, A., Knisel, W.G., Bergstrom, L.F., Bengtson, R., Ward, A., Reyes, M., Manguerra, H., King, K. 2001. GLEAMS Model, Agricultural Non-point Source Water Quality Models: Their Use and Application. Southern Cooperative Series Bulletin #398, 69-82. Southern Association of Agricultural Experiment Station Directors.
Šimůnek et al., 2011	User Manual	HYDRUS	Šimůnek, J.; van Genuchten, M.Th.; Šejna, M. The HYDRUS Software Package for Simulating Two- and Three- Dimensional Movement of Water, Heat, and Multiple Solutes in Variably Saturated Media. Technical Manual, Version 2.0, PC Progress, Prague, Czech Republic, 2011, 258 pp.
Suarez, 2005	User Manual	PRZM-3	Suarez, L.A. 2005. PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.12.2. Publication No. EPA/600/R-05/111
Tiktak et al., 1994	User Manual	PESTRAS	Tiktak, A.; van der Linden, A.M.A.; Swartjes, F. PESTRAS: A One Dimensional Model for Assessing Leaching and Accumulation of Pesticides in Soil. RIVM report 715501003, Bilthoven, the Netherlands. 1994, 99 pp.; Freijer, J.I.; Tiktak, A.; Hassanizadeh, S.M.; van der Linden, A.M.A. PESTRAS Version 3.1.: A One Dimensional Model for Assessing Leaching, Accumulation and Volatilization of Pesticides in Soil. RIVM Report No. 715501007, Bilthoven, Netherlands. 1996. 130 pp.

Citation	Article Type	Summary	Reference
US EPA, 2008	User Manual	FIRST	US Environmental Protection Agency. 2008. FIRST: A Screening Model to Estimate Pesticide Concentrations in Drinking Water, Version 1.1.1. https://archive.epa.gov/epa/pesticide-science-and-assessing-pesticide-risks/first-version-111-description.html
US EPA, 2020	User Manual	SCI-GROW	US EPA. 2020. SCI-GROW Description. US EPA Web Archive.
van den Berg et al., 2016	User Manual	PESTLA	Van den Berg, F.; Boesten, J. J. T. I. Pesticide Leaching and Accumulation Model (PESTLA): Version 3.4, Description and User's Guide, Technical Document 43; Agricultural Research Department, Winand Staring Centre for Integrated Land, Soil, and Water Research: Wageningen, The Netherlands, 1998, 150 pp.
vanclooster et al., 1996	User Manual	WAVE	Vanclooster, M., Viaene, P., Christiaens, K., and Ducheyne, S.: WAVE, A Mathematical Model for Simulating Water and Agrochemicals in the Soil and the Vadose Environment, Reference and User's Manual, Release 2.1, Institute for Land and Water Management, Katholieke Universiteit Leuven, Belgium, 1996, 15 pp.
Walker and Barnes, 1981	User Manual	N/A	Walker, A.; Barnes, A. Simulation of Herbicide Persistence in Soil: A Revised Computer Model. Pest. Sci. 1981, 12, 123–132.
Winston, 2009	User Manual	MODFLOW	Winston, R. B. (2009). *Model Muse-A Graphical User Interface for MODFLOW-2005 and PHAST* . Retrieved May 5, 2020, from http://pubs.usgs.gov/tm/tm6A29.
Yeh et al., 1992	User Manual	3DFEMWATER/3DLEWASTE	Yeh, G.T., Sharp-Hansen, S., Lester, B., Strobl, R., Scarbrough, J. 1992. 3DFEMWATER/3DLEWASTE: Numerical codes for delineating wellhead protection areas in agricultural regions based on the assimilative capacity criterion. Publication No. EPA/600/R-92/223.
Young and Fry (2014)	User Manual	PRZM5	Young, D., & Fry, M. (2014). *PRZM5 A Model for Predicting Pesticide in Runoff, Erosion, and Leachate: User Manual USEPA/OPP 734F14002 . June 2014* , 53. https://doi.org/10.13140/2.1.1828.6408
Young, 2015	User Manual	PWC	Young, D. F. (2015). *Pesticide in Water Calculator User Manual (Version 1.50) Overview* . http://www.epa.gov/pesticide-

APPENDIX B: MODEL SUMMARIES AND RANKING

Model	Defensibility	Applicability (real-world sterilants transport)	Availability	Ease of Use	Novel Features	IW/FAL pathways	Total	Summary	Identified Mechanics	Pros	Cons	Comments	User Manual/Reference
PEARL	3	3	3	2	2	IW/FAL	15	*models pesticide transport throughout the soil profile, *can model transport to groundwater and surface water bodies,* used regularly for EU groundwater modelling, *leaching, runoff, migration, *PEARL is based on PESTRAS	*PEARL integrates the SAWP model and uses Richard's equation for water flow in the unsaturated zone	*handles transformation products well, *allows for variable weather dependent infiltration rates, *models vertical transport and lateral transport within the saturated zone by considering solute flux	* tied to agricultural applications, *requires many inputs that may not be easily accessible, *standard scenarios are only relevant to the EU context	*evaluated further, see Appendix C	Leistra et al., 2001
3DFEMWATER/3DLEWASTE	3	3	3	1	2	IW/FAL	14	*3DFEMWATER is used to model water flow through variably saturated media. 3DLEWASTE models waste transport through the saturated zone. These models can be combined in tandem and used to model pesticide transport. The model was developed as a tool to delineate wellhead protection zones within agricultural regions.	*relies on numerical modelling, *transport through the saturated zone is based on a Lagrangian-Eulerian Finite Element Model *transport through both the saturated and unsaturated zone are considered *multiple point sources and sinks are considered *processes that may retard contaminant transport are considered	*advanced model which incorporates many hydrogeological parameters, *has the capacity to model transport through bot the unsaturated and saturated zone *has the capacity to model pesticides	*relies on advanced mathematical methods and coding, *is recommended by the US EPA to be used only by advanced numerical modellers with a strong hydrogeological background, *many input parameters are required, *not user friendly, *necessary site-specific input parameters may be difficult to acquire	*may be useful for advanced modellers but not for typical users, therefore not included in further review	Yeh et al., 1992
BIOSCREEN	3	2	3	3	2	FAL	14	*designed to support decision making about petroleum fuel releases, * the approach is to determine the significance of natural attenuation in transport through the saturated zone	*solution of the 3D-advection dispersion model describing transport through the saturated zone is solved using Domenico's (1987) method, *advection, dispersion, decay, and a finite source are considered	*applies similar methods to the Tier 2 approach, requires only inputs that are available or calculatable from the AEP, *Analytical solutions allows for easier interpretation of mathematical methods, *considers dissipation of the source	* only transport through the saturated zone is considered,	*may be incorporated into the current Tier 2 model, included in further review	Newell et al., 1996
MODFLOW	3	3	3	1	2	IW/FAL	14	*modular hydrologic model, was originally designed strictly as a groundwater model but with the incorporation of specific packages, has the capacity to model solute transport	*MT3D-USGS is the groundwater solute transport simulator for MODFLOW, is primarily covers unsaturated zone transport, considers partitioning	*an international standard model for predicting groundwater and groundwater-surface water interactions,* many optional packages exist for further specification, *	*requires extensive site specific input parameters, boundary conditions, and graphical input requirements, * more effective for saturated zone transport	*not considered for further due to highly specific nature more appropriate for site-specific risk assessment	Winston, 2009
PWC	3	2	3	2	3	IW	14	*most current and available version of PRZM, integrated with the surface water concentration calculator, *assess pesticide movement to groundwater as well as movement to surface water bodies via run-off	*same as PRZM for Tier 2 relevant pathways	*considers transport to groundwater including advection dispersion, decay, adsorption, *variable infiltration rates are considered in conjunction with meteorological data, *impacts of runoff and plant-soil relations are accounted for	*requires many input parameters, many of which are not found in AEP guidance documents, *does not include lateral transport, *requires selection of specific parameters to meet the Tier 2 CSM	*evaluated further see Appendix C	Young, 2015
SWAP	3	3	2	2	2	IW/FAL	14	*models water, solutes, and heat transport in unsaturated and saturated soils, *field scale model,	*Richards' equation is soled numerical to model water transport through the unsaturated zone, *solute transport is based on convection, dispersion, adsorption, and decomposition, *each of the water, solute, and heat flux modules interact at each timestep, *a vertical one-dimensional transport model is used for the unsaturated zone and a field scale model is used for the three-dimensional saturated zone	*considers all elements of the Tier 2 CSM, *considers the impact of macropores and water repellency, *snow storage module exists to account for Nordic environments, *variable infiltration rates are considered, *impacts of transpiration are considered	*more complicated than the Tier 2 model, requires more inputs, designed originally for a European context	*examined further in the context of PEARL, difficulty in acquiring executable SWAP files	Kroes et al., 2008
HYDRUS	3	3	2	1	2	IW/FAL	13	*finite element model that allows for simulation of solute transport in one, two, or three dimensions, *	*Richard's equation is used to simulate water flow through the unsaturated zone	*has the capacity to consider three-dimensional transport,*accounts for hysteresis,	*requires extensive site specific input parameters and, boundary conditions, and graphical input requirements, * more effective for unsaturated zone transport	*not considered for further due to highly specific nature more appropriate for site-specific risk assessment	Šimůnek et al., 2011
SHAW	3	2	3	2	2	IW	13	*simulates freezing, thawing, water and solute transfer within a one-dimensional profile,*can be used to determine groundwater seepage	*climatic effects are considered, impacts of vegetation are considered but not required to complete a run, *seasonal changes are considered for infiltration, * time step flux is used as the main transport approach	*impacts of soil freezing on solute transport are considered,	*complex and requires many input parameters, * less developed solute transport component, focuses mainly on water relations	*not examined further due to limited solute transport capabilities, but snowmelt considerations would be of interest to the Canadian context	Flerchinger, 2000

Model	Defensibility	Applicability (real-world sterilants transport)	Availability	Ease of Use	Novel Features	IW/FAL pathways	Total	Summary	Identified Mechanics	Pros	Cons	Comments	User Manual/Reference
RZWQM	3	3	3	N/A	2	IW	12	*one dimensional model of all processes within an agricultural crop system, * agrochemicals can be modelled within the root zone and below the root zone, a quasi-two-dimensional macropore/lateral flow element is included	*one-dimensional numerical model, uses Richard's equation for water movement through the unsaturated zone, *solute movement is also solved numerically, adsorption, degradation and transport are all considered	*allows for the consideration of movement through macropores, *redistribution of chemicals within the soil profile can be considered between rainfall or irrigation events	*relatively complex model, requires many inputs specific to agricultural systems	*not examined further due to the complexity of the model, agricultural nature may not fit the Tier 2 CSM	Ahuja et al., 2000
AF/RF-GIS	2	1	3	3	1	N/A	10	Constructed by an academic group, attenuation/retardation factor model considers herbicide transport through the unsaturated zone, * in tended to improve decisions making regarding the leaching of agrochemicals to groundwater, *result of the model is a risk factor for the given agrochemical	*analytical method based on simple relationships, *attenuation is considered based on decay and infiltration, retardation is considered based on partitioning	*simple to apply, *relatively few inputs required that are relatively easy to determine, *mathematic expressions are easy to interpret, *considers site-specific water balance	*not intended to model transport below the root zone, *is designed primarily as a tool to assess risk of contamination to groundwater	*not readily applicable to desired pathways, not included in further review	de Paz and Rubio, 2006
GLEAMS	2	2	2	1	2	IW	10	* field scale model used to evaluate pesticide transport to groundwater, *based on an agricultural setting the model can help with decision making regarding application dates, rates, and land use practices	* the model has three modules: - Hydrology (ET, percolation, infiltration, runoff) - Soil erosion (migration through overland flow and sediment transport) - Pesticide or nutrient transport (simulates effects of pesticide loss in runoff and percolation below the rooting zone)	*hydrology model may allow for region specific modifications based on climate data, *consideration of overland flow may provide a more accurate infiltration rate, and potentially pesticide loss	*considers only unsaturated transport, *requirements relating to the agricultural setting may not parallel sufficiently with the Tier 2 CSM, *soil parameters may be overly specific	*requires DOS programming and was not considered further	Shirmohammadi et al., 2001
LEACHP	2	2	1	2	2	IW	10	*models the vertical movement of solutes, particularly pesticides, through the unsaturated zone, *can be used to predict groundwater contamination	*mechanistic model, *water flow is calculated using Richard's equation, *degradation is considered and is temperature dependent, *considers partitioning based on Freundlich isotherms	*variable infiltration is considered, *considers climatic factors,	*requires extensive input parameters that may require estimation, * does not allow for an optional constant sorption coefficient	*not considered further due to lack of access	Hutson, 2003
SWAT	2	2	2	1	2	IW	10	*basin-scale soil and water assessment tool, *created to determine the impact of water and agrochemical use practices over large and variable watershed	*physically based model, many input parameters are used in place of regression equations, *	*uses inputs typically available from government agencies, *allows for a wide variety of applications, complex scenarios, large scale investigations	*does not simulate leaching, *overly complex, many input parameters required which may not be available	*note examined due to input parameter requirements, not relevant to CSM	Neitsch et al., 2005
VS2DT	2	2	2	1	2	IW	10	*intended to assess water and solute movement in variably saturated porous media,	*applies a finite difference method to model flow, both Darcy's equation and the advection-dispersion equation are considered, *decay, adsorption and ion exchange are considered	*many optional features are included, *considers other factors such as ponding, evaporation, transpiration, and seepage	*written in Fortran 77, *requires many input parameters, relatively complicated	*overly complicated, not examined further	Healy, 1990
CMLS	3	2	2	N/A	1	IW	9	*designed to help manage agrochemicals, * the model estimates the depth and concentrations of the center of mass of non-polar chemicals with respect to time,	*applies a "tipping-bucket" type flow model, infiltration, evapotranspiration, sorption, and considered, *dispersion is not considered,	*requires soil and chemical parameters which are readily available, *includes graphical outputs, *includes a stochastic weather generator, *includes Monte Carlo simulations for weather	*does not consider dispersion as a factor influencing chemical transport, *	*expected to behave similarly to PRZM, not investigated further due to lack of access	Nofziger et al., 2005
MACRO	2	2	2	N/A	2	IW	9	*numerical model of solute and water transport in the unsaturated zone of fields	*Richard's equation is used to simulate water flow through the unsaturated zone, *micropores and gravity flow through macropores is considered, *solute transport is considered using flow domains with flow rate and solute concertation, degradation is considered as well as sorption	*allows for prediction of preferential flow,*considers perched water tables, macropores and micropores,	*very slow, *does not consider transport through the saturated zone, relatively complicated, requires extensive input parameters, current version specific to Europe, excellent soil physics knowledge is required to select appropriate parameters	*not considered further due to specificity of available version	Jarvis, 1994
PELMO	2	2	2	N/A	2	IW	9	*based on the PRZM model, and adapted to meet German regulatory requirements,	see PRZM	*contains adapted runoff and volatilization modules	*specific to the German regulatory context	*not considered further due to specificity and lack of applicability to the CSM	Klein, 1995

Model	Defensibility	Applicability (real-world sterilants transport)	Availability	Ease of Use	Novel Features	IW/FAL pathways	Total	Summary	Identified Mechanics	Pros	Cons	Comments	User Manual/Reference
PESTRAS	2	3	1	N/A	2	IW	9	*modified version of PESTLA	*relies on the SWAP model for transport through the unsaturated zone	*updated version of PESTLA	*no longer available, specific to the Dutch regulatory context	*not considered further due to specificity and lack of applicability to the CSM	Tiktak et al., 1994
PHREEQC	2	1	3	1	2	N/A	9	*model of aqueous geochemical processes	*complex aqueous geochemical modelling, allows for reactive-transport simulation,	*allows for consideration of complex chemical systems	*difficult implementation, requires C++ programming	*not considered further due to complexity	Parkhurst, 2020
PRZM	3	2	1	N/A	2	IW	9	Models pesticide fate and transport in crop rooting zone	*one-dimensional finite difference model that determines pesticide transport through the crop root zone, *versions more recent than PRZM 3 contain VADOFT which models pesticide transport through the vadose zone, *	- can model up to three chemicals at once - provides a more sophisticated method of modelling vertical transport through the rooting zone	* does not have a much room for site-specific parameters - incorporates many inputs which would likely require significant effort to make Alberta-specific	*archived, not considered further in this version	Suarez, 2005
PRZM-GW	3	2	1	N/A	2	IW	9	*model was used in Tier 1 assessments for drinking water, *considers not only the root zone but transport to a groundwater source well	*similar to PRZM but extends the soil zone in consideration down and into the groundwater table	*US EPA Tier 1 model for groundwater evaluation, * considers transport into saturated soils, *considers variable infiltration rates, evapotranspiration etc.	- only models vertical transport, not lateral, *not currently available	*archived, not considered further in this version	Barrett et al., 2015
CRACK-NP	3	1	2	N/A	2	N/A	8	*model describes nitrogen and pesticide movement through cracked clay soils	*model assumes that water will sorb and desorb to soil but no vertical flux will occur* designed for soils where transport occurs primarily through macropores, *partitioning and degradation (temperature dependent) are considered	*would be useful in determining pesticide transport in cracked clay soils	*only applicable to cracked clay soils	*overly specific and not generally useful for Tier 2 CSM, not considered for further investigation	Armstrong et al., 2000
PESTLA	2	2	1	N/A	2	IW	8	*used to evaluate pesticide leaching to groundwater,	*relies on the SWAP model for transport through the unsaturated zone	*purported to provide a more user-friendly interface	*no longer available, specific to the Dutch regulatory context	*not considered further due to specificity and lack of applicability to the CSM	van den Berg et al., 2016
PRZM/EXAMS	3	2	1	N/A	2	N/A	8	*links PRZM to a n ecosystem model that examines transport of pesticides from and other materials to water bodies	Links chemical properties to limnological parameters that control the kinetics of fate and transport of chemicals in aquatic ecosystems	*considers aquatic systems	- very similar to PRZM, *transport to aquatic systems is primarily driven by runoff, * could be useful in confirming surface water guidelines, but not soil quality guidelines	*archived, not considered further in this version	Burns, 2006
VLEACH	2	1	3	N/A	1	IW	8	*models the leaching of volatile sorbed contaminants in the vadose zone	*one-dimensional model, *applies numerical methods, *contains four main processes: liquid-phase advection, solid-phase sorption, vapour-phase diffusion, and three-phase equilibrium	*provides area-weighted assessment of groundwater impacts	*does not consider degradation, *limited to a portion of the CSM	*not applicable to CSM, to examined further	Ravi and Johnson, 1997
WAVE	2	2	1	N/A	2	IW	8	*models transport and transformation of agrochemicals in the soil, crop, and vadose zone	*one-dimensional numerical model, *Richard's equation is used to calculate water transport through the vadose zone, *convection, dispersion, diffusion, adsorption, and decay are considered as parameters that impact solute transport	*consider transport to groundwater	*model requires calibration, challenging to acquire, does not consider process that occur within groundwater	*not examined further due to access difficulty	vanclooster et al., 1996
WhAEM	2	1	3	N/A	1	N/A	7	*groundwater geohydrology program intended to delineate protection zones around wellheads in the united states	*an analytical element method is used to consider geohydrologic modelling, * hydrological boundaries are considered, *recharge is considered	*available as a groundwater model on the US EPA Website	*not applicable to sterilants or the CSM	*not examined further due to lack of applicability	Kraemer and Haitjeman, 2018
FIRST	3	1	1	N/A	1	N/A	6	*used to estimate pesticide concentrations in drinking water sourced from surface water bodies to protect ecological health, examines exposure mainly as a result of spray drift and runoff	*examines dimensions and dynamics of surface water bodies as well as using percent crop area (PCA) to estimate the influx of pesticides into a water body	*uses few basic chemical specific parameters, * parallels the PRAZM/EXAMS model in one process, *is able to predict peak and long term concentrations of pesticides in water bodies	*model application does not align with Tier 2 model	*not applicable to the desired scenarios, not considered further	US EPA, 2008
SCIGROW	2	1	1	N/A	1	IW	6	*Used to estimate pesticide concentrations in "vulnerable" groundwater	*considers degradation, sorption, and application rates, *results are based on existing data from groundwater-monitoring studies	*can be used for vulnerable groundwater scenarios	*model produces screening guidelines and may be overly conservative, *no lateral transport component is considered, input parameters may not be suitable to he Tier 2 CSM	*not examined further due to lack of access and overly conservative nature	US EPA, 2020

Model	Defensibility	Applicability (real-world sterilants transport)	Availability	Ease of Use	Novel Features	IW/FAL pathways	Total	Summary	Identified Mechanics	Pros	Cons	Comments	User Manual/Reference
VARLEACH	1	2	1	N/A	1	IW	6	*chromatographic model	* meteorological data is used to determine moisture content of surface soil, *herbicide leaching is determined using a simulation model, *		*limited resources available	*not available, not examined further	Walker and Barnes, 1981
	1-limited model testing and evaluation, 2-moderate testing and evaluation, 3-rigorous testing and evaluation	1-not relevant to the CSM, 2-some relevance to the CSM but incomplete, 3- converse all elements of the CSM in some way	1- not available or archived, 2-available but difficult to execute, 3- available and simple to execute	1-challenging to use, requires advanced coding or other skills, 2-somewhat challenging interface, 3-simple and easy to use	1-does not contain novel elements relative to the Tier 2 model, 2- contains some novel elements relevant to the Tier 2 CSM, 3-contains many novel elements relevant to the Tier 2 CSM	studies transport to groundwater (relevant to the IW pathway) studies transport through the saturated zone to freshwater bodies (relevant to the FAL pathway), both or neither	score based on a maximum value of 17						

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In this appendix, the mechanisms and approaches in selected models are compared to the equivalent processes used in the AEP (2019a) model. The approach used by the AEP to derive soil and groundwater quality guidelines (SQG and GQG) for the protection of IW and FAL divides contaminant transport into four discrete processes.

The four processes are:

1. Soil-Leachate Partitioning (DF1)

2. Transport through the unsaturated zone (DF2)

3. Groundwater Mixing (DF3)

4. Lateral transport through the saturated zone (DF4)

BIOSCREEN, PWC, and PEARL were identified as three candidate models which could be used at the tier 2 level based on their availability, ease of use, applicability to the CSM, and inclusion of novel features not currently present within the Tier 2 model. A mechanistic review of these three models was completed by examining the methods through which each of the models address the above processes. The user manuals for each of the models was the main source for the mechanistic review however background information and historical user manuals and guidance documents were also reviewed. Where models did not directly

line up with the AEP processes an effort was made to describe parallels and differences. Novel features were also reviewed and are discussed in section C1.5

1. SOIL-LEACHATE PARTITIONING

The AEP model is based largely on the CCME (2006) protocol for deriving SQG. The AEP dilution factor 1 (DF1) describes the dilution that occurs as a result of partitioning between soil water, air, and sorbed to particles. In the CCME (2006) protocol, the portion of the model which describes soil-leachate partitioning was derived from US EPA soil screening guidance (SSG), where the total concentration of the contaminant in soil can be described as the sum of the contaminant present in soil water, air, and sorbed to soil particles (CCME, 2006; US EPA, 1996).

$$C_t = \frac{C_s\rho_b + C_w\theta_w + C_a\theta_a}{\rho_b}$$

C_t	total concentration of contaminant in soil (mg/kg)
C_s	concentration of contaminant adsorbed to soil particles (mg/kg)
C_w	concentration of contaminant in aqueous phase (mg/L)
C_a	concentration of contaminant in vapour phase (mg/L)
ρ_b	soil dry bulk density (kg/L)
θ_a	water-filled porosity (L-water/L-soil) = air-filled porosity (L-air/L-soil)

Based on the assumption that C_s can be related to C_w via the partition coefficient K_d (Freundlich equation where n =1) and C_a can be related to C_w via Henry's Law constant H', the equation can be simplified to the following presented in CCME (2006):

$$SQG_{GW} = C_L(K_d + \frac{\theta_w + H'\theta_a}{\rho_b})$$

where:

SQG_{GW}	soil quality guideline for the protection of groundwater (mg/kg)
C_L	allowable leachate concentration at source (mg/L) – calculated below
K_d	partition coefficient (cm^3/g)
θ_w	is the moisture-filled porosity (unitless)
H'	dimensionless Henry's Law Constant (Hx42.32)
H	is the Henry's Law Constant (atm-m^3/mol)
θ_a	is the vapour-filled porosity (unitless)
ρ_b	is the dry soil bulk density (g/cm^3)

This standard method of determining contaminant partitioning is used by both the CCME and the US EPA. The Tier 2 model, BIOSCREEN, and PWC all use this approach for addressing partitioning. The Tier 2 model does however specify the use of K_{oc}*f_{oc} in place of K_d. The PEARL model also applies a similar approach but allows for pH dependent sorption as well as non-equilibrium sorption.

2. CONTAMINANT TRANSPORT THROUGH THE UNSATURATED ZONE

The AEP dilution factor 2 (DF2) describes the dilution that occurs as solutes move through the unsaturated zone. It is based on the CCME (2006) method for calculating the acceptable concentration of a contaminate in leachate at the source. The one-dimensional analytical method for the steady state solution is described as:

$$C_L = \frac{C_z}{exp\left[\frac{b}{2\partial_u} - \frac{b}{2\partial_u}\left(1 + \frac{4\partial_u L_S}{v_u}\right)^{1/2}\right]}$$

where:

C_L allowable chemical concentration in leachate at the source (mg/L)
Cz allowable chemical concentration in leachate at the water table (mg/L) calculated below
b thickness of zone below the source (m) = d – Z
d depth from surface to shallowest DUA (m)
Z depth to bottom of contaminated soil (m)
∂_u dispersivity in the unsaturated zone (m) = 0.1b
L_S decay constant for chemical in unsaturated zone (y^{-1}):

$$L_S = \frac{0.693}{t_{1/2S}}(e^{-0.07d})$$

$t_{1/2S}$ chemical half-life in saturated zone (years)

v_u average linear leachate velocity (m/y)

$$v_u = \frac{I}{\theta_w R_u}$$

I infiltration rate/recharge (m/y)
θ_w water-filled porosity in unsaturated zone (unitless)
R_u retardation factor in unsaturated zone (unitless):

$$R_u = 1 + \frac{\rho_b}{\theta_w} K_{oc} f_{oc}$$

ρ_b soil bulk density in unsaturated zone (g/cm^3)
K_{oc} organic carbon-water partition coefficient (L/kg)
f_{oc} fraction organic carbon (g/g) in unsaturated zone

In the Tier 2 model, infiltration rate is assumed to be constant and does not consider hydrological variation and soil properties (Golder, 2005). This oversimplification can be avoided using water balance models coupled with meteorological data or numerical models that are based on Richard's equation. PRZM applies a water balance model and PEARL applies Richard's equation (see section 1.5).

The CCME method was itself derived from a method developed by Kool et al. (1994) (BC MOE, 2016). Kool et al's (1994) method considered spatially uniform, unidirectional downward flow based on Darcy's law. The equation developed by Kool et al. (1994) was an advection-dispersion equation that included a decay chain.

$$\frac{\partial}{\partial_z}\left(D_l \frac{\partial_{Cl}}{\partial_z}\right) - V\frac{\partial_{Cl}}{\partial_z} = \theta R_l \frac{\partial_{Cl}}{\partial_t} + \theta Q_l \lambda_{lCl} - \sum_{m=1}^{M} \theta \in_{lm} Q_m \lambda_m c$$

Where:

C_l	concentration of species l (g/m^3)
D_l	the apparent dispersion coefficient (m^2/yr)
z	depth (m)
V	Darcy velocity
I	Infiltration rate (m/yr)
Θ	volumetric water content
Rl	retardation factor
λ	first order decay constant (/yr)
Q	coefficient for decay in the sorbed phase
M	total number of parent species
m	parents species index
∈lm	fraction of a parent species that transforms into ach daughter species

BIOSCREEN does not consider vertical transport of solutes through the unsaturated zone. However, both PWC and PEARL use different approaches to modelling solute transport through the unsaturated zone.

2.1 PWC

PWC is the current US EPA model for pesticide transport to groundwater and surface water bodies. It is an amalgamation of several archived models including PRZM. The most recent version, PRZM5, is used within PWC to determine vertical transport through the unsaturated zone. PRZM5 assesses transport via advection and dispersion of the solute through time. The concentration of the contaminant in the dissolved, sorbed, and vapour phase is determined by simultaneously considering plant uptake, runoff, erosion, decay, volatilization, foliar washoff, advection, dispersion and retardation (Young and Fry, 2014).

The following equation is used by PRZM5:

$$\frac{\partial \mathrm{m}_w}{\partial \mathrm{t}} + \frac{\partial \mathrm{m}_s}{\partial \mathrm{t}} = -k_w V_w C_w - k_s M_s C_s - q(z) C_w - E(z) C_s - I\frac{\partial_w}{\partial_z}\Delta z + DA\frac{\partial^2 C_w}{\partial z^2}\Delta z$$

Where:

m_w	solute mass in the water phase of the compartment (M)
m_s	solute mass in the sorbed phase of the compartment (M)
k_w	first order degradation coefficient for water phase of the compartment (/T)
k_s	first order coefficient for sorbed phase of the compartment (/T)
V_w	volume of water in the compartment (L^3)
M_s	mass of soil in compartment (M)

q(z)	runoff flow associated with depth z (L^3/T)
E(z)	erosion flow associated with depth z (M/T)
I	infiltration flow (L^3/T)
C_w	concentration in water (M/L^3)
C_s	concentration on soil (M/M)
D	dispersion coefficient (L^2/T)
A	area of effective dispersion (L^2) = $A_T\theta$
Z	vertical dimension (L)

Several substitutions result in the following:

$$(\theta + \rho_b K_d)\frac{\partial c_w}{\partial t} = -k_w \theta c_w - k_s \rho_b k_d c_w - \left(\frac{D_{R(z)}}{\Delta z}\right) c_{w-} \left(\frac{E_{N(z)}}{\Delta z}\right) K'_d c_w - v\frac{\partial c_w}{\partial z} + D\theta\frac{\partial^2 c_w}{\partial z^2}$$

K_d	sorption coefficient (L^3/M)
$K_{d'}$	erosion-specific enhanced sorption coefficient (L^3/M)
V_T	total volume of compartment (L^3)
ρ_b	bulk density (M/L^3)
D_R	area-normalized runoff intensity ($q(z)/A_{field}$) associated with depth z, (L/T)
E_N	area-normalized erosion intensity ($E(z)/A_{field}$) associated with depth z, ($M/L^2/T$)
v	infiltration velocity based on full area (L/T)
Δz	compartment length in vertical dimension (L)
D	dispersion coefficient (L^2/T)
k_w	first order degradation coefficient for water phase of the compartment (/T)
k_s	first order coefficient for sorbed phase of the compartment (/T)
k_d	first order sorption coefficient (/T)
c_w	concentration in water (M/L^3)
Δt	time step (day)
Θ	the soil water content (cm^3/cm^3)

PRZM5 does not use an analytical approach to solve this equation but rather applies a numerical approach and solves the equation using the implicit backwards spatial differencing method. Backwards differencing allows for the approximation of the derivative by following the assumption that the value of the derivative at any given point *i* is approximately equal to the difference between $f(x_i)$ and $(fx_i\text{-}1)$.

2.2 PEARL

The PEARL model integrates the Soil-Water-Atmosphere-Plant (SWAP) model to simulate solute transport through the vadose zone. SWAP uses Richard's equation to simulate water movement through the unsaturated zone, see section 4.4.5.2. However, convection, dispersion, adsorption, and decomposition are considered as the governing factors that influence the concentration of solutes within the soil mass. Within the vadose zone, SWAP is a one-dimensional vertical direction model.

The transport equation applied by SWAP for solute transport through the unsaturated zone is a combination of the following three equations:

1) Conservation of mass:

$$\frac{\partial X}{\partial t} = -\frac{\partial J}{\partial z} - S_s$$

Where:

X	Total solute concentration int eh soil system (g/cm^3)
J	Total solute flux (g/cm^{2}d)
S_s	Solute sink term (g/cm^{3}d)

Where solute sink (S_s) accounts for linear decomposition:

$$S_s = \mu(\theta c + \rho_b Q) + K_r S_c$$

Where:

S_s	Solute sink
μ	First order rate coefficient of transformation (/day)
K_r	Root uptake preference factor (-)
S_c	Root water extraction rate (/day)

2) Total solute flux equation:

$$J = J_{con} + J_{dif} + J_{dis} = qc - \theta\left(D_{dif} + D_{dis}\right)\frac{\partial c}{\partial z}$$

Where:

$$J_{dif} = -\theta D_{dif}\frac{\partial c}{\partial z} \quad ; \quad D_{dif} = D_w \frac{\theta^{\frac{7}{3}}}{\Phi_{por}^2} \quad ; \quad J_{con} = qc \quad ; \quad J_{dis} = -\theta D_{dis}\frac{\partial c}{\partial z} \quad ; \quad D_{dis} = L_{dis}|v|$$

Where:

J_{dif}	Solute flux (g/cm^{2}d)
Θ	Water content (-)
C	Solute concentration (g/cm^3)
z	Depth
D_{dif}	Diffusion coefficient (cm^2/d)
D_w	Solute diffusion coefficient in free water (cm^2/d)
Φ_{por}	Soil porosity (cm^3/cm^3)
J_{con}	Convective flux (g/cm^{2}d)
q	Darcy flux (cm/d)
J_{dis}	Dispersion flux (g/cm^{2}d)
D_{dis}	Dispersion coefficient (cm^2/d)
L_{dis}	Dispersion length (cm)
V	Pore water velocity (v=q/θ)

3) Total solute concentration in the soil system:

$$X = \theta_c + \rho_b Q$$

X	Total solute concentration in the soil system
Θ_c	Solutes dissolved in the soil water
ρ_b	Dry soil bulk density (g/cm^3)
Q	Amount of compound adsorbed (g/g)

Where amount of compound adsorbed (Q):

$$Q = K_f c_{ref} \left(\frac{c}{c_{ref}}\right)^{N_f}$$

Where:

Q	Amount of compound adsorbed (g/g)
K_f	Freundlich coefficient (cm^3/g)
N_f	Freundlich exponent (-)
C	Solute concentration (g/cm^3)
C_{ref}	Reference value of the solute concentration (g/cm^3)

The resulting equation is the following:

$$\frac{\partial(\theta_c + \rho_b Q)}{\partial t} = -\frac{\partial(qc)}{\partial z} + \frac{\partial[\theta\left(D_{dif} + D_{dis}\right)\frac{\partial c}{\partial z}]}{dz} - \mu(\theta_c + \rho_b Q) - K_r Sc$$

Where:

Θ_c	Solutes dissolved in the soil water
ρ_b	Dry soil bulk density (g/cm^3)
Q	Amount of compound adsorbed (g/g)
q	Darcy flux (cm/d)
z	Depth (cm)
t	time (d)
Θ	Water content (-)
D_{dif}	Diffusion coefficient (cm^2/d)
D_{dis}	Dispersion coefficient (cm^2/d)
μ	First order rate coefficient of transformation (/day)
K_r	Root uptake preference factor (-)
S_c	Root water extraction rate (/day)

This equation is valid for one-dimensional, convective-dispersive mass transport including non-linear adsorption, linear decay and proportional root uptake in unsaturated/saturated soil (Kroes et al., 2008). It is solved by explicit, central finite difference scheme.

2.3 Summary

Contaminant Transport through the unsaturated zone is not handled by BIOSCREEN and differs significantly between the Tier 2 model, PWC, and PEARL. The Tier 2 method is based on a one-dimensional analytical method developed by Kool et al (1994). It considers dispersion, retardation, and chemical decay. The PWC model employs the PRZM5 module to model solute transport through the unsaturated zone. The transport model developed by Young and Fry (2014) considers one-dimensional vertical transport with advection and dispersion. Plant uptake in the rooting zone, runoff, erosion, chemical decay, volatilization, foliar washoff, advection, dispersion, and retardation are all considered as potential factors that may influence the concentration of the compound dissolved within the soil water. The model is solved using numerical methods. The PEARL model employs the SWAP model to determine solute transport through the unsaturated zone. This one-dimensional model is based on convective-dispersive mass transport and considers adsorption (optional non-linear), linear decay, and root uptake. This model is also solved using numerical methods.

3. GROUNDWATER MIXING

The AEP dilution factor 3 (DF3) describes the dilution that occurs as solutes move from leachate in the unsaturated zone into the saturated zone. It is based on the CCME (2006) method for calculating the acceptable concentration of a contaminate in leachate at the source. The CCME method was based on a method developed by the US EPA SSG and can be described as:

$$C_z = C_{gw}\left\{1 + \frac{Z_d K_H i}{IX}\right\}$$

where:

C_z	allowable chemical concentration in leachate at the water table (mg/L)
C_{gw}	allowable chemical concentration in groundwater at the source (mg/L) – calculated below
Z_d	average thickness of mixing zone (m) – calculated below
K_H	hydraulic conductivity in the saturated zone (m/y)
i	hydraulic gradient (unitless)
I	infiltration rate (m/y) = precipitation minus runoff and evapotranspiration
X	length of source parallel to groundwater flow (m)

$$Z_d = r + s$$

r	mixing depth available due to dispersion and diffusion (m) = 0.01 X
X	length of source parallel to groundwater flow (m)
S	mixing depth available due to infiltration rate and groundwater flow rate

$$s = d_a\{1 - e^{\frac{-2.178XI}{K_H i d_a}}$$

d_a	depth of unconfined aquifer (m)
I	infiltration rate (m/y) = precipitation minus runoff and evapotranspiration
K_H	hydraulic conductivity in the saturated zone (m/y)
i	hydraulic gradient (unitless)

BIOSCREEN does not consider groundwater mixing. Within the PWC and former PRZM-GW guidance documents it is unclear how mixing of leachate with groundwater is considered. PRZM was not originally designed to handle saturated conditions however the development of PRZM-GW allowed for the inclusion of saturated conditions by modifying the field capacity input parameter. Subsequent model evaluations found this method to be sufficiently accurate (USEPA/OPP, 2012). The PEARL model does consider groundwater mixing scenarios based on a mass balance approach.

3.1 PEARL-SWAP

PEARL integrates the SWAP model for vertical solute movement through the soil column. The bottom boundary can be set as either the top of the saturated zone or the upper portion of the saturated zone where soil water movement transitions to three-dimensional flow (Kroes and van Dam, 2003). The SWAP module includes eight options for the lower boundary conditions:

- Prescribe groundwater level (Dirichlet-field scale)
- Prescribe bottom flux (q_{bot}) (Neumann-regional scale)
- Calculate bottom flux from hydraulic head of deep aquifer (Cauchy-regional scale)
- Calculate bottom flux as a function of groundwater level (Cauchy-regional scale)
- Prescribe soil water pressure head of bottom compartment (Cauchy-field scale)
- Bottom flux equals zero (Neumann-field scale)
- Free drainage of soil profile (Neuman-field scale)
- Free outflow at soil-air interface (Neumann-field scale)

Dirichlet conditions are a prescribed pressure head. Neuman conditions are typically used when a geological barrier is present. Cauchy conditions are typically applied when unsaturated flow models are combined with regional groundwater flow models (Kroes and van Dam, 2003).

Solute movement from the unsaturated zone into the saturated zone is represented as a solute drainage flux:

$$J_{drain} = \sum_{i=n_{gwl}}^{n} q_{drain,i} c_i$$

Where:

J_{drain}	the solute flux that leaves the one dimensional soil profile
n_{gwl}	groundwater level compartment
q_{drain}	water drainage flux
c_i	concentration in the compartment

This is the typical case of infiltration however PEARL also has the capacity to model upward flow from groundwater into the unsaturated zone.

3.2 Summary

The Tier 2 model considers groundwater mixing based on methods developed by the US EPA soil screening guidance (SSG) and is based on mass balance. BIOSCREEN does not consider groundwater mixing as the CSM used in this model assumes a plume within the saturated zone. Mixing into the groundwater zone is not clearly defined within the PWC guidance documents but appears not be handled as a separate

process. PEARL applies a mass balance approach to groundwater mixing. The SWAP model within PEARL allows for the differentiation of a bottom boundary over which solute flux can occur from the one-dimensional unsaturated transport zone to the three-dimensional saturated transport zone.

4. LATERAL TRANSPORT THROUGH THE SATURATED ZONE

The Tier 2 model applies a solution of the 3D advection-dispersion equation developed by Domenico and Robbing (1985) to model lateral transport of solutes through the saturated zone. The equation contains terms that account for advection, dispersion, and decay. However, the Domenico and Robbins solution assumes that no vertical dispersion occurs downgradient of the source area.

The 3D advection-dispersion equation considered by Domenico and Robbins is as follows (Srinivasan et al., 2007):

$$\frac{\partial c}{\partial t} = -v\frac{\partial c}{\partial x} + D_x\frac{\partial^2 c}{\partial x^2} + D_y\frac{\partial^2 c}{\partial y^2} + D_z\frac{\partial^2 c}{\partial z^2} - kc$$

The first term (left of the equal sign) is the change in solute concentration over time, the second term evaluates advection, the third, fourth, and fifth terms evaluate dispersion in each of the cartesian directions, and the sixth term considers decay of the solute.

Domenico and Robbins developed an analytical solution on which the fourth dilution factor of the AEP Tier 2 model is based.

Domenico and Robbins analytical solution:

$$c_{(x,y,z,t)} = \left(\frac{c_{gw}}{4}\right)\exp\left\{\frac{x}{2\,\partial_x}\left[1-\left(1+\frac{4L_s\,\partial_x}{v}\right)^{\frac{1}{2}}\right]\right\} erfc\left[\frac{x - vt(1+\frac{4L_s\,\partial_x}{v})^{\frac{1}{2}}}{2(\partial_x vt)^{\frac{1}{2}}}\right]$$

$$\left\{erfc\left[\frac{y+\frac{Y}{2}}{2(\alpha_x x)^{\frac{1}{2}}}\right] - erfc\left[\frac{y-\frac{Y}{2}}{2(\alpha_x x)^{\frac{1}{2}}}\right]\right\}$$

$$V = Ki$$

$$v = \frac{Ki}{n_e R_f}$$

$$R_f = 1 + \frac{\rho_b}{n}K_d$$

$$L_s = \frac{0.693}{t_{1/2s}}(e^{-0.07d})$$

Cw allowable chemical concentration in water at receptor (mg/L)

X	distance from source to receptor (m)
x,y,z	Cartesian coordinates relating source and receptor (m); y, z assumed to be 0
t	time since contaminant release (years)
C_{gw}	allowable chemical concentration in groundwater at source (mg/L)
∂_x	longitudinal dispersivity tensor = 0.1x
∂_y	lateral dispersivity tensor = 0.1∂x
L_s	decay constant (y-1) in saturated zone
d	depth from surface to groundwater surface (m)
$t_{1/2S}$	biodegradation half-life (y)
v	velocity of contaminant (m/y)
K_H	hydraulic conductivity in the saturated zone (m/y)
i	hydraulic gradient (unitless)
n	total porosity of soil = 1 - ρb/2.65 (unitless)
n_e	effective soil porosity (unitless)
Y	source width (m) perpendicular to groundwater flow
R_f	retardation factor (unitless)
ρ_b	soil bulk density in saturated zone (g/cm^3)
K_d	distribution coefficient (cm^3/g)

Saturated zone-transport is time-dependent in this model and the CCME (2006) solution evaluates chemical concentrations at 100 years.

The Tier 2 AEP process, based on Domenico and Robbins (1985) analytical solution of the advection-dispersion model is listed below:

$$DF4 = \frac{2}{exp(A) \cdot erfc(B) \cdot [erf(C) - erf(D)]}$$

where:

DF4	=	dilution factor 4
er	=	error function;
A	=	equation group A ;
B	=	equation group B ;
C	=	equation group C ; and
D	=	equation group D .

The equation group A was calculated as follows:

$$A = \frac{x}{2 \cdot D_x} \cdot \left[1 - \left(1 + \frac{4 \cdot L_s \cdot D_x}{v} \right)^{1/2} \right]$$

where:

A	=	equation group A;
x	=	downgradient distance to receptor (m);
D_x	=	dispersivity in the direction of groundwater flow (m);
L_s	=	decay constant (1/y); and
v	=	velocity of the contaminant (m/y).

The dispersivity in the direction of groundwater flow was calculated as follows:

$$D_x = 0.1 \cdot x$$

where:

D_x	=	dispersivity in the direction of groundwater flow (m); and
x	=	downgradient distance to receptor (m).

The decay constant was calculated as follows:

$$L_s = \frac{0.6931}{t_{1/2s}} \cdot \exp(-0.07 \cdot d)$$

where:

L_s	=	decay constant (1/y);
$t_{1/2s}$	=	decay half-life of the contaminant in the saturated zone (y);
d	=	depth to groundwater table (m).

The velocity of the contaminant was calculated as follows:

$$v = \frac{V}{\theta_t \cdot R_s}$$

where:

v	=	velocity of the contaminant (m/y);
V	=	Darcy velocity of groundwater (m/y);
θ_t	=	total soil porosity; and
R_s	=	retardation factor in the saturated zone.

The retardation factor in the saturated zone was calculated as follows:

$$R_s = 1 + \frac{\rho_b \cdot K_{oc} \cdot f_{oc}}{\theta_t}$$

where:

R_s	=	retardation factor in the saturated zone;
ρ_b	=	dry soil bulk density (g/cm^3);
K_{oc}	=	organic carbon partition coefficient (L/kg);

f_{oc}	=	fraction of organic carbon (g/g); and
θ_t	=	total soil porosity.

The equation group C was calculated as follows:

$$C = \frac{y + Y/2}{2 \cdot \left(D_y \cdot x\right)^{1/2}}$$

where:

C	=	equation group C;
y	=	perpendicular distance to the receptor (m);
Y	=	source width (m);
D_y	=	dispersivity perpendicular to groundwater flow (m); and
x	=	downgradient distance to receptor (m).

The dispersivity perpendicular to groundwater flow was calculated as follows:

$$D_y = 0.01 \cdot x$$

where:

D_y	=	dispersivity perpendicular to groundwater flow (m); and
x	=	downgradient distance to receptor (m).

The equation group D was calculated as follows:

$$D = \frac{y - Y/2}{2 \cdot \left(D_y \cdot x\right)^{1/2}}$$

where:

D	=	equation group D;
y	=	perpendicular distance to the receptor (m);
Y	=	source width (m);
D_y	=	dispersivity perpendicular to groundwater flow (m); and
x	=	downgradient distance to receptor (m).

The PWC model does not consider lateral transport through the unsaturated zone however, in the original PRZM-GW model a basic plug flow model was suggested post processing to simulate lateral transport between the source and vulnerable groundwater. Both the BIOSCREEN and PEARL models consider saturated transport.

4.1 BIOSCREEN

BIOSCREEN is based on the same 3D advection-dispersion equation as that used in the Tier 2 model, however BIOSCREEN is based on a slightly different solution, produced by Domenico in 1987. This solution accounts for a depleting source mass. Domenico's (1987) solution is based on the Ogata-Banks (1961) equation and the Bear (1979) equation.

Ogata-Banks equation:

$$c_x = \left(\frac{c_o}{2}\right) erfc \frac{(x - vt)}{2(\alpha_x vt)^{1/2}}$$

Where

c_x	concentration at any distance x
x	distance
c_o	source concentration
v	velocity of the constituent
t	time
αx:	dispersivity

Bear equation for a plug flow model with longitudinal dispersion and continuous decay (a variant of the Ogata-Banks expression):

$$c_{(x,t)} = \left(\frac{c_o}{2}\right) \exp\left\{\frac{2}{\alpha_x}\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v}\right)^{\frac{1}{2}}\right]\right\} erfc\left\{\frac{x - vt\left(1 + \frac{4\lambda\alpha_x}{v}\right)^{\frac{1}{2}}}{2(\alpha_x vt)^{1/2}}\right\}$$

Domenico (1987) solution:

$$c_{(x,y,z)} = \left(\frac{c_o}{4}\right) \exp\left\{\frac{x}{2\alpha_x}\left[1 - \left(1 + \frac{4\lambda\alpha_x}{v}\right)^{\frac{1}{2}}\right]\right\}$$

$$\left\{erfc\left[\frac{y + \frac{Y}{2}}{2(\alpha_x x)^{\frac{1}{2}}}\right] - erfc\left[\frac{y - \frac{Y}{2}}{2(\alpha_x x)^{\frac{1}{2}}}\right]\right\}$$

$$\left\{erfc\left[\frac{z + \frac{Z}{2}}{2(\alpha_x x)^{\frac{1}{2}}}\right] - erfc\left[\frac{z - \frac{Z}{2}}{2(\alpha_x x)^{\frac{1}{2}}}\right]\right\}$$

Where:

C	Centerline concentration
c_o	Source concentration

αx:	Dispersivity
x,y,z	Distance in the Cartesian directions
λ	Decay constant
Y, Z	Source dimensions
erf	Error function

4.2 PEARL

Solute transport through groundwater is considered in three dimensions. Solute transport is associated with the soil hydrology which is considered in depth within the PEARL model. Saturated transport is described using analytical drainage formulas including lateral drainage flux. Lateral drainage can be set as a sink term within the Richard's equation. Further, saturated transport to FAL is assumed to be mediated by the difference in pressure head between the average groundwater elevation and the surface water level. The Ernst equation is used to describe the relationship between drainage flux and groundwater elevation. Transport through the saturated zone is considered at the field scale but can be scaled to regional systems.

A modified version of the Ernst equation is used:

$$q_{drain} = \frac{\Phi_{gwl} - \Phi_{drain}}{\gamma_{entr} + \gamma_{rad} + \frac{L_{drain}^2}{8KD}}$$

Where:

q_{drain}	drainage flux
Φ_{gwl}	groundwater level
$\Phi_{drain,n}$	drainage level
γ_{entr}	minimum resistance
γ_{rad}	reference resistance
L_{drain}	distance to drainage
K	aquifer volume
D	aquifer thickness

However other modified Hooghoudt and Ernst equations are used to describe other drainage situations.

The user manual does not directly describe solute flux within the saturated unit however a mass balance approach is used and a breakthrough curve is derived and describe as follows:

$$\frac{\partial(\theta_s c_{gr} + \rho_b k_{ads} c_{gr})}{\partial t} = \frac{q_{drain}}{d_{aquif}}(c_{in} - c_{gr}) - \mu_{gr}(\theta_s c_{gr} + \rho_b k_{ads} c_{gr})$$

Where:

Θ_s	saturated water content (cm^3/cm^3)
c_{gr}	solute concentration in groundwater (g/cm^3)
ρ_b	bulk density (g/cm^3)
k_{ads}	linear adsorption coefficient in the saturated zone (cm^3/g)
q_{drain}	drainage flux (cm/d)

d_{aquif} thickness of the aquifer (cm)
c_{in} solute concentration of water percolating from the unsaturated zone (g/cm^3)
μ_{gr} first order rate coefficient for transformation in the saturated zone (/d)

4.3 Summary

While the PWC model allows for calculation of transport to surface water bodies this is based predominantly on overland flow rather than groundwater transport. Lateral transport through the saturated zone is not considered by this model. The Tier 2 approach to lateral saturated transport is based on Domenico and Robbins' (1985) analytical solution of the three-dimensional advection dispersion equation. It considers advection, dispersion and decay but assumes no vertical dispersion or source depletion. BIOSCREEN's approach is very similar to the Tier 2 approach but is based on a slightly updated version of the previous analytical solution, published by Domenico in 1987. This solution accounts for source depletion over time. The method employed by the PEARL model for saturated transport is based on mass flux throughout the saturated zone and relies on a modified Ernst equation.

5. OTHER FEATURES

Both PWC and PEARL contain several other features that make them suitable for modelling pesticides however not all are relevant to the AEP CSM. One element that may be useful is the method with which these models calculate infiltration. The Tier 2 approach uses a constant infiltration rate for each of two defined soil textures. However PWC and PEARL use a more sophisticated method and allow the evaluation of infiltration on a time dependent and/or weather dependent basis.

5.1 PWC

PWC applies PRZM5 to calculate water through the unsaturated zone (D'Andrea et al., 2019). PRZM5 utilizes a "tipping bucket" method to evaluate the infiltration of water from above. This method dictates the soil water content at any point along the soil column. It is represented by:

$$\theta_{i,t+1} = v_{i,t}\frac{\Delta t}{\Delta z_i} - ET_{i,t}\frac{\Delta t}{\Delta z_i} + \theta_{i,t}$$

$\theta_{i,t+1}$ the soil water content of *i* at the end of the current time step (cm3/cm3)
$\theta_{i,t}$ the soil water content of *i* at the start of the current time step (cm3/cm3)
v_i the water velocity entering compartment *i* from the above compartment (cm/day)
ET_i the evapotranspiration at depth *i* (cm/day)
Δt time step (day)
Δz_i compartment *i* thickness (cm)

When infiltration exceeds the soil's field capacity (thefc), the excess water is used for flow to the next compartment

$$v_{i+1} = (\theta_{i,t+1} - \theta_{i,thefc})\frac{\Delta z_i}{\Delta t}$$

When infiltration exceeds field capacity

$$\theta_{i,t+1} = \theta_{i,thefc}$$

5.2 PEARL

PEARL employs the SWAP module to handle the majority of hydrological processes including the calculation of variable infiltration rates. SWAP itself solves Richard's equation for transport through the variably saturated zone. Richard's equation describes how water moves through unsaturated soil and allows for different soil moisture content at different time steps based on variable infiltration. The methods employed within this module allow for a robust number of considerations such as preferential flow through macropores, frozen ground and snow melt in cold climates, and hydrophobic soil conditions.

However, at the most basic level Richard's equation is applied as follows:

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z}\left[K(\theta)\left(\frac{\partial h}{\partial z} + 1\right)\right]$$

Where:

Θ	water content
t	time
z	depth
h	hydraulic head
K	hydraulic conductivity

PEARL also has the capacity to consider lateral flow through unsaturated soil via interflow and is described as follows:

$$q_{drain,n} = \frac{\Phi_{gwl} - \Phi_{drain,n}}{\max\left(\Phi_{gwl}, 1 \cdot \Phi_{gwl} - \gamma_{ref}\right)}$$

Where:

q_{drain}	interflow flux (cm/d)
Φ_{gwl}	groundwater level
$\Phi_{drain,n}$	reference level
γ_{min}	minimum resistance
γ_{ref}	reference resistance

When the groundwater level is above the reference level, interflow is calculated as:

$$q_{drain,n} = A_{interflow}(\Phi_{gwl} - \Phi_{drain,n})^{B_{interflow}}$$

Where:

q_{drain}	interflow flux (cm/d)
Φ_{gwl}	groundwater level
$\Phi_{drain,n}$	reference level
$A_{interflow}$	conductance parameter(cm/d)

$B_{interflow}$ exponent of the empirical relation (-)

5.3 Summary

The Tier 2 model assumes that all input variables are constant over space and time, including infiltration. However, meteorological variability can result in significant variation in this parameter. The PRZM module of PWC accounts for the variability by accounting for infiltration using a “tipping bucket” approach paired with meteorological data. PEARL also considers variable infiltration rates but uses Richard’s equation to model water flow through the unsaturated zone.

APPENDIX D: INPUT PARAMETERS

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1. Tier 2 Input Parameters D-1
2. BIOSCREEN Input Parameters D-2
3. PWC Input Parameters D-3
4. PEARL Input Parameters D-7
5. Meteorological Parameters D-11

This report evaluated and compared three models identified in the literature with the Alberta Tier 1 and Tier 2 models. To do this, a parameter set was required for each. This appendix identifies the parameter set used for the evaluation of each model and provides the rationale for parameter value selection.

1. TIER 2 INPUT PARAMETERS

Input parameters used in the Tier 2 model were selected from tables C-2, C-3, and C-6 (AEP, 2019a). The inputted values are summarized in Tables D1 through D3.

Table D1 Soil and Hydrogeological Parameters

Parameter	Unit	Fine-grained soil	Coarse-grained soil	Source
Dry soil bulk density (ρ_b)	g/cm^3	1.4	1.7	AEP, 2019a
Total soil porosity (θ_t)	vol/vol	0.47	0.36	AEP, 2019a
Water filled porosity (θ_w)	vol/vol	0.168	0.119	AEP, 2019a
Air filled porosity (θ_a)	vol/vol	0.302	0.241	AEP, 2019a
Fraction organic carbon (f_{oc})	g/g	0.005	0.005	AEP, 2019a
Saturated Hydraulic Conductivity (K)	m/y	32	320	AEP, 2019a
Hydraulic Gradient (i)	m/m	0.028	0.028	AEP, 2019a
Infiltration rate (I)	m/y	0.012	0.06	AEP, 2019a
Soil permeability to vapour flow (kv)	cm^2	10^{-9}	$6x10^{-8}$	AEP, 2019a

Table D2 Site Characteristics

Parameter	Unit	Value	Source
Contaminant Source Width Perpendicular to Groundwater Flow (Y)	m	10	AEP, 2019a
Contaminant Source Length Parallel to Groundwater Flow (X)	m	10	AEP, 2019a
Contaminant Source Depth (Z)	m	3	AEP, 2019a
Distance to Surface Water (x)	m	10	AEP, 2019a

Table D2 Site Characteristics			
Parameter	**Unit**	**Value**	**Source**
Distance to Agricultural Water User (x)	m	0	AEP, 2019a
Depth to groundwater (d)	m	3	AEP, 2019a
Depth of unconfined aquifer (d_a)	m	5	AEP, 2019a
Transport time (t)	yr	500	AEP, 2019a
Thickness of zone below the source (b)	m	1	*theoretical CSM for Tier 2

Table D3 Chemical Specific Information				
Parameter	**Unit**	**Bromacil**	**Tebuthiuron**	**Source**
Organic Carbon Partition Coefficient (Koc)	mL/g	66.6	23	AEP, 2019a
Henry's law constant	Dimensionless	5.27×10^{-9}	4.91×10^{-9}	AEP, 2019a
Solubility	mg/L	815	2500	AEP, 2019a
*Half-life	Years	0.75	1.5	*Half-life based on results of literature review of Project 7, Task 1

2. BIOSCREEN Input Parameters

Input parameters used in the assessment of the BIOSCREEN model were based largely on those provided in tables C2, C3, and C6 of the AEP Tier 1 (2019a). BIOSCREEN is a USEPA model and uses a mix of imperial and metric units. Unit conversions were applied to AEP values as required. Other parameter values were sourced as indicated below. A summary of the input parameters is included in Table D4 to D9.

Table D4 Hydrogeological Parameters				
Parameter	**Unit**	**Fine-grained soil**	**Coarse-grained soil**	**Source**
Saturated Hydraulic Conductivity (K)	cm/s	1×10^{-4}	1×10^{-3}	AEP, 2019a
Hydraulic Gradient (i)	ft/ft	0.028	0.028	AEP, 2019a
Total soil porosity (θ_t)	vol/vol	0.47	0.36	AEP, 2019a

Table D5 Dispersion Parameters				
Parameter	**Unit**	**Fine-grained soil**	**Coarse-grained soil**	**Source**
Estimated plume length	ft	32.8	32.8	AEP, 2019a

Table D6 Adsorption Parameters				
Parameter	**Unit**	**Fine-grained soil**	**Coarse-grained soil**	**Source**
Dry soil bulk density (ρ_b)	Kg/L	1.4	1.7	AEP, 2019a

Table D6 Adsorption Parameters				
Parameter	**Unit**	**Fine-grained soil**	**Coarse-grained soil**	**Source**
Fraction organic carbon (f_{oc})	g/g	0.005	0.005	AEP, 2019a
		Bromacil	**Tebuthiuron**	
Organic Carbon Partition Coefficient (Koc)	L/kg	66.6	23	AEP, 2019a

Table D7 Biodegradation Parameters				
Parameter	**Unit**	**Fine-grained soil**	**Coarse-grained soil**	**Source**
Half-life	Yrs	0.75	1.5	literature review of Project 7, Task 1

Table D8 Site Parameters				
Parameter	**Unit**	**Fine-grained soil**	**Coarse-grained soil**	**Source**
Modeled area length	ft	32.8	32.8	AEP, 2019a
Modeled area width	ft	32.8	32.8	AEP, 2019a
Simulation time	yr	variable	variable	Time of max concentration at 10 m downgradient

Table D9 Source Data						
Parameter	**Unit**	**Fine-grained soil**		**Coarse-grained soil**		**Source**
Source thickness in saturated zone	ft	9.84		9.84		AEP, 2019a
Groundwater concentration	mg/L	variable		variable		Desired variable
		Bromacil-Fine	Bromacil-Coarse	Tebuthiuron-Fine	Tebuthiuron-Coarse	
Soluble Mass	kg	3.7×10^{-4}	4.4×10^{-4}	4.0×10^{-5}	4.9×10^{-5}	Calculated from AEP, 2019a

3. PWC Input Parameters

Where possible input parameters for the PWC model were derived from AEP values however the PWC model uses many parameters not included in the AEP models, and values for these were selected from ranges provided within the user manual, literature sources, or approximations. Values selected and their associated source/rationale are summarized in Tables D10 through D14.

Table D10 Chemical Specific Parameters

Chemical Parameters	Unit	Tebuthiuron	Bromacil	Source
Koc	ml/g	23	66.6	AEP, 2019a
Soil Half life	days	$1x10^6$ or 547.5	$1x10^6$ or 275	Mimic no half life/Task 1 literature derived
Soil reference Temperature	°C	20	20	Approximate/ Task 1 literature derived
Molecular Weight	g/mol	228.3	261.1157	NLM, 2020
Vapour Pressure	torr	300 (at 25 °C)	0.0008 (at 100 °C)	NLM, 2020
Solubility	mg/L	2500	815	AEP, 2019a
Henry's la constant	dimensionless	$5.27 x10^{-9}$	$4.91 x 10^{-9}$	Modified from AEP, 2019a
Heat of Henry	J/mol	59000	59000	Young, 2015; Young and Fry, 2014, Suarez, 2005
Q10	N/A	2	2	Young, 2015; Young and Fry, 2014, Suarez, 2005

*can include daughter products if desired

Table D11 Application Parameters			
	Unit	**All scenarios**	**Source/Explanation**
Number of applications	N/A	1	One initial application to mimic Tier 1 CSM
Days since emergence	days	0	Sets application at beginning of time period
Amount	Kg/ha	varied for sensitivity analysis	Desired variable
Application method	N/A	Uniform below	Distributes amount evenly between surface and defined depth to mimic Tier 2 CSM
Depth	cm	300	
Reservoir efficiency	--	0.95	Suggested values in user manual, Young, 2015; Young and Fry, 2014, Suarez, 2005
Reservoir Drift	--	0.05	
Pond efficiency	--	0.95	
Pond drift	--	0.05	
Custom efficiency	--	0.95	
Custom drift	--	0.05	
Application occurs every	yrs	30	Number of years included in weather file
Application occurs from year	N/A	1	Application occurs at begging
Application occur to year	N/A	Last	Irrelevant due to set application frequency

Table D12 Crop/Land Parameters				
Crop/Land	**Unit**	**Fine-grained**	**Coarse-grained**	**Source/Rational**
Scenario	N/A	Standard Oregon Grass Seed	Standard Oregon Grass Seed	Grass selected as most likely scenario (Young, 2015)
Meteorological files	N/A	Great Fall, Montana	Great Fall, Montana	See section D5
Growth descriptors				
Emergence date	N/A	16/09	16/09	Predefined by scenario
Mature date	N/A	15/05	15/05	Predefined by scenario
Harvest date	N/A	30/06	30/06	Predefined by scenario
Root depth	cm	60	60	Predefined by scenario
Canopy cover	%	100	100	Predefined by scenario
Canopy height	cm	50	50	Predefined by scenario
Canopy holdup	cm	0.1	0.1	Predefined by scenario
Hydrological Factors				
Pan factor	N/A	0.74	0.74	Predefined by scenario
Snowmelt factor	cm/°C/day	0.36	0.36	Predefined by scenario
Evaporation depth	cm	17.5	17.5	Predefined by scenario
Post-harvest foliage	N/A	Surface applied	Surface applied	Irrelevant due to inject scenario, but selection required
Irrigation	N/A	none	none	CSM
Soil Layers				
Number of horizons	N/A	1	1	CSM
Thick	cm	1000	1000	AEP, 2019a
Bulk density (ρ)	g/cm^3	1.4	1.7	AEP, 2019a
Max Cap (field capacity)	cm^3/cm^3	0.312	0.312	Predefined by scenario
Min. Cap. (wilting point)	cm^3/cm^3	0.132	0.132	Predefined by scenario
OC	%	0.5	0.5	AEP, 2019a
N		100	100	Predefined by scenario

Table D13 Runoff Parameters			
	Unit	**All scenarios**	**Source/Explanation**
Number of Time-Varying Factors	N/A	29	All values predefined by scenario
Day	N/A	time-varying factor-29 values	All values predefined by scenario
Month	N/A	time-varying factor-29 values	All values predefined by scenario
CN	N/A	79	Curve number, predefined by scenario
USLE-C	N/A	time-varying factor-29 values	USLE (universal soil loss equation) cover management factor, all values predefined by scenario
N	N/A	1	Number of chemicals in the simulation
USLE K	N/A	0.43	Soil erodibility, predefined by scenario
USLE LS	N/A	0.2	Topographic factor, predefined by scenario
USLE P	N/A	1	Practice factor, predefined by scenario
IREG	N/A	3	Location of NRCS 24 hrs hyetograph (relates to weather file)
Slope	%	1	Slope of hydraulic flow path, predefined by scenario
PRZM Runoff & Erosion Extraction			
Runoff Depth	cm	2.0	Lowest depth at which runoff interacts with soil, predefined by scenario
Runoff Decline	1/cm	1.55	Exponential decline of runoff interaction as a function of depth, predefined by scenario
Efficiency	N/A	0.266	Amount of runoff that interacts with soil, predefined by scenario
Erosion Depth	cm	0.1	Lowest depth that erosion interacts with soil, predefined by scenario
Erosion Decline	1/cm	0	Exponential decline of erosion interaction as a function of depth, predefined by scenario
Efficiency	N/A	1.0	Fraction of eroded soil that interacts with the surface for compound removal, predefined by scenario

Table D14 Watershed Parameters			
	Unit	**All scenarios**	**Source**
Simulation Type	N/A	Groundwater	CSM
Watershed and Water Body Dimensions			
Field Area	m^2	100	AEP, 2019a
Water body area	m^2	12	Not active for groundwater simulation
Initial Depth	m	3	AEP, 2019a
Max Depth	m	3	AEP, 2019a
Hydraulic Length	M	600	Predefined by scenario
Cropped Area Fraction	N/A	1.0	Predefined by scenario
Base Flow	m^3/s	0.0	Predefined by scenario
Water Body Physical Parameters	N/A	USEPA/OPP defaults	Not active for groundwater simulation
Sediment Accounting	N/A	No Burial	Not active for groundwater simulation

4. PEARL Input Parameters

Where possible, input parameters for the PEARL model were derived from AEP values however the PEARL model uses many parameters not included in the AEP models, and values for these were selected from ranges provided within the user manual, literature sources, or approximations. Values selected and their associated source/rationale are summarized in Tables D15 through D17.

Table D15 Location Parameters				
	Unit	**Fine grained**	**Coarse grained**	**Source/Explanation**
Location	N/A	Alberta, Canada	Alberta, Canada	Scenario Name
Longitude	Decimal Degrees	47.506187	47.506187	Pertains to meteorological file, same as PWC
Latitude	Decimal Degrees	-111.283691	-111.283691	
Altitude	masl	1015	1015	
Max ponding depth	m	0	0	Suggested in user manual (Tiktak and Boesten, 2000)
Initial Soil temperature at bottom of profile	°C	10	10	Suggested in user manual (Tiktak and Boesten, 2000)
Air boundary thickness layer thickness	m	0.01	0.01	Suggested in user manual (Tiktak and Boesten, 2000)

Table D15 Location Parameters				
	Unit	**Fine grained**	**Coarse grained**	**Source/Explanation**
Soil Profile				
Relative diffusion coefficient	N/A	Millington Quirk	Millington Quirk	Suggested in user manual (Tiktak and Boesten, 2000)
Number of Soil Horizons	N/A	1	1	CSM
Thickness of horizon	m	10	10	AEP, 2019a
Number of numerical components	N/A	12	12	Suggested in user manual (Tiktak and Boesten, 2000)
Dispersion length	m	0.05	0.05	Suggested in user manual (Tiktak and Boesten, 2000)
Soil Building Block				
Sand	%	0.319	0.67	Estimated for soil type
Silt	%	0.428	0.26	
Clay	%	0.253	0.067	
Foc	%	0.005	0.005	AEP, 2019a
pH	N/A	7.0	7.0	Estimated
Dry bulk density	kg/m3	1700	1400	AEP
Van Genuchten parameters				
Theta Sat	m3/m3	0.434	0.37	Suggested in user manual (Tiktak and Boesten, 2000)
Theta Res	m3/m3	0.01	0.03	
Alpha dry	1/cm	0.033	0.0126	
Alpha wet	1/cm	0.066	0.0252	
Lambda	N/A	-3.162	0.5	
K Sat	m/day	0.0864	0.877	AEP, 2019a
n	N/A	1.2	1.57	Suggested in user manual (Tiktak and Boesten, 2000)
Meteostation				
Source	N/A	Great Falls, Montana, USA		see section D5
Longitude	Decimal Degrees	47.506187	47.506187	Pertains to weather file
Latitude	Decimal Degrees	-111.283691	-111.283691	
Altitude	masl	1015	1015	
Lower boundary	N/A	Time dependent groundwater level	Time dependent groundwater level	Estimated based on user manual (Tiktak and Boesten, 2000)

Table D15 Location Parameters				
	Unit	**Fine grained**	**Coarse grained**	**Source/Explanation**
Crop Calendar	N/A	No crops-fallow soil	No crops-fallow soil	CSM
Irrigation	N/A	No irrigation	No irrigation	CSM
Tillage	N/A	No tillage	No tillage	CSM
Repeat Interval	N/A	No repeat	No repeat	CSM

Table D16 Chemical Specific Parameters				
Substance	**Unit**	**Tebuthiuron**	**Bromacil**	**Source**
General				
Molar mass	g/mol	228.3	261.1157	NLM, 2020
Saturated vapour pressure		39996.7	0.107	NLM, 2020
Measured at	°C	20	25	NLM, 2020
Molar enthalpy of vaporisation	kg/mol	95	95	Estimated based on user manual (Tiktak and Boesten, 2000)
Solubility in water	mg/L	2500	815	AEP, 2019a
Measured at	°C	20	20	Estimated
Molar enthalpy of dissolution	kg/mol	27	27	Estimated based on user manual (Tiktak and Boesten, 2000)
Freundlich sorption				
Option	N/A	Kom, pH-independent	Kom, pH-independent	AEP, 2019a
Kom	ml/g	23	66.6	AEP, 2019a
Measured at	°C	20	20	Estimated
Molar enthalpy of sorption	kJ/mol	0	0	Estimated based on user manual (Tiktak and Boesten, 2000)
Reference concentration in liquid phase	mg/L	1	1	
Freundlich sorption exponent	N/A	0.9	0.9	
Desorption rate coefficient	1/day	0	0	
Factor relating CofFreNeq and CofFreEql	N/A	0	0	

Table D16 Chemical Specific Parameters				
Substance	**Unit**	**Tebuthiuron**	**Bromacil**	**Source**
Transformation				
Half-life	day	550	275	Literature derived, see Task 1
Measured at	°C	20	20	
Liquid content in incubation experiment	Kg/kg	1	1	Estimated based on user manual (Tiktak and Boesten, 2000)
Exponent for the effect of liquid	N/A	0.7	0.7	
Molar activation energy	kg/mol	65.4	65.4	
Diffusion				
Reference temperature for diffusion	°C	20	20	Estimated based on user manual (Tiktak and Boesten, 2000)
Reference diffusion coefficient in water	m^2/day	$4.3x10^{-5}$	$4.3x10^{-5}$	
Reference diffusion coefficient in air	m^2/day	0.43	0.43	
Crop				
Wash-off factor	N/A	0.0001	0.0001	Suggested by user manual (Tiktak and Boesten, 2000)
Half-life on crop surface	Day	$1x10^6$	$1x10^6$	
Coefficient for plant uptake	N/A	0.5	0.5	
***option to create transformation schemes				

Table D17 Application Parameters			
Application	**Unit**	**All Scenarios**	**Source/Explanation**
Application type		Injection	Mimics CSM
Date	(dd/mm/yyyy)	01/01/1961	Irrelevant
Dosage	Kg/ha	0	Set initial conditions rather than addition
Depth (m)	m	1	Maximum depth allowed
Initial Conditions			
Depth (m)	m	3	AEP, 2019a
Concentration (mg/kg)	mg/kg	variable	Desired variable
Deposition	N/A	No deposition	CSM
Initial Groundwater Conditions			
Initial groundwater level	cm	-300	AEP, 2019a

5. METEOROLOGICAL PARAMETERS

Both PWC and PEARL require weather files to determine infiltration rates and complete a simulation. Site specific meteorological data can be acquired from and on-site weather station or proximal weather stations. The files can then be formatted based on the guidelines found within the PWC and PEARL user manuals. Formatted weather files for PWC have been created for sites across the United States and are available for download on the Environmental Modeling Community of Practice Meteorological Data webpage. For simplicity, the closest US city to Alberta with a weather file available in the US EPA database (Great Falls, Montana) was selected for the model analysis. Located approximately 300 km southeast of Lethbridge, AB it is expected to be representative of southern Alberta (Figure D1). This weather file was then modified to meet the PEARL formatting requirements.

The selected weather file contains hourly historical meteorological data from 1961 to 1990. For reference, a summary of the water balance generated by PEARL is included in Figure D2.

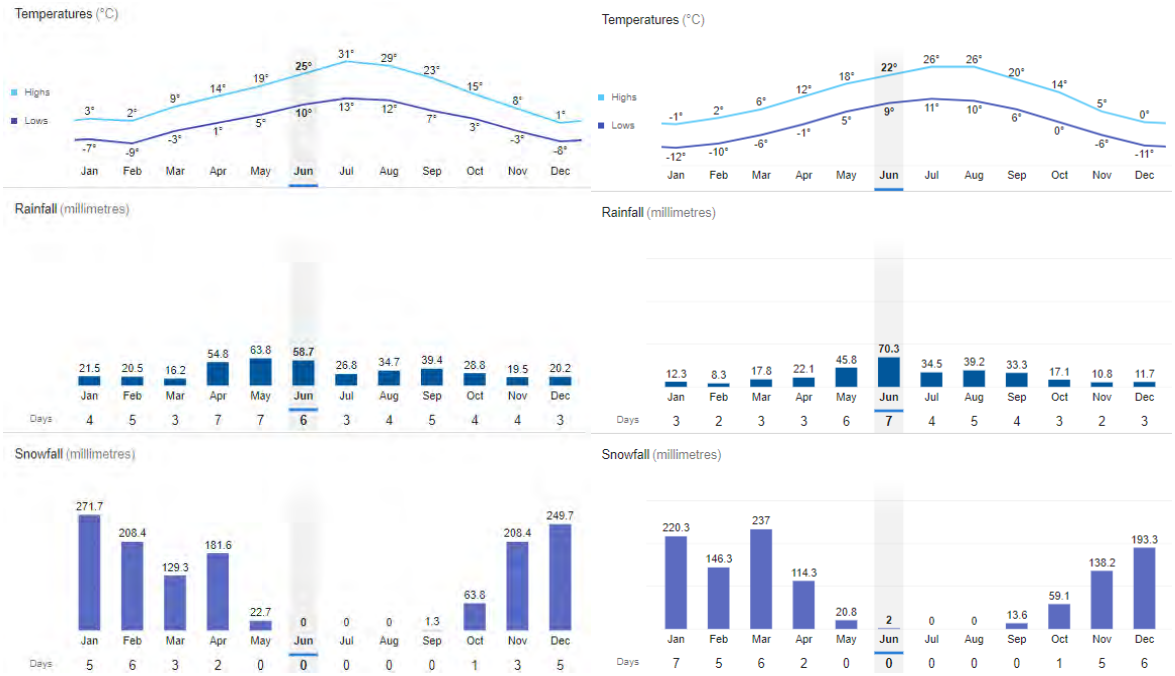

Figure D1: Average monthly climatic data for a) great falls, MT and b) Lethbridge, AB [from National Oceanic and Atmospheric Administration (NOAA), 2020]

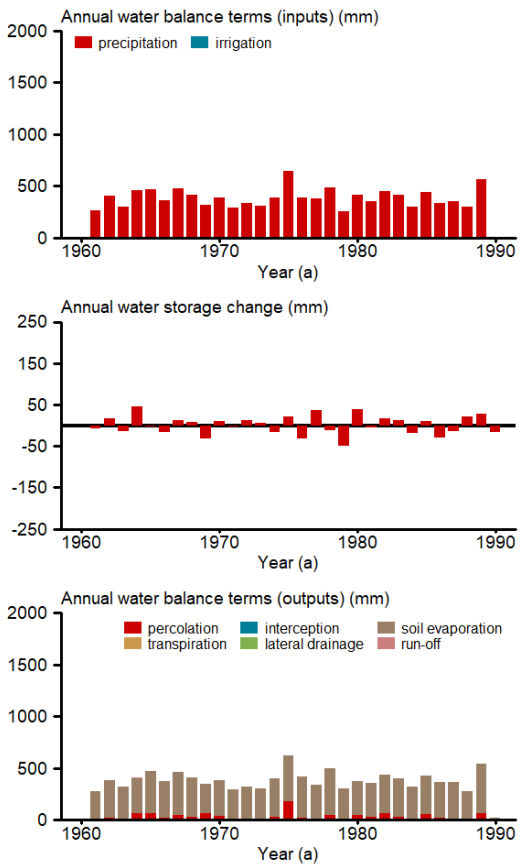

Figure D1: Local water balances from 1961 to 1990.

APPENDIX E MODEL ANALYSIS AND COMPARISONS

Table of Contents

1. BIOSCREEN E-1
2. PWC E-5
3. PEARL E-8

1. BIOSCREEN

The objective of the analysis of BIOSCREEN was to determine the maximum allowable concentration at the source that would produce a groundwater concentration 10 m downgradient (the receptor) that is within surface water guidelines for the FAL pathway. Four scenarios were considered: bromacil in fine grained soil, bromacil in coarse grained soil, tebuthiuron in fine grained soil, and tebuthiuron in coarse grained soil. Within each BIOSCREEN run both 'no degradation' and first-order degradation scenarios are considered.

In order to assess the model, it was necessary to define some novel inputs. One parameter that is not included within the Tier 2 guidelines but is required by BIOSCREEN is the mass of the source. The source mass can be determined on a site-specific basis, however for the sake of the model analysis it was estimated based on the groundwater concentration and the organic carbon partition coefficient. BIOSCREEN also requires a set duration for the simulation. Within the AEP Tier 2 model the time is set to 500 years, however given that BIOSCREEN accounts for source depletion, when a long simulation time was used, the source was depleted and the concentration 10 m downgradient was consistently low. Therefore, the time at which the sterilant concentration peaked at the receptor was determined before proceeding with the model analysis. Peak times were approximately 10 and 8 years for bromacil and tebuthiuron respectively under fine-grained conditions and approximately 1 and 0.5 years respectively under coarse grained conditions (Figure E1).

The relationship between the source concentration and the concentration 10 m downgradient was then evaluated at the peak time (Figure E2). The maximum allowable groundwater concentration at the source such that the downgradient concentration did not exceed the FAL guideline was then determined (Table E1).

Table E1 Theoretical groundwater guidelines for the FAL pathway based on BIOSCREEN model

		Maximum groundwater concentration at the source (mg/L)	
		Fine	**Coarse**
Bromacil	No Degradation	0.01	0.011
	1st Order Degradation	2.94	0.02
Tebuthiuron	No Degradation	0.0032	0.0056
	1st Order Degradation	0.029	0.0067

While the source mass was selected for simplicity, it represents a relatively small source that may not be representative of the majority of impacted site in Alberta. Thus, the relationship between the source mass and the concentration of sterilant 10 m downgradient was also evaluated to assess the sensitivity of the model to this parameter (Figure E3). When only the source mass was varied, the downgradient groundwater concentration followed a sigmoidal relationship and plateaued with a mass size between 0.1 and 1 kg.

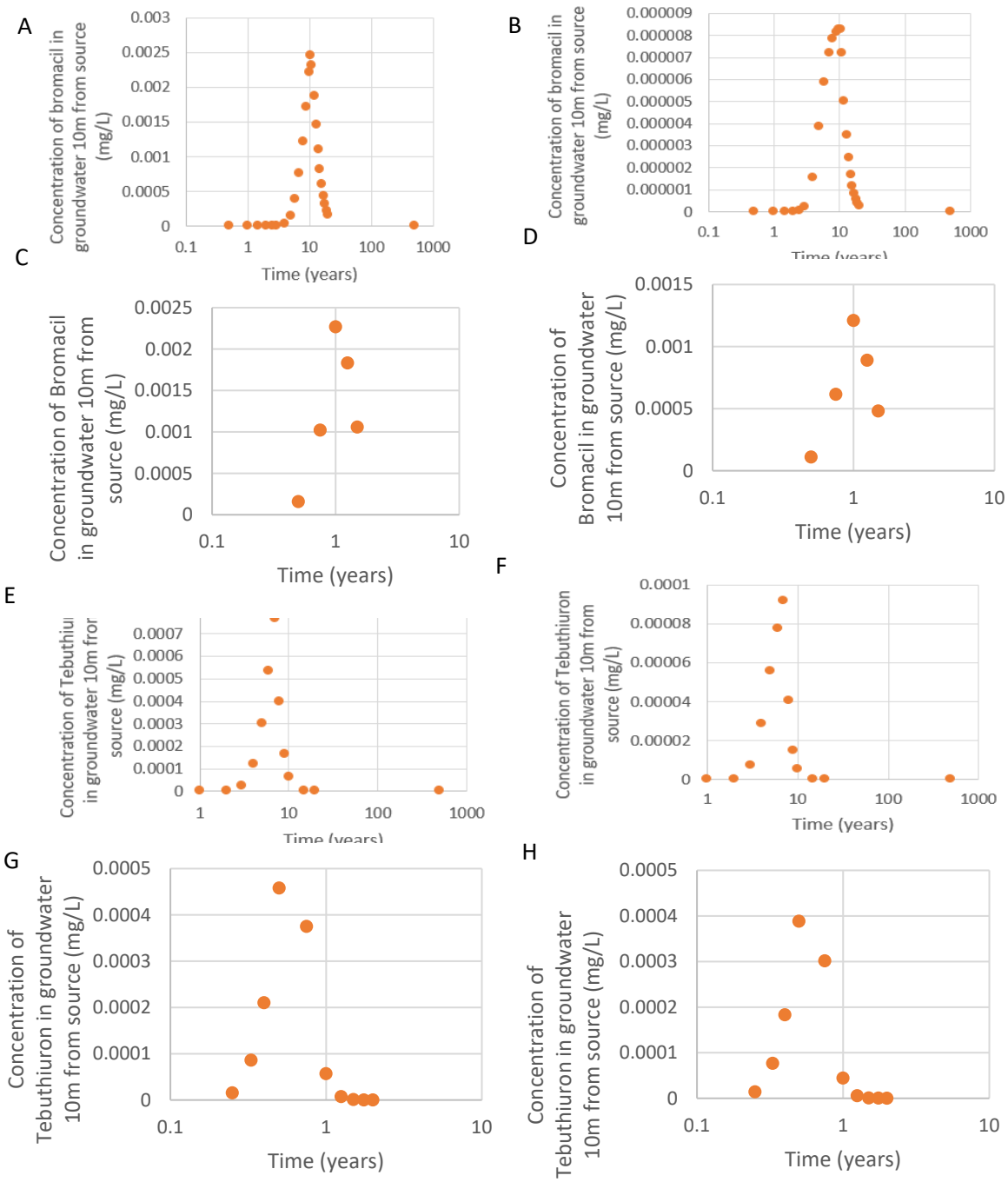

Figure E1: Peak time of sterilant concentration at the receptor. A) bromacil in fine grained soil with no degradation, b) bromacil in fine grained soil with first order degradation, c) bromacil in coarse grained soil with no degradation, d) bromacil in coarse grained soil with first order degradation, e) tebuthiuron in fine grained soil with no degradation, f) tebuthiuron in fine grained soil with first order degradation, g) tebuthiuron in coarse grained soil with no degradation, h) tebuthiuron in coarse grained soil with first order degradation

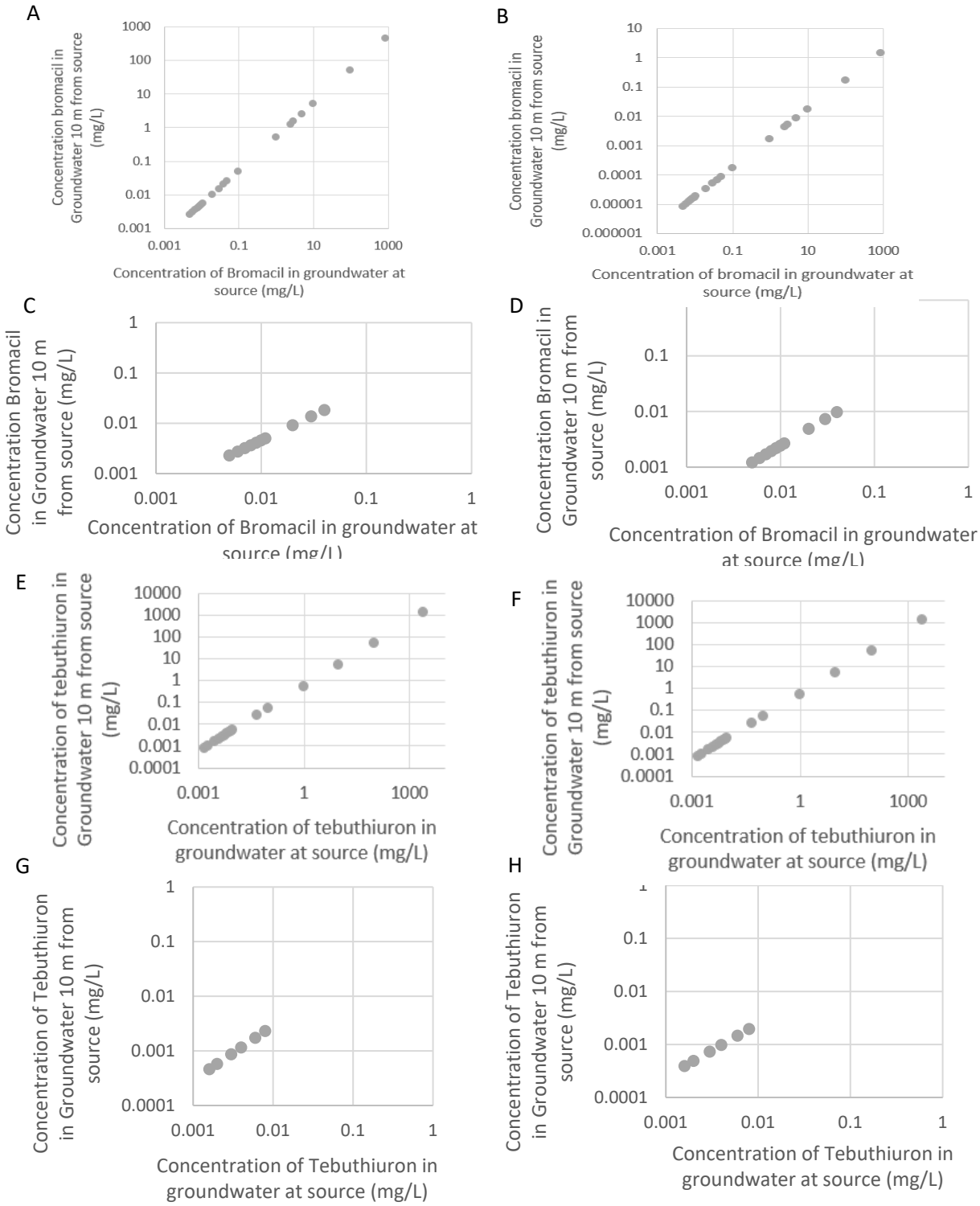

Figure E2: Concentration of sterilant 10 m downgradient with respect to the concentration at the source. A) bromacil in fine grained soil with no degradation, b) bromacil in fine grained soil with first order degradation, c) bromacil in coarse grained soil with no degradation, d) bromacil in coarse grained soil with first order degradation, e) tebuthiuron in fine grained soil with no degradation, f) tebuthiuron in fine grained soil with first order degradation, g) tebuthiuron in coarse grained soil with no degradation, h) tebuthiuron in coarse grained soil with first order degradation.

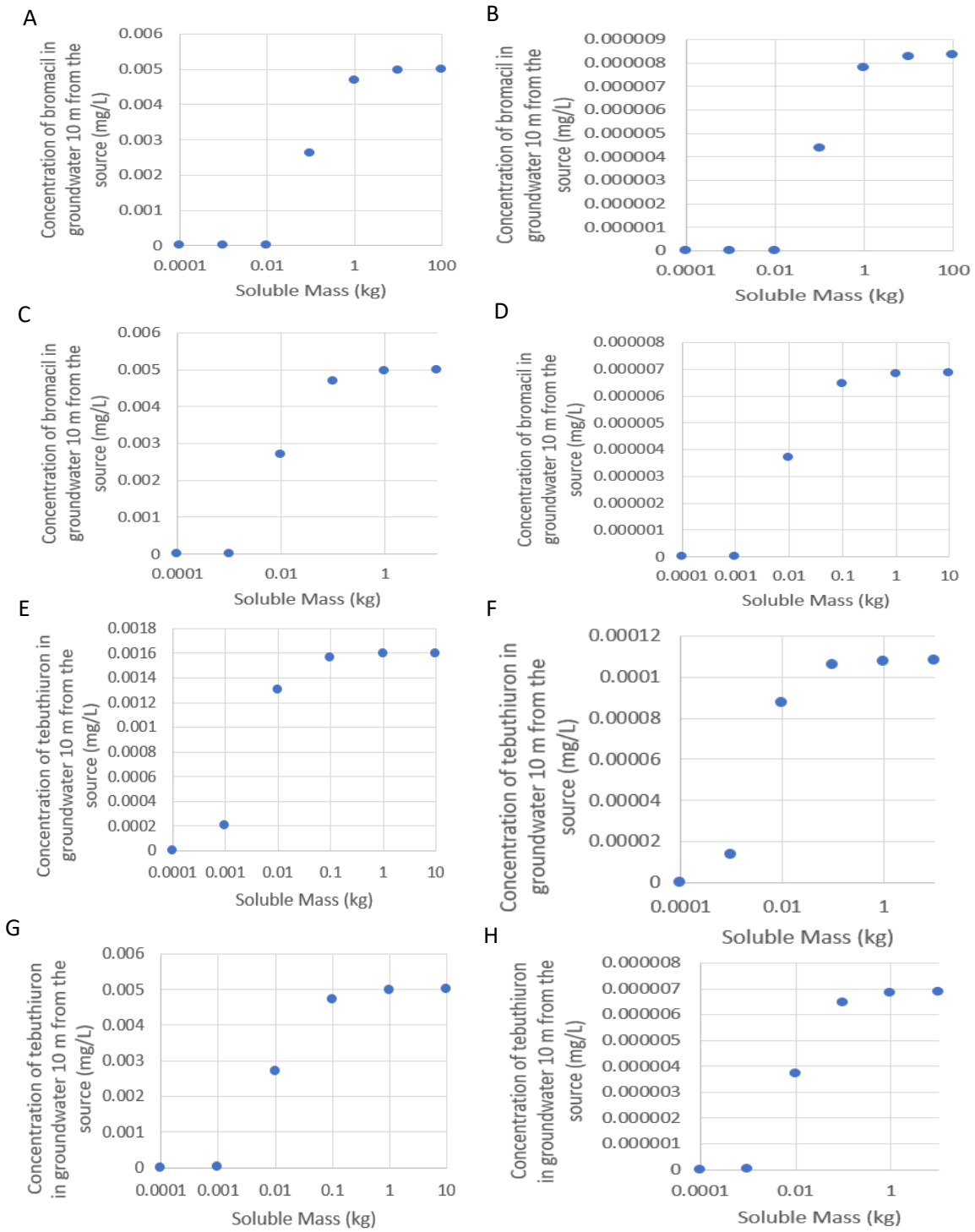

Figure E3: Concentration of sterilant 10 m downgradient with respect to the source mass. A) bromacil in fine grained soil with no degradation, b) bromacil in fine grained soil with first order degradation, c) bromacil in coarse grained soil with no degradation, d) bromacil in coarse grained soil with first order degradation, e) tebuthiuron in fine grained soil with no degradation, f) tebuthiuron in fine grained soil with first order degradation, g) tebuthiuron in coarse grained soil with no degradation, h) tebuthiuron in coarse grained soil with first order degradation.

2. PWC

PWC has the capacity to model agrochemical transport to groundwater but does not consider lateral transport through the saturated zone. The objective of the analysis of PWC was to determine the maximum allowable concentration within the soil at the source that would produce a groundwater concentration that is within the IW groundwater guideline. Four scenarios were considered: bromacil in fine grained soil, bromacil in coarse grained soil, tebuthiuron in fine grained soil, and tebuthiuron in coarse grained soil. For each scenario transport was considered both with and without degradation.

The relationship between the source concentration and the groundwater concentration was evaluated and the maximum allowable groundwater concentration at the source was determined (Table E2). Similar to BIOSCREEN, a linear relationship was observed between the source concentration and the concentration in groundwater (Figure E4).

Table E2 Theoretical soil guidelines for the IW pathway based on PWC model

		Maximum soil concentration at the source (mg/kg)	
		Fine	**Coarse**
Bromacil	No Degradation	0.00035	0.0004
	1st order degradation	0.00036	0.0004
Tebuthiuron	No Degradation	0.00043	0.00047
	1st order degradation	0.00045	0.00048

At the completion of a model run, PWC produces a figure that presents the concentration of the agrochemical within the top of the groundwater with respect to the duration of the simulation (Figure E5). The weather file used in this model evaluation included the year 1961 to 1990 and the sterilant was “applied” within the first year. Based on the model predictions, the peak concentration occurred within the first year of application for each scenario, but concentrations decreased through time when biodegradation was considered (Figure 5b,d,f,h). The sudden and rapid increase in sterilant concentration within the groundwater during the first year of the simulation was surprising and suggests that further investigation into the unsaturated transport component of PWC may be necessary.

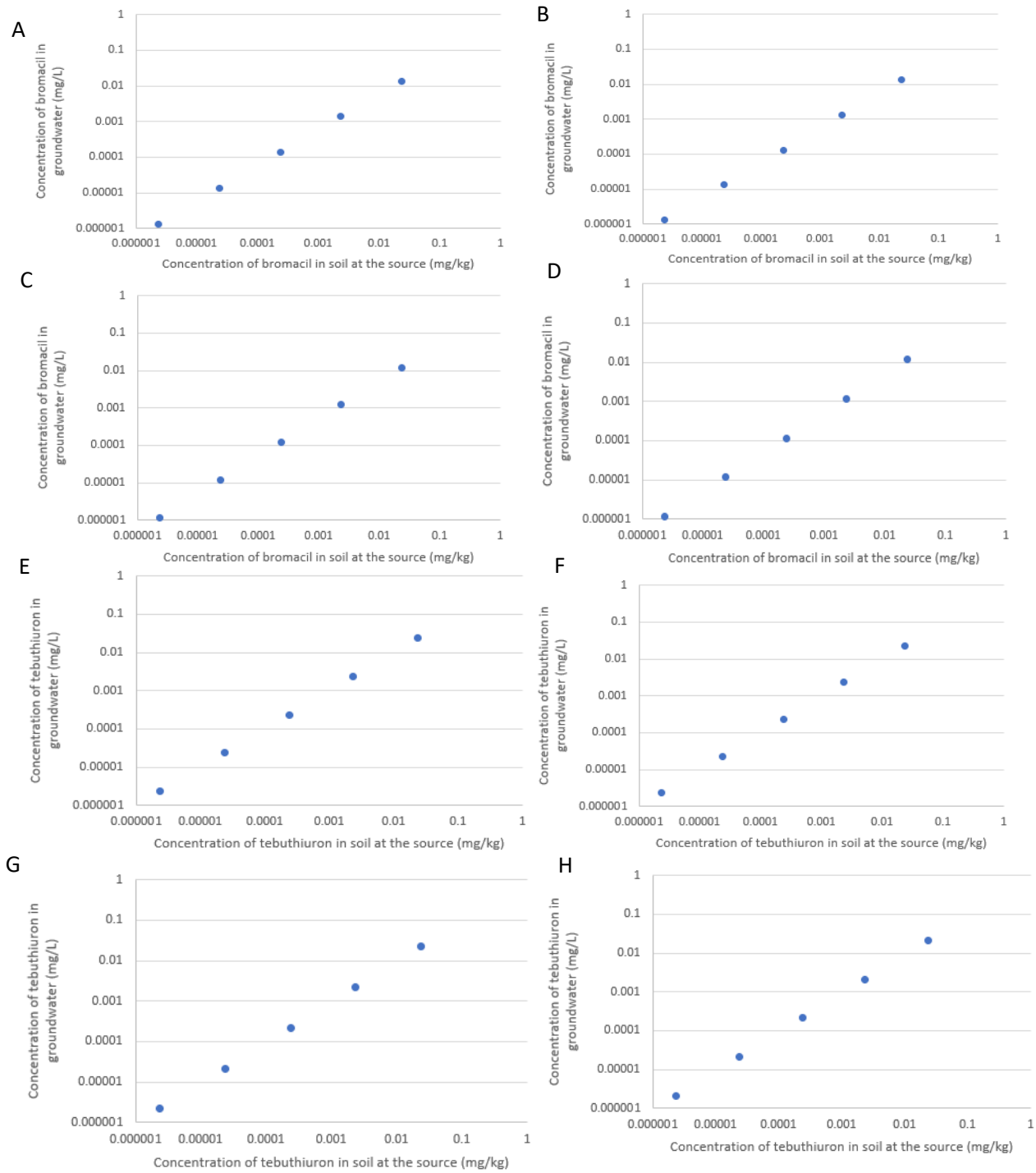

Figure E4: Concentration of sterilant in groundwater with respect to the concentration at the source. A) bromacil in fine grained soil with no degradation, b) bromacil in fine grained soil with first order degradation, c) bromacil in coarse grained soil with no degradation, d) bromacil in coarse grained soil with first order degradation, e) tebuthiuron in fine grained soil with no degradation, f) tebuthiuron in fine grained soil with first order degradation, g) tebuthiuron in coarse grained soil with no degradation, h) tebuthiuron in coarse grained soil with first order degradation.

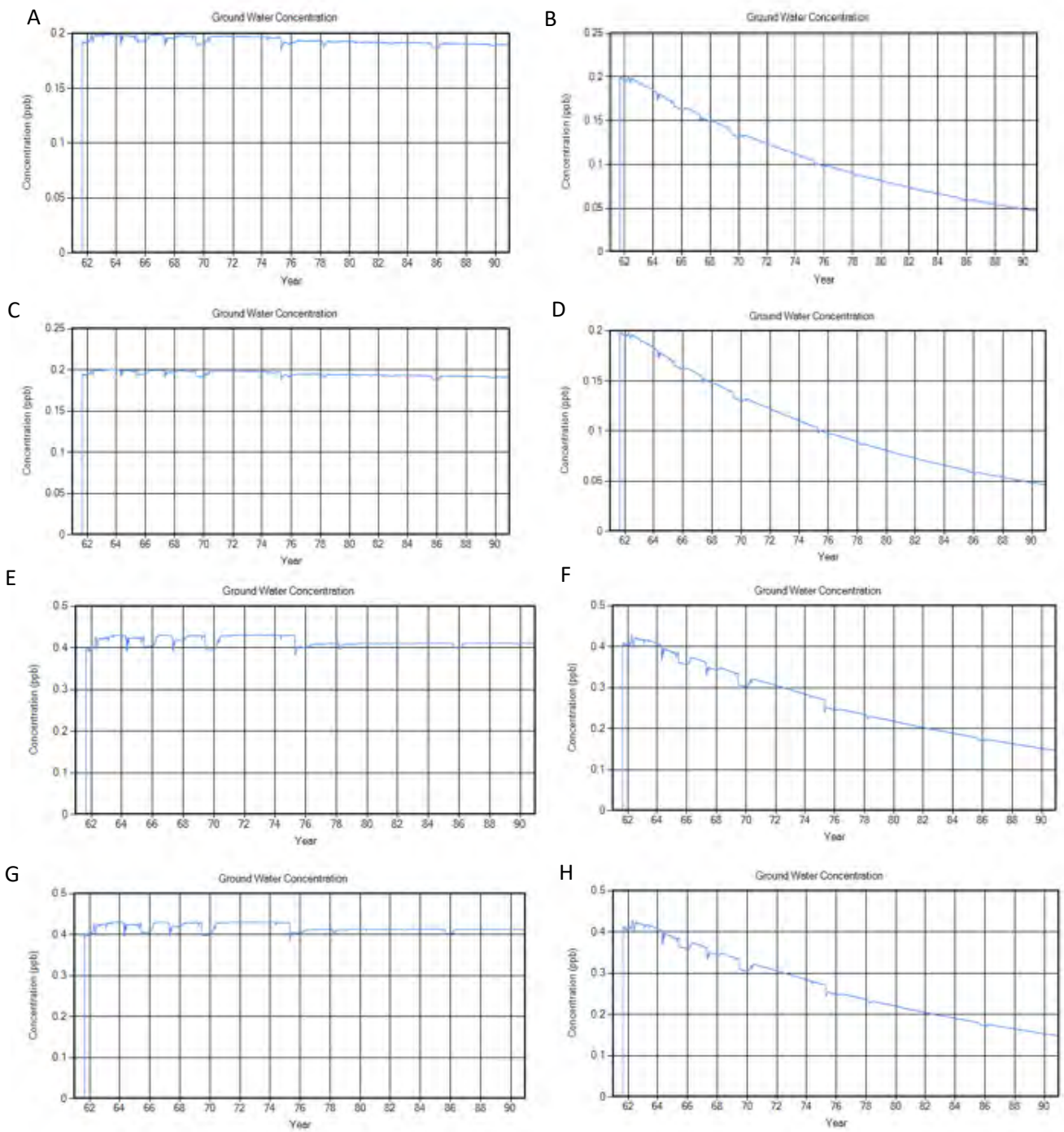

Figure E5: Maximum concentration of sterilant in groundwater with respect to time. A) bromacil in fine grained soil with no degradation, b) bromacil in fine grained soil with first order degradation, c) bromacil in coarse grained soil with no degradation, d) bromacil in coarse grained soil with first order degradation, e) tebuthiuron in fine grained soil with no degradation, f) tebuthiuron in fine grained soil with first order degradation, g) tebuthiuron in coarse grained soil with no degradation, h) tebuthiuron in coarse grained soil with first order degradation.

3. PEARL

The analysis of PEARL had two objectives. The first was to determine the maximum allowable concentration within the soil at the source that would produce a groundwater concentration that was within the IW groundwater guideline. The second was to determine the maximum allowable concentration within the soil at the source that would produce a groundwater concentration 10 m downgradient that was within the FAL surface water guideline. Four scenarios were considered: bromacil in fine grained soil, bromacil in coarse grained soil, tebuthiuron in fine grained soil, and tebuthiuron in coarse grained soil. The inclusion/exclusion of a half-life was also considered but did not have an impact on the allowable concentrations even when a 1 m separation unit was included.

The relationship between the source concentration and the groundwater concentration was evaluated and the maximum allowable groundwater concentration at the source was determined (Table E3). The relationship between the source concentration and the concentration of the sterilant in the upper groundwater was once again linear (Figure E6).

Table E3 Theoretical soil guidelines for the IW pathway based on PEARL model

		Maximum soil concentration at the source (mg/kg)	
		Fine	**Coarse**
Bromacil	No Degradation	1.45×10^{-4}	1.4×10^{-4}
	1st order degradation	1.45×10^{-4}	1.4×10^{-4}
Tebuthiuron	No Degradation	1.67×10^{-4}	1.25×10^{-4}
	1st order degradation	1.67×10^{-4}	1.25×10^{-4}

Upon completion of a simulation, PEARL produces numerous figures which may be of interest to the user. Similar to PWC, an output file showing the concentration of bromacil within the upper groundwater over the course of the simulation (in this case 1961 to 1990) can be generated. In the simulations considering bromacil both under fine-grained and coarse-grained conditions, the concentration of the sterilant in the groundwater gradually increased over the course of the simulation period. In the simulations considering tebuthiuron, sterilant concentrations within the groundwater increased to a maximum approximately halfway through the simulation then decreased with time (Figure E7).

The second objective of the analysis of PEARL was not completed due to incomplete results from the model. The PEARL model is purported to model both transport through the unsaturated zone as well as the saturated zone. One of the output files created at the end of a PEARL simulation is a mass balance of the agrochemical in the soil over time (Figure E8 A,B). In all simulations the concentration increased during the first year as the sterilant is 'applied' and was lost over time as a result of processes including transformation, vertical and lateral leaching, volatilization, and plant uptake. A breakdown of the magnitude of the contribution of each of these processes is also provided (Figure E8 C,D). Under all scenarios, transformation (degradation) was the main process through which sterilants were lost from the soil profile followed by vertical leaching. A greater contribution from leaching was observed for tebuthiuron which reflects the lower K_{oc} of this sterilant. Lateral leaching was negligible under all

scenarios evaluated which suggests that further refinement of some input parameters may be necessary.

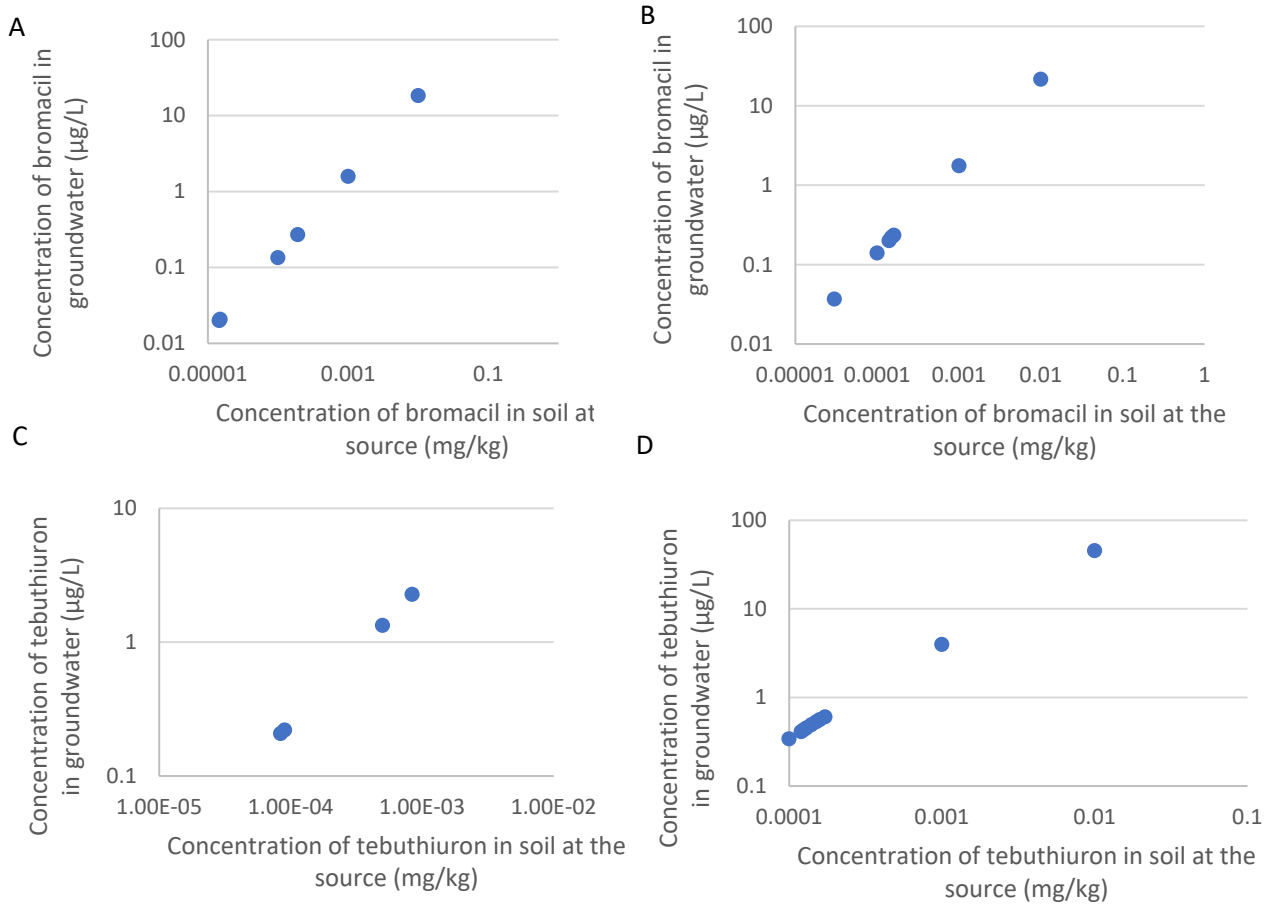

Figure E6: Concentration of sterilant in groundwater with respect to the concentration at the source. A) bromacil in fine grained soil, b) bromacil in coarse grained soil, c) tebuthiuron in fine grained soil, d) tebuthiuron in coarse grained soil.

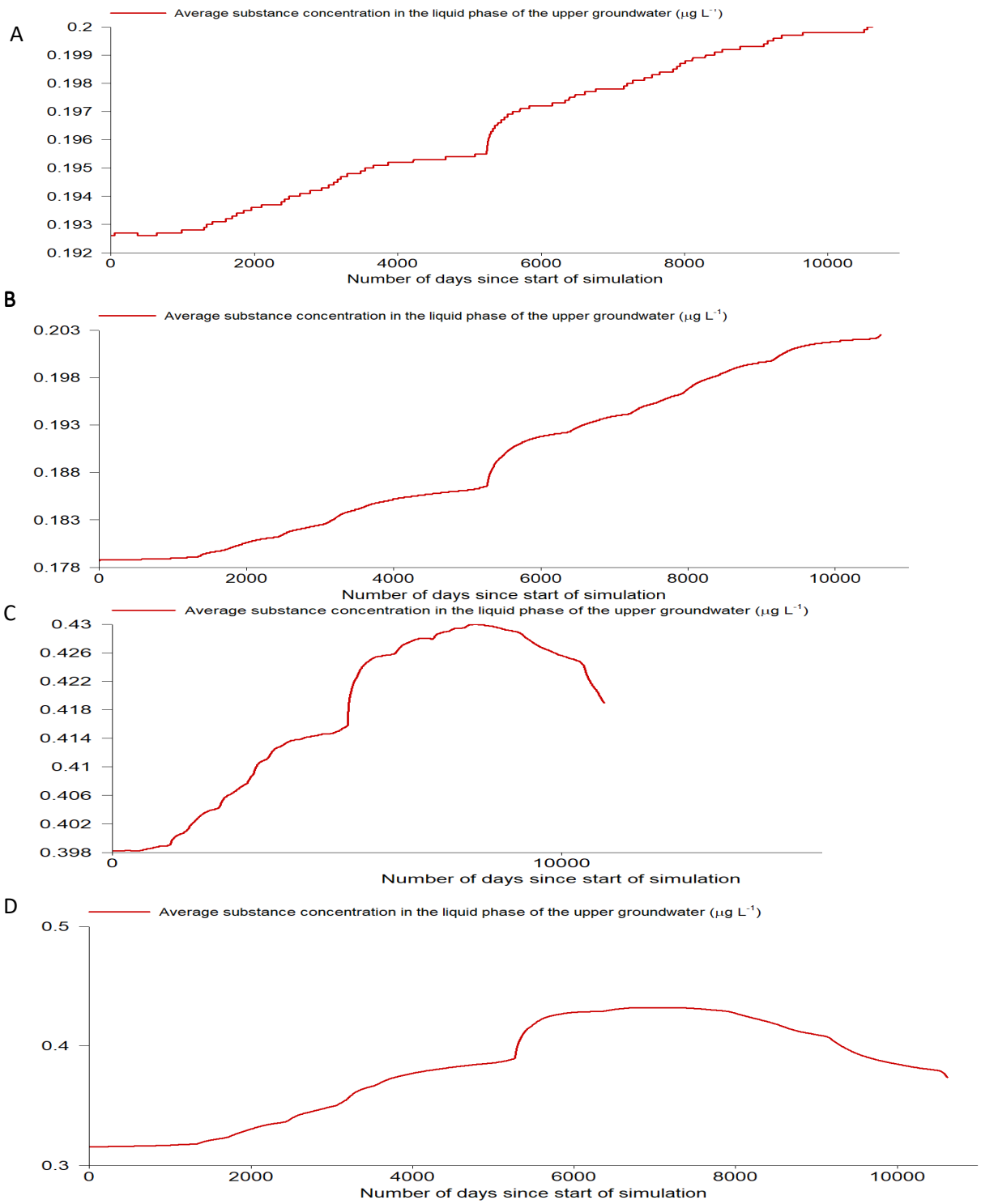

Figure E7: Maximum concentration of sterilant in groundwater with respect to time. A) bromacil in fine grained soil, b) bromacil in coarse grained soil, c) tebuthiuron in fine grained soil, d) tebuthiuron in coarse grained soil.

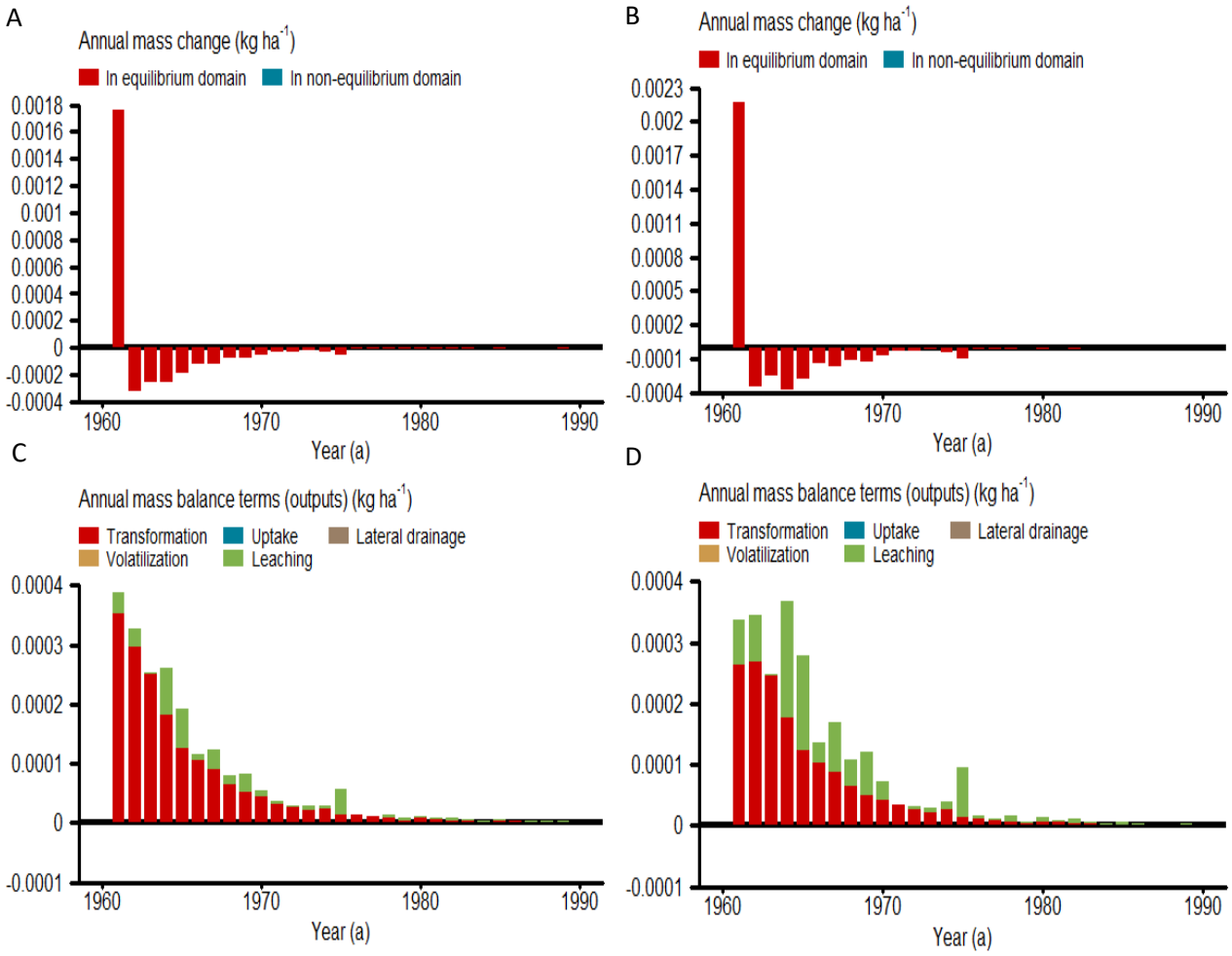

Figure E8: Annual mass balance of sterilants in fine grained soil. A) annual mass change of bromacil in fine grained soil, b) annual mass change of tebuthiuron in fine grained soil c) mass balance of bromacil in fine grained soil by transfer component d) mass balance of tebuthiuron in fine grained soil by transfer component

Appendix A5-3: Soil-Water and Organic Carbon-Water Partitioning Coefficients

Bachmann, V. and M. Tindal, 2023. Determination of Soil-Water and Organic Carbon-Water Partitioning Coefficients for Bromacil and Tebuthiuron. Report SSP-7C prepared by InnoTech Alberta and Millennium EMS Solutions Ltd. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 15 pp.

Determination of Soil-Water and Organic Carbon-Water Partitioning Coefficients for Bromacil and Tebuthiuron

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Report Prepared for
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April 24, 2023

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EXECUTIVE SUMMARY

Soil sterilants were commonly used from the 1960s to late 1990s to control weeds on rangelands, pipeline right of ways, oil and gas wells, railways, sawmills, pulp mills, and other industrial sites across Alberta. Sterilants are typically non-selective, residual, and persistent; they control all plants they contact and because they persist in soil, vegetation growth on sterilant-impacted sites is often inhibited. Sterilants tend to be highly mobile, which can result in off-site contamination via leaching, surface runoff, and wind. Two of the most used soil sterilants in Alberta are bromacil and tebuthiuron.

A related project being conducted by Millennium EMS Solutions Ltd. (MEMS) will use the data generated through the experiments as model input parameters for establishing Alberta Tier 1 guidelines for bromacil and tebuthiuron for the protection of irrigation water and freshwater aquatic life. The chemical properties and interactions with soil are poorly understood for bromacil and tebuthiuron. To inform the model input parameters, more understanding of these soil interactions is required.

The objectives of this Soil Sterilants Program Project were to establish accurate adsorption coefficient (K_d and K_{oc}) values for bromacil and tebuthiuron in soils with a range of organic carbon matter and to determine whether additional testing would be beneficial in further refining input parameters. The project used the OECD *Guideline for Testing of Chemicals: Adsorption–Desorption Using a Batch Equilibrium Method*. Three soils were selected from InnoTech Alberta's available stock of test soils that had a range of organic carbon.

The soils used had total organic carbon (TOC) contents of 4.96%, 1.14%, and 0.05% and had textures of silty loam, sandy loam, and sand, respectively. Tebuthiuron showed higher concentrations in soil than bromacil after the adsorption test. With both sterilants, the amount of sterilant in soil was higher with higher TOC and finer soil texture. K_d values were consistent with sterilants concentrations in the soil; finer textured and higher TOC soils had higher K_d than coarse textured and low TOC soils. On average, K_d values were 3.31 mL/g for fine soil, 1.63 mL/g for sandy loam, and 0.45 mL/g for coarse soil. The K_{oc} values were 66.8 mL/g for fine soil, 142.8 mL/g for sandy loam, and 907.3 mL/g for coarse soil.

The chemical interactions with soil and groundwater are poorly understood for bromacil and tebuthiuron. Work to better understand these relationships are out of the scope of this project. The results produced by this project provide sufficient data to be used as model input parameters for other projects within the Soil Sterilants Program.

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1.0 INTRODUCTION

1.1 Background

Soil sterilants are non-selective, broad-spectrum herbicides used for vegetation control on industrial land. In Alberta, they were introduced in the 1960s and were used on a variety of industrial sites until their use was halted in the 1990s due to observed offsite migration and extended persistence. Decades after ceasing treatment with sterilant products, impacts can persist in soil and water. Soil sterilants are considered unique and challenging contaminants to manage (Drozdowski et al., 2018).

1.2 Historical Project Activities

The Soil Sterilants Program (SSP) was designed to address several knowledge gaps related to the assessment, risk management, and remediation of sterilant-impacted sites. Many of the knowledge gaps identified include the chemical properties of these sterilants and their interactions with soil and groundwater. These chemical properties are necessary to develop accurate models for the transport and fate of sterilants in impacted sites. The objective of the Project is to refine input parameters related to contaminant fate, mobility, and degradation that more realistically reflect Alberta-specific field conditions, are protective of receptors at Alberta sites, and can be used to inform Alberta Tier 1 and Guideline modification. Previous preliminary sensitivity analysis for bromacil identified that sterilant half-life and water–organic carbon partition coefficient (K_{oc}), fraction of soil organic carbon (f_{oc}), soil bulk density, and infiltration rate were controlling parameters for the model.

Marquez et al. (2020), evaluated the sensitivity of the Domenico and Robbins groundwater transport model (Domenico model) used to develop Alberta Environment and Parks (AEP) Tier 1 and Tier 2 guidelines (Alberta Environment and Parks, 2022a, b). Model sensitivity was evaluated with sterilant half-life, K_{oc}, f_{oc}, soil bulk density, and infiltration rate. Based on model sensitivity to half-life and water–organic carbon partition coefficient (K_{oc}), it was recommended that experiments be carried out with Alberta soils to generate model input parameters [1].

A half-life experiment is underway in collaboration with BV Laboratories, and a preliminary adsorption isotherm experiment was conducted by the University of Guelph (Houston et al., 2020), with experiments aimed to determine the soil-water partition coefficient (K_d) and organic carbon-water partition coefficient (K_{oc}) for bromacil and tebuthiuron in two subsoils collected from Alberta sites. The experiments were based on methods provided in *OECD #106 Guideline for the Testing of Chemicals: Adsorption–Desorption Using a Batch Equilibrium Method* (Organisation for Economic Cooperation and Development, 2000). The method followed was indirect, whereby a solution of known concentration was prepared of the test substance in 0.01 M $CaCl_2$. The solution was added to a container with a specified soil at a ratio of 5:1 and the mixture was agitated, centrifuged, and the aqueous phase was analyzed. The amount of test substance adsorbed on the soil sample was calculated as the difference between the amount of test substance initially present in solution and the amount remaining at the end of the experiment.

Using the indirect method and subsoils collected from Alberta sites, the K_{oc} values calculated separately from each individual measurement of the final aqueous concentration had very wide ranges. Upon

[1] Relevant to adsorption is Dilution Factor 1 (DF1): A linear distribution coefficient was used to describe the partitioning between the sorbed, aqueous, and gaseous phases in soils. The partitioning of non-polar chemicals is a function of the organic carbon-water partitioning coefficient (K_{oc}) of the contaminant and the amount of organic carbon in the soil (fraction of organic carbon [f_{oc}]).

review, it was determined that the indirect method created uncertainties and that the soils used had very low fractions of organic carbon (f_{oc}), further contributing to variability in results. The OECD direct method is recommended when the difference in the solution concentration of the substance cannot be accurately determined, and includes analysis of stock solution, supernatant, and soil.

The OECD method also describes three tiers of assessment: Tier 1 is a preliminary study; Tier 2 is a screening test with 5 distinct soils, and Tier 3 is the determination of Freundlich adsorption isotherms or the study of desorption by means of desorption kinetics/Freundlich desorption isotherms.

2.0 OBJECTIVE AND SCOPE

The current project was proposed as a modified Tier 2 assessment with three soils, rather than five soils. The objectives of the project were as follows:

1. Establish accurate K_d and K_{oc} with soils containing sufficient quantities (i.e., >0.5%) fraction of organic carbon.
2. Determine whether additional testing (i.e., OECD #106 Tier 3) would be beneficial in further refining input parameters.

3.0 METHODOLOGY

3.1 Soil Identification and Characterization

InnoTech Alberta (InnoTech) has a stock of a variety soils for use in small scale experiments. Soils for potential use in this test was identified through historical analysis. Millennium EMS Solutions Ltd. (MEMS) reviewed the preliminary data, provided recommendations for additional analyses, and selected the soils used for experiments.

Soils were analyzed for physical and chemical characteristics. Three soils identified from the review of historical data were analyzed for the parameters in Table 1.

Table 1. Schedule of analytical tests in this project.

Analysis	Individual parameters	Samples from each soil type
Particle Size Analysis (PSA)	%Sand, %Silt, %Clay, Texture	3
Detailed salinity	pH (by $CaCl_2$), saturated paste EC, % saturation, Ca, Mg, Na, SO_4-S, SO_4, Cl, K, SAR, TGR, reported in mg/kg. Includes Cl in mg/L	3
Cation exchange capacity	(Pending info from Element)	3
Metals	Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mo, Ni, Se, Ag, Tl, Sn, U, V, Zn, Cr^{6+}, saturated paste B (mg/L), Hg.	3
Fraction of organic carbon (f_{oc})	Total organic carbon	3
Bromacil (soil or water)	Bromacil	1
Tebuthiuron (soil or water)	Tebuthiuron	1

Samples were taken as random grab samples from previously homogenized soil by cone and quarter method. Soils were assumed to not have been in contact with bromacil or tebuthiuron; therefore, only one sample each was analyzed for confirmation.

3.2 Experimental Design

The method used in this experiment was modelled after the Adsorption–Desorption Using a Batch Equilibrium Method, which is an OECD guideline for the testing of chemicals (Organisation for Economic Cooperation and Development, 2000).

3.2.1 Preparation of Stock Solutions

The analytical grade chemical compounds used in the experiment were the bromacil PESTANAL® analytical standard (CAS number 314-40-9) (MilliporeSigma, 2023a) and the tebuthiuron PESTANAL® analytical standard (CAS number 34014-18-1) (MilliporeSigma, 2023b).

Sterilant in stock solution was prepared to achieve approximately 1 mg/kg equivalent soil concentration based on review of tabulated site information [2]. Using serial dilution, the bromacil and tebuthiuron stock solutions were prepared to a concentration of 0.214 mg/L each in 0.01 M $CaCl_2$ deionized water. Sufficient stock solutions were prepared for analysis and use in all adsorption experiments for each sterilant. Once prepared, the stock solutions were kept in sealed glass containers under refrigeration at 4 °C.

3.2.2 Experimental Setup

3.2.2.1 Soil Sample Preparation

Prior to initiation of the adsorption experiments, the following sample-preparation steps were completed:

1. The soils were air dried at ambient temperature (21 °C) and sieved to a particle size ≤2 mm. The soils were previously homogenized. A subsample of each soil to be used in the experiment was homogenized.
2. The moisture content of each soil was determined through the oven-dry method (i.e., drying at 105 °C until no change in weight) (ASTM International, 2019). All masses used and calculated refers to oven dry mass (i.e., the weight of soil is corrected for moisture content).

3.2.2.2 Adsorption Experiments

After sample preparation, the following adsorption experiment steps were completed:

1. Forty (40) grams of air-dried soil per replicate and per soil type (see Table 2) were weighed, and each soil replicate was placed into a glass sample tube.
2. A total of 200 mL of 0.01 M $CaCl_2$ spiked to 0.214 mg/L with bromacil or tebuthiuron was added to each sample tube.
3. One control sample for each sterilant was prepared (i.e., centrifuge tube containing only 0.01 M $CaCl_2$ spiked to 0.214 mg/L of sterilant).

[2] An option for poorly soluble substances is to add the test substance to the test system by spiking: the test substance is dissolved in an organic solvent, an aliquot of which is added to the system of soil and 0.01 M solution of $CaCl_2$ in distilled or de-ionized water. The content of organic solvent in the aqueous phase should be kept as low as possible, normally not exceeding 0.1%.

4. The soil pH was measured before and after the previously mentioned reagents were introduced to the soil. The pH probe was cleaned between samples.
5. Samples were agitated with a wrist action shaker to ensure full reagent contact and were mixed for 12 h on a shaker table at 130 rpm.
6. After 12 h, the sample tubes were removed from the shaker table and centrifuged for 20 min at 7,000 rpm to separate suspended soil particles from the solution.
7. For each replicate and the control, the supernatant was decanted, and aqueous solution and soils were analyzed for analyte concentrations. A 200 mL sample was provided to Element Laboratories for analysis.
8. All remaining soil, which was approximately 40 g, was collected in an amber glass jar and submitted to Element Laboratories for analysis.

3.2.3 Adsorption Coefficient Calculation

The distribution coefficient K_d is the ratio between the content of the substance in the soil phase and the mass concentration of the substance in the aqueous solution, under the test conditions, when adsorption equilibrium is reached:

$$K_d = \frac{C_s^{ads}(eq)}{C_{aq}^{ads}(eq)} = \frac{m_s^{ads}(eq)}{m_{aq}^{ads}(eq)} \cdot \frac{V_0}{m_{soil}} \quad (cm^3 \cdot g^{-1}) \qquad 1$$

where:

- $C_s^{ads}(eq)$ is the content of the substance adsorbed on the soil at adsorption equilibrium ($\mu g \cdot g^{-1}$).
- $C_{aq}^{ads}(eq)$ is the mass concentration of the substance in the aqueous phase at adsorption equilibrium ($\mu g \cdot cm^{-3}$); this concentration is analytically determined considering the values given by the control samples.
- $m_s^{ads}(eq)$ is the mass of the test substance adsorbed on the soil at adsorption equilibrium (μg).
- $m_{aq}^{ads}(eq)$ is the mass of the test substance in the solution at adsorption equilibrium (μg).
- m_{soil} is the quantity of the soil phase, expressed in dry mass of soil (g).
- V_0 is the initial volume of the aqueous phase in contact with the soil (cm^3).

3.2.4 Organic Carbon Normalized Adsorption Coefficient Calculation

K_{oc} coefficient represents a single value which characterizes the partitioning mainly of non-polar organic chemicals between the organic carbon in the soil or sediment and water. The adsorption of these compounds is correlated with the organic content of the sorbing solid; thus, K_{oc} values depend on the specific characteristics of the humic fractions which differ considerably in sorption capacity, due to differences in origin, genesis, etc.

The organic carbon normalized adsorption coefficient K_{oc} relates the distribution coefficient K_d to the content of organic carbon of the soil sample:

$$K_{oc} = \frac{K_d}{\%_{oc}} \cdot 100\% \quad (cm^3 \cdot g^{-1}) \qquad 2$$

where $\%_{oc}$ is the percentage of organic carbon in the soil sample ($g \cdot g^{-1}$).

4.0 RESULTS AND DISCUSSION

4.1 Soil Identification and Characterization

Three soils were selected for the experiment based on texture and organic carbon content: fine soil, sandy loam, and coarse soil. The fine soil is a silt loam with a TOC of 4.96%, sourced from InnoTech's experimental farm facility in Vegreville, AB. The sandy loam has a TOC of 1.14% and the coarse soil is sand with a TOC of 0.05%. The sandy loam and coarse soils were taken from InnoTech's standard soils inventory. See APPENDIX A: Soil Characteristics for full soil characteristic analyses.

Table 2. Select properties of the three soil types used in the experiment.

Parameter	Units	Soil Type		
		Fine Soil	Sandy Loam	Coarse Soil
Texture description	—	Silt Loam	Sandy Loam	Sand
Percent particle size	% Sand	29	77	90
	% Silt	54	13	5
	% Clay	17	10	5
Organic matter	%	9.92	2.28	0.1
Total organic carbon	%	4.96	1.14	0.05
pH	—	5.2	7.1	6.5
EC	dS/m	1.98	2.66	0.06

4.2 Sterilants Adsorption Results

4.2.1 Analytical Results

Soil moisture content for each of the soils prior to oven drying was 4.3% ± 0.1% for the fine soil, 0.19% ± 0.02% for the coarse soil, and 6.6% ± 0.3% for the sandy loam soil. Refer to Appendix A for full results of moisture content.

After the adsorption test, the amount of bromacil remaining in the aqueous solution varied among the soil types (Figure 1). When compared to the bromacil control (241 µg/L), less than half of the bromacil remained in aqueous solution for all soils. The amount of tebuthiuron remaining in aqueous solution differed more widely between the different soils than for bromacil. Compared to the tebuthiuron control (232 µg/L), the amount remaining in solution varied from 96% for coarse soil to 42% for fine soil. Lab results for each sample can be found in Table 3.

Table 3. Bromacil and tebuthiuron concentrations for each soil and water in each repetition after OECD batch equilibrium method.

Sample	Total Organic Carbon (%)	Bromacil in Soil (µg/g)	Bromacil in Water (µg/L)	Tebuthiuron in Soil (µg/g)	Tebuthiuron in Water (µg/L)
Fine Soil R1	4.96	0.239	66.2	0.460	97.2
Fine Soil R2	4.96	0.215	64.8	0.498	97.2
Fine Soil R3	4.96	0.183	60.8	0.391	95.9
Sandy Loam R1	1.14	0.126	94.5	0.332	167
Sandy Loam R2	1.14	0.144	85.1	0.348	162
Sandy Loam R3	1.14	0.148	79.7	0.282	170

Sample	Total Organic Carbon (%)	Bromacil in Soil (µg/g)	Bromacil in Water (µg/L)	Tebuthiuron in Soil (µg/g)	Tebuthiuron in Water (µg/L)
Coarse Soil R1	0.05	0.040	85.1	0.158	223
Coarse Soil R2	0.05	0.038	79.7	0.143	224
Coarse Soil R3	0.05	0.033	79.7	0.141	227
Control	n/a	n/a	241	n/a	232

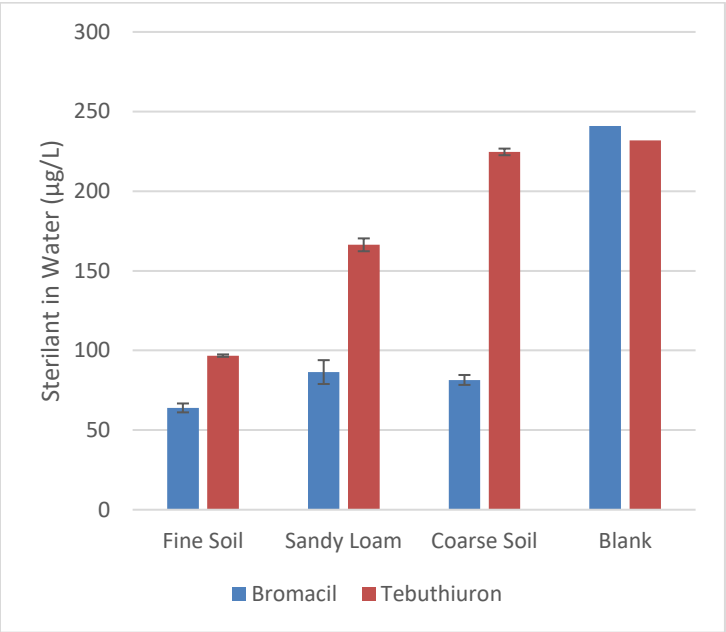

Figure 1. Bromacil and tebuthiuron remaining in aqueous solution after adsorption test. Note: Control samples represent one repetition. Soils represent means (n=3), and error bars indicate the standard deviation.

The amount of bromacil in soil varied between soil type after the adsorption test; with more bromacil in finer textured, higher TOC soil than in sandy loam and coarse soil (Figure 2). The concentration of bromacil in soil was 0.21 ± 0.03 mg/kg for fine soil, 0.14 ± 0.01 mg/kg for sandy loam, and 0.037 ± 0.004 mg/kg for coarse soil. Tebuthiuron seemed to adsorb more strongly on soil than bromacil; concentrations in soil were higher than bromacil for all soil types. Like bromacil, tebuthiuron concentrations were higher in fine textured, higher TOC soil than sandy loam or coarse soil. The concentration of tebuthiuron in soil was 0.45 ± 0.5 mg/kg for fine soil, 0.32 ± 0.03 mg/kg for sandy loam, and 0.15 ± 0.01 mg/kg for coarse soil.

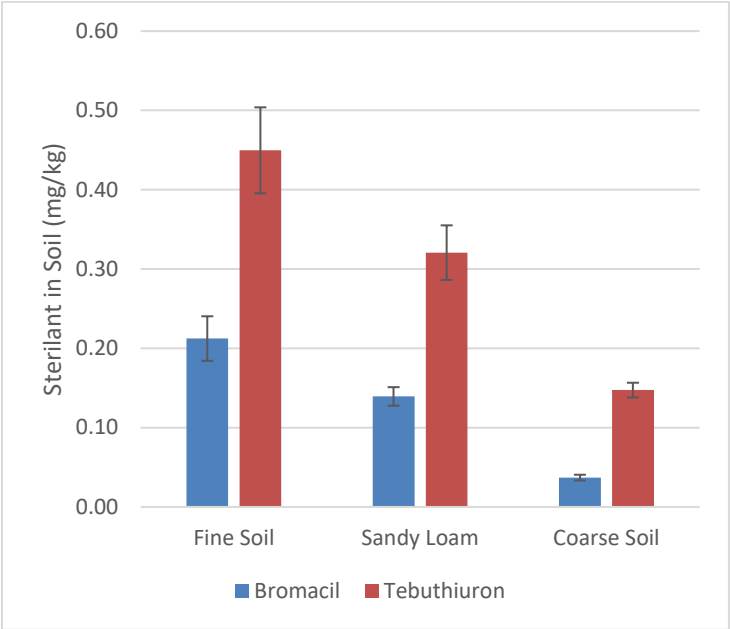

Figure 2. Final bromacil and tebuthiuron concentrations retained on the soil after adsorption test. Note: Bars represent means (n=3), and error bars indicate standard deviation.

4.2.2 Adsorption Coefficients

Distribution coefficients were calculated using the results from the adsorption test and the values followed the same trend; the amount of sterilant adsorbed varied depending on soil textured and/or TOC and there was more tebuthiuron in soil than bromacil in soil (Figure 3). Calculated distribution coefficients for each soil, sterilant, and repetition can be found in Table 4.

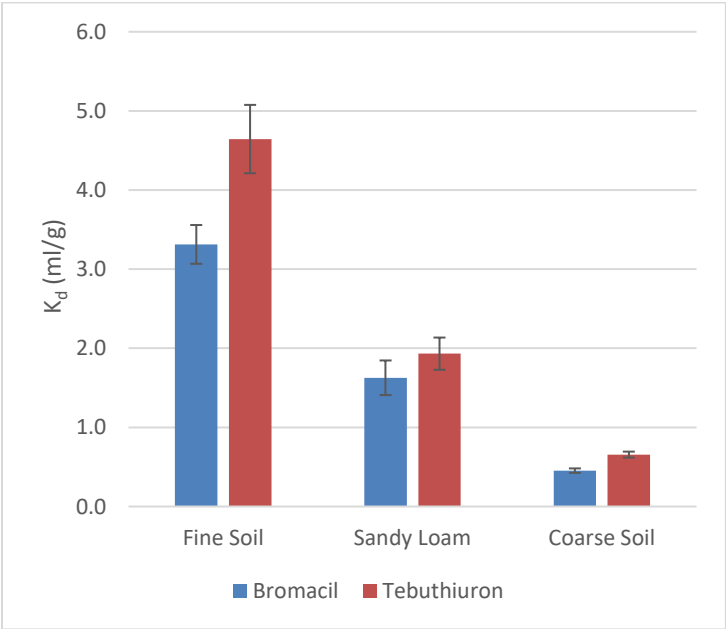

Figure 3. The average distribution coefficient, K_d, for fine soil, sandy loam, and coarse soil and bromacil and tebuthiuron.
Note: Bars represent means (n=3) and error bars indicate standard deviation.

The organic carbon normalized adsorption coefficient (K_{oc}) was greatly affected by TOC, particularly evident in coarse soil (Figure 4). Calculated K_{oc} for each soil, sterilant, and repetition can be found in Table 4.

Table 4. The distribution coefficients, K_d, and organic carbon normalized adsorption coefficients, K_{oc}, of bromacil and tebuthiuron for each repetition of the tested soils.

Sample	Bromacil K_d (mL/g)	Bromacil K_{oc} (mL/g)	Tebuthiuron K_d (mL/g)	Tebuthiuron K_{oc} (mL/g)
Fine Soil R1	3.61	72.79	4.73	95.41
Fine Soil R2	3.32	66.89	5.12	103.30
Fine Soil R3	3.01	60.68	4.08	82.20
Sandy Loam R1	1.33	116.96	1.99	174.39
Sandy Loam R2	1.69	148.43	2.15	188.43
Sandy Loam R3	1.86	162.89	1.66	145.51
Coarse Soil R1	0.47	940.07	0.71	1,417.04
Coarse Soil R2	0.48	953.58	0.64	1,276.79
Coarse Soil R3	0.41	828.11	0.62	1,242.29

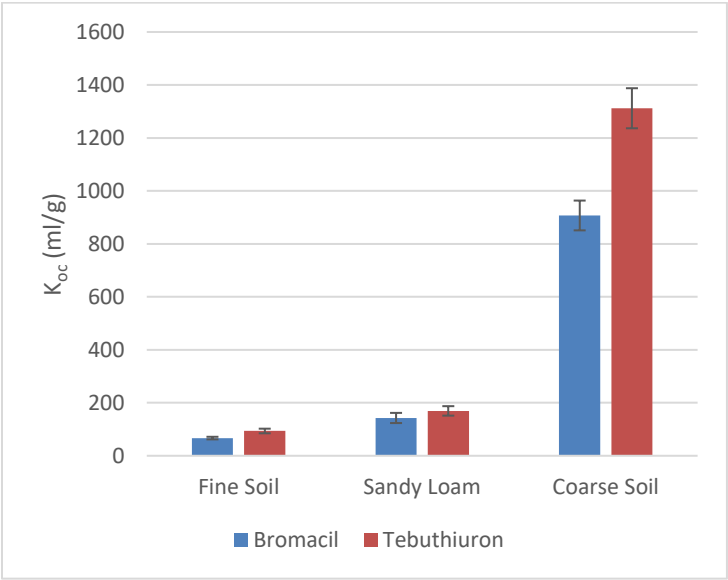

Figure 4. Organic carbon normalized adsorption coefficient, K_{oc}, for fine soil, sandy loam, and coarse soil and bromacil and tebuthiuron.
Note: Bars represent means (n=3), and error bars indicate standard deviation.

5.0 CONCLUSIONS AND RECOMMENDATIONS

The adsorption characteristics for bromacil and tebuthiuron were tested on three different soils using a modified OECD batch equilibrium method with the goal of establishing accurate distribution coefficients (K_d) and organic carbon normalized adsorption coefficients (K_{oc}). The soils used had TOC of 4.96%, 1.14%, and 0.05% and textures of Silt Loam, Sandy Loam, and Sand respectively. Tebuthiuron showed

higher concentrations in soil than bromacil after the adsorption test. With both sterilants, the amount of sterilant in soil was higher with higher TOC and finer soil texture. K_d values were consistent with sterilant concentrations in the soil; finer textured and higher TOC soils had higher K_d than coarse textured and low TOC soils. On average, K_d values were 3.31 mL/g for fine soil, 1.63 mL/g for sandy loam, and 0.45 mL/g for coarse soil. The K_{oc} values were 66.8 mL/g for fine soil, 142.8 mL/g for sandy loam, and 907.3 mL/g for coarse soil.

The method used is intended to test the effect of TOC on the adsorption rate of the bromacil and tebuthiuron. Interactions with other chemical parameters are poorly understood for bromacil and tebuthiuron. While the different soils used had different amounts of TOC, there were other differences between the soil types that can influence adsorption. Variation in soil texture, pH, and CEC, among other chemical parameters, in the soils used may affect the adsorption characteristics of these sterilants. Further work isolating the different chemical parameters and reducing confounding factors, outside the scope of this project, may be required to understand these interactions. The results produced by this project satisfy the purposes of informing model input parameters for projects conducted by Millennium EMS Solutions Ltd. and no further work is required.

6.0 ACKNOWLEDGEMENTS

This project was completed through a collaborative effort of Millennium EMS Solutions and InnoTech Alberta researchers and technicians. The authors would like to thank everyone who helped with soil and solutions preparations, laboratory operations, and data analysis, including, but not limited to Eric Ruan and Brittany Orfino. Furthermore, the authors would like to thank the Soil Sterilants Program Committee for funding this research.

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8.0 APPENDIX A: Soil Characteristics

Table A1. Baseline soil characterization for soils used in the adsorption experiment.

Parameter	Units	Fine Soil	Sandy Loam	Coarse Soil
Texture		Silt Loam	Sandy Loam	Sand
	% Sand	29	77	90
	% Silt	54	13	5
	% Clay	17	10	5
Organic Matter	%	9.92	2.28	0.1
Total Organic Carbon	%	4.96	1.14	0.05
pH		5.2	7.1	6.5
EC	dS/m	1.98	2.66	0.06
SAR		0.3	0.4	0.2
% Saturation	%	71	49	49
Calcium	mg/kg	174	211	2.7
Magnesium	mg/kg	63.8	42	0.9
Sodium	mg/kg	17	19	<1
Potassium	mg/kg	28	13	1
Chloride	mg/kg	16	32	2
Sulfate (SO4)	mg/kg	116	214	<3.0
Sulfate-S	mg/kg	38.8	71.5	<1.0
TGR (Theoretical Gypsum Requirement)	T/ac	<0.1	<0.1	<0.1
Boron	mg/L	0.57	<0.5	<0.05
Antimony	mg/kg	0.3	0.2	<0.2
Arsenic	mg/kg	7.3	3.2	0.9
Barium	mg/kg	191	60	21
Beryllium	mg/kg	0.5	0.2	<0.1
Cadmium	mg/kg	0.43	0.1	0.02
Chromium	mg/kg	14.2	5.5	2.3
Cobalt	mg/kg	8.7	3.1	1
Copper	mg/kg	16.9	5.5	1.1
Lead	mg/kg	10	4.4	1.2
Mercury	mg/kg	<0.05	<0.05	<0.05
Molybdenum	mg/kg	<1.0	<1.0	<1.0
Nickel	mg/kg	18.1	8.2	2.1
Selenium	mg/kg	0.7	<0.3	<0.3
Silver	mg/kg	<0.10	<0.10	<0.10
Thallium	mg/kg	0.15	0.06	<0.05
Tin	mg/kg	<1.0	<1.0	<1.0
Uranium	mg/kg	1	0.8	<0.5
Vanadium	mg/kg	25.3	9.7	3.8
Zinc	mg/kg	86	26	6
Chromium (VI)	mg/kg	<0.05	<0.05	<0.05

Table A2. Soil moisture content for the soils used in the adsorption experiment.

Sample	Moisture Content (%)	Average Moisture (%)	Standard Deviation (%)
Coarse Soil R1	0.23	0.19	0.03
Coarse Soil R2	0.18		
Coarse Soil R3	0.18		
Fine Soil R1	4.42	4.31	0.10
Fine Soil R2	4.23		
Fine Soil R3	4.27		
Sandy Loam R1	6.26	6.59	0.31
Sandy Loam R2	6.62		
Sandy Loam R3	6.88		
Note. Moisture content was determined by ASTM D2216, *Standard Test Methods for Laboratory Determination of Water* (*Moisture*) *Content of Soil and Rock by Mass*.			

9.0 APPENDIX B: Confirmations Of Analysis

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APPENDIX A6: NATIVE SPECIES TOXICITY EVALUATION

This project produced two reports.

Appendix A6-1. Sterilant Toxicity to Native Plants

Thacker, S., 2021. Toxicity of Bromacil and Tebuthiuron to Alberta Native Species. Report SSP-9 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 54 pp.

Toxicity of Bromacil and Tebuthiuron to Alberta Native Plant Species

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CITATION

This report may be cited as:

Thacker, S., 2021. Toxicity of Bromacil and Tebuthiuron to Alberta Native Plant Species. Report SSP-9A prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 49 pp.

EXECUTIVE SUMMARY

Soil sterilants were commonly used from the 1960s to late 1990s to control weeds on rangelands, pipeline right of ways, oil and gas wells, railways, sawmills, pulp mills, and other industrial sites across Alberta. Sterilants are typically non-selective, residual, and persistent; they control all plants they contact and because they persist in soil, vegetation growth on sterilant-impacted sites is often inhibited. Sterilants also tend to be highly mobile, which can result in off-site contamination (via leaching, surface runoff, and wind). Two of the most used soil sterilants in Alberta are bromacil and tebuthiuron.

Cost-effective strategies for managing sterilant-impacted sites are needed, but knowledge gaps exist regarding effective management practices for such sites. There is a need to better understand the sensitivity of Alberta native plant species to soil sterilants. Ecological direct contact guidelines for soil sterilants in the current Alberta Tier 1 Soil and Groundwater Remediation Guidelines have largely been developed using agronomic species. Agronomic species may differ in their sensitivity to soil sterilants compared to native species. An opportunity exists to develop data for remedial endpoints in natural areas of the province where native species would be the primary receptors in surface soil. The goal of this project was to evaluate the toxicity of two common soil sterilants, bromacil and tebuthiuron, to typical Alberta native plant species. Information from this project is intended to be used for the development of revised direct soil eco-contact guidelines for non-agricultural areas of the province.

Definitive toxicity tests were conducted using a modified Environment Canada test method at InnoTech Alberta's greenhouse facility in Vegreville. Prior to definitive testing, a range-finding test was conducted to refine the optimal target concentration for definitive testing. Toxicity tests were conducted with various native grass species (*Agropyron dasystachyum, Bouteloua gracilis, Festuca hallii, Koeleria macrantha, Nassella viridula, Pascopyrum smithii*) exposed to either bromacil or tebuthiuron in soil. Most of the seed used in the study was sourced locally, with the exception of *B. gracilis* and *K. macrantha*. The toxicity tests ran for six weeks. At the end of the test, data for biological endpoints were collected, including emergence, root and shoot length, and root and shoot biomass.

Results from the toxicity tests were used to generate regression models and inhibition concentration (IC_p) values for each endpoint from each species/sterilant test. The IC_p values indicated that while the data tended to be variable within a species and endpoint, species-specific effects were observed. For example, *B. gracilis* was more tolerant to the sterilants than other species. Generally, the species tested tended to be more sensitive to bromacil than tebuthiuron. There was not a clear difference in toxicity between root and shoots parameters. The IC_p values for *B. gracilis* in the current study were compared to values obtained from previous work by Stantec Consulting Ltd. Differences in toxicity were observed; these differences might be due to the growth period, type of sterilant products used, and/or soil properties.

Millennium EMS Solutions Ltd. (MEMS) was retained to develop species sensitivity distributions using IC_ps and to propose revised soil quality guidelines. Potential revised guidelines were generated based on native plants data from the current study, plant data (including agronomic species) from historical studies, and invertebrate data from historical studies. The revised guidelines were more stringent than the current Alberta Tier 1 Guidelines for ecological direct contact surface soil quality guidelines for fine-grained soil, and were a function of new data indicating that the native species tested in the current study appeared more sensitive to bromacil and tebuthiuron than species that have been historically studied. Overall, outcomes from this project constitute a valuable resource for decision makers regarding the management of sterilant-impacted sites in Alberta.

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1 INTRODUCTION

1.1 Project Background

Soil sterilants were commonly used from the 1960s to late 1990s to control weeds on rangelands, pipeline right of ways, oil and gas wells, railways, saw mills, pulp mills, and other industrial sites across Alberta (Bessie et al., 2012; Drozdowski et al., 2018). Sterilants are typically residual and non-selective, meaning they control all plant material they contact regardless of species or growth form (i.e., grass versus broadleaf). Sterilants present in the environment are of concern because these compounds are typically highly mobile, which can result in off-site contamination (via leaching, surface runoff, and wind), and persist in soil, meaning vegetation establishment on these sites is often inhibited. Cotton and Sharma (1993) estimated that there could be as many as 61,750 oil and gas sites in Alberta with residual soil sterilants; two of the most used soil sterilants in Alberta are bromacil and tebuthiuron, both of which are considered mobile and persistent in soil (Drozdowski et al., 2018; Rakewich and Bakker, 2011).

1.2 Scope and Rationale for Research

There is a need for cost-effective strategies to manage such sites and achieve regulatory site closure; however, knowledge gaps exist regarding effective management practices for sites impacted by residual soil sterilants. For example, in the current Alberta Tier 1 Soil and Groundwater Remediation Guidelines (Tier 1 Guidelines; AEP, 2019), ecological direct contact guidelines for soil sterilants have largely been developed using agronomic species, which may be more sensitive to soil sterilants than locally-adapted native species. If this is true, there is an opportunity to develop data for site specific remedial endpoints for natural areas of the province where native species would be the primary receptors, assuming all other exposure pathways are eliminated. To achieve this, there is first a need to understand the toxicity of common soil sterilants to relevant Alberta native species.

1.3 Research Objectives

The goal of this project is to evaluate the toxicity of two common soil sterilants, bromacil and tebuthiuron, to Alberta native plant species. Information from this project is intended to be used to develop recommendations for direct soil eco-contact guidelines for non-agricultural areas of the province. This project relates to the overarching goal of the Sterilants Program as it works to inform proven, cost-effective practices for managing sites in Alberta impacted by soil sterilants. The outcome of this project, and contribution to the Sterilants Program, is pertinent information regarding the toxicity of common soil sterilants to Alberta native species, and recommendations for guidelines and best management practices regarding sterilant concentrations in soil and their impacts on the growth of native vegetation.

The project was completed in two phases: (1) range-finding testing and (2) definitive toxicity testing. These phases of the project, and relevant results and outcomes, are described here.

2 RANGE FINDING TEST

2.1 Introduction

Range-finding tests were conducted to determine which concentrations of bromacil and tebuthiuron would be appropriate for definitive tests with the different selected species. Data from the range-finding

tests were used only to inform definitive testing, and the data from these tests are not presented in detail in this report. Data used to inform decision making are shown in Subsection 2.3.

2.2 Experimental Design

The experimental design for the range-finding test is detailed in Table 1. Environment Canada's (2007) recommendations for range-finding tests were followed, except for the test length. Because we expected toxicity to increase with time, and we intended to run the definitive tests for six weeks as opposed to three (Environment Canada, 2007), we chose to run the range-finding test for six weeks.

Table 1. Experimental design for the range-finding test with bromacil and tebuthiuron.

Treatments/Parameters	**Number**	**Description**	
Test Soil	1	Solonetzic Brown Chernozem (loam)	
Soil Sterilants	2	Bromacil Tebuthiuron	
Soil Sterilant Concentrations (mg/kg)	8	Negative control (unamended Brown Chernozem) 7 concentrations for each sterilant (see Table 3)	
Plant Species	5 for bromacil; 4 for tebuthiuron	**Bromacil** *Bouteloua gracilis* *Pascopyrum smithii* *Nassella viridula* *Festuca hallii* *Koeleria macrantha*	**Tebuthiuron** *Bouteloua gracilis* *Nassella viridula* *Agropyron dasystachyum* *Festuca hallii*
Replicates	2	Duplicates recommended for range finding test (Environment Canada, 2007)	
Total # Pots = 138			

Locally adapted seed was used when possible. A list of species Latin and common names is provided in Appendix A. All species were wild collected within Alberta, except for *B. gracilis* and *K. macrantha* for which commercially available seed was used (sourced from Hannas Seeds in Lacombe). Species selection was based on those species commonly used in reclamation seed mixes (Powter et al., 2017) and through conversations with advisors who were familiar with sterilant-impacted sites.

The soil used in this experiment was a loam sourced from Brooks Asphalt and Aggregates (Brooks, AB). We chose to source soil from the Brown Soil Zone of Alberta, as this is more representative of the types of sites typically impacted by soil sterilants in the province. While the exact soil classification could not be determined, as the site had been stripped of topsoil, two soil pits were dug just off site. Based on soil maps (Government of Alberta, 2020), data from the soil pits, and soil analysis (Table 2), the soil was likely an Orthic or Solonetzic Brown Chernozem (Appendix B).

Table 2. Properties of the soil collected near Brooks, Alberta.
The average and standard deviation are based on n=3.

Parameter	Units	Average	Standard Deviation
Texture		Loam	-
	% Sand	46	2.31
	% Silt	35	2.52
	% Clay	18	1.53
75 µm sieve		Fine-Grained	-
	% Retained	42	0.31
Organic Matter	%	3.44	0.55
Organic Carbon	%	1.73	0.28
pH		7.60	0.10
EC	dS/m	1.40	0.04
SAR		4.00	0.10
% Saturation		48	1.73
Calcium	mg/kg	49.0	0.18
Magnesium	mg/kg	13.0	1.56
Sodium	mg/kg	85.0	0.06
Potassium	mg/kg	13.7	0.40
Chloride	mg/kg	18.3	0.21
Sulfate (SO_4)	mg/kg	130	1.00
Sulfate-S	mg/kg	43.3	0.03
TGR (Theoretical Gypsum Requirement)	T/ac	<0.1	-

2.2.1 Spiking Soil with Bromacil and Tebuthiuron

The soil was brought to InnoTech Alberta's research facility in Vegreville. The soil (approximately 1 yd^3, or 0.75 m^3) was homogenized using a large soil mixer (Bouldin & Lawson LLC, Tennessee, USA). The soil was first spiked for the range finding test with bromacil (Hyvar® X-L, liquid, 21.9% lithium salt of bromacil) and tebuthiuron (Spike® 80DF, granule, 80% tebuthiuron). Based on previous findings (Stantec Consulting Ltd., 2008, 2012) and personal communication (Stephenson, 2019), the target sterilant concentrations were derived (Table 3).

Table 3. Sterilant concentrations in soil for acute testing.
Values in parentheses represent the standard deviation (n = 2).

Sterilant	Target Concentration (mg/kg)	Actual Concentration (mg/kg)*
Control (no sterilants)	0	0 (0)
Bromacil	0.01	<0.008 (0)**
	0.1	0.064 (0.004)
	0.5	0.43 (0.02)
	1	0.93 (0.20)
	5	6.52 (0.73)
	10	10.7 (2.45)
	100	101 (20)

Sterilant	Target Concentration (mg/kg)	Actual Concentration (mg/kg)*
Tebuthiuron	0.05	0.069
	0.1	0.164
	0.5	0.697
	1	1.3
	5	5.22
	30	21.3
	300	439

* Bromacil actual concentrations represent the mean value of two replicates. Tebuthiuron actual concentrations represent a single replicate.
** While soil was spiked with bromacil, resulting concentrations were below detection limits.

To spike soil with bromacil, dilutions of liquid Hyvar® X-L were made (Figure 1); this was the most accurate way to spike soils with bromacil. Five solutions ranging from 100 g/L bromacil to 0.01 g/L bromacil were made. Given the mass of soil, we calculated the required volume of dilution to achieve the target concentration in soil. Water was mixed with the solution which was spread onto the soil. To spike soil with tebuthiuron, the required amount of Spike® 80DF for each concentration was weighed on a microbalance; because the product was granular and could be weighed accurately, dilutions were not required. The product was then dissolved in water, which was spread onto the soil.

To mix the sterilants into soil, a pre-weighed amount of soil was added to a mixing bin; the same process was followed for each concentration, for both bromacil and tebuthiuron. The soil was homogenized with a spatula and three trenches were made. The bromacil or tebuthiuron solution (as described in the previous paragraph) was then poured into the trenches (Figure 1). Using the spatula, soil was gently mixed. Then, soil was mixed with an electric hand mixer until uniform in colour. The soil was mixed by hand with the spatula once more to distribute throughout the mixing bin, and then another pass was made with the hand mixer. Once homogenized, samples were taken to confirm the sterilant concentration. Samples were sent to Element Materials Technology (Edmonton, AB). High-performance liquid chromatography/mass spectrometry (HPLC/MS) was used to analyze sterilant concentrations in soil (bromacil minimum detection limit (MDL) = 0.0015 reporting at 0.008 mg/kg; tebuthiuron MDL = 0.0012 reporting at 0.005 mg/kg). Spiked soils were then transferred to designated buckets and stored at 4°C until the start of definitive toxicity tests.

Actual concentrations varied somewhat from the target concentrations (Table 3); Appendix E provides the raw values for each replicate as reported by the analytical laboratory. Soils were re-spiked as needed to get as close as possible to the target. Lessons learned from the range finding test were applied when spiking soils for the definitive tests (section 3.0). An important learning was that generally, variability was low within a target concentration. For this reason, when spiking for definitive tests, we initially sent a subset of samples for analysis. Based on the results of the initial subset, we either submitted the third sample or re-spiked if required. This method helped keep the laboratory analysis portion of the project on budget.

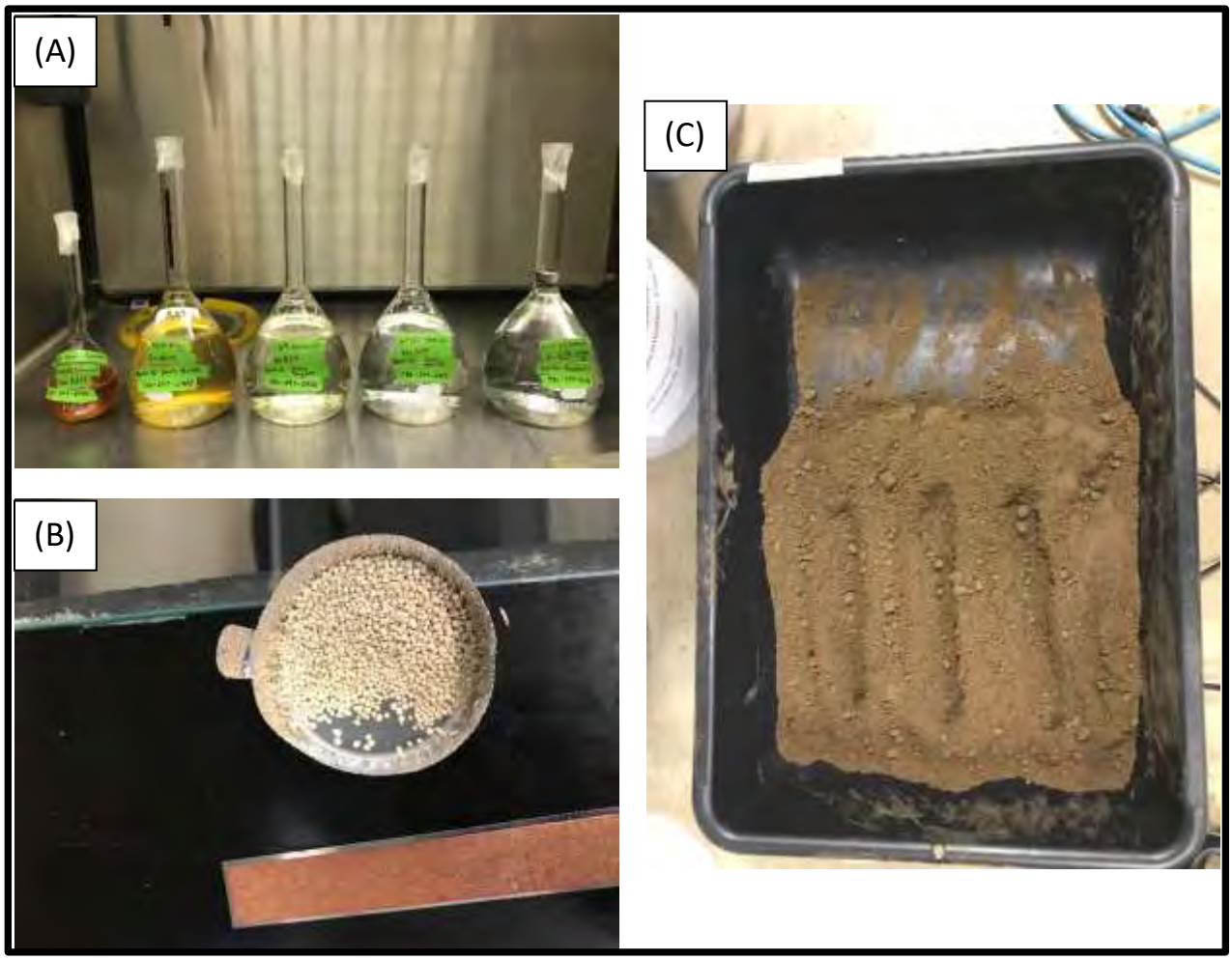

Figure 1. Soil spiking with sterilants.
(A) bromacil dilutions, (B) tebuthiuron to be weighed on microbalance, and (C) soil mixing set-up.

2.2.2 Experiment Set-Up

Germination was assessed before the start of the range-finding test by planting the seeds in small pots filled with test soil moistened to approximately 30% of the soil's water holding capacity (Environment Canada, 2007). Pots were kept covered to maintain soil moisture. The number of germinated plants was assessed after 14 days. Germination tests revealed that for many of the species (*A. dasystachyum, P. smithii, N. viridula*), seeds required cold stratification. Seeds were cold stratified for one month in uncontaminated soil. However, even with cold stratification, germination of *B. gracilis* and *K. macrantha* was low (<40%); for these two species, broadcast seeding was utilized. While broadcast seeding results in a lack of emergence data, emergence was not expected to be greatly impacted by sterilants (Stantec Consulting Ltd., 2008, 2012). For species that were broadcast seeded, plants were culled to 12 per pot after two weeks of growth.

One day prior to seeding, 1 L polypropylene pots were filled with approximately 0.5 L of soil. Based on the current moisture content for each sterilant concentration, water was added to each pot to achieve a moisture content approximately 16% gravimetric moisture, which is approximately 30% of the soil's water

holding capacity (Environment Canada, 2007). For each species and sterilant concentration, there were two replicate pots (n=2), which were placed randomly in the greenhouse to minimize localized effects.

Plants were grown in a greenhouse at InnoTech Alberta's facility in Vegreville. The greenhouse had a 16-h photoperiod with day/night temperatures of 24/15°C, respectively. Lids were kept on the pots for seven days to keep the soil moist and facilitate germination. After one week, lids were removed. Plants were watered at the surface as needed with reverse osmosis water, generally once a day once lids were removed. After six weeks of growth, shoot height was measured on each surviving plant per pot.

2.2.3 Data Analysis

Statistical analysis was not conducted, given that each treatment had only two replicates. Rather, we averaged the two replicates for each species/treatment combination and compared the results among treatments for both emergence and shoot length. To assist in determining which concentrations to target for definitive tests, we compared shoot length within sterilant-impacted soils to the control. Using this method, we identified the concentrations that resulted in an approximately 25% or 50% reduction in shoot length. In this report, all concentrations for sterilants in soil are provided on a dry weight basis.

2.3 Results and Discussion

There was no consistent trend in emergence with increasing sterilant concentration, for any species or either sterilant. Instead, emergence appeared relatively unaffected by sterilant concentration, and plants emerged even at the highest concentrations of bromacil and tebuthiuron. In fact, 80% to 90% emergence was observed for all species at the highest concentration for each sterilant (values based on individual pot data, not averages). Interestingly, toxicity appeared to increase over time. For example, concentrations which were not lethal after three weeks became lethal after six weeks. Tables 4 and 5 indicate the approximate concentrations at which a 25% or 50% reduction in shoot length occurred; these data were used to inform the target concentrations for definitive testing. Appendix C provides photos of plants from the range finding test.

Table 4. Bromacil concentrations (mg/kg) in soil at which approximately a 25% or 50% reduction in shoot length occurred after six weeks of growth.

Species	**25% reduction***	**50% reduction***
Koeleria macrantha	Plants dead higher than 0.1 mg/kg; IC25 and 50 not reached	-
Bouteloua gracilis	Between 0.1 and 0.5, closer to 0.1 mg/kg	Between 0.1 and 0.5, closer to 0.5 mg/kg
Pascopyrum smithii	Between 0.01 and 0.1 mg/kg	Between 0.1 and 0.5 mg/kg
Nassella viridula	0.1 mg/kg	All plants dead above 0.1 mg/kg
Festuca hallii	IC25 and IC50 above 0.1 mg/kg, but all plants dead above 0.1 mg/kg	-

*Sterilant concentrations given in this table are based on the target concentrations; note that there are some differences between target and actual concentrations (Table 3), which were accounted for when determining concentrations for definitive testing.

Table 5. Tebuthiuron concentrations (mg/kg) in soil at which approximately a 25% or 50% reduction in shoot length occurred after six weeks of growth.

Species	25% reduction	50% reduction
Festuca hallii	0.1 mg/kg	All plants dead at 0.5 mg/kg or higher
Bouteloua gracilis	0.5 mg/kg	Between 1 and 5 mg/kg
Agropyron dasystachyum	0.1 mg/kg	All plants dead at 0.5 mg/kg or higher
Nassella viridula	0.05 mg/kg	Between 0.1 to 0.5 mg/kg

*Sterilant concentrations given in this table are based on the target concentrations; note that there are some differences between target and actual concentrations (Table 3), which were accounted for when determining concentrations for definitive testing.

2.4 Implications for Definitive Toxicity Testing

The range-finding test results indicated that lower concentrations of both sterilants were required to obtain an appropriate range of effects for definitive testing. The species differed in their sensitivity, with *K. macrantha* and *F. hallii* tending to be most sensitive, and *B. gracilis* tending to be most resistant to the impacts of sterilants on growth, at least in terms of shoot length.

3 DEFINITIVE TOXICITY TESTING

3.1 Introduction

Results from the range finding test were used to inform target concentrations for definitive testing. The goal of definitive toxicity testing was to evaluate the toxicity of bromacil and tebuthiuron in soil for various native grass species. Further understanding of the effects of soil sterilants on native species can inform and improve reclamation practices on sterilant-impacted sites and inform remediation guidelines.

3.2 Experimental Design

The experimental design for definitive toxicity testing followed Environment Canada's (2007) protocol for terrestrial plants exposed to contaminants in soil, with some modifications. Modifications were made because the protocol was designed mainly for agronomic species, but there are special considerations to consider with native species. Modifications included test duration (plants were grown for six weeks to account for slow growth of native species) and no reference toxicity tests were conducted (determined not to be a critical component of the test, given the allocated budget and project goals). An overview of the experimental design is provided in Table 6.

Table 6. Overview of the experimental design for definitive toxicity testing.

Treatments/Parameters	Number	Description
Test Soil	1	Solonetzic Brown Chernozem (loam)
Artificial Soil	1	Prepared as described by Environment Canada (2007); included for QA/QC, not as experimental control

Treatments/Parameters	Number	Description	
Soil Sterilants	2	Bromacil Tebuthiuron	
Soil Sterilants Concentrations (mg/kg)	12	Negative control (unamended Brown Chernozem) 11 concentrations for each sterilant spiked into Brown Chernozem(see Table 7)	
Plant Species	5 for bromacil; 4 for tebuthiuron	**Bromacil** *Bouteloua gracilis* *Pascopyrum smithii* *Nassella viridula* *Festuca hallii* *Koeleria macrantha*	**Tebuthiuron** *Bouteloua gracilis* *Nassella viridula* *Agropyron dasystachyum* *Festuca hallii*
Replicates	Unbalanced	6 for negative control and artificial soil 4 for the lowest six test concentrations 3 for the highest five test concentrations	
Total # Pots = 423			

The experiment was conducted as three staggered trials. Each trial consisted of two species. The same species used in the range finding test were used in the definitive tests. The same loam soil sourced from Brooks, AB was used for definitive testing.

3.2.1 Spiking Soil with Bromacil and Tebuthiuron

The same spiking method described in section 2.2.1 was utilized for the definitive tests. However, different concentrations were targeted. Table 7 provides an overview of the target and actual concentrations of bromacil and tebuthiuron used for definitive testing; Appendix F provides the raw values for each replicate as reported by the analytical laboratory. The experimental control was the unamended Brown Chernozem which was virtually free of residues of bromacil and tebuthiuron. The artificial soil was included in the experimental design for QA purposes.

Table 7. Sterilant concentrations in soil for definitive testing.
Standard deviation based on n = 3.

Sterilant	Target Concentration (mg/kg)	Actual Concentration (mg/kg)	Standard Deviation (mg/kg)
Control (no sterilants)	0	0	-*
Bromacil	0.01	0.012	0.001
	0.05	0.021	0.002
	0.07	0.032	0.003
	0.1	0.068	0.015
	0.2	0.15	0.01
	0.3	0.24	0.00
	0.5	0.44	0.04
	0.75	0.62**	0.07
	1	0.93**	0.21
	3	1.80	0.45
	5	8.02**	0.30

Sterilant	Target Concentration (mg/kg)	Actual Concentration (mg/kg)	Standard Deviation (mg/kg)
Tebuthiuron	0.01	0.012	0.004
	0.05	0.040	0.004
	0.1	0.066	0.014
	0.2	0.12	0.02
	0.3	0.21	0.01
	0.5	0.39	0.02
	0.75	0.75	0.11
	1	1.33**	0.15
	3	2.53	0.31
	5	4.31	0.25
	15	12.9	1.07

* All replicates were below the detection limits for bromacil and tebuthiuron in soil.

** Average concentration based on two replicates.

3.2.2 Experiment Set-Up

The experimental set-up described in section 2.2.2 was also used for definitive toxicity testing. In short, pots (1 L capacity) were filled with approximately 0.5 L of soil one day prior to seeding. Water was added to the surface of the soil in each pot to achieve a moisture content of approximately 16% gravimetric moisture, which was approximately 30% of the soil's water holding capacity. Twelve seeds were sown per pot, except in the case of *B. gracilis* and *K. macrantha*, which were broadcast seeded. When broadcast seeding was used, plants were culled randomly to 20 per pot after seven days of growth, and 12 per pot after 14 days. Lids were kept on the pots for the first seven days to facilitate germination, after which the lids were removed.

Plants were grown in a greenhouse at InnoTech Alberta's facility in Vegreville. The greenhouse had a 16-hour photoperiod with day/night temperatures of 24/15°C, respectively. Plants were watered as needed with reverse osmosis water. After six weeks of growth, root washing was performed. Plant roots were separated from the soil by gently loosening the soil by hand and shaking the plants prior to washing with water. Root and shoot length were measured using a ruler within 1 mm accuracy. Root and shoot biomass were dried at 60°C for one week, then weighed on a four decimal point scale.

3.2.3 Data Analysis

3.2.3.1 Statistical analysis

Data exploration, analysis and visualization were carried out using the R language and environment for statistical computing (R Core Team, 2019) and the additional packages tidyr (Wickham and Henry, 2019), dplyr (Wickham et al., 2019), purrr (Henry and Wickham, 2019), ggplot2 (Wickham, 2016), nlme (Pinheiro, 2019), and emmeans (Lenth et al., 2019). Statistical differences between sterilant concentrations (for each sterilant) for day 21 emergence (the number of seedlings that have emerged 3 mm above the soil surface), root and shoot length, and root and shoot biomass were assessed using generalized least squares (GLS) ($\alpha = 0.05$); GLS was used due to the unbalanced study design. Data were inspected to determine if assumptions of normality and homogeneity of variance were met; in cases where assumptions were not met, transformation was used. If no plants germinated in a pot, root and shoot length and weight values

were set as NA, as suggested in Environment Canada (2005). In this report, all concentrations for sterilants in soil are provided on a dry weight basis.

To determine the effective concentration (EC_p) for emergence and inhibition concentration (IC_p) for other growth parameters, the R package drc was used (Ritz and Streibig, 2016). First, an appropriate non-linear regression function was fit to each data set. When deciding which regression model was appropriate for each data set, data were inspected visually. Visual assessment, along with the ShapiroWilk test for normality and Levene's test for homogeneity of variance, were used to assess whether assumptions were met for each regression model. In cases where assumptions of normality and equal variance were violated, a BoxCox transformation was used. There were cases where a BoxCox transformation did not improve the variance heterogeneity (i.e., where only one or two replicates existed for higher concentrations, where all replicates were equal to zero for emergence, or when model fitting would not allow for BoxCox transformation), and in these cases we proceeded with the analysis assuming the model was robust in the face of these violations, and if the regression outputs were reasonable.

Multiple regression models were tested, and the one with the lowest residual standard error was selected as the best fit. The modelFit function in drc was also used to assess fit. Each fitted regression, with data points displayed, is shown in Appendix D. After regression fitting, IC_p values were determined using the ED function in drc. Ritz et al. (2015) and Ritz and Streibig (2012) were used for troubleshooting with the drc package and integrating with ggplot2.

3.2.3.2 Uncertainty

To address potential uncertainty in the data, outliers were considered, power analyses were conducted, and the regression outputs were investigated to determine whether results were reasonable. When outliers were present, especially in the control data, regression models were fit to the data with the outlier included and with the outlier removed. Generally, the resulting IC_p values did not differ between the two models. In some cases, the model confidence bands were wide (Appendix D). Given the data variability, ANOVA-based power analyses were run to assess the statistical strength to detect a 25% reduction in each parameter. The power analyses indicated that most models had sufficient power; for those that did not, the data are still presented, and power was considered when developing the species sensitivity distribution. Additionally, as described in Subsection 3.2.3.1, regression outputs were evaluated to determine whether assumptions of normality and equal variance were met, and regression outputs were compared to the raw data to confirm that the outputs were reasonable.

3.3 Results and Discussion

3.3.1 Soil Sterilant Concentrations

The concentrations of bromacil and tebuthiuron in soil are presented in Table 7 (Subsection 3.2.2). In general, the actual concentrations of bromacil and tebuthiuron were lower than the target concentrations. Soil samples were analyzed at Element Materials Technology. High-performance liquid chromatography/mass spectrometry (HPLC/MS) was used to analyze sterilant concentrations in soil. For bromacil, the MDL was 0.0015 mg/kg, reporting at 0.008 mg/kg. For tebuthiuron, the MDL was 0.0012, reporting at 0.005 mg/kg.

3.3.2 Toxicity Testing

For each species and sterilant, the mean and standard deviation for each endpoint measured are provided in Tables 8 to 13. In general, despite targeting a more appropriate range of concentrations via the range finding test, the species tended to have low survival even at low concentrations. As a result, there were few data points for some species. *B. gracilis* tended to have the best survival and tolerance to both sterilants. Despite a longer growth period (six weeks as opposed to the standard three weeks), *F. hallii* plants were very small compared to the other species tested, which made measurement of some root parameters challenging. The species tested tended to be more sensitive to bromacil than tebuthiuron, with lower IC_p values when exposed to bromacil (Table 14). There was no clear difference in the sensitivity of root versus shoot parameters; in general, when comparing IC_p values for root versus shoot length or root versus shoot weight, there was not a large difference between these values (Table 14). Regression models could not be fit for emergence data, and emergence tended not to be significantly impacted by increasing sterilant concentrations (Tables 8 to 13). Appendix C provides select photos of plants during definitive testing.

Table 8. *Bouteloua gracilis* endpoint data for artificial soil, control soil, and soil spiked to different concentrations of bromacil and tebuthiuron.
The endpoint data (shoot/root weight and shoot/root length) are means with standard deviations in parentheses. Different lowercase letters indicate significant differences between sterilant concentrations within an endpoint, based on generalized least squares (GLS) analysis.

Soil/Sterilant	Sterilant Concentration (mg/kg)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Artificial Soil	0	19.8 (2.45)	19.0 (3.14)	124.23 (4.85)	195.79 (7.79)
Control	0	68.8 (6.05)a	29.1 (6.81)a	222.26 (31.76)a	186.75 (14.94)a
Bromacil	0.012	54.3 (10.33)ab	24.0 (1.65)a	230.73 (29.52)a	151.2 (27.01)ab
	0.021	50.6 (4.61)b	23.7 (3.32)a	223.08 (18.53)a	174.48 (28.73)a
	0.032	52.9 (4.04)b	16.1 (6.37)ab	219.21 (22.27)a	182.04 (31.83)ab
	0.068	26.8 (2.5)c	10.5 (2.82)b	195.21 (5.74)a	142.52 (13.24)b
	0.15	10.1 (0.8)d	3.02 (0.7)c	139.31 (5.3)b	106.17 (19.78)bc
	0.24	3.75 (2.93)e	0.99 (0.39)d	71.74 (22.25)c	45.92 (20.10)c
	0.44	1.48 (0.4)e	0.8 (0.28)d	49.5 (6.36)c	35.5 (33.23)abc
	0.62	-	-	-	-
	0.93	0.10 (NA)	0.35 (NA)	9.5 (NA)	18 (NA)
	1.8	-	-	-	-
	8	-	-	-	-

Soil/Sterilant	Sterilant Concentration (mg/kg)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Control	0	68.8 (6.05)a	29.1 (6.81)a	222.26 (31.76)ab	186.75 (14.94)abc
Tebuthiuron	0.012	93.2 (15.68)ab	23.8 (3.37)a	235.13 (27.85)ab	199.22 (8.39)ab
	0.04	86.63 (20.33)abc	24.75 (6.15)abcd	229.32 (20.7)ab	212.71 (10.86)a
	0.066	90.7 (27.38)abcd	30.0 (5.72)a	259.13 (40.93)a	191.8 (13.03)abc
	0.12	63.0 (15.13)abcd	25.8 (6.25)abcd	232.72 (39.41)ab	149.55 (14.35)d
	0.21	52.1 (5.12)bcd	23.2 (5.66)ab	224 (18.61)ab	163.91 (14.45)cd
	0.39	44.8 (6.75)cd	16.2 (4.71)abcd	205.43 (10.3)ab	168.71 (15.24)bcd
	0.75	11.6 (3.25)ef	3.74 (0.9)cd	191.21 (12.72)bc	150.48 (2.5)cd
	1.3	27.7 (6.21)de	11.1 (2.6)bcd	144.59 (22.86)c	111.76 (19.08)e
	2.5	4.4 (0.82)f	0.84 (0.55)d	81.46 (7.13)d	33.02 (13.92)f
	4.3	4.2 (0.57)f	0.5 (0.42)d	61.5 (14.85)d	30.5 (10.61)f
	13	-	-	-	-

Concentrations with only one replicate with surviving plants were not included in generalized least squares (GLS) analysis.
Artificial soil was not included in GLS analysis.
Emergence data were not available as *B. gracilis* was broadcast seeded and culled.
A dash indicates no data available (no living plants).

Table 9. *Koeleria macrantha* endpoint data for artificial soil, control soil, and soil spiked to varying concentrations of bromacil.
The endpoint data (shoot/root weight and shoot/root length) are means with standard deviations in parentheses. Different lowercase letters indicate significant differences between sterilant concentrations within an endpoint, based on generalized least squares (GLS) analysis.

Soil/Sterilant	Sterilant Concentration (mg/kg)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Artificial Soil	0	12.2 (0.51)	21.8 (2.79)	51.92 (2.45)	181.28 (23.79)
Control	0	26.3 (5.78)a	16.62 (3.81)a	74.83 (7.6)a	160.19 (15.06)a
Bromacil	0.012	12.4 (3.59)b	5.68 (1.32)b	53.71 (4.21)b	139.78 (34.42)ab
	0.021	12.2 (7.17)bc	7.09 (5.67)abc	52.76 (13.59)ab	166.94 (12.44)a
	0.032	2.62 (2.26)c	0.61 (0.32)c	40.69 (7.4)b	93.25 (18.03)b
	0.068	0.40 (NA)	0.10 (NA)	15 (NA)	21 (NA)
	0.15	-	-	-	-
	0.24	-	-	-	-
	0.44	0.31 (NA)	0.03 (NA)	14 (NA)	10.67 (NA)
	0.62	-	-	-	-
	0.93	-	-	-	-
	1.8	-	-	-	-
	8	-	-	-	-

Concentrations with only one replicate with surviving plants were not included in generalized least squares (GLS) analysis.
Artificial soil was not included in GLS analysis.
Emergence data were not available as *K. macrantha* was broadcast seeded and culled.
A dash indicates no data available (no living plants).

Table 10. *Nassella viridula* endpoint data for artificial soil, control soil, and soil spiked to varying concentrations of bromacil and tebuthiuron.
The endpoint data (shoot/root weight and shoot/root length) are means with standard deviations in parentheses. Different lowercase letters indicate significant differences between sterilant concentrations within an endpoint, based on generalized least squares (GLS) analysis.

Soil/Sterilant	Sterilant Concentration (mg/kg)	Emergence (%)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Artificial Soil	0	50 (12)	40.91 (5.84)	51.6 (13.33)	160.61 (10.26)	179.7 (26.93)
Control	0	49 (10)	60.9 (11.33)a	65.9 (6.68)a	178.2 (24.08)a	181.6 (19.56)a
Bromacil	0.012	33 (7)	39.23 (11.59)a	40.80 (15.67)ab	162.75 (24.81)a	179.4 (17.68)a
	0.021	40 (25)	18.88 (4.04)b	10.1 (1.82)b	142.31 (22.3)ab	204.4 (36.75)a
	0.032	35 (8)	7.24 (2.75)c	1.3 (1.54)c	93.31 (18.38)b	167.7 (5.19)a
	0.068	58 (20)	-	-	-	-
	0.15	38 (11)	-	-	-	-
	0.24	33 (12)	-	-	-	-
	0.44	44 (19)	-	-	-	-
	0.62	53 (5)	-	-	-	-
	0.93	33 (22)	-	-	-	-
	1.8	50 (8)	-	-	-	-
	8	33 (8)	-	-	-	-

Soil/Sterilant	Sterilant Concentration (mg/kg)	Emergence (%)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Control	0	49 (10)	60.9 (11.33)a	65.9 (6.68)a	178.2 (24.08)a	181.6 (19.56)b
Tebuthiuron	0.012	35 (21)	63.99 (9.22)a	85.69 (35.11)ab	173.78 (23.6)a	195.3 (33.41)abc
	0.04	27 (17)	36.7 (17.97)abc	29.1 (7.43)bc	158.8 (52.83)a	215.6 (62.88)abc
	0.066	48 (12)	27.91 (12.87)b	14.1 (5.69)c	160.21 (19.24)ab	227 (7.97)a
	0.12	27 (10)	5.69 (0.29)c	1.3 (0.16)d	99.38 (6.16)b	144.7 (8.1)c
	0.21	40 (10)	1.57 (0.49)d	0.4 (0.56)d	53.92 (12.92)b	41.3 (20.86)abc
	0.39	23 (12)	-	-	-	-
	0.75	33 (17)	-	-	-	-
	1.3	42 (8)	-	-	-	-
	2.5	39 (10)	-	-	-	-
	4.3	47 (10)	-	-	-	-
	13	50 (17)	-	-	-	-

Concentrations with only one replicate with surviving plants were not included in generalized least squares (GLS) analysis.
Artificial soil was not included in GLS analysis.
A dash indicates no data available (no living plants).

Table 11. *Agropyron dasystachyum* endpoint data for artificial soil, control soil, and soil spiked to varying concentrations of tebuthiuron.
The endpoint data (shoot/root weight and shoot/root length) are means with standard deviations in parentheses. Different lowercase letters indicate significant differences between sterilant concentrations within an endpoint, based on generalized least squares (GLS) analysis.

Soil/Sterilant	Sterilant Concentration (mg/kg)	Emergence (%)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Artificial Soil	0	81 (13)	34.85 (4.29)	48.2 (6.35)	224.24 (15.48)	180 (18.49)
Control	0	72 (10)	136.09 (41.67)a	76.9 (27.26)ab	277.14 (28.94)a	165.3 (15.06)a
Tebuthiuron	0.012	73 (4)	85.23 (10.79)a	60.9 (6.44)a	229.83 (13.12)a	144.3 (6.04)a
	0.04	71 (8)	79.45 (25.4)a	40.9 (6.18)b	247.93 (9.23)a	141.7 (12.03)a
	0.066	81 (13)	11.88 (3.5)b	6.8 (3.11)c	153.14 (9.51)b	152.6 (30.21)ab
	0.12	75 (7)	2.2 (0.24)c	0.7 (0.3)c	73.62 (20.25)c	93 (12.06)b
	0.21	92 (10)	-	-	-	-
	0.39	63 (11)	-	-	-	-

Soil/Sterilant	Sterilant Concentration (mg/kg)	Emergence (%)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
	0.75	75 (17)	-	-	-	-
	1.3	86 (5)	-	-	-	-
	2.5	61 (34)	-	-	-	-
	4.3	83 (14)	-	-	-	-
	13	81 (13)	-	-	-	-

Concentrations with only one replicate with surviving plants were not included in generalized least squares (GLS) analysis.
Artificial soil was not included in GLS analysis.
A dash indicates no data available (no living plants).

Table 12. *Festuca hallii* endpoint data for artificial soil, control soil, and soil spiked to varying concentrations of bromacil and tebuthiuron.
The endpoint data (shoot/root weight and shoot/root length) are means with standard deviations in parentheses. Different lowercase letters indicate significant differences between sterilant concentrations within an endpoint, based on generalized least squares (GLS) analysis.

Soil/Sterilant	Sterilant Concentration (mg/kg)	Emergence (%)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Artificial Soil	0	47 (18)	3.4 (0.87)	2.77 (2.31)	58.1 (9.93)	70.41 (45.42)
Control	0	57 (18)	4.5 (1.97)ab	3.78 (1.67)a	64.8 (12.87)a	105.66 (19.41)a
Bromacil	0.012	35 (8)	4.8 (1.41)a	2.64 (1.31)ab	62.9 (9.83)a	66.23 (21.98)ab
	0.021	40 (23)	2.24 (1.57)ab	1.90 (0.75)ab	48.6 (7.21)ab	37.21 (18.41)bc
	0.032	40 (13)	2.00 (0.64)b	0.43 (0.19)b	41.2 (1.6)b	22.67 (5.01)c
	0.068	38 (16)	0.5 (NA)	-*	26 (NA)	17 (NA)
	0.15	52 (22)	-	-	-	-
	0.24	46 (26)	-	-	-	-
	0.44	58 (14)	-	-	-	-
	0.62	58 (8)	-	-	-	-
	0.93	31 (21)	-	-	-	-
	1.8	47 (5)	-	-	-	-
	8	44 (24)	-	-	-	-

Soil/Sterilant	Sterilant Concentration (mg/kg)	Emergence (%)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Control	0	57 (18)	4.5 (1.97)a	3.78 (1.67)a	64.8 (12.87)a	105.66 (19.41)a
Tebuthiuron	0.012	44 (23)	3.93 (1.23)a	2.94 (1.46)ab	54.9 (13.75)a	108.41 (35.50)a
	0.04	60 (13)	4.85 (2.26)ab	1.24 (0.7)ab	65.3 (12.48)a	72.25 (12.17)a
	0.066	40 (28)	4.12 (0.96)a	2.38 (1.46)ab	61.7 (7.08)a	97.62 (28.82)a
	0.12	38 (34)	1.31 (0.72)b	0.18 (0.08)b	43.5 (13.18)a	17.38 (1.58)b
	0.21	48 (21)	0.63 (NA)	-*	25.8 (NA)	-*
	0.39	40 (18)	0.3 (NA)	-*	25 (NA)	-*
	0.75	42 (17)	-	-	-	-
	1.3	44 (10)	-	-	-	-
	2.5	33 (8)	-	-	-	-
	4.3	42 (8)	-	-	-	-
	13	28 (13)	-	-	-	-

Concentrations with only one replicate with surviving plants were not included in generalized least squares (GLS) analysis.
Artificial soil was not included in GLS analysis.
*Value missing because accurate measurement were not possible.
A dash indicates no data available (no living plants).

Table 13. *Pascopyrum smithii* endpoint data for artificial soil, control soil, and soil spiked to varying concentrations of bromacil.
The endpoint data (shoot/root weight and shoot/root length) are means with standard deviations in parentheses. Different lowercase letters indicate significant differences between sterilant concentrations within an endpoint, based on generalized least squares (GLS) analysis.

Soil/Sterilant	Sterilant Concentration (mg/kg)	Emergence (%)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
Artificial Soil	0	44 (7)	34.8 (9.71)	40.28 (13.94)	184.1 (21.73)	201.25 (49.06)
Control	0	52 (14)	55 (24.75)a	36.82 (21.33)a	209.3 (20.29)a	179.81 (34.02)a
Bromacil	0.012	27 (23)	1.9 (1.03)b	2.33 (1.11)b	106.1 (34.86)ab	159.11 (70.21)a
	0.021	42 (12)	22 (20.31)ab	18.53 (21.85)ab	167.1 (77.02)bc	198.54 (112.05)a
	0.032	35 (8)	0.3 (NA)ab	-*	30 (NA)c	8 (NA)a
	0.068	44 (18)	-	-	-	-
	0.15	40 (10)	-	-	-	-
	0.24	42 (8)	-	-	-	-
	0.44	33 (8)	-	-	-	-
	0.62	28 (10)	-	-	-	-

Soil/Sterilant	Sterilant Concentration (mg/kg)	Emergence (%)	Shoot Weight (mg)	Root Weight (mg)	Shoot Length (mm)	Root Length (mm)
	0.93	39 (5)	-	-	-	-
	1.8	39 (5)	-	-	-	-
	8	28 (17)	-	-	-	-

Concentrations with only one replicate with surviving plants were not included in generalized least squares (GLS) analysis.
Artificial soil was not included in GLS analysis.
*Value missing because accurate measurement were not possible.
A dash indicates no data available (no living plants).

Figures 2 to 4 provide a visual of differences in toxicity between bromacil and tebuthiuron, and among species.

The data tended to be variable within a species and endpoint. Variability may have been introduced through the longer growth period. For example, when plants germinated at three weeks as opposed to within the first week, they tended to be smaller. However, the longer growth period better captures the germination time of these native species and allowed for sufficient biomass production for some of the slower growing species. Another possible source of variability could be the use of wild-collected seed. Only *B. gracilis* and *K. macrantha* were sourced commercially – all other species were wild-collected locally. While seed was only selected for the experiment if it showed a healthy germplasm, commercially available seed has been selected over time for seed production and consistent growth. The wild-collected seed does not have the same degree of selection and, therefore, is likely to have more variable growth. As described in section 3.2.3, the data were run with significant outliers removed, and this did not change the IC_p values greatly compared to when all data were included.

The IC_p values for *B. gracilis* in the current study were compared to values obtained historically by Stantec Consulting Ltd. (2008, 2012). IC_p values between the two studies were comparable for tebuthiuron. However, IC_p values for bromacil in the current study tended to be an order of magnitude lower than those in Stantec Consulting Ltd. (2012). Toxicity tends to increase with time (i.e., exposure duration) (Stephenson, 2019), thus it is not surprising that IC_p values would occur at lower concentrations when the experiment was run for six weeks as opposed to three weeks. Additionally, the difference for bromacil between the two studies could be due in part to the product used to spike soil. In the current study we used Hyvar® X-L, a liquid which contains other compounds such as ethylene glycol, ethanol, and methanol which could impact soil organisms (Stantec Consulting Ltd., 2012). In Stantec Consulting Ltd. (2012) Hyvar® X was used, which is a solid that does not contain ethylene glycol, ethanol, and methanol. It is possible that a difference in toxicity was observed due to the use of different bromacil products to spike soil. Additionally, the soil used in the current study was not the same as the soils used in Stantec Consulting Ltd., 2008, 2012; different soil properties could have resulted in differing results for *B. gracilis* between studies.

Table 14. Summary of the regression analyses for each measurement endpoint, for each species and sterilant combination. Inhibition concentrations (IC_p values) and confidence intervals were obtained using the drc package in R. A dash indicates no data available.

Species	Sterilant	Parameter	Model*	Model Residual Standard Error	IC20 (mg/kg)	IC20 Standard Error	Lower Confidence Limit	Upper Confidence Limit	IC25 (mg/kg)	IC25 Standard Error	Lower Confidence Limit	Upper Confidence Limit	IC50 (mg/kg)	IC 50 Standard Error	Lower Confidence Limit	Upper Confidence Limit
Bouteloua gracilis	Bromacil	Shoot length	LL.3	20.83	0.09	0.01	0.06	0.11	0.10	0.01	0.08	0.13	0.18	0.01	0.15	0.21
		Root length	LL.3	24.54	0.08	0.02	0.04	0.12	0.09	0.02	0.05	0.13	0.17	0.02	0.13	0.21
		Shoot weight	W1.3	5.81	0.02	0.00	0.01	0.03	0.02	0.00	0.02	0.03	0.06	0.01	0.04	0.07
		Root weight	W1.3	3.98	0.01	0.00	0.01	0.02	0.02	0.00	0.01	0.03	0.05	0.01	0.03	0.06
	Tebuthiuron	Shoot length	LL.3, BoxCox transformation	0.22	0.64	0.11	0.42	0.85	0.79	0.12	0.55	1.03	1.78	0.15	1.48	2.09
		Root length	NA	-	Could not fit a model											
		Shoot weight	BC.4	14.04	0.175	0.033	0.108	0.242	0.198	0.037	0.123	0.273	0.406	0.092	0.219	0.593
		Root weight	BC.4	5.48	0.243	0.057	0.128	0.359	0.275	0.057	0.160	0.390	0.476	0.079	0.316	0.637
Koeleria macrantha	Bromacil	Shoot length	LL.3	9.04	0.010	0.004	0.001	0.018	0.013	0.004	0.003	0.022	0.038	0.008	0.020	0.055
		Root length	LL.3	22.63	0.030	0.003	0.024	0.036	0.031	0.002	0.026	0.035	0.033	0.001	0.030	0.036
		Shoot weight	W1.3	5.17	0.004	0.003	-0.002	0.011	0.006	0.003	-0.002	0.013	0.013	0.004	0.005	0.021
		Root weight	EXD.2	3.56	0.003	0.001	0.002	0.005	0.004	0.001	0.002	0.006	0.011	0.002	0.006	0.015
Nassella viridula	Bromacil	Shoot length	W1.3	22.11	0.020	0.004	0.013	0.028	0.023	0.003	0.016	0.030	0.033	0.003	0.027	0.039
		Root length	NA	-	Could not fit a model											
		Shoot weight	LL.3	8.63	0.009	0.002	0.005	0.012	0.010	0.002	0.006	0.013	0.015	0.002	0.012	0.018
		Root weight	LL.3	8.08	0.010	0.001	0.007	0.012	0.010	0.001	0.008	0.012	0.014	0.001	0.012	0.015
	Tebuthiuron	Shoot length	LL.3	24.39	0.078	0.014	0.049	0.108	0.089	0.014	0.060	0.117	0.142	0.015	0.111	0.172
		Root length	LL.3	32.28	0.113	0.011	0.091	0.135	0.120	0.011	0.098	0.142	0.151	0.015	0.120	0.180
		Shoot weight	LL.3	10.39	0.029	0.007	0.015	0.044	0.033	0.007	0.019	0.048	0.053	0.007	0.039	0.068
		Root weight	BC.4	14.47	0.029	0.006	0.015	0.042	0.030	0.006	0.017	0.043	0.039	0.006	0.026	0.051

Species	Sterilant	Parameter	Model*	Model Residual Standard Error	IC20 (mg/kg)	IC20 Standard Error	Lower Confidence Limit	Upper Confidence Limit	IC25 (mg/kg)	IC25 Standard Error	Lower Confidence Limit	Upper Confidence Limit	IC50 (mg/kg)	IC 50 Standard Error	Lower Confidence Limit	Upper Confidence Limit
Agropyron dasystachyum	Tebuthiuron	Shoot length	NA	-	Could not fit a model											
		Root length	W1.3, BoxCox transformation	1.97	0.102	0.020	0.060	0.145	0.108	0.015	0.076	0.139	0.128	0.010	0.107	0.149
		Shoot weight	EXD.2	29.17	0.010	0.002	0.005	0.014	0.012	0.003	0.007	0.018	0.030	0.006	0.017	0.043
		Root weight	W1.3	15.74	0.023	0.018	-0.014	0.060	0.026	0.017	-0.010	0.062	0.040	0.011	0.016	0.064
Festuca hallii	Bromacil	Shoot length	LL.3	9.33	0.019	0.005	0.010	0.029	0.023	0.005	0.013	0.033	0.045	0.009	0.025	0.065
		Root length	LL.3	14.34	0.008	0.002	0.004	0.013	0.010	0.002	0.005	0.014	0.017	0.002	0.013	0.022
		Shoot weight	LL.3	1.55	0.015	0.005	0.005	0.025	0.017	0.005	0.007	0.027	0.025	0.006	0.013	0.037
		Root weight	W1.3, BoxCox transformation	0.38	0.014	0.005	0.004	0.024	0.015	0.005	0.005	0.025	0.021	0.004	0.013	0.029
	Tebuthiuron	Shoot length	LL.3	12.44	0.100	0.027	0.042	0.157	0.116	0.029	0.056	0.176	0.208	0.060	0.082	0.335
		Root length	NA	-	Could not fit a model											
		Shoot weight	LL.3	1.50	0.082	0.028	0.023	0.141	0.086	0.026	0.031	0.141	0.104	0.018	0.067	0.141
		Root weight	EXD.2	1.29	0.013	0.005	0.003	0.023	0.017	0.006	0.004	0.030	0.041	0.015	0.010	0.073
Pascopyrum smithii	Bromacil	Shoot length	NA	-	Could not fit a model											
		Root length	NA	-	Could not fit a model											
		Shoot weight	NA	-	Could not fit a model											
		Root weight	NA	-	Could not fit a model											

*No models could be fit for emergence, as there was no statistical difference in 3-week germination observed for all species. Model abbreviations are:
LL = log-logistic
W1 = Weibull
EXD = exponential
BC = Brain-Cousens modified log-logistic
NA = Not applicable, could not fit a model

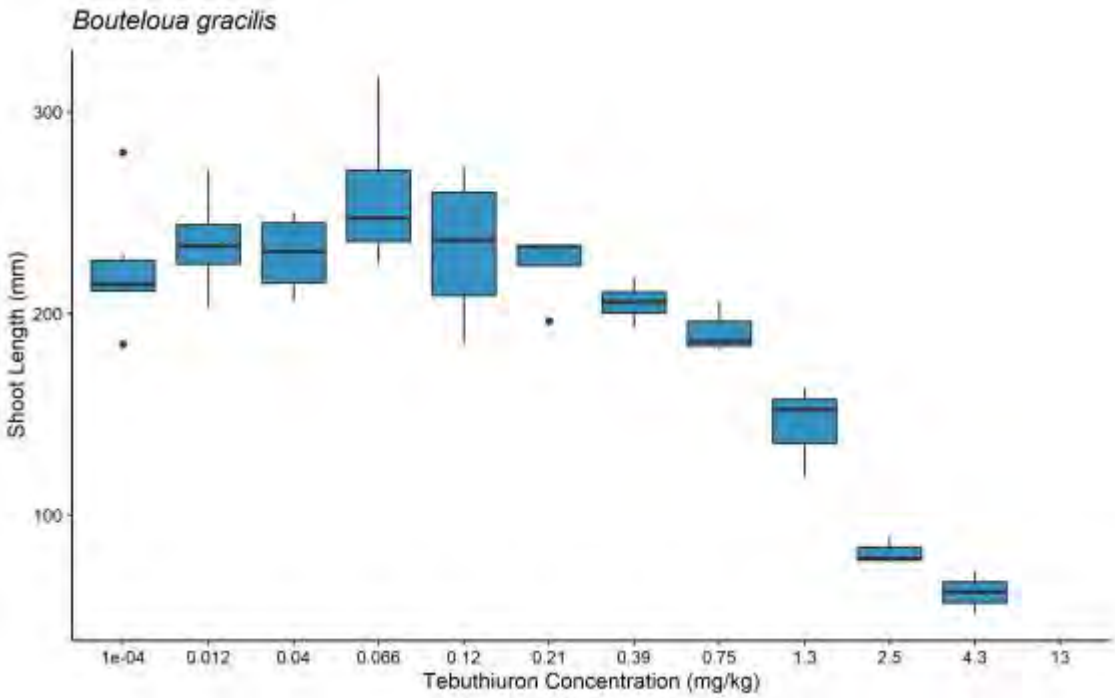

Figure 2. *Bouteloua gracilis* shoot length (mm) when exposed to varying concentrations of tebuthiuron (mg/kg).
The median value at each concentration is represented by a horizontal black line, and the box indicates the 25th and 75th percentiles. Whiskers represent the largest or smallest value, up to 1.5 times the interquartile range (IQR). Data points beyond the whiskers are outlying points.

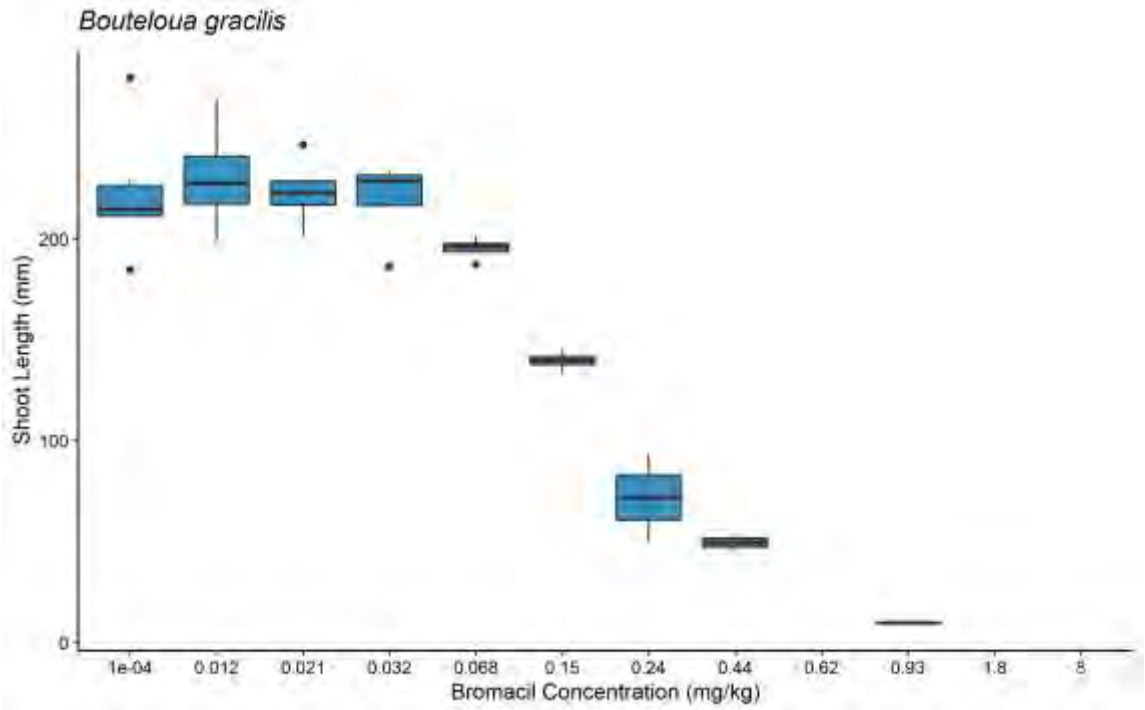

Figure 3. *Bouteloua gracilis* shoot length (mm) when exposed to varying concentrations of bromacil (mg/kg).
The median value at each concentration is represented by a horizontal black line, and the box indicates the 25th and 75th percentiles. Whiskers represent the largest or smallest value, up to 1.5 times the interquartile range (IQR). Data points beyond the whiskers are outlying points.

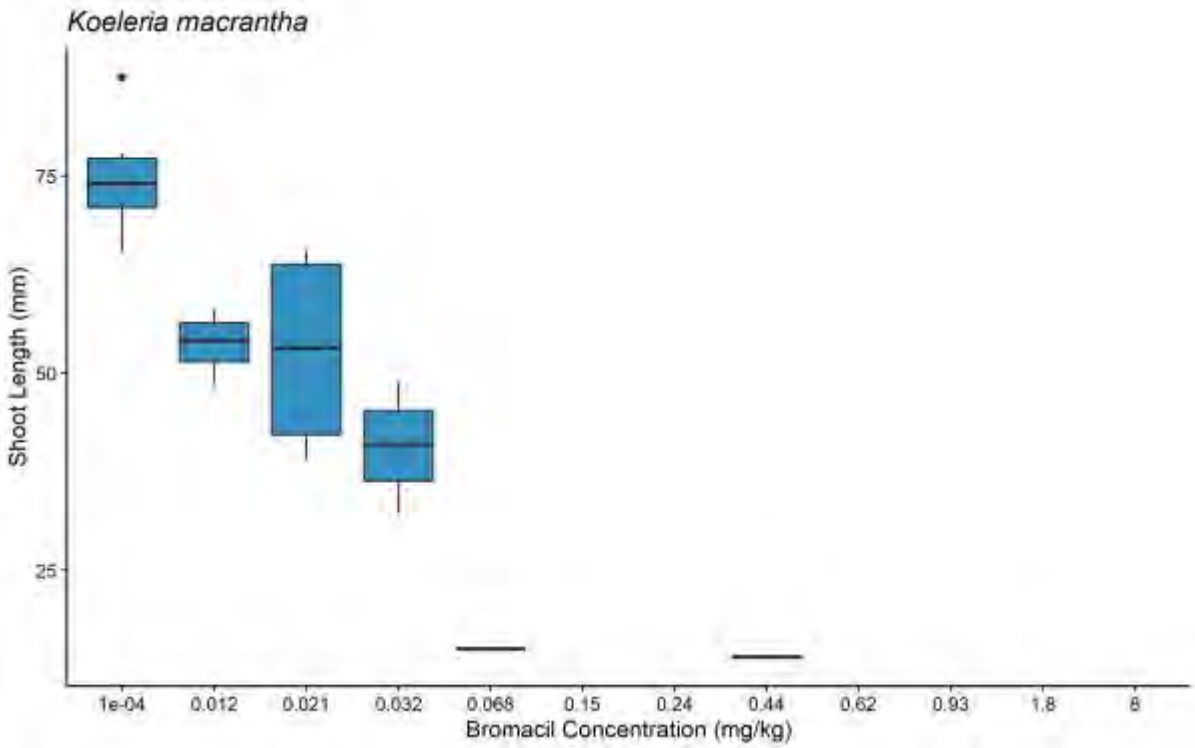

Figure 4. *Koeleria macrantha* shoot length (mm) when exposed to varying concentrations of bromacil (mg/kg).
The median value at each concentration is represented by a horizontal black line, and the box indicates the 25th and 75th percentiles. Whiskers represent the largest or smallest value, up to 1.5 times the interquartile range (IQR). Data points beyond the whiskers are outlying points.

3.3.3 Species Sensitivity Distribution

Millennium EMS Solutions Ltd. (MEMS) was retained as part of this project to develop species sensitivity distributions based on the data and to develop potential revised ecological direct contact surface soil quality guidelines for Alberta. The work completed by MEMS can be found in the report Litalien and Tindal (2021), which accompanies the current report. Here, we summarized and discussed the pertinent findings by Litalien and Tindal (2021).

MEMS used data from the current report and historical data used in the development of Alberta Tier 1 guidelines for bromacil and tebuthiuron (Stantec Consulting Ltd., 2008, 2012). MEMS assessed three different datasets: (1) all plants + invertebrates, (2) native plants + invertebrates, and (3) agronomic plants + invertebrates. The ecological direct contact surface soil quality guidelines developed by MEMS for fine-textured soil were based on all the data (all plants + invertebrates). The current Tier 1 guidelines and revised guidelines are provided in Table 15. Because the current report is focused on fine-textured soil, MEMS did not recommend modifications to the guidelines for coarse-textured soils.

Table 15. Revised ecological direct contact surface soil quality guidelines for fine-textured soil.

	Guideline	Natural/Residential/Agricultural	Commercial/Industrial
Bromacil	Current Tier 1 (mg/kg	0.20	0.49
	Revised[1] (mg/kg)	0.028	0.21
Tebuthiuron	Current Tier 1 (mg/kg	0.046	0.60
	Revised[1] (mg/kg)	0.018	0.15

Table adapted from Litalien and Tindal (2021).

[1] Based on an expanded dataset which includes more native plant species than the current Tier 1 guidelines.

MEMS also discussed potential alternate guidelines using native and agronomic species datasets more selectively. For example, guidelines for natural land use could be based on the native plants and invertebrates data set, guidelines for agricultural land use could be based on the agronomic plants and invertebrates data, and the complete dataset could be utilized for residential, commercial, and industrial land uses. The alternative guidelines are presented in Table 16, although there was not sufficient data for the agronomic plants and invertebrates data set.

Table 16. Potential alternate ecological direct contact surface soil quality guidelines for fine-textured soil.

	Guideline	Natural	Residential	Agricultural	Commercial/Industrial
Bromacil	Current Tier 1 (mg/kg	0.20			0.49
	Alternate (mg/kg)	0.014	0.028	0.37	0.21
Tebuthiuron	Current Tier 1 (mg/kg	0.046			0.60
	Alternate (mg/kg)	0.023	0.018	0.018	0.15

Table adapted from Litalien and Tindal (2021).

The revised guidelines from MEMS are more stringent than current Tier 1 guidelines. This is based on the inclusion of new data for native species, which appeared to be more sensitive to bromacil and tebuthiuron than the species that were historically studied. MEMS found that *K. macrantha*, *F. hallii*, and *N. viridula* were generally the most sensitive to bromacil; *F. hallii*, *A. dasystachyum*, and *N. viridula* were generally the most sensitive to tebuthiuron.

As discussed in section 3.3.1, *B. gracilis* was used both in the current and historical studies. Differences were observed for *B. gracilis* between the current and historical studies, and these may be attributed to different growth period (three versus six weeks), differing bromacil product (Hyvar® X vs. Hyvar® X-L), and/or differing soil properties. While the native species tested in the current study had a longer growth period than was used historically, this modification was made given the slow growth of many native species, which required a longer growth period to obtain accurate and meaningful results. Native species that were not tested historically were included in the current study, and many of the seed sources were local (within Alberta); typically, commercial seed is sourced from outside of Canada. Further investigation would be required to determine whether seed source plays a role in sensitivity to soil sterilants for native species.

The revised guidelines determined by MEMS (Litalien and Tindal, 2021) indicate a lower guideline concentration limit for tebuthiuron compared to bromacil. This may seem counterintuitive, as the native species tested in the current study tended to be more sensitive to bromacil. However, the data used to develop revised guidelines includes the current study and historical data for plants and invertebrates. When looking at the potential alternate guidelines for natural areas (Table 16), the bromacil guideline is more stringent. This is because this alternate guideline is based on the native species and invertebrates and does not include agronomic species. It should also be noted that the revised guideline for bromacil is an order of magnitude lower than the current Tier 1 guideline, while the revised guideline for tebuthiuron is approximately two times lower than the Tier 1 guideline value.

3.4 Implications for Reclamation

The results indicate that native species may be more sensitive to the effects of bromacil and tebuthiuron than agronomic species and invertebrates. It is important to note that all but two species were sourced locally from within Alberta. A direct comparison between locally-adapted and non-local seed sources would be needed to determine whether seed source plays a role in sensitivity to sterilants. Of the species tested in the current study, *B. gracilis* appeared to be the least sensitive to both sterilants. Native species tended to be more sensitive to bromacil than tebuthiuron in the current study.

The revised ecological direct contact surface soil quality guidelines generated by MEMS (Litalien and Tindal, 2021) indicate lower guideline limits than the current Tier 1 guidelines, and are a function of new data indicating that native species are more sensitive to bromacil and tebuthiuron than species studied historically. The results of this study can be used to inform potential modifications to current ecological direct contact surface soil quality guidelines for fine-grained soil in Alberta, and constitute a valuable resource for decision makers regarding the management of sterilant-impacted sites.

4 SUMMARY AND CONCLUSIONS

4.1 Summary

The goal of the Project was to evaluate the toxicity of two common soil sterilants, bromacil and tebuthiuron, to Alberta native species. Data from this project were used to develop potential revisions for direct soil eco-contact guidelines by Millennium EMS Solutions (MEMS). This project relates to the overarching goal of the Soil Sterilants Program as it works to inform proven, cost-effective management practices for soil sterilant impacted sites in Alberta.

Toxicity tests were conducted on various native grass species (*Agropyron dasystachyum, Bouteloua gracilis, Festuca hallii, Koeleria macrantha, Nassella viridula, Pascopyrum smithii*) exposed to either bromacil or tebuthiuron in soil. Endpoints such as emergence, root and shoot length, and root and shoot biomass were assessed. Results from the toxicity tests were used to generate regression models and inhibition concentration (IC_p) values for each endpoint from each species/sterilant test. While the data tended to be variable within a species and endpoint, species-specific effects were observed. Some species, such as *B. gracilis*, were more tolerant to the sterilants than others. In general, the species tested tended to be more sensitive to bromacil than tebuthiuron. There was no clear difference in sensitivity between root and shoots parameters.

The IC_p values for *B. gracilis* in the current study were compared to values obtained from Stantec Consulting Ltd. (2008, 2012). IC_p values between the two studies were comparable for tebuthiuron. However, IC_p values for bromacil in the current study tended to be an order a magnitude lower than those obtained in Stantec Consulting Ltd. (2012). Differences in toxicity might be due to the length of the growth period (six weeks in the current study versus three weeks historically), the difference in sterilant products used (i.e., Hyvar® X versus Hyvar® X -L), and/or soil properties.

Potential revised guidelines were generated by MEMS based on native plants data from the current study, plant data (including agronomic species) from historical studies, and invertebrate data from historical studies. The revised guidelines are more stringent than the current Alberta Tier 1 guidelines for ecological direct contact surface soil quality guidelines for fine-grained soil; this was because the native species tested in the current study appeared to be more sensitive to bromacil and tebuthiuron than species that have been historically studied.

4.2 Conclusions and Recommendations

The Project has provided pertinent information regarding the toxicity of common soil sterilants to Alberta native species, and potential revisions to consider for Alberta Tier 1 guidelines. The native species tested in the current study were more sensitive to soil sterilants than species that were studied historically, indicating that more stringent soil guidelines might be appropriate for some land uses. It is recommended that:

- Revised soil quality guidelines derived by MEMS be considered for Tier 1 ecological direct contact surface soil quality guidelines for fine-grained soil, for non-commercial and non-industrial land uses.
- The potential revised guidelines are:
  - Bromacil – Natural/Residential/Agricultural: 0.028 mg/kg
  - Tebuthiuron – Natural/Residential/Agricultural: 0.018 mg/kg
- The potential alternate guidelines indicated by MEMS (Table 16) could also be considered for natural, residential, and/or agricultural land uses.

Data obtained from the current study indicated that native species were more sensitive to bromacil and tebuthiuron than the plants studied historically. For *B. gracilis*, differences were observed between the current study and historical studies, possibly due to differences in growth period, bromacil product, and soil properties. Additionally, the potential impact of seed source could not be addressed under the scope of the current study. Recommendations for areas of future work include:

- *Toxicity testing with a range of native species grown in soils with varying chemical and physical properties from within Alberta.* This would give a more complete picture of the range of effects sterilants may have on native plants in Alberta.
- *Toxicity testing with a range of native species in a coarse-grained soil.* The current study focused on fine-grained soils, but given the recommended guideline modifications, further information on the toxicity of sterilants to native species in coarse-grained soil could provide further guideline recommendations.
- *Direct comparison of locally-adapted versus non-local native seed sources.* Assessing whether species grown from locally-adapted seed vary in their sensitivity to sterilants compared to seed from non-local sources could have important implications for reclamation best management practices.

The information gained from this Project includes toxicity information for a range of Alberta native species when exposed to bromacil and tebuthiuron in soil. Potential revised guidelines for Alberta Tier 1 ecological direct contact surface soil quality guidelines for fine-grained soil were derived and were more stringent than current guidelines; the revised guidelines were a function of new data indicating that native species were more sensitive to sterilants than those species historically studied. This project has contributed to the Soil Sterilants Program and constitutes a valuable resource for decision makers regarding the management of sterilant-impacted sites in Alberta.

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APPENDIX A: SPECIES LIST

A list of species used in the case studies is provided below. Scientific naming convention follows Alberta Conservation Information Management System (ACIMS) (Kershaw, 2015) and common names follow Alberta Agriculture and Forestry (2016).

Latin Name with Authority	Common Name
Agropyron dasystachyum (Hook.) Scribn. & J.G. Sm.	Northern Wheatgrass
Bouteloua gracilis (Willd. ex Kunth) Lag. ex Griffiths	Blue Grama
Festuca hallii (Vasey) Piper	Plains Rough Fescue
Koeleria macrantha (Ledeb.) Schult.	June Grass
Nassella viridula (Trin.) Barkworth	Green Needle Grass
Pascopyrum smithii (Rydb.) Á. Löve	Western Wheatgrass

APPENDIX B: SOIL PIT PHOTOS

Figure B.1. Soil sampling area located on a site near Brooks, Alberta and soil pits.

APPENDIX C: EXPERIMENT PHOTOS

RANGE FINDING TEST

Figure C.1. *Koeleria macrantha* (control) at the end of the six-week experiment.

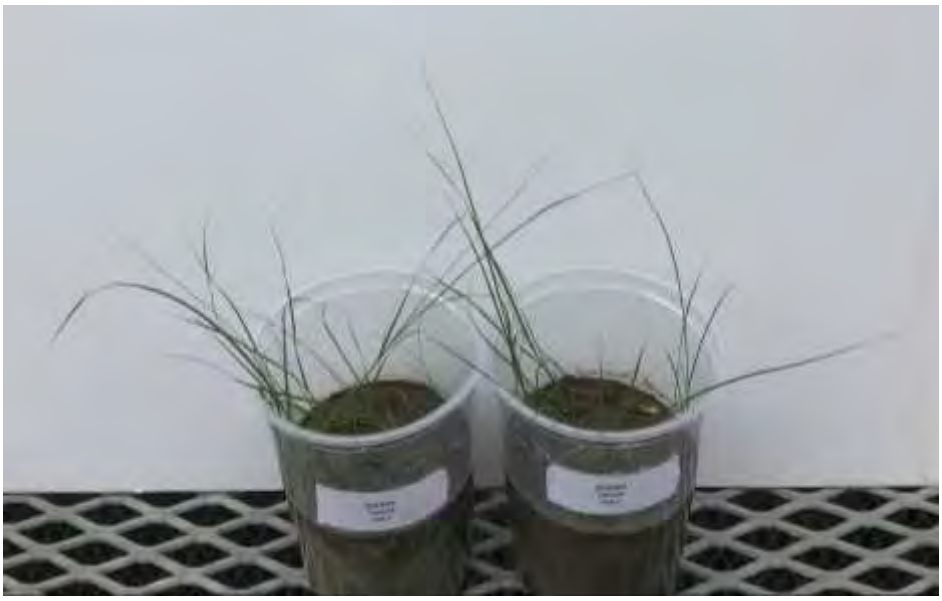


Figure C.2. *Bouteloua gracilis* (control) at the end of the six-week experiment.

Figure C.3. *Pascopyrum smithii* (control) at the end of the six-week experiment.

Figure C.4. *Nassella viridula* (control) at the end of the six-week experiment.

Figure C.5. *Festuca hallii* (control) at the end of the six-week experiment.

Figure C.6. *Agropyron dasystachyum* (control) at the end of the six-week experiment.

DEFINITIVE TESTING

Select photos to illustrate differences in toxicity between the two sterilants on a single species (*Bouteloua gracilis*), and differences in toxicity among species (*Bouteloua gracilis* versus *Pascopyrum smithii*).

Figure C.7. *Bouteloua gracilis* from the lowest the highest tebuthiuron concentration (left to right).

Figure C.8. *Bouteloua gracilis* from the lowest the highest bromacil concentration (left to right).

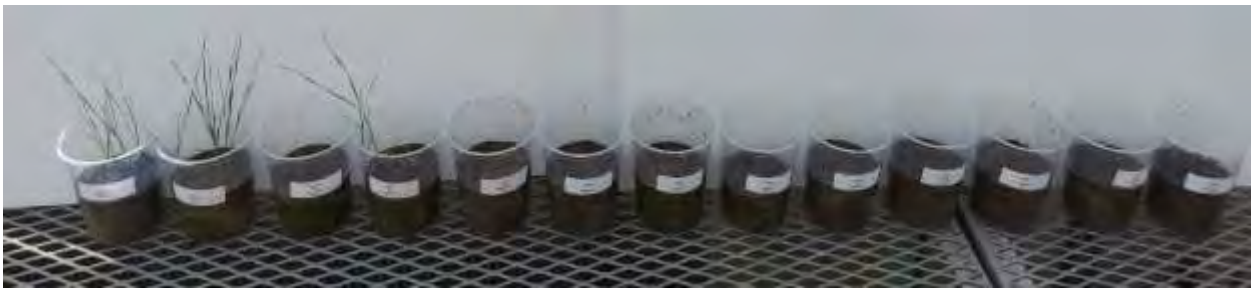


Figure C.9. *Pascopyrum smithii* from the lowest the highest bromacil concentration (left to right).

APPENDIX D: REGRESSIONS

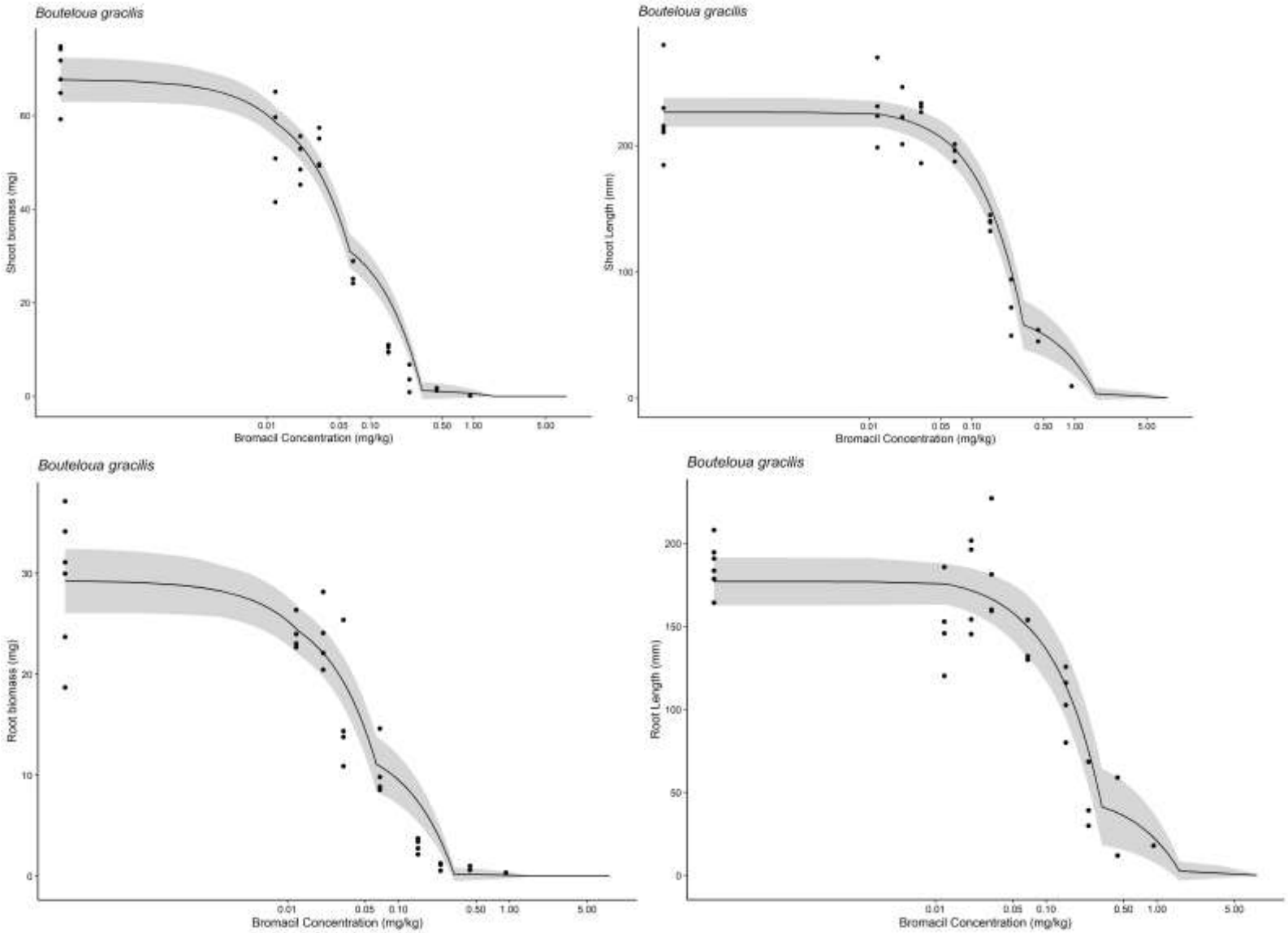


Figure D.1. *Bouteloua gracilis* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of bromacil.

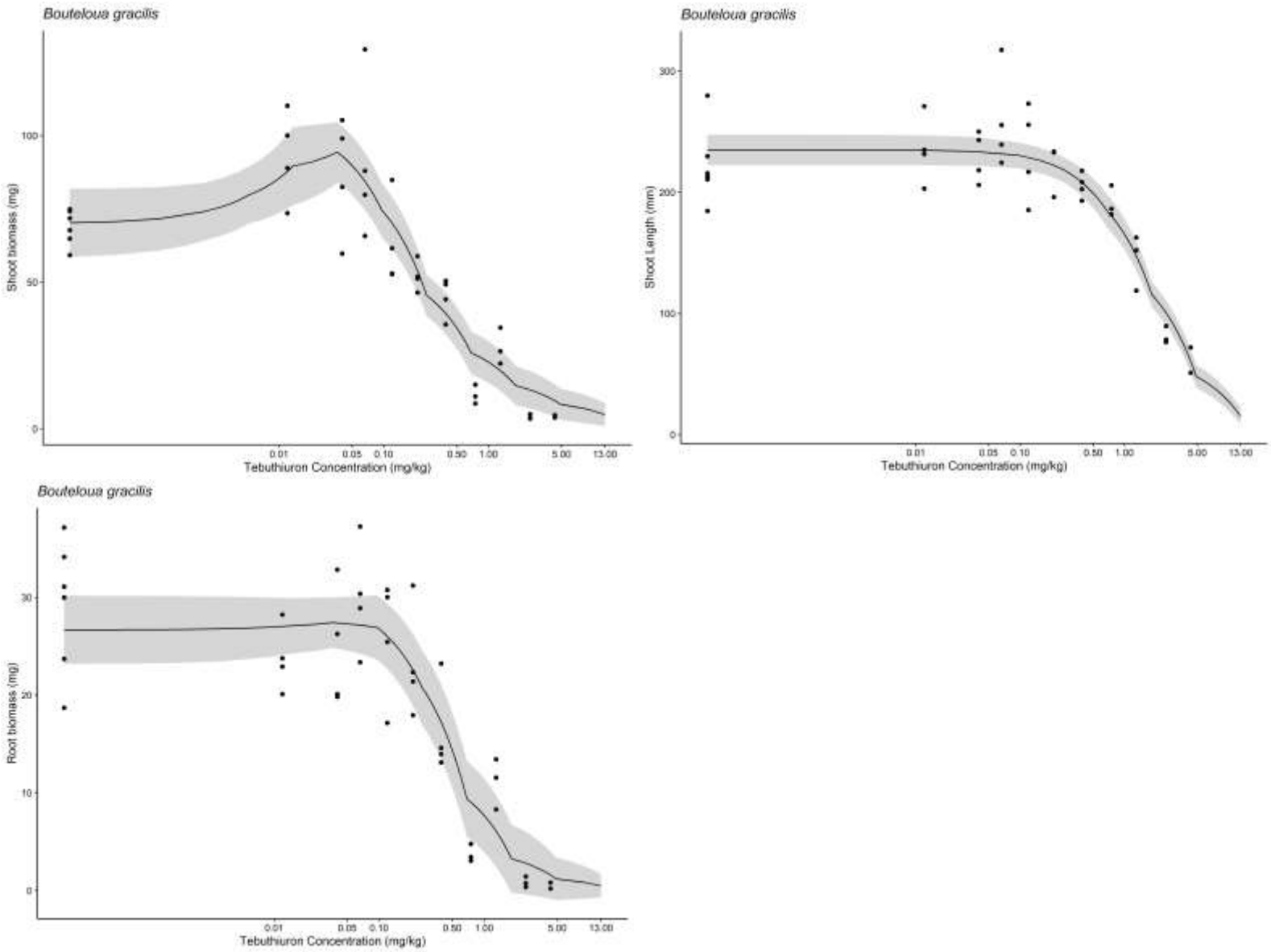
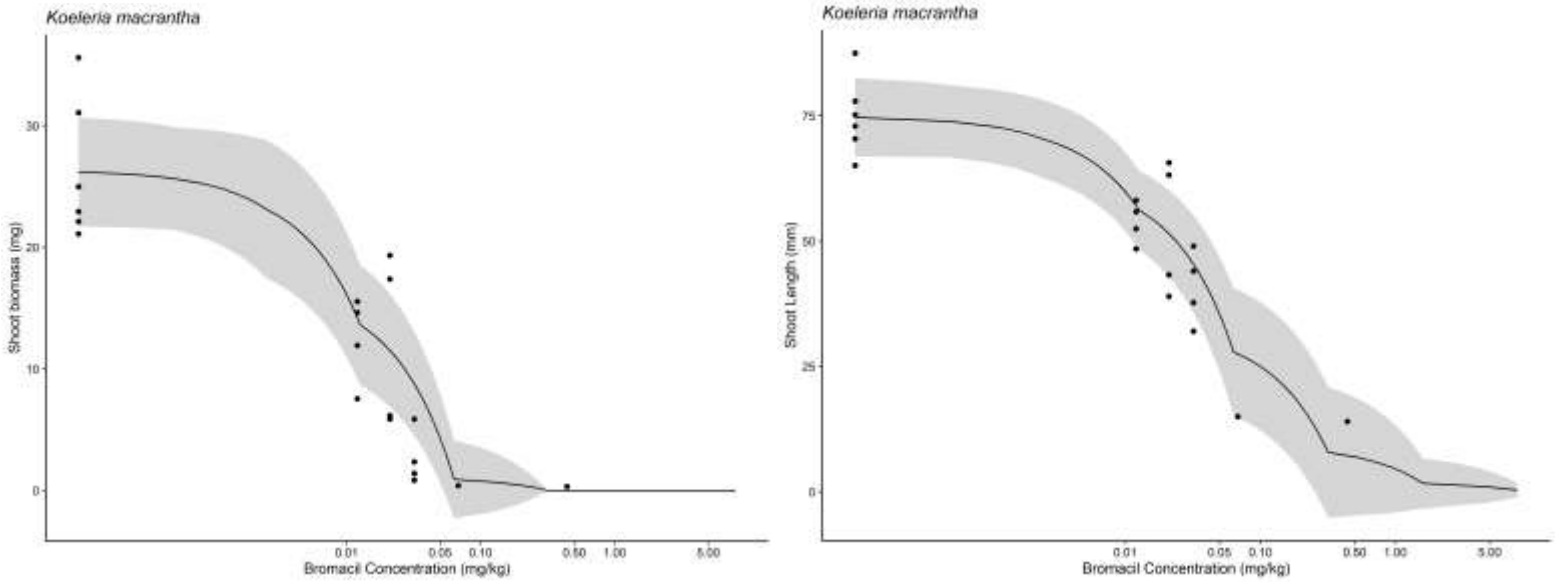


Figure D.2. *Bouteloua gracilis* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of tebuthiuron.



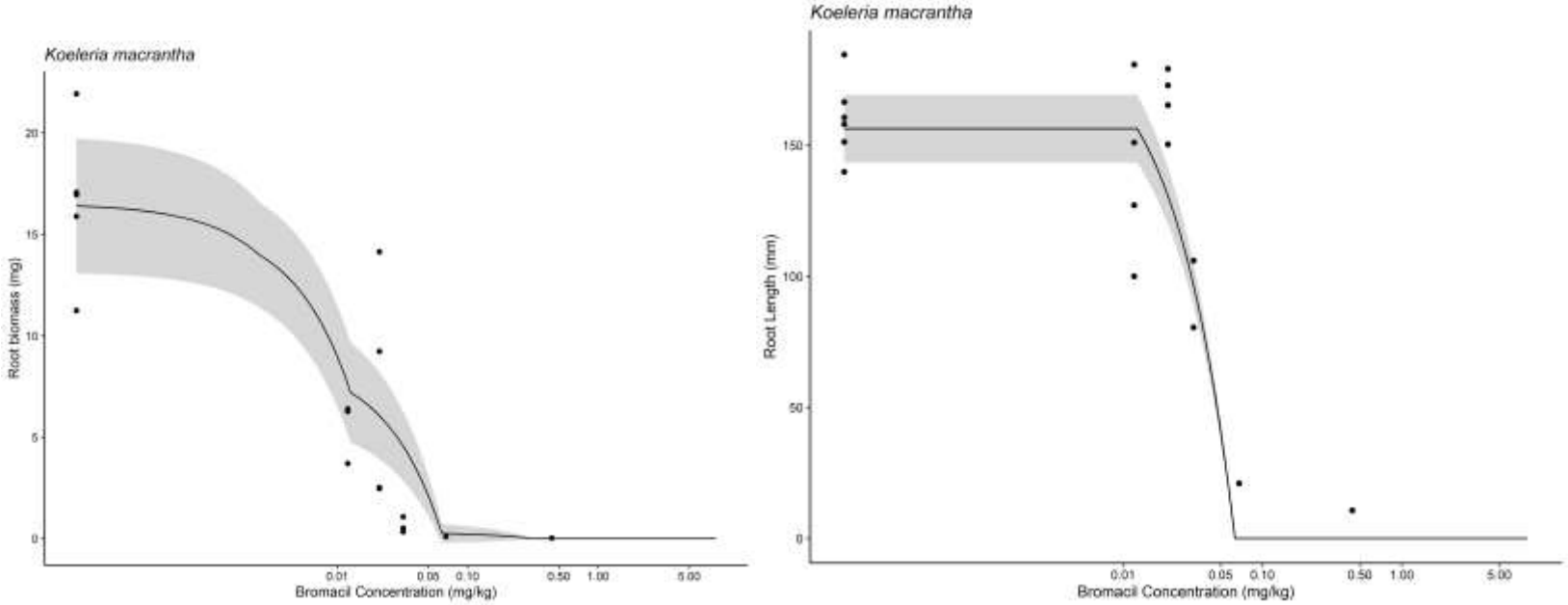
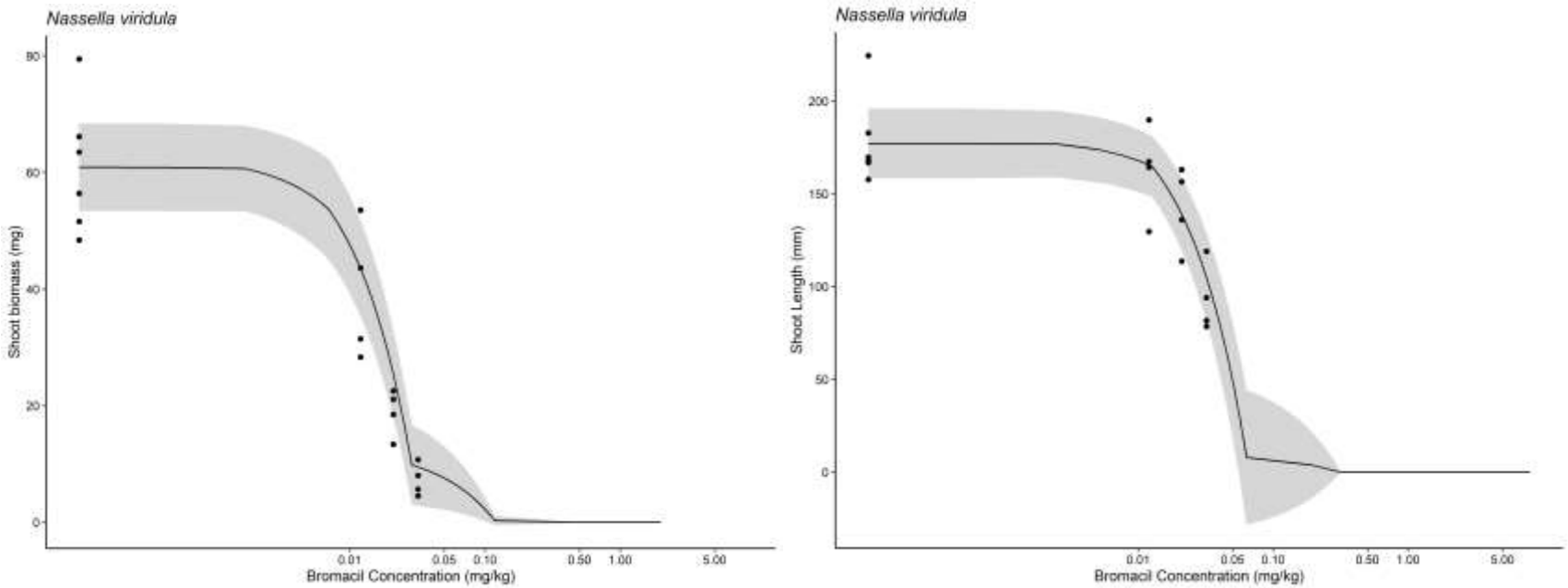


Figure D.3. *Koeleria macrantha* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of bromacil.



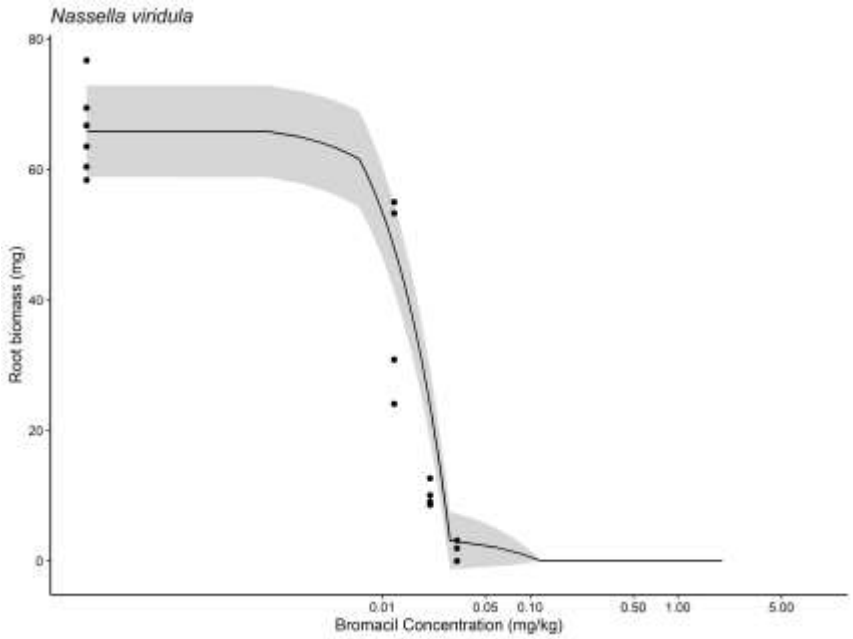


Figure D.4. *Nassella viridula* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of bromacil.

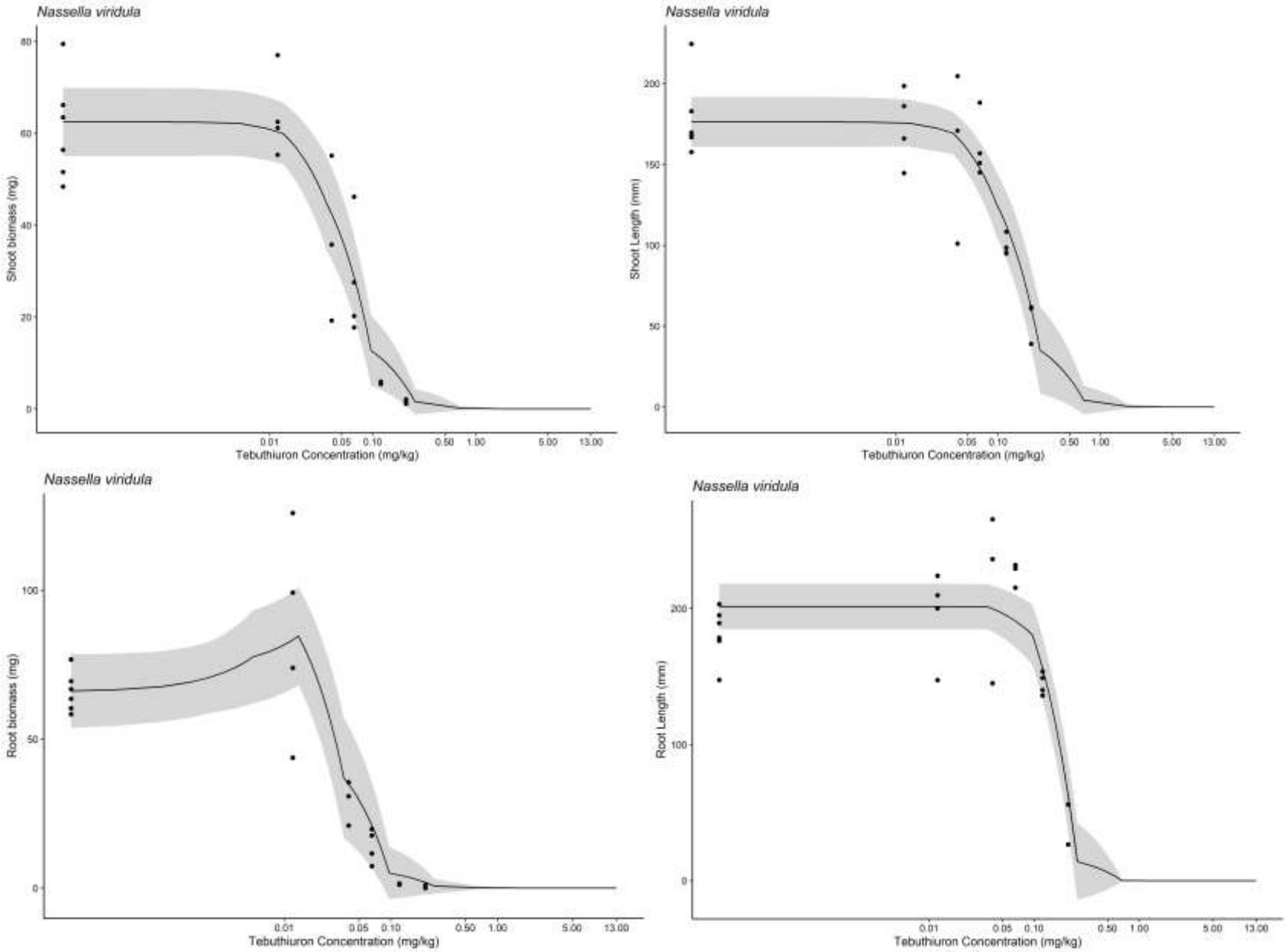


Figure D.5. *Nassella viridula* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of tebuthiuron.

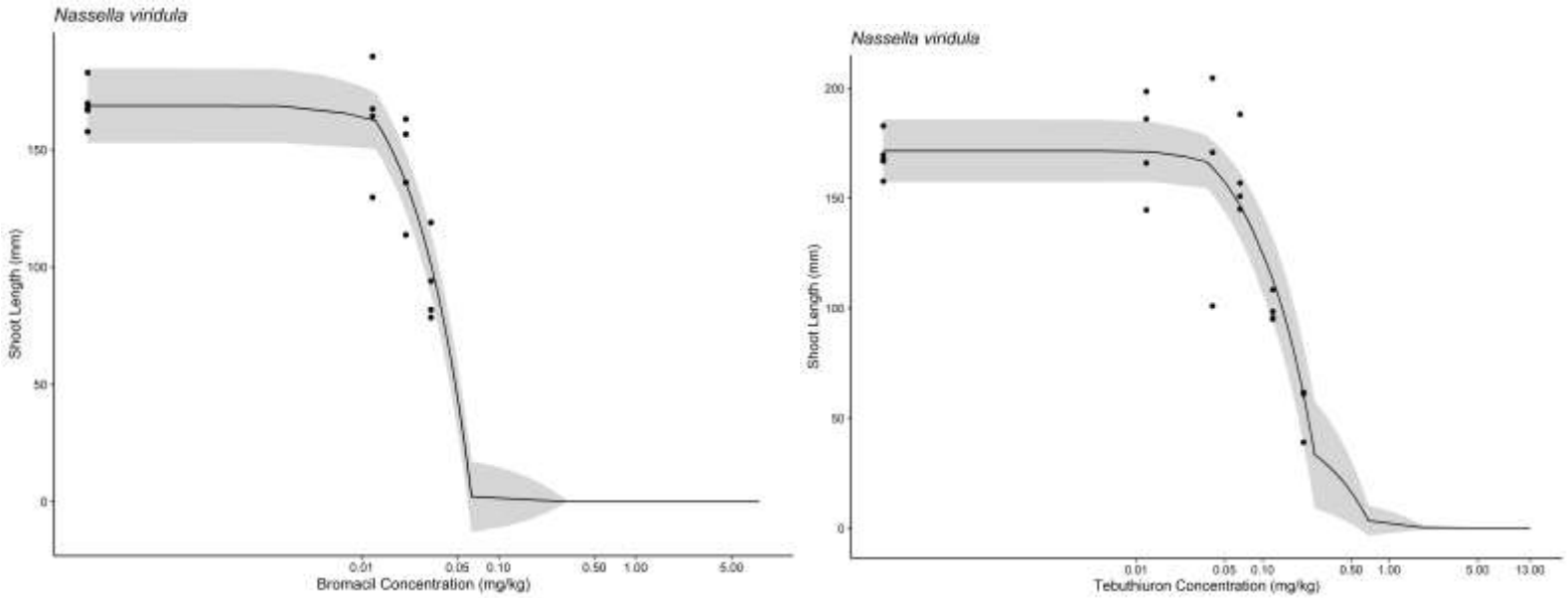
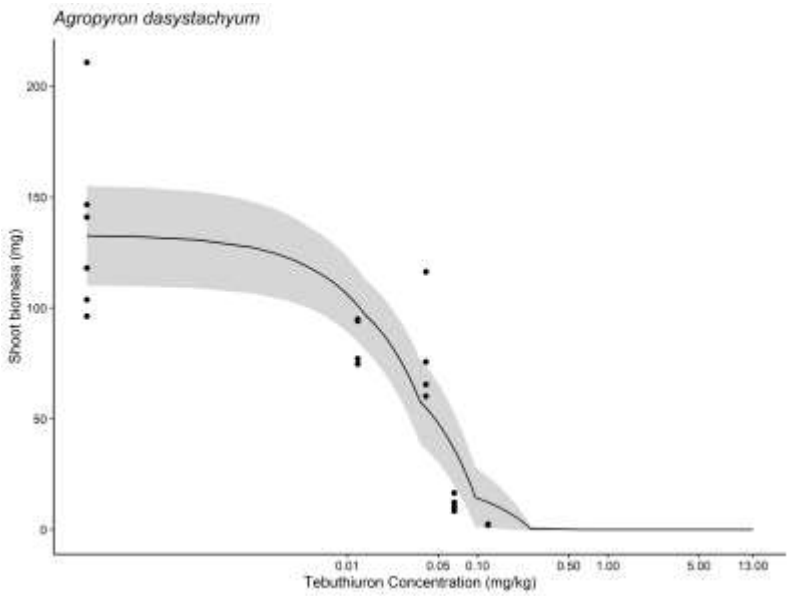
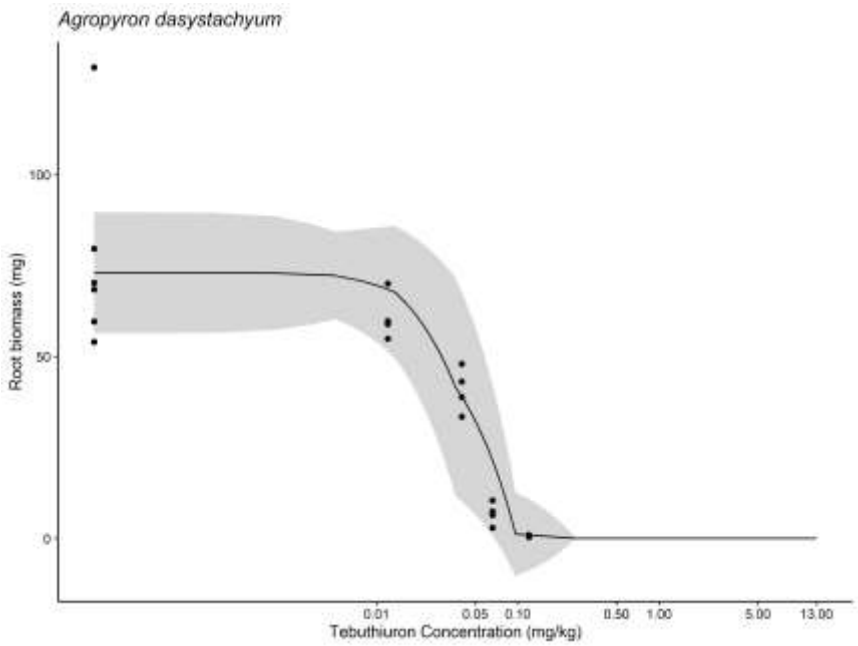


Figure D.6. *Nassella viridula* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of bromacil and tebuthiuron. These regressions had replicates from the control treatment removed to assess the impact on IC_p values; impacts were deemed minimal and these regressions are shown for information only.


Agropyron dasystachyum
Shoot biomass (mg)
200
150
100
50
0
0.01
0.05
0.10
0.50
1.00
5.00
13.00
Tebuthiuron Concentration (mg/kg)


Agropyron dasystachyum
Root biomass (mg)
100
50
0
0.01
0.05
0.10
0.50
1.00
5.00
13.00
Tebuthiuron Concentration (mg/kg)

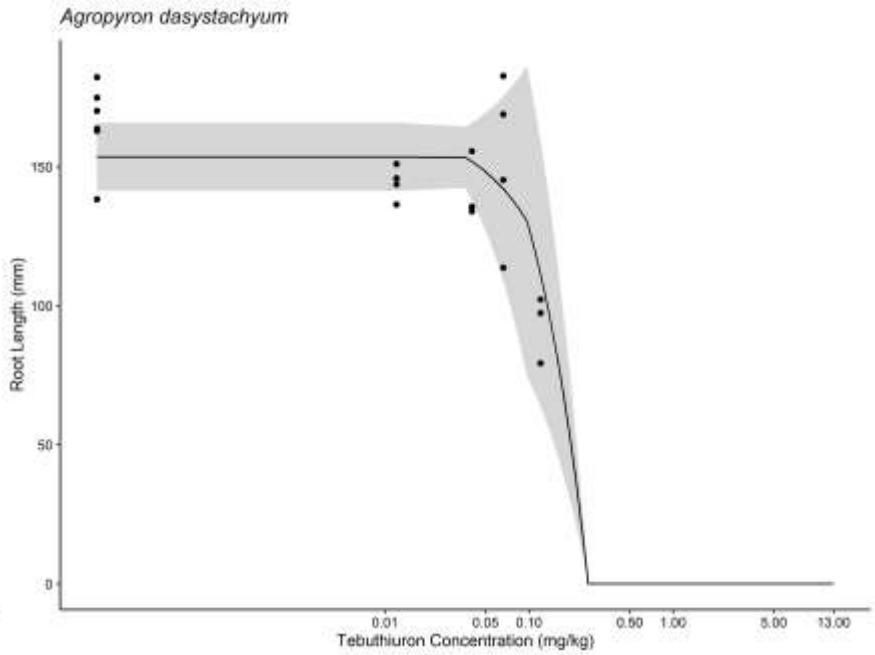

Agropyron dasystachyum
Root Length (mm)
150
100
50
0
0.01
0.05
0.10
0.50
1.00
5.00
13.00
Tebuthiuron Concentration (mg/kg)

Figure D.7. *Agropyron dasystachyum* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of tebuthiuron.

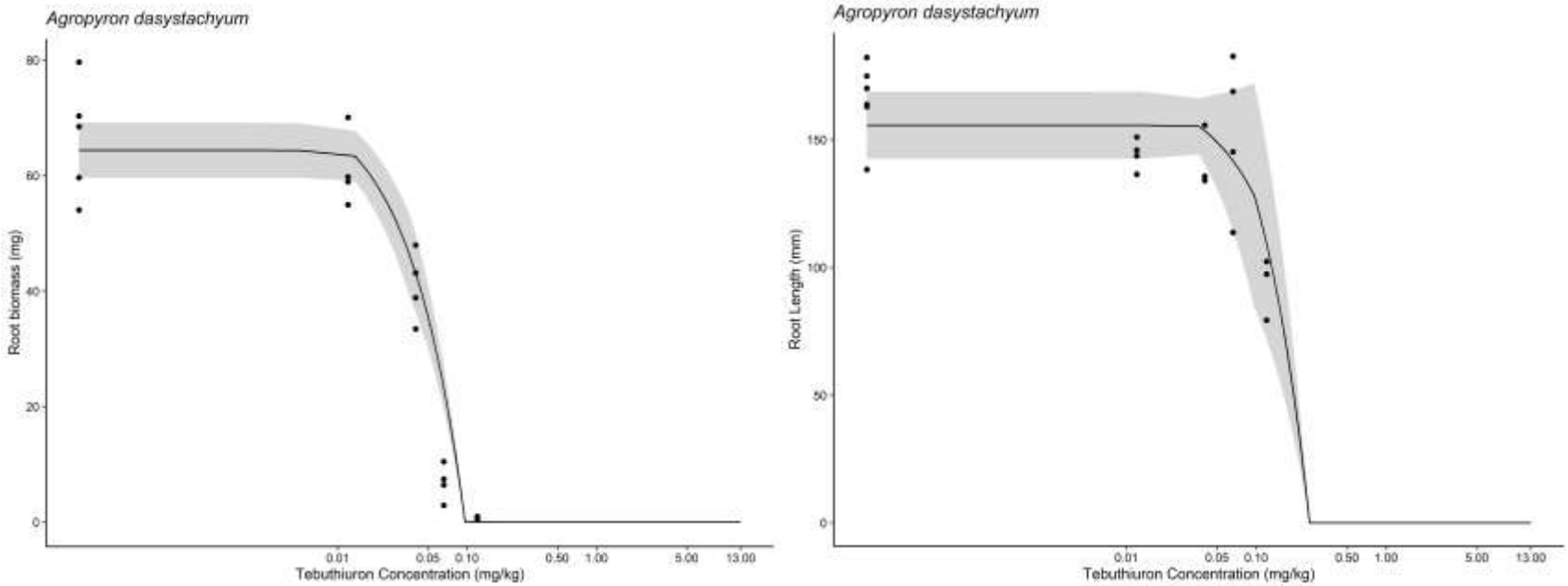


Figure D.8. *Agropyron dasystachyum* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of tebuthiuron. These regressions had replicates from the control treatment removed to assess the impact on IC_p values; impacts were deemed minimal and these regressions are shown for information only.

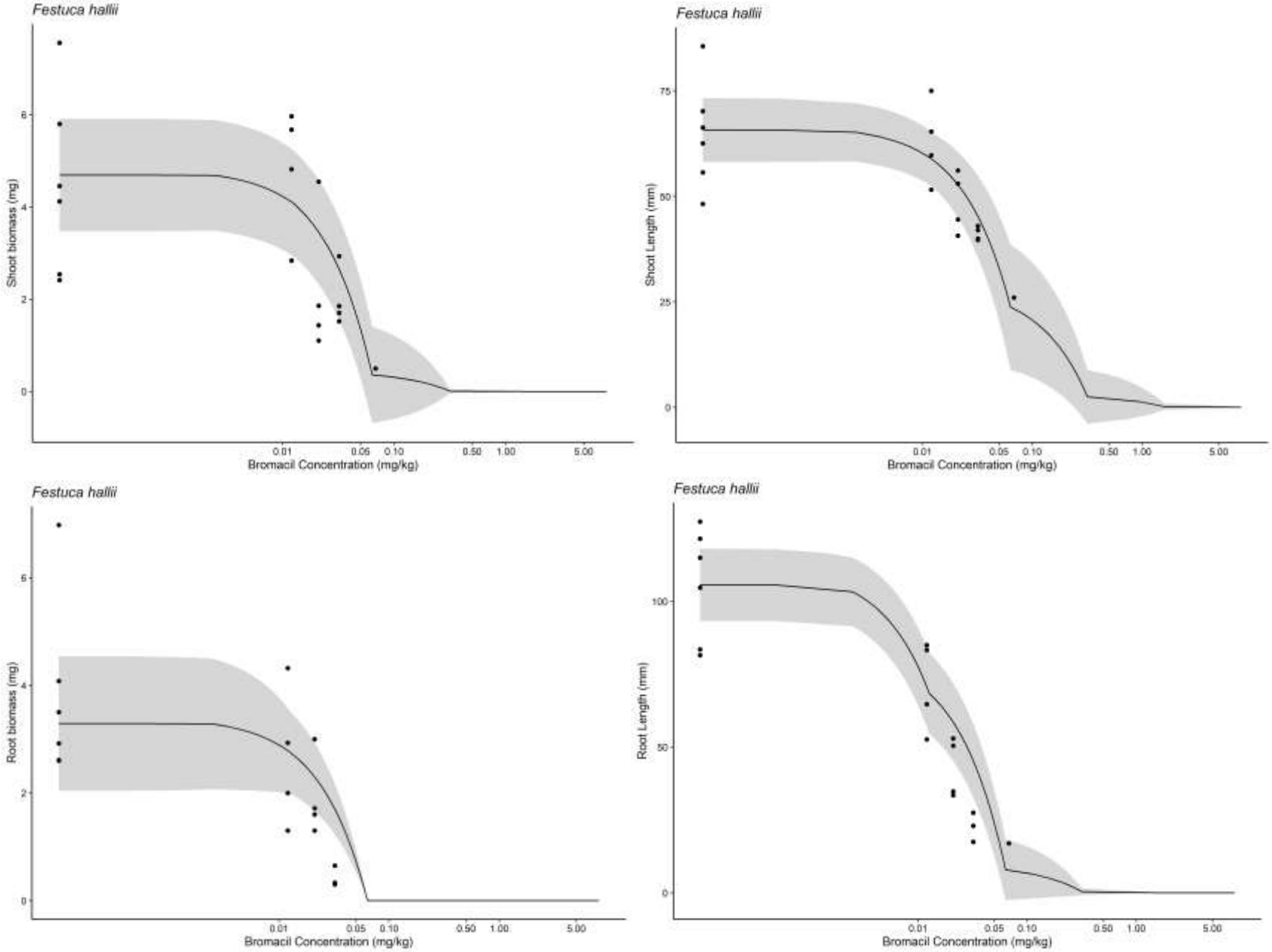


Figure D.9. *Festuca hallii* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of bromacil.

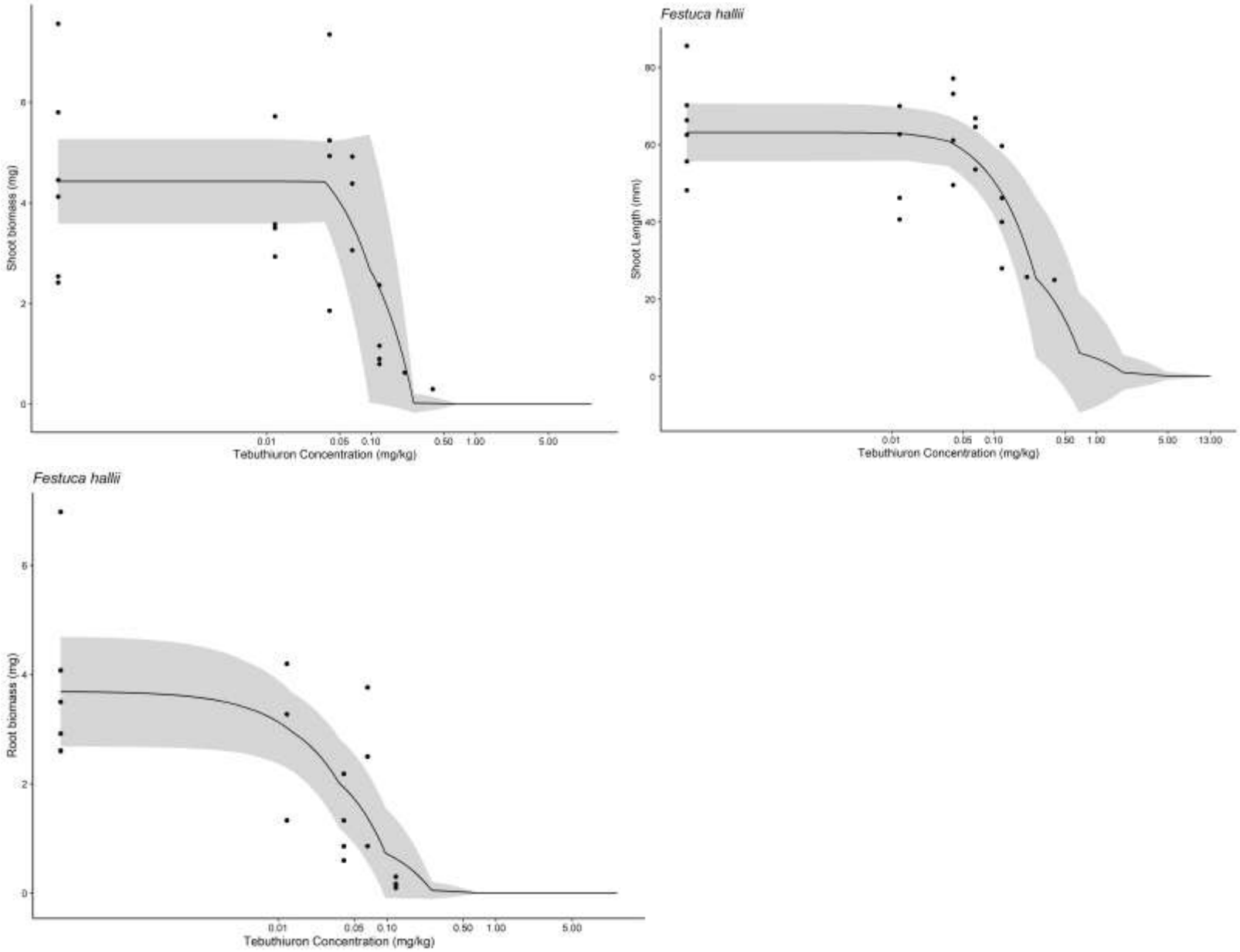


Figure D.10. *Festuca hallii* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of tebuthiuron.

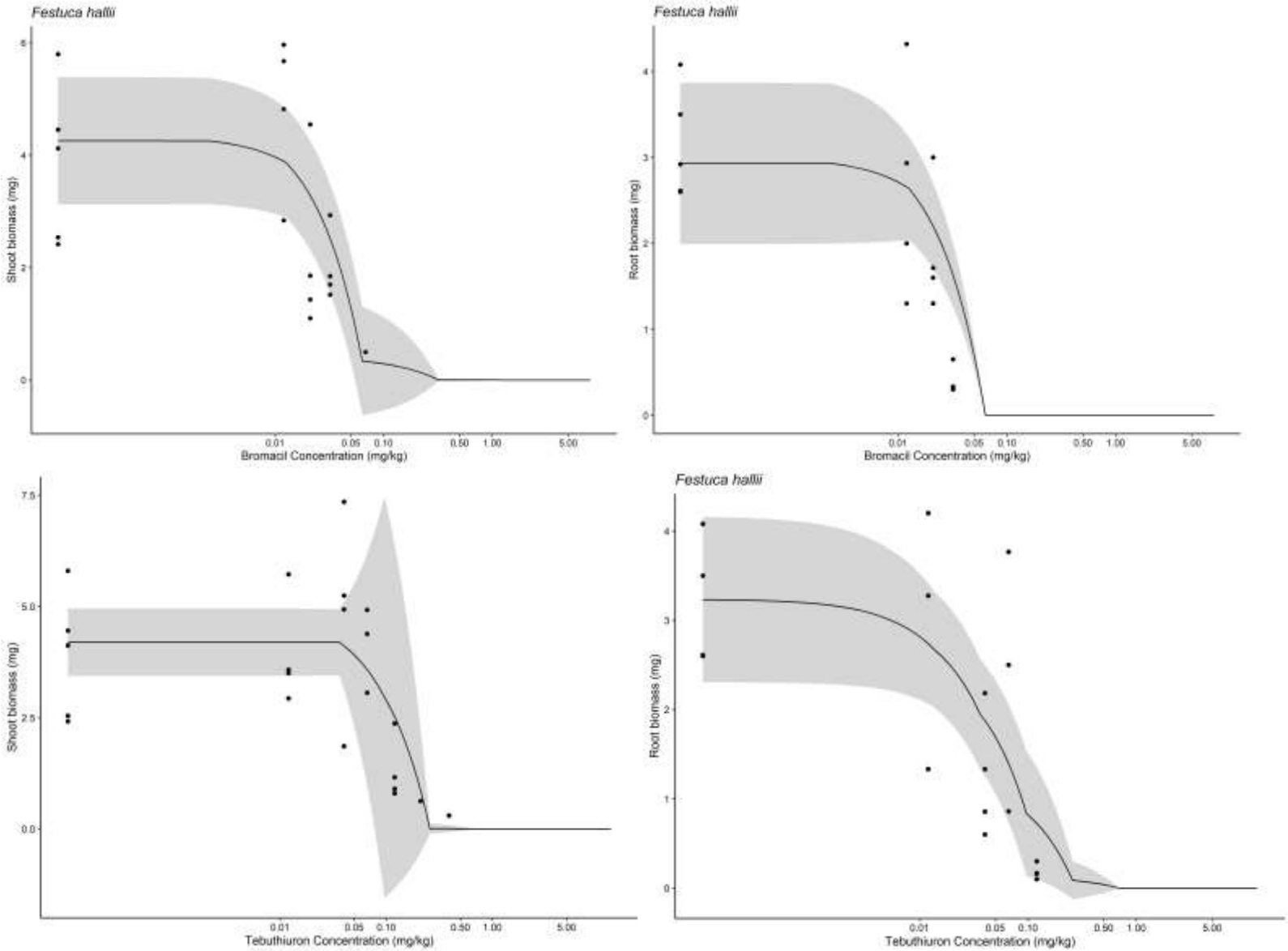


Figure D.11. *Festuca hallii* regression curves for shoot and root parameters exposed to soil spiked with varying concentrations of bromacil and tebuthiuron. These regressions had replicates from the control treatment removed to assess the impact on IC_p values; impacts were deemed minimal and these regressions are shown for information only.

APPENDIX E: RANGE FINDING TEST – STERILANT CONCENTRATIONS IN SOIL

The table below provides the raw concentrations of bromacil (mg/kg) as reported by the laboratory, showing the value for each replicate of the target concentrations.

Sterilant	Target Concentration (mg/kg)	Replicate	Actual Concentration (mg/kg)
Bromacil	0.01	1	<0.008*
		2	<0.008*
	0.1	1	0.067
		2	0.061
	0.5	1	0.447
		2	0.417
	1	1	0.783
		2	1.07
	5	1	6
		2	7.03
	10	1	8.93
		2	12.4
	100	1	86.5
		2	115

* Values below the laboratory detection limit.

The table below provides the raw concentrations of tebuthiuron (mg/kg) as reported by the laboratory, showing the value for each replicate of the target concentrations.

Sterilant	Target Concentration (mg/kg)	Replicate	Actual Concentration (mg/kg)
Tebuthiuron	0.05	1	0.069
	0.1	1	0.164
	0.5	1	0.697
	1	1	1.3
	5	1	5.22
	30	1	21.3
	300	1	439

APPENDIX F: DEFINITIVE TOXICITY TESTING – STERILANT CONCENTRATIONS IN SOIL

The table below provides the raw concentrations of bromacil (mg/kg) as reported by the laboratory, showing the value for each replicate of the target concentrations.

Sterilant	Target Concentration (mg/kg)	Replicate	Actual Concentration (mg/kg)
Bromacil	0.01	1	0.013
		2	0.013
		3	0.011
	0.05	1	0.02
		2	0.021
		3	0.023
	0.07	1	0.029
		2	0.032
		3	0.034
	0.1	1	0.052
		2	0.071
		3	0.082
	0.2	1	0.165
		2	0.138
		3	0.144
	0.3	1	0.239
		2	0.245
		3	0.236
	0.5	1	0.409
		2	0.411
		3	0.486
	0.75	1	0.672
		2	0.573
	1	1	0.782
		2	1.08
	3	1	2.32
		2	1.56
		3	1.53
	5	1	8.23
		2	7.8

The table below provides the raw concentrations of tebuthiuron (mg/kg) as reported by the laboratory, showing the value for each replicate of the target concentrations.

Sterilant	Target Concentration (mg/kg)	Replicate	Actual Concentration (mg/kg)
Tebuthiuron	0.01	1	0.011
		2	0.016
		3	0.009
	0.05	1	0.044
		2	0.038
		3	0.037
	0.1	1	0.058
		2	0.082
		3	0.059
	0.2	1	0.133
		2	0.098
		3	0.123
	0.3	1	0.213
		2	0.194
		3	0.21
	0.5	1	0.405
		2	0.387
		3	0.363
	0.75	1	0.636
		2	0.736
		3	0.863
	1	1	1.43
		2	1.22
	3	1	2.29
		2	2.88
		3	2.41
	5	1	4.03
		2	4.37
		3	4.52
	15	1	12
		2	12.7
		3	14.1

Appendix A6-2: Ecological Contact Guideline Development

Litalien, A. and M. Tindal, 2021. Ecological Contact Guideline Development for Bromacil and Tebuthiuron. Report SSP-9B prepared by Millennium EMS Solutions for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 16 pp. plus Appendices.

Ecological Contact Guideline Development for Bromacil and Tebuthiuron

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Canada

January 2021

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EXECUTIVE SUMMARY

Species sensitivity distributions for bromacil and tebuthiuron were developed based on the 2006 CCME protocol for development of soil quality guidelines for the protection of the ecological direct contact pathway. Datasets included the ecotoxicological responses of invertebrates and native and/or agronomic plant species in fine-grained soils. The datasets were based on both recent data collected as part of the Soil Sterilants Program as well as historical data used in the development of Tier 1 Guidelines for bromacil and tebuthiuron.

Revised soil quality guidelines for the ecological direct contact pathway are as follows:

- Bromacil – Natural/Residential/Agricultural: 0.028 mg/kg;
- Bromacil – Commercial/Industrial: 0.21 mg/kg;
- Tebuthiuron – Natural/Residential/Agricultural: 0.018 mg/kg; and
- Tebuthiuron – Commercial/Industrial: 0.15 mg/kg tebuthiuron.

The updated guidelines are more conservative than previous guidelines based on the incorporation of new data developed as part of the Soil Sterilants Program. The native species examined appear to be more sensitive to bromacil and tebuthiuron than those species examined historically.

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1. INTRODUCTION

The historical use of soil sterilants for vegetation management at many upstream oil and gas facilities as well as industrial sites throughout Alberta presents a challenge to decommissioning and remediation. Soil sterilants such as bromacil and tebuthiuron are persistent and even low concentrations can negatively impact plant survival and growth. Guidelines for the ecological direct contact pathway for both bromacil and tebuthiuron currently exist within the Alberta documentation (Tier 1 Guidelines; AEP, 2019). However, these guidelines were based on the combined ecotoxicological endpoints of native plants and agronomic species. Given that native plant species and crop plants may differ in their sensitivity to bromacil and tebuthiuron, further ecotoxicological testing on native species has been conducted as part of this project. By incorporating these new ecotoxicological endpoints, guidelines may be produced which better reflect native plant species.

As part of the Soil Sterilants Program, InnoTech Alberta (InnoTech) retained Millennium EMS Solutions Ltd. (MEMS) to support the analysis and reporting of the results of Thacker (2021) as well as develop revised eco-contact guidelines for bromacil and tebuthiuron with respect to native species and/or a combination of agronomic and native species (Task 5). This report summarizes Task 5 work.

Task 5 focused on evaluating new ecotoxicological data for native plant species exposed to bromacil and tebuthiuron to propose new soil remediation guidelines for use in Alberta if appropriate. This task focused on ecotoxicological data produced by Thacker (2021) and did not include a literature search of other recent ecotoxicological studies.

Task 5 work involved:

1. Generating and interpreting species sensitivity distributions for each sterilant based on ecotoxicological studies conducted by Thacker (2021).
2. Developing proposed soil remediation guidelines protective of the ecological direct contact pathway consistent with current Alberta Environment and Parks protocols. Datasets for native and agronomic species were considered both separately and combined to develop the most appropriate revised guidelines.
3. Completing a written interpretation of the species sensitivity distributions, potential guideline recommendation, risk assessment, and management recommendations.

2. METHODOLOGY

2.1 DERIVATION OF SOIL QUALITY GUIDELINES FOR SOIL CONTACT PATHWAYS

Consistent with Alberta Environment and Parks protocols, CCME methodology was applied to developing the sensitivity distributions and associated ecotoxicological guidelines. CCME (2006) outlines three methods for the development of soil quality guidelines for the protection of soil ecological contact. These include:

1. Weight of Evidence Method
    a. Guidelines are developed based on “Threshold Effects Concentration” (TEC) for agricultural or residential/parkland uses and “Effect Concentration-Low” (ECL) values for

commercial and industrial uses which are in turn derived from a dataset of Effects concentration (EC_{25}/IC_{25}) values.

2. LOEC Method
    a. Guidelines are developed based on TEC and ECL values that are extrapolated from lowest effects concentration (LOEC) values.
3. Median Effects Method
    a. Guidelines are developed based on TEC and ECL values which are extrapolated from Median Effective Concentration (EC_{50} or LC_{50}) values.

The weight of evidence approach is preferred where data quality and quantity are sufficient and was adopted for this project based on the available dataset. Data requirements are discussed in section 2.2.

2.2 DATA SOURCES

Ecotoxicological data was included from both Tacker (2021) and the historical studies used to develop the existing AEP (2019) Tier 1 Guidelines for the ecological direct contact pathway. Sections 2.2.1 and 2.2.2 briefly summarize the studies and the resulting ecotoxicological data used for the development of the updated guidelines.

2.2.1 Tier 1 Ecotoxicological Studies

Two ecotoxicological studies were commissioned to develop Tier 1 Guidelines for bromacil (Stantec, 2012) and tebuthiuron (Stantec, 2008), respectively.

2.2.1.1 Bromacil

Definitive ecotoxicological tests were conducted by Stantec (2012) on three plant species and two soil invertebrate species in both fine grained and coarse-grained soils. The authors applied the test methods and procedures outlined by Environment Canada (2004, 2005, 2007). Table 1 outlines the species studied and their selection criteria.

Table 1. Species selected by Stantec (2012) for definitive ecotoxicity testing of bromacil.

Species	Selection Criteria	Agronomic or Native Species	Endpoints
Plants			
Durum wheat (*Triticum durum*)	Representative of Monocots	Agronomic	Shoot Length Root Length Shoot Dry Mass Root Dry Mass
Blue grama grass (*Bouteloua gracilis*)		Native	Survival

Species	Selection Criteria	Agronomic or Native Species	Endpoints
Alfalfa (*Medicago sativa*)	Representative of Dicots	Agronomic	Shoot Length Root Length Shoot Dry Mass Root Dry Mass
Invertebrates			
Red wiggler worm (*Eisenia andrei*)	Representative of earthworms		Progeny Production
Springtail (Collembola – *Folsomia candida*)	Representative of soil arthropods		Adult Survival Progeny Production Progeny Dry Mass Progeny Wet Mass

Stantec (2012) developed IC_{25} values and plotted species sensitivity distributions as per the CCME methods outlined in section 2.1 and 2.3 to determine appropriate soil quality guidelines. The resulting values were:

- Fine – TEC (agricultural/residential) – 0.25 mg/kg
- Fine – ECL (commercial/industrial) – 0.93 mg/kg
- Coarse – TEC (agricultural/residential) – 0.11 mg/kg
- Coarse – ECL (commercial/industrial) – 0.1 mg/kg

However, the current Tier 1 eco-contact guidelines for bromacil (AEP, 2019) are based on the sensitivity distribution of IC_{25} values from plant species alone. While using a dataset based on plant species alone did not meet requirements of the Weight of Evidence approach, Stantec (2012) determined that a more cautious approach was necessary based on the differences in sensitivity between the plant and invertebrate datasets.

2.2.1.2 Tebuthiuron

Definitive ecotoxicological tests were conducted by Stantec (2008) on four plant species and two soil invertebrates in topsoil and subsoil collected from a site in Alberta to develop Tier 2 site-specific soil quality guidelines for tebuthiuron. The authors applied the test methods and procedures outlined by Environment Canada (2004, 2005, 2007). Table 2 outlines the species studied and their selection criteria.

Table 2. Species selected by Stantec (2008) for definitive ecotoxicity testing of tebuthiuron.

Species	Selection Criteria	Agronomic or Native Species	Endpoints
Plants			
Durum wheat (*Triticum durum*)		Agronomic	Shoot Length

Species	Selection Criteria	Agronomic or Native Species	Endpoints
Blue grama grass (*Bouteloua gracilis*)	Recommended species in Environment Canada Test Methods	Native	Root Length Shoot Dry Mass Root Dry Mass
Western wheatgrass (*Pascopyrum smithii*) Silver sagebrush (*Artemisia cana* subsp. *cana*)	Site-specific species, provide more ecologically relevant endpoints	Native	Emergence (IC_{50} only) Shoot Length Root Length Shoot Dry Mass Root Dry Mass
Invertebrates			
Red wiggler worm (*Eisenia andrei*)	Representative of earthworms		Adult Survival (IC_{50} only) Progeny Production Progeny Dry Mass Progeny Wet Mass
Springtail (Collembola – *Folsomia candida*)	Representative of soil arthropods		Adult Survival (IC_{50} only) Progeny Production

The study objective was site-specific, and the authors did not develop species sensitivity distributions. However, IC_{25} values for each endpoint were calculated and are included in the current assessment.

2.2.2 Tier 1 Ecological Direct Contact Pathway Guidelines for Bromacil and Tebuthiuron

The current Tier 1 Guidelines for the ecological direct contact pathway of bromacil and tebuthiuron are based on the ecotoxicity studies discussed in sections 2.2.1.1 and 2.2.1.2 and summarized in Table 3.

Table 3. Tier 1 surface soil quality guidelines for the ecological direct contact pathway.

		Natural / Agricultural / Residential (mg/kg)	Commercial / Industrial (mg/kg)
Bromacil	Fine	0.20	0.49
	Coarse	0.12	0.20
Tebuthiuron	Fine	0.046	0.60
	Coarse	0.046	0.60

2.2.3 Ecotoxicological Studies

Definitive ecotoxicological tests were conducted by InnoTech in 2020 in order to assess the toxicity of bromacil and tebuthiuron on native plant species in fine-grained soil (Thacker, 2021). Tests were

conducted using Environmental Canada standard tests methods and procedures; however the growth period was extended to 6 weeks and no reference toxicity tests were performed (Environment Canada, 2007; Thacker, 2021). Table 4 indicates the species and endpoints used in the ecotoxicity tests.

Table 4. Species and endpoints selected by Thacker (2021) for the ecotoxicity testing of bromacil and tebuthiuron.

Sterilant	Species	Endpoints
Bromacil	*Bouteloua gracilis*	Shoot Length Root Length Shoot Weight Root Weight
	Pascopyrum smithii	
	Nassella viridula	
	Festuca hallii	
	Koeleria macrantha	
Tebuthiuron	*Bouteloua gracilis*	Shoot Length Root Length – IC_{25} could not be determined Shoot Weight Root Weight
	Nassella viridula	Shoot Length Root Length Shoot Weight Root Weight
	Agropyron dasystachyum	
	Festuca hallii	
	Pascopyrum smithii	Shoot Length Root Length Shoot Weight Root Weight

IC_{25} values were produced from these ecotoxicity tests and utilized in the development of species sensitivity distributions. Response curves used to develop IC_{25} values are presented in Appendix A.

2.3 WEIGHT OF EVIDENCE DATA REQUIREMENTS

The CCME lists several requirements and recommendations for the application of the weight of evidence approach (Section 7.5.5.1 CCME, 2006) in the development of species sensitivity distributions. Table 5 indicates the requirements and how they were met using the datasets discussed in section 2.2.

Table 5. Requirements for the application of the weight of evidence approach.

Requirement or Recommendation	Was the requirement met/applied?	How was the requirement met or mitigated?
A minimum of 10 data points are required from a minimum of three separate studies.	Partially	The number of data points criterion was met for both bromacil and tebuthiuron. Only two studies were available for each chemical, and therefore the requirement for three separate studies was not met. However, it is our professional opinion that the nature of the studies used provides sufficient quality and quantity of data to meet the intent of the requirements. The studies used for the development of the species sensitivity distributions here were designed specifically for the purpose of evaluating the ecological direct contact pathway for bromacil and tebuthiuron. A large number of high quality datapoints are available for each species.
A minimum of two data points from invertebrates and two data points from plant species must be represented.	Yes	For each sterilant, greater than 10 data points were available for native plant species, however less than 10 were available for crop plants and invertebrates. The following datasets were considered, and each included a minimum of two data points for plants and invertebrates: All plants + all invertebrates Native plants + all invertebrates Crop plants + all invertebrates (tebuthiuron had a dataset of <10 total)
When a sufficient dataset is available, plant and invertebrate data points should be evaluated separately. Soil Quality Guidelines (SQG) should be derived from the lowest guideline of the two datasets. However, plant and invertebrate data may be combined to meet dataset requirements.	No	
Redundant data points for a single species should be composited and the geomean presented.	Yes	Redundant endpoints were available for blue gramma grass (*Bouteloua gracilis*) exposed to both bromacil and tebuthiuron. The respective endpoints were composited. Endpoints for the wet weight and dry weight of invertebrates were also composited as these are considered to be causally connected.
When different response levels are available, only the EC_{25}/IC_{25} (or closest) values should be included.	Yes	Only EC_{25}/IC_{25} values were included for the development of the species sensitivity distributions.

Requirement or Recommendation	Was the requirement met/applied?	How was the requirement met or mitigated?
When sufficient data exists, coarse-grained and fine-grained soils should be considered separately. However, data points from different soil types of the same species and response level may be combined based on professional judgement.	No	Insufficient data was available for coarse-grained scenarios; therefore, only fine-grained scenarios were examined.
An uncertainty factor should be applied if: • Only 3 studies are available, • Fewer than 3 taxonomic groups are represented, • Greater than 50% of the data for either plant of invertebrates is below the 25th percentile, • Toxicity studies were short-term, • More than 50% of studies were based on low bioavailability conditions	No	While only 2 studies were available, the data presented within each were of high quality. More than three taxonomic groups were represented, and endpoints for plants and invertebrates were well distributed. The studies were not short term and were not conducted under conditions of low bioavailability.

2.4 SPECIES SENSITIVITY DISTRIBUTIONS

The term species sensitivity distribution refers to the distribution of how the concentration at which effects are seen varies across a range of different species and endpoints. Species sensitivity distributions were calculated in this document from EC_{25}/IC_{25} values based on guidance provided in the CCME (2006) protocol. Data points for the group of species and endpoints being considered were compiled and assigned a rank from smallest to largest. Rank percentile was then determined using the following equation:

$$j = \left(\frac{i}{n+1}\right)100$$

Where:

j = rank percentile

i = rank of the data point in the data set

n = total number of data points in the data set

A distribution of rank percentile versus soil concentration was developed in R version 4.0.3 and the 25th and 50th percentile of the distribution was determined based on a logarithmic regression of the data. The Estimated Species Sensitivity Distribution – 25th percentile ($ESSD_{25}$) and the Estimated Species Sensitivity Distribution – 50th percentile ($ESSD_{50}$) are the 25th and 50th percentile values of the distribution, respectively. TEC and ECL values are then generated from the ESSD values. The ECL is equivalent to the $ESSD_{50}$, the TEC is the quotient of the $ESSD_{25}$ and an uncertainty factor. The uncertainty factor was set as a value of 1 given the quality of the studies used as discussed in section 2.2.

3. RESULTS AND DISCUSSION

3.1 SUMMARY OF AVAILABLE DATA

IC_{25} values were taken from Stantec (2008, 2012) and Thacker (2021) ecotoxicity studies and used to develop three datasets:

- all data;
- native plants plus all invertebrate data; and,
- agronomic plants plus all invertebrate data.

One of the objectives of the project was to evaluate the sensitivity of native plant species to bromacil and tebuthiuron. All available data were examined to give the most complete dataset for the development of the SSD. However, following the procedures and minimum data requirements outlined in section 2.3, it is also possible to separate datapoints for plants based on if they were native or agronomic species. By developing these three datasets it was possible to evaluate the difference in sensitivity between native and agronomic plant species while also considering a larger dataset with greater confidence.

IC_{25} data are summarized in Tables 6 and 7 and full datasets are available in Appendix B.

Table 6. Summary of IC_{25} datapoints used in the development of species sensitivity distributions for bromacil.

Dataset	Source	IC_{25} Datapoints			
		Native Plants	Crop Plants	Invertebrates	Total
All data	Thacker (2021)	11	0	0	11
	Stantec (2012)	1	9	4	14
	Geomean of both studies	4	0	0	4
	Total	16	9	4	29
Native+ Invertebrates	Thacker (2021)	11	0	0	11
	Stantec (2012)	1	0	4	5
	Geomean of both studies	4	0	0	4
	Total	16	0	4	20

Dataset	Source	IC_{25} Datapoints			
		Native Plants	Crop Plants	Invertebrates	Total
Crop + Invertebrates	Thacker (2021)	0	0	0	0
	Stantec (2012)	0	9	4	13
	Geomean of both studies	0	0	0	0
	Total	0	9	4	13

Table 7. Summary of IC_{25} datapoints used in the development of species sensitivity distributions for tebuthiuron.

Dataset	Source	IC_{25} Datapoints			
		Native Plants	Crop Plants	Invertebrates	Total
All data	Thacker (2021)	10	0	0	10
	Stantec (2008)	8	4	3	15
	Geomean of both studies	3	0	0	3
	Total	21	4	3	28
Native+ Invertebrates	Thacker (2021)	10	0	0	10
	Stantec (2008)	8	0	3	11
	Geomean of both studies	3	0	0	3
	Total	21	0	3	24
Crop + Invertebrates	Thacker (2021)	0	0	0	0
	Stantec (2008)	0	4	3	7
	Geomean of both studies	0	0	0	0
	Total	0	4	3	7

IC_{25} values were provided by Thacker (2021) based on ecotoxicity datasets which either included or excluded outliers as determined from the species response regressions presented in Appendix A. Species sensitivity distributions were developed for both types of dataset (including outliers or excluding outliers).

3.2 SPECIES SENSITIVITY DISTRIBUTIONS

Species sensitivity distributions (SSD) were developed for bromacil and tebuthiuron considering three datasets (all data, native plants + invertebrates, and crop plants +invertebrates) as indicated in section 3.1. Figures 1 to 3 show SSDs for bromacil while Figures 4 to 6 show those of tebuthiuron. In all Figures, the red line represents the predicted regression while the blue lines represent bootstrapped values and dashed lines the confidence intervals. Arrows indicate the 25th and 50th percentile.

As indicated in section 3.1, data were made available from the Thacker (2021) studies which either included or excluded outliers. Little variability was observed between the SSDs based on datasets that included outliers versus those that excluded outliers, therefore only the SSDs with the most complete dataset (including outliers) are presented below. The minor variation in TEC and ECL values between datasets with and without outliers are summarized in section 3.3.

The associated regressions presented in Figures 1 to 6 were generally of good fit. Of the species examined, *Koeleria macrantha*, *Festuca hallii*, and *Nassella viridula* were generally the most sensitive to bromacil and *Festuca hallii*, *Agropyron dasystachyum*, and *Nassella viridula* were generally the most sensitive to tebuthiuron. Therefore, the most sensitive species to both sterilants were native plants.

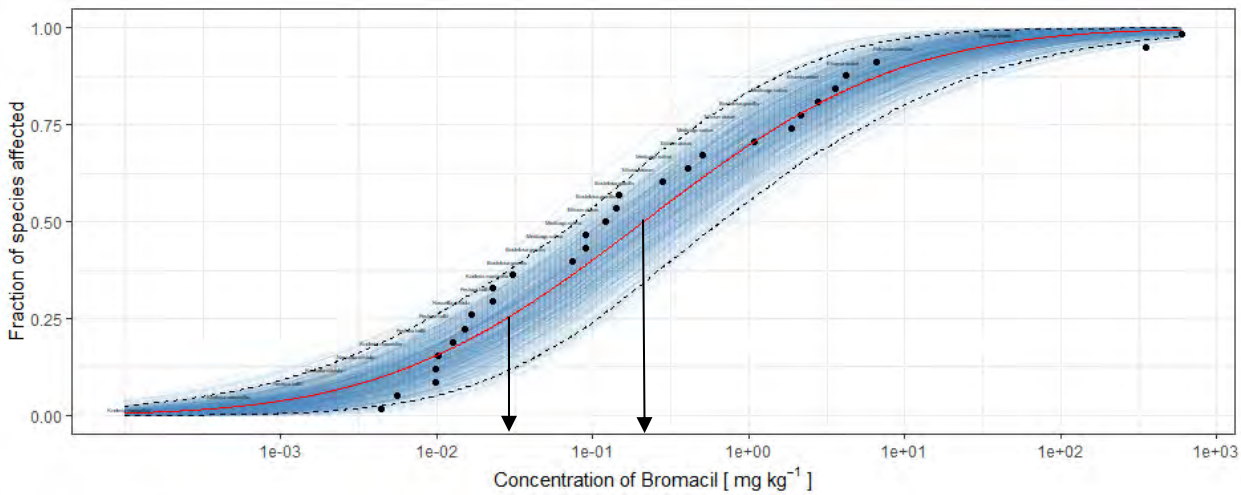

Figure 1. Species sensitivity distributions for all plant + invertebrate species exposed to bromacil.

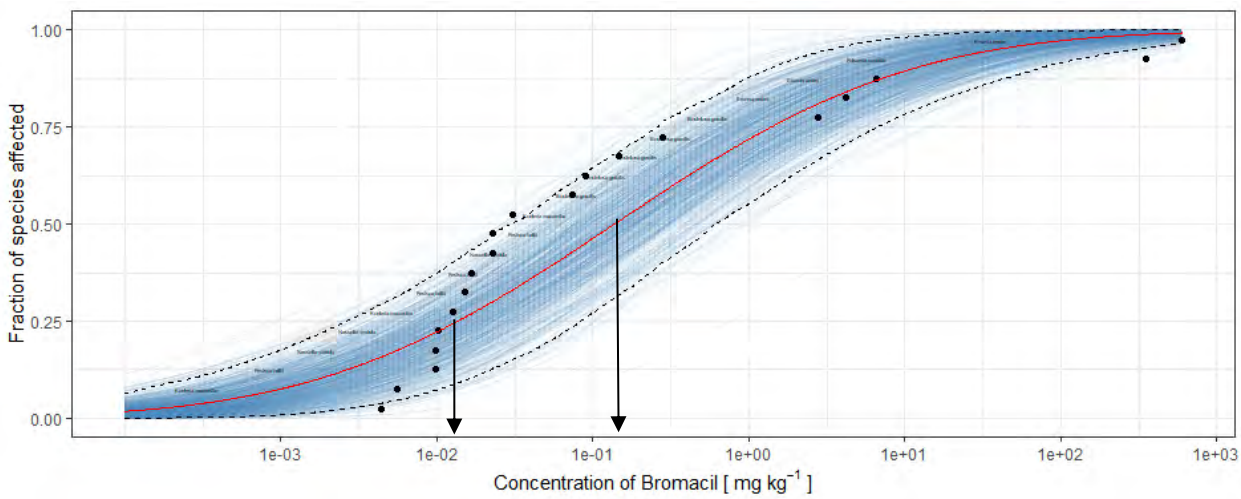

Figure 2. Species sensitivity distributions for native plant + invertebrate species exposed to bromacil.

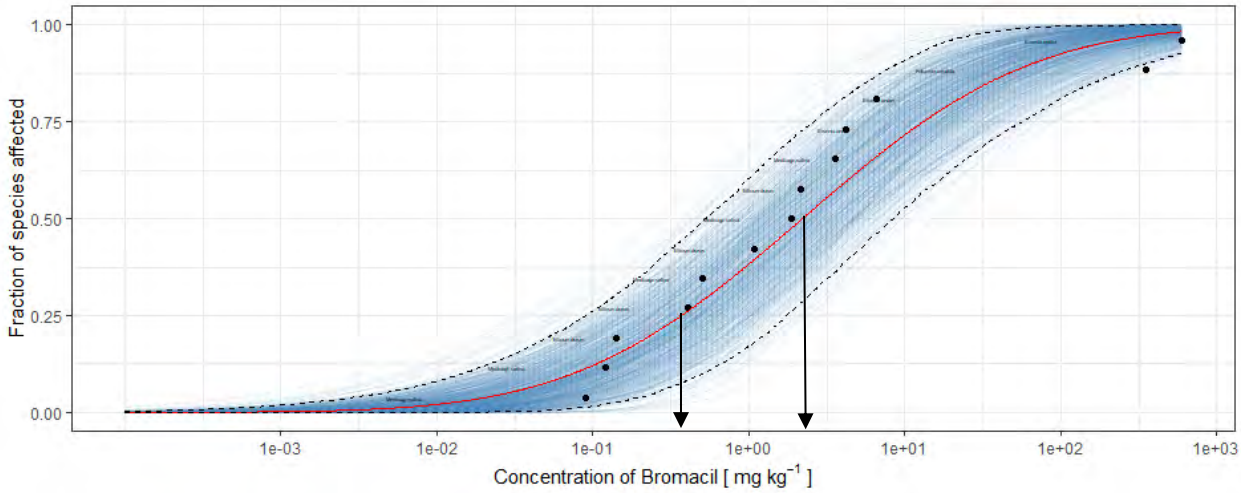

Figure 3. Species sensitivity distributions for crop plants + invertebrate species exposed to bromacil.

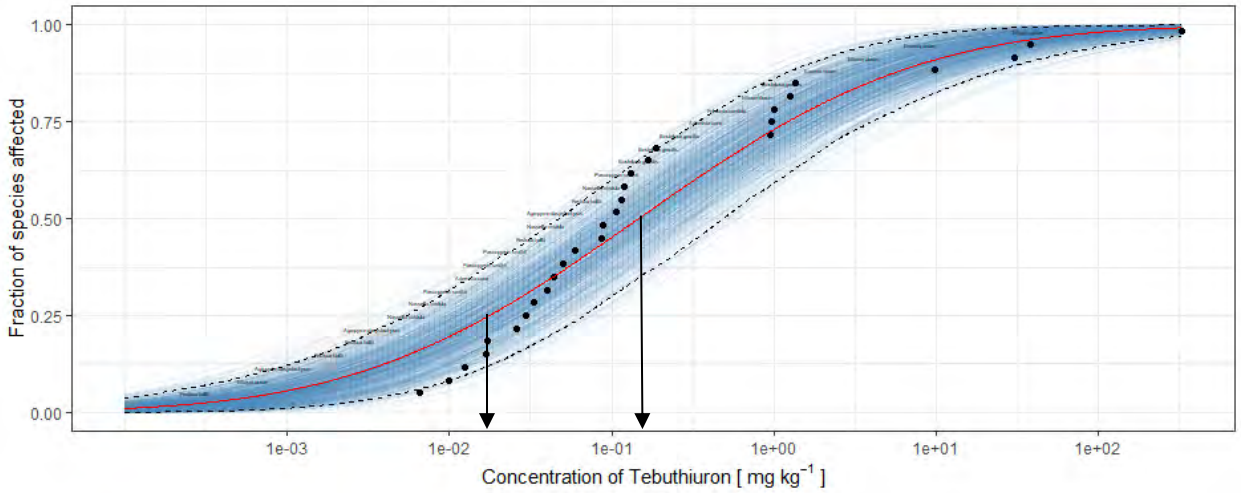

Figure 4. Species sensitivity distributions for all plant + invertebrate species exposed to tebuthiuron.

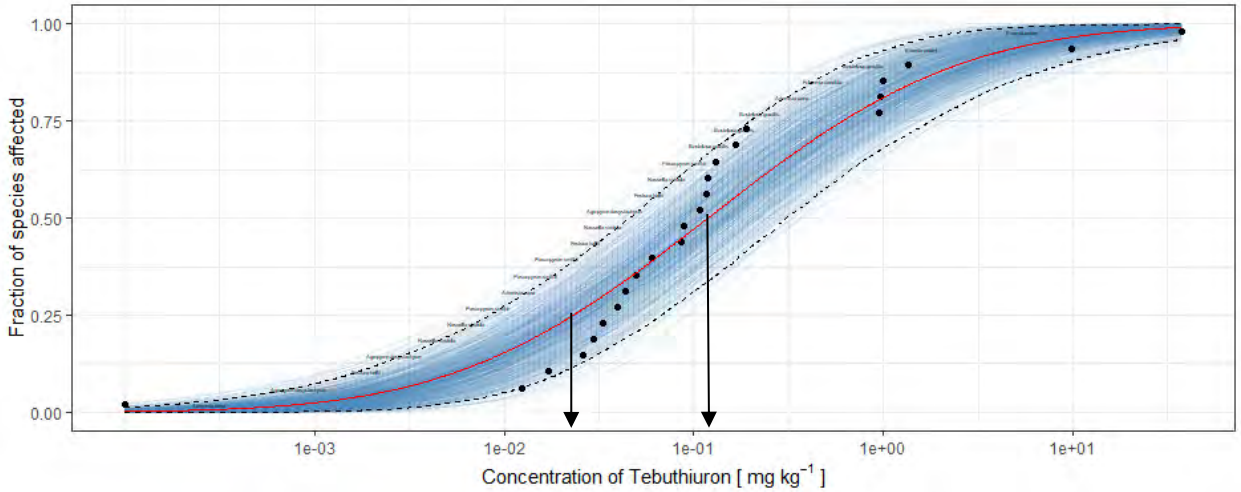

Figure 5. Species sensitivity distributions for native plant + invertebrate species exposed to tebuthiuron.

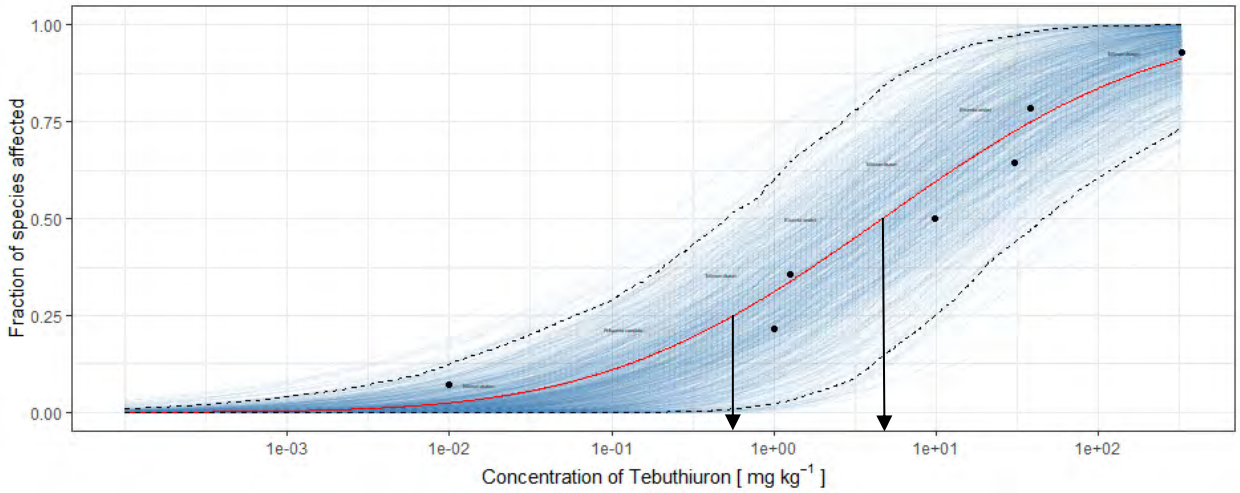

Figure 6. Species sensitivity distributions for crop plant and invertebrate species exposed to tebuthiuron.

3.3 DERIVED EFFECTS CONCENTRATIONS

IC_{25} values were provided by Thacker (2021) based on ecotoxicity datasets which either included or excluded outliers as determined from the species response regressions presented in Appendix A. For each dataset (i.e., all plants + invertebrates), the 25th and 50th percentiles (TEC and ECL) were determined based on IC_{25} values which either included all original data or excluded outliers. There was little variation between the resulting 25th and 50th percentiles of the datasets which used IC_{25} values with outliers and those that did not (Table 8). Therefore, the TEC and ECL values based on the larger dataset (including outliers) were carried forward (Table 9). This dataset included a larger number of datapoints and therefore provided a higher degree of confidence in the distribution.

Table 8. Comparison of results including or excluding outliers.

Sterilant	Dataset	Outliers*	25th percentile (mg/kg)	50th percentile (mg/kg)	n studies	n independent data points
Bromacil	All data	Included	0.027841	0.211355	2	29
		Excluded	0.028365	0.213916	2	29
	Native plants + Invertebrates	Included	0.013588	0.137198	2	20
		Excluded	0.013923	0.139615	2	20
	Crop plants + Invertebrates	Included	0.3693	2.198001	1	13
		Excluded	0.3693	2.198001	1	13

Sterilant	Dataset	Outliers*	25th percentile (mg/kg)	50th percentile (mg/kg)	n studies	n independent data points
Tebuthiuron	All data	Included	0.017649	0.146087	2	28
		Excluded	0.018194	0.149373	2	28
	Native plants + Invertebrates	Included	0.023225	0.118818	2	24
		Excluded	0.02416	0.122168	2	24
	Crop plants + Invertebrates	Included	0.56378	4.639896	1	7
		Excluded	0.56378	4.639896	1	7

*TEC and ECL values were calculated based on IC_{25} data that included or excluded outliers

Table 9. Derived effects concentrations.

Sterilant	Dataset	TEC (25th percentile) (mg/kg)	ECL (50th percentile) (mg/kg)	n studies	n independent data points
Bromacil	All data	0.028	0.21	2	29
	Native plants + Invertebrates	0.014	0.14	2	20
	Crop plants + Invertebrates	0.37	2.2	1	13
Tebuthiuron	All data	0.018	0.15	2	28
	Native plants + Invertebrates	0.023	0.12	2	24
	Crop plants + Invertebrates	0.56	4.6	1	7

3.4 SOIL QUALITY GUIDELINES FOR THE ECOLOGICAL SOIL CONTACT PATHWAY

The CCME (2006) protocol for determining soil quality guidelines (SQG) for the protection of the ecological direct contact pathway indicates that the TEC value may be used to derive the SQGs for the natural, agricultural, and residential land uses and the ECL can be used to determine the SQGs for the commercial and industrial land uses. The standard practice is to develop soil quality guidelines based on the complete dataset of plants and invertebrates and therefore, Table 10 provides revised Tier 1 Guidelines for the ecological direct contact pathway from bromacil and tebuthiuron based on the TEC and ECL values of the "All Data" datasets, as indicated in Table 6.

Table 10. Ecological direct contact surface soil quality guidelines – Fine.

Sterilant	Guideline	Natural/Residential/ Agricultural	Commercial/Industrial
Bromacil	Current Tier 1 (mg/kg)	0.20	0.49
	Revised[1] (mg/kg)	0.028	0.21
Tebuthiuron	Current Tier 1 (mg/kg)	0.046	0.60
	Revised[1] (mg/kg)	0.018	0.15

[1]Based on an expanded dataset which includes a greater number of native plant species than the original Tier 1 Guidelines.

The SQGs guidelines which include the new data developed by Thacker (2021) for native plants species are generally lower than those based on the historical dataset used to develop the Tier 1 Guidelines alone. The species sensitivity distributions presented in section 3.2 indicate that several of the native plants evaluated in Thacker (2021) were the most sensitive to both sterilants.

Given the quality and quantity of data available, it was also possible to generate separate datasets for native plant species and agronomic plant species as well as a combined dataset for both. Alternative guidelines could be based on the datasets which separated the plant data based on their status as native or crop plants. The SQG for the natural land use could be based on the TEC of the native plants + invertebrates dataset, while the SQG for the agricultural land use could be based on the TEC of the crop plants + invertebrates dataset. The full dataset would be relevant for residential land (using the TEC to derive the SQGs) and for commercial and industrial land (using the ECL to derive the SQGs). However, an insufficient number of datapoints are available for tebuthiuron based solely on crop plants + invertebrates (n=<10), therefore the SQG for the agricultural land use would need to be based on both native and agronomic species. These alternative values are presented in Table 11.

Table 11. Possible alternative ecological direct contact surface soil quality guidelines – Fine.

Sterilant	Guideline	Natural	Residential	Agricultural	Commercial/ Industrial
Bromacil	Current Tier 1 (mg/kg)	0.20			0.49
	Alternate (mg/kg)	0.014	0.028	0.37	0.21
Tebuthiuron	Current Tier 1 (mg/kg)	0.046			0.60
	Alternate (mg/kg)	0.023	0.018	0.018	0.15

Given that native plant species were found to be the most sensitive to both bromacil and tebuthiuron, the inclusion of these species in a dataset significantly impacted the conservatism of the overall guideline. The resulting guidelines were lowest when datasets included only native plants, highest when only crop plants were included and intermediate when both native and agronomic plant species were included. It should be noted that the alternate Commercial/Industrial guideline in Table 11 for bromacil is more conservative than the Agricultural guideline in Table 11. This is counterintuitive, and likely does not make practical sense, but is because the agricultural guideline was based on a dataset which included only agronomic plant species, while the Commercial/Industrial guideline was based on both agronomic and

native species. For this reason, it may be most appropriate to use the internally consistent set of guidelines presented in Table 10.

The current investigation focused solely on fine-grained soils and therefore modifications to the current coarse-grained guidelines are not provided here. However, it is noted that the current Tier 1 Guidelines for tebuthiuron in coarse soils were developed based on fine-grained studies due to the absence of any appropriate data in coarse-grained soils.

4. SUMMARY AND CONCLUSIONS

This project expanded the existing ecotoxicological dataset for bromacil and tebuthiuron by assessing their toxicity to a range of native plant species. The work reported here developed revised soil quality guidelines protective of the ecological direct contact exposure pathway for bromacil and tebuthiuron based on species sensitivity distributions from the expanded datasets. The revised soil quality guidelines are based on species sensitivity distributions of the complete available datasets including both native plant species and agronomic plant species. Possible alternative guidelines using the native and agronomic plant datasets more selectively were discussed in Section 3. Guidelines were developed for fine-grained soil only because the new ecotoxicological data were based on tests conducted in fine-grained soils.

The revised SQGs based on the complete available datasets of both native and agronomic plant species are as follows:

- Bromacil – Natural/Residential/Agricultural: 0.028 mg/kg
- Bromacil – Commercial/Industrial: 0.21 mg/kg
- Tebuthiuron – Natural/Residential/Agricultural: 0.018 mg/kg.
- Tebuthiuron – Commercial/Industrial: 0.15 mg/kg tebuthiuron.

The revised guidelines are more conservative than previous guidelines based on the incorporation of new data for native plant species which appear to be more sensitive to bromacil and tebuthiuron than those species examined historically.

5. REFERENCES

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6. ACKNOWLEDGEMENTS

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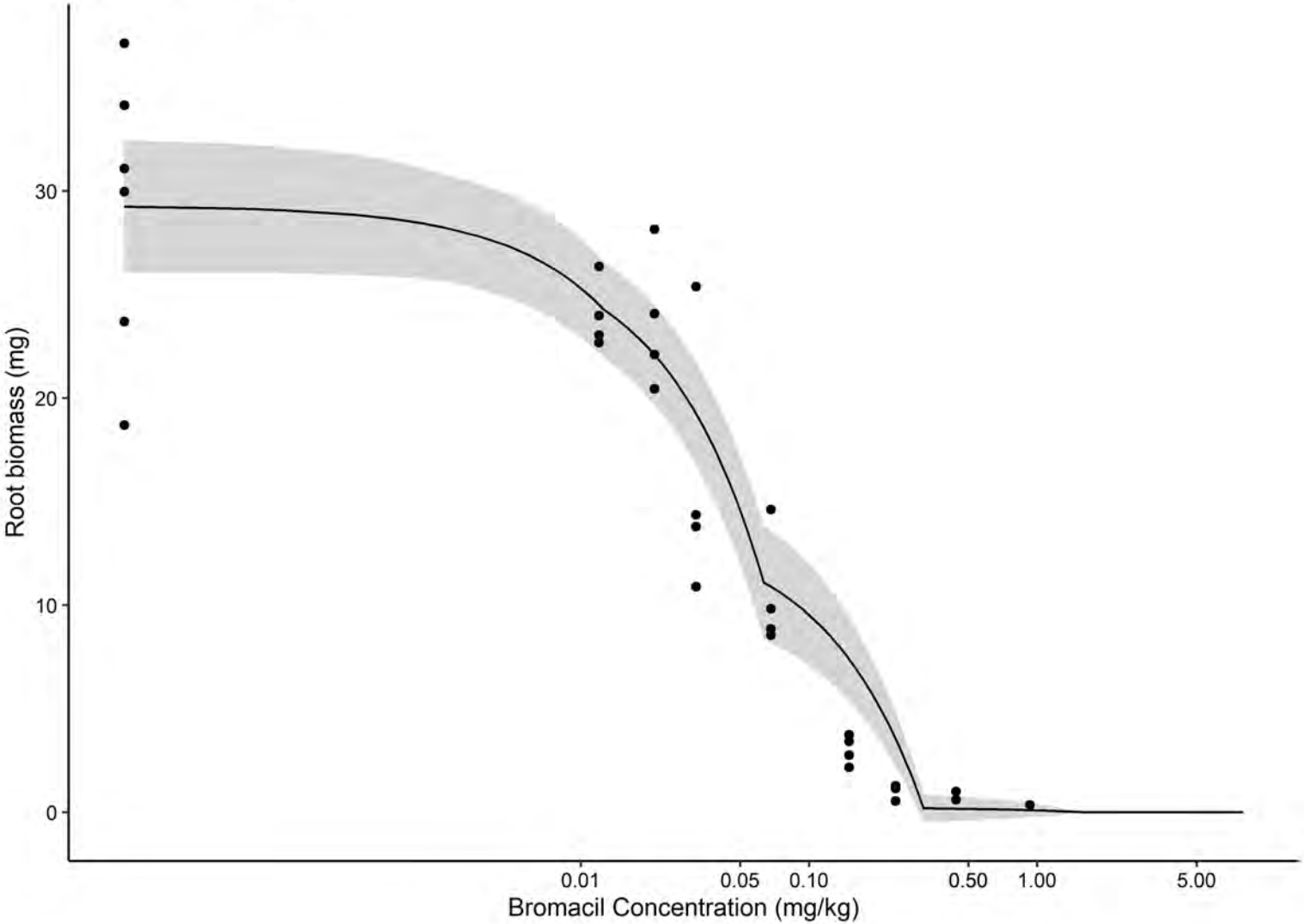
7. LIST OF APPENDICES

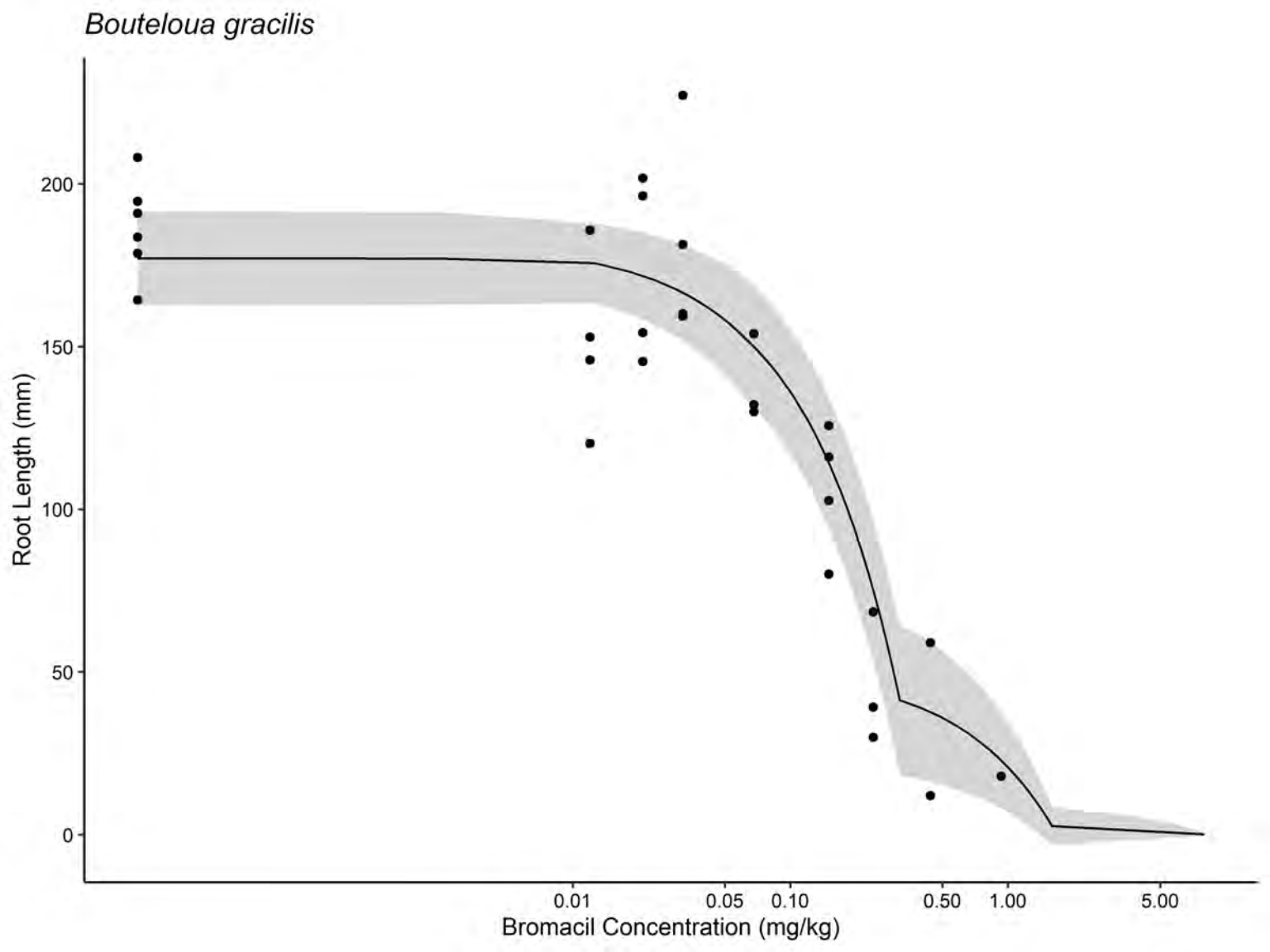
APPENDIX A: IC_{25} Endpoint Regressions

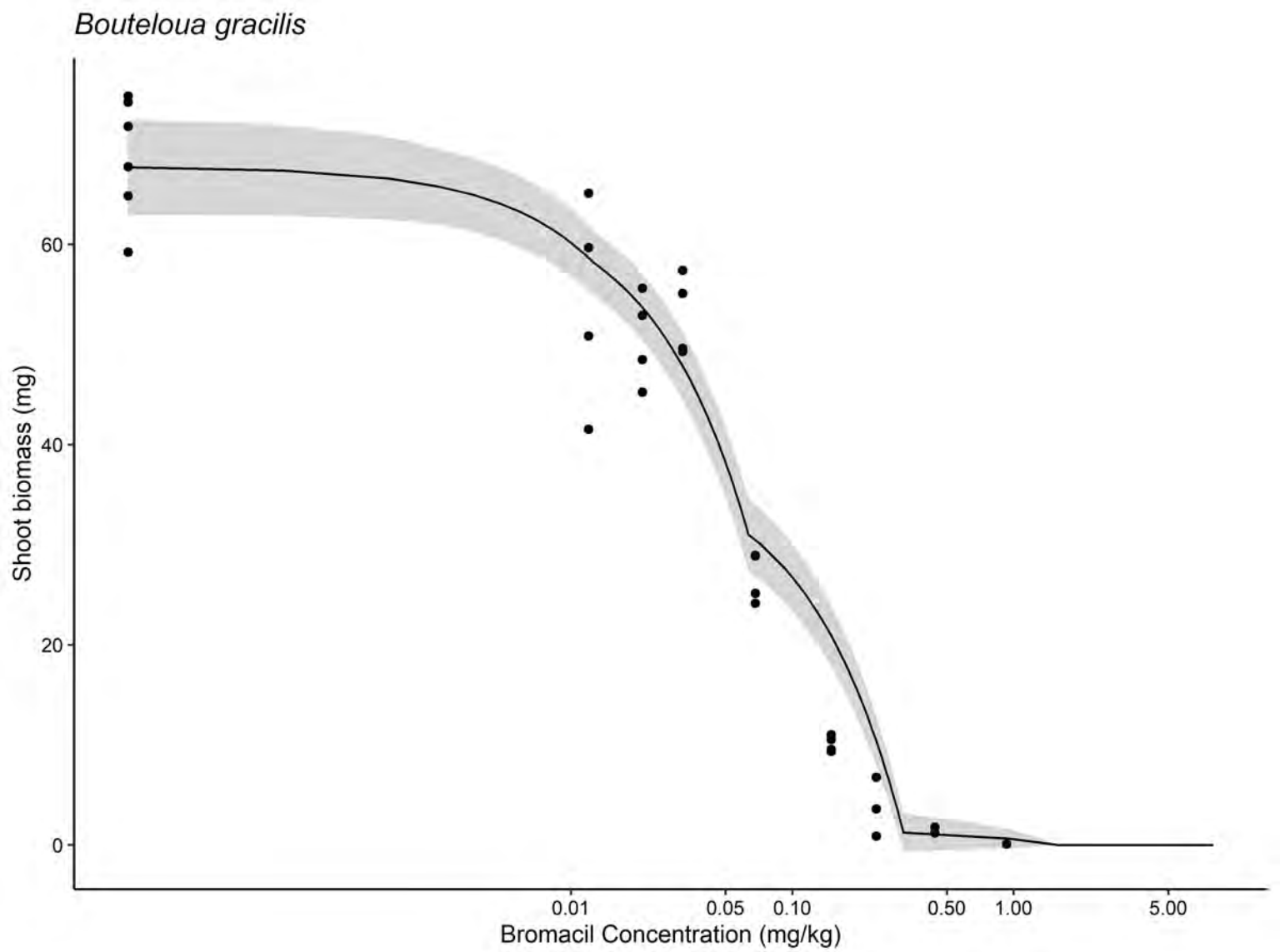
APPENDIX B: IC_{25} Data Summary

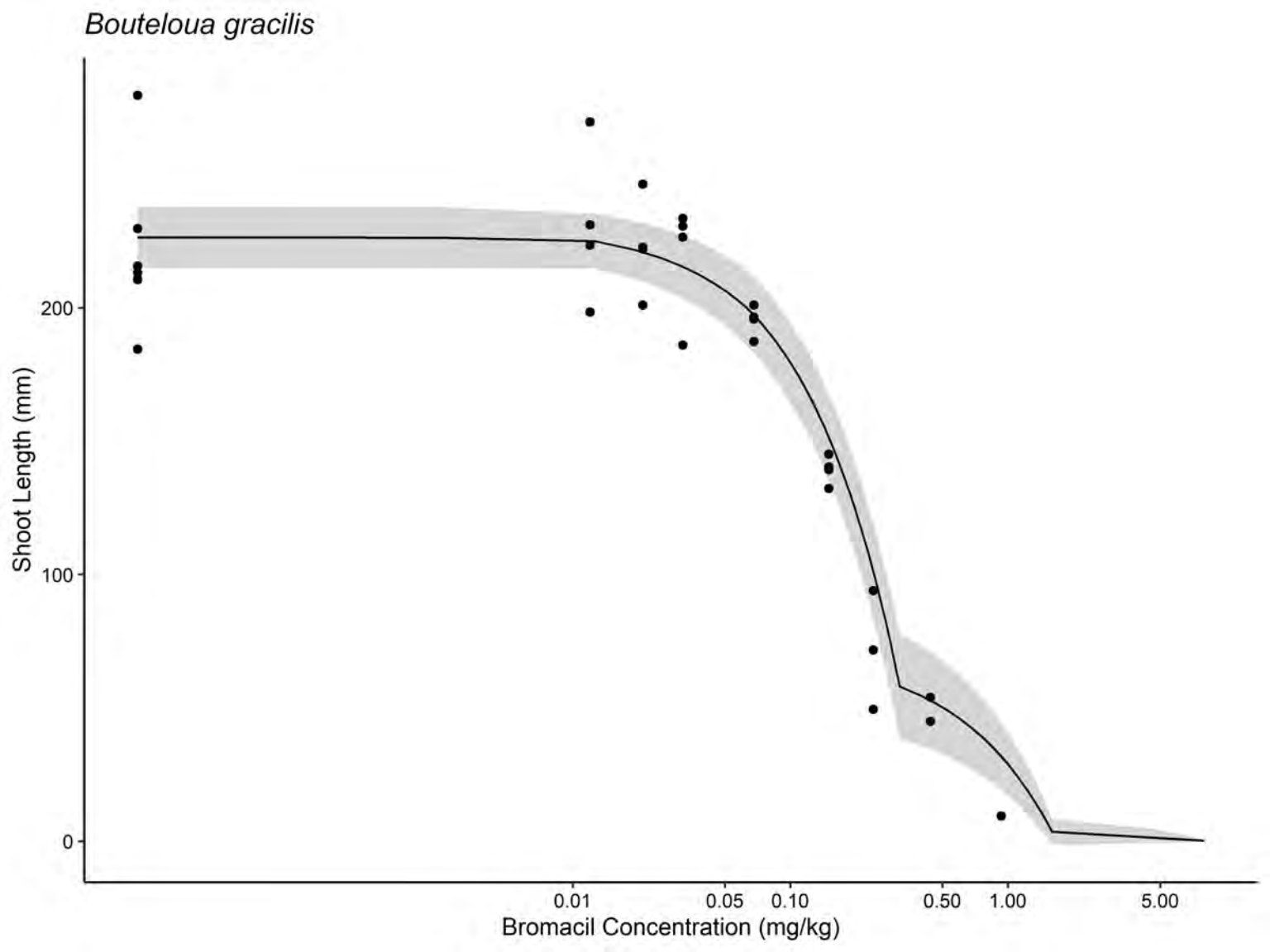
APPENDIX A: IC_{25} Endpoint Regressions

Bouteloua gracilis

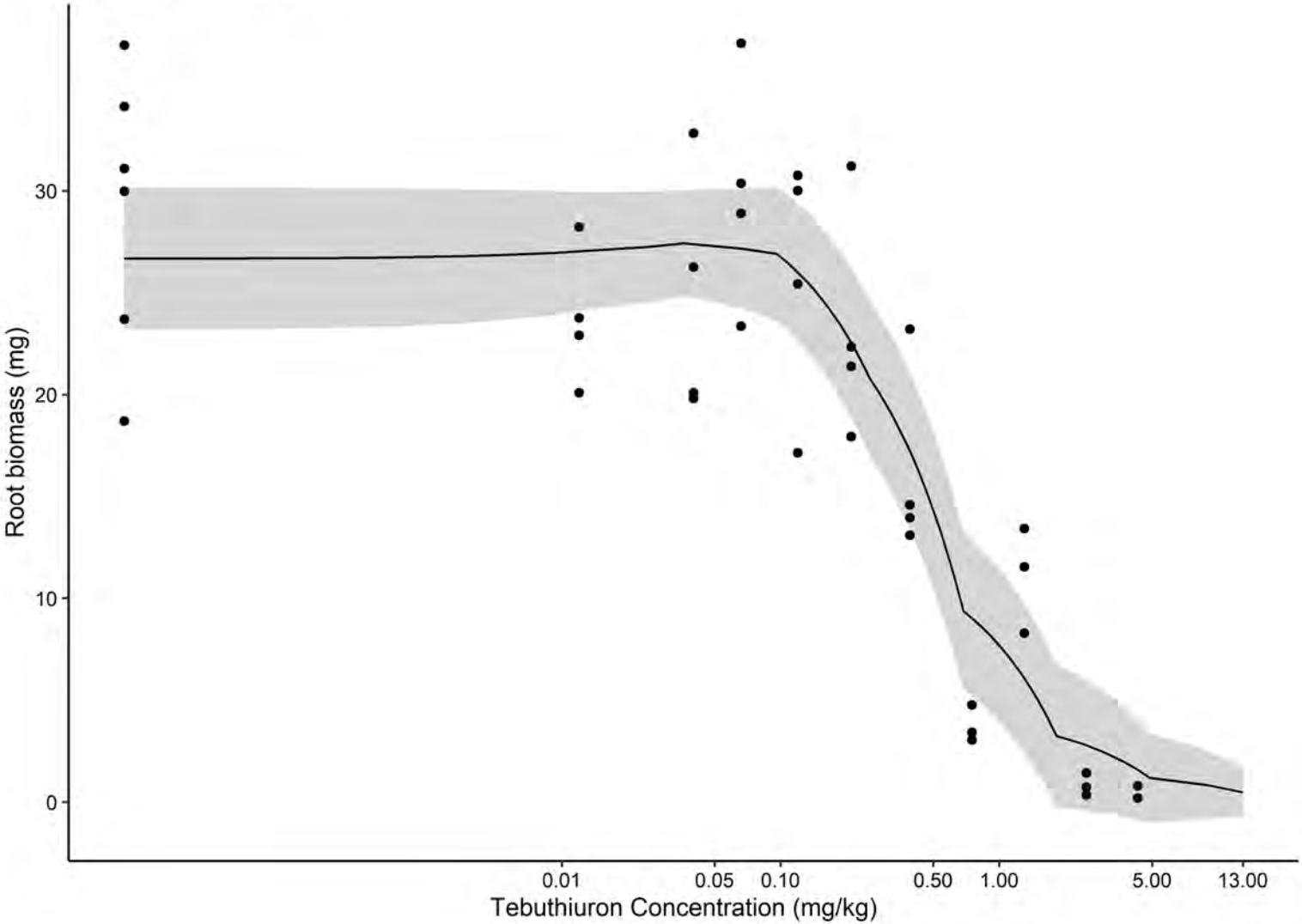


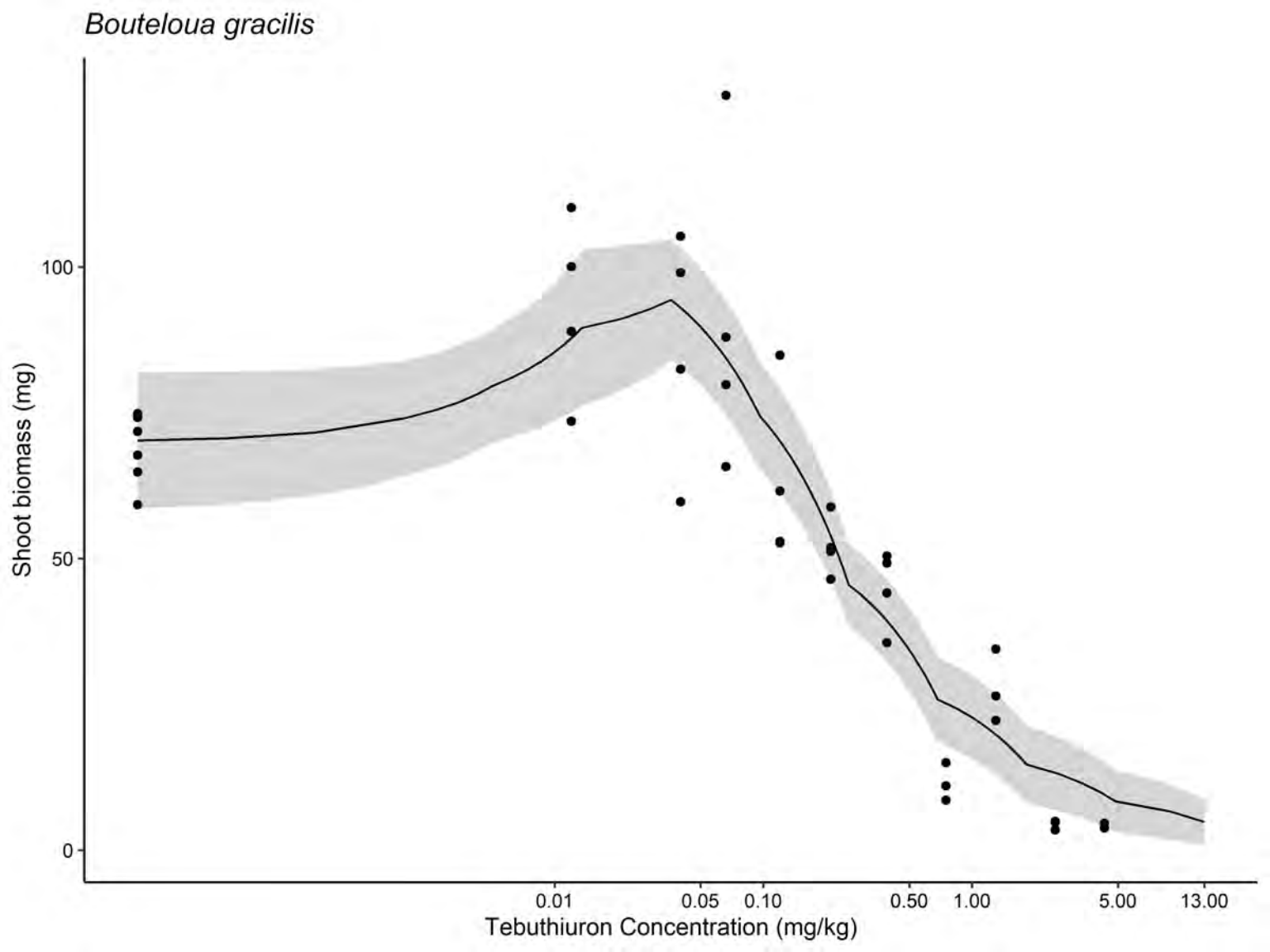

Bouteloua gracilis
Root Length (mm)
200
150
100
50
0
0.01
0.05
0.10
0.50
1.00
5.00
Bromacil Concentration (mg/kg)

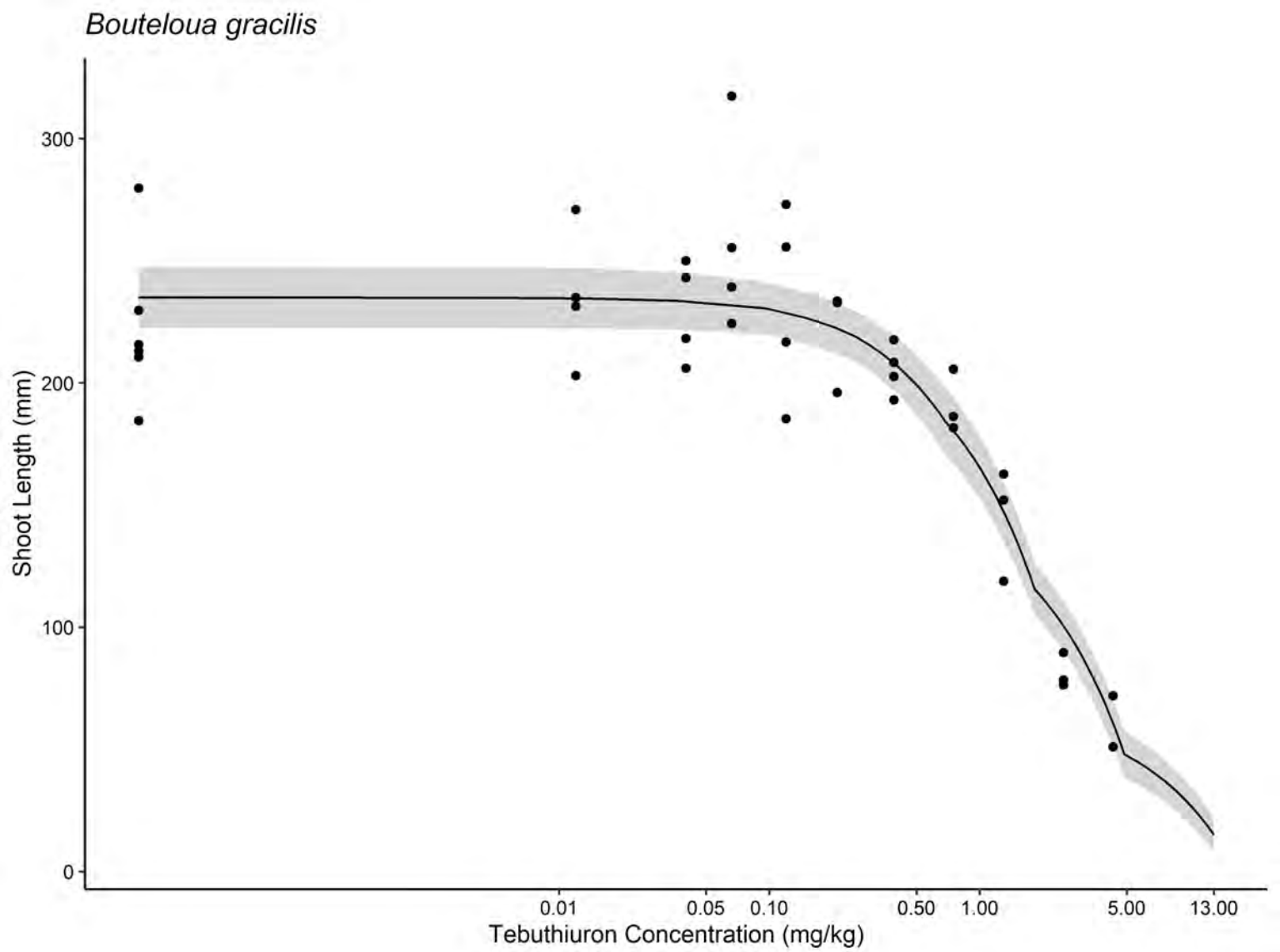

Bouteloua gracilis
Shoot biomass (mg)
60
40
20
0
0.01
0.05
0.10
0.50
1.00
5.00
Bromacil Concentration (mg/kg)

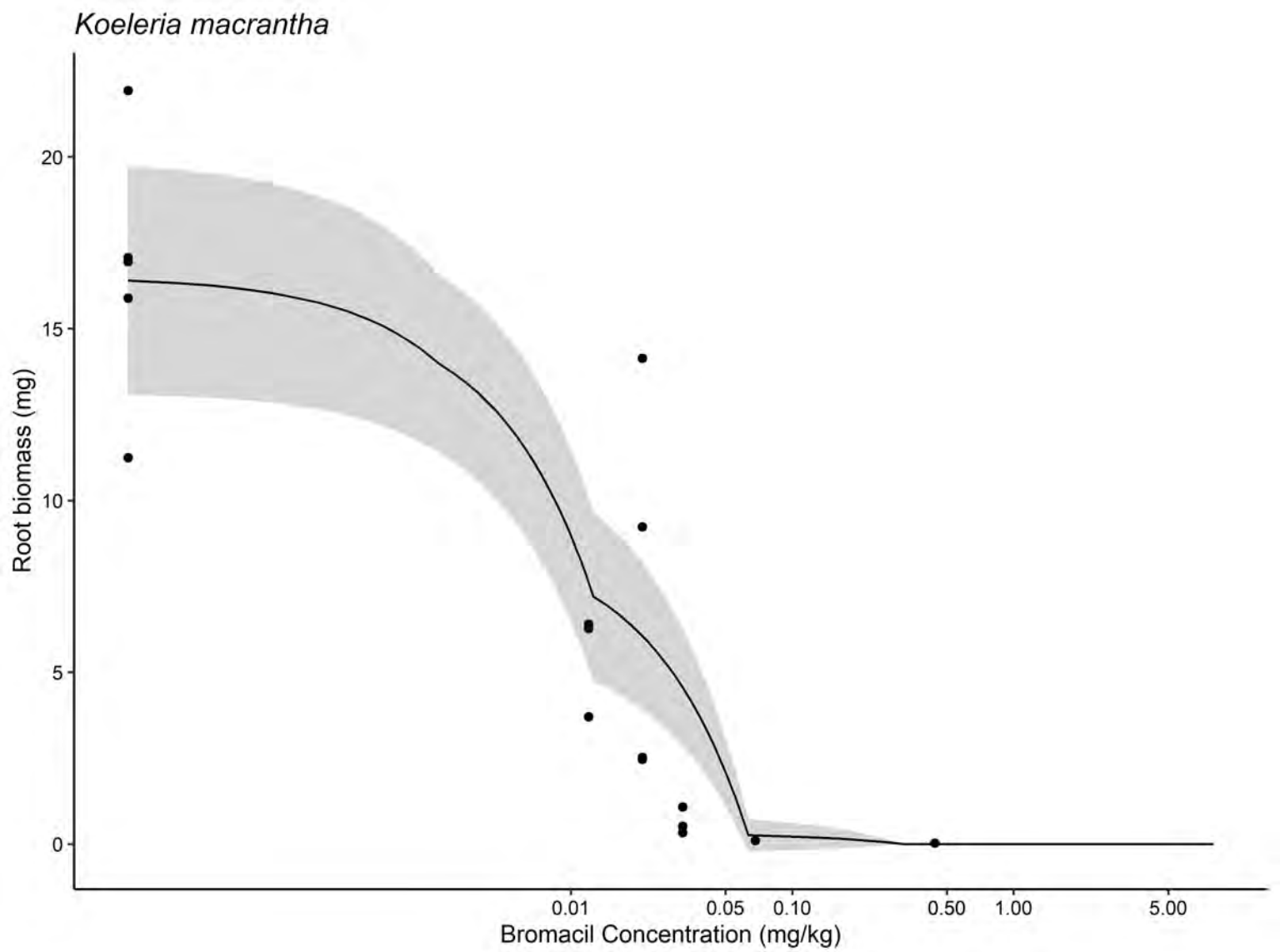

Bouteloua gracilis
Shoot Length (mm)
200
100
0
0.01
0.05
0.10
0.50
1.00
5.00
Bromacil Concentration (mg/kg)

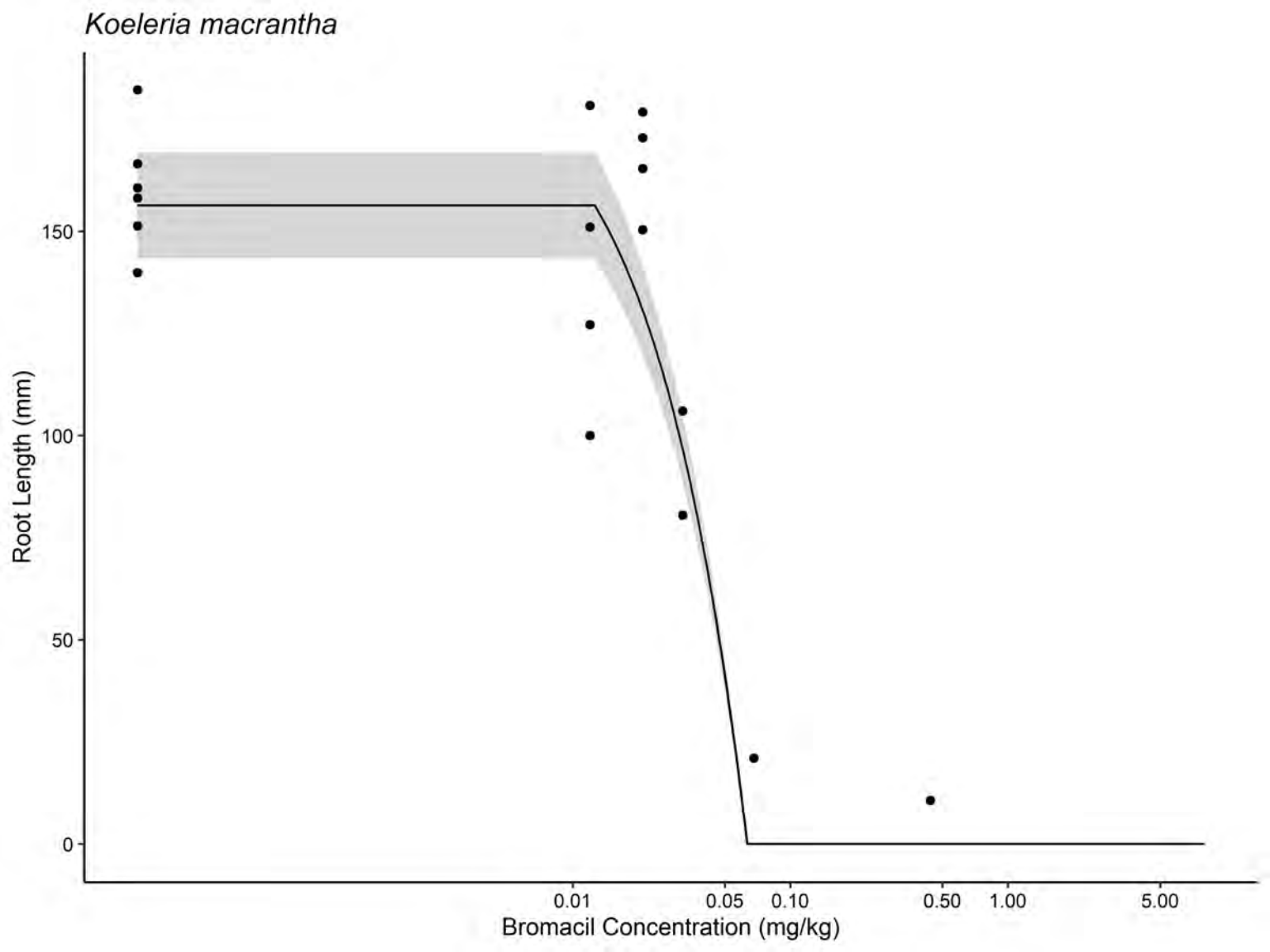
Bouteloua gracilis

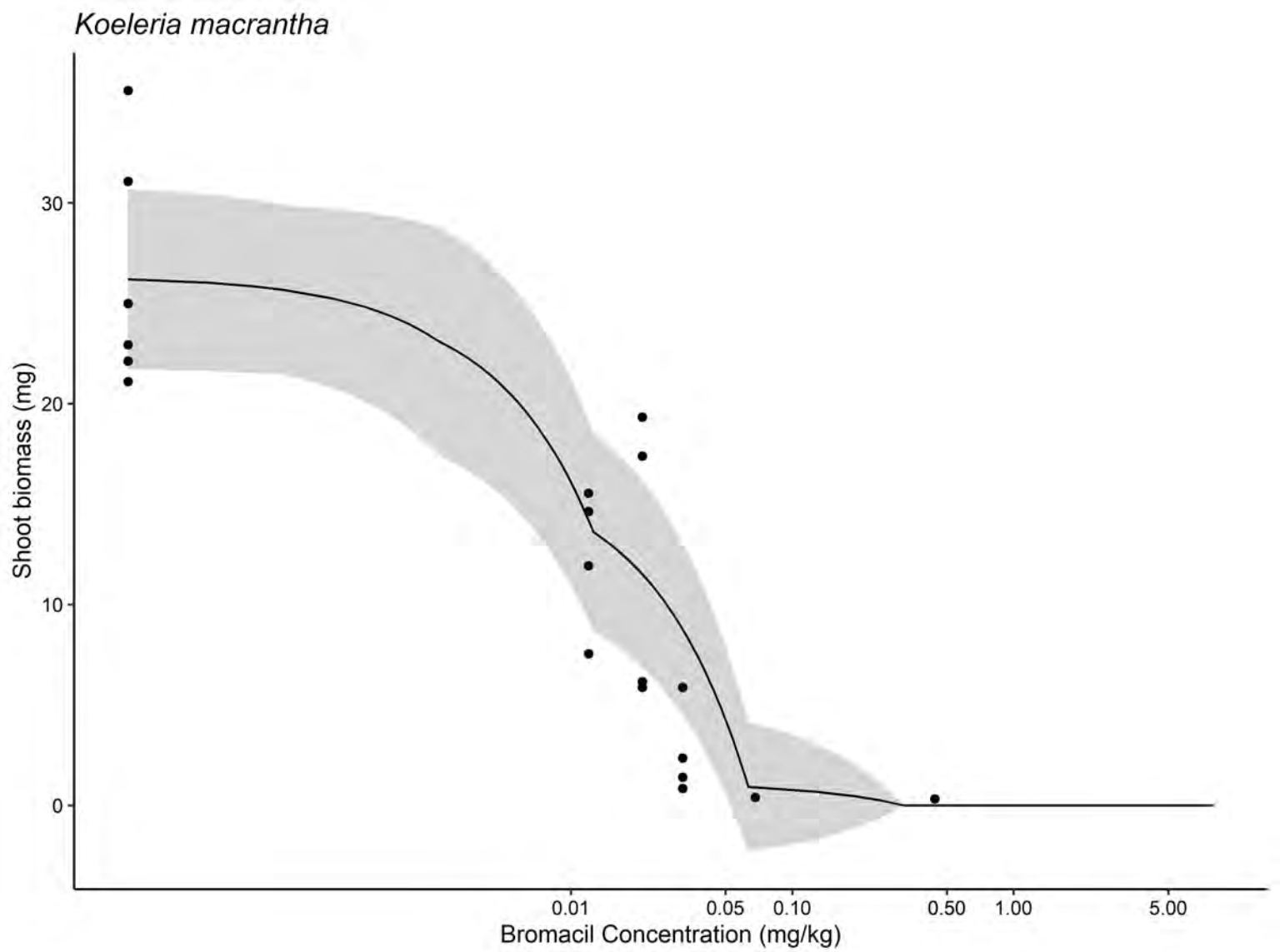


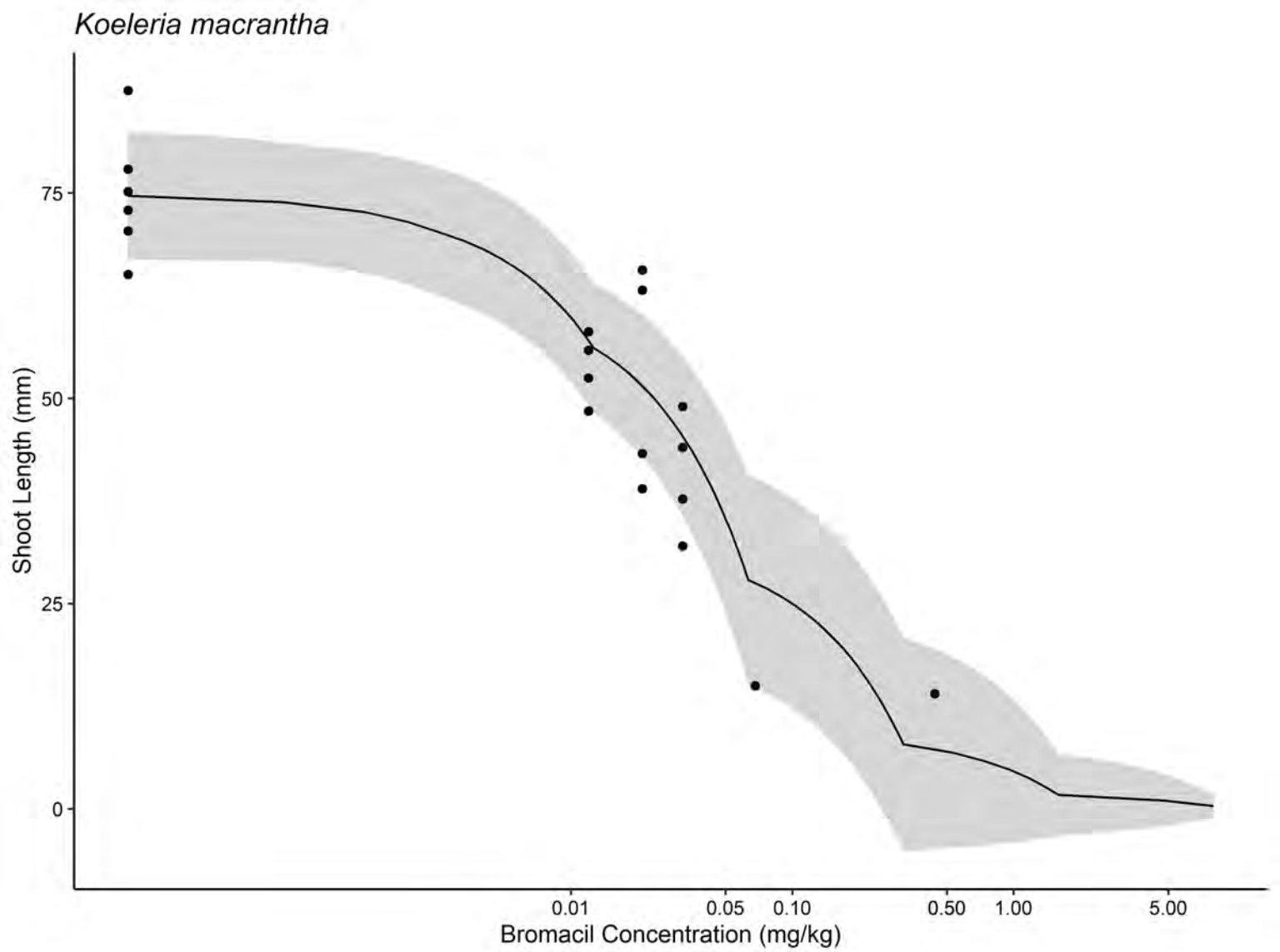

Bouteloua gracilis
Shoot biomass (mg)
100
50
0
0.01
0.05
0.10
0.50
1.00
5.00
13.00
Tebuthiuron Concentration (mg/kg)


Bouteloua gracilis
Shoot Length (mm)
300
200
100
0
0.01
0.05
0.10
0.50
1.00
5.00
13.00
Tebuthiuron Concentration (mg/kg)


Koeleria macrantha
Root biomass (mg)
20
15
10
5
0
0.01
0.05
0.10
0.50
1.00
5.00
Bromacil Concentration (mg/kg)


Koeleria macrantha
Root Length (mm)
150
100
50
0
0.01
0.05
0.10
0.50
1.00
5.00
Bromacil Concentration (mg/kg)


Koeleria macrantha
Shoot biomass (mg)
30
20
10
0
0.01
0.05
0.10
0.50
1.00
5.00
Bromacil Concentration (mg/kg)


Koeleria macrantha
Shoot Length (mm)
75
50
25
0
0.01
0.05
0.10
0.50
1.00
5.00
Bromacil Concentration (mg/kg)

APPENDIX B: IC_{25} Data Summary

Table B1. Bromacil All Data

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Crop	*Medicago sativa*	root dry mass	0.12
		Medicago sativa	root length	0.09
		Medicago sativa	shoot dry mass	0.5
		Medicago sativa	shoot length	1.87
		Medicago sativa	survival	3.56
		Triticum durum	root dry mass	0.14
		Triticum durum	root length	1.08
		Triticum durum	shoot dry mass	0.41
		Triticum durum	Shoot length	2.14
	Invertebrate	*Eisenia andrei*	adult survival	600
		Eisenia andrei	progeny production	6.63
		Folsomia candida	progeny production	350.75
	Native	*Bouteloua gracilis*	survival	2.78
Geomean	Invertebrate	*Eisenia andrei*	progeny mass	4.20014
	Native	*Bouteloua gracilis*	root dry mass	0.08986
		Bouteloua gracilis	Root length	0.14588
		Bouteloua gracilis	shoot dry mass	0.07374
		Bouteloua gracilis	Shoot length	0.28098
Innotech	Native	*Festuca hallii*	Root length	0.00981
		Festuca hallii	Root weight	0.01513
		Festuca hallii	Shoot length	0.02302
		Festuca hallii	Shoot weight	0.01681
		Koeleria macrantha	Root length	0.03058
		Koeleria macrantha	Root weight	0.00438
		Koeleria macrantha	Shoot length	0.01265
		Koeleria macrantha	Shoot weight	0.00554
		Nassella viridula	Root weight	0.01032
		Nassella viridula	Shoot length	0.02283
		Nassella viridula	Shoot weight	0.00992

Table B2. Bromacil All Data - No Outliers

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Crop	*Medicago sativa*	root dry mass	0.12
		Medicago sativa	root length	0.09
		Medicago sativa	shoot dry mass	0.5
		Medicago sativa	shoot length	1.87
		Medicago sativa	survival	3.56
		Triticum durum	root dry mass	0.14
		Triticum durum	root length	1.08
		Triticum durum	shoot dry mass	0.41
		Triticum durum	Shoot length	2.14
	Invertebrate	*Eisenia andrei*	adult survival	600
		Eisenia andrei	progeny production	6.63
		Folsomia candida	progeny production	350.75
	Native	*Bouteloua gracilis*	survival	2.78
Geomean	Invertebrate	*Eisenia andrei*	progeny mass	4.20014
	Native	*Bouteloua gracilis*	root dry mass	0.08986
		Bouteloua gracilis	Root length	0.14588
		Bouteloua gracilis	shoot dry mass	0.07374
		Bouteloua gracilis	Shoot length	0.28098
Innotech	Native	*Festuca hallii*	Root dry mass control rep 3 removed	0.01736
		Festuca hallii	Root length	0.00981
		Festuca hallii	Shoot dry mass control rep 3 removed	0.01895
		Festuca hallii	Shoot length	0.02302
		Koeleria macrantha	Root dry mass	0.00438
		Koeleria macrantha	Root length	0.03058
		Koeleria macrantha	Shoot dry mass	0.00554
		Koeleria macrantha	Shoot length	0.01265
		Nassella viridula	Root dry mass	0.01032
		Nassella viridula	Shoot dry mass	0.00992
		Nassella viridula	Shoot length control rep 4 removed	0.02503

Table B3. Bromacil Native Plants and Invertebrates

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Native	*Bouteloua gracilis*	survival	2.78
	Invertebrate	*Eisenia andrei*	progeny production	6.63
		Folsomia candida	progeny production	350.75
		Eisenia andrei	adult survival	600
Geomean	Native	*Bouteloua gracilis*	shoot dry mass	0.07374
		Bouteloua gracilis	root dry mass	0.08986
		Bouteloua gracilis	Root length	0.14588
		Bouteloua gracilis	Shoot length	0.28098
	Invertebrate	*Eisenia andrei*	progeny mass	4.20014
Innotech	Native	*Koeleria macrantha*	Root weight	0.00438
		Koeleria macrantha	Shoot weight	0.00554
		Festuca hallii	Root length	0.00981
		Nassella viridula	Shoot weight	0.00992
		Nassella viridula	Root weight	0.01032
		Koeleria macrantha	Shoot length	0.01265
		Festuca hallii	Root weight	0.01513
		Festuca hallii	Shoot weight	0.01681
		Nassella viridula	Shoot length	0.02283
		Festuca hallii	Shoot length	0.02302
		Koeleria macrantha	Root length	0.03058

Table B4. Bromacil Native Plants and Invertebrates - No Outliers

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Native	*Bouteloua gracilis*	survival	2.78
	Invertebrate	*Eisenia andrei*	progeny production	6.63
		Folsomia candida	progeny production	350.75
		Eisenia andrei	adult survival	600
Geomean	Native	*Bouteloua gracilis*	shoot dry mass	0.07374
		Bouteloua gracilis	root dry mass	0.08986
		Bouteloua gracilis	Root length	0.14588
		Bouteloua gracilis	Shoot length	0.28098
	Invertebrate	*Eisenia andrei*	progeny mass	4.20014
Innotech	Native	*Koeleria macrantha*	Root dry mass	0.00438
		Koeleria macrantha	Shoot dry mass	0.00554
		Festuca hallii	Root length	0.00981
		Nassella viridula	Shoot dry mass	0.00992
		Nassella viridula	Root dry mass	0.01032
		Koeleria macrantha	Shoot length	0.01265
		Festuca hallii	Root dry mass control rep 3 removed	0.01736
		Festuca hallii	Shoot dry mass control rep 3 removed	0.01895
		Festuca hallii	Shoot length	0.02302
		Nassella viridula	Shoot length control rep 4 removed	0.02503
		Koeleria macrantha	Root length	0.03058

Table B5. Bromacil Agronomic Plants and Invertebrates

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Crop	*Medicago sativa*	root length	0.09
		Medicago sativa	root dry mass	0.12
		Triticum durum	root dry mass	0.14
		Triticum durum	shoot dry mass	0.41
		Medicago sativa	shoot dry mass	0.5
		Triticum durum	root length	1.08
		Medicago sativa	shoot length	1.87
		Triticum durum	Shoot length	2.14
		Medicago sativa	survival	3.56
	Invertebrate	*Eisenia andrei*	progeny production	6.63
		Folsomia candida	progeny production	350.75
		Eisenia andrei	adult survival	600
Geomean	Invertebrate	*Eisenia andrei*	progeny mass	4.20014

Table B6. Bromacil Agronomic Plants and Invertebrates - No Outliers

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Crop	*Medicago sativa*	root length	0.09
		Medicago sativa	root dry mass	0.12
		Triticum durum	root dry mass	0.14
		Triticum durum	shoot dry mass	0.41
		Medicago sativa	shoot dry mass	0.5
		Triticum durum	root length	1.08
		Medicago sativa	shoot length	1.87
		Triticum durum	Shoot length	2.14
		Medicago sativa	survival	3.56
	Invertebrate	*Eisenia andrei*	progeny production	6.63
		Folsomia candida	progeny production	350.75
		Eisenia andrei	adult survival	600
Geomean	Invertebrate	*Eisenia andrei*	progeny mass	4.20014

Table B7. Tebuthiuron All Data

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Native	Artemisia cana	root length	0.00001
		Pascopyrum smithii	root dry mass	0.04
		Artemisia cana	root dry mass	0.044
		Pascopyrum smithii	shoot dry mass	0.05
		Pascopyrum smithii	shoot length	0.06
		Pascopyrum smithii	root length	0.13
		Artemisia cana	shoot length	0.973
		Bouteloua gracilis	root length	1.35
	Invertebrate	Folsomia candida	number of progeny	1
		Eisenia andrei	number of progeny	9.8
	Crop	Triticum durum	shoot dry mass	0.01
		Triticum durum	root dry mass	1.26
		Triticum durum	shoot length	30.27
		Triticum durum	root length	328.1
Geomean	Native	Bouteloua gracilis	shoot dry mass	0.1663481
		Bouteloua gracilis	root dry mass	0.1890746
		Bouteloua gracilis	Shoot length	0.9491857
	Invertebrate	Eisenia andrei	mass of individual progeny	37.752218
Innotech	Native	Agropyron dasystachyum	Shoot dry mass	0.0124801
		Festuca hallii	Root dry mass	0.0171684
		Agropyron dasystachyum	Root dry mass	0.025914
		Nassella viridula	Root dry mass	0.0299076
		Nassella viridula	Shoot dry mass	0.0332128
		Festuca hallii	Shoot dry mass	0.086085
		Nassella viridula	Shoot length	0.088709
		Agropyron dasystachyum	Root length	0.1075923
		Festuca hallii	Shoot length	0.116079
		Nassella viridula	Root length	0.119664

Table B8. Tebuthiuron All Data - No Outliers

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Native	Artemisia cana	root length	0
		Pascopyrum smithii	root dry mass	0.04
		Artemisia cana	root dry mass	0.044
		Pascopyrum smithii	shoot dry mass	0.05
		Pascopyrum smithii	shoot length	0.06
		Pascopyrum smithii	root length	0.13
		Artemisia cana	shoot length	0.973
		Bouteloua gracilis	root length	1.35
	Invertebrate	Folsomia candida	number of progeny	1
		Eisenia andrei	number of progeny	9.8
	Crop	Triticum durum	shoot dry mass	0.01
		Triticum durum	root dry mass	1.26
		Triticum durum	root length	328.1
		Triticum durum	shoot length	30.27
Geomean	Native	Bouteloua gracilis	shoot dry mass	0.1663481
		Bouteloua gracilis	root dry mass	0.1890746
		Bouteloua gracilis	Shoot length	0.9491857
	Invertebrate	Eisenia andrei	mass of individual progeny	37.752218
Innotech	Native	Festuca hallii	Shoot dry mass control rep 3 removed	0.0933006
		Nassella viridula	Shoot length control rep 4 removed	0.093965
		Agropyron dasystachyum	Root length control rep 1 removed	0.105177
		Festuca hallii	Shoot length	0.116079
		Nassella viridula	Root length control rep 2 removed	0.1178986
		Agropyron dasystachyum	Shoot dry mass control rep 6 removed	0.0139275
		Festuca hallii	Root dry mass control rep 3 removed	0.0204736
		Nassella viridula	Root dry mass	0.0299076
		Nassella viridula	Shoot dry mass	0.0332128
		Agropyron dasystachyum	Root dry mass control rep 6 removed	0.0343268

Table B9. Tebuthiuron Native Plants and Invertebrates

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Native	Artemisia cana	root length	0
		Pascopyrum smithii	root dry mass	0.04
		Artemisia cana	root dry mass	0.044
		Pascopyrum smithii	shoot dry mass	0.05
		Pascopyrum smithii	shoot length	0.06
		Pascopyrum smithii	root length	0.13
		Artemisia cana	shoot length	0.973
		Bouteloua gracilis	root length	1.35
	Invertebrate	Eisenia andrei	number of progeny	9.8
		Folsomia candida	number of progeny	1
Geomean	Native	Bouteloua gracilis	shoot dry mass	0.1663481
		Bouteloua gracilis	root dry mass	0.1890746
		Bouteloua gracilis	Shoot length	0.9491857
	Invertebrate	Eisenia andrei	mass of individual progeny	37.752218
Innotech	Native	Agropyron dasystachyum	Shoot dry mass	0.0124801
		Festuca hallii	Root dry mass	0.0171684
		Agropyron dasystachyum	Root dry mass	0.025914
		Nassella viridula	Root dry mass	0.0299076
		Nassella viridula	Shoot dry mass	0.0332128
		Festuca hallii	Shoot dry mass	0.086085
		Nassella viridula	Shoot length	0.088709
		Agropyron dasystachyum	Root length	0.1075923
		Festuca hallii	Shoot length	0.116079
		Nassella viridula	Root length	0.119664

Table B10. Tebuthiuron Native Plants and Invertebrates - No Outliers

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Native	Artemisia cana	root length	0
		Pascopyrum smithii	root dry mass	0.04
		Artemisia cana	root dry mass	0.044
		Pascopyrum smithii	shoot dry mass	0.05
		Pascopyrum smithii	shoot length	0.06
		Pascopyrum smithii	root length	0.13
		Artemisia cana	shoot length	0.973
		Bouteloua gracilis	root length	1.35
	Invertebrate	Folsomia candida	number of progeny	1
		Eisenia andrei	number of progeny	9.8
Geomean	Native	Bouteloua gracilis	shoot dry mass	0.1663481
		Bouteloua gracilis	root dry mass	0.1890746
		Bouteloua gracilis	Shoot length	0.9491857
	Invertebrate	Eisenia andrei	mass of individual progeny	37.752218
Innotech	Native	Agropyron dasystachyum	Shoot dry mass control rep 6 removed	0.0139275
		Festuca hallii	Root dry mass control rep 3 removed	0.0204736
		Nassella viridula	Root dry mass	0.0299076
		Nassella viridula	Shoot dry mass	0.0332128
		Agropyron dasystachyum	Root dry mass control rep 6 removed	0.0343268
		Festuca hallii	Shoot dry mass control rep 3 removed	0.0933006
		Nassella viridula	Shoot length control rep 4 removed	0.093965
		Agropyron dasystachyum	Root length control rep 1 removed	0.105177
		Festuca hallii	Shoot length	0.116079
		Nassella viridula	Root length control rep 2 removed	0.1178986

Table B11. Tebuthiuron Agronomic Plants and Invertebrates

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Crop	Triticum durum	shoot dry mass	0.01
		Triticum durum	root dry mass	1.26
		Triticum durum	shoot length	30.27
		Triticum durum	root length	328.1
	Invertebrate	Folsomia candida	number of progeny	1
		Eisenia andrei	number of progeny	9.8
Geomean	Invertebrate	Eisenia andrei	mass of individual progeny	37.752218

Table B12. Tebuthiuron Agronomic Plants and Invertebrates - No Outliers

Data Origin	Classification	Species	Parameter	IC25
				mg/kg
Stantec	Crop	Triticum durum	shoot dry mass	0.01
		Triticum durum	root dry mass	1.26
		Triticum durum	shoot length	30.27
		Triticum durum	root length	328.1
	Invertebrate	Folsomia candida	number of progeny	1
		Eisenia andrei	number of progeny	9.8
Geomean	Invertebrate	Eisenia andrei	mass of individual progeny	37.752218

APPENDIX A7: INVESTIGATION OF LONG-TERM EFFECTS OF ACTIVATED CARBON

Thacker, S., 2022. Investigation of Long-Term Effects of Activated Carbon in Immobilization of Bromacil and Tebuthiuron in Alberta Soils. Report SSP-10 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 50 pp.

Investigation of the Long-Term Effectiveness of Activated Carbon in Immobilization of Bromacil and Tebuthiuron

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CITATION

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EXECUTIVE SUMMARY

Soil sterilants were commonly used from the 1960s to late 1990s to control weeds on pipeline right of ways, oil and gas wells, railways, sawmills, pulp mills, and other industrial sites across Alberta. Sterilants are typically non-selective, residual, and persistent; they control all plants they contact and because they persist in soil, vegetation growth on sterilant-impacted sites is often inhibited. Sterilants tend to be highly mobile, which can result in off-site contamination (via leaching, surface runoff, wind). Two of the most used soil sterilants in Alberta were bromacil and tebuthiuron.

There is a need for cost-effective strategies to manage sterilant-impacted sites and achieve regulatory site closure; however, knowledge gaps exist regarding effective management practices for sites impacted by residual soil sterilants. Activated carbon (AC) has long been considered one of the most effective in-situ remediation technologies for soil sterilants, adsorbing sterilants to immobilize them, thus preventing uptake by plants or leaching through the soil. However, there is hesitation from a regulatory perspective to accept immobilization as a long-term solution for managing sterilant-impacted soils due to uncertainty regarding the longevity of immobilization. Both industry and government are seeking confirmation that AC can effectively be considered a permanent remediation technology whereby a sterilant-impacted site treated with AC could be considered for regulatory closure (i.e., receive a reclamation certificate).

This project was completed in two phases to meet the overall objective of assessing the long-term immobilization of soil sterilants by AC to validate AC's applicability as a remediation technology. The first phase included a literature review to summarize information on the stability and potential degradation of AC over time; factors that could influence desorption from AC; and methods of conducting artificial weathering experiments.

The second part of Phase 1 included desorption experiments via modified Synthetic Precipitation Leaching Procedure (SPLP) to assess the percentage of each sterilant retained by AC. Experiments included 'low' and 'high' bromacil and tebuthiuron concentrations in coarse- and fine-grained soils. Results from Phase 1 were used to inform Phase 2, an artificial weathering experiment using multiple freeze-thaw cycles of a sterilant-spiked topsoil to assess the longevity of sterilant immobilization by AC compared with soil that was not amended with AC.

The SPLP method was used to assess leaching after weathering in Phase 2; additionally, total and phytoaccessible (i.e., the fraction available to plants) sterilant concentrations were measured pre- and post-weathering. Use of the SPLP and phytoaccessible methods was required to assess the fraction of labile sterilant (i.e., not sorbed to activated carbon), as the total concentration would represent both the labile and sorbed fractions.

Results of Phase 1 showed that AC was effective at immobilizing soil sterilants when applied at a rate of 400:1 (AC:sterilant, weight basis) with significantly lower sterilant leaching in soil amended with AC compared non-amended soil. In Phase 1, desorption, assessed via SPLP, ranged from 0 to 14% in AC-amended soil, with higher desorption in coarse-grained soil compared to fine-grained soil. In Phase 2 (topsoil), desorption ranged from 1% to 3% after weathering of AC-amended soil. AC amendment significantly lowered phytoaccessible sterilant concentrations. Based on results following artificial weathering, it is interpreted that AC effectively sorbs the majority of bromacil and tebuthiuron in the long-term.

Long-term sterilant sorption to AC may be complicated by many factors, including weathering and climactic conditions, environmental conditions, sterilant properties (i.e., propensity to solubilize), competition between the sterilant and other compounds in soil for sorption sites, and the types of bonds formed between the sterilant and AC. The data from Phases 1 and 2 indicate that the majority of the bromacil and tebuthiuron remained sorbed to AC after physical weathering. In many cases AC amendment lowered phytoaccessible sterilant concentrations below limits outlined in the Alberta Tier 1 Soil and Groundwater Remediation Guidelines, indicating that the phytoaccessible laboratory method is a valuable risk assessment tool. Including AC as a remediation technology in meso- or field-scale demonstrations within the Soil Sterilants Program should be considered, along with the development of best management practices for the use of AC as an immobilization technique.

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GLOSSARY

Activated Carbon (AC)
A carbon-rich material derived from the pyrolysis of biomass at higher temperatures than that of biochar, derived at pyrolysis temperatures of approximately 1,000°C and above; often used as an absorbent.

Biochar
A carbon-rich material derived from the pyrolysis of biomass in the absence of oxygen, derived at pyrolysis temperatures below 1000°C; often used as a soil amendment.

Black Carbon (BC)
A carbon-rich material derived from incomplete combustion of vegetation and fossil fuels, as well as mineral weathering; activated carbon and biochar are forms of black carbon.

ACRONYMS

AC	Activated Carbon
BC	Black Carbon
SPLP	Synthetic Precipitation Leaching Procedure
SSP	Soil Sterilants Program

1. INTRODUCTION

Soil sterilants were commonly used from the 1960s to late 1990s to control weeds on rangelands, pipeline right of ways, oil and gas wells, railways, sawmills, pulp mills, and other industrial sites across Alberta (Bessie et al., 2012; Drozdowski et al., 2018). The presence of sterilants in the environment is of concern because these compounds are typically highly mobile, which can result in off-site contamination (via leaching, surface runoff, and wind), and persist in soil, meaning vegetation establishment on these sites is often inhibited. Two of the most used soil sterilants in Alberta were bromacil and tebuthiuron, both of which are considered mobile and persistent in soil and water (Drozdowski et al., 2018; Rakewich and Bakker, 2011).

There is a need for cost-effective strategies to manage sterilant-impacted sites and achieve regulatory site closure; however, knowledge gaps exist regarding effective management practices for sites impacted by residual soil sterilants. Activated carbon (AC) was initially used to improve vegetation growth on sterilant-impacted sites by immobilizing soil sterilants. Activated carbon has long been considered one of the most effective in-situ remediation technologies, adsorbing soil sterilants to immobilize them, thus preventing uptake by plants or leaching through the soil column. However, there is hesitation from a regulatory perspective to accept immobilization as a long-term solution for managing sterilant-impacted soils due to uncertainty regarding the longevity of immobilization. Both industry and government representatives are seeking confirmation that AC can effectively be considered a permanent remediation technology whereby a sterilant-impacted site treated with AC could be considered for regulatory closure (i.e., receive a reclamation certificate). Based on anecdotal evidence, there are numerous factors that may influence desorption and potential for leaching, such as pH, temperature, and competition with other adsorptive compounds in soil and water.

1.1 Scope and Rationale for Research

The original objective of this project was to assess the long-term immobilization of soil sterilants by AC in soil by obtaining samples from sites historically amended with AC to determine whether a portion of sterilant could be considered leachable or phytoaccessible. The purpose of the assessment was to validate AC's effectiveness as a remediation technology. The focus was on bioaccessibility of sterilants to vegetation and was closely tied to another Soil Sterilants Program (SSP) project to develop a method to determine total versus phytoaccessible soil sterilants (Maxwell, 2022). It was assumed that at sites selected for this analysis, specifics regarding the original AC treatment were known (i.e., quantity of AC used, type of AC, incorporation depth), sterilant data was available, and that the sites were accessible over 20 to 30 years after original AC amendment.

When this project commenced, we began the process of reaching out to expert advisors to find sites that would be suitable for the project. Information such as the rate of AC applied, sterilant concentrations, and depth of AC application were considered important in site selection. However, only two potential sites were identified, which were research plots set up by Michelle Cotton and Paul Sharma in Vegreville and Devon, respectively. We were able to get access to the Devon site and speak with the site managers, who indicated that the research plot area had been extensively disturbed in the years since the experiment ended. In Vegreville, the plots are not visibly evident and have been farmed for years, which has likely shifted the location of the original plots. Additionally, portions of the plots have likely been disturbed via construction work on site and may no longer be accessible.

Given the difficulties in finding suitable sites to meet the original goals of the project, we undertook preliminary activities to gain a better understanding of how sterilants may desorb over time and how AC was typically applied in the field. In discussion with various people with expertise in chemistry, sterilants, and adsorption technologies, it has been indicated that there could be desorption of sterilants from AC over time; however, the factors affecting the potential release of sterilants have not been confirmed. In addition, practitioners who historically amended soils with AC indicated that practices varied, and that both amendment ratios and distribution may have been inconsistent.

1.2 Research Objectives

Based on the lack of appropriate sites with historical AC amendment and information received during the preliminary activities in this project, a change in objective and scope for the project was approved by the Soil Sterilants Program Steering Committee. The project addressed the following research questions:

1. What is the percent effectiveness of AC in immobilizing soil sterilants when applied to soil at ratios established in previous research (i.e., 400:1)?
2. If proven sufficiently effective in immobilizing soil sterilants, under what conditions could AC release soil sterilants, thus making them available to vegetation and/or leaching through the soil profile?

Answering these questions will provide clarity for regulators and practitioners regarding whether AC is a viable permanent remediation technology, whereby a sterilant-impacted site treated with AC could be considered for regulatory closure.

1.3 Approach

To achieve the research objectives identified above, a phased approach was implemented for the project. Phase 1 included a literature review (Section 2) and aggressive desorption experiment (Section 3). The literature review was intended to increase understanding of factors that influence sterilant longevity in soil and the ability of compounds to desorb from AC over time. The desorption experiment provided information on the effectiveness of AC in sorbing sterilants under conditions intended to aggressively desorb and leach them from soil.

Both the literature review and leaching experiment were used to inform Phase 2 of the project, which is described in Section 4. Phase 2 was an artificial weathering experiment, aimed at assessing the effectiveness of AC in retaining sterilants after weathering (in this case, exposure to freeze-thaw cycles).

2. LITERATURE REVIEW

The literature review focused on topics related to AC sorption that are key to understanding how and where the technology could effectively be applied in Alberta and aimed to support decision making regarding the applicability of AC as a remediation technology with sound science. Three key components investigated were:

1. The potential for AC to degrade over time.
    - This is considered a key knowledge gap that would influence reclamation certification. If AC is documented to degrade in the environment, then this would not be a suitable long-term remediation strategy.

- On the other hand, if there is evidence to suggest the AC will be relatively unaltered over long time scales (i.e., sufficient time to be considered a permanent remediation technology), then the technology has potential.
- The literature review included different forms of AC (i.e., granular, powder).

2. Factors that influence desorption from AC.
   - Understanding which factors are most influential on the desorption of sterilants from AC will inform other stages of the project and provide pertinent information for practitioners and regulators regarding which sites are most likely to have successful remediation with AC.
   - The literature review focused on sorption bonds between sterilants and AC, and factors that could influence these bonds such as charge, competition between sorption and propensity to dissolve, and competition with other sorptive compounds in soil. Other factors were also considered: texture, pH, organic carbon, temperature, and moisture.
3. Weathering
   - The intent of this review was both to understand factors that influence desorption and determine how AC in soil could be artificially weathered to simulate processes that occur in soil over time.
   - This portion of the literature review was used to inform potential lab-based methods to assess the longevity of sterilant immobilization with AC.

Similar compounds, such as biochar, were considered in the literature review. Various herbicides and similar compounds were also considered. These compounds did not necessarily have the same chemistry and persistence as bromacil and tebuthiuron, but provided information on AC sorption dynamics where information specific to bromacil and tebuthiuron was not available.

2.1 AC Stability, Sorption Dynamics, and Degradation Over Time

As indicated in Hilber and Bucheli (2010), there is a lack of information regarding the stability of AC in soil and sediment, despite this being an important consideration for remediation in the long term (10+ years). The term black carbon (BC) is used to refer to carbon-rich material derived from incomplete combustion of vegetation and fossil fuels, as well as mineral weathering (Nguyen et al., 2008). Biochar and AC are forms of BC, and these compounds have many similarities. Research related to biochar and BC can provide insights for AC.

A study by Cho et al. (2011) found that the amount of AC present, and sorption capacity of AC for PCBs, was maintained after five years in the field, indicating AC and its sorption bonds may be stable over time. However, this study investigated PCBs and not herbicides; PCBs can be strongly adsorbed to AC, and therefore may offer a less conservative representation of desorption potential over time (Lanouette, 1990; McDonough et al., 2008; Wang et al., 2019). Additionally, the study by Cho et al. (2011) was conducted in an intertidal mudflat in San Francisco, as opposed to upland soils. Studies over longer time periods would be beneficial. While black carbon is known to be a recalcitrant compound (Cheng et al., 2008b), and the study cited above indicates stability over a five year period, other researchers indicate that biochar and AC have the potential to degrade over time (Zimmerman, 2010).

Zimmerman (2010) conducted a one-year laboratory incubation to understand degradation of biochar over time. They found that the presence of microbes resulted in higher carbon release compared to abiotic conditions; carbon released under abiotic conditions was 50% to 90% of carbon released when microbes were present. One-hundred-year C losses for biochar were modelled and estimated to be 3% to 26%. Biochar C half-lives were modelled and ranged from 10^2 to 10^7 years. Interestingly, biochars with higher

charring temperature tended to have lower C release. For example, 100-year C losses for oak biochar with a charring temperature of 250°C were estimated at 20%, while losses were estimated at 6% for oak biochar with a 650°C charring temperature (Zimmerman, 2010). In general, AC is charred at higher temperatures than biochar (i.e., 1,000°C; Hilber and Bucheli, 2010), which indicates AC is likely to be more recalcitrant over time. However, the results from Zimmerman (2010) indicate the potential for degradation over time.

Other authors have assessed the stability of biochar after exposure to physical weathering. Naisse et al. (2015) simulated physical weathering with both wetting/drying and freeze/thaw cycles. Geochemical weathering of biochar was performed with and without humic acid in a modified Soxhlet reactor and used to inform effects on mineral availability (i.e., K, S, Ca, Mg and P, N) (Yao et al., 2010). Interestingly, abiotic factors appeared to impact sorption dynamics and oxidation of BC more strongly than biotic factors (i.e., microorganisms) (Cheng et al., 2006; Hale et al., 2011).

In a study investigating changes to BC particles and BC stocks in soil (top 10 cm) cleared with fire 2 to 100 years prior, BC content decreased quickly in the first 30 years post-fire, after which BC content decreased slowly up to 100 years post-fire (Nguyen et al., 2008). Molecular properties of BC also changed more rapidly in the first 30 years post-fire and were observed to change more rapidly at the surface of the BC. The changes in BC content in soil in the first 30 years are likely not only the result of decomposition, but also erosion and movement below the depth being sampled (Nguyen et al., 2008).

In a study investigating the effect of climate and soil factors on changes to surface charge and molecular structure of black carbon (BC), the authors compared field-collected, historical black carbon (collected along a climosequence) to newly produced black carbon (Cheng et al., 2008a). The authors found that historical BC was oxidized substantially after 130 years in soil compared to newly produced BC or BC incubated for one year. Natural oxidation of BC resulted in the following changes:

- Change in elemental composition: historical BC had more oxygen and less carbon in its structure compared to new BC.
- Oxygen-containing functional groups: historical BC saw the formation of carboxylic and phenolic functional groups.
- Change in charge: historical BC samples saw the loss of a positive surface charge, and a surface negative charge after one year incubation.

Natural BC oxidation increased significantly with time of exposure. Long-term oxidation was most evident on the surface of BC. The changes in molecular structure and charge indicate the potential for changes in sorption over time. While there are many factors that influence sorption, the surface charge of BC, or more specifically AC, is important. Changes in the surface charge of BC observed by Cheng et al. (2008a) indicate a potential for desorption of sterilants to occur over time. Additionally, the loss of C from BC noted in Cheng et al. (2008b) indicates degradation of BC overtime. While AC is more recalcitrant than biochar, this study indicates both the potential for BC to degrade over time, and the potential for loss of surface charge which could result in desorption of sterilants.

The studies reviewed indicate that:

- BC can degrade and change in structure over time, and sorption dynamics can also change.
- AC can be relatively stable over time (i.e., five years).
- AC is likely more stable than biochar, given its higher charring temperature.

- While AC is recalcitrant in soil, weathering processes have the potential to degrade AC and change sorption dynamics over time.
    - The extent of this change has not been evaluated under conditions relevant to Alberta.

2.2 Factors Influencing Desorption From AC

2.2.1 Environmental Factors

Sterilant sorption to soil particles and AC is dependent on numerous factors, including environmental conditions. These factors have recently been reviewed by Drozdowski et al. (2018). For example, bromacil is adsorbed more strongly by organic matter than clay and is more likely to be found at the surface in soils with higher organic matter (Drozdowski et al., 2018). Tebuthiuron leaching is lowest in soils with high clay or organic matter content (Drozdowski et al., 2018). Similar results have been found for other herbicides. In a study with 2,4-D, organic matter and clay content were both considered important factors influencing the sorptive capacity of soil (Akma et al., 2009).

Orduz et al. (2021) demonstrated that the desorption of herbicide from AC is affected by the pH of the solution it is desorbed in. Liu et al. (2010) found that pH and temperature affected diuron adsorption in soil, while organic matter was the only factor that significantly impacted desorption. The soil with the lowest organic content had the highest desorption of diuron (Liu et al., 2010).

Adsorption and desorption of the herbicide fluroxypyr was observed on activated carbon under different pH and temperature conditions (Pastrana-Martínez et al., 2009). The pH is important because it influences surface charge of the adsorbent (in this case, AC), dissociation of the adsorbate, and desorption of the adsorbate (Pastrana-Martínez et al., 2009). Changes in adsorption with pH were attributed to changes in herbicide solubility and dispersive and electrostatic adsorbent-adsorbate interactions. The authors concluded that the highest amount of fluroxypyr was thermally desorbed when there were only non-electrostatic interactions between herbicide molecules and the AC surface (Pastrana-Martínez et al., 2009). The data indicates that the type of bonds between the herbicide and AC impact desorption kinetics. While pH influenced adsorption and desorption in this study, soils in Alberta are generally well buffered, and therefore pH is not likely to be a driving factor in sterilant sorption dynamics in most Alberta soils.

2.2.2 Sterilant Characteristics

In most soils, there will be competition for adsorption sites on AC between herbicide and naturally-occurring organic compounds (A. Seech, personal communication, March 3, 2021). Herbicides such as bromacil and tebuthiuron are more hydrophilic than many organic compounds in soil (i.e., humic and fulvic acids), indicating that such naturally-occurring organic compounds may be more likely to sorb to AC. The solubility of the herbicide impacts its likelihood to sorb and stay sorbed overtime (A. Seech, personal communication, March 3, 2021). For example, low solubility pesticides such as DDT are less likely to desorb compared to compounds with high solubility/hydrophilicity. It is likely that some desorption of bromacil and tebuthiuron from AC could occur in soil given their hydrophilic nature and the complex matrices of organic matter and clay that constitute most soils; however, sterilant sorption to AC is complicated by many environmental and climatic factors, as well as competition with other compounds and the types of bonds formed between the sterilant and AC.

2.2.3 Weathering

Weathering is a key consideration in the long-term immobilization of sterilants with AC in soil. While AC is considered recalcitrant, papers explored in Section 2.1 indicated that BC can be degraded over time and that the molecular composition can change. Biological, chemical, and physical weathering processes occur in soil, and can impact the stability and sorption dynamics of AC (Cheng et al., 2006; Hale et al., 2011; Naisse et al., 2015). Hale et al. (2011) investigated the effect of chemical, physical, and biological aging on the sorption of pyrene to AC and biochar. While pyrene is not a herbicide, this study provides evidence for the effect of artificial weathering on the sorptive capacity of AC. The types of aging investigated were:

- Biological: exposure to nutrients and microorganisms
- Thermal/Chemical: exposure to 60°C and 110°C
- Physical: exposure to freeze-thaw cycles

Chemical aging caused the greatest change to the physico-chemical properties of materials and resulted in the greatest desorption of pyrene (Hale et al., 2011).

In a study using wheat ash as an adsorbant for diuron, Yang and Sheng (2003) evaluated diuron sorption in ash-amended soil that was either not aged, or aged for 1, 3, 6, or 12 months. The unaged ash-amended soil showed the highest diuron adsorption, with all aged soils having lower sorption. However, the aged ash-amended soils did have higher adsorption than unaged soil without ash amendment. While aged ash still adsorbed the sterilant, aging decreased adsorption compared to unaged material. The temperatures used to create the wheat ash used in the study by Yang and Sheng (2003) were likely much lower than the temperatures used to create activated carbon, and other researchers have indicated that higher charring temperatures tend to have slower rates of black carbon degradation (Zimmerman, 2010).

Harvey (1973) investigated the effect of freeze-thaw cycles on the effectiveness of AC at preventing atrazine injury to plants in silica sand. A two-week storage period with alternating temperatures of -27°C and 25°C (five freeze-thaw cycles) reduced the effectiveness of AC such that there was no statistically significant difference between soil with and without AC (AC amendment rate of 0.4 mg/kg was used with atrazine concentrations of 0, 5, and 10 mg/kg). While this study was conducted in silica sand, and not natural soils, it suggests that natural weathering processes could change sterilant sorption to AC.

Given the observation that abiotic factors influence sorption dynamics of BC more strongly than biotic factors, chemical or physical artificial weathering methods are likely best suited to assess the long-term immobilization of sterilants in soil. Considering the climate in Alberta, which includes annual freeze/thaw cycles, physical weathering would be a suitable method for an artificial weathering experiment with Alberta soils.

3. STERILANT DESORPTION EXPERIMENT

3.1 Introduction

The purpose of the desorption experiment was to assess the percent effectiveness of AC in immobilizing soil sterilants when applied to soil at ratios established in previous research. To provide a conservative approach for assessing sterilant immobilization, we utilized an aggressive procedure to assess the “worst case scenario” of sterilant desorption from AC in soil.

3.2 Methods

3.2.1 Overview

To assess the "worst case scenario" desorption potential of sterilants in soil amended with AC, and the percent effectiveness of AC, the Synthetic Precipitation Leaching Procedure (SPLP) (US EPA, 1994) was used as a basis for the experimental method. The SPLP method was heavily modified for the specific research questions being asked and the scenario being addressed (Section 3.2.4). Table 1 provides an overview of the experimental design.

Table 1. Experimental design for the desorption experiment.

Treatments/Parameters	Number	Description
Soil	2	Topsoil* Silica sand
Soil Sterilants	2	Bromacil (Hyvar® X-L, liquid, 21.9% lithium salt of bromacil) Tebuthiuron (Spike® 80DF, granule, 80% tebuthiuron)
Soil Sterilants Concentrations	2	High concentration Low concentration
AC Product	1	Powdered (Darco® 100-mesh particle size)
AC Application Rate	2	400:1** No AC
Replicates	5	However, sterilant analysis was conducted on 3 replicates. The remaining 2 replicates were stored at 4°C.

* Solonetzic Brown Chernozem (loam) sourced near Brooks, AB.
** The AC application rate was selected based on those rates utilized by Cotton and Sharma (1993) in laboratory and field experiments and is on a weight basis.

Two different soil materials were used for the desorption trial. Silica sand was used to provide information regarding sterilant desorption in the absence of clay particles and organic compounds (clay and organic matter provide sorption sites for sterilants, and organic compounds can compete with sterilants for sorption sites). A loam topsoil sourced near Brooks, AB was also used; this soil was selected as it is representative of the soils that occur in many areas with sterilant impacts in Alberta.

The loam topsoil was already spiked with bromacil or tebuthiuron for another SSP project, and soil with a high and low concentration of each sterilant was selected for use in the current project. See Section 3.2.2 for a detailed description of the spiking process. In Cotton and Sharma (1993), bromacil and tebuthiuron concentrations of 0.8 and 2.4 mg/kg were used in both lab and field trials to study the effect of AC amendment on plant growth in sterilant-impacted soils; the low rate was representative of carryover from a single application a couple years prior, whereas the high concentration was representative of sterilant build up after multiple applications. Similar concentrations were used in the current experiment for both silica sand and topsoil but depended on the concentrations available from the other SSP project. Both soil materials were amended with AC. The sterilant concentrations and amount of AC added are provided in Table 2.

Table 2. Total bromacil and tebuthiuron concentrations (mg/kg) of spiked topsoil and silica sand used in the desorption experiment.

Treatment	Soil Material	Sterilant	Sterilant Concentration (mg/kg soil)*
Top-B-High	Topsoil	Bromacil	1.83
Sand-B-High	Sand		2.71
Top-B-Low	Topsoil		0.65
Sand-B-Low	Sand		0.96
Top-T-High	Topsoil	Tebuthiuron	2.14
Sand-T-High	Sand		2.45
Top-T-Low	Topsoil		0.72
Sand-T-Low	Sand		0.59

* Average concentrations based on duplicate samples (n=2), except for Top-B-High and Top-T-High, which are based on triplicate samples (n=3).

Soil was amended with powdered AC (Darco® 100-mesh particle size), as powdered AC has most commonly been applied in field projects in Alberta (K. Bessie, personal communication, April 6, 2021). See Section 3.2.3 for a detailed description of the process for amending soil and silica sand with AC. Based on the ratio that proved effective at preventing injury to vegetation in previous field experiments in Alberta (Cotton and Sharma, 1993), an AC:sterilant ratio of 400:1 (by weight) was used. Drozdowski et al. (2018) reviewed the quantity of AC needed to inactivate herbicides in soil; the review indicates that using a 400:1 ratio is conservative. Additionally, sterilant-spiked silica sand and topsoil without AC amendment were included in the experiment to provide information regarding the amount of sterilant sorbed by the soil itself.

Laboratory analysis included total and phytoaccessible sterilants in soils prior to the experiment, total sterilants in the filtrate (see Section 3.2.4, and total sterilants in the soils after the experiment. Total sterilants analysis utilized the standard method conducted at Element Materials Technology (Calgary). Phytoaccessible sterilant levels were determined based on the method in Maxwell (2022) (Appendix A). The goal was to generate a mass balance for sterilants.

3.2.2 Spiking Soil

The topsoil was spiked in 2020 as part of another SSP project (Thacker, 2021). The topsoil was brought to InnoTech Alberta's research facility in Vegreville. The topsoil (approximately 1 yd^3, or 0.75 m^3) was homogenized using a large soil mixer (Bouldin and Lawson LLC, Tennessee). Both the topsoil and silica sand were spiked with bromacil (Hyvar® X-L, liquid, 21.9% lithium salt of bromacil) or tebuthiuron (Spike® 80DF, granule, 80% tebuthiuron). The spiking method was the same for both the topsoil and silica sand.

To spike soil with bromacil, dilutions of liquid Hyvar® X-L were made. Five solutions ranging from 100 g/L bromacil to 0.01 g/L bromacil were made. Given the mass of soil, we calculated the required volume of dilution to achieve the target concentration in soil. Water was mixed with the solution which was spread onto the soil. To spike soil with tebuthiuron, the required amount of Spike® 80DF for each concentration was weighed on a microbalance and dissolved in water.

To mix the sterilants into soil, a pre-weighed amount of soil was added to a mixing bin; the same process was followed for each concentration, for both bromacil and tebuthiuron. The soil was homogenized with a spatula and three trenches were made. The bromacil or tebuthiuron solution (as described in the previous paragraph) was then poured into the trenches. Using the spatula, the soil was gently mixed. Then, the soil was mixed with an electric hand mixer until uniform in colour. The soil was mixed by hand with the spatula once more to distribute throughout the mixing bin, and then another pass was made with the hand mixer. Once homogenized, samples were taken to confirm the sterilant concentration. Samples were sent to Element Materials Technology (Edmonton). High-performance liquid chromatography/mass spectrometry (HPLC/MS) was utilized to analyze sterilant concentrations in soil (bromacil MDL = 0.0015 reporting at 0.008 mg/kg; tebuthiuron MDL = 0.0012 reporting at 0.005 mg/kg). Spiked soils were transferred to designated buckets and stored at 4°C.

The same spiking method was used for silica sand in 2021.

3.2.3 Amending Soil

For each treatment, 2.5 kg of spiked soil was weighed. The amount of powdered AC required to amend each treatment was calculated prior to amending the soils. A 0.0001 g microbalance was used to weigh the required amount of AC. The AC was mixed into a small sub-fraction of the spiked soil with a glass stirring rod. The sub fraction with AC was then added to the remainder of the spiked soil and mixed five times following the cone-and-quarter method (Schumacher et al., 1990). The amended soil was put into a glass jar and rolled on an electric roller for one hour.

Once amended with AC, the soils were aged at 4°C for four weeks prior to the start of the trial. Aging the samples was important to ensure there was sufficient time for the sterilants to sorb to the AC. Silica sand was aged for two weeks. Given that there was no organic matter or clay present in the silica sand, it was determined that a shorter aging period was acceptable. The selected aging periods were based on data from Gan et al. (1999) and Northcott and Jones (2000).

3.2.4 Desorption Trial

Sterilant desorption was assessed using a modified SPLP method. The SPLP method offers an aggressive approach for assessing potential leaching/desorption of a chemical from soil. To account for the volumes of material needed for analysis and the conditions present in Alberta soils, we modified the standard SPLP method by: (1) using a larger volume of soil, (2) decreasing the extractant to soil ratio to 10:1, and (3) using 0.01M $CaCl_2$ as the extractant rather than an acid solution. In SPLP, nitric and sulfuric acids are used as the extractant, but because we wanted to more closely approximate real soil conditions, 0.01M $CaCl_2$ was used to simulate groundwater, without significantly altering soil pH.

Soil or silica sand (150 g, oven-dried equivalent) was weighed into 2 L glass jars. The soil material was at approximately 70% of field capacity when weighed into the jars; samples were not dried prior to extraction to maintain as close to field conditions as possible, and because wetting/drying cycles can weather AC (Naisse et al., 2015). To each jar, 1,500 mL of 0.01M $CaCl_2$ was added as the extractant (10:1 ratio of extractant to soil).

The jars containing soil and $CaCl_2$ solution were placed on a back-and-forth-shaker (Eberbach Corporation, Michigan), at approximately 160 oscillations per minute, for 18 hours. The long shaking time offers an aggressive method for assessing desorption, providing a conservative estimate for

determining AC percent effectiveness in retaining sterilants. After 18 hours of agitation, the jars were left overnight to allow the soil to settle out of the water column; Figure 1 shows jars of silica sand after the settling period. The extractant was then vacuum-filtered through a glass-fibre filter with a particle retention size of 0.7 µm. The soil was dried on the filter paper until water was no longer observed dripping through the filter paper, and the soil was then transferred to a glass vial and sent for analysis of sterilant concentration. The moisture content of the soil after filtering was determined for mass balance calculations (Section 3.3). The filtrate was sent for laboratory analysis. Data obtained from the trial included sterilant concentration in the filtrate and sterilant concentration in the soil after shaking and filtration.

Figure 1. Jars containing silica sand, after being shaken for 18 hours and allowed to settle. The jar on the left was amended with activated carbon, and the jar on the right was not.

3.2.5 Desorption and Mass Balance Calculation

Desorption/immobilization and mass balance were calculated based on the initial concentration of sterilant in soil and the amount of sterilant in the filtrate. The sterilant concentration in the soil after shaking and filtration could not be factored into mass balance calculations, as explained in Section 3.3.2. First, the mass of sterilant in initial soil and in the filtrate was calculated:

$$Mass\ of\ sterilant\ in\ inital\ soil = concentration\ of\ sterilant\ in\ inital\ soil\ \times dry\ soil\ weight$$

$$Mass\ of\ sterilant\ in\ filtrate = concentration\ of\ sterilant\ in\ filtrate\ \times volume\ of\ filtrate$$

Next, the percentage of sterilant immobilized and desorbed was calculated.

$$\%\ sterilant\ desorbed = \frac{mass\ of\ sterilant\ in\ filtrate}{mass\ of\ sterilant\ in\ inital\ soil} \times 100$$

$$\%\ sterilant\ immobilized = 100\ - \%\ sterilant\ desorbed$$

The mass of sterilant in soil after shaking and filtering was calculated.

$$Mass\ of\ sterilant\ in\ filtered\ soil = concentration\ of\ sterilant\ in\ filtered\ soil\ \times inital\ dry\ soil\ weight$$

Soils after shaking and filtration were generally moister than the initial soil condition. To account for the sterilant concentration contributed by filtrate present in the filtered soil, the following calculation was used:

$$Final\ soil\ weight = inital\ dry\ soil\ weight\ \times (1\ +\ final\ soil\ moisture)$$

$$Mass\ of\ water\ in\ filtered\ soil\ (g) = final\ soil\ weight\ - inital\ dry\ soil\ weight$$

$$Sterilant\ contribution\ from\ water = mass\ of\ water\ in\ filtered\ soil\ \times sterilant\ concentration\ in\ filtrate$$

The phytoaccessible portion of the sterilants in soil were calculated as follows:

$$Mass\ of\ phytoaccessible\ sterilant\ in\ soil = phytoaccessible\ concentration\ of\ sterilant\ in\ soil\ \times initial\ dry\ soil\ weight$$

$$\%\ phytoaccessible = \frac{mass\ of\ phytoaccessible\ sterilant}{mass\ of\ total\ sterilant\ in\ inital\ soil} \times 100$$

3.2.6 Statistical Analysis

Data exploration, analysis, and visualization were carried out using the R language and environment for statistical computing (R Core Team, 2019) and the additional packages *tidyr* (Wickham and Henry, 2019), *dplyr* (Wickham et al., 2019), *purrr* (Henry and Wickham, 2019), *ggplot2* (Wickham, 2016), and *emmeans* (Lenth et al., 2019). In this report, the term "significant" is used to describe statistically significant relationships ($\alpha = 0.05$). For all statistical tests, data were explored to determine whether assumptions of normality and homogeneity of variance were met; this included visual examination of data and residuals, Shapiro-Wilk test, and Levene's test. Statistical differences between the % of sterilant desorbed in AC-amended versus non-amended soil, for each soil material and sterilant combination, were determined with pairwise t-tests.

3.3 Results and Discussion

3.3.1 Sterilant Immobilization

AC effectively immobilized the majority of the sterilants present in soil (Figures 2 and 3). Sterilant desorption in the presence of AC was significantly lower than without AC for all treatments. Even with the aggressive conditions applied during the trial, which were intended to facilitate desorption, soils and sand amended with AC exhibited low rates of desorption (0 to 14% on average, depending on the soil material and sterilant concentration) (Appendix B). In AC-amended soils, there was no clear difference in the proportion of sterilant desorbed between topsoil and silica sand. Raw data is provided in Appendix C.

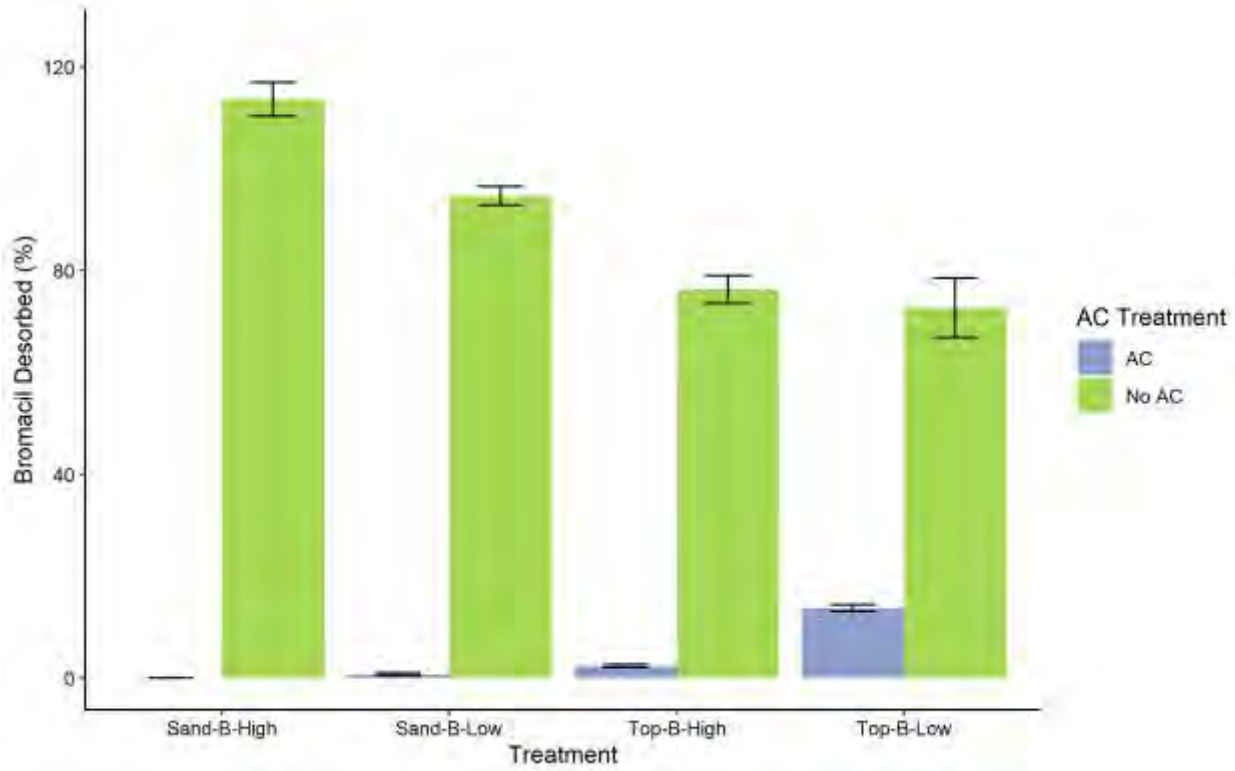

Figure 2. Desorption (%) of bromacil in topsoil and silica sand, either amended with activated carbon (AC), or non-amended.
Bars represent means (n=3) and error bars indicate the standard error. Desorption data was determined after 18-hour shaking in 0.01M $CaCl_2$. Note that in treatment names, Sand = silica sand, Top = topsoil, and B = bromacil. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

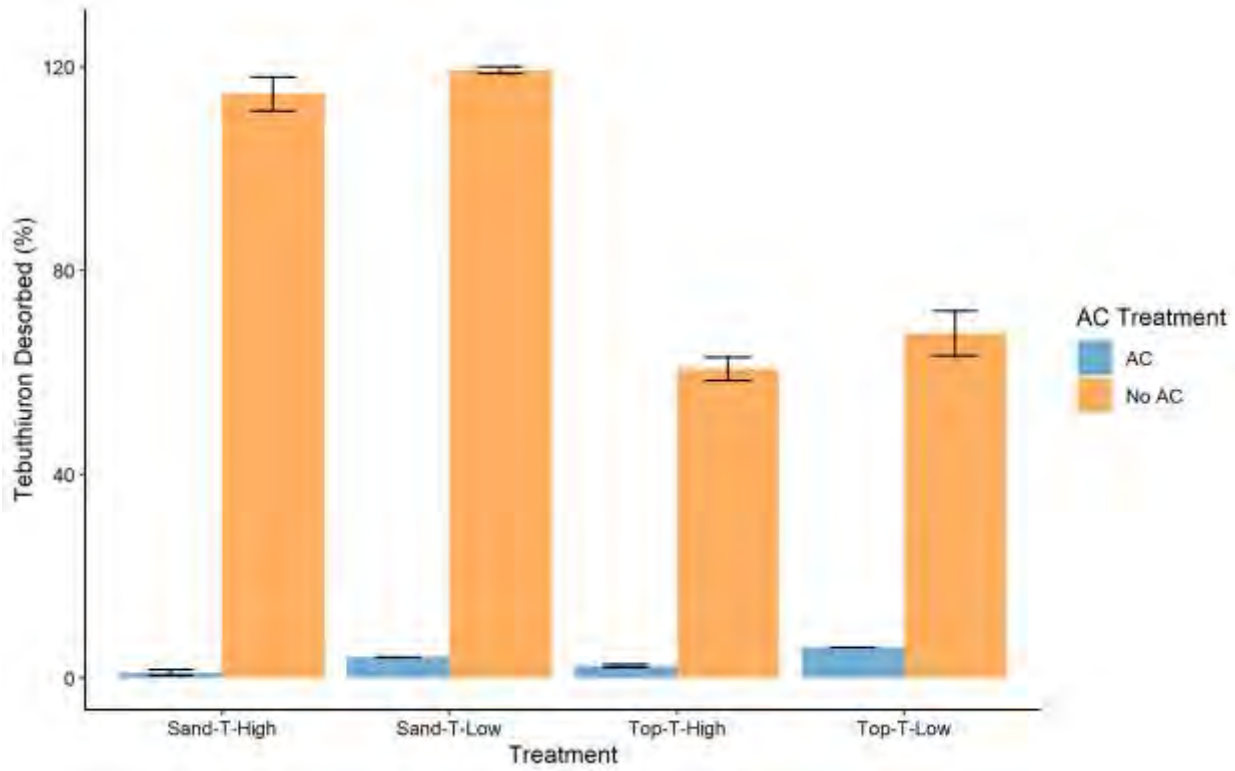

Figure 3. Desorption (%) of tebuthiuron in topsoil and silica sand, either amended with activated carbon (AC), or non-amended.
Bars represent means (n=3) and error bars indicate the standard error. Desorption data was determined after 18-hour shaking in 0.01M $CaCl_2$. Note that in treatment names, Sand = silica sand, Top = topsoil, and T = tebuthiuron. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

Soils with the higher bromacil concentration tended to have a higher proportion of bromacil desorb, compared to the low bromacil concentration (in the absence of AC); the opposite was true for tebuthiuron. However, it should be noted that the differences were relatively small. We expected higher desorption proportions with the higher sterilant concentration, as Cotton and Sharma (1993) found that AC amendment provided protection to plants against herbicide when the sterilant concentration was 0.8 mg/kg, but not when it was 2.4 mg/kg, in controlled environment studies. With AC amendment, there was no clear difference between high and low bromacil concentrations, in terms of desorption; for tebuthiuron, the proportion desorbed was slightly higher at low concentrations. Overall, the initial concentration of each sterilant used did not have a strong impact on the amount of sterilant that desorbed.

In the absence of activated carbon, the topsoil retained more of the sterilants than the silica sand. This observation was expected given that the topsoil contains clay and organic matter (which provide sorption sites for sterilants), while the sand did not. Topsoil retained 23% to 39% of the sterilant added, depending on the sterilant and concentration (Appendix B). The silica sand data is harder to interpret, as often greater than 100% desorption was calculated. It is unclear why >100% desorption was observed in many silica sand treatments (Appendix B). While efforts were made to homogenize the soil material well, some heterogeneity likely still existed, and contributed to this result.

3.3.2 Mass Balance

When calculating a mass balance for each treatment, it was assumed that the following equation should be true:

$$Initial\ sterilant\ in\ soil = sterilant\ in\ filtrate + sterilant\ in\ filtered\ soil\ *$$

*Note that the sterilant in filtered soil excludes the sterilant concentration from water (see Section 3.3).

Without the addition of AC, the mass of sterilant approximately balanced for each treatment. However, with AC amendment, the mass of sterilant in the filtrate and filtered soil combined was clearly less than the initial sterilant mass in soil (Figures 4 and 5). These calculations work on the assumption that the laboratory extraction was for "total sterilants" (i.e., majority of the sterilant present in the sample is removed in the extraction). The imbalance in AC-amended soils is due to the sterilant concentration observed in filtered soil; the concentration is lower than expected. It appears that not all the sterilant mass was extracted, due to bonds with AC. This is further evidenced by surrogate recovery in AC-amended soil. The laboratory adds a surrogate to samples as a QA/QC procedure; the surrogate is a compound with similar behaviour and characteristics as the target compound, and when bromacil or tebuthiuron is the target compound, monuron is used as the surrogate. In general, surrogate recovery is lower in soils amended with AC compared to soils without AC. This indicates that something (in this case, AC) is preventing the surrogate from being extracted. Because the surrogate behaves like the sterilants, we can presume that the same effect is happening for bromacil and tebuthiuron. Differences in surrogate recovery between AC-amended and non-AC soil was most evident at the high sterilant concentration. Because of this observed effect, the sterilant concentration in the soil after shaking and filtration could not be factored into mass balance calculations.

The initial mass of sterilant in soil was based on the analysis of samples without AC amendment. To test the theory suggested above, we sent AC-amended samples (which had not undergone the desorption experiment process) for "total sterilants" analysis. The data is provided in Table 4, and supports the conclusion that, in AC-amended soils, bonds with AC prevent the sterilant and surrogate from being fully extracted. Therefore, in AC-amended soils, standard lab analysis for sterilants is not representative of the total sterilant concentration in soil.

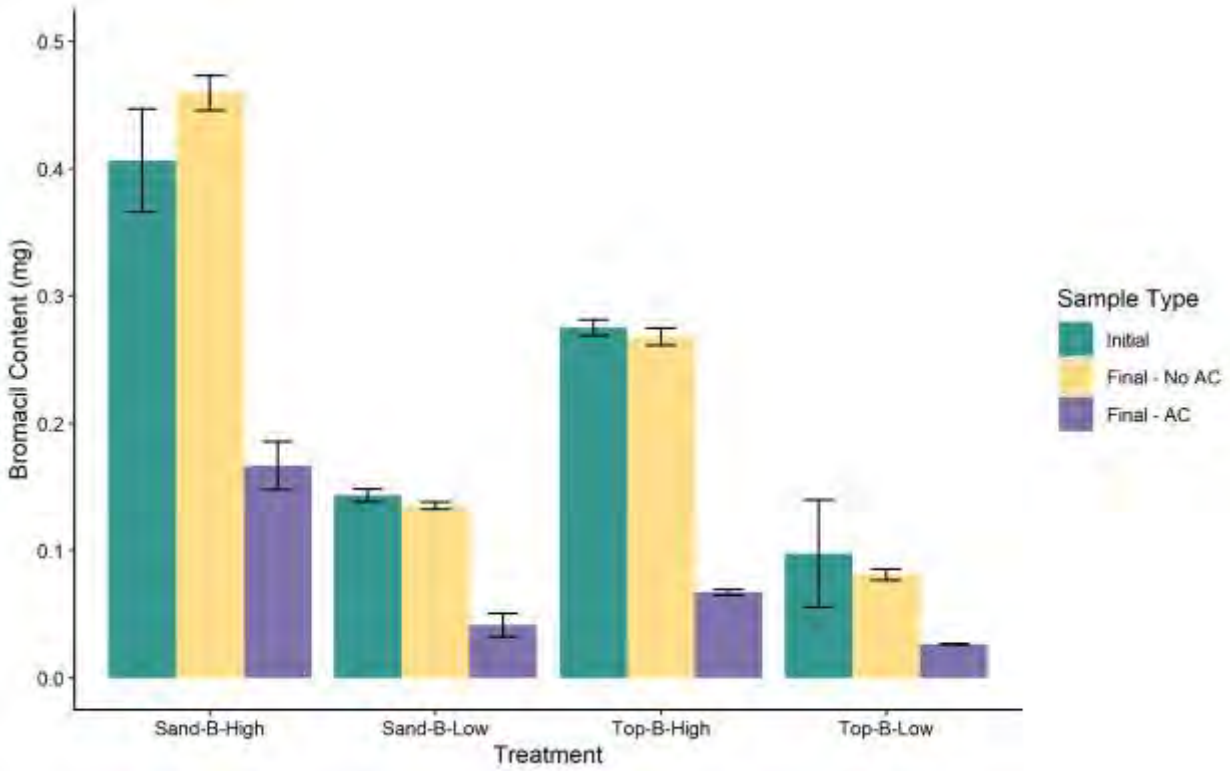

Figure 4. Bromacil (mg) either measured initially before the desorption experiment (in topsoil or silica sand), or at the end of the desorption experiment.
Bars represent means (n=3) and error bars indicate the standard error. Final bromacil concentrations were determined by combining the sterilant mass in the filtrate and filtered soil. Final concentrations are presented both for soil amended with activated carbon (AC) or non-amended (No AC). Bromacil content is based on the soil sample size of 150 g. Note that in treatment names, Sand = silica sand, Top = topsoil, and B = bromacil. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

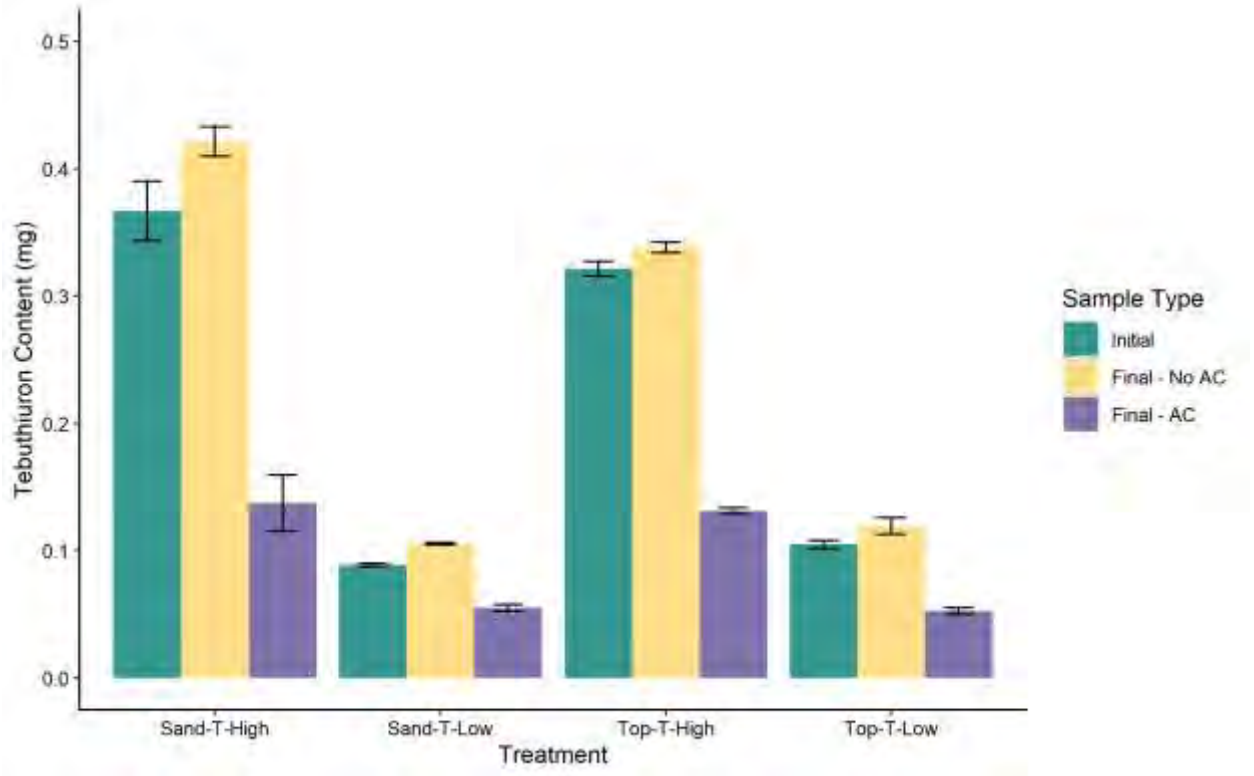

Figure 5. Tebuthiuron (mg) either measured initially before the desorption experiment (in topsoil or silica sand), or at the end of the desorption experiment.
Bars represent means (n=3) and error bars indicate the standard error. Final tebuthiuron concentrations were determined by combining the sterilant mass in the filtrate and filtered soil. Final concentrations are presented both for soil amended with activated carbon (AC) or non-amended (No AC). Tebuthiuron content is based on the soil sample size of 150 g. Note that in treatment names, Sand = silica sand, Top = topsoil, and T = tebuthiuron. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

Table 3. Sterilant concentration in topsoil (sampled before the desorption trial) with either no AC amendment or AC amendment.

Treatment	Sterilant	Sterilant Concentration (mg/kg soil)*	% Difference Between AC-amended and Non-amended Concentration	# of Replicates
Top-B-High (non-amended)	Bromacil	1.83	27	3
Top-B-High (AC-amended)		0.49		1
Top-T-High (non-amended)	Tebuthiuron	2.14	44	3
Top-T-High (AC-amended)		0.95		1

* Average concentrations based on triplicate samples (n=3).

3.3.3 Phytoaccessible Sterilants

The phytoaccessible sterilant fraction, measured using Maxwell's (2022) method, was lower than the initial, total sterilant concentration in soil (Figure 6). The only exception was for the non-amended silica sand spiked with tebuthiuron to 0.59 mg/kg (Appendix D). The results suggest that Maxwell's method may provide a reasonable approximation of the phytoaccessible fraction of sterilants in soil.

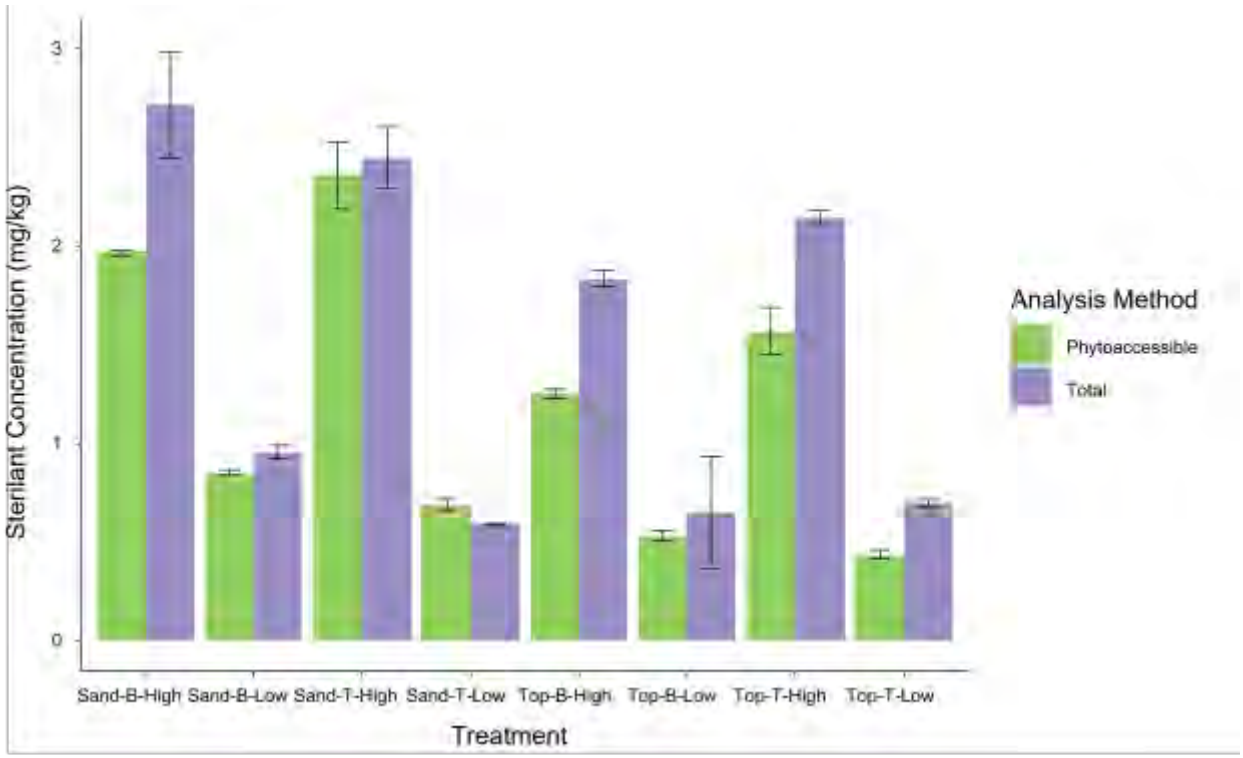

Figure 6. Sterilant concentration (mg/kg) in topsoil and silica sand, without activated carbon (AC) amendment, determined by either phytoaccessible or total sterilant analysis. Bars represent means and error bars indicate the standard error. Phytoaccessible and total sterilant analysis were conducted on samples prior to the desorption experiment. Note that in treatment names, Sand = silica sand, Top = topsoil, B = bromacil, T = tebuthiuron. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

The phytoaccessible fraction in soils amended with AC was much lower compared to the non-amended soil, indicating that the sorption of sterilants to AC reduced phytoaccessibility (Figures 7 and 8, Appendix D). In soils amended with AC, the phytoaccessible fraction was typically greater than the desorbed fraction (Figures 9 and 10), indicating that a portion of the sterilants present may be available to plants but may not readily desorb from AC.

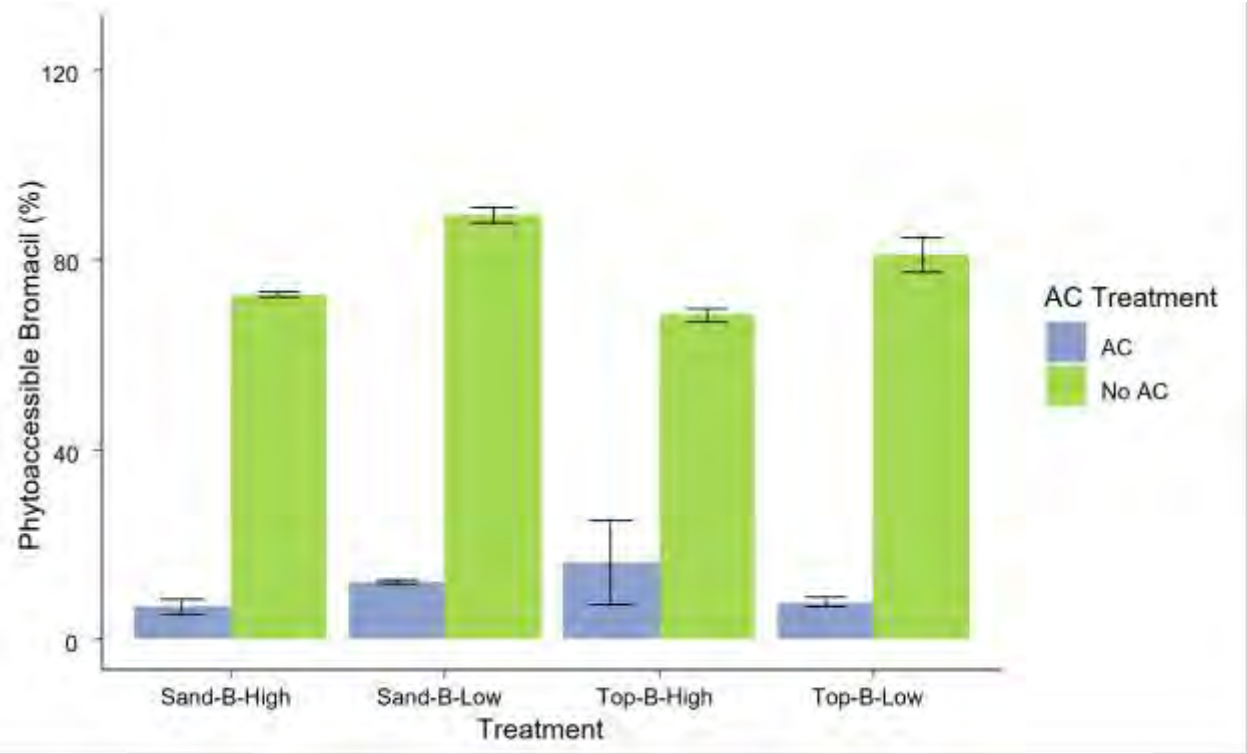

Figure 7. Phytoaccessible bromacil (%) in topsoil and silica sand, either amended with activated carbon (AC), or non-amended.
Bars represent means (n=3) and error bars indicate the standard error. Phytoaccessible analysis was conducted on samples prior to the desorption experiment. Note that in treatment names, Sand = silica sand, Top = topsoil, and B = bromacil. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

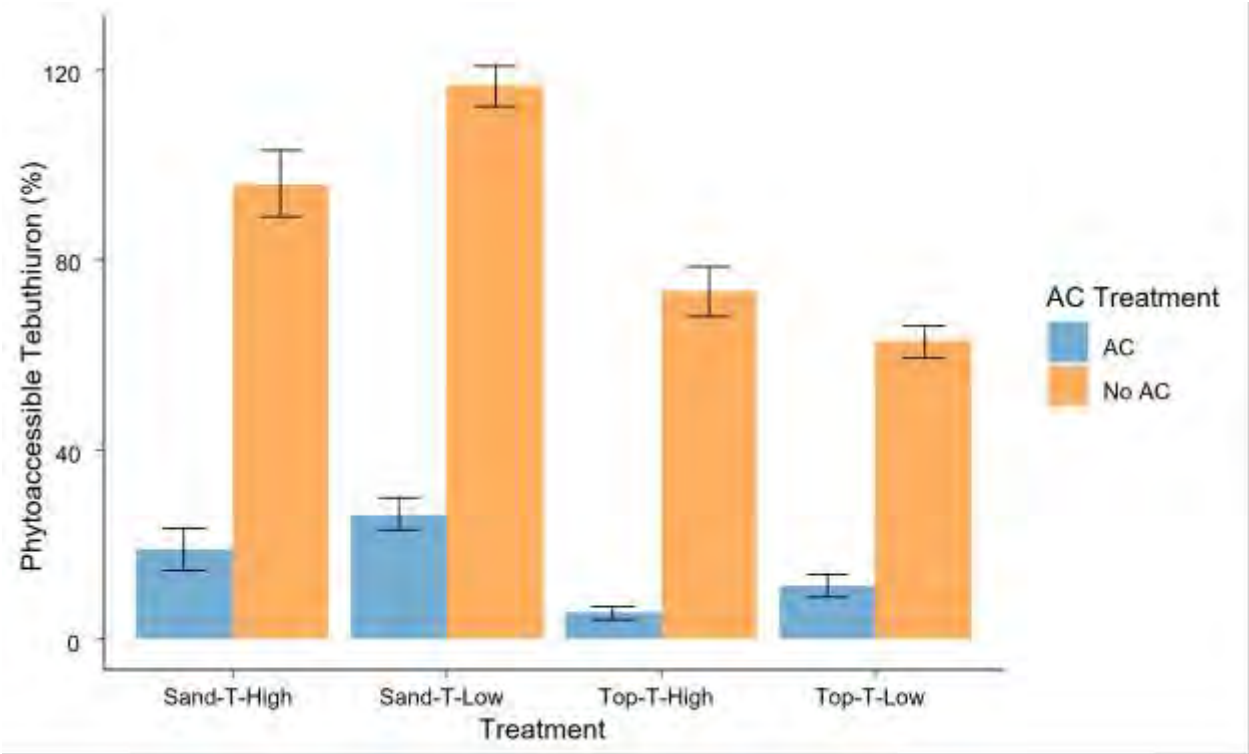

Figure 8. Phytoaccessible tebuthiuron (%) in topsoil and silica sand, either amended with activated carbon (AC), or non-amended.
Bars represent means (n=3) and error bars indicate the standard error. Phytoaccessible analysis was conducted on samples prior to the desorption experiment. Note that in treatment names, Sand = silica sand, Top = topsoil, and T = tebuthiuron. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

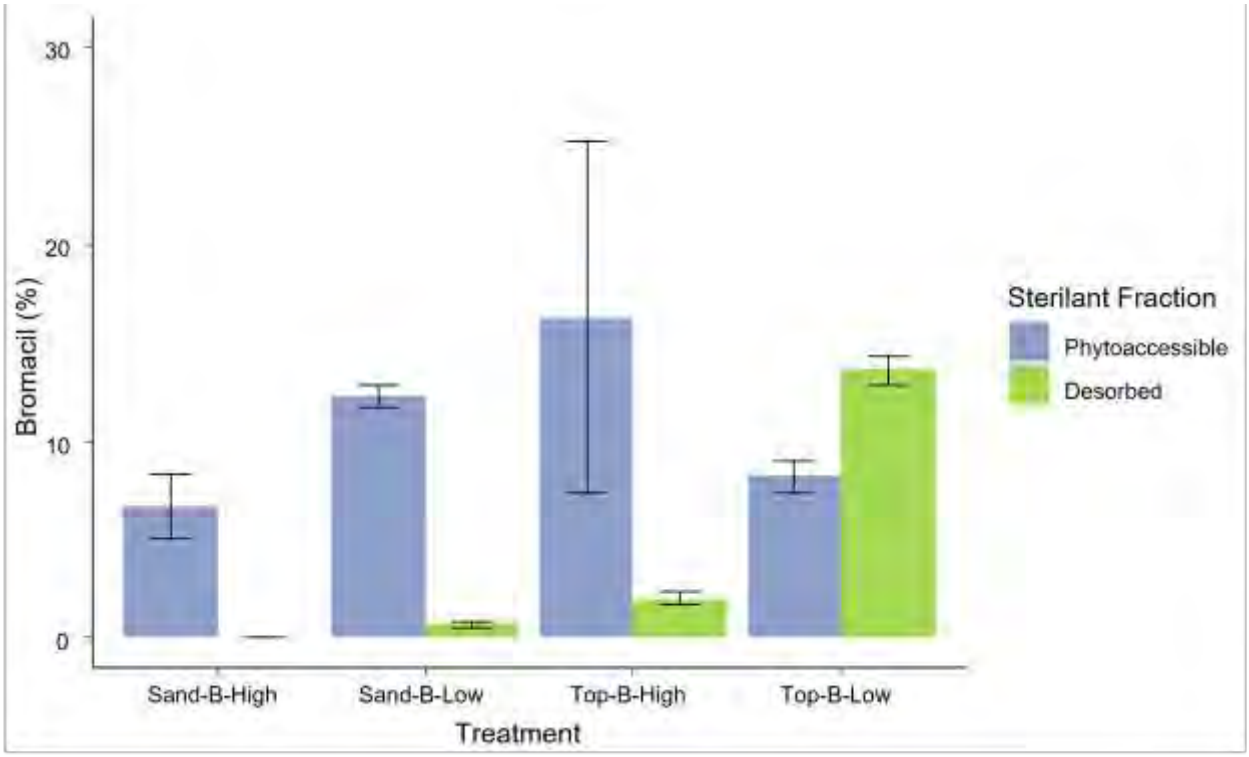

Figure 9. Phytoaccessible or desorbed bromacil (%) in topsoil and silica sand amended with activated carbon (AC).
Bars represent means (n=3) and error bars indicate the standard error. Phytoaccessible analysis was conducted on samples prior to the desorption experiment. The desorbed fraction of bromacil was determined from the desorption experiment. Note that in treatment names, Sand = silica sand, Top = topsoil, and B = bromacil. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

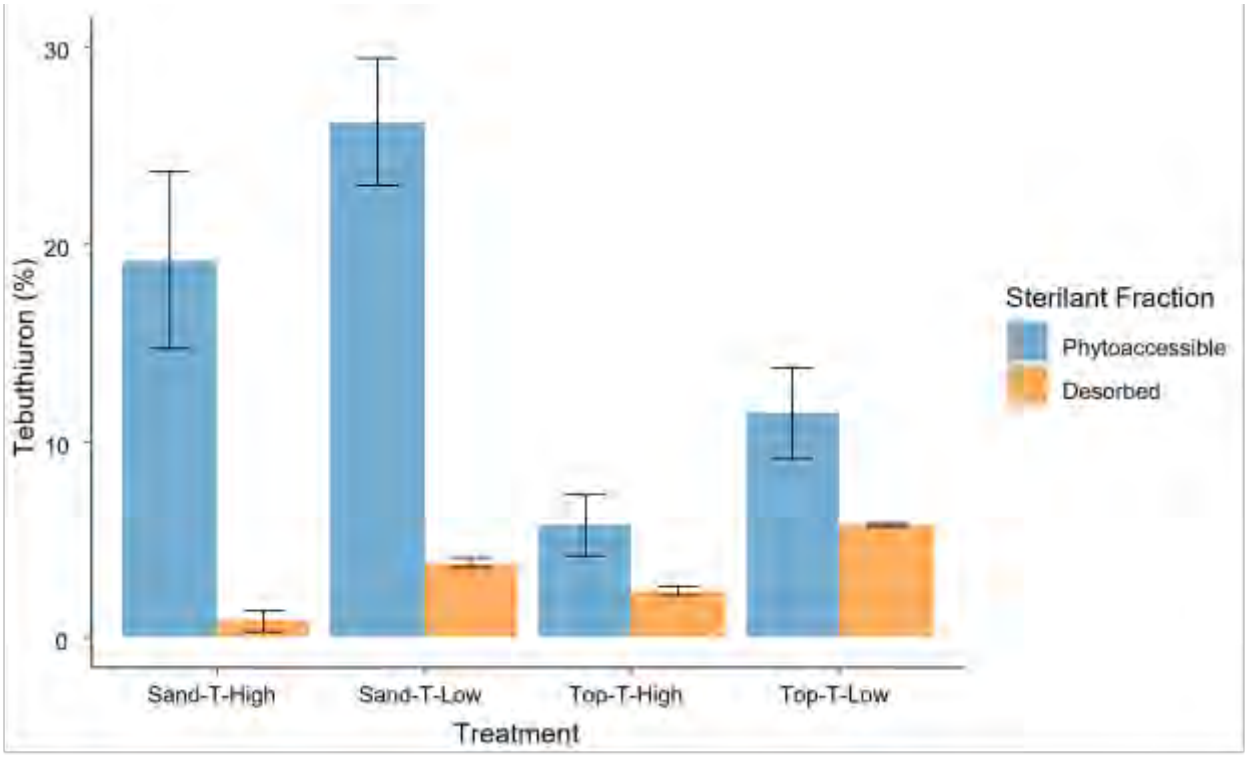

Figure 10. Phytoaccessible or desorbed tebuthiuron (%) in topsoil and silica sand amended with activated carbon (AC).
Bars represent means (n=3) and error bars indicate the standard error. Phytoaccessible analysis was conducted on samples prior to the desorption experiment. The desorbed fraction of tebuthiuron was determined from the desorption experiment. Note that in treatment names, Sand = silica sand, Top = topsoil, and T = tebuthiuron. High refers to the higher sterilant concentration (target 2.4 mg/kg), and low refers to the lower sterilant concentration (target 0.8 mg/kg).

3.4 Phase 1 Summary and Recommendations

3.4.1 Summary

The literature review provided evidence that black carbon may degrade over time. However, degradation studies often focused on biochar, and not activated carbon. Higher charring temperatures tend to lead to more recalcitrant black carbon compounds, indicating that AC is likely more recalcitrant than biochar, given the high charring temperatures used to create AC. Additionally, it appears likely that some desorption of bromacil and tebuthiuron from AC could occur in soil given their hydrophilic nature and the complex matrices of organic matter and clay that constitute most soils.

The literature indicated that researchers have used various means of artificial weathering (physical, chemical, and biological) to assess desorption of compounds from AC and similar compounds.

After an aggressive 18-hour shaking period, a strong sorption of sterilants to AC was observed. The percentage of sterilant desorbed was significantly less in soils amended with AC, compared to non-amended soils, for all treatments.

In soils with strong sorptive agents such as AC, common laboratory extraction for “total” sterilants does not appear to effectively extract sterilants bound to AC. This may lead to an underestimation of the total sterilant concentration in soils with sorptive amendments.

3.4.2 Recommendations

The longevity of sterilant immobilization with AC remains a question. Longevity was identified by Alberta Environment and Parks (AEP) as an important consideration in assessing the feasibility of AC as a suitable remediation technology for achieving site closure. Therefore, the recommendation for Phase 2 of this project is to conduct an artificial weathering experiment using physical weathering methods (i.e., freeze/thaw cycles). Phase 2 is detailed in Section 4.

4. ARTIFICIAL WEATHERING EXPERIMENT

4.1 Introduction

Exposure of AC and biochar to freeze-thaw cycles has been shown to increase desorption of compounds such as atrazine and pyrene and cause weathering of the AC or biochar itself (Hale et al., 2011; Harvey, 1973; Naisse et al., 2015). Weathering AC via exposure to freeze-thaw is relevant to Alberta’s climate. Therefore, in Phase 2, freeze-thaw cycles were used to artificially weather AC and sterilants in soil to assess the longevity of immobilization by AC.

4.2 Methods

4.2.1 Overview

Soils were previously spiked with either bromacil or tebuthiuron (Thacker, 2021) and amended with AC at an AC:sterilant ratio of 400:1 by weight. In Phase 1, soils with a sterilant concentration of approximately 0.8 and 2.4 mg/kg were used, however soils with other concentrations of bromacil and tebuthiuron were amended with AC as back-up. There was not sufficient soil remaining after Phase 1 to use the same materials in Phase 2. Therefore, soils from Phase 1 spiked to a concentration of approximately 1.5 mg/kg bromacil or tebuthiuron were used in the artificial weathering experiment. Given that these soils were amended with AC during Phase 1, they were considered sufficiently aged prior to beginning the artificial weathering experiment.

Soil (300 g, oven-dried equivalent) was placed into glass Mason jars with screw-top lids and exposed to the freeze-thaw cycle treatments. The number of freeze-thaw cycles was based on a literature review of similar studies (Hale et al., 2011; Harvey, 1973; Naisse et al., 2015). Each freeze-thaw cycle included 24 hours at approximately -15°C followed by 24 hours at approximately 20°C, allowing for complete freezing and thawing of the soil. Samples were weighed between freeze-thaw cycles and water added if needed to maintain a consistent moisture content. An overview of the experimental design is provided in Table 4.

Table 4. Experimental design for the artificial weathering experiment.

Treatments/Parameters	Number	Description
Soil	1	Brooks topsoil*
Soil Sterilants	2	Bromacil (Hyvar® X-L, liquid, 21.9% lithium salt of bromacil) Tebuthiuron (Spike® 80DF, granule, 80% tebuthiuron)
Soil Sterilants Concentration	1	Bromacil (mg/kg): 1.95 (0.62) *mean (standard deviation)* Tebuthiuron (mg/kg): 1.20 (9.09) *mean (standard deviation)*
AC Product	1	Powdered (Darco® 100-mesh particle size)
AC Application Rate	2	400:1** No AC
# of Freeze Thaw Cycles	2	10 and 20 freeze/thaw cycles
Replicates	3	

* Solonetzic Brown Chernozem (fine-grained loam) sourced near Brooks, AB.
** The AC application rate was selected based on those rates utilized by Cotton and Sharma (1993) in laboratory and field experiments and is on a weight basis.

Prior to conducting the freeze-thaw cycles, total sterilants and phytoaccessible sterilants analyses were performed on the soils to have an understanding of sterilant concentrations in non-weathered soil. Data from Phase 1 revealed that in the presence of AC, much of the sterilant remains adsorbed to AC during the extraction for total sterilants, and therefore is not accounted for in the analysis; this analytical method therefore becomes useful to assess if weathering changes the sorption of sterilants to AC. After the prescribed number of freeze-thaw cycles were completed, soil was sampled and analyzed for total and phytoaccessible sterilants. Sterilant concentrations after weathering were compared to the concentrations before weathering to assess if weathering changed the sorption of sterilants to AC or changed sterilant availability.

In addition to collecting soil samples for total and phytoaccessible sterilants after weathering, the modified SPLP extraction used in Phase 1 was performed on soils after weathering. Analysis included the filtrate collected after shaking and filtration; this analysis provided data on the quantity of sterilant that desorbed from soil and/or AC after weathering followed by an aggressive shaking procedure, providing a "worst case scenario" of sterilant desorption. The filtrate was also analyzed for total organic carbon (TOC) to determine if degradation of AC could be quantified. The soil was also analyzed for total sterilants after the modified SPLP extraction, as well as TOC and total inorganic carbon (TIC). The weathered soils with and without AC amendment were included in this analysis. However, due to a shortage of soil, the only non-weathered soil used in the modified SPLP extraction was the non-AC amended bromacil-spiked soil. The same desorption and mass balance equations described in Section 3.3 were used in Phase 2 for the modified SPLP extraction samples.

4.2.2 Statistical Analysis

Data exploration, analysis, and visualization were carried out using the R language and environment for statistical computing (R Core Team, 2019) and the additional packages *tidyr* (Wickham and Henry, 2019), *dplyr* (Wickham et al., 2019), *purrr* (Henry and Wickham, 2019), *ggplot2* (Wickham, 2016), and *emmeans* (Lenth et al., 2019). In this report, the term "significant" is used to describe statistically significant relationships ($\alpha = 0.05$). For all statistical tests, data were explored to determine whether assumptions of normality and homogeneity of variance were met; this included visual examination of data and residuals, Shapiro-Wilk test, and Levene's test.

To compare phytoaccessible soil concentrations in non-weathered and weathered soil, analysis of variance (ANOVA) followed by pairwise t-tests were used. Data transformation was required to meet assumptions or normality and homogeneity of variance. Phytoaccessible bromacil and tebuthiuron data were both log-transformed. In some cases, the reported sterilant concentration was below the laboratory detection limit (0.008 mg/kg for bromacil; 0.005 mg/kg for tebuthiuron) – in these cases, for the purposes of statistical analysis, the concentration was assumed to be either 0.008 or 0.005 mg/kg, respectively.

To compare total sterilant concentrations in non-weathered and weathered soil, ANOVA followed by pairwise t-tests were used. Data transformation was required to meet assumptions or normality and homogeneity of variance. Total bromacil and tebuthiuron data were both log-transformed.

To compare carbon (%) between treatments before and after modified-SPLP and between AC-amended and non-amended soil, ANOVA followed by pairwise t-tests were used. Statistical comparison was made among AC amendment and weathering treatments for each carbon source: total organic carbon (TOC) in soil, total inorganic carbon (TIC) in soil, and TOC in filtrate. The carbon sources were not compared. TIC was not measured in filtrate water due to a miscommunication with the lab. TOC in the filtrate was reported as mg/L, and was converted to a percentage for ease of comparison as in Section 3.3.3.3.

4.3 Results and Discussion

4.3.1 Phytoaccessible Sterilants – Non-Weathered and Weathered Soil

We were interested in comparing the bioaccessibility of soil sterilants before and after artificial weathering. In soil not amended with AC, bioaccessibility of bromacil increased significantly with weathering (after both 10 and 20 freeze-thaw cycles) [Figure 11]. This indicates that weathering may have changed the bonds between soil particles (i.e., clay, organic matter) and bromacil, resulting in an increase in bioaccessibility. In soil amended with AC, while 20 freeze-thaw cycles resulted in a significantly higher phytoaccessible bromacil concentration compared to non-weathered soil and 10 freeze-thaw cycles, the change in bioaccessibility with weathering was much smaller compared to the non-AC amended soil. After 20 freeze-thaw cycles, the data indicates that weathering resulted in either a change in the bonds between AC and bromacil, or possibly degradation of AC, resulting in an increase in the phytoaccessible bromacil concentration. Regardless of the weathering treatment, AC amendment resulted in significantly lower phytoaccessible bromacil concentrations compared to soil with no AC.

In soils amended with AC, phytoaccessible bromacil concentrations were below the total bromacil concentrations defined by the Alberta Tier 1 Soil Remediation Guidelines when non-weathered or after 10 freeze-thaw cycles, but were above the guideline (0.009 mg/kg for natural area, agricultural, and residential/parkland land uses) after 20 freeze-thaw cycles (AEP, 2019). When considering the ecological direct soil contact pathway, soil amended with AC and exposed to 20 freeze-thaw cycles had a phytoaccessible bromacil concentration below the guideline values (Figure 11). Without AC amendment, all weathering treatments resulted in phytoaccessible bromacil concentrations above the guidelines indicated in Figure 11.

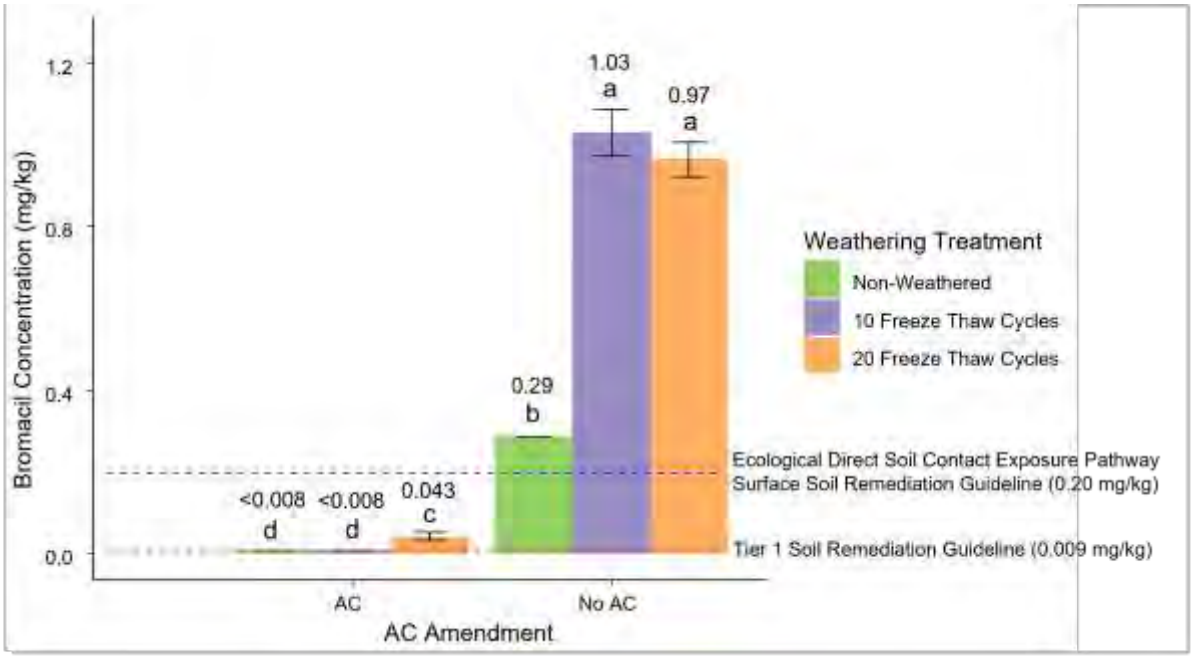

Figure 11. Phytoaccessible bromacil concentration (mg/kg) in soil amended with activated carbon (AC) or not amended (no AC).
The two AC amendment treatments were exposed to three different weathering treatments: no weathering, 10 freeze-thaw cycles, or 20 freeze-thaw cycles. Bars are means (n=3) with error bars representing the standard error. Average values are provided above each bar. Different lowercase letters indicate significant differences among the treatments. The red line indicates the total bromacil Alberta Tier 1 Soil Remediation Guidelines for fine-textured soil for natural area, agricultural, and residential/parkland land uses (AEP, 2019); the limiting pathway is the protection of freshwater aquatic life. The blue line indicates the fine-textured ecological direct soil contact exposure pathway Surface Soil Remediation Guideline Values for natural area, agricultural, and residential/parkland land uses for total bromacil (AEP, 2019).

Changes in bioaccessibility with weathering differed for tebuthiuron compared to bromacil (Figure 12). In non-AC amended soil, there were no significant differences in the bioaccessibility of tebuthiuron between weathered and non-weathered soil; weathering did not appear to influence the bonds between soil particles and tebuthiuron. In soil amended with AC, soil that underwent 10 freeze-thaw cycles had higher phytoaccessible tebuthiuron concentrations than soils that were non-weathered or underwent 20 freeze-thaw cycles. However, the phytoaccessible concentration in AC-amended soil, regardless of the weathering treatment, was low (<0.005 mg/kg in non-weathered and 20 freeze-thaw cycle treatments, 0.032 mg/kg in the 10 freeze-thaw cycle treatment; Appendix E). Regardless of the weathering treatment, AC amendment resulted in significantly lower phytoaccessible tebuthiuron concentrations compared to soil with no AC. Additionally, soils amended with AC were below the Alberta Tier 1 Soil Remediation Guidelines value for total tebuthiuron (0.046 mg/kg for natural area, agricultural, and residential/parkland land uses) regardless of the weathering treatment. Without AC amendment, all weathering treatments resulted in phytoaccessible tebuthiuron concentrations above the guidelines indicated in Figure 12.

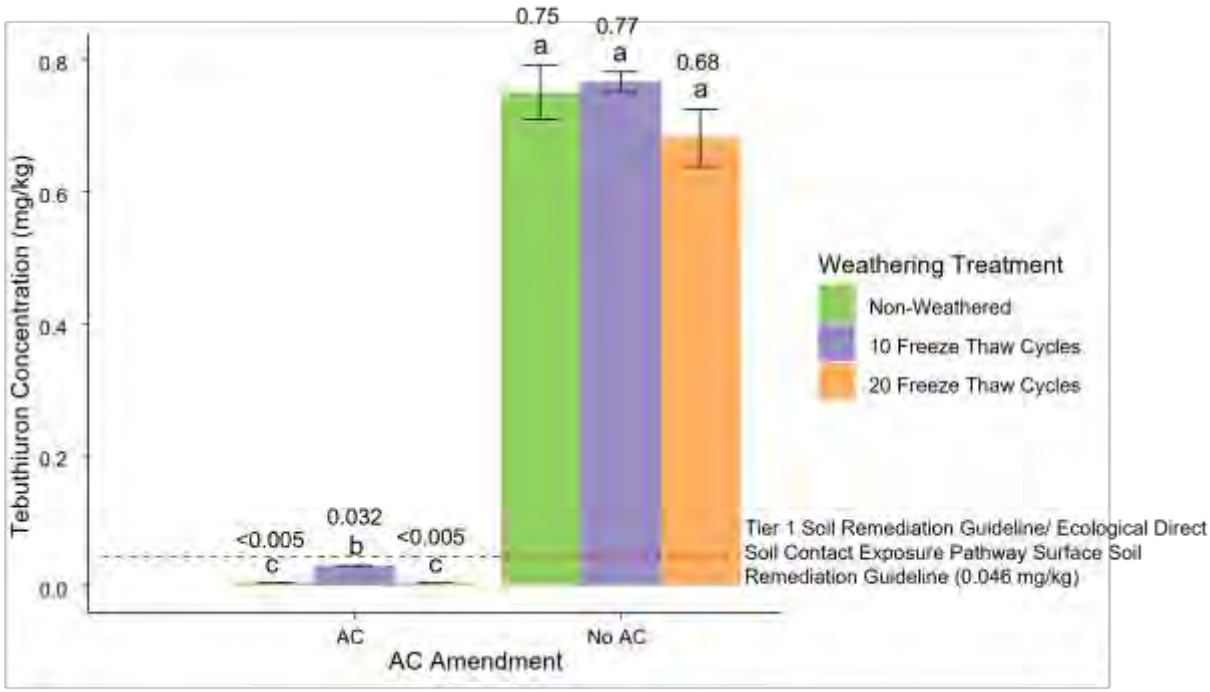

Figure 12. Phytoaccessible tebuthiuron concentration (mg/kg) in soil amended with activated carbon (AC) or not amended (no AC).
The two AC amendment treatments were exposed to three different weathering treatments: no weathering, 10 freeze-thaw cycles, or 20 freeze-thaw cycles. Bars are means (n=3) with error bars representing the standard error. Average values are provided above each bar. Different lowercase letters indicate significant differences among the treatments. The red line indicates the total tebuthiuron Alberta Tier 1 Soil Remediation Guidelines – as well as ecological direct soil contact exposure pathway Surface Soil Remediation Guideline Values – for fine-textured soil for natural area, agricultural, and residential/parkland land uses; the limiting pathway is ecological direct soil contact (AEP, 2019).

4.3.2 Total Sterilants – Non-Weathered and Weathered Soil

Total sterilant concentrations were affected by AC amendment and weathering (Figure 13 and 14; Appendix E). As identified in Phase 1, reported total sterilant concentrations were impacted by the presence of AC. In the absence of weathering, total bromacil and tebuthiuron concentrations were significantly lower when soil was amended with AC. This is an important finding, indicating that the laboratory method used to extract "total" sterilants may not be sufficient when a strong sorptive material, such as AC, is present in soil.

In soils amended with AC, total bromacil concentrations were above the total bromacil concentrations defined by the Alberta Tier 1 Soil Remediation Guidelines (0.009 mg/kg for natural area, agricultural, and residential/parkland land uses) regardless of the weathering treatment. When considering the ecological direct soil contact pathway, soil amended with AC had total bromacil concentrations below the guideline values for all weathering treatments (Figure 13). Without AC amendment, all weathering treatments resulted in total bromacil concentrations above the guidelines indicated in Figure 13.

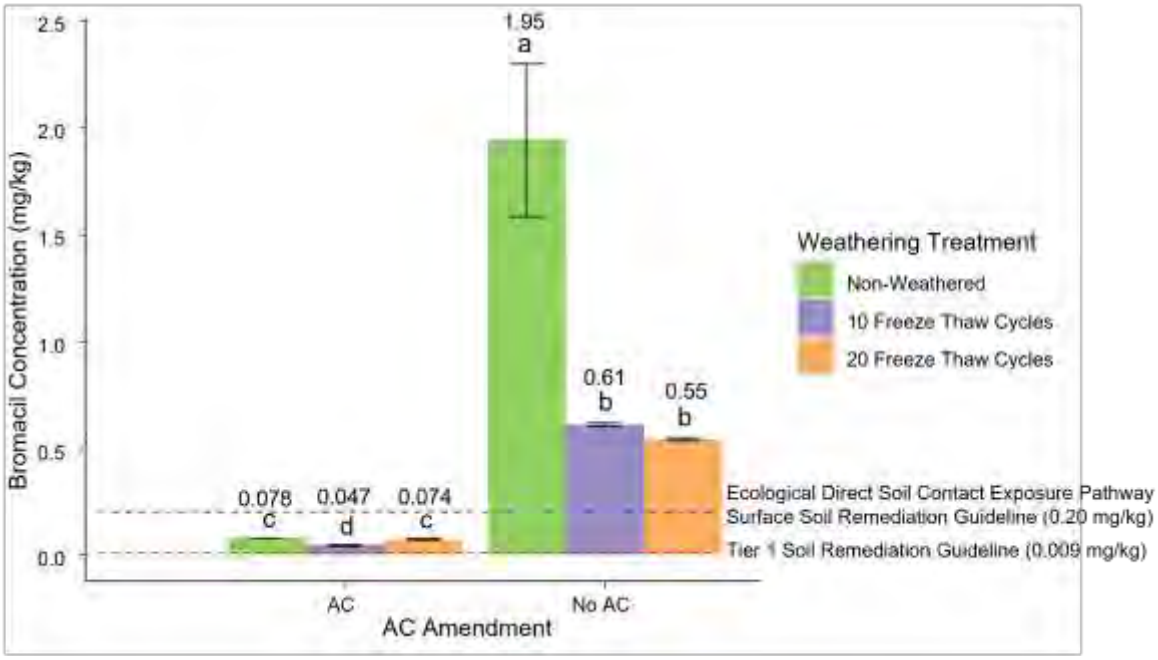

Figure 13. Total bromacil concentration (mg/kg) in soil amended with activated carbon (AC) or not amended (no AC).
The two AC amendment treatments were exposed to three different weathering treatments: no weathering, 10 freeze-thaw cycles, or 20 freeze-thaw cycles. Bars are means (n=3) with error bars representing the standard error. Average values are provided above each bar. Different lowercase letters indicate significant differences among the treatments. The red line indicates the total bromacil Alberta Tier 1 Soil Remediation Guidelines for fine-textured soil for natural area, agricultural, and residential/parkland land uses (AEP, 2019); the limiting pathway is the protection of freshwater aquatic life. The blue line indicates the fine-textured ecological direct soil contact exposure pathway Surface Soil Remediation Guideline Values for natural area, agricultural, and residential/parkland land uses for total bromacil (AEP, 2019).

In terms of total tebuthiuron, all soils tested were above the Alberta Tier 1 Soil Remediation Guidelines value for total tebuthiuron (0.046 mg/kg for natural area, agricultural, and residential/parkland land uses) regardless of the weathering or AC treatment (Figure 14). However, it is important to note that the reported total sterilant concentrations are influenced by the presence of AC as described in the previous paragraph.

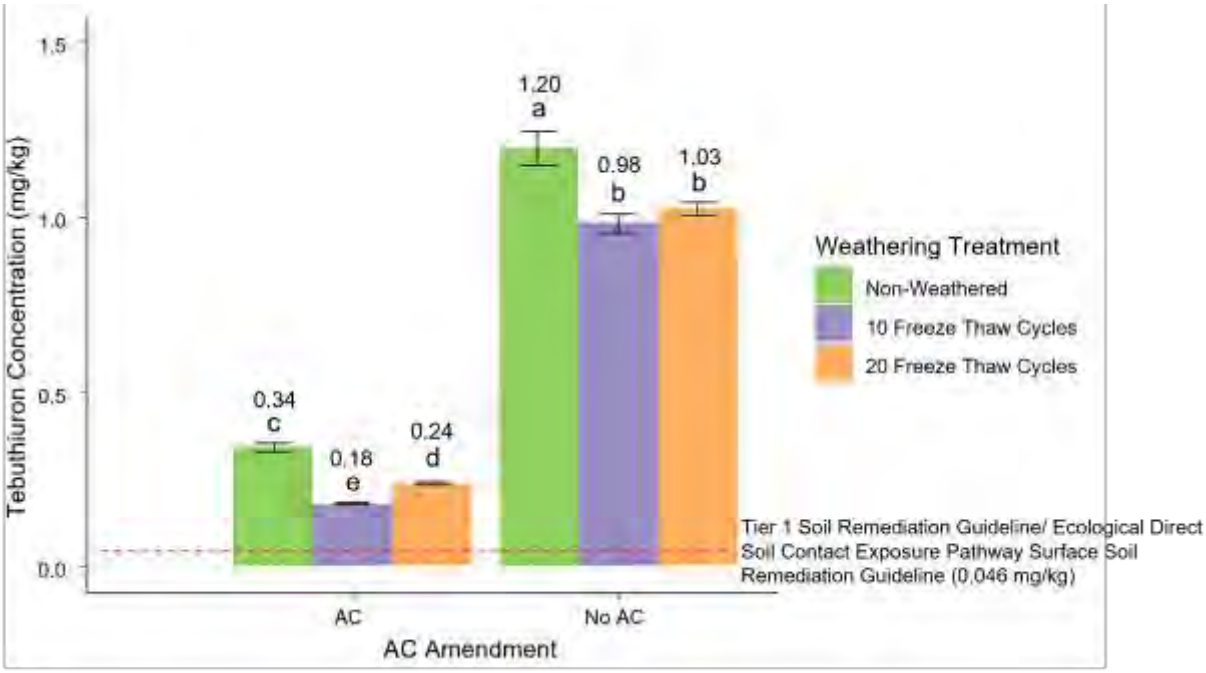

Figure 14. Total tebuthiuron concentration (mg/kg) in soil amended with activated carbon (AC) or not amended (no AC).
The two AC amendment treatments were exposed to three different weathering treatments: no weathering, 10 freeze-thaw cycles, or 20 freeze-thaw cycles. Bars are means (n=3) with error bars representing the standard error. Average values are provided above each bar. Different lowercase letters indicate significant differences among the treatments. The red line indicates the total tebuthiuron Alberta Tier 1 Soil Remediation Guidelines – as well as ecological direct soil contact exposure pathway Surface Soil Remediation Guideline Values – for fine-textured soil for natural area, agricultural, and residential/parkland land uses; the limiting pathway is ecological direct soil contact (AEP, 2019).

Total sterilant concentrations tended to decrease with weathering for both bromacil and tebuthiuron, especially in soil with no AC amendment (Figure 13 and 14). This observation was unexpected, especially for bromacil, given that phytoaccessible concentrations of bromacil increased with weathering (Section 4.3.1). Total sterilant concentrations were not expected to change, given that no sterilants were removed from the system. Total sterilant concentrations might decrease if weathering results in degradation of sterilants, but if this were the case, one would not expect phytoaccessible bromacil to increase with weathering. Total sterilant concentrations could decrease if sterilants were to sorb to the container during the freeze-thaw cycles, but given that glass containers were used, this is considered unlikely.

Interestingly, the surrogate recovery (previously explained in Section 2.4.2) was similar from AC-amended and no AC soils after weathering, for both bromacil and tebuthiuron (i.e., 73% versus 68% in bromacil-spiked soil not amended with AC or AC-amended after 20 freeze-thaw cycles, respectively; Appendix E). In non-weathered soil, a difference in surrogate recovery was observed (81% versus 61% in bromacil-spiked soil not amended with AC or AC-amended, respectively; Appendix E). In Phase 1, AC-amended soils tended to have lower surrogate recovery, indicating that sterilants were strongly sorbed to AC and that the analytical extraction method may not have been sufficient to recover sterilants when strongly sorptive materials were present. In Phase 2, it is unclear why the laboratory analysis shows

total sterilant concentrations to be much lower in AC-amended soil, but without a considerably lower surrogate recovery also observed in AC-amended soil after weathering.

4.3.3 Desorption Experiment

4.3.3.1 Sterilant immobilization

A modified SPLP extraction was performed on the soils after exposure to freeze-thaw cycles to further assess the impact of weathering on sterilant desorption. Due to a shortage of soil, the only non-weathered soil used in the modified SPLP extraction was the non-AC amended bromacil-spiked soil. The percent desorption of bromacil and tebuthiuron, after exposure to an aggressive 18-hour shaking period, is shown in Figure 15 and 16.

The percentage of bromacil desorbed did not differ significantly between the non-weathered soil and 20 freeze-thaw cycle treatment in soil with no AC amendment. However, the percentage of bromacil desorbed after 10 freeze-thaw cycles was significantly less than in the non-weathered soil; this result is surprising, and one would expect higher desorption in weathered soil due to changes in the bonds between soil particles and the sterilant. After an aggressive shaking procedure, bromacil desorption in AC-amended soil was significantly lower than soils that were not amended with AC. However, AC did not completely prevent bromacil desorption in weathered soil (2% and 1% desorption after 10 and 20 freeze-thaw cycles, respectively; Table 5).

The percentage of tebuthiuron desorbed was not significantly affected by the freeze-thaw cycles (10 or 20 cycles) [Figure 16]. Desorption was significantly lower in AC-amended soils compared to soils that were not amended with AC. After weathering, AC did not completely prevent tebuthiuron desorption (2% and 3% desorption after 10 and 20 freeze-thaw cycles, respectively; Table 5).

Considering the results from both Phase 1 and 2, it is clear that amendment with AC can prevent a significant amount of sterilant leaching, even after the soil has been weathered via 20 freeze-thaw cycles. However, amendment with AC did not result in complete immobilization of bromacil or tebuthiuron after an aggressive, “worst case scenario” shaking procedure.

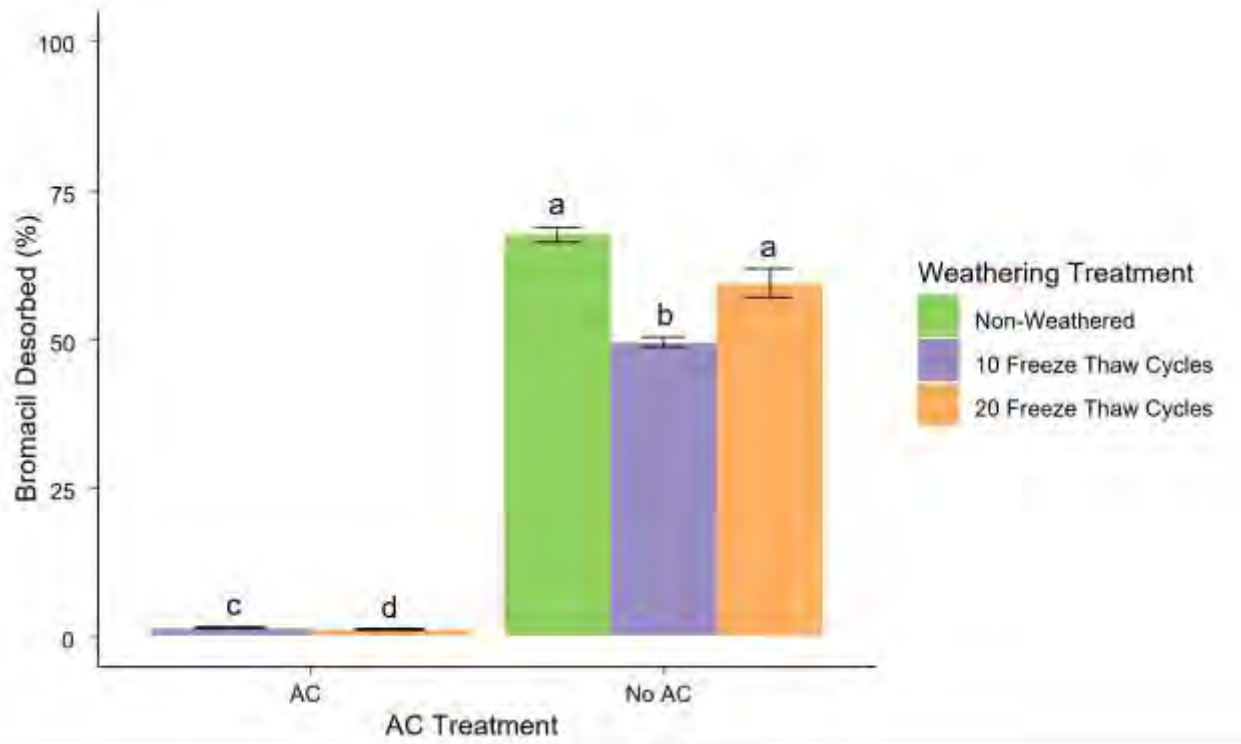

Figure 15. Desorption (%) of bromacil in soil amended with activated carbon (AC) or not amended (no AC).
The two AC amendment treatments were exposed to three different weathering treatments: no weathering, 10 freeze-thaw cycles, or 20 freeze-thaw cycles. Bars represent means (n=3) and error bars indicate the standard error. Desorption data was determined after 18-hour shaking in 0.01M $CaCl_2$.

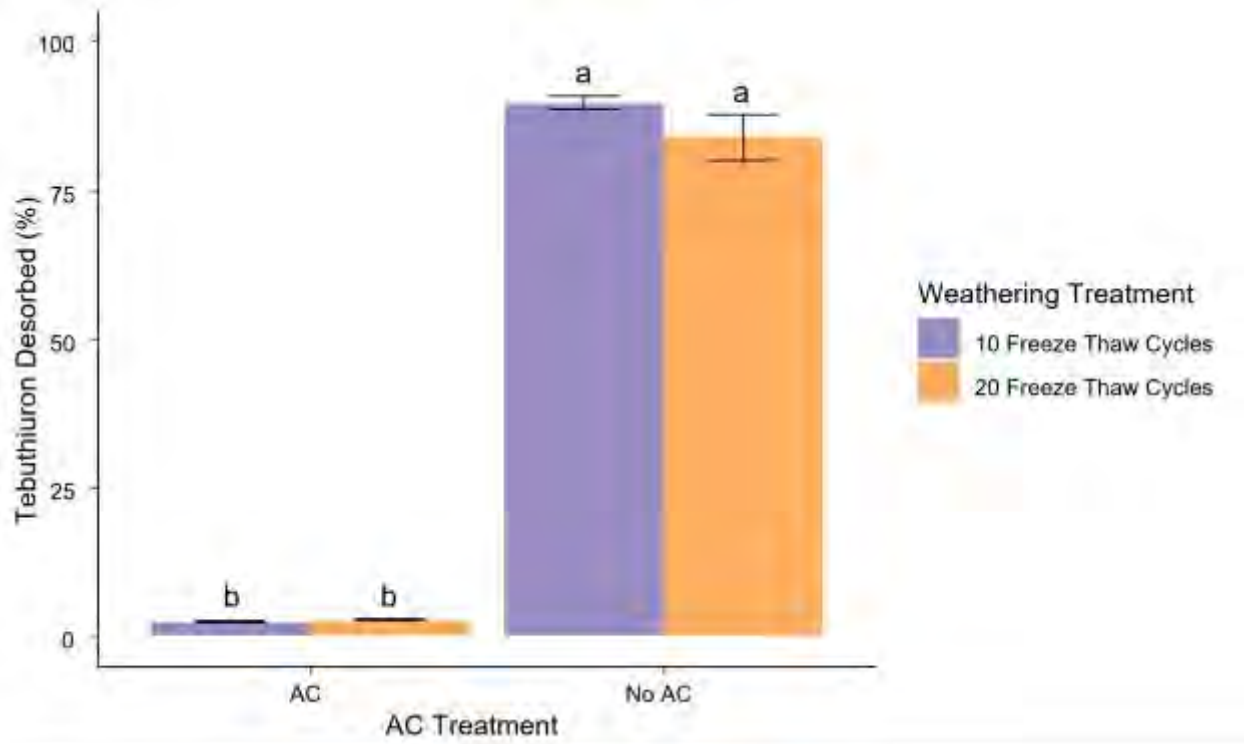

Figure 16. Desorption (%) of tebuthiuron in soil amended with activated carbon (AC) or not amended (no AC).
The two AC amendment treatments were exposed to two different weathering treatments: 10 freeze-thaw cycles, or 20 freeze-thaw cycles. Bars represent means (n=3) and error bars indicate the standard error. Desorption data was determined after 18-hour shaking in 0.01M $CaCl_2$.

4.3.3.2 Mass balance

As was observed in Phase 1, after the desorption experiment, mass did not balance between the initial sterilant content versus the content in the filtrate and filtered soil (Table 5). When AC was present, this observation was more pronounced. Despite low recovery in AC-amended soil, the surrogate recovery was comparable to that of the non-amended soil; this differed from the findings in Phase 1. In Phase 2, the mass of bromacil also did not balance in soil that was not amended with AC; in non-AC amended soil, the mass of tebuthiuron roughly balanced. The sterilant concentrations measured in the filtered soil used total sterilant measurements from the laboratory. Given the complications observed with total sterilant analysis and interpretation (Section 4.2 and 4.3.2), there is a need to better understand what quantity of sterilants are extracted during this analysis, especially when AC (or other sorptive materials) are present.

Table 5. Sterilant mass and desorption data obtained during the desorption experiment.

Values are means (n=3). Yellow shading is used to highlight the fact that sterilant mass did not balance in soils amended with AC.

Sterilant	**AC Treatment**	**Weathering Treatment**	Initial sterilant in soil (mg)	Sterilant in filtrate (mg)	Sterilant in filtered soil* (mg)	Sterilant in filtrate + filtered soil* (mg)	% of sterilant desorbed	% of sterilant retained	Average surrogate recovery in filtered soil (%)**
Bromacil	No AC	Non-Weathered	0.292	0.196	0.007	0.203	67	33	70
		10 Freeze Thaw Cycles	0.292	0.144	0.008	0.152	49	51	67
		20 Freeze Thaw Cycles	0.292	0.173	0.010	0.183	59	41	69
	AC	10 Freeze Thaw Cycles	0.292	0.004	0.006	0.011	2	98	65
		20 Freeze Thaw Cycles	0.292	0.004	0.010	0.014	1	99	69
Tebuthiuron	No AC	10 Freeze Thaw Cycles	0.180	0.161	0.038	0.199	90	10	79
		20 Freeze Thaw Cycles	0.180	0.150	0.030	0.181	84	16	69
	AC	10 Freeze Thaw Cycles	0.180	0.004	0.040	0.044	2	98	81
		20 Freeze Thaw Cycles	0.180	0.005	0.025	0.030	3	97	68

*Note that the sterilant in filtered soil excludes the sterilant concentration from the filtrate (0.01M $CaCl_2$) (see Section 3.3).

**The laboratory adds a surrogate to samples as a QA/QC procedure. The surrogate is a compound with similar behaviour and characteristics as the target compound, and when bromacil or tebuthiuron is the target compound, monuron is used as the surrogate.

4.3.3.3 Carbon in soil and filtrate

Carbon in soil and filtrate was measured to determine whether it was possible to use these analyses to observe potential degradation of AC. Of the weathered soils, only soils spiked with bromacil and weathered via 20 freeze-thaw cycles were used for this analysis (in the interest of cost savings). They were compared to non-weathered soil either amended with AC or non-amended. The percentage of bromacil desorbed after the 18-hour shaking period was very low (Section 3.3.3.1), indicating that AC degradation due to weathering was likely low. While TOC in AC-amended soil after weathering and modified-SPLP was lower than that of non-weathered soil prior to SPLP, the difference was not significant (Figure 17). There were also no significant differences in TIC within AC-amended soil before and after SPLP, and no significant difference between AC-amended and non-amended soils post-SPLP. There was no significant difference in TOC measured within the filtrate of AC-amended and non-amended soil. Measurement of TOC or TIC did not appear to indicate degradation of AC after 20 freeze-thaw cycles, although it would be beneficial to include analysis of TIC in the filtrate for confirmation.

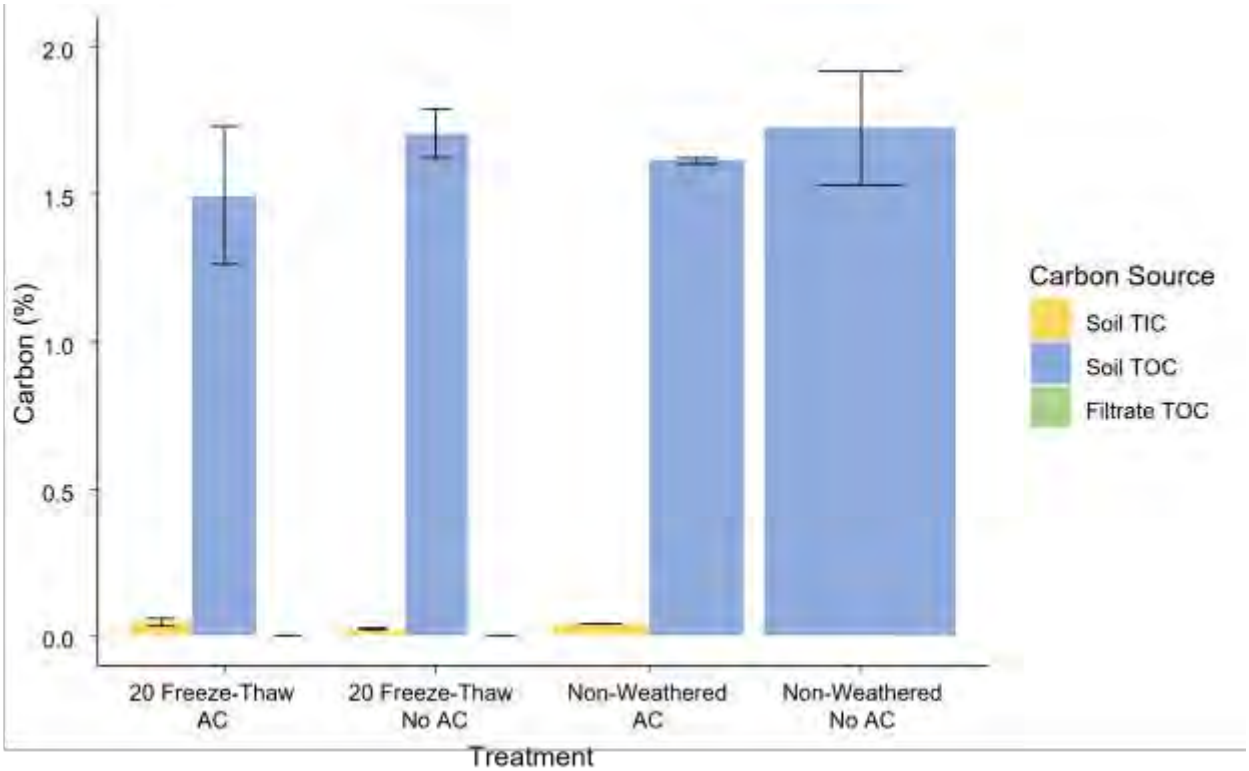

Figure 17. Carbon (%) in soil and filtrate, before and after the desorption experiment. Three carbon sources were investigated: total inorganic carbon (TIC) in soil, total organic carbon (TOC) in soil, and TOC in filtrate water. The treatments included soil either amended with activated carbon (AC) or non-amended, and soil that was exposed to 20 freeze-thaw cycles that underwent a modified SPLP desorption experiment or non-weathered soil prior to SPLP. Bars represent means (n=3) and error bars indicate the standard error. Desorption data was determined after 18-hour shaking in 0.01M $CaCl_2$.

4.4 Phase 2 Summary

Sterilants (bromacil and tebuthiuron) and AC in soil were artificially weathered via 10 or 20 freeze-thaw cycles, with the goal of assessing the longevity of sterilant immobilization by AC in soil. In some cases, weathering resulted in increased sterilant phytoaccessibility in soils amended with AC, but the difference was relatively small. *Regardless of the weathering treatment, AC amendment resulted in significantly lower phytoaccessible sterilant concentrations compared to soil with no AC*. Results from the modified-SPLP extraction indicated that only 1% to 3% of sterilant mass desorbed in AC-amended topsoil. In fact, desorption percentages observed after SPLP in Phase 2 were lower than those observed for non-weathered topsoil in Phase 1 (2% to 14% of sterilant mass desorbed in AC-amended topsoil). Additionally, results from Phase 2 further emphasized the need to better understand the laboratory extraction process for total sterilants, and how it is impacted by sorptive compounds such as AC.

5. OVERALL SUMMARY AND CONCLUSIONS

The overall objective of this project was to assess the long-term immobilization of soil sterilants by AC. The purpose of the assessment was to validate AC's effectiveness as a remediation technology. As the project began, two pertinent research questions were identified:

1. What is the percent effectiveness of AC in immobilizing soil sterilants when applied to soil at ratios established in previous research (i.e., 400:1)?
2. If proven sufficiently effective in immobilizing soil sterilants, under what conditions could AC release soil sterilants, thus making them available to vegetation and/or leaching through the soil profile?

To evaluate these research questions, the project was completed in two phases. Phase 1 included a literature review and desorption experiment. The desorption experiment was designed to simulate the worst-case scenario of sterilant leaching in soil. Phase 2 was an artificial weathering experiment to assess the longevity of sterilant immobilization by AC.

In general, AC was effective at immobilizing soil sterilants when applied at a rate of 400:1 (AC:sterilant, weight basis). In both Phase 1 and Phase 2 desorption experiments, sterilant desorption was significantly lower in soil amended with AC compared non-amended soil. Across the experiments, desorption rates ranged from 0 to 14%, and the soil type tended to influence desorption more strongly than the sterilant concentration. In general, phytoaccessible concentrations of bromacil and tebuthiuron were below direct soil contact guidelines after weathering when soils were amended with activated carbon.

In Phase 2, in topsoil, desorption rates ranged from 1% to 3% after weathering, indicating that AC may effectively sorb the majority of bromacil and tebuthiuron in the long-term, but some desorption and leaching may still occur. Additionally, weathering influenced the phytoaccessibility of soil sterilants. In some cases, weathering resulted in increased sterilant phytoaccessibility in soils amended with AC, but the difference was relatively small. Regardless of the weathering treatment, AC amendment resulted in significantly lower phytoaccessible sterilant concentrations compared to soil with no AC.

There are numerous factors that could result in AC releasing soil sterilants, including weathering and climactic conditions, environmental conditions, and properties of the sterilant itself. In Phase 2, weathering increased the bioaccessibility of bromacil and tebuthiuron in some cases, but phytoaccessibility was significantly lower compared to soil that was not amended with AC. The literature

review also indicated that weathering can result in desorption of sterilants and other compounds from AC. Weathering may also degrade black carbon over time, causing changes in structure, charge, and sorption dynamics; AC is likely more recalcitrant than other black carbon materials such as biochar, but it is plausible that these changes could occur in AC. Environmental conditions such as clay content, organic matter, pH, and temperature influence sterilant sorption to AC. Clay and organic matter can provide sorption sites for AC, and changes to the clay or organic matter content over time could impact sorption. There will be competition for adsorption sites on AC between herbicide and naturally-occurring organic compounds. Temperature and pH influence sorption and desorption. Additionally, the type of bonds formed between the herbicide and AC impact desorption kinetics.

This project aimed to address regulatory hesitation in accepting immobilization as a long-term solution for managing sterilant-impacted soils, due to uncertainty regarding the longevity of immobilization. Desorption of bromacil and tebuthiuron from AC in the tested topsoil was low after weathering (1% to 3%), indicating that majority of the sterilants remained sorbed to AC after physical weathering. In many cases, AC amendment lowered phytoaccessible sterilant concentrations below limits outlined in the Tier 1 Soil Remediation Guidelines, indicating that the phytoaccessible laboratory method is a valuable risk assessment tool. It is recommended that SSP members seek regulatory input regarding the results of this project, to determine whether any additional validation of AC's long-term effectiveness is required. Additionally, this research has highlighted the need to better understand the extraction process used to determine total sterilant concentrations, and how this may be affected by the presence of strongly sorptive materials such as AC.

Including AC as a remediation technology in meso- or field-scale demonstrations within the SSP should be considered. This could lead to development of best practices for the use of AC as an immobilization technique, including factors such as:

- The type of AC (i.e., feedstock and charring temperature);
- Methods of incorporation into soil;
- Comparison of immobilization by AC to other remediation technologies; and,
- Incorporation of the phytoaccessible method (Maxwell, 2022) for proving effective retention of sterilants to justify regulatory site closure.

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APPENDIX A: PHYTOACCESSIBLE STERILANT EXTRACTION METHOD

The method below was developed in Maxwell (2021).

February 1, 2021 Adopted Method

1) From Garrett et al. (2009): **[Use 1 g soil to 40 mL extractant]**. A sample weight to extractant ratio of 1 g soil per 40 mL extractant was selected, based on previous research (e.g., Hall et al., 1996a,b,c, 1998), as being optimum.[45] Less volume of extractant per g of soil tends to create a less efficient extraction, and a larger volume of extractant impairs detection limits.[45] The soil is extracted with a solution what has more or less the same ionic strength as the average salt concentration in many soil solutions.[46]
2) Use brief (less than 10 seconds), vigorous hand-shaking to break-up and suspend soil in calcium chloride.
3) Shake horizontally for 50 minutes on mechanical shaker at 385 oscillations or shakes per minute.[45]
4) Centrifuge samples for 10 min at a Relative Centrifugal Force (RCF) of [3200].[45]
5) Decant supernatant into a new pre-cleaned 50-mL polypropylene (PP) tube.[45]
6) Re-centrifuge the supernatant for 20 min at a RCF of [3200].[45]
7) Pipette 5 mL of the supernatant into a new, clean 15-mL PP centrifuge tube
8) Dilute the sample twofold (add 5 mL) with 2% HNO3 into a 15-mL PP centrifuge tube, mix by vortexing, and centrifuge immediately for 20 min at a RCF of [3600].[45] (i) Acidification of the drawn supernatant is done to prevent elemental adsorption to the glass or polythene of the reaction vessel and to prevent growth of bacteria, (ii) The acidified supernatant can be stored without a change in composition.[46]
9) The prepared sample will be submitted to Element Materials Technology (Calgary, AB) for analysis on HPLC/MSD for bromacil and tebuthiuron concentrations. Element filters the sample through a syringe filter. The extract will be injected into the HPLC.

APPENDIX B: DESORPTION EXPERIMENT AVERAGED DATA

Sterilant mass and desorption data obtained during the desorption experiment. Values are means (n=3).

Yellow shading is used to highlight the fact that sterilant mass did not balance in soils amended with AC.

Treatment	Sterilant	AC treatment	Initial sterilant in soil (mg)	Sterilant in filtrate (mg)	Sterilant in filtered soil* (mg)	Sterilant in filtrate + filtered soil* (mg)	% of sterilant desorbed	% of sterilant retained	Average surrogate recovery in filtered soil (%)**
Top-B-High	Bromacil	No AC	0.275	0.210	0.058	0.268	77	23	69
		AC	0.275	0.005	0.062	0.067	2	98	39
Sand-B-High		No AC	0.407	0.462	-0.002	0.459	114	-14	78
		AC	0.407	0.000	0.166	0.167	0	100	10
Top-B-Low		No AC	0.098	0.071	0.010	0.081	73	27	68
		AC	0.098	0.013	0.013	0.026	14	86	60
Sand-B-Low		No AC	0.143	0.136	-0.001	0.135	95	5	82
		AC	0.143	0.001	0.040	0.041	1	99	12
Top-T-High	Tebuthiuron	No AC	0.321	0.195	0.143	0.338	61	39	59
		AC	0.321	0.008	0.123	0.131	2	98	42
Sand-T-High		No AC	0.368	0.420	0.001	0.421	114	-14	73
		AC	0.368	0.003	0.134	0.137	1	99	10
Top-T-Low		No AC	0.105	0.071	0.048	0.119	67	33	75
		AC	0.105	0.006	0.047	0.053	6	94	63
Sand-T-Low		No AC	0.089	0.105	0.000	0.105	119	-19	82
		AC	0.089	0.003	0.052	0.055	4	96	10

*Note that the sterilant in filtered soil excludes the sterilant concentration from the filtrate (0.01M $CaCl_2$) (see Section 3.3).

**The laboratory adds a surrogate to samples as a QA/QC procedure. The surrogate is a compound with similar behaviour and characteristics as the target compound, and when bromacil or tebuthiuron is the target compound, monuron is used as the surrogate.

APPENDIX C: DESORPTION EXPERIMENT RAW DATA

The following tables presents the raw data obtained from laboratory analysis of samples in the desorption experiment, providing an indication of variability in the data.

Bromacil Data

Treatment	AC treatment	Initial sterilant concentration in soil (mg/kg)	Sterilant concentration in filtered soil (mg/kg)	Sterilant concentration in filtrate (ug/L)	Phytoaccessible concentration in soil (mg/kg)	% of sterilant phytoaccessible	% of sterilant desorbed	% of sterilant retained
Top-B-High	No AC	1.83	0.40	147.00	1.30	71	80	20
		1.83	0.45	143.00	1.23	67	78	22
		1.83	0.42	131.00	1.23	67	71	29
	AC	1.83	0.42	4.90	0.13	7	3	97
		1.83	0.39	3.10	0.14	8	2	98
		1.83	0.43	2.90	0.62	34	2	98
Sand-B-High	No AC	2.71	0.02	317.00	2.00	74	117	-17
		2.71	0.02	318.00	1.95	72	117	-17
		2.71	0.01	289.00	1.95	72	107	-7
	AC	2.71	0.87	0.10	0.21	8	0	100
		2.71	1.29	0.10	0.24	9	0	100
		2.71	1.17	0.10	0.10	4	0	100

Treatment	AC treatment	Initial sterilant concentration in soil (mg/kg)	Sterilant concentration in filtered soil (mg/kg)	Sterilant concentration in filtrate (ug/L)	Phytoaccessible concentration in soil (mg/kg)	% of sterilant phytoaccessible	% of sterilant desorbed	% of sterilant retained
Top-B-Low	No AC	0.65	0.10	39.80	0.58	88	61	39
		0.65	0.07	51.60	0.51	79	79	21
		0.65	0.06	50.90	0.50	76	78	22
	AC	0.65	0.10	8.40	0.05	7	13	87
		0.65	0.10	8.40	0.06	10	13	87
		0.65	0.08	9.80	0.05	7	15	85
Sand-B-Low	No AC	0.96	0.00	86.90	0.88	92	91	9
		0.96	0.00	93.00	0.83	87	97	3
		0.96	0.00	91.70	0.85	89	96	4
	AC	0.96	0.39	0.70	0.11	12	1	99
		0.96	0.20	0.40	0.13	13	0	100
		0.96	0.22	0.90	0.11	12	1	99

Tebuthiuron Data

Treatment	AC treatment	Initial sterilant concentration in soil (mg/kg)	Sterilant concentration in filtered soil (mg/kg)	Sterilant concentration in filtrate (ug/L)	Phytoaccessible concentration in soil (mg/kg)	% of sterilant phytoaccessible	% of sterilant desorbed	% of sterilant retained
Top-T-High	No AC	2.14	0.99	136.00	1.63	76	63	37
		2.14	1.06	119.00	1.73	81	56	44
		2.14	0.92	135.00	1.34	63	63	37
	AC	2.14	0.86	5.00	0.18	8	2	98
		2.14	0.81	4.40	0.13	6	2	98
		2.14	0.80	6.00	0.06	3	3	97
Sand-T-High	No AC	2.45	0.01	288.00	2.19	89	118	-18
		2.45	0.01	288.00	2.19	89	118	-18
		2.45	0.01	264.00	2.70	110	108	-8
	AC	2.45	0.79	0.30	0.69	28	0	100
		2.45	1.16	4.70	0.37	15	2	98
		2.45	0.73	1.60	0.35	14	1	99
Top-T-Low	No AC	0.70	0.43	45.80	0.48	69	66	34
		0.70	0.31	42.70	0.43	62	61	39
		0.70	0.26	53.00	0.40	57	76	24
	AC	0.70	0.28	4.10	0.06	9	6	94
		0.70	0.32	3.90	0.11	16	6	94
		0.70	0.34	4.00	0.06	9	6	94

Treatment	AC treatment	Initial sterilant concentration in soil (mg/kg)	Sterilant concentration in filtered soil (mg/kg)	Sterilant concentration in filtrate (ug/L)	Phytoaccessible concentration in soil (mg/kg)	% of sterilant phytoaccessible	% of sterilant desorbed	% of sterilant retained
Sand-T-Low	No AC	0.59	0.01	70.80	0.67	114	120	-20
		0.59	0.00	69.90	0.66	111	118	-18
		0.59	0.00	70.80	0.74	125	120	-20
	AC	0.59	0.31	2.50	0.19	33	4	96
		0.59	0.36	2.20	0.14	24	4	96
		0.59	0.37	2.10	0.13	22	4	96

APPENDIX D: PHYTOACCESSIBLE STERILANT DATA AND COMPARISON

Comparison of phytoaccessible sterilant data with initial, sterilant concentration data for each treatment. Values are means (n=3).

Treatment	Sterilant	AC treatment	Phytoaccessible concentration (mg/kg)	Phytoaccessible sterilant in soil (mg)	% Phytoaccessible	Initial sterilant concentration (mg/kg soil)	Initial sterilant in soil (mg)	% of sterilant desorbed	% of sterilant retained
Top-B-High	Bromacil	No AC	1.253	0.188	68	1.83	0.275	77	23
		AC	0.299	0.045	16	1.83	0.275	2	98
Sand-B-High		No AC	1.967	0.295	73	2.71	0.407	114	-14
		AC	0.181	0.027	7	2.71	0.407	0	100
Top-B-Low		No AC	0.528	0.079	81	0.65	0.098	73	27
		AC	0.053	0.008	8	0.65	0.098	14	86
Sand-B-Low		No AC	0.853	0.128	89	0.96	0.143	95	5
		AC	0.117	0.018	12	0.96	0.143	1	99
Top-T-High	Tebuthiuron	No AC	1.567	0.235	73	2.14	0.321	61	39
		AC	0.123	0.018	6	2.14	0.321	2	98
Sand-T-High		No AC	2.360	0.354	96	2.45	0.368	114	-14
		AC	0.469	0.070	19	2.45	0.368	1	99
Top-T-Low		No AC	0.437	0.066	63	0.72	0.105	67	33
		AC	0.080	0.012	11	0.72	0.105	6	94
Sand-T-Low		No AC	0.688	0.103	117	0.59	0.089	119	-19
		AC	0.155	0.023	26	0.59	0.089	4	96

APPENDIX E: PHYTOACCESSIBLE AND TOTAL STERILANT CONCENTRATIONS AFTER WEATHERING

Phytoaccessible and total sterilant concentration (mg/kg) in soil amended with activated carbon (AC) or not amended (no AC). The two AC amendment treatments were exposed to three different weathering treatments: no weathering, 10 freeze-thaw cycles, or 20 freeze- thaw cycles. Values are means (n=3) with the standard deviation in parentheses.

Sterilant	AC Treatment	Weathering Treatment	Phytoaccessible Sterilant Concentration (mg/kg)	Total Sterilant Concentration (mg/kg)	Average Surrogate Recovery (%)*
Bromacil	No AC	Non-Weathered	0.29 (0)	1.95 (0.62)	81
		10 Freeze Thaw Cycles	1.03 (0.09)	0.61 (0.01)	77
		20 Freeze Thaw Cycles	0.97 (0.07)	0.55 (0.01)	73
	AC	Non-Weathered	<0.008 (0)	0.078 (0.001)	61
		10 Freeze Thaw Cycles	<0.008 (0)	0.047 (0.002)	71
		20 Freeze Thaw Cycles	0.043 (0.02)	0.074 (0.005)	68
Tebuthiuron	No AC	Non-Weathered	0.75 (0.07)	1.20 (0.09)	71
		10 Freeze Thaw Cycles	0.77 (0.03)	0.98 (0.05)	67
		20 Freeze Thaw Cycles	0.68 (0.08)	1.03 (0.03)	68
	AC	Non-Weathered	<0.005 (0)	0.34 (0.02)	61
		10 Freeze Thaw Cycles	0.032 (0)	0.18 (0.004)	65
		20 Freeze Thaw Cycles	<0.005 (0)	0.24 (0.01)	62

* The laboratory adds a surrogate to samples as a QA/QC procedure. The surrogate is a compound with similar behaviour and characteristics as the target compound, and when bromacil or tebuthiuron is the target compound, monuron is used as the surrogate. Surrogate recovery was measured on total sterilant samples, and is not representative of phytoaccessible sterilant soil samples.

APPENDIX A8: BENCH-SCALE TESTING OF CHEMICAL AMENDMENTS TO REMEDIATE BROMACIL AND TEBUTHIURON IN SOIL

This project produced three reports.

Appendix A8-1: Chemical Amendments

Bendouz, M. and J. Paré, 2022. Bench-scale Testing of Chemical Amendments to Remediate Bromacil and Tebuthiuron in Soil. Report SSP-11A prepared by Chemco Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 45 pp.

Bench-scale Testing of Chemical Amendments to Remediate Bromacil and Tebuthiuron in Soil

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Chemco Inc. ("Chemco")

Prepared for Soil Sterilants Program

InnoTech Alberta Inc.

Edmonton, Alberta

October 05, 2022

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EXECUTIVE SUMMARY

Bench-scale testing was conducted to evaluate the ability of chemical oxidation and reduction amendments to degrade bromacil and tebuthiuron in soil with and without the use of surfactants. Results showed that the reductive amendment called DARAMEND was highly effective in the treatment of bromacil in the tested soil samples. Overall treatment product cost was approximately C$55/MT of impacted soil (product only) using a 1 % w/w loading rate. This approach enabled a rapid, cost-effective, and long-lasting treatment.

Interestingly, contaminant destruction was obtained without tilling the sample after a 30-days contact period. For field deployment, this would mean that a single pass application with proper wetting could help to reach the remedial objective.

The hydrogen peroxide oxidation process using the VTX catalyst and surfactant was a little more expensive than the DARAMEND technology at C$99/MT of impacted soil (product only) for the destruction of 1.0 mg/kg contaminant concentration. For tebuthiuron, the ISCO approach with alkaline activated Klozur® persulfate successfully reduced tebuthiuron concentration by 76% without adding the surfactant using a low dosage of Klozur® persulfate. This gives a treatment cost of C$5/MT of impacted soil (product only) per 1 mg/kg removal of tebuthiuron (without surfactant) compared to C$17/MT of impacted soil (with the use of surfactant). For groundwater contamination, the fact that the targeted compound is already in the water phase would facilitate its destruction via oxidative pathways.

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1 INTRODUCTION AND PROJECT OBJECTIVES

Soil sterilants are non-selective, broad-spectrum herbicides used for vegetation control on industrial land. In Alberta, they were introduced in the 1960s and were used on a variety of industrial sites until they were banned in the 1990s due to their ability to migrate offsite and their extreme persistence. Decades after ceasing treatment with sterilant products, impacts can persist in soil and water. As sterilants are unique and challenging contaminants to manage, the Soil Sterilants Program (SSP) was designed to address several knowledge gaps related to the assessment, remediation, and risk management of sterilant-impacted sites.

In the design phase of the SSP, and through an SSP project that evaluated remediation technologies, a review of available remediation technologies for sterilants in soil and water was conducted (Drozdowski et al., 2018; Levy et al., 2021). To align with the needs of the Soil Sterilants Program, potential technologies were evaluated to determine their applicability to Alberta conditions and specific site challenges, while considering cost, logistics of application, and sustainability. Interviews were held with technology providers to evaluate technology readiness levels and application to three key challenges:

1. Treatment of sterilants at depths greater than 50 cm below ground surface in unsaturated soil, thus inaccessible to treatment at surface (ideally in situ).
2. Sterilant destruction in soil where immobilization is not considered an acceptable option (in situ or ex situ).
3. In situ treatment of saturated fine-grained till soils and groundwater.

After evaluating and short-listing the technologies, bench-scale testing was proposed to evaluate chemical oxidation and reduction products in their ability alone, and with the use of surfactants, to degrade bromacil and tebuthiuron. Surfactants may be integrated to desorb and thus make the compounds accessible to treatment.

This report includes a description of methods, data compilation and analysis, conclusions, and recommendations for next steps for further demonstrating the effectiveness of remediation technologies in a meso- or field-scale demonstration. As part of the SSP mandate to support stakeholders in effective remediation of soil sterilants, the report also includes evaluation of cost, logistics, safety, and potential secondary soil impacts of recommended treatment technologies.

2 TECHNOLOGY SELECTION AND APPROACH

Based on the findings of Levy et al. (2021), select remedial technologies were identified for bench-scale testing. A description of remediation treatment technologies investigated or considered for removal or degradation of sterilants OR primarily used to treat pesticide-impacted soils is provided below. The trials completed in this study aimed to identify remedial technologies capable of degrading bromacil or tebuthiuron in soil and to establish effective remedial agent concentrations and activator combinations, if required.

2.1 REDUCTIVE TREATMENT PATHWAY

2.1.1 Treatment Option 1: Daramend Reagent

At this time, only the use of the DARAMEND reagent is recommended for testing as it has the greatest potential for success in treatment of bromacil based on results with similar contaminants of concern; it has

been deemed unlikely to be effective in treating tebuthiuron due to absence of evidence that it degrades anaerobically (A. Seech, pers. comm.). The product and approach also have a low risk of associated residual impacts to soil.

DARAMEND is composed of controlled-release organic carbon substrate combined with zero valent iron (ZVI). It is used for the treatment of groundwater or saturated soil impacted by persistent halogenated compounds, including chlorinated solvents, pesticides, and organic explosives. DARAMEND provides the in situ chemical reduction (ISCR) benefits of very strongly reducing conditions targeting the contaminant via both biotic and abiotic degradation mechanisms. The balance between the organic carbon substrate and the ZVI allows the product to operate at near–neutral pH. Fermentable carbon in the product typically persists for 5 to 10 years depending on site-specific conditions. Treatment may be repeated every 3 to 6 weeks until the target contaminant endpoint concentration is reached; however, for the purpose of the stated experiments there will only be one application. Treated soils will be incubated for a period of 4 to 8 weeks at room temperature.

A 14- to 21-day delay is normally required to establish the optimal reductive condition after amendment introduction to the soil matrix. This delay can be influenced by site specification conditions including temperature, geology, soil moisture, etc.

2.2 OXIDATIVE TREATMENT PATHWAY

2.2.1 Treatment Option 2: Potassium Persulfate Activated with Hydrated Lime

This treatment provides a long-term (i.e., 1 to 3 year) chemical oxidation based on low solubility of both oxidant and activator. The persulfate releases minimal gas upon reaction and has a relatively low Soil Oxidant Demand (SOD) compared with other proposed amendments. These properties, combined with longer persistence, are ideal for lower permeability soil and bedrock. This blend of oxidant and activator also has minimal reactivity with carbon steel or concrete underground infrastructure. For treatment of contaminants of concern in soil, the oxidant and activator could be incorporated into the soil as a solid and mixed directly while adding water. Solubilization of the compound via groundwater flow or high humidity content would treat the contaminant of concern.

2.2.2 Treatment Option 3: Sodium Persulfate Activated with Calcium Peroxide

This amendment is composed of 50% sodium persulfate and 50% calcium peroxide. The sodium persulfate portion will lead to the chemical oxidation of contaminants in aqueous phase within the soil matrix. Oxidation time is between 4 to 12 weeks. Calcium peroxide lasts 3 to 6 months and promotes aerobic biodegradation when soils are sufficiently but not excessively moist.

Products are incorporated via soil mixing or as a solid suspension due to the calcium peroxide portion of the product. The chemical oxidation destroys or partially oxidizes the contaminant, making it easier to degrade via biological processes that follow. The use of a calcium-based product with the sodium persulfate serves to limit the amount of residual salt in the aquifer as calcium and sulphate ions will precipitate as gypsum. Potassium persulfate is a secondary option if sodium is deemed problematic, although there may be effectiveness or cost implications. Long persistence and treatment potential makes this a suitable technology for low solubility amendment or fine-grained geologies where sorption and desorption processes are slow.

2.2.3 Treatment Option 4: Sodium Persulfate activated with Sodium Hydroxide

This option provides 4 to 12 weeks of active chemical oxidation of the target contaminant per application event. However, with both products containing sodium, soil and aquifer impacts may occur and this approach should only be taken when sodium and sodium adsorption ratios (SAR) at a site can

accommodate additional sodium. Sodium persulfate and sodium hydroxide can, however, be exchanged for their potassium equivalents, if required. As an oxidant, sodium persulfate releases minimal gas and has a relatively low SOD. This, in addition to relatively long persistence. is ideal for lower permeability soil and bedrock. This blend of oxidant and activator also has minimal reactivity with carbon steel or concrete underground infrastructure.

These components are both fully soluble and can be pre-mixed at the surface before application and sprayed as a true aqueous solution.

2.2.4 Treatment Option 5: Hydrogen Peroxide Alone or Activated Using VTX

This option will provide 2 to 4 weeks of chemical oxidation per application event. Residual oxygen released from the hydrogen peroxide decomposition could promote biological degradation of the contaminants once the oxidation phase is completed. Peroxide degradation by-products are water, oxygen, and carbon dioxide, thus not adding any salt ions into the soil or aquifer. The need for the use of the catalyst will be dependent on the Natural Oxidant Demand (NOD) value for the soil and groundwater; if the NOD is high, a catalyst would not be required, thus reducing the cost.

To increase the reactivity with the targeted contaminants and the rate of destruction, in situ chemical oxidation (i.e., ISCO) can be combined with a surfactant (*i.e.*, S-ISCO approach). The use of a surfactant would improve contaminant availability for oxidative destruction in the water phase. The surfactant helps to desorb contaminants from soil components and decreases water's surface tension, allowing for improved distribution of amendments in fine-grained soils. Selected surfactants must be compatible with the selected oxidant and be biodegradable. For soil delivery, a solution may be introduced to the soil composed of diluted catalyst, surfactant, and oxidant.

3 PROJECT METHODOLOGY

The following sections detail methods employed in soil characterization, preliminary technology screening, and technology optimization.

3.1 Soil Preparation

3.1.1 Soil Characterization

A loam topsoil sourced near Brooks, AB was used for the tests described here. The soil was selected as it is representative of the soils that occur in many areas with sterilant impacts in Alberta.

Prior to conducting experiments, the soil was analyzed for physical and chemical characteristics:

- Texture
- Detailed salinity
- pH (by $CaCl_2$), saturated paste EC, % saturation, Ca, Mg, Na, SO_4-S, SO_4, K, SAR, TGR, reported in mg/kg; Cl in mg/L
- Metals (Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mo, Ni, Se, Ag, Tl, Sn, U, V, Zn, Cr_6^+, saturated paste B (mg/L), Hg)
- Total Organic Carbon
- Nutrients (nitrogen, phosphorus, potassium; incl. nitrogen species (TKN, NO_2, NO_3, ammonia) and ortho phosphate)
- Heterotrophic plate count
- Water holding capacity

- Soil base buffering capacity (Amount of alkali required to bring the soil into alkaline range when using alkaline activated persulfate oxidation processes)
- Natural Oxidant Demand (lost amount of oxidant to the mineral or organic portion of the contaminated soil)

3.1.2 Soil Spiking and Weathering

Batches of the soil were spiked with Hyvar X-L (bromacil) and Spike (tebuthiuron) to a concentration of approximately 2 mg/kg. Soil was aged[1] for 30 days prior to testing to allow for weathering and interactions in the soil matrix. Soils were thoroughly homogenized to ensure that samples taken initially were representative of the starting concentration of the sterilants for all subsequent experiments.

3.1.3 Soil Oxidant Demand (SOD)

For SOD measurement, three bromacil-spiked soil samples were used (photo in Appendix E.1).

Tests were performed to measure the amount of oxidant naturally consumed by the soil organic or mineral matrix (Soil Oxidant Demand) during treatment. The amount and rate of oxidant consumption is used to determine oxidant dosing and optimize the reaction conditions for soil and groundwater treatment. Tests were performed using a soil to water ratio of 40 g:200 mL.

Hydrogen peroxide oxidant was tested using 1, 5, and 25 g/L concentration. After 24 hours, the oxidant concentration in the solution was measured by a standard back titration with sodium thiosulphate.

The sodium persulfate oxidizer system was tested with activation using 1, 5, 25, and 125 g/L persulfate concentrations. To activate the sodium persulfate, we evaluated alkaline activation using sodium hydroxide (dosing 2 moles of NaOH per mole of sodium persulfate). After 48 hours, the persulfate concentration in the solution was measured by a standard back titration with permanganate. The SOD was determined as:

$$SOD = V \times (C0 - Cf)/ms$$

Where V = volume of the groundwater used in the sample
$C0$ = initial concentration of persulfate at time 0
Cf = concentration of persulfate after 48 hours
ms = mass of soil used in the sample

The SOD was determined by averaging the 3 lowest SOD values for the different initial peroxide concentrations.

3.2 Stage 1: Preliminary Technology Screening

3.2.1 Surfactant Screening Test

As the first step of the project, a list of surfactants was developed for potential effectiveness in desorbing sterilants from the soil matrix:

- TWEEN 80
- DECONIT
- CHEMSOL DL3
- CHEMSOL DL4
- IVEYSOL 106CL
- FFT

[1] Aging consisted of 10 freeze-thaw cycles every 3 days over a 30-day period.

Surfactants were screened based on biodegradability, availability in Alberta, and approval for use in Canada. The physicochemical properties of the surfactants selected for testing are included in Appendix F.

3.2.2 Reductive Technology Testing

The DARAMEND amendment is a combination of controlled-release carbon and zero-valent iron and can be spread onto the soil and incorporated using specialized rotary tillers. Once incorporated into the soil, water is added to achieve the desired moisture content. Alternatively, DARAMEND could be pre-mixed with water and introduced as a slurry to the soil. This step initiates the reductive phase of the treatment. Native microorganisms in the soil utilize the carbon and nutrients provided by the DARAMEND to drive the oxidation reduction potential (ORP) down. Corrosion of the iron, as intended, further reduces the ORP. This combination of processes creates an environment where the contaminants are destroyed.

The DARAMEND[2] product was recommended for treatment of bromacil and tebuthiuron based on success in treatment of similar contaminants of concern. The product and approach also have a low risk of associated residual impacts to soil.

To evaluate both abiotic and biotic remediation of bromacil, the experiment was conducted over a 60-day period with sacrificial sampling at 30 days of incubation. The experiment was set up initially with the most effective surfactant identified through the screening process in section 3.2.1. Samples were saturated and tested periodically using an ORP probe to assess redox condition.

Tests were set up in duplicate and tested Daramend at 1% and 3% dosing rate, with and without tilling at 30 days, and both with and without TWEEN 80 surfactant.

3.2.3 Oxidative Testing Protocol: No Surfactant

The oxidants and activators were added together into duplicate vials. The persulfates (sodium or potassium) and the alkaline activation the tests were incubated for a period of approximately 30 days with monitoring to assess time to oxidant consumption.

An additional replicate was added to the highest concentrations with additional water to exceed full soil saturation to analyze the persulfate residual at the end of the testing period. This will enable calculation of the stoichiometry between the contaminant of concern and the oxidant to obtain the number of g of persulfate to dose per kg of soil on the targeted contaminant and understand the rate of consumption of the oxidant in the natural soil matrix. The treatment testing approach for oxidative technologies for treatment of bromacil (Table 1) and tebuthiuron (Table 2) are outlined below. No surfactants were used in this stage of testing.

[2] A DARAMEND brand that does *not* contain activated carbon was used for the trial to ensure there is not retention of bromacil that may result in under-reported concentration post-treatment.

Table 1. Experimental design for oxidative testing for bromacil (no surfactant).

Treatment	Dosage	Oxidant (g/kg)	Activator (g/kg)
Control	Dry blank – Time Zero	-	-
	Wet blank (water only) – End of testing time	-	-
	Dry blank – end of testing time	-	-
Potassium persulfate activated with calcium-based product (hydrated lime)	Potassium persulfate 100% per kg of soil + Ca $(OH)_2$ 100% per kg of soil (low dosage)	1.20	3.40
	Potassium persulfate 100% per kg of soil + Ca $(OH)_2$ 100% per kg of soil (median dosage)	2.70	3.89
	Potassium persulfate 100% per kg of soil + Ca $(OH)_2$ 100% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	4.72
Sodium persulfate activated with calcium-based product (calcium peroxide FG)	Sodium persulfate 100% per kg of soil + de calcium peroxide FG 100% per kg of soil (low dosage)	1.20	1.20
	Sodium persulfate 100% per kg of soil + de calcium peroxide FG 100% per kg of soil (median dosage)	2.70	2.70
	Dosage 3 - Sodium persulfate 100% per kg of soil + Ca $(OH)_2$ 100% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	5.20
Sodium persulfate activated with alkaline base (sodium hydroxide)	Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil (low dosage)	1.20	13.6
	Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil (median dosage)	2.70	15.6
	Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	18.9
Hydrogen Peroxide alone	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) (low dosage)	10.2	-
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) (median dosage)	20.2	-
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) (high dosage)	40.2	-
Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10.2	1.02
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	20.2	2.02
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	40.2	4.02

Table 2. Experimental design for oxidative testing for tebuthiuron (no surfactant).

Treatment	Dosage	Oxidant (g/kg)	Activator (g/kg)
Control	Dry blank – Time Zero		
	Wet blank (water only) – End of testing time		
	Dry blank – end of testing time		
Potassium persulfate activated with calcium-based product (hydrated lime)	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (low dosage)	1.20	4.4
	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (median dosage)	2.70	4.9
	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	5.7
Sodium persulfate activated with calcium-based product (calcium peroxide FG)	Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (low dosage)	1.20	1.20
	Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (median dosage)	2.70	2.70
	Sodium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	5.20
Sodium persulfate activated with alkaline base (sodium hydroxide)	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	1.20	17.6
	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	2.70	19.6
	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	22.9
Hydrogen Peroxide alone	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1 (low dosage)	10.2	-
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) (median dosage)	20.2	-
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) (high dosage)	40.2	-
Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10:1) + VTX 22% (low dosage)	10.2	1.02
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	20.2	2.02
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	40.2	4.02

3.3 Stage 2: Remedial Technology Optimization

The experiment outlined in Table 3 was conducted using the two best technologies for treatment of bromacil and tebuthiuron, respectively, as identified through wider testing outlined in Tables 1 and 2. and optimized surfactants as established through the screening test outlined in section 3.2.1.

Table 3. Experimental design for oxidative testing for bromacil and tebuthiuron treatment with surfactant.

Soil Type	Treatment	Dosage	Oxidant (g/kg)	Activator (g/kg)	Surfactant (g/kg)
Bromacil-spiked soil	**Sodium persulfate + NaOH**	Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil (low dosage)	1.20	13.6	1
		Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil (median dosage)	2.70	15.6	1
		Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	18.9	1
	Sodium persulfate + NaOH + Surfactant (DL4)	Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil (low dosage)	1.20	13.6	1
		Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil (median dosage)	2.70	15.6	1
		Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	18.9	1
	Hydrogen peroxide + VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10:1) + VTX 22% (low dosage)	10.2	1.02	1
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20:1) + VTX 22% (median dosage)	20.2	2.02	1
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30:1) + VTX% 22 (high dosage)	40.2	4.02	1
	Hydrogen peroxide + VTX + Surfactant (TWEEN)	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10:1) + VTX 22% (low dosage)	10.2	1.02	1
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20:1) + VTX 22% (median dosage)	20.2	2.02	1
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	40.2	4.02	1
Tebuthiuron-spiked soil	**Sodium persulfate + NaOH**	Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil (low dosage)	1.20	17.6	1
		Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil (median dosage)	2.70	19.6	1
		Sodium persulfate 100% per kg of soil + NaOH 25% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	22.9	1

Soil Type	Treatment	Dosage	Oxidant (g/kg)	Activator (g/kg)	Surfactant (g/kg)
	Sodium persulfate + NaOH + Surfactant (DECONIT)	Sodium persulfate 100 % per kg of soil + NaOH 25% per kg of soil (low dosage)	1.20	17.6	1
		Sodium persulfate 100 % per kg of soil + NaOH 25% per kg of soil (median dosage)	2.70	19.6	1
		Sodium persulfate 100 % per kg of soil + NaOH 25% per kg of soil + rep 3 enough water to measure the residual persulfate) (high dosage)	5.20	22.9	1
	Hydrogen peroxide + VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10.2	1.02	1
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20:1) + VTX 22% (median dosage)	20.2	2.02	1
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30:1) + VTX% 22 (high dosage)	40.2	4.02	1
	Hydrogen peroxide + VTX + Surfactant (TWEEN)	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10:1) + VTX 22% (low dosage)	10.2	1.02	1
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	20.2	2.02	1
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30:1) + VTX% 22 (high dosage)	40.2	4.02	1

4 RESULTS AND DISCUSSION

4.1 Soil Preparation

4.1.1 Soil Characterization

Characterization parameters for a batch of Brooks topsoil, unspiked and containing no soil sterilants (analysis provided by Element laboratories, October 2019) is presented in Table 4. Original laboratory reports are included in Appendix A.

Table 4. Soil characterization results.

Parameter	Units	Average (n=3)	Standard Deviation
Texture		Loam	-
	% Sand	46	2.31
	% Silt	35	2.52
	% Clay	18	1.53
75 um sieve		Fine-Grained	-
	% Retained	42	0.31
Organic Matter	%	3.44	0.55
Organic Carbon	%	1.73	0.28
pH		7.60	0.10
EC	dS/m	1.40	0.04
SAR		4.00	0.10
% Saturation		48	1.73
Calcium	mg/kg	49.0	0.18
Magnesium	mg/kg	13.0	1.56
Sodium	mg/kg	85.0	0.06
Potassium	mg/kg	13.7	0.40
Chloride	mg/kg	18.3	0.21
Sulfate (SO_4)	mg/kg	130	1.00
Sulfate-S	mg/kg	43.3	0.03
TGR	T/ac	<0.1	-

4.1.2 Soil Spiking and Weathering

Three random grab samples were obtained for characterization of the spiked soils to be used for the treatability study at the end of the 30-day weathering period (Table 5). Additional sterilant data is included in Appendix C.

Table 5. Concentrations of bromacil and tebuthiuron in spiked soil analyses following a 30-day weathering period.

Parameter	Laboratory Detection limit	Bromacil			Tebuthiuron			Average
		Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	
Bromacil (mg/kg)	0.008	1.35	1.39	1.33	-	-	-	**1.36**
Tebuthiuron (mg/kg)	0.005	-	-	-	2.07	2.10	2.13	**2.10**

4.1.3 Soil Oxidant Demand

The SOD value obtained for the hydrogen peroxide alone is 30 g of H_2O_2 50% lost per kg of soil (Table 6). This is a little bit higher than the normal range for hydrogen peroxide for which expected values range around 25 g per kg of soil.

With such values, the use of a catalyst could be necessary to generate the necessary free radicals, but laboratory bench scale testing tests will make it possible to validate the performance gain associated with the use of a catalyst against the targeted contaminant. The lab testing has demonstrated that the use of a catalyst improved contaminant destruction.

Table 6. Results of soil oxidant demand testing.

Soil (Oxidant + Activation Method)	SOD
Soil sample (Hydrogen peroxide alone)	30 g of H_2O_2 50% per kg of soil
Soil sample (Persulfate + NaOH)	41 g of persulfate 100% lost per kg of soil

The SOD values for the soil sample using activated sodium persulfate exceeded the normal expected range of 1 to 5 g of 100% sodium persulfate lost per kg of soil. This may result in some extra cost for the use of this oxidant; however, in the case of high SOD values, it may be advisable to use a dose of oxidant at a fraction of the values obtained (e.g., ¼ or ½ of the SOD) instead of the usual stoichiometric ratios. This is because the degradation reactions of the oxidants with the mineral or organic matrix of the soil compete with the reaction with the targeted contaminants.

Therefore, it is possible to economically conduct the chemical oxidation of the targeted contaminants despite the high SOD. To validate the exact reaction pathways, it is recommended that laboratory or pilot scale treatment tests are employed to validate the exact amounts of oxidant required to achieve the desired levels of decontamination.

The alkaline activation process of the persulfate oxidant requires an optimal pH that is around 11.0 (10.0 being the minimum acceptable).

To raise the pH to 11 for samples TP01, the soil required 1.875 g of sodium hydroxide 100% per kg of soil. This amount is based on a 1:2 molar ratio for the sodium persulfate: sodium hydroxide, thus the initial pH for TP01 was 7.97 and it became 11.58 after adding the sodium hydroxide 100%.

4.2 Stage 1: Preliminary Technology Screening

4.2.1 Surfactant Screening Test

Six surfactants were investigated in laboratory studies with bromacil and tebuthiuron. The extraction tests were done using 3 different concentrations for each surfactant. The analysis of the results shows that the surfactants have different performance profiles. Surfactant screening included tests to establish both contaminant extraction and reactivity with oxidants.

4.2.1.1 Bromacil

Among the 6 surfactants selected, three were found applicable after the screening: TWEEN, DL3 and DL4. TWEEN was the most effective surfactant providing the highest level of bromacil concentration at 1 g/kg with an extraction percentage of 74%, followed by DL3 which provided 38% bromacil extraction at 5 g/kg, and then DL4 at 1 g/kg with 28% bromacil extraction (Table 7).

Table 7. Surfactant screening test for bromacil.

	Description	Type of surfactant	Dosage (g/kg)	Contaminant Concentration (ppb)	% Increase	Comments
BROMACIL - TEMOIN 1 - BLANK	Leachate of Spiked soil with bromacil without surfactant					
BROMACIL - TEMOIN 2 - BLANK	Leachate of Spiked soil with bromacil without surfactant			323		
BROMACIL - TEMOIN 3 - BLANK	Leachate of Spiked soil with bromacil without surfactant			258		
BROMACIL - TEMOIN 4 - BLANK	Leachate of Spiked soil with bromacil without surfactant			427		
BROMACIL - TWEEN - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant TWEEN at dosage of 1 g/kg	TWEEN	1	**583**	**74**	**Best results**
BROMACIL - TWEEN - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant TWEEN at dosage of 5 g/kg	TWEEN	5	483	44	
BROMACIL - TWEEN - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant TWEEN at dosage of 10 g/kg	TWEEN	10	527	57	
BROMACIL - DECONIT - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant DECONIT at dosage of 1 g/kg	DECONIT	1	376	12	
BROMACIL - DECONIT - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant DECONIT at dosage of 5 g/kg	DECONIT	5	264	-21	
BROMACIL - DECONIT – 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant DECONIT at dosage of 10 g/kg	DECONIT	10			
BROMACIL - DL3 - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL3 at dosage of 1 g/kg	DL3	1	413	23	
BROMACIL - DL3 - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL3 at dosage of 5 g/kg	DL3	5	**465**	**38**	**2nd best**
BROMACIL - DL3 - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL3 at dosage of 10 g/kg	DL3	10	395	18	
BROMACIL - DL4 - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL4 at dosage of 1 g/kg	DL4	1	**430**	**28**	**3rd best**
BROMACIL - DL4 - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL4 at dosage of 5 g/kg	DL4	5			
BROMACIL - DL4 - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL4 at dosage of 10 g/kg	DL4	10	343	2	
BROMACIL - 106-CL - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant 106 CL at dosage of 1 g/kg	106 CL	1	280	-17	
BROMACIL - 106-CL - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant 106 CL at dosage of 5 g/kg	106 CL	5	218	-35	
BROMACIL - 106-CL - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant 106 CL at dosage of 10 g/kg	106 CL	10	393	17	
BROMACIL - FFT - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant FFT at dosage of 1 g/kg	FFT	1	393	17	
BROMACIL - FFT - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant FFT at dosage of 5 g/kg	FFT	5			
BROMACIL - FFT - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant FFT at dosage of 10 g/kg	FFT	10	424	26	

4.2.1.2 Tebuthiuron

For tebuthiuron, TWEEN was the most effective surfactant, providing the highest level of the contaminant extraction in the efficacy trials. The best increase was observed with TWEEN at 5 g/kg (54% tebuthiuron extraction), followed by DECONIT at 5 g/kg (47% extraction) and TWEEN at 1 g/kg with 31% extraction (Table 8).

Table 8. Surfactant screening test for tebuthiuron.

Essay	Description	Type of surfactant	Dosage (g/kg)	Contaminant Concentration (ppb)	% Increase	Comments
TBT - TEMOIN 1 - BLANK	Leachate of Spiked soil with Tebuthiuron without Surfactant			282		
TBT - TEMOIN 2 - BLANK	Leachate of Spiked soil with Tebuthiuron without Surfactant			316		
TBT - TEMOIN 3 - BLANK	Leachate of Spiked soil with Tebuthiuron without Surfactant					
TBT - TEMOIN 4 - BLANK	Leachate of Spiked soil with Tebuthiuron without Surfactant			347		
TBT - TWEEN - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant TWEEN at dosage of 1 g/kg	TWEEN	1	**413**	**31**	**3 th best**
TBT - TWEEN - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant TWEEN at dosage of 5 g/kg	TWEEN	5	**487**	**54**	**Best results**
TBT - TWEEN - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant TWEEN at dosage of 10 g/kg	TWEEN	10	363	15	
TBT - DECONIT - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DECONIT at dosage of 1 g/kg	DECONIT	1	189	-40	
TBT - DECONIT - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DECONIT at dosage of 5 g/kg	DECONIT	5	**462**	**47**	**2nd best**
TBT - DECONIT - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DECONIT at dosage of 10 g/kg	DECONIT	10	333	6	
TBT - DL3 - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL3 at dosage of 1 g/kg	DL3	1	323	2	
TBT - DL3 - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL3 at dosage of 5 g/kg	DL3	5	288	-9	
TBT - DL3 - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL3 at dosage of 10 g/kg	DL3	10	285	-10	
TBT - DL4 - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL4 at dosage of 1 g/kg	DL4	1	267	-15	
TBT - DL4 - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL4 at dosage of 5 g/kg	DL4	5	304	-3	
TBT - DL4 - 10 g/kg	Leachate Spiked soil with Tebuthiuron +Surfactant DL4 at dosage of 10 g/kg	DL4	10	202	-36	
TBT - 106-Ckg - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant 106 CL at dosage of 1 g/kg	106 CL	1	158	-50	
TBT - 106-Ckg - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant 106 CL at dosage of 5 g/kg	106 CL	5	181	-42	
TBT - 106-Ckg - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant 106 CL at dosage of 10 g/kg	106 CL	10	128	-59	
TBT - FFT - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant FFT at dosage of 1 g/kg	FFT	1			
TBT - FFT - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant FFT at dosage of 5 g/kg	FFT	5			
TBT - FFT - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant FFT at dosage of 10 g/kg	FFT	10	256	-19	

The addition of surfactants increased contaminant extraction for both bromacil and tebuthiuron. However, the range of increased extraction observed in tebuthiuron was less than the range observed for bromacil.

The reactivity of the selected surfactants (TWEEN, DECONIT, DL3, and DL4) towards potential oxidants (persulfate and hydrogen peroxide) was also investigated. The results showed that TWEEN and DL3 react

with persulfate but do not react with hydrogen peroxide, while DECONIT and DL4 are compatible with both persulfate and hydrogen peroxide.

The choice of surfactants for various tests was:

- Surfactant DL4: For bromacil with persulfate activated with NaOH.
- Surfactant TWEEN: For bromacil and tebuthiuron with hydrogen Peroxide activated with VTX.
- Surfactant DECONIT: For tebuthiuron persulfate activated with NaOH.

4.2.2 Reductive Technology Testing

The application of Daramend was able to reduce bromacil concentration by over 98% using a dosage of 3% (wt/wt basis) with no tilling, and 97% at a dosage of 1% (wt/wt basis) with a tilling at 30 days. The dosage of 1% (wt/wt basis) was accomplished by adding 10 g of Daramend per kg of dry soil and using water to increase moisture content to 60% of the soil's water holding capacity (WHC). The results are presented in Figure 1.

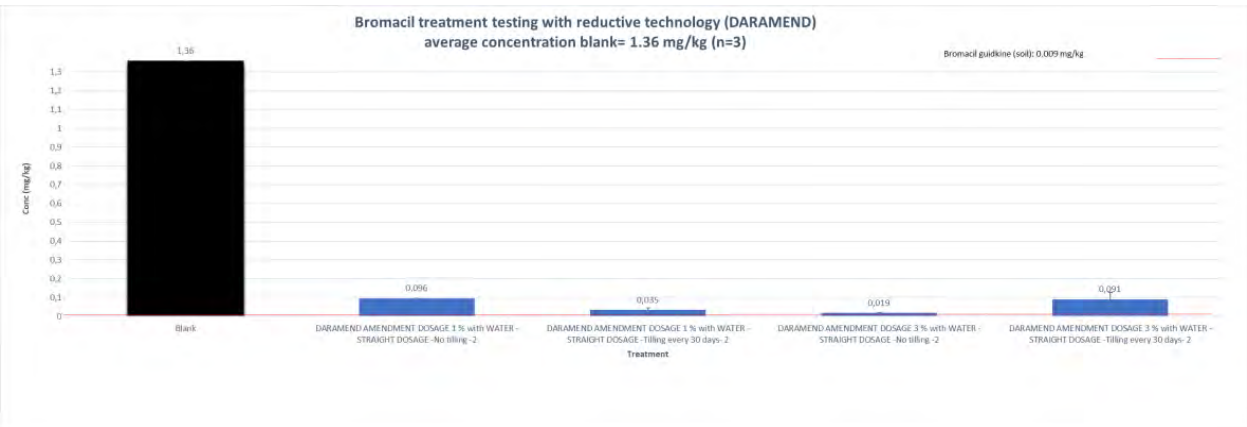


Figure 1. Effect of Daramend treatment on bromacil concentrations in soil.

Laboratory results obtained for the different treatments conducted with reductive testing for bromacil are provided in Appendix D.

4.2.3 Oxidative Testing Protocol: No Surfactant

For the treatment option using oxidative approaches (without surfactant) the treatment with hydrogen peroxide and VTX (catalyst) gave the best removal rates for bromacil and tebuthiuron after 30 days of soil contact (Figures 2 and 3). These results were obtained with a 40:1 oxidant to sterilant dosage. A total of 40.2 g of hydrogen peroxide 50% plus 4 g VTX per kg of dry soil was required for a removal of 70% of bromacil (where a concentration of 0.401 mg/kg was obtained after 30 days of reaction) and a reduction of 55% of tebuthiuron (where a concentration of 0.95 mg/kg was obtained after 30 days of reaction). All the injected oxidant had been consumed or decomposed at a complete reaction of the dosed oxidant.

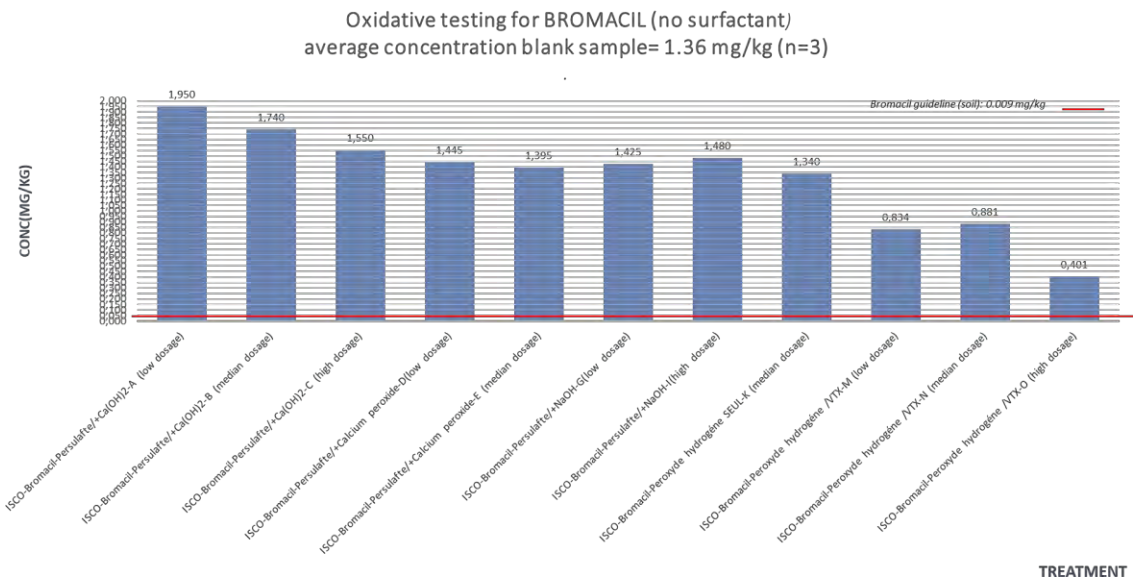


Figure 2. Effect of oxidative treatment on bromacil concentration without adding surfactant.

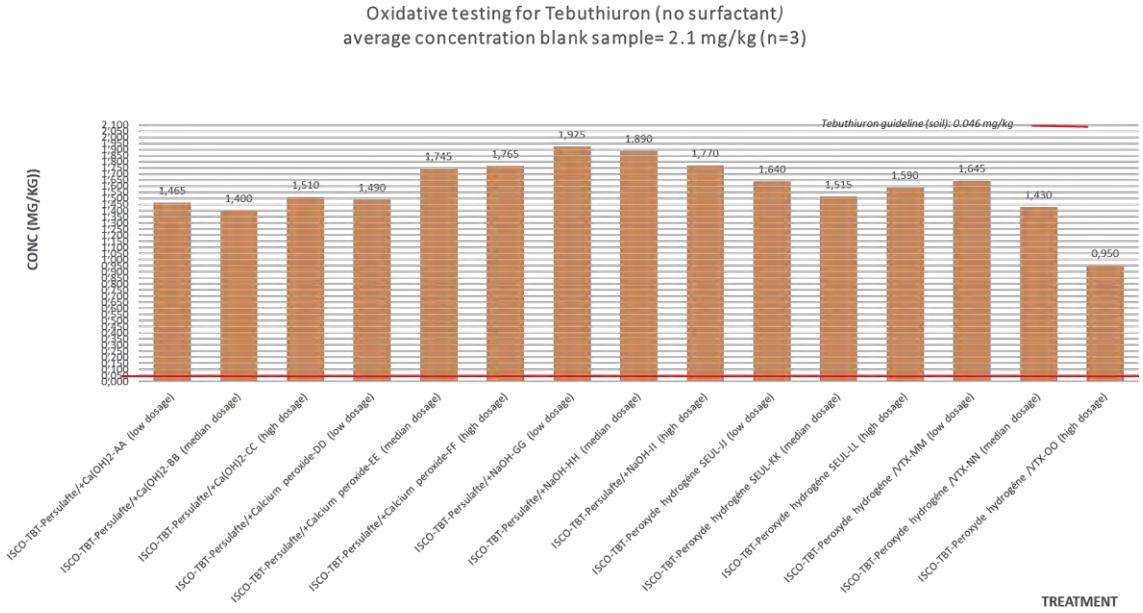


Figure 3. Effect of oxidative treatment on tebuthiuron concentration without adding surfactant.

The results obtained for the different treatments conducted with Oxidative Testing (without surfactant) for bromacil and tebuthiuron are summarized in Appendix D.

Some dosages do not appear in Figures 2 and 3 or in Appendix D of this treatment series due to the loss of samples that were broken during transport. The list of the samples broken during transport to the analysis laboratory are presented in Appendix D.

4.3 Stage 2: Remedial Technology Optimization

4.3.1 DARAMEND Reductant Bench Scale Testing With Surfactant

The results of the treatment with DARAMEND using the surfactant TWEEN are summarized in Figure 4 (a and b) for bromacil, and 5 (a and b) for tebuthiuron. Figures 4(b) and 5(b) show the Influence of DARAMEND treatment on bromacil and tebuthiuron in soil treated after a treatment cycle of 30 days and 60 days.

For bromacil, the average removal ranged from 31% to 59% after 30 days, although it was reduced by 98% after a treatment cycle of 60 days by tilling 1% DARAMEND with the addition of surfactant TWEEN into the soil and using water to increase soil moisture content to 60% of the soil's water holding capacity (WHC). The tilling process served to aerate and homogenize the soil.

For bromacil, it might be that surfactant was detrimental to successful treatment with DARAMEND after 30 days, due to microbial cell wall interference. However, after a treatment cycle of 60 days, the Bromacil concentrations were reduced from 1,36 mg/kg to 0,016 mg/kg showing a significant reduction of 99%.

For tebuthiuron, the average percentage removal was between 36 % and 45% after a treatment cycle of 30 days, and it was reduced by an average of 40 and 42% after a treatment cycle of 60 days using DARAMEND at a dosage of 1 and 3 % (wt/wt basis) respectively.

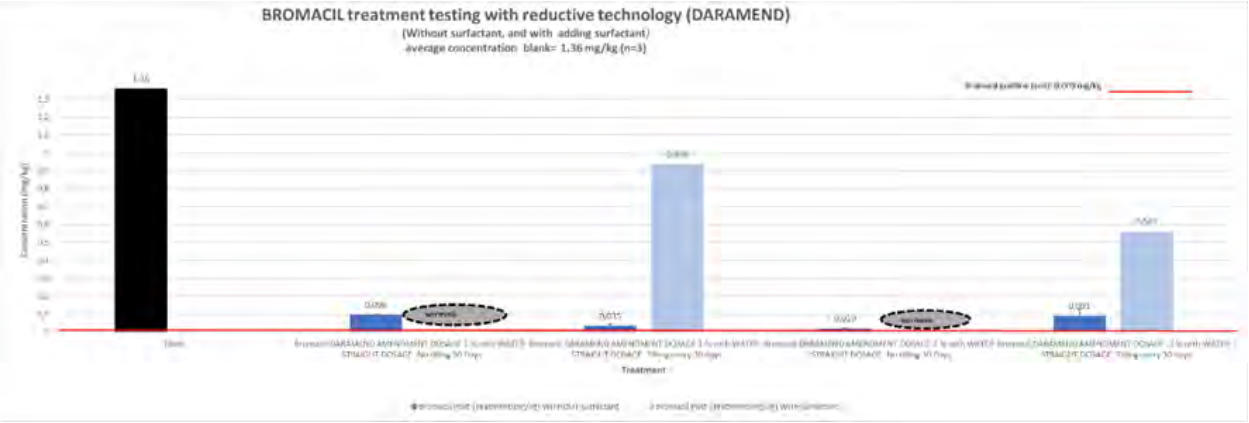
The results obtained for the different treatments conducted with reductive testing (with surfactant) for bromacil and tebuthiuron are summarized in Appendix D.

4.3.2 Oxidative Treatment Technology Testing with Surfactant(s)

For bromacil, the oxidative treatment results indicate very good sterilant removal with the use of hydrogen peroxide activated with VTX at high dosage combined with the addition of the surfactant TWEEN (Figure 6). The bromacil concentrations were reduced from baseline levels of 1.36 mg/kg to a concentration level of 0.316 mg/kg (a destruction of 76%). These results were obtained with a high dosage of hydrogen peroxide (40:1 oxidant to contaminant dosage) by using 40.2 g of hydrogen peroxide 50% plus 4 g/kg VTX, which ensured the optimal generation of hydroxyl radicals and desorption of contaminants from the soil. Adding the surfactant TWEEN (1 g per kg of soil) to the chemical oxidation process (S-ISCO) increased the solubility of contaminants that are immiscible with water and pulls sorbed contaminants from the soil, making them available for simultaneous oxidative destruction.

For tebuthiuron, the use of alkaline activated sodium persulfate without surfactant was successful. The treatment with alkaline activated persulfate showed a destruction of 76% tebuthiuron in low dosage (without the surfactant), comparing to 80% of destruction with the use of the surfactant at the same dosage (Figure 7). It was observed that the addition of the surfactant does not improve degradation of tebuthiuron. **For this reason, the use of a surfactant is not recommended for this treatment.**

a) With and without adding of the Tween surfactant.



b) After 30 and 60 days of reaction with surfactant

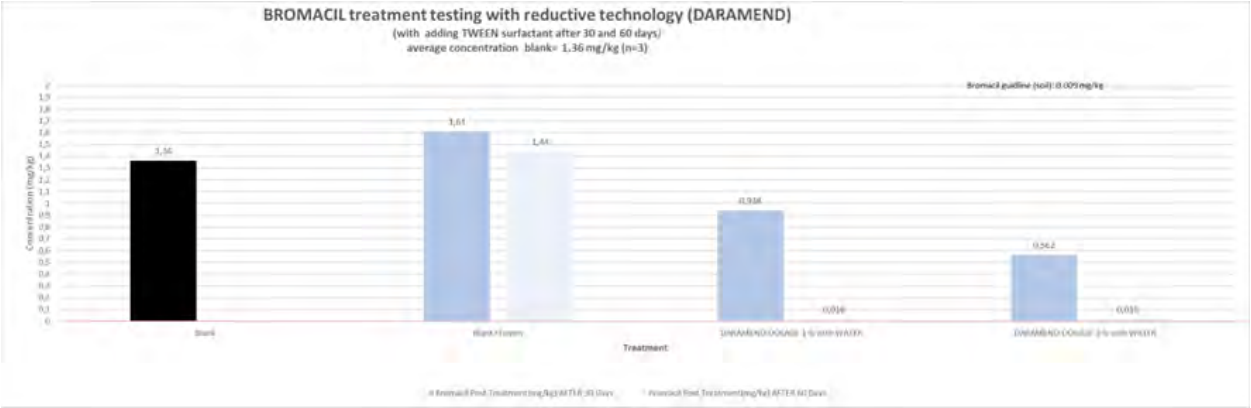
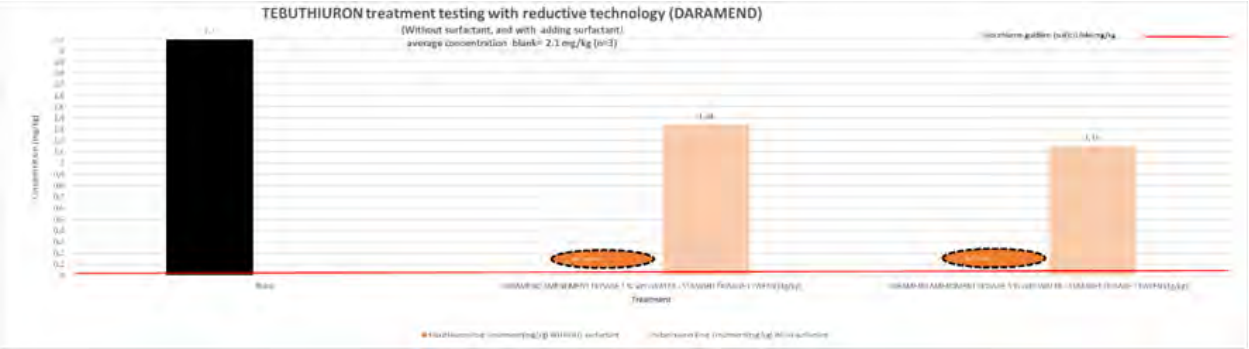


Figure 4. Comparing the effect of reductive treatment on bromacil with and without addition of surfactant.

a) With addition of Tween surfactant



b) After 30 and 60 days of reaction with surfactant

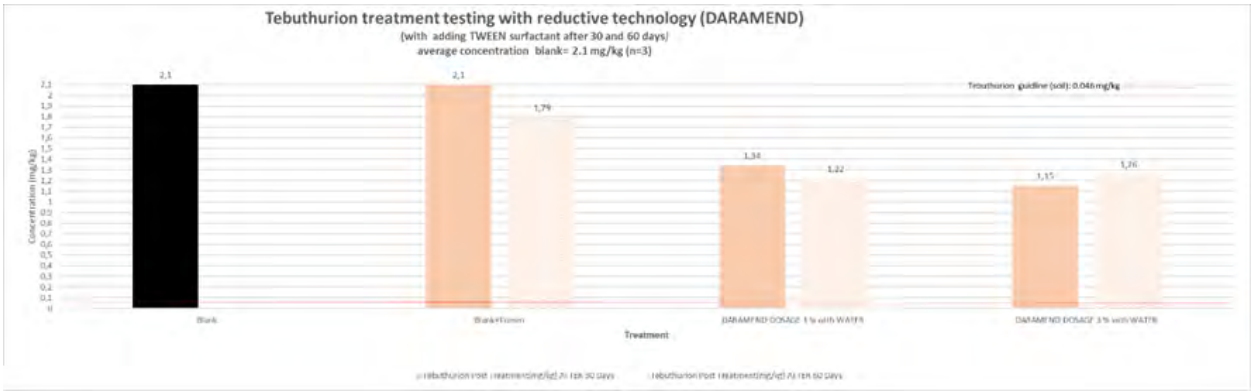


Figure 5. Results of reductive treatment on tebuthiuron with the addition of surfactant.

Note that no residual sodium persulfate was measured in the sacrificial samples after 30 and 60 days of treatment. This means that all the injected oxidant has been consumed or degraded within the test period. For the purposes of the economics calculations in the next section, we assumed 100% of the injected mass of the oxidant has been used. The high SOD value obtained for the submitted soil might have limited contaminant destruction by this oxidant in the submitted soil samples.

Note that the Blank concentration in Figure 6 is found to be lower than the post-treatment value, this might be associated to the soil heterogeneity. Another potential issue would be associated with the interference of residual persulfate oxidant with the lab reagent used for bromacil extraction and testing. This would need to be further investigated when submitting additional samples.

The results obtained from the different treatments conducted with oxidative testing (with surfactant) for bromacil and tebuthiuron are summarized in Appendix D.

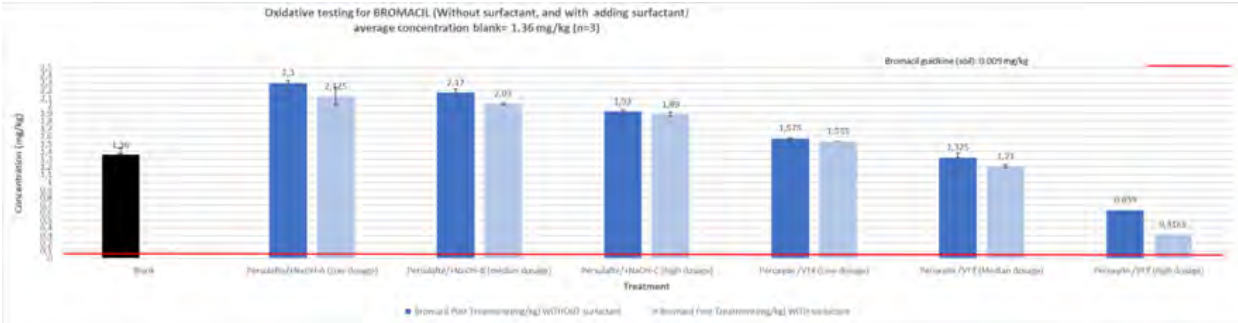


Figure 6. Results of oxidative treatment on bromacil with and without the addition of surfactant.

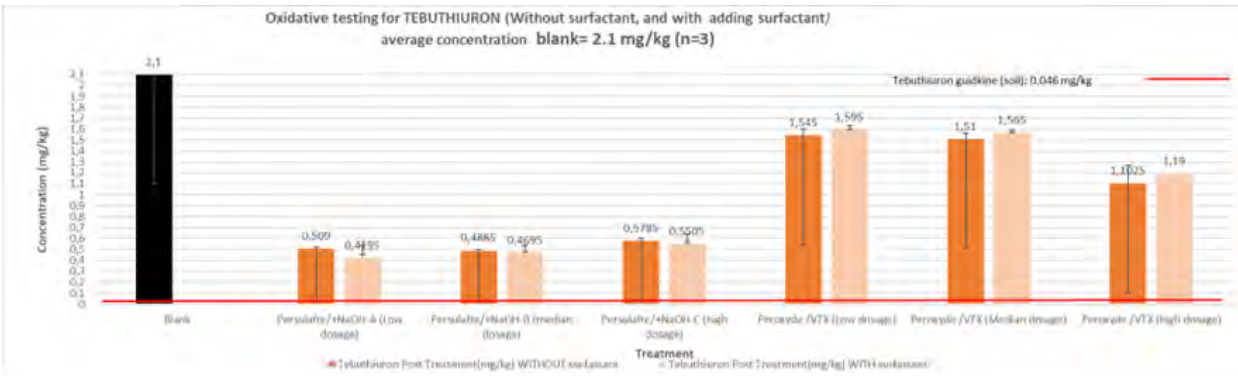


Figure 7. The effect of oxidative treatment on tebuthiuron with and without the addition of surfactant.

5 ECONOMIC EVALUATION

The previous portions of the report presented the results obtained for sterilant destruction rate versus the untreated soil sample for different amendment concentrations and combinations.

In this section, we are adding the economic aspects related to the destruction of the *mass* of contaminant to validate what is the best approach on the cost of amendment for each 1 mg/kg of sterilant (bromacil or tebuthiuron) removed. By calculating the amount of oxidant or reductive amendment needed to remove 1 mg of sterilant per kg of soil, we can then better estimate the costs for products for the treatments for the best degradation rates observed. These economic estimates are based on the available data and are only *estimates* of the product costs; they do NOT include the costs of onsite activities (i.e., soil handling, amendment incorporation, and monitoring).

5.1 Bromacil

By calculating the quantity of amendment necessary to eliminate 1 mg/kg of bromacil, we can conclude that the use of DARAMEND is the most advantageous option (Table 9). Thus, the treatment cost for the products is $42/MT of soil treated to destroy 1 mg/kg of bromacil. Note that the soil contained 1.36 mg/kg of bromacil and a similar dosage rate of DARAMEND could also treat higher concentration for the SAME cost structure but no test using a lower dosage was conducted.

Table 9. Economic evaluation of bromacil treatment costs (product only).

Treatment		Dosage of H_2O_2 50% / or DARAMEND consumed (g/kg)	Dosage of surfactant consumed (g/kg)	Bromacil reduced (mg/kg)	Quantity of H_2O_2 50% / or DARAMEND to destroy 1 mg/kg of bromacil [1] (g)	Quantity of the surfactant to extract 1 mg/kg of bromacil (kg)
ISCO	Hydrogen Peroxide/VTX (high dosage)	40.20	0	0.96	42	0
S-ISCO	Hydrogen Peroxide /VTX (high dosage) + TWEEN	40.20	1.00	1.04	39	1
ISCR	Daramend @ 1% (WT/WT)	10	0	1.33	8	0
		Cost of H_2O_2 50% ($/MT)	**Cost of VTX 22% ($/MT)**	**Cost of surfactant TWEEN ($/MT)**	**Cost of DARAMEND ($/MT)**	**Total treatment cost $/MT**
	Hydrogen Peroxide/VTX (high dosage)	52				52
	Hydrogen Peroxide /VTX (high dosage) + TWEEN	48	37	14		99
	Daramend @ 1 % (WT/WT)				42	42

[1] Same quantity required to destroy 1g/MT soil of bromacil.

The cost for remediation of 1 mg/kg of bromacil with DARAMEND was estimated based on results of the experiment. We introduced an initial 1% w/w dosage of DARAMEND into the soil matrix that was left to react for a period of 30 days. **Note that the DARAMEND would only work in saturated conditions (or high-water content soil) as the contaminant destruction pathway would not be efficient if the water content is insufficient.** We would target a 90% soil water holding capacity.

5.2 Tebuthiuron

For tebuthiuron, using sodium persulfate activated by sodium hydroxide, at low dosage without surfactant is more advantageous compared to the addition of the surfactant (Table 10). This gives a

treatment cost of $5/MT (product only) per 1 mg/kg removal of tebuthiuron (without surfactant) compared to $17/MT (with the use of surfactant).

5.3 Product Prices

Prices of the products, FOB Calgary warehouse, AB, used in the cost calculations:

- DARAMEND Reagent Tote @ $5.55/kg
- Hydrogen Peroxide 50% Tote @ $1.25/kg
- VTX22% Tote @ $9.50/kg
- TWEEN 80 –surfactant– 200kg drums or 1000kg totes – $15.00CDN/kg
- DECONIT –surfactant– 200kg drums or 1000kg totes – $21.00CDN/kg
- Sodium Persulfate 100%-Tote @ $5.55/kg
- Sodium Hydroxide 50% Tote @ $1.25/kg

*****Applicable Terms and Conditions: All prices are for the chemical only, FOB Calgary warehouse, subject to change without notice based on current inventory and freight cost at the moment of order.

All Taxes Extra.

Net 30 days.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 Bromacil Treatment

The reductive Daramend approach was highly effective in the treatment of bromacil in the tested soil samples. ***Overall treatment product cost was approximately C$55/MT (product only) of soil using a 1% w/w loading rate.*** This approach enabled rapid, cost- effective, and long-lasting treatment. Note that a lower DARAMEND dosage, like 0.25 % or 0.5 % w/w, could be tested or implemented in the field given that we have sufficient soil moisture and contact time for the reductive processes to take place. We could also potentially tackle higher bromacil concentrations with a similar amendment dosage rate, but this threshold would need to be tested to understand minimal dosage rate.

DARAMEND requires a treatment approach where the soil is normally cycled between reducing conditions and aerobic conditions. ***Interestingly, bromacil destruction was obtained WITHOUT tilling the sample after a 30-day contact time and sterilant removal rates were over 99% after 60 days showing that additional contact time under proper conditions would keep the reaction between the DARAMEND and the bromacil going.*** For field deployment, this would mean that a single pass application with proper wetting could help us reach the remedial objective given sufficient contact time.

Table 10. Economic evaluation of tebuthiuron treatment costs (product only).

Treatment		Dosage of H_2O_2 50% or DARAMEND consumed (g/kg)	Dosage of surfactant consumed (g/kg)	Tebuthiuron reduced (mg/kg)	Quantity of H_2O_2 50% or persulphate to destroy 1 mg/kg of tebuthiuron (g)	Quantity of the surfactant to extract 1 mg/kg of tebuthiuron (kg)	Quantity of H_2O_2 50% or DARAMEND to destroy 1 kg/MT of tebuthiuron (kg)
ISCO	Persulfate/NaOH (low dosage)	1.2	0	1.59	1	0	1
	Peroxide/VTX (high dosage)	40.2	0	1.15	35	0	35
S-ISCO	Persulfate/NaOH (low dosage) + DECONIT	1.2	1	1.68	1	0.6	1
		Cost of H_2O_2 50% ($/MT)	**Cost of VTX 22% ($/MT)**	**Cost of surfactant DECONIT ($/MT)**	**Cost of NaOH 50% ($/MT)**	**Cost of sodium persulfate 100% ($/MT)**	**Total treatment cost ($/MT)**
	Hydrogen Peroxide/VTX (high dosage)				1	4	5
	Hydrogen Peroxide /VTX (high dosage) + TWEEN	44	33				77
	Daramend@1% (WT/WT)			12	11	4	17

If necessary, after completing the initial reductive phase, the soil could be tilled again to dry it to a lower moisture content and introduce oxygen into the soil. This process allows further bromacil breakdown of the and prepares the soil for further treatment cycles using DARAMEND if needed. In this case, only one treatment cycle was required to obtain a 0.016 mg/kg bromacil concentration after 60 days. This is close to the 0.009 mg/kg remedial objective but considering the low ORP and usual DARAMEND persistency (5 to 7 years), additional sample submission after 60 days would likely have shown results below the remedial objective. Field testing will allow to confirm typical treatment time.

In addition, the treatment method is very sustainable, allowing the soil to be treated on site as opposed to using landfill space. The process uses little energy and very few resources. Finally, bromacil is destroyed, not just transported for storage or future treatment off-site.

The hydrogen peroxide oxidation process using the VTX catalyst and surfactant is more costly than the DARAMEND technology at **C$99/MT** (product only) for the destruction of 1.0 mg/kg bromacil concentration. This product combination would be an alternative treatment method for a combined soil and groundwater issue.

For groundwater contamination, the fact that the targeted compound is already in the water phase would facilitate its destruction via oxidative pathways. The remediation of the sorbed bromacil would however be influenced by the sorption/desorption mechanism to make the bromacil available in the water phase. It is important to note that final concentrations obtained during the lab scale treatment were not as low as with Daramend.

In the case of groundwater contamination only, the use of a surfactant would not bring any benefit; therefore, treatment costs would be **C$52/MT** (product only). In that regard, it is important to note that either for oxidative or reductive treatment pathways, surfactants are adding a significant cost versus their measured effectiveness. In the case of reductive processes using biotic pathways, they can even hinder treatment, possibly due to microbial interference.

6.2 Tebuthiuron Treatment

The ISCO approach with a low dosage of alkaline activated Klozur® persulfate reduced tebuthiuron concentration by 76% without adding a surfactant. The stability of persulfate, which can last weeks to months in the soil, provides a large radius of influence, and maximizes contact time with contaminants. Another factor that increases the effectiveness of persulfate in treating chlorinated compounds is that after oxidative reactions have ceased, a reducing environment can be created by fostering sulfate-reducing bacteria that will continue to degrade contaminants. This was not evaluated in this study.

The treatment cost was **C$5/MT** (product only) per 1 mg/kg tebuthiuron removed (without surfactant) compared to **C$17/MT** (with the use of surfactant). Additional persulfate injection in the soil matrix could the done after the completion of the initial oxidative phase to obtain higher sterilant removal rate. This is related to the fact that the remediation of the sorbed soil sterilant is limited by the oxidant persistence and the sorption/desorption mechanism to bring the sterilant to the water phase for final destruction.

This reactivity between the alkaline activated persulfate and tebuthiuron could also be an alternative treatment method in the case of a combined soil and groundwater issue. For groundwater contamination, the fact that the tebuthiuron is already in the water phase would facilitate its destruction via oxidative pathways.

Additional field demonstration would be required to validate exact loading rate versus tebuthiuron destruction.

7 REFERENCES

Drozdowski, B., C.B. Powter, and S. Levy, 2018. *Management of Sterilant Impacted Sites: Literature Synthesis*. InnoTech Alberta, Edmonton, Alberta. 62 pp. Available at https://www.cclmportal.ca/resource/management-sterilant-impacted-sites-literature-synthesis

Levy, S., X. Mo and V. Bachmann, 2021. *Evaluation and Comparison of Soil Sterilant Remediation Technologies*. Report SSP-13 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 30 pp.

APPENDIX A: BROOKS TOPSOIL CHARACTERIZATION

Characterization parameters for a batch of 'Brooks topsoil;' unspiked and containing no soil sterilants (analysis provided by Element laboratories, October 2019). Average and standard deviation from three random grab samples from entire batch.

Parameter	Units	Average	Standard Deviation
Texture		Loam	-
	% Sand	46	2.31
	% Silt	35	2.52
	% Clay	18	1.53
75 um sieves		Fine-Grained	-
	% Retained	42	0.31
Organic Matter	%	3.44	0.55
Organic Carbon	%	1.73	0.28
pH		7.60	0.10
EC	dS/m	1.40	0.04
SAR		4.00	0.10
% Saturation		48	1.73
Calcium	mg/kg	49.0	0.18
Magnesium	mg/kg	13.0	1.56
Sodium	mg/kg	85.0	0.06
Potassium	mg/kg	13.7	0.40
Chloride	mg/kg	18.3	0.21
Sulfate (SO4)	mg/kg	130	1.00
Sulfate-S	mg/kg	43.3	0.03
TGR	T/ac	<0.1	-

Testing protocol for surfactant evaluation:

1. Take a representative mass of soil (1,000 to 1,500 g) and mix it well. Collect three (3) baseline samples for contaminant analysis;
2. Take 3 x (300 g) of soil for each of three (3) tests. Let us call them A, B, and C;
3. Wet each of A, B, and C test samples with water to at least 100 % moisture content, note how much water added to each;
4. Add 1 g of surfactant 1 (Liquid) to A, 5 g of Surfactant 1 to B, and 10 g of Surfactant 1 to C (To allow for a calibration curve).
5. Mix each on an orbital or arm shaker of A, B, and C for a period of 24 to 48 hours max, note actual time of mixing;
6. Drain water off each test sample into a vial, label each separately for each surfactant;
7. Rinse each with 50 to 75 ml of water 2 to 3 times (Just note what you did), and add wash water into the marked vials from (6);
8. Then mix e send half or the entire sample for contaminant analysis;
9. Tabulate and plot the results for each A, B, C on separate and combined graphs.

C.1 Open scan – Spike (Tebuthiuron) contents

BUREAU VERITAS

Results of Characterization Analysis by GC/MSD (Extractable Organics)

Client: Innotech Alberta Inc.
Sample ID: LSZ741
Bureau Veritas Job No. C007564
Analysis Date: 2020-01-21
File ID: MS12JG54.D
Internal Standard: D10-Phenanthrene:
Area = 3625320 R.T. = 14.18 min

Compound Name	Retention Time	Match %	CAS No.	Area	Approximate Conc. (ug/g)
Propylene Glycol	2.76	80	000057-55-6	2157890	230
oxygenated hydrocarbon	6.51	N/A	N/A	82948	9.1
unknown	10.71	N/A	N/A	398192	43
unknown	11.71	N/A	N/A	547479	60
Tebuthiuron	12.79	97	34014-18-1	417195133	46000
unknown	14.09	N/A	N/A	1326270	140
unknown	15.93	N/A	N/A	325703	36
Cyclic octaatomic sulfur	16.61	91	010544-50-0	322473	35
unknown	16.99	N/A	N/A	941421	100
2-Butenedioic acid (E)-, bis(2-ethylhexyl) ester	17.75	91	000141-02-6	18247800	2000
unknown	20.06	N/A	N/A	745454	81
unknown	24.18	N/A	N/A	456655	50

Legend:
Match % = Probability of a match between the unknown peak and the closest Library Match
CAS No. = CAS Registry Number which represents the best compound match in the NIST Library
Approximate Conc. = Approximate value based on a 1:1 area response with the Internal Standard.

Approved by: Approval date:2020/01/24

Validated by: Validation date: 2020/01/24

C2. Open scan – Hyvar (Bromacil) contents

BUREAU VERITAS

Results of Characterization Analysis by GC/MSD (Extractable Organics)

Client: Innotech Alberta Inc.
Sample ID: LNF660
Bureau Veritas Job No. B9Y6235
Analysis Date: 2019-12-13
File ID: MS12DB61.D
Internal Standard: D10-Phenanthrene:
Area = 4385800 R.T. = 13.72 min

Compound Name	Retention Time	Match %	CAS No.	Area	Approximate Conc. (ug/g)
2-Pentanone, 4-hydroxy-4-methyl-	3.66	56	000123-42-2	1029390	460
Brominated Compound	6.68	N/A	N/A	80476	36
Nitrogen Containing Compound	8.36	N/A	N/A	2666760	1200
unknown	10.38	N/A	N/A	271481	120
unknown	12.93	N/A	N/A	541570	240
unknown	14.26	N/A	N/A	1152810	520
Bromacil	15.30	96	000314-40-9	91173300	41000
unknown	15.36	N/A	N/A	949821	420

Legend:
Match % = Probability of a match between the unknown peak and the closest Library Match
CAS No. = CAS Registry Number which represents the best compound match in the NIST Library
Approximate Conc. = Approximate value based on a 1:1 area response with the Internal Standard.

Approved by: Approval date:2020/01/08

Validated by: Validation date: 2020/01/08

Table D.1- ISCR (DARAMEND) with and without surfactant – Bromacil

Treatment	Start date of testing	Reaction time (days)	Repetition	Additive	Surfactant	Surfactant (g/kg)	Bromacil Initial Concentration (mg/kg)	Average Bromacil Post Treatment Concentration (mg/kg) after 30 days	average Bromacil Post Treatment Concentration (mg/kg) after 60 days	Reduction in Bromacil Concentration (%) after 30 days	Reduction in Bromacil Concentration (%) after 60 days
DARAMEND AMENDMENT DOSAGE 1 % with WATER - STRAIGHT DOSAGE -No tilling 30 Days	08-February 2022	30	2	DARAMEND	None	**0**	1,36	0,096	Not tested	93	Not tested
DARAMEND AMENDMENT DOSAGE 1 % with WATER - STRAIGHT DOSAGE -Tilling every 30 days	08-February 2022	30	2	DARAMEND	None	0	1,36	0,035	Not tested	97	Not tested
DARAMEND AMENDMENT DOSAGE 3 % with WATER - STRAIGHT DOSAGE -No tilling 30 Days	08-February 2022	30	2	DARAMEND	None	0	1,36	0,019	Not tested	**99**	Not tested
DARAMEND AMENDMENT DOSAGE 3 % with WATER - STRAIGHT DOSAGE -Tilling every 30 days	08-February 2022	30	2	DARAMEND	None	0	1,36	0,091	Not tested	93	Not tested
DARAMEND AMENDMENT DOSAGE 1 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN**	5 May 2022	30 -60	1	DARAMEND	TWEEN	1	1,36	0,938	0,016	31	**99**
DARAMEND AMENDMENT DOSAGE 3 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN**	5 May 2022	30-60	1	DARAMEND	TWEEN	1	1,36	0,562	0,015	59	**99**

Table D.2- ISCR (DARAMEND) with surfactant – Tebuthiuron

Treatment	Start date of testing	Reaction time (days)	Repetition	Additive	Surfactant	Surfactant (g/kg)	Bromacil Initial Concentration (mg/kg)	Average Tebuthiuron Post Treatment Concentration (mg/kg) after 30 days	average Tebuthiuron Post Treatment Concentration (mg/kg) after 60 days	Reduction in Bromacil Concentration (%) after 30 days	Reduction in Bromacil Concentration (%) after 60 days
TEBUTHIURON without Surfactant		30	Not tested	Not tested	Not tested	0	Not tested	Not tested	Not tested	Not tested	Not tested
DARAMEND AMENDMENT DOSAGE 1 % **with SURFACTANT** - STRAIGHT DOSAGE + **TWEEN**	5 May 2022	30 -60	1	DARAMEND	TWEEN	1	2,1	1,34	1,22	36	42
DARAMEND AMENDMENT DOSAGE 3 % **with SURFACTANT** - STRAIGHT DOSAGE + **TWEEN**	5 May 2022	30-60	1	DARAMEND	TWEEN	1	2,1	1,15	1,26	**45**	**40**

Table D.3- ISCO – BROMACIL

Treatment		Start date of testing	Reaction time	Repetition	Surfactant	Oxidant Concentration: H_2O_2 OR Persulfate (g/kg)	Activator (g/kg)	Bromacil Initial Concentration (mg/kg)	Bromacil Post Treatment Concentration (mg/kg)	Reduction in Bromacil Concentration (%)
Potassium persulfate activated with calcium-based product (hydrated lime)	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (low dosage)	08 -02- 2022	30	2	none	1.20	3.40	1,36	1,95	-43
	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (median dosage)	08 February 2022	30	2	none	2.70	3.89	1,36	1,74	-28
	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (high dosage)	08 February 2022	30	2	none	5.20	4.72	1,36	1,55	-14
Sodium persulfate activated with calcium-based product (calcium peroxide FG)	Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (low dosage)	08 February 2022	30	2	none	1.20	1.20	1,36	1,445	-6
	Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (median dosage)	08 February 2022	30	2	none	2.70	2.70	1,36	1,395	-3
	Dosage 3 - Sodium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (high dosage)	08 February 2022	30	2	none	5.20	5.20	1,36	Broken	Broken
Sodium persulfate activated with alkaline base (sodium hydroxide)	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	08 February 2022	30	2	none	1.20	13.6	1,36	1,425	-5
	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	08 February 2022	30	2	none	2.70	15.6	1,36	Broken	Broken
	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	08 February 2022	30	2	none	5.20	18.9	1,36	1,48	-9
Hydrogen Peroxide alone	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1(low dosage)	08 February 2022	30	2	none	10.2	0	1,36	broken	Broken
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) (median dosage)	08 February 2022	30	2	none	20.2	0	1,36	1,34	1
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) (high dosage)	08 February 2022	30	2	none	40.2	0	1,36	Broken	Broken
Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	08 February 2022	30	2	none	10.2	1.02	1,36	0,834	39
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	08 February 2022	30	2	none	20.2	2.02	1,36	0,881	35
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	08 February 2022	30	2	none	40.2	4.02	1,36	0,401	**71**

Table D.4- ISCO – Tebuthiuron

Treatment		Start date of testing	Reaction time (days)	Repetition	Surfactant	Oxidant Concentration : H2O2 OR Persulfate (g/kg)	Activator (g/kg)	Tebuthiuron Initial Concentration (mg/kg)	Tebuthiuron Post Treatment Concentration (mg/kg)	Reduction in Tebuthiuron Concentration (%)
Potassium persulfate activated with calcium-based product (hydrated lime)	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (low dosage)	08 February 2022	30	2	none	1.20	4.4	2,1	1,47	30
	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (median dosage)	08 February 2022	30	2	none	2.70	4.9	2,1	1,40	33
	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (high dosage)	08 February 2022	30	2	none	5.20	5.7	2,1	1,51	28
Sodium persulfate activated with calcium-based product (calcium peroxide FG)	Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (low dosage)	08 February 2022	30	2	none	1.20	1.20	2,1	1,49	29
	Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (median dosage)	08 February 2022	30	2	none	2.70	2.70	2,1	1,75	17
	Sodium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (high dosage)	08 February 2022	30	2	none	5.20	5.20	2,1	1,77	16
Sodium persulfate activated with alkaline base (sodium hydroxide)	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	08 February 2022	30	2	none	1.20	17.6	2,1	1,93	8
	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	08 February 2022	30	2	none	2.70	19.6	2,1	1,89	10
	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	08 February 2022	30	2	none	5.20	22.9	2,1	1,77	16
Hydrogen Peroxide alone	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio 10: 1(low dosage)	08 February 2022	30	2	none	10.2	0	2,1	1,64	22
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio 20: 1) (median dosage)	08 February 2022	30	2	none	20.2	0	2,1	1,52	28
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio 30: 1) (high dosage)	08 February 2022	30	2	none	40.2	0	2,1	1,59	24
Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio 10: 1) + VTX 22% (low dosage)	08 February 2022	30	2	none	10.2	1.02	2,1	1,65	22
	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	08 February 2022	30	2	none	20.2	2.02	2,1	1,43	32
	Hydrogen peroxide 50% per kg of soil (oxidant: Contaminant ratio 30: 1) + VTX% 22 (high dosage)	08 February 2022	30	2	none	40.2	4.02	2,1	0,95	55

Table D.5 - S-ISCO: Bromacil and Tebuthiuron Surfactant-Enhanced Oxidative Testing

Sterilant	Treatment		Start date of testing	Reaction time	Repetition	Surfactant (dosage de surfactant (1 g/kg))	Oxidant Concentration: H2O2 OR Persulfate (g/kg)	Activator (g/kg)	Sterilant Initial Concentration (mg/kg)	Sterilant Post Treatment Concentration (mg/kg)	Reduction in Sterilant Concentration (%)
BROMACIL	Sodium persulfate + NaOH	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	10 May 2022	30	2	None	1.20	13.6	1,36	2,3	-69
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	10 May 2022	30	2	none	2.70	15.6	1,36	2,17	-60
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil) (high dosage)	10 May 2022	30	2	none	5.20	18.9	1,36	1,93	-42
	Sodium persulfate + NaOH + **DL4**	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	10 May 2022	30	2	DL4	1.20	13.6	1,36	2,125	-56
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	10 May 2022	30	2	DL4	2.70	15.6	1,36	2,03	-49
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	10 May 2022	30	2	DL4	5.20	18.9	1,36	1,89	-39
	Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10 May 2022	30	2	none	10.2	1.02	1,36	1,575	-16
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	10 May 2022	30	2	none	20.2	2.02	1,36	1,325	3
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	10 May 2022	30	2	none	40.2	4.02	1,36	0,639	**53**
	Hydrogen Peroxide activated using VTX +**TWEEN**	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10 May 2022	30	2	TWEEN	10.2	1.02	1,36	1,535	-13
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	10 May 2022	30	2	TWEEN	20.2	2.02	1,36	1,21	11
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	10 May 2022	30	2	TWEEN	40.2	4.02	1,36	0,3165	**77**

Sterilant	Treatment		Start date of testing	Reaction time	Repetition	Surfactant (dosage de surfactant (1 g/kg))	Oxidant Concentration: H2O2 OR Persulfate (g/kg)	Activator (g/kg)	Sterilant Initial Concentration (mg/kg)	Sterilant Post Treatment Concentration (mg/kg)	Reduction in Sterilant Concentration (%)
TEBUTHIURON	Sodium persulfate + NaOH	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	10 May 2022	30	2	none	1.20	17.6	2,1	0,509	76
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	10 May 2022	30	2	none	2.70	19.6	2,1	0,4885	77
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	10 May 2022	30	2	none	5.20	22.9	2,1	0,5785	72
	Sodium persulfate + NaOH + **DECONIT**	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	10 May 2022	30	2	DECONIT	1.20	17.6	2,1	0,4195	80
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	10 May 2022	30	2	DECONIT	2.70	19.6	2,1	0,4695	78
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	10 May 2022	30	2	DECONIT	5.20	22.9	2,1	0,5505	74
	Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10 May 2022	30	2	none	10.2	1.02	2,1	1,545	26
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	10 May 2022	30	2	none	20.2	2.02	2,1	1,51	28
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	10 May 2022	30	2	none	40.2	4.02	2,1	1,1025	48
	Hydrogen Peroxide activated using VTX +**TWEEN**	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10 May 2022	30	2	TWEEN	10.2	1.02	2,1	1,595	24
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	10 May 2022	30	2	TWEEN	20.2	2.02	2,1	1,565	25
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	10 May 2022	30	2	TWEEN	40.2	4.02	2,1	1,19	43

Table D.6- List of the samples broken during transport to the analysis laboratory

	Treatment	Sample ID	Delivered to Element on	
Without surfactant	Bromacil-Persulfate/+Ca(OH)2	ISCO-Bromacil-Persulfate/+Ca(OH)2-A2	2022-03-21	BROKEN
		ISCO-Bromacil-Persulfate/+Ca(OH)2-C2	2022-03-21	BROKEN
	Bromacil-Persulfate/+Calcium peroxide	ISCO-Bromacil-Persulfate/+Calcium peroxide-F1	2022-03-21	BROKEN
		ISCO-Bromacil-Persulfate/+Calcium peroxide-F2	2022-03-21	BROKEN
	Bromacil-Persulfate/+NaOH	ISCO-Bromacil-Persulfate/+NaOH-H1	2022-03-21	BROKEN
		ISCO-Bromacil-Persulfate/+NaOH-H2	2022-03-21	BROKEN
	Bromacil-Hydrogen peroxide alone	ISCO-Bromacil-Hydrogen peroxide alone-J1	2022-03-21	BROKEN
		ISCO-Bromacil-Hydrogen peroxide alone-J2	2022-03-21	BROKEN
		ISCO-Bromacil-Hydrogen peroxide alone-L1	2022-03-21	BROKEN
		ISCO-Bromacil-Hydrogen peroxide alone-L2	2022-03-21	BROKEN
	Bromacil-Hydrogen peroxide /VTX	ISCO-Bromacil-Hydrogen peroxide /VTX-M2	2022-03-21	BROKEN
		ISCO-Bromacil-Hydrogen peroxide /VTX-N1	2022-03-21	BROKEN
	Tebuthiuron- BLANK	Tebuthiuron-DRY BLANK-time zero	2022-03-21	BROKEN
		Tebuthiuron-WET BLANK-end of testing	2022-03-21	BROKEN
	Tebuthiuron-Persulfate/+Ca(OH)2	ISCO-Tebuthiuron-Persulfate/+Ca(OH)2-BB2	2022-03-21	BROKEN
	Tebuthiuron-Persulfate/+Calcium peroxide	ISCO-Tebuthiuron-Persulfate/+Calcium peroxide-DD2	2022-03-21	BROKEN
	Tebuthiuron-Persulfate/+NaOH	ISCO-Tebuthiuron-Persulfate/+NaOH-II1	2022-03-21	BROKEN
	Tebuthiuron-Hydrogen peroxide alone	ISCO-Tebuthiuron-Hydrogen peroxide alone--LL2	2022-03-21	BROKEN
	Tebuthiuron-Hydrogen peroxide /VTX	ISCO-Tebuthiuron-Hydrogen peroxide /VTX-NN2	2022-03-21	BROKEN
		ISCO-Tebuthiuron-Hydrogen peroxide /VTX-OO1	2022-03-21	BROKEN
With surfactant (+TWEEN)	Bromacil Hydrogen peroxide /VTX+surfactant TWEEN	Bromacil-Peroxide /VTX +TWEEN K2-20	10-06-2022	BROKEN
	Tebuthiuron Hydrogen peroxide /VTX+surfactant TWEEN	Tebuthiuron-Peroxide /VTX +TWEEN X2-40	10-06-2022	BROKEN

Table D.7- Summary results of the treatments and combinations which met Tier 1 guidelines.

Met the criteria	Close to the criteria (>50% reduction)	no or slight reduction

	Treatment		Start date of testing	Sterilant (mg/kg)	Reduction (%)	Reaching The Criterion
ISCO- BROMACIL	Potassium persulfate activated with calcium-based product (hydrated lime)	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (low dosage)	08 -2- 2022	1,95	-43	
		Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (median dosage)	08 -2- 2022	1,74	-28	
		Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (high dosage)	08 -2- 2022	1,55	-14	
	Sodium persulfate activated with calcium-based product (calcium peroxide FG)	Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (low dosage)	08 -2- 2022	1,445	-6	
		Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (median dosage)	08 -2- 2022	1,395	-3	
		Dosage 3 - Sodium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (high dosage)	08 -2- 2022	Broken	Broken	
	Sodium persulfate activated with alkaline base (sodium hydroxide)	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	08 -2- 2022	1,425	-5	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	08 -2- 2022	Broken	Broken	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	08 -2- 2022	1,48	-9	
	Hydrogen Peroxide alone	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1(low dosage)	08 -2- 2022	broken	Broken	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) (median dosage)	08 -2- 2022	1,34	1	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) (high dosage)	08 -2- 2022	Broken	Broken	
	Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	08 -2- 2022	0,834	39	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	08 -2- 2022	0,881	35	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	08 -2- 2022	0,401	**71**	
	Sodium persulfate + NaOH	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	10 -5- 2022	2,3	-69	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	10 -5- 2022	2,17	-60	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	10 -5- 2022	1,93	-42	
	Sodium persulfate + NaOH + **DL4**	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	10 -5- 2022	2,125	-56	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	10 -5- 2022	2,03	-49	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	10 -5- 2022	1,89	-39	
	Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10 -5- 2022	1,575	-16	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	10 -5- 2022	1,325	3	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	10 -5- 2022	0,639	**53**	
	Hydrogen Peroxide activated using VTX +**TWEEN**	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10 -5- 2022	1,535	-13	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	10 -5- 2022	1,21	11	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	10 -5- 2022	0,3165	**77**	
SCR- BROMACIL	DARAMEND WITHOUT SURFACTANT	DARAMEND AMENDMENT DOSAGE 1 % with WATER - STRAIGHT DOSAGE -No tilling 30 Days	08 -2- 2022	0,096	**93**	
		DARAMEND AMENDMENT DOSAGE 1 % with WATER - STRAIGHT DOSAGE -Tilling every 30 days	08 -2- 2022	0,035	**97**	
		DARAMEND AMENDMENT DOSAGE 3 % with WATER - STRAIGHT DOSAGE -No tilling 30 Days	08 -2- 2022	0,019	**99**	
		DARAMEND AMENDMENT DOSAGE 3 % with WATER - STRAIGHT DOSAGE -Tilling every 30 days	08 -2- 2022	0,091	93	
	DARAMEND + SURFACTANT (**TWEEN)**	DARAMEND AMENDMENT DOSAGE 1 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN (30 days)**	05-5-2022	0,938	31	
		DARAMEND AMENDMENT DOSAGE 3 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN (30 days)**	05-5-2022	0,562	59	
		DARAMEND AMENDMENT DOSAGE 1 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN (60 days)**	05-5-2022	0,016	**99**	
		DARAMEND AMENDMENT DOSAGE 3 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN (60 days)**	05-5-2022	0,015	**99**	

ISCO- TEBUTHIURON	Potassium persulfate activated with calcium-based product (hydrated lime)	Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (low dosage)	08 -2- 2022	1,47	30	
		Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (median dosage)	08 -2- 2022	1,40	33	
		Potassium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (high dosage)	08 -2- 2022	1,51	28	
	Sodium persulfate activated with calcium-based product (calcium peroxide FG)	Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (low dosage)	08 -2- 2022	1,49	29	
		Sodium persulfate 100 % per kg of soil + de calcium peroxide FG 100% per kg of soil (median dosage)	08 -2- 2022	1,75	17	
		Dosage 3 - Sodium persulfate 100 % per kg of soil + Ca $(OH)_2$ 100% per kg of soil (high dosage)	08 -2- 2022	1,77	16	
	Sodium persulfate activated with alkaline base (sodium hydroxide)	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	08 -2- 2022	1,93	8	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	08 -2- 2022	1,89	10	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	08 -2- 2022	1,77	16	
	Hydrogen Peroxide alone	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1(low dosage)	08 -2- 2022	1,64	22	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) (median dosage)	08 -2- 2022	1,52	28	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) (high dosage)	08 -2- 2022	1,59	24	
	Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	08 -2- 2022	1,65	22	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	08 -2- 2022	1,43	32	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	08 -2- 2022	0,95	55	
	Sodium persulfate + NaOH	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	10 -5- 2022	0,509	76	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	10 -5- 2022	0,4885	77	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	10 -5- 2022	0,5785	72	
	Sodium persulfate + NaOH + **DECONIT**	Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (low dosage)	10 -5- 2022	0,4195	**80**	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (median dosage)	10 -5- 2022	0,4695	78	
		Sodium persulfate 100 % per kg of soil + NaOH 25 % per kg of soil (high dosage)	10 -5- 2022	0,5505	74	
	Hydrogen Peroxide activated using VTX	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10 -5- 2022	1,545	26	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	10 -5- 2022	1,51	28	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	10 -5- 2022	1,1025	48	
	Hydrogen Peroxide activated using VTX +**TWEEN**	Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 10: 1) + VTX 22% (low dosage)	10 -5- 2022	1,595	24	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 20: 1) + VTX 22% (median dosage)	10 -5- 2022	1,565	25	
		Hydrogen peroxide 50% per kg of soil (oxidant: contaminant ratio of 30: 1) + VTX% 22 (high dosage)	10 -5- 2022	1,19	43	
ISCR- TEBUTHIURON	DARAMEND WITHOUT SURFACTANT	TEBUTHIURON without Surfactant was not tested				
	DARAMEND + SURFACTANT (**TWEEN)**	DARAMEND AMENDMENT DOSAGE 1 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN (30 days)**	05-5-2022	1,34	**36**	
		DARAMEND AMENDMENT DOSAGE 3 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN (30 days)**	05-5-2022	1,15	**45**	
		DARAMEND AMENDMENT DOSAGE 1 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN (60 days)**	05-5-2022	1,22	42	
		DARAMEND AMENDMENT DOSAGE 3 % **with SURFACTANT** - STRAIGHT DOSAGE +**TWEEN (60 days)**	05-5-2022	1,26	40	

E.1 picture of the soil sample (SOD tests)

Surfactant	Composition/information on ingredients	Physical and chemical properties
TWEEN 80	Name of substance: Tween® 80 CAS: No 9005-65-6	**Physical state**: liquid **Form**: viscous **Colour**: yellow **Odour**: odourless **Melting point/freezing point:** not determined **Boiling point or initial boiling point and boiling range:** >100 °C at 1.013 hPa **Flammability** : this material is combustible, but will not ignite readily **Lower and upper explosion limit**: not determined **Flash point**: >113 °C (c.c.) **Auto-ignition temperature**: not determined **Decomposition temperature**: not relevant **pH (value)**: neutral **Kinematic viscosity**: 300 – 500 mm^2/s at 25 °C **Water solubility** : soluble **Partition coefficient n-octanol/water (log value)**: not available **Vapour pressure**: <1,33 hPa **Density**: 1,06 – 1,09 g/cm^3 at 25 °C **Relative vapour density** : not available **Particle characteristics**: not relevant (liquid) **Oxidising properties:** none
DECONIT	Chemical Name / CAS No. / By volume%* DECON-IT® A - Biodegradable Non-ionic Surfactants / 9002-93-1 / 1 – 5%* DECON-IT® B - Biodegradable Non-ionic Surfactants / 9002-93-1 / 1 – 5%* DECON-IT® C- Biodegradable Non-ionic Surfactants / 9081-99-6 / 1 – 5%* DECON-IT® D- Biodegradable Non-ionic Surfactants / 9036-19-5 / 1 – 5%* DECON-IT® E - Biodegradable Non-ionic Surfactants / 89004-38-5 / 1 – 5%* DECON-IT® J - Biodegradable Non-ionic Surfactants / 9036-19-5 / 1 – 5%* Preservative** / Not Available / <0.01% Scent** / Not Available / 0.1 – 1%* Water / 7732-18-5 / 60 – 80%*	**Appearance:** Colourless/slight white liquid **Specific Gravity (water = 1):** 0.99 – 1.04 **Odour:** Mild. **Solubility in Water**: Completely miscible **Odour Threshold**: Not Available **Solubility in Other Liquids**: Not Available **pH:** Not Available (near 7) **Partition Coefficient,n-Octanol / Water (Log Kow):** Not Available **Melting Point and Freezing Point**: ~0°C **Auto-Ignition Temperature**: Not Applicable **Initial Boiling Point and Boiling Range**: Not Available **Decomposition Temperature:** Not Available **Flash Point:** None (Tag Closed Cup) **Viscosity:** Not Available **Evaporation Rate** : <0.01 **Flammability (solid, gas):** Not Applicable (Liquid) **Vapour Density (air = 1):** >1 (air = 1) **Upper and Lower Flammability or Explosive Limit:**Not Applicable **Vapour Pressure:** <0.01 mm Hg **% Volatile**: Not Available
CHEMSOL DL3	Chemical name / CAS Number / Concentration Ethoxylated Alcohol / 68439-46-3 / 60-100%	**Appearance:** Liquid. Hazy. **Odour:** Mild. **Odour threshold:** Not available. **pH:** 6.5 **Melting point:** 36 - 59°F (2.22 - 15°C) **Freezing point:** Not available. **Initial boiling point and boiling range:** > 491°F (>255°C) **Flash point (method):** 306°F (152.2°C) **Evaporation rate (BuAe=1):** Not available. **Flammability (solid, gas):** Not applicable.

		Lower flammable limit (% by vol.): Not applicable. **Upper flammable limit (% by vol.):** Not applicable. **Vapour pressure:** Not available. **Vapour density:** Not available. **Relative density / Specific gravity:** 0 981 **Solubility in water:** Slightly soluble. **Partition coefficient:** Not available. **Auto-ignition temperature:** Not applicable. **Decomposition temperature:** Not available. **Viscosity:** 50 mPa.s at 100˚F (37.77˚C) **Molecular weight:** Not available. **Oxidizing properties:** Not available.
CHEMSOL DL4	Chemical name: Sodium petroleum sulfonate CAS Number: 68608-26-4 Concentration: 15-40%	**Appearance:** Liquid. Yellowish, clear. **Odour:** Characteristic. **Odour threshold:** Not available. **pH:** Around 7 (20 g/L) **Pour point:** -3˚C **Freezing point:** Not available. **Initial boiling point and boiling range:** > 100˚C **Flash point (method):** > 100˚C **Evaporation rate (BuAe=1):** Not available. **Flammability (solid, gas):** Not applicable. **Lower flammable limit (% by vol.):** Not applicable. **Upper flammable limit (% by vol.):** Not applicable. **Vapour pressure:** Approx. 3 kPa (25˚C) **Vapour density:** Not available. **Relative density / Specific gravity:** Approx. 1.05 g/cm³ (20˚C) **Solubility in water:** Soluble (25˚C). **Partition coefficient:** Not available. **Auto-ignition temperature:** Not applicable. **Decomposition temperature:** > 250˚C **Viscosity:** 160 mPa.s (30˚C) **Molecular weight:** Not available. **Oxidizing properties:** Not available.
IVEYSOL 106CL	Chemical name / CAS Number / Concentration(v/v) Biodegradable Non-ionic Surfactant 1 / Proprietary / 1-10% Biodegradable Non-ionic Surfactant 2 / Proprietary / 1-10% Biodegradable Non-ionic Surfactant 3 / Proprietary / 1-10% Biodegradable Non-ionic Surfactant 4 / Proprietary / 1-10% Biodegradable Non-ionic Surfactant 5 / Proprietary / 1-10% Biodegradable Non-ionic Surfactant 6 / Proprietary / 1-10% Preservative / 4080-31-3 / <90% Scent / 8016 / <1% water / 7732-18-5 / <90%	**Appearance:** Liquid, cloudy **Odour:** Mild **Odour threshold:** Not available **pH:** 7 (+/- 0.5) (1% solution) **Melting Point:** ~0°C **Freezing point:** ~0°C **Boiling Point:** Not available **Flash Point:** Not applicable **Evaporation Rate:** <0.01 **Flammability:** Not applicable **Lower flammable/ explosive limit:** Not applicable **Upper flammable/Explosive Limit:** Not applicable **Vapour Pressure:** <0.01 mm Hg **Vapour Density:** >1 **Relative Density:** 0 99-1.04 **Solubility:** 100% (Completely miscible in water) **Partition Coefficient:** Not available (n-octanol / water) **Auto-Ignition Temperature:** Not applicable **Decomposition Temperature:** Not available **Viscosity:** Not available

FFT	Chemical Name	CAS No.	Range (%)	**Appearance and Odor:** Liquid, Blue color, Hydrocarbon odor **pH:** ND **Vapor Pressure:** > 80 hPa @ 38°C / 100°F 4.1 kPa @ 20°C / 68°F **Vapor Density (Air = 1):** >2 **Boiling Point:** ND **Solubility:** Soluble in hydrocarbons; insoluble in water **Flash Point:** <50°F **Freezing Point:** NA **Melting Point:** NA **Specific Gravity:** 0.75 @ 15 6 °C / 15.6 °C **Volatile Organic Compounds (VOC):** ND **Viscosity (40 °C):** ND
	Solvent Naphtha (Petroleum), Light Aliphatic	64742-89-8l	<50	
	Synthetic Hydrocarbon Base Oil	Proprietary	<100	

Appendix A8-2: Electrocoagulation Technology

Saint-Fort, R. and S. Levy, 2022. Proof of Concept of Electrocoagulation Technology to Remediate Water Contaminated with Bromacil and Tebuthiuron. Report SSP-11B prepared by Mount Royal University and InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 11 pp. plus appendix.

Proof of Concept of Electrocoagulation Technology to Remediate Water Contaminated with Bromacil and Tebuthiuron

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July 11, 2022

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CITATION

This report may be cited as:

Saint-Fort, R. and S. Levy, 2022. Proof of Concept of Electrocoagulation Technology to Remediate Water Contaminated with Bromacil and Tebuthiuron. Report SSP-11B prepared by Mount Royal University and InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 7 pp. plus Appendix.

EXECUTIVE SUMMARY

Bromacil and tebuthiuron are pesticides used in Alberta and around the world as sterilants for non-selective vegetation control on industrial sites. This study aimed to investigate the removal of bromacil and tebuthiuron by electrocoagulation based on two types of electrodes (Fe and Al) using a batch mode approach. The reactor was operated with four electrodes in a bipolar connection, held vertically and parallel. The gap between each electrode was 1.25 cm and each electrode had an effective area of 102 cm^2. The simulated water contained bromacil and tebuthiuron at a concentration of 4 mg/L (4,000 µg/L), respectively. The ionic strength was adjusted with the addition of 20 g of NaCl. The simulated water solution had a pH of 5.92, TDS of 2,850 mg/L, EC of 3.04 mS, and turbidity 0.55 NTU.

Overall, the removal efficiency by the electrocoagulation process for bromacil ranged from 0 to 23.40%, while for tebuthiuron it was from 0 to 16%. Both removal processes involving the Fe electrodes system and Al electrodes system were relatively low. Comparatively, removal of the pesticides was generally higher with the Fe electrodes with the highest value being 23.40% while for the Al electrodes the maximum value was 16%. The low removal from the systems could be attributed to a lack of significant oxidative destruction and chemical transformation mechanisms under the applied electrocoagulation treatments. It also appears that there was no significant formation of a stable complexation mechanism that could have led to the removal of bromacil and tebuthiuron.

The following recommendations for further testing are made considering the low removal efficiency according to the study findings:

1. *The effectiveness of a four-cell Fe-graphite electrodes system and a four-cell Al-graphite electrodes system, respectively*. Both electrode systems will be configured in a bipolar arrangement. The removal efficiency of each electrode system will be tested using Treatment (T4) (i.e., 30 volts and 90 sec). In both electrode arrangement systems, graphite will be the non-sacrificial electrode. The rationale for this recommendation is the potential synergistic effect of hydroxyl radicals (*OH) and hypochlorous acid (HOCl) generation in the reactor during treatment. This has the potential to result in significant degradation and removal of the hydrophilic pesticides.
2. *The effect of increasing the surface area of the electrodes (cm^2) to volume (L) ratio, (S/V)*. Higher S/V ratio increases the surface area available for electrolytic reactions to occur in the reactor, which in return can have an integral effect on the pesticide removal efficiency.
3. *The effect of varying the inter electrode distance*. As an operational factor, the process efficiency can be improved by varying the distance between the electrodes. At minimum inter electrode distance, the resistance for current flow in the reactor is lowered. In this case, removal efficiency may occur due to higher current reaching the electrodes and lower resistivity in the solution to the electrical current. Optimal distance is highly characteristic of the solution matrix to be treated.
4. *The effect of voltage increase*. An increase in the voltage causes higher current to pass through the reactor. Concurrently, current density (A/m^2), which is current delivered to the electrode (A) divided by the electrode's area (m^2), also goes up. Increase in applied voltage or current density has the effect of increasing the rate of reactions in the reactor. However, voltage increase leads to higher energy consumption; economic considerations may render this approach less attractive.

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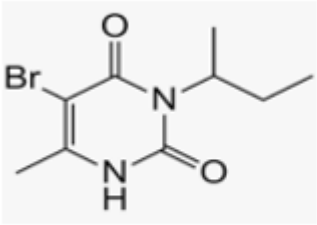
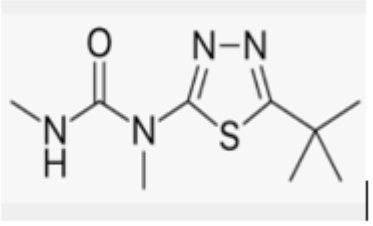
1.0 BACKGROUND

Bromacil and tebuthiuron (Figure 1) are pesticides used in Alberta and around the world as sterilants for non-selective vegetation control on industrial sites. Their mass transport along with their metabolites in the vadose zone has resulted in their leaching into the groundwater while runoff has led to contamination of surface water. Management of these impacted ecosystems through a cost-effective remediation program is needed for protecting public health, maintaining environmental quality, and ensuring sustainable development and prosperity.



Bromacil



Tebuthiuron

Figure 1. Chemical structure of bromacil and tebuthiuron.

The goal of this project was to conduct a proof of concept to ascertain the feasibility of using electrocoagulation to remediate water contaminated with bromacil and tebuthiuron. The Tier 1 Groundwater Remediation Guideline for natural areas is 0.005 mg/L for bromacil and 0.0016 mg/L for tebuthiuron.[1]

The primary objective of this research project was to investigate in a laboratory setting the application of electrocoagulation for treating water spiked with bromacil and tebuthiuron using a batch mode approach.

2.0 MATERIALS AND METHOD

A volume of 10 L of deionized water was added to a 19 L glass. The analytical grade pesticides used in the study were purchased from Sigma. The water was spiked with bromacil and tebuthiuron pesticides to a concentration of 4 mg/L, respectively, and the ionic strength of the water was adjusted with the addition of 20 g of NaCl. The mixture was dissolved gently on a magnetic stirrer for an hour. When not in use, the solution was kept refrigerated at 6°C. The resulting solution had a pH of 5.92, TDS of 2,850 mg/L, EC of 3.04 mS and turbidity 0.55 NTU.

The electrocoagulation treatments were investigated at room temperature in a 0.50 L reactor capacity (Figure 2). In each run, 400 ml of the solution was quantitatively transferred into the electrolytic reactor. The cell was operated with four reactors that were made of either aluminum of iron. Each electrode had the dimensions of 34 cm x 3 cm x 0.30 cm. The four (4) electrodes were held vertically and parallel with a 1.25 cm gap between each electrode in a bipolar connection. Each electrode had an effective area of

[1] AEP (Alberta Environment and Parks). 2019a. *Alberta Tier 1 Soil and Groundwater Remediation Guidelines*. Land Policy Branch, Policy and Planning Division. 198 pp. Available at https://open.alberta.ca/publications/1926-6243

102 cm^2. The reactor was stirred gently during a treatment process. At the end of each treatment investigation, the cell and the electrodes were washed thoroughly with diluted alcohol.

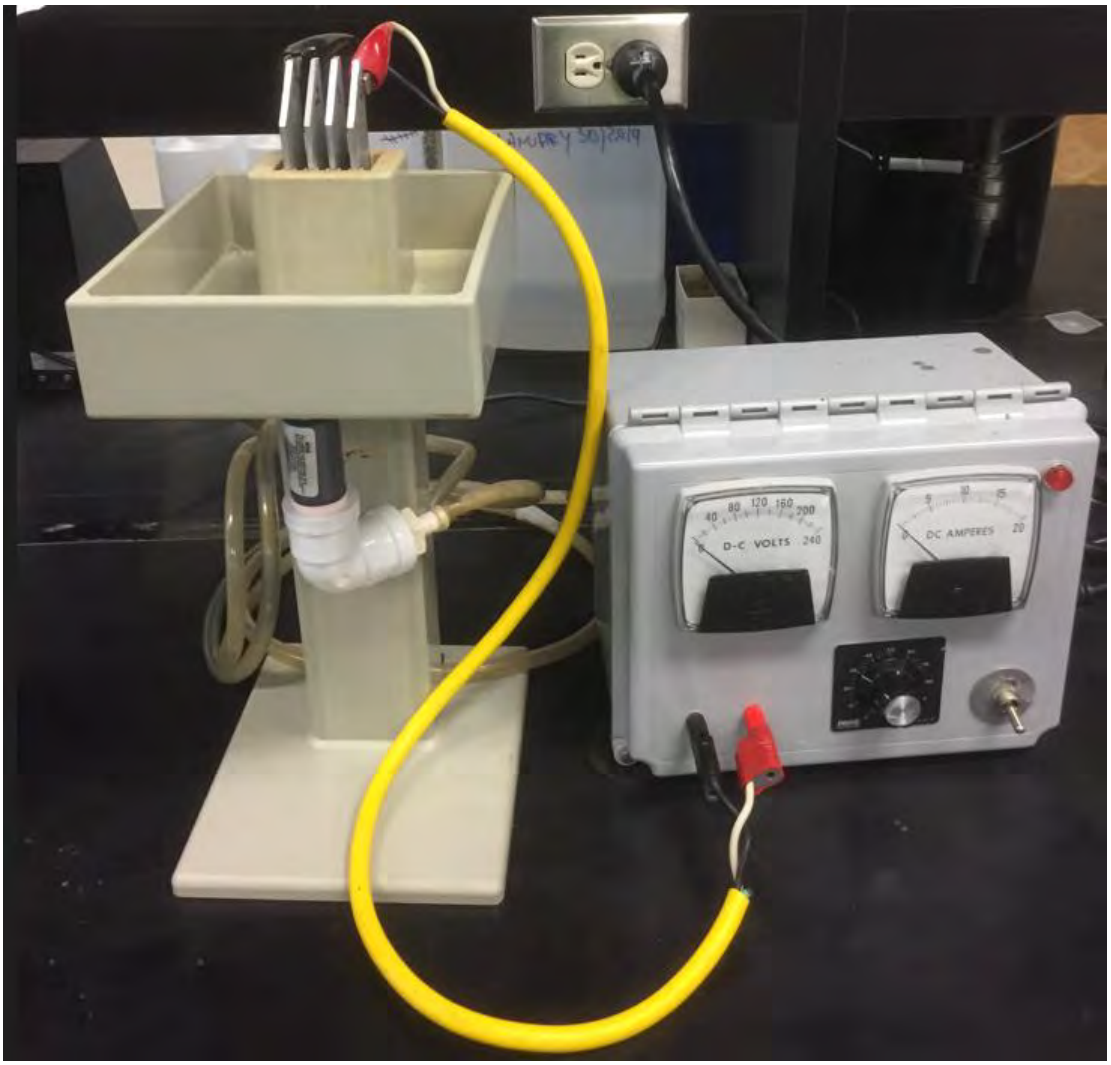


Figure 2. The electrocoagulation unit.

The first treatment testing approach is shown in Table 1 and Table 2. A second treatment testing program was also conducted later (Table 3). In the latter case, following the electrocoagulation treatment, the treated sample was transferred in a 500 mL beaker, sealed with parafilm and stored overnight at room temperature in the dark. The samples were then filtered the next morning through Whatman® filter paper #2 to remove the coagulant. The control was also filtered in the same manner as the treated samples.

Table 1. Experimental design using Al electrodes.

	TRT#	Knob Volts / and Time (s)	Matrix read	
			Volts	A
Rep 1	T1	20 Volts / 45 sec	4	1.025
	T2	20 Volts / 90 sec	4	1.075
	T3	30 Volts / 45 sec	9	2
	T4	30 Volts / 90 sec	10	2.05
Rep2	T5	20 Volts / 45 sec	4	1.025
	T6	20 Volts / 90 sec	4	1.075
	T7	30 Volts / 45 sec	11	2.05
	T8	30 Volts / 90 sec	11	2.05

Table 2. Experimental design using Fe electrodes.

	TRT#	Knob Volts / Time (s)	Matrix read	
			Volts	A
Rep1	T9	20 Volts / 45 sec	4	1
	T10	20 Volts / 90 sec	4	1
	T11	30 Volts / 45 sec	12	2.025
	T12	30 Volts /90 sec	12	2.1
Rep2	T13	20 Volts /45 sec	4	1.025
	T14	20 Volts /90 sec	6	1.05
	T15	30 Volts /45 sec	11.8	2
	T16	30 Volts /90 sec	11.8	2.25

Table 3. Reduced experimental design.

TRT#	Knob Volts / and Time (s)	Matrix read		Comments (samples filtered)
		Volts	A	
T17	30 Volts / 90 sec	10	2.05	Al electrode
T18	30 Volts / 90 sec	10	2.05	Al electrode
T19	30 Volts / 90 sec	12	2.1	Fe electrode
T20	30 Volts / 90 sec	12	2.1	Fe electrode

At the end of an experiment, the sample was transferred in a 500 mL amber bottle, capped, labelled, and stored in the fridge overnight. Subsequently, the stored samples were put in a cooler with dry ice and delivered to Element Laboratory in Calgary for analysis within 24 hours.

The removal efficiency (RE%) of bromacil and tebuthiuron associated with a particular treatment was calculated according to the equation:

$$RE\% = \left(\frac{X_{o-}X}{X_o}\right) 100$$

where Xo and X represent initial concentration and final concentration, respectively of a pesticide in a given run.

3.0 RESULTS

The analytical reports generated by Element for the project are in Appendix 1. The average values for the first experiment removal efficiency for the various electrocoagulation treatments are summarized in Table 4 and Table 5.

Table 4. Removal efficiency of bromacil by the electrocoagulation treatments.

Treatment	Residual concentration (µg/L)	% Removal efficiency
T1 and T5 (Al electrodes)	3,350	1.47
T2 and T6 (Al electrodes)	3,235	4.85
T3 and T7 (Al electrodes)	4,220	0
T4 and T8 (Al electrodes)	3,325	2.21
T9 and T13 (Fe electrodes)	3,350	1.47
T10 and T14 (Fe electrodes)	3,570	0
T11 and T15 (Fe electrodes)	3,240	4.71
T12 and T16 (Fe electrodes)	3,040	10.59

Table 5. Removal efficiency of tebuthiuron by the electrocoagulation treatments.

Treatment	Residual concentration (µg/L)	% Removal efficiency
T1 and T5 (Al electrodes)	3,000	2.67
T2 and T6 (Al electrodes)	2,950	4.22
T3 and T7 (Al electrodes)	3,560	0
T4 and T8 (Al electrodes)	2,990	2.92
T9 and T13 (Fe electrodes)	2,910	5.52
T10 and T14 (Fe electrodes)	3,145	0
T11 and T15 (Fe electrodes)	2,855	7.31
T12 and T16 (Fe electrodes)	2,595	16

Table 6 shows the removal efficiency values of bromacil and tebuthiuron for the second set of experiments.

Table 6. Removal efficiency of bromacil and tebuthiuron by the electrocoagulation treatments.

	Residual concentration (µg/L		% Removal efficiency	
Treatment	Bromacil	Tebuthiuron	Bromacil	Tebuthiuron
T17 and T18 (Al electrodes)	2,080	2,370	16	4.43
T19 and T20 (Fe electrodes)	1,900	2,290	23.40	7.66

4.0 FINDINGS

Under the sets of experimental conditions used, the results indicate that the electrocoagulation treatments were ineffective at remediating bromacil and tebuthiuron in the spiked water matrix. The Fe electrodes system was relatively more effective than the aluminum electrode system. Fe ions dissolved in its cationic form were able to form more diverse polyvalent polyhydroxide complexes such as $Fe(OH)_2$ or $Fe(OH)_3$. In return, these Fe complexes were more effective than the Al complexes at interacting and removing the pesticides via adsorption and entrapment onto the flocs. Pesticides oxidation is also induced at the electrode surfaces by the accumulation of the flocs. The Al electrodes achieved a removal efficiency ranging from 0 to 4.85% for bromacil. On the other hand, the Fe electrodes system had a removal efficiency for bromacil ranging from 0 to 10.59%. With respect to tebuthiuron, the removal efficiency with the Al electrodes ranged from 0 to 4.22% and for the Fe electrodes, it ranged from 0 to 16%. Additionally, for the filtered samples, with the Al electrodes, removal efficiency for bromacil was 16% and 23.40%, respectively. In the case of tebuthiuron, the removal efficiency with the Fe electrodes system was 4.43% and 7.66%, respectively.

Overall, the removal efficiency of bromacil ranged from 0 to 23.40 %, while for tebuthiuron it ranged from 0 to 16%. In essence, there were no significant oxidative destruction and/or chemical transformation mechanisms of the pesticides under the applied treatments. It also appears that there was no significant formation of stable complexation mechanism involving the pesticides. This process would have led to their adhesion to the coagulant and resulting in their removal from the matrix.

5.0 RECOMMENDATIONS

The following recommendations for further testing are made considering the low removal efficiency according to the study findings:

1. *The effectiveness of a four-cell Fe-graphite electrodes system and a four-cell Al-graphite electrodes system, respectively*. Both electrode systems will be configured in a bipolar arrangement. The removal efficiency of each electrode system will be tested using Treatment (T4) (i.e., 30 volts and 90 sec). In both electrode arrangement systems, graphite will be the non-sacrificial electrode. The rationale for this recommendation is the potential synergistic effect of hydroxyl radicals (*OH) and hypochlorous acid (HOCl) generation in the reactor during treatment. This has the potential to result in significant degradation and removal of the hydrophilic pesticides.
2. *The effect of increasing the surface area of the electrodes (cm^2) to volume (L) ratio, (S/V)*. Higher S/V ratio increases the surface area available for electrolytic reactions to occur in the reactor, which in return can have an integral effect on the pesticide removal efficiency.
3. *The effect of varying the inter electrode distance*. As an operational factor, the process efficiency can be improved by varying the distance between the electrodes. At minimum inter electrode distance, the resistance for current flow in the reactor is lowered. In this case, removal efficiency may occur due to higher current reaching the electrodes and lower resistivity in the solution to the electrical current. Optimal distance is highly characteristic of the solution matrix to be treated.
4. *The effect of voltage increase*. An increase in the voltage causes higher current to pass through the reactor. Concurrently, current density (A/m^2), which is current delivered to the electrode (A) divided by the electrode's area (m^2), also goes up. Increase in applied voltage or current density has the effect of increasing the rate of reactions in the reactor. However, voltage increase leads to higher energy consumption; economic considerations may render this approach less attractive.

APPENDIX 1: ELEMENT LABORATORY ANALYTICAL RESULTS

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Report Transmission Cover Page

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-InnoTech	Lot ID:	**1570018**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgary MRU	Date Received:	May 9, 2022
		LSD:		Date Reported:	May 17, 2022
		P.O.:	71376	Report Number:	2746001
Attn:	Accounts Payable	Proj. Acct. code:			
Sampled By:					
Company:	MRU				

Contact	Company	Address
Accounts Payable	**InnoTech Alberta Inc.**	PO Box 8330, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5133 Fax: (780) 450-5542 Email: innotech-finance@albertainnovates.ca

Delivery	Format	Deliverables
Email - Single Report	PDF	COC / Invoice
Email - Single Report	PDF	Test Report

Notes To Clients:

- May 16, 2022 - sample 1 to 17:The extract was diluted 20000 times during analysis to bring results into the analytical range.

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Analytical Report

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Attn: Accounts Payable
Sampled By:
Company: MRU

Project ID: SSP-InnoTech
Project Name: Electrocoagulation
Project Location: Calgary MRU
LSD:
P.O.: 71376
Proj. Acct. code:

Lot ID: **1570018**
Control Number:
Date Received: May 9, 2022
Date Reported: May 17, 2022
Report Number: 2746001

	Reference Number	1570018-1	1570018-2	1570018-3	
	Sample Date	May 08, 2022	May 08, 2022	May 08, 2022	
	Sample Time	NA	NA	NA	
	Sample Location				
	Sample Description	Control / Water / 8.6°C	TRT#1 [Al] / Treated Water / 8.6°C	TRT#2 [Al] / Treated Water / 8.6°C	
	Matrix	Water	Water	Water	
Analyte	**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Water					
Bromacil	µg/L	3400	3380	3240	0.1
Tebuthiuron	µg/L	3080	3010	2950	0.1
Sterilants - Water - Surrogate Recovery					
Monuron Surrogate	%	100	83	105	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-InnoTech	Lot ID:	**1570018**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgary MRU	Date Received:	May 9, 2022
		LSD:		Date Reported:	May 17, 2022
		P.O.:	71376	Report Number:	2746001
Attn:	Accounts Payable	Proj. Acct. code:			
Sampled By:					
Company:	MRU				

	Reference Number	1570018-4	1570018-5	1570018-6	
	Sample Date	May 08, 2022	May 08, 2022	May 08, 2022	
	Sample Time	NA	NA	NA	
	Sample Location				
	Sample Description	TRT#3 [AI] / Treated Water / 8.6°C	TRT#4 [AI] / Treated Water / 8.6°C	TRT#5 [AI] / Treated Water / 8.6°C	
	Matrix	Water	Water	Water	
Analyte	**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Water					
Bromacil	µg/L	4180	3160	3320	0.1
Tebuthiuron	µg/L	3710	2870	2990	0.1
Sterilants - Water - Surrogate Recovery					
Monuron Surrogate	%	105	105	83	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-InnoTech	Lot ID:	**1570018**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgary MRU	Date Received:	May 9, 2022
		LSD:		Date Reported:	May 17, 2022
		P.O.:	71376	Report Number:	2746001
Attn:	Accounts Payable	Proj. Acct. code:			
Sampled By:					
Company:	MRU				

	Reference Number	1570018-7	1570018-8	1570018-9	
	Sample Date	May 08, 2022	May 08, 2022	May 08, 2022	
	Sample Time	NA	NA	NA	
	Sample Location				
	Sample Description	TRT#6 [Al] / Treated Water / 8.6°C	TRT#7 [Al] / Treated Water / 8.6°C	TRT#8 [Al] / Treated Water / 8.6°C	
	Matrix	Water	Water	Water	
Analyte	**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Water					
Bromacil	µg/L	3230	4260	3470	0.1
Tebuthiuron	µg/L	2950	3950	3110	0.1
Sterilants - Water - Surrogate Recovery					
Monuron Surrogate	%	103	104	105	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-InnoTech	Lot ID:	**1570018**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgary MRU	Date Received:	May 9, 2022
		LSD:		Date Reported:	May 17, 2022
		P.O.:	71376	Report Number:	2746001
Attn:	Accounts Payable	Proj. Acct. code:			
Sampled By:					
Company:	MRU				

		Reference Number	1570018-10	1570018-11	1570018-12	
		Sample Date	May 08, 2022	May 08, 2022	May 08, 2022	
		Sample Time	NA	NA	NA	
		Sample Location				
		Sample Description	TRT#9 [Fe] / Treated Water / 8.6°C	TRT#10 [Fe] / Treated Water / 8.6°C	TRT#11 [Fe] / Treated Water / 8.6°C	
		Matrix	Water	Water	Water	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Water						
Bromacil		µg/L	3320	3220	3130	0.1
Tebuthiuron		µg/L	2940	2810	2720	0.1
Sterilants - Water - Surrogate Recovery						
Monuron	Surrogate	%	83	83	103	50-140

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Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-InnoTech	Lot ID:	**1570018**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgary MRU	Date Received:	May 9, 2022
		LSD:		Date Reported:	May 17, 2022
		P.O.:	71376	Report Number:	2746001
Attn:	Accounts Payable	Proj. Acct. code:			
Sampled By:					
Company:	MRU				

	Reference Number	1570018-13	1570018-14	1570018-15	
	Sample Date	May 08, 2022	May 08, 2022	May 08, 2022	
	Sample Time	NA	NA	NA	
	Sample Location				
	Sample Description	TRT#12 [Fe] / Treated Water / 8.6°C	TRT#13 [Fe] / Treated Water / 8.6°C	TRT#14 [Fe] / Treated Water / 8.6°C	
	Matrix	Water	Water	Water	
Analyte	**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Water					
Bromacil	µg/L	3530	3380	3920	0.1
Tebuthiuron	µg/L	3060	2880	3480	0.1
Sterilants - Water - Surrogate Recovery					
Monuron Surrogate	%	83	83	104	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-InnoTech	Lot ID:	**1570018**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgary MRU	Date Received:	May 9, 2022
		LSD:		Date Reported:	May 17, 2022
		P.O.:	71376	Report Number:	2746001
Attn:	Accounts Payable	Proj. Acct. code:			
Sampled By:					
Company:	MRU				

		Reference Number	1570018-16	1570018-17	
		Sample Date	May 08, 2022	May 08, 2022	
		Sample Time	NA	NA	
		Sample Location			
		Sample Description	TRT#15 [Fe] / Treated Water / 8.6°C	TRT#16 [Fe] / Treated Water / 8.6°C	
		Matrix	Water	Water	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Water						
Bromacil		µg/L	3350	2550		0.1
Tebuthiuron		µg/L	2990	2130		0.1
Sterilants - Water - Surrogate Recovery						
Monuron	Surrogate	%	104	62		50-140

Approved by:

Jimmy Tran
Operations Manager

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Quality Control

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-InnoTech	Lot ID:	**1570018**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgary MRU	Date Received:	May 9, 2022
		LSD:		Date Reported:	May 17, 2022
		P.O.:	71376	Report Number:	2746001
Attn:	Accounts Payable	Proj. Acct. code:			
Sampled By:					
Company:	MRU				

Sterilants in Water

Blanks	Units	Measured	Lower Limit	Upper Limit		Passed QC
Bromacil	ng	0	-1.5	1.5		yes
Tebuthiuron	ng	0	-1.5	1.5		yes
Date Acquired:	May 09, 2022					
Calibration Check	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	ng	100.00	80	120		yes
Tebuthiuron	ng	101.00	80	120		yes
Date Acquired:	May 09, 2022					
Replicates	**Units**	**Replicate 1**	**Replicate 2**	**% RSD Criteria**	**Absolute Criteria**	**Passed QC**
Bromacil	µg/L	1.4	1.6	22	2.0	yes
Tebuthiuron	µg/L	2.1	2.3	22	2.0	yes
Date Acquired:	May 09, 2022					
Matrix Spike	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	µg/L	72	40	140		yes
Tebuthiuron	µg/L	104	40	140		yes
Date Acquired:	May 09, 2022					

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Methodology and Notes

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-InnoTech	Lot ID:	**1570018**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgary MRU	Date Received:	May 9, 2022
		LSD:		Date Reported:	May 17, 2022
		P.O.:	71376	Report Number:	2746001
Attn:	Accounts Payable	Proj. Acct. code:			
Sampled By:					
Company:	MRU				

Method of Analysis

Method Name	Reference	Method	Date Analysis Started	Location
Sterilants - Water	Alta. Env. Method	* Alta. Env. method, A119.0	May 9, 2022	Element Calgary
Sterilants - Water	USGS	* Determination of Pesticides in Water by Graphitized Carbon-Based SPE & HPLC/MS, O-2060-1	May 9, 2022	Element Calgary

** Reference Method Modified*

References

Alta. Env. Method	Alberta Environment Method
USGS	U.S. Geological Survey National Water Quality Laboratory

Comments:

- May 16, 2022 - sample 1 to 17:The extract was diluted 20000 times during analysis to bring results into the analytical range.

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Analytical Report

Bill To:	InnoTech Alberta Inc.	Project ID:	SSP-Innotech	Lot ID:	**1581020**
	Financial Services	Project Name:	Electrocoagulation	Control Number:	
	250 Karl Clark Road	Project Location:	Calgaru MRU	Date Received:	Jun 27, 2022
	Edmonton, AB, Canada	LSD:		Date Reported:	Jul 6, 2022
	T6N 1E4	P.O.:	71376	Report Number:	2761867
Attn:	Accounts Payable: Brenda	Proj. Acct. code:			
Sampled By:	Roger Saint-Fort				
Company:	MRU				

		Reference Number	1581020-1	1581020-2	1581020-3
		Sample Date	Jun 27, 2022	Jun 27, 2022	Jun 27, 2022
		Sample Time	NA	NA	NA
		Sample Location			
		Sample Description	Control / Filtered / 12.3°C	TRT #17 [Al] / Treated H2O/Filtered / 12.3°C	TRT #18 [Al] / Treated H2O/Filtered / 12.3°C
		Matrix	Water	Water	Water
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Water						
Bromacil		µg/L	2480	2160	2000	0.1
Tebuthiuron		µg/L	2070	2580	2160	0.1
Sterilants - Water - Surrogate Recovery						
Monuron	Surrogate	%	100	120	100	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc.	Project ID:	SSP-Innotech	Lot ID:	**1581020**
	Financial Services	Project Name:	Electrocoagulation	Control Number:	
	250 Karl Clark Road	Project Location:	Calgaru MRU	Date Received:	Jun 27, 2022
	Edmonton, AB, Canada	LSD:		Date Reported:	Jul 6, 2022
	T6N 1E4	P.O.:	71376	Report Number:	2761867
Attn:	Accounts Payable: Brenda	Proj. Acct. code:			
Sampled By:	Roger Saint-Fort				
Company:	MRU				

	Reference Number	1581020-4	1581020-5		
	Sample Date	Jun 27, 2022	Jun 27, 2022		
	Sample Time	NA	NA		
	Sample Location				
	Sample Description	TRT #19 [Fe] / Treated H2O/Filtered / 12.3°C	TRT #20 [Fe] / Treated H2O/Filtered / 12.3°C		
	Matrix	Water	Water		
Analyte	**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants In Water					
Bromacil	µg/L	2000	1820		0.1
Tebuthiuron	µg/L	2160	2420		0.1
Sterilants - Water - Surrogate Recovery					
Monuron Surrogate	%	90	110		50-140

Approved by:

Jimmy Tran
Operations Manager

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Quality Control

Bill To:	InnoTech Alberta Inc. Financial Services 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-Innotech	Lot ID:	**1581020**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgaru MRU	Date Received:	Jun 27, 2022
		LSD:		Date Reported:	Jul 6, 2022
		P.O.:	71376	Report Number:	2761867
Attn:	Accounts Payable: Brenda	Proj. Acct. code:			
Sampled By:	Roger Saint-Fort				
Company:	MRU				

Sterilants in Water

Blanks	Units	Measured	Lower Limit	Upper Limit		Passed QC
Bromacil	ng	0	-1.5	1.5		yes
Tebuthiuron	ng	0	-1.5	1.5		yes
Date Acquired:	July 03, 2022					
Calibration Check	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	ng	101.00	80	120		yes
Tebuthiuron	ng	102.50	80	120		yes
Date Acquired:	July 03, 2022					
Replicates	**Units**	**Replicate 1**	**Replicate 2**	**% RSD Criteria**	**Absolute Criteria**	**Passed QC**
Bromacil	µg/L	1.6	1.4	22	2.0	yes
Tebuthiuron	µg/L	2.1	1.8	22	2.0	yes
Date Acquired:	July 03, 2022					
Matrix Spike	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	µg/L	80	40	140		yes
Tebuthiuron	µg/L	104	40	140		yes
Date Acquired:	July 03, 2022					

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Methodology and Notes

Bill To:	InnoTech Alberta Inc. Financial Services 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP-Innotech	Lot ID:	**1581020**
		Project Name:	Electrocoagulation	Control Number:	
		Project Location:	Calgaru MRU	Date Received:	Jun 27, 2022
		LSD:		Date Reported:	Jul 6, 2022
		P.O.:	71376	Report Number:	2761867
Attn:	Accounts Payable: Brenda	Proj. Acct. code:			
Sampled By:	Roger Saint-Fort				
Company:	MRU				

Method of Analysis

Method Name	Reference	Method	Date Analysis Started	Location
Sterilants - Water	Alta. Env. Method	* Alta. Env. method, A119.0	Jul 3, 2022	Element Calgary
Sterilants - Water	USGS	* Determination of Pesticides in Water by Graphitized Carbon-Based SPE & HPLC/MS, O-2060-1	Jul 3, 2022	Element Calgary

** Reference Method Modified*

References

Alta. Env. Method	Alberta Environment Method
USGS	U.S. Geological Survey National Water Quality Laboratory

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Appendix A8-3: Trap & Treat® and Zero Valent Iron

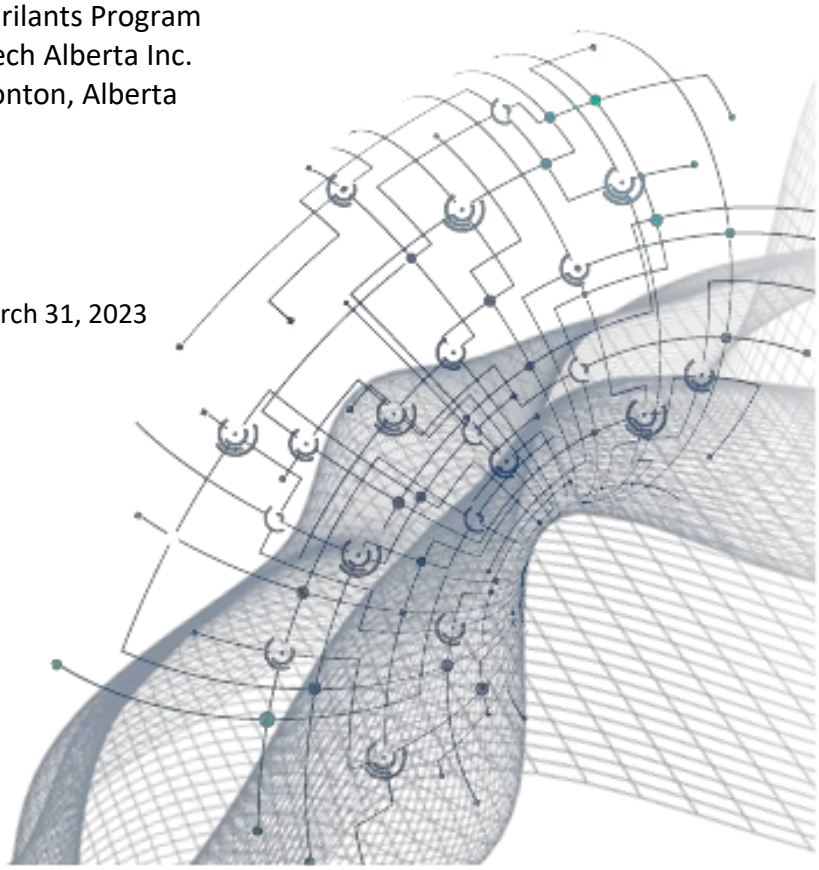
French, K., E. Cowan and A. Neufeld, 2023. Bench Scale Treatability Study using Trap & Treat® and Zero Valent Iron for Bromacil and Tebuthiuron in Alberta Soils. Report SSP-11C prepared by Vertex Environmental Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 20 pp. plus lab data.

Bench-scale Treatability Study Using Trap & Treat® and Zero Valent Iron for Bromacil and Tebuthiuron in Alberta Soils

Kevin French, Eric Cowan, and Alyson Neufeld
Vertex Environmental Inc.
Kitchener, ON

Prepared for
Soil Sterilants Program
InnoTech Alberta Inc.
Edmonton, Alberta

March 31, 2023



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CITATION

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French, K., E. Cowan and A. Neufeld, 2023. Bench-scale Treatability Study using Trap & Treat® and Zero Valent Iron for Bromacil and Tebuthiuron in Alberta Soils. Report SSP-11C prepared by Vertex Environmental Inc. for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 20 pp. plus lab data.

EXECUTIVE SUMMARY

Vertex Environmental Inc. (Vertex Environmental) was retained by InnoTech Alberta Inc. ("InnoTech") to undertake bench-scale treatability studies evaluating in-situ treatment of bromacil and tebuthiuron using samples of impacted soil from Alberta. Currently, no in-situ destructive technologies are known for bromacil and tebuthiuron and therefore the current study aimed to assess the performance, efficiency and degradation rates of newly developed treatment media Trap & Treat® BOS 200+® and Trap & Treat® CAT 100. Micro-scale zero valent iron (ZVI) was also evaluated for the same parameters, with and without pH control. Trap & Treat® BOS 200+®'s treatment approach utilizes bio stimulation and inoculation, whereas Trap & Treat® CAT 100's treatment approach utilizes chemical reduction, bio stimulation and inoculation, and ZVI's treatment approach utilizes chemical reduction alone. Trap & Treat® BOS 200+® and Trap & Treat® CAT 100 also contain activated carbon which is designed to trap the contaminants, increasing the contact time between the treatment media and the contaminants to further promote biodegradation and/or chemical reduction. To isolate treatment effects from adsorption to the activated carbon, the study compared the full formulations of the treatment media with simulated formulations, where the components of the treatment media are used in the absence of activated carbon. The impact of surfactant was also investigated.

The methodology included assembling static batch reactors filled with the bromacil or tebuthiuron impacted soils mixed with remedial amendments. The reactors were kept under dark and anoxic conditions for four months. The following test reactors were assembled for each contaminant:

- Test Reactor #1 contained only the contaminated soil with no added reagents or amendments.
- Test Reactor #2 contained 1.2% by weight Trap & Treat® BOS 200+®.
- Test Reactor #3 contained 0.7% by weight Trap & Treat® CAT 100.
- Test Reactor #4 contained the components of Trap & Treat® BOS 200+® at the same weight percentage as Test Reactor #2 but without any activated carbon component. The mass of each component was equal to that used in the Trap & Treat® BOS 200+® reactor.
- Test Reactor #5 contained the components of Trap & Treat® CAT 100 at the same weight percentage as Test Reactor #3 but without any activated carbon component and with ZVI substituting for the iron component in the Trap & Treat® CAT 100.
- Test Reactor #6 contained 5% by weight ZVI.
- Test Reactor #7 contained 5% by weight ZVI with 3.5% by weight aluminum sulphate.
- Test Reactor #8 contained 1.2% by weight Trap & Treat® BOS 200+® with 0.2% by weight Tween 80 surfactant.
- Test Reactor #9 contained 0.7% by weight Trap & Treat® CAT 100 with 0.2% by weight Tween 80 surfactant.
- Test Reactor #10 contained 0.2% by weight Tween 80 surfactant with the components of Trap & Treat® BOS 200+® at the same weight percentage as Test Reactor #2, but without any activated carbon component. The mass of each component was equal to that used in the Trap & Treat® BOS 200+® reactor.
- Test Reactor #11 contained 0.2% by weight Tween 80 surfactant with the components of Trap & Treat® CAT 100 at the same weight percentage as Test Reactor #3, but without any activated

carbon component and with ZVI substituting for the iron component in the Trap & Treat® CAT 100.

During testing, bromacil treatment reactors were monitored for bromacil concentration, pH, Heterotrophic Plate Count (HPC) and bromide concentration at four (4) sampling times: two weeks, one month, two months, and four months durations from test start. During testing, tebuthiuron treatment reactors were monitored for tebuthiuron concentration, pH and HPC at four (4) sampling times: two weeks, one month, two months, and four months durations from test start. The target treatment for both bromacil and tebuthiuron was to reduce measured concentrations in the soil samples to below 0.009 mg/kg.

For bromacil, Trap & Treat® CAT 100, Trap & Treat® BOS 200+ and ZVI were all able to destructively remove bromacil from the soil, dropping concentrations to within the target withing the four-month testing period. The reactor with surfactant added to the simulated Trap & Treat® CAT 100 had the fastest degradation rate for bromacil. However, if treatment is required in the form of a permeable reactive barrier, immobilization via activated carbon and no surfactant is beneficial. Under these requirements, Trap & Treat® BOS 200+® was the best performing media.

For tebuthiuron, only Trap & Treat® BOS 200+® was successful at destructively removing tebuthiuron from the soil at a rate fast enough to reach the target within the 4-month testing period. Surfactant slowed the degradation for both Trap & Treat® reagents.

Based on the bench-scale treatability testing, both bromacil and tebuthiuron are susceptible to adsorption and degradation by Trap & Treat® BOS 200+®. Further mesocosm studies or pilot or field scale trials are recommended to confirm the suitability for treating both soil sterilants using Trap & Treat® BOS 200+®.

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1.0 INTRODUCTION

Soil sterilants were commonly used from the 1960s to late 1990s for non-selective vegetation control on industrial sites in Alberta. Soils treated with sterilants often become a source of contamination to adjacent lands and waterbodies. The Soil Sterilants Program (SSP) was formed to establish proven, technical, and cost-effective strategies and best management practices sites impacted by residual soil sterilants, with the goal of achieving regulatory site closure in a timely and efficient manner.

Drozdowski et al. (2018) completed a literature synthesis report outlining the current research on the ecological impact of sterilant impacted sites and possible treatment approaches. In-situ approaches for remediating bromacil and tebuthiuron were limited to adsorption technologies including various types of activated carbon. However, this approach can hinder the degradation of the sterilants and has the potential to adsorb future herbicide applications. As such, there is a need for further research into destructive technologies that can remove these sterilants from soil and groundwater, without negatively impacting the soil or groundwater quality for future use.

Vertex Environmental Inc. (Vertex Environmental) was retained by InnoTech Alberta Inc. (InnoTech) to undertake bench-scale treatability testing for the in-situ treatment of bromacil and tebuthiuron in Alberta soils using newly developed treatment amendments Trap & Treat® BOS 200+® and Trap & Treat® CAT 100, as well as micro-scale zero-valent iron (ZVI). Nano-scale ZVI has been successfully used to treat other soil sterilants through chemical reduction. Lowering the pH has successfully promoted the chemical reduction for some sterilants and thus this was also investigated for bromacil and tebuthiuron treatment. Trap & Treat® BOS 200+® is based on trapping the contaminant with activated carbon and promoting degradation treatment through nutrient addition and time-released terminal electron acceptors to support the growth of degrading microbes. Trap & Treat® CAT 100 is again based on trapping the contaminant using carbon and the catalytic reduction treatment through iron and bacterial mechanisms.

The following bench-scale treatability study aimed to isolate the degradation mechanisms from the adsorption to activated carbon by mixing the contaminated soil with simulated Trap & Treat® BOS 200+® and simulated Trap & Treat® CAT 100, each containing essentially all the components of the proprietary, engineered remedial amendments but without the activated carbon content. The impact of adding surfactant to the mixtures was also tested, as surfactants can help desorb contamination from soil to make it more available to react with remedial amendments.

2.0 OBJECTIVE AND SCOPE

Currently, there are no proven in-situ destructive approaches to permanently remove bromacil and tebuthiuron from soil and groundwater. The objective of this study was to test three remedial amendments including Trap & Treat® BOS 200+®, Trap & Treat® CAT 100, and micro-scale ZVI at bench-scale to identify amendments worth investigating further at a pilot- or field-scale. Simulated amendment formulation reactors were used to isolate treatment from adsorption for Trap & Treat® BOS 200+® and Trap & Treat® CAT 100. These simulated reactors were built with the components of either Trap & Treat® BOS 200+® and Trap & Treat® CAT 100 at the same concentrations as the full formulation test reactors but without the activated carbon component. Reactors were also built to test if surfactants can promote degradation by Trap & Treat® BOS 200+® and Trap & Treat® CAT 100 and if lowering the pH can promote the chemical reduction using ZVI.

The scope of work included assembling twenty-two anaerobic static reactors containing water saturated bromacil- and tebuthiuron-impacted soil mixed with varying treatment amendments outlined below. Soil testing included baseline testing for bromacil or tebuthiuron concentration, total organic carbon (TOC), heavy metals, nutrients, pH, moisture content, and Heterotrophic Plate Count (HPC) to determine suitability for use in the reactors. Additionally, bromacil/tebuthiuron concentration, pH, HPC, and bromide concentration (bromacil-impacted soils only) were analyzed during testing for soil collected at two weeks, one month, two months, and four months. No soil remained to be frozen for possible future analysis. This report summarizes the analytical data with accompanying analysis on performance and efficiency of treatment, bromacil and tebuthiuron degradation rates, as well as recommendations for further testing and pilot or field scale applications. The timeline of the testing completed is outlined in Appendix A.

3.0 METHODOLOGY

InnoTech provided Vertex Environmental with soil contaminated with bromacil and soil contaminated with tebuthiuron. Twenty-two test reactors were assembled, eleven for each type of contaminant. Approximately 2.5 kg of contaminated soil was mixed with remedial amendments, saturated with water, and placed into a 3 L clear glass jar for each of the reactors. Each reactor lid was equipped with an inlet valve and a water-sealed check valve to allow nitrogen gas to be injected into the headspace of the reactor without letting in air/oxygen, thus maintaining anaerobic conditions in the reactors (Figure 1).

Figure 1. Example of Reactor Design.

Reactors were covered with a black cloth to prevent any photochemistry from occurring and were purged with nitrogen on a daily basis to keep the reactors under anaerobic condition. For the first two weeks, the soils in each of the reactors were thoroughly mixed on a daily basis to ensure good contact between the remedial amendments and the contaminants. Following this, the reactors were mixed weekly until the two-month sampling event, and then left without mixing for the final two months of the testing program.

The following reactor configurations were assembled for each type of contaminated soil. Each of the reactors was given an abbreviated name used to refer to the reactor in tables and figures. These names are given below in brackets.

- Test Reactor #1 contained only the contaminated soil with no added reagents or amendments (control).
- Test Reactor #2 contained 1.2% by weight Trap & Treat® BOS 200+® (BOS 200+).
- Test Reactor #3 contained 0.7% by weight Trap & Treat® CAT 100 (CAT 100).
- Test Reactor #4 contained the components of Trap & Treat® BOS 200+® at the same weight percentage as Test Reactor #2 but without any activated carbon component. The mass of each component was equal to that used in the Trap & Treat® BOS 200+® reactor (Sim BOS 200+).

- Test Reactor #5 contained the components of Trap & Treat® CAT 100 at the same weight percentage as Test Reactor #3 but without any activated carbon component and with ZVI substituting for the iron component in the Trap & Treat® CAT 100 (Sim CAT 100).
- Test Reactor #6 contained 5% by weight ZVI (ISCR).
- Test Reactor #7 contained 5% by weight ZVI with 3.5% by weight aluminum sulphate (ISCR +).
- Test Reactor #8 contained 1.2% by weight Trap & Treat® BOS 200+® with 0.2% by weight Tween 80 surfactant (BOS 200+ & Surf).
- Test Reactor #9 contained 0.7% by weight Trap & Treat® CAT 100 with 0.2% by weight Tween 80 surfactant (CAT 100 & Surf).
- Test Reactor #10 contained 0.2% by weight Tween 80 surfactant with the components of Trap & Treat® BOS 200+® at the same weight percentage as Test Reactor #2, but without any activated carbon component. The mass of each component was equal to that used in the Trap & Treat® BOS 200+® reactor (Sim BOS 200+ & Surf).
- Test Reactor #11 contained 0.2% by weight Tween 80 surfactant with the components of Trap & Treat® CAT 100 at the same weight percentage as Test Reactor #3, but without any activated carbon component and with ZVI substituting for the iron component in the Trap & Treat® CAT 100 (Sim CAT 100 & Surf).

4.0 RESULTS AND DISCUSSION

4.1 Bromacil

Before loading the static reactors, baseline analysis was performed on the bromacil-impacted soil including detection of nutrients, organic matter and metal content. The results are summarized in Table 1 in Appendix B. The soil was determined to be appropriate for the proposed bench-scale testing.

4.1.1 Trap & Treat® BOS 200+®

Figure 2 depicts the bromacil concentrations in the test reactors investigating the ability of Trap & Treat® BOS 200+® to treat bromacil. All four configurations of Trap & Treat® BOS 200+® (with and without activated carbon and with and without surfactant) lowered bromacil concentrations to greater extents than the control and brought the bromacil concentrations below detection limits in all but the reactor containing Trap & Treat® BOS 200+® and surfactant (Table 2, Appendix B). At the two-week sampling event, there was a more substantial drop in bromacil concentration in the Trap & Treat® BOS 200+® reactors compared to the simulated Trap & Treat® BOS 200+® reactors. This is likely indicative of an initial adsorption onto the activated carbon. For the remaining three sampling events, the simulated Trap & Treat® BOS 200+® reactors outperformed the Trap & Treat® BOS 200+® reactors, indicating that Trap & Treat® BOS 200+® (and its simulation) is able to degrade bromacil in soil.

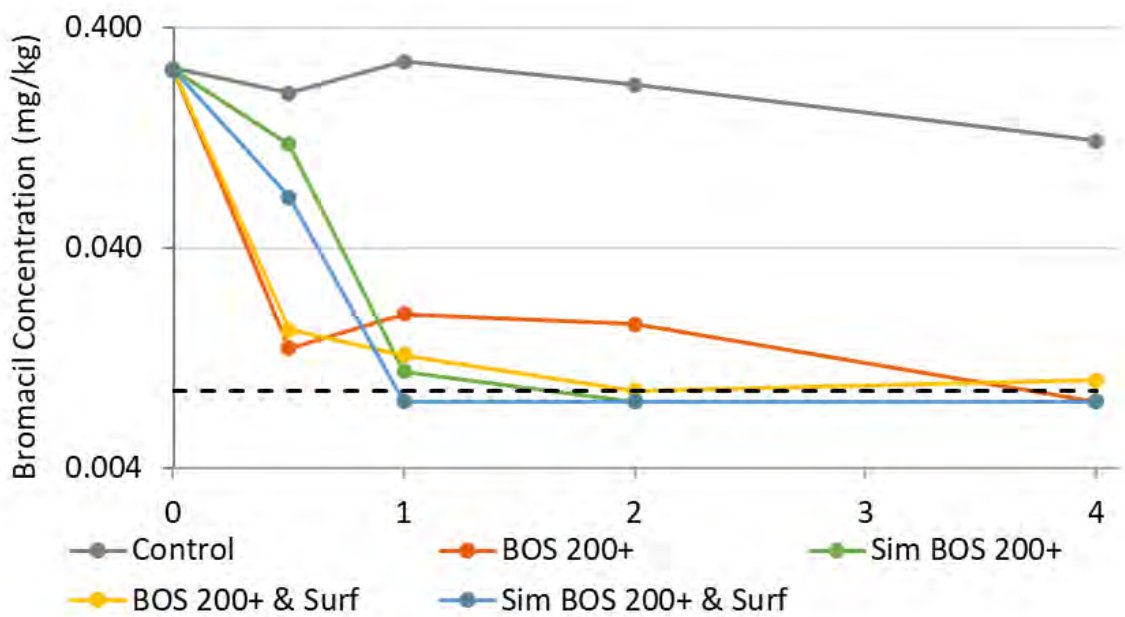

Figure 2. Bromacil Concentration in Reactors with Trap & Treat® BOS 200+®. The black dashed line is the target bromacil concentration.

The degradation of the bromacil is further inferred from elevated bromide concentration in all these reactors in comparison to the control (Table 3, Appendix B). Bromide is a likely breakdown product of bromacil, thus elevated concentrations indicate that there is a destructive mechanism at play, not merely sorption onto the activated carbon. For both the Trap & Treat® BOS 200+® and simulated Trap & Treat® BOS 200+® reactors, the surfactant resulted in a more rapid degradation of bromacil than the

surfactant-free reactors, indicating the surfactant was successful at helping to mobilize the bromacil, increasing its availability for degradation.

Further insight into the performance of the reactors can be gleaned from HPC measurements, a measure of bacterial activity in the reactors. The HPC increased in all the reactors including the control (Table 4, Appendix B). However, the treatment reactors all had more significant increases than the control, consistent with expectations based on the addition of microbes to each of these reactors. The HPC in the Trap & Treat® BOS 200+® reactor peaked at approximately half that of the other reactors, which could indicate one of the factors that caused a slower decrease in bromacil concentrations in this reactor in comparison to the others. The reason for the smaller bacterial colony in this reactor is unknown.

4.1.2 Trap & Treat® CAT 100

Figure 3 depicts the bromacil concentrations in the test reactors investigating the ability of Trap & Treat® CAT 100 to treat bromacil. All four configurations of Trap & Treat® CAT 100 (with and without activated carbon and with and without surfactant) lowered bromacil concentrations to a greater extent than the control (Table 2, Appendix B). However, only the simulated Trap & Treat® CAT 100 reactors brought bromacil concentrations down to below the detection limit, indicating that Trap & Treat® CAT 100 is also able to degrade bromacil. The degradation of the bromacil is further inferred from the elevated bromide concentration in all of these reactors in comparison to the control (Table 3, Appendix B).

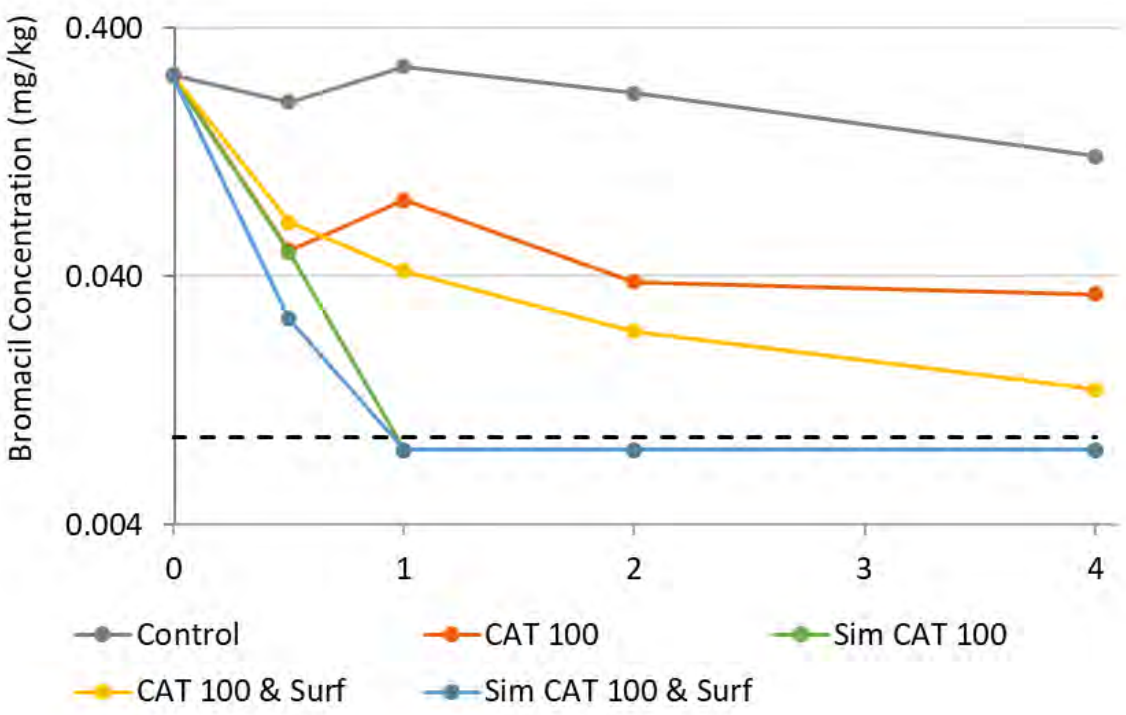

Figure 3. Bromacil Concentration in Reactors with Trap & Treat® CAT 100. The black dashed line is the target bromacil concentration.

The simulated Trap & Treat® CAT 100 reactors were more effective at lowering the bromacil concentration than the Trap & Treat® CAT 100 reactors. The simulated Trap & Treat® CAT 100 reactors used ZVI to substitute for the iron component in the Trap & Treat® CAT 100. The enhanced reactivity

seen in the simulated formulations may be due to the iron being more accessible with the ZVI particles in contrast to the iron incorporated into Trap & Treat® CAT 100. For both the simulated Trap & Treat® CAT 100 and Trap & Treat® CAT 100 reactors, the addition of surfactant resulted in a more rapid degradation of bromacil, suggesting that the surfactant was successful at mobilizing the bromacil, increasing its availability for degradation. The HPC increased in all the reactors beyond that in the control reactor. Unlike the Trap & Treat® BOS 200+® reactors, there was a peak in HPC for most reactors during the two-month sampling event (Table 4, Appendix B). The reactors with surfactant, showed slower HPC growth than the reactors without surfactant.

4.1.3 In-Situ Chemical Reduction

Figure 4 depicts the bromacil concentrations in the test reactors investigating the ability of ZVI to treat bromacil. The ISCR reactor with only ZVI was effective at lowering the bromacil concentration below the detection limit in two months (Table 2, Appendix B). In contrast, in the ISCR reactor with pH adjustment using aluminum sulphate (i.e., ISCR+), there was only a slight drop in bromacil concentration. The addition of aluminum sulfate in the ISCR+ reactor dropped the pH to between 4.4 and 5.3, depending on the sampling event. It also caused the HPC to drop below detection limits at two weeks, rebounding to less than that detected in the control for the following three sampling events (Table 4, Appendix B). In comparison to the simulated Trap & Treat® CAT 100 reactor, also containing elemental iron but at a lower concentration, the bromacil concentration dropped more slowly for the ISCR reactor, indicating the importance of the biological degradation stimulated in the simulated Trap & Treat® CAT 100® reactor. Despite there being no microbes added to the ISCR reactor, the peak HPC reached 19,200,000 CFU/g, in the two-month sampling event, like the other treatment reactors.

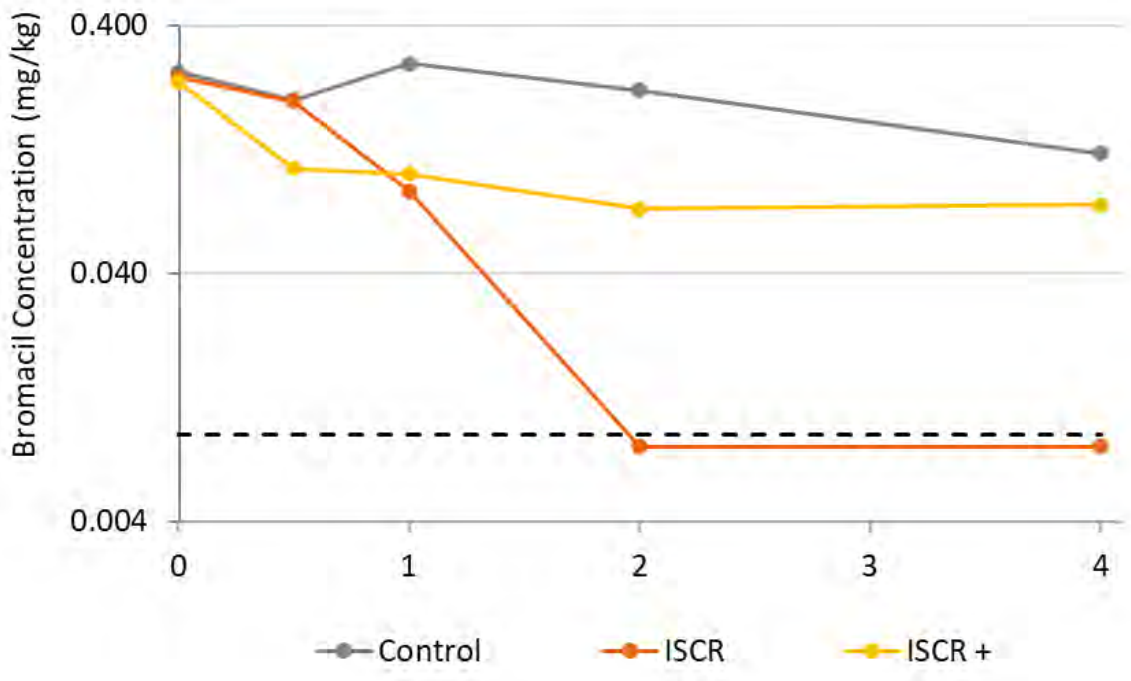

Figure 4. Bromacil Concentration in Reactors with ZVI.
The black dashed line is the target bromacil concentration.

4.1.4 Bromacil Summary

All three treatment approaches, Trap & Treat® BOS 200+®, Trap & Treat® CAT 100, and ZVI, resulted in a drop in bromacil concentration in the soil. There was accelerated degradation in the absence of activated carbon and there was formation of bromide in all the treatment reactors. Both observations support the conclusion that there was destruction of bromacil not just adsorption.

Trap & Treat® BOS 200+® removed the bromacil at a faster rate and more completely than Trap & Treat® CAT 100 (both with and without surfactant). In contrast, the simulated Trap & Treat® BOS 200+® was slightly slower than Trap & Treat® CAT 100 (both with and without surfactant). In both the full and simulated formulations, surfactant enhanced the treatment efficacy. ISCR was also effective at dropping bromacil concentration, but it was slower than the simulated Trap & Treat® BOS 200+® and Trap & Treat® CAT 100 reactors.

Overall, the simulated Trap & Treat® CAT 100 with surfactant was the fastest and best performing in terms of destruction of bromacil in soil for general plume treatment. For a potential permeable reactive barrier (PRB) application the additional activated carbon component is desirable for longevity and the absence of surfactant is desirable for adsorptive strength and longevity. Therefore, the preferred formulation for a PRB application to treat plumes of bromacil in groundwater is Trap & Treat® BOS 200+®.

4.2 Tebuthiuron

Before loading the static reactors, baseline analytical was performed on the tebuthiuron-impacted soil including detection of nutrients, organic matter, and metal content. The results are summarized in Table 1 in Appendix B. The soil was determined to be appropriate for the proposed bench-scale testing.

4.2.1 Trap & Treat® BOS 200+®

Figure 5 depicts the tebuthiuron concentrations in the test reactors investigating the ability of Trap & Treat® BOS 200+® to treat tebuthiuron. Only Trap & Treat® BOS 200+® was effective at removing tebuthiuron from the soil, the simulated versions were indistinguishable from the control reactor (Table 5, Appendix B). Unlike bromacil, tebuthiuron treatment was negatively impacted by the addition of surfactant, decreasing the rate of removal for tebuthiuron. The HPC was higher in the simulated Trap & Treat® BOS 200+® reactors than in the Trap & Treat® BOS 200+® reactors, which had only slightly elevated HPC in comparison to the control (Table 7, Appendix B). The addition of surfactant appeared to delay the growth of bacteria in both the full and simulated formulations. Despite the elevated bacterial count in the simulated Trap & Treat® BOS 200+® reactors, the degradation of tebuthiuron was not enhanced.

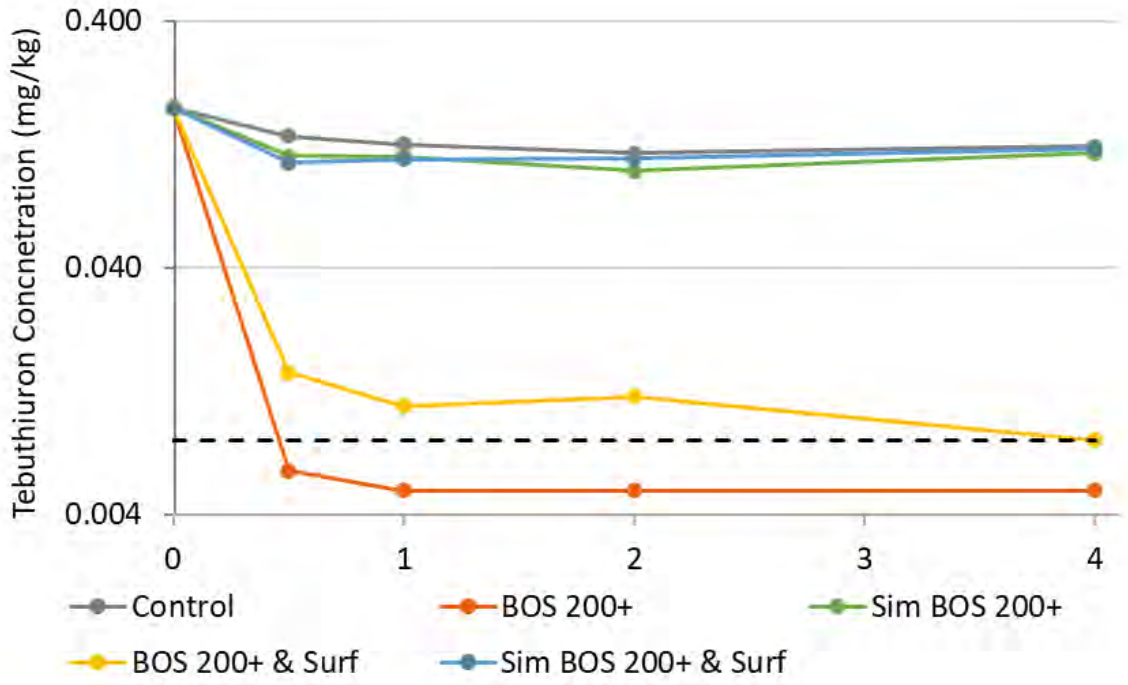

Figure 5. Tebuthiuron Concentration in Reactors with Trap & Treat® BOS 200+®. The black dashed line is the target tebuthiuron concentration.

4.2.2 CAT 100

Figure 6 depicts the tebuthiuron concentrations in the test reactors investigating the ability of Trap & Treat® CAT 100 to treat tebuthiuron. None of the reactors with Trap & Treat® CAT 100 decreased the tebuthiuron concentration below the target concentration, however, the full formulations were more successful at decreasing the concentration of tebuthiuron than the simulated versions, which, like the simulated Trap & Treat® BOS 200+® reactors, were indistinguishable from the control (Table 5, Appendix B). The Trap & Treat® CAT 100 reactor without surfactant, initially showed enhanced removal of tebuthiuron in comparison to the Trap & Treat® CAT 100 reactor with surfactant. After one month, however, the measured concentration of tebuthiuron in the Trap & Treat® CAT 100 concentration rebounded in comparison to the Trap & Treat® CAT 100 reactor with surfactant which continued to decrease. The HPC count was enhanced in all of the Trap & Treat® CAT 100 reactors in comparison to the control (Table 7, Appendix B). The reactors with surfactant, had delayed HPC growth in comparison to the ones without, like what was observed in the Trap & Treat® BOS 200+® reactors. The reactors with simulated Trap & Treat® CAT 100 had higher HPC than the full formulations.

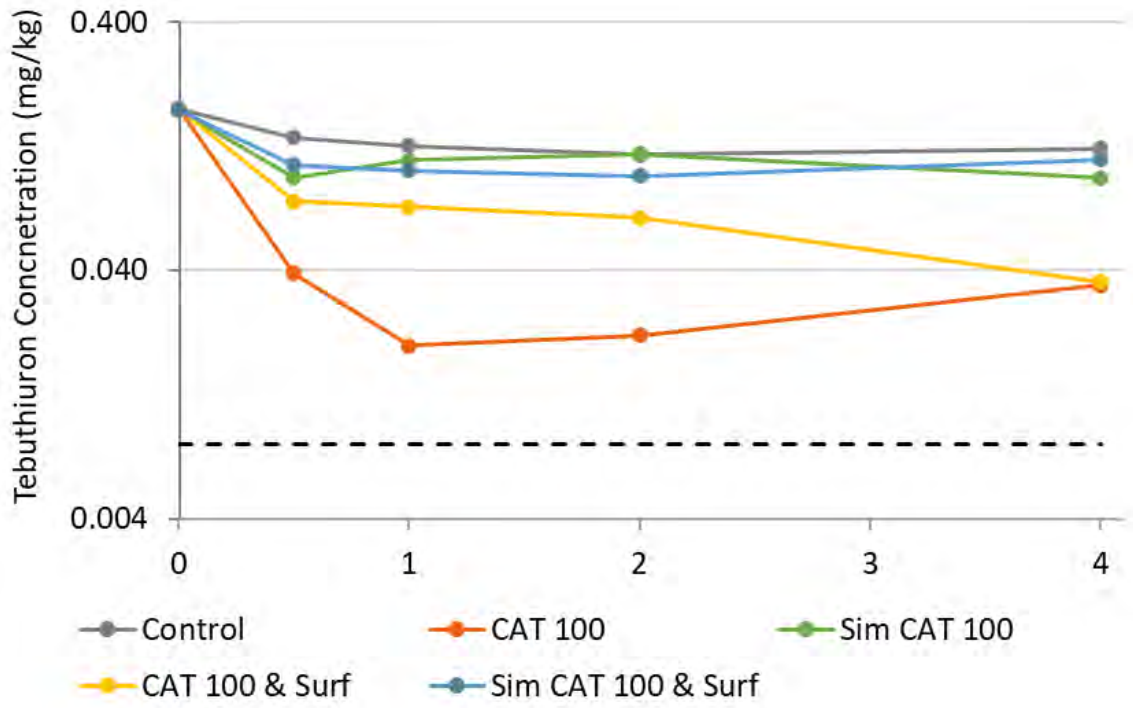

Figure 6. Tebuthiuron Concentration in Reactors with Trap & Treat® CAT 100. The black dashed line is the target tebuthiuron concentration.

4.2.3 In-situ Chemical Reduction

Figure 7 depicts the tebuthiuron concentrations in the test reactors investigating the ability of ZVI to treat tebuthiuron. Neither of the chemical reduction reactors dropped the concentration of tebuthiuron below the target (Table 5, Appendix B). The ISCR+ reactor with pH adjustment, showed a more significant impact on the tebuthiuron concentration than the ISCR reactor without pH adjustment, however, neither showed a clear downward trend in concentration. The addition of aluminum sulfate in the ISCR+ reactor dropped the pH to between 4.5 and 4.6, depending on the sampling event (Table 6, Appendix B). It also caused the HPC to drop below the HPC measured in the control reactor. In contrast, the HPC in the ISCR was similar to that measured in the control reactor (Table 7, Appendix B).

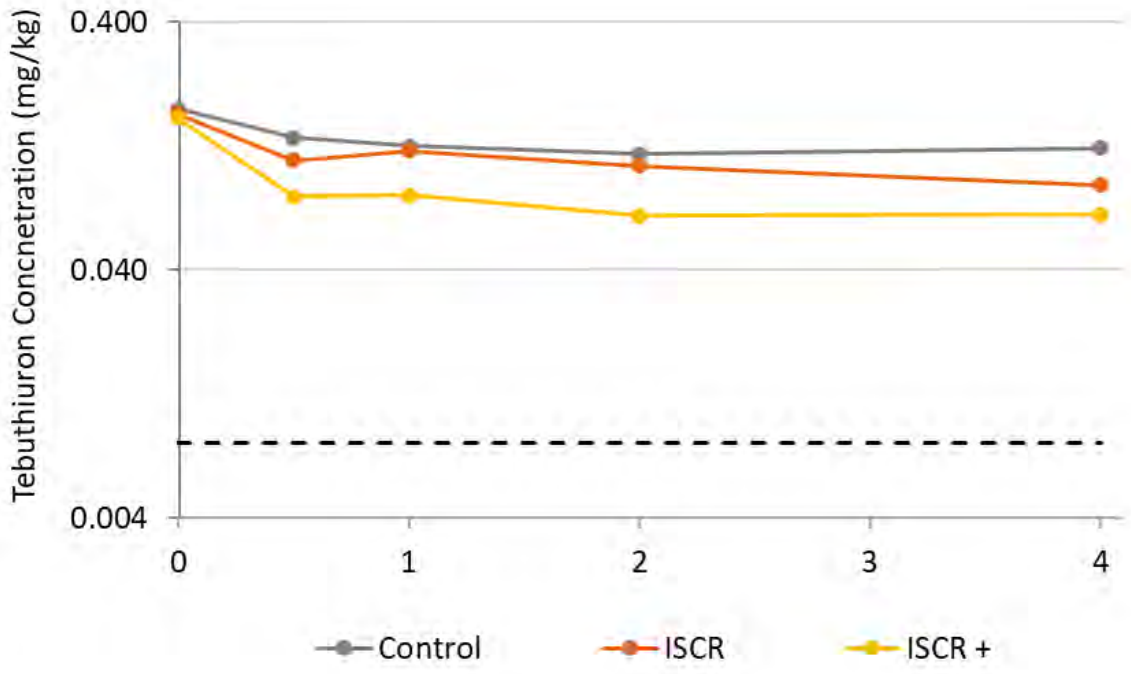

Figure 7. Tebuthiuron Concentration in Reactors with ZVI.
The black dashed line is the target tebuthiuron concentration.

4.2.4 Tebuthiuron Summary

Trap & Treat® BOS 200+® with and without surfactant performed better than Trap & Treat® CAT 100 with and without surfactant. The enhanced treatment using Trap & Treat® BOS 200+® versus Trap & Treat® CAT 100 suggests that the reduction in tebuthiuron concentrations in soil is due to destruction of tebuthiuron and not carbon adsorption alone because Trap & Treat® BOS 200+® has a lower activated carbon percentage than Trap & Treat® CAT 100.

Unlike for bromacil treatment, neither of the simulated formulations with or without surfactant, or ZVI showed effective treatment within the four-month treatment study. Also different than for bromacil, the addition of surfactant overall had a negative impact on performance.

Based on the above, the Trap & Treat® BOS 200+® without surfactant is recommended for the overall fastest and best performance in terms of destruction. As discussed above, Trap & Treat® BOS 200+® is also well-suited for a PRB application.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 Overall Conclusions from the Treatability Testing of Bromacil in Soil

Both Trap & Treat® CAT 100 and Trap & Treat® BOS 200+® can treat bromacil in soil. For plume treatment, the removal of activated carbon and the addition of surfactant could increase the reaction rates for both treatment media, with Trap & Treat® CAT 100 expected to have a quicker degradation rate under these conditions. However, for a PRB application, the lack of mobility promoted by activated carbon and no surfactant is preferred. Under these circumstances Trap & Treat® BOS 200+® is expected to the best performing treatment media.

5.2 Overall Conclusions from the Treatability Testing of Tebuthiuron in Soil

The only treatment approach that was successful at reducing tebuthiuron below the target within the four-month trial was Trap & Treat® BOS 200+®. In this case, surfactant slowed the reaction rate. Therefore Trap & Treat® BOS 200+® is expected to be the best performing media for both plume and PRB treatment of tebuthiuron-impacted soil.

5.3 Recommendations

Based on the bench-scale treatability testing, both bromacil and tebuthiuron are susceptible to adsorption and degradation by Trap & Treat® BOS 200+®. Further mesocosm studies or pilot- or field-scale trials are recommended to confirm the suitability for treating both soil sterilants using Trap & Treat® BOS 200+®.

6.0 ACKNOWLEDGEMENTS

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8.0 APPENDIX A: Timeline of Work

The project proceeded as per the following timeline**:**

- May 18, 2022 –Two 20 L pails of bromacil-impacted soil and two 20 L pails of tebuthiuron-impacted soil were received at the Vertex Environmental laboratory.
- June 1, 2022 – Baseline samples were submitted to ALS Environmental and Element for analytical testing.
- July 4, 2022 – Reactors were assembled as per the above-noted design.
- July 19, 2022 – Two-week samples were collected from the reactors and submitted to ALS environmental and Element for analytical testing.
- August 4, 2022 – One-month samples were collected from the reactors and submitted to ALS environmental and Element for analytical testing.
- September 6, 2022 – Two-month samples were collected from the reactors and submitted to ALS environmental and Element for analytical testing. Mixing of the reactors was discontinued.
- November 4, 2022 – Four-month samples were collected from the reactors and submitted to ALS environmental and Element for analytical testing.

9.0 APPENDIX B: Data Tables

Table 1. Baseline Analysis of Bromacil and Tebuthiuron Impacted Soils.

Analyte	Units	Bromacil Baseline	Tebuthiuron Baseline
Leachable Anions & Nutrients			
Kjeldahl nitrogen, total [TKN]	%	0.156	0.139
leachable bromide	mg/kg	<0.50	
Ortho phosphate (as P)	mg/kg	1.70	1.95
Aggregate Organics			
Total Organic Carbon [TOC]	%	1.38	1.41
organic matter	%	2.38	2.43
Physical Tests			
moisture	%	12.1	11.1
pH	pH units	7.33	7.33
Metals			
aluminum	mg/kg	10100	10400
antimony	mg/kg	0.30	0.30
arsenic	mg/kg	5.74	5.73
barium	mg/kg	205	194
beryllium	mg/kg	0.43	0.42
bismuth	mg/kg	<0.20	<0.20
boron	mg/kg	5.9	5.8
cadmium	mg/kg	0.304	0.283
calcium	mg/kg	3540	3370
chromium	mg/kg	12.4	12.3
cobalt	mg/kg	6.96	6.73
copper	mg/kg	13.2	12.7
iron	mg/kg	12000	11800
lead	mg/kg	7.92	7.78
lithium	mg/kg	5.3	5.2
magnesium	mg/kg	2460	2400
manganese	mg/kg	460	462
mercury	mg/kg	0.0237	0.0237
molybdenum	mg/kg	0.54	0.57
nickel	mg/kg	14.8	14.3
phosphorus	mg/kg	401	385
potassium	mg/kg	1800	1780
selenium	mg/kg	0.29	0.26
silver	mg/kg	<0.10	<0.10

Analyte	Units	Bromacil Baseline	Tebuthiuron Baseline
sodium	mg/kg	332	327
strontium	mg/kg	29.7	28.8
sulfur	mg/kg	<1000	<1000
thallium	mg/kg	0.168	0.165
tin	mg/kg	<2.0	<2.0
titanium	mg/kg	137	142
tungsten	mg/kg	<0.50	<0.50
uranium	mg/kg	0.739	0.738
vanadium	mg/kg	23.8	23.4
zinc	mg/kg	50.6	49.5
zirconium	mg/kg	2.5	2.5

Table 2. Bromacil Concentrations and Estimated Half-Life in the Bromacil Reactors.

Bromacil Concentration (mg/kg)						Estimated Half Life (months)
Reactor ID	Sampling Date					
	Baseline 2022-06-08	2 Weeks 2022-07-18	1 Month 2022-08-04	2 Months 2022-09-06	4 Months 2022-11-04	
Control	0.260	0.201	0.281	0.219	0.122	3.66
BOS 200+	0.257	0.014	0.020	0.018	<0.008	0.52
BOS 200+ & Surf	0.257	0.017	0.013	0.009	0.010	0.23
Sim BOS 200+	0.258	0.118	0.011	<0.008	<0.008	0.22
Sim BOS 200+ & Surf	0.258	0.068	<0.008	<0.008	<0.008	0.20
CAT 100	0.258	0.051	0.081	0.038	0.034	1.37
CAT 100 & Surf	0.258	0.066	0.042	0.024	0.014	0.95
Sim CAT 100	0.257	0.050	<0.008	<0.008	<0.008	0.20
Sim CAT 100 & Surf	0.257	0.027	<0.008	<0.008	<0.008	0.15
ISCR	0.248	0.198	0.086	<0.008	<0.008	0.40
ISCR+	0.239	0.106	0.101	0.073	0.076	2.42

Table 3. Bromide Concentration in the Bromacil Reactors.

Bromide (mg/kg)					
Reactor ID	Sampling Date				
	Baseline 2022-06-01	2 Weeks 2022-07-18	1 Month 2022-07-18	2 Months 2022-09-06	4 Months 2022-11-04
Control	<0.50	<0.51	0.09	0.07	<0.2
BOS 200+	<0.50	<0.50	0.48	0.49	<0.2
Sim BOS 200+	<0.50	<0.50	0.72	0.71	<0.2
BOS 200+ & Surf	<0.50	<0.50	0.64	0.53	<0.2

Bromide (mg/kg)					
Reactor ID	Sampling Date				
	Baseline 2022-06-01	2 Weeks 2022-07-18	1 Month 2022-07-18	2 Months 2022-09-06	4 Months 2022-11-04
Sim BOS 200+ & Surf	<0.50	<0.50	0.59	0.63	<0.2
CAT 100	<0.50	<0.50	0.75	0.69	<0.2
Sim CAT 100	<0.50	<0.50	0.77	0.60	<0.2
CAT 100 & Surf	<0.50	<0.51	0.59	0.76	<0.2
Sim CAT 100 & Surf	<0.50	<0.50	0.79	0.71	<0.2
ISCR	<0.50	<0.50	0.89	0.94	<0.2
ISCR+	<0.50	0.70	0.49	0.57	<0.2

Table 4. Heterotrophic Plate Counts in the Bromacil Reactors**.**

Heterotrophic Plate Count (HPC) (CFU/g)					
Reactor ID	Sampling Date				
	Baseline 2022-06-01	2 Weeks 2022-07-18	1 Month 2022-08-4	2 Months 2022-09-06	4 Months 2022-11-04
Control	8,055	25,100	3,630,000	3,750,000	1,270,000
BOS 200+	8,055	468,000	9,730,000	8,410,000	5,700,000
Sim BOS 200+	8,055	257,000	21,700,000	18,500,000	5,420,000
BOS 200+ & Surf	8,055	25,200	25,600,000	12,300,000	3,080,000
Sim BOS 200+ & Surf	8,055	375,000	3,790,000	17,400,000	5,290,000
CAT 100	8,055	328,000	20,600,000	18,700,000	N/A
Sim CAT 100	8,055	1,600,000	18,400,000	23,100,000	3,950,000
CAT 100 & Surf	8,055	342,000	3,780,000	17,600,000	3,820,000
Sim CAT 100 & Surf	8,055	458,000	4,780,000	31,100,000	3,180,000
ISCR	8,055	37,100	6,550,000	19,200,000	1,200,000
ISCR+	8,055	<10	1,220,000	2,180,000	464,000

Table 5. Tebuthiuron Concentrations and Estimated Half-life in Tebuthiuron Reactors**.**

Tebuthiuron (mg/kg)						Estimated Half Life (Months)
Reactor ID	Sampling Date					
	Baseline 2022-06-08	2 Weeks 2022-07-18	1 Month 2022-08-4	2 Months 2022-09-06	4 Months 2022-11-04	
Control	0.179	0.137	0.127	0.117	0.124	7.55
BOS 200+	0.177	0.006	<0.005	<0.005	<0.005	0.19
BOS 200+ & Surf	0.177	0.015	0.011	0.012	0.008	0.52
Sim BOS 200+	0.178	0.114	0.113	0.099	0.117	6.64
Sim BOS 200+ & Surf	0.178	0.107	0.110	0.111	0.121	7.23
CAT 100	0.178	0.039	0.020	0.022	0.035	1.70

Tebuthiuron (mg/kg)						Estimated Half Life (Months)
Reactor ID	Sampling Date					
	Baseline 2022-06-08	2 Weeks 2022-07-18	1 Month 2022-08-4	2 Months 2022-09-06	4 Months 2022-11-04	
CAT 100 & Surf	0.178	0.076	0.072	0.065	0.036	1.74
Sim CAT 100	0.177	0.095	0.111	0.118	0.094	4.39
Sim CAT 100 & Surf	0.177	0.106	0.101	0.096	0.112	6.07
ISCR	0.170	0.111	0.121	0.105	0.088	4.19
ISCR+	0.164	0.079	0.080	0.066	0.067	3.09

Table 6. pH of Tebuthiuron Reactors.

pH				
Reactor ID	Sampling Date			
	Baseline 2022-06-01	2 Weeks 2022-07-18	1 Month 2022-08-4	2 Months 2022-09-06
Control	7.33	7.38	7.33	7.48
BOS 200+	7.33	7.70	7.46	7.36
Sim BOS 200+	7.33	7.41	7.48	7.22
BOS 200+ & Surf	7.33	7.49	8.09	7.21
Sim BOS 200+ & Surf	7.33	7.52	8.12	7.28
CAT 100	7.33	7.48	7.36	7.2
Sim CAT 100	7.33	7.18	7.06	7.06
CAT 100 & Surf	7.33	7.20	7.43	7.16
Sim CAT 100 & Surf	7.33	7.14	7.32	6.92
ISCR	7.33	7.51	7.41	7.12
ISCR+	7.33	4.59	4.50	4.57

Table 7. Heterotrophic Plate Count in Tebuthiuron Reactors

HPC (CFU/g)					
Reactor ID	Sampling Date				
	Baseline 2022-06-01	2 Weeks 2022-07-18	1 Month 2022-08-4	2 Months 2022-09-06	4 Months 2022-11-04
Control	6,280	368,000	9,040,000	3,580,000	1,260,000
BOS 200+	6,280	539,000	12,400,000	6,060,000	4,280,000
Sim BOS 200+	6,280	32,500,000	32,400,000	7,470,000	2,520,000
BOS 200+ & Surf	6,280	326,000	6,210,000	11,300,000	2,020,000
Sim BOS 200+ & Surf	6,280	388,000	67,300,000	14,900,000	3,150,000
CAT 100	6,280	29,900,000	14,900,000	14,900,000	4,600,000
Sim CAT 100	6,280	59,500,000	51,700,000	24,300,000	2,060,000
CAT 100 & Surf	6,280	265,000	25,300,000	23,500,000	1,940,000

HPC (CFU/g)					
Reactor ID	Sampling Date				
	Baseline 2022-06-01	2 Weeks 2022-07-18	1 Month 2022-08-4	2 Months 2022-09-06	4 Months 2022-11-04
Sim CAT 100 & Surf	6,280	422,000	29,800,000	29,000,000	2,760,000
ISCR	6,280	50,800	4,460,000	8,600,000	1,360,000
ISCR+	6,280	36,700	1,080,000	2,010,000	356,000

9.0 APPENDIX C: Certificates of Analysis

LABORATORY CERTIFICATES OF ANALYSES

BASELINE SAMPLING EVENT

Vertex Environmental Inc.
ATTN: Eric Cowan
40 McBrine Dr
Kitchener ON N2R 1E7

Date Received: 01-JUN-22
Report Date: 10-JUN-22 21:27 (MT)
Version: FINAL

Client Phone: 519-653-8444

Certificate of Analysis

Lab Work Order #: L2711558

Project P.O. #:	NOT SUBMITTED
Job Reference:	VE 1034
C of C Numbers:	20-948703
Legal Site Desc:	

Rick Hawthorne
Account Manager

[This report shall not be reproduced except in full without the written authority of the Laboratory.]

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2711558-1 BROMACIL BASELINE Sampled By: MJ on 01-JUN-22 @ 12:15 Matrix: SOIL							
Physical Tests							
% Moisture	12.6		0.25	%	08-JUN-22	09-JUN-22	R5795794
Bacteriological Tests							
Heterotrophic Plate Count	8950		10	CFU/g dwt	07-JUN-22	07-JUN-22	R5796604
L2711558-2 TEBUTHIURON BASELINE Sampled By: MJ on 01-JUN-22 @ 12:15 Matrix: SOIL							
Physical Tests							
% Moisture	11.5		0.25	%	08-JUN-22	09-JUN-22	R5795794
Bacteriological Tests							
Heterotrophic Plate Count	6280		10	CFU/g dwt	07-JUN-22	07-JUN-22	R5796604

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

Reference Information

Test Method References:

ALS Test Code	Matrix	Test Description	Method Reference**
HPC-SOLID-MF-WT	Soil	HPC on sludge or solid	SM 9215D
MOISTURE-WT	Soil	% Moisture	CCME PHC in Soil - Tier 1 (mod)

** ALS test methods may incorporate modifications from specified reference methods to improve performance.

The last two letters of the above test code(s) indicate the laboratory that performed analytical analysis for that test. Refer to the list below:

Laboratory Definition Code	Laboratory Location
WT	ALS ENVIRONMENTAL - WATERLOO, ONTARIO, CANADA

Chain of Custody Numbers:

20-948703

GLOSSARY OF REPORT TERMS

Surrogates are compounds that are similar in behaviour to target analyte(s), but that do not normally occur in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery. In reports that display the D.L. column, laboratory objectives for surrogates are listed there.
mg/kg - milligrams per kilogram based on dry weight of sample
mg/kg wwt - milligrams per kilogram based on wet weight of sample
mg/kg lwt - milligrams per kilogram based on lipid weight of sample
mg/L - unit of concentration based on volume, parts per million.
< - Less than.
D.L. - The reporting limit.
N/A - Result not available. Refer to qualifier code and definition for explanation.

Test results reported relate only to the samples as received by the laboratory.
UNLESS OTHERWISE STATED, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.
Analytical results in unsigned test reports with the DRAFT watermark are subject to change, pending final QC review.

Quality Control Report

Workorder: L2711558 Report Date: 10-JUN-22

Client: Vertex Environmental Inc.
40 McBrine Dr
Kitchener ON N2R 1E7

Contact: Eric Cowan

Test	Matrix	Reference	Result	Qualifier	Units	RPD	Limit	Analyzed
HPC-SOLID-MF-WT	**Soil**							
Batch R5796604								
WG3735221-3 DUP		**L2711558-1**						
Heterotrophic Plate Count		8950	7160		CFU/g dwt	22	50	07-JUN-02
WG3735221-1 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	07-JUN-02
MOISTURE-WT	**Soil**							
Batch R5795794								
WG3737267-3 DUP		**L2711558-2**						
% Moisture		11.5	11.6		%	0.3	20	09-JUN-22
WG3737267-2 LCS								
% Moisture			99.98		%		90-110	09-JUN-22
WG3737267-1 MB								
% Moisture			<0.25		%		0.25	09-JUN-22

Quality Control Report

Legend:

Limit	ALS Control Limit (Data Quality Objectives)
DUP	Duplicate
RPD	Relative Percent Difference
N/A	Not Available
LCS	Laboratory Control Sample
SRM	Standard Reference Material
MS	Matrix Spike
MSD	Matrix Spike Duplicate
ADE	Average Desorption Efficiency
MB	Method Blank
IRM	Internal Reference Material
CRM	Certified Reference Material
CCV	Continuing Calibration Verification
CVS	Calibration Verification Standard
LCSD	Laboratory Control Sample Duplicate

Quality Control Report

Hold Time Exceedances:

ALS Product Description	Sample ID	Sampling Date	Date Processed	Rec. HT	Actual HT	Units	Qualifier
Bacteriological Tests							
HPC on sludge or solid							
	1	01-JUN-22 12:15	07-JUN-22 13:50	48	146	hours	EHT
	2	01-JUN-22 12:15	07-JUN-22 13:50	48	146	hours	EHT

Legend & Qualifier Definitions:

EHTR-FM:	Exceeded ALS recommended hold time prior to sample receipt. Field Measurement recommended.
EHTR:	Exceeded ALS recommended hold time prior to sample receipt.
EHTL:	Exceeded ALS recommended hold time prior to analysis. Sample was received less than 24 hours prior to expiry.
EHT:	Exceeded ALS recommended hold time prior to analysis.
Rec. HT:	ALS recommended hold time (see units).

Notes*:
Where actual sampling date is not provided to ALS, the date (& time) of receipt is used for calculation purposes.
Where actual sampling time is not provided to ALS, the earlier of 12 noon on the sampling date or the time (& date) of receipt is used for calculation purposes. Samples for L2711558 were received on 01-JUN-22 15:20.

ALS recommended hold times may vary by province. They are assigned to meet known provincial and/or federal government requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by the US EPA, APHA Standard Methods, or Environment Canada (where available). For more information, please contact ALS.

The ALS Quality Control Report is provided to ALS clients upon request. ALS includes comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against pre-determined data quality objectives to provide confidence in the accuracy of associated test results.

Please note that this report may contain QC results from anonymous Sample Duplicates and Matrix Spikes that do not originate from this Work Order.

Chain of Custody (COC) / Analytical Request Form

COC Number: 20 - 948703

Canada Toll Free: 1 800 668 9878

Page of

Report To	Contact and company name below will appear on the final report
Company:	Vertex environmental inc.
Contact:	Eric Cowan
Phone:	
	Company address below will appear on the final report
Street:	40 McBrine Dr.
City/Province:	Kitchener
Postal Code:	
Invoice To	Same as Report To ☐ YES ☑ NO
	Copy of Invoice with Report ☑ YES ☐ NO
Company:	Vertex environmental inc.
Contact:	Accounting

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 ericc@vertexenvironmental.ca

Email 3 mahshidj@vertexenvironmental.ca

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 accountspayable@vertexenvironmental.ca

Turnaround Time (TAT) Requested

☑ Routine [R] if received by 3pm
☐ 4 day [P4] if received by 3pm
☐ 3 day [P3] if received by 3p
☐ 2 day [P2] if received by 3p
☐ 1 day [E] if received by 3pm
☐ Same day [E2] if received by may apply to rush requests on

L2711558-COFC

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please contact your AM to confirm availability.

Project Information

ALS Account # / Quote #:

Job #: VE 1034

PO / AFE:

LSD:

ALS Lab Work Order # (ALS use only): L2711558 HJT2204831

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#

Major/Minor Code: Routing Code:

Requisitioner:

Location:

ALS Contact: Rick H. Sampler: MJ

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	TOC	Heavy metals	Total nitrogen	ortho-P	pH	moisture content	Bromide	Heterotrophic plate count	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	Bromacil Baseline	01-06-22	12:15	Soil	3	✓	✓	✓	✓	✓	✓	✓	✓			
	Tebuthiuron Baseline	01-06-22	12:15	Soil	3	✓	✓	✓	✓	✓	✓		✓			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments Identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C: FINAL COOLER TEMPERATURES °C: 21.3

SHIPMENT RELEASE (client use)			INITIAL SHIPMENT RECEPTION (ALS use only)			FINAL SHIPMENT RECEPTION (ALS use only)		
Released by: Mahshid Jannati	Date: 01-06-22	Time: 2pm	Received by:	Date:	Time:	Received by: HDJ	Date: JUNE 1	Time: 15:20

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION WHITE - LABORATORY COPY YELLOW - CLIENT COPY

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a Regulated Drinking Water (DW) System, please submit using an Authorized DW COC form.

ALS Environmental

CERTIFICATE OF ANALYSIS

Work Order	: **WT2204831**	Page	: 1 of 4
Client	: **Vertex Environmental Inc.**	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo ON Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: VE 1034	Date Samples Received	: 01-Jun-2022 15:20
PO	: ----	Date Analysis Commenced	: 01-Jun-2022
C-O-C number	: 20-948703	Issue Date	: 14-Jun-2022 13:15
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 2		
No. of samples analysed	: 2		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. This document shall not be reproduced, except in full.

This Certificate of Analysis contains the following information:

- General Comments
- Analytical Results
- Surrogate Control Limits

Additional information pertinent to this report will be found in the following separate attachments: Quality Control Report, QC Interpretive report to assist with Quality Review and Sample Receipt Notification (SRN).

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is conducted in accordance with US FDA 21 CFR Part 11.

Signatories	*Position*	*Laboratory Department*
Adam Boettger	Team Leader - LCMS	LCMS, Waterloo, Ontario
Amanda Ganouri-Lumsden	Department Manager - Microbiology and Prep	Centralized Prep, Waterloo, Ontario
Colby Bingham	Quality Systems Coordinator	Inorganics, Saskatoon, Saskatchewan
Greg Pokocky	Supervisor - Inorganic	Inorganics, Waterloo, Ontario
Greg Pokocky	Supervisor - Inorganic	Metals, Waterloo, Ontario
Jon Fisher	Department Manager - Inorganics	Inorganics, Waterloo, Ontario
Jon Fisher	Department Manager - Inorganics	Metals, Waterloo, Ontario
joshua kodama		Centralized Prep, Waterloo, Ontario

General Comments

The analytical methods used by ALS are developed using internationally recognized reference methods (where available), such as those published by US EPA, APHA Standard Methods, ASTM, ISO, Environment Canada, BC MOE, and Ontario MOE. Refer to the ALS Quality Control Interpretive report (QCI) for applicable references and methodology summaries. Reference methods may incorporate modifications to improve performance.

Where a reported less than (<) result is higher than the LOR, this may be due to primary sample extract/digestate dilution and/or insufficient sample for analysis.

Where the LOR of a reported result differs from standard LOR, this may be due to high moisture content, insufficient sample (reduced weight employed) or matrix interference.

Please refer to Quality Control Interpretive report (QCI) for information regarding Holding Time compliance.

Key : CAS Number: Chemical Abstracts Services number is a unique identifier assigned to discrete substances
LOR: Limit of Reporting (detection limit).

Unit	*Description*
-	No Unit
%	percent
mg/kg	milligrams per kilogram
pH units	pH units

<: less than.

>: greater than.

Surrogate: An analyte that is similar in behavior to target analyte(s), but that does not occur naturally in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery.

Test results reported relate only to the samples as received by the laboratory.

UNLESS OTHERWISE STATED on SRN or QCI Report, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.

Qualifiers

Qualifier	*Description*
DLHC	*Detection Limit Raised: Dilution required due to high concentration of test analyte(s).*
PEHT	*Parameter exceeded recommended holding time prior to analysis.*

Analytical Results

Sub-Matrix: Soil/Solid (Matrix: Soil/Solid)				Client sample ID	BROMACIL BASELINE	THBUTHIURON BASELINE	----	----	----
				Client sampling date / time	01-Jun-2022 12:15	01-Jun-2022 12:15	----	----	----
Analyte	CAS Number	Method	LOR	Unit	WT2204831-001	WT2204831-002	--------	--------	--------
					Result	Result	----	----	----
Sample Preparation									
Dummy Analyte	----	EP357	1	-	Not Authorised	Not Authorised	----	----	----
Physical Tests									
moisture	----	E144	0.25	%	12.1	11.1	----	----	----
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.33	7.33	----	----	----
Metals									
aluminum	7429-90-5	E440	50	mg/kg	10100	10400	----	----	----
antimony	7440-36-0	E440	0.10	mg/kg	0.30	0.30	----	----	----
arsenic	7440-38-2	E440	0.10	mg/kg	5.74	5.73	----	----	----
barium	7440-39-3	E440	0.50	mg/kg	205	194	----	----	----
beryllium	7440-41-7	E440	0.10	mg/kg	0.43	0.42	----	----	----
bismuth	7440-69-9	E440	0.20	mg/kg	<0.20	<0.20	----	----	----
boron	7440-42-8	E440	5.0	mg/kg	5.9	5.8	----	----	----
cadmium	7440-43-9	E440	0.020	mg/kg	0.304	0.283	----	----	----
calcium	7440-70-2	E440	50	mg/kg	3540	3370	----	----	----
chromium	7440-47-3	E440	0.50	mg/kg	12.4	12.3	----	----	----
cobalt	7440-48-4	E440	0.10	mg/kg	6.96	6.73	----	----	----
copper	7440-50-8	E440	0.50	mg/kg	13.2	12.7	----	----	----
iron	7439-89-6	E440	50	mg/kg	12000	11800	----	----	----
lead	7439-92-1	E440	0.50	mg/kg	7.92	7.78	----	----	----
lithium	7439-93-2	E440	2.0	mg/kg	5.3	5.2	----	----	----
magnesium	7439-95-4	E440	20	mg/kg	2460	2400	----	----	----
manganese	7439-96-5	E440	1.0	mg/kg	460	462	----	----	----
mercury	7439-97-6	E510	0.0050	mg/kg	0.0237	0.0237	----	----	----
molybdenum	7439-98-7	E440	0.10	mg/kg	0.54	0.57	----	----	----
nickel	7440-02-0	E440	0.50	mg/kg	14.8	14.3	----	----	----
phosphorus	7723-14-0	E440	50	mg/kg	401	385	----	----	----
potassium	7440-09-7	E440	100	mg/kg	1800	1780	----	----	----
selenium	7782-49-2	E440	0.20	mg/kg	0.29	0.26	----	----	----
silver	7440-22-4	E440	0.10	mg/kg	<0.10	<0.10	----	----	----

Analytical Results

Sub-Matrix: Soil/Solid (Matrix: Soil/Solid)				Client sample ID	BROMACIL BASELINE	THBUTHIURON BASELINE	----	----	----
				Client sampling date / time	01-Jun-2022 12:15	01-Jun-2022 12:15	----	----	----
Analyte	CAS Number	Method	LOR	Unit	WT2204831-001	WT2204831-002	--------	--------	--------
					Result	Result	----	----	----
Metals									
sodium	7440-23-5	E440	50	mg/kg	332	327	----	----	----
strontium	7440-24-6	E440	0.50	mg/kg	29.7	28.8	----	----	----
sulfur	7704-34-9	E440	1000	mg/kg	<1000	<1000	----	----	----
thallium	7440-28-0	E440	0.050	mg/kg	0.168	0.165	----	----	----
tin	7440-31-5	E440	2.0	mg/kg	<2.0	<2.0	----	----	----
titanium	7440-32-6	E440	1.0	mg/kg	137	142	----	----	----
tungsten	7440-33-7	E440	0.50	mg/kg	<0.50	<0.50	----	----	----
uranium	7440-61-1	E440	0.050	mg/kg	0.739	0.738	----	----	----
vanadium	7440-62-2	E440	0.20	mg/kg	23.8	23.4	----	----	----
zinc	7440-66-6	E440	2.0	mg/kg	50.6	49.5	----	----	----
zirconium	7440-67-7	E440	1.0	mg/kg	2.5	2.5	----	----	----
Leachable Anions & Nutrients									
bromide, leachable	24959-67-9	E235.Br	0.50	mg/kg	<0.50	----	----	----	----
Kjeldahl nitrogen, total [TKN]	----	E319	0.020	%	0.156	0.139	----	----	----
phosphate, ortho- (as P)	14265-44-2	E378	0.080	mg/kg	1.70 DLHC	1.95 DLHC	----	----	----
Aggregate Organics									
carbon, total organic [TOC]	----	E357	0.10	%	1.38 PEHT	1.41 PEHT	----	----	----
organic matter	----	E357	0.20	%	2.38	2.43	----	----	----
Herbicides									
bromacil	314-40-9	E706A	0.00500	mg/kg	0.431 DLHC	<0.00500	----	----	----
Herbicides Surrogates									
dichlorophenylacetic acid, 2,4-	19719-28-9	E706A	0.010	%	91.6	83.1	----	----	----
Pesticides									
tebuthiuron	34014-18-1	E751D	0.000040	mg/kg	0.000182	0.193 DLHC	----	----	----

Please refer to the General Comments section for an explanation of any qualifiers detected.

QUALITY CONTROL INTERPRETIVE REPORT

Work Order	: **WT2204831**	Page	: 1 of 8
Client	: **Vertex Environmental Inc.**	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo, Ontario Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: VE 1034	Date Samples Received	: 01-Jun-2022 15:20
PO	: ----	Issue Date	: 14-Jun-2022 13:15
C-O-C number	: 20-948703		
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 2		
No. of samples analysed	: 2		

This report is automatically generated by the ALS LIMS (Laboratory Information Management System) through evaluation of Quality Control (QC) results and other QA parameters associated with this submission, and is intended to facilitate rapid data validation by auditors or reviewers. The report highlights any exceptions and outliers to ALS Data Quality Objectives, provides holding time details and exceptions, summarizes QC sample frequencies, and lists applicable methodology references and summaries.

Key

Anonymous: Refers to samples which are not part of this work order, but which formed part of the QC process lot.
CAS Number: Chemical Abstracts Service number is a unique identifier assigned to discrete substances.
DQO: Data Quality Objective.
LOR: Limit of Reporting (detection limit).
RPD: Relative Percent Difference.

Workorder Comments

Holding times are displayed as "---" if no guidance exists from CCME, Canadian provinces, or broadly recognized international references.

Summary of Outliers

Outliers : Quality Control Samples

- No Method Blank value outliers occur.
- No Duplicate outliers occur.
- No Laboratory Control Sample (LCS) outliers occur
- No Matrix Spike outliers occur.
- No Test sample Surrogate recovery outliers exist.

Outliers: Reference Material (RM) Samples

- No Reference Material (RM) Sample outliers occur.

Outliers : Analysis Holding Time Compliance (Breaches)

- No Analysis Holding Time Outliers exist.

Outliers : Frequency of Quality Control Samples

- No Quality Control Sample Frequency Outliers occur.

Analysis Holding Time Compliance

This report summarizes extraction / preparation and analysis times and compares each with ALS recommended holding times, which are selected to meet known provincial and /or federal requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by organizations such as CCME, US EPA, APHA Standard Methods, ASTM, or Environment Canada (where available). Dates and holding times reported below represent the first dates of extraction or analysis. If subsequent tests or dilutions exceeded holding times, qualifiers are added (refer to COA).

If samples are identified below as having been analyzed or extracted outside of recommended holding times, measurement uncertainties may be increased, and this should be taken into consideration when interpreting results.

Where actual sampling date is not provided on the chain of custody, the date of receipt with time at 00:00 is used for calculation purposes.

Where only the sample date without time is provided on the chain of custody, the sampling date at 00:00 is used for calculation purposes.

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Aggregate Organics : Total Organic Carbon by Wet Oxidation and Titration										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E357	01-Jun-2022	----	----	----		09-Jun-2022	28 days	8 days	✓
Aggregate Organics : Total Organic Carbon by Wet Oxidation and Titration										
Glass soil jar/Teflon lined cap THBUTHIURON BASELINE	E357	01-Jun-2022	----	----	----		09-Jun-2022	28 days	8 days	✓
Herbicides : Phenoxy Acid Herbicides in Soil by LC-MS-MS										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E706A	01-Jun-2022	04-Jun-2022	14 days	3 days	✓	06-Jun-2022	40 days	2 days	✓
Herbicides : Phenoxy Acid Herbicides in Soil by LC-MS-MS										
Glass soil jar/Teflon lined cap THBUTHIURON BASELINE	E706A	01-Jun-2022	04-Jun-2022	14 days	3 days	✓	06-Jun-2022	40 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E235.Br	01-Jun-2022	09-Jun-2022	----	----		13-Jun-2022	28 days	12 days	✓
Leachable Anions & Nutrients : Ortho-phosphate by Colorimetry (1:10 Soil:Water) (mg/kg)										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E378	01-Jun-2022	09-Jun-2022	----	----		13-Jun-2022	28 days	12 days	✓
Leachable Anions & Nutrients : Ortho-phosphate by Colorimetry (1:10 Soil:Water) (mg/kg)										
Glass soil jar/Teflon lined cap THBUTHIURON BASELINE	E378	01-Jun-2022	09-Jun-2022	----	----		09-Jun-2022	28 days	8 days	✓

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation: Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis: Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Leachable Anions & Nutrients : Total Kjeldahl Nitrogen by Colourimetry										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E319	01-Jun-2022	06-Jun-2022	----	----		07-Jun-2022	365 days	6 days	✓
Leachable Anions & Nutrients : Total Kjeldahl Nitrogen by Colourimetry										
Glass soil jar/Teflon lined cap THBUTHIURON BASELINE	E319	01-Jun-2022	06-Jun-2022	----	----		07-Jun-2022	365 days	6 days	✓
Metals : Mercury in Soil/Solid by CVAAS										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E510	01-Jun-2022	07-Jun-2022	----	----		07-Jun-2022	28 days	6 days	✓
Metals : Mercury in Soil/Solid by CVAAS										
Glass soil jar/Teflon lined cap THBUTHIURON BASELINE	E510	01-Jun-2022	07-Jun-2022	----	----		07-Jun-2022	28 days	6 days	✓
Metals : Metals in Soil/Solid by CRC ICPMS										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E440	01-Jun-2022	07-Jun-2022	----	----		07-Jun-2022	180 days	6 days	✓
Metals : Metals in Soil/Solid by CRC ICPMS										
Glass soil jar/Teflon lined cap THBUTHIURON BASELINE	E440	01-Jun-2022	07-Jun-2022	----	----		07-Jun-2022	180 days	6 days	✓
Pesticides : Pesticides in Soil by LC-MS/MS (POS1 List)										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E751D	01-Jun-2022	04-Jun-2022	28 days	3 days	✓	06-Jun-2022	28 days	2 days	✓
Pesticides : Pesticides in Soil by LC-MS/MS (POS1 List)										
Glass soil jar/Teflon lined cap THBUTHIURON BASELINE	E751D	01-Jun-2022	04-Jun-2022	28 days	3 days	✓	06-Jun-2022	28 days	2 days	✓
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL BASELINE	E144	01-Jun-2022	----	----	----		01-Jun-2022	----	----	

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap										
THBUTHIURON BASELINE	E144	01-Jun-2022	----	----	----		01-Jun-2022	----	----	
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL BASELINE	E108A	01-Jun-2022	06-Jun-2022	----	----		06-Jun-2022	30 days	5 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
THBUTHIURON BASELINE	E108A	01-Jun-2022	06-Jun-2022	----	----		06-Jun-2022	30 days	5 days	✓

Legend & Qualifier Definitions

Rec. HT: ALS recommended hold time (see units).

Quality Control Parameter Frequency Compliance

The following report summarizes the frequency of laboratory QC samples analyzed within the analytical batches (QC lots) in which the submitted samples were processed. The actual frequency should be greater than or equal to the expected frequency.

Matrix: **Soil/Solid**

Evaluation: × = *QC frequency outside specification*; ✓ = *QC frequency within specification.*

Quality Control Sample Type			Count		Frequency (%)		
Analytical Methods	*Method*	*QC Lot #*	*QC*	*Regular*	*Actual*	*Expected*	*Evaluation*
Laboratory Duplicates (DUP)							
Leachable Bromide in Soil/Solid by IC	E235.Br	517214	1	1	100.0	5.0	✓
Mercury in Soil/Solid by CVAAS	E510	513192	1	2	50.0	5.0	✓
Metals in Soil/Solid by CRC ICPMS	E440	513191	1	18	5.5	5.0	✓
Moisture Content by Gravimetry	E144	507792	1	20	5.0	5.0	✓
Ortho-phosphate by Colorimetry (1:10 Soil:Water) (mg/kg)	E378	517251	2	3	66.6	5.0	✓
Pesticides in Soil by LC-MS/MS (POS1 List)	E751D	511464	1	10	10.0	5.0	✓
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A	512070	1	20	5.0	5.0	✓
Phenoxy Acid Herbicides in Soil by LC-MS-MS	E706A	511465	1	10	10.0	5.0	✓
Total Kjeldahl Nitrogen by Colourimetry	E319	512789	1	3	33.3	5.0	✓
Total Organic Carbon by Wet Oxidation and Titration	E357	512644	1	3	33.3	5.0	✓
Laboratory Control Samples (LCS)							
Leachable Bromide in Soil/Solid by IC	E235.Br	517214	2	1	200.0	10.0	✓
Mercury in Soil/Solid by CVAAS	E510	513192	2	2	100.0	10.0	✓
Metals in Soil/Solid by CRC ICPMS	E440	513191	2	18	11.1	10.0	✓
Moisture Content by Gravimetry	E144	507792	1	20	5.0	5.0	✓
Ortho-phosphate by Colorimetry (1:10 Soil:Water) (mg/kg)	E378	517251	2	3	66.6	5.0	✓
Pesticides in Soil by LC-MS/MS (POS1 List)	E751D	511464	1	10	10.0	5.0	✓
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A	512070	1	20	5.0	5.0	✓
Phenoxy Acid Herbicides in Soil by LC-MS-MS	E706A	511465	1	10	10.0	5.0	✓
Total Kjeldahl Nitrogen by Colourimetry	E319	512789	2	3	66.6	10.0	✓
Total Organic Carbon by Wet Oxidation and Titration	E357	512644	2	3	66.6	10.0	✓
Method Blanks (MB)							
Leachable Bromide in Soil/Solid by IC	E235.Br	517214	1	1	100.0	5.0	✓
Mercury in Soil/Solid by CVAAS	E510	513192	1	2	50.0	5.0	✓
Metals in Soil/Solid by CRC ICPMS	E440	513191	1	18	5.5	5.0	✓
Moisture Content by Gravimetry	E144	507792	1	20	5.0	5.0	✓
Ortho-phosphate by Colorimetry (1:10 Soil:Water) (mg/kg)	E378	517251	2	3	66.6	5.0	✓
Pesticides in Soil by LC-MS/MS (POS1 List)	E751D	511464	1	10	10.0	5.0	✓
Phenoxy Acid Herbicides in Soil by LC-MS-MS	E706A	511465	1	10	10.0	5.0	✓
Total Kjeldahl Nitrogen by Colourimetry	E319	512789	1	3	33.3	5.0	✓
Total Organic Carbon by Wet Oxidation and Titration	E357	512644	1	3	33.3	5.0	✓
Matrix Spikes (MS)							
Ortho-phosphate by Colorimetry (1:10 Soil:Water) (mg/kg)	E378	517251	2	3	66.6	5.0	✓
Pesticides in Soil by LC-MS/MS (POS1 List)	E751D	511464	1	10	10.0	5.0	✓
Phenoxy Acid Herbicides in Soil by LC-MS-MS	E706A	511465	1	10	10.0	5.0	✓

Methodology References and Summaries

The analytical methods used by ALS are developed using internationally recognized reference methods (where available), such as those published by US EPA, APHA Standard Methods, ASTM, ISO, Environment Canada, BC MOE, and Ontario MOE. Reference methods may incorporate modifications to improve performance (indicated by "mod").

Analytical Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A Waterloo - Environmental	Soil/Solid	MOEE E3137A	pH is determined by potentiometric measurement with a pH electrode, and is conducted at ambient laboratory temperature (normally 20 ± 5°C) and is carried out in accordance with procedures described in the Analytical Protocol (prescriptive method). A minimum 10g portion of the sample, as received, is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling, or decanting and then analyzed using a pH meter and electrode.
Moisture Content by Gravimetry	E144 Waterloo - Environmental	Soil/Solid	CCME PHC in Soil - Tier 1	Moisture is measured gravimetrically by drying the sample at 105°C. Moisture content is calculated as the weight loss (due to water) divided by the wet weight of the sample, expressed as a percentage.
Leachable Bromide in Soil/Solid by IC	E235.Br Waterloo - Environmental	Soil/Solid	CSSS Ch. 15 (mod)/EPA 300.1 (mod)	Inorganic anions are analyzed by Ion Chromatography with conductivity and/or UV detection using a soil sample that has been added in a defined ratio of soil to deionized water, then shaken well and allowed to settle. Anions are measured in the fluid that is observed in the upper layer.
Total Kjeldahl Nitrogen by Colourimetry	E319 Saskatoon - Environmental	Soil/Solid	CSSS (2008) 22.2.3	The soil is digested with sulfuric acid in the presence of CuSO4 and K2SO4 catalysts. Ammonia in the soil extract is determined colrimetrically at 660 nm.
Total Organic Carbon by Wet Oxidation and Titration	E357 Waterloo - Environmental	Soil/Solid	CSSS (2008) 21.3.2 (mod)	Total Organic Carbon is determined by wet oxidation digestion using potassium dichromate and sulfuric acid (Walkley-Black). Oxidized organic carbon is determined by back-titration with ferrous ammonium sulfate. Organic matter is estimated from the organic carbon result using the Van Bemmelon factor.
Ortho-phosphate by Colorimetry (1:10 Soil:Water) (mg/kg)	E378 Waterloo - Environmental	Soil/Solid	EPA 300.0 (mod)	Orthophosphate is determined colourimetrically on a soil sample that has been extracted and filtered through a 0.45 micron membrane filter.
Metals in Soil/Solid by CRC ICPMS	E440 Waterloo - Environmental	Soil/Solid	EPA 6020B (mod)	This method is intended to liberate metals that may be environmentally available. Samples are dried, then sieved through a 2 mm sieve, and digested with HNO3 and HCl. Dependent on sample matrix, some metals may be only partially recovered, including Al, Ba, Be, Cr, Sr, Ti, Tl, V, W, and Zr. Silicate minerals are not solubilized. Volatile forms of sulfur (including sulfide) may not be captured, as they may be lost during sampling, storage, or digestion. This method does not adequately recover elemental sulfur, and is unsuitable for assessment of elemental sulfur standards or guidelines. Analysis is by Collision/Reaction Cell ICPMS.
Mercury in Soil/Solid by CVAAS	E510 Waterloo - Environmental	Soil/Solid	EPA 200.2/1631 Appendix (mod)	Samples are dried, then sieved through a 2 mm sieve, and digested with HNO3 and HCl, followed by CVAAS analysis.

Analytical Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
Phenoxy Acid Herbicides in Soil by LC-MS-MS	E706A Waterloo - Environmental	Soil/Solid	MOE E3552	Soil samples are extracted using 2% formic acid in acetonitrile. The extract is solvent exchanged to 20% acetonitrile in water and analyzed using liquid chromatography tandem mass spectrometry (LC-MS/MS).
Pesticides in Soil by LC-MS/MS (POS1 List)	E751D Waterloo - Environmental	Soil/Solid	MOECC 3501(mod)	Sample is derivatized and injected directly. Each compound is separated by reversed phase HPLC and analyzed by Electro Spray Ionization MS/MS detection using Triple Quadrupole MS/MS detector. Internal standards are used for quantitation.

Preparation Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
Leach 1:2 Soil : 0.01CaCl2 - As Received for pH	EP108A Waterloo - Environmental	Soil/Solid	MOEE E3137A	A minimum 10g portion of the sample, as received, is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling or decanting and then analyzed using a pH meter and electrode.
Kjeldahl Digestion for soils	EP319 Saskatoon - Environmental	Soil/Solid	CSSS (2008) 22.2.3	The soil is digested with sulfuric acid in the presence of CuSO4 and K2SO4 catalysts.
Digestion for Metals and Mercury	EP440 Waterloo - Environmental	Soil/Solid	EPA 200.2 (mod)	Samples are dried, then sieved through a 2 mm sieve, and digested with HNO3 and HCl. This method is intended to liberate metals that may be environmentally available.
Leach for Metals and Anions	EP441 Waterloo - Environmental	Soil/Solid	In-House	This analysis is carried out using a leaching procedure which involves the gentle tumbling of the sample in a specified leaching solution (typically deionized water) for a specific length of time.
Preparation of Phenoxy Acid Herbicides in Soil by LC-MS-MS	EP706 Waterloo - Environmental	Soil/Solid	MOE E3552	Soil samples are extracted using 2% formic acid in acetonitrile. The extract is solvent exchanged to 20% acetonitrile in water and analyzed using liquid chromatography tandem mass spectrometry (LC-MS/MS).
Preparation of Pesticides in Soil by LC-MS/MS	EP751D Waterloo - Environmental	Soil/Solid	MOECC 3501(mod)	An aliquot of 2.0 ± 0.01 g of homogenized soil sample is spiked with positive and negative internal standards, then extracted with 20 mL acetonitrile and 10mL methanol:1% formic acid in water (9:1). The extracts are concentrated and then analyzed by LC-MS/MS.
Dry and Grind	EPP442 Saskatoon - Environmental	Soil/Solid	Soil Sampling and Methods of Analysis, Carter 2008	After removal of any coarse fragments and reservation of wet subsamples a portion of homogenized sample is set in a tray and dried at less than 60°C until dry. The sample is then particle size reduced with an automated crusher or mortar and pestle, typically to <2 mm. Further size reduction may be needed for particular tests.

QUALITY CONTROL REPORT

Work Order	: **WT2204831**	Page	: 1 of 11
Client	: Vertex Environmental Inc.	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo, Ontario Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: VE 1034	Date Samples Received	: 01-Jun-2022 15:20
PO	: ----	Date Analysis Commenced	: 01-Jun-2022
C-O-C number	: 20-948703	Issue Date	: 14-Jun-2022 13:22
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 2		
No. of samples analysed	: 2		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. This document shall not be reproduced, except in full.

This Quality Control Report contains the following information:

- Laboratory Duplicate (DUP) Report; Relative Percent Difference (RPD) and Data Quality Objectives
- Matrix Spike (MS) Report; Recovery and Data Quality Objectives
- Reference Material (RM) Report; Recovery and Data Quality Objectives
- Method Blank (MB) Report; Recovery and Data Quality Objectives
- Laboratory Control Sample (LCS) Report; Recovery and Data Quality Objectives

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is conducted in accordance with US FDA 21 CFR Part 11.

Signatories	*Position*	*Laboratory Department*
Adam Boettger	Team Leader - LCMS	Waterloo LCMS, Waterloo, Ontario
Amanda Ganouri-Lumsden	Department Manager - Microbiology and Prep	Waterloo Centralized Prep, Waterloo, Ontario
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Jon Fisher	Department Manager - Inorganics	Waterloo Metals, Waterloo, Ontario
joshua kodama		Waterloo Centralized Prep, Waterloo, Ontario

General Comments

The ALS Quality Control (QC) report is optionally provided to ALS clients upon request. ALS test methods include comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against predetermined Data Quality Objectives (DQOs) to provide confidence in the accuracy of associated test results. This report contains detailed results for all QC results applicable to this sample submission. Please refer to the ALS Quality Control Interpretation report (QCI) for applicable method references and methodology summaries.

Key :

Anonymous = Refers to samples which are not part of this work order, but which formed part of the QC process lot.
CAS Number = Chemical Abstracts Service number is a unique identifier assigned to discrete substances.
DQO = Data Quality Objective.
LOR = Limit of Reporting (detection limit).
RPD = Relative Percent Difference
# = Indicates a QC result that did not meet the ALS DQO.

Workorder Comments

Holding times are displayed as "---" if no guidance exists from CCME, Canadian provinces, or broadly recognized international references.

Laboratory Duplicate (DUP) Report

A Laboratory Duplicate (DUP) is a randomly selected intralaboratory replicate sample. Laboratory Duplicates provide information regarding method precision and sample heterogeneity. ALS DQOs for Laboratory Duplicates are expressed as test-specific limits for Relative Percent Difference (RPD), or as an absolute difference limit of 2 times the LOR for low concentration duplicates within ~ 4-10 times the LOR (cut-off is test-specific).

Sub-Matrix: **Soil/Solid**

					Laboratory Duplicate (DUP) Report						
Laboratory sample ID	*Client sample ID*	*Analyte*	*CAS Number*	*Method*	*LOR*	*Unit*	*Original Result*	*Duplicate Result*	*RPD(%) or Difference*	*Duplicate Limits*	*Qualifier*
Physical Tests (QC Lot: 507792)											
WT2204788-001	Anonymous	moisture	----	E144	0.25	%	14.3	14.2	0.435%	20%	----
Physical Tests (QC Lot: 512070)											
WT2204797-001	Anonymous	pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	8.12	8.16	0.04	Diff <2x LOR	----
Metals (QC Lot: 513191)											
WT2204831-001	BROMACIL BASELINE	aluminum	7429-90-5	E440	50	mg/kg	10100	10400	2.86%	40%	----
		antimony	7440-36-0	E440	0.10	mg/kg	0.30	0.30	0.0002	Diff <2x LOR	----
		arsenic	7440-38-2	E440	0.10	mg/kg	5.74	6.03	4.94%	30%	----
		barium	7440-39-3	E440	0.50	mg/kg	205	208	1.41%	40%	----
		beryllium	7440-41-7	E440	0.10	mg/kg	0.43	0.42	0.009	Diff <2x LOR	----
		bismuth	7440-69-9	E440	0.20	mg/kg	<0.20	<0.20	0	Diff <2x LOR	----
		boron	7440-42-8	E440	5.0	mg/kg	5.9	6.0	0.1	Diff <2x LOR	----
		cadmium	7440-43-9	E440	0.020	mg/kg	0.304	0.288	5.64%	30%	----
		calcium	7440-70-2	E440	50	mg/kg	3540	3530	0.453%	30%	----
		chromium	7440-47-3	E440	0.50	mg/kg	12.4	12.7	2.55%	30%	----
		cobalt	7440-48-4	E440	0.10	mg/kg	6.96	6.94	0.279%	30%	----
		copper	7440-50-8	E440	0.50	mg/kg	13.2	13.4	1.74%	30%	----
		iron	7439-89-6	E440	50	mg/kg	12000	12200	1.34%	30%	----
		lead	7439-92-1	E440	0.50	mg/kg	7.92	8.10	2.21%	40%	----
		lithium	7439-93-2	E440	2.0	mg/kg	5.3	5.4	0.04	Diff <2x LOR	----
		magnesium	7439-95-4	E440	20	mg/kg	2460	2460	0.0357%	30%	----
		manganese	7439-96-5	E440	1.0	mg/kg	460	463	0.481%	30%	----
		molybdenum	7439-98-7	E440	0.10	mg/kg	0.54	0.52	3.10%	40%	----
		nickel	7440-02-0	E440	0.50	mg/kg	14.8	15.1	2.11%	30%	----
		phosphorus	7723-14-0	E440	50	mg/kg	401	413	3.07%	30%	----
		potassium	7440-09-7	E440	100	mg/kg	1800	1850	3.09%	40%	----
		selenium	7782-49-2	E440	0.20	mg/kg	0.29	0.30	0.01	Diff <2x LOR	----
		silver	7440-22-4	E440	0.10	mg/kg	<0.10	<0.10	0	Diff <2x LOR	----
		sodium	7440-23-5	E440	50	mg/kg	332	340	2.45%	40%	----
		strontium	7440-24-6	E440	0.50	mg/kg	29.7	29.6	0.272%	40%	----
		sulfur	7704-34-9	E440	1000	mg/kg	<1000	<1000	0	Diff <2x LOR	----
		thallium	7440-28-0	E440	0.050	mg/kg	0.168	0.169	0.0009	Diff <2x LOR	----

Sub-Matrix: **Soil/Solid**

					Laboratory Duplicate (DUP) Report						
Laboratory sample ID	*Client sample ID*	*Analyte*	*CAS Number*	*Method*	*LOR*	*Unit*	*Original Result*	*Duplicate Result*	*RPD(%) or Difference*	*Duplicate Limits*	*Qualifier*
Metals (QC Lot: 513191) - continued											
WT2204831-001	BROMACIL BASELINE	tin	7440-31-5	E440	2.0	mg/kg	<2.0	<2.0	0	Diff <2x LOR	----
		titanium	7440-32-6	E440	1.0	mg/kg	137	144	5.26%	40%	----
		tungsten	7440-33-7	E440	0.50	mg/kg	<0.50	<0.50	0	Diff <2x LOR	----
		uranium	7440-61-1	E440	0.050	mg/kg	0.739	0.776	4.86%	30%	----
		vanadium	7440-62-2	E440	0.20	mg/kg	23.8	24.2	2.07%	30%	----
		zinc	7440-66-6	E440	2.0	mg/kg	50.6	51.8	2.44%	30%	----
		zirconium	7440-67-7	E440	1.0	mg/kg	2.5	2.6	0.1	Diff <2x LOR	----
Metals (QC Lot: 513192)											
WT2204831-001	BROMACIL BASELINE	mercury	7439-97-6	E510	0.0050	mg/kg	0.0237	0.0249	0.0012	Diff <2x LOR	----
Leachable Anions & Nutrients (QC Lot: 512789)											
VA22B2210-001	Anonymous	Kjeldahl nitrogen, total [TKN]	----	E319	2000	mg/kg	1.85 %	18900	400	Diff <2x LOR	----
Leachable Anions & Nutrients (QC Lot: 517213)											
WT2204831-001	BROMACIL BASELINE	phosphate, ortho- (as P)	14265-44-2	E378	0.791	mg/kg	1.70	1.70	0.0007	Diff <2x LOR	----
Leachable Anions & Nutrients (QC Lot: 517214)											
WT2204831-001	BROMACIL BASELINE	bromide, leachable	24959-67-9	E235.Br	0.50	mg/kg	<0.50	<0.50	0	Diff <2x LOR	----
Leachable Anions & Nutrients (QC Lot: 517251)											
WT2204725-001	Anonymous	phosphate, ortho- (as P)	14265-44-2	E378	0.080	mg/kg	0.241	0.233	0.008	Diff <2x LOR	----
Aggregate Organics (QC Lot: 512644)											
WT2204831-001	BROMACIL BASELINE	carbon, total organic [TOC]	----	E357	0.10	%	1.38	1.39	0.803%	20%	----
Herbicides (QC Lot: 511465)											
SK2202468-018	Anonymous	bromacil	314-40-9	E706A	0.00050	mg/kg	<0.00050	<0.00050	0	Diff <2x LOR	----
Pesticides (QC Lot: 511464)											
SK2202468-018	Anonymous	tebuthiuron	34014-18-1	E751D	0.000500	mg/kg	<0.000500	<0.000500	0	Diff <2x LOR	----

Method Blank (MB) Report

A Method Blank is an analyte-free matrix that undergoes sample processing identical to that carried out for test samples. Method Blank results are used to monitor and control for potential contamination from the laboratory environment and reagents. For most tests, the DQO for Method Blanks is for the result to be < LOR.

Sub-Matrix: **Soil/Solid**

Analyte	CAS Number	Method	LOR	Unit	Result	Qualifier
Physical Tests (QCLot: 507792)						
moisture	----	E144	0.25	%	<0.25	----
Metals (QCLot: 513191)						
aluminum	7429-90-5	E440	50	mg/kg	<50	----
antimony	7440-36-0	E440	0.1	mg/kg	<0.10	----
arsenic	7440-38-2	E440	0.1	mg/kg	<0.10	----
barium	7440-39-3	E440	0.5	mg/kg	<0.50	----
beryllium	7440-41-7	E440	0.1	mg/kg	<0.10	----
bismuth	7440-69-9	E440	0.2	mg/kg	<0.20	----
boron	7440-42-8	E440	5	mg/kg	<5.0	----
cadmium	7440-43-9	E440	0.02	mg/kg	<0.020	----
calcium	7440-70-2	E440	50	mg/kg	<50	----
chromium	7440-47-3	E440	0.5	mg/kg	<0.50	----
cobalt	7440-48-4	E440	0.1	mg/kg	<0.10	----
copper	7440-50-8	E440	0.5	mg/kg	<0.50	----
iron	7439-89-6	E440	50	mg/kg	<50	----
lead	7439-92-1	E440	0.5	mg/kg	<0.50	----
lithium	7439-93-2	E440	2	mg/kg	<2.0	----
magnesium	7439-95-4	E440	20	mg/kg	<20	----
manganese	7439-96-5	E440	1	mg/kg	<1.0	----
molybdenum	7439-98-7	E440	0.1	mg/kg	<0.10	----
nickel	7440-02-0	E440	0.5	mg/kg	<0.50	----
phosphorus	7723-14-0	E440	50	mg/kg	<50	----
potassium	7440-09-7	E440	100	mg/kg	<100	----
selenium	7782-49-2	E440	0.2	mg/kg	<0.20	----
silver	7440-22-4	E440	0.1	mg/kg	<0.10	----
sodium	7440-23-5	E440	50	mg/kg	<50	----
strontium	7440-24-6	E440	0.5	mg/kg	<0.50	----
sulfur	7704-34-9	E440	1000	mg/kg	<1000	----
thallium	7440-28-0	E440	0.05	mg/kg	<0.050	----
tin	7440-31-5	E440	2	mg/kg	<2.0	----
titanium	7440-32-6	E440	1	mg/kg	<1.0	----
tungsten	7440-33-7	E440	0.5	mg/kg	<0.50	----
uranium	7440-61-1	E440	0.05	mg/kg	<0.050	----

Sub-Matrix: **Soil/Solid**

Analyte	CAS Number	Method	LOR	Unit	Result	Qualifier
Metals (QCLot: 513191) - continued						
vanadium	7440-62-2	E440	0.2	mg/kg	<0.20	----
zinc	7440-66-6	E440	2	mg/kg	<2.0	----
zirconium	7440-67-7	E440	1	mg/kg	<1.0	----
Metals (QCLot: 513192)						
mercury	7439-97-6	E510	0.005	mg/kg	<0.0050	----
Leachable Anions & Nutrients (QCLot: 512789)						
Kjeldahl nitrogen, total [TKN]	----	E319	200	mg/kg	<200	----
Leachable Anions & Nutrients (QCLot: 517213)						
phosphate, ortho- (as P)	14265-44-2	E378	0.08	mg/kg	<0.080	----
Leachable Anions & Nutrients (QCLot: 517214)						
bromide, leachable	24959-67-9	E235.Br	0.5	mg/kg	<0.50	----
Leachable Anions & Nutrients (QCLot: 517251)						
phosphate, ortho- (as P)	14265-44-2	E378	0.08	mg/kg	<0.080	----
Aggregate Organics (QCLot: 512644)						
carbon, total organic [TOC]	----	E357	0.1	%	<0.10	----
Herbicides (QCLot: 511465)						
bromacil	314-40-9	E706A	0.0005	mg/kg	<0.00050	----
Pesticides (QCLot: 511464)						
tebuthiuron	34014-18-1	E751D	0.00004	mg/kg	<0.000040	----

Laboratory Control Sample (LCS) Report

A Laboratory Control Sample (LCS) is an analyte-free matrix that has been fortified (spiked) with test analytes at known concentration and processed in an identical manner to test samples. LCS results are expressed as percent recovery, and are used to monitor and control test method accuracy and precision, independent of test sample matrix.

Sub-Matrix: **Soil/Solid**

					Laboratory Control Sample (LCS) Report				
					Spike	Recovery (%)	Recovery Limits (%)		
Analyte	CAS Number	Method	LOR	Unit	Concentration	LCS	Low	High	Qualifier
Physical Tests (QCLot: 507792)									
moisture	----	E144	0.25	%	50 %	99.8	90.0	110	----
Physical Tests (QCLot: 512070)									
pH (1:2 soil:CaCl2-aq)	----	E108A	----	pH units	7 pH units	100	98.0	102	----
Metals (QCLot: 513191)									
aluminum	7429-90-5	E440	50	mg/kg	200 mg/kg	97.6	80.0	120	----
antimony	7440-36-0	E440	0.1	mg/kg	100 mg/kg	103	80.0	120	----
arsenic	7440-38-2	E440	0.1	mg/kg	100 mg/kg	99.4	80.0	120	----
barium	7440-39-3	E440	0.5	mg/kg	25 mg/kg	98.3	80.0	120	----
beryllium	7440-41-7	E440	0.1	mg/kg	10 mg/kg	89.7	80.0	120	----
bismuth	7440-69-9	E440	0.2	mg/kg	100 mg/kg	92.4	80.0	120	----
boron	7440-42-8	E440	5	mg/kg	100 mg/kg	90.8	80.0	120	----
cadmium	7440-43-9	E440	0.02	mg/kg	10 mg/kg	100	80.0	120	----
calcium	7440-70-2	E440	50	mg/kg	5000 mg/kg	97.4	80.0	120	----
chromium	7440-47-3	E440	0.5	mg/kg	25 mg/kg	99.2	80.0	120	----
cobalt	7440-48-4	E440	0.1	mg/kg	25 mg/kg	98.4	80.0	120	----
copper	7440-50-8	E440	0.5	mg/kg	25 mg/kg	96.4	80.0	120	----
iron	7439-89-6	E440	50	mg/kg	100 mg/kg	97.6	80.0	120	----
lead	7439-92-1	E440	0.5	mg/kg	50 mg/kg	99.0	80.0	120	----
lithium	7439-93-2	E440	2	mg/kg	25 mg/kg	87.0	80.0	120	----
magnesium	7439-95-4	E440	20	mg/kg	5000 mg/kg	103	80.0	120	----
manganese	7439-96-5	E440	1	mg/kg	25 mg/kg	98.4	80.0	120	----
molybdenum	7439-98-7	E440	0.1	mg/kg	25 mg/kg	97.4	80.0	120	----
nickel	7440-02-0	E440	0.5	mg/kg	50 mg/kg	97.8	80.0	120	----
phosphorus	7723-14-0	E440	50	mg/kg	1000 mg/kg	98.2	80.0	120	----
potassium	7440-09-7	E440	100	mg/kg	5000 mg/kg	103	80.0	120	----
selenium	7782-49-2	E440	0.2	mg/kg	100 mg/kg	99.0	80.0	120	----
silver	7440-22-4	E440	0.1	mg/kg	10 mg/kg	80.9	80.0	120	----
sodium	7440-23-5	E440	50	mg/kg	5000 mg/kg	98.8	80.0	120	----
strontium	7440-24-6	E440	0.5	mg/kg	25 mg/kg	101	80.0	120	----
sulfur	7704-34-9	E440	1000	mg/kg	5000 mg/kg	91.0	80.0	120	----
thallium	7440-28-0	E440	0.05	mg/kg	100 mg/kg	96.7	80.0	120	----
tin	7440-31-5	E440	2	mg/kg	50 mg/kg	98.4	80.0	120	----
titanium	7440-32-6	E440	1	mg/kg	25 mg/kg	97.2	80.0	120	----

Sub-Matrix: **Soil/Solid**

					Laboratory Control Sample (LCS) Report				
					Spike	Recovery (%)	Recovery Limits (%)		
Analyte	CAS Number	Method	LOR	Unit	Concentration	LCS	Low	High	Qualifier
Metals (QCLot: 513191) - continued									
uranium	7440-61-1	E440	0.05	mg/kg	0.5 mg/kg	94.1	80.0	120	----
vanadium	7440-62-2	E440	0.2	mg/kg	50 mg/kg	101	80.0	120	----
zinc	7440-66-6	E440	2	mg/kg	50 mg/kg	95.9	80.0	120	----
zirconium	7440-67-7	E440	1	mg/kg	10 mg/kg	97.4	80.0	120	----
Metals (QCLot: 513192)									
mercury	7439-97-6	E510	0.005	mg/kg	0.1 mg/kg	91.5	80.0	120	----
Leachable Anions & Nutrients (QCLot: 512789)									
Kjeldahl nitrogen, total [TKN]	----	E319	200	mg/kg	1000 mg/kg	84.0	80.0	120	----
Leachable Anions & Nutrients (QCLot: 517213)									
phosphate, ortho- (as P)	14265-44-2	E378	0.08	mg/kg	0.0424 mg/kg	105	70.0	130	----
Leachable Anions & Nutrients (QCLot: 517214)									
bromide, leachable	24959-67-9	E235.Br	0.5	mg/kg	1 mg/kg	102	70.0	130	----
Leachable Anions & Nutrients (QCLot: 517251)									
phosphate, ortho- (as P)	14265-44-2	E378	0.08	mg/kg	0.106 mg/kg	101	70.0	130	----
Aggregate Organics (QCLot: 512644)									
carbon, total organic [TOC]	----	E357	0.1	%	42.1 %	99.2	80.0	120	----
Herbicides (QCLot: 511465)									
bromacil	314-40-9	E706A	0.0005	mg/kg	0.01 mg/kg	95.5	60.0	140	----
Pesticides (QCLot: 511464)									
tebuthiuron	34014-18-1	E751D	0.00004	mg/kg	0.0004 mg/kg	97.0	70.0	130	----

Matrix Spike (MS) Report

A Matrix Spike (MS) is a randomly selected intra-laboratory replicate sample that has been fortified (spiked) with test analytes at known concentration, and processed in an identical manner to test samples. Matrix Spikes provide information regarding analyte recovery and potential matrix effects. MS DQO exceedances due to sample matrix may sometimes be unavoidable; in such cases, test results for the associated sample (or similar samples) may be subject to bias. ND – Recovery not determined, background level >= 1x spike level.

Sub-Matrix: **Soil/Solid**

					Matrix Spike (MS) Report					
					Spike		Recovery (%)	Recovery Limits (%)		
Laboratory sample ID	Client sample ID	Analyte	CAS Number	Method	Concentration	Target	MS	Low	High	Qualifier
Leachable Anions & Nutrients (QCLot: 517213)										
WT2204831-001	BROMACIL BASELINE	phosphate, ortho- (as P)	14265-44-2	E378	ND mg/kg	0.098 mg/kg	ND	70.0	130	----
Leachable Anions & Nutrients (QCLot: 517251)										
WT2204725-001	Anonymous	phosphate, ortho- (as P)	14265-44-2	E378	ND mg/kg	0.098 mg/kg	ND	70.0	130	----
Herbicides (QCLot: 511465)										
SK2202468-018	Anonymous	bromacil	314-40-9	E706A	0.00933 mg/kg	0.01 mg/kg	93.3	50.0	130	----
Pesticides (QCLot: 511464)										
SK2202468-018	Anonymous	tebuthiuron	34014-18-1	E751D	0.000407 mg/kg	0.0004 mg/kg	104	60.0	140	----

Reference Material (RM) Report

A Reference Material (RM) is a homogenous material with known and well-established analyte concentrations. RMs are processed in an identical manner to test samples, and are used to monitor and control the accuracy and precision of a test method for a typical sample matrix. RM results are expressed as percent recovery of the target analyte concentration. RM targets may be certified target concentrations provided by the RM supplier, or may be ALS long-term mean values (for empirical test methods).

Sub-Matrix:

					Reference Material (RM) Report				
					RM Target	Recovery (%)	Recovery Limits (%)		
Laboratory sample ID	Reference Material ID	Analyte	CAS Number	Method	Concentration	RM	Low	High	Qualifier
Metals (QCLot: 513191)									
	RM	aluminum	7429-90-5	E440	9817 mg/kg	114	70.0	130	----
	RM	antimony	7440-36-0	E440	3.99 mg/kg	109	70.0	130	----
	RM	arsenic	7440-38-2	E440	3.73 mg/kg	102	70.0	130	----
	RM	barium	7440-39-3	E440	105 mg/kg	110	70.0	130	----
	RM	beryllium	7440-41-7	E440	0.349 mg/kg	102	70.0	130	----
	RM	boron	7440-42-8	E440	8.5 mg/kg	116	40.0	160	----
	RM	cadmium	7440-43-9	E440	0.91 mg/kg	105	70.0	130	----
	RM	calcium	7440-70-2	E440	31082 mg/kg	102	70.0	130	----
	RM	chromium	7440-47-3	E440	101 mg/kg	107	70.0	130	----
	RM	cobalt	7440-48-4	E440	6.9 mg/kg	105	70.0	130	----
	RM	copper	7440-50-8	E440	123 mg/kg	105	70.0	130	----
	RM	iron	7439-89-6	E440	23558 mg/kg	105	70.0	130	----
	RM	lead	7439-92-1	E440	267 mg/kg	98.5	70.0	130	----
	RM	lithium	7439-93-2	E440	9.5 mg/kg	96.5	70.0	130	----
	RM	magnesium	7439-95-4	E440	5509 mg/kg	108	70.0	130	----
	RM	manganese	7439-96-5	E440	269 mg/kg	106	70.0	130	----
	RM	molybdenum	7439-98-7	E440	1.03 mg/kg	104	70.0	130	----
	RM	nickel	7440-02-0	E440	26.7 mg/kg	103	70.0	130	----
	RM	phosphorus	7723-14-0	E440	752 mg/kg	98.7	70.0	130	----
	RM	potassium	7440-09-7	E440	1587 mg/kg	111	70.0	130	----
	RM	silver	7440-22-4	E440	4.06 mg/kg	115	70.0	130	----
	RM	sodium	7440-23-5	E440	797 mg/kg	109	70.0	130	----
	RM	strontium	7440-24-6	E440	86.1 mg/kg	103	70.0	130	----
	RM	thallium	7440-28-0	E440	0.0786 mg/kg	102	40.0	160	----
	RM	tin	7440-31-5	E440	10.6 mg/kg	103	70.0	130	----
	RM	titanium	7440-32-6	E440	839 mg/kg	115	70.0	130	----
	RM	uranium	7440-61-1	E440	0.52 mg/kg	105	70.0	130	----
	RM	vanadium	7440-62-2	E440	32.7 mg/kg	107	70.0	130	----
	RM	zinc	7440-66-6	E440	297 mg/kg	101	70.0	130	----

Sub-Matrix:

Laboratory sample ID	Reference Material ID	Analyte	CAS Number	Method	Reference Material (RM) Report: RM Target Concentration	Recovery (%): RM	Recovery Limits (%): Low	Recovery Limits (%): High	Qualifier
Metals (QCLot: 513191) - continued									
	RM	zirconium	7440-67-7	E440	5.73 mg/kg	114	70.0	130	----
Metals (QCLot: 513192)									
	RM	mercury	7439-97-6	E510	0.0585 mg/kg	115	70.0	130	----
Leachable Anions & Nutrients (QCLot: 512789)									
	RM	Kjeldahl nitrogen, total [TKN]	----	E319	1040 mg/kg	91.2	80.0	120	----
Leachable Anions & Nutrients (QCLot: 517214)									
	RM	bromide, leachable	24959-67-9	E235.Br	70.3 mg/kg	97.7	60.0	140	----
Aggregate Organics (QCLot: 512644)									
	RM	carbon, total organic [TOC]	----	E357	0.437 %	125	70.0	130	----

Chain of Custody (COC) / Analytical Request Form

COC Number: 20 - 948703

Canada Toll Free: 1 800 668 9878

Page of

ALS www.alsglobal.com

Environmental Division Waterloo
Work Order Reference
WT2204831

Telephone : +1 519 886 6910

Report To	Contact and company name below will appear on the final report
Company:	Vertex environmental inc.
Contact:	Eric Cowon
Phone:	
	Company address below will appear on the final report
Street:	40 McBrine Dr.
City/Province:	Kitchener
Postal Code:	
Invoice To	Same as Report To ☐ YES ☑ NO
	Copy of Invoice with Report ☑ YES ☐ NO
Company:	Vertex environmental inc.
Contact:	Accounting

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 ericc@vertexenvironmental.ca

Email 3 mahshidj@vertexenvironmental.ca

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 accountspayable@vertexenvironmental.ca

Turnaround Time (TAT) Requested

☑ Routine [R] if received by 3pm M-F - no surcharges apply

☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimun

☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimu

☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimu

☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimur

☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Addi may apply to rush requests on weekends, statutory holidays and non-rc

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please

Project Information

ALS Account # / Quote #:

Job #: VE 1034

PO / AFE:

LSD:

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#

Major/Minor Code: Routing Code:

Requisitioner:

Location:

ALS Lab Work Order # (ALS use only): WT2204831

ALS Contact: Rick H. Sampler: MJ

Analysis Re

Indicate Filtered (F), Preserved (P) or Filtered ar

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	TOC	Heavy metals	Total nitrogen	ortho-P	pH	moisture content	Bromide	Heterotrophic plate count	SAMPLES ON HOLD	EXTENDED STORAGE REQUIR	SUSPECTED HAZARD (see not
	Bromacil Baseline	01-06-22	12:15	soil	3	✓	✓	✓	✓	✓	✓	✓	✓			
	Tebuthiuron Baseline	01-06-22	12:15	soil	3	✓	✓	✓	✓	✓	✓		✓			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C				FINAL COOLER TEMPERATURES °C			
				21.3			

SHIPMENT RELEASE (client use)

Released by:	Date:	Time:
Mahshid Jannati	01-06-22	2pm

INITIAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:

FINAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:
HDJ	JUNE 1	1520

WHITE - LABORATORY COPY YELLOW - CLIENT COPY

AUG 2020 FRONT

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a **Regulated Drinking Water (DW) System**, please submit using an **Authorized DW COC form**.

LABORATORY CERTIFICATES OF ANALYSES

TWO-WEEK SAMPLING EVENT

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Report Transmission Cover Page

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1587245**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Jul 21, 2022
		LSD:		Date Reported:	Jul 28, 2022
		P.O.:	71376	Report Number:	2770579
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

Contact	Company	Address
Accounts Payable: **Brenda Dziwenka**	**InnoTech Alberta Inc.**	Financial Services, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5133 Fax: (780) 450-5542 Email: innotech-finance@albertainnovates.ca

Delivery	Format	Deliverables
Email - Multiple Deliverables By Lot	PDF	COC / Invoice
Email - Single Deliverable	PDF	Test Report

Les Spink	**InnoTech Alberta Inc.**	PO Box 8330, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5033 Fax: (780) 450-5083 Email: leslie.spink@albertainnovates.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / Invoice

Simone Levy	**InnoTech Alberta Inc.**	Bag 4000, Hwy 16A & 75 Street Vegreville, AB T9C 1T4 Phone: (780) 450-5474 Fax: (780) 913-0178 Email: Simone.levy@innotechalberta.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / COA
Email - Merge Deliverables	PDF	COC / Test Report
Email - Merge Deliverables	PDF	COC / Test Report / Invoice
Email - Single Deliverable	Standard Crosstab Without Tabs	Test Report

Victor Bachmann	**InnoTech Alberta Inc.**	1 Oil Path Dr. Devon, AB T9G 1A8 Phone: (780) 987-8635 Fax: (780) 450-5333 Email: victor.bachmann@innotechalberta.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	Test Report

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Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1587245**
Control Number:
Date Received: Jul 21, 2022
Date Reported: Jul 28, 2022
Report Number: 2770579

		Reference Number	1587245-1	1587245-2	1587245-3
		Sample Date	Jul 18, 2022	Jul 18, 2022	Jul 18, 2022
		Sample Time	16:00	16:00	16:00
		Sample Location			
		Sample Description	Bromacil- Control / soil / 23.1°C	Bromacil- BOS 200+ / soil / 23.1°C	Bromacil- CAT 100 / soil / 23.1°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.202	0.014	0.051	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	104	92	99	50-140

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Analytical Report

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		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Jul 21, 2022
		LSD:		Date Reported:	Jul 28, 2022
		P.O.:	71376	Report Number:	2770579
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

		Reference Number	1587245-4	1587245-5	1587245-6	
		Sample Date	Jul 18, 2022	Jul 18, 2022	Jul 18, 2022	
		Sample Time	16:00	16:00	16:00	
		Sample Location				
		Sample Description	Bromacil- Sim BOS 200+ / soil / 23.1°C	Bromacil- Sim CAT 100 / soil / 23.1°C	Bromacil- ISCR / soil / 23.1°C	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.118	0.050	0.198	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	110	109	112	50-140

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		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Jul 21, 2022
		LSD:		Date Reported:	Jul 28, 2022
		P.O.:	71376	Report Number:	2770579
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

		Reference Number	1587245-7	1587245-8	1587245-9
		Sample Date	Jul 18, 2022	Jul 18, 2022	Jul 18, 2022
		Sample Time	16:00	16:00	16:00
		Sample Location			
		Sample Description	Bromacil- ISCR+ / soil / 23.1°C	Bromacil- BOS200+ Surf / soil / 23.1°C	Bromacil- CAT 100 Surf / soil / 23.1°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.106	0.017	0.066	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	97	88	88	50-140

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Analytical Report

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PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1587245**
Control Number:
Date Received: Jul 21, 2022
Date Reported: Jul 28, 2022
Report Number: 2770579

		Reference Number	1587245-10	1587245-11	1587245-12
		Sample Date	Jul 18, 2022	Jul 18, 2022	Jul 18, 2022
		Sample Time	16:00	16:00	16:00
		Sample Location			
		Sample Description	Bromacil- Sim BOS Surf / soil / 23.1°C	Bromacil- Sim CAT Surf / soil / 23.1°C	Teb- Control / soil / 23.1°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.068	0.027		0.008
Tebuthiuron	Dry Weight	mg/kg			0.137	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	87	90	92	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1587245**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Jul 21, 2022
		LSD:		Date Reported:	Jul 28, 2022
		P.O.:	71376	Report Number:	2770579
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

		Reference Number	1587245-13	1587245-14	1587245-15	
		Sample Date	Jul 18, 2022	Jul 18, 2022	Jul 18, 2022	
		Sample Time	16:00	16:00	16:00	
		Sample Location				
		Sample Description	Teb- BOS 200+ / soil / 23.1°C	Teb- CAT 100 / soil / 23.1°C	Teb- Sim BOS 200+ / soil / 23.1°C	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.006	0.039	0.114	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	61	96	102	50-140

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Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1587245**
Control Number:
Date Received: Jul 21, 2022
Date Reported: Jul 28, 2022
Report Number: 2770579

		Reference Number	1587245-16	1587245-17	1587245-18
		Sample Date	Jul 18, 2022	Jul 18, 2022	Jul 18, 2022
		Sample Time	16:00	16:00	16:00
		Sample Location			
		Sample Description	Teb- Sim CAT 100 / soil / 23.1°C	Teb- ISCR / soil / 23.1°C	Teb- ISCR+ / soil / 23.1°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.095	0.111	0.079	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	91	98	89	50-140

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Analytical Report

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Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1587245**
Control Number:
Date Received: Jul 21, 2022
Date Reported: Jul 28, 2022
Report Number: 2770579

		Reference Number	1587245-19	1587245-20	1587245-21
		Sample Date	Jul 18, 2022	Jul 18, 2022	Jul 18, 2022
		Sample Time	16:00	16:00	16:00
		Sample Location			
		Sample Description	Teb- BOS200+ Surf / soil / 23.1°C	Teb- CAT 100 Surf / soil / 23.1°C	Teb- Sim BOS Surf / soil / 23.1°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.015	0.076	0.107	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	81	81	83	50-140

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Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1587245**
Control Number:
Date Received: Jul 21, 2022
Date Reported: Jul 28, 2022
Report Number: 2770579

Reference Number	1587245-22
Sample Date	Jul 18, 2022
Sample Time	16:00
Sample Location	
Sample Description	Teb- Sim CAT Surf / soil / 23.1°C
Matrix	Soil

Analyte		Units	Results	Results	Results	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.106			0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	90			50-140

Approved by:

Jimmy Tran
Operations Manager

Data have been validated by Analytical Quality Control and Element's Integrated Data Validation System (IDVS).
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Quality Control

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1587245**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Jul 21, 2022
		LSD:		Date Reported:	Jul 28, 2022
		P.O.:	71376	Report Number:	2770579
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

Sterilants in Soil

Blanks	**Units**	**Measured**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	ng	0	-0.030	0.030		yes
Date Acquired:	July 24, 2022					
Calibration Check	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	ng	105.00	80	120		yes
Date Acquired:	July 24, 2022					
Replicates	**Units**	**Replicate 1**	**Replicate 2**	**% RSD Criteria**	**Absolute Criteria**	**Passed QC**
Bromacil	mg/kg	0.202	0.200	50	0.040	yes
Date Acquired:	July 24, 2022					
Matrix Spike	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	mg/kg	73	40	140		yes
Date Acquired:	July 24, 2022					

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Methodology and Notes

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1587245**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Jul 21, 2022
		LSD:		Date Reported:	Jul 28, 2022
		P.O.:	71376	Report Number:	2770579
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

Method of Analysis

Method Name	Reference		Method	Date Analysis Started	Location
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Jul 24, 2022	Element Calgary
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Jul 28, 2022	Element Calgary

** Reference Method Modified*

References

US EPA	US Environmental Protection Agency Test Methods

Please direct any inquiries regarding this report to our Client Services group.
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ALS Environmental

CERTIFICATE OF ANALYSIS

Work Order	: **WT2207889**	Page	: 1 of 4
Client	: **Vertex Environmental Inc.**	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo ON Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 19-Jul-2022 14:00
PO	: ----	Date Analysis Commenced	: 19-Jul-2022
C-O-C number	: 20-955327	Issue Date	: 25-Jul-2022 14:51
Sampler	: MJ		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 22		
No. of samples analysed	: 22		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. This document shall not be reproduced, except in full.

This Certificate of Analysis contains the following information:

- General Comments
- Analytical Results

Additional information pertinent to this report will be found in the following separate attachments: Quality Control Report, QC Interpretive report to assist with Quality Review and Sample Receipt Notification (SRN).

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is conducted in accordance with US FDA 21 CFR Part 11.

Signatories	*Position*	*Laboratory Department*
Greg Pokocky	Supervisor - Inorganic	Inorganics, Waterloo, Ontario
Joseph Scharbach		Centralized Prep, Waterloo, Ontario

General Comments

The analytical methods used by ALS are developed using internationally recognized reference methods (where available), such as those published by US EPA, APHA Standard Methods, ASTM, ISO, Environment Canada, BC MOE, and Ontario MOE. Refer to the ALS Quality Control Interpretive report (QCI) for applicable references and methodology summaries. Reference methods may incorporate modifications to improve performance.

Where a reported less than (<) result is higher than the LOR, this may be due to primary sample extract/digestate dilution and/or insufficient sample for analysis.

Where the LOR of a reported result differs from standard LOR, this may be due to high moisture content, insufficient sample (reduced weight employed) or matrix interference.

Please refer to Quality Control Interpretive report (QCI) for information regarding Holding Time compliance.

Key : CAS Number: Chemical Abstracts Services number is a unique identifier assigned to discrete substances
LOR: Limit of Reporting (detection limit).

Unit	*Description*
%	percent
mg/kg	milligrams per kilogram
pH units	pH units

<: less than.

>: greater than.

Surrogate: An analyte that is similar in behavior to target analyte(s), but that does not occur naturally in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery.

Test results reported relate only to the samples as received by the laboratory.

UNLESS OTHERWISE STATED on SRN or QCI Report, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.

Analytical Results

Sub-Matrix: Soil (Matrix: Soil/Solid)				Client sample ID	TEB-CONTROL	TEB-BOS 200+	TEB-CAT 100	TEB-SIM BOS 200+	TEB-SIM CAT 100
				Client sampling date / time	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00
Analyte	CAS Number	Method	LOR	Unit	WT2207889-001	WT2207889-002	WT2207889-003	WT2207889-004	WT2207889-005
					Result	Result	Result	Result	Result
Physical Tests									
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.38	7.70	7.48	7.41	7.18

Please refer to the General Comments section for an explanation of any qualifiers detected.

Analytical Results

Sub-Matrix: Soil (Matrix: Soil/Solid)				Client sample ID	TEB-ISCR	TEB-ISCR+	TEB-BOS 200+ SURF	TEB-CAT 100 SURF	TEB-SIM BOS SURF
				Client sampling date / time	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00
Analyte	CAS Number	Method	LOR	Unit	WT2207889-006	WT2207889-007	WT2207889-008	WT2207889-009	WT2207889-010
					Result	Result	Result	Result	Result
Physical Tests									
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.51	4.59	7.49	7.20	7.52

Please refer to the General Comments section for an explanation of any qualifiers detected.

Analytical Results

Sub-Matrix: Soil (Matrix: Soil/Solid)				Client sample ID	TEB-SIM CAT SURF	BROMACIL-CONTROL	BROMACIL-BOS 200+	BROMACIL-CAT 100	BROMACIL-SIM BOS 200+
				Client sampling date / time	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00
Analyte	CAS Number	Method	LOR	Unit	WT2207889-011	WT2207889-012	WT2207889-013	WT2207889-014	WT2207889-015
					Result	Result	Result	Result	Result
Physical Tests									
moisture	----	E144	0.25	%	----	32.2	29.2	28.0	30.2
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.14	7.30	7.41	7.22	7.42
Leachable Anions & Nutrients									
bromide, leachable	24959-67-9	E235.Br	0.50	mg/kg	----	<0.51	<0.50	<0.50	<0.50

Please refer to the General Comments section for an explanation of any qualifiers detected.

Analytical Results

Sub-Matrix: Soil (Matrix: Soil/Solid)				Client sample ID	BROMACIL-SIM CAT 100	BROMACIL-ISC R	BROMACIL-ISC R+	BROMACIL-BOS 200+ SURF	BROMACIL-CAT 100 SURF
				Client sampling date / time	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00	18-Jul-2022 16:00
Analyte	CAS Number	Method	LOR	Unit	WT2207889-016	WT2207889-017	WT2207889-018	WT2207889-019	WT2207889-020
					Result	Result	Result	Result	Result
Physical Tests									
moisture	----	E144	0.25	%	29.2	31.4	29.7	29.2	23.0
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.10	7.53	4.64	7.46	7.12
Leachable Anions & Nutrients									
bromide, leachable	24959-67-9	E235.Br	0.50	mg/kg	<0.50	<0.50	0.70	<0.50	<0.51

Please refer to the General Comments section for an explanation of any qualifiers detected.

Analytical Results

Sub-Matrix: Soil (Matrix: Soil/Solid)				Client sample ID	BROMACIL-SIM BOS SURF	BROMACIL-SIM CAT SURF	----	----	----
				Client sampling date / time	18-Jul-2022 16:00	18-Jul-2022 16:00	----	----	----
Analyte	CAS Number	Method	LOR	Unit	WT2207889-021	WT2207889-022	--------	--------	--------
					Result	Result	----	----	----
Physical Tests									
moisture	----	E144	0.25	%	29.7	23.8	----	----	----
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.58	7.09	----	----	----
Leachable Anions & Nutrients									
bromide, leachable	24959-67-9	E235.Br	0.50	mg/kg	<0.50	<0.50	----	----	----

Please refer to the General Comments section for an explanation of any qualifiers detected.

QUALITY CONTROL INTERPRETIVE REPORT

Work Order	: **WT2207889**	Page	: 1 of 10
Client	: **Vertex Environmental Inc.**	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo, Ontario Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 19-Jul-2022 14:00
PO	: ----	Issue Date	: 25-Jul-2022 14:51
C-O-C number	: 20-955327		
Sampler	: MJ		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 22		
No. of samples analysed	: 22		

This report is automatically generated by the ALS LIMS (Laboratory Information Management System) through evaluation of Quality Control (QC) results and other QA parameters associated with this submission, and is intended to facilitate rapid data validation by auditors or reviewers. The report highlights any exceptions and outliers to ALS Data Quality Objectives, provides holding time details and exceptions, summarizes QC sample frequencies, and lists applicable methodology references and summaries.

Key

Anonymous: Refers to samples which are not part of this work order, but which formed part of the QC process lot.
CAS Number: Chemical Abstracts Service number is a unique identifier assigned to discrete substances.
DQO: Data Quality Objective.
LOR: Limit of Reporting (detection limit).
RPD: Relative Percent Difference.

Workorder Comments

Holding times are displayed as "---" if no guidance exists from CCME, Canadian provinces, or broadly recognized international references.

Summary of Outliers

Outliers : Quality Control Samples

- No Method Blank value outliers occur.
- No Duplicate outliers occur.
- No Laboratory Control Sample (LCS) outliers occur
- No Test sample Surrogate recovery outliers exist.

Outliers: Reference Material (RM) Samples

- No Reference Material (RM) Sample outliers occur.

Outliers : Analysis Holding Time Compliance (Breaches)

- No Analysis Holding Time Outliers exist.

Outliers : Frequency of Quality Control Samples

- No Quality Control Sample Frequency Outliers occur.

Analysis Holding Time Compliance

This report summarizes extraction / preparation and analysis times and compares each with ALS recommended holding times, which are selected to meet known provincial and /or federal requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by organizations such as CCME, US EPA, APHA Standard Methods, ASTM, or Environment Canada (where available). Dates and holding times reported below represent the first dates of extraction or analysis. If subsequent tests or dilutions exceeded holding times, qualifiers are added (refer to COA).

If samples are identified below as having been analyzed or extracted outside of recommended holding times, measurement uncertainties may be increased, and this should be taken into consideration when interpreting results.

Where actual sampling date is not provided on the chain of custody, the date of receipt with time at 00:00 is used for calculation purposes.

Where only the sample date without time is provided on the chain of custody, the sampling date at 00:00 is used for calculation purposes.

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-BOS 200+	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-BOS 200+ SURF	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-CAT 100	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-CAT 100 SURF	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-CONTROL	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-ISCR	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-ISCR+	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation: Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis: Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-SIM BOS 200+	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-SIM BOS SURF	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-SIM CAT 100	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Leachable Anions & Nutrients : Leachable Bromide in Soil/Solid by IC										
Glass soil jar/Teflon lined cap BROMACIL-SIM CAT SURF	E235.Br	18-Jul-2022	20-Jul-2022	----	----		20-Jul-2022	28 days	2 days	✓
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-BOS 200+	E144	18-Jul-2022	----	----	----		19-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-BOS 200+ SURF	E144	18-Jul-2022	----	----	----		19-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-CAT 100	E144	18-Jul-2022	----	----	----		19-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-CAT 100 SURF	E144	18-Jul-2022	----	----	----		20-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-CONTROL	E144	18-Jul-2022	----	----	----		19-Jul-2022	----	----	

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-ISCR	E144	18-Jul-2022	----	----	----		19-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-ISCR+	E144	18-Jul-2022	----	----	----		19-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-SIM BOS 200+	E144	18-Jul-2022	----	----	----		19-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-SIM BOS SURF	E144	18-Jul-2022	----	----	----		20-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-SIM CAT 100	E144	18-Jul-2022	----	----	----		19-Jul-2022	----	----	
Physical Tests : Moisture Content by Gravimetry										
Glass soil jar/Teflon lined cap BROMACIL-SIM CAT SURF	E144	18-Jul-2022	----	----	----		20-Jul-2022	----	----	
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-BOS 200+	E108A	18-Jul-2022	20-Jul-2022	----	----		21-Jul-2022	30 days	3 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-CAT 100	E108A	18-Jul-2022	20-Jul-2022	----	----		21-Jul-2022	30 days	3 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-CONTROL	E108A	18-Jul-2022	20-Jul-2022	----	----		21-Jul-2022	30 days	3 days	✓

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-BOS 200+	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-BOS 200+ SURF	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-CAT 100	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-CAT 100 SURF	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-CONTROL	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-ISCR	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-ISCR+	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-SIM BOS 200+	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-SIM BOS SURF	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-SIM CAT 100	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap BROMACIL-SIM CAT SURF	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-BOS 200+ SURF	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-CAT 100 SURF	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-ISCR	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-ISCR+	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-SIM BOS 200+	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-SIM BOS SURF	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-SIM CAT 100	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation: Preparation Date	Holding Times: Rec	Holding Times: Actual	Eval	Analysis: Analysis Date	Holding Times: Rec	Holding Times: Actual	Eval
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
TEB-SIM CAT SURF	E108A	18-Jul-2022	20-Jul-2022	----	----		22-Jul-2022	30 days	4 days	✓

Legend & Qualifier Definitions

Rec. HT: ALS recommended hold time (see units).

Quality Control Parameter Frequency Compliance

The following report summarizes the frequency of laboratory QC samples analyzed within the analytical batches (QC lots) in which the submitted samples were processed. The actual frequency should be greater than or equal to the expected frequency.

Matrix: **Soil/Solid**

Evaluation: × = *QC frequency outside specification*; ✓ = *QC frequency within specification.*

Quality Control Sample Type			Count		Frequency (%)		
Analytical Methods	*Method*	*QC Lot #*	*QC*	*Regular*	*Actual*	*Expected*	*Evaluation*
Laboratory Duplicates (DUP)							
Leachable Bromide in Soil/Solid by IC	E235.Br	569420	1	11	9.0	5.0	✓
Moisture Content by Gravimetry	E144	569288	2	37	5.4	5.0	✓
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A	569419	2	25	8.0	5.0	✓
Laboratory Control Samples (LCS)							
Leachable Bromide in Soil/Solid by IC	E235.Br	569420	2	11	18.1	10.0	✓
Moisture Content by Gravimetry	E144	569288	2	37	5.4	5.0	✓
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A	569419	2	25	8.0	5.0	✓
Method Blanks (MB)							
Leachable Bromide in Soil/Solid by IC	E235.Br	569420	1	11	9.0	5.0	✓
Moisture Content by Gravimetry	E144	569288	2	37	5.4	5.0	✓

Methodology References and Summaries

The analytical methods used by ALS are developed using internationally recognized reference methods (where available), such as those published by US EPA, APHA Standard Methods, ASTM, ISO, Environment Canada, BC MOE, and Ontario MOE. Reference methods may incorporate modifications to improve performance (indicated by "mod").

Analytical Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A Waterloo - Environmental	Soil/Solid	MOEE E3137A	pH is determined by potentiometric measurement with a pH electrode, and is conducted at ambient laboratory temperature (normally 20 ± 5°C) and is carried out in accordance with procedures described in the Analytical Protocol (prescriptive method). A minimum 10g portion of the sample, as received, is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling, or decanting and then analyzed using a pH meter and electrode.
Moisture Content by Gravimetry	E144 Waterloo - Environmental	Soil/Solid	CCME PHC in Soil - Tier 1	Moisture is measured gravimetrically by drying the sample at 105°C. Moisture content is calculated as the weight loss (due to water) divided by the wet weight of the sample, expressed as a percentage.
Leachable Bromide in Soil/Solid by IC	E235.Br Waterloo - Environmental	Soil/Solid	CSSS Ch. 15 (mod)/EPA 300.1 (mod)	Inorganic anions are analyzed by Ion Chromatography with conductivity and/or UV detection using a soil sample that has been added in a defined ratio of soil to deionized water, then shaken well and allowed to settle. Anions are measured in the fluid that is observed in the upper layer.

Preparation Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
Leach 1:2 Soil : 0.01CaCl2 - As Received for pH	EP108A Waterloo - Environmental	Soil/Solid	MOEE E3137A	A minimum 10g portion of the sample, as received, is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling or decanting and then analyzed using a pH meter and electrode.
Leach for Metals and Anions	EP441 Waterloo - Environmental	Soil/Solid	In-House	This analysis is carried out using a leaching procedure which involves the gentle tumbling of the sample in a specified leaching solution (typically deionized water) for a specific length of time.

QUALITY CONTROL REPORT

Work Order	: **WT2207889**	Page	: 1 of 4
Client	: Vertex Environmental Inc.	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo, Ontario Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 19-Jul-2022 14:00
PO	: ----	Date Analysis Commenced	: 19-Jul-2022
C-O-C number	: 20-955327	Issue Date	: 25-Jul-2022 14:51
Sampler	: MJ		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 22		
No. of samples analysed	: 22		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. This document shall not be reproduced, except in full.

This Quality Control Report contains the following information:

- Laboratory Duplicate (DUP) Report; Relative Percent Difference (RPD) and Data Quality Objectives
- Reference Material (RM) Report; Recovery and Data Quality Objectives
- Method Blank (MB) Report; Recovery and Data Quality Objectives
- Laboratory Control Sample (LCS) Report; Recovery and Data Quality Objectives

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is conducted in accordance with US FDA 21 CFR Part 11.

Signatories	*Position*	*Laboratory Department*
Greg Pokocky	Supervisor - Inorganic	Waterloo Inorganics, Waterloo, Ontario
Joseph Scharbach		Waterloo Centralized Prep, Waterloo, Ontario

General Comments

The ALS Quality Control (QC) report is optionally provided to ALS clients upon request. ALS test methods include comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against predetermined Data Quality Objectives (DQOs) to provide confidence in the accuracy of associated test results. This report contains detailed results for all QC results applicable to this sample submission. Please refer to the ALS Quality Control Interpretation report (QCI) for applicable method references and methodology summaries.

Key :

Anonymous = Refers to samples which are not part of this work order, but which formed part of the QC process lot.
CAS Number = Chemical Abstracts Service number is a unique identifier assigned to discrete substances.
DQO = Data Quality Objective.
LOR = Limit of Reporting (detection limit).
RPD = Relative Percent Difference
# = Indicates a QC result that did not meet the ALS DQO.

Workorder Comments

Holding times are displayed as "---" if no guidance exists from CCME, Canadian provinces, or broadly recognized international references.

Laboratory Duplicate (DUP) Report

A Laboratory Duplicate (DUP) is a randomly selected intralaboratory replicate sample. Laboratory Duplicates provide information regarding method precision and sample heterogeneity. ALS DQOs for Laboratory Duplicates are expressed as test-specific limits for Relative Percent Difference (RPD), or as an absolute difference limit of 2 times the LOR for low concentration duplicates within ~ 4-10 times the LOR (cut-off is test-specific).

Sub-Matrix: **Soil/Solid**

					Laboratory Duplicate (DUP) Report						
Laboratory sample ID	*Client sample ID*	*Analyte*	*CAS Number*	*Method*	*LOR*	*Unit*	*Original Result*	*Duplicate Result*	*RPD(%) or Difference*	*Duplicate Limits*	*Qualifier*
Physical Tests (QC Lot: 569288)											
WT2207254-039	Anonymous	moisture	----	E144	0.25	%	8.57	9.49	10.2%	20%	----
Physical Tests (QC Lot: 569419)											
WT2207889-004	TEB-SIM BOS 200+	pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.41	7.39	0.02	Diff <2x LOR	----
Physical Tests (QC Lot: 569438)											
WT2207916-001	Anonymous	moisture	----	E144	0.25	%	3.41	3.84	11.9%	20%	----
Physical Tests (QC Lot: 569551)											
WT2207861-017	Anonymous	pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.08	7.11	0.03	Diff <2x LOR	----
Leachable Anions & Nutrients (QC Lot: 569420)											
WT2207889-012	BROMACIL-CONTROL	bromide, leachable	24959-67-9	E235.Br	0.50	mg/kg	<0.51	<0.50	0.50	Diff <2x LOR	----

Method Blank (MB) Report

A Method Blank is an analyte-free matrix that undergoes sample processing identical to that carried out for test samples. Method Blank results are used to monitor and control for potential contamination from the laboratory environment and reagents. For most tests, the DQO for Method Blanks is for the result to be < LOR.

Sub-Matrix: **Soil/Solid**

Analyte	CAS Number	Method	LOR	Unit	Result	Qualifier
Physical Tests (QCLot: 569288)						
moisture	----	E144	0.25	%	<0.25	----
Physical Tests (QCLot: 569438)						
moisture	----	E144	0.25	%	<0.25	----
Leachable Anions & Nutrients (QCLot: 569420)						
bromide, leachable	24959-67-9	E235.Br	0.5	mg/kg	<0.50	----

Laboratory Control Sample (LCS) Report

A Laboratory Control Sample (LCS) is an analyte-free matrix that has been fortified (spiked) with test analytes at known concentration and processed in an identical manner to test samples. LCS results are expressed as percent recovery, and are used to monitor and control test method accuracy and precision, independent of test sample matrix.

Sub-Matrix: **Soil/Solid**

					Laboratory Control Sample (LCS) Report				
					Spike	Recovery (%)	Recovery Limits (%)		
Analyte	CAS Number	Method	LOR	Unit	Concentration	LCS	Low	High	Qualifier
Physical Tests (QCLot: 569288)									
moisture	----	E144	0.25	%	50 %	100	90.0	110	----
Physical Tests (QCLot: 569419)									
pH (1:2 soil:CaCl2-aq)	----	E108A	----	pH units	7 pH units	99.8	98.0	102	----
Physical Tests (QCLot: 569438)									
moisture	----	E144	0.25	%	50 %	100	90.0	110	----
Physical Tests (QCLot: 569551)									
pH (1:2 soil:CaCl2-aq)	----	E108A	----	pH units	7 pH units	100	98.0	102	----
Leachable Anions & Nutrients (QCLot: 569420)									
bromide, leachable	24959-67-9	E235.Br	0.5	mg/kg	2.5 mg/kg	104	70.0	130	----

Reference Material (RM) Report

A Reference Material (RM) is a homogenous material with known and well-established analyte concentrations. RMs are processed in an identical manner to test samples, and are used to monitor and control the accuracy and precision of a test method for a typical sample matrix. RM results are expressed as percent recovery of the target analyte concentration. RM targets may be certified target concentrations provided by the RM supplier, or may be ALS long-term mean values (for empirical test methods).

Sub-Matrix:

					Reference Material (RM) Report				
					RM Target	Recovery (%)	Recovery Limits (%)		
Laboratory sample ID	Reference Material ID	Analyte	CAS Number	Method	Concentration	RM	Low	High	Qualifier
Leachable Anions & Nutrients (QCLot: 569420)									
	RM	bromide, leachable	24959-67-9	E235.Br	23.9 mg/kg	87.4	60.0	140	----

Chain of Custody (COC) / Analytical Request Form

COC Number: 20

Page

Canada Toll Free: 1 800 668 9878

www.alsglobal.com

Environmental Division Waterloo
Work Order Reference
WT2207889

Telephone : – 1 519 886 6910

Report To — Contact and company name below will appear on the final report

Company:	Vertex environmental inc.
Contact:	Eric Cowan
Phone:	

Company address below will appear on the final report

Street:	40 McBrine Dr.
City/Province:	Kitchener
Postal Code:	

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)
Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A
☐ Compare Results to Criteria on Report - provide details below if box checked
Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax	
Email 2	eric@vertexenvironmental.ca
Email 3	mahshidj@vertexenvironmental.ca

Turnaround Time (TAT) Requested

- ☐ Routine [R] if received by 3pm M-F - no surcharges apply
- ☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum
- ☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum
- ☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum
- ☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum
- ☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additi may apply to rush requests on weekends, statutory holidays and non-rou

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please contact your AM to confirm availability.

Invoice To

Same as Report To	☐ YES ☑ NO
Copy of Invoice with Report	☑ YES ☐ NO
Company:	Vertex environmental inc.
Contact:	Accounting

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax	
Email 2	accountspayable@vertexenvironmental.ca

Project Information

ALS Account # / Quote #:	
Job #:	VE 1034
PO / AFE:	
LSD:	

Oil and Gas Required Fields (client use)

AFE/Cost Center:	PO#
Major/Minor Code:	Routing Code:
Requisitioner:	
Location:	

ALS Lab Work Order # (ALS use only): WT2207889

ALS Contact: Rick H. Sampler: MJ

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	pH	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	Teb - control	18-07-22	4 pm	soil	2	✓	✓			
	Teb - BOS 200+	↓	↓	↓	2	✓	✓			
	Teb - CAT 100				2	✓	✓			
	Teb - Sim BOS 200+				2	✓	✓			
	Teb - Sim CAT 100				2	✓	✓			
	Teb - ISCR				2	✓	✓			
	Teb - ISCR+				2	✓	✓			
	Teb - BOS 200+ surf				2	✓	✓			
	Teb - CAT 100 surf				2	✓	✓			
	Teb - Sim BOS surf				2	✓	✓			
	Teb - Sim CAT surf				2	✓	✓			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☑ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C				FINAL COOLER TEMPERATURES °C		
					24.8	

SHIPMENT RELEASE (client use)

Released by:	Date:	Time:
Mahshid Jannati	19-07-22	

INITIAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:

FINAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:
	7/19/22	14:00

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION

WHITE - LABORATORY COPY YELLOW - CLIENT COPY

AUG 2020 FRONT

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a **Regulated Drinking Water (DW) System**, please submit using an **Authorized DW COC form**.

Chain of Custody (COC) / Analytical Request Form

COC Number: 20

Page

Canada Toll Free: 1 800 668 9878

www.alsglobal.com

Environmental Division Waterloo
Work Order Reference
WT2207889

Telephone : +1 519 886 6910

Report To	Contact and company name below will appear on the final report
Company:	Vertex environmental inc.
Contact:	Eric Cowan
Phone:	
	Company address below will appear on the final report
Street:	40 McBrine Dr.
City/Province:	Kitchener
Postal Code:	
Invoice To	Same as Report To ☐ YES ☑ NO
	Copy of Invoice with Report ☑ YES ☐ NO
Company:	Vertex environmental inc.
Contact:	Accounting

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 ericc@vertexenvironmental.ca

Email 3 mahshidj@vertexenvironmental.ca

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 accountspayable@vertexenvironmental.ca

Turnaround Time (TAT) Requested

- ☐ Routine [R] if received by 3pm M-F - no surcharges apply
- ☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum
- ☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum
- ☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum
- ☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum
- ☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additio may apply to rush requests on weekends, statutory holidays and non-rout

Date and Time Required for all E&P TATs: dd-mmm-yy hh:mm am/pm

For all tests with rush TATs requested, please contact your AM to confirm availability.

Project Information

ALS Account # / Quote #:

Job #: VE 1034

PO / AFE:

LSD:

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#

Major/Minor Code: Routing Code:

Requisitioner:

Location:

ALS Lab Work Order # (ALS use only): WT2207889

ALS Contact: Rick H. Sampler: MJ

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	pH	Bromide	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	Bromacil - Control	18-07-22	4 pm	soil	2	✓	✓	✓			
	Bromacil - BOS 200+	↓	↓	↓	2	✓	✓	✓			
	Bromacil - CAT 100				2	✓	✓	✓			
	Bromacil - sim BOS 200+				2	✓	✓	✓			
	Bromacil - sim CAT 100				2	✓	✓	✓			
	Bromacil - ISCR				2	✓	✓	✓			
	Bromacil - ISCR+				2	✓	✓	✓			
	Bromacil - BOS 200+ Surf				2	✓	✓	✓			
	Bromacil - CAT 100 Surf				2	✓	✓	✓			
	Bromacil - sim BOS surf				2	✓	✓	✓			
	Bromacil - sim CAT surf				2	✓	✓	✓			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☑ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C				FINAL COOLER TEMPERATURES °C			
							24-3

SHIPMENT RELEASE (client use)

Released by:	Date:	Time:
Mahshid Jamali	19-07-22	

INITIAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:

FINAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:
[signature]	7/19/22	14:00

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION

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Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a **Regulated Drinking Water (DW) System**, please submit using an **Authorized DW COC form**.

Vertex Environmental Inc.
ATTN: Eric Cowan
40 McBrine Dr
Kitchener ON N2R 1E7

Date Received: 19-JUL-22
Report Date: 28-JUL-22 09:37 (MT)
Version: FINAL

Client Phone: 519-653-8444

Certificate of Analysis

Lab Work Order #: L2723328

Project P.O. #: NOT SUBMITTED
Job Reference: VE 1034
C of C Numbers: 20-955326, 20-955327
Legal Site Desc:

Rick Hawthorne
Account Manager

[This report shall not be reproduced except in full without the written authority of the Laboratory.]

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2723328-1 TEB-CONTROL Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.0		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	37		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-2 TEB-BOS 200+ Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	29.2		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	54		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-3 TEB-CAT 100 Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	30.0		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	299000		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-4 SIM BOS 200+ Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.2		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	325000		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-5 TEB-SIM CAT 100 Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	25.2		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	595000		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-6 TEB-ISCR Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	28.5		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	508		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-7 TEB-ISCR+ Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	25.8		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	367		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2723328-7 TEB-ISCR+ Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Bacteriological Tests							
L2723328-8 TEB-BOS 200+ SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.4		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	3260		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-9 TEB-CAT 100 SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	28.1		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	2650		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-10 TEB-SIM BOS SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.5		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	3880		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-11 TEB-SIM CAT SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.9		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	4220		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-12 BROMACIL-CONTROL Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.8		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	251		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-13 BROMACIL-BOS 200+ Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	28.1		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	4680		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-14 BROMACIL-CAT 100 Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2723328-14 BROMACIL-CAT 100 Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.9		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	3280		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-15 BROMACIL-SIM BOS 200+ Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	29.3		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	2570		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-16 BROMACIL-SIM CAT 100 Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	28.7		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	16000		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-17 BROMACIL-ISCR Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.5		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	371		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-18 BROMACIL-ISCR + Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.3		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	<10		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-19 BROMACIL-BOS 200+ SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	28.0		0.25	%	19-JUL-22	20-JUL-22	R5825276
Bacteriological Tests							
Heterotrophic Plate Count	3160		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-20 BROMACIL-CAT 100 SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	25.8		0.25	%	22-JUL-22	23-JUL-22	R5828106
Bacteriological Tests							
Heterotrophic Plate Count	3420		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2723328-20 BROMACIL-CAT 100 SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Bacteriological Tests							
L2723328-21 BROMACIL-SIM BOS SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	29.7		0.25	%	22-JUL-22	23-JUL-22	R5828106
Bacteriological Tests							
Heterotrophic Plate Count	3750		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337
L2723328-22 BROMACIL-SIM CAT SURF Sampled By: MJ on 18-JUL-22 @ 16:00 Matrix: SOIL							
Physical Tests							
% Moisture	28.6		0.25	%	22-JUL-22	23-JUL-22	R5828106
Bacteriological Tests							
Heterotrophic Plate Count	1140		10	CFU/g dwt	20-JUL-22	20-JUL-22	R5829337

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

Reference Information

QC Samples with Qualifiers & Comments:

QC Type Description	Parameter	Qualifier	Applies to Sample Number(s)
Duplicate	Heterotrophic Plate Count	DUP-H	L2723328-1, -10, -11, -12, -13, -14, -15, -16, -17, -18, -19, -2, -20, -21, -22, -3, -4, -5, -6, -7, -8, -9
Duplicate	Heterotrophic Plate Count	DUP-H,J	L2723328-1, -10, -11, -12, -13, -14, -15, -16, -17, -18, -19, -2, -20, -21, -22, -3, -4, -5, -6, -7, -8, -9

Sample Parameter Qualifier key listed:

Qualifier	Description
DUP-H	Duplicate results outside ALS DQO, due to sample heterogeneity.
DUP-H,J	Duplicate results outside ALS DQO, due to sample heterogeneity. Duplicate results and limits are expressed in terms of absolute difference.

Test Method References:

ALS Test Code	Matrix	Test Description	Method Reference**
HPC-SOLID-MF-WT	Soil	HPC on sludge or solid	SM 9215D
MOISTURE-WT	Soil	% Moisture	CCME PHC in Soil - Tier 1 (mod)

** ALS test methods may incorporate modifications from specified reference methods to improve performance.

The last two letters of the above test code(s) indicate the laboratory that performed analytical analysis for that test. Refer to the list below:

Laboratory Definition Code	Laboratory Location
WT	ALS ENVIRONMENTAL - WATERLOO, ONTARIO, CANADA

Chain of Custody Numbers:

20-955326 20-955327

GLOSSARY OF REPORT TERMS

Surrogates are compounds that are similar in behaviour to target analyte(s), but that do not normally occur in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery. In reports that display the D.L. column, laboratory objectives for surrogates are listed there.
mg/kg - milligrams per kilogram based on dry weight of sample
mg/kg wwt - milligrams per kilogram based on wet weight of sample
mg/kg lwt - milligrams per kilogram based on lipid weight of sample
mg/L - unit of concentration based on volume, parts per million.
< - Less than.
D.L. - The reporting limit.
N/A - Result not available. Refer to qualifier code and definition for explanation.

Test results reported relate only to the samples as received by the laboratory.
UNLESS OTHERWISE STATED, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.
Analytical results in unsigned test reports with the DRAFT watermark are subject to change, pending final QC review.

Quality Control Report

Workorder: L2723328 Report Date: 28-JUL-22

Client: Vertex Environmental Inc.
40 McBrine Dr
Kitchener ON N2R 1E7

Contact: Eric Cowan

Test	Matrix	Reference	Result	Qualifier	Units	RPD	Limit	Analyzed
HPC-SOLID-MF-WT	**Soil**							
Batch R5829337								
WG3750871-3 DUP		**L2723328-1**						
Heterotrophic Plate Count		37	12	DUP-H,J	CFU/g dwt	25	20	20-JUL-22
WG3750871-6 DUP		**L2723328-22**						
Heterotrophic Plate Count		1140	4580	DUP-H	CFU/g dwt	120	50	20-JUL-22
WG3750871-1 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	20-JUL-22
WG3750871-2 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	20-JUL-22
WG3750871-4 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	20-JUL-22
WG3750871-5 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	20-JUL-22
MOISTURE-WT	**Soil**							
Batch R5825276								
WG3750543-3 DUP		**L2723328-2**						
% Moisture		29.2	28.3		%	3.1	20	20-JUL-22
WG3750543-2 LCS								
% Moisture			99.9		%		90-110	20-JUL-22
WG3750543-1 MB								
% Moisture			<0.25		%		0.25	20-JUL-22
Batch R5828106								
WG3751707-2 LCS								
% Moisture			100.9		%		90-110	23-JUL-22
WG3751707-1 MB								
% Moisture			<0.25		%		0.25	23-JUL-22

Quality Control Report

Legend:

Limit	ALS Control Limit (Data Quality Objectives)
DUP	Duplicate
RPD	Relative Percent Difference
N/A	Not Available
LCS	Laboratory Control Sample
SRM	Standard Reference Material
MS	Matrix Spike
MSD	Matrix Spike Duplicate
ADE	Average Desorption Efficiency
MB	Method Blank
IRM	Internal Reference Material
CRM	Certified Reference Material
CCV	Continuing Calibration Verification
CVS	Calibration Verification Standard
LCSD	Laboratory Control Sample Duplicate

Sample Parameter Qualifier Definitions:

Qualifier	Description
DUP-H	Duplicate results outside ALS DQO, due to sample heterogeneity.
DUP-H,J	Duplicate results outside ALS DQO, due to sample heterogeneity. Duplicate results and limits are expressed in terms of absolute difference.

Hold Time Exceedances:

All test results reported with this submission were conducted within ALS recommended hold times.

ALS recommended hold times may vary by province. They are assigned to meet known provincial and/or federal government requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by the US EPA, APHA Standard Methods, or Environment Canada (where available). For more information, please contact ALS.

The ALS Quality Control Report is provided to ALS clients upon request. ALS includes comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against pre-determined data quality objectives to provide confidence in the accuracy of associated test results.

Please note that this report may contain QC results from anonymous Sample Duplicates and Matrix Spikes that do not originate from this Work Order.

Chain of Custody (COC) / Analytical Request

L2723328-COFC

5320

Canada Toll Free: 1 800 668 9878

ALS www.alsglobal.com

Report To	Contact and company name below will appear on the final report
Company:	[illegible]
Contact:	[illegible]
Phone:	
	Company address below will appear on the final report
Street:	[illegible]
City/Province:	Kitchener
Postal Code:	
Invoice To	Same as Report To ☐ YES ☑ NO
	Copy of invoice with Report ☑ YES ☐ NO
Company:	[illegible]
Contact:	Accounting

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 [illegible]

Email 3 [illegible]

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 [illegible]

Turnaround Time (TAT) Requested

☐ Routine [R] if received by 3pm M-F - no surcharges apply

☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum

☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum

☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum

☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum

☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additional fees may apply to rush requests on weekends, statutory holidays and non-routine tests

AFFIX ALS BARCODE LABEL HERE (ALS use only)

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please contact your AM to confirm availability.

Project Information

ALS Account # / Quote #:

Job #: [illegible]

PO / AFE:

LSD:

ALS Lab Work Order # (ALS use only): L2723328

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#:

Major/Minor Code: Routing Code:

Requisitioner:

Location:

ALS Contact: [illegible] Sampler: [illegible]

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	pH	Bromide	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	[illegible]	18-07-22	[illegible]	[illegible]	2	✓	✓	✓			
	[illegible]				2	✓	✓	✓			
	[illegible] CAT 100				2	✓	✓	✓			
	[illegible] Sim BOS 200+				2	✓	✓	✓			
	[illegible] Sim CAT 100				2	✓	✓	✓			
	[illegible] TSCR				2	✓	✓	✓			
	[illegible] TSCR+				2	✓	✓	✓			
	[illegible] BOS 200+ Surf				2	✓	✓	✓			
	[illegible] CAT 100 Surf				2	✓	✓	✓			
	[illegible] Sim BOS Surf				2	✓	✓	✓			
	[illegible] Sim CAT Surf				2	✓	✓	✓			
						✓					

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☑ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C: FINAL COOLER TEMPERATURES °C: 24-3

SHIPMENT RELEASE (client use)

Released by: [illegible] Date: 19-07-22 Time:

INITIAL SHIPMENT RECEPTION (ALS use only)

Received by: Date: Time:

FINAL SHIPMENT RECEPTION (ALS use only)

Received by: [illegible] Date: 7/19/22 Time: 14:00

WHITE - LABORATORY COPY YELLOW - CLIENT COPY

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a Regulated Drinking Water (DW) System, please submit using an Authorized DW COC form.

Chain of Custody (COC) / Analytical Request Form

Canada Toll Free: 1 800 668 9878

L2723328-COFC

ALS www.alsglobal.com

Report To	Contact and company name below will appear on the final report
Company:	[illegible]
Contact:	[illegible]
Phone:	
	Company address below will appear on the final report
Street:	[illegible]
City/Province:	[illegible]
Postal Code:	
Invoice To	Same as Report To ☐ YES ☑ NO
	Copy of Invoice with Report ☑ YES ☐ NO
Company:	[illegible]
Contact:	[illegible]

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 [illegible]

Email 3 [illegible]

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2 [illegible]

Turnaround Time (TAT) Requested

☐ Routine [R] if received by 3pm M-F - no surcharges apply

☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum

☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum

☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum

☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum

☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additional fees may apply to rush requests on weekends, statutory holidays and non-routine tests

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please contact your AM to confirm availability.

AFFIX ALS BARCODE LABEL HERE (ALS use only)

Project Information

ALS Account # / Quote #:

Job #: [illegible]

PO / AFE:

LSD:

ALS Lab Work Order # (ALS use only): L2723328

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#

Major/Minor Code: Routing Code:

Requisitioner:

Location:

ALS Contact: [illegible] Sampler: MJ

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	[illegible]	NUMBER OF CONTAINERS	pH	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	[illegible]	18-[illegible]	4 pm	Soil	2	✓	✓			
	[illegible] BOS 200+				2	✓	✓			
	[illegible] CAT 100				2	✓	✓			
	Tab - Sim BOS 200+				2	✓	✓			
	Tab - Sim CAT 100				2	✓	✓			
	Tab - [illegible]				2	✓	✓			
	Tab - [illegible]				2	✓	✓			
	Tab - BOS 200+ Surf				2	✓	✓			
	Tab - CAT 100 Surf				2	✓	✓			
	Tab - Sim BOS Surf				2	✓	✓			
	Tab - Sim CAT Surf				2	✓	✓			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☒ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C: FINAL COOLER TEMPERATURES °C: 24.8

SHIPMENT RELEASE (client use)			INITIAL SHIPMENT RECEPTION (ALS use only)			FINAL SHIPMENT RECEPTION (ALS use only)		
Released by: [illegible]	Date: 19-01-22	Time:	Received by:	Date:	Time:	Received by: [illegible]	Date: 7/19/22	Time: 14:00

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION WHITE - LABORATORY COPY YELLOW - CLIENT COPY

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a Regulated Drinking Water (DW) System, please submit using an Authorized DW COC form.

LABORATORY CERTIFICATES OF ANALYSES

ONE-MONTH SAMPLING EVENT

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Report Transmission Cover Page

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1590784**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Aug 8, 2022
		LSD:		Date Reported:	Aug 16, 2022
		P.O.:	71376	Report Number:	2775541
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

Contact	Company	Address
Accounts Payable: **Brenda Dziwenka**	**InnoTech Alberta Inc.**	Financial Services, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5133 Fax: (780) 450-5542 Email: innotech-finance@albertainnovates.ca

Delivery	Format	Deliverables
Email - Multiple Deliverables By Lot	PDF	COC / Invoice
Email - Single Deliverable	PDF	Test Report

Les Spink	**InnoTech Alberta Inc.**	PO Box 8330, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5033 Fax: (780) 450-5083 Email: leslie.spink@albertainnovates.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / Invoice

Simone Levy	**InnoTech Alberta Inc.**	Bag 4000, Hwy 16A & 75 Street Vegreville, AB T9C 1T4 Phone: (780) 450-5474 Fax: (780) 913-0178 Email: Simone.levy@innotechalberta.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / COA
Email - Merge Deliverables	PDF	COC / Test Report
Email - Merge Deliverables	PDF	COC / Test Report / Invoice
Email - Single Deliverable	Standard Crosstab Without Tabs	Test Report

Victor Bachmann	**InnoTech Alberta Inc.**	1 Oil Path Dr. Devon, AB T9G 1A8 Phone: (780) 987-8635 Fax: (780) 450-5333 Email: victor.bachmann@innotechalberta.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	Test Report

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Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1590784**
Control Number:
Date Received: Aug 8, 2022
Date Reported: Aug 16, 2022
Report Number: 2775541

		Reference Number	1590784-1	1590784-2	1590784-3
		Sample Date	Aug 04, 2022	Aug 04, 2022	Aug 04, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil- Control / soil / 20.4°C	Bromacil- BOS 200+ / soil / 20.4°C	Bromacil- CAT 100 / soil / 20.4°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	<0.2	<0.2	<0.2	0.03
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.281	0.020	0.081	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	95	83	97	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1590784**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Aug 8, 2022
		LSD:		Date Reported:	Aug 16, 2022
		P.O.:	71376	Report Number:	2775541
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

		Reference Number	1590784-4	1590784-5	1590784-6
		Sample Date	Aug 04, 2022	Aug 04, 2022	Aug 04, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil- Sim BOS 200+ / soil / 20.4°C	Bromacil- Sim CAT 100 / soil / 20.4°C	Bromacil- ISCR / soil / 20.4°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	<0.2	<0.2	<0.2	0.03
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.011	<0.008	0.086	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	89	99	94	50-140

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Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1590784**
Control Number:
Date Received: Aug 8, 2022
Date Reported: Aug 16, 2022
Report Number: 2775541

		Reference Number	1590784-7	1590784-8	1590784-9
		Sample Date	Aug 04, 2022	Aug 04, 2022	Aug 04, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil- ISCR+ / soil / 20.4°C	Bromacil- BOS200+ Surf / soil / 20.4°C	Bromacil- CAT 100 Surf / soil / 20.4°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	<0.2	<0.2	<0.2	0.03
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.101	0.013	0.042	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	87	78	82	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1590784**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Aug 8, 2022
		LSD:		Date Reported:	Aug 16, 2022
		P.O.:	71376	Report Number:	2775541
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

		Reference Number	1590784-10	1590784-11		
		Sample Date	Aug 04, 2022	Aug 04, 2022		
		Sample Time	11:00	11:00		
		Sample Location				
		Sample Description	Bromacil- Sim BOS Surf / soil / 20.4°C	Bromacil- Sim CAT Surf / soil / 20.4°C		
		Matrix	Soil	Soil		
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	<0.2	<0.2		0.03

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Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1590784**
Control Number:
Date Received: Aug 8, 2022
Date Reported: Aug 16, 2022
Report Number: 2775541

		Reference Number	1590784-10	1590784-11	1590784-12
		Sample Date	Aug 04, 2022	Aug 04, 2022	Aug 04, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil- Sim BOS Surf / soil / 20.4°C	Bromacil- Sim CAT Surf / soil / 20.4°C	Teb- Control / soil / 20.4°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	<0.008	<0.008		0.008
Tebuthiuron	Dry Weight	mg/kg			0.127	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	77	87	88	50-140

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T1Y 5L3, Canada

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1590784**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Aug 8, 2022
		LSD:		Date Reported:	Aug 16, 2022
		P.O.:	71376	Report Number:	2775541
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

		Reference Number	1590784-13	1590784-14	1590784-15	
		Sample Date	Aug 04, 2022	Aug 04, 2022	Aug 04, 2022	
		Sample Time	11:00	11:00	11:00	
		Sample Location				
		Sample Description	Teb- BOS 200+ / soil / 20.4°C	Teb- CAT 100 / soil / 20.4°C	Teb- Sim BOS 200+ / soil / 20.4°C	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	<0.005	0.020	0.113	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	81	89	95	50-140

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Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1590784**
Control Number:
Date Received: Aug 8, 2022
Date Reported: Aug 16, 2022
Report Number: 2775541

		Reference Number	1590784-16	1590784-17	1590784-18
		Sample Date	Aug 04, 2022	Aug 04, 2022	Aug 04, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Sample A / soil / 20.4°C	Teb- ISCR / soil / 20.4°C	Teb- ISCR+ / soil / 20.4°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.111	0.121	0.080	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	94	100	82	50-140

Element
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Calgary, Alberta
T1Y 5L3, Canada

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F: +1 (403) 291-2021
E: info.Calgary@element.com
W: www.element.com

Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Mahshid Jannati
Company: Vertex Environmental Inc

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1590784**
Control Number:
Date Received: Aug 8, 2022
Date Reported: Aug 16, 2022
Report Number: 2775541

		Reference Number	1590784-19	1590784-20	1590784-21
		Sample Date	Aug 04, 2022	Aug 04, 2022	Aug 04, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Teb- BOS200+ Surf / soil / 20.4°C	Teb- CAT 100 Surf / soil / 20.4°C	Teb- Sim BOS Surf / soil / 20.4°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.011	0.072	0.110	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	75	77	77	50-140

Element
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W: www.element.com

Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1590784**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Aug 8, 2022
		LSD:		Date Reported:	Aug 16, 2022
		P.O.:	71376	Report Number:	2775541
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

Reference Number	1590784-22
Sample Date	Aug 04, 2022
Sample Time	11:00
Sample Location	
Sample Description	Sample B / soil / 20.4°C
Matrix	Soil

Analyte		Units	Results	Results	Results	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.101			0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	83			50-140

Approved by:

Benjamin Morris, B.Sc
Operations Manager

Data have been validated by Analytical Quality Control and Element's Integrated Data Validation System (IDVS).
Generation and distribution of the report, and approval by the digitized signature above, are performed through a secure and controlled automatic process.

Terms and Conditions: https://www.element.com/terms/terms-and-conditions

Element
Bay #5, 2712-37 Avenue N.E.
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T1Y 5L3, Canada

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E: info.Calgary@element.com
W: www.element.com

Quality Control

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1590784**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Aug 8, 2022
		LSD:		Date Reported:	Aug 16, 2022
		P.O.:	71376	Report Number:	2775541
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

Sterilants in Soil

Blanks	Units	Measured	Lower Limit	Upper Limit		Passed QC
Bromacil	ng	0	-0.030	0.030		yes
Tebuthiuron	ng	0	-0.008	0.008		yes
Date Acquired:	August 12, 2022					
Calibration Check	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	ng	103.50	80	120		yes
Tebuthiuron	ng	101.50	80	120		yes
Date Acquired:	August 12, 2022					
Replicates	**Units**	**Replicate 1**	**Replicate 2**	**% RSD Criteria**	**Absolute Criteria**	**Passed QC**
Bromacil	mg/kg	<0.008	<0.008	50	0.040	yes
Tebuthiuron	mg/kg	<0.005	<0.005	50	0.010	yes
Date Acquired:	August 12, 2022					
Matrix Spike	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	mg/kg	100	40	140		yes
Tebuthiuron	mg/kg	90	40	140		yes
Date Acquired:	August 12, 2022					

Water Soluble Parameters

Blanks	Units	Measured	Lower Limit	Upper Limit		Passed QC
Chromium (VI)	mg/L	0	-0.10	0.10		yes
Date Acquired:	August 11, 2022					
Client Sample Replicates	**Units**	**Replicate 1**	**Replicate 2**	**% RSD Criteria**	**Absolute Criteria**	**Passed QC**
Chromium (VI)	mg/kg	0.07	0.06	10	0.01	yes
Date Acquired:	August 11, 2022					

Element
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T1Y 5L3, Canada

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W: www.element.com

Methodology and Notes

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1590784**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Aug 8, 2022
		LSD:		Date Reported:	Aug 16, 2022
		P.O.:	71376	Report Number:	2775541
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Mahshid Jannati				
Company:	Vertex Environmental Inc				

Method of Analysis

Method Name	Reference		Method	Date Analysis Started	Location
1:5 Water Soluble Extraction	APHA	*	Single-Column Ion Chromatography with Electronic Suppression, 4110 C	Aug 11, 2022	Element Edmonton - Roper Road
1:5 Water Soluble Extraction	McKeague	*	Soluble Salts in Extracts of 1:5 Soil:Water Mixtures, 3.23	Aug 11, 2022	Element Edmonton - Roper Road
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Aug 9, 2022	Element Calgary
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Aug 11, 2022	Element Calgary
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Aug 12, 2022	Element Calgary

** Reference Method Modified*

References

APHA	Standard Methods for the Examination of Water and Wastewater
McKeague	Manual on Soil Sampling and Methods of Analysis
US EPA	US Environmental Protection Agency Test Methods

Please direct any inquiries regarding this report to our Client Services group.
Results relate only to samples as submitted.
The test report shall not be reproduced except in full, without the written approval of the laboratory.

Vertex Environmental Inc.
ATTN: Mashid Jannati
40 McBrine Dr
Kitchener ON N2R 1E7

Date Received: 05-AUG-22
Report Date: 10-AUG-22 12:39 (MT)
Version: FINAL

Client Phone: 519-653-8444

Certificate of Analysis

Lab Work Order #: L2726971
Project P.O. #: NOT SUBMITTED
Job Reference: VE-1034
C of C Numbers:
Legal Site Desc:

Rick Hawthorne
Account Manager

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ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2726971-1 BROMACIL-CONTROL Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.4		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	3630000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-2 BROMACIL-BOS 200+ Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	28.5		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	9730000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-3 BROMACIL-CAT 100 Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	30.1		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	20600000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-4 BROMACIL-SIM BOS 200+ Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	29.3		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	21700000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-5 BROMACIL-SIM CAT100 Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	31.0		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	18400000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-6 BROMACIL-ISCR Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	28.1		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	6550000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-7 BROMACIL-ISCR+ Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	26.5		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	1220000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2726971-7 BROMACIL-ISCR+ Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Bacteriological Tests							
L2726971-8 BROMACIL-BOS 200+ SURF Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	29.1		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	25600000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-9 BROMACIL-CAT 100 SURF Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.9		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	3780000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-10 BROMACIL-SIM BOS SURF Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	28.3		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	3790000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726971-11 BROMACIL-SIM CAT SURF Sampled By: CLIENT on 04-AUG-22 Matrix: SOIL							
Physical Tests							
% Moisture	24.8		0.25	%	07-AUG-22	08-AUG-22	R5837165
Bacteriological Tests							
Heterotrophic Plate Count	4780000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

Reference Information

QC Samples with Qualifiers & Comments:

QC Type Description	Parameter	Qualifier	Applies to Sample Number(s)
Duplicate	Heterotrophic Plate Count	DUP-H	L2726971-1, -10, -11, -2, -3, -4, -5, -6, -7, -8, -9

Sample Parameter Qualifier key listed:

Qualifier	Description
DUP-H	Duplicate results outside ALS DQO, due to sample heterogeneity.

Test Method References:

ALS Test Code	Matrix	Test Description	Method Reference**
HPC-SOLID-MF-WT	Soil	HPC on sludge or solid	SM 9215D
MOISTURE-WT	Soil	% Moisture	CCME PHC in Soil - Tier 1 (mod)

** ALS test methods may incorporate modifications from specified reference methods to improve performance.

The last two letters of the above test code(s) indicate the laboratory that performed analytical analysis for that test. Refer to the list below:

Laboratory Definition Code	Laboratory Location
WT	ALS ENVIRONMENTAL - WATERLOO, ONTARIO, CANADA

Chain of Custody Numbers:

GLOSSARY OF REPORT TERMS

Surrogates are compounds that are similar in behaviour to target analyte(s), but that do not normally occur in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery. In reports that display the D.L. column, laboratory objectives for surrogates are listed there.
mg/kg - milligrams per kilogram based on dry weight of sample
mg/kg wwt - milligrams per kilogram based on wet weight of sample
mg/kg lwt - milligrams per kilogram based on lipid weight of sample
mg/L - unit of concentration based on volume, parts per million.
< - Less than.
D.L. - The reporting limit.
N/A - Result not available. Refer to qualifier code and definition for explanation.

Test results reported relate only to the samples as received by the laboratory.
UNLESS OTHERWISE STATED, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.
Analytical results in unsigned test reports with the DRAFT watermark are subject to change, pending final QC review.

Quality Control Report

Workorder: L2726971 Report Date: 10-AUG-22

Client: Vertex Environmental Inc.
40 McBrine Dr
Kitchener ON N2R 1E7

Contact: Mashid Jannati

Test	Matrix	Reference	Result	Qualifier	Units	RPD	Limit	Analyzed
HPC-SOLID-MF-WT	**Soil**							
Batch R5839362								
WG3755227-6 DUP		**L2726971-11**						
Heterotrophic Plate Count		4780000	2790000	DUP-H	CFU/g dwt	53	50	06-AUG-22
WG3755227-1 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	06-AUG-22
WG3755227-2 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	06-AUG-22
WG3755227-4 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	06-AUG-22
WG3755227-5 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	06-AUG-22
MOISTURE-WT	**Soil**							
Batch R5837165								
WG3755265-2 LCS								
% Moisture			100.6		%		90-110	08-AUG-22
WG3755265-1 MB								
% Moisture			<0.25		%		0.25	08-AUG-22

Quality Control Report

Legend:

Limit	ALS Control Limit (Data Quality Objectives)
DUP	Duplicate
RPD	Relative Percent Difference
N/A	Not Available
LCS	Laboratory Control Sample
SRM	Standard Reference Material
MS	Matrix Spike
MSD	Matrix Spike Duplicate
ADE	Average Desorption Efficiency
MB	Method Blank
IRM	Internal Reference Material
CRM	Certified Reference Material
CCV	Continuing Calibration Verification
CVS	Calibration Verification Standard
LCSD	Laboratory Control Sample Duplicate

Sample Parameter Qualifier Definitions:

Qualifier	Description
DUP-H	Duplicate results outside ALS DQO, due to sample heterogeneity.

Quality Control Report

Hold Time Exceedances:

ALS Product Description	Sample ID	Sampling Date	Date Processed	Rec. HT	Actual HT	Units	Qualifier
Bacteriological Tests							
HPC on sludge or solid							
	1	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	2	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	3	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	4	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	5	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	6	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	7	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	8	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	9	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	10	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL
	11	04-AUG-22	06-AUG-22 16:40	48	53	hours	EHTL

Legend & Qualifier Definitions:

EHTR-FM:	Exceeded ALS recommended hold time prior to sample receipt. Field Measurement recommended.
EHTR:	Exceeded ALS recommended hold time prior to sample receipt.
EHTL:	Exceeded ALS recommended hold time prior to analysis. Sample was received less than 24 hours prior to expiry.
EHT:	Exceeded ALS recommended hold time prior to analysis.
Rec. HT:	ALS recommended hold time (see units).

Notes*:
Where actual sampling date is not provided to ALS, the date (& time) of receipt is used for calculation purposes.
Where actual sampling time is not provided to ALS, the earlier of 12 noon on the sampling date or the time (& date) of receipt is used for calculation purposes. Samples for L2726971 were received on 05-AUG-22 14:20.

ALS recommended hold times may vary by province. They are assigned to meet known provincial and/or federal government requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by the US EPA, APHA Standard Methods, or Environment Canada (where available). For more information, please contact ALS.

The ALS Quality Control Report is provided to ALS clients upon request. ALS includes comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against pre-determined data quality objectives to provide confidence in the accuracy of associated test results.

Please note that this report may contain QC results from anonymous Sample Duplicates and Matrix Spikes that do not originate from this Work Order.

Chain of Custody (COC) / Analytical Request Form

L2726971-COFC

746

Canada Toll Free: 1 800 668 9878

www.alsglobal.com

Report To	Contact and company name below will appear on the final report
Company:	Vertex Environmental
Contact:	Mahshid Jannati
Phone:	226 339 6943
Company address below will appear on the final report	
Street:	40 McBrine Dr
City/Province:	Kitchener ON
Postal Code:	N2R 1E7
Invoice To	Same as Report To ☐ YES ☐ NO
	Copy of Invoice with Report ☐ YES ☐ NO
Company:	
Contact:	

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax mahshid@vertexenvironmental.ca

Email 2 eric@vertexenvironmental.ca

Email 3

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2

Turnaround Time (TAT) Requested

☑ Routine [R] if received by 3pm M-F - no surcharges apply

☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum

☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum

☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum

☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum

☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additional fees may apply to rush requests on weekends, statutory holidays and non-routine tests

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please contact your AM to confirm availability.

AFFIX ALS BARCODE LABEL HERE (ALS use only)

Project Information

ALS Account # / Quote #:

Job #: VE-1034

PO / AFE:

LSD:

ALS Lab Work Order # (ALS use only): L2726971

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#

Major/Minor Code: Routing Code:

Requisitioner:

Location:

ALS Contact: Sampler:

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

Only pH & HPC

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	pH	~~HPC~~	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	Bromacil - Control	04/08/22	12:00	Soil	2	X	X	X			
	Bromacil - BOS 200+				2	X	X	X			
	Bromacil - CAT 100				2	X	X	X			
	Bromacil - Sim BOS 200+				2	X	X	X			
	Bromacil - Sim CAT 100				2	X	X	X			
	Bromacil - ISCR				2	X	X	X			
	Bromacil - ISCR+				2	X	X	X			
	Bromacil - BOS 200+ Surf				2	X	X	X			
	Bromacil - CAT 100 Surf				2	X	X	X			
	Bromacil - Sim BOS Surf				2	X	X	X			
	Bromacil - Sim CAT Surf				2	X	X	X			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☐ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C				FINAL COOLER TEMPERATURES °C			
				18.8			

SHIPMENT RELEASE (client use)			INITIAL SHIPMENT RECEPTION (ALS use only)			FINAL SHIPMENT RECEPTION (ALS use only)		
Released by:	Date:	Time:	Received by:	Date:	Time:	Received by: MA	Date: 2022-08-05	Time: 14:20

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION WHITE - LABORATORY COPY YELLOW - CLIENT COPY

AUG 2020 FRONT

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a Regulated Drinking Water (DW) System, please submit using an Authorized DW COC form.

Vertex Environmental Inc.
ATTN: Mashid Jannati
40 McBrine Dr
Kitchener ON N2R 1E7

Date Received: 05-AUG-22
Report Date: 10-AUG-22 12:38 (MT)
Version: FINAL

Client Phone: 519-653-8444

Certificate of Analysis

Lab Work Order #: L2726970
Project P.O. #: NOT SUBMITTED
Job Reference: VE-1034
C of C Numbers:
Legal Site Desc:

Rick Hawthorne
Account Manager

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ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2726970-1 TEB-CONTROL Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	30.1		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	9040000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-2 TEB-BAS 200+ Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.1		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	12400000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-3 TEB-CAT 100 Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.8		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	14900000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-4 TEB-SIM BOS 200+ Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.6		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	32400000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-5 TEB-SIM CAT 100 Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	28.4		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	51700000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-6 TEB-ISCR Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.6		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	4460000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-7 TEB-ISCRT Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	24.5		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	1080000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2726970-7 TEB-ISCRT Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Bacteriological Tests							
L2726970-8 TEB-BOS 200+ SURF Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.5		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	6210000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-9 TEB- CAT100 SURF Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	28.3		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	25300000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-10 TEB-SIM BOS SURF Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	24.7		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	67300000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362
L2726970-11 TEB-SIM CAT SURF Sampled By: CLIENT on 04-AUG-22 @ 13:00 Matrix: SOIL							
Physical Tests							
% Moisture	27.2		0.25	%	07-AUG-22	08-AUG-22	R5837164
Bacteriological Tests							
Heterotrophic Plate Count	29800000		10	CFU/g dwt	06-AUG-22	06-AUG-22	R5839362

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

Reference Information

QC Samples with Qualifiers & Comments:

QC Type Description	Parameter	Qualifier	Applies to Sample Number(s)

Sample Parameter Qualifier key listed:

Qualifier	Description

Test Method References:

ALS Test Code	Matrix	Test Description	Method Reference**
HPC-SOLID-MF-WT	Soil	HPC on sludge or solid	SM 9215D
MOISTURE-WT	Soil	% Moisture	CCME PHC in Soil - Tier 1 (mod)

** ALS test methods may incorporate modifications from specified reference methods to improve performance.

The last two letters of the above test code(s) indicate the laboratory that performed analytical analysis for that test. Refer to the list below:

Laboratory Definition Code	Laboratory Location
WT	ALS ENVIRONMENTAL - WATERLOO, ONTARIO, CANADA

Chain of Custody Numbers:

GLOSSARY OF REPORT TERMS

Surrogates are compounds that are similar in behaviour to target analyte(s), but that do not normally occur in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery. In reports that display the D.L. column, laboratory objectives for surrogates are listed there.
mg/kg - milligrams per kilogram based on dry weight of sample
mg/kg wwt - milligrams per kilogram based on wet weight of sample
mg/kg lwt - milligrams per kilogram based on lipid weight of sample
mg/L - unit of concentration based on volume, parts per million.
< - Less than.
D.L. - The reporting limit.
N/A - Result not available. Refer to qualifier code and definition for explanation.

Test results reported relate only to the samples as received by the laboratory.
UNLESS OTHERWISE STATED, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.
Analytical results in unsigned test reports with the DRAFT watermark are subject to change, pending final QC review.

Quality Control Report

Workorder: L2726970 Report Date: 10-AUG-22

Client: Vertex Environmental Inc.
40 McBrine Dr
Kitchener ON N2R 1E7

Contact: Mashid Jannati

Test	Matrix	Reference	Result	Qualifier	Units	RPD	Limit	Analyzed
HPC-SOLID-MF-WT	**Soil**							
Batch R5839362								
WG3755227-3 DUP		**L2726970-1**						
Heterotrophic Plate Count		9040000	6460000		CFU/g dwt	33	50	06-AUG-22
WG3755227-1 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	06-AUG-22
WG3755227-2 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	06-AUG-22
MOISTURE-WT	**Soil**							
Batch R5837164								
WG3755266-2 LCS								
% Moisture			98.2		%		90-110	08-AUG-22
WG3755266-1 MB								
% Moisture			<0.25		%		0.25	08-AUG-22

Quality Control Report

Legend:

Limit	ALS Control Limit (Data Quality Objectives)
DUP	Duplicate
RPD	Relative Percent Difference
N/A	Not Available
LCS	Laboratory Control Sample
SRM	Standard Reference Material
MS	Matrix Spike
MSD	Matrix Spike Duplicate
ADE	Average Desorption Efficiency
MB	Method Blank
IRM	Internal Reference Material
CRM	Certified Reference Material
CCV	Continuing Calibration Verification
CVS	Calibration Verification Standard
LCSD	Laboratory Control Sample Duplicate

Quality Control Report

Hold Time Exceedances:

ALS Product Description	Sample ID	Sampling Date	Date Processed	Rec. HT	Actual HT	Units	Qualifier
Bacteriological Tests							
HPC on sludge or solid							
	1	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	2	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	3	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	4	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	5	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	6	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	7	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	8	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	9	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	10	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL
	11	04-AUG-22 13:00	06-AUG-22 16:40	48	52	hours	EHTL

Legend & Qualifier Definitions:

EHTR-FM:	Exceeded ALS recommended hold time prior to sample receipt. Field Measurement recommended.
EHTR:	Exceeded ALS recommended hold time prior to sample receipt.
EHTL:	Exceeded ALS recommended hold time prior to analysis. Sample was received less than 24 hours prior to expiry.
EHT:	Exceeded ALS recommended hold time prior to analysis.
Rec. HT:	ALS recommended hold time (see units).

Notes*:
Where actual sampling date is not provided to ALS, the date (& time) of receipt is used for calculation purposes.
Where actual sampling time is not provided to ALS, the earlier of 12 noon on the sampling date or the time (& date) of receipt is used for calculation purposes. Samples for L2726970 were received on 05-AUG-22 14:20.

ALS recommended hold times may vary by province. They are assigned to meet known provincial and/or federal government requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by the US EPA, APHA Standard Methods, or Environment Canada (where available). For more information, please contact ALS.

The ALS Quality Control Report is provided to ALS clients upon request. ALS includes comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against pre-determined data quality objectives to provide confidence in the accuracy of associated test results.

Please note that this report may contain QC results from anonymous Sample Duplicates and Matrix Spikes that do not originate from this Work Order.

Chain of Custody (COC) / Analytical Request Form

ALS www.alsglobal.com

Canada Toll Free: 1 800 668 9878

L2726970-COFC

Report To	Contact and company name below will appear on the final report
Company:	Vertex Environmental
Contact:	Makhid Jamrah
Phone:	226 339 6993
	Company address below will appear on the final report
Street:	40 McBaine Dr
City/Province:	~~Cam~~ Kitchener ON
Postal Code:	N2R 1E7

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax: makhid@vertexenvironmental.ca

Email 2: criec@vertexenvironmental.ca

Email 3:

Turnaround Time (TAT) Requested

☑ Routine [R] if received by 3pm M-F - no surcharges apply

☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum

☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum

☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum

☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum

☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additional fees may apply to rush requests on weekends, statutory holidays and non-routine tests

AFFIX ALS BARCODE LABEL HERE (ALS use only)

Date and Time Required for all E&P TATs: dd-mmm-yy hh:mm am/pm

For all tests with rush TATs requested, please contact your AM to confirm availability.

Invoice To	
	Same as Report To ☐ YES ☐ NO
	Copy of Invoice with Report ☐ YES ☐ NO
Company:	
Contact:	

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax:

Email 2:

Project Information

ALS Account # / Quote #:

Job #: ~~VE-1033~~ VE-1034

PO / AFE:

LSD: FH

ALS Lab Work Order # (ALS use only): L2726970

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#:

Major/Minor Code: Routing Code:

Requisitioner:

Location:

ALS Contact: Sampler:

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	PH	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	Teb - Control	04/08/22	1100	Soil	2	X	X			
	Teb - BOS 200+	↓	↓	↓	2	X	X			
	Teb - CAT 100				2	X	X			
	Teb - Sim BOS 200+				2	X	X			
	Teb - Sim CAT 100				2	X	X			
	Teb - ISCR				2	X	X			
	Teb - ISCR+				2	X	X			
	Teb - BOS 200+ Surf				2	X	X			
	Teb - CAT 100 Surf				2	X	X			
	Teb - Sim BOS Surf				2	X	X			
	Teb - Sim CAT Surf				2	X	X			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C				FINAL COOLER TEMPERATURES °C			
				18.8			

SHIPMENT RELEASE (client use)			INITIAL SHIPMENT RECEPTION (ALS use only)			FINAL SHIPMENT RECEPTION (ALS use only)		
Released by:	Date:	Time:	Received by:	Date:	Time:	Received by: MA	Date: 2022-08-05	Time: ~~13:20~~ 14:20

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION

WHITE - LABORATORY COPY YELLOW - CLIENT COPY

AUG 2020 FRONT

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a **Regulated Drinking Water (DW) System**, please submit using an **Authorized DW COC form**.

ALS Environmental

CERTIFICATE OF ANALYSIS

Work Order	: **WT2209786**	Page	: 1 of 3
Client	: **Vertex Environmental Inc.**	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo ON Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 05-Aug-2022 14:20
PO	: ----	Date Analysis Commenced	: 08-Aug-2022
C-O-C number	: ----	Issue Date	: 11-Aug-2022 17:12
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 11		
No. of samples analysed	: 11		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. This document shall not be reproduced, except in full.

This Certificate of Analysis contains the following information:

- General Comments
- Analytical Results

Additional information pertinent to this report will be found in the following separate attachments: Quality Control Report, QC Interpretive report to assist with Quality Review and Sample Receipt Notification (SRN).

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is conducted in accordance with US FDA 21 CFR Part 11.

Signatories	*Position*	*Laboratory Department*
Greg Pokocky	Supervisor - Inorganic	Inorganics, Waterloo, Ontario

General Comments

The analytical methods used by ALS are developed using internationally recognized reference methods (where available), such as those published by US EPA, APHA Standard Methods, ASTM, ISO, Environment Canada, BC MOE, and Ontario MOE. Refer to the ALS Quality Control Interpretive report (QCI) for applicable references and methodology summaries. Reference methods may incorporate modifications to improve performance.

Where a reported less than (<) result is higher than the LOR, this may be due to primary sample extract/digestate dilution and/or insufficient sample for analysis.

Where the LOR of a reported result differs from standard LOR, this may be due to high moisture content, insufficient sample (reduced weight employed) or matrix interference.

Please refer to Quality Control Interpretive report (QCI) for information regarding Holding Time compliance.

Key : CAS Number: Chemical Abstracts Services number is a unique identifier assigned to discrete substances
LOR: Limit of Reporting (detection limit).

Unit	*Description*
pH units	pH units

<: less than.

>: greater than.

Surrogate: An analyte that is similar in behavior to target analyte(s), but that does not occur naturally in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery.

Test results reported relate only to the samples as received by the laboratory.

UNLESS OTHERWISE STATED on SRN or QCI Report, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.

Analytical Results

Sub-Matrix: Soil/Solid (Matrix: Soil/Solid)				Client sample ID	TEB-CONTROL	TEB-BOS 200+	TEB- CAT 100	TEB-SIM BOS 200+	TEB-SIM CAT 100
				Client sampling date / time	04-Aug-2022 01:00	04-Aug-2022 01:00	04-Aug-2022 01:00	04-Aug-2022 01:00	04-Aug-2022 01:00
Analyte	CAS Number	Method	LOR	Unit	WT2209786-001	WT2209786-002	WT2209786-003	WT2209786-004	WT2209786-005
					Result	Result	Result	Result	Result
Physical Tests									
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.33	7.46	7.36	7.48	7.06

Please refer to the General Comments section for an explanation of any qualifiers detected.

Analytical Results

Sub-Matrix: Soil/Solid (Matrix: Soil/Solid)				Client sample ID	TEB-ISCR	TEB-ISCR+	TEB-BOS 200+ SURF	TEB-CAT 100 SURF	TEB-SIM BOS SURF
				Client sampling date / time	04-Aug-2022 01:00	04-Aug-2022 01:00	04-Aug-2022 01:00	04-Aug-2022 01:00	04-Aug-2022 01:00
Analyte	CAS Number	Method	LOR	Unit	WT2209786-006	WT2209786-007	WT2209786-008	WT2209786-009	WT2209786-010
					Result	Result	Result	Result	Result
Physical Tests									
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.41	4.50	8.09	7.43	8.12

Please refer to the General Comments section for an explanation of any qualifiers detected.

Analytical Results

Sub-Matrix: Soil/Solid (Matrix: Soil/Solid)				Client sample ID	TEB-SIM CAT SURF	----	----	----	----
				Client sampling date / time	04-Aug-2022 01:00	----	----	----	----
Analyte	CAS Number	Method	LOR	Unit	WT2209786-011	--------	--------	--------	--------
					Result	----	----	----	----
Physical Tests									
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.32	----	----	----	----

Please refer to the General Comments section for an explanation of any qualifiers detected.

QUALITY CONTROL INTERPRETIVE REPORT

Work Order	: **WT2209786**	Page	: 1 of 5
Client	: **Vertex Environmental Inc.**	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo, Ontario Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 05-Aug-2022 14:20
PO	: ----	Issue Date	: 11-Aug-2022 17:20
C-O-C number	: ----		
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 11		
No. of samples analysed	: 11		

This report is automatically generated by the ALS LIMS (Laboratory Information Management System) through evaluation of Quality Control (QC) results and other QA parameters associated with this submission, and is intended to facilitate rapid data validation by auditors or reviewers. The report highlights any exceptions and outliers to ALS Data Quality Objectives, provides holding time details and exceptions, summarizes QC sample frequencies, and lists applicable methodology references and summaries.

Key

Anonymous: Refers to samples which are not part of this work order, but which formed part of the QC process lot.
CAS Number: Chemical Abstracts Service number is a unique identifier assigned to discrete substances.
DQO: Data Quality Objective.
LOR: Limit of Reporting (detection limit).
RPD: Relative Percent Difference.

Workorder Comments

Holding times are displayed as "---" if no guidance exists from CCME, Canadian provinces, or broadly recognized international references.

Summary of Outliers

Outliers : Quality Control Samples

- No Duplicate outliers occur.
- No Laboratory Control Sample (LCS) outliers occur
- No Test sample Surrogate recovery outliers exist.

Outliers: Reference Material (RM) Samples

- No Reference Material (RM) Sample outliers occur.

Outliers : Analysis Holding Time Compliance (Breaches)

- No Analysis Holding Time Outliers exist.

Outliers : Frequency of Quality Control Samples

- No Quality Control Sample Frequency Outliers occur.

Analysis Holding Time Compliance

This report summarizes extraction / preparation and analysis times and compares each with ALS recommended holding times, which are selected to meet known provincial and /or federal requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by organizations such as CCME, US EPA, APHA Standard Methods, ASTM, or Environment Canada (where available). Dates and holding times reported below represent the first dates of extraction or analysis. If subsequent tests or dilutions exceeded holding times, qualifiers are added (refer to COA).

If samples are identified below as having been analyzed or extracted outside of recommended holding times, measurement uncertainties may be increased, and this should be taken into consideration when interpreting results.

Where actual sampling date is not provided on the chain of custody, the date of receipt with time at 00:00 is used for calculation purposes.

Where only the sample date without time is provided on the chain of custody, the sampling date at 00:00 is used for calculation purposes.

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB- CAT 100	E108A	04-Aug-2022	08-Aug-2022	----	----		10-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-BOS 200+	E108A	04-Aug-2022	08-Aug-2022	----	----		10-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-BOS 200+ SURF	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-CAT 100 SURF	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-CONTROL	E108A	04-Aug-2022	08-Aug-2022	----	----		10-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-ISCR	E108A	04-Aug-2022	08-Aug-2022	----	----		10-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap TEB-ISCR+	E108A	04-Aug-2022	08-Aug-2022	----	----		10-Aug-2022	30 days	6 days	✓

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
TEB-SIM BOS 200+	E108A	04-Aug-2022	08-Aug-2022	----	----		10-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
TEB-SIM BOS SURF	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
TEB-SIM CAT 100	E108A	04-Aug-2022	08-Aug-2022	----	----		10-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
TEB-SIM CAT SURF	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓

Legend & Qualifier Definitions

Rec. HT: ALS recommended hold time (see units).

Quality Control Parameter Frequency Compliance

The following report summarizes the frequency of laboratory QC samples analyzed within the analytical batches (QC lots) in which the submitted samples were processed. The actual frequency should be greater than or equal to the expected frequency.

Matrix: **Soil/Solid**

Evaluation: × = *QC frequency outside specification*; ✓ = *QC frequency within specification.*

Quality Control Sample Type			Count		Frequency (%)		
Analytical Methods	*Method*	*QC Lot #*	*QC*	*Regular*	*Actual*	*Expected*	*Evaluation*
Laboratory Duplicates (DUP)							
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A	592375	2	25	8.0	5.0	✓
Laboratory Control Samples (LCS)							
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A	592375	2	25	8.0	5.0	✓

Methodology References and Summaries

The analytical methods used by ALS are developed using internationally recognized reference methods (where available), such as those published by US EPA, APHA Standard Methods, ASTM, ISO, Environment Canada, BC MOE, and Ontario MOE. Reference methods may incorporate modifications to improve performance (indicated by "mod").

Analytical Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A Waterloo - Environmental	Soil/Solid	MOEE E3137A	pH is determined by potentiometric measurement with a pH electrode, and is conducted at ambient laboratory temperature (normally 20 ± 5°C) and is carried out in accordance with procedures described in the Analytical Protocol (prescriptive method). A minimum 10g portion of the sample, as received, is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling, or decanting and then analyzed using a pH meter and electrode.

Preparation Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
Leach 1:2 Soil : 0.01CaCl2 - As Received for pH	EP108A Waterloo - Environmental	Soil/Solid	MOEE E3137A	A minimum 10g portion of the sample, as received, is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling or decanting and then analyzed using a pH meter and electrode.

QUALITY CONTROL REPORT

Work Order	: **WT2209786**	Page	: 1 of 3
Client	: Vertex Environmental Inc.	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo, Ontario Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 05-Aug-2022 14:20
PO	: ----	Date Analysis Commenced	: 08-Aug-2022
C-O-C number	: ----	Issue Date	: 11-Aug-2022 17:13
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 11		
No. of samples analysed	: 11		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. This document shall not be reproduced, except in full.

This Quality Control Report contains the following information:

- Laboratory Duplicate (DUP) Report; Relative Percent Difference (RPD) and Data Quality Objectives
- Laboratory Control Sample (LCS) Report; Recovery and Data Quality Objectives

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is conducted in accordance with US FDA 21 CFR Part 11.

Signatories	*Position*	*Laboratory Department*
Greg Pokocky	Supervisor - Inorganic	Waterloo Inorganics, Waterloo, Ontario

General Comments

The ALS Quality Control (QC) report is optionally provided to ALS clients upon request. ALS test methods include comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against predetermined Data Quality Objectives (DQOs) to provide confidence in the accuracy of associated test results. This report contains detailed results for all QC results applicable to this sample submission. Please refer to the ALS Quality Control Interpretation report (QCI) for applicable method references and methodology summaries.

Key :

Anonymous = Refers to samples which are not part of this work order, but which formed part of the QC process lot.
CAS Number = Chemical Abstracts Service number is a unique identifier assigned to discrete substances.
DQO = Data Quality Objective.
LOR = Limit of Reporting (detection limit).
RPD = Relative Percent Difference
# = Indicates a QC result that did not meet the ALS DQO.

Workorder Comments

Holding times are displayed as "---" if no guidance exists from CCME, Canadian provinces, or broadly recognized international references.

Laboratory Duplicate (DUP) Report

A Laboratory Duplicate (DUP) is a randomly selected intralaboratory replicate sample. Laboratory Duplicates provide information regarding method precision and sample heterogeneity. ALS DQOs for Laboratory Duplicates are expressed as test-specific limits for Relative Percent Difference (RPD), or as an absolute difference limit of 2 times the LOR for low concentration duplicates within ~ 4-10 times the LOR (cut-off is test-specific).

Sub-Matrix: **Soil/Solid**

					Laboratory Duplicate (DUP) Report						
Laboratory sample ID	*Client sample ID*	*Analyte*	*CAS Number*	*Method*	*LOR*	*Unit*	*Original Result*	*Duplicate Result*	*RPD(%) or Difference*	*Duplicate Limits*	*Qualifier*
Physical Tests (QC Lot: 592375)											
WT2209568-001	Anonymous	pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.56	7.65	0.09	Diff <2x LOR	----
Physical Tests (QC Lot: 592583)											
WT2208980-001	Anonymous	pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	8.06	8.13	0.07	Diff <2x LOR	----

Laboratory Control Sample (LCS) Report

A Laboratory Control Sample (LCS) is an analyte-free matrix that has been fortified (spiked) with test analytes at known concentration and processed in an identical manner to test samples. LCS results are expressed as percent recovery, and are used to monitor and control test method accuracy and precision, independent of test sample matrix.

Sub-Matrix: **Soil/Solid**

					Laboratory Control Sample (LCS) Report				
					Spike	Recovery (%)	Recovery Limits (%)		
Analyte	CAS Number	Method	LOR	Unit	Concentration	LCS	Low	High	Qualifier
Physical Tests (QCLot: 592375)									
pH (1:2 soil:CaCl2-aq)	----	E108A	----	pH units	7 pH units	98.8	98.0	102	----
Physical Tests (QCLot: 592583)									
pH (1:2 soil:CaCl2-aq)	----	E108A	----	pH units	7 pH units	100	98.0	102	----

only PH on this COC

Chain of Custody (COC) / Analytical Request Form

CO

Environmental Division Waterloo
Work Order Reference
WT2209786

Telephone : + 1 519 886 6910

ALS www.alsglobal.com

Canada Toll Free: 1 800 668 9878

Report To	Contact and company name below will appear on the final report
Company:	Vertex Environmental
Contact:	Makshid Jamati
Phone:	226 339 6993
	Company address below will appear on the final report
Street:	40 McBrine Dr
City/Province:	~~Cam~~ Kitchener ON
Postal Code:	N2R 1E7
Invoice To	Same as Report To ☐ YES ☐ NO
	Copy of Invoice with Report ☐ YES ☐ NO
Company:	
Contact:	

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax makshid@vertexenvironmental.ca

Email 2 eric@vertexenvironmental.ca

Email 3

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax

Email 2

Turnaround Time (TAT) R

☑ Routine [R] if received by 3pm M-F - no surcl
☐ 4 day [P4] if received by 3pm M-F - 20% rus
☐ 3 day [P3] if received by 3pm M-F - 25% ru
☐ 2 day [P2] if received by 3pm M-F - 50% ru
☐ 1 day [E] if received by 3pm M-F - 100% ru
☐ Same day [E2] if received by 10am M-S - 200% may apply to rush requests on weekends, statuto

EL HERE

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please contact your AM to confirm availability.

Project Information

ALS Account # / Quote #:

Job #: ~~VE-1042~~ VE-1034

PO / AFE:

LSD:

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#

Major/Minor Code: Routing Code:

Requisitioner:

Location:

ALS Lab Work Order # (ALS use only): WT2209786 AMTS

ALS Contact: Sampler:

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	PH	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	Teb - Control	04/08/22	1:00	Soil	2	X	X			
	Teb - BOS 200+	↓	↓	↓	2	X	X			
	Teb - CAT 100	↓	↓	↓	2	X	X			
	Teb - Sim BOS 200+	↓	↓	↓	2	X	X			
	Teb - Sim CAT 100	↓	↓	↓	2	X	X			
	Teb - ISCR	↓	↓	↓	2	X	X			
	Teb - ISCR+	↓	↓	↓	2	X	X			
	Teb - BOS 200+ Surf	↓	↓	↓	2	X	X			
	Teb - CAT 100 Surf	↓	↓	↓	2	X	X			
	Teb - Sim BOS Surf	↓	↓	↓	2	X	X			
	Teb - Sim CAT Surf	↓	↓	↓	2	X	X			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C

FINAL COOLER TEMPERATURES °C 18.8

SHIPMENT RELEASE (client use)			INITIAL SHIPMENT RECEPTION (ALS use only)			FINAL SHIPMENT RECEPTION (ALS use only)		
Released by:	Date:	Time:	Received by:	Date:	Time:	Received by: MA	Date: 2022-08-05	Time: ~~13:20~~ 14:20

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION WHITE - LABORATORY COPY YELLOW - CLIENT COPY

AUG 2020 FRONT

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a **Regulated Drinking Water (DW) System**, please submit using an **Authorized DW COC form**.

ALS Environmental

CERTIFICATE OF ANALYSIS

Work Order	: **WT2209787**	Page	: 1 of 3
Client	: **Vertex Environmental Inc.**	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo ON Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 05-Aug-2022 14:20
PO	: ----	Date Analysis Commenced	: 08-Aug-2022
C-O-C number	: ----	Issue Date	: 11-Aug-2022 17:12
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 11		
No. of samples analysed	: 11		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. This document shall not be reproduced, except in full.

This Certificate of Analysis contains the following information:

- General Comments
- Analytical Results

Additional information pertinent to this report will be found in the following separate attachments: Quality Control Report, QC Interpretive report to assist with Quality Review and Sample Receipt Notification (SRN).

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is conducted in accordance with US FDA 21 CFR Part 11.

Signatories	*Position*	*Laboratory Department*
Greg Pokocky	Supervisor - Inorganic	Inorganics, Waterloo, Ontario

General Comments

The analytical methods used by ALS are developed using internationally recognized reference methods (where available), such as those published by US EPA, APHA Standard Methods, ASTM, ISO, Environment Canada, BC MOE, and Ontario MOE. Refer to the ALS Quality Control Interpretive report (QCI) for applicable references and methodology summaries. Reference methods may incorporate modifications to improve performance.

Where a reported less than (<) result is higher than the LOR, this may be due to primary sample extract/digestate dilution and/or insufficient sample for analysis.

Where the LOR of a reported result differs from standard LOR, this may be due to high moisture content, insufficient sample (reduced weight employed) or matrix interference.

Please refer to Quality Control Interpretive report (QCI) for information regarding Holding Time compliance.

Key : CAS Number: Chemical Abstracts Services number is a unique identifier assigned to discrete substances
LOR: Limit of Reporting (detection limit).

Unit	*Description*
pH units	pH units

<: less than.

>: greater than.

Surrogate: An analyte that is similar in behavior to target analyte(s), but that does not occur naturally in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery.

Test results reported relate only to the samples as received by the laboratory.

UNLESS OTHERWISE STATED on SRN or QCI Report, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.

Analytical Results

Sub-Matrix: Soil/Solid (Matrix: Soil/Solid)				Client sample ID	BROMACIL - CONTROL	BROMACIL - BOS 200+	BROMACIL- CAT 100	BROMACIL- SIM BOS 200+	BROMACIL - SIM CAT 100
				Client sampling date / time	04-Aug-2022 12:00	04-Aug-2022 12:00	04-Aug-2022 12:00	04-Aug-2022 12:00	04-Aug-2022 12:00
Analyte	CAS Number	Method	LOR	Unit	WT2209787-001	WT2209787-002	WT2209787-003	WT2209787-004	WT2209787-005
					Result	Result	Result	Result	Result
Physical Tests									
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.45	7.83	7.48	7.84	7.20

Please refer to the General Comments section for an explanation of any qualifiers detected.

Analytical Results

Sub-Matrix: Soil/Solid (Matrix: Soil/Solid)				Client sample ID	BROMACIL- ISCR	BROMACIL- ISCR+	BROMACIL- BOS 200+ SURF	BROMACIL- CAT 100 SURF	BROMACIL- SIM BOS SURF
				Client sampling date / time	04-Aug-2022 12:00	04-Aug-2022 12:00	04-Aug-2022 12:00	04-Aug-2022 12:00	04-Aug-2022 12:00
Analyte	CAS Number	Method	LOR	Unit	WT2209787-006	WT2209787-007	WT2209787-008	WT2209787-009	WT2209787-010
					Result	Result	Result	Result	Result
Physical Tests									
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.57	5.31	7.93	7.40	8.10

Please refer to the General Comments section for an explanation of any qualifiers detected.

Analytical Results

Sub-Matrix: Soil/Solid (Matrix: Soil/Solid)				Client sample ID	BROMACIL- SIM CAT SURF	----	----	----	----
				Client sampling date / time	04-Aug-2022 12:00	----	----	----	----
Analyte	CAS Number	Method	LOR	Unit	WT2209787-011	--------	--------	--------	--------
					Result	----	----	----	----
Physical Tests									
pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.08	----	----	----	----

Please refer to the General Comments section for an explanation of any qualifiers detected.

QUALITY CONTROL INTERPRETIVE REPORT

Work Order	: **WT2209787**	Page	: 1 of 5
Client	: **Vertex Environmental Inc.**	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo, Ontario Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 05-Aug-2022 14:20
PO	: ----	Issue Date	: 11-Aug-2022 17:13
C-O-C number	: ----		
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 11		
No. of samples analysed	: 11		

This report is automatically generated by the ALS LIMS (Laboratory Information Management System) through evaluation of Quality Control (QC) results and other QA parameters associated with this submission, and is intended to facilitate rapid data validation by auditors or reviewers. The report highlights any exceptions and outliers to ALS Data Quality Objectives, provides holding time details and exceptions, summarizes QC sample frequencies, and lists applicable methodology references and summaries.

Key

Anonymous: Refers to samples which are not part of this work order, but which formed part of the QC process lot.
CAS Number: Chemical Abstracts Service number is a unique identifier assigned to discrete substances.
DQO: Data Quality Objective.
LOR: Limit of Reporting (detection limit).
RPD: Relative Percent Difference.

Workorder Comments

Holding times are displayed as "---" if no guidance exists from CCME, Canadian provinces, or broadly recognized international references.

Summary of Outliers

Outliers : Quality Control Samples

- No Duplicate outliers occur.
- No Laboratory Control Sample (LCS) outliers occur
- No Test sample Surrogate recovery outliers exist.

Outliers: Reference Material (RM) Samples

- No Reference Material (RM) Sample outliers occur.

Outliers : Analysis Holding Time Compliance (Breaches)

- No Analysis Holding Time Outliers exist.

Outliers : Frequency of Quality Control Samples

- No Quality Control Sample Frequency Outliers occur.

Analysis Holding Time Compliance

This report summarizes extraction / preparation and analysis times and compares each with ALS recommended holding times, which are selected to meet known provincial and /or federal requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by organizations such as CCME, US EPA, APHA Standard Methods, ASTM, or Environment Canada (where available). Dates and holding times reported below represent the first dates of extraction or analysis. If subsequent tests or dilutions exceeded holding times, qualifiers are added (refer to COA).

If samples are identified below as having been analyzed or extracted outside of recommended holding times, measurement uncertainties may be increased, and this should be taken into consideration when interpreting results.

Where actual sampling date is not provided on the chain of custody, the date of receipt with time at 00:00 is used for calculation purposes.

Where only the sample date without time is provided on the chain of custody, the sampling date at 00:00 is used for calculation purposes.

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation				Analysis			
			Preparation Date	Holding Times Rec	Holding Times Actual	Eval	Analysis Date	Holding Times Rec	Holding Times Actual	Eval
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL - BOS 200+	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL - CONTROL	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL - SIM CAT 100	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL- BOS 200+ SURF	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL- CAT 100	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL- CAT 100 SURF	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL- ISCR	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓

Matrix: **Soil/Solid**

Evaluation: × = Holding time exceedance ; ✓ = Within Holding Time

Analyte Group / Container / Client Sample ID(s)	Method	Sampling Date	Extraction / Preparation: Preparation Date	Holding Times: Rec	Holding Times: Actual	Eval	Analysis: Analysis Date	Holding Times: Rec	Holding Times: Actual	Eval
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL- ISCR+	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL- SIM BOS 200+	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL- SIM BOS SURF	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓
Physical Tests : pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received										
Glass soil jar/Teflon lined cap										
BROMACIL- SIM CAT SURF	E108A	04-Aug-2022	08-Aug-2022	----	----		09-Aug-2022	30 days	6 days	✓

Legend & Qualifier Definitions

Rec. HT: ALS recommended hold time (see units).

Quality Control Parameter Frequency Compliance

The following report summarizes the frequency of laboratory QC samples analyzed within the analytical batches (QC lots) in which the submitted samples were processed. The actual frequency should be greater than or equal to the expected frequency.

Matrix: **Soil/Solid**

Evaluation: × = *QC frequency outside specification*; ✓ = *QC frequency within specification.*

Quality Control Sample Type			Count		Frequency (%)		
Analytical Methods	*Method*	*QC Lot #*	*QC*	*Regular*	*Actual*	*Expected*	*Evaluation*
Laboratory Duplicates (DUP)							
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A	592294	1	13	7.6	5.0	✓
Laboratory Control Samples (LCS)							
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A	592294	1	13	7.6	5.0	✓

Methodology References and Summaries

The analytical methods used by ALS are developed using internationally recognized reference methods (where available), such as those published by US EPA, APHA Standard Methods, ASTM, ISO, Environment Canada, BC MOE, and Ontario MOE. Reference methods may incorporate modifications to improve performance (indicated by "mod").

Analytical Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
pH by Meter (1:2 Soil:0.01M CaCl2 Extraction) - As Received	E108A Waterloo - Environmental	Soil/Solid	MOEE E3137A	pH is determined by potentiometric measurement with a pH electrode, and is conducted at ambient laboratory temperature (normally 20 ± 5°C) and is carried out in accordance with procedures described in the Analytical Protocol (prescriptive method). A minimum 10g portion of the sample, as received, is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling, or decanting and then analyzed using a pH meter and electrode.

Preparation Methods	Method / Lab	Matrix	Method Reference	Method Descriptions
Leach 1:2 Soil : 0.01CaCl2 - As Received for pH	EP108A Waterloo - Environmental	Soil/Solid	MOEE E3137A	A minimum 10g portion of the sample, as received, is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil by centrifuging, settling or decanting and then analyzed using a pH meter and electrode.

QUALITY CONTROL REPORT

Work Order	: **WT2209787**	Page	: 1 of 3
Client	: Vertex Environmental Inc.	Laboratory	: Waterloo - Environmental
Contact	: Mahshid Jannati	Account Manager	: Rick Hawthorne
Address	: 40 McBrine Dr Kitchener ON Canada N2R 1E7	Address	: 60 Northland Road, Unit 1 Waterloo, Ontario Canada N2V 2B8
Telephone	: ----	Telephone	: +1 519 886 6910
Project	: P22-020	Date Samples Received	: 05-Aug-2022 14:20
PO	: ----	Date Analysis Commenced	: 08-Aug-2022
C-O-C number	: ----	Issue Date	: 11-Aug-2022 17:20
Sampler	: ----		
Site	: ----		
Quote number	: P22-020 Q88766		
No. of samples received	: 11		
No. of samples analysed	: 11		

This report supersedes any previous report(s) with this reference. Results apply to the sample(s) as submitted. This document shall not be reproduced, except in full.

This Quality Control Report contains the following information:

- Laboratory Duplicate (DUP) Report; Relative Percent Difference (RPD) and Data Quality Objectives
- Laboratory Control Sample (LCS) Report; Recovery and Data Quality Objectives

Signatories

This document has been electronically signed by the authorized signatories below. Electronic signing is conducted in accordance with US FDA 21 CFR Part 11.

Signatories	*Position*	*Laboratory Department*
Greg Pokocky	Supervisor - Inorganic	Waterloo Inorganics, Waterloo, Ontario

General Comments

The ALS Quality Control (QC) report is optionally provided to ALS clients upon request. ALS test methods include comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against predetermined Data Quality Objectives (DQOs) to provide confidence in the accuracy of associated test results. This report contains detailed results for all QC results applicable to this sample submission. Please refer to the ALS Quality Control Interpretation report (QCI) for applicable method references and methodology summaries.

Key :

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CAS Number = Chemical Abstracts Service number is a unique identifier assigned to discrete substances.
DQO = Data Quality Objective.
LOR = Limit of Reporting (detection limit).
RPD = Relative Percent Difference
# = Indicates a QC result that did not meet the ALS DQO.

Workorder Comments

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Laboratory Duplicate (DUP) Report

A Laboratory Duplicate (DUP) is a randomly selected intralaboratory replicate sample. Laboratory Duplicates provide information regarding method precision and sample heterogeneity. ALS DQOs for Laboratory Duplicates are expressed as test-specific limits for Relative Percent Difference (RPD), or as an absolute difference limit of 2 times the LOR for low concentration duplicates within ~ 4-10 times the LOR (cut-off is test-specific).

Sub-Matrix: **Soil/Solid**

					Laboratory Duplicate (DUP) Report						
Laboratory sample ID	Client sample ID	Analyte	CAS Number	Method	LOR	Unit	Original Result	Duplicate Result	RPD(%) or Difference	Duplicate Limits	Qualifier
Physical Tests (QC Lot: 592294)											
WT2209787-001	BROMACIL - CONTROL	pH (1:2 soil:CaCl2-aq)	----	E108A	0.10	pH units	7.45	7.41	0.04	Diff <2x LOR	----

Laboratory Control Sample (LCS) Report

A Laboratory Control Sample (LCS) is an analyte-free matrix that has been fortified (spiked) with test analytes at known concentration and processed in an identical manner to test samples. LCS results are expressed as percent recovery, and are used to monitor and control test method accuracy and precision, independent of test sample matrix.

Sub-Matrix: **Soil/Solid**

					Laboratory Control Sample (LCS) Report				
					Spike	Recovery (%)	Recovery Limits (%)		
Analyte	CAS Number	Method	LOR	Unit	Concentration	LCS	Low	High	Qualifier
Physical Tests (QCLot: 592294)									
pH (1:2 soil:CaCl2-aq)	----	E108A	----	pH units	7 pH units	99.8	98.0	102	----

Chain of Custody (COC) / Analytical Request Form

www.alsglobal.com

Canada Toll Free: 1 800 668 9878

COC Number: 20 - 1000740

Page

Environmental Division Waterloo
Work Order Reference
WT2209787

Telephone : +1 519 886 6910

only pH on this COC

Report To	Contact and company name below will appear on the final report
Company:	Vertex Environmental
Contact:	Mahshid Javadi
Phone:	226 339 6943
	Company address below will appear on the final report
Street:	90 Mobile Dr
City/Province:	Kitchener ON
Postal Code:	N2R 1E7
Invoice To	Same as Report To ☐ YES ☐ NO
	Copy of Invoice with Report ☐ YES ☐ NO
Company:	
Contact:	

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)
Merge QC/QCI Reports with COA ☐ YES ☐ NO ☐ N/A
☐ Compare Results to Criteria on Report - provide details below if box checked
Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX
Email 1 or Fax mahshid.j@vertexenvironmental.ca
Email 2 eric@vertexenvironmental.ca
Email 3

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX
Email 1 or Fax
Email 2

Turnaround Time (TAT) Requested

☑ Routine [R] if received by 3pm M-F - no surcharges apply
☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum
☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum
☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum
☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum
☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additio may apply to rush requests on weekends, statutory holidays and non-rout

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please con

Project Information

ALS Account # / Quote #:
Job #: VE-1034
PO / AFE:
LSD:

Oil and Gas Required Fields (client use)

AFE/Cost Center: PO#
Major/Minor Code: Routing Code:
Requisitioner:
Location:

ALS Lab Work Order # (ALS use only): WT2209787-S
ALS Contact: Sampler:

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

Only pH & HPC

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	pH	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	Biomacil - Control	04/08/22	12:00	Sol	2	X	X			
	Biomacil - BOS 200+	↓	↓	↓	2	X	X			
	Biomacil - CAT 100				2	X	X			
	Biomacil - Sim BOS 200+				2	X	X			
	Biomacil - Sim CAT 100				2	X	X			
	Biomacil - ISCR				2	X	X			
	Biomacil - ISCR+				2	X	X			
	Biomacil - BOS 200+ Surf				1	X	X			
	Biomacil - CAT 100 Surf				2	X	X			
	Biomacil - Sim BOS Surf				2	X	X			
	Biomacil - Sim CAT Surf				2	X	X			
					2	X	X			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO
Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☐ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED
Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO
Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C				FINAL COOLER TEMPERATURES °C			
				18.8			

SHIPMENT RELEASE (client use)

Released by:	Date:	Time:

INITIAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:

FINAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:
MA	2022-08-05	14:20

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION

WHITE - LABORATORY COPY YELLOW - CLIENT COPY

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

If any water samples are taken from a Regulated Drinking Water (DW) System, please submit using an Authorized DW COC form.

AUG 2020 FRONT

LABORATORY CERTIFICATES OF ANALYSES

TWO-MONTH SAMPLING EVENT

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Report Transmission Cover Page

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1598380**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Sep 12, 2022
		LSD:		Date Reported:	Sep 20, 2022
		P.O.:	71376	Report Number:	2786293
Attn:	Les Spink	Proj. Acct. code:	33910461.3002		
Sampled By:	Mahshid				
Company:	Vertex				

Contact	Company	Address
Accounts Payable: **Brenda Dziwenka**	**InnoTech Alberta Inc.**	Financial Services, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5133 Fax: (780) 450-5542 Email: innotech-finance@albertainnovates.ca

Delivery	Format	Deliverables
Email - Multiple Deliverables By Lot	PDF	COC / Invoice
Email - Single Deliverable	PDF	Test Report

Les Spink	**InnoTech Alberta Inc.**	PO Box 8330, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5033 Fax: (780) 450-5083 Email: leslie.spink@albertainnovates.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / Invoice

Simone Levy	**InnoTech Alberta Inc.**	Bag 4000, Hwy 16A & 75 Street Vegreville, AB T9C 1T4 Phone: (780) 450-5474 Fax: (780) 913-0178 Email: Simone.levy@innotechalberta.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / COA
Email - Merge Deliverables	PDF	COC / Test Report
Email - Merge Deliverables	PDF	COC / Test Report / Invoice
Email - Single Deliverable	Standard Crosstab Without Tabs	Test Report

Victor Bachmann	**InnoTech Alberta Inc.**	PO Box 8330, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5474 Fax: (780) 913-0178 Email: victor.bachmann@albertainnovates.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / COA
Email - Merge Deliverables	PDF	COC / Test Report
Email - Single Deliverable	Standard Crosstab Without Tabs	Test Report

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Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Mahshid
Company: Vertex

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002

Lot ID: **1598380**
Control Number:
Date Received: Sep 12, 2022
Date Reported: Sep 20, 2022
Report Number: 2786293

		Reference Number	1598380-1	1598380-2	1598380-3
		Sample Date	Sep 06, 2022	Sep 06, 2022	Sep 06, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil Control	Bromacil BOS 200+	Bromacil CAT100
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	0.07	0.49	0.69	0.03
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.219	0.018	0.038	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	97	94	93	50-140

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Attn: Les Spink
Sampled By: Mahshid
Company: Vertex

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002

Lot ID: **1598380**
Control Number:
Date Received: Sep 12, 2022
Date Reported: Sep 20, 2022
Report Number: 2786293

		Reference Number	1598380-4	1598380-5	1598380-6	
		Sample Date	Sep 06, 2022	Sep 06, 2022	Sep 06, 2022	
		Sample Time	11:00	11:00	11:00	
		Sample Location				
		Sample Description	Bromacil Sim BOS 200+	Bromacil Sim CAT 100	Bromacil ISCR	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	0.71	0.60	0.94	0.03
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	<0.008	<0.008	<0.008	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	88	89	89	50-140

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Attn: Les Spink
Sampled By: Mahshid
Company: Vertex

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002

Lot ID: **1598380**
Control Number:
Date Received: Sep 12, 2022
Date Reported: Sep 20, 2022
Report Number: 2786293

		Reference Number	1598380-7	1598380-8	1598380-9
		Sample Date	Sep 06, 2022	Sep 06, 2022	Sep 06, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil ISCR+	Bromacil BOS200+ Surf	Bromacil CAT 100 Surf
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	0.57	0.53	0.76	0.03
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.073	0.009	0.024	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	87	72	74	50-140

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Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1598380**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Sep 12, 2022
		LSD:		Date Reported:	Sep 20, 2022
		P.O.:	71376	Report Number:	2786293
Attn:	Les Spink	Proj. Acct. code:	33910461.3002		
Sampled By:	Mahshid				
Company:	Vertex				

		Reference Number	1598380-10	1598380-11		
		Sample Date	Sep 06, 2022	Sep 06, 2022		
		Sample Time	11:00	11:00		
		Sample Location				
		Sample Description	Bromacil Sim BOS Surf	Bromacil Sim CAT Surf		
		Matrix	Soil	Soil		
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	0.63	0.71		0.03

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Sampled By: Mahshid
Company: Vertex

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002

Lot ID: **1598380**
Control Number:
Date Received: Sep 12, 2022
Date Reported: Sep 20, 2022
Report Number: 2786293

		Reference Number	1598380-10	1598380-11	1598380-12
		Sample Date	Sep 06, 2022	Sep 06, 2022	Sep 06, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil Sim BOS Surf	Bromacil Sim CAT Surf	Teb Control
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	<0.008	<0.008		0.008
Tebuthiuron	Dry Weight	mg/kg			0.117	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	73	76	79	50-140

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Company: Vertex

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002

Lot ID: **1598380**
Control Number:
Date Received: Sep 12, 2022
Date Reported: Sep 20, 2022
Report Number: 2786293

		Reference Number	1598380-13	1598380-14	1598380-15
		Sample Date	Sep 06, 2022	Sep 06, 2022	Sep 06, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Teb BOS 200+	Teb CAT100	Teb Sim BOS 200+
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	<0.005	0.022	0.099	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	75	80	78	50-140

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Attn: Les Spink
Sampled By: Mahshid
Company: Vertex

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002

Lot ID: **1598380**
Control Number:
Date Received: Sep 12, 2022
Date Reported: Sep 20, 2022
Report Number: 2786293

		Reference Number	1598380-16	1598380-17	1598380-18	
		Sample Date	Sep 06, 2022	Sep 06, 2022	Sep 06, 2022	
		Sample Time	11:00	11:00	11:00	
		Sample Location				
		Sample Description	Teb Sim CAT 100	Teb ISCR	Teb ISCR+	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.118	0.105	0.066	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	92	89	72	50-140

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Analytical Report

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Attn: Les Spink
Sampled By: Mahshid
Company: Vertex

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002

Lot ID: **1598380**
Control Number:
Date Received: Sep 12, 2022
Date Reported: Sep 20, 2022
Report Number: 2786293

		Reference Number	1598380-19	1598380-20	1598380-21
		Sample Date	Sep 06, 2022	Sep 06, 2022	Sep 06, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Teb BOS200+ Surf	Teb CAT 100 Surf	Teb Sim BOS Surf
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.012	0.065	0.111	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	82	82	81	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1598380**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Sep 12, 2022
		LSD:		Date Reported:	Sep 20, 2022
		P.O.:	71376	Report Number:	2786293
Attn:	Les Spink	Proj. Acct. code:	33910461.3002		
Sampled By:	Mahshid				
Company:	Vertex				

Reference Number	1598380-22
Sample Date	Sep 06, 2022
Sample Time	11:00
Sample Location	
Sample Description	Teb Sim CAT Surf
Matrix	Soil

Analyte		Units	Results	Results	Results	Nominal Detection Limit
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.096			0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	73			50-140

Approved by:

Benjamin Morris, B.Sc
Operations Manager

Data have been validated by Analytical Quality Control and Element's Integrated Data Validation System (IDVS).
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Quality Control

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Attn: Les Spink
Sampled By: Mahshid
Company: Vertex

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002

Lot ID: **1598380**
Control Number:
Date Received: Sep 12, 2022
Date Reported: Sep 20, 2022
Report Number: 2786293

Sterilants in Soil

Blanks	Units	Measured	Lower Limit	Upper Limit		Passed QC
Bromacil	ng	0	-0.030	0.030		yes
Tebuthiuron	ng	0	-0.008	0.008		yes
Date Acquired:	September 13, 2022					

Calibration Check	Units	% Recovery	Lower Limit	Upper Limit		Passed QC
Bromacil	ng	102.00	80	120		yes
Tebuthiuron	ng	103.00	80	120		yes
Date Acquired:	September 13, 2022					

Replicates	Units	Replicate 1	Replicate 2	% RSD Criteria	Absolute Criteria	Passed QC
Bromacil	mg/kg	0.219	0.212	50	0.040	yes
Tebuthiuron	mg/kg	<0.005	<0.005	50	0.010	yes
Date Acquired:	September 13, 2022					

Matrix Spike	Units	% Recovery	Lower Limit	Upper Limit		Passed QC
Bromacil	mg/kg	100	40	140		yes
Tebuthiuron	mg/kg	103	40	140		yes
Date Acquired:	September 13, 2022					

Water Soluble Parameters

Blanks	Units	Measured	Lower Limit	Upper Limit		Passed QC
Bromide	mg/L	0	-0.45	0.57		yes
Date Acquired:	September 13, 2022					

Client Sample Replicates	Units	Replicate 1	Replicate 2	% RSD Criteria	Absolute Criteria	Passed QC
Bromide	mg/kg	0.76	0.83	10	0.04	yes
Date Acquired:	September 13, 2022					

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Methodology and Notes

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1598380**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Sep 12, 2022
		LSD:		Date Reported:	Sep 20, 2022
		P.O.:	71376	Report Number:	2786293
Attn:	Les Spink	Proj. Acct. code:	33910461.3002		
Sampled By:	Mahshid				
Company:	Vertex				

Method of Analysis

Method Name	Reference		Method	Date Analysis Started	Location
1:5 Water Soluble Extraction	APHA	*	Single-Column Ion Chromatography with Electronic Suppression, 4110 C	Sep 13, 2022	Element Edmonton - Roper Road
1:5 Water Soluble Extraction	McKeague	*	Soluble Salts in Extracts of 1:5 Soil:Water Mixtures, 3.23	Sep 13, 2022	Element Edmonton - Roper Road
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Sep 13, 2022	Element Calgary

** Reference Method Modified*

References

APHA	Standard Methods for the Examination of Water and Wastewater
McKeague	Manual on Soil Sampling and Methods of Analysis
US EPA	US Environmental Protection Agency Test Methods

Please direct any inquiries regarding this report to our Client Services group.
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40 McBrine Dr
Kitchener ON N2R 1E7

Date Received: 06-SEP-22
Report Date: 26-SEP-22 13:26 (MT)
Version: FINAL

Client Phone: 519-653-8444

Certificate of Analysis

Lab Work Order #: L2731736

Project P.O. #:	NOT SUBMITTED
Job Reference:	VE 1034
C of C Numbers:	20-955307
Legal Site Desc:	

Rick Hawthorne
Account Manager

[This report shall not be reproduced except in full without the written authority of the Laboratory.]

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2731736-1 BROMACIL- CONTROL Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.4		0.25	%	07-SEP-22	08-SEP-22	R5855818
pH	7.45		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	3750000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-2 BROMACIL- BOS 200+ Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	25.4		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.22		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	8410000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-3 BROMACIL- CAT100 Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.1		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.19		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	18700000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-4 BROMACIL- SIM BOS 200+ Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	26.5		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.41		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	18500000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-5 BROMACIL- SIM CAT 100 Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	29.2		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	6.97		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	23100000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-6 BROMACIL- ISCR Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	29.1		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.24		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	19200000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2731736-7 BROMACIL- ISCR+ Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	25.1		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	4.44		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	2180000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-8 BROMACIL- BOS 200+ SURF Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	26.2		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.23		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	12300000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-9 BROMACIL- CAT100 SURF Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.8		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.08		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	17600000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-10 BROMACIL- SIM BOS SURF Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.3		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.22		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	17400000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-11 BROMACIL- SIMCAT SURF Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	29.9		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	6.86		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	31100000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-12 TEB- CONTROL Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	26.5		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.48		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	3580000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2731736-13 TEB- BOS 200+ Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	25.0		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.36		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	6060000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-14 TEB- CAT 100 Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	26.9		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.20		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	14900000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-15 TEB- SIM BOS 200+ Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.1		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.22		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	7470000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-16 TEB- SIM CAT 100 Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	25.3		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.06		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	24300000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-17 TEB- ISCR Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	26.1		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.12		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	8600000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-18 TEB- ISCR+ Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	23.1		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	4.57		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	2010000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2731736-19 TEB- ROS 200+ SURF Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	25.1		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.21		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	11300000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-20 TEB- CAT 100 SURF Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	26.7		0.25	%	12-SEP-22	13-SEP-22	R5858621
pH	7.16		0.10	pH units		21-SEP-22	R5865221
Bacteriological Tests							
Heterotrophic Plate Count	23500000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-21 TEB- SIM BOS SURF Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.0		0.25	%	14-SEP-22	15-SEP-22	R5860956
pH	7.28		0.10	pH units		22-SEP-22	R5865657
Bacteriological Tests							
Heterotrophic Plate Count	14900000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681
L2731736-22 TEB- SIM CAT SURF Sampled By: CLIENT on 06-SEP-22 Matrix: SOIL							
Physical Tests							
% Moisture	27.9		0.25	%	14-SEP-22	15-SEP-22	R5860956
pH	6.92		0.10	pH units		22-SEP-22	R5865657
Bacteriological Tests							
Heterotrophic Plate Count	29000000	PEHT	10	CFU/g dwt	13-SEP-22	13-SEP-22	R5861681

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

Reference Information

Sample Parameter Qualifier key listed:

Qualifier	Description
PEHT	Parameter Exceeded Recommended Holding Time Prior to Analysis

Test Method References:

ALS Test Code	Matrix	Test Description	Method Reference**
HPC-SOLID-MF-WT	Soil	HPC on sludge or solid	SM 9215D
MOISTURE-WT	Soil	% Moisture	CCME PHC in Soil - Tier 1 (mod)
PH-WT	Soil	pH	MOEE E3137A

A minimum 10g portion of the sample is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil and then analyzed using a pH meter and electrode.

Analysis conducted in accordance with the Protocol for Analytical Methods Used in the Assessment of Properties under Part XV.1 of the Environmental Protection Act (July 1, 2011).

** ALS test methods may incorporate modifications from specified reference methods to improve performance.

The last two letters of the above test code(s) indicate the laboratory that performed analytical analysis for that test. Refer to the list below:

Laboratory Definition Code	Laboratory Location
WT	ALS ENVIRONMENTAL - WATERLOO, ONTARIO, CANADA

Chain of Custody Numbers:

20-955307

GLOSSARY OF REPORT TERMS

Surrogates are compounds that are similar in behaviour to target analyte(s), but that do not normally occur in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery. In reports that display the D.L. column, laboratory objectives for surrogates are listed there.
mg/kg - milligrams per kilogram based on dry weight of sample
mg/kg wwt - milligrams per kilogram based on wet weight of sample
mg/kg lwt - milligrams per kilogram based on lipid weight of sample
mg/L - unit of concentration based on volume, parts per million.
< - Less than.
D.L. - The reporting limit.
N/A - Result not available. Refer to qualifier code and definition for explanation.

Test results reported relate only to the samples as received by the laboratory.
UNLESS OTHERWISE STATED, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.
Analytical results in unsigned test reports with the DRAFT watermark are subject to change, pending final QC review.

Quality Control Report

Workorder: L2731736 Report Date: 26-SEP-22

Client: Vertex Environmental Inc.
40 McBrine Dr
Kitchener ON N2R 1E7

Contact: Eric Cowan

Test	Matrix	Reference	Result	Qualifier	Units	RPD	Limit	Analyzed
HPC-SOLID-MF-WT	**Soil**							
Batch R5861681								
WG3762587-21 DUP		**L2731736-1**						
Heterotrophic Plate Count		3750000	3510000		CFU/g dwt	6.6	50	13-SEP-22
WG3762587-24 DUP		**L2731736-21**						
Heterotrophic Plate Count		14900000	13700000		CFU/g dwt	8.7	50	13-SEP-22
WG3762587-19 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	13-SEP-22
WG3762587-20 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	13-SEP-22
WG3762587-22 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	13-SEP-22
WG3762587-23 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	13-SEP-22
MOISTURE-WT	**Soil**							
Batch R5855818								
WG3761624-3 DUP		**L2731736-1**						
% Moisture		27.4	27.3		%	0.6	20	08-SEP-22
WG3761624-2 LCS								
% Moisture			101.0		%		90-110	08-SEP-22
WG3761624-1 MB								
% Moisture			<0.25		%		0.25	08-SEP-22
Batch R5858621								
WG3762199-3 DUP		**L2731736-14**						
% Moisture		26.9	26.7		%	0.6	20	13-SEP-22
WG3762199-2 LCS								
% Moisture			99.6		%		90-110	13-SEP-22
WG3762199-1 MB								
% Moisture			<0.25		%		0.25	13-SEP-22
Batch R5860956								
WG3762892-2 LCS								
% Moisture			99.8		%		90-110	15-SEP-22
WG3762892-1 MB								
% Moisture			<0.25		%		0.25	15-SEP-22
PH-WT	**Soil**							
Batch R5865221								
WG3762200-1 DUP		**L2731736-12**						
pH		7.48	7.43	J	pH units	0.05	0.3	21-SEP-22
WG3764176-1 LCS								
pH			6.95		pH units		6.9-7.1	21-SEP-22

Quality Control Report

Test	Matrix	Reference	Result	Qualifier	Units	RPD	Limit	Analyzed
PH-WT	**Soil**							
Batch R5865657								
WG3764307-1 LCS								
pH			7.04		pH units		6.9-7.1	22-SEP-22

Quality Control Report

Legend:

Limit	ALS Control Limit (Data Quality Objectives)
DUP	Duplicate
RPD	Relative Percent Difference
N/A	Not Available
LCS	Laboratory Control Sample
SRM	Standard Reference Material
MS	Matrix Spike
MSD	Matrix Spike Duplicate
ADE	Average Desorption Efficiency
MB	Method Blank
IRM	Internal Reference Material
CRM	Certified Reference Material
CCV	Continuing Calibration Verification
CVS	Calibration Verification Standard
LCSD	Laboratory Control Sample Duplicate

Sample Parameter Qualifier Definitions:

Qualifier	Description
J	Duplicate results and limits are expressed in terms of absolute difference.

Quality Control Report

Hold Time Exceedances:

ALS Product Description	Sample ID	Sampling Date	Date Processed	Rec. HT	Actual HT	Units	Qualifier
Bacteriological Tests							
HPC on sludge or solid							
	1	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	2	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	3	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	4	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	5	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	6	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	7	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	8	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	9	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	10	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	11	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	12	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	13	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	14	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	15	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	16	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	17	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	18	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	19	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	20	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	21	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT
	22	06-SEP-22	13-SEP-22 13:55	48	170	hours	EHT

Legend & Qualifier Definitions:

EHTR-FM:	Exceeded ALS recommended hold time prior to sample receipt. Field Measurement recommended.
EHTR:	Exceeded ALS recommended hold time prior to sample receipt.
EHTL:	Exceeded ALS recommended hold time prior to analysis. Sample was received less than 24 hours prior to expiry.
EHT:	Exceeded ALS recommended hold time prior to analysis.
Rec. HT:	ALS recommended hold time (see units).

Notes*:
Where actual sampling date is not provided to ALS, the date (& time) of receipt is used for calculation purposes.
Where actual sampling time is not provided to ALS, the earlier of 12 noon on the sampling date or the time (& date) of receipt is used for calculation purposes. Samples for L2731736 were received on 06-SEP-22 18:00.

ALS recommended hold times may vary by province. They are assigned to meet known provincial and/or federal government requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by the US EPA, APHA Standard Methods, or Environment Canada (where available). For more information, please contact ALS.

The ALS Quality Control Report is provided to ALS clients upon request. ALS includes comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against pre-determined data quality objectives to provide confidence in the accuracy of associated test results.

Please note that this report may contain QC results from anonymous Sample Duplicates and Matrix Spikes that do not originate from this Work Order.

Ch: L2731736-COFC

COC Number: 20 - 955309

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Report To	Contact and company name below will appear on the final report	Reports / Recipients	Turnaround Time (TAT) Requested
Company:	Vertex Environmental Inc	Select Report Format: ☑ PDF ☐ EXCEL ☐ EDD (DIGITAL)	☑ Routine [R] if received by 3pm M-F - no surcharges apply
Contact:	Eric Cowan	Merge QC/QCI Reports with COA ☑ YES ☐ NO ☐ N/A	☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum
Phone:	519 573 5228	☐ Compare Results to Criteria on Report - provide details below if box checked	☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum
	Company address below will appear on the final report	Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX	☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum
Street:	40 McBride Dr	Email 1 or Fax eric@vertexenvironmental.ca	☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum
City/Province:	Kitchener Ontario	Email 2	☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additional fees may apply to rush requests on weekends, statutory holidays and non-routine tests
Postal Code:	N2R 1E7	Email 3	Date and Time Required for all E&P TATs:
Invoice To	Same as Report To ☑ YES ☐ NO	Invoice Recipients	For all tests with rush TATs requested, please contact your AM to confirm availability.
	Copy of Invoice with Report ☐ YES ☑ NO	Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX	
Company:		Email 1 or Fax accounting@vertexenvironmental.ca	
Contact:		Email 2	

AFFIX ALS BARCODE LABEL HERE (ALS use only)

Project Information		Oil and Gas Required Fields (client use)	
ALS Account # / Quote #		AFE/Cost Center:	PO#
Job #:	VE0310	Major/Minor Code:	Routing Code:
PO / AFE:		Requisitioner:	
LSD:	50	Location:	
ALS Lab Work Order # (ALS use only):	L2731736	ALS Contact:	Sampler:

Analysis Request — Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	pH	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
12	Teb- Control	06/09/22		Soil		✓	✓			
13	Teb- BOS200+					✓	✓			
14	Teb- CAT100					✓	✓			
15	Teb- Sim BOS200+					✓	✓			
16	Teb- Sim CAT100					✓	✓			
17	Teb- FSCR					✓	✓			
18	Teb- FSCR+					✓	✓			
19	Teb- BOS200+ Surf					✓	✓			
20	Teb- CAT100 Surf					✓	✓			
21	Teb- Sim BOS Surf					✓	✓			
22	Teb- Sim CAT Surf					✓	✓			

Drinking Water (DW) Samples[1] (client use)	Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)
Are samples taken from a Regulated DW System? ☐ YES ☐ NO	
Are samples for human consumption/ use? ☐ YES ☐ NO	

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☒ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C				FINAL COOLER TEMPERATURES °C			
				20.7			

SHIPMENT RELEASE (client use)			INITIAL SHIPMENT RECEPTION (ALS use only)			FINAL SHIPMENT RECEPTION (ALS use only)		
Released by: Melody Sang	Date: 09/06/22	Time:	Received by:	Date:	Time:	Received by:	Date: 9/6/22	Time: 1800

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION — WHITE - LABORATORY COPY YELLOW - CLIENT COPY

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a Regulated Drinking Water (DW) System, please submit using an Authorized DW COC form.

AUG2022FRONT

Ch L2731736-COFC

COC Number: 20 - 955307

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Report To	Contact and company name below will appear on the final report
Company:	Vertex Environmental Inc
Contact:	Eric Conan
Phone:	519 573 5228
	Company address below will appear on the final report
Street:	40 McBrine Dr
City/Province:	Kitchener ON
Postal Code:	N2R 1C7
Invoice To	Same as Report To ☑ YES ☐ NO
	Copy of Invoice with Report ☐ YES ☑ NO
Company:	
Contact:	

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☑ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax: eric@vertexenvironmental.ca

Email 2:

Email 3:

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax: accounting@vertexenvironmental.ca

Email 2:

Turnaround Time (TAT) Requested

- ☑ Routine [R] if received by 3pm M-F - no surcharges apply
- ☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum
- ☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum
- ☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum
- ☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum
- ☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additional fees may apply to rush requests on weekends, statutory holidays and non-routine tests

AFFIX ALS BARCODE LABEL HERE (ALS use only)

Date and Time Required for all E&P TATs:

For all tests with rush TATs requested, please contact your AM to confirm availability.

Project Information

ALS Account # / Quote #:	
Job #:	VE1034
PO / AFE:	
LSD:	JD
ALS Lab Work Order # (ALS use only):	L2731736

Oil and Gas Required Fields (client use)

AFE/Cost Center:	PO#:
Major/Minor Code:	Routing Code:
Requisitioner:	
Location:	
ALS Contact:	Sampler:

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS: pH	HPC	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
1	Bromacil - Control	06-Sep-22		Soil	✓	✓			
2	Bromacil - BOS 200+				✓	✓			
3	Bromacil - CAT100				✓	✓			
4	Bromacil - Sim BOS 200+				✓	✓			
5	Bromacil - Sim CAT 100				✓	✓			
6	Bromacil - ISCR				✓	✓			
7	Bromacil - ISCR+				✓	✓			
8	Bromacil - BOS200+ SURF				✓	✓			
9	Bromacil - CAT100 Surf				✓	✓			
10	Bromacil - Sim BOS Surf				✓	✓			
11	Bromacil - Sim CAT Surf				✓	✓			

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☐ NO

Are samples for human consumption/ use? ☐ YES ☐ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☑ NONE ☐ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C	FINAL COOLER TEMPERATURES °C
	20.7

SHIPMENT RELEASE (client use)			INITIAL SHIPMENT RECEPTION (ALS use only)			FINAL SHIPMENT RECEPTION (ALS use only)		
Released by: Melody Sangt	Date: 09/06/22	Time:	Received by:	Date:	Time:	Received by:	Date: 9/6/22	Time: 1800

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION

WHITE - LABORATORY COPY YELLOW - CLIENT COPY

AUG 2020 FRONT

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a **Regulated Drinking Water (DW) System**, please submit using an **Authorized DW COC form**.

LABORATORY CERTIFICATES OF ANALYSES

FOUR-MONTH SAMPLING EVENT

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Report Transmission Cover Page

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1613658**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Nov 8, 2022
		LSD:		Date Reported:	Nov 22, 2022
		P.O.:	71376	Report Number:	2814794
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Alyson Neufeld				
Company:	Vertex Environmental Inc.				

Contact	Company	Address
Accounts Payable	**InnoTech Alberta Inc.**	Financial Services, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5133 Fax: (780) 450-5542 Email: innotech-finance@albertainnovates.ca

Delivery	Format	Deliverables
Email - Multiple Deliverables By Lot	PDF	COC / Invoice
Email - Single Deliverable	PDF	Test Report

Alyson Neufeld	**InnoTech Alberta Inc.**	Kitchener, ON Phone: (519) 653-8444 Fax: Email: alysonn@vertexenvironmental.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / Test Report

Emily Herdman	**InnoTech Alberta Inc.**	Bag 4000, Hwy 16A & 75 Street Vegreville, AB T9C 1T4 Phone: (780) 450-5474 Fax: (780) 913-0178 Email: Emily.Herdman@innotechalberta.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / COA
Email - Merge Deliverables	PDF	COC / Test Report
Email - Merge Deliverables	PDF	COC / Test Report / Invoice
Email - Single Deliverable	Standard Crosstab Without Tabs	Test Report

Les Spink	**InnoTech Alberta Inc.**	PO Box 8330, 250 Karl Clark Road Edmonton, AB T6N 1E4 Phone: (780) 450-5033 Fax: (780) 450-5083 Email: leslie.spink@albertainnovates.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	COC / Invoice

Victor Bachmann	**InnoTech Alberta Inc.**	1 Oil Path Dr. Devon, AB T9G 1A8 Phone: (780) 987-8635 Fax: (780) 450-5333 Email: victor.bachmann@innotechalberta.ca

Delivery	Format	Deliverables
Email - Merge Deliverables	PDF	Test Report

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Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
250 Karl Clark Road
Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Alyson Neufeld
Company: Vertex Environmental Inc.

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1613658**
Control Number:
Date Received: Nov 8, 2022
Date Reported: Nov 22, 2022
Report Number: 2814794

		Reference Number	1613658-1	1613658-2	1613658-3
		Sample Date	Nov 07, 2022	Nov 07, 2022	Nov 07, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil- Control / soil / 4.5°C	Bromacil- BOS 200+ / soil / 4.5°C	Bromacil- CAT 100 / soil / 4.5°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	<0.2	<0.2	<0.2	0.03
Soil % Moisture						
Moisture	Soil % Moisture	% by weight	22.20	24.50	24.10	
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.122	0.008	0.034	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	108	95	110	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1613658**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Nov 8, 2022
		LSD:		Date Reported:	Nov 22, 2022
		P.O.:	71376	Report Number:	2814794
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Alyson Neufeld				
Company:	Vertex Environmental Inc.				

		Reference Number	1613658-4	1613658-5	1613658-6
		Sample Date	Nov 07, 2022	Nov 07, 2022	Nov 07, 2022
		Sample Time	11:00	11:00	11:00
		Sample Location			
		Sample Description	Bromacil- Sim BOS 200+ / soil / 4.5°C	Bromacil- Sim CAT 100 / soil / 4.5°C	Bromacil- ISCR / soil / 4.5°C
		Matrix	Soil	Soil	Soil
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	<0.2	<0.2	<0.2	0.03
Soil % Moisture						
Moisture	Soil % Moisture	% by weight	23.70	24.90	23.70	
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	<0.008	<0.008	<0.008	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	107	102	111	50-140

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Analytical Report

Bill To: InnoTech Alberta Inc.
PO Box 8330
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Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Alyson Neufeld
Company: Vertex Environmental Inc.

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1613658**
Control Number:
Date Received: Nov 8, 2022
Date Reported: Nov 22, 2022
Report Number: 2814794

		Reference Number	1613658-7	1613658-8	1613658-9	
		Sample Date	Nov 07, 2022	Nov 07, 2022	Nov 07, 2022	
		Sample Time	11:00	11:00	11:00	
		Sample Location				
		Sample Description	Bromacil- ISCR+ / soil / 4.5°C	Bromacil- BOS200+ Surf / soil / 4.5°C	Bromacil- CAT 100 Surf / soil / 4.5°C	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	<0.2	<0.2	<0.2	0.03
Soil % Moisture						
Moisture	Soil % Moisture	% by weight	21.80	23.10	24.60	
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	0.076	0.010	<0.008	0.008
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	114	101	103	50-140

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Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1613658**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Nov 8, 2022
		LSD:		Date Reported:	Nov 22, 2022
		P.O.:	71376	Report Number:	2814794
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Alyson Neufeld				
Company:	Vertex Environmental Inc.				

		Reference Number	1613658-10	1613658-11	
		Sample Date	Nov 07, 2022	Nov 07, 2022	
		Sample Time	11:00	11:00	
		Sample Location			
		Sample Description	Bromacil- Sim BOS Surf / soil / 4.5°C	Bromacil- Sim CAT Surf / soil / 4.5°C	
		Matrix	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Water Soluble Parameters						
Bromide	Water Soluble	mg/kg	<0.2	<0.2		0.03

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		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Nov 8, 2022
		LSD:		Date Reported:	Nov 22, 2022
		P.O.:	71376	Report Number:	2814794
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Alyson Neufeld				
Company:	Vertex Environmental Inc.				

		Reference Number	1613658-10	1613658-11	1613658-12	
		Sample Date	Nov 07, 2022	Nov 07, 2022	Nov 07, 2022	
		Sample Time	11:00	11:00	11:00	
		Sample Location				
		Sample Description	Bromacil- Sim BOS Surf / soil / 4.5°C	Bromacil- Sim CAT Surf / soil / 4.5°C	Teb- Control / soil / 4.5°C	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Soil % Moisture						
Moisture	Soil % Moisture	% by weight	25.20	23.80	23.10	
Sterilants in Soil						
Bromacil	Dry Weight	mg/kg	<0.008	0.014		0.008
Tebuthiuron	Dry Weight	mg/kg			0.124	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	101	99	107	50-140

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Bill To: InnoTech Alberta Inc.
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Edmonton, AB, Canada
T6N 1E4
Attn: Les Spink
Sampled By: Alyson Neufeld
Company: Vertex Environmental Inc.

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1613658**
Control Number:
Date Received: Nov 8, 2022
Date Reported: Nov 22, 2022
Report Number: 2814794

		Reference Number	1613658-13	1613658-14	1613658-15	
		Sample Date	Nov 07, 2022	Nov 07, 2022	Nov 07, 2022	
		Sample Time	11:00	11:00	11:00	
		Sample Location				
		Sample Description	Teb- BOS 200+ / soil / 4.5°C	Teb- CAT 100 / soil / 4.5°C	Teb- Sim BOS 200+ / soil / 4.5°C	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Soil % Moisture						
Moisture	Soil % Moisture	% by weight	23.70	23.40	23.40	
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	<0.005	0.035	0.117	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	94	105	99	50-140

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Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1613658**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Nov 8, 2022
		LSD:		Date Reported:	Nov 22, 2022
		P.O.:	71376	Report Number:	2814794
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Alyson Neufeld				
Company:	Vertex Environmental Inc.				

		Reference Number	1613658-16	1613658-17	1613658-18	
		Sample Date	Nov 07, 2022	Nov 07, 2022	Nov 07, 2022	
		Sample Time	11:00	11:00	11:00	
		Sample Location				
		Sample Description	Teb- Sim CAT 100 / soil / 4.5°C	Teb- ISCR / soil / 4.5°C	Teb- ISCR+ / soil / 4.5°C	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Soil % Moisture						
Moisture	Soil % Moisture	% by weight	21.70	23.00	21.90	
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.094	0.088	0.067	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	105	102	108	50-140

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Attn: Les Spink
Sampled By: Alyson Neufeld
Company: Vertex Environmental Inc.

Project ID: SSP11
Project Name: VE-1034
Project Location:
LSD:
P.O.: 71376
Proj. Acct. code: 33910461.3002 (Vertex)

Lot ID: **1613658**
Control Number:
Date Received: Nov 8, 2022
Date Reported: Nov 22, 2022
Report Number: 2814794

		Reference Number	1613658-19	1613658-20	1613658-21	
		Sample Date	Nov 07, 2022	Nov 07, 2022	Nov 07, 2022	
		Sample Time	11:00	11:00	11:00	
		Sample Location				
		Sample Description	Teb- BOS200+ Surf / soil / 4.5°C	Teb- CAT 100 Surf / soil / 4.5°C	Teb- Sim BOS Surf / soil / 4.5°C	
		Matrix	Soil	Soil	Soil	
Analyte		**Units**	**Results**	**Results**	**Results**	Nominal Detection Limit
Soil % Moisture						
Moisture	Soil % Moisture	% by weight	23.40	23.30	23.80	
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.121	0.036	0.008	0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	102	112	99	50-140

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Analytical Report

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1613658**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Nov 8, 2022
		LSD:		Date Reported:	Nov 22, 2022
		P.O.:	71376	Report Number:	2814794
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Alyson Neufeld				
Company:	Vertex Environmental Inc.				

Reference Number	1613658-22
Sample Date	Nov 07, 2022
Sample Time	11:00
Sample Location	
Sample Description	Teb- Sim CAT Surf / soil / 4.5°C
Matrix	Soil

Analyte		Units	Results	Results	Results	Nominal Detection Limit
Soil % Moisture						
Moisture	Soil % Moisture	% by weight	23.60			
Sterilants in Soil						
Tebuthiuron	Dry Weight	mg/kg	0.112			0.005
Sterilants - Soil - Surrogate Recovery						
Monuron	Surrogate	%	101			50-140

Approved by:

Randy Neumann, BSc
Director

Data have been validated by Analytical Quality Control and Element's Integrated Data Validation System (IDVS).
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Quality Control

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1613658**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Nov 8, 2022
		LSD:		Date Reported:	Nov 22, 2022
		P.O.:	71376	Report Number:	2814794
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Alyson Neufeld				
Company:	Vertex Environmental Inc.				

Sterilants in Soil

Blanks	Units	Measured	Lower Limit	Upper Limit		Passed QC
Bromacil	ng	0	-0.030	0.030		yes
Tebuthiuron	ng	0	-0.008	0.008		yes
Date Acquired:	November 16, 2022					
Calibration Check	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Bromacil	ng	107.50	80	120		yes
Tebuthiuron	ng	102.00	80	120		yes
Date Acquired:	November 16, 2022					
Matrix Spike	**Units**	**% Recovery**	**Lower Limit**	**Upper Limit**		**Passed QC**
Tebuthiuron	mg/kg	105	40	140		yes
Date Acquired:	November 16, 2022					
Replicates	**Units**	**Replicate 1**	**Replicate 2**	**% RSD Criteria**	**Absolute Criteria**	**Passed QC**
Tebuthiuron	mg/kg	0.124	0.118	50	0.010	yes
Date Acquired:	November 16, 2022					

Water Soluble Parameters

Blanks	Units	Measured	Lower Limit	Upper Limit		Passed QC
Bromide	mg/L	0	-0.45	0.57		yes
Chromium (VI)	mg/L	0	-0.10	0.10		yes
Date Acquired:	November 20, 2022					
Client Sample Replicates	**Units**	**Replicate 1**	**Replicate 2**	**% RSD Criteria**	**Absolute Criteria**	**Passed QC**
Chromium (VI)	mg/kg	<0.05	<0.05	10	0.01	yes
Date Acquired:	November 20, 2022					

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Methodology and Notes

Bill To:	InnoTech Alberta Inc. PO Box 8330 250 Karl Clark Road Edmonton, AB, Canada T6N 1E4	Project ID:	SSP11	Lot ID:	**1613658**
		Project Name:	VE-1034	Control Number:	
		Project Location:		Date Received:	Nov 8, 2022
		LSD:		Date Reported:	Nov 22, 2022
		P.O.:	71376	Report Number:	2814794
Attn:	Les Spink	Proj. Acct. code:	33910461.3002 (Vertex)		
Sampled By:	Alyson Neufeld				
Company:	Vertex Environmental Inc.				

Method of Analysis

Method Name	Reference		Method	Date Analysis Started	Location
1:5 Water Soluble Extraction	APHA	*	Single-Column Ion Chromatography with Electronic Suppression, 4110 C	Nov 20, 2022	Element Edmonton - Roper Road
1:5 Water Soluble Extraction	McKeague	*	Soluble Salts in Extracts of 1:5 Soil:Water Mixtures, 3.23	Nov 20, 2022	Element Edmonton - Roper Road
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Nov 15, 2022	Element Calgary
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Nov 16, 2022	Element Calgary
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Nov 17, 2022	Element Calgary
Sterilants - Soil	US EPA	*	Solvent Extractable Nonvolatile Compounds by HPLC/TS/MS or UV Detection, 8321 B	Nov 17, 2022	Element Calgary

** Reference Method Modified*

References

APHA	Standard Methods for the Examination of Water and Wastewater
McKeague	Manual on Soil Sampling and Methods of Analysis
US EPA	US Environmental Protection Agency Test Methods

Please direct any inquiries regarding this report to our Client Services group.
Results relate only to samples as submitted.
The test report shall not be reproduced except in full, without the written approval of the laboratory.

element
www.Element.com

Project Information

Project ID:	SSP11
Project Name:	VE-1034
Project Location:	
Legal Location:	
PO/AFE#:	
Proj. Acct. Code:	33910461.3002 (Vertex)
Quote #:	PO#71376

Invoice To

Company:	Alberta Innovates
Address:	250 Karl Clark Rd NW
	Edmonton, AB
Attention:	Les Spink
Phone:	
Cell:	780.450.5170
Fax:	
E-mail 1:	les.spink@albertainnovates.ca
Agreement ID:	92141
Copy of Report:	No

Report To

Company:	Innotech Alberta
Address:	250 Karl Clark Rd.
	Edmonton, AB
Attention:	Simone Levy
Phone:	780-450-5210
Cell:	
Fax:	
E-mail 1:	Simone.Levy@InnotechAlberta.ca
E-mail 2:	
Copy of Invoice:	YES

Additional Reports to

1) Name:	Victor Bachmann
E-mail:	or.bachmann@innotechalberta
2) Name:	Alyson Neufeld
E-mail:	lysonn@vertexenvironmental.c

Sample Custody

Sampled by:	Alyson Neufeld
Company:	Vertex Environmental Inc

I authorize Element to proceed with the work indicated on this form:

Signature:	AN
Date/Time:	7-Nov-22

RUSH Priority

- ☐ Same Day (200%)
- ☐ Next Day/Two Day (100%)
- ☐ Three or Four Days (50%)
- ☑ 5 to 7 Days (Regular TAT)

Date Required _____

When "ASAP" is requested, turn around will default to a 100% RUSH priority, with pricing and turn around time to match. Please contact the lab prior to submitting RUSH samples. If not all samples require RUSH, please indicate in the special instructions.

Report Results

- ☑ Email
- ☑ QA/QC
- ☐ Online
- ☑ PDF
- ☐ Fax
- ☑ Excel

Requirements

- ☐ HCDWORG
- ☐ SPIGEC
- ☐ AB Tier 1
- ☐ BCCSR

Other (list below)

Special Instructions/Comments (please include contact information including phone number if different from above).

Please Include Orthophosphate in nutrient analysis, TKN

	Site I.D.	Sample Description	Depth start in cm	Depth end in cm	Date/Time sampled	Matrix	Sampling method	Number of Containers #	MeOH Field Preserved? ✓	Bromacil	Tebuthiuron	water-soluble bromide by me									
										Enter tests above (✓ relevant samples below)											
1	Bromacil- Control	soil			2022/7/11 11:00			1		✓		✓									
2	Bromacil- BOS 200+	soil			2022/7/11 11:00			1		✓		✓									
3	Bromacil- CAT 100	soil			2022/7/11 11:00			1		✓		✓									
4	Bromacil- Sim BOS 200+	soil			2022/7/11 11:00			1		✓		✓									
5	Bromacil- Sim CAT 100	soil			2022/7/11 11:00			1		✓		✓									
6	Bromacil- ISCR	soil			2022/7/11 11:00			1		✓		✓									
7	Bromacil- ISCR+	soil			2022/7/11 11:00			1		✓		✓									
8	Bromacil- BOS200+ Surf	soil			2022/7/11 11:00			1		✓		✓									
9	Bromacil- CAT 100 Surf	soil			2022/7/11 11:00			1		✓		✓									
10	Bromacil- Sim BOS Surf	soil			2022/7/11 11:00			1		✓		✓									
11	Bromacil- Sim CAT Surf	soil			2022/7/11 11:00			1		✓		✓									
12	Teb- Control	soil			2022/7/11 11:00			1			✓										
13	Teb- BOS 200+	soil			2022/7/11 11:00			1			✓										
14	Teb- CAT 100	soil			2022/7/11 11:00			1			✓										
15	Teb- Sim BOS 200+	soil			2022/7/11 11:00			1			✓										
16	Teb- Sim CAT 100	soil			2022/7/11 11:00			1			✓										
17	Teb- ISCR	soil			2022/7/11 11:00			1			✓										
18	Teb- ISCR+	soil			2022/7/11 11:00			1			✓										
19	Teb- BOS200+ Surf	soil			2022/7/11 11:00			1			✓										
20	Teb- CAT 100 Surf	soil			2022/7/11 11:00			1			✓										
21	Teb- Sim BOS Surf	soil			2022/7/11 11:00			1			✓										
22	Teb- Sim CAT Surf	soil			2022/7/11 11:00			1			✓										

Please indicate any potentially hazardous samples

Submission of this form acknowledges acceptance of Element's Standard of terms and conditions (https://www.element.com/terms/terms-and-conditions)

Page 1 of 1

ED 120-005

Control #

Lot: 1613658 COC

Temp. received: 4.5 °C

Date/Time stamp: NOV 8 8:34?a

Delivery Method:

Waybill:

Received by: RM

Vertex Environmental Inc.
ATTN: Alyson Neufeld
40 McBrine Dr
Kitchener ON N2R 1E7

Date Received: 04-NOV-22
Report Date: 08-DEC-22 12:28 (MT)
Version: FINAL REV. 2

Client Phone: 519-653-8444

Certificate of Analysis

Lab Work Order #: L2739411
Project P.O. #: NOT SUBMITTED
Job Reference: VE 1034
C of C Numbers:
Legal Site Desc:

Comments: ADDITIONAL 07-DEC-22 08:34

8-DEC-2022 with Ph

Rick Hawthorne
Account Manager

[This report shall not be reproduced except in full without the written authority of the Laboratory.]

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2739411-1 BROM-CONTROL Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.4		0.25	%	08-NOV-22	09-NOV-22	R5889076
pH	7.80		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	1270000		10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-2 BROM-BOS 200+ Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.7		0.25	%	08-NOV-22	09-NOV-22	R5889076
pH	7.37		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	5700000	MBER	10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-3 BROM-CAT 100 Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	24.7		0.25	%	08-NOV-22	09-NOV-22	R5889076
pH	7.41		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	NR	NDOGHPC	10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-4 BROM-SIM BOS 200+ Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.3		0.25	%	08-NOV-22	09-NOV-22	R5889076
pH	7.34		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	5420000	MBER	10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-5 BROM-SIM CAT 100 Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.5		0.25	%	08-NOV-22	09-NOV-22	R5889076
pH	7.13		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	3950000		10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-6 BROM-ISCR Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	25.7		0.25	%	08-NOV-22	09-NOV-22	R5889076
pH	7.20		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	1200000		10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

ALS ENVIRONMENTAL ANALYTICAL REPORT

Sample Details/Parameters	Result	Qualifier*	D.L.	Units	Extracted	Analyzed	Batch
L2739411-7 BROM-ISCR+ Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	21.8		0.25	%	08-NOV-22	09-NOV-22	R5889076
pH	5.01		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	464000		10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-8 BROM-BOS 200+ & SURF Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	22.3		0.25	%	08-NOV-22	09-NOV-22	R5889076
pH	7.30		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	3080000		10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-9 BROM-CAT 100 & SURF Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	25.9		0.25	%	09-NOV-22	10-NOV-22	R5889085
pH	7.00		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	3180000		10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-10 BROM-SIM BOS 200+ & SURF Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	26.2		0.25	%	09-NOV-22	10-NOV-22	R5889085
pH	7.38		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	5290000	MBER	10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743
L2739411-11 BROM-SIM CAT 100 & SURF Sampled By: AN on 04-NOV-22 @ 09:00 Matrix: SOIL							
Physical Tests							
% Moisture	24.1		0.25	%	09-NOV-22	10-NOV-22	R5889085
pH	7.27		0.10	pH units		08-DEC-22	R5903780
Bacteriological Tests							
Heterotrophic Plate Count	3820000		10	CFU/g dwt	05-NOV-22	05-NOV-22	R5897743

* Refer to Referenced Information for Qualifiers (if any) and Methodology.

Reference Information

Sample Parameter Qualifier key listed:

Qualifier	Description
MBER	Estimated Result (Microbiological test). Colony count outside ideal range. Result calculated from most nearly acceptable value.
NDOGHPC	NO DATA: Overgrown with HPC

Test Method References:

ALS Test Code	Matrix	Test Description	Method Reference**
HPC-SOLID-MF-WT	Soil	HPC on sludge or solid	SM 9215D
MOISTURE-WT	Soil	% Moisture	CCME PHC in Soil - Tier 1 (mod)
PH-WT	Soil	pH	MOEE E3137A

A minimum 10g portion of the sample is extracted with 20mL of 0.01M calcium chloride solution by shaking for at least 30 minutes. The aqueous layer is separated from the soil and then analyzed using a pH meter and electrode.

Analysis conducted in accordance with the Protocol for Analytical Methods Used in the Assessment of Properties under Part XV.1 of the Environmental Protection Act (July 1, 2011).

** ALS test methods may incorporate modifications from specified reference methods to improve performance.

The last two letters of the above test code(s) indicate the laboratory that performed analytical analysis for that test. Refer to the list below:

Laboratory Definition Code	Laboratory Location
WT	ALS ENVIRONMENTAL - WATERLOO, ONTARIO, CANADA

Chain of Custody Numbers:

GLOSSARY OF REPORT TERMS

Surrogates are compounds that are similar in behaviour to target analyte(s), but that do not normally occur in environmental samples. For applicable tests, surrogates are added to samples prior to analysis as a check on recovery. In reports that display the D.L. column, laboratory objectives for surrogates are listed there.
mg/kg - milligrams per kilogram based on dry weight of sample
mg/kg wwt - milligrams per kilogram based on wet weight of sample
mg/kg lwt - milligrams per kilogram based on lipid weight of sample
mg/L - unit of concentration based on volume, parts per million.
< - Less than.
D.L. - The reporting limit.
N/A - Result not available. Refer to qualifier code and definition for explanation.

Test results reported relate only to the samples as received by the laboratory.
UNLESS OTHERWISE STATED, ALL SAMPLES WERE RECEIVED IN ACCEPTABLE CONDITION.
Analytical results in unsigned test reports with the DRAFT watermark are subject to change, pending final QC review.

Quality Control Report

Workorder: L2739411 Report Date: 08-DEC-22

Client: Vertex Environmental Inc.
40 McBrine Dr
Kitchener ON N2R 1E7

Contact: Alyson Neufeld

Test	Matrix	Reference	Result	Qualifier	Units	RPD	Limit	Analyzed
HPC-SOLID-MF-WT	**Soil**							
Batch R5897743								
WG3771540-6 DUP		**L2739411-11**						
Heterotrophic Plate Count		3820000	2980000		CFU/g dwt	25	50	05-NOV-22
WG3771540-1 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	05-NOV-22
WG3771540-2 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	05-NOV-22
WG3771540-4 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	05-NOV-22
WG3771540-5 MB								
Heterotrophic Plate Count			<10		CFU/g dwt		10	05-NOV-22
MOISTURE-WT	**Soil**							
Batch R5889076								
WG3771955-2 LCS								
% Moisture			99.4		%		90-110	09-NOV-22
WG3771955-1 MB								
% Moisture			<0.25		%		0.25	09-NOV-22
Batch R5889085								
WG3771966-3 DUP		**L2739411-10**						
% Moisture		26.2	25.9		%	1.2	20	10-NOV-22
WG3771966-2 LCS								
% Moisture			99.99		%		90-110	10-NOV-22
WG3771966-1 MB								
% Moisture			<0.25		%		0.25	10-NOV-22
PH-WT	**Soil**							
Batch R5903780								
WG3775377-1 DUP		**L2739411-1**						
pH		7.80	7.80	J	pH units	0.00	0.3	08-DEC-22
WG3775554-1 LCS								
pH			7.00		pH units		6.9-7.1	08-DEC-22

Quality Control Report

Legend:

Limit	ALS Control Limit (Data Quality Objectives)
DUP	Duplicate
RPD	Relative Percent Difference
N/A	Not Available
LCS	Laboratory Control Sample
SRM	Standard Reference Material
MS	Matrix Spike
MSD	Matrix Spike Duplicate
ADE	Average Desorption Efficiency
MB	Method Blank
IRM	Internal Reference Material
CRM	Certified Reference Material
CCV	Continuing Calibration Verification
CVS	Calibration Verification Standard
LCSD	Laboratory Control Sample Duplicate

Sample Parameter Qualifier Definitions:

Qualifier	Description
J	Duplicate results and limits are expressed in terms of absolute difference.

Quality Control Report

Hold Time Exceedances:

ALS Product Description	Sample ID	Sampling Date	Date Processed	Rec. HT	Actual HT	Units	Qualifier
Physical Tests							
pH							
	1	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	2	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	3	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	4	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	5	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	6	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	7	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	8	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	9	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	10	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT
	11	04-NOV-22 09:00	07-DEC-22 12:00	30	33	days	EHT

Legend & Qualifier Definitions:

EHTR-FM:	Exceeded ALS recommended hold time prior to sample receipt. Field Measurement recommended.
EHTR:	Exceeded ALS recommended hold time prior to sample receipt.
EHTL:	Exceeded ALS recommended hold time prior to analysis. Sample was received less than 24 hours prior to expiry.
EHT:	Exceeded ALS recommended hold time prior to analysis.
Rec. HT:	ALS recommended hold time (see units).

Notes*:
Where actual sampling date is not provided to ALS, the date (& time) of receipt is used for calculation purposes.
Where actual sampling time is not provided to ALS, the earlier of 12 noon on the sampling date or the time (& date) of receipt is used for calculation purposes. Samples for L2739411 were received on 04-NOV-22 18:30.

ALS recommended hold times may vary by province. They are assigned to meet known provincial and/or federal government requirements. In the absence of regulatory hold times, ALS establishes recommendations based on guidelines published by the US EPA, APHA Standard Methods, or Environment Canada (where available). For more information, please contact ALS.

The ALS Quality Control Report is provided to ALS clients upon request. ALS includes comprehensive QC checks with every analysis to ensure our high standards of quality are met. Each QC result has a known or expected target value, which is compared against pre-determined data quality objectives to provide confidence in the accuracy of associated test results.

Please note that this report may contain QC results from anonymous Sample Duplicates and Matrix Spikes that do not originate from this Work Order.

Cha rm

L2739411-COFC

COC Number: 20 -

Page of

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Report To	Contact and company name below will appear on the final report
Company:	Vertex Environmental
Contact:	Alyson Neufeld
Phone:	1(437)774-1862
	Company address below will appear on the final report
Street:	40 McBrine Dr
City/Province:	Kitchener, ON
Postal Code:	N2R 1E7
Invoice To	Same as Report To ☐ YES ☑ NO
	Copy of Invoice with Report ☐ YES ☑ NO
Company:	Vertex Environmental
Contact:	Tiberiu Lefter

Project Information

ALS Account # / Quote #:	
Job #:	VE 1034
PO / AFE:	
LSD:	

Reports / Recipients

Select Report Format: ☑ PDF ☑ EXCEL ☐ EDD (DIGITAL)

Merge QC/QCI Reports with COA ☑ YES ☐ NO ☐ N/A

☐ Compare Results to Criteria on Report - provide details below if box checked

Select Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax	alysonn@vertexenvironmental.ca
Email 2	mahshidj@vertexenvironmental.ca
Email 3	ericc@vertexenvironmental.ca

Invoice Recipients

Select Invoice Distribution: ☑ EMAIL ☐ MAIL ☐ FAX

Email 1 or Fax	accounting@vertexenvironmental.ca
Email 2	

Oil and Gas Required Fields (client use)

AFE/Cost Center:	PO#
Major/Minor Code:	Routing Code:
Requisitioner:	
Location:	

Turnaround Time (TAT) Requested

- ☑ Routine [R] if received by 3pm M-F - no surcharges apply
- ☐ 4 day [P4] if received by 3pm M-F - 20% rush surcharge minimum
- ☐ 3 day [P3] if received by 3pm M-F - 25% rush surcharge minimum
- ☐ 2 day [P2] if received by 3pm M-F - 50% rush surcharge minimum
- ☐ 1 day [E] if received by 3pm M-F - 100% rush surcharge minimum
- ☐ Same day [E2] if received by 10am M-S - 200% rush surcharge. Additional fees may apply to rush requests on weekends, statutory holidays and non-routine tests

Date and Time Required for all E&P TATs: dd-mmm-yy hh:mm am/pm

For all tests with rush TATs requested, please contact your AM to confirm availability.

AFFIX ALS BARCODE LABEL HERE (ALS use only)

Analysis Request

Indicate Filtered (F), Preserved (P) or Filtered and Preserved (F/P) below

ALS Lab Work Order # (ALS use only): L2739411	ALS Contact: Rick H	Sampler: AN

ALS Sample # (ALS use only)	Sample Identification and/or Coordinates (This description will appear on the report)	Date (dd-mmm-yy)	Time (hh:mm)	Sample Type	NUMBER OF CONTAINERS	HPC, soil moisture	SAMPLES ON HOLD	EXTENDED STORAGE REQUIRED	SUSPECTED HAZARD (see notes)
	Brom - Control	4-Nov-22	9:00	soil		R			
	Brom - BOS 200+	4-Nov-22	9:00	soil		R			
	Brom - CAT 100	4-Nov-22	9:00	soil		R			
	Brom - Sim BOS 200+	4-Nov-22	9:00	soil		R			
	Brom - Sim CAT 100	4-Nov-22	9:00	soil		R			
	Brom - ISCR	4-Nov-22	9:00	soil		R			
	Brom -ISCR +	4-Nov-22	9:00	soil		R			
	Brom -BOS 200+ & Surf	4-Nov-22	9:00	soil		R			
	Brom -CAT 100 & Surf	4-Nov-22	9:00	soil		R			
	Brom -Sim BOS 200+ & Surf	4-Nov-22	9:00	soil		R			
	Brom -Sim CAT 100 & Surf								

Drinking Water (DW) Samples[1] (client use)

Are samples taken from a Regulated DW System? ☐ YES ☑ NO

Are samples for human consumption/ use? ☐ YES ☑ NO

Notes / Specify Limits for result evaluation by selecting from drop-down below (Excel COC only)

SAMPLE RECEIPT DETAILS (ALS use only)

Cooling Method: ☐ NONE ☑ ICE ☐ ICE PACKS ☐ FROZEN ☐ COOLING INITIATED

Submission Comments identified on Sample Receipt Notification: ☐ YES ☐ NO

Cooler Custody Seals Intact: ☐ YES ☐ N/A Sample Custody Seals Intact: ☐ YES ☐ N/A

INITIAL COOLER TEMPERATURES °C				FINAL COOLER TEMPERATURES °C			
				4.8			

SHIPMENT RELEASE (client use)

Released by:	Date:	Time:

INITIAL SHIPMENT RECEPTION (ALS use only)

Received by:	Date:	Time:

FINAL SHIPMENT RECEPTION (ALS use only)

Received by: MA	Date: 2022-11-04	Time: 1830

WHITE - LABORATORY COPY YELLOW - CLIENT COPY

REFER TO BACK PAGE FOR ALS LOCATIONS AND SAMPLING INFORMATION

Failure to complete all portions of this form may delay analysis. Please fill in this form LEGIBLY. By the use of this form the user acknowledges and agrees with the Terms and Conditions as specified on the back page of the white - report copy.

1. If any water samples are taken from a Regulated Drinking Water (DW) System, please submit using an Authorized DW COC form.

MA SOI-495

AUG 2020 FRONT

APPENDIX A9: EX-SITU FIELD TRIALS

Appendix A9-1: Ex-situ Field Demonstration

Bachmann, V. and R.J. Thiessen, 2023. Ex-situ Field Demonstration for the Remediation of Bromacil in Soil. Report SSP-12A prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 23 pp.

Ex Situ Field Demonstration for the Remediation of Bromacil in Soil

Victor Bachmann, InnoTech Alberta

Ron J. Thiessen, InnoTech Alberta

PREPARED FOR
SOIL STERILANTS PROGRAM STEERING COMMITTEE
BY INNOTECH ALBERTA INC.

InnoTech Alberta Inc. (InnoTech)

Environmental Impacts

250 Karl Clark Road

Edmonton, Alberta T6N 1E4

Canada

August 25, 2024

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CITATION

This report can be sited as:

Bachmann, V. and R.J. Thiessen, 2024. Sterilant Sampling Best Management Practices. Report SSP-12A prepared by InnoTech Alberta for Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 23 pp.

EXECUTIVE SUMMARY

Bromacil and tebuthiuron are persistent, non-selective, broad-spectrum soil sterilants used for vegetation control on industrial land. In Alberta, they were introduced in the 1960s and were used on a variety of industrial sites until their use was halted in the 1990s. Decades after ceasing treatment, bromacil and tebuthiuron impacts persist in soil and water at sites in Alberta.

A 12-week, mesoscale experiment at InnoTech Alberta's Vegreville Research Facility focused on bromacil degradation and immobilization in soil obtained from a bromacil-impacted site in Alberta. Based on previous work done by the Soil Sterilants Program (SSP), the following remediation technologies were tested: (1) chemical oxidation with a surfactant using hydrogen peroxide, VTX® catalyst, and Tween®-80 surfactant; (2) adsorption using ChemCarb PAC 800 activated carbon; and (3) chemical and biological reduction using Daramend®. The primary objectives were to evaluate the ability of these technologies to reduce total bromacil concentrations to meet the Alberta Tier 1 soil remediation guideline of 0.009 mg/kg and assess the operational application and safety of the treatment technologies.

Two of the technologies were effective in reducing total bromacil concentrations: activated carbon and Daramend®. Activated carbon reduced total bromacil concentration by 74%. Daramend® reduced total bromacil concentrations by 58%. However, final concentrations for activated carbon- and Daramend®-treated soils were an order of magnitude greater than Tier 1 soil remediation guideline for bromacil. Daramend® can actively remediate soil for up to five years and this 12-week study does not evaluate the long-term performance of Daramend®.

Phytoaccessible bromacil in activated carbon-treated soil was below the detection limit of 0.008 mg/kg two weeks after treatment. The detection limit is below the Alberta Tier 1 guideline for bromacil. Activated carbon can be effective as a risk management tool at bromacil-impacted sites.

Chemical oxidation with hydrogen peroxide, VTX® catalyst, and Tween®-80 was not effective in reducing bromacil concentration. In this experiment, the components of the chemical oxidant were not applied according to supplier recommended practices. No conclusions or recommendations on the use of this technology can be made based on the results of this experiment.

Based on the results of this experiment, the following actions are recommended:

1. Further testing of activated carbon to extend the findings in this report and work completed in SSP #10 (Thacker, 2022). The objective would be to determine the long-term efficacy of immobilizing bromacil in a field study.
2. Perform a similar mesoscale experiment to refine the application of Daramend® and evaluate its performance over multiple seasons. A corresponding lab component would confirm the degradation of bromacil and evaluate if lab-scale optimization is related to field performance. The objective would be to optimize the application of Daramend®, determine its long-term effectiveness in reducing bromacil concentrations, and confirm whether bromacil is being degraded or adsorbed by Daramend®.

ACKNOWLEDGEMENTS

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1.0 INTRODUCTION

1.1 PROJECT BACKGROUND

Bromacil and tebuthiuron are non-selective, broad-spectrum soil sterilants used for vegetation control on industrial land. In Alberta, they were introduced in the 1960s and were used on a variety of industrial sites until their use was halted in the 1990s due to their ability to migrate offsite and their extreme persistence. Decades after ceasing treatment with sterilant products, impacts can persist in soil and water (Drozdowski et al., 2018).

Bromacil and tebuthiuron are unique and challenging contaminants to manage. To address several knowledge gaps related to the assessment, remediation, and risk management of sites impacted by these sterilants, the Soil Sterilants Program (SSP) was designed as a 5-year joint industry program that was initiated in 2019.

In the design phase of the SSP and through a completed SSP project titled *Soil Sterilants Program Project 13—Evaluation and Comparison of Remediation Technologies*, a review of available remediation technologies for bromacil and tebuthiuron in soil and water was conducted (Drozdowski et al., 2018; Levy et al., 2021). To align with the needs of the SSP, potential remediation technologies were evaluated to determine their applicability to Alberta's conditions and specific site challenges, while considering cost, logistics of application, and sustainability.

After evaluating and short-listing the technologies identified, bench-scale testing was conducted to evaluate the ability of chemical oxidation and reduction products alone, and with the use of surfactants, to degrade bromacil and tebuthiuron in soil (Bendouz and Paré, 2022; French et al., 2023). Based on the results of the bench-scale testing, a field demonstration was proposed to test and compare three leading treatment technologies for the remediation of one of the sterilants, bromacil, in soil collected from a representative sterilant-impacted site in Alberta owned by one of the SSP funders, ATCO Electric Ltd.

2.0 OBJECTIVES

The project was a meso-scale demonstration of the remediation technologies that were short-listed through the desktop review (Levy, Mo, & Bachmann, 2021) and bench-scale lab testing (Bendouz and Paré, 2022). The project evaluated the following three remediation technologies for their ability to decrease total Bromacil concentrations in soil, with the objective of achieving Alberta Tier 1 Regulatory Guidelines (Alberta Environment and Parks, 2022) concentrations or possibly an alternative guideline based on contaminant pathway exclusion:

1. In-Situ Chemical Oxidation (ISCO) with a surfactant via PeroxyChem 50% hydrogen peroxide, VTX®, and Tween®-80 (PVT): Hydrogen peroxide is a commonly used oxidant for ISCO. VTX® is a catalyst that accelerates oxidation and produces highly reactive hydroxyl radicals at near-neutral pH in soil and groundwater. Tween®-80 is an environmentally safe polysorbate surfactant that is used to solubilize some contaminants.
2. Activated Carbon (AC) via ChemCarb PAC 800 Powdered Activated Carbon (PAC): Coal derived activated carbon. Powdered activated carbon was selected because of its high surface-area and ability to apply in an aqueous slurry, which facilitates greater contact with soil contaminants.

3. In-Situ Chemical Reduction (ISCR) with anaerobic bioremediation via Daramend®: Daramend® is an amendment with Zero Valent Iron (ZVI) and organic matter to facilitate chemical and anaerobic reduction of halogenated organic compounds. It is an established remediation amendment used in the treatment of chlorinated VOCs, chlorinated pesticides, and organic explosives.

In addition to treatment efficacy, the technologies were compared based on cost, health and safety, and environmental considerations. Recommended best practices (i.e. operational considerations) were also proposed.

The scope of work comprised the following tasks:

1. Soil sourcing, transportation, and delivery of bromacil-impacted soil to InnoTech's Above-Ground Mesocosm Facility (AGMF) at the research facility in Vegreville;
2. Soil homogenization and treatment cell setup;
3. Plot amendment with remediation products;
4. Sampling, monitoring, and decommissioning; and
5. Data analysis, reporting and recommendations.

3.0 METHODS

3.1 SOIL SOURCING

Approximately 90 m^3 of loose bromacil-impacted soil was provided by ATCO Electric Ltd. from its former Trochu substation at NE-17-033-23 W4M. During phase 2 and 3 Environmental Site Assessments (ESAs), soil on the site was analyzed for other potential co-contaminants including salt, metals, hydrocarbons, and phenols. All parameters were within site-specific guidelines. Pentachlorophenol was elevated in two samples but met site-specific guidelines. The soil was characterized as silty-clay and had a total bromacil concentration ranging from 0.242 mg/kg to 1.76 mg/kg.

Soil from the top 2.5 m immediately below the gravel surface was excavated and loaded into 10 tandem axle trucks. Excavation targeted areas with the highest bromacil concentrations. A soil sample was taken from each excavator bucket load as it went into the trucks. The samples were composited by truck load and sent for rush analysis to Element Materials Technology for total bromacil concentrations.

3.2 SITE PREPARATION

The Above-Ground Mesocosm Facility (AGMF) at InnoTech's Vegreville Research Centre (Figure 1) is a 10 m by 30 m containment pad consisting of two integrated liners, impermeable membrane, berms, and a catchment pond for collecting surface water.

Figure 1. Above-Ground Mesocosm Facility prior to setup.

To prevent contamination of the gravel in the AGMF with bromacil, a 0.6 mm thick polyethylene liner was placed on the AGMF (Figure 2). Sandbags were used to hold the liner in place until soil was delivered. A rig mat was placed at the north end of the AGMF to allow for direct dumping of soil into the containment area without damaging the berm.

Figure 2. Containment cell after placement of liner, sandbags, and rig mat.

3.3 SOIL HOMOGENIZATION AND CHARACTERIZATION

Once the tandem trucks reached the AGMF, soil was deposited onto the liner within the AGMF. An excavator at the outside edge of the AGMF moved the soil into a pile until all the trucks had been unloaded. To homogenize the soil, the excavator spread the soil around the liner area using an Allu® bucket to screen the soil. Then the spread-out soil was collected into one pile using the Allu® bucket (Figure 4). This spreading and piling through the Allu® bucket was done four times. Finally, the soil was

piled at the north end of the containment cell. Composite samples were taken from the pile and analyzed for parameters in Table 1.

Figure 3. Bromacil-impacted soil delivery and placement.

Figure 4. Soil homogenization and piling using Allu® bucket on excavator.

Table 1. Soil characterization parameters.

Analysis	Rationale	Number of samples	Laboratory
Available nutrients	Characterize general soil physical and chemical parameters	3	Element
Particle size distribution			
Detailed salinity			
Heterotrophic plate count	Characterize the soil's ability to degrade contaminants via biological processes		
Natural oxidant demand	Estimate the amount of oxidant that could be scavenged by non-targeted organic and inorganic constituents in soil	1	Chemco Inc. (Chemco)
Water holding capacity	Support calculations of the amount of water to be added to soil	3	Chemco
Gravimetric moisture content	Monitor actual soil moisture against the optimal moisture content equivalent to a percentage of the soil's water holding capacity	5	InnoTech Alberta

3.4 TREATMENT CELL CONSTRUCTION

After soil homogenization, 12 treatment cells were constructed on top of the liner. Three cells were allocated for each of the three treatments, and the remaining three cells were assigned as controls.

Each treatment cell consisted of (1) a squared, soil bermed area, (2) a blue 3.7 m by 4.3 m tarp placed within the bermed area to isolate the cell and reagents, (3) approximately 5.4 m^3 of bromacil-impacted soil from the pile placed on the tarp to form a 3.0 m by 3.0 m pile 0.6 m tall, (4) treatment amendments mixed into the soil, (5) soil temperature and moisture content sensors inserted into the soil, and (6) another blue tarp placed on top to cover the soil and maintain consistent soil moisture content throughout the experiment. Sandbags were placed on the perimeter of the upper tarps to keep them in place. All treatments were applied by Trium Environmental Inc. (Trium), a remediation consulting company.

3.4.1 Hydrogen Peroxide with VTX® Catalyst and Tween®-80 Surfactant (PVT)

For PVT, approximately 250 kg of 50% hydrogen peroxide solution, 30 kg of 22% VTX® catalyst solution, and 10 kg of Tween®-80 surfactant supplied by Chemco were applied to each treatment cell. Appropriate application of the PVT requires that the chemical reaction occurs while in direct contact with the contaminants in the soil. VTX® catalyst reacts immediately when in contact with hydrogen peroxide and produces the short acting free radicals that destroy compounds in the soil. When not in contact with soil, hydrogen peroxide is consumed during the reaction by both the catalyst reaction and reaction with the free radicals produced by the catalyst reaction. Product supplier instructions stated

that the treatment was to be applied in two steps: (1) apply the VTX® catalyst and Tween®-80 to the soil, then (2) apply hydrogen peroxide to the VTX® and Tween®-80 treated soil. The application weights were calculated by Chemco based on the natural oxidant demand of the bromacil-impacted soil.

Application rate was 495 kg of 50% hydrogen peroxide, 50 kg of VTX® catalyst, and 16kg of Tween®-80 for each treatment cell. For application to each treatment cell, Trium diluted the 50% hydrogen peroxide solution with municipal drinking water to a range of 15% to 20% concentration. Then VTX® catalyst was added to the diluted hydrogen peroxide in the mixing vessel (Figure 5). Finally, the Tween®-80 surfactant was added to make approximately 600 L of solution. There was a strong reaction when VTX® catalyst was added to the diluted hydrogen peroxide and Tween®-80 application rate had to be reduced to approximately 1.6 kg per treatment cell.

Figure 5. Mixing vessel.

For each treatment cell, the combined reagent solution was mixed with soil by spreading thin layers of soil across the treatment cell area and applying the reagent solution until the soil was saturated (Figure 6). The layering and saturation were repeated until the target soil volume was reached and all the prepared reagent solution was incorporated.

Figure 6. Application of PVT with surfactant to bromacil-impacted soil.

3.4.2 Activated Carbon

For each treatment cell, a total of 75 kg of powdered activated carbon (PAC), ChemcaCarb PAC 800, supplied by Chemco was mixed on-site with 600 L of municipal drinking water (Figure 5) to form a slurry. The mixing vessel was first filled with PAC and water was slowly added while blending with a slow paddle mixer. The PAC slurry was applied to the soil in each treatment cell like the PVT treatment: layers of soil were saturated with PAC slurry until the target volume of soil was saturated with the prepared slurry. Approximately 27 L/m^3 of slurry was applied to each PAC treatment cell.

3.4.3 Daramend®

Approximately 265 kg of Daramend®, supplied by Chemco, was directly added to each of the three treatment cells. Small layers of soil were spread over the tarp, Daramend® was spread on the soil layer, then municipal drinking water was sprayed on the surface until saturated. This was repeated until all the soil and Daramend® had been added. Then the excavator was used to mix the Daramend® treated soil and more water was added to achieve ≥80% water holding capacity.

Figure 7. Applying Daramend® to soil.

3.4.4 Control

The remaining soil was used to construct the control cells. Each cell was mixed using the excavator to ensure that the soil was handled in a similar manner as the treatment cells. Water was added to the control cells to achieve ≥80% water holding capacity.

3.5 MONITORING, WATERING, AND TREATMENT SAMPLING

3.5.1 Monitoring

Meter Group ECH_2O 5TE soil sensors were installed into the soil of each treatment cell to monitor volumetric water content and soil temperature. Each sensor was connected to one of three Meter Group Em50 data loggers to record hourly measurements. The data were downloaded during sampling events on weeks 2, 4, 8, and 12. During data download, real-time volumetric water content data was reviewed to determine if any treatment cells required additional water to maintain target moisture content.

Ambient weather conditions recorded at the on-site Environment and Climate Change Canada weather station were used to assess whether early-autumn air temperatures were suitable for the continuation of the experiment after week 8.

3.5.2 Watering

Additional water was added to the control cells at weeks 2 and 3 and Daramend® treatment cells on weeks 2, 3, and 4 by spraying municipal drinking water over the surface of the piles until the surface was saturated and most of the water sprayed ran off the soil surface.

On week 7, a small excavator was used to incorporate additional municipal drinking water into the entire soil volume of the Daramend® treatment cells. Each treatment cell was uncovered, and the soil sensors were removed. The excavator shifted the soil into a pile on one half of the bottom tarp. Then water was added as the excavator moved the pile into the other half of the tarp. Finally, the excavator

put the soil back into the original dimensions (Figure 8). Soil sensors were inserted into the soil and the treatment cells we covered by tarps.

Figure 8. Water addition to Daramend® treatment cells in week 7.

3.5.3 Treatment Sampling

The soil in each cell was periodically sampled and analyzed for total bromacil, gravimetric water content, and oxidation-reduction potential (ORP). Three discreet samples were taken from each cell for analysis. The standard USEPA Method 8321B was used for total bromacil in soil. Periodic gravimetric analysis of gravimetric soil moisture content was performed to confirm the field measurements from the soil sensors. ORP was measured to determine if the soil was in oxidizing or reducing conditions.

To determine the plant accessible or leachable bromacil after adsorption, AC treated piles were analyzed for phytoaccessible bromacil using the method developed by Maxwell (2022). Phytoaccessible bromacil was analyzed using the same samples used for total bromacil.

3.5.4 Statistical Analysis

Data exploration, analysis, and visualization were carried out using the R language and environment for statistical computing (R Core Team, 2023). In this report, the term “significant” is used to describe statistically significant relationships ($p = 0.05$). For all statistical tests, data were explored to determine whether assumptions of normality and homogeneity of variance were met; this included visual examination of data and residuals, Shapiro-Wilk test, and Levene’s test.

Analysis of covariance (ANCOVA) with a fitted linear model and treatment and time as factors was used to compare total bromacil concentrations of treatments against the control concentrations. Significance was identified using Tukey multiple comparisons of means. Interaction of time and

To compare total bromacil concentrations of treatments against the control concentrations, analysis of covariance (ANCOVA) using a fitted linear model with treatment and time since treatment as factors was used. Significance was identified using Tukey multiple comparisons of means. Phytoaccessible bromacil

concentrations had too many below detection limit results (reported as <0.008 mg/kg) so no statistical analysis was done on the phytoaccessible data.

4.0 RESULTS AND DISCUSSION

4.1 SOIL SOURCE CONCENTRATIONS

The 10 composite samples from the excavation site in Trochu had an average total bromacil concentration of 0.58±0.41 mg/kg. Total bromacil concentration ranged from 0.053 mg/kg to 1.59 mg/kg. Soil excavation targeted the highest concentration soil and the highest bromacil concentration was from the first truck load. Based on results from past ESAs, bromacil concentrations were as expected. See Appendix A for full results.

4.2 SOIL HOMOGENIZATION AND CHARACTERIZATION

Results from the samples taken from each treatment cell during setup show that soils were well homogenized with an average total bromacil concentration of 0.544 mg/kg and a standard deviation of 0.05 mg/kg. Three samples were outside the interquartile range: 0.407 mg/kg, 0.410 mg/kg, and 0.671 mg/kg. These samples came from 2 different activated carbon treatment cells. The z-score for all values were less than |3| and, given the initial heterogeneity of the source soil, these samples were not considered outliers.

Soil texture was classified as fine-grained, clay loam with 33% sand, 23% silt, and 25% clay, consistent with past ESAs. The soil was non-saline and non-sodic with a mean electrical conductivity of 1.25 dS/m, sodium adsorption ratio of 1.3, and pH of 7.8. Soil nutrients analysis showed high potassium, and low nitrogen and carbon. See Appendix A for full results.

4.3 TREATMENT APPLICATION AND EFFICACY

4.3.1 Hydrogen Peroxide with VTX® Catalyst and Tween®-80 Surfactant (PVT)

Mixing all the reagents prior to application rather than Chemco's recommendation of applying the catalyst and surfactant to the soil then applying hydrogen peroxide resulted in the hydrogen peroxide reacting strongly with the catalyst directly in the mixing vessel. The strong reaction made adding and mixing of Tween®-80 difficult and the application rate of Tween®-80 was reduced from 16 kg to approximately 1.6 kg per treatment cell. Production of short-lasting, highly reactive free radicals happened when the mixing vessel and the entire volume of reagents for each treatment cell was mixed prior to application. Free radicals produced in this reaction have a lifetime in the order of seconds to minutes. By the time the treatment was applied to the first layer of soil, most of the free radicals would have been self-consumed and none would have been active during the application to most of the soil volume.

The treatment was reacting strongly as it was being sprayed over the soil surface, producing vapours, fumes, and foam as show in Figure 9. The temperature of the soil rose 10°C above the ambient air temperature. By the time soil sensors had been installed the next day, soil in each treatment cell had returned to ambient temperature.

Figure 9. Reaction of chemical oxidant with soil.

Soil temperature for the PVT treatment cells followed the same temperature trend as control cells and was approximately 2°C higher than control (Figure 10). Considering the short acting time of PVT, the slight temperature increase is not evidence that continuing chemical reactions were occurring.

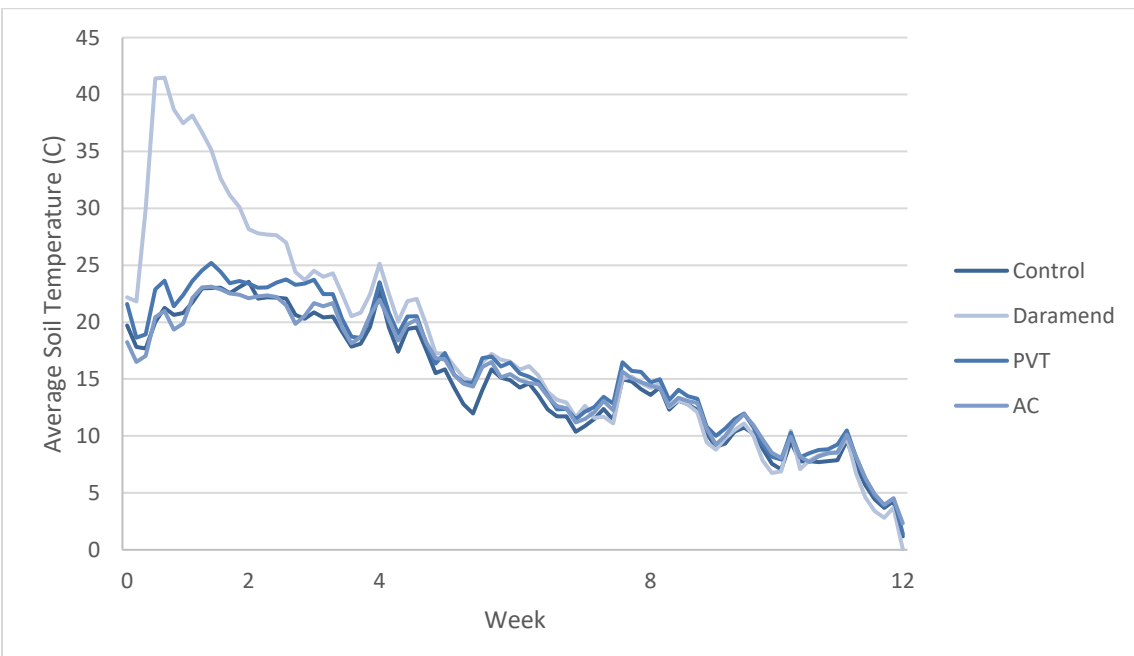

Figure 10. Average soil temperature for treatment and control cells (n=3) during the experiment.

PVT soil moisture was initially 0.07 m^3/m^3 higher than controls at 0.26 m^3/m^3. Moisture gradually decreased over the course of the experiment (Figure 11). No additional water was added to the PVT treatment cells after initial treatment.

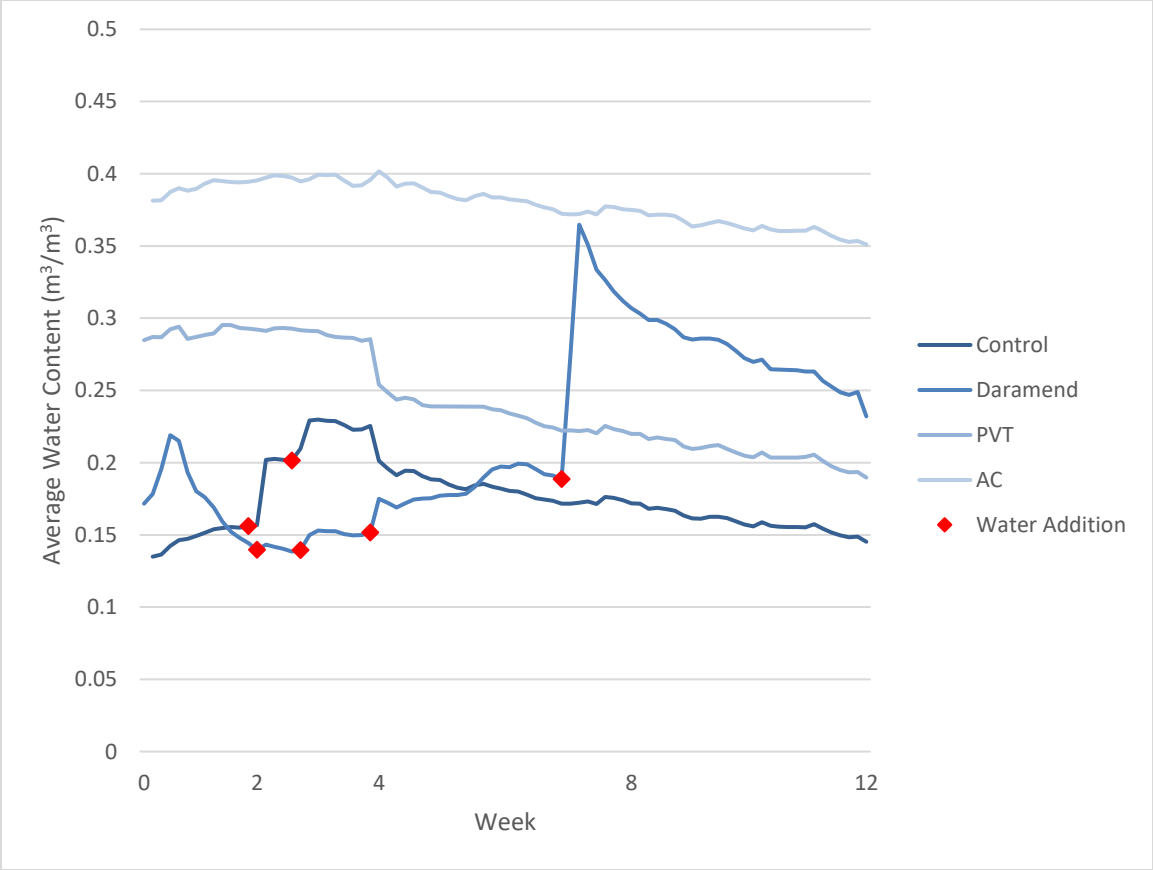

Figure 11. Average water content (m^3/m^3) for treatment and control cells (n=3) during the experiment.

PVT did not have a statistically significant effect on total bromacil concentration compared to control cells (Figure 12). As discussed in methods, PVT was not mixed according to manufacturer's instructions: VTX® catalyst was mixed with the hydrogen peroxide in the mixing vessel prior to application to the soil. Chemical reactions were likely self-consumed before they were able to act on the bromacil in the soil and the desired effects were not seen.

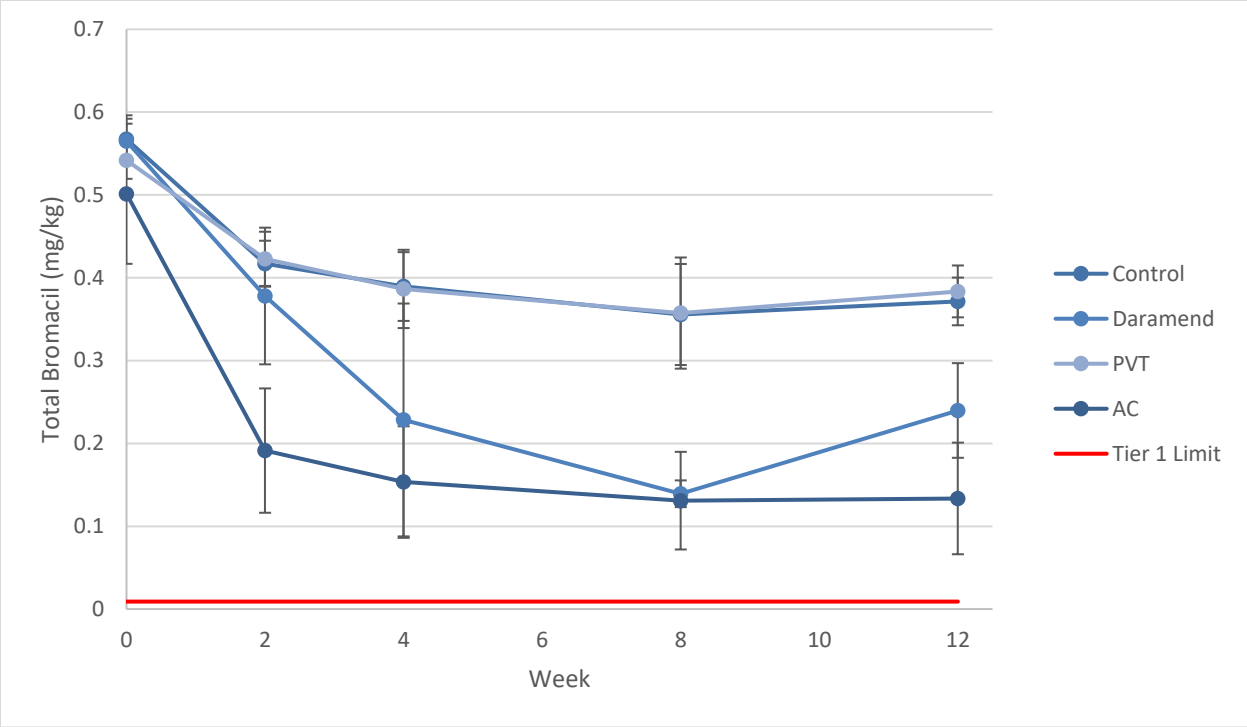

Figure 12. Average total bromacil concentrations (mg/kg) in treatment and control cells (n=9) during the 12 weeks of the experiment.
Error bars indicate standard deviation. Alberta Tier 1 Guideline for bromacil (0.009 mg/kg) is indicated in red.

4.3.2 Activated Carbon (AC)

The slurry application of the AC treatment brought moisture content in those piles to, on average, 0.40 m^3/m^3 and reached 0.35 m^3/m^3 by the end of the experiment (Figure 11). The water holding capacity of soil was 34.3% (w/w). The amount of water added with the AC treatment exceeded the water holding capacity of the soil and free-standing water could be seen during treatment application (Figure 13). When all the slurry had been applied, the treatment cells were a saturated paste. At this level of saturation, the AC suspension would have had full contact with the soil volume. No additional water was added to these treatment cells. Soil temperatures in AC treatment cells did not differ from control cells at any point during the experiment (Figure 10).

Figure 13. Application of AC in slurry to a treatment cell. Free water can be seen on the soil surface.

Total bromacil concentration was reduced 62%, from 0.50 mg/kg to 0.19±0.08 mg/kg, 2 weeks after treatment (statistically significant at p<<0) (Figure 12). At 12 weeks, total bromacil concentrations had been reduced by 74% from the starting concentration to 0.13±0.07 mg/kg. There was variability with the treatment cells and differences between weeks 2 and 12 are likely due to sample variation.

Average initial phytoaccessible bromacil concentration in AC treatment cells was 0.060 mg/kg, 12% of the initial total bromacil concentration. Phytoaccessible bromacil was below the detection limit of 0.008 mg/kg and the Tier 1 soil remediation guidelines of 0.009 mg/kg for bromacil (Alberta Environment and Parks, 2022) by week 2 and no detectable phytoaccessible bromacil was found for the remainder of the experiment (Figure 14).

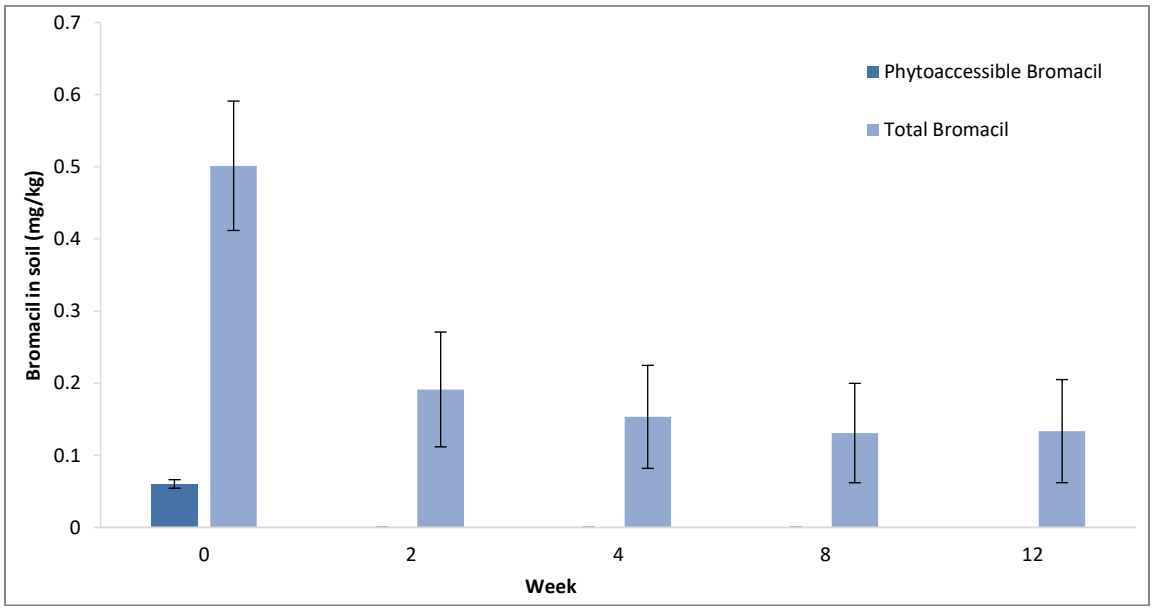

Figure 14. Total and phytoaccessible bromacil in AC treated soil.
There was no detectible phytoaccessible after treatment with AC.

4.3.3 Daramend®

Daramend® treatment cells had a moisture content of 17.7% 2 weeks after treatment and moisture content was between 16% and 18% until week 7 (Figure 11). The treatment cells were surface watered at weeks 2, 3 and 4. The fine texture of the soil prevented water from penetrating the soil surface and watering was not effective in increasing soil moisture. The lower moisture content compared to the treatments was due to the application method. AC and PVT were applied directly as a liquid in relatively high volumes compared to the soil volume. Daramend® was applied as a powder in layers and water was added using a low flow hose. Also, the organic component of Daramend® has a high water holding capacity and absorbs soil moisture. This can be seen in the reduction of soil moisture despite surface water addition over the first 3 weeks after treatment in Figure 11. Control treatments had a lower initial water content, but soil moisture increased when the control cells were surface watered (Figure 11) even though water did not appear to penetrate the soil surface.

The excavation and water addition at week 7 increased soil moisture content from 18.9% to 36.4%. Moisture in Daramend® treatments significantly decreased over the remainder of the experiment to 23.2%; whereas the other treatments had a gradual or negligible decrease in moisture (Figure 11).

Daramend® treatment cells had a significant 20°C increase in temperature during the three days after treatment, up to 41°C (Figure 10). The temperature gradually decreased over the first 3 weeks after treatment and followed ambient air temperature trends after 3 weeks. Temperatures remained elevated, compared to control cells and ambient air temperature for 5 weeks after treatment. After 5 weeks, Daramend® treatment cell soil temperatures were similar to control cells.

Daramend® treatment cells had a statistically significant reduction in total bromacil concentrations (Figure 12). The lowest total bromacil concentration was at week 8, 0.14±0.02 mg/kg (Figure 12). There was a rebound in bromacil concentrations and week 12 concentrations had increased to 0.24±0.06 mg/kg. The rebound was not statistically significant ($p=0.10$). There was a similar dip and rebound in total bromacil concentrations at weeks 8 and 12 in PVT treatment and control cells. Just before the rebound, the decrease from the initial total bromacil concentration was approximately 60%.

The oxidation-reduction potential measurements for Daramend® treatment and control cells can be seen in Figure 15. ALS Ltd. analyzed samples for ORP from samples taken at weeks 2 and 4. ORP was determined by field measurements on weeks 8 and 12. Due to the different methods and high variability between results, individual Daramend® treatment and control cell replicates are reported. ORP for the control cells were all positive, over 100 mV, for the entire experiment, indicating that the soil was in oxidizing conditions (Figure 15). The Daramend® treatment cells were positive for most of the experiment. On week 8, one week after excavation and watering, ORP in 2 of the Daramend® treatment cells were negative, -455 mV and -508 mV, indicating that the soils were in strongly reducing conditions (Figure 15). By week 12, only one of the Daramend® treatment cells was in reducing conditions with an ORP of -60 mV (Figure 15). Daramend® treatment cells with negative ORP did not have different bromacil concentrations compared to the Daramend® treatment cell that always had positive ORP.

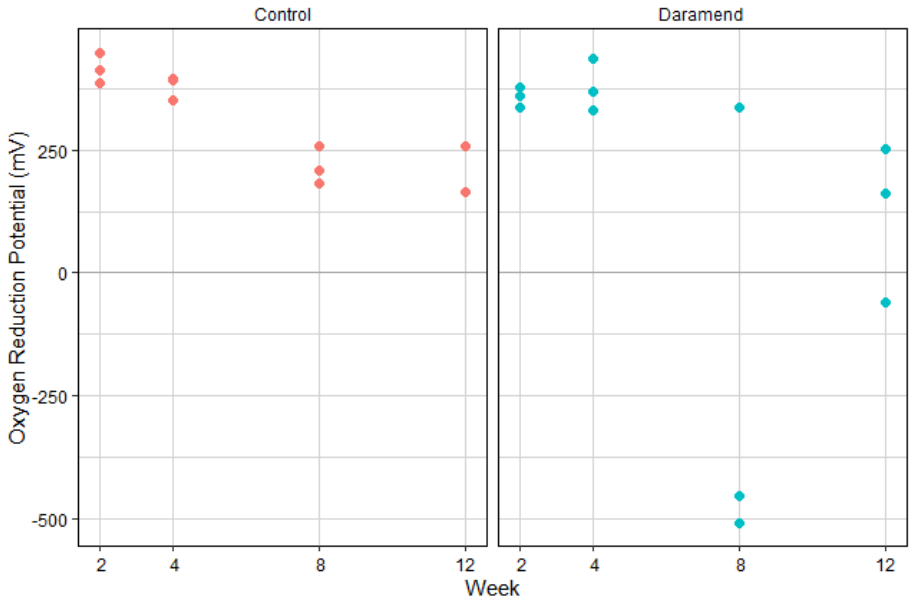

Figure 15. Oxidation-reduction potential (ORP) of Daramend® treatment and control cells. The measurement from each replicate is presented.

4.3.4 Treatment Efficacy Comparison

Control cells had an initial statistically significant decrease in total bromacil concentration in week 2 then remained constant to week 12 (Figure 12). A similar decrease over the same period is seen in PVT treatment cells. Samples collected at week 0 were prior to treatment or watering. Aerobic degradation of weathered bromacil was not expected, PVT treatment cells were saturated and in anaerobic conditions, and no further degradation was seen in control cells. The initial decrease is likely due to dilution from watering during setup.

In control, PVT, and Daramend® treatment cells there was a dip in concentrations in week 8 samples and concentrations returned to week 4 levels on week 12 (Figure 12). The decrease in week 8 was statistically significant for weeks 0 and 2 but not significant for weeks 4 and 12 when compared within their respective treatments. This dip was not seen in AC treatment samples. Element analyzed AC treatment samples separately from the others so that phytoaccessible analysis could be done. The decrease in week 8 in reported total bromacil concentration in control, PVT, and Daramend® treatment cells could be due to the different analysis for week 8. The results from week 12 samples were reported beyond the holding time for week 8 samples so the week 8 samples were not reanalyzed to confirm results.

AC treatment was the most effective in reducing total bromacil concentrations, with a total reduction of 74% (Table 2). Daramend® was effective in reducing bromacil concentrations, with a total reduction in bromacil concentrations of 58%. PVT was not effective in reducing bromacil concentrations compared to control. None of the treatments were able to reduce total bromacil concentrations to meet Alberta Tier 1 soil remediation guideline of 0.009 mg/kg for bromacil (Alberta Environment and Parks, 2022).

Table 2. Average percent reduction with standard deviation in total bromacil concentrations for each treatment cell and controls by weeks after treatment application.

Week	Average Percent Reduction in Bromacil			
	Control	Daramend®	PVT	AC
2	26%±3%	33%±5%	22%±6%	62%±7%
4	31%±5%	60%±7%	29%±4%	69%±2%
8	37%±8%	75%±2%	34%±10%	74%±4%
12	34%±5%	58%±2%	29%±3%	74%±12%

PVT was not applied in using recommended methods and the short-acting chemical reactions that treat soil contaminants were occurring before it was in contact with the soil. Total bromacil concentration in PVT treatment cells was not statistically different from controls cells. Saturation of the soil by the PVT treatment includes contact with Tween®-80 surfactant and higher bromacil concentrations would be expected from surfactant mobilization. Oxidation degradation from hydrogen peroxide and from free radicals produced from catalyst reactions is non-specific and will degrade most organic compounds they contact. Mixing all 3 compounds within the same mixing vessel may have caused the degradation of Tween®-80 before contacting the soil. Based on the misapplication of the PVT treatment, no conclusions can be made on its efficacy in reducing bromacil concentrations in soil.

In previous work, phytoaccessible bromacil concentrations were ~2/3 of total bromacil concentrations (Maxwell, 2022). Initial phytoaccessible bromacil concentrations were 10% of the total bromacil concentration in the AC treatment cells in this experiment (Figure 14). Post-AC treatment, phytoaccessible concentrations were below detection limits (Figure 14). Bromacil in the AC treatment cells remains within the soil volume, adsorbed to the applied AC. While total bromacil analysis shows how much bromacil is in the soil, phytoaccessible analysis is related to the leachability and potential mobility of bromacil (Maxwell, 2022). In a leaching and artificial AC weathering study, AC was able to retain the majority of adsorbed bromacil with bromacil retention increasing with artificial weathering (Thacker, 2022). While AC would not be eligible for remediation certification under current regulations, AC treatment should be considered as part of an environmental risk management plan to immobilize bromacil and reduce its impact on plant receptors.

Daramend® also had a statistically significant 58% reduction in total bromacil concentrations at week 12 (Figure 12). While total bromacil concentrations did not meet Tier 1 guidelines for bromacil of 0.009 mg/kg, Daramend® is a long-acting, freeze/thaw stable, multi-year remediation amendment. Further total bromacil reduction would be expected in subsequent years if Daramend® is degrading bromacil in the soil. Bromacil does adsorb to soil organic matter and bromacil in the Daramend® treatment cells could be adsorbing to the organic matter component of Daramend®. The USEPA method uses a solvent to extract bromacil from the soil samples and is assumed to be able to desorb all bromacil sorbed to soil organic matter (Maxwell, 2022; USEPA, 2007). It is likely that the reduction in total bromacil is due to degradation and not due to adsorption. Analysis of degradation byproducts would be required to confirm whether Daramend® degrades bromacil. Bromide is the primary byproduct produced in bromacil degradation and is produced in low concentrations relative to bromacil, by mass. Bromide was not analyzed in his experiment.

4.4 RELATIVE TREATMENT COSTS

Table 3 summarizes the costs of the two effective treatments, activated carbon (ChemCarb PAC 800) and Daramend®, based on unit volume of loose soil. Relative costs should be considered since earthworks and amendment costs will differ with volume of soil and the amendment amount required is dependent on bromacil concentration in the soil. Unit costs are based on treating approximately 16 m^3 of soil with only one treatment application as applied in this experiment. This information is for relative cost comparisons and not for remediation cost estimation. When comparing costs, it should be noted that no additional reduction in total bromacil concentration would be expected in AC treatment cells whereas Daramend® can actively remediate for as long as five years.

Table 3. Relative cost comparison for activated carbon and Daramend®. Earthworks costs comprise mobilization and demobilization, excavating and mixing soil with amendment, and soil placement. Daramend® includes additional handling for mid-experiment watering.

Aspect	Treatment	
	ChemCarb PAC 800	Daramend®
Treatment cost per m^3 of soil	$53	$99
Earthworks cost per m^3 of soil	$154	$182
Total cost per m^3 of soil	$206	$281

4.5 HEALTH, SAFETY, OPERATIONAL, AND ENVIRONMENTAL CONSIDERATIONS

4.5.1 Activated Carbon

Some of the AC became wind-borne during slurry mixing, potentially exposing workers to dust. The MSDS requires the use of safety glasses and respirators with particulate filters when handling the ChemCarb Pac 800 in poorly ventilated spaces (ClearTech Industries Inc., 2022). Granular activated carbon does not pose the same dust hazard but has poorer performance due to reduced contact with soil and contaminants. Activated carbon is not considered hazardous and no special transportation, handling, or spill response methods are required. Some sources of AC contain heavy metals that can pose an environmental risk. AC produced from organic sources and characterization of the AC product can mitigate potential heavy metal impacts.

During mixing, some of the AC particles were slightly hydrophobic and caused issues blending with water in the vessel. The AC treatment cells were small scale compared to operational scale remediation projects. Mixing AC slurry at operational scales would require in-situ mixing equipment to ensure contact with the soil volume. The size of the AC particles in powdered activated carbon would be small enough to infiltrate into the soil profile in coarse textured soils but complete contaminant contact would not be ensured. Creating a slurry for operational-scale applications requires access to large volumes of water, additional earth moving, and geotechnical issues that would need to be addressed. There are other techniques for AC treatment application that should be considered when using AC for bromacil treatment (Levy et al., 2021).

4.5.2 Daramend®

Daramend® can be an eye and respiratory irritant and the MSDS requires eye protection and respirators with particulate filters. In poorly ventilated areas, Daramend® can form a combustible dust (Evonik

Active Oxygens, LLC, 2021). Steps should be taken to prevent dust formation. No environmental hazards are associated with Daramend® and no special transportation handling or spill response methods are required, aside from preventing dust generation.

Ex-situ, on-site mixing of Daramend® into the soil allows for full contact for maximum efficacy but may not be feasible for large volumes of soil in operational-scale projects or for deep impacts where excavation is not feasible. Daramend® can be used as a permeable reactive barrier (PRB) to intercept and treat bromacil plumes, limiting the size of excavation required and providing a risk management option for off-site migration. It is also available in forms that can be injected below ground, eliminating the need for excavation. PRB and injectable forms were not tested in this experiment and would require further investigation to determine their effectiveness.

Maintaining high moisture content to ensure reducing conditions is the primary challenge when using Daramend®. Large amounts of water must be available on-site to reach target moisture content in the soil. When applied to fine-textured soil, common in Alberta, reaching target moisture content then handling moistened fine-textured soil is challenging and time-consuming. Monitoring, adding water to maintain moisture content, and/or wrapping the soil to prevent moisture loss are required to ensure Daramend® effectiveness.

5.0 SUMMARY AND RECOMMENDATIONS

5.1 SUMMARY

This project was a 12-week, mesoscale experimental demonstration of three remediation technologies to reduce and immobilize bromacil in soil obtained from an ATCO Electric former substation. The three technologies were: (1) chemical oxidation using hydrogen peroxide, VTX® catalyst, and Tween®-80 surfactant; (2) activated carbon (AC) adsorption using ChemCarb PAC 800; and (3) biological and chemical reduction with Daramend®.

The objective was to evaluate the ability of these technologies to decrease total bromacil concentrations in soil, achieving Alberta Tier 1 soil remediation guideline for bromacil of 0.009 mg/kg (Alberta Environment and Parks, 2022) or risk management through pathway exclusion.

Two technologies were identified as effective in reducing total bromacil concentrations, activated carbon and Daramend®. Activated carbon reduced total bromacil concentrations by 74% (±12%) and Daramend® by 58% (±2%). Neither technology was able to achieve Tier 1 guideline by the end of the 12-week experiment; final levels were 0.13 mg/kg (±0.07 mg/kg) and 0.24 mg/kg (±0.06 mg/kg) for AC and Daramend®, respectively. No additional reduction in total bromacil from AC treatment was expected. Daramend® is a long-acting remediation amendment and bromacil reduction could occur for up to five years (Peroxychem, 2017).

Two weeks after treatment with activated carbon, phytoaccessible bromacil was below the detection limit of 0.008 mg/kg from an initial concentration of 0.060 mg/kg. Bromacil reduction from AC treatment is through adsorption and the bromacil is not degraded or removed. Using AC would be effective in risk management on bromacil-impacted soil and reducing or eliminating the effects of bromacil on plants growing in the impacted soil.

Handling of AC and Daramend® requires standard personal protective equipment for workers and, in poorly ventilated areas, respirators with particulate filters. In poorly ventilated areas, Daramend® can form combustible dust when handling and care is required in such conditions. AC and Daramend® are

not considered hazardous to the environment and no spill response or transport of dangerous goods documents are required.

AC and Daramend® have similar operational considerations. Both require large volumes of water on-site; AC requires enough water to form a slurry and have full contact with the soil volume and Daramend® requires large volumes of water to reach the minimum moisture content of 70% of the soils water holding capacity. To ensure full contact with the bromacil-impacted soil, excavation and mixing of the amendments with the soil is required. Ex-situ mixing used in this experiment limits the application of AC and Daramend® to surface soil. Other forms of AC with in-situ and below ground application should be investigated but their efficacy will vary. Daramend® can be applied as a permeable reactive barrier that can intercept bromacil plumes, eliminating the need for full excavation of all impacted soil and giving options for risk management of bromacil migration off-site. There is an injectable form of Daramend® that can be used as a below-ground in-situ treatment should be investigated for bromacil remediation. AC is half the cost of Daramend® at \$53 per m^3 and \$99 per m^3 of soil treated, respectively.

Oxidation using hydrogen peroxide, VTX® catalyst, and Tween®-80 (PVT) was not effective in reducing total bromacil concentration. PVT was not applied according to supplier recommendations that VTX® and Tween®-80 should be applied and mixed into the soil before mixing in hydrogen peroxide. In this experiment, all three components of VTX® were mixed in a vessel prior to application. Due to the misapplication, PVT can not be evaluated for its efficacy in treating bromacil in soil.

5.2 RECOMMENDATIONS

Soil Sterilants Project #12 has provided some meso-scale information on the use of Daramend®, activated carbon, and hydrogen peroxide with VTX® catalyst and surfactant. None of the treatments used was able to reach Alberta Tier 1 guidelines. The 12-week trial was not able to assess long-term remediation efficacy of these amendments. It is recommended that:

1. Further testing of activated carbon technologies to extend the findings in this report and work completed in SSP #10 (Thacker, 2022). The objective would be to determine the long-term efficacy of immobilizing bromacil in a field study.
2. Perform a similar mesoscale experiment to refine the application of Daramend® and evaluate its performance over multiple seasons. A corresponding lab component would confirm the degradation of bromacil and evaluate if lab-scale optimization is related to field performance. The objective would be to optimize the application of Daramend®, determine its long-term effectiveness in reducing bromacil concentrations, and confirm whether bromacil is being degraded or adsorbed by Daramend®.
3. Repeat the test of hydrogen peroxide with VTX and Tween®-80 on bromacil impacted soil using manufacturer's recommended application methods. The objective would be to assess the effectiveness of chemical oxidation in reducing bromacil in soil.

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Table 4. Bromacil concentrations from samples taken during excavation at source in Trouchu, AB on July 27, 2022.

Sample	Sample Location	Bromacil (mg/kg)	Monuron (%)
20220727-SSP12-Baseline1	Trochu NE 17-033-23W4M	1.59	110
20220727-SSP12-Baseline2	Trochu NE 17-033-23W4M	0.538	102
20220727-SSP12-Baseline3	Trochu NE 17-033-23W4M	0.628	108
20220727-SSP12-Baseline4	Trochu NE 17-033-23W4M	0.879	96
20220727-SSP12-Baseline5	Trochu NE 17-033-23W4M	0.688	98
20220728-SSP12-Baseline6	Trochu NE 17-033-23W4M	0.206	101
20220728-SSP12-Baseline7	Trochu NE 17-033-23W4M	0.326	101
20220728-SSP12-Baseline8	Trochu NE 17-033-23W4M	0.379	99
20220728-SSP12-Baseline9	Trochu NE 17-033-23W4M	0.053	100
20220728-SSP12-Baseline10	Trochu NE 17-033-23W4M	0.552	100

Table 5. Nutrient, carbon, and microbial analysis of 3 composite soil samples from Trochu on August 3, 2022, after homogenization.

Sample	Nitrate (µg/g)	Phosphorus (µg/g)	Potassium (µg/g)	Sulfate (mg/kg)	Ammonium (mg/kg)	Organic Matter (%)	Inorganic Carbon (%)	Organic Carbon (%)	Heterotrophic Count (CFU/g)
20220803-SSP12-PileComp-1	3	16	255	180	0.5	1.7	0.51	0.86	76000
20220803-SSP12-PileComp-2	3	14	256	131	<0.3	2.09	0.48	1.05	300000
20220803-SSP12-PileComp-3	3	13	256	137	<0.4	1.8	0.54	0.88	67000

Table 6. Texture and particle size analysis of 3 composite soil samples from Trochu on August 3, 2022, after homogenization.

Sample	Texture	Sand (% by weight)	Silt (% by weight)	Clay (% by weight)	Texture	75 micron sieve (% by weight)
20220803-SSP12-PileComp-1	Silty Clay Loam	15	46	38	Fine-Grained	34.2
20220803-SSP12-PileComp-2	Sandy Clay Loam	46	21	33	Fine-Grained	34.4
20220803-SSP12-PileComp-3	Clay Loam	38	28	34	Fine-Grained	36.9

Table 7. Detailed salinity of 3 composite soil samples from Trochu on August 3, 2022, after homogenization.

Sample	pH	Electrical Conductivity (dS/m)	SAR	% Saturation	Calcium (mg/kg)	Magnesium (mg/kg)	Sodium (mg/kg)	Potassium (mg/kg)	Chloride (mg/kg)	Sulfate (SO4) (mg/kg)	Sulfate-S (mg/kg)	TGR (T/ac)
20220803-SSP12-PileComp-1	7.8	1.18	1.3	82	94.6	43.0	56	13	19	409	136	<0.1
20220803-SSP12-PileComp-2	7.7	1.32	1.3	66	83.3	38.6	48	11	18	370	123	<0.1
20220803-SSP12-PileComp-3	7.9	1.26	1.4	75	86.9	41.5	55	12	17	395	132	<0.1

APPENDIX A10: EVALUATION AND COMPARISON OF REMEDIATION TECHNOLOGIES

Levy, S., X. Mo and V. Bachmann, 2021. Evaluation and Comparison of Soil Sterilant Remediation Technologies. Report SSP-13 prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 30 pp.

Appendix A9-2: Optimization of Daramend®

Bachmann, V., 2024. Optimization of Daramend® for the Remediation of Bromacil in Soil. Report SSP-12B prepared by InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 27 pp.

Optimization of Daramend® for the Remediation of Bromacil in Soil

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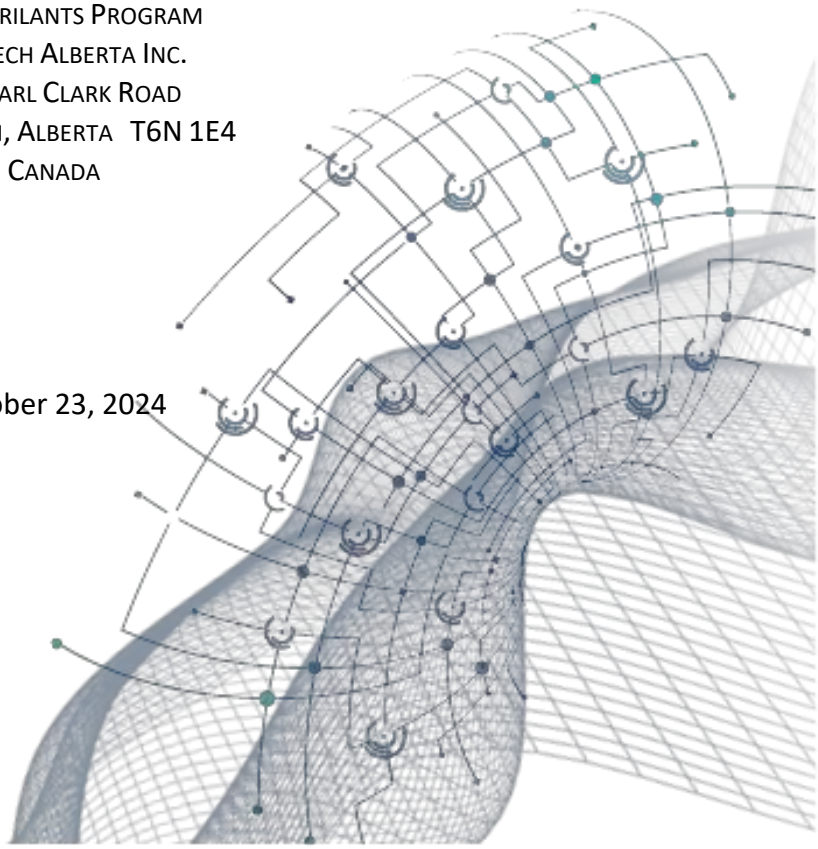

October 23, 2024

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EXECUTIVE SUMMARY

Bromacil and tebuthiuron are non-selective, broad-spectrum soil sterilants used for vegetation control on industrial land. In Alberta, they were introduced in the 1960s and were used on a variety of industrial sites until their use was halted in the 1990s due to their ability to migrate offsite and their extreme persistence. Decades after ceasing treatment with sterilant products, impacts can persist in soil and water. These sterilants are unique and challenging contaminants to manage. To address several knowledge gaps related to the assessment, remediation, and risk management of sites impacted by these sterilants, the Soil Sterilants Program (SSP) was designed as a 5-year joint industry program that was initiated in 2019.

A year-long, mesoscale study at InnoTech Alberta's Vegreville Research Facility was executed to optimize the use of Daramend® for the remediation of bromacil in soil obtained from a contaminated site in Alberta. A parallel lab-scale experiment was performed to assess the use of bench-scale scale studies for Daramend® optimization for field planning. Daramend® was applied at 2 dosages, 0.5% and 2% by dry soil weight, with control treatments (0% Daramend®). Additionally, two application practices were compared, (1) single application of Daramend® and water (Moisture Regime 1), and (2) two applications of Daramend® and three applications of water (Moisture Regime 2). The primary objective was to determine the optimum Daramend® dosage and management practice to maximize bromacil reduction to achieve the Alberta Tier 1 soil remediation guideline of 0.009 mg/kg and minimize remediation costs.

None of the treatments in the mesoscale study were able to reach the Alberta Tier 1 target of 0.009 mg/kg. Control treatments in Moisture Regime 2 had an increase in bromacil concentrations. By the end of the treatment, Daramend® treatments did not have statistically significant different bromacil concentrations from the initial concentrations. In Moisture Regime 2, the final bromacil concentrations for both 0.5% and 2% Daramend® were significantly lower than the final bromacil concentration for the control treatment. At week 38, the first sampling event after the winter season, there was an increase in bromacil concentrations from the previous measurement for all treatments; the control treatment in Moisture Regime 2 increased to more than double the initial concentration. The week 38 increase was less for all Daramend® treatments. Bromide concentrations increased for all Daramend® treatments in Moisture Regime 2, and 2% Daramend® treatments in Moisture Regime 1, indicating that bromacil was being destructively remediated in those treatments. There appeared to be an interaction between bromides and the soil. All increases in bromides were in the surface samples; bromide concentrations in the centre of the treatments did not change over the course of the experiment, even after mixing of Moisture Regime 2 treatments.

The bromacil concentration for all treatments in the lab study decreased to within 0.003 mg/kg of the minimum detection limit (0.008 mg/kg) by week 37 and were not significantly different from each other. Bromacil concentration in the control treatment did not start decreasing until 12 weeks after treatment. In Daramend® treatments, bromacil concentrations started decreasing 2 weeks after treatment. Increases in bromacil concentration were seen at week 8 for control treatment, but the increase was not statistically significant. Bromide concentrations increased for all treatments indicating destructive remediation of bromacil. Daramend® treatments had higher bromide concentrations than controls. There were decreases in bromide concentrations at week 4 for some treatments and at week 12 for 2% Daramend® treatments showing that bromides were interacting with soil.

For this soil, it appears that the limiting factor for bromacil degradation was moisture content and Daramend® was able to enhance degradation. The addition of water seems to release more bromacil from the soil phase and the application of Daramend® buffers this release by degrading the released bromacil. Bromacil is degraded via reductive debromination, an anaerobic process. Achieving and maintaining the

required moisture content on fine-textured surface soil in in-situ applications of Daramend® is logistically unfeasible. Daramend® and other anaerobic technologies maybe better suited for application in ex-situ reactors where the prolonged saturation of the impacted soil can be achieved and maintained.

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1.0 INTRODUCTION

1.1 Purpose and Background

Soil sterilants are non-selective, broad-spectrum herbicides used for vegetation control on industrial land. In Alberta, they were introduced in the 1960s and were used on a variety of industrial sites until their use was halted in the 1990s due to their ability to migrate offsite and their extreme persistence. Decades after ceasing treatment with sterilant products, impacts can persist in soil and water.

Soil sterilants are unique and challenging contaminants to manage. To address several knowledge gaps related to the assessment, remediation and risk management of sterilant-impacted sites, the Soil Sterilants Program (SSP) was designed as a 5-year joint industry program that was initiated in 2019.

After bench-scale testing of identified remediation technologies in SSP Project #11 and meso-scale testing in Project #12 *Ex Situ Field Demonstration for the Remediation of Bromacil in Soil* (Bachmann & Thiessen, 2023), Daramend® was shown to reduce the concentration of bromacil in soil. A field site was selected to test the efficacy of Daramend® in reducing bromacil concentration in soil in a real-world application.

Work done in SSP projects #11 and #12 showed Daramend® was effective in reducing bromacil concentration in soil. However, dosage rates, reapplication, soil moisture, and soil tilling to maximize the efficacy of Daramend® have yet to be optimized. Optimizing Daramend® application for bromacil remediation is necessary before applying the treatment in full-scale operations. A smaller scale experiment was conducted to determine the optimal field application practices of Daramend® to maximize the reduction of bromacil in soil. The optimization trial included a smaller, lab-scale component run in parallel to the field component. The lab component will be used to assess whether lab scale tests have similar results as field tests and could be used to optimize future field projects at the planning stage to optimize future field projects.

2.0 PROJECT OBJECTIVES

The overall objective of the project was to identify optimal conditions for treatment of bromacil-impacted soils with Daramend® to maximize contaminant reduction. Specific project objectives include:

1. Evaluate the optimal application rate, reapplication frequency, mixing, and controllable soil parameters of bromacil-impacted soil treated with Daramend® with the objective of maximizing bromacil reduction and achieving Tier 1[1] regulatory guideline concentration.
2. Determine the correlation between lab (4 L test jars) and field remediation results to inform the design of future remediation programs.

[1] Alberta Tier 1 Soil and Groundwater Remediation Guidelines (EPA, 2024). The limit for bromacil in all soils is 0.009 mg/kg.

3.0 PROJECT METHODOLOGY

3.1 Soil Sourcing, Homogenization, and Characterization

3.1.1 Soil Sourcing

Bromacil impacted soil was provided by ATCO utilities near Bow Island, AB. The soil was excavated on August 17th, 2023, as part of site closure, and the soil was delivered to the InnoTech Alberta facility in Vegreville the same day.

Based on analysis from November 2021, the impacted soil has a bromacil concentration ranging from 0.032 mg/kg to 1.980 mg/kg. Alberta Tier 1 Guidelines for bromacil in soil is 0.009 mg/kg (Alberta Environment and Parks, 2022).

3.1.2 Experimental Design

The aboveground mesocosm containment pad (~10 m x 30 m) at the Vegreville research facility was used for the experiment. The containment pad was constructed with two integrated liners, berms, and a catchment pond for collecting surface water. Permission to use the containment pad for the project was obtained from the committee overseeing its use.

Treatment soils were amended with 2 Daramend® dosage levels, 0.5% and 2% by dry soil weight; a control soil had no Daramend®. Soil water content was managed according to 2 moisture regimes. Moisture Regime 1 had water added to the soil during Daramend® application and plots were covered for the duration of the study. Moisture Regime 2 had water added to the soil during Daramend® application and again 4 weeks later. Moisture Regime 2 treatments in the field study had an additional application of Daramend® and water 44 weeks after initial treatment. Four replicates of 4 m^3 treatment cells for each treatment were used for the field study. Four replicates of 4 L jars were used for each treatment for the lab study. The experimental design is shown in Table 1.

Table 1. Experimental design.

Parameter	Quantity	Description
Soil	1	Bromacil impacted soil from Bow Island, AB.
Daramend®	3	Control (0%), 0.5%, 2.0% by dry soil weight
Moisture Regime	2	Moisture Regime 1: Initial moistening only, initial moistening and moistening 30 days after amendment
		Moisture Regime 2: Initial moistening and moistening 28 days after amendment. Additional Daramend® and water application 44 weeks after initial amendment (field study only).
Replicates	4	4 m^3 treatment cells or 4 L jars
Total	24	Total number of treatment cells

3.1.3 Homogenization

Once the soils reached the Vegreville site, they were directly deposited from the trucks onto the liner within the containment cell. A backhoe with an Allu® SMH 3-12 screener crusher bucket ("Allu® bucket") attachment was onsite to redistribute and homogenize the soils from outside the containment cell. An Allu® bucket is a heavy equipment attachment consisting of an open ended bucket with rotating drums and hammers to crush, mix, and/or aerate soil (ALLU Finland Oy., n.d.) (Figure 1). Homogenization was

conducted by scooping soil with the Allu® bucket, processing the soil through the bucket 4 times, and redistributing to mix all the soil and achieve homogeneity. After processing, the homogenized soil was piled on the north end of the containment pad.

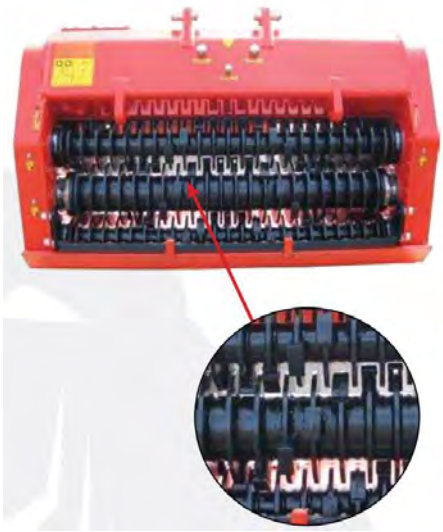

Figure 1. SMH series Allu Bucket (exact model used not shown).
Inset shows the drums with hammers for processing soil.
The SMH 3-12 used had 3 drums with hammers for soil processing (ALLU Finland Oy., n.d.).

Following homogenization, three composite samples from the homogenized pile were taken and submitted to Element Materials Technology analytical laboratories for baseline characterization parameters listed in Table 2. Another 6 random grab samples were taken for initial bromacil and bromides[2] concentration and variation. Subsamples from the composite samples were tested at InnoTech Inc. for moisture content and water holding capacity using the ASTM Standard Test Method for Determination of Water Content (ASTM Standard D4959-16, 2016).

3.2 Field Study

3.2.1 Treatment Cells

Each treatment cell was comprised of 3 m^3 of soil wrapped in a polyurethane tarp. The tarps were 4 m x 8 m. They were spread out and 3 m^3 of soil was piled on one half of the tarp.

3.2.2 Daramend® and Water Application

Each Allu® bucket was 1 m^3 and the soil was assumed to have a density of 1.6 t/m^3 based on its texture and the bulk densities of soils in Alberta. For 3 m^3 of soil, the weight of the soil was approximately 4.8 t. Soils were amended at three concentrations: 0% (control), 0.5%, and 2% by dry soil weight. For 0.5% treatments, 24 kg of Daramend® was required for each treatment cell; for 2% treatments, 96 kg of Daramend® was required for each treatment cell. The weight of Daramend® added to each treatment cell can be found in Appendix A.

[2] The degradation of bromacil releases bromide ions. Analysis of soluble bromides was used as an indicator of bromacil degradation.

Table 2. Soil characterization analyses.

Analysis	Replicates	Soil volume (total)	Provider
Texture	3	3 x 250 mL bags	Elemental Materials Technology
Total Organic Carbon	3		
Detailed salinity			
(pH (by CaCl2), saturated paste EC, % saturation, Ca, Mg, Na, SO4-S, SO4, Cl, K, SAR, TGR, reported in mg/kg. Includes Cl in mg/L)	3		
Bromacil	6 (random grab)	6 x 125 mL jars	
Moisture Content	3	3 x 100 g	InnoTech Alberta
Water holding capacity	3	3 x 100 g	

Daramend® for each treatment cell was weighed out and divided into three plastic totes for 0.5% treatments and 9 plastic totes for 2% treatments. Each treatment cell required three full Allu® buckets. For each bucket, the operator filled the Allu® bucket approximately 1/3 with soil and approximately 1/3 of the required Daramend® for 1 m^3 was spread evenly over the surface of the soil inside the bucket (Figure 2a). The operator scooped more soil and another 1/3 of the Daramend® was spread over the surface (Figure 2b). This was repeated until the required Daramend® was added. Then the bucket was topped off with soil to 1 m^3 of soil. The Allu® bucket processed the soil and Daramend®, mixing it and depositing the amended soil onto the tarp.

Figure 2. Mixing the Daramend® treatment soil.
a) Adding Daramend® to the soil in the Allu® bucket. b) Mixing and depositing the amended soil onto the treatment cell.

The facility in Vegreville has an on-site water filling station that provides City of Edmonton municipal drinking water. A 2,300 L water tanker with a 3.0 hp gas powered water pump and hose was filled with

water from this filling station. Soil from the Allu® bucket was dumped onto the tarp in thin layers. Each layer was sprayed with water until saturated before the next layer was added (Figure 3). Water was sprayed on the soil as it was being dumped out of the Allu® bucket and saturated before the next layer was added.

Figure 3. Adding water to the treatment piles.
a) as the treated soil comes out of the Allu bucket and b) until the layer is saturated with water.

3.2.3 4-Week Water Application

On week 4, Moisture Regime 2 treatment cells had additional municipal drinking water incorporated into entire soil volume. Each treatment cell was uncovered, and the soil sensors were removed. The excavator piled the soil into one half of the treatment cell. Then water was added as the excavator moved the soil back onto the other half of the treatment cell. Water was added using 20 L buckets. The excavator would lay down a layer of soil and 2 buckets full of water was spread over the top of the layer (Figure 4). To keep the water within the treatment cells, the excavator made a basin of the piles to pour the water in before mixing (Figure 4a). This was repeated until the soil was saturated. The soil was deemed saturated when it would no longer absorb water, and additional water would prevent the soil from forming a cohesive pile. The amount of water added ranged from ~180 L to ~200 L. Finally, the excavator put the soil back into a single 4 m^3 pile, soil sensors were installed, and the treatment cells were covered by tarps. Between treatment replicates, the excavator bucket was scraped off into the treatment cell using clean shovels. Between treatments, the excavator bucket and shovels were washed thoroughly with a pressure washer. The volume of water added to each treatment cell can be found in Appendix B.

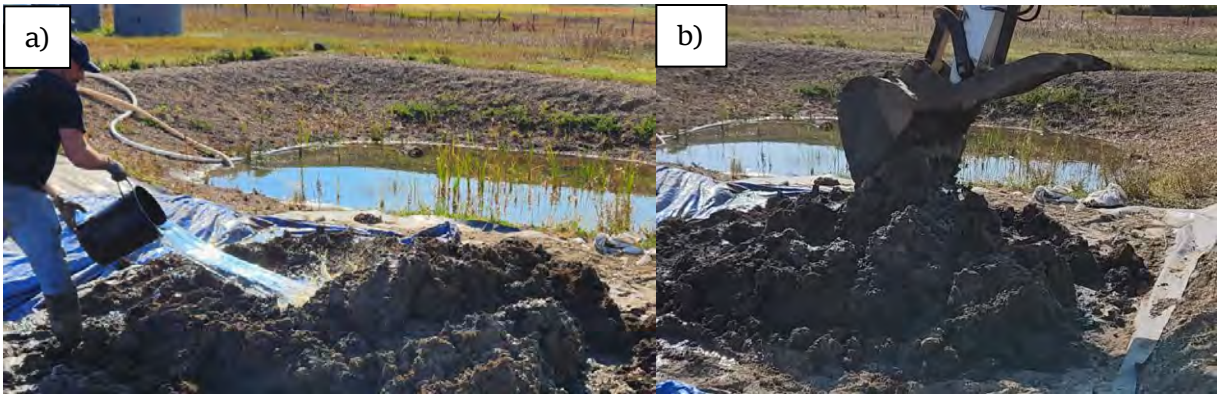

Figure 4. Add water to moisture regime 2 treatments.
Water was a) added to the soil by pouring buckets of water on the piles and b) incorporated using the small excavator.

3.2.4 44-Week Daramend and Water Application

On week 44, Moisture Regime 2 treatment cells had an additional application of water and Daramend® at similar dosage levels as the initial Daramend® application (0%, 0.5%, and 2% by dry soil weight). Water was applied using the same method as in section 3.2.3 (Figure 5a). Each pile took approximately 180 L to 220 L of water. Daramend® for each treatment cell was weighed in plastic totes. Daramend® was added during the water application. To add the additional Daramend®, a portion of total required Daramend® was spread over each soil layer then water was spread over the soil and Daramend® (Figure 5b). This was repeated until each pile had the required Daramend® applied and the soil was saturated with water. Mass of Daramend® and volume of water added to each treatment cell can be found in Appendix B.

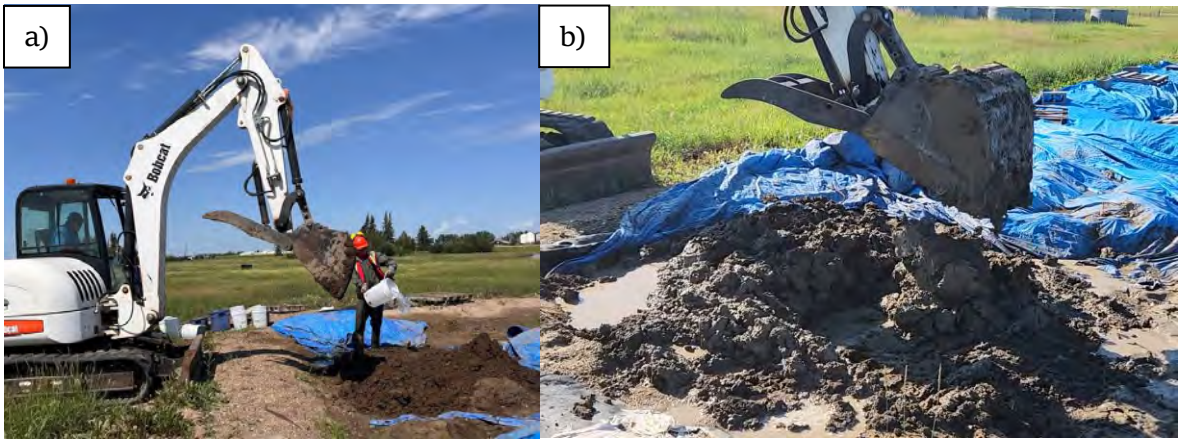

Figure 5. Adding water and Daramend® to moisture regime 2 treatments at week 44.
a) Adding water on top of Daramend® to moisture regime 2 treatments and b) incorporating the additional water and Daramend® to the soil.

3.2.5 Sampling and Monitoring

The soil in each treatment cell was periodically sampled and analyzed for total bromacil, soluble bromides, gravimetric water content, and oxidation-reduction potential (ORP). Two composite samples were taken from each cell. One composite sample from the top surface and one composite sample from the centre of mass of each treatment cell. The bottom of the treatment cells was avoided to account for potential cross contamination from run-off during water application and precipitation events. Soil samples were taken using a Dutch auger. Nitrile gloves were worn during sampling and replaced between treatment

replicates. All sampling equipment and ORP meter were washed using the triple-rinse method described in *Sterilant Sampling Best Management Practices* (Hemsley et al., 2021). The sampling schedule and dates are show in Table 3.

Table 3. Sample schedule for bromacil and bromides analysis.

Date	Week
8/24/2023	0
9/7/2023	2
9/21/2023	4
10/19/2023	8
Winter (7 months)	
5/16/2024	38
6/25/2024	44
8/22/2024	52

ORP was measured with an Oakton ORPTestr 10 using a modified version of the ISO field method for determination of redox potential (ISO, 2022). Using a shovel or auger, soil was exposed to a depth of 15 cm to 30 cm (Figure 6). The ORP meter was inserted into the soil and readings were taken according to the ORPTestr 10 instructions, when the ORP value had stabilized, typically after 5 minutes. The redox potential is used to assess whether the soil was in an aerobic and anaerobic state.

Figure 6. Oakton ORPTestr 10 taking a measurement in one of the treatment piles.

Each treatment cell had a Meter Group ECH_2O 5TE soil sensor installed to monitor volumetric water content (VWC) and soil temperature. Each sensor was connected to one of six Meter Group Em50 data loggers to record hourly measurements. Logger data were downloaded from the loggers during sampling.

Ambient weather conditions were taken from Environment and Climate Change Canada (ECCC) which has a weather station located approximately 600m from the above ground mesocosm facility. Hourly and daily weather data from the weather station was downloaded from the ECCC historical climate data website (ECCC, 2024).

3.3 Lab Study

3.3.1 Screening and Homogenization

A 120 L subsample of the soil from Bow Island, AB was taken after it was homogenized on site. The subsample was screened to 2 mm to remove rocks and other debris. The subsample was homogenized using the cone and quarter method (Schumacher et al., 1990). The soil was divided it into four large bins. Then scoops of soil were taken in sequence from each bin and placed into a fifth bin until all the soil was combined. The soil was divided again by scoops, sequentially, into the four bins. This process was repeated five times to achieve homogenization. Ten samples were randomly taken after homogenization and used to determine water content using the ASTM method (ASTM Standard D4959-16, 2016).

3.3.2 Daramend® and Water Addition

Approximately 3 kg of soil was used for each treatment replicate. The soil was spread out in a bin and the required amount of Daramend® was spread over the surface of the soil (Figure 7a). Then the Daramend® was incorporated into the soil via the cone and quarter method (Schumacher et al., 1990). For 3 kg of soil approximately 600 mL of water was required to reach 90% of the soil's water holding capacity. A third of the amended soil was put into a 4 L jar and mixed with 600 ml of deionized water using a glass stir rod (Figure 7b). The remainder of the soil was added to the jar in increments and mixed (Figure 7c).

Figure 7. Application of Daramend® and water to soil in the lab study.
a) Amending soil with Daramend®, b) mixing amended soil with water, and c) final soil after amendment and water incorporation.

The jars were sealed with lids and kept in a 20℃ room. An additional replicate for each treatment was setup for temperature and volumetric water content monitoring.

3.3.3 Freeze Thaw Cycles

To simulate weathering from winter conditions, the lab study went through 3 cold-warm cycles starting 16 weeks after treatment. Each cycle comprised 2 weeks at -15°C or 4°C followed by 2 weeks exposure at 20°C. Soil temperature was recorded using the sensors in the monitoring vessels. A final sample was taken from each replicate at week 37 for bromacil and bromides analysis.

3.3.4 Sampling and Monitoring

A composite sample of soil from each Daramend® dosage treatment was taken for analysis of bromacil and bromides prior to amendment. Treatment jars were sampled and analyzed for bromacil and bromides at 2, 4, 8, 12, and 37 weeks after setup. During sampling, ORP of each replicate was measured with an Oakton ORPTestr 10. The additional replicates were monitored for soil temperature and volumetric water content using Meter Group ECH_2O 5TE soil sensors connected to one of two Em50 dataloggers.

3.4 Statistical Analysis

All data exploration, analysis, and visualization was done using the R Project for Statistical Computing (R Core Team, 2024). All data were tested for normality using Shapiro-Wilk's Test and homogeneity of variance using Levene's test. Normal and equal variance data were tested for significance using analysis of variance (ANOVA) and post-hoc analysis was done using Tukey's honest significance test. For non-normal or unequal variance data, data were log transformed and analyzed by ANOVA and Tukey's test. When log-transformed data were not normal, the data were tested using general linear models (GLM) with a gamma distribution and a log link function. Statistical differences for bromacil and bromide concentrations were determined between Daramend® dosages, moisture regimes, and sample depth. Comparisons were made between the different treatments and within treatments between initial and final concentrations.

4.0 RESULTS

4.1 Soil Homogenization and Characterization

Five composite samples taken after homogenization had an average total bromacil concentration of 0.027±0.005 mg/kg. Total bromacil concentration ranged from 0.019 mg/kg to 0.035 mg/kg. Soil texture was classified as fine-grained, sandy clay loam with 1.0±0.2% Total Organic Carbon. The soil had a mean electrical conductivity of 5.3±0.4 dS/m, "Poor" according to Alberta's salt remediation guidelines (Alberta Environment, 2001), and a Sodium Adsorption Ratio (SAR) of 5.2±0.3, "Fair" according to Alberta's salt remediation guidelines. Full characterization results can be found in Appendix A.

4.2 Field Study

4.2.1 Moisture Content and Soil Temperature

The soil had an average moisture content of 11.7±0.8% (by weight) prior to initial treatment. After treatment, the treatments had an average moisture content of 20±2% (by weight) (Figure 8). There was no significant difference in moisture content between Daramend® and moisture regime treatments ($p > 0.05$).

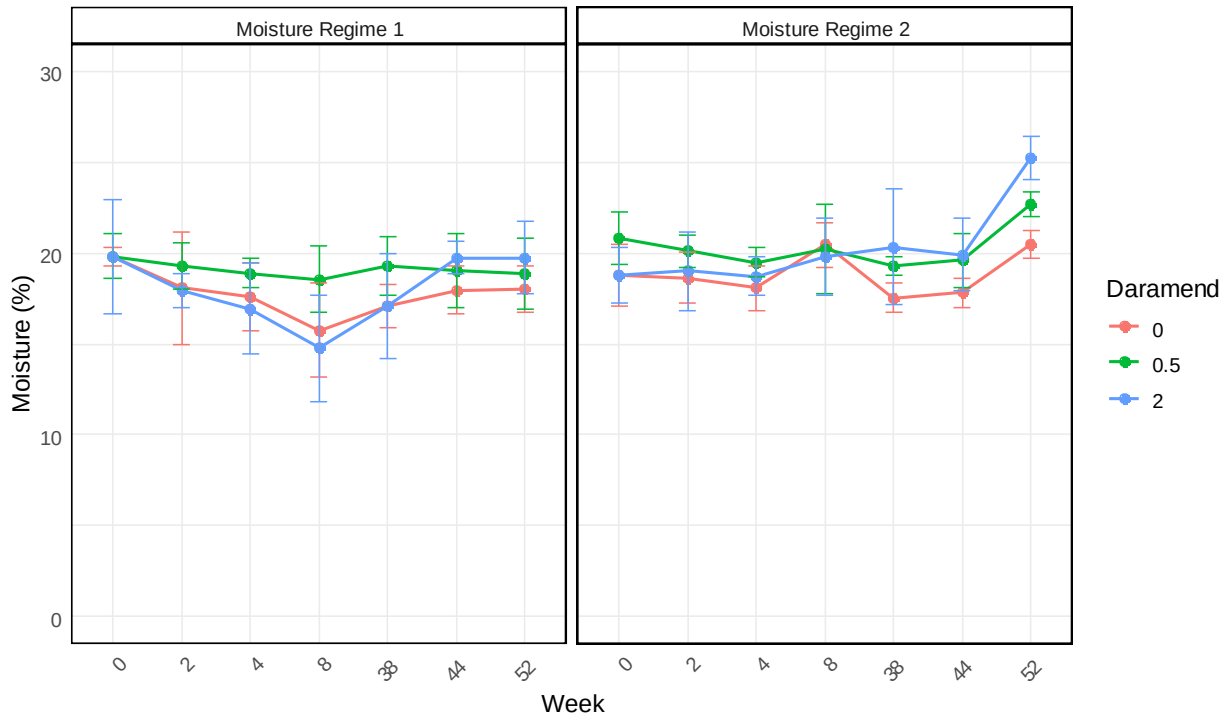

Figure 8. Moisture content of each treatment of the field study for the duration of the experiment. Moisture content was taken from analytical reports of the sampling events. The moisture content is an average of top, centre of mass, and replicates of each treatment.

In Moisture Regime 1 treatments, 0% and 2% Daramend® dosage treatments had a gradual decrease in moisture content for the first 8 weeks to 14±3% and 13±3% respectively. At week 38, 0% and 2% Daramend® treatments had increased moisture content to 17±1%. Moisture content continued to increase in Daramend® 2% treatment to 20±1% by week 44. The 0.5% Daramend® treatments had a consistent moisture content for the duration of the experiment.

The moisture content of Moisture Regime 2 treatments was consistent until the final week. Control treatments had an increase in moisture content at week 8. The control samples were taken after the 2nd water application and the 0.5% and 2% Daramend® treatments were sampled before the 2nd water application. The water application is reflected for all Moisture Regime 2 treatments in the soil sensor data and in the lab data at week 52.

The soil sensors had frequent failures that resulted in data loss. Available data are shown in Appendix C. Reported VWC was influenced by sensor placement and soil temperature. Cold temperatures had lower reported VWC values; day/night temperature changes can be seen in reported VWC values, and the sensors were unable to report VWC below 2°C. Soil temperature generally followed air temperature with expected day and night variations. There was no effect on soil temperature from Daramend® application ($p > 0.05$).

4.2.2 Bromacil Concentrations

Initial bromacil concentrations were below the expected concentrations of 0.1 mg/kg by an order of magnitude at 0.027±0.005 mg/kg. The lower concentration was likely due to dilution during homogenization with low to no bromacil containing soil. The soil was excavated as part of site closure and all excavated soil was diverted to Vegreville for this experiment. To achieve closure, the site would have

had soil outside the delineated bromacil-impacted area excavated to ensure all the target soil was removed from the site. After homogenization, bromacil concentrations were above the Tier 1 guideline of 0.009 mg/kg and would require remediation in real-world settings.

Bromacil concentrations were consistent during the first 8 weeks of the experiment. Moisture Regime 1 treatments started with an average bromacil concentration of 0.023 mg/kg (Figure 9) and at week 8 bromacil concentrations were at 0.023±0.003 mg/kg, 0.018±0.003 mg/kg, and 0.021±0.003 mg/kg for control, 0.5%, and 2% Daramend® treatments, respectively. In Moisture Regime 2 treatments, bromacil concentrations decreased during this time with an initial concentration of approximately 0.025 mg/kg and at week 8, 0.019±0.001mg/kg, 0.018±0.002 mg/kg, and 0.017±0.001 mg/kg for control, 0.5%, and 2% Daramend® treatments, respectively.

In the spring at week 38, there was an increase in bromacil concentrations for all treatments, exceeding the initial concentrations at week 0. The increase was more pronounced in control treatments and nearly double the initial bromacil concentration at 0.06±0.02 mg/kg in Moisture Regime 2. There was high variability between replicates for that treatment with concentrations ranging from 0.03 mg/kg to 0.09 mg/kg. Results from this week were confirmed within method variance.

There were many samples (18 of 46 total samples) from week 44 that did not meet the method acceptance standard with the surrogate recovery below the method criteria of 50%. Of the 18 samples that did not meet criteria, 8 were from control treatments, 5 from 0.5% Daramend®, and 4 from 2% Daramend® treatments in both moisture regimes. The samples that did not meet criteria were removed from statistical analysis. All other samples from the experiment were within specified method acceptance criteria.

At week 52, bromacil concentrations in Daramend® treatments were significantly lower than controls for Moisture Regime 2 ($p < 0.05$). There were no significant differences in bromacil concentration for Moisture Regime 1; initial (week 0) and final (week 52) bromacil concentrations were not significantly different for any treatment combination. Bromacil concentrations in centre of mass and surface samples were not significantly different.

4.2.3 Bromide Concentrations

Bromide concentrations generally increased for all treatments over the course of the experiment except between weeks 38 and 44, where there was a large decrease (Figure 9). Increases in bromide indicates that decreases in bromacil concentration were due to debromination of bromacil molecules. Changes in bromide concentrations were primarily in surface samples. Soil mixing during water and Daramend® reapplication in Moisture Regime 2 treatments did not affect the difference in concentrations between surface and centre of mass samples (Figure 10).

At week 52, bromide concentrations were significantly different for sample depth and Daramend® dosage ($p < 0.05$). The 2% Daramend® treatment had significantly higher bromide concentration than 0.5% Daramend® and controls for both moisture regimes. Bromide concentrations for 0.5% Daramend® and controls were not significantly different for depth or moisture regime.

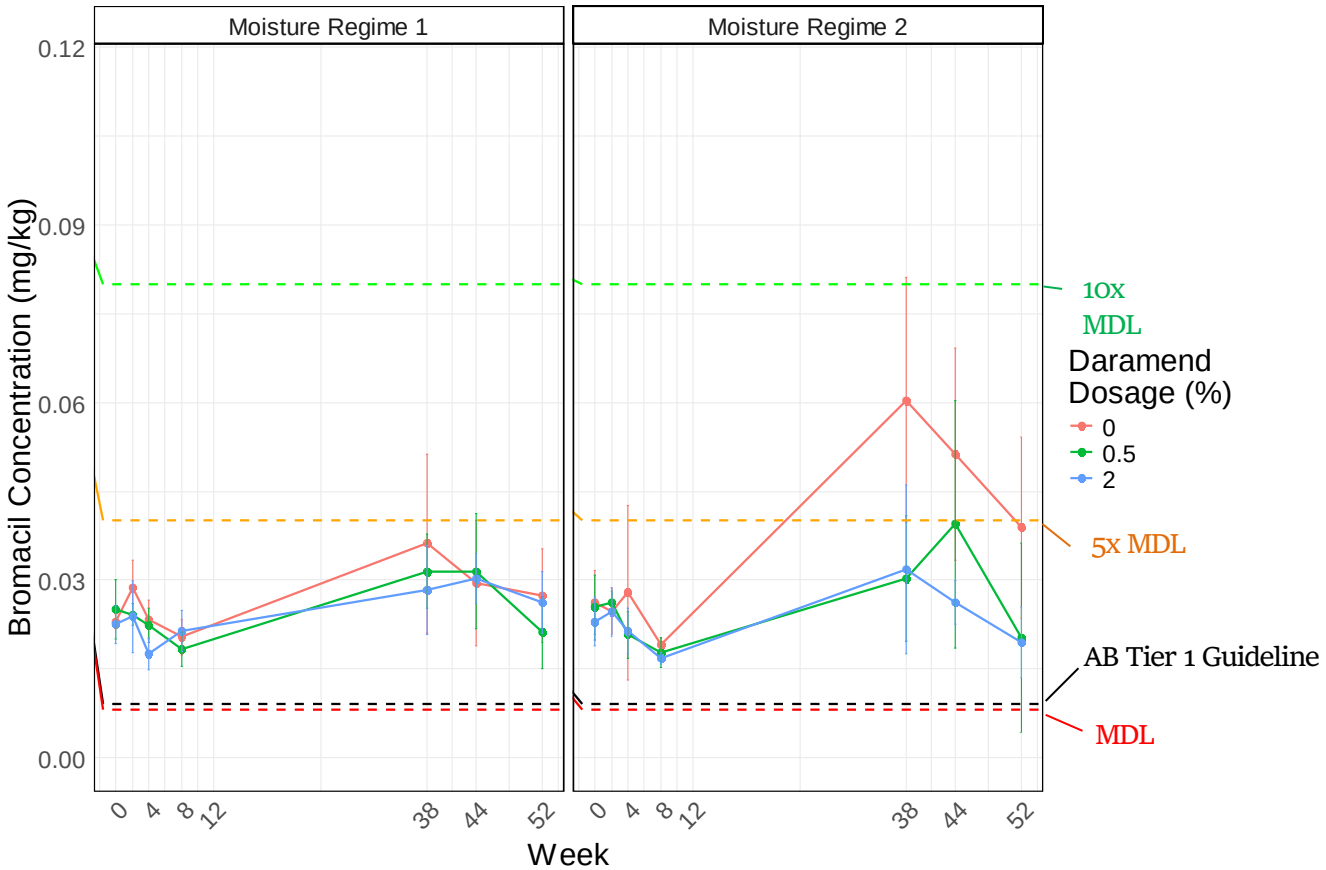

Figure 9. Average bromacil concentration for each treatment.
Error bars indicate standard deviation. Minimum detection limit (MDL) for bromacil is shown as a red dashed line, Alberta Tier 1 Guideline limit for bromacil is shown as a black dashed line. Five times the MDL is shown as an orange dashed line, and ten times the MDL as a green dashed line.

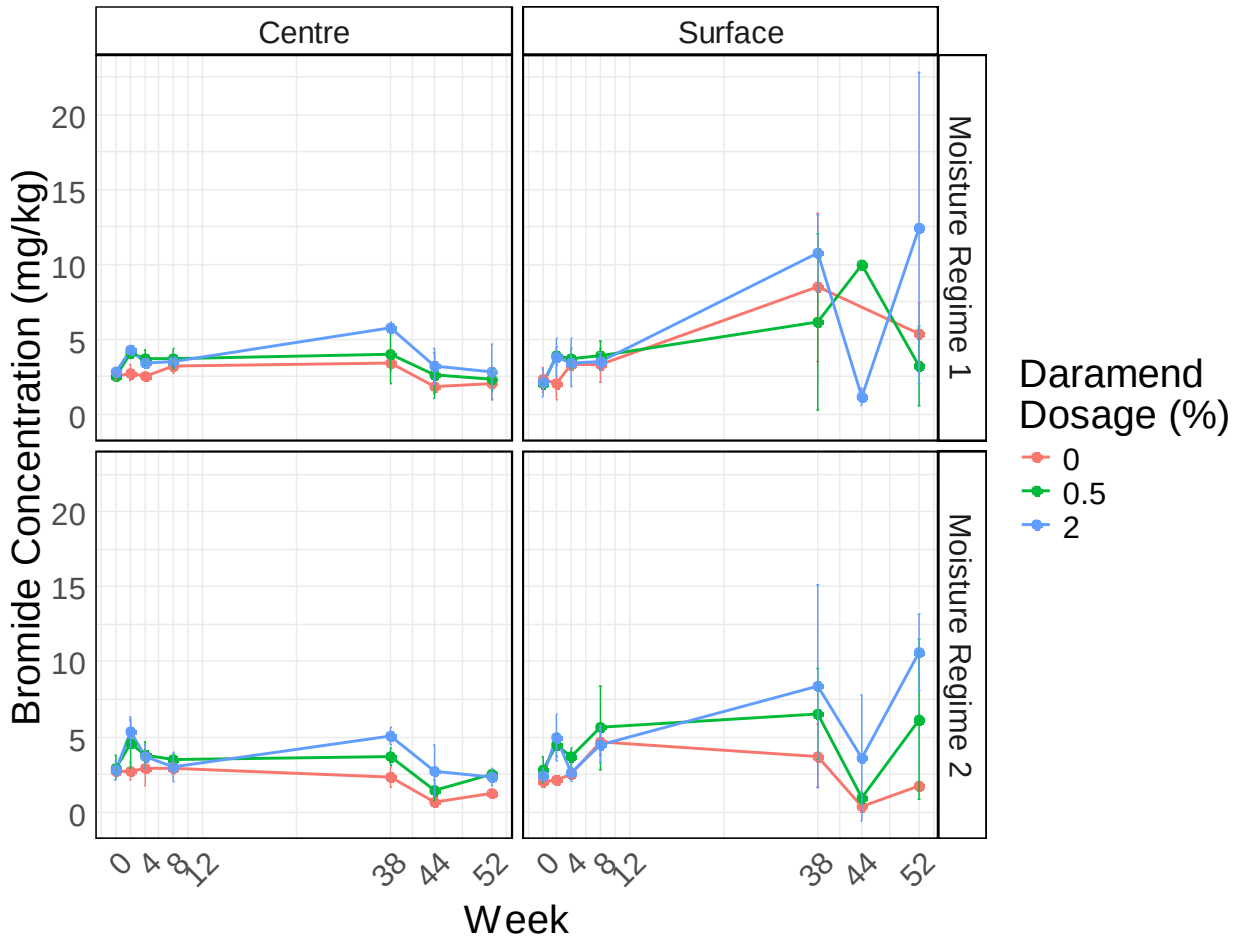

Figure 10. Average bromide concentrations for each treatment and sample depth for the duration of the experiment.

4.2.4 Oxidation-Reduction Potential

The ORP was highly variable between treatments, replications, and measurements. ORP was generally lower for Daramend® treatments than control treatments. Control treatments had an ORP above 200 mV for most of the experiment (Figure 11), showing that they were in aerobic conditions.

In the spring, the ORP for all treatments was above 200 mV and decreased for the Daramend® treatments. In moisture regime 1, 2% Daramend® was < -200 mV in the first season then > 100 mV in the spring and rest of the experiment. The 0.5% Daramend® was above 0 mV in the first season and after the spring, steadily decreased to -40 mV by week 52. In moisture regime 2, 0.5% Daramend® had the lowest ORP in the spring (~-200 mV on week 8) and remained >50 mV in the spring and rest of the experiment. The 2% Daramend® treatment steadily decreased in ORP in the spring to -43 mV by week 52, after the last Daramend® application.

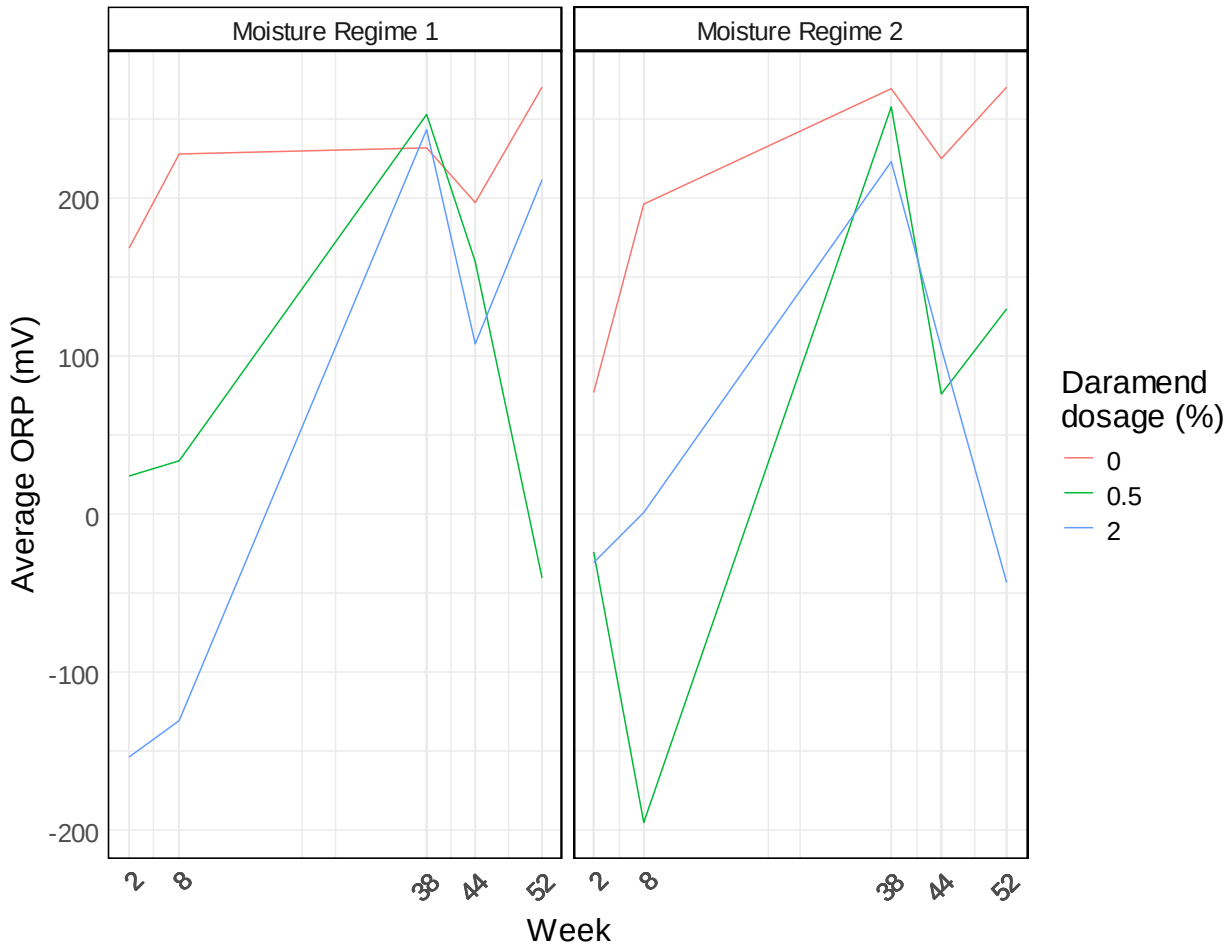

Figure 11. Average ORP for each treatment.

4.3 Lab Study

4.3.1 Moisture Content

The soil had an average moisture content of 6±2% (by weight) prior to initial treatment. After treatment, the soil had an average moisture content of 25±1% (by weight) (Figure 12). There was no significant difference in moisture content between Daramend® treatments ($p > 0.05$). After the second water addition, Moisture Regime 2 treatments had significantly higher ($p < 0.05$) moisture content than Moisture Regime 1 for the duration of the study. In Moisture Regime 1, the control consistently had higher moisture content (~27%) than Daramend® (~25%) treatments, but the difference was not statistically significant. Moisture Regime 2 had significantly higher ($p > 0.05$) moisture content than Moisture Regime 1 after the second water addition.

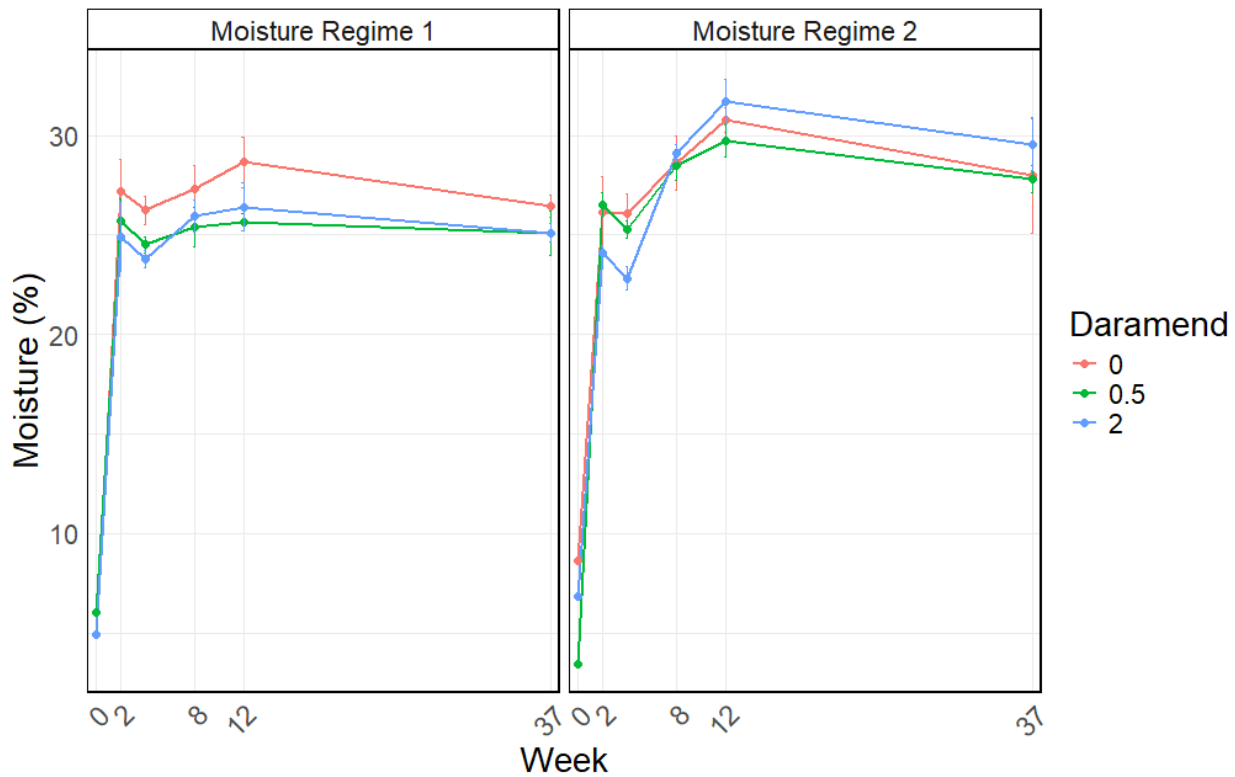

Figure 12. Moisture content of each treatment of the lab study for the duration of the experiment. Moisture content was taken from analytical reports of the sampling events. The moisture content is an average of the four replicates for each treatment.

4.3.2 Bromacil Concentrations

Initial bromacil concentration for all treatments was 0.025±0.04 mg/kg. All treatments gradually decreased in bromacil concentration over the duration of the experiment. The control treatment in Moisture Regime 1 had an increase in bromacil concentration at week 8, to 0.031±0.004 mg/kg. For the control treatments, bromacil concentration did not start decreasing until after week 8. Final average bromacil concentration for all treatments was between 0.009 mg/kg and 0.011 mg/kg, with multiple individual samples at the MDL of 0.008 mg/kg.

None of the treatments were significantly different from each other ($p > 0.05$) at week 37 and the rate of bromacil reduction was consistent for Daramend ® treatments. There was a delay in bromacil reduction for control treatments and reduction did not occur until after week 8.

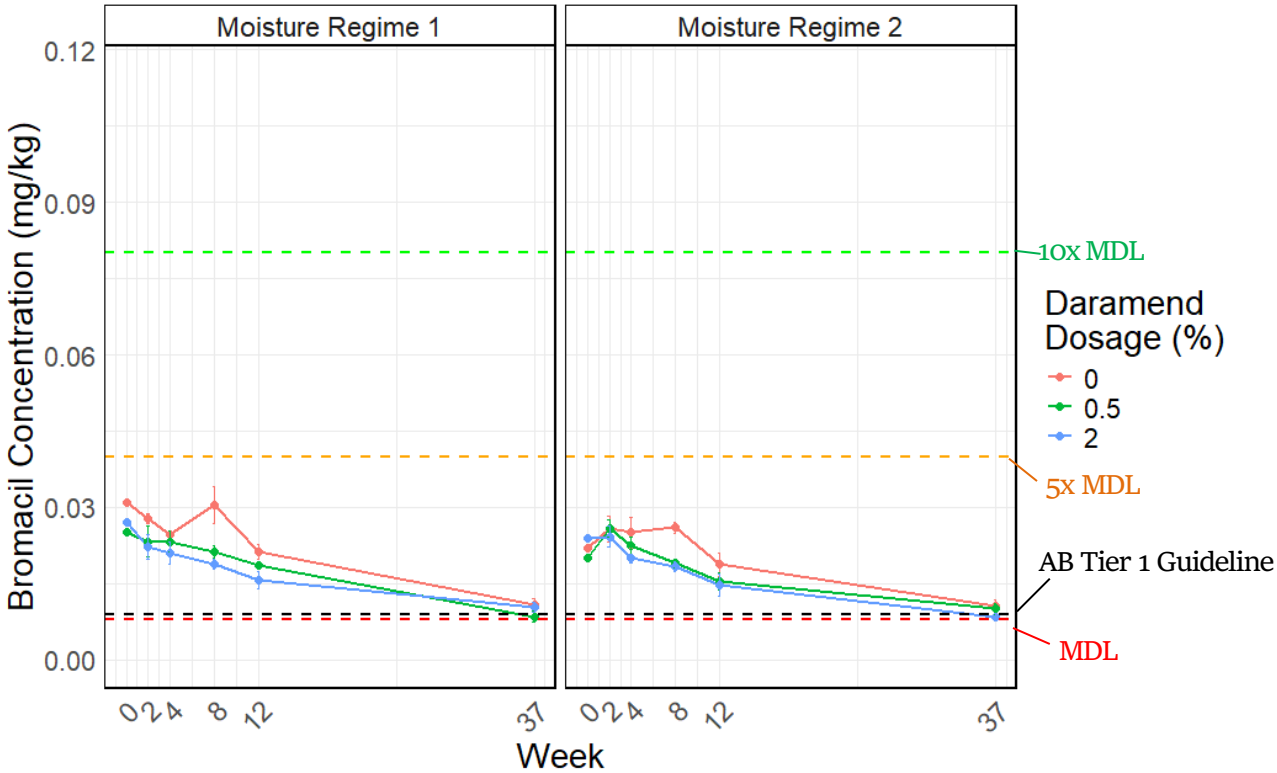

Figure 13. Average bromacil concentration for each treatment in the lab study for the duration of the experiment.

4.3.3 Bromide Concentrations

Bromide concentrations fluctuated during the study (Figure 14). The initial bromide concentration was 2.1±0.2 mg/kg. The 2% Daramend® treatments generally increased with a spike in concentrations at week 8. In Moisture Regime 2, control had lower bromide concentration than Daramend® treatments. By week 37, the Daramend® treatments had significantly higher ($p < 0.05$) bromide concentrations than control treatments.

4.3.4 Oxidation-Reduction Potential

For both moisture regimes, 2% Daramend® treatments had the lowest ORP, reaching a low at week 12 (-324 mV in Moisture Regime 1 and -410 mV in Moisture Regime 2). In Moisture Regime 1, control and 0.5% Daramend® treatments ORP peaked at ~50 mV on week 4 then decreased and remained between -80 mV and -150 mV for the duration of the experiment. Control and 0.5% Daramend® in Moisture Regime 2 was between -100 mV and -160 mV for most of the experiment. In both moisture regimes, 2% Daramend® treatments increased in ORP after freezing and thawing. In Moisture Regime 1, the ORP increased after each cold cycle (Figure 15). Temperature data from the soil sensors can be found in Appendix C.

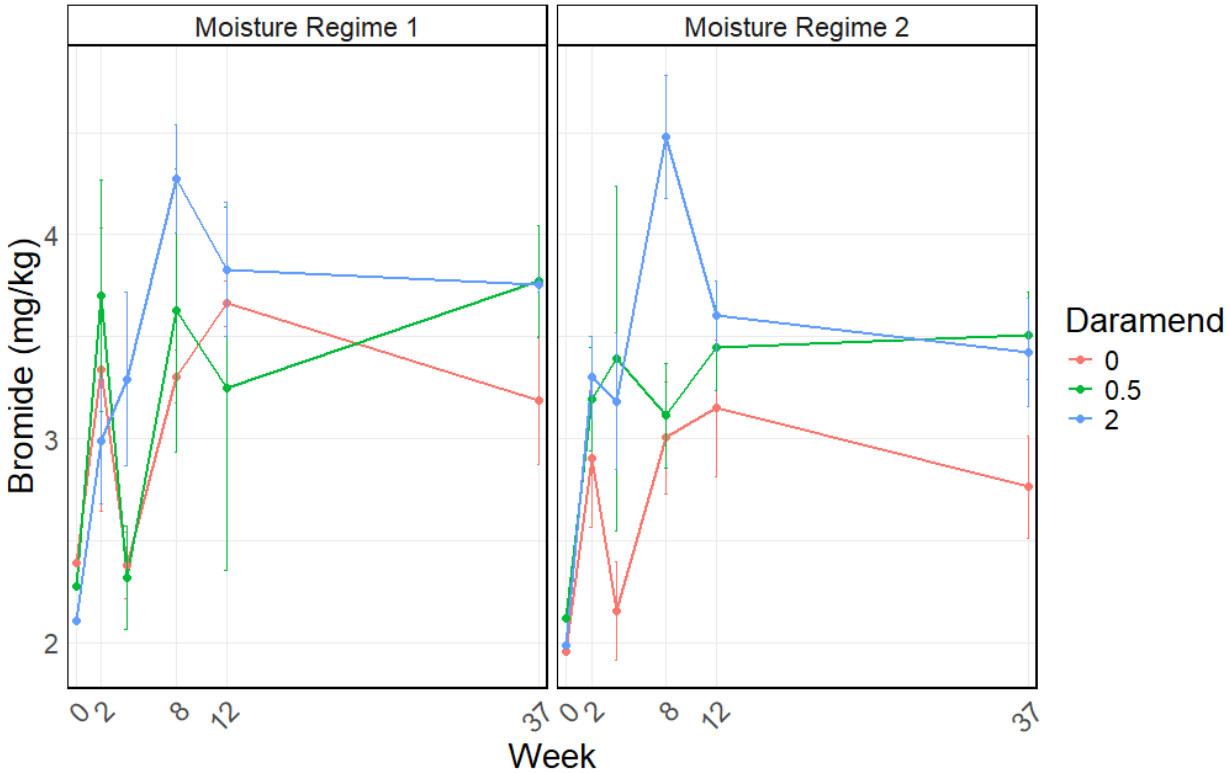

Figure 14. Average bromide concentrations in each treatment and moisture regime for the bench study.

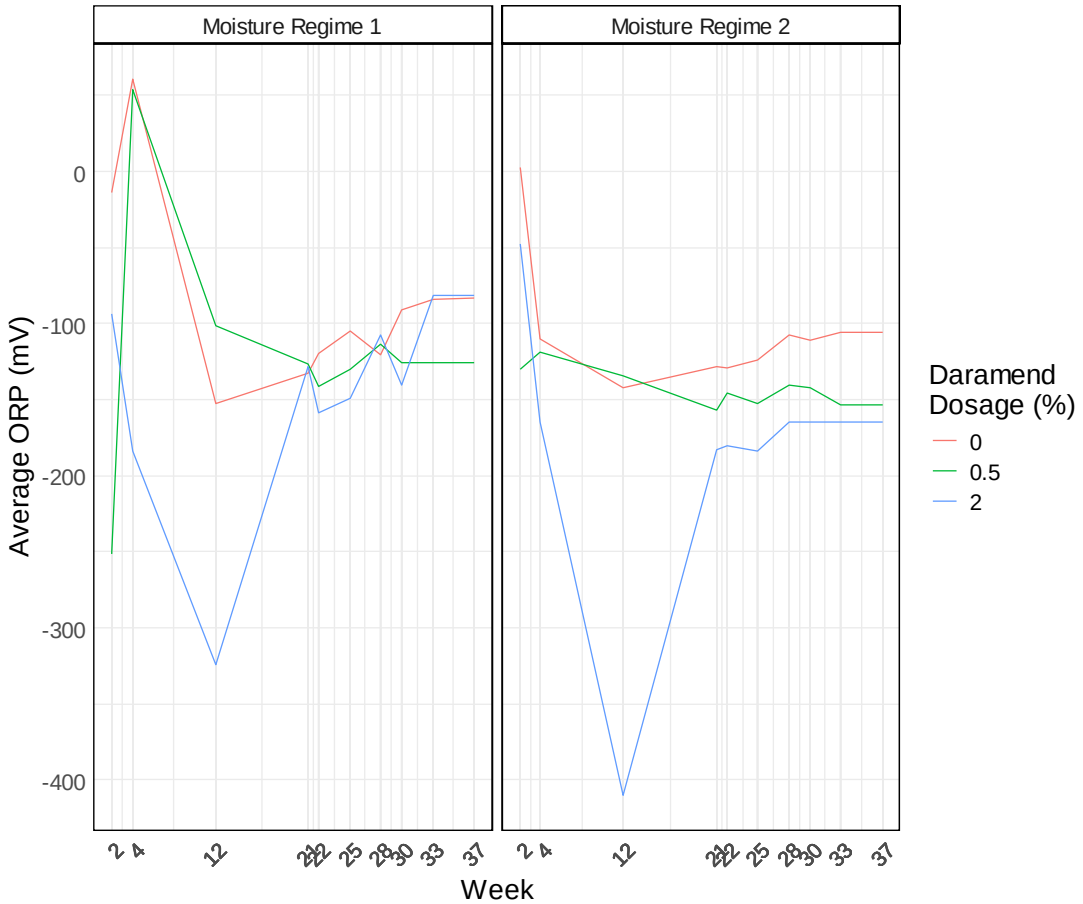

Figure 15. Average ORP for each treatment in the lab study.

5.0 DISCUSSION

5.1 Bromacil Reduction

None of the treatments in the field study had a statistically significant net decrease in bromacil concentration. In Moisture Regime 2, the control treatment appeared to have a net increase in bromacil concentration at the end of the study, but the difference was not statistically significant ($p = 0.998$). All treatments had a rebound in bromacil concentration over the winter, with the highest reading at the first sampling event in the spring (week 38, Figure 10). The bromacil concentrations rebounded to the starting concentrations for all treatments in Moisture Regime 1 and Daramend® treatments in Moisture Regime 2.

Cross-contamination from spring thaw and run-off was considered. Evaluation of the moisture trends from the soil sensors (Appendix C) and laboratory analyses (Figure 8) did not show an increase in moisture content in the spring from thaw and the treatments with the lowest moisture content had the greatest spring increase in bromacil concentrations. All samples were preferentially taken at the top of each treatment replicate for the surface samples or the centre of mass, avoiding the bottom third for the centre samples and there is no consistent difference between surface and centre bromacil concentrations. The entire study area was covered with poly tarps before the first snow fall and remained covered until the end of the experiment. This makes the likelihood of spring thaw contaminating the treatment cells unlikely.

Similar rebound was observed for control treatments in the lab study (Figure 13) and on the Daramend® treatment in a previous field study (Bachmann & Thiessen, 2023). There was no second water addition to the control treatments in the previous field study, so post-watering rebound could not be assessed. The Daramend® treatments in the lab study did not have any rebound in bromacil concentration (Figure 13). This suggests that (1) there could be solubilization of bromacil from the soil-phase and (2) Daramend® acts as a buffer by degrading the solubilized bromacil.

All treatments in the lab study had similar decrease in bromacil concentration. The Daramend® treatments showed no rebound in bromacil at week 8 and had a faster reduction in bromacil concentration than the control treatments. However, all treatments reached the MDL of 0.008 mg/kg by week 37 (Figure 9). After week 12, all treatments were in reducing conditions with ORPs below 0 mV and the 2% Daramend® treatments were in reducing conditions for the entire experiment (Figure 15). For the control treatments, the timing of the reducing conditions matches the start of decreasing bromacil concentrations. From the lab study, it appears that the limiting factor for bromacil degradation is the redox status of the soil. The increased water holding capacity from the organic matter and reduction potential of the zero valent iron in the Daramend® seems to enhance and accelerate bromacil degradation.

The 2% Daramend® treatments had significantly higher ($p < 0.05$) bromide concentration than controls in both moisture regimes. The 0.5% Daramend® treatments were not statistically different from controls. However, when comparing surface samples to centre of mass samples, no changes in bromide concentration occurred in the centre of mass of any treatment; all increases in bromide concentration occurred at the surface (Figure 10). Bromacil does not significantly photodegrade in soil (Acher et al., 1994), the soil treatments were coved by at least one layer of poly tarp for the entire study, and bromide concentration did not significantly increase in control treatments. For Moisture Regime 2, the difference between surface and centre bromide concentrations remained after mixing during water application events at week 8 and 44.

While bromide is generally non-reactive in mineral soil, in high organic soil and arable soils, bromide is transformed into organic bromines (Albers & Rosenbom, 2023). The method used to determine bromide content detects only soluble bromides, so if there is any process that transforms the bromine into organic bromides they would not be detected. 2% Daramend® dosages in both moisture regimes and in both field and lab studies had the largest spikes and subsequent drops in bromide concentrations (Figure 10 and Figure 14). In the closed and controlled conditions of the lab study, any decrease in bromide concentration would be from biological or geochemical processes in the soil. Increased organic matter and microbial activity in the higher Daramend® dosage could lead to interferences that prevent the detection of bromide and explain why bromide concentrations did not change after mixing.

5.2 Application and Required Moisture Content

Previous bench-scale testing (Bendouz & Pare, 2022; French et al., 2023) of remediation amendments and the known degradation pathways of bromacil (Adrian & Suflita, 1990, 1994; Gawel et al., 2020) have identified that anaerobic/reducing conditions are required for the degradation of bromacil. During initial application, reaching the required moisture content was unfeasible. The fine texture of the soil made water uptake slow and once the soil was above 50% water holding capacity it was difficult to handle (Figure 16). Previous testing of Daramend® on fine-grained soil (Bachmann & Thiessen, 2023) showed that surface watering was not able to penetrate the soil mass and sufficiently wet beyond the soil surface.

Working on or around sufficiently saturated soil would cause a number of logistical and safety issues due to the unstable surface.

Figure 16. Third water addition to one of the moisture regime 2 treatments.

To ensure that the soil has reached the required moisture levels for Daramend® (and other anaerobic technologies), the soil should be wetted until it becomes a slurry and maintained until target bromacil concentrations have been achieved. Such a process is best suited to sealed reactors and unsuitble for in-situ application of Daramend®.

5.3 Minimum Detection Limit

The soil had a lower bromacil concentration than expected and it was near the method's minimum detection limit of 0.008 mg/kg. At the time of the experiment, lower detection limit methods were not available. The lab performing the analyses stated that at the concentrations being analyzed, there can be an uncertainty of ±0.024 mg/kg. While the high variability of bromacil concentrations in the field study could be explained by analytical uncertainty near the MDL, the results from the lab study did not show the same variability and had bromacil concentrations closer to the MDL. For the final week in the lab study, concentrations were at or within one significant digit of the minimum detection limit and differences between treatments cannot be evaluated. At bromacil concentrations within one significant digit of the MDL, differences between samples are obscured and may result in type II errors from statistical analysis.

6.0 SUMMARY AND CONCLUSIONS

This project was a year-long, mesoscale experiment optimizing the application of Daramend® on surface soil for the remediation of bromacil in soil obtained from an ATCO Electric site. Daramend® was applied at two concentrations, 0.5% and 2% by dry soil weight with control treatments, and managed using 2 moisture regimes: (1) single application of Daramend® and water and (2) two applications of Daramend® and three applications of water. A parallel lab study was conducted with the same parameters to assess the ability of bench-scale testing to optimize field applications. The field study was conducted in an outdoor containment pad at InnoTech Alberta's Vegreville research facility.

The objective was to determine the optimal dosage of Daramend® and soil management practices for the destructive remediation of bromacil to the Alberta Tier 1 soil remediation guideline concentration of 0.009 mg/kg.

None of the Daramend® treatments in the field study were able to reach the objective of bromacil concentrations below 0.009 mg/kg. Control treatments had a net increase in bromacil at the end of the experiment. After spring thaw, control treatments had a substantial increase in bromacil concentration with Moisture Regime 1 increasing to 157% and Moisture Regime 2 increasing to 230% of the original concentrations. By the end of the experiment, the control treatments were 119% and 148% of the original concentrations for Moisture Regime 1 and 2, respectively. The Daramend® treatments had a smaller increase in bromacil concentrations after spring thaw. At the end of the experiment, none of the Daramend® treatments had statistically significant differences in bromacil concentration compared to starting concentrations. In Moisture Regime 1, none of the treatments were statistically different. For Moisture Regime 2, both Daramend® treatments had similar bromacil concentrations and both were significantly lower than the control treatment.

All treatments in the lab study had a significant decrease in bromacil concentration, reaching the MDL of 0.008 mg/kg by week 37. There was an 8-week delay in bromacil reduction for the control treatments, after which the bromacil reduction rate was similar to the Daramend® treatments. The bench study did not have similar results to the field study. Moisture and temperature conditions in the bench study did not match the field study.

The degradation of bromacil is a reductive process that occurs in anaerobic/saturated conditions. For the optimal performance of Daramend® in the treatment of bromacil, prolonged saturation of the soil is required. Application of Daramend® on fine-textured surface soil and wetting to and maintenance of sufficient moisture content is logistically impractical. It would require large amounts of water to be slowly and/or repeatedly applied to reach saturation then covered or contained to maintain the saturation.

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APPENDIX A: Initial Soil Characterization

Table 4. Initial soil characterization results for soil received from Bow Island, AB.

Sample	Total Organic Carbon (%)	Texture	Sand (% by weight)	Silt (% by weight)	Clay (% by weight)	% retained on 75 micron sieve
Baseline1	1.16	Sandy Clay Loam	53	22	25	42.4
Baseline2	0.97	Loam	46	29	25	37.6
Baseline3	1.4	Sandy Clay Loam	52	23	25	38.2
Average	1	Sandy Clay Loam	50	25	25	39.4
Stdev	0.18		3	3	0	2.1

	Saturated Paste							
Sample	pH	Electrical Conductivity (dS/m)	Sodium Adsorption Ration	% Saturation	Calcium (meq/L)	Calcium (mg/kg)	Magnesium (meq/L)	Magnesium (mg/kg)
Baseline1	7.8	5.45	5.4	71	27.1	388	19	164
Baseline2	7.9	4.67	4.7	98	21.9	427	15	178
Baseline3	7.8	5.65	5.4	74	26.1	384	18.5	164
Average	7.8	5.26	5.2	81	25.0	400	17.5	169
Stdev	0.05	0.4	0.3	12	2.3	19	1.78	6.6

	Saturated Paste										
Sample	Sodium (meq/L)	Sodium (mg/kg)	Potassium (meq/L)	Potassium (mg/kg)	Chloride (meq/L)	Chloride (mg/kg)	Sulfate (SO4) (meq/L)	Sulfate (SO4) (mg/kg)	Sulfate-S (meq/L)	Sulfate-S (mg/kg)	TGR (T/ac)
Baseline1	26.1	428	0.66	19	23.8	602	45.7	1570	45.7	523	<0.1
Baseline2	20.2	454	0.56	21	17.3	597	36.6	1720	36.6	572	<0.1
Baseline3	25.3	428	0.64	18	23.1	603	43.2	1520	43.2	508	<0.1
Average	23.9	437	0.62	19	21.4	601	41.8	1603	41.8	534	<0.1
Stdev	2.6	12	0.04	1.2	2.9	2.6	3.8	85	3.8	27.3	n/a

APPENDIX B: Mass Of Daramend and Volume of Water Added to Treatments

Table 5. Mass of Daramend® added to each treatment cell at week 0.

Daramend® Dosage	Moisture Regime	Replicate	Daramend® (kg)
0.5%	1	1	24.050
		2	23.914
		3	23.854
		4	24.086
	2	1	24.002
		2	24.714
		3	24.066
		4	24.290
2.0%	1	1	95.920
		2	95.878
		4	95.990
	2	1	95.836
		2	95.848
		3	95.964
		4	95.138

Table 6. Mass of Daramend and volume of water added to Moisture Regime 2 treatments on week 44.

Daramend Dosage	Moisture Regime	Replicate	Daramend (kg)	Water (L)
0.0%		1	0	126
		2		162
		3		198
		4		180
0.5%	2	1	20.160	126
		2	20.022	126
		3	20.136	108
		4	20.008	126
2.0%		1	80.102	198
		2	80.046	198
		3	80.050	198
		4	80.114	180

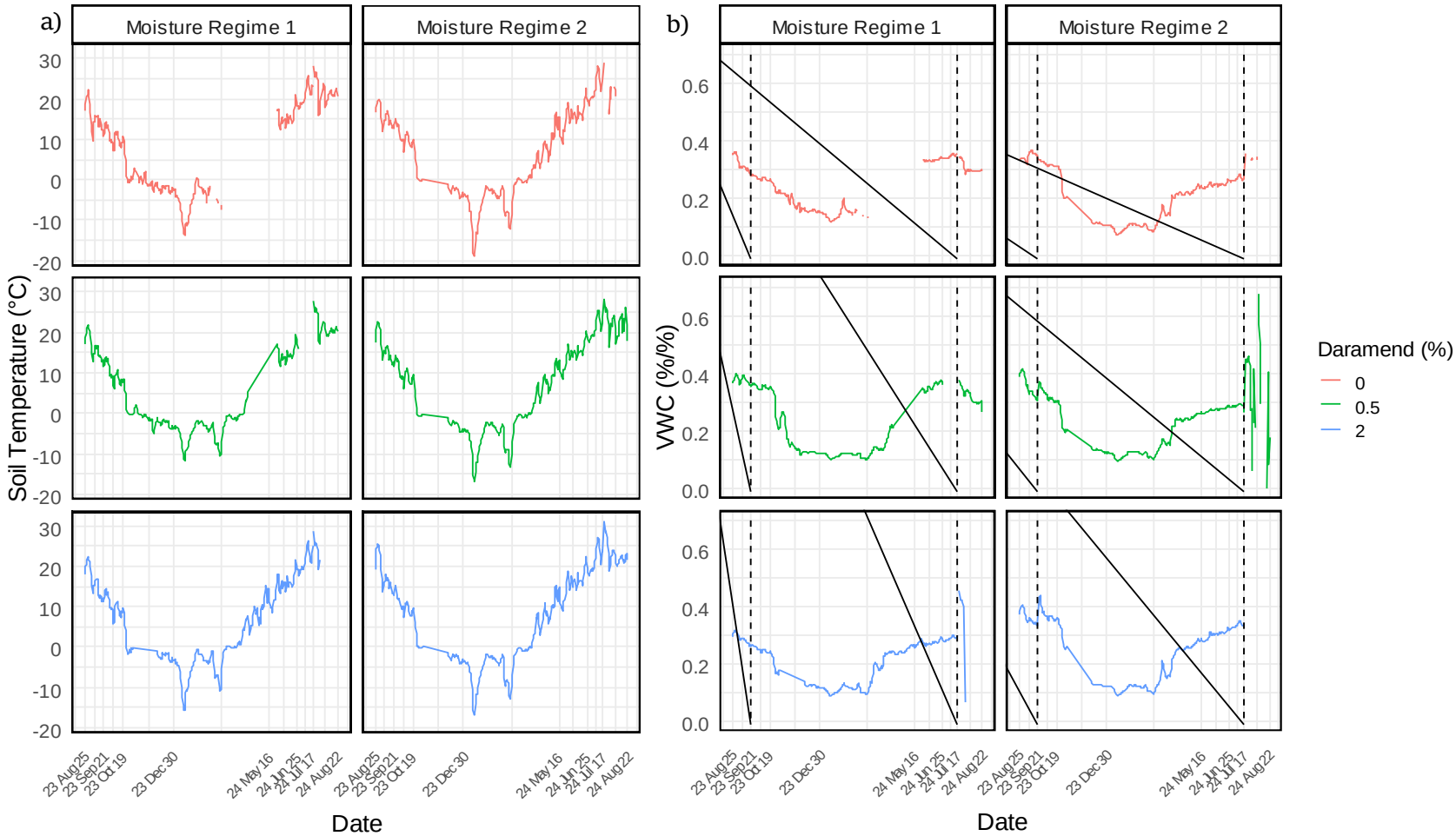

Figure 17. Available soil sensor data from field study.

a) Average soil temperature (°C) and b) average volumetric water content (%/%) for each Daramend® dosage and moisture regime.

The vertical dotted lines show the second and third water applications (third with additional Daramend®)

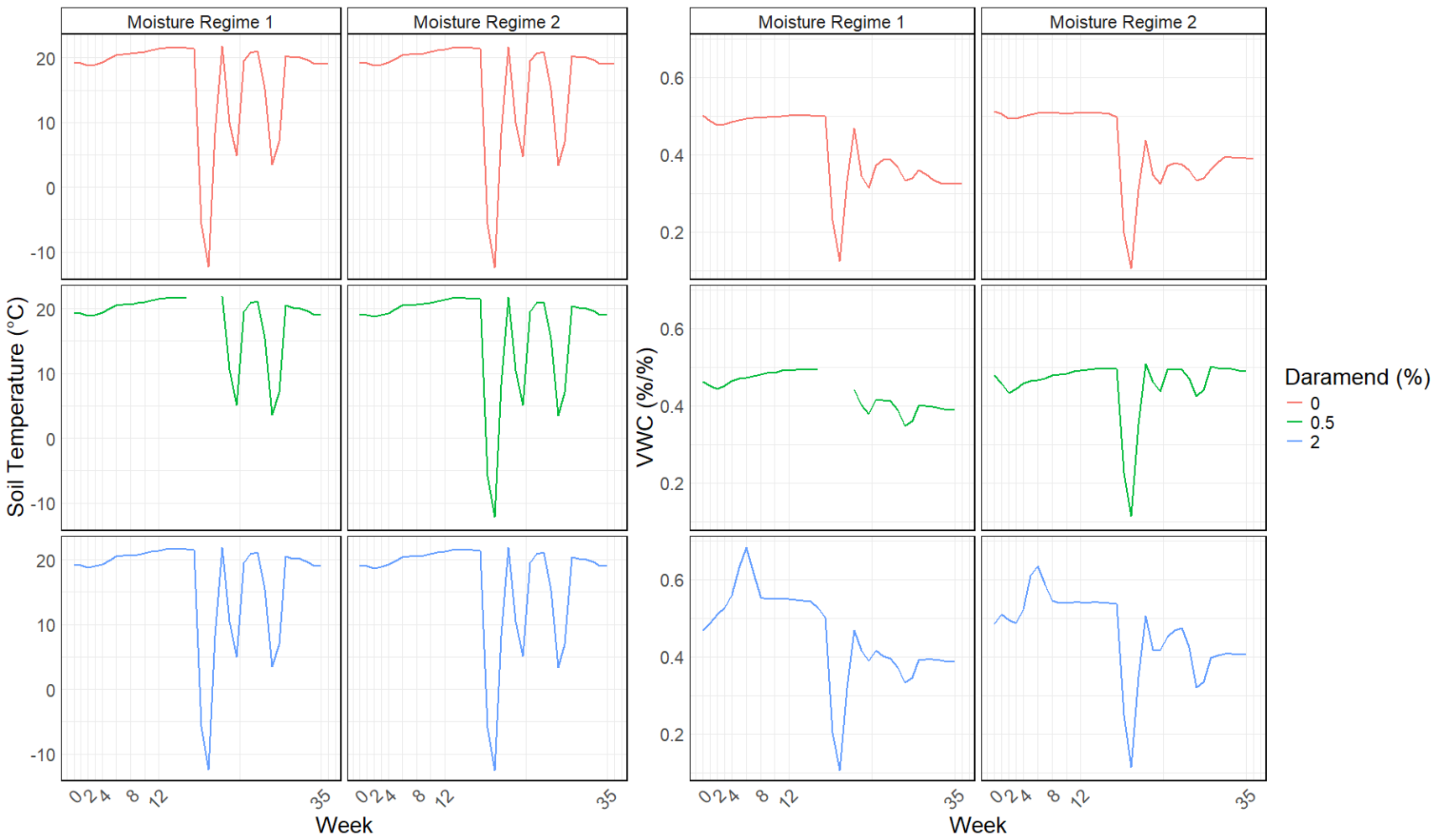

Figure 18. Available soil sensor data from lab study.
a) Soil temperature (°C) and b) volumetric water content (%/%) for each Daramend® dosage and moisture regime.

Evaluation and Comparison of Soil Sterilant Remediation Technologies

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EXECUTIVE SUMMARY

This project was undertaken to complement previous reviews conducted on the remediation of soil sterilants. Based on input from the community of practice, additional review was needed to identify cost-effective and efficient technologies specific to remediation of bromacil and tebuthiuron. In addition, to align with the needs of the Soil Sterilants Program, potential technologies were evaluated to determine their applicability to Alberta conditions and specific site challenges, while also taking into account cost, logistics of application, and sustainability.

The scope of this project was expanded to include a review of applicable site types and industry challenges, and to identify high-potential technologies that could be evaluated at bench- and meso-scale to first de-risk through a series of testing stages, then potentially deploy at field scale.

Methods included review of historical Soil Sterilants Program documentation, review of bromacil and tebuthiuron characteristics, and identification of high priority concerns in sterilant management. Three key challenges were defined for the purpose of evaluating and testing remediation technologies:

1. Sterilants at depths greater than 50 cm below ground surface in unsaturated soil, thus inaccessible to treatment at surface, were identified as a remediation challenge. Ideally the technologies to address deeper sterilants would function *in situ* to minimize excavation of overlying soil.
2. Soil treatment requirements where sterilant destruction is required, and immobilization is not considered an acceptable option, are challenging to implement. Technologies for this application could be *in situ* or *ex situ*.
3. Saturated fine-grained till soils and groundwater impacted by sterilants pose a remediation challenge. *In situ* technologies and/or combinations thereof to avoid remedial excavation and disposal of >5,000 to 10,000 tonnes of soil and underlying groundwater, generally where sterilants are widely dispersed, would be beneficial.

A review of literature, and interviews conducted with subject matter experts from the consulting industry and technology providers, were used to gather more information and develop a list of potential technologies. All identified technologies were evaluated to determine if they were proven for treatment of sterilants, impractical to meet objectives of the research and testing program, or potential technologies for inclusion in the program.

Recommendations were made for staged bench-, meso- and field-scale testing and demonstration to test and potentially prove out technologies for use at the field scale. A proposed technology testing program was developed, which will be used to guide Project Service Providers in other Soil Sterilants Program remediation projects, for testing remediation technologies and running a field demonstration project.

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ACRONYMS

AC	Activated Carbon
AEP	Alberta Environment and Parks
AER	Alberta Energy Regulator
bgs	Below Ground Surface
DUA	Drinking Use Aquifer
ERH	Electrical Resistivity Heating
GAC	Granular Activated Carbon
ISTR	In-situ Thermal Remediation
OM	Organic Matter
PRB	Permeable Reactive Barrier
PRZ	Permeable Reactive Zone
RFP	Request for Proposals
SEE	Steam Enhanced Extraction
SSP	Soil Sterilants Program
TCH	Thermal Conductive Heating
UV	Ultraviolet
VUV	Vacuum Ultraviolet
ZVI	Zero Valent Iron

1. INTRODUCTION

Soil sterilants are non-selective, broad-spectrum herbicides that were used for vegetation control on industrial land. In Alberta, the use of these compounds for vegetation control began in the 1960s and continued for more than three decades before being terminated in the late 1990s. Some sites where soil sterilants were used have residual compounds in soil and groundwater, even decades after treatment with sterilant products ceased. Where concentrations are elevated, sterilants in soil may act as a continuous source of contamination, becoming dispersed in soil, leaching into groundwater, and potentially migrating beyond a site's boundaries.

The Soil Sterilants Program (SSP) aims to address several knowledge gaps related to the management of sterilant-impacted sites. In the design phase of the SSP, a review of available remediation technologies for sterilants in soil and water was conducted (Drozdowski et al., 2018b). The design phase also included a workshop where stakeholders within the community of practice gathered to identify priorities for the SSP (Drozdowski et al., 2018a). Through the workshop and with input from the SSP's expert advisory committee, a need was identified to further investigate remedial technologies that could be implemented for effective treatment of bromacil and tebuthiuron in soil and water.

To address sterilant-impacted sites, a considerable amount of literature review and experimentation has occurred over the past 20 years in Alberta. Several technologies have successfully treated sterilants in soil and water, both *in situ* and *ex situ*. These include immobilization using activated carbon (Cotton and Sharma, 1993), thermal desorption (Bessie, 2009; EBA Engineering, 2007), and chemical oxidation (Gunasekara, 2004; Lazorko-Connon, 2008; Rosas et al., 2014; Shea et al., 2004). However, based on input from the community of practice, excavation and disposal remain the most common method of soil remediation, and challenges are encountered in remediation of groundwater to meet applicable endpoints for regulatory site closure (AEP, 2019). Thus, it was requested that additional technologies be investigated for potential use in treating the two most common soil sterilants in Alberta, bromacil and tebuthiuron, evaluating them in terms of applicability to specific site challenges, cost, logistics of application, and sustainability.

1.1 OBJECTIVE AND SCOPE

The original scope of work for this project was to identify, evaluate and compare potential remediation technologies for bromacil and tebuthiuron impacts in soil and water, with the specific objective of identifying suitable candidates for field-scale demonstration. The scope was expanded to include a review of applicable site types and industry challenges, and to identify high-potential technologies that could be evaluated at bench- and meso-scale to first de-risk, then potentially deployed at field scale.

2. METHODS

To meet the objectives set out for this project, the following tasks were completed:

1. Historical SSP documentation summarized in previous documents prepared for the SSP (Drozdowski et al., 2018a, b) was reviewed to identify characteristics of bromacil and tebuthiuron pertinent to remediation and to summarize technologies previously identified for the remediation of soil sterilants.
2. To understand field conditions for identifying high priority challenges in sterilant management, previous documentation was reviewed and summarized including detailed site descriptions, followed by consultation with representative site owners and managers. Interview questions focused on the history and pattern of sterilant application, remedial objectives, and end land uses to select potentially applicable remediation technologies. Defined industry challenges were then short-listed for matching with potential remediation technologies.
3. To identify potential candidate technologies beyond those initially identified, a review was conducted of:
   a. Technologies that have been trialed with soil sterilants, specifically bromacil and tebuthiuron, preferably under field conditions, both nationally and internationally, and;
   b. Technologies identified as potential candidates for bromacil and tebuthiuron remediation in either soil or water, based on the mechanisms of the technology and treatment of similar contaminants.

   Searches were conducted through multiple sources including conference proceedings; databases; peer reviewed journals; industry, government, and public reports; and the Internet to find literature related to the themes within the scope of the project.
4. Interviews were conducted with subject matter experts from the consulting industry and technology providers with knowledge and experience in the implementation and operational aspects of relevant remedial technologies, and potential emerging remedial technologies.
5. All identified technologies were evaluated to determine if they were proven for treatment of sterilants, impractical to meet objectives of the research and testing program, or potential technologies for inclusion in the program.
6. Recommendations were made for bench-, meso- and field-scale testing and demonstration.

3. BACKGROUND

This background section is intended to complement the information provided in the SSP design phase document (Drozdowski et al., 2018b), and only the information pertinent to decision making regarding potential remediation technologies[1] is included.

3.1 REGULATORY GUIDELINES

Alberta Tier 1 Soil and Groundwater Remediation Guidelines (Tier 1 Guidelines) for bromacil and tebuthiuron are provided in Table 1 (AEP, 2019). Achieving Tier 1 Guidelines concentrations in a remediation program can be challenging and is one of the reasons that remedial excavation and disposal, or risk management and exposure control, are often selected as the approach of choice at sterilant-impacted sites. Other SSP projects aim to provide data for guideline adjustment, where permitted, based on site characteristics. Where guidelines can be adjusted and the result is a guideline that is less stringent than Tier 1, there is potential to employ different remediation technologies that may address sterilants at higher concentrations.

Table 1. Alberta Tier 1 Guidelines for bromacil and tebuthiuron (fine- and coarse-grained soils, natural land use).

Sterilant	Groundwater	Soil
Tebuthiuron	0.00043 mg/L	0.046 mg/kg
Bromacil	0.0002 mg/L	0.009 mg/kg

Characteristics of bromacil and tebuthiuron that have potential to influence both fate and transport and the potential effectiveness of remedial technologies are listed in Table 2.

[1] Technologies include physical, chemical, and biological processes and products used for decontamination of soil and water.

Table 2. Summary of relevant chemical specific parameters with potential impact to remediation technology selection.

Parameter	Sterilant	
	Bromacil	**Tebuthiuron**
Water Solubility	• 815 mg/L at 25°C • Increases with higher pH	• 2,500 mg/L at 25°C
Soil/Organic matter (OM) sorption coefficient (K_d/K_{oc}); Octanol-water partition coefficient (log K_{ow})	• K_{oc}: 32 g/mL (Dube et al., 2009) • K_d/K_{oc}: variable from 2.3 to 289 in soils ranging from sand to peat. • Log (Koc): 1.86 (average) for soil; 1.61 (average for sediments). • Log K_{ow}: 2.11	• K_{oc}: 80 mg/ • K_d: 0.2 to 10.0 • Log K_{ow}: 1.79
Mobility	• Highly likely to be mobile in soils low in OM. • Moves horizontally on surface and vertically with water. • Moderate mobility in soils high in OM and clay content.	• Influenced by soil texture and organic matter content (higher mobility in sandy soils and soils low in OM; lower in clay loam soils or highly organic soils).
Leaching Potential	• High • Restricted by high water table. • An important dissipation process. • Readily leached.	• Medium • High solubility in water, weak adsorption to soil particles and is highly persistent, therefore has high potential to leach.
Adsorption/ Desorption	• Lower than other herbicides (Landsburg and Fedkenheuer, 1990). • Sorption to soils increases with clay and OM content. • Will not partition to suspended particles or sediments in aquatic systems (remain dissolved in water column).	• Relatively poor soil sorption. • Sorption to soils highest in soils high in OM content followed by clay content • <1% at soil OM of 0.3% and 40% with soil OM of 4.8%.
Vapour Pressure	• 4.10×10^{-02} mPa @20°C (negligible volatility) (Lewis et al., 2016)	• 0.27 mPa @20°C (negligible volatility) (Lewis et al., 2016)
Microbial Degradation	• Bromacil is slowly debrominated by microflora under anaerobic, methanogenic conditions but is not degraded under denitrifying or sulphate-reducing conditions. • Wolf and Martin (1974) reported a microbially mediated half-life of 144 days in anaerobic sandy loam soil.	• Biodegradation of tebuthiuron in aerobic soil is expected to be slow; it also shows little biodegradation in anaerobic soils. • Similarly, tebuthiuron does not degrade appreciably in water.

Based on the relatively high solubility of both bromacil and tebuthiuron, they will enter surface and groundwater where there is insufficient sorptive capacity in soil; soils with higher organic or clay contents will help to limit sterilant dispersion. Where sterilant remediation in groundwater is required, a challenge can be encountered in their sorption to saturated soils, which limits their capacity for complete removal.

Conversely, technologies that use adsorption and absorption to surfaces, such as activated carbon, have been used successfully for trapping these compounds. However, additional studies are being conducted under the SSP to evaluate the longevity of sorption to determine whether they can be used for effective long-term treatment, enabling regulatory closure of sites where they have been used. If proven successful, the application of various activated carbon technologies, ideally to both trap and allow bioremediation of the sterilants, could be further explored.

The low vapour pressures of sterilants result in little volatilization, making technologies applicable for treatment of other common contaminants, such as petroleum hydrocarbons, inapplicable for sterilants.

Finally, remediation strategies based on biodegradation may require timeframes on the order of months to years. Based on available literature, dehalogenation of bromacil under anaerobic conditions may be considered in evaluating potential remediation options that involve reductive conditions.

4. SITE CHARACTERISTICS SUMMARY

To understand the challenges facing the community of practice in the management and remediation of bromacil and tebuthiuron in Alberta, three sources of information were reviewed. The first was a compilation of survey responses provided in the report from the SSP design workshop held in 2018 (Drozdowski et al., 2018a). The second is based on a compilation of information on sterilant-impacted sites provided by a consultant, including sites from several clients and with distribution throughout Alberta. The third source of information was interviews conducted with SSP Steering Committee members regarding their challenges in remediating sterilant-impacted sites.

4.1 WORKSHOP FEEDBACK

Based on the 2018 workshop findings (Drozdowski et al., 2018a) and literature synthesis (Drozdowski et al., 2018b):

- In Alberta, most of the issues are associated with bromacil and tebuthiuron, which have largely moved from the surface to depths inaccessible to conventional in-situ soil remediation technologies (i.e., below 50 cm).
- Elevated bromacil and tebuthiuron concentrations at the surface were primarily addressed through application and mixing of activated carbon (AC). Minimal long-term data are available to verify the length of time sterilants remain adsorbed to AC, whether concentrations decrease over time through biodegradation, and the contact and retention effectiveness of AC.
- Soil sterilants are often heterogeneously distributed throughout a site based on surface application, their stability and mobility, as well as the time elapsed at many sites since they were applied (i.e., 1970s to 1990s). Accurate delineation is a challenge, and heterogeneous distribution is difficult to address where immobilization or chemical contact are required at specific ratios.
- Where present in soil, bromacil and tebuthiuron are often found at levels exceeding regulatory guidelines in groundwater. Low endpoint concentrations required for site closure (Table 1), based

on regulatory guidelines, make *in situ* groundwater remediation challenging; however, some remediation technologies are able to reduce concentrations by orders of magnitude, thus effectively controlling risk despite challenges in complete elimination. Groundwater that is extracted via pump and treat can be successfully remediated using carbon filters and through photolysis. However, reaching target endpoints is extremely challenging as mass removal rates decline and the system becomes dominated by diffusion and desorption (K. French, *pers. comm.*).

- Research on other sterilants in other jurisdictions has proven that combinations of treatment technologies can be more successful at remediating residual pesticides than individual technologies. There is a need to test treatment combinations (e.g., AC to bind plus oxidant or enzymes to degrade) or a sequential approach to bring high concentrations down, followed by a polishing step.
- The cost for any remediation program must be equivalent to or less than a remedial excavation and disposal approach unless there are significant sustainability considerations to support an alternative remediation approach.

4.2 CONSULTANT SITES SUMMARY

While not a complete list of sterilant-impacted sites in Alberta, a list of 50 sites with a summary of select site parameters was compiled by an SSP partner consultant (Houston et al., 2020). Parameters included site location, sterilant type and maximum concentration in soil and groundwater, soil lithology, groundwater data (hydraulic conductivity, gradient and depth), delineation status, and presence of co-contaminants in soil or groundwater. A summary of relevant information is provided here; however, based on the data structure some interpretation was required.

- All sites had sterilant impacts in soil, with 46 having bromacil impacts and 10 with tebuthiuron impacts. Where tebuthiuron was present, bromacil was always present as a co-contaminant. Over half the sites also had reported impacts in groundwater, but not all were evaluated.
- Sixteen sites were identified as having coarse-grained soil as the dominant soil type influencing contaminant migration, with the remainder having fine-grained soil.
- Fifteen sites had sterilants restricted to surface soil (<50 cm). The average soil impact depth was 2.75 m below ground surface (bgs), and maximum was 6 m bgs.
- Full delineation of sterilant impacts was achieved at approximately half of the sites.
- Groundwater depth at the sites, where evaluated, was found at an average of 2.13 m bgs, ranging from 0.23 to 9.46 m bgs. Hydraulic conductivity at the sites spanned two orders of magnitude, from approximately 1×10^{-6} to 1×10^{-8} m/s.
- Most sites with groundwater impacts had co-contaminants. These included phenols, pentachlorophenol, boron, petroleum hydrocarbons, polycyclic aromatic hydrocarbons, chloride (majority), other sterilants, metals and sulphate.

In summary, bromacil was the more prevalent sterilant. Sites had both fine- and coarse-grained soil; often both soil types were encountered at a given site, but the dominant soil type influencing sterilant migration was listed. Most sites had impacts below surface and into shallow groundwater. Sterilant delineation was achieved at approximately half the sites, indicating challenges in full delineation. Finally, co-contaminants were found at most sites, potentially influencing management and remediation choices for soil sterilants.

4.3 SSP STEERING COMMITTEE FEEDBACK

Finally, interviews were conducted with SSP steering committee members to understand the challenges faced on their sites or those they were familiar with; remediation technologies employed; and what bench-scale testing and field-scale testing may be needed for greater confidence in selecting treatment technologies.

4.3.1 Site Characteristics and Sterilant Distribution

- At some sites the distribution of sterilants is near fence lines and around buildings and gates. For these cases, *in situ* treatment would be favourable because soils in these locations are generally not found with co-contaminants and are therefore not usually being excavated.
- Vegetation impacts cannot always be used to identify sterilant impacts, as sites may be graveled. Dormant sites may not be regularly monitored.
- Small 'hot spots' are often found across a site in soil.
- As sterilant use was halted in the late 1990s, surface soil can meet guidelines but sterilants at the same sites can be found deeper in the profile (i.e., ~1 to 3 m bgs and sometimes in groundwater) due to migration time.

4.3.2 Remediation and Management Strategies

- Risk assessment and risk management were most frequently employed in sterilant management, followed by remedial excavation and disposal where risk could not be managed otherwise.
- For one site with groundwater impacts, bench-scale testing was completed to evaluate the potential effectiveness of a permeable reactive barrier (PRB) with BOS100. The technology uses sorption to trap the contaminants, followed by treatment through a reductive dechlorination process. The technology was not employed at the site, however, as contaminant concentrations fell below a key risk threshold and were instead monitored.
- A pump and treat program is ongoing at one site where groundwater is extracted followed by filtration through a granular activated carbon (GAC) unit. At the same site, *in situ* treatment using an oxidant technology was ineffective at treating the sterilants.
- Some sites had soils treated using thermal desorption where it was found to be economical to use that technology.
- Several sites had AC applied, but there was some uncertainty regarding effectiveness and longevity.

- Assessment at a site without sterilant impacts but in the vicinity of sterilant-impacted sites included shallow surface soil bacterial counts to evaluate potential natural degradation vs. active remediation. Data could be made available for understanding microbial populations in the region.

4.3.3 Remediation Goals

Some sites with high sterilant concentrations require lowering to Tier 1 endpoint concentrations; in other cases, a risk management approach is required, where concentrations are deemed not to affect vegetation growth and there is no risk of migration. Example sites with the latter scenario are those where land is returned to a landowner for productive use without the site receiving a full reclamation certificate, or where co-contaminants prevent full closure.

Sites in agricultural areas generally face more scrutiny when claims of low risk are made compared to those in non-agricultural areas. Development of site-specific remedial objectives needs to be done in conjunction with relevant regulatory agencies, either the Alberta Energy Regulator (AER) or Alberta Environment and Parks (AEP).

In summary, there are a variety of treatment options available but limited experience in their implementation for treatment of sterilants in Alberta. In addition, treatment options need to consider a range of endpoint concentrations based on different site requirements.

4.4 KEY REMEDIATION CHALLENGES

Based on the information presented above, three key challenges were defined for the purpose of evaluating and testing remediation technologies:

1. Sterilants at depths greater than 50 cm bgs in unsaturated soil, thus inaccessible to treatment at surface, were identified as a remediation challenge. Ideally the technologies to address deeper sterilants would function in situ to minimize excavation of overlying soil.
2. Soil treatment where sterilant destruction is required, and immobilization is not considered an acceptable option, are challenging to implement. Technologies for this application could be *in situ* or *ex situ*.
3. Saturated fine-grained till soils and groundwater impacted by sterilants pose a remediation challenge. Where sterilants are widely dispersed, in situ technologies and/or combinations thereof to avoid remedial excavation and disposal of >5,000 to 10,000 tonnes of soil and underlying groundwater, would be beneficial.

A consideration in all the above scenarios is whether the primary goal is to address high concentrations to reduce risk, or lower concentrations to meet remediation endpoints. In some cases, technologies may be more applicable at higher versus lower concentrations, and it is recommended this be addressed through the testing program. In addition, some technologies may be more applicable to either bromacil or tebuthiuron or may be applicable only to a particular soil type (i.e., coarse- or fine-grained; specific organic matter content).

5. REMEDIATION TECHNOLOGY REVIEW

Remediation technologies applicable for treating soil and groundwater impacted by soil sterilants were previously identified in Drozdowski et al. (2018b). Additional review of literature, conference proceedings and other sources revealed few new applicable technologies, and none tested at field scale for the specific treatment of bromacil or tebuthiuron.

5.1 SUMMARY OF REMEDIATION TECHNOLOGIES AND SCREENING FOR SSP

Technologies are summarized in Table 3 (*Ex situ* soil remediation technologies), Table 4 (*In situ* soil remediation technologies), Table 5 (*Ex situ* water remediation technologies) and Table 6 (*In situ* water remediation technologies). Typical remediation costs, where available, are provided in Appendix A.

Based on the key challenges identified in Section 4.4[2] and the review of applicable site types in Alberta, technologies were organized by the authors into one of three categories:

1. **Proven** for treatment of sterilants – requires no further evaluation unless providers can identify explicit requirements for testing to significantly refine the process.
2. **Impractical** for application for reasons as specified (e.g., low effectiveness and/or longevity, elevated cost, or potential residual impacts to treated media, such as incomplete remediation resulting in harmful daughter products or impact to soil quality).
3. **Potential** to evaluate through bench-, meso-, pilot- or field-scale trials, pending additional review and prioritization.

Additional notes were also included in the tables with justification for each of the rankings, and potential follow-up tests required.

Further evaluation of those technologies deemed 'potential' in Tables 3 to 6 was conducted by locating and interviewing service providers to better understand the application of technologies, their availability, and their ability to treat the two sterilants of concern. All providers and/or technologies listed in Tables 7 and 8 would be available for projects in Alberta. Results of interviews providing additional information on

[2] Key remediation challenges (section 4.4) are defined as follows:

1. Sterilants at depths greater than 50 cm bgs in unsaturated soil, thus inaccessible to treatment at surface, were identified as a remediation challenge. Ideally the technologies to address deeper sterilants would function in situ to minimize excavation of overlying soil.
2. Soil treatment requirements where sterilant destruction is required, and immobilization is not considered an acceptable option, are challenging to implement. Technologies for this application could be in situ or ex situ.
3. Saturated fine-grained till soils and groundwater impacted by sterilants pose a remediation challenge. In situ technologies and/or combinations thereof to avoid remedial excavation and disposal of >5,000 to 10,000 tonnes of soil and underlying groundwater, generally where sterilants are widely dispersed, would be beneficial.

the technologies are included in Tables 7 and 8, including their potential for addressing the key challenges identified by industry representatives in section 4.4.

Table 3. Ex situ remediation technologies for sterilants in soil[3].

Technology	Applicable Sterilants	Contaminant Removal Process	Conditions for use/Limitations	Advantages	Evaluation for SSP Treatment Trial*	Recommendation/Comment
Immobilization (with Activated Carbon)	All	Immobilization by adsorption to activated carbon particles	Requires thorough incorporation into soil and addition of water. Requires regulator approval with scientific backing to certify sites treated with activated carbon as a remediation technology.	Low cost, proven technology	Proven	Regularly used successfully both *in situ* and *ex situ*; longevity in question by regulators and is under review via SSP#10
Remedial Excavation and Disposal	All	Physically excavate and haul contaminated soil to appropriate landfill facility	Landfill acceptance (Landsburg and Fedkenheuer, 1990) Difficult to ensure contaminant delineation due to mobility and length of time in the environment; destructive; Requires fill material	Complete removal of contaminant from the site	Proven	Regularly used successfully; cost and sustainability questionable
Thermal Desorption	Atrazine, tebuthiuron, bromacil (Bessie, 2009; EBA Engineering, 2007)	Contaminants are destroyed by heating soil to moderate temperatures – ranging from 200°F to 1,000°F depending on the contaminant (Lin, 2009)	Dewatering may be necessary to excavate soils for treatment (Bessie, 2009) Cost effective at volumes greater than 5,000 m^3; OM and clay rich soils bind contaminants and increase reaction time required for processing (EBA Engineering, 2007)	Highly effective	Proven	Used successfully for bromacil and tebuthiuron
Landfarming, Biopiles and Composting	Atrazine (and other similar compounds) (Morillo and Villaverde, 2017); bromacil, diuron, simazine (high pH conditions), linuron (EBA Engineering, 2007)	Mixing of contaminated soil with non-hazardous organic amendments and nutrient solutions to encourage the development of bacterial populations or other organisms, which can degrade pollutants via co-metabolic pathways (Niti et al., 2013; Ortíz et al., 2013; Rubio-Bellido et al., 2015; Silva et al., 2004)	Success is influenced by microbial bioaccessibility to the pollutants, which is determined both by the mechanical conditions (mixing, moisture content, soil composition), the properties of the applied amendment and contaminant properties; length of time required to remediate soil is years to decades; leaching concerns; may result in less uniform treatment	Can be performed *in situ* or *ex situ*; most applicable when time is not a limiting factor; easy to implement; does not require heavy infrastructure; cost-efficient; uses naturally occurring microbes, stimulated by natural (and synthetic) amendments and mechanical aeration	Impractical	Only potentially effective for remediation of tebuthiuron based on degradation via oxidation
Slurry Bioreactors	Unknown (chlorinated pesticides) (Morillo and Villaverde, 2017)	Wastewater residue is mixed with contaminated soil to obtain a slurry of a predetermined consistency; an aqueous suspension in the range of 10% to 30% w/v. The system can work under aerobic or anaerobic conditions and in different feed modes: continuous, semi-continuous, and batch (Morillo and Villaverde, 2017)	High cost, which must be justified for each application; lack of good medium- to full-scale successful demonstration (Morillo and Villaverde, 2017)	Accurate control of bioremediation process, which can be optimized by setting and monitoring the most critical parameters (Morillo and Villaverde, 2017)	Impractical	High cost makes it an unlikely candidate for treatment of sterilants
Soil Washing	All (dependent on solvent, surfactant)	Excavated contaminated soil is mixed with water containing extractants (solvent, (bio or synthetic) surfactant, and/or cyclodextrin) and agitated. After washing, soil particles settle out, and washing solutions are separated and regenerated or disposed of (Morillo and Villaverde, 2017)	Only works effectively in soils containing at least 50% sand and gravel (Morillo and Villaverde, 2017); Solvent extraction is typically low on very high molecular weight pesticides (Morillo and Villaverde, 2017); Solvents can be toxic to soil microbial populations (Pavel and Gavrilescu, 2008)	Proven to work effectively if applied appropriately	Impractical	Not suitable for most Alberta soils (fine-textured)

1. **Proven** for treatment of sterilants – requires no further evaluation (beige rows)
2. **Impractical** for application due to cost, Alberta soil types, or potential residual impact from technology/product (blue rows)
3. **Potential** to evaluate through bench-, meso-, pilot- or field-scale evaluation (green rows)

[3] Requires soils to be excavated, treated, and then replaced. Soil layers, especially topsoil and subsoil, cannot be mixed and therefore two treatments are required where both are present. Dewatering may also be required where soils are saturated, and water management in an open excavation may also be required.

Table 4. In situ remediation technologies for sterilants in soil.

Technology	Applicable Sterilants	Contaminant Removal Process	Conditions for use/Limitations	Advantages	Evaluation for SSP Treatment Trial*	Recommendation/Comment
Immobilization (with Activated Carbon)	All	Immobilization by adsorption to activated carbon particles	Requires thorough incorporation into soil and addition of water. Requires regulator approval with scientific backing to certify sites treated with activated carbon as a remediation technology. Care must be taken not to admix topsoil and subsoil layers when incorporating AC	Low cost, proven technology	Proven	Regularly used successfully; longevity in question by regulators
Bioremediation and Natural Attenuation	Atrazine, bromacil, diuron (Morillo and Villaverde, 2017), linuron, simazine (Bessie, 2009); tebuthiuron (Cotton and Sharma, 1993); atrazine (Henderson et al., 2006); simazine (Gunasekara, 2004)	Natural bioremediation – Existing native microflora (microbes or fungi) degrade the target contaminants; bioaugmentation – inoculation of enriched/acclimated consortia or single pollutant degrading strains of microbes or fungi to enhance degradation of contaminants (Cotton and Sharma, 1993); biostimulation – addition of appropriate nutrients (nitrogen, phosphorus, trace elements) and/or small amounts of secondary carbon sources to provide microorganisms with an environment which favors the development of metabolic pathways for contaminant biodegradation	Limited control; not proven to be effective for many contaminants under field conditions	Low cost; can be completed *in-situ*	Impractical	Likely ineffective based on known degradation rates (very slow)
Enhanced Microbial Degradation	Not available	Earthmaster Environmental Strategies Inc. provides phytoremediation with bioaugmentation or use of microbial pre-treatment to remediate soil contamination. The approach is considered experimental and would require validation on a 'proof of concept' prior to moving forward in further refinement.	To be determined	Low cost solution for surface impact	Impractical	Based on challenges as identified, surficial remediation is not a priority based on proven technologies.
Enzymatic Remediation	Atrazine (Henderson et al., 2006) – All (unknown)	Enzymes and enzymatic proteins are added to soil to facilitate the breakdown of organic contaminants	Enzymes for specific contaminants or by products may not be identified; incomplete conversion can create undesirable or hazardous by-products; sourcing enzymes may be difficult and/or costly; relatively new and unproven at field scale	Can be used to target specific contaminants or broad range of contaminants; can be used where microbial activity would be limited either by environment or high toxicity; can completely convert contaminants to harmless inorganic by-products	Impractical	See Limitations

Technology	Applicable Sterilants	Contaminant Removal Process	Conditions for use/Limitations	Advantages	Evaluation for SSP Treatment Trial*	Recommendation/Comment
In-situ Thermal Remediation (ISTR)	Unknown – All	Various methods where heat can be transferred to the subsurface including: (1) direct conduction of heat away from heaters placed in trenches or wells (thermal conductive heating or TCH), (2) electrical resistivity heating (ERH) of the subsurface by passing electrical currents through the soil, and (3) steam injection or steam enhanced extraction (SEE). Often paired with both vapour and liquid recovery for contaminant removal (U.S. Army Corps of Engineers, 2006)	Some of the ISTR methods may not be appropriate for remediation of very low volatility organics, such as pesticides; requires full site characterization	Thermal conductivity of media within the vadose and non-vadose zones vary less than permeability which allows much more uniform heating and treatment within a contaminated zone when compared to delivery of reagents	Impractical	Provider in Alberta could not be located; questionable effectiveness due to low vapour pressure of sterilants
Phytoremediation	Atrazine, linuron (Bessie, 2009; EBA Engineering, 2007) Atrazine (Henderson et al., 2006; Russell, 2011)	Compounds are transported across plant membranes and removed from the soil. Compounds can be released through leaves via evapotranspiration processes (phytovolatilization); degraded (phytodegradation) or become non-toxic via enzymatic modification and sequestration in plants (phytoextraction); or are degraded by microorganisms in the rhizosphere (rhizodegradation)	Long durations to effective remediation (Belden et al., 2004) (may never reach remedial endpoints); Highly dependent on climatic conditions, contaminant concentration and bioavailability, plant tolerance to contaminants, contamination areal extent and depth (limited by the rhizosphere or the root zone) or the disposal of plant wastes (EBA Engineering, 2007; Morillo and Villaverde, 2017); Plant selection is crucial, and little information is known about Alberta species; limited ability to measure "bioavailable" concentrations of herbicide residue to determine if this technology is applicable	Low cost; reduced erosion rates, improved chemical, physical and biological soil properties which may stabilize herbicide residues, decreasing potential for leaching and uptake (Belden et al., 2004); Land aesthetic improvement	Impractical	Unlikely to be effective based on plant susceptibility to sterilants
TRIUM SRT - Immobilization/Stabilization	None	Fly ash and polymer-based immobilization technology; may act as soil stabilizer	Early testing phase in Canada, limitations unknown at present	Waste to use product; activated carbon alternative	Impractical	Very early technology readiness level and immobilization is questioned as long-term solution
Fertilizers	Bromacil, tebuthiuron (Cotton and Sharma, 1993)	Enhance microbial degradation (Cotton and Sharma, 1993)	Not a permanent solution	Low cost	Impractical	Likely ineffective based on known degradation rates (very slow).
Manure / Organic Amendments	Atrazine, diuron, bromacil, tebuthiuron (Cotton and Sharma, 1993)	Improve soil structure, cation exchange, nutrients and enhance biodegradation; Amendments include peat and sawdust (Cotton and Sharma, 1993) , green wastes and compost (Morillo and Villaverde, 2017); Large amounts can retard degradation by providing more readily degradable carbon sources (Shea, 1985)	Increases pH and electrical conductivity (Landsburg and Fedkenheuer, 1990); Not effective alone or with activated carbon at high sterilant levels in lab study (Cotton and Sharma, 1993); Manure age has an impact of effectiveness – older is better (Cotton and Sharma, 1993)	Large volumes commercially available (Cotton and Sharma, 1993); Some amendments will require fertilizer (N) addition to maintain appropriate C:N ratios (Cotton and Sharma, 1993); Adding manure or peat and fertilizer improved plant productivity (Cotton and Sharma, 1993) and subsequent degradation	Impractical	Likely ineffective for long-term sequestration
Soil Flushing	Atrazine, bromacil, tebuthiuron (Bessie, 2009)	Extraction eluents with additives that enhance contaminant solubility are injected in the ground to dissolve soluble contaminants and then physically move the contaminants to an area where they may be extracted from the ground and treated or disposed of (Lin, 2009)	Requires water source and recovery/treatment system (Lin, 2009)	Proven to work effectively for soluble contaminants if applied appropriately and with sufficient soil transmissivity	Impractical	Typically used for flushing salts; unknown if used or applicable for sterilants. Unlikely as a candidate for soil treatment based on cost, logistics, and timelines, in comparison to proven technologies.

Technology	Applicable Sterilants	Contaminant Removal Process	Conditions for use/Limitations	Advantages	Evaluation for SSP Treatment Trial*	Recommendation/Comment
Activated Carbon Slurry	None	Adsorption to activated carbon	Has not been tested with sterilants; results in adsorption to activated carbon but long-term effectiveness must be ensured for regulatory site closure	Potential application at depth without removing overlying soil via backhoe (surface to 6m bgs) or injection grid	Potential	Requires testing
Chemical Oxidation	Diuron (Rosas et al., 2014); atrazine (Shea et al., 2004); simazine (Gunasekara, 2004)	Advanced oxidation processes (Fenton processes, TiO_2 photocatalysis) produce strong oxidizing intermediates (mainly OH• radicals) and their reaction with organic contaminants (pesticides/sterilants) leads to their destruction and mineralization	nZVI (zero valent iron) and surfactants can be toxic to resident microbial populations, plants or earthworms; a portion of nZVI is lost due to reaction with dissolved oxygen, oxide minerals and organic matter, which needs to be compensated for in application rates; adsorption of surfactant onto soils is sometimes high; success is dependent on solvent/surfactant concentration, contact time and effectiveness and temperature; Fenton process can lead to losses in soil organic matter; difficulties of diffusion through heterogeneous soil matrices	Can be done both *in situ* and *ex situ*	Potential	Chemical oxidation is challenging in highly calcareous till soils found in Alberta and should only be used if proven effective in bench-scale testing
Chemical Reduction (DARAMEND®)	Possible treatment of bromacil based on mode of action; unlikely to be successful in treating tebuthiuron	Daramend® reagents are composed of micro-scale zero valent iron (ca. 40% w/w) + solid organic carbon (ca. 60% w/w, processed plant material), and food grade binding agent: • Elemental iron powder (ZVI) promotes chemical dehalogenation while high quality organic carbon + nutrients push microbial growth and oxygen/nitrate/sulfate consumption • Together these processes drive the treated soil to a highly reduced state (i.e., strongly negative Eh)	Applied in a cycled anaerobic/aerobic mode for chlorinated organics in soil; Treatment of fine-grained soils requires careful attention to soil moisture content, irrigation, and soil mixing protocols; requires bench-scale testing prior to use	Combination of adsorbent and enhanced microbial degradation	Potential	Reduction can be a slow process. In addition, these technologies may not be effective in treating very low concentrations. Need to confirm no risk of chemical by-products or lowered quality of soil post-treatment.
Electrokinetic Remediation**	Pesticides identified as potential target contaminants with limitations (Federal Round Table on Remediation Technologies, 2020). See Fact Sheet for additional information (Government of Canada, 2019).	Electric field is applied across the soil using electrodes initiating physical, chemical and electrokinetic processes in the soil causing favourable transport and removal of contaminants. Electrokinetics can be used to transport treatment agents required for other technologies, such as zero-valent iron nanoparticles, oxidants (peroxide, permanganate or other), or biological amendments. The use of electrokinetics has previously been used in conjunction with a phytoremediation treatment, or during the use of surfactants or ultrasound treatments.	No field-scale data to verify effectiveness; may require integration of other technologies (chemical oxidation) to work effectively; requires full site characterization. A system for recovering and treating contaminants that can accumulate around the electrodes may be required. Most effective in saturated, low permeability soils.	Applicable in fine-grained soils with low hydraulic conductivities and large specific surface areas; capable of treating fine and low permeability materials	Potential	Bench-scale trial required with suitable technology provider

N/A = Not applicable

*Technology evaluation for potential trials

**Various forms of electrokinetic remediation have been identified including some *in situ* and *ex situ*

1. **Proven** for treatment of sterilants – requires no further evaluation (beige rows)
2. **Impractical** for application due to cost, Alberta soil types or potential residual impact from technology/product (blue rows)
3. **Potential** to evaluate through bench-, meso-, pilot- or field-scale evaluation (green rows)

Table 5. Ex situ remediation technologies for sterilants in water.

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages	Evaluation for SSP Treatment Trial*	Recommendation/Comment
Activated Carbon Filtration	Atrazine (Lazorko-Connon, 2008); linuron (EBA Engineering, 2007)	Adsorbed (Lazorko-Connon, 2008); water is pumped through vessels containing activated carbon; Sorption to organo-zeolites (Lazorko-Connon, 2008)	Interference from natural organic matter and suspended solids (>50 mg/L); multiple contaminants can influence performance (oil and grease >10 mg/L); not effective for highly water-soluble contaminants (EBA Engineering, 2007)	Effective for low concentrations of contaminants (EBA Engineering, 2007); Increased adsorption with increased adsorbent concentration (Lazorko-Connon, 2008); may be applicable both *in-situ* and *ex-situ*	Proven	Testing not necessary
Chemical Oxidation and Reduction	Atrazine (Lazorko-Connon, 2008); simazine (photo-Fenton reaction) (Gunasekara, 2004)	Water is pumped out and treated in a reaction chamber using ultraviolet light (UV) catalyzed hydrogen peroxide (or other oxidizing chemical) oxidation and sterilization; Oxidizing chemicals (peroxides, ozone, permanganates) are injected into the contaminated zone and contaminants are rapidly oxidized.	Forms bromate in high bromide waters (Lazorko-Connon, 2008); atrazine difficult to oxidize (Lazorko-Connon, 2008); inefficient without surfactants and solvents; Contaminants can/will be sorbed on soil, even after repeated pump and treat cycles; not effective for contaminants that are not soluble in water or adsorb strongly to soil; chemicals involved can be highly toxic to environment, public, workers; incomplete oxidation can create hazardous by-products	Used in pump and treatment. Can remediate a wide range of contaminants; can be applied both *in-situ* and *ex-situ* depending on site characteristics	Proven	Oxidation has been effective in treating tebuthiuron but requires consideration of groundwater chemistry, geology and hydrogeology. May be ineffective at treating low sterilant concentrations. Reductants may also be ineffective in treating bromacil as dehalogenation is microbially mediated. Chemical inputs can be costly.
Deep Well Injection	All (Bessie, 2009)	Contaminants are injected below drinking use aquifer (DUA)	Requires aquifer characterization; due to soil sorption, complete contaminant removal may not be possible	Injected into saline zones below DUA zone; permanent storage in the subsurface	Proven	Additional validation of this remediation method is unnecessary.
Photocatalysis	Atrazine, bromacil, diuron (Bessie, 2009)	Oxidation enhanced by UV light	May result in the production of by-products (i.e., incomplete conversion to CO_2 and water)	Effective for all concentrations	Proven	Unnecessary cost for *ex situ* treatment compared with activated carbon filter
Chlorination	Bromacil	Chlorination and chemical oxidation processes have been proven effective to degrade bromacil in water at suitable temperature and pH (Hu et al., 2019)	Likely cost prohibitive compared with existing carbon filtration technology	Potentially effective treatment	Impractical	Cost elevated compared with proven technology in activated carbon filtration
Electro/photoelectro-Fenton process	Tebuthiuron	Electro-Fenton and photoelectro-Fenton processes were proven effective in lab studies to degrade tebuthiuron in acidic solution at low pH (Gozzi et al., 2018), with sulfate and nitrate as the predominant ions released from the destruction. The intermediates could not be photodegraded by UVA light and may need to be treated further, which will increase the cost of this technology.	*Ex situ* treatment requires water removal; may be cost prohibitive compared with existing carbon filtration technology	Potentially effective treatment of bromacil	Impractical	Cost may be more than that for proven technology in activated carbon filtration
Nanofiltration/Reverse Osmosis	Atrazine (Lazorko-Connon, 2008)	Adsorbed (Lazorko-Connon, 2008) ; water is pumped through vessels containing nanofilters for capture of contaminants of concern	Interference from natural organic matter (Lazorko-Connon, 2008)	Not concentration dependent (Lazorko-Connon, 2008)	Impractical	Cost may be more than that for proven technology in activated carbon filtration
Photoelectrocatalysis Using WO_3 and H_2O_2, H_2SO_4 and H_2O_2 as Supporting Electrolyte	Bromacil	Electrochemical degradation process; one was activated by photoelectrocatalysis using WO_3 nanosheets/nanorods (Roselló-Márquez et al., 2019)	*Ex situ* treatment requires water removal; may be cost prohibitive compared with existing carbon filtration technology	Potentially effective treatment of bromacil	Impractical	Cost may be more than that for proven technology in activated carbon filtration

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages	Evaluation for SSP Treatment Trial*	Recommendation/Comment
Synergistic Vacuum Ultraviolet/Ultraviolet/ Chlorine Process	Bromacil	Another novel advanced oxidation process, a combination of vacuum ultraviolet/ultraviolet/chlorine (VUV/UV/chlorine process) was tested on six pesticides including bromacil, showing a high removal efficiency of over 95% after 60 seconds (Yang and Zhang, 2019)	*Ex situ* treatment requires water removal; may be cost prohibitive compared with existing carbon filtration technology	Potentially effective treatment of bromacil	Impractical	Cost may be more than that for proven technology in activated carbon filtration

1. **Proven** for treatment of sterilants – requires no further evaluation (beige rows)
2. **Impractical** for application due to cost, Alberta soil types or potential residual impact from technology/product (blue rows)
3. **Potential** to evaluate through bench-, meso-, pilot- or field-scale evaluation (green rows)

Table 6. In situ remediation technologies for sterilants in water.

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages	Evaluation for SSP Treatment Trial*	Recommendation/Comment
Bioremediation	Atrazine, diuron, simazine (Bessie, 2009)	Biodegradation	Without enhancement seems to be very slow	Aerobic or anaerobic conditions and *in situ* or *ex situ* (Bessie, 2009)	Impractical	Same rate as monitored natural attenuation/dissipation
Phytoremediation	Linuron, simazine (Bessie, 2009), (EBA Engineering, 2007)	Sterilants absorbed through the roots	Limited to shallow groundwater and surface water (EBA Engineering, 2007) ; Seasonal process	Poplar trees have been shown to be effective given the large amount of water they draw (EBA Engineering, 2007)	Impractical	Tolerant species would need to be sourced and tested
Sorption + AOP with Micron Trap-Ox Zeolites FeBEA35 and H_2O_2	Bromacil	Nano-remediation using injectable reactive and sorption-active particles, including a composite material consisting zerovalent nano irons (nZVI) and colloidal activated carbon, and a proprietary mixture of zeolites and Fenton reagents, may prove effective for cleanup of bromacil-polluted groundwater *in situ* or *ex situ*, by chemical reduction or oxidation including advanced oxidation processes such as Fenton reactions (Gawel et al., 2020)	Unknown – only tested at bench scale	Unknown – only tested at bench scale	Impractical	Provider of technology would need to be located; studies conducted at bench scale. May be covered under ChemOx approach.
Activated Colloidal Carbon Slurry + ChemOx	Bromacil, other to be determined	*In situ* remediation with PRB or permeable reactive zone (PRZ), may also be applicable as *in situ*, *ex situ* and on-site water treatment; sorption + reduction with micron Colloidal Carbon-Iron (AC+nZVI). PlumeStop® is a colloidal carbon slurry that is injectable and has been used for sequestering perfluorinated compounds, which may have similarities to sterilants	Challenges in using PlumeStop® include regulatory permission for its use, with a need to demonstrate control over the product once delivered to ensure no offsite migration. Extensive site characterization data and monitoring are therefore required to use PlumeStop. In addition, the product may not be effective at low concentrations due to difficulty in contact between colloidal activated carbon and dissolved sterilants.	Sorption and treatment technology combination	Potential	Requires bench scale testing by technology provider; applicable only to PRB/PRZ (not *ex situ* soil)
Enhanced Biodegradation (*in situ*)	Diuron, atrazine (aerobic or anaerobic), simazine (EBA Engineering, 2007)	Oxygen or dilute hydrogen peroxide solutions are introduced by air sparging below the water table; nitrate solutions are added to create anaerobic conditions for enhancing microbial activity	Solutions are difficult to deliver in heterogeneous systems; peroxide solutions must be <100 to 200 ppm; nitrate injections can have impacts on DUA; *ex situ* requires removal from aquifers so compounds must be soluble; dilute concentrations of contaminants often will not support microbial populations in bioreactors; influenced by climate (constructed wetlands) (EBA Engineering, 2007)	May increase the rate of microbial degradation which is very slow under natural conditions	Potential	Unlikely to be effective for bromacil (oxic conditions); slow treatment of tebuthiuron. Potential option for combination treatment if success demonstrated by technology provider
Permeable Reactive Barrier (PRB) with Embedded BOS[4] and Reductant	Bromacil (Vertex Env, *pers comm*)	Adsorption to activated carbon embedded in permeable reactive barrier with reductant for bromacil destruction; may be enhanced with enhanced biodegradation	Requires suitable groundwater flow for capture of impacted water; may be more applicable as risk management tool versus remediation	Potential *in situ* technology	Potential	Potentially effective treatment; likely most effective in high permeability aquifer

[4] BOS 100® consists of activated carbon impregnated with metallic iron. First, contaminants are "trapped" by the carbon, and then "treated" by reaction with the metallic iron. BOS 200® consists of activated carbon, terminal electron acceptors, nutrients and a facultative blend of aerobic and anaerobic bacteria. First, contaminants are "trapped" by the carbon, and then "treated" by biological degradation (Vertex Environmental Inc., 2020).

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages	Evaluation for SSP Treatment Trial*	Recommendation/Comment
Surfactant-Enhanced Removal	None – theoretical	Surfactant (Ivey-Sol) to remove sterilants sorbed to organic and clay particle surfaces with soil washing (where applicable)	Likely most effective in coarse-grained soils; requires groundwater well network with injection and recovery potential	Effective for other contaminant types; may allow treatment in fine-grained aquifers	Potential	Test at bench-scale to prove, then work up to meso-scale or pilot; ensure regulatory approval of approach

1. **Proven** for treatment of sterilants - requires no further evaluation (beige rows)
2. **Impractical** for application due to cost, Alberta soil types or potential residual impact from technology/product (blue rows)
3. **Potential** to evaluate through bench-scale, meso-scale, pilot- or field-scale evaluation (green rows)

Table 7. Summary of remediation technologies for sterilants in soil identified for potential testing.

Technology	Applicable Sterilants	Additional Information Provider	Additional Information on Treatment Technology	Primary Remediation Challenges Addressed by the Technologies[4]	Potential Testing Stage Based on Provider Feedback
Chemical Oxidation (*in situ* and *ex situ*)	Diuron (Rosas et al., 2014); atrazine (Shea et al., 2004); simazine (Gunasekara, 2004)	Brant Smith – ChemCo/Evonik and Jean Pare – Chemco (Evonik Active Oxygens, LLC, n.d.; Chemco Inc., 2020)	ChemCo/PeroxyChem/Evonik provided information on various chemical oxidation options. Key to identifying suitable treatment products and combinations would be to run in-house lab studies to short-list products and refine a treatment approach. Deployment methods include localized incorporation as well as large scale slurry incorporation into soil via deep drill. Additional considerations in using oxidative treatments include potential effectiveness at low concentrations (i.e., likelihood of contact between contaminant and product), activation technology, consumption rate, and cost.	2) Sterilant destruction	Stage 1
	To be determined[5]	Oskar Pula – Operations manager TRIUM	TRIUM Environmental Inc. provided information on their chemical oxidation (ChemOx®). Chemical treatment capabilities include hydrogen peroxide, sodium persulfate, potassium and sodium permanganate, ozone, and sodium percarbonate. Oxidants are combined with various activators and stabilizing agents. Soil testing would be required to identify suitable products and combinations, and treatment via oxidation would likely only be suitable for tebuthiuron. TRIUM has a large mulcher that is used for product delivery and incorporation to avoid some issues around effective distribution in soils (*ex situ*).	2) Sterilant destruction	Stage 2 (pending information from TCE trials)
Activated Carbon Slurry	None	Kevin French – Vertex Environmental Ltd. (Vertex Environmental Inc., 2020)	Deep drill and/or injection of activated carbon powder slurry – A variety of other solid or particulate AC-based remedial amendments exist, including simply powdered AC, that can be injected and can be controlled so as not to pose a risk of migration (K. French, pers. comm.).	1) Sterilants at depths greater than 50 cm bgs in unsaturated soil	Provider recommended assessment of adsorptive capacity and flow through column testing Stage to be determined; also requires assessing incorporation mechanism >50 cm bgs

[5] SSP Steering Committee members noted recent project with TRIUM; results requested for review but are currently pending.

Technology	Applicable Sterilants	Additional Information Provider	Additional Information on Treatment Technology	Primary Remediation Challenges Addressed by the Technologies[4]	Potential Testing Stage Based on Provider Feedback
Chemical Reduction (DARAMEND) *in situ* or *ex situ*	Possible treatment of bromacil based on mode of action; unlikely to be successful in treating tebuthiuron	ChemCo/Evonik representative – Remediation treatment chemical provider (Dr. Alan Seech – Evonik; Jean Pare – ChemCo)	DARAMEND®is an *in situ* chemical reduction (ISCR) product successful for use in treatment of other pesticides. Suppliers believe it would be suitable for treatment of bromacil impacts but were uncertain about treatment of tebuthiuron. The product works through reductive dehalogenation with FeO as reducing compound and by providing nutrients and feedstock to soil microbes, which contribute to reducing conditions in pore space.	2) Sterilant destruction	Stage 1
Electrokinetic Remediation**	Pesticides identified as potential target contaminants with limitations	Ron Lutz (Signum Environmental Ltd., 2020) Shaun Kavalinas, Ed Hanna – ElectroKinetic Solutions (EKS, 2020) Ground Effects (SK) (Ground Effects Environmental Services Inc., 2020)	Signum Environmental Ltd., ElectroKinetic Solutions (EKS) and Ecoventure Inc. provided information on their electrokinetic treatment technologies. None have been specifically trialed with sterilant treatment and would require refinement for potential use. Ecoventure technology deemed unfit due to issue with degrading electrodes during treatment. EKS suggested that chelating agents and an ionic solution would require development for specific treatment of bromacil and/or tebuthiuron. Ground Effects electroosmosis technology has not been specifically trialed with sterilants; potential for electro-osmosis *in situ*; technology has been more successful in fine-textured than coarse-textured soils (for treating salinity)	1) Sterilants at depths greater than 50 cm bgs in unsaturated soil 2) Sterilant destruction 3) Saturated fine-grained till soils and groundwater	Stage 1

Table 8. Summary of remediation technologies for sterilants in water identified for potential testing.

Technology	Applicable Sterilants	Additional Information Provider	Additional Information on Treatment Technology	Primary Remediation Challenges Addressed by the Technologies[4]	Potential Testing Stage Based on Provider Feedback
Activated Colloidal Carbon Slurry + ChemOx	All	Andrew Punsoni – ReGenesis Remediation Solutions	REGENESIS representatives were contacted to determine whether their liquid activated carbon product, PlumeStop®, could be used for immobilization of sterilants, possibly in combination with an oxidant to facilitate bioremediation. Column studies are typically completed to evaluate product effectiveness and optimal loading rate.	2) Sterilant destruction 3) Saturated fine-grained till soils and groundwater	Stage 1
Enhanced Biodegradation (*in-situ*)	Diuron, atrazine (aerobic or anaerobic), simazine (EBA Engineering, 2007)	SiREM	SiREM's cultured dehalogenating bacteria could facilitate debromination of bromacil under anaerobic conditions paired with chemical alteration of redox conditions. Other services offered by SiREM include treatability testing using a variety of remediation approaches (e.g., oxidation, reduction, electrokinetic enhanced in situ biological and chemical remediation).	2) Sterilant destruction 3) Saturated fine-grained till soils and groundwater	Stage 1
Permeable Reactive Barrier (PRB) with Embedded BOS and Reductant	Bromacil	Kevin French – Vertex Environmental Ltd.	Bench-scale testing was completed to evaluate the potential effectiveness of a permeable reactive barrier (PRB) with BOS100. The technology uses sorption to trap the contaminants, followed by treatment through a reductive dechlorination process.	2) Sterilant destruction 3) Saturated fine-grained till soils and groundwater	Stage 2/3 based on prior bench-scale tests
Surfactant-Enhanced Removal	None – theoretical	Bud Ivey – Ivey International Inc. (2020)	Where sterilants are highly sorbed to organic matter or clay particles, solvents may enhance desorption for subsequent flushing or *in situ* enhanced bioremediation. Potential combination technology.	3) Saturated fine-grained till soils and groundwater	Stage 1

5.2 POTENTIAL OPTIONS FOR COMBINING TREATMENT TECHNOLOGIES

Opportunities for concurrent as well as sequential treatment require further review. In some cases, adding amendments to other treatment technologies, such as thermal desorption, may enhance the process to generate more effective treatment, or to achieve acceptable concentrations to meet regulatory closure requirements. Various chemical oxidation and reduction combinations may also be targeted to the remediation of bromacil and tebuthiuron under various conditions. In other cases, different technologies may be required for treating high concentrations, with 'polishing' technologies at lower concentrations.

Given the heterogeneous distribution of sterilants and unique conditions at most sites, a variety of approaches may be required depending on remedial objectives for the site or area. Highly specialized oversight of such a project would be required, which may have to be sought in addition to the treatment providers.

6. RECOMMENDATIONS

6.1 BENCH-SCALE REMEDIATION TECHNOLOGY TESTING

Given that there are several different needs in addressing the challenges around sterilant remediation in soil and that *in situ* groundwater remediation can be highly site-specific, a strategy for bench- and field-scale testing of remediation technologies for maximum effectiveness is required. It is recommended that a directed Request for Proposals (RFP) be provided to short-listed technology providers to provide additional justification for testing of their technologies, and an outline of the testing that would be conducted with associated cost. It is also recommended that the SSP project manager follow up with any service providers who do not submit a proposal for technology testing to gain more information, especially where they deem their technology to be inapplicable to the treatment of soil sterilants.

Based on interviews with technology providers and practitioners, a flexible and staged approach was requested for the assessment of potential remediation technologies. Technology testing stages are described as follows:

1. **Stage 1 – Preliminary bench-scale testing**: Where technologies or products are available and deemed *potentially* effective for sterilant remediation, providers will be given flexibility in a preliminary trial of their technologies with spiked samples of known bromacil and/or tebuthiuron concentration. The sterilant concentrations used, soil and/or water types would be limited to those deemed most effective for evaluating a technology's suitability for remediation of bromacil and/or tebuthiuron. This will be a 'low cost' effort aimed at screening technologies for applicability prior to conducting additional testing in Stage 2. Where testing has been completed at a Stage 1 level and satisfactory results can be provided to the SSP, Stage 2 testing would be considered.
2. **Stage 2 – Extended bench-scale testing**: Following successful Stage 1 testing or where technologies have been previously tested, further validation will be proposed through a greater range of sterilants concentrations, soil types and/or water composition.

3. **Stage 3 – Meso- and/or field-scale testing:** Where extended bench scale testing proves a technology to be successful and providers wish to conduct additional testing at meso- or field-scale (or their technology functions at meso-scale), testing facilities available at InnoTech Alberta would be put forward in a collaborative joint proposal for the project. Alternatively, onsite field testing could be carried out, provided sufficient controls were put in place for evaluation of product effectiveness and regulatory permission to conduct testing.

Proposed recipients of a directed RFP based on recommendations in Tables 7 and 8 include:

- Chemco Inc.
- ElectroKinetic Solutions
- Evonik Industries AG
- Ground Effects Environmental Services Inc.
- Ivey International Inc.
- ReGenesis
- Signum Environmental Ltd.
- SiREM
- TRIUM Environmental Inc.
- Vertex Environmental Ltd.

It is recommended that the SSP Steering Committee review the proposed recipients of a directed RFP to determine whether there may be any conflicts of interest in including the proposed providers, or whether their technology or approach is considered too early in readiness level to be considered. Select Expert Advisory Committee members with expertise in contaminant remediation will review proposals and evaluate their merit.

6.2 MESO- TO FIELD-SCALE REMEDIATION DEMONSTRATION

As additional *ex situ* groundwater remediation technologies are deemed unnecessary, *in situ* testing will be the focus of the remediation demonstration. Discussions are required with the steering committee to determine a path forward for a remediation demonstration approach.

1. **Site identification**: Several sites have been put forward as potential candidates for remediation trials. The sites have been defined as having the following characteristics:
    - Bromacil or tebuthiuron plume of some significance and concentrations to enable observable decreases in sterilant concentrations
    - Fine-grained till soils
    - Impacts in soil and groundwater, fully delineated

- Existing monitoring well network
- Ideally near a major centre without access or onsite infrastructure restrictions

Note: One site has been identified as a potential candidate and additional delineation is proposed for June 2021, which will confirm site characteristics including soil type and sterilant concentrations.

2. **Technology suppliers and advisors meeting**: Once one or more sites have been identified as potential candidates for a remediation trial, several providers of remediation services will be gathered to discuss options for evaluation of one or more treatment technologies. Those listed in Table 8 would be invited to the discussion along with key Expert Advisory Committee members.
3. **Trial design**: As the research organization, InnoTech will oversee the field level remediation project. InnoTech will work closely with the site owner's current consultants and the remediation technology providers chosen to provide services for the site remediation. Where required, InnoTech will design the onsite research experiments to evaluate the chosen technologies in consultation with service providers.
4. **Work plan and cost estimate**: Once the design and suppliers have been selected, a final work plan and cost estimate, including contingencies, will be established for the field scale demonstration project(s).

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8. ACKNOWLEDGEMENTS

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The authors would like to acknowledge the funding support provided by the SSP Steering Committee via InnoTech Alberta to initiate this project.

We would also like to thank all the individuals who have provided information, documents and insights to kick start this initiative, particularly Kathryn Bessie, who has been instrumental in previous sterilant research and providing guidance for future direction

APPENDIX A: Typical Remediation Costs for Soil and Water

Table A1. Soil remediation treatments costs.

Remediation Technology	Cost Associated with Remediation (US$ and/or C$)
Excavation and landfilling	US$2,200 to US$2,400/ton (Weber et al., 2011) C$100 to C$200/ton depending on distance to landfill (EBA Engineering, 2007)
Immobilization (w/Activated Carbon)	C$15/m^3 to C$35/m^3 (EBA Engineering, 2007)
Land treatment	Biopiles C$35 to C$260/m^3 (Shea et al., 2004) Landspreading US$39/m^3 (Shea et al., 2004) Composting C$45 to C$180/m^3 (EBA Engineering, 2007) Landfarming C$5 to C$100/m^3 (EBA Engineering, 2007)
Biosurfactants and surfactants	US$1 to US$60/kg US$1 to US$2/kg surfactant (Mao et al., 2015)
Electrokinetic	US$50 to US$117/m^3 (Federal Round Table on Remediation Technologies, 2020)
Phytoremediation	$10 and $50/ton; $12 to 60/m^3 (Gerhardt et al., 2009) C$50 to C$147/m^3 (EBA Engineering, 2007)
Chemical Oxidation (DARAMEND® and EHC®)	$17/m^3 ($12.5/yd^3) (Seech et al., 2008) $29 to $63/ton (Seech et al., 2008) US$77 to USS94/m^3; nZVI alone, nZVI + acetic acid, nZVI + aluminum sulphate or nZVI + acetic acid + aluminum sulphate (Shea et al., 2004)
Soil washing and flushing	$50 to $104/m^3 for in situ treatments, and $150 to $200/m^3 for *ex situ* treatments (Bini, 2011; Iturbe et al., 2004) C$19 to C$191/m^3 (EBA Engineering, 2007)
Bioremediation (using microorganisms)	$6.4 to $150/m^3 (Bini, 2011; Gavrilescu, 2005) ($50 to $100/m^3 for *in situ* or $150 to $500/m^3 for *ex situ*)
w/ use of Cyclodextrin	$220/ton (Gruiz et al., 2011)
Thermal desorption	C$44 to C$252/m^3 (EBA Engineering, 2007)
Removal and incineration	US$261 to US$1,961/m^3 (Shea et al., 2004)

*Unless otherwise referenced, value was adapted from Sterilants Literature Review conducted by EBA Engineering in 2007 (EBA Engineering, 2007) which predominantly used the Federal Remediation Technologies Roundtable (FRTR) Remediation Technologies Screening Matrix V. 4.0 (http://www.frtr.gov/matrix2.section4/)

Table A2. Water remediation treatment costs.

Remediation Technology	Cost Associated with Remediation **Literature** (EBA Engineering, 2007)* **(US$)**
ChemOx (EHC®)	$6.0/m^3 of treated aquifer (Seech et al., 2008)
Enhanced biodegradation (aerobic) – air sparging	$10 to 20/m^3

Remediation Technology	Cost Associated with Remediation **Literature** (EBA Engineering, 2007)*** (US$)**
Enhanced biodegradation (anaerobic) – chemical hydrolysis and nitrate enhanced	$40 to 60/L
Enhanced biodegradation (*ex situ*)	$6.1 to 8.6/$m^3$ bioreactor unit
Adsorption by activated carbon	$0.32 to 1.7/$m^3$ (flow rate of 0.4 M L/day)

*Unless otherwise referenced, value was adapted from Sterilants Literature Review conducted by EBA Engineering in 2007 (EBA Engineering, 2007) which predominantly used the Federal Remediation Technologies Roundtable (FRTR) Remediation Technologies Screening Matrix V. 4.0 (http://www.frtr.gov/matrix2.section4/

APPENDIX B: 2024 ANNUAL SHARING EVENT PRESENTATIONS

APPENDIX B1: INTRODUCTION TO THE 2024 SHARING EVENT

SSP Soil Sterilants Program

TC Energy | ATCO | ALBERTA INNOVATES | InnoTech ALBERTA

SOIL STERILANTS PROGRAM (SSP) – 2024 FINAL SHARING EVENT

INTRODUCTION

BONNIE DROZDOWSKI

SEPTEMBER 10, 2024

WELCOME, SAFETY MOMENT AND AGENDA

SSP Soil Sterilants Program

Time	Activity/Project # and Title	Presenter
Introduction		
9:00	Introduction and program information	Bonnie Drozdowski
Identification and Delineation		
9:15	Sterilant Sampling Best Management Practices	Kathryn Bessie
9:40	Laboratory Method Investigation	Adam Malcolm
10:05	**BREAK- Coffee**	
10:20	Detection of Bioaccessible Sterilants	Jackie Maxwell
10:45	Field Screening Technologies for Bromacil and Tebuthiuron	Kevin French
Risk Assessment and Management		
11:10	Native Species Toxicity Evaluation	Stefan Schreiber
11:30	**Lunch**	
12:40	Risk Assessment for Management of Sterilant Impacted Sites	Cory Kartz
13:20	Investigation of the Long-term Effectiveness of Activated Carbon and Immobilization of Bromacil and Tebuthiuron	Chris Powter
Remediation		
13:40	Bench-scale Testing of Chemical Amendments to Remediate Bromacil and Tebuthiuron in Soil	Jean Pare
14:05	Bench-scale Treatability Study of Bromacil and Tebuthiuron in Alberta Soils	Kevin French
14:35	Ex-situ Field Demonstration and Optimization of the use of Daramend for the Remediation of Bromacil in Soil	Victor Bachmann
15:00	Summary and Conclusions	InnoTech Alberta and ATCO

SSP Soil Sterilants Program

BACKGROUND

- Soil sterilants used from 1960's to 1990's for non-selective vegetation control
- Site management challenges due to persistence and mobility

SSP Soil Sterilants Program

TC Energy | ATCO | ALBERTA INNOVATES | InnoTech ALBERTA

OBJECTIVE:

To establish **proven, technical** and **cost-effective** strategies and best practices for management of sites impacted by residual soil sterilants, with the goal of supporting regulatory site closure.

PROGRAM DELIVERY

- 5 year program
  - Initiated in 2019
- Scope
  - Address challenges specific to AB
  - Applied research
  - Focus on Bromacil and Tebuthiuron

SSP Soil Sterilants Program

Governance and Management

Program Participants (Steering Committee) Strategic direction, funding, guidelines and policies, project approval

Program Director (ITA) Coordinate/Liaise with SC; Program and Project Oversight; Synthesis

Expert Advisory Committee Volunteer; Subject Matter Expertise for project selection and steering

Project Execution

Project Service Providers

Identification and Delineation | **Risk Assessment and Management** | **Remediation**

Data Synthesis and Knowledge Transfer

STEERING COMMITTEE

- Monica Brightwell, ATCO Pipelines
- Darcy Bye, TC Energy
- Larry D'Silva, TC Energy
- Dallas Johnson, Alberta Innovates
- Jason Pentland, ATCO Electric
- Bonnie Drozdowski, InnoTech Alberta

EXPERT ADVISORY COMMITTEE

- Kathryn Bessie, Retired (Formerly TetraTech)
- Alfred Burk, Verdant Environmental
- Gordon Dinwoodie, Retired (Formerly AEPA)
- Catherine Evans, Alberta Energy Regulator
- Kevin French, Vertex Environmental
- Premee Mohamed, Alberta Environment and Protected Areas
- Terry Obal, (Formerly Maxxam Analytics)
- Chris Powter, Enviro Q&A Services
- Roger Saint-Fort, Mount Royal University
- Ron Sawatsky, Independent (Formerly InnoTech)
- Gladys Stephenson, Aquaterra Environmental Consulting
- Ron Thiessen, University of Calgary (Formerly Advisian)

IDENTIFICATION AND DELINEATION

Project	Project Description	Project Service Provider(s)
Sampling Best Management Practices	Develop best management practices for sampling methodologies to ensure quality analytical results are available to inform management decisions.	TetraTech
Laboratory Method Investigation	Develop a method to increase effectiveness and/or efficiency in laboratory analysis for detection of total bromacil and tebuthiuron in soil and water.	InnoTech Alberta
Detection of Bioavailable Sterilants	Develop and validate laboratory analytical method(s) for detection of bioaccessible bromacil and tebuthiuron, required for evaluating effectiveness of immobilization technologies and for supporting risk assessment.	University of Alberta InnoTech Alberta
Field Screening Technologies	Investigate the potential to develop field screening or proxy lab analytical methods to minimize costs associated with delineation of bromacil and/or tebuthiuron.	Vertex Environmental Inc.

- Kathryn Bessie, Tyrel Hemsley, and Aziz Shiakh
- Victor Bachmann, Graham Knox, Simone Levy, Alberto Pereira, Julius Petrolius, Eric Ruan, Sarah Thacker, Ron Thiessen, and Xinghuo Mo
- Eric Cowan, Kevin French, Emily Terpstra, and Alyson Neufeld
- Jackie Maxwell and Sylvie Quideau
- Chris Powter

RISK ASSESSMENT AND MANAGEMENT

- Sarah Thacker, Victor Bachmann, Simone Levy, and Stefan Schreiber
- Cory Kartz, Amélie Litalien, Ian Mitchell, and Miles Tindal
- Amy Grainger, Steven Hardy, Adele Houston, Gil Marquez, Aaron Tangedal, Ron Thiessen, and Tiona Todoruk
- Ryan Prosser
- Barry Loescher
- Chris Powter

Project	Project Description	Project Service Provider(s)
Sterilant-Specific Model Input Data	Develop sterilant-specific model input data relevant to Alberta (soil half-life, mobility, etc.).	Advisian, University of Guelph and BV Labs
Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life	Determine appropriate risk model(s) and model parameters to develop screening guidelines for bromacil and tebuthiuron deemed to be protective of the irrigation watering and freshwater aquatic life pathways and better reflect the contaminant's "real-world" fate and mobility in the subsurface under Alberta field conditions.	Millennium EMS Solutions
Investigating Sterilant Fate and Mobility in Alberta	Investigate bromacil mobility in groundwater under Alberta conditions to inform guideline modification and/or acceptance for Tier 2 approaches.	Advisian
Native Species Toxicity Evaluation	Undertake Alberta native plant species toxicity evaluation.	InnoTech Alberta

REMEDIATION

Project	Project Description	Project Service Provider(s)
Investigation of Long-term Effects of Activated Carbon	Investigate longevity of immobilized bromacil and/or tebuthiuron with activated carbon, a common historical amendment for preventing migration of soil sterilants.	InnoTech Alberta
Bench-scale Testing of Sterilant Remediation Technologies	Identify and test candidate technologies for immobilization or remediation of bromacil and/or tebuthiuron in soil and water.	Chemco Inc. Mount Royal University and InnoTech Alberta Vertex Environmental Inc. Evonik
Remediation Demonstration(s)	Undertake operational-scale demonstration of management of representative sterilant-impacted site:multiple technology approach.	InnoTech Alberta

- Victor Bachmann, Simone Levy, Sarah Thacker, Stefan Schreiber, Ryan James, Ron Thiessen, and Bonnie Drozdowski
- Chris Powter
- Eric Cowan, Kevin French, Emily Terpstra, and Alyson Neufeld
- Allan Seech
- Malika Bendouz and Jean Paré
- Roger Saint-Fort
- Oskar Pula

DATA SYNTHESIS/KNOWLEDGE TRANSFER

Project	Project Description	Project Service Provider(s)
Technology Evaluation and Comparison	Evaluate and compare remediation technologies, including cost and benefit analysis (including treatment logistics).	InnoTech Alberta
Knowledge Synthesis and Extension	Hold Annual sharing events to update project status. Present non-proprietary information through publications and conferences. Prepare a series of Program Summary reports for Sterilant Program members and, where approved, for public dissemination.	InnoTech Alberta Enviro Q&A Services

Enviro Q&A Services

- Simone Levy, Bonnie Drozdowski, Sarah Thacker, Victor Bachmann, Xinghuo Mo
- Chris Powter

SSP FINAL SHARING EVENT OBJECTIVES:

1. Share SSP project info with relevant stakeholders, including:
   - Other service providers and members of 'community of practice'
   - SSP Steering Committee (funders)
   - Expert advisory committee members
2. Summarize how project results support decision making for sterilant-impacted sites

QUESTIONS?

APPENDIX B2: SUMMARY OF THE 2024 SHARING EVENT

SSP Soil Sterilants Program

TC Energy | ATCO | ALBERTA INNOVATES | InnoTech ALBERTA

SOIL STERILANTS PROGRAM (SSP) – 2024 FINAL SHARING EVENT

SUMMARY AND CONCLUSIONS

BONNIE DROZDOWSKI, JASON PENTLAND AND MONICA BRIGHTWELL

SEPTEMBER 10, 2024

What did we learn initially w/in the program?

- Majority of sterilant impacts in Alberta are associated with **bromacil** and **tebuthiuron**
- Sites are **primarily** located in **central** and **southern Alberta**
- Alberta **Tier 1** Soil and Groundwater Remediation Guidelines (EPA 2023) are **conservative** and based on data generated outside Alberta
- Lack of available information for use in **risk assessment models**
- **Remediation technologies** have been **successfully** used to reduce or eliminate sterilant impacts – **more research required** for Alberta conditions and at larger scale

Drozdowski, B., C.B. Powter, S. Levy, 2018. Management of Sterilant Impacted Sites: Literature Synthesis. InnoTech Alberta, Edmonton, Alberta. 49 pp.

Drozdowski, B., S. Levy and C.B. Powter, 2018. Remediating Soil Sterilant-Affected Lands: Summary of Stakeholder Discussions. InnoTech Alberta, Edmonton, Alberta. 42 pp.

PROGRAM DELIVERY

SSP Soil Sterilants Program

- 5 year program
  - Initiated in 2019
- Scope
  - Address challenges specific to Alberta
  - Applied research
  - Focus on Bromacil and Tebuthiuron

The SSP aimed to synthesize information so that practitioners, site owners and regulators have the tools needed to assess, remediate, reclaim, and effectively manage risk surrounding sterilant impacts.

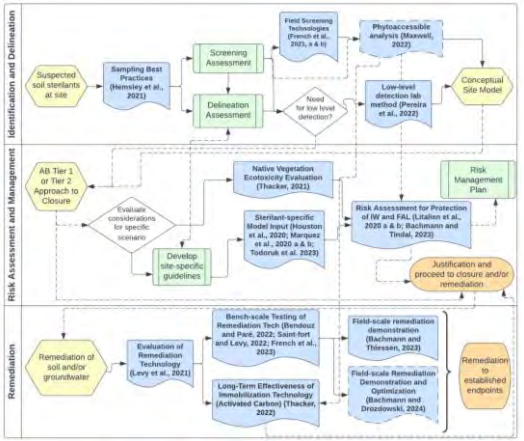
SSP Soil Sterilants Program

TC Energy | ATCO | ALBERTA INNOVATES | InnoTech ALBERTA

KNOWLEDGE GAPS AND INTENDED SSP OUTCOMES

SSP Soil Sterilants Program

Program Area	Intended Outcome of the Program
Identification and Delineation	a) The uncertainty associated with the methods used to identify when/where sterilant impacts occur is reduced. b) Technologies, best practices, and analytical methods are developed to more accurately and cost-effectively assess and delineate impacts.
Risk Assessment and Management	a) Uncertainty associated with empirical data inputs to risk assessment models for protection of ecological pathways is reduced. b) Conclusive evidence is generated regarding long-term effectiveness of immobilization technologies.
Remediation	a) Optimal, state-of-the-art technologies and/or processes are demonstrated under Alberta conditions to address specific challenges faced by the community of practice.
Knowledge Transfer	a) A community of practice consisting of practitioners, industry and government representatives is developed and retained. b) Technical information is disseminated through annual workshops and external presentations.



SSP Soil Sterilants Program

PROGRAM DELIVERABLES

SSP Soil Sterilants Program

- Drozdowski, B. and C.B. Powter, 2024. Soil Sterilants Program: **Knowledge Synthesis, Recommended Practices and Gaps**. Report SSP-14B prepared by InnoTech Alberta and Enviro Q&A Services for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 65 pp.
- Powter, C.B. and B. Drozdowski, 2024. Soil Sterilants Program: **Project Report Compilation**. Report SSP-14A prepared by Enviro Q&A Services and InnoTech Alberta for Soil Sterilants Program, InnoTech Alberta, Edmonton, Alberta. 46 pp. plus appendices.
- Sawchuk, S., B. Drozdowski and C.B. Powter, 2024. Soil Sterilants Program: **Steering Committee Minutes and Quarterly and Annual Reports**. Report SSP-14C prepared for InnoTech Alberta, Soil Sterilants Program, Edmonton, Alberta. 200 pp.

STERILANT IMPACTED SITES AND CHALLENGES

SSP Soil Sterilants Program

Site Summary Information	
• Bromacil is the more prevalent sterilant. • Co-contaminants are found at most sterilant-impacted sites. • Sites often have both fine- and coarse-grained soils, with majority dominated by fine-grained. • Vegetation impacts cannot always be used to identify sterilant impacts, as sites may be graveled. • Small soil 'hot spots' are often found across a site.	• Majority of sites have sterilant impacts below surface and into shallow groundwater. • Vertical and horizontal sterilant delineation is challenging and only achieved approximately 50% of the time. • Inactive and dormant sites may not be regularly monitored. • Surface soil can meet guidelines but sterilants at the same sites can be found deeper in the profile

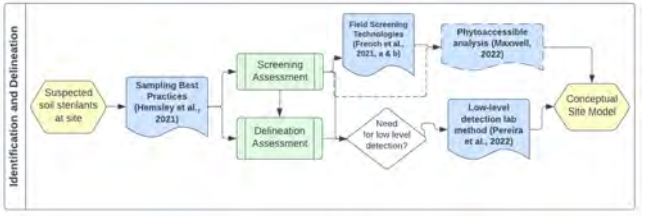
High Priority Risk Management and/or Remediation Challenges
Sterilants within surface soil (≤ 0.5 m bgs)
Sterilants at depths > 0.5 mbgs in unsaturated soil
Soil treatment requirements where sterilant destruction is required, and immobilization is not considered an acceptable option
Saturated fine-grained till soils and groundwater impacted by sterilants
Groundwater impacted by sterilants

IDENTIFICATION AND DELINEATION

SSP Soil Sterilants Program

PROBLEM

- Sterilants are widespread and difficult to detect due to mobility
- Analytical methods have variable detection limits, sometimes higher than guideline levels and only represent total concentrations



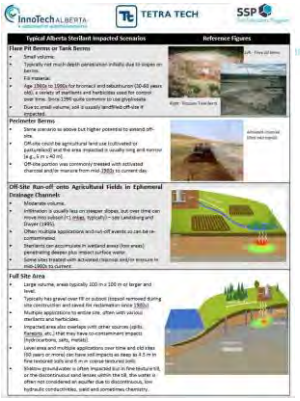
LEARNINGS AND SOLUTIONS

Site Characterization Steps

Identify Potential for Sterilant Use
- Phase 1 ESA: historical site activities, topography and potential receptors, vegetation and surface assessment (see p.2 for more info).

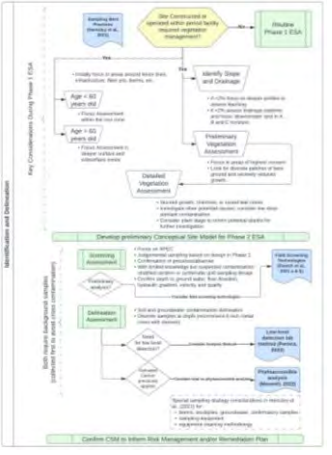
Preliminary Phase 2 ESA
- Soil characterization and sampling by stratigraphic unit (Fig. 1) via solid stem auger unless otherwise specified.
- Collect samples in jars with Teflon™-lined lids.
- Sterilant screen analysis in case various types used.

Sterilant Delineation/Confirmatory Sampling
- Low contaminant (ppb or ppt range) sampling techniques (e.g. core sampling; scrape samples prior to placing in jars; isolate suspected high concentration from low concentration samples).
- Special care must be taken to prevent cross-contamination.
- Follow QA/QC protocols (see p.3).
- Increase sampling frequency for delineation (vertical and horizontal) and confirmatory sampling.
- Equipment decontamination via Triple Rinse Method recommended (see p.3)
- Analyze individual relevant sterilants.
- Install groundwater monitoring wells where potential for impacts and delineation in groundwater.



LEARNINGS AND SOLUTIONS

- Application of the sampling methods BMPs is essential for preventing cross-contamination to detect low concentrations
  - **WORTH THE INVESTMENT**
- Field screening technologies do not currently have the sensitivity required to be useful to detect presence/absence
  - **FOCUS ON HOW AND WHAT TO SAMPLE TO MANAGE DELINATION COSTS**
- Lower detection limits and greater accuracy are possible analytically – need to assess when and why
  - **USEFUL FOR CONFIDENCE IN SSRA**
- Total (non-soluble) and phyto-accessible (soluble) concentrations are not equivalent
  - **USEFUL FOR ASSESSING RISK THROUGH SSRA**

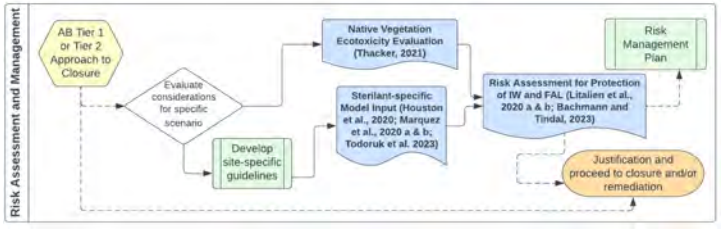


RISK ASSESSMENT AND MANAGEMENT

SSP Soil Sterilants Program

PROBLEM

- IW and FAL < DSC guidelines and often below detection limits
- Models do not include a degradation half-life
- Uncertainty in the input parameters to assess for SSRA
- Toxicity data for Alberta native species incomplete or missing



LEARNINGS AND SOLUTIONS

SSP Soil Sterilants Program

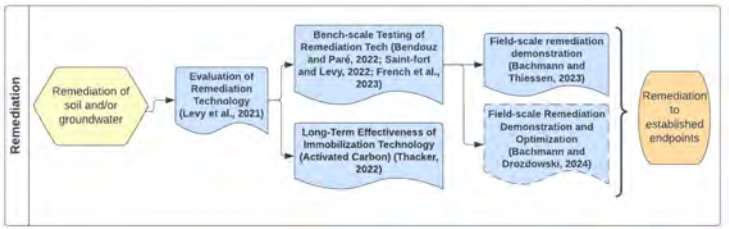
- Evaluation of FAL and IW pathway elimination is the first step in any risk analysis
- Site specific data collection is essential for use of the Alberta Risk Framework
  - **FOCUS ON GROUNDWATER MONITORING WELLS AT THE "POINT OF CONTACT" AND Kd**

REMEDIATION

SSP Soil Sterilants Program

PROBLEM

- Uncertainty in longevity and acceptability of Immobilization technologies
- Lack of demonstrated remediation success at operational scale



SSP Soil Sterilants Program

DISCUSSION?

SSP Soil Sterilants Program

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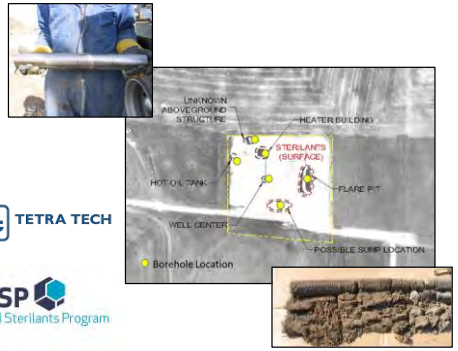
LEARNINGS AND SOLUTIONS

SSP Soil Sterilants Program

- Immobilization technologies were definitively proven with and without weathering to reduce phyto-accessible Br and Tb concentrations
- Essential to complete SOD validation prior to selecting an oxidation remediation technology
- Bench-scale testing demonstrated the benefit of BOS200+ with and without AC and surfactant
- Operational considerations influence practical application

APPENDIX B3: SAMPLING BEST MANAGEMENT PRACTICES



TETRA TECH

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PROJECT #2 - STERILANT SAMPLING BEST MANAGEMENT PRACTICES

KATHRYN BESSIE (RETIRED)
TYREL HEMSLEY, M.SC., P.AG, (EPA)
AZIZ SHAIKH, M.SC., P.ENG (TETRA TECH CANADA INC.)

SSP Soil Sterilants Program

PROJECT OBJECTIVE

- Develop *Sterilant Sampling Best Management Practices* (BMP) to provide specific sampling guidance for low level concentrations of bromacil and tebuthiuron (sterilants) in soil and groundwater in Alberta.

BMP REPORT ACHIEVEMENTS

SSP Soil Sterilants Program

- Documents the historical use of sterilants in Alberta and provides real case scenarios showing fate and exposure related to sterilant application history, the age of the site and site conditions. The history also identifies the high horizontal and vertical variability of sterilant concentrations in soils, mobility risk to groundwater, co-contaminant issues, and historical use of activated charcoal for topsoil treatment (remediation). END USER COMES UP TO SPEED QUICKLY AND UNDERSTANDS LIMITATIONS OF PRE-2000 ASSESSMENTS.
- Consolidates sampling methodology appropriate for sterilants from practical experience, AEP 2016, CCME 2016 and also EPA 2020 sampling methods for low level ("trace") concentrations less than 0.2 ppm (200 ppb). BMP CONSOLIDATES AND EDUCATES BUT DOESN'T RECREATE THE WHEEL
- Outlines sampling methods that vary depending upon the stage of assessment: preliminary, delineation and confirmatory sampling. LEADS TO COST EFFICIENCY AND ALLOWS USE OF COMMON ALBERTA SAMPLING PRACTICES FOR PRELIMINARY STAGE

EXAMPLE ALBERTA SCENARIO

SSP Soil Sterilants Program

Perimeter Berms

- Higher potential to extend off-site
- Off-site could be agricultural land use (cultivated or pasture land) and the area impacted is usually long and narrow (e.g. 5 m x 40 m)
- Off-site portion was commonly treated with activated charcoal and/or manure from mid 1980s to current day

SCENARIOS ALLOW MANAGERS TO GROUP SITES THAT CAN THEN BE MANAGED APPROPRIATELY BASED ON RISK AND TYPE OF RECEPTORS IMPACTED

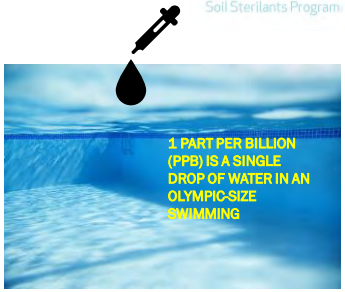
BMP REPORT ACHIEVEMENTS

- Preliminary assessments include practical, cost-effect sampling methods for shallow (<1.5 m) soils using direct sampling from walls of shovel holes or testpit.
- A vegetation assessment is an important tool for assessment since it can be potentially used for delineation or for receptor impact assessments. Sterilant-impacted soils tend to have a lack of vegetation, rust coloured or sparse vegetation but suspect areas must also be tested to ensure the cause isn't due to poor growth medium, salts or other contaminants.
- Delineation and confirmatory sampling methods recommended for subsoil delineation include standard methods and tools that are not always be used in Alberta but that are very important at trace concentrations for preventing potential cross-contamination, such as: use of soil sampling tools with smaller lengths of soil smearing such as the California split barrel sampler with liners, EPA triple rinse of sampling equipment between sample depths, and QA/QC samples (equipment, field and trip blanks and duplicate samples). For groundwater, piezometers with smaller screen lengths and low-flow purging and sampling methods are recommended.
- FLEXABILITY OF EQUIPMENT WITH GOAL OF MINIMIZING CROSS-CONTAMINATION

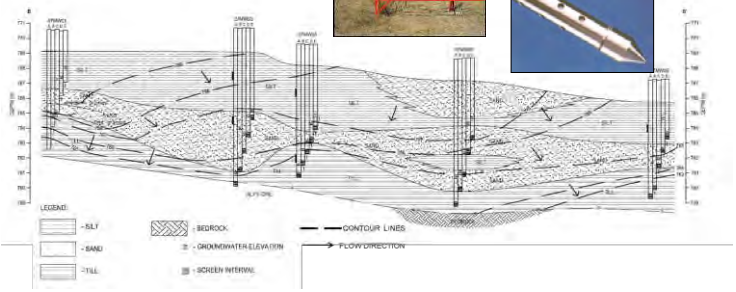
POTENTIAL FOR CROSS-CONTAMINATION

- High Potential for Cross Contamination for "trace" concentrations (ppm, ppb, ppt)
- Low Level Sampling (≤0.2 mg/kg; USEPA 2020)
- Need for Equipment Blanks

EXAMPLES: Groundwater – detecting glove components; Soil – collecting lab sample from interior of an undisturbed core or directly from a excavation face



GROUNDWATER SAMPLING



BMP FACTSHEET

- A practical tool that is simple to use (3 pages) and easy to understand by end users for planning sampling strategies.
  - Page 1 – challenges, site and equipment considerations, stage of assessment
  - Page 2 – Typical Alberta scenarios of sterilant impacts
  - Page 3 – Recommended sampling procedures for "trace" concentrations

BMP FACTSHEET

SYNERGIES WITH OTHER PROJECTS

- Since sterilants cannot be seen and do not have an odour in soils or groundwater, more samples and analysis are needed. The additional data is useful for a statistical sampling and data analysis approach that is generally required anyways for risk assessment (Project #8) and/or closure sampling.
- Field screening, which can be very useful in reducing analytical costs during delineation and remediation, is not currently available for sterilants at the guideline levels (Project #3)
- Site history must document if activated charcoal was used for treatment. If long-term effectiveness of activated charcoal as a remedial treatment could be confirmed (Project #10), then bioaccessability analysis (Project #4) could be added to site assessments and used to possibly eliminate some projects from requiring further remediation or show that risks to vegetation and from leaching are managed.
- Vegetation assessments are recommended for sites with shallow impacts and are useful as field data to collaborate with laboratory toxicity tests, especially for native prairie (Project #9).

SYNERGIES WITH OTHER PROJECTS

- The depths, concentrations and soil/groundwater separation distance of sterilants were further categorized in a data review from over 40 sites during Project #6 (Houston et.al. 2020). All of the sites had sterilants detected below 1 mbgs with a maximum depth range of 6 m for bromacil and 4.5 m for tebuthiuron and about half the sites had groundwater impacts.
- One of the challenges with sterilant assessment is that the Alberta Tier 1 Guidelines have groundwater guidelines as Below the Detection Limit (BDL) of the current laboratory analytical method. Project #3, lab method, uses specialized equipment that allows a lower detectable limit that when used with the "trace" sampling methods will allow better assessment and delineation.

HOW BMP MIGHT AFFECT SITE MANAGEMENT

- For sites that have had activated charcoal treatment, resampling the layer treated and analysis for both total and bioaccessible bromacil (Project #4) may allow topsoil conservation and reuse if it is suitable. Less risk of leaching and impact to underlying layers so less remediation may be required at end of day.
- For preliminary assessments, simple ways of collecting samples directly from sidewalls of shovel or testpits with nitrile gloves after cleaning smears away prevent equipment cross-contamination.
- For delineation and confirmatory sampling, the methods for trace concentrations may be more expensive but should be offset by reducing volume and area estimate errors from cross-contamination. Assessments are generally less expensive than remediation (except for small volume sites). Cost savings are expected by having more sites able to take a risk assessments approach instead of remediation.

RECOMMENDATIONS AND/OR DATA GAPS

- These sampling methods and equipment are currently available, so it comes down to education and requiring them to be used where appropriate.
- Site data reviewers should use the BMP to understand the lack of information likely available for historical sites and "scenario".
- Site managers need to make sure the consultants are using methods suitable for "trace" concentrations and are documenting quality assurance that cross-contamination is not occurring.
- When and if new technology becomes available for field screening at the concentrations needed and that are practical to use in the field, it would potentially cut costs for delineation and confirmatory assessments.

QUESTIONS?

APPENDIX B4: LABORATORY METHOD INVESTIGATION FOR DETECTION OF BROMACIL AND TEBUTHIURON IN WATER AND SOIL

SSP Soil Sterilants Program

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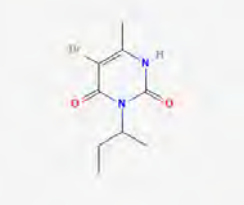
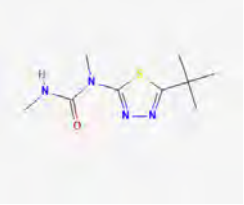
PROJECT 3 - LABORATORY METHOD INVESTIGATION FOR DETECTION OF BROMACIL AND TEBUTHIURON IN WATER AND SOIL

1. PROJECT GOAL AND OBJECTIVE(S)

SSP Soil Sterilants Program

Bromacil	Tebuthiuron
$C_9H_{13}BrN_2O_2$	$C_9H_{16}N_4OS$
CAS #: 314-40-9	CAS #: 34014-18-1
A substituted uracil herbicide. Non-selective weed and bush control on non-cropland.	A substituted urea herbicide. Non-selective broad spectrum to control weeds, woody and herbaceous plants and sugar cane.





ENVIRONMENTAL QUALITY GUIDELINE

SSP Soil Sterilants Program

WATER	Drinking Water	Irrigation Water	Livestock Water	Aquatic Life
Bromacil (µg/L)	950	0.2	1,100	5
Tebuthiuron (µg/L)	660	0.43	130	1.6

SOIL	Fine
Bromacil (µg/kg)	9
Tebuthiuron (µg/kg)	46

Ref 1: Environmental Quality Guidelines for Alberta Surface Waters [2018]
Ref 2: Alberta Tier 1 Soil and Groundwater Remediation Guidelines [2024]

ANALYTICAL PAIN POINTS

SSP Soil Sterilants Program

- Existing methods are time consuming; manual extraction
- Existing MDLs were too high for monitoring at or near the Tier 1 guidelines

	Soil (µg/kg)	Lowest Tier 1	Water (µg/L)	Lowest Tier 1
Bromacil	5	9	0.1	0.2
Tebuthiuron	5	46	0.1	0.43

PROJECT GOAL AND OBJECTIVE(S)

- a) Develop new sample prep and extraction method:
  - **Use solid phase extraction (SPE) for water sample**
  - **Use Accelerated solvent extraction (ASE) for soil and sediment sample**
- b) Develop a new instrument analysis method with Liquid Chromatography coupled to tandem mass spectrometry (LC-MS/MS) and/or high-resolution mass spectrometry (HRMS)
- c) Target method with Method detection limit (MDL):

	Soil (µg/kg)	Water (µg/L)
Bromacil	0.1	0.001
Tebuthiuron	0.1	0.001

SOLID PHASE EXTRACTION (SPE) METHOD FOR ANALYSIS ON WATER SAMPLES

Autotrace 280

Solid Phase Extraction

1 L of Sample

↓

Elution 5 mL methanol and 5 mL dichloromethane

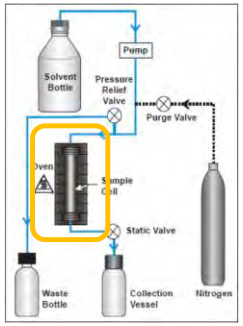
↓

Concentrate to 100 µL

↓

LC-MS

ACCELERATED SOIL EXTRACTION (ASE METHOD FOR SOIL SAMPLES



5 g of soil

↓

Extraction at 110°C
Static time 10 min
Purge time 5 min
Hexane/acetone (80/20, v/v)

↓

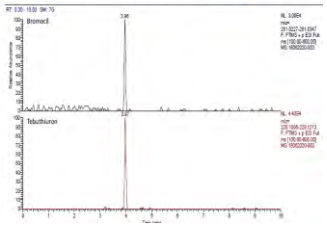
Concentrate to 100 µL

↓

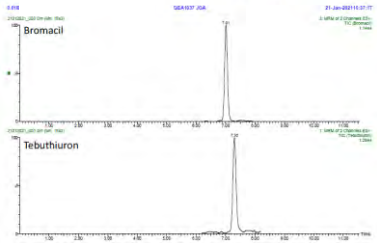
LC-MS

SELECTIVITY: LC-CHROMATOGRAMS AT LOQ CONCENTRATION

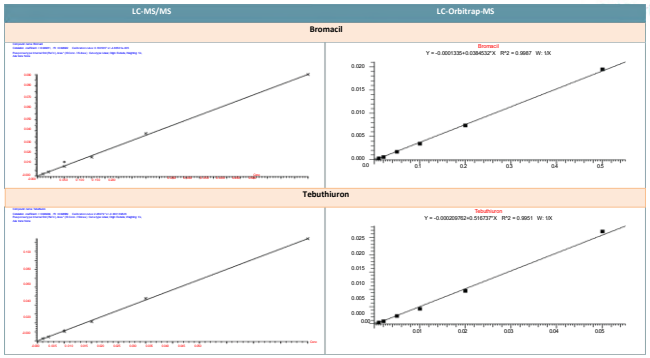
LC-Orbitrap/MS



LC-MS/MS



CALIBRATION:



ACCURACY AND PRECISION

	Bromacil	Tebuthiuron
Soil		
Accuracy (Low)	92%	114%
Accuracy (High)	113%	121%
Precision (Low)	1.9%	3.2%
Precision (High)	10%	11.3%
Water		
Accuracy (Low)	102%	103%
Accuracy (High)	115%	122%
Precision (Low)	1.5%	5.6%
Precision (High)	5.2%	17.4%

METHOD DETECTION LIMIT (MDL)

	Soil (µg/kg or ppb)		Water (µg/L or ppb)	
	LC-orbitrap/MS	LC-MS/MS	LC-orbitrap/MS	LC-MS/MS
Bromacil	0.034	0.013	0.000063	0.00011
Tebuthiuron	0.006	0.003	0.000036	0.000045

Target	Soil (µg/kg)	Tier 1 Soil	Comm. MDL	Water (µg/L)	Tier 1 Water	Comm. MDL
Bromacil	0.1	5	~5	0.001	0.2	~0.1
Tebuthiuron	0.1	46	~5	0.001	0.43	~0.1

Ref: USEPA document *Definition and procedure for the determination of Method Detection Limits* published in December 2016.

PERFORMANCE EVALUATION

Commercial Extraction	MeOH (Soil) Liq.-Liq. DCM (Water)		**InnoTech Extraction**	ASE (Soil) SPE (Water)
	$ - $$			$$ - $$$
	▸			▸▸
Commercial Dectection	HPLC-UV or MS GC-MS		**InnoTech Detection**	3Q-LC-MS/MS LC-Orbitrap-MS

PRAGMATIC EVALUATION AND CONCLUSIONS

	Scenario 1: Trending field samples high above Tier 1 limits	*Scenario 2*: Trending field samples near Tier 1 limits (within same OoM)	*Scenario 3*: Trending field samples below Tier 1 limits (1+ OoM less)
Analytical Need	Method with MDL near Tier 1 limit (Same Order of Magnitude [OoM])	Method with MDL ~1 OoM less than Tier 1 limit More refined precision and accuracy statements	Method with MDL as low as possible (maximum OoM less than Tier 1)
Method Available	Most commercial services	✗	InnoTech
Method Possible	✓	✓	✓

LOOKING FORWARD

- Identify instrumentation appropriate for MDLs only 1-OoM less than Tier 1 guidelines
  - OR
- Optimization or revalidation of existing commercial methods using ASE or SPE sample prep
- (Assess market viability of such a method; who is best suited to provide the service)
- Interlaboratory study (ILS) and Proficiency Testing (PT) needed

Thank you

SSP Soil Sterilants Program

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APPENDIX B5: DEVELOPMENT OF AN EXTRACTION METHOD FOR ESTIMATING PHYTOACCESSIBILITY OF BROMACIL AND TEBUTHIURON

SSP Soil Sterilants Program

Mitacs

InnoTech ALBERTA

UNIVERSITY OF ALBERTA

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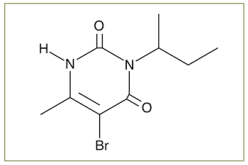
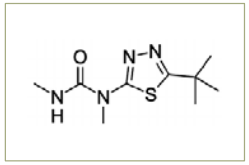
PROJECT 4 – DEVELOPMENT OF AN EXTRACTION METHOD FOR ESTIMATING PHYTOACCESSIBILITY OF BROMACIL & TEBUTHIURON

JACKIE MAXWELL, M.SC., P.AG., SLR CONSULTING (CANADA) LTD.

SOIL STERILANTS BROMACIL & TEBUTHIURON





Bromacil	Tebuthiuron
• Solubility in water 815 mg/L • Solubility in methanol 14,000 mg/L • Linear K_{oc} 32 mg/L	• Solubility in water 2,500 mg/L • Solubility in methanol 170,000 mg/L • Linear K_{oc} 80 mg/L

DROZDOWSKI, B., POWTER, C., & LIEW, S. (2018). MANAGEMENT OF STERILANT IMPACTED LANDS: LITERATURE SYNTHESIS; PESTICIDE PROPERTIES DATABASE. (2021). *TEBUTHIURON (REF: EL 103)*; PESTICIDE PROPERTIES DATABASE. (2021). *BROMACIL (REF: DPX N3976)*

RESEARCH QUESTION 01

SSP Soil Sterilants Program

How can the soluble / phytoaccessible portion of bromacil and tebuthiuron be estimated?

TOTAL, BIOAVAILABLE, BIO/PHYTO-ACCESSIBLE CONCENTRATIONS OF SOIL STERILANTS

	Total	Bioavailable	Bioaccessible	Phytoaccessible
Definition	ALL possible sterilant, adsorbed and solubilized	Solubilized sterilant in contact with cell membrane	Bioavailable, plus that which may become available	Desorbed and solubilized at one point in time
Method	99% MeOH, shake, concentrate, filter, HPLC/MSD	Individual measurements of processes leading to cell membrane contact	Individual measurements of processes	Wait for it!

METHODS TO ESTIMATE PHYTOACCESSIBILITY

SSP Soil Sterilants Program

Nutrients

- 'Classical' extractants specific to macro-or-micronutrient(s)
- These do not destroy soil structure or change pH
- e.g., 0.073 sodium acetate, 0.01 M calcium chloride

Application Rates

- Rates tested by bioassays
- Different soils tested
- Extract spiked soil with 0.01 N or 0.01 M calcium chloride
- Soil or extract concentration measured

Contaminants

- Adsorption/desorption studies using different ionic strengths of calcium chloride
- Bioassay experiments and measure concentration in tissues

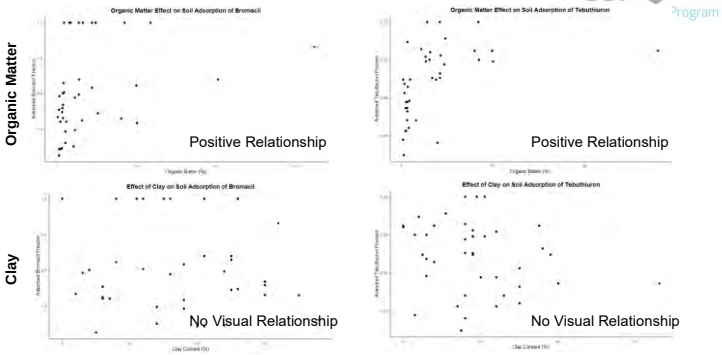
RESEARCH QUESTION 02

SSP Soil Sterilants Program

Do higher percentages of clay and organic matter significantly increase adsorption of bromacil or tebuthiuron?

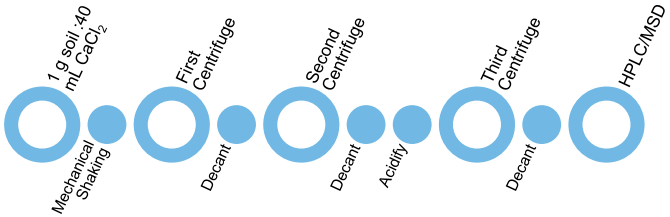
EXPLORATORY DATA ANALYSIS

SSP Program



Q01 METHOD:

SSP Soil Sterilants Program



GARRETT, R. G., HALL, G. E. M., VAIVE, J. E., & PELCHAT, P. (2009). A WATER-LEACH PROCEDURE FOR ESTIMATING BIOACCESSIBILITY OF ELEMENTS IN SOILS FROM TRANSECTS ACROSS THE UNITED STATES AND CANADA. APPLIED GEOCHEMISTRY, 24, 1438–1453.; HOUBA, V. J. G., TEMMINGHOFF, E. J. M., GAIKHORST, G. A., & VAN VARK, W. (2000). SOIL ANALYSIS PROCEDURES USING 0.01 M CALCIUM CHLORIDE AS EXTRACTION REAGENT. COMMUNICATIONS IN SOIL SCIENCE AND PLANT ANALYSIS, 31(9–10), 1299–1396.; ALVA, A. K., & SINGH, M. (1991). SORPTION-DESORPTION OF HERBICIDES IN SOIL AS INFLUENCED BY ELECTROLYTE CATIONS AND IONIC STRENGTH. JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH, 26(2), 147–163.; MCKENZIE, R. H. (2016). DETERMINING PLANT AVAILABLE PHOSPHORUS. TOP CROP MANAGER WEST, 40, 41, 59...ETC!

Q02 METHOD:

$$Adsorbed\ Fraction = \frac{Total - Extract}{Total}$$

where:

Total = total sterilant concentration (mg/kg), estimated by 99 percent methanol extraction, or the spiked amount

Extract = sterilant extracted by 0.01 M calcium chloride (mg/kg)

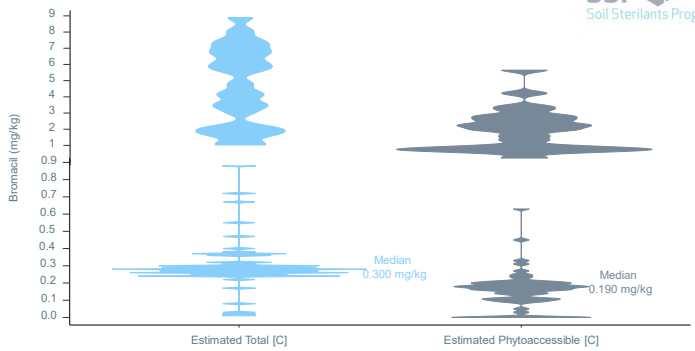
Q02 METHOD: SELECTED CATEGORIES FOR ORGANIC MATTER & CLAY

A 2x2 ANOVA tested 1) if higher %OM increases adsorption, 2) if higher %clay increased adsorption, and 3) if there is an interactive effect b/w %OM & %clay

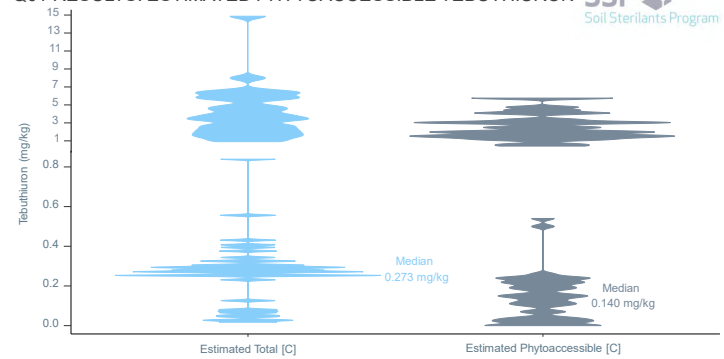
Bromacil	High Clay Content (18-38%)	Low Clay Content (0-16%)
High Organic Matter (3.24-64.6%)	10	10
Low Organic Matter (0.00-2.92%)	10	10
Tebuthiuron	**High Clay Content (18-66%)**	**Low Clay Content (0-16%)**
High Organic Matter (5.29-66%)	10	10
Low Organic Matter (0.28-4.34%)	10	10

RENR 581: Introduction to Exploratory Data Analysis, and RENR 582: Elementary Statistics in the Applied Sciences

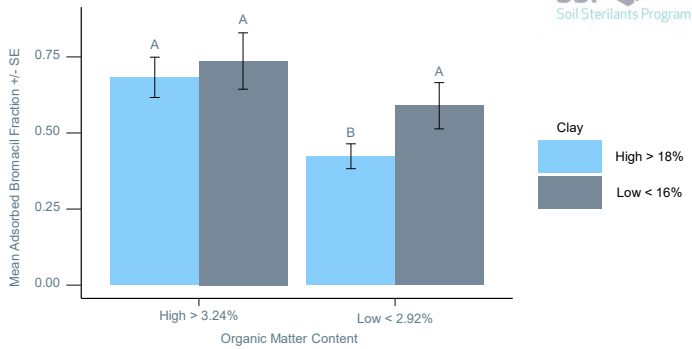
Q01 RESULTS: ESTIMATED PHYTOACCESSIBLE BROMACIL



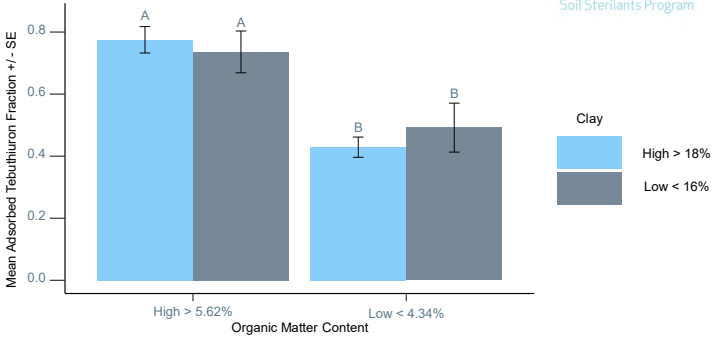
Q01 RESULTS: ESTIMATED PHYTOACCESSIBLE TEBUTHIURON



Q02 RESULTS: OM & CLAY EFFECT ON BROMACIL ADSORPTION

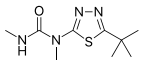


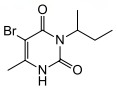
Q02 RESULTS: OM & CLAY EFFECT ON TEBUTHIURON ADSORPTION



QUESTIONS?

APPENDIX B6: FIELD SCREENING TECHNOLOGIES FOR BROMACIL AND TEBUTHIURON





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PROJECT 5 - FIELD SCREENING TECHNOLOGIES FOR BROMACIL AND TEBUTHIURON

KEVIN FRENCH,
VEI CONTRACTING INC.

OVERVIEW

- Project Team
- Project Goal and Objective
- Project Overview
  - Literature Review & Preliminary Testing of Existing Technologies
- Methods & Results
  - Instruments & Biosensors Assessed
  - Compounds/Media Tested
  - Specific Instrument/Technology Results
- Project Status & Next Steps
- Data Gaps, Challenges & Learnings
- Relationships to Other Projects
- Questions

PROJECT TEAM

VEI CONTRACTING
Formerly Vertex Environmental Inc.

UNIVERSITY OF WATERLOO
Bionanotechnology & Interfaces Laboratory

Kevin French

Eric Cowan

Dr. Juewen Liu

PROJECT GOAL & OBJECTIVE

- Key knowledge gap identified relates to the current ability, or lack thereof, to identify and delineate bromacil and tebuthiuron impacts in soil and/or water in the field
- No field-ready technologies available to achieve the goal of on-site detection, identification, quantification and delineation
- Results in high costs and long timelines for site investigation and/or remedial excavation since sample collection and laboratory analysis must be relied upon
- Objective was:
  - ***"to develop detection/field screening or proxy laboratory analytical methods to minimize the costs associated with identification, quantification and delineation of bromacil and/or tebuthiuron in soil and/or water at impacted sites."***

PROJECT OVERVIEW

- Project designed to be completed in two Phases with Phase 1 being "proof-of-concept" and Phase 2 being "validation and optimization" of the technology or technologies
- Phase 1 (this phase) endeavors to identify a technology or technologies that:
  - Can accurately and consistently detect bromacil and/or tebuthiuron in soil and/or water
  - Is practical and safe to use in the field
  - Costs a fraction of the cost of current laboratory analytical methods
  - Can be completed on-site in under 4 hours
- Based on the results of the Phase 1 literature review and preliminary, proof-of-concept testing of existing technology, promising technology(ies) will be recommended for advancement to Phase 2 (next phase) of the Project
- Phase 2 (not included) was to attempt to validate the applicability of the technology(ies), identify potential matrix interference effects and likely lowest reliable detection limits, establish testing protocols

PROJECT OVERVIEW

- Literature Review of Existing Technologies
  - Research into instruments that are field-ready and intended (or adaptable) for use in detecting specific physical, chemical, optical or other properties of compounds
    - Potential to detect/measure some known physical, chemical, optical or other property of bromacil and tebuthiuron
  - Review of literature related to particular biosensor technologies that have shown promise in the detection of bromacil
- Preliminary Testing of Existing Technologies
  - Technologies/instruments that showed potential were carried forward for proof-of-concept testing
  - No further testing of biosensor technologies included in this phase of the Project

METHODS & RESULTS – TECHNOLOGIES

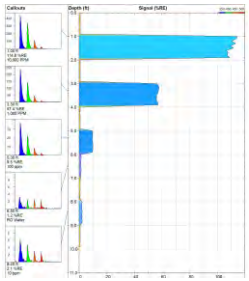
- Instruments assessed:
  - Ultraviolet laser induced fluorescence (UVOST® or OIP®)
  - Visible light laser induced fluorescence (TarGOST® or OIP-G®)
  - Near infrared reflectance spectroscopy (NIRS)
  - X-ray fluorescence (XRF)
  - Portable gas chromatography/photoionization detector (GC/PID)
  - Raman spectroscopy
  - Laser-induced breakdown spectroscopy (LIBS)
  - Gas Chromatography/Thermionic Ionization Detector (GC/TID)
- Biosensors assessed:
  - Single-stranded DNA molecular recognition element (ssDNA MRE)
  - Enzyme-linked immunosorbent assays (ELISA)

METHODS & RESULTS – COMPOUNDS/MEDIA

- Compounds/media used in proof-of-concept testing:
  - Bromacil – laboratory grade, 100% pure, solid
  - Alligare Bromacil 80 WG – commercial, 80% bromacil, solid
  - Hyvar® X-L – commercial, 20% bromacil, liquid
  - Spike® 80DF – commercial, 80% tebuthiuron, solid
  - Silica sand and/or distilled water spiked with the above compounds (completed)

METHODS & RESULTS – INTERPRETATION

- Readings/measurements/outputs from each of the instruments were examined and evaluated to assess (on a preliminary basis) whether:
  - The sterilant appears to have been detected in one or more of the samples
  - The pattern of detection appears to be unique
  - The response appears to vary in a predictable manner in relation to spike concentration

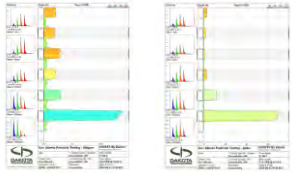


UVOST® response for varying concentrations of sand spiked with Alligare Bromacil 80 WG

METHODS & RESULTS – INSTRUMENT DETAILS

- Technology: **Ultraviolet laser induced fluorescence (UVOST® or OIP®)**
- Basis of Detection: Non-destructive, optical (UV), fluorescence response
- **Literature Review Findings: Potentially viable**
- Potential Applicability: Bromacil and tebuthiuron in soil and water

- **Preliminary Testing Results: Potentially viable for bromacil and tebuthiuron, but likely not practical**
  - Proportional response recorded with concentration for spiked water samples but detection limits very high
  - May be recording non-sterilant constituents in the compounds used to create spikes

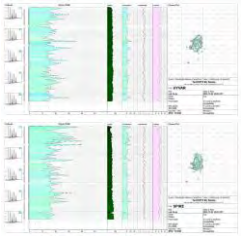


UVOST® response for varying concentrations of sand spiked with Alligare Bromacil 80 WG (L) and Spike® 80DF (R)

METHODS & RESULTS – INSTRUMENT DETAILS

- Technology: **Visible light laser induced fluorescence (TarGOST® or OIP-G®)**
- Basis of Detection: Non-destructive, optical (visible), fluorescence response
- **Literature Review Findings: Potentially viable**
- Potential Applicability: Bromacil and tebuthiuron in soil and water

- **Preliminary Testing Results: Not viable**
  - No variation in response to spiked soil samples with different concentrations of compounds

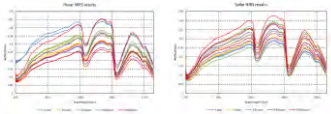


TarGOST® response for varying concentrations of sand spiked with Hyvar® X-L (T) and Spike® 80DF (B)

METHODS & RESULTS – INSTRUMENT DETAILS

- Technology: **Near infrared reflectance spectroscopy (NIRS)**
- Basis of Detection: Non-destructive, optical (IR), scatter and adsorption response
- **Literature Review Findings: Potentially viable**
- Potential Applicability: Bromacil and tebuthiuron in soil only

- **Preliminary Testing Results: Potentially viable for bromacil and tebuthiuron in soil only, but likely not practical**
  - No distinct response reported for any spiked samples tested
  - Requires hundreds of samples with known concentrations of sterilants to allow machine learning algorithms to identify distinct signatures
  - Likely 50 ppm minimum detection limits in soil without extraction

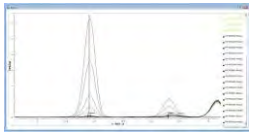


NIRS response for varying concentrations of sand spiked with Hyvar® X-L (T) and Spike® 80DF (B)

METHODS & RESULTS – INSTRUMENT DETAILS

- Technology: **X-ray fluorescence (XRF)**
- Basis of Detection: Non-destructive, optical (x-ray), fluorescence response
- **Literature Review Findings: Potentially viable**
- Potential Applicability: Bromacil and tebuthiuron in soil only

- **Preliminary Testing Results: Potentially viable for bromacil and tebuthiuron in soil only, but likely not practical**
  - Proportional response recorded with concentration for spiked soil samples by detecting single elements only (i.e., Br in bromacil and S in tebuthiuron)
  - Likely too high detection limits due to background / matrix interference from naturally-occurring sulphur



XRF response (Br) for varying concentrations of sand spiked with Alligare Bromacil 80 WG

METHODS & RESULTS – INSTRUMENT DETAILS

- Technology: **Portable gas chromatography/ photoionization detector (GC/PID)**
- Basis of Detection: Destructive, volatilization, separation, ionization detection
- **Literature Review Findings: Not viable**; bromacil and tebuthiuron only volatilize at temperatures too high (i.e., >120°C) for existing field instrumentation
- Potential Applicability: None

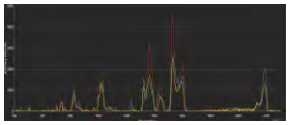
- **Preliminary Testing Results: Not tested based on results of literature review**

METHODS & RESULTS – INSTRUMENT DETAILS

- Technology: **Raman spectroscopy**
- Basis of Detection: Non-destructive (direct) and destructive (surface-enhanced), optical (visible/UV), scatter spectra
- **Literature Review Findings: Potentially viable**
- Potential Applicability: Bromacil and tebuthiuron in soil and water

- **Preliminary Testing Results: Potentially viable for bromacil and tebuthiuron in soil and water, but likely not practical**
  - Proportional response recorded with concentration for spiked water samples via identification of compounds (i.e., not only elements)
  - Solvent (i.e., methanol) extraction and concentration could lower detection limits, but likely not enough relative to standards

MISA Raman response for varying concentrations of water spiked with Hyvar® X-L

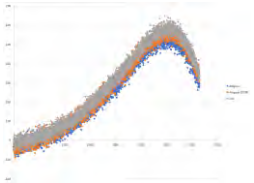


METHODS & RESULTS – INSTRUMENT DETAILS

- Technology: **Laser-induced breakdown spectroscopy (LIBS)**
- Basis of Detection: Destructive, plasmatization, spectra
- **Literature Review Findings: Potentially viable**
- Potential Applicability: Bromacil and tebuthiuron in soil only

- **Preliminary Testing Results: Not viable**
  - No variation in response to spiked samples with different concentrations of compounds
  - Not available with laser of adequate wavelength for sterilants

LIBS response for varying concentrations of sand spiked with Alligare Bromacil 80 WG

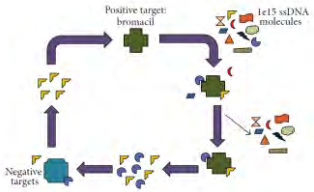


METHODS & RESULTS – INSTRUMENT DETAILS

- Technology: **Gas Chromatography/Thermionic Ionization Detector (GC/TID)**
- Basis of Detection: Destructive, volatilization, separation, ionization
- **Literature Review Findings: Potentially viable**
- Potential Applicability: Bromacil and tebuthiuron in soil and water
- **Preliminary Testing Results: Not tested**; currently not available as a commercial portable or field ready device

METHODS & RESULTS – BIOSENSOR DETAILS

- Technology: **Single-stranded DNA molecular recognition element (ssDNA MRE)**
- Basis of Detection: Biosensor (aptamer)
- **Literature Review Findings: Reported results for bromacil were not considered reliable**; however, the approach may work provided different aptamers can be identified
- Potential Applicability: Bromacil and tebuthiuron in soil and water
- **Preliminary Testing Results: Not tested**



METHODS & RESULTS – BIOSENSOR DETAILS

- Technology: **Enzyme-linked immunosorbent assays (ELISA)**
- Basis of Detection: Biosensor (antibody)
- **Literature Review Findings: Reported results for bromacil were considered reliable; however, the approach was not considered feasible** for on-site field applications (too complicated and sensitive). Recommendation to consider developing an Au nanoparticle-based immunochromatographic assay instead.
- Potential Applicability: Bromacil and tebuthiuron in soil and water
- **Preliminary Testing Results: Not tested**

METHODS & RESULTS – SUMMARY

- Instruments assessed:
  - Ultraviolet laser induced fluorescence (UVOST® or OIP®)
  - Visible light laser induced fluorescence (TarGOST® or OIP-G®)
  - Near infrared reflectance spectroscopy (NIRS)
  - X-ray fluorescence (XRF)
  - Portable gas chromatography/photoionization detector (GC/PID)
  - Raman spectroscopy
  - Laser-induced breakdown spectroscopy (LIBS)
  - Gas Chromatography/Thermionic Ionization Detector (GC/TID)
- Results:
  - **Potentially viable but likely not practical**
  - **Not viable**
  - **Potentially viable but likely not practical**
  - **Potentially viable but likely not practical**
  - **Not viable; not tested**
  - **Potentially viable but likely not practical**
  - **Not viable**
  - **Not tested; not available**
- Biosensors assessed:
  - Single-stranded DNA molecular recognition element (ssDNA MRE)
  - Enzyme-linked immunosorbent assays (ELISA)
- Results:
  - **Potentially viable; not tested**
  - **Potentially viable but likely not practical**

PROJECT STATUS & NEXT STEPS

- Literature Review of Existing Technologies:
  - Completed
- Preliminary Testing of Existing Technologies:
  - First round "proof-of-concept" instrument testing completed for spiked soil and water samples
  - No instrument testing completed on "real-world" samples
  - No testing completed on biosensor technologies
  - Completed
- Next Steps:
  - None
  - No recommendations for Phase 2 Testing (i.e., technology validation, matrix interference, extraction/concentration, detection limits, formal testing protocols, etc.)

DATA GAPS, CHALLENGES & LEARNINGS

- Ultraviolet laser induced fluorescence (UVOST® or OIP®)
- Near infrared reflectance spectroscopy (NIRS)
- X-ray fluorescence (XRF)
- Raman spectroscopy
  - All potentially applicable; however, unlikely to be able to achieve adequate detection limits required even with extraction (and possibly concentration) for better sensitivity
- Single-stranded DNA molecular recognition element (ssDNA MRE)
  - Potentially applicable; different aptamers would need to be identified and tested
- Enzyme-linked immunosorbent assays (ELISA)
  - Potentially applicable; however, not considered a feasible approach for field testing
  - An Au nanoparticle-based immunochromatographic assay is a recommended alternative for field use

RELATIONSHIPS TO OTHER PROJECTS

- Apply same sampling methodologies (Project #2) to collect and pre-screen environmental samples for selection for laboratory analysis and ideally allow a correlation of field screening results to laboratory analytical results (potential time and cost savings)
- Insight from the laboratory methodology optimization (Project #3) and bioavailability (Project #4) could inform environmental sample extraction and/or concentration in the field for improved detection limits and better pre-screening of sites
- If and when an appropriate and optimized field screening technology has been developed, apply the technology to not only identify and preliminarily characterize sterilant impacted sites, but also:
  - Assist in investigating the longevity of immobilized bromacil and/or tebuthiuron with Activated Carbon at existing treated sites (Project #10)
  - Assist in identifying and characterizing suitable sites (or plots within sites) to subject to proof-of-concept or full-scale demonstration of remedial technologies and monitoring the on-going effectiveness of the remedial technologies over time in conjunction with traditional laboratory analysis (Projects #11 and #12)

QUESTIONS?

APPENDIX B7: NATIVE SPECIES TOXICITY EVALUATION

SOIL STERILANTS PROGRAM (SSP) – ANNUAL SHARING EVENT

PROJECT #9 – NATIVE SPECIES ECOTOXICITY EVALUATION

STEFAN SCHREIBER ON BEHALF OF SARAH THACKER

INNOTECH ALBERTA

CHALLENGE

- Soil quality guidelines for sterilants in Alberta largely based on agronomic species
- Uncertainty regarding sensitivity of native species to soil sterilants

https://www.country-guide.ca/crops/what-you-should-know-before-marketing-durum-wheat/

GOALS OF EXPERIMENT

- Evaluate the toxicity of bromacil and tebuthiuron to Alberta native species
- Develop potential alternatives for direct soil contact guidelines for the province

https://blog.cwf-fcf.org/index.php/en/pfra-community-pastures/

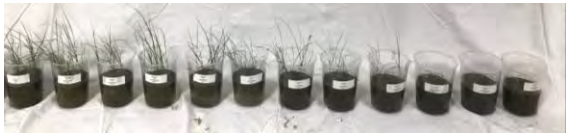
EXPERIMENTAL DESIGN

- Followed an Environment Canada (2007) method
- **6-week** greenhouse experiment (fine textured soil and locally adapted seeds)

Treatments/Parameters	Number	Description	
Test Soil	1	Solonetzic Brown Chernozem (loam)	
Soil Sterilants	2	Bromacil Tebuthiuron	
Soil Sterilants Concentrations (mg/kg)	12	Negative control 11 concentrations spiked with each sterilant	
Plant Species	5 for bromacil; 4 for tebuthiuron	Bromacil Blue grama Western wheatgrass Green needle grass Plains rough fescue Junegrass	Tebuthiuron Blue grama Green needle grass Northern wheatgrass Plains rough fescue
Replicates	Unbalanced	6 for negative control and artificial soil 4 for the lowest six test concentrations 3 for the highest five test concentrations	

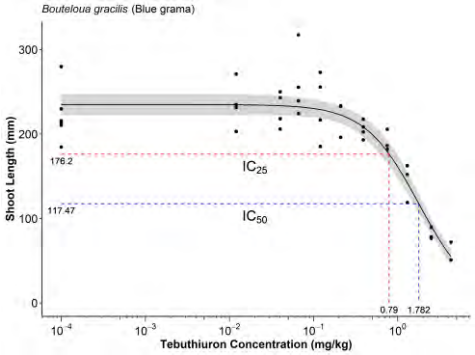
EXPERIMENTAL DESIGN

- Estimate Inhibition Concentrations for:
  - Emergence
  - Shoot length
  - Root length
  - Shoot weight
  - Root weight



RESULTS – INHIBITION CONCENTRATIONS

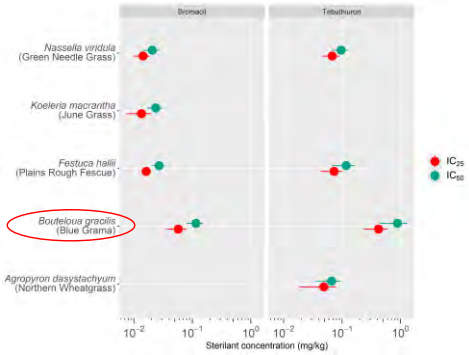
- Regressions for each species-sterilant endpoints (IC_{25}, IC_{50})
  - Emergence
  - Root length
  - Shoot length
  - Root weight
  - Shoot weight
- Determine inhibition concentrations (IC_p)



RESULTS – INHIBITION CONCENTRATIONS

- Bromacil tended to be more toxic than tebuthiuron
- Blue Grama the least sensitive of the tested native grasses

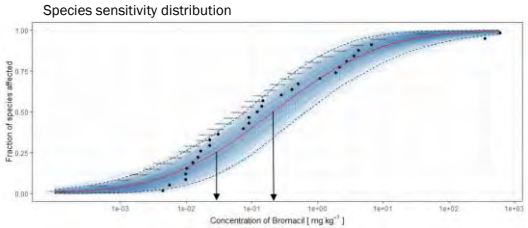
- IC_{25} values were then used to build species sensitivity distributions (*done by Millennium EMS Solutions Ltd.*)



RESULTS – SOIL QUALITY GUIDELINE DEVELOPMENT

Work conducted by Millennium EMS Solutions Ltd. using current and historical data

- Species sensitivity distributions (IC_{25}) completed for:
  - All plants + invertebrates used for SQG

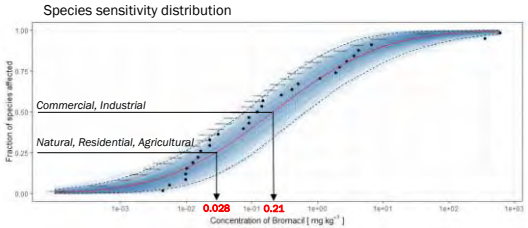


CCME 2006 protocol for the development of soil quality guidelines/eco-contact pathway guidelines

RESULTS – SOIL QUALITY GUIDELINE DEVELOPMENT

Work conducted by Millennium EMS Solutions Ltd. using current and historical data

- Species sensitivity distributions (IC_{25}) completed for:
  - All plants + invertebrates used for SQG



CCME 2006 protocol for the development of soil quality guidelines/eco-contact pathway guidelines

ALTERNATIVE SOIL QUALITY GUIDELINES

- Proposing alternative guidelines for the ecological direct soil contact pathway for fine textured soil
  - Species sensitivity distributions including new data on native species more sensitive to the effects of bromacil and tebuthiuron than species studied historically
  - Alternative guidelines more stringent than current Tier 1 Guidelines

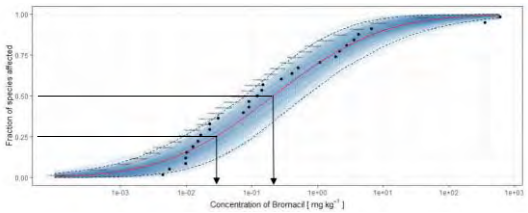
	Tier 1 Guideline	Natural/Residential/Agricultural (25th percentile of SSD)	Commercial/Industrial (50th percentile of SSD)
Bromacil	Current Tier 1 (mg/kg)	0.20	0.49
	Revised[1] (mg/kg)	0.028	0.21
Tebuthiuron	Current Tier 1 (mg/kg)	0.046	0.60
	Revised[1] (mg/kg)	0.018	0.15

Table adapted from Litalien and Tindal (2021)
[1] Based on an expanded dataset which includes more native plant species than the current Tier 1 guidelines.

RESULTS – SOIL QUALITY GUIDELINE DEVELOPMENT

Work conducted by Millennium EMS Solutions Ltd. using current and historical data

- Species sensitivity distributions (IC_{25}) completed for:
  - All plants + invertebrates ⇨ Residential land use
  - Native plants + invertebrates ⇨ Natural land use
  - Agronomic plants + invertebrates ⇨ Agricultural land use



CCME 2006 protocol for the development of soil quality guidelines/eco-contact pathway guidelines

ALTERNATIVE SOIL QUALITY GUIDELINES

- Proposing alternative guidelines for the ecological direct soil contact pathway for fine textured soil
  - With the additional number of species, it may even be possible to look at individual guidelines for natural (*native plants/invert.*), residential (*native plants/crop plants/invert.*) and agriculture lands (*crop plants/invert.*)

	Tier 1 Guideline	Natural (25th percentile of SSD)	Residential (25th percentile of SSD)	Agricultural (25th percentile of SSD)	Commercial/ Industrial (50th percentile of SSD)
Bromacil	Current Tier 1 (mg/kg)		0.20		0.49
	Revised (mg/kg)	0.014	0.028	0.37	0.21
Tebuthiuron	Current Tier 1 (mg/kg)		0.046		0.60
	Revised (mg/kg)	0.023	0.018	0.018*	0.15

Table adapted from Litalien and Tindal (2021)

*insufficient number of datapoints are available for tebuthiuron based solely on crop plants and invertebrates (n=<10), therefore the SQG for the agricultural land use would need to be based on both native and agronomic species (i.e., *residential* land use)

CONCLUSIONS AND KEY LEARNINGS

- Native species appear to be more sensitive to the effects of bromacil and tebuthiuron than agronomic species and invertebrates
- Additional data collection allowed to look at a more granular level to provide potential separate guidelines for different land uses, but more data is needed (soils, species etc.)
- We need to be more cognitive of the species present on site when comparing to existing SQG because they are likely not protective of those species
- Important to identify when a practitioner should consider a more conservative guideline to be protective of species present on site

SSP
Soil Sterilants Program

QUESTIONS?

APPENDIX B8: RISK ASSESSMENT FOR PROTECTION OF IRRIGATION WATER AND FRESHWATER AQUATIC LIFE

SOIL STERILANTS PROGRAM (SSP) – 2024 ANNUAL SHARING EVENT

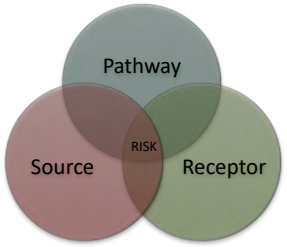
Risk Assessment for Management of Sterilant Impacted Sites

Cory Kartz and Miles Tindal
Millennium EMS Solutions Ltd

TIER 1 SOIL GUIDELINES - AGRICULTURAL LAND USE

	Bromacil		Tebuthiuron	
	Fine (mg/kg)	Coarse (mg/kg)	Fine (mg/kg)	Coarse (mg/kg)
Tier 1 Guideline	0.009	0.009	0.046	0.046

INTRODUCTION TO RISK ASSESSMENT



Key Concepts:

- Exposure Pathway
  - How Sources can reach Receptors
- Land Use
  - Relevant Exposure Pathways
  - Receptor Sensitivity

LAND USE

- Natural Area
- Agricultural
- Residential
- Commercial
- Industrial

EXPOSURE PATHWAYS

- Direct exposure pathways
  - Human direct contact pathway
  - Ecological direct contact pathway
- Indirect exposure pathways
  - Protection of freshwater aquatic life (FAL)
  - Protection of irrigation water (IW)
  - Protection of drinking water (DUA)
  - Protection of livestock water (LW)

TIER 1 SOIL GUIDELINES BY EXPOSURE PATHWAY - AGRICULTURAL LAND USE

	Bromacil		Tebuthiuron	
	Fine (mg/kg)	Coarse (mg/kg)	Fine (mg/kg)	Coarse (mg/kg)
Human Soil Contact	2,000	2,000	1,600	1,600
Drinking Water (DUA)	7	10	2.5	3.7
Livestock Water (LW)	2	2	0.12	0.11
Ecological Soil Contact	0.2	0.12	0.046	0.046
Freshwater Aquatic Life (FAL)	0.009	0.009	BDL	BDL
Irrigation Water (IW)	BDL	BDL	BDL	BDL

BDL = below detection limit – assessment by groundwater monitoring REQUIRED for Tier 1 soil guideline application

TIER 1 SOIL GUIDELINES BY EXPOSURE PATHWAY - AGRICULTURAL LAND USE

	Bromacil		Tebuthiuron	
	Fine (mg/kg)	Coarse (mg/kg)	Fine (mg/kg)	Coarse (mg/kg)
Human Soil Contact	2,000	2,000	1,600	1,600
Drinking Water (DUA)	7	10	2.5	3.7
Livestock Water (LW)	2	2	0.12	0.11
Ecological Soil Contact	0.2	0.12	0.046	0.046
Freshwater Aquatic Life (FAL)	0.009	0.009	BDL	BDL
Irrigation Water (IW)	BDL	BDL	BDL	BDL

BDL = below detection limit – assessment by groundwater monitoring REQUIRED for Tier 1 soil guideline application
Overall Tier 1 guidelines in red

TIER 1 SOIL GUIDELINES BY EXPOSURE PATHWAY - AGRICULTURAL LAND USE

	Bromacil		Tebuthiuron	
	Fine (mg/kg)	Coarse (mg/kg)	Fine (mg/kg)	Coarse (mg/kg)
Human Soil Contact	2,000	2,000	1,600	1,600
Drinking Water (DUA)	7	10	2.5	3.7
Livestock Water (LW)	2	2	0.12	0.11
Ecological Soil Contact	0.2	0.12	0.046	0.046
Freshwater Aquatic Life (FAL)	0.009	0.009	BDL	BDL
Irrigation Water (IW)	BDL	BDL	BDL	BDL

BDL = below detection limit – assessment by groundwater monitoring REQUIRED for Tier 1 soil guideline application

TIER 1 SOIL GUIDELINES BY EXPOSURE PATHWAY - AGRICULTURAL LAND USE

	Bromacil		Tebuthiuron	
	Fine (mg/kg)	Coarse (mg/kg)	Fine (mg/kg)	Coarse (mg/kg)
Human Soil Contact	2,000	2,000	1,600	1,600
Drinking Water (DUA)	7	10	2.5	3.7
Livestock Water (LW)	2	2	0.12	0.11
Ecological Soil Contact	0.2	0.12	0.046	0.046
Freshwater Aquatic Life (FAL)	0.009	0.009	BDL	BDL
Irrigation Water (IW)	BDL	BDL	BDL	BDL

BDL = below detection limit – assessment by groundwater monitoring REQUIRED for Tier 1 soil guideline application

TIER 1 SOIL GUIDELINES BY EXPOSURE PATHWAY - AGRICULTURAL LAND USE

	Bromacil		Tebuthiuron	
	Fine (mg/kg)	Coarse (mg/kg)	Fine (mg/kg)	Coarse (mg/kg)
Human Soil Contact	2,000	2,000	1,600	1,600
Drinking Water (DUA)	7	10	2.5	3.7
Livestock Water (LW)	2	2	0.12	0.11
Ecological Soil Contact	0.2	0.12	0.046	0.046
Freshwater Aquatic Life (FAL)	0.009	0.009	BDL	BDL
Irrigation Water (IW)	BDL	BDL	BDL	BDL

BDL = below detection limit – assessment by groundwater monitoring REQUIRED for Tier 1 soil guideline application

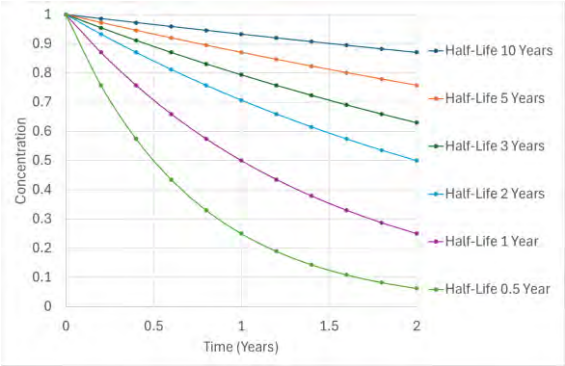
CALCULATING GUIDELINES FOR INDIRECT EXPOSURE PATHWAYS

- Models (equations)
  - Standard Tier 1 models
  - Other models
- Parameters
  - Site (soil, groundwater, geometry) parameters
    - Tier 1 default value for fine and coarse soils
  - Chemical-specific parameters
    - Degradation half-life ($t_{1/2}$)
    - Sorption coefficient (K_{oc} or K_d)

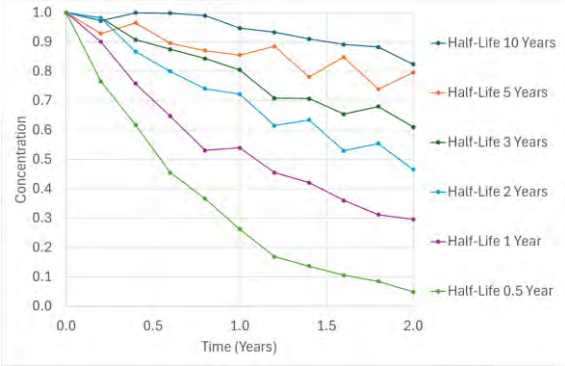
CHEMICAL-SPECIFIC PARAMETER VALUES - EXISTING TIER 1 VALUES

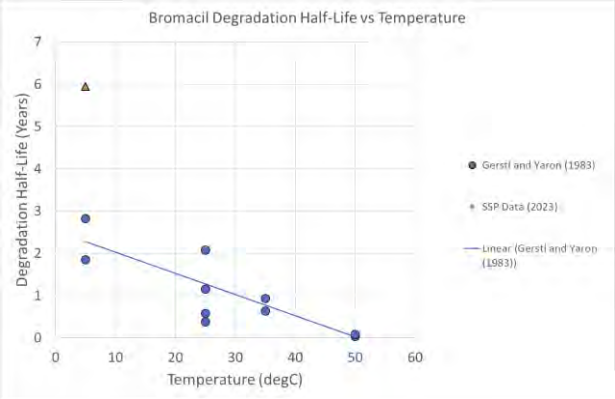
Parameter	Unit	Bromacil	Tebuthiuron
Degradation half-life ($t_{1/2}$)	(years)	(no value)	(no value)
Sorption coefficient (K_{oc})	(ml/g)	66.6	23

MEASURING A SLOW DEGRADATION RATE



MEASURING A SLOW DEGRADATION RATE





CHEMICAL-SPECIFIC PARAMETER VALUES - EXISTING TIER 1 VALUES

Parameter	Unit	Bromacil	Tebuthiuron
Degradation half-life ($t_{1/2}$)	(years)	(no value)	(no value)
Sorption coefficient (K_{oc})	(ml/g)	66.6	23

PRACTICAL APPLICATION

	Bromacil		Tebuthiuron	
	Fine (mg/kg)	Coarse (mg/kg)	Fine (mg/kg)	Coarse (mg/kg)
Human Soil Contact	2,000	2,000	1,600	1,600
Drinking Water (DUA)	7	10	2.5	3.7
Livestock Water (LW)	2	2	0.12	0.11
Ecological Soil Contact	0.2	0.12	0.046	0.046
Freshwater Aquatic Life (FAL)	0.009	0.009	BDL	BDL
Irrigation Water (IW)	BDL	BDL	BDL	BDL

BDL = below detection limit – assessment by groundwater monitoring REQUIRED for Tier 1 soil guideline application
Overall Tier 1 guidelines in red

GROUNDWATER MONITORING TO OVERRIDE SOIL GUIDELINES

- Groundwater monitoring strongly recommended:
  - Both bromacil and tebuthiuron
  - All land uses
- Groundwater monitoring should access reasonable worst-case location
- Groundwater below surface water guideline for aquatic life or irrigation:
  - overrides corresponding soil guideline
- Note that groundwater monitoring is REQUIRED for Tier 1 soil guideline application:
  - For any pathways noted as BDL in soil guideline tables
- Groundwater above surface water guidelines > Tier 2 approach recommended

FRESHWATER AQUATIC LIFE (FAL) – TIER 2 PATHWAY APPLICABILITY

- Formal Tier 2 pathway exclusion not available
- FAL pathway applicable in all land uses
- Other site-specific approaches to assess pathway relevance:
  - Transit time to water body
  - Tier 2 guideline recalculation

TIER 2 FAL APPLICABILITY - DISTANCE TRAVELLED IN 500 YEARS

	Bromacil		Tebuthiuron	
	Fine (m)	Coarse (m)	Fine (m)	Coarse (m)
Distance Travelled in 500 Years	500	5,000	700	8,000

These cut-off apply equally in all land uses

TIER 2 FAL APPLICABILITY - DISTANCE FOR FAL PATHWAY NOT TO BE LIMITING

	Distance to Surface Water			
Source Size (Width)	Bromacil		Tebuthiuron	
(m)	Fine (m)	Coarse (m)	Fine (m)	Coarse (m)
10 m	410	360	590	950
20 m	(530)	720	(770)	1,900
30 m	(600)	1,100	(870)	2,800
50 m	(680)	1,800	(1,000)	4,400
100 m	(790)	3,100	(1,200)	6,500

These calculations are an example only based on:
- apply to natural area or agricultural land use
- Current Tier 1 ecological direct contact , different values would be calculated for industrial land use

Distances in parentheses are greater than the 500-year cutoffs in the previous slide

TIER 2 IRRIGATION WATER PATHWAY APPLICABILITY – LAND USE CONSIDERATIONS

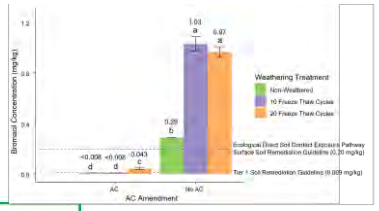
- The irrigation water pathway applies only to agricultural land
- Tier 1 guidance indicates irrigation water can come from either:
  - An “irrigation use aquifer” (Section 2.3.5)
  - A dugout (Section C.5.2)
- Bromacil or tebuthiuron in groundwater in agricultural land use:
  - Will require exposure control

RECOMMENDED BEST MANAGEMENT PRACTICES

- Always plan to assess groundwater when bromacil or tebuthiuron are present
- Compare worst case groundwater concentration to:
  - FAL surface water guideline
  - Irrigation water guideline
- Groundwater below guideline overrides soil guideline for corresponding pathways
- Applicable guideline will then be the ecological soil contact guideline
- Groundwater above guidelines > Tier 2 approach recommended
- If Tier 2 approaches are not available or do not resolve the issue
  - Remediation or exposure control may be required

QUESTIONS?

APPENDIX B9: INVESTIGATION OF THE LONG-TERM EFFECTIVENESS OF ACTIVATED CARBON AND IMMOBILIZATION OF BROMACIL AND TEBUTHIURON



Enviro Q&A Services

SSP Soil Sterilants Program

InnoTech ALBERTA
A SUBSIDIARY OF ALBERTA INNOVATES

SOIL STERILANTS PROGRAM (SSP) – 2024 ANNUAL SHARING EVENT

PROJECT #10 - INVESTIGATION OF THE LONG-TERM EFFECTIVENESS OF ACTIVATED CARBON IN IMMOBILIZATION OF BROMACIL AND TEBUTHIURON

CHRIS POWTER ON BEHALF OF SARAH THACKER, INNOTECH ALBERTA

SSP Soil Sterilants Program

PROBLEM STATEMENT

- Activated carbon (AC) has long been considered one of the most effective in-situ remediation technologies for soil sterilants, adsorbing sterilants to immobilize them, thus preventing uptake by plants or leaching through the soil.
- However, there is **hesitation** from a regulatory perspective to accept immobilization as a long-term solution for managing sterilant-impacted soils **due to uncertainty** about the longevity of immobilization.

Does Activated Carbon effectively immobilize bromacil and tebuthiuron such that AC can be considered a permanent remediation technology?

SSP Soil Sterilants Program

RESEARCH APPROACH

- Literature review
  - Potential for AC degradation
  - Factors influencing sorption and desorption
  - Weathering
- Desorption experiment
  - Designed to simulate worst-case scenario of sterilant leaching in soil and assess the percentage of each sterilant retained by AC
- Weathering experiment
  - Freeze-thaw cycles used to artificially weather AC and sterilants to assess the longevity of sterilant immobilization by AC

SSP-4: Phytoaccessible Sterilants

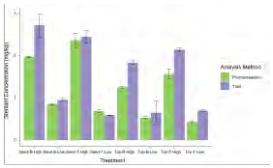
SSP-10

SSP-9A: Native Species Toxicity

SSP Soil Sterilants Program

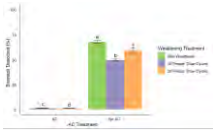
RESULTS – DESORPTION

- Sterilant desorption in the presence of AC was significantly lower than without AC for all treatments.
- Desorption ranged from 0% to 14% in AC-amended soil, with higher desorption in coarse-grained soil compared to fine-grained soil.
- Phyto-accessible fraction in soils amended with AC was much lower compared to the non-amended soil.
- Phyto-accessible fraction was typically greater than the desorbed fraction in AC amended soils.



RESULTS – WEATHERING

- In unamended soil, phyto-accessibility of bromacil increased significantly with weathering.
- In topsoil, desorption ranged from 1% to 3% after weathering of AC-amended soil; however, there were cases where the phyto-accessibility was increased after weathering, though still below levels in soils without AC.
- AC amendment significantly lowered phyto-accessible sterilant concentrations, in many cases below Tier 1 Guidelines.
- AC was effective at immobilizing soil sterilants when applied at a rate of 400:1 with significantly lower sterilant leaching in soil amended with AC compared non-amended soil.
- In the absence of weathering, total bromacil and tebuthiuron concentrations were significantly lower in AC-amended soil.



IMPLICATIONS FOR STERILANT-IMPACTED SITES

- Activated Carbon was shown to effectively sorb and retain the majority of bromacil and tebuthiuron in the long-term which should lead to greater acceptance by practitioners and regulators of this remediation technology.
- Sterilant-specific and soil-specific approaches to AC treatment are required.
- Phyto-accessible sterilants is a better measure of potential sterilant impacts than total sterilants.
- Total sterilant levels may be underestimated in AC-amended soils due to AC binding.

RECOMMENDATIONS

- Evaluate the type of AC (i.e., feedstock and charring temperature)
- Optimize methods of incorporation into soil
- Compare AC immobilization to other remediation technologies (cost, efficiency, longevity)

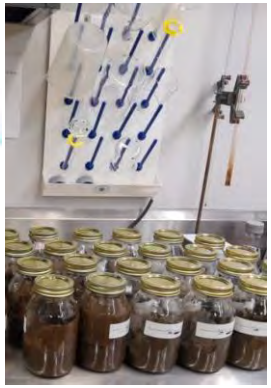
QUESTIONS?

APPENDIX B10: BENCH-SCALE TESTING OF CHEMICAL AMENDMENTS TO REMEDIATE BROMACIL AND TEBUTHIURON IN SOIL

SSP Soil Sterilants Program

InnoTech ALBERTA

CHEMCO ENVIRONMENT



SOIL STERILANTS PROGRAM (SSP) – BENCH-SCALE TESTING OF CHEMICAL AMENDMENTS TO REMEDIATE BROMACIL AND TEBUTHIURON IN SOIL

MALIKA BENDOUZ AND JEAN PARE - CHEMCO INC.

SIMONE LEVY AND VICTOR BACHMANN – INNOTECH ALBERTA

BENCH-SCALE TESTING OF REMEDIATION TECHNOLOGIES

SSP Soil Sterilants Program

Technology identification

- Applicable media
- Feasibility
- In/Ex-situ

Validation

- Establish effectiveness limits and influential factors
- Evaluate costs and logistics

Scaled testing

- Decision support for potential users
- Information for providers/developers

REMEDIATION PROJECTS OVERVIEW

SSP Soil Sterilants Program

Note **key characteristics** of bromacil and tebuthiuron that influence potential for remediation → Review and short-list **industry challenges** in managing sites impacted by sterilants → Evaluate **existing technologies** for applicability – separate proven from 'potential' or 'adjacent' → Search for **additional technologies** or approaches that could help address challenges → Consult with **technology providers** and those with experience in remediating sterilants → Develop **testing proposals** and **project advisory committee** → **Project #11**: **Bench-scale** screening and refinement → **Project #12**: Meso- and field-scale **remediation demonstration(s)**

#13/11. SCREENING AND BENCH-SCALE TESTING OF REMEDIATION TECHNOLOGIES

SSP Soil Sterilants Program

Key Challenges
1) Sterilant **destruction** in soil where immobilization is not considered an acceptable option (*in situ* or *ex situ*)
2) Treatment of sterilants at **depths greater than 50 cm bgs** in unsaturated soil, thus inaccessible to treatment at surface (ideally treated *in situ*)
3) *In situ* treatment of **saturated fine-grained till soils and groundwater**
4) **Cost-effective** *ex situ* water remediation

#13/11. SCREENING AND BENCH-SCALE TESTING OF REMEDIATION TECHNOLOGIES

SSP Soil Sterilants Program

Key Challenge	Bench-Scale Testing
1) Destruction of sterilants (ideally to guideline levels) 2) Treatment of sterilants at depths greater than 50 cm bgs in unsaturated soil, thus inaccessible to treatment at surface (ideally treated *in situ*)	Chemical oxidation and reduction approaches, with and without surfactants CHEMCO
3) *In situ* treatment of saturated fine-grained till soils and groundwater	*In situ* biostimulation, with and without surfactants VERTEX Environmental Inc.
4) Cost-effective *ex situ* water remediation	In situ Biostimulation, with and without surfactants AND Electrocoagulation (*ex situ*) trial MOUNT ROYAL UNIVERSITY

DESTRUCTIVE TECHNOLOGY – IN SITU CHEMICAL OXIDATION

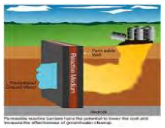
SSP Soil Sterilants Program

- ✓ Water is the carrier for the oxidants used in chemical oxidation (except for ozone)
- ✓ Surfactant enhanced Chemical Oxidation might be considered Oxidants are non-specific and will react with the targeted contaminants AND with the soil organic and/or mineral soil matrix content Soil Oxidant Demand - SOD).
- ✓ If you have enough oxidant present and sufficient time you will push the destruction toward to FULL mineralization (CO_2, H_2O, Cl^-) of the contaminant of concern
- ✓ Kinetics of the chemical oxidation reaction is thus influence by the contaminant of concern solubility and availability in the groundwater or moisture phase
- ✓ Surfactants can be combined with the oxidant to increase distribution and contaminant availability (S-ISCO)
- ✓ Sorbed phase contamination might be challenging to remediate (less available)
- ✓ Back diffusion of the contamination (rebound) can persist because of high hydrophobic properties or geological consideration
- ✓ Application/Injection technique must induce proper contact between the contaminant and the oxidant for a proper duration for the required reaction to occurs (kinetics)

DESTRUCTIVE TECHNOLOGY – IN SITU CHEMICAL REDUCTION

SSP Soil Sterilants Program

- ✓ Introduction of a reducing material or generating reducing species to help degrade toxic organic compounds or immobilize metals in the desired area
- ✓ The most commonly used reductant is zero valent iron (ZVI)
- ✓ Possible introduction of organic substrates to produce enhanced conditions to conduct microbial reduction
- ✓ Degradation / Immobilization of contaminants by abiotic or biotic processes
- ✓ Transfer of electrons from reduced metals (ZVI, ferrous iron) or reduced minerals (magnetite, pyrite) to contaminants including chlorinated organics and heavy metals
- ✓ Permeable Reactive Barriers (PRB's) constructed using ZVI = example of simple ISCR
- ✓ Combined ZVI/fermentable carbon reagents are an example of advanced ISCR



Source: EPA

STERILANT CHARACTERISTICS

SSP Soil Sterilants Program

Parameter	Sterilant	
	Bromacil	Tebuthiuron
Water Solubility	815 mg/L at 25 °C; increases with higher pH	2,500 mg/L at 25 °C
Soil/organic matter sorption coefficient (K_d/K_{oc}); Octanol-water partition coefficient (log K_{ow})	K_{oc}: 32 g/mL ; K_d/K_{oc}: variable from 2.3 to 289 in soils ranging from sand to peat; Log (Koc): 1.86 (average) for soil; 1.61 (average for sediments) Log K_{ow}: 2.11	K_{oc}: 80 mg/; K_d: 0.2-10.0; Log K_{ow}: 1.79
Mobility	Highly likely to be mobile in soils low in organic matter; Moves horizontally on surface and vertically with water; Moderate mobility in soils high in OM and clay content	Influenced by soil texture and organic matter content (higher mobility in sandy soils and soils low in OM; lower in clay loam soils or highly organic soils)
Leaching Potential	High; important dissipation process; readily leached	Medium; High solubility in water, weak adsorption to soil particles and is highly persistent, therefore has high potential to leach
Adsorption/ Desorption	Lower than other herbicides; sorption to soils increases with clay and OM content; will not partition to suspended particles or sediments in aquatic systems (remains dissolved in water column)	Relatively poor soil sorption; Sorption to soils highest in soils high in OM content followed by clay content; <1% at soil OM of 0.3% and 40% with soil OM of 4.8%
Volatilization	Minor importance	Not volatile
Microbial degradation	Bromacil is slowly debrominated by microflora under anaerobic, methanogenic conditions but is not degraded under denitrifying or sulphate-reducing conditions.	Biodegradation of tebuthiuron in aerobic soil is expected to be slow. It also shows little biodegradation in anaerobic soils. Similarly, tebuthiuron does not degrade appreciably in water.

BENCH SCALE IN SITU CHEMICAL OXIDATION/REDUCTION – CHEMCO INC.

BENCH-SCALE TESTING APPROACH

1. Surfactant screening – 6 different types (anionic, cationic and non-ionic) to ENHANCE contaminant availability
2. Reductive treatment testing – with and without surfactant (Daramend only tilled)
3. Oxidative treatment testing – without surfactant; two best candidates with surfactant (staged approach)
   - Potassium persulfate activated with calcium-based product (hydrated lime)
   - Sodium persulfate activated with calcium-based product (calcium peroxide FG)
   - Sodium persulfate activated with alkaline base (sodium hydroxide)
   - Hydrogen Peroxide alone or activated using VTX (organic catalyst)

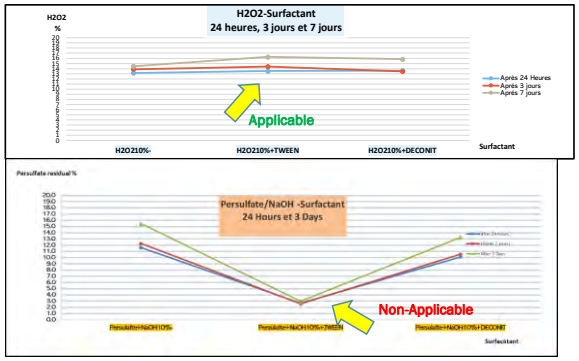
SURFACTANTS SCREENING RESULTS (BROMACIL)

Essay	Description	Type of surfactant	Dosage (g/kg)	Contaminant Concentration (ppb)	% Increase	comments
BROMACIL - TEMOIN 1 - BLANK	Leachate of Spiked soil with bromacil without surfactant					
BROMACIL - TEMOIN 2 - BLANK	Leachate of Spiked soil with bromacil without surfactant			323		
BROMACIL - TEMOIN 3 - BLANK	Leachate of Spiked soil with bromacil without surfactant			258		
BROMACIL - TEMOIN 4 - BLANK	Leachate of Spiked soil with bromacil without surfactant			427		
BROMACIL - TWEEN - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant TWEEN at dosage of 1 g/kg	TWEEN	1	583	74	Best results
BROMACIL - TWEEN - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant TWEEN at dosage of 5 g/kg	TWEEN	5	483	44	
BROMACIL - TWEEN - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant TWEEN at dosage of 10 g/kg	TWEEN	10	527	57	
BROMACIL - DECONIT - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant DECONIT at dosage of 1 g/kg	DECONIT	1	376	12	
BROMACIL - DECONIT - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant DECONIT at dosage of 5 g/kg	DECONIT	5	264	-21	
BROMACIL - DECONIT - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant DECONIT at dosage of 10 g/kg	DECONIT	10			
BROMACIL - DL3 - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL3 at dosage of 1 g/kg	DL3	1	413	23	
BROMACIL - DL3 - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL3 at dosage of 5 g/kg	DL3	5	465	38	2nd best
BROMACIL - DL3 - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL3 at dosage of 10 g/kg	DL3	10	395	18	
BROMACIL - DL4 - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL4 at dosage of 1 g/kg	DL4	1	438	28	3th best
BROMACIL - DL4 - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL4 at dosage of 5 g/kg	DL4	5			
BROMACIL - DL4 - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant DL4 at dosage of 10 g/kg	DL4	10	343	2	
BROMACIL - 106-CL - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant 106 CL at dosage of 1 g/kg	106 CL	1	280	-17	
BROMACIL - 106-CL - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant 106 CL at dosage of 5 g/kg	106 CL	5	218	-35	
BROMACIL - 106-CL - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant 106 CL at dosage of 10 g/kg	106 CL	10	393	17	
BROMACIL - FFT - 1 g/kg	Leachate of Spiked soil with bromacil+Surfactant FFT at dosage of 1 g/kg	FFT	1	383	17	
BROMACIL - FFT - 5 g/kg	Leachate of Spiked soil with bromacil+Surfactant FFT at dosage of 5 g/kg	FFT	5			
BROMACIL - FFT - 10 g/kg	Leachate of Spiked soil with bromacil+Surfactant FFT at dosage of 10 g/kg	FFT	10	424	26	

SURFACTANTS SCREENING RESULTS (TEBUTHIURON)

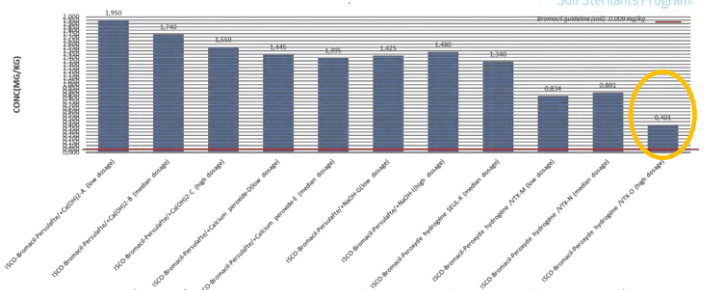
Essay	Description	Type of surfactant	Dosage (g/kg)	Contaminant Concentration (ppb)	% Increase	comments
TBT - TEMOIN 1 - BLANK	Leachate of Spiked soil with Tebuthiuron without Surfactant			282		
TBT - TEMOIN 2 - BLANK	Leachate of Spiked soil with Tebuthiuron without Surfactant			316		
TBT - TEMOIN 3 - BLANK	Leachate of Spiked soil with Tebuthiuron without Surfactant					
TBT - TEMOIN 4 - BLANK	Leachate of Spiked soil with Tebuthiuron without Surfactant			347		
TBT - TWEEN - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant TWEEN at dosage of 1 g/kg	TWEEN	1	413	31	3 rh best
TBT - TWEEN - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant TWEEN at dosage of 5 g/kg	TWEEN	5	487	54	Best results
TBT - TWEEN - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant TWEEN at dosage of 10 g/kg	TWEEN	10	363	15	
TBT - DECONIT - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DECONIT at dosage of 1 g/kg	DECONIT	1	189	-40	
TBT - DECONIT - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DECONIT at dosage of 5 g/kg	DECONIT	5	462	47	2nd best
TBT - DECONIT - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DECONIT at dosage of 10 g/kg	DECONIT	10	333	6	
TBT - DL3 - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL3 at dosage of 1 g/kg	DL3	1	323	2	
TBT - DL3 - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL3 at dosage of 5 g/kg	DL3	5	288	-9	
TBT - DL3 - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL3 at dosage of 10 g/kg	DL3	10	285	-10	
TBT - DL4 - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL4 at dosage of 1 g/kg	DL4	1	267	-15	
TBT - DL4 - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant DL4 at dosage of 5 g/kg	DL4	5	304	-3	
TBT - DL4 - 10 g/kg	Leachate Spiked soil with Tebuthiuron +Surfactant DL4 at dosage of 10 g/kg	DL4	10	202	-36	
TBT - 106-Clig - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant 106 CL at dosage of 1 g/kg	106 CL	1	158	-50	
TBT - 106-Clig - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant 106 CL at dosage of 5 g/kg	106 CL	5	181	-42	
TBT - 106-Clig - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant 106 CL at dosage of 10 g/kg	106 CL	10	128	-59	
TBT - FFT - 1 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant FFT at dosage of 1 g/kg	FFT	1			
TBT - FFT - 5 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant FFT at dosage of 5 g/kg	FFT	5			
TBT - FFT - 10 g/kg	Leachate of Spiked soil with Tebuthiuron +Surfactant FFT at dosage of 10 g/kg	FFT	10	256	-19	

SURFACTANT REACTIVITY TESTING VERSUS OXIDANT



OXIDATIVE TESTING NO SURFACTANT (BROMACIL)

average concentration blank sample= 1.36 mg/kg (n=3)

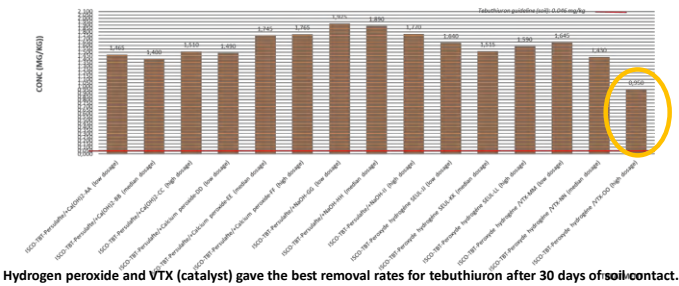


Hydrogen peroxide and VTX (catalyst) gave the best removal rates for bromacil after 30 days of soil contact. (40:1 oxidant to contaminant dosage: 40.2 g of hydrogen peroxide 50% + 4 g/kg VTX per kg of dry soil)

- **70% of Bromacil destruction obtained @ final concentration of 0.401 mg/kg after 30 days of reaction**

OXIDATIVE TESTING NO SURFACTANT (TEBUTHIURON)

Oxidative testing for Tebuthiuron (no surfactant)
average concentration blank sample= 2.1 mg/kg (n=3)



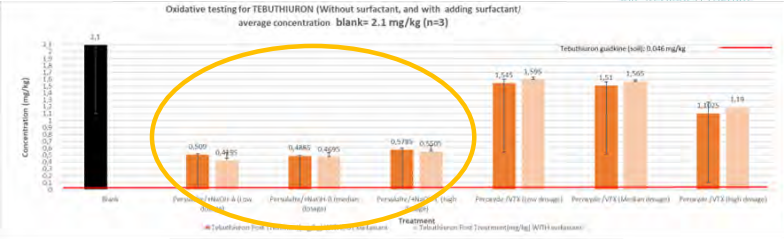
Hydrogen peroxide and VTX (catalyst) gave the best removal rates for tebuthiuron after 30 days of soil contact. (40:1 oxidant to contaminant dosage: 40.2 g of hydrogen peroxide 50% + 4 g/kg VTX per kg of dry soil)

- **55% of Tebuthiuron destruction @ final concentration of 0,95 mg/kg after 30 days of reaction**

OXIDATIVE TREATMENT ON BROMACIL WITH AND WITHOUT THE ADDITION OF SURFACTANT

- ✓ Very good contaminant removal with the use of Hydrogen peroxide activated with VTX at high dosage combined with the addition of the surfactant (TWEEN®).: high dosage of Hydrogen peroxide (40:1 oxidant to contaminant dosage) by using 40.2 g of hydrogen peroxide 50% plus 4 g/kg VTX, + surfactant TWEEN (1 g per kg of soil)
- ✓ The Bromacil destruction = 76 %.

OXIDATIVE TREATMENT ON TEBUTHIURON WITH AND WITHOUT THE ADDITION OF SURFACTANT

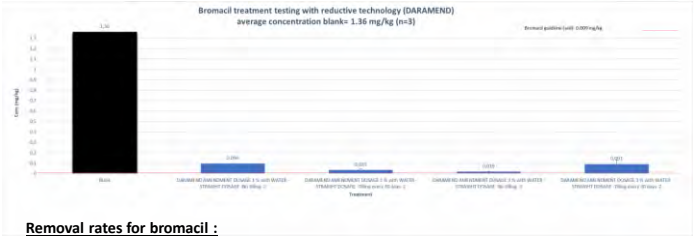


- ✓ The use of Alkaline activated Sodium persulfate without surfactant was successful.
- ✓ Tebuthiuron destruction = 76% (without the surfactant) AND 80% (with the surfactant)

- the use of a surfactant will not be recommended for this treatment

The high SOD value obtained (41 g of sodium persulfate per kg of soil) for the submitted soil might have limited contaminant destruction by this oxidant in the submitted soil samples

EFFECT OF DARAMEND® TREATMENT CONCENTRATIONS IN SOIL ON BROMACIL

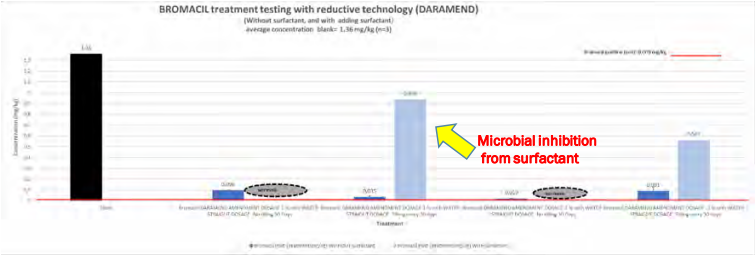


Removal rates for bromacil :

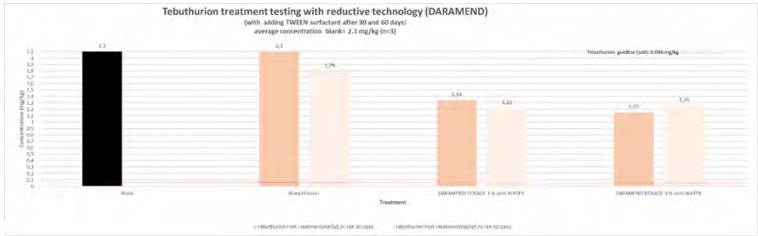
- Daramend®@ 3% (wt/wt basis) with no tilling : 98%
- Daramend®@ 1% (wt/wt basis) with a tilling every 30 days: 97%

Note: 1% (wt/wt basis) = 10 g of Daramend® per kg of dry soil and using water to increase moisture content to 90% WHC

COMPARING THE EFFECT OF REDUCTIVE TREATMENT ON BROMACIL WITH AND WITHOUT ADDITION OF SURFACTANT



COMPARING THE EFFECT OF REDUCTIVE TREATMENT ON TEBUTHIURON WITH AND WITHOUT ADDITION OF SURFACTANT



Bromacil:

- ✓ Average percentage removal ranged from **31% to 59% after 30 days, although it was reduced by 98% after a treatment cycle of 60 days by tilling 1 % of DARAMEND amendment** with the addition of surfactant TWEEN into the soil and using water to increase soil moisture content to 60% of the soil's water holding capacity (WHC). The tilling process served to aerate and homogenize the soil. **The Bromacil concentrations were reduced from 1.36 mg/kg to 0.016 mg/kg showing a significant reduction of 99%**.

➢ **The surfactant was detrimental to successful treatment with DARAMEND after 30 days, due to microbial cell wall interference**

Tebuthiuron

- ✓ Average percentage removal was between 36% and 45% after a treatment cycle of 30 days, and it was reduced by an average of 40% and 42% after a treatment cycle of 60 days using DARAMEND at a dosage of 1% and 3% (wt/wt basis) respectively.

SUMMARY & LESSONS LEARNED

- **Destructive Technology targeting Bromacil:**
  - ✓ Daramend approach was highly effective in the treatment of **Bromacil** in the tested soil samples. Overall treatment product cost was approximately $55/MT (product only) of soil using a 1% w/w loading rate.
  - ✓ DARAMEND would only work in saturated conditions (or high-water content soil) as the contaminant destruction pathway would not be efficient if the water content is insufficient.
  - ✓ The hydrogen peroxide oxidation process using the VTX catalyst and surfactant more costly than the DARAMEND technology at $99/MT (product only) for the destruction of 1.0 mg/kg contaminant concentration. This product combination would be an alternative treatment method for a combined soil and groundwater issue.
  - ✓ These approaches enabled a rapid, cost- effective, and long-lasting treatment., very sustainable

SUMMARY & LESSONS LEARNED

- **Destructive Technology Targeting Tebuthiuron**
  - ✓ ISCO approach with alkaline activated Klozur® persulfate study has been successful allow a reduction of 76% of the Tebuthiuron without adding the surfactant using a low dosage of Klozur® persulfate.
  - ✓ The stability of persulfate, can last weeks to months in the soil, provides a large radius of influence, and maximizes contact time with contaminants
  - ✓ Treatment cost of $5/MT (product only) per 1 mg/kg removal of Tebuthiuron (without surfactant)
  - ✓ This reactivity between the alkaline activated persulfate and the Tebuthiuron could also be an alternative treatment method in the case of a combined soil and groundwater issue.

Notes:

- The use of a surfactant will not be recommended for this treatment.
- No residual sodium persulfate was measured in the sacrificial samples
- The high SOD value obtained for the submitted soil might have limited contaminant destruction by this oxidant in the submitted soil samples.

NEXT STEPS AND TAKEAWAY

In Situ / Ex situ Destructive Technologies

- ✓ Soil Oxidant Demand (SOD) validation for any oxidation destructive is HIGHLY RECOMMENDED
- ✓ Potassium persulfate vs. Sodium Persulfate for additional persistency and face
- ✓ DARAMEND dosage optimization to obtain lower treatment cost need to be evaluated
- ✓ EHC could be applicable In situ as a Permeable reactive barrier setting for the saturated zone
- ✓ Mixing optimization and Water integration and maintenance for better reductive processes ex situ

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QUESTIONS?

SSP
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TC Energy | ATCO | ALBERTA INNOVATES | InnoTech ALBERTA

APPENDIX B11: BENCH-SCALE TREATABILITY STUDY OF BROMACIL AND TEBUTHIURON IN ALBERTA SOILS

SOIL STERILANTS PROGRAM (SSP) – 2024 FINAL SHARING EVENT

PROJECT 11 – BENCH-SCALE TREATABILITY TESTING OF BROMACIL AND TEBUTHIURON ALBERTA SOILS

KEVIN FRENCH,
VEI CONTRACTING INC.

OVERVIEW

- Project Team
- Project Goal and Objective
- Project Overview
  - Literature Review of Existing Technologies
- Methods & Results
  - Technologies Assessed
  - Compounds/Media Tested
  - Testing Procedure
  - Reactor Configuration
  - Test Results & Summary
- Project Status & Next Steps
- Data Gaps, Challenges & Learnings
- Relationships to Other Projects
- Questions

PROJECT TEAM

Kevin French

Eric Cowan

Dr. Alyson Neufeld

PROJECT GOAL & OBJECTIVE

- Key technology gap identified relates to the current lack of known in-situ destructive technologies for bromacil and tebuthiuron impacts in soil and/or water in the field
- Current state of remedial technologies is limited to adsorption/immobilization using activated carbon (AC), biochar, etc., but the effectiveness and permanence of this treatment technology was unknown (i.e., see SSP Project #10)
- There is an interest in determining whether any newly developed in-situ remedial technologies could provide a cost-effective and permanent destruction mechanism for sterilants in soil and groundwater
- Objective is:
  - ***"to test three remedial amendments including different formulations of Trap & Treat® BOS 200+®, Trap & Treat® CAT 100, and micro-scale zero-valent iron (ZVI) at bench-scale to identify amendments worth investigating further at a pilot- or field-scale."***

PROJECT OVERVIEW

- Literature Review of Existing Technologies:
  - Research suggested that bromacil may be amenable to destruction via CAT 100® which combines activated carbon, elemental iron, complex carbohydrates and facultative microbes.
  - Similarly, tebuthiuron may be amenable to destruction via BOS 200+® which combines activated carbon, nitrate, sulphate, complex carbohydrates and facultative microbes.
  - Both bromacil and tebuthiuron are highly sorbed by activated carbon (AC). Therefore, the bench-scale testing simulated the destruction mechanisms of CAT 100® and BOS 200+® in the absence of AC.
  - Nano-scale ZVI has been successfully used to treat other soil sterilants through chemical reduction. Lowering the pH has successfully promoted the chemical reduction for some sterilants and thus this was also investigated for bromacil and tebuthiuron treatment.
  - The impact of adding surfactant to the mixtures was also tested, as surfactants can help desorb contamination from soil to make it more available to react with remedial amendments.

METHODS & RESULTS – TECHNOLOGIES ASSESSED

- Remedial technologies assessed:
  - Trap & Treat® BOS 200+®
  - Trap & Treat® CAT 100
  - Simulated Trap & Treat® BOS 200+® (i.e., no AC)
  - Simulated Trap & Treat® CAT 100 (i.e., no AC)
  - Zero-valent iron (ZVI)
  - ZVI with aluminum sulphate
  - Trap & Treat® BOS 200+® with surfactant
  - Trap & Treat® CAT 100 with surfactant
  - Simulated Trap & Treat® BOS 200+® with surfactant
  - Simulated Trap & Treat® CAT 100 with surfactant

METHODS & RESULTS – COMPOUNDS/MEDIA

Hyvar® X-L – commercial, 20% bromacil, liquid

Spike® 80DF – commercial, 80% tebuthiuron, solid

- Compounds/media tested:
  - Actual samples of sterilant impacted soils from Alberta provided by InnoTech
  - Samples had detectable concentrations of sterilants above the standards:
    - Bromacil: baseline = 0.210 mg/kg
    - Tebuthiuron: baseline = 0.136 mg/kg
  - Soils were impacted with Hyvar® or Spike®
  - Samples were not previously augmented with AC
  - **Required degree of treatment to meet standards from baseline concentrations:**
    - **Bromacil: 95.7%**
    - **Tebuthiuron: 93.4%**

METHODS & RESULTS – TESTING PROCEDURE

- Approx. 2.5 kg of impacted soil was mixed with remedial amendments, saturated with distilled water and placed into a 3 L glass jar for each of the reactors and configurations.
- Reactors were equipped with an inlet valve and a water-sealed check valve to allow nitrogen gas to be injected into the headspace of the reactor to maintain anaerobic conditions.
- Reactors were covered with a black cloth to prevent any photochemistry from occurring.
- The soils in each reactor was thoroughly mixed on a daily basis for the first 2 weeks to ensure good contact between the remedial amendments and the sterilants. Following this, the reactors were mixed weekly until the 2-month sampling event, and then left without mixing for the final 2 months of the testing program.

METHODS & RESULTS – REACTOR CONFIGURATION

- #1 – Control reactor; only the contaminated soil with no added reagents or amendments
- #2 - 1.2% wt. Trap & Treat® BOS 200+®
- #3 - 0.7% wt. Trap & Treat® CAT 100
- #4 – same components and weight percentages as #2 but without any AC component
- #5 – same components and weight percentages as reactor #3 but without any AC component
- #6 - 5% wt. ZVI
- #7 - 5% wt. ZVI with 3.5% wt. aluminum sulphate
- #8 – same as reactor #2 with 0.2% wt. Tween 80 surfactant
- #9 - same as reactor #3 with 0.2% wt. Tween 80 surfactant
- #10 - same as reactor #4 with 0.2% wt. Tween 80 surfactant
- #11 - same as reactor #5 with 0.2% wt. Tween 80 surfactant

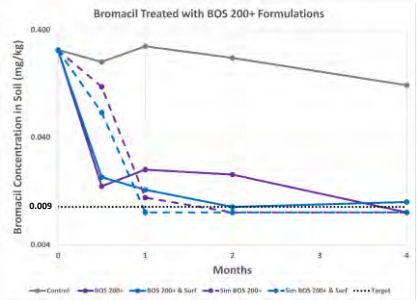
METHODS & RESULTS – BROMACIL RESULTS

Analytical Results Summary Table - Bromacil-Impacted Soils

Reactor ID	Bromacil Concentrations in Soil (mg/kg)							Final Percent Reduction
	Sampling Dates							
	Mixed Soil Baseline 2022-04-27	Starting Baseline 2022-06-08	Adjusted Starting Baseline 2022-06-08	2 Weeks 2022-07-18	1 Month 2022-08-04	2 Months 2022-09-06	4 Months 2022-11-04	
Control	0.210	0.260	0.260	0.201	0.281	0.219	0.122	53.1%
BOS 200+	0.210	0.260	0.257	0.014	0.020	0.018	0.008	96.9%
BOS 200+ & Surf	0.210	0.260	0.257	0.017	0.013	0.009	0.010	96.1%
Sim BOS 200+	0.210	0.260	0.258	0.118	0.011	0.008	0.008	96.9%
Sim BOS 200+ & Surf	0.210	0.260	0.258	0.068	0.008	0.008	0.008	96.9%
CAT 100	0.210	0.260	0.258	0.051	0.081	0.038	0.034	86.8%
CAT 100 & Surf	0.210	0.260	0.258	0.066	0.042	0.024	0.014	94.6%
Sim CAT 100	0.210	0.260	0.257	0.050	0.008	0.008	0.008	96.9%
Sim CAT 100 & Surf	0.210	0.260	0.257	0.027	0.008	0.008	0.008	96.9%
ISCR	0.210	0.260	0.248	0.198	0.086	0.008	0.008	96.8%
ISCR +	0.210	0.260	0.239	0.106	0.101	0.073	0.076	68.2%
Target Standard	0.009							

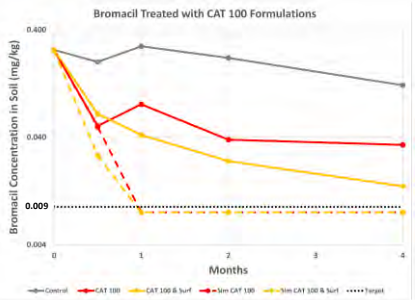
METHODS & RESULTS – BROMACIL RESULTS

- Technology: Bromacil-impacted soils treated with BOS 200+ formulations:
  - All configurations of BOS 200+ lowered bromacil concentrations to greater extents than in the control
  - All configurations of BOS 200+ brought the bromacil concentrations below the target concentration except for the reactor containing BOS 200+ and surfactant
  - These results indicate that **BOS 200+ (with or without its AC component) is able to degrade bromacil in soil to below the target concentration** within four (4) months



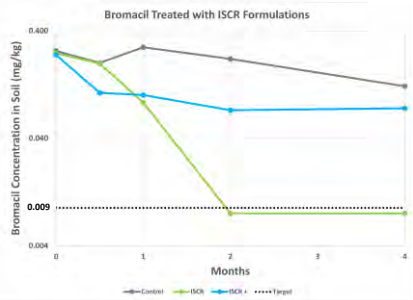
METHODS & RESULTS – BROMACIL RESULTS

- Technology: Bromacil-impacted soils treated with CAT 100 formulations:
  - All configurations of CAT 100 lowered bromacil concentrations to greater extents than in the control
  - Only the configurations of simulated CAT 100 (without its AC component) brought the bromacil concentrations below the target concentration
  - These results indicate that **simulated CAT 100 (without its AC component) is able to degrade bromacil in soil to below the target concentration** within four (4) months



METHODS & RESULTS – BROMACIL RESULTS

- Technology: Bromacil-impacted soils treated with ISCR formulations:
  - Both configurations of ISCR lowered bromacil concentrations to greater extents than in the control
  - Only ISCR (ZVI) brought the bromacil concentration below the target concentration
  - These results indicate that **ISCR (ZVI) is able to degrade bromacil in soil to below the target concentration** within four (4) months



METHODS & RESULTS – BROMACIL RESULTS SUMMARY

- Technology Summary: Treatment of bromacil-impacted soils
  - All three treatment approaches, BOS 200+, CAT 100 and ISCR, resulted in a drop in bromacil concentration in the soil
  - The formation of bromide in all of the treatment reactors support the conclusion that there was destruction of bromacil, not just carbon adsorption; plus bromacil reductions were observed in reactors containing no AC
  - BOS 200+ removed the bromacil at a faster rate and/or more completely than CAT 100 or ISCR
  - In both the full and simulated BOS 200+ and CAT 100 formulations, surfactant enhanced the treatment efficacy
  - **Overall, the simulated CAT 100 (without its AC component) and with surfactant was the fastest and best performing in terms of destruction of bromacil in soil and would be applicable for general plume treatment**
  - For a potential permeable reactive barrier (PRB) application the additional AC component is desirable for longevity and the absence of surfactant is desirable for adsorptive strength and longevity
  - **Therefore, the preferred formulation for a PRB application to treat migrating plumes of bromacil in groundwater is the full formulation of BOS 200+ (with its AC component) and without surfactant**

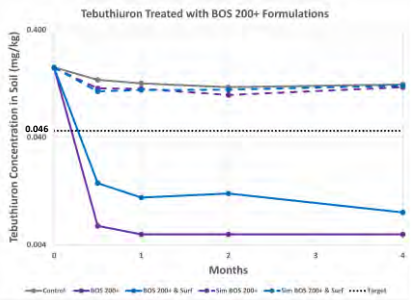
METHODS & RESULTS – TEBUTHIURON RESULTS

Analytical Results Summary Table - Tebuthiuron-Impacted Soils

Reactor ID	Tebuthiuron Concentrations in Soil (mg/kg)							Final Percent Reduction
	Sampling Dates							
	Mixed Soil Baseline 2022-04-27	Starting Baseline 2022-06-08	Adjusted Starting Baseline 2022-06-08	2 Weeks 2022-07-18	1 Month 2022-08-04	2 Months 2022-09-06	4 Months 2022-11-04	
Control	0.136	0.179	0.179	0.137	0.127	0.117	0.1240	30.7%
BOS 200+	0.136	0.179	0.177	0.006	0.005	0.005	0.0050	97.2%
BOS 200+ & Surf	0.136	0.179	0.177	0.015	0.011	0.012	0.0080	95.5%
Sim BOS 200+	0.136	0.179	0.178	0.114	0.113	0.099	0.1170	34.1%
Sim BOS 200+ & Surf	0.136	0.179	0.178	0.107	0.110	0.111	0.1210	31.9%
CAT 100	0.136	0.179	0.178	0.039	0.020	0.022	0.0350	80.3%
CAT 100 & Surf	0.136	0.179	0.178	0.076	0.072	0.065	0.0360	79.8%
Sim CAT 100	0.136	0.179	0.177	0.095	0.111	0.118	0.0940	46.8%
Sim CAT 100 & Surf	0.136	0.179	0.177	0.106	0.101	0.096	0.1120	36.7%
ISCR	0.136	0.179	0.170	0.111	0.121	0.105	0.0880	48.4%
ISCR +	0.136	0.179	0.164	0.079	0.080	0.066	0.0670	59.2%
Target Standard	0.046							

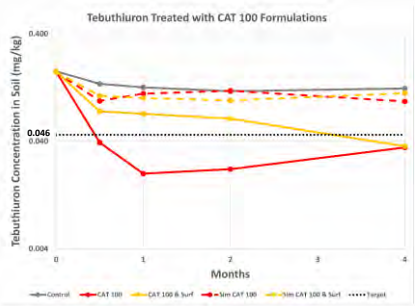
METHODS & RESULTS – TEBUTHIURON RESULTS

- Technology: Tebuthiuron-impacted soils treated with BOS 200+ formulations:
  - The full formulations of BOS 200+ lowered tebuthiuron concentrations to greater extents than the control; the simulated versions (without its AC component) were indistinguishable from the control
  - The full formulations of BOS 200+ (with and without surfactant) brought the tebuthiuron concentrations below the target concentration
  - These results indicate that the **full formulation of BOS 200+ (with and without surfactant) is able to degrade tebuthiuron in soil to below the target concentration** within four (4) months



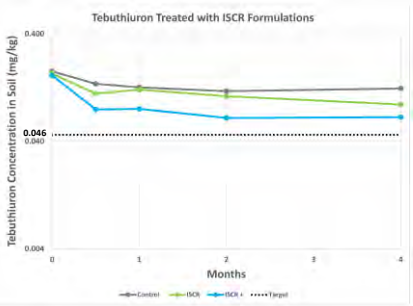
METHODS & RESULTS – TEBUTHIURON RESULTS

- Technology: Tebuthiuron-impacted soils treated with CAT 100 formulations:
  - The full formulations of CAT 100 lowered tebuthiuron concentrations to greater extents than the control; the simulated versions (without its AC component) were indistinguishable from the control
  - The full formulations of CAT 100 (with and without surfactant) brought the tebuthiuron concentrations below the target concentration
  - These results indicate that the **full formulation of CAT 100 (with and without surfactant) is able to degrade tebuthiuron in soil to below the target concentration** within four (4) months



METHODS & RESULTS – TEBUTHIURON RESULTS

- Technology: Tebuthiuron-impacted soils treated with ISCR formulations:
  - Both configurations of ISCR lowered tebuthiuron concentrations to marginally greater extents than in the control
  - None of the configurations of ISCR brought the tebuthiuron concentrations below the target concentration
  - These results indicate that **ISCR formulations are unable to degrade tebuthiuron in soil to below the target concentration** within four (4) months



METHODS & RESULTS – TEBUTHIURON RESULTS SUMMARY

- Technology Summary: Treatment of tebuthiuron-impacted soils
  - All three treatment approaches, BOS 200+, CAT 100 and ISCR, resulted in a drop in bromacil concentration in the soil
  - BOS 200+ (with and without surfactant) was better performing than CAT 100 (with and without surfactant)
  - The greater treatment using BOS 200+ versus CAT 100 suggests that the reduction in tebuthiuron concentrations in soil is due to the destruction of tebuthiuron and not carbon adsorption alone since BOS 200+ has a lower AC percentage than CAT 100
  - In both the full and simulated BOS 200+ and CAT 100 formulations, surfactant reduced the treatment efficacy
  - **Overall, the full formulation of BOS 200+ (with its AC component) and without surfactant was the fastest and best performing in terms of destruction of tebuthiuron in soil and would be applicable for general plume treatment**
  - **Similarly, overall, the preferred formulation for a PRB application to treat migrating plumes of tebuthiuron in groundwater is the full formulation of BOS 200+ (with its AC component) and without surfactant**

METHODS & RESULTS – OVERALL SUMMARY

- **Permanent destructive technologies were demonstrated for both bromacil and tebuthiuron in Alberta soils**
- **For sites with bromacil impacts:**
  - **Simulated CAT 100 (without its AC component) and with surfactant** was the fastest and best performing in terms of destruction of bromacil and would be applicable for **general plume treatment**
  - The **full formulation of BOS 200+ (with its AC component) and without surfactant** is the preferred formulation for a PRB application to treat **migrating plumes of bromacil in groundwater**
- **For sites with tebuthiuron impacts:**
  - The **full formulation of BOS 200+ (with its AC component) and without surfactant** was the fastest and best performing in terms of destruction of tebuthiuron and would be applicable for **general plume treatment**
  - The **full formulation of BOS 200+ (with its AC component) and without surfactant** is the preferred formulation for a PRB application to treat **migrating plumes of tebuthiuron in groundwater**

PROJECT STATUS & NEXT STEPS

- Bench-Scale Treatability Testing of Remedial Technologies:
  - Completed and demonstrated effective on samples of sterilant-impacted Alberta soils
  - No testing completed on sterilant-impacted groundwater
    - Not considered necessary as destructive treatment has already been demonstrated in soils
- Next Steps:
  - Further mesocosm studies, or pilot- or field-scale trials are recommended to confirm the suitability for treating bromacil and tebuthiuron in soil and/or groundwater under real-world conditions at Alberta sites

DATA GAPS, CHALLENGES & LEARNINGS

- Several remedial amendments were assessed and shown to be effective in reducing bromacil and tebuthiuron concentrations in Alberta soils to below target concentrations and with greater than 95% reduction rates
- Permanent destruction of bromacil was demonstrated through the generation of bromide in the samples
- Permanent destruction of tebuthiuron was inferred based on indirect metrics in the absence of an indicator parameter like bromide
- The treatment reactors were dosed with standard remedial amendment loading rates commonly used at other types of impacted sites, confirming financial viability of treatment
- The preferred remedial amendments can be applied under field conditions via soil mixing or injection approaches
- The preferred remedial amendments are all applicable to subsurface applications (at or below the water table) as they work under anaerobic conditions
- Approaches for general plume treatment and for permeable reactive barrier (PRB) applications are feasible

RELATIONSHIPS TO OTHER PROJECTS

- Remedial technologies tested were demonstrated to have the ability to adsorb and permanently destroy bromacil and tebuthiuron in soil and groundwater thereby reducing mobility (Project #8) and protecting irrigation water and freshwater aquatic life (Project #7)
- Several remedial technologies testing include AC in their matrix to provide adsorptive capacity for bromacil and tebuthiuron while the destruction mechanisms proceed and, as such, also provides interim level of treatment/protection (Project #10)
- Remedial technologies tested were demonstrated to be effective under anaerobic conditions and are therefore suitable to permanent treatment of bromacil and tebuthiuron impacts located at and below the water table (as opposed to in surface soils) (Project #11)
- Remedial technologies tested are now suitable remediation demonstration (Project #12)

QUESTIONS?

APPENDIX B12: EX-SITU FIELD DEMONSTRATION AND OPTIMIZATION OF THE USE OF DARAMEND FOR THE REMEDIATION OF BROMACIL IN SOIL

SOIL STERILANTS PROGRAM (SSP) – 2024 FINAL SHARING EVENT

PROJECT #12 – EX-SITU FIELD DEMONSTRATION AND OPTIMIZATION OF THE USE OF DARAMEND FOR THE REMEDIATION OF BROMACIL IN SOIL

VICTOR BACHMANN
INNOTECH ALBERTA

GOALS AND OBJECTIVES

- Are the remediation technologies identified in **Longevity of Activated Carbon** and **Bench Scale Testing of Remediation** projects effective in treating bromacil in field effective soils at larger scales?
  - Field demonstration– how do activated carbon, chemical oxidation by hydrogen peroxide, and Daramend® perform in the remediation of bromacil at meso-scales?
  - Optimization of Daramend®– what are the optimal dosage rates, application frequencies, and soil moisture management practices for bromacil remediation by Daramend®?

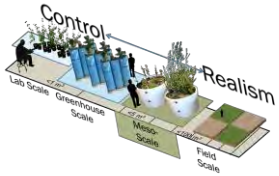
TECHNOLOGY SELECTION

- Criteria
  - Currently available
  - On-site application
  - Destructive remediation
  - Effective in SSP bench scale studies
  - Effective on bromacil
- Technologies selected
  - Hydrogen peroxide with VTX catalyst and Tween 80® surfactant (PVT)
  - Activated Carbon
  - Darmend®

Bench testing of various remediation technologies

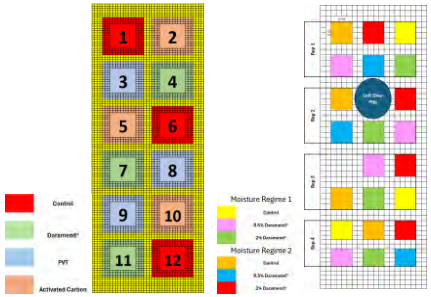
METHODS

- Field Demonstration
  - 5.4m³ soil treatment cells, 3 replicates for each treatment
  - 12-week long demonstration trial
  - Remediation technologies:
    - Hydrogen peroxide with VTX® catalyst and Tween®-80 surfactant (PVT)
    - Powdered activated carbon
    - Daramend®
- Optimization of Daramend®
  - 4m³ soil treatment cells, 3-4 replications for each treatment
  - 1-year long demonstration trial
  - Daramend® dosage levels: 0% (control), 0.5% and 2%
  - 2 Daramend® and water application frequencies:
    - Initial application only
    - 2 Daramend® and 3 water applications



PROJECT SETUP

- 10m x 30m double lined containment pad at InnoTech Alberta's Vegreville location
- Individual treatment cells within a small berm
- Each treatment cell lined with poly tarp on the bottom and covered
- Entire area covered over winter



DEMONSTRATION OF REMEDIATION TECHNOLOGIES - APPLICATION

PVT

Daramend®

- PVT
  - All components mixed prior to application
  - Applied directly to the soil making a slurry
- Activated Carbon
  - Activated carbon mixed into water on-site
  - Soil spread in layers
  - Each soil layer sprayed with AC as a slurry until saturated
- Daramend®
  - Spread over soil in layers
  - Each Daramend® layer watered until saturated
  - Soil mixed with excavator after treatment

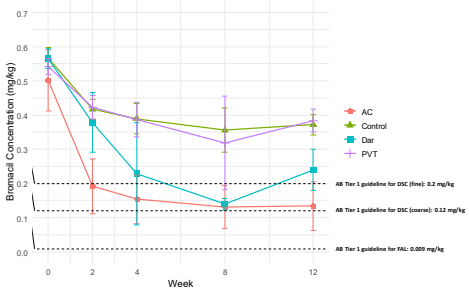
Activated Carbon

OPTIMIZATION OF DARAMEND® – APPLICATION

- Initial Daramend® and water application
  - Daramend® added to soil in Allu® bucket
  - Amended soil deposited in layers
  - Each soil layer watered until saturated
- Subsequent applications (Moisture Regime 2)
  - Soil excavated and shifted to one half of cell
  - Daramend® and water added in layers
  - Second Daramend ® dosage the same as first
  - 160L to 220L of water added on 2nd and 3rd application
  - 2nd water application after 8 weeks
  - 2nd Daramend® and 3rd water application following spring

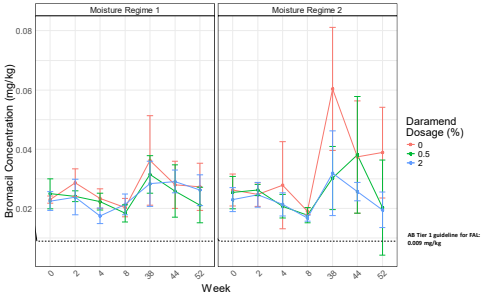
DEMONSTRATION OF REMEDIATION TECHNOLOGIES – RESULTS

- Control
  - 34% reduction in bromacil
  - Reduction occurred in the first 2 weeks
- PVT
  - 29% reduction in bromacil
  - Peroxide likely consumed by catalyst prior to contact with soil
- AC
  - 74% reduction in bromacil
  - Majority of reduction in the first 4 weeks
  - No further bromacil reduction after week 4
- Daramend®
  - 58% reduction in bromacil
  - Rebound in bromacil concentrations after week 8



OPTIMIZATION OF DARAMEND® – RESULTS

- Bromacil concentrations stable over first 8 weeks
- Rebound in bromacil concentrations in the spring
- Moisture regime 1 bromacil some decrease in during summer
- Moisture regime 2 bromacil decreasing after 2nd Daramend® application



OPTIMIZATION OF DARAMEND® – RESULTS

- No net decrease in bromacil concentrations
- Control treatments had an overall increase in bromacil concentrations
- Moisture regime 1 Daramend® at 0.5% had 33% lower bromacil than control
- Moisture regime 2 Daramend® treatments had 50% lower bromacil than control

Daramend Applications	Water applications	Daramend Dosage (%)	Bromacil Concentration Initial (mg/kg)	Bromacil Concentration Final (mg/kg)	% of Initial	% of Control
1	1	0	0.023	0.027	119%	100%
		0.5	0.025	0.021	85%	77%
		2	0.023	0.026	116%	96%
2	3	0	0.026	0.039	148%	100%
		0.5	0.025	0.015	80%	38%
		2	0.023	0.020	85%	50%

APPLICATIONS ON BROMACIL-IMPACTED SITES

- Hydrogen Peroxide with VTX catalyst (PVT)
  - No effect on bromacil concentrations
  - Mixing of components prior to application likely consumed oxidant
  - Additional pilot testing required to evaluate technology
  - Hazardous chemicals require specialized handling
  - Not typically applied at surface
  - Reagent cost \$135 m^{-3} (\$257 m^{-3} with earthworks)

APPLICATIONS ON BROMACIL-IMPACTED SITES

- Activated Carbon
  - No further bromacil reduction after 4 weeks
  - Bromacil not removed or destroyed - risk management
  - Achieving 74% reduction required excavation of soil and application of activated carbon to the entire soil mass
  - Other application methods
    - Surface broad casting and tilling
    - Surface slurry application
    - Injection
    - Permeable Reactive Barrier
  - Widely available with many service providers
  - \$53 m^{-3} (\$206 with earthworks)

APPLICATIONS ON BROMACIL-IMPACTED SITES

- Daramend®
  - Field testing not consistent with bench scale
  - Application rates and methods need further optimization
  - Achieving & maintaining required moisture logistically challenging
  - May not be effective on sites approaching Tier 1 levels
  - Further optimization and piloting required using different application methods
  - Daramend® cost $99 m-3 2% dosage rate ($185 m-3 with earthworks), $25 m-3 at 0.5% ($111 m-3 with earthworks)

PROJECT CONCLUSIONS

- Bromacil remains difficult to remediate
- No technologies achieved AB Tier 1 of 0.009 mg/kg
- Activated carbon effective as a risk management practice
  - Reduce off-site migration
  - Long-term sequestration
- Daramend® performance inconsistent with varying bromacil concentrations and soil types
  - Consider different application methods
- Emerging technologies need further testing
  - BOS 200+
  - Zero Valent Iron
- Testing done only on surface soils

QUESTIONS?