



SOIL STERILANTS PROGRAM: KNOWLEDGE SYNTHESIS, RECOMMENDED PRACTICES AND GAPS

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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 were bromacil and tebuthiuron.

This report provides lessons learned and a summary of the remaining knowledge gaps derived from the research projects undertaken through the 5-year Soil Sterilants Program. Recommendations arising from the Program include:

Improving sterilant identification and sampling

- To reduce overall site management costs, emphasize quality environmental sites assessments (ESAs) to inform conceptual site models (CSMs). This is required for both risk-based and remediation management approaches.
 - Leverage guidance and support tools to identify sites and areas on a site most likely to be impacted by sterilants. Assume sterilants could be present if site was operational prior to 2000, particularly in agricultural regions of Alberta.
 - Leverage best practices described herein and associated SSP documents to inform CSM through Phase 1 and 2 ESA.
 - Do not rely on vegetation assessments as indicators of sterilant presence/absence.
- Install groundwater monitoring wells in initial Phase 2 ESA; data is required for CSM's and in Tier 2 Risk Assessment approaches.
- Develop strong QA/QC program.
- Collect soil and water samples in a manner that reduces potential cross-contamination.
 - Focus on how and what to sample to manage costs rather than application of field screening technologies.

Improving detection and delineation of soil sterilants in soil and groundwater

- Phyto-accessible (soluble) analytical method may provide useful data and "line of evidence" when applying a Tier 2 risk assessment approach and the Freshwater Aquatic Life (FAL) pathway can be eliminated OR if immobilization technologies are being (or have been) applied as a management tool.
 - Demonstrate the difference between total (non-soluble and soluble) and phyto-accessible (soluble) concentrations to develop a site-specific guideline to accompany Phase 2 data.
- Use accelerated solvent extraction (ASE) for soil samples and the solid-phase extraction method with an Autotrace 280 SPE for water samples. Analyze the extractant by LC-MS/MS or LC-Orbitrap-MS when low-level precision and accuracy are essential to project success.



Improving risk assessment and management

- Compare Phase 1 and 2 ESA and CSM to Tier 1 Guidelines as a first step to determine management options.
 - Always plan to assess groundwater when bromacil or tebuthiuron are present; install groundwater monitoring wells during the initial Phase 2 ESA in areas representative of "worst-case" scenario.
- Exclude pathways where applicable and determine if additional site-specific non-chemicalspecific data (Db, foc, porosity, etc.) or chemical-specific parameters (half-life, Koc) would be beneficial for calculation of modified Guidelines through a Tier 2 approach.
 - Exclude FAL pathway if no surface water bodies are present within 300 m by (1) assessing the groundwater and monitoring sterilant plume characteristics; and (2) applying a conservative degradation half-life justified through literature or site-specific data.
 - Exclude Irrigation Water pathway if outside agricultural regions.
- Consider where the site is located and if agronomic or native species are intended for reclamation.
- To reduce risk to receptors, if equivalent land capability requires native grass species for reclamation consider using the alternate soil quality guidelines for Tier 1 ecological direct contact surface soil quality guidelines for fine-grained soil in non-commercial and non-industrial land uses.

Improving remediation (unless otherwise specified, the recommendations apply to both bromacil and tebuthiuron)

Sterilants within surface soil (≤ 0.5 metres below ground surface (mbgs))

- Conduct bench-scale tests with impacted soil to assess treatment application rates based on soil properties and Phase 2 ESA data for sterilant concentrations.
- Destructive and immobilization technologies must be applied in slurry form to optimize in-situ soil contact (recommended moisture content 80% of soil water holding capacity).
- Apply immobilization technologies (i.e., Activated Carbon) in-situ.
- For destructive remediation technologies excavate impacted soil for treatment in a constructed treatment cell (on- or off-site).
 - Construct treatment cell to enable impacted soil depth within the cell to be ≥0.6 m.
- Bromacil: In-situ Chemical Reduction (ISCR) technology DARAMEND[®]
 - Monitor soil moisture during treatment to maintain moisture conditions and reducing soil environment.
 - Activated Carbon
- Tebuthiuron:
 - In-situ Chemical Oxidation (ISCO) H₂O₂ with catalyst and surfactant (requires further investigation).
 - Activated Carbon



Sterilants at depths greater >0.5 mbgs in unsaturated soil

- Excavate un-impacted soil to expose impacted zone and store on-site for reclamation.
 - Excavate impacted soil and treat in a constructed treatment cell (on- or off-site) in the same manner as described above.

Saturated fine-grained till soils and groundwater impacted by sterilants

• Ex-situ – technologies and recommended practices described above apply.

Groundwater impacted by sterilants

• Applicable technologies for groundwater treatment described in Levy et al. (2021).



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GLOSSARY

Black Carbon

Carbon-rich material derived from incomplete combustion of vegetation and fossil fuels, as well as mineral weathering. Biochar and activated carbon are forms of black carbon.

Closure (Regulatory)

The written approval and acceptance by a regulatory authority of remediation work at or offsite of a property in connection with a release.

Community of Practice

A collection of individuals involved in various aspects of the management of sterilant impacted sites, including practitioners, industry representatives, researchers, and regulators.



Phyto-accessible

Amount of a contaminant that is available to affect vegetation (i.e., is soluble and not bound to soil particles).

Risk Assessment

In the context of the Soil Sterilants Program, risk assessment involves identifying appropriate risk model(s) and model parameters to develop screening guidelines for bromacil and tebuthiuron deemed to be protective of relevant pathways based on the contaminants' real-world fate and mobility in the subsurface under Alberta field conditions (Litalien et al., 2020).

Risk Management

The identification of risk and the application of control measures, such as remediation and exposure controls, to reduce or eliminate risks (*Alberta Risk Management Plan Guide*; AEP, 2017).

Risk Management Plan

A plan employing the use of exposure control to manage risks posed by one or more contaminants of potential concern within one or more areas of potential concern.

Tier 1 Guidelines

Alberta Environment and Parks, 2019¹. 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. <u>https://open.alberta.ca/dataset/842becf6-dc0c-4cc7-8b29-</u> <u>e3f383133ddc/resource/a5cd84a6-5675-4e5b-94b8-0a36887c588b/download/albertatier1guidelines-</u> <u>jan10-2019.pdf</u>

Tier 2 Guidelines

Alberta Environment and Parks, 2019¹. 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. <u>https://open.alberta.ca/dataset/aa212afe-2916-4be9-8094-42708c950313/resource/157bf66c-370e-4e19-854a-3206991cc3d2/download/albertatier2guidelines-jan10-2019.pdf</u>

AC	Activated Carbon
APEC	Area of Potential Environmental Concern
ASE	Accelerated Solvent Extraction
bgs	Below Ground Surface

¹ Most of the SSP reports referred to the 2019 Alberta Tier 1 Guidelines and Alberta Tier 2 Guidelines for bromacil and tebuthiuron guideline values. These guidelines were updated in 2022 (<u>https://open.alberta.ca/publications/1926-6243</u>), however none of the bromacil or tebuthiuron guideline values changed.



CSM	Conceptual Site Model
DSC	Direct Soil Contact
EPA	Alberta Environment and Protected Areas
ESA	Environmental Site Assessment
ELISA	Enzyme-linked Immunosorbent Assays
FAL	Freshwater Aquatic Life
foc	Fraction of Organic Carbon
GC/TID	Gas Chromatography / Thermionic Ionization Detector
GC/PID	Portable Gas Chromatography / Photoionization Detector
GWQG	Groundwater Quality Guidelines
HPLC-MS	High-performance Liquid Chromatography Coupled to Mass Spectrometry
ІСр	Inhibition Concentration
ISCO	In-situ Chemical Oxidation
ISCR	In-situ Chemical Reduction
IW	Irrigation Water
Kd	Distribution Coefficient
Кос	Organic Carbon Normalized Adsorption Coefficient
LC-MS	Liquid Chromatography Coupled to Mass Spectrometry
LC-MS/MS	Liquid Chromatography Coupled to Tandem Mass Spectrometry
LIBS	Laser-induced Breakdown Spectroscopy
mbgs	Metres Below Ground Surface
MDL	Minimum Detection Limit / Method Detection Limit
NAPL	Non-aqueous Phase Liquid
NIRS	Near Infrared Reflectance Spectroscopy
OIP	Optical Image Profiler
OM	Organic Matter
ORP	Oxidation Reduction Potential
PID	Photoionization Detector
PRB	Permeable Reactive Barrier
ssDNA MRE	Single-stranded DNA Molecular Recognition Element
SOP	Standard Operating Procedure
SPE	Solid-phase Extraction
SPLP	Synthetic Precipitation Leaching Procedure



SQG	Soil Quality Guidelines
SSP	Soil Sterilants Program
ТОС	Total Organic Carbon
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
v/v	Volume to Volume
XRF	X-ray Fluorescence
ZVI	Zero Valent Iron



1.0 INTRODUCTION

Soil sterilants were commonly used from the 1960s to late 1990s for non-selective vegetation control on industrial sites in Alberta. Sterilants are unique contaminants that pose challenges for traditional assessment and delineation, remediation, and risk assessment and management. In addition, common soil types and hydrogeology in Alberta contribute to challenges in the management of soil sterilants. Bromacil and tebuthiuron were identified as the primary sterilants of concern in Alberta based on a literature review (Drozdowski et al., 2018a), and stakeholder consultation (Drozdowski et al., 2018b). Common characteristics of these two sterilants are provided in Appendix A. Many impacted industrial sites are either starting to be decommissioned or stalled at the remediation phase resulting in delayed reclamation and certification. Soils treated with sterilants can become a source of contamination to adjacent land and waterbodies through leaching, surface runoff, and wind dispersion.

The Soil Sterilants Program (SSP), funded by government and industry, 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 or acceptable risk management for site owners.

This report provides learnings, recommended practices and a summary of the remaining knowledge gaps derived from the research projects undertaken through the 5-year Soil Sterilants Program in the areas of: (1) Identification and Delineation, (2) Risk Assessment and Management, and (3) Remediation (Figure 1). A report compiling the SSP research reports has been prepared (Powter and Drozdowski, 2025).



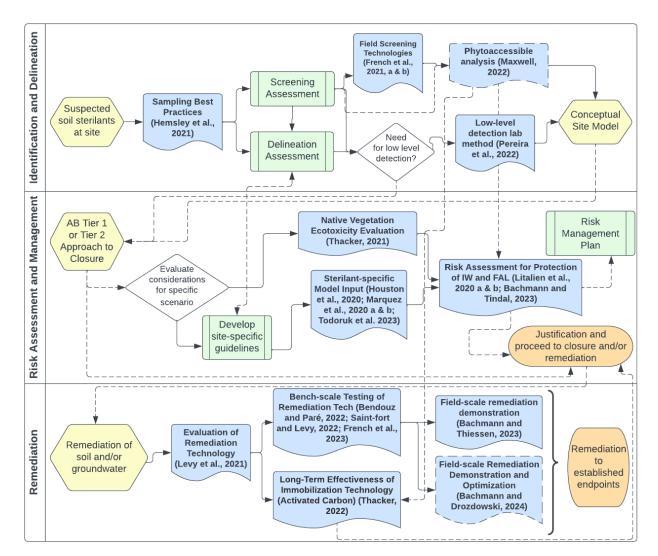


Figure 1. Research projects and interdependencies of projects undertaken through the Soil Sterilants Program in the areas of: (1) Identification and Delineation, (2) Risk Assessment and Management, and (3) Remediation. Note – blue shapes indicate projects and references generated from the SSP.



1.1 Applicable Regulatory Considerations

Alberta's environmental regulatory framework is outlined within the *Environmental Protection and Enhancement Act* (EPEA; Government of Alberta, 2000) and associated Regulations. All findings from the SSP are intended to be used in conjunction with this framework. The management of contaminated sites is guided through the *Contaminated Sites Policy Framework* (EPA, 2023) with support from the *Alberta Environmental Site Assessment Standard* (AEP, 2016a), *Alberta Tier 1 Soil and Groundwater Remediation Guidelines* (Tier 1 Guidelines) (AEP, 2022a), *Alberta Tier 2 Soil and Groundwater Remediation Guidelines* (Tier 2 Guidelines) (AEP, 2022b), *Alberta Risk Management Plan Guide* (AEP, 2017) and the *Alberta Exposure Control Guide* (AEP, 2016b). The Tier 1 Guideline values for bromacil and tebuthiuron are very low and in some cases are less than the current laboratory detection limits (Table 1 and Table 2).

Soil	Alberta Tier 1 Guidelines (Agriculture Land Use) ¹												
Sterilant	Soil (Coarse-grained; mg/kg)							Soil (Fine-grained; mg/kg)					
	Hum	cal Huma			nan	an Ecological							
	Direct Soil Contact	Domestic Use Aquifer	Direct Soil Contact	Freshwater Aquatic Life	Irrigation Water	Livestock Water	Direct Soil Contact	Domestic Use Aquifer	Direct Soil Contact	Freshwater Aquatic Life	Irrigation Water	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	
	 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. 												

Table 1.	Alberta Tier 1 soil guidelines for bromacil and tebuthiuron (agricultural land use).
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Table 2. Alberta Tier 1 groundwater guidelines for bromacil and tebuthiuron (agricultural land us

Alberta Tier 1 Guidelines (Agriculture Land Use) ¹												
Groundwater (Coarse-grained; mg/L)							Groundwater (Fine-grained; mg/L)					
Hur	man		Ecological			Human			Ecological			
Potable	Vapour Inhalation	Direct Soil Contact	Freshwater Aquatic Life	Irrigation Water	Livestock Water	Potable	Vapour Inhalation	Direct Soil Contact	Freshwater Aquatic Life	Irrigation Water	Livestock Water	
0.95	-	0.44	0.005	0.0002	1.1	0.95	-	0.30	0.005	0.0002	1.1	
0.66	-	0.20	0.0016	0.00043	0.13	0.66	-	0.25	0.0016	0.00043	0.13	
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2022 Alberta Tier 1 groundwater remediation guideline; BDL – below detection limit; groundwater as comparison to groundwater remediation guidelines necessary; **Bold** – lowest applicable guideline.

1.2 Alberta Context – Bromacil- and Tebuthiuron-impacted Sites

To enable a better understanding of sterilant presence, distribution and behaviour in field conditions in Alberta, interviews and a practitioner/industry survey of sites impacted by bromacil and tebuthiuron were conducted. The information was used to inform research priorities, experimental designs and ultimately to support sampling, risk management and remediation best practices.



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 collated by reviewing data from 51 sites currently or historically impacted by bromacil and/or tebuthiuron across Alberta (Table 3) (Houston et al., 2020; Todoruk et al., 2023). Earlier literature and consultation indicated there were thousands of sterilant impacted sites across Alberta (Drozdowski et al., 2018a, b) suggesting data from 51 sites was a reasonable sample size to generate data from.

Sixteen of the 51 sites were identified as having coarse-grained soils while the remainder were finegrained. Overall, bromacil and tebuthiuron concentrations were greater at depths greater than 1 mbgs. All sites with tebuthiuron also had bromacil as a co-contaminant; this complicates the risk management and remedial options since the two sterilants have distinct characteristics and properties and respond differently to treatment methods. Bromacil was absent from groundwater at sites with both coarse-grained (6 sites) and fine-grained (10 sites) soils, a range of hydraulic conductivities (10⁻⁶ to 10⁻⁹ m/s), and variable depths to groundwater (0.96 to 11 mbgs). Co-contaminants at sites where groundwater was unimpacted by sterilants were generally limited to chloride and/or metals or were not present. Conversely, organic contaminants were more prevalent at the sites where groundwater was impacted by sterilants. Collectively, these data suggest that the fate and transport of sterilants in the environment are complex processes and support the idea that biodegradation is an important consideration at sterilant impacted sites in Alberta.

Description	Bromacil	Tebuthiuron	
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	0.19 mg/kg to 3.0 mg/kg	0.48 mg/kg to 1.81 mg/kg	
Number of sites impacted (Groundwater impacted)	46 (27 sites)	10 (co-located with bromacil) (3 of 27 sites)	
Vertical separation between impacted soil and measured groundwater depth – 0 m (Groundwater impacted)	18 sites (14 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 (0 of 1 site)	
Vertical separation between impacted soil and measured groundwater depth – >5 m to 10 m (Groundwater impacted)	4 sites (1 of 3 sites)	None	

Table 3. Summary of bromacil and tebuthiuron impacts within coarse- and fine-textured soils.

Table adapted from Hemsley et al. (2021) with information from Houston et al. (2020) and Gainer and Todoruk (2023).

Table 4 summarizes sterilant distribution at Alberta sites (Drozdowski et al., 2018; Gainer and Todoruk, 2023; Houston et al. 2020; Levy et al., 2021).



Table 4. Summary information related to sterilant-impacted sites in Alberta.

	Summary Information						
•	Bromacil is the more prevalent sterilant. Co-contaminants are found at most sterilant-	 Majority of sites have sterilant impacts below surface and into shallow groundwater. 					
	 Co-contaminants are found at most sterilant- impacted sites. Sites often have both fine- and coarse-grained soils, with the majority dominated by fine- grained. 	Sterilant delineation is challenging and only					
•		 achieved approximately 50% of the time. Inactive and dormant sites may not be regularly monitored. 					
•	Vegetation impacts cannot always be used to identify sterilant impacts, as sites may be graveled.	• Surface soil can meet guidelines but sterilants at the same sites can be found deeper in the profile.					
•	Small soil 'hot spots' are often found across a site.						

1.3 Management Practices and Challenges Related to Sterilant-impacted Sites in Alberta

Literature review and consultation yielded the following information on historical and current activities related to management of sterilant-impacted sites in Alberta (Drozdowski et al., 2018a, b; Levy et al., 2021):

- Risk assessment (i.e., Tier 2 approaches including site specific risk assessment (SSRA)) and risk management (i.e., exposure control, administrative or engineering controls) were most often employed in sterilant management, followed by remedial excavation and disposal where risk could not be managed otherwise.
- Several remediation technologies have been trialed and used with varying degrees of success for management of sterilant-impacted sites, including, but not limited to, thermal desorption, activated carbon, permeable reactive barrier and/or pump and treat with chemical oxidants, and photocatalysis. A detailed evaluation of ex-situ and in-situ soil and water remediation technologies was completed by Levy et al. (2021) and technologies were categorized by proven, impractical, and potential application for management of sterilant-impacted sites.

High priority risk management and remediation challenges were identified through the literature review and consultation process and were used to identify research priorities and technology selection to inform best practices for sterilant impacted sites (Table 5; Levy et al., 2021). A key consideration for all scenarios identified is whether the primary goal is to address high concentrations to reduce risk, or lower concentrations to meet remediation endpoints. Technologies and management strategies should be selected according to the end goal. Given the heterogeneous distribution of sterilants on sites and unique conditions at most sites, a variety of approaches may be required at each site.



Table 5.High priority risk management and/or remediation challenges and technology
considerations.

High Priority Risk Management and/or Remediation Challenges	Considerations for Technology Application
Sterilants within surface soil (≤ 0.5 mbgs)	 Accessible via in-situ technologies. Validation of remediation endpoints required to assess applicability of Tier 1 or Tier 2 Guidelines.
Sterilants at depths > 0.5 mbgs in unsaturated soil	 Inaccessible to treatment at surface. Ideally the technologies to address deeper sterilants would function in-situ to minimize excavation of overlying soil.
Soil treatment requirements where sterilant destruction is required, and immobilization is not considered an acceptable option	• Technologies for this application could be in-situ <i>or</i> ex-situ.
Saturated fine-grained till soils and groundwater impacted by sterilants	 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.
Groundwater impacted by sterilants	 Technologies that can prevent off-site migration. Technologies that can treat impacts in-situ or ex-situ.



2.0 IDENTIFICATION AND DELINEATION

2.1 Problem Statement

Sterilant impacts are often widespread and difficult to detect due to the amount of time they have had to migrate therefore practitioners are uncertain about when and where to screen for soil sterilants, leading to unnecessary intrusive sampling following Phase I environmental sites assessments (ESA), excessive and/or uncertain analysis due to cross contamination (and associated cost), and identification of sterilants late in the assessment process that cause reclamation delays.

Additionally, analytical methods currently used in Alberta to characterize sterilants found in soil and/or water have variable detection limits, sometimes higher than guideline levels, and only provide total (soluble and non-soluble), rather than phyto-accessible (soluble), concentrations.

The SSP addressed these challenges through assessment of sampling practices and analytical technologies and methods (Figure 2).

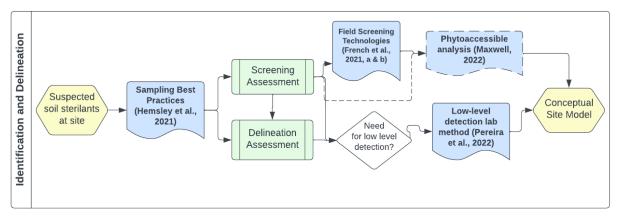


Figure 2. Identification and delineation projects.

2.2 Sterilant Identification and Sampling Best Management Practices

A sampling Best Management Practices report was prepared for practitioners involved in environmental site assessment or remediation and reclamation activities at sterilant-impacted sites (Hemsley et al., 2021). The document provides guidance on regulatory considerations, site evaluations, soil and groundwater characterization (e.g., soil sampling, groundwater sampling), and data evaluation and interpretation specific to bromacil and tebuthiuron. To ensure sterilants are effectively identified and delineated, the following should be considered when developing a sampling program:

- Site historical information and characteristics (e.g., age of site, likelihood of sterilant application, low-lying areas, slopes, soil classification, hydraulic characteristics).
- 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.
- Situations with 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 in a short distance.

The high potential for cross-contamination when sampling for sterilants requires special sampling techniques that address the low detection limits of bromacil and tebuthiuron analysis (Table 6). Specific considerations for identifying and delineating sterilants in Phase 1 and 2 ESAs are summarized in Figure 3.

General Guidance	Soil	Groundwater		
Take at least 1 field duplicate for every 10 samples and 1 trip blank per shipping container and 1 field equipment blank per day to	Start sampling the areas where you expect the lowest sterilant levels and work progressively towards the areas with the	Install groundwater monitoring wells to delineate suspected sources and impacts.		
confirm the presence or absence of cross-contamination during field activities, travel, or laboratory analysis for soils and groundwater.	highest expected sterilant levels.	Change sampling equipment between well development, purging and sampling.		
Collect and analyse decontaminated equipment rinsate to document the absence of cross-	Collect samples using a hollow stem auger with an 18" (45 cm) split barrel spoon with 6"	Obtain at least two groundwater samples on different days from any monitoring well.		
contamination.	(15 cm) x 2.5" (6 cm) stainless steel sleeves every 1.0 m down to a depth of 7.5 m or until bedrock. Collect at least 100 g for lab analysis.	Establish discrete monitoring points within different water bearing lithological units to avoid mixing of groundwater during drilling and sampling.		
Keep samples cool (around 4°C) and out of direct sunlight during transportation and storage.	Seal each soil-filled sleeve with Teflon [™] tape and plastic caps and submit directly to the laboratory for analysis.	Use low flow purging and sampling for shallow depths.		
Triple-rinse equipment using Liquinox and distilled water before each sample is taken.	Store soil samples in amber glass wide-mouth jars with Teflon [™] -lined lids.	Collect water samples in one-litre amber glass bottles and fill so there is no headspace.		

 Table 6.
 Sampling guidance for sterilant-impacted soil and groundwater.



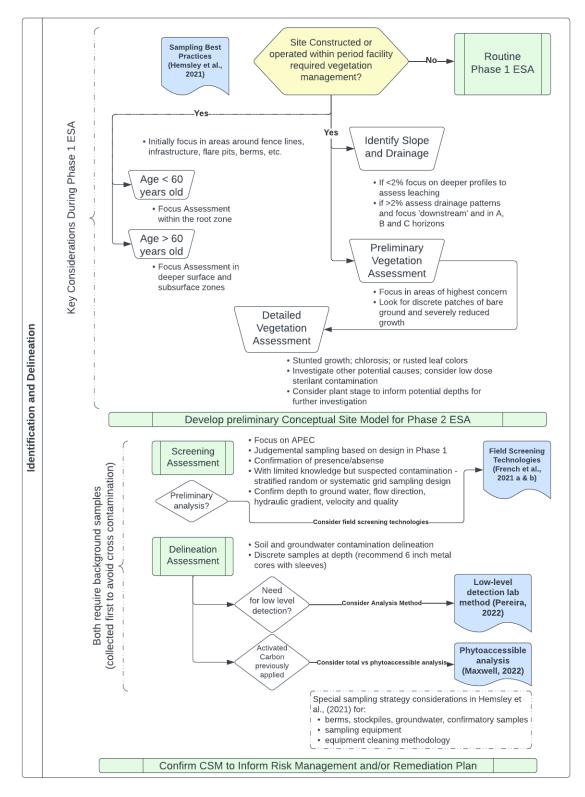


Figure 3. Considerations for identifying, assessing, and delineating sterilants. Information extracted from Hemsley et al. (2021); French et al. (2021a, b); Pereira et al. (2022); and Maxwell (2022).



2.3 Sterilant Detection and Analysis

2.3.1 Field Screening Technologies

Preliminary technologies for screening sterilants in the field were investigated to minimize the costs and timelines associated with identification, quantification, and delineation of bromacil and/or tebuthiuron in soil and/or water at impacted sites. A literature review, preliminary testing, and interviews completed in relation to the potential application of existing field screening technologies concluded that only two of the technologies evaluated were suitable for further testing. Technologies were evaluated based on their ability to detect bromacil or tebuthiuron in spiked silica sand or spiked distilled water, and the following technologies were recommended for further investigation and/or optimization (French et al., 2021a, b):

- X-ray fluorescence (XRF): potentially for bromacil in soil samples; and
- Raman spectroscopy: potentially for bromacil and tebuthiuron in soil and water samples.

Upon further study and evaluation, the detection limits and/or portability of the equipment make the technologies unsuitable for field screening for soil sterilants without further technology development and advancement. In addition, two biosensor technologies were investigated (ssDNA MRE and ELISA), both of which were deemed unsuitable for field screening of bromacil or tebuthiuron (French et al., 2021b). However, immunochromatographic assays with nanomaterials have been developed for portable monitoring and could be considered for development in field screening for bromacil. Table 7 provides a summary and recommendations for field screening technologies for bromacil and tebuthiuron investigated in the SSP.



Table 7.	Summary and recommendations for field screening technologies for bromacil and tebuthiuron investigated in SSP.
	From French et al. (2021 a, b).

Technology/Analysis	Technology Summary	Preliminary Testing Results
Ultraviolet laser induced	Uses ultraviolet laser to excite molecules of the compound of interest to produce fluorescence.	 UVOST detects bromacil-based Alligare 80 at 1,000 mg/L in water and tebuthiuron at 100 mg/L.
fluorescence (UVOST [®] or OIP [®])	 Usually used for non-aqueous phase liquids in a direct-push platform. Can be used in ex-situ samples. 	• Did not detect bromacil-based Hyvar XL.
	 Typically used for high concentration NAPLs and not dissolved phase contaminants. 	 Detection limits too high for field screening and refinement to target minimum detection limit (MDL) unlikely.
Visible light laser induced fluorescence	 Same technology as UVOST and optical image profiler (OIP) with a green visible wavelength. 	 Not successful at detecting bromacil or
(TarGOST [®] or OIP-G [®])	 Does not identify dissolved-phase compounds. Detects high molecular weight like coal tar and heavy crudes. 	tebuthiuron.
	 Uses near IR reflectance spectrometry to detect compounds. Scatter and absorption are unique to certain molecules. 	
Near infrared reflectance	 Non-destructive, portable, and can detect as low as ppb with previous confirmed bromacil detection. 	 Not successful at detecting bromacil or tebuthiuron at low level concentrations.
spectroscopy (NIRS)	 High water content soils interfere with readings. Can theoretically directly test water samples. Tebuthiuron may be detectible by NIRS, but not confirmed. 	
	 Uses the scattering and absorption of x-ray light to determine the chemical properties of a sample. 	 XRF successful in detecting bromacil at 100 mg/kg and tebuthiuron at
X-ray fluorescence (XRF)	 Non-selective and shows a spectrum of the relative amounts of components within a sample. 	1,000 mg/kg in spiked soil.Optimization for bromacil detection in
	 Detects at the ppm range and is not capable of extremely low detection limits. Has been used to identify foliar applied herbicides but not for bromacil and tebuthiuron. 	soil initially recommended.Detection limit too high and refinement to target MDL unlikely for tebuthiuron.



Technology/Analysis	Technology Summary	Preliminary Testing Results
MISA Raman spectroscopy	 Uses laser light scattering on molecules. Can be set up in lab or field for non-destructive testing of soil or water. Has been used to measure bromacil degradation in soil. No information on using it to detect tebuthiuron. 	 Successful in detecting bromacil at 100 mg/L in aqueous solutions with no extraction and 10 mg/L with chloroform extraction. Optimization may reach target MDL for this technology.
Laser-induced breakdown spectroscopy (LIBS)	 Uses high energy laser pulse to ionize and excite atoms in a sample that evaporates some of the sample in the production of plasma. The light from the plasma is analyzed to determine the chemical components of the sample. Appears that bromacil and tebuthiuron are in the range of identification of currently available LIBS instruments, but they have not been used specifically for these sterilants. 	 Not successful at detecting bromacil or tebuthiuron.
Gas chromatography/ thermionic ionization detector (GC/TID)	 No easily field deployable instrument is available for this technology. There are field trucks fitted with these instruments, but they are specialized vehicles designed for GC investigations. 	 No testing completed.
Portable gas chromatography/ photoionization detector (GC/PID)	 PIDs are suitable for volatile organic compounds. Bromacil and tebuthiuron are not volatile at ambient temperatures and PID instruments do not have bromacil or tebuthiuron as detectible compounds. GC has been used to determine bromacil and tebuthiuron in lab settings. There are no field-ready setups to detect these compounds. 	 No testing completed.
Single-stranded DNA molecular recognition element (ssDNA MRE)	 ssDNA aptamer for bromacil not reliable. Selected aptamer does not bind to bromacil. Aptamer approach could be viable, though new aptamer selection experiments would be required. 	 Not suitable for field screening.
Enzyme-linked immunosorbent assays (ELISA)	 Antibody test reliable and sensitive. The process requires multiple incubation and washing steps. Takes 4 hours in a typical assay. 	 Not suitable for field screening. Immunochromatographic assays with nanomaterials have been developed for portable monitoring and should be considered for development in field screening for bromacil.



2.3.2 Phyto-accessible Sterilants Analytical Method

Tier 1 Guidelines currently assume that the sterilants present in soil are always 100% accessible to plants under all conditions. However, sterilants adsorbed to the soil (organic matter, clay, or immobilization treatment technology) are not phyto-accessible, therefore using a phyto-accessible analytical method for analysing bromacil and tebuthiuron is more applicable as plants are the most sensitive receptor when considering the Direct Soil Contact (DSC) pathway (Stantec Consulting Ltd., 2008, 2012). Analyzing soil samples for total sterilant concentration precludes immobilization as a remedial method. Measuring phyto-accessible or soluble herbicide concentrations in soil rather than total concentrations can inform actual risk to susceptible receptors, confirming the validity of immobilization remediation technologies and resulting in less need for ex-situ soil treatment or landfilling.

Methods employed to assess total sterilant concentration use methanol as an extractant, which results in a measurement that does not differentiate between adsorbed and water-soluble fractions. A 0.01 M calcium chloride (CaCl₂) solution is often used to assess soluble (phyto-accessible) concentrations of nutrients and to conduct adsorption/desorption studies of metals and organics.

Maxwell (2022) used 0.01 M CaCl₂ as an extractant to estimate the phyto-accessible concentrations of bromacil and tebuthiuron in soil, demonstrating that phyto-accessible concentrations were approximately 50% *less than* total sterilant concentrations. The study also confirmed that soil organic matter is a significant naturally-occurring adsorbent of bromacil and tebuthiuron resulting in reduced phyto-accessibility. Adsorbed bromacil and tebuthiuron increased with increased organic matter but not with increased clay content. Thacker (2022) investigated use of the phyto-accessible method compared to total sterilant analysis in conjunction with sterilant immobilization experiments in topsoil and silica sand with and without amendment with activated carbon. The phyto-accessible sterilant fraction was lower than the initial, total sterilant concentration in soil, except for one treatment in unamended soils (Figure 4A). The phyto-accessible fraction in soils amended with activated carbon was much lower compared to the non-amended soil, indicating that the sorption of sterilants to activated carbon reduced phyto-accessibility (Figure 4B).

Site-specific conceptual models can be informed by the conclusions from Maxwell (2022) [and Thacker, 2022] to manage bromacil and tebuthiuron soil impacts in-situ with activated carbon.

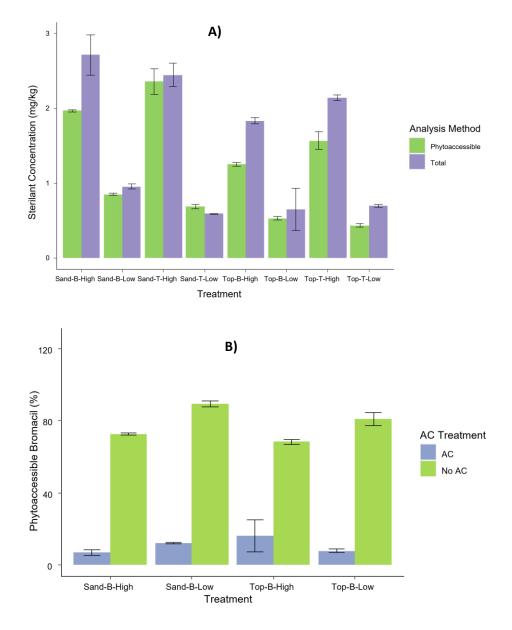


Figure 4. Total and phyto-accessible sterilant concentrations and the effect of activated carbon on phyto-accessible sterilant levels.

A) Sterilant concentration (mg/kg) in topsoil and silica sand, without activated carbon (AC) amendment, determined by either phyto-accessible or total sterilant analysis.

B) phyto-accessible bromacil (%) in topsoil and silica sand, either amended with activated carbon (AC), or non-amended. Bars represent means and error bars indicate the standard error.

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).

From Thacker (2022).

2.3.3 Low-level Laboratory Analytical Method

Analytical methods related to total sterilant concentrations in Alberta 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 academic research between 1984 and 2020 also used the same analytical techniques, however in later years methods 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. However, despite advances in both analytical and extraction methods, detection limits in commercial laboratories are still very near Tier 1 Guidelines (AEP, 2022a) and results often vary between laboratories.

Development of test methods to increase the effectiveness and efficiency in laboratory analytical methodologies for detection of total bromacil and tebuthiuron focused on two components of the chemical measurement process: optimization of extraction approach and instrumentation (Pereira et al., 2022). New analytical methods for analysis of bromacil and tebuthiuron using reverse-phase liquid chromatography paired with either a linear ion trap-Orbitrap mass spectrometer or a triple quadrupole mass spectrometer were successfully developed and validated with detection limits between two and three orders of magnitude lower than available through commercial laboratories. Specific details associated with the revised, low level analysis methods can be found in Pereira et al. (2022). Table 8 provides a comparison of the methods and associated detection limits.

Laboratory Method	Bro	macil	Tebut	hiuron		
	Soil/Sediment Water		Soil/Sediment	Water		
Commercial Laboratory Extraction Method	99% methanol Dichloromethan methylene chloride**		99% methanol	Dichloromethane, methylene chloride**		
Commercial Laboratory Detection Method	High performance liquid chromatography with ultraviolet detection (HPLC-UV), high performance liquid chromatography coupled to mass spectrometry (HPLC-MS), gas chromatography coupled to mass spectrometry (GC-MS)					
Commercial Laboratory Detection Limit*	>5 μg/kg	≥ 0.1 µg/L	≥ 5 μg/kg	≥ 0.1 µg/L		
Tier 1 Guideline	9 μg/kg	0.2 μg/L (IW)	46 µg/kg	0.43 μg/L (IW)		
Low Level Extraction Method***	ASE	SPE	ASE	SPE		
Low Level Detection Method	n Method Reverse-phase liquid chromatography paired with either a triple quadrupole mass spectrometer (LC-MS/MS) or a linear ion trap-Orbitrap mass spectrometer (LC-Orbitrap-MS)					
LC/MS (LC-MS/MS)	0.013 µg/kg	0.0001 μg/L	0.003 µg/kg	0.000004 μg/L		
LC-Orbitrap-MS	0.032 μg/kg	0.00006 μg/L	0.006 μg/kg	0.000004 μg/L		

Table 8.Summary of laboratory extraction and detection methods for analysis of bromacil and
tebuthiuron in soil and water.

* Varies based on detection method; ** Varies based on the laboratory; ***ASE = Accelerated Solvent Extraction; SPE = Solid-Phase Extraction

Use of low-level soil/sediment sample extraction (accelerated solvent extraction (ASE)) and water sample extraction (solid-phase extraction (SPE)) coupled with LC/MS or LC-Orbitrap were able to achieve detection limits between two and three orders of magnitude lower than available through commercial laboratories. However, the cost of the extraction and analysis is significantly higher due to the additional equipment required and may not be warranted. Detection limits for bromacil and tebuthiuron were improved by both the revised sample preparation and extraction methods and the analytical instruments used. Depending on the sterilant concentrations at a site relative to the laboratory method detection limit different analytical approaches could be applied (Table 9). A study to assess the benefits of the sample preparation and extraction methods with conventional analytical instruments to determine if better precision and accuracy could be achieved to assess impacts near Tier 1 limits more cost effectively is recommended.

Sterilant Impacts	Analytical Need	Method Available	Method Possible √	
Sterilant concentrations well above Tier 1 limits	Method with MDL* near Tier 1 limit (Same Order of Magnitude [OoM])	Most commercial laboratory services		
Sterilant concentrations near Tier 1 limits (within same order of magnitude)	1 limits (within same More refined precision and		ASE or SPE coupled with conventional analytical instruments (HPLC-UV, HPLC-MS, or GC-MS)	
Sterilant concentrations below Tier 1 limits (greater than one order of magnitude)	Method with MDL as low as possible (maximum OoM less than Tier 1)	InnoTech Alberta (ASE or SPE coupled with LC-MS/MS or LC-Orbitrap-MS)	v	

Table 9. Applicable analytical methods based on required Method Detection Limit.

*Method detection limit

2.4 Knowledge Gaps and Recommended Practices

Remaining and/or new knowledge gaps associated with identification and delineation of soil sterilants that would support more effective management of sites impacted by soil sterilants include:

- Field Screening Technologies
 - Use of X-ray fluorescence (XRF) for detection of bromacil in soil samples in the field and Raman spectroscopy for bromacil and tebuthiuron in soil and water samples in the field would significantly reduce delineation costs and timelines for remediation and reclamation. Technologies are currently either too difficult or time consuming to use effectively in the field or not sensitive enough to inform meaningful decisions. Further research and development in low-level, portable detection technologies would be beneficial for more effective identification and delineation of sterilant impacted sites.
- Analytical Methods
 - To ensure acceptance of the phyto-accessible (soluble) detection method further investigation is required to
 - correlate phyto-accessible sterilant levels with vegetative survival and growth, and

- test a broader range of soil clay (Maxwell (2022) used soil clay contents ranging from 16% to 18%) and organic contents.
- The low-level analytical method investigated through the SSP indicated that lower detection levels could be accomplished using conventional analytical equipment if an alternative extraction method was utilized. Further investigation is required for confirmation followed by an interlaboratory study and proficiency testing.

Table 10 provides a summary of recommended practices for effective identification, detection and delineation of bromacil and tebuthiuron in soil and groundwater.

Site Management Stage	Recommended Practices
Sterilant identification and sampling	 To reduce overall site management costs, emphasize quality environmental sites assessments (ESAs) to inform conceptual site models (CSMs). This is required for both risk-based and remediation management approaches. Leverage guidance and support tools to identify sites and areas on a site most likely to be impacted by sterilants. Assume sterilants could be present if site was operational prior to 2000, particularly in agricultural regions of Alberta. Leverage best practices described herein and associated SSP documents to inform CSM through Phase 1 and 2 ESA.
	 Do not rely on vegetation assessments as indicators of sterilant presence/absence.
	 Install groundwater monitoring wells in initial Phase 2 ESA; data is required for CSM's and in Tier 2 Risk Assessment approaches.
	Develop strong QA/QC program.
	 Collect soil and water samples in a manner that reduces potential cross-contamination. o Focus on how and what to sample to manage costs rather than application of field screening technologies.
Detection and delineation of soil sterilants in soil and groundwater	 Phyto-accessible (soluble) analytical method may provide useful data and "line of evidence" when applying a Tier 2 risk assessment approach and the Freshwater Aquatic Life (FAL) pathway can be eliminated OR if immobilization technologies are being (or have been) applied as a management tool. Demonstrate the difference between total (non-soluble and soluble) and phyto-accessible (soluble) concentrations to develop a site-specific guideline to accompany Phase 2 data.
	 Use accelerated solvent extraction (ASE) for soil samples and the solid-phase extraction method with an Autotrace 280 SPE for water samples. Analyze the extractant by LC-MS/MS or LC-Orbitrap-MS when low-level precision and accuracy are essential to project success.

 Table 10.
 Recommended practices associated with effective identification and delineation of bromacil and tebuthiuron.

3.0 RISK ASSESSMENT AND MANAGEMENT

3.1 Problem Statement

Under Alberta's framework for the management of contaminated sites (EPA, 2023) three options exist: Tier 1, Tier 2, and exposure control. Where Tier 1 takes 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. 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 (IW) and freshwater aquatic life (FAL) pathways. EPA's risk assessment model considers partitioning of solutes, unsaturated transport, groundwater mixing, and lateral transport. With Tier 2 Guidelines, some site-specific factors can be included but are still limited which may result in overly conservative guidelines.

Specific challenges as they relate to application of these Guidelines to bromacil and tebuthiuron include:

- The values of the irrigation water (IW) and freshwater aquatic life (FAL) soil and groundwater guidelines calculated under the current Alberta Tier 1 framework (AEP, 2022a) are lower than the corresponding ecological direct contact guidelines and in some cases are below current analytical detection limits.
- The current Alberta Tier 1 guideline document does not include a value for degradation half-life for either bromacil or tebuthiuron. The lack of a degradation half-life is a major challenge to the overall management of these sterilants.
- Sterilant toxicity data for Alberta native plant species is incomplete or missing.

The SSP addressed these challenges through a thorough investigation of applicable risk models and input parameters applicable to soil sterilants (Figure 5).

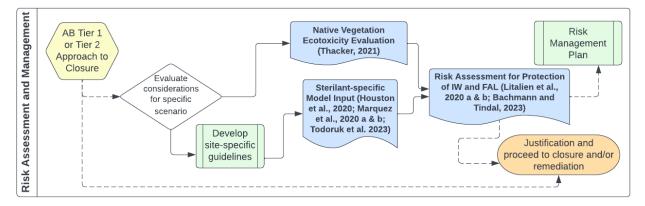


Figure 5. Risk assessment and management projects.

3.2 Risk Assessment Modelling

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 (Litalien et al., 2020). 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 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 objective of analysis and experimentation in the SSP 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 and better reflect the contaminants "real-world" fate and mobility in the subsurface under Alberta field conditions.

Risk assessment 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 Tier 2 Guideline calculations for site closure are required. Remedial endpoint (i.e., guideline) modification using the available Alberta Tier 2 risk assessment models (AEP, 2022a, b) to develop Tier 2 Soil and Groundwater Remediation Guidelines (AEP, 2022b) can be an effective and relatively inexpensive approach to site management when sterilants are present. The intent of Tier 2 Guidelines is to provide a level of protection equivalent to Tier 1 Guidelines. 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 (Litalien et al., 2020a; Marquez et al., 2019).

The Tier 1 guidelines use the Domenico and Robbins groundwater transportation model (Domenico model; Domenico, 1987; Domenico and Robbins, 1985) which 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. The Tier 1 and 2 model for calculating soil guidelines protective of the IW and FAL pathways is comprised of four dilution factors (DF) including:

-	
DF1	 Represents partitioning of the contaminant between soil, pore water, and soil vapour. Considers how a contaminant may sorb to soil organic matter and mineral soil particles.
DF2	 Represents the ratio of the concentration of the contaminant in porewater at the source to that of the porewater just above groundwater.
	 Includes dilution due to biodegradation and dispersion as the contaminant moves down through the soil profile.
	• Equal to 1 in Tier 1 (assumed source of contamination extends to shallow groundwater).
DF3	 Represents the ratio of the concentration of the contaminant in porewater just above groundwater to the concentration in groundwater.
	 Addresses mixing between vadose zone pore water and groundwater.
DF4	• Represents the dilution that occurs due to dispersion and biodegradation as groundwater travels downgradient from the source to a receptor.
	• Calculated based on assumption that distance between source and FAL receptor is 10 m in Tier 1.

For Tier 2 guideline adjustments, some site-specific factors can be included but are limited, which may result in overly conservative guidelines for application to Alberta sites. Additional research and analysis were required to inform Tier 2 Guideline modifications and calculations that are acceptable to regulators and more realistically reflect Alberta-specific field conditions and are protective of receptors:

• Undertake sensitivity analysis to determine key model input parameters influencing soil and groundwater Guidelines for bromacil and tebuthiuron.

- Conduct laboratory experiments using Alberta field soils to measure half-life under varying conditions and estimate soil organic-carbon partition coefficients (Koc) for bromacil and tebuthiuron.
- Evaluate alternative models that could adjust IW and FAL pathways for bromacil and tebuthiuron.
- Review literature to identify degradation mechanisms and associated metabolites for bromacil and tebuthiuron to inform analytical methods and risk evaluation.

This information is also useful and applicable for Tier 2 Site Specific Risk Assessment data collection.

3.2.1 Model Sensitivity Analysis

Domenico model sensitivity analysis included several model input parameters to evaluate the effects on soil and/or groundwater guidelines (Marquez et al. 2020a, Todoruk et al., 2023). Modifications to the input parameters leading in changes to the resulting guidelines of at least 10-times, 5- to 10-times, and 1- to 5-times were considered to have a significant, moderate, and limited influence, respectively. Key findings from the sensitivity analysis are summarized in Table 11 and included:

- The Domenico model has higher sensitivity to half-life, fraction of organic carbon (foc; in both fine- and coarse-grained soil), and infiltration rate (in coarse-grained soil) than other parameters, especially at the lower end of the ranges assessed (Marquez et al., 2020a).
- The half-life and infiltration rate inputs into the model that influenced resulting guidelines are directly related to the modelled geometric and flow parameters that could vary across sites.
- Within the model, higher dilution factors correlate directly to higher guideline values. Organic carbon-water partitioning coefficient (Koc) in the model is influenced by foc and half-life. The analysis indicates that the model has moderate sensitivity to Koc, with potential dilution increasing linearly as values increase and foc may influence the overall dilution factors, however, the sensitivity to these parameters is interdependent.
- The model did not show high sensitivity to soil bulk density which directly calculates total porosity, vapour filled- and moisture-filled porosity in the model in the absence of site parameter data. Soil moisture and particle density are modifying factors for bulk density and the estimated porosities and should be further evaluated to refine the model.
- Half-life was generally a sensitive parameter at the lower ends of the included ranges with the largest variation in dilution factors within the 0.25- to 4-year half-life range. The trends observed in outcomes were similar between coarse- and fine-grained soils. Half-life is generally considered to have a significant influence on soil and groundwater guideline outcomes.

	Bromacil (Coarse)				Tebuthiuron (Coarse)					
	Half Life (years)	foc (g/g)	Koc (mL/g)	Dry Bulk Density (g/cm³)	Infiltration Rate (m/yr)	Koc (mL/g)	foc	Koc (mL/g)	Bulk Density (g/cm³)	Infiltration Rate (m/yr)
DF1	ø	↑ with increasing foc	↔ with increasing Koc	\checkmark	Ø	ø	↑ with increasing foc	↔ with increasing Koc	\checkmark	Ø
DF2	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø	Ø
DF3	Ø	Ø	ø	Ø	↑ at low rates	Ø	Ø	ø	Ø	↑ at low rates
DF4	↑ impact at lower half-life range	↑ with increasing foc	↔ with increasing Koc	\checkmark	Ø	↑ impact at lower half-life range	↑ with increasing foc	↔ with increasing Koc	\checkmark	Ø
Range Tested	0.25 to 64	0 to 6	4 to 157	1.0 to 2.0	0.001 to 0.5	0.25 to 64	0 to 6	4 to 157	1.0 to 2.0	0.001 to 0.5
Default Tier 1	1,000,000	0.005	66.6	1.7 (coarse); 1.4 (fine)	0.006 (coarse); 0.012 (fine)	1,000,000	0.005	23	1.7 (coarse); 1.4 (fine)	0.006 (coarse); 0.012 (fine)

Table 11.Degree of influence of various parameters on dilution factors within the Domenico Robbins groundwater model for calculating Tier 1
Guideline modifications and Tier 2 Guidelines in coarse-textured soils.

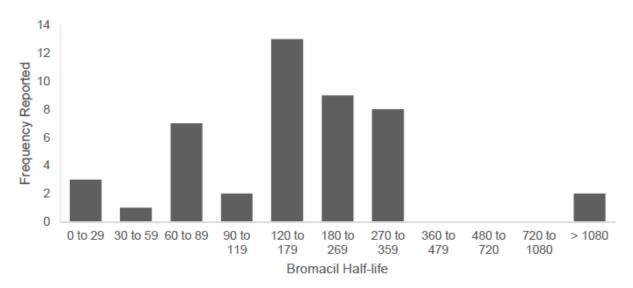
DF1 – soil-leachate partitioning; DF2 – transport through unsaturated zone; DF3 – groundwater mixing; DF4 – lateral transport through saturated zone; foc = fraction of organic carbon; Koc = water-organic carbon partition coefficient

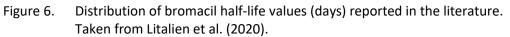
 \emptyset indicates no influence; \uparrow indicates significant influence; \leftrightarrow indicates moderate influence; \downarrow indicates limited to no influence

3.2.2 Guideline Calculation for Irrigation Water and Freshwater Aquatic Life Pathways

Water quality guidelines in Canada, 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 (Litalien et al., 2020). A review of the applicable guidelines (Litalien et al., 2020) indicated:

- The CCME water quality guideline for Protection of Aquatic Life (CWQG-PAL) for both bromacil (5.0 μg/L) and tebuthiuron (1.6 μg/L) was used to develop the Alberta Tier 1 surface water guideline for the FAL pathway.
- The CCME water quality guideline for the protection of agricultural water uses (CWQG-IW) for both bromacil (0.2 μg/L) and tebuthiuron (0.27 μg/L) was used to develop Alberta Tier 1 surface water guideline for the IW pathway.
- Reported toxicity values for several algal and crop species are on the same order of magnitude as the current Alberta surface water quality guideline for bromacil and tebuthiuron suggesting that FAL and IW surface water quality guideline values are not overly conservative, when applicable (see Litalien et al. (2020) for a summary of the literature).
- The 2019 update to the Alberta Tier 1 Guidelines included a time cap consideration on lateral groundwater transport. The influence of the 500-year transportation cap on the soil quality guidelines for the protection of the FAL pathway was investigated and found to have no impact on Guidelines for either fine- or coarse-grained soils.
- The EPA Tier 1 (2023) guidance document does not indicate a half-life, or degradation rate for bromacil or tebuthiuron resulting in an assumption that the chemical does not degrade and the default factor in the model is 1,000,000 years.
- Although bromacil half-life is highly variable in the literature, ranging from 14 to 1,494 days there is strong evidence to suggest that degradation does in fact occur (Litalien et al., 2020). Of the 42 sources reviewed, ten sources reported half-lives of less than 90 days; 30 reported halflives between 6 months and 1 year; and the most cited half-lives ranged between 120 days and 180 days (Figure 6).
- Although most of the data were generated from experiments conducted under standard laboratory conditions or in field studies conducted in tropical regions, the data confirms degradation occurs.
- Incorporation of a half-life into Tier 2 Risk Assessment Guideline derivation allows for both the FAL and IW pathway guidelines to be raised above laboratory detection limits for bromacil and tebuthiuron.





3.2.3 Sterilant-specific Model Input Data

Laboratory studies were developed to refine two of the model input parameters considered sensitive: half-life and partition coefficients for each sterilant (Houston et al., 2020).

3.2.3.1 Half-life Estimation

To estimate half-life, coarse- and fine-grained uncontaminated Alberta soils were spiked with bromacil and tebuthiuron and evaluated in a series of microcosms in varying saturated conditions over 105 weeks (2 years) (Todoruk et al., 2023). Variables included concentration of sterilants (high versus low); weathering (fresh versus aged); presence / absence of chloride; mass / volume of the sample; and source of formulation (Table 12).

Treatments/ Parameters	Description and Justification for Treatment/Parameter		
Soil type	Coarse- and fine-grained soil.		
Contaminant	 Bromacil (Hyvar[®] X-L) and Tebuthiuron (Spike[®] 80DF). 		
Commercial Formulation	• To identify whether differences in degradation rates were observed with a commercial formulation as compared to laboratory standards, a "commercial formulation" treatment in coarse-grained soil was added.		
	 The high concentration was intended to conservatively reflect fresh application rates (Bromacil – 10 mg/kg; Tebuthiuron – 4 mg/kg). 		
Concentration	 The low concentration was intended to reflect weathered concentrations without accounting for changes in bioavailability that may accompany weathering (Bromacil – 2 mg/kg; Tebuthiuron – 0.9 mg/kg). 		

Table 12.
Table 12.

Treatments/ Parameters	Description and Justification for Treatment/Parameter		
Weathering / Aging	 Bromacil contamination is reflective of unweathered and weathered conditions. Unweathered treatments were spiked with known concentrations of bromacil. Soils from a site with field-weathered bromacil were included. Field-weathered tebuthiuron-impacted soils were not included as sites were not identified where tebuthiuron was the only contaminant of concern in soils. 		
Salinity	2,500 mg/kg chloride (similar order of magnitude to chloride levels found in Houston et al. (2020)).		
Mass / Volume	 To identify whether the mass of soil and volume of incubation jar influenced degradation rates, a "bulk incubation" treatment in coarse-grained soil was added to the experiment. The bulk incubation setup had the same ratio of soil volume to headspace volume as the primary experiment (one replicate). 		
Soil Moisture	 Intended to be reflective of Alberta subsoil conditions – suboptimal moisture percentages were selected (12% for fine-grained; 7% for coarse-grained) 		
Temperature	 Intended to be reflective of Alberta subsoil conditions – experimental conditions were maintained at 5°C. 		
Controls	Unspiked for bromacil and tebuthiuron for each soil type.		

Key findings from the study were:

- Data analysis and visualization of the experimental half-life data indicated degradation of bromacil and tebuthiuron was generally limited under the experimental conditions investigated (i.e., cool temperatures (4 to 5°C; fine-grained soil or coarse-grained soil; high or low concentrations), though did occur.
- A significant *decrease* in sterilant concentrations was found for *bromacil* in the *low concentration* (2 mg/kg) treatment in combination with *fine soil*, although the effect size was minimal, and the overall results imply **very slow degradation**.
- When initial *bromacil* concentrations were *high* (10 mg/kg) no meaningful signal of degradation can be estimated from the measured data for either *fine- or coarse*-textured soil.
- No meaningful signal of degradation can be estimated from the measured data for *tebuthiuron* in either concentration or soil treatment.

Limited, or slow degradation, for soil sterilants is aligned with the literature. Litalien et al. (2020) conducted a literature review and sensitivity analysis on bromacil and tebuthiuron half-lives. While over 50 peer reviewed papers report on the dissipation, migration and or half-lives of sterilants, only a limited number of the studies were from temperate climates or under controlled temperatures in the lab, and the majority were conducted on surface soil (i.e., <1.5 m below ground surface). According to the literature reviewed by Litalien et al. (2020), bromacil half-lives from the relevant studies ranged between 60 and 270 days with cooler temperature, drier climates, and higher soil organic carbon content having been noted as major drivers resulting in slower degradation. This is aligned with the experimental results from the half-life experiments which demonstrated slow degradation under cool temperatures.

Similarly, half-lives reported in the literature for tebuthiuron are variable ranging from days to >8 years, with the majority reported as less than 1 year with significant influences from temperature and annual precipitation. Few studies are available with directly applicable degradation estimates or half-lives for

tebuthiuron in northern climates, though the data available does confirm degradation occurs, albeit slowly.

The EPA Tier 1 (2023) guidelines are based on a highly conservative approach which does not indicate a half-life, or degradation rate for bromacil or tebuthiuron (defaults to > 1,000,000 years) resulting in soil quality guidelines for FAL and IW pathways below laboratory method detection limits. Inclusion of a half-life for bromacil and tebuthiuron has meaningful impacts on the Soil Quality Guidelines for the FAL and IW pathways, while still ensuring the appropriate level of protection to receptors, particularly when initial soil concentrations are low. Although the estimated half-lives observed in the laboratory experiments are subject to uncertainties, when combined with literature data and field observations, there is weight of evidence to suggest that a half-life, however conservative, should be included in Tier 2 Guideline development. Based on these results, the following is recommended:

- When sites are identified with **fine-textured soils** and **low initial starting concentrations** of **bromacil** (~2 mg/kg) a conservative half-life value could be applied when using a Tier 2 Risk Assessment approach.
 - A half-life of 10 years is recommended for Tier 2 applications under specific site conditions (i.e., fine-textured soils with low initial concentrations of bromacil). A value of 10 years provides a conservative degradation rate based on experimental results for low initial concentrations and is greater than half-lives reported in the literature under all environmental conditions.
 - Additional experimentation is recommended to refine degradation rates for inclusion in Tier 2 risk assessment, particularly for tebuthiuron. Further study is required to determine the initial concentration recommendations for bromacil and tebuthiuron in coarse- and finetextured soils.

3.2.3.2 Partition Coefficients

The 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 with a value less than 100 indicating that a compound is very mobile (Branham et al., 1995). The current EPA Tier 1 document includes Koc values of 66.6 mL/g and 23 mL/g for bromacil and tebuthiuron, respectively. These values are sourced from the Oak Ridge National Laboratory Risk Assessment Information System which in turn uses values from the US EPA EPI (Estimation Programs Interface) Suite. Thus, the Koc values used in the EPA Tier 1 guidelines are based on chemical estimation methods, rather than on measured data. Accordingly, a program was initiated to measure the Koc for these two chemicals.

A modified Tier 2 OECD #106 [*Guideline for the Testing of Chemicals: Adsorption-Desorption Using a Batch Equilibrium Method*] assessment, utilizing three soils rather than five, was used to develop adsorption isotherms based on the organic carbon content of uncontaminated Alberta subsoils (Bachmann and Tindal, 2023b). Measured parameters in the laboratory study conducted included water-organic carbon partition coefficient (Koc) and sorption distribution coefficient (Kd) for bromacil and tebuthiuron in soils with variable texture and total organic carbon (TOC) (Table 12) (Bachmann and Tindal, 2023b).

Study results indicated:

• Sorption of bromacil and tebuthiuron is complex and dependant on multiple factors.

- Adsorption of bromacil was higher in all three soils investigated experimentally than tebuthiuron, as expected based on published Koc values and chemical formula.
- Greater adsorption occurred in fine-grained soil compared to coarse-grained soil which may be attributable to higher organic carbon measured in the fine-grained soils and/or lower porosity that can restrict migration of organic contaminants.
- Experimental data were inconclusive to inform defensible Koc values for bromacil and tebuthiuron in Alberta coarse- and fine-textured soils. However, further investigation or experimentation to confirm Koc's relevant to the Alberta context is not recommended based on further literature and model sensitivity analysis:
 - The Koc value for bromacil (66.6 mL/g) used in the development of bromacil Tier 1 screening guidelines using the Domenico model (AEP, 2019) is slightly higher than the most cited value range (30 to 40 mL/g) (Litalien et al., 2020). The soil quality guideline for the protection of the FAL pathway is moderately sensitive to changes in Koc's for Bromacil, however the IW pathway was not very sensitive.
 - The Koc value for tebuthiuron (23 mL/g) used in the development of Tier 1 screening guidelines is less than the most cited value (80 mL/g) (Litalien et al., 2020) in the literature.
- Finer textured and higher TOC soils had higher distribution coefficients (Kd values) than coarsetextured and low-TOC soils for both sterilants; Kd values were consistent with sterilant concentrations in the soil.
 - Insufficient data was generated through experimentation to inform defensible recommendations for sorption coefficients in guideline calculations. Further investigation is recommended both through literature review of Kd/Foc relationships and experimentation.

3.2.4 Alternative Model Evaluation

Alternative risk models were evaluated that could be used to derive soil and groundwater guidelines for bromacil and tebuthiuron that would be both protective of the irrigation water (IW) and freshwater aquatic life (FAL) pathways (Litalien et al., 2020). 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. Results of the analysis indicated that none of the models reviewed could effectively replace all elements of the Tier 2 model however they could be useful supplements:

- 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.
 - Groundwater quality guidelines (GWQGs) and soil quality guidelines (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 alternative 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 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. 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.
 - Soil Quality Guidelines (SQGs) for the IW pathway produced by the model were similar if slightly more conservative than those of the Tier 2 model.
 - Given the similarity of the results to the Tier 2 model coupled with 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 (e.g., surface runoff) and thus sites where these factors vary significantly from the typical conceptual site model could benefit from the application of this model.
- 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 (including upward and downward migration, solute accounting between soil, water, and gas phases, as well as advanced water balances) that could be of interest on a site-specific basis.
 - SQGs for the IW pathway were approximately twice as conservative as those of the Tier 2 guidelines.

3.2.5 Degradation Mechanisms and Metabolites

A literature review investigating mechanisms and resultant metabolites of aerobic biodegradation, anaerobic biodegradation, and metabolism by flora and fauna was completed to identify degradation processes and metabolites of bromacil and tebuthiuron in soil (Marquez et al., 2020b). The purpose of generating a better understanding of degradation process and mechanisms and potential metabolites was to use the information for potential field screening technologies and to inform risk management and remediation plans or monitoring activities targeting exposure pathways for which risks are predicted. For example, if metabolites could be identified, it could be demonstrated that degradation is occurring, providing lines of evidence for risk management strategies. Findings included:

- Nine bromacil and eight tebuthiuron degradation products and their associated degradation processes were identified from laboratory studies (Appendix B).
- No chemical-specific information related to the metabolites was identified (e.g., relevant toxicity data).
- 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, as well as their metabolites, were characterized as having low soil 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 may occur more rapidly than in soil based on laboratory estimated half-lives.
- Metabolites were not identified in samples analyzed from the half-life or Koc experiments.

3.3 Sterilant Toxicity to Native Plants

Ecological direct contact guidelines for soil sterilants in the Tier 1 Guidelines have been developed using agronomic species which may differ in their sensitivity to soil sterilants compared to native species. Toxicity of bromacil and tebuthiuron to typical Alberta native grassland vegetation species can be used to develop revised direct soil eco-contact guidelines for non-agricultural areas of the province.

Toxicity tests were conducted in a greenhouse study using modified Environment Canada test methods with various native grass species (northern wheatgrass (*Agropyron dasystachyum*), blue grama (*Bouteloua gracilis*), plains rough fescue (*Festuca hallii*), June grass (*Koeleria macrantha*), green needle grass (*Nassella viridula*), and Western wheatgrass (*Pascopyrum smithii*)) exposed to either bromacil or tebuthiuron in soil sourced from the brown soil zone in Alberta (Thacker, 2021). The study only focused on fine-textured soil, therefore no recommendations were made for coarse-textured soils.

Generally, the species tested tended to be more sensitive to bromacil than tebuthiuron. Inhibition concentration (ICp) values for each endpoint from each species/sterilant test were generated and used to develop species sensitivity distributions and to propose alternate soil quality guidelines for the ecological direct soil contact pathway for fine-textured soil. The study 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. Data generated from the SSP (Litalien and Tindal, 2021 and Thacker, 2021) were combined with historical data used in the development of Tier 1 Guidelines (Stantec Consulting Ltd., 2008, 2012) to produce alternate guidelines recommendations for land use based on the applicable data sets (Table 13). For example, alternate guidelines for natural land use are based on the native plants and invertebrate data, guidelines for agricultural land use are based on the agronomic plants and invertebrate data, and the complete dataset was used for residential, commercial, and industrial land uses. Table 13 summarizes the alternative guidelines, with the caveat that there was not sufficient data for the agronomic plants and invertebrate data set. In most cases, the alternate guidelines were more conservative.

Table 13.	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 ¹ (mg/kg)	0.014	0.028	0.37	0.21
Tebuthiuron	Current Tier 1 (mg/kg)		0.046		0.60
	Alternate ¹ (mg/kg)	0.023	0.018	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.

3.4 Knowledge Gaps and Recommended Practices

3.4.1 Knowledge Gaps Associated with a Risk-Based Approach to Management of Sterilant Impacted Sites

Knowledge gaps associated with chemical-specific parameters used in risk assessment and modeling remain. Further knowledge generation is required for half-life, soil sorption coefficients and sterilant toxicity to inform defensible recommendations for use in Tier 2 Guideline modifications. Recommendations for further study include:

Half-life and Sterilant Degradation

- A full asymptotic decline in degradation rates was not observed in treatments / replications during the SSP half-life experiments indicating the need for longer-duration half-life experiments.
 - Additional literature meta-analysis is recommended to correlate half-life with temperature, moisture content and organic carbon. Data analysis was based on half-life ranges rather than individual half-life values which could inform a defensible conservative degradation rate, particularly for bromacil.
 - Additional experimentation is recommended to refine degradation rates for Alberta conditions for inclusion in Tier 2 risk assessment, potentially in larger batch-scale vessels to allow ongoing sampling from a single bulk source for the duration of experiment, particularly for tebuthiuron.
 - Further study is required to determine the influence of initial concentration of bromacil and tebuthiuron on degradation rates in coarse- and fine-textured soils.

Partition Coefficient

- Insufficient data was generated through experimentation to inform defensible recommendations for alternative sorption coefficients in guideline calculations.
 - Further investigation is recommended both through literature review and experimentation.
 - Extract Kd/foc data points from literature and conduct a meta-analysis to inform Koc values for both bromacil and tebuthiuron.

Sterilant toxicity

- Test toxicity with a range of native species in a coarse-grained soil (Thacker (2021) focused on fine-grained soils) and species from other ecological zones (Thacker (2021) focused on native grassland species).
- Test toxicity with a range of native species grown in soils with varying chemical and physical properties from within Alberta to give a more complete picture of the range of effects sterilants may have on native plants.

3.4.2 Recommendations for a Risk-Based Approach for Management of Sterilant-impacted Sites

A summary of recommended practices and opportunities for improved risk assessment and management of bromacil- and tebuthiuron-impacted sites is provided below. Figure 7 shows considerations for practical application of the information.

- Compare Phase 1 and 2 ESA and CSM to Tier 1 Guidelines as a first step to determine management options.
 - Practitioners should plan to assess groundwater when bromacil or tebuthiuron are present; install groundwater monitoring wells during the initial Phase 2 ESA in areas representative of "worst-case" scenario.
- Determine the most limiting applicable exposure pathway based on Tier 1 Guidelines. Compare worst case groundwater concentration to Irrigation Water (IW) and Freshwater Aquatic Life (FAL) surface water.
 - Groundwater < guideline = applicable guideline will be ecological soil contact guideline.
 - Groundwater > guideline = Tier 2 approach recommended.
- Exclude pathways where applicable and determine if additional site-specific non-chemicalspecific data (Db, foc, porosity, etc.) or chemical-specific parameters (half-life, Koc) would be beneficial for calculation of modified Guidelines through a Tier 2 approach.
 - Exclude FAL pathway if no surface water bodies are present within 300 m by (1) assessing the groundwater and monitoring sterilant plume characteristics; and (2) applying a conservative degradation half-life justified through literature or site-specific data.
 - Exclude IW pathway if outside agricultural regions.
 - Consider where the site is located and if agronomic or native species are intended for reclamation.
 - To reduce risk to receptors, if equivalent land capability requires native grass species for reclamation consider using the alternate soil quality guidelines for Tier 1 ecological direct contact surface soil quality guidelines for fine-grained soil in non-commercial and non-industrial land uses (Thacker, 2021).

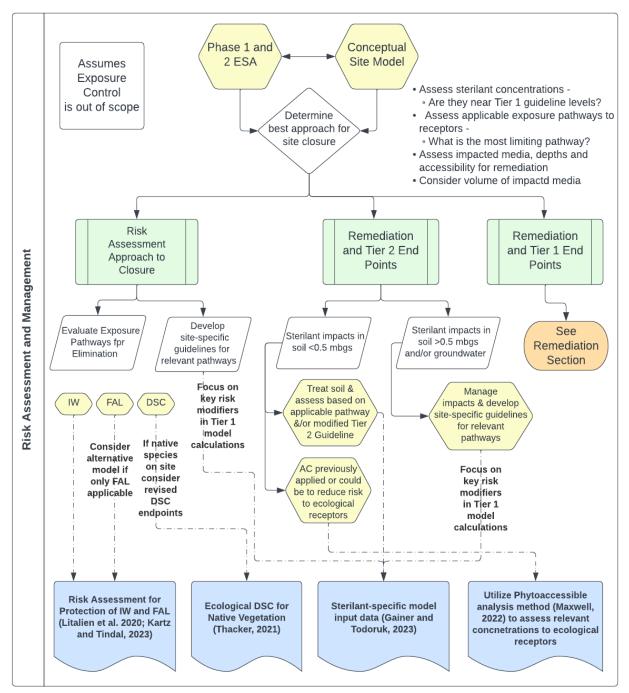


Figure 7. Considerations for application of the Tier 1 and 2 Risk Assessment Approaches for more effective management of sterilant impacted sites.
 ESA – environmental site assessment; IW – irrigation water pathway; FAL – freshwater aquatic life pathway; DSC – direct soil contact pathway

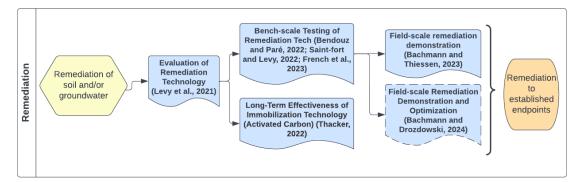
4.0 **REMEDIATION**

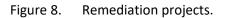
4.1 Problem Statement

Several challenges were identified associated with remediation of sterilant-impacted sites including:

- Long-term evaluations of remediation treatment longevity, which is particularly relevant for immobilization treatments that rely on sterilant adsorption, are not available.
- Detailed, publicly accessible data on operational-scale treatment demonstrations in Alberta (e.g., target sterilant(s) and concentrations, co-contaminants, methods, rates, and costs) are not available.
- Information on the potential for, and value of, combining treatment technologies to increase remediation success is lacking.

The SSP addressed these challenges by investigating commercial-ready and near-commercial technologies for their suitability for remediation of bromacil and tebuthiuron (Figure 8).





4.2 Evaluation of Remediation Technologies

Potential sterilant remediation technologies were evaluated to determine their applicability to Alberta conditions and specific site challenges, while also considering cost, logistics of application, and sustainability. In addition, a review of applicable site types and industry challenges was completed and high-potential technologies that could be de-risked at bench- and meso-scale testing stages, prior to field-scale evaluation were identified.

Technologies were split into four treatment types: (1) Ex-situ soil remediation technologies, (2) In-situ soil remediation technologies, (3) Ex-situ water remediation technologies, and (4) In-situ water remediation technologies (Levy et al., 2021). Typical remediation costs, where available, were identified. Technologies were ranked as:

- 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.

In addition, for practical application, treatment options needed to consider: (1) a range of endpoint concentrations based on different site requirements, (2) sterilant (bromacil or tebuthiuron or both), and (3) soil type (i.e., coarse- or fine-grained; specific organic matter content). Table 14 provides a summary of the technologies evaluated and their applicability to sterilant impacted sites.

Technology Type	Proven	Impractical	Potential
Ex-situ Soil Remediation Technologies	 Immobilization (with Activated Carbon) Remedial Excavation and Disposal Thermal Desorption 	 Landfarming, Bio-piles and Composting Slurry Bioreactors Soil Washing 	• N/A
In-situ Soil Remediation Technologies	• Immobilization (with Activated Carbon)	 Bioremediation and Natural Attenuation Enhanced Microbial Degradation Enzymatic Remediation In-situ Thermal Remediation Phytoremediation TRIUM SRT – Immobilization / Stabilization Fertilizers Manure/ Organic Amendments Soil Flushing 	 Activated Carbon Slurry Chemical Oxidation Chemical Reduction Electrokinetic Remediation
Ex-situ Water Remediation Technologies	 Activated Carbon Filtration Chemical Oxidation and Reduction Deep Well Injection Photocatalysis 	 Chlorination Electro/Photoelectron Fenton Processes Nanofiltration/Reverse Osmosis Photoelectrocatalysis using WO₃ and H₂O₂, H₂SO₄, and H₂O₂ as supporting electrolyte Synergistic Vacuum Ultraviolet / Chlorine Process 	• N/A

Table 14.Ex-situ and in-situ soil and water remediation technologies evaluated.From Levy et al. (2021).

Technology Type	Proven	Impractical	Potential
In-situ Water		BioremediationPhytoremediation	 Activated Colloidal Carbon Slurry + ChemOx Enhanced Biodegradation
Remediation Technologies	• N/A	• Sorption + AOP with Micron Trap-Ox Zeolites FeBEA35 and H ₂ O ₂	 Permeable Reactive Barrier (PRB) with Embedded Reductant
			Surfactant- Enhanced Removal

N/A = Not Applicable

The study found there are a variety of treatment options available but limited experience in their implementation for treatment of sterilants in Alberta (Levy et al., 2021). Thermal desorption was the only ex-situ remediation technology previously proven and remains a viable option for management of sterilant impacted sites. Immobilization remediation technology (i.e., activated carbon) was prioritized for laboratory experimentation and destructive remediation technologies ranked as "potential" (Table 14) were prioritized for further testing at bench-scale prior to field-scale demonstration. Concurrent as well as sequential treatments were also identified as opportunities to address sterilant-impacted sites that warrant further investigation.

4.3 Immobilization Technologies for Management of Sterilant Impacted Sites

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. Table 15 summarizes the literature review results.

Literature Review Component	Review Findings		
	• Black carbon ² can degrade and change in structure over time, and sorption dynamics can also change.		
Potential for AC to degrade over time	 AC can be relatively stable over time (i.e., five years) and 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 Alberta conditions. 		

Table 15.Factors influencing Activated Carbon (AC) sorption in soils.Literature review findings from Thacker (2022).

² Black carbon refers to carbon-rich material derived from incomplete combustion of vegetation and fossil fuels, as well as mineral weathering – biochar and AC are forms of black carbon.

Literature Review Component	Review Findings		
	 Sterilant sorption is dependant on clay and organic matter (OM) content: Bromacil – absorbed more strongly by OM than clay and more likely to be found at the surface in soils with ↑ OM. Tebuthiuron – leaching is lowest in soils with high clay or OM. 		
Factors influencing sorption and desorption	 Desorption of sterilants can be affected by pH and temperature, though OM has the most influence. Alberta soils are generally well buffered; therefore, pH is not likely to be a driving factor in sorption dynamics. 		
	Co-contaminants compete for adsorption sites on AC.		
	 Solubility of sterilant and co-contaminant impacts likelihood to sorb and stay sorbed. Compounds with ↓ solubility = ↑ likelihood to sorb therefore influencing sterilant immobilization. 		
	 Aging factors influencing AC degradation include biological (exposure to nutrients and microorganisms), thermal/chemical (exposure to high temperatures), physical (exposure to freeze-thaw cycles). 		
Weathering	 Abiotic factors have the greatest influence on sorption dynamics: Exposure to high temperature influenced physiochemical properties of AC which resulted in ↑ desorption. Freeze-thaw cycles ↓ effectiveness of AC. 		

No suitable sites could be found with sufficient information about AC application rates and sterilant concentrations to inform research questions related to long-term immobilization of sterilants by AC. Therefore, a laboratory study was conducted focused on 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 (Thacker, 2022). Laboratory work was informed by the literature review (Thacker, 2021) and conducted to assess:

- 1. The percentage of each sterilant retained by AC (based on desorption experiments via modified Synthetic Precipitation Leaching Procedure (SPLP)).
- 2. The longevity of sterilant immobilization by AC compared with soil that was not amended with AC (based on an artificial weathering experiment using multiple freeze-thaw cycles of sterilant-spiked topsoil).
- 3. Phyto-accessible sterilant concentrations pre- and post-weathering compared to total sterilant concentrations.

The results of the studies are summarized in Table 16. In general, phyto-accessible concentrations of bromacil and tebuthiuron were below Tier 1 Direct Soil Contact (DSC) Guidelines after weathering when soils were amended with AC (and below Tier 1 Soil Guidelines for many samples). It is difficult to extrapolate the results to the long-term sorption stability as there are other processes that may influence stability over time however, based on the artificial weathering study, it is interpreted that AC effectively sorbs the majority of bromacil and tebuthiuron over time. It was noted that bromacil and tebuthiuron behaved differently, indicating sterilant-specific approaches to AC treatment are required. It was recommended to include AC as a remediation technology in meso- or field-scale demonstrations to develop best practices for use of AC as an immobilization remediation technology.

Table 16.	Summary of research from the immobilization studies.
	From Thacker (2022).

Parameter and Purpose of Inclusion	Experimental Results and Interpretation
Desorption: Sterilant immobilization and phyto-accessibility Designed to simulate worst-case scenario of sterilant leaching in soil and assess the percentage of each sterilant retained by AC	 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. Initial sterilant concentration did not have a strong influence on amount of sterilant desorbed. Phyto-accessible fraction in soils amended with AC was much lower compared to the non-amended soil, indicating that the sorption of sterilants to AC reduced phyto-accessibility. Phyto-accessible fraction was typically greater than the desorbed fraction in AC amended soils, indicating that a portion of the sterilants present may be available to plants but may not readily desorb from AC.
	 In the absence of weathering, total bromacil and tebuthiuron concentrations were significantly lower in AC-amended soil. This indicates 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.
Weathering: Freeze- thaw cycles used to artificially weather AC and sterilants to assess the longevity of sterilant immobilization by AC	 In soil not amended with AC, phyto-accessible 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, indicating that a majority of the sterilants remained sorbed to AC after physical weathering (phyto-accessible bromacil concentrations depicted in Figure 9). Changes in phyto-accessibility with weathering differed for tebuthiuron compared to bromacil. 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 to non-amended soil.

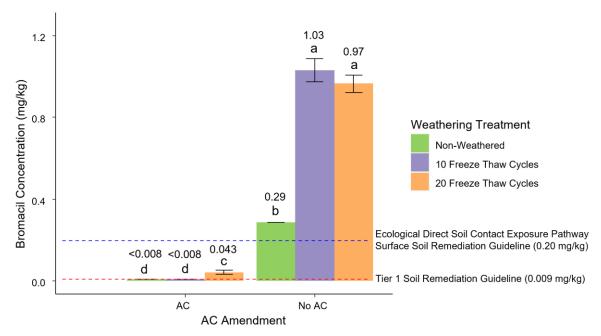


Figure 9. Phyto-accessible bromacil concentration in soil amended with activated carbon (AC) or not amended (no AC).

From Thacker (2022).

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. Average values are provided above each bar. Different lowercase letters indicate significant differences among the treatments.

4.4 Bench-scale Evaluation of Destructive Remediation Technologies

Based on the remediation technology evaluation and interviews with technology providers and practitioners (Levy et al., 2021), a two-stage bench-scale testing program evaluated promising destructive remediation technologies to assess their potential for field-scale trials:

- In-situ chemical oxidation (ISCO) and reduction (ISCR) technologies (Bendouz and Paré, 2022):
 - DARAMEND[®] (ISCR),
 - Potassium persulfate (activated with hydrated lime) (ISCO),
 - Sodium persulfate (activated with calcium peroxide) (ISCO),
 - o Sodium persulfate (activated with sodium hydroxide) (ISCO),
 - Hydrogen peroxide (H₂O₂) (utilising VTX catalyst) (ISCO),
- Trap & Treat[®] BOS 200+[®] (ISCO), Trap & Treat[®] CAT 100 (ISCO), Micro-scale Zero Valent Iron (ZVI) (ISCR) (French et al., 2023), and
- Electrocoagulation (Saint-Fort and Levy, 2022).

Several surfactants were evaluated for their ability to enhance the rate of contaminant destruction when combined with ISCR and ISCO (Bendouz and Paré, 2022). Table 17 summarizes the technologies and bench-scale test results.

Technology	Technology Summary	Bench-Scale Test Results*
DARAMEND [®] (ISCR)	 Composed of a controlled-release organic carbon substrate combined with zero valent iron (ZVI). 	• 2 dosing rates (1% and 3%), with and without tilling at 30 days, with and without TWEEN 80 surfactant.
	 Requires strongly anaerobic (saturated) conditions to maintain reducing conditions; requires incorporation (generally with specialized rotary 	 Highly effective in the treatment of bromacil (98% reduction using 3% dosage without tilling; 97% reduction using 1% with tilling @ 30 days) (Bendouz and Paré, 2022). Sterilant destruction was obtained without tilling the sample after a 30-days contact
	tillers).Native microorganisms in the soil use the carbon	time indicating a single pass application with appropriate wetting conditions could achieve remedial objectives.
	and nutrients provided by DARAMEND® to drive	Benefit of surfactant (TWEEN) application was inconclusive.
	 the oxidation reduction potential (ORP) down. Corrosion of the iron, as intended, further reduces the ORP creating conditions for contaminant destruction. Primarily selected for treatment of bromacil. 	 Lowest overall cost for application (\$55/MT soil (product only) using a 1% w/w loading rate).
		 DARAMEND[®] will only work in saturated (or high-water content soil conditions (90% water holding capacity)) as contaminant destruction pathway will be ineffective if water content is insufficient.
		• Deemed unlikely to be effective in treating tebuthiuron due to absence of evidence that it degrades anaerobically.
		 Recommended to test lower DARAMEND[®] dosage rates (0.25% or 0.5% w/w given sufficient soil moisture and contact time).
Potassium persulfate activated with hydrated lime (ISCO)	 Treatment provides a long-term (i.e., 1 to 3 year) chemical oxidation environment based on low solubility of both oxidant and activator. Persulfate releases minimal gas upon reaction and has a relatively low Soil Oxidant Demand compared with other ISCO amendments. These properties, combined with longer persistence, are ideal for lower permeability soil and bedrocks. 	 Stage 1 Testing Low, medium, and high dose for both bromacil and tebuthiuron. Oxidant and alkaline activator added together and incubated for 30 days; preliminary screening did not include surfactants. Minimal reduction in bromacil or tebuthiuron concentration (Bendouz and Paré, 2022). Technology not selected for Stage 2 testing.
	 This blend of oxidant and activator also has minimal reactivity with carbon steel or concrete underground infrastructure. 	

Table 17. Summary and results of technologies selected for bench-scale remediation testing.

Technology	Technology Summary	Bench-Scale Test Results*
Sodium persulfate activated with calcium peroxide (ISCO)	 Treatment consisted of 50% sodium persulfate and 50% calcium peroxide, with the sodium persulfate portion leading to the chemical oxidation of contaminants in aqueous phase within the soil matrix. Oxidation time for this technology is typically between 4 to 12 weeks. Calcium peroxide lasts 3 to 6 months and 	 Stage 1 Testing Low, medium, and high dose for both bromacil and tebuthiuron. Oxidant and alkaline activator added together and incubated for 30 days; preliminary screening did not include surfactants. Minimal reduction in bromacil or tebuthiuron concentration (Bendouz and Paré, 2022). Technology not selected for Stage 2 testing.
	promotes aerobic biodegradation when soils are sufficiently but not excessively moistened.	
Sodium persulfate activated with sodium hydroxide (ISCO)	 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. 	 Stage 1 Testing Low, medium, and high dose for both bromacil and tebuthiuron. Oxidant and alkaline activator added together and incubated for 30 days; preliminary screening did not include surfactants. 76% reduction in tebuthiuron concentration at low dosage application (Bendouz and Paré, 2022). Technology selected for Stage 2 testing with surfactants.
	 Sodium persulfate releases minimal gas and has a relatively low Soil Oxidant Demand. This, in addition to relatively long persistence, is ideal for lower permeability soil and bedrock. 	 Stage 2 Testing Included surfactant CHEMSOL DL4 (for bromacil) and DECONIT (for tebuthiuron). 80% reduction in tebuthiuron concentration at low dosage application; determined that surfactant did not improve degradation enough to warrant inclusion.
	 Components are both fully soluble and can be pre- mixed at the surface before application and sprayed as a true aqueous solution. 	 Recommended for tebuthiuron treatment without surfactant.

Technology	Technology Summary	Bench-Scale Test Results*
Hydrogen peroxide (H ₂ O ₂) alone or activated using VTX (catalyst) (ISCO)	 Provides 2 to 4 weeks of chemical oxidation per application event. Residual oxygen released from the H₂O₂ 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 is dependent on the Natural Oxidant Demand value for the soil and groundwater; if the demand is high, a catalyst would not be required, thus reducing cost. 	 Stage 1 Testing Low, medium, and high dose for both bromacil and tebuthiuron. Treatment reduced bromacil concentration by 70% of the initial concentration and tebuthiuron concentration by 55% of initial concentration (with addition of 40.2 g of 50% H₂O₂ and 4 g/kg VTX catalyst) (Bendouz and Paré, 2022). The H₂O₂ oxidation process using the VTX catalyst and surfactant was more expensive than the DARAMEND® technology at C\$99/tonne of impacted soil (product only) for the destruction of 1.0 mg/kg contaminant concentration. Technology selected for Stage 2 testing with surfactants. Stage 2 Testing Included surfactant TWEEN (for bromacil and tebuthiuron). Treatment reduced bromacil concentration by 76% of the initial and reduced tebuthiuron concentration by 55% of initial concentration (with 40:1 oxidant to contaminant dosage and 4 g/kg VTX catalyst).
Surfactants	 Often used to improve contaminant availability for oxidative destruction in water phase as they help to desorb contaminants from soil components and decrease water surface tension, allowing for improved distribution of amendments in fine-grained soils. Screened based on biodegradability, availability in Alberta and approval for use in Canada: TWEEN 80; DECONIT; CHEMSOL DL3; CHEMSOL DL4; IVEYSOL 106CL; FFT. 	 3 concentrations of each surfactant were tested with bromacil and tebuthiuron. 3 of 6 surfactants were applicable for bromacil: TWEEN at 1 g/kg (74% bromacil extracted), DL3 at 5 g/kg (38%), and DL4 at 1 g/kg (28%). 3 of 6 surfactants were applicable for tebuthiuron: TWEEN at 5 g/kg (54%), DECONIT at 5 g/kg (47%), and TWEEN at 1 g/kg (31%) (Bendouz and Paré, 2022). 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.

Technology	Technology Summary	Bench-Scale Test Results*
Trap & Treat [®] BOS 200+ [®]	 Trap & Treat[®] BOS 200+[®]'s treatment approach uses bio-stimulation and inoculation. Contains activated carbon, which is designed to trap the contaminants, increasing the contact time between the treatment media and the 	 Static batch reactors filled with bromacil- and tebuthiuron-impacted soils mixed with amendment. Tested with and without activated carbon component. Tested with and without TWEEN 80 surfactant (and with and without activated carbon component and with ZVI).
	contaminants to further promote biodegradation and/or chemical reduction.	• Able to destructively remove bromacil from the soil, dropping concentrations to within the target (0.009 mg bromacil/kg soil) within the four-month testing period.
	• Evaluated for use in permeable reactive barrier (PRB) for groundwater treatment.	 If treatment is required in the form of a PRB, immobilization via activated carbon and no surfactant is beneficial. Under these requirements, Trap & Treat[®] BOS 200+[®] was the best performing treatment.
		 Successful at destructively removing tebuthiuron from the soil at a rate fast enough to reach the target (0.009 mg tebuthiuron/kg soil) within the 4-month testing period (French et al., 2023).
		 Likely a good option for treating bromacil- and tebuthiuron-impacted sites; further testing required.
Trap & Treat® CAT 100	 Trap & Treat[®] CAT 100's treatment approach uses chemical reduction, bio-stimulation and inoculation. Contains activated carbon, which is designed to trap the contaminants, increasing the contact 	 Static batch reactors filled with bromacil- and tebuthiuron-impacted soils mixed with amendment. Tested with and without activated carbon component. Tested with and without TWEEN 80 surfactant (and with and without activated carbon component and with ZVI).
	time between the treatment media and the contaminants to further promote biodegradation and/or chemical reduction.	• Able to destructively remove bromacil from the soil, dropping concentrations to within the target (0.009 mg bromacil/kg soil) within the four-month testing period (French et al., 2023).
		 The reactor with surfactant added to the simulated Trap & Treat[®] CAT 100 had the fastest degradation rate for bromacil.
		 Not successful at destructively removing tebuthiuron from the soil at a rate fast enough to reach the target (0.009 mg tebuthiuron/kg soil) within the 4-month testing period.
Micro-scale zero valent iron (ZVI)	• ZVI's treatment approach uses chemical reduction alone.	 Static batch reactors filled with bromacil- and tebuthiuron-impacted soils mixed with amendment. Tested with and without aluminum sulphate as a pH control.
		• Able to destructively remove bromacil from the soil, dropping concentrations to within the target (0.009 mg bromacil/kg soil) within the four-month testing period (French et al., 2023).
		 Not successful at destructively removing tebuthiuron from the soil at a rate fast enough to reach the target (0.009 mg tebuthiuron/kg soil) within the 4-month testing period.

Technology	Technology Summary	Bench-Scale Test Results*
Electrocoagulation	• Bromacil- and tebuthiuron-spiked water samples were added to an electrocoagulation cell with either Al or Fe electrodes and were subjected to various combinations of voltage and voltage application (time) cycles.	 The removal efficiency by the electrocoagulation process for bromacil ranged from 0% to 23.40%, while for tebuthiuron it was from 0 to 16% (Saint-Fort and Levy, 2022). Removal of the sterilants 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 levels 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 stable complexation mechanism that could have led to the removal of bromacil and tebuthiuron.	
		Further testing recommended.

* For experiments conducted by Bendouz and Paré (2022) initial bromacil and tebuthiuron concentrations were 1.36 mg/kg and 2.1 mg/kg, respectively; for experiments conducted by French et al. (2023) initial bromacil and tebuthiuron concentrations were 0.26 mg/kg and 0.79 mg/kg, respectively; for experiments conducted by Saint-Fort and Levy (2022) initial bromacil and tebuthiuron concentrations were 0.26 mg/kg and 0.79 mg/kg, respectively; for experiments conducted by Saint-Fort and Levy (2022) initial bromacil and tebuthiuron concentrations were 1.36 mg/kg and 0.79 mg/kg, respectively; for experiments conducted by Saint-Fort and Levy (2022) initial bromacil and tebuthiuron concentrations were 4 mg/L (simulated water).

Table 18 provides a summary of the technologies that successfully reduced (or were assumed to reduce) bromacil and tebuthiuron concentrations. Based on lab, bench-scale testing, economic analysis, and technology availability, it was recommended that ISCR technology (DARAMEND[®]) is suitable for treatment of surface soils (<0.5 mbgs) impacted by bromacil. Further testing is required to ensure no other challenges are created through technology application that may influence site closure. Additional testing was also recommended for ISCO (H₂O₂ with VTX catalyst and without surfactant) technology for groundwater and saturated soil impacted by either bromacil or tebuthiuron (Bendouz and Paré, 2022) and activated carbon (AC) (Thacker, 2022). 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 soil contamination would however be influenced by the sorption/desorption mechanism to make the sterilant available in the water phase. If selecting an ISCO remediation technology, it is recommended to conduct laboratory or pilot scale treatment tests to validate the amount of oxidant required to achieve the desired level of decontamination.

High Priority Risk Management and/or Remediation Challenges	Bromacil	Tebuthiuron
	Activated Carbon (in-situ)	Activated Carbon (in-situ)
	DARAMEND [®] (ISCR)	• H ₂ O ₂ with VTX catalyst
Sterilant impacts in soil < 0.5 mbgs	• Trap & Treat [®] BOS 200+ [®]	(ISCO)
	(ISCO)	Trap & Treat [®] BOS 200+ [®]
	• Trap & Treat [®] CAT 100 (ISCO)	(without surfactant) (ISCO)
	Activated Carbon (ex-situ)	Activated Carbon (ex-situ)
Sterilant impacts in unsaturated soil > 0.5 mbgs	 Trap & Treat[®] BOS 200+[®] (ISCO) 	 Trap & Treat[®] BOS 200+[®] (without surfactant) (ISCO)
	• Trap & Treat [®] CAT 100 (ISCO)	
Sterilant impacts in saturated soil > 0.5 mbgs and groundwater	 Trap & Treat[®] CAT 100 (without activated carbon and with surfactant) – unconfirmed 	 Trap & Treat[®] BOS 200+[®] (without surfactant) (ISCO) – unconfirmed

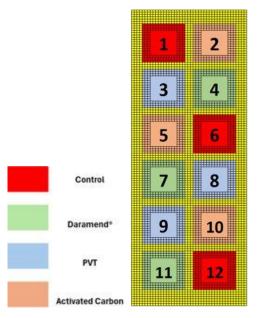
Table 18.Summary of technologies that showed promising results for immobilization and/or
reduction of bromacil and/or tebuthiuron at the bench scale.

* All technologies require further evaluation in the field to confirm efficacy and potential side-effects.

Three commercially available remediation technologies were recommended for meso-scale demonstration: (1) ISCO with H_2O_2 , catalyst (VTX[®]) and surfactant (Tween[®]80); (2) immobilization with AC (Chemcarb PAC 800 powdered AC); and (3) ISCR with DARAMEND[®].

4.5 Meso-scale Ex-situ Remediation Technology Field Trial

A 12-week, outdoor meso-scale experiment focused on bromacil degradation and immobilization in soil was conducted in 2022 to evaluate the effectiveness of three technologies for remediating bromacilimpacted soil sourced from a former substation near Trochu, Alberta (Bachmann and Thiessen, 2023). No sites were available as a source of tebuthiuron-impacted soil, therefore the meso-scale experiment only focused on bromacil. Approximately 90 m³ of silty clay soil impacted by bromacil ranging from 0.24 to 1.76 mg/kg, was hauled to a lined treatment cell in Vegreville, Alberta, homogenized and divided into 12 unique, 3.0 x 3.0 x 0.6 m (5.4 m³) cells. Experimental design consisted of three replicates of three treatments (1 application rate/ treatment) and three control replicates randomized on the treatment cell (Figure 10). Each cell was isolated and covered with a polyethylene multipurpose liner to prevent interference between treatments and maintain a consistent soil moisture content throughout the experiment. Table 19 provides a summary of the meso-scale remediation trial and the associated results from the experiment.



- Figure 10. Meso-scale field experiment design evaluating immobilization and destructive remediation technologies.
- Table 19.Experimental results from a meso-scale ex-situ remediation trial evaluating immobilization
and destructive remediation technologies.From Bachmann and Thiessen (2023).

Experimental Treatment	Results
 Immobilization technology – AC (Chemcarb PAC 800 powdered AC) (Replicate #'s 2, 5 and 10 in Figure 10) 75 kg powdered product applied in 	 Statistically significant decrease in total bromacil concentrations (73 ± 6% reduction from 0.50 ± 0.2 mg/kg to 0.13 ± 0.07 mg/kg total bromacil concentration (i.e., total)) over 12 weeks.
slurry form.	Phyto-accessible bromacil concentrations reduced from
• Mixed with water in a blending container prior to application to soil.	0.06 mg/kg (which was 8% of initial bromacil concentration measured by solvent extraction) to <0.008 mg/kg (the
• Targeted moisture content >80% of soil water holding capacity.	laboratory detection limit) within 2 weeks.
In-situ Chemical Oxidation (H ₂ O ₂ , catalyst (VTX [®]) and surfactant (Tween [®] 80)) Replicate #'s 3, 8 and 9 in Figure 10)	 ISCO technology was handled and applied incorrectly – catalyst, surfactant and H₂O₂ were mixed in a blending container prior to application to soil resulting in the
 250 kg 50% H₂O₂, 30 kg 22% VTX[®] catalyst, and 10 kg Tween[®]80 	desired reaction occurring before being applied to the sterilant impacted soil.
surfactant.Reagents mixed in a blending container	 As a result, the treatment was not effective at reducing bromacil concentrations in impacted soil.
with water prior to application to soil.	 Recommended for further testing with tebuthiuron- impacted soils as halogenated contaminants such as bromacil generally require reductive mechanisms for efficient contaminant degradation or transformation.

Experimental Treatment	Results
In-situ Chemical Reduction (DARAMEND®) Replicate #'s 4, 7 and 11 in Figure 10)	 57 ± 1% decrease in total (i.e., total) bromacil concentrations (0.56 ± 0.09 mg/kg to 0.24 ± 0.01 mg/kg).
 265 kg DARAMEND[®] powder applied in slurry form. 	 Multiple applications may be required to achieve Tier 1 Soil Guideline (0.009 mg/kg) concentrations.
 Mixed with in a blending container prior to application to soil. 	
• Targeted moisture content >80% of soil water holding capacity.	

Further testing was recommended for optimization of ISCR technology (DARAMEND[®]) application rates and moisture conditions. ISCO technologies should be re-evaluated and tested for treatment of groundwater impacted by sterilants. Important learnings from executing the meso-scale field trial for practical application of either immobilization or reductive remediation technologies include (Bachmann and Thiessen, 2023):

- Powdered adsorbent or ISCR technologies require mixing with water in a blending container prior to application to impacted soil. For field-scale application, this may require a caisson drill or other similar mixing equipment. Specialized PPE may be required when handling the AC or ISCR technologies.
- The slurry required to optimize in-situ contact between the treatment technology and impacted soil at field-scale applications will result in additional water access, earth moving, and geotechnical considerations.
- The source of activated carbon should be considered to avoid the release of unintended contaminants (e.g., heavy metals) to the environment (e.g., walnut shells vs. coal-based activated carbon).

4.6 Optimization Meso-scale Field Trial

A one-year field optimization trial was established at the InnoTech Alberta mesocosm facility in Vegreville to evaluate DARAMEND[®] dosage rate, application frequency, and moisture content on bromacil-impacted soil in a mesocosm setting (Table 20; Bachmann, 2024). A lab study was also performed to assess the use of bench-scale scale studies for Daramend[®] optimization for field planning.

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 1: Initial moistening only, initial moistening and moistening 30 days after amendment	
Moisture Regime	2	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	

Table 20.	Experimental design	n for the field study.
		/

None of the treatments in the mesoscale study were able to reach the Alberta Tier 1 target of 0.009 mg/kg (Figure 11). 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) and treatments were not significantly different from each other.

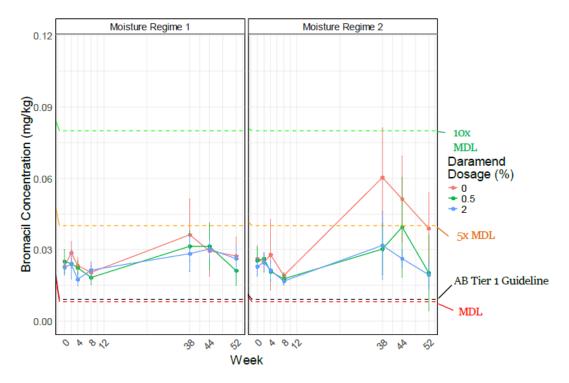


Figure 11. Average bromacil concentration for each treatment.

Bromide concentrations increased for all field Daramend[®] treatments in Moisture Regime 2, and 2% Daramend[®] treatments in Moisture Regime 1, indicating that bromacil was being destructively remediated in those treatments. In the lab study, Daramend[®] treatments had higher bromide concentrations than controls.

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.

4.7 Knowledge Gaps and Recommended Practices

Fate and behavior of soil sterilants in the environment is complex and influenced by multiple environmental and chemical-specific factors. Four priority remediation challenges were identified for potential solutioning through the SSP: (1) sterilants within surface soil (≤ 0.5 mbgs); (2) sterilants at depths greater >0.5 mbgs in unsaturated soil; (3) saturated fine-grained till soils and groundwater impacted by sterilants and (4) groundwater impacted by sterilants. Several knowledge gaps remain associated with remediation technologies applicable to bromacil- and tebuthiuron-impacted soil and groundwater including:

In-situ Remediation Technologies

- The effectiveness of new and novel in-situ destructive remediation technologies such as electrocoagulation.
- Best practices for the use of AC as an immobilization technique, including factors such as:
 - Type of AC (feedstock and charring temperature)
 - o Methods of incorporation into soil (including moisture content)
 - The influence of AC on the extraction and analysis of total bromacil and tebuthiuron concentrations using the accelerated solvent extraction method (ASE) investigated in the SSP.
- In-situ remediation of saturated fine-grained till soils and groundwater impacted by sterilants.
- Remediation of groundwater impacted by sterilants.
- The suitability for treating bromacil and tebuthiuron alone and in combination using Trap & Treat[®] BOS 200+[®], particularly for application in a permeable reactive barrier to prevent off-site migration.

Ex-situ Remediation Technologies

- The potential for concurrent or sequential application of different treatment technologies and risk assessment methods for achieving closure.
- Practical methods for maintaining reductive soil conditions (i.e., moisture conditions) to enable ISCR technology (DARAMEND[®]) to work effectively.
- The effectiveness of new and novel ex-situ destructive remediation technologies.
- Updated cost and greenhouse gas emission analysis for ex-situ technologies including thermal desorption, ISCR technology (DARAMEND[®]) and landfilling.

A summary of recommended practices and opportunities for improved management practices associated with remediation of bromacil and tebuthiuron impacted sites is provided in Table 21.

High Priority	Recommended Practices		
Remediation Challenges	Bromacil	Tebuthiuron	
	 Conduct bench-scale tests with impacted soil to assess treatment application rates based on soil properties and Phase 2 ESA data for sterilant concentrations. Destructive and immobilization technologies must be applied in slurry form to optimize in-situ soil contact 		
	(recommended moisture content – 80% of soil water holding capacity).		
	Apply immobilization technologies (i.e., AC) in-situ.		
Sterilants within surface soil (≤ 0.5 mbgs)	 For destructive remediation technologies excavate impacted soil for treatment in a constructed treatment cell (on- or off-site). ○ Construct treatment cell to enable impacted soil depth within the cell to be ≥0.6 m. 		
	 ISCR technology DARAMEND[®] Monitor soil moisture during treatment to maintain moisture conditions and reducing soil environment. 	 ISCO H₂O₂ with catalyst and surfactant (requires further investigation). AC 	
	• AC	Thermal desorption.	
	Thermal desorption.		
Sterilants at depths greater	• Excavate un-impacted soil to expose impacted zone and store on-site for reclamation.		
>0.5 mbgs in unsaturated soil	• Excavate impacted soil and treat in a constructed treatment cell (on- or off-site) in the same manner as described above, or with previously proven technologies such as thermal desorption.		
Saturated fine-grained till soils and groundwater impacted by sterilants	Ex-situ – technologies and recommended practices described above apply.		
Groundwater impacted by sterilants	• Applicable technologies for groundwater treatment described in Levy et al. (2021).		

Table 21. Recommended practices associated with high priority remediation challenges for bromacil- and tebuthiuron-impacted sites.

ISCR – In-Situ Chemical Reduction; ISCO – In-Situ Chemical Oxidation; AC – Activated Carbon

5.0 SSP OUTCOMES

The SSP goal was to develop proven, technical, and cost-effective strategies and best practices for management of sites impacted by residual soil sterilants, with the goal of achieving regulatory site closure through remediation or acceptable risk assessment strategies.

The program was structured following the basic steps in a remediation program: (1) Identification and Delineation, (2) Risk Assessment, and (3) Remediation. For each of these steps, a list of Problem Statements was developed to guide a suite of research projects to address knowledge gaps. Table 22 lists the SSP outcomes for each of these Problem Statements. Another goal of the SSP was to share knowledge with program participants and a broader base of practitioners; outcomes of knowledge transfer activities are also provided in Table 22.

Effective management of sterilant-impacted sites has many interdependencies between identification and delineation of the contaminants and the best risk management and/or remediation approach to closure. The SSP projects were intended to break new ground in the management of sterilant-affected soil and water. As such, many of the findings need to be validated through evaluation of sites from a variety of Alberta conditions to confirm broad applicability. Among others, conditions such as sterilant levels, co-contaminants, site age (sterilant weathering), site soil and/or groundwater characteristics, and climate considerations need to be evaluated.

A key consideration for all scenarios identified is whether the primary goal is to address high concentrations to reduce risk, or lower concentrations to meet remediation endpoints. Technologies and management strategies should be selected according to the end goal. Given the heterogeneous distribution of sterilants and unique conditions at most sites, a variety of approaches may be required at each site.

SSP Program Component	SSP Knowledge Gap	SSP Outcome
Identification and	Practitioners are uncertain about when and where to screen for soil sterilants, leading to unnecessary intrusive sampling following Phase I environmental sites assessments, excessive analysis with associated costs, and identification of sterilants late in the assessment process that cause reclamation delays.	 Detailed sampling protocols for soil and water were developed that will reduce the potential for cross-contamination and sample dilution. Potential technologies for field-screening soil and water to provide for more efficient sampling were revied and two potential technologies were identified as promising.
Delineation	Analytical methods currently used in Alberta to characterize sterilants found in soil and/or water have variable detection limits, sometimes higher than guideline levels, and only provide total, rather than plant- accessible, concentrations.	 A new laboratory analytical procedure was developed that provides significantly more precise measures of bromacil and tebuthiuron in soil and water samples with minimum detection limits that are below Tier 1 Guidelines values. A sample extraction procedure was developed to analyze phyto-accessible levels of sterilants in soils which will more realistically represent the amount of sterilant in a sample that will affect vegetation.

Table 22. SSP outcomes achieved for each knowledge gap.

SSP Program Component	SSP Knowledge Gap	SSP Outcome
Risk Assessment	Accurate Alberta-specific chemical data for bromacil and tebuthiuron for use in risk assessment models (e.g., half- life, Koc, Kd) are not available.	 A laboratory study established adsorption coefficient (Kd and Koc) values for bromacil and tebuthiuron in Alberta soils with varying organic matter contents and textures.
	Alberta Tier 1 regulatory guidelines are limited by the ecological contact pathways for the protection of irrigation water and freshwater aquatic life.	 Thirty risk assessment 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 subjected to a detailed mechanistic review and model analysis based on standard Tier 1 input values and parameters derived from the literature when necessary. None of the models reviewed could effectively replace all elements of the Tier 2 model however they could be useful supplements.
	Sterilant toxicity data for Alberta native plant species is incomplete or missing.	 Toxicity of sterilants to six native grass species was shown to be greater than the agricultural crops used in the Tier 1 Guidelines – revised guidelines based on these data were more stringent than the current Tier 1 guidelines for ecological direct contact surface soil quality for fine- grained soil.
	Long-term evaluations of remediation treatment longevity, which is particularly relevant for immobilization treatments that rely on sterilant adsorption such as activated carbon, are not available.	 Activated Carbon was shown to effectively sorb the majority of bromacil and tebuthiuron in the long-term which should lead to greater acceptance by practitioners and regulators of this remediation technology.
Remediation	Detailed, publicly accessible data on operational-scale treatment demonstrations in Alberta (e.g., target sterilant(s) and concentrations, co- contaminants, methods, rates, and costs) are not available.	 This was confirmed as an ongoing need through a literature review and discussions with practitioners.
	Information on the potential for, and value of, combining treatment technologies to increase remediation success is lacking.	 Several lab- and field-scale trials were conducted using various treatment technologies with and without catalysts and surfactants. Results varied by sterilant.

SSP Program Component	SSP Knowledge Gap	SSP Outcome		
	Other remediation outcomes – Inventory and ranking of remediation technologies	 A catalogue and ranking of existing remediation technologies was developed to assist practitioners in screening potential technologies for use at their site. Three promising remediation technologies (DARAMEND[®], 		
		 Electrocoagulation, and Trap & Treat[®] and Zero Valent Iron) were tested at the bench-scale. DARAMEND[®] was found to be suitable for use in treatment of bromacil in soil and water but is not able to treat tebuthiuron. Trap & Treat[®] BOS 200+[®] was successful in adsorbing and degrading both bromacil and tebuthiuron. Electrocoagulation removed limited amounts of sterilants in soil and requires further development if it is to be considered for field deployment. 		
	Other remediation outcomes – Meso-scale evaluation of three remediation technologies	 A mesoscale experiment tested three commercially available remediation technologies: (1) chemical oxidation with a surfactant via PeroxyChem 50% hydrogen peroxide, VTX®, and Tween®-80 (the oxidant); (2) adsorption with Chemcarb PAC 800 powdered activated carbon (the adsorbent); and (3) biological and chemical reduction with DARAMEND® (the reductant) of bromacil degradation and immobilization in soil: Total bromacil concentrations were reduced, however they remained an order of magnitude greater than the Tier 1 Guideline suggesting these technologies may be appropriate for contaminated sites where a less stringent Tier 2 soil remediation guideline is applicable or where a risk management plan is implemented. Phyto-accessible bromacil in the activated carbontreated soil decreased to below the Tier 1 Guideline which supports the use of the tested adsorbent as a risk management tool at bromacil-impacted sites. An optimization trial of DARAMEND® resulted in none of the treatments in the mesoscale study reaching the Alberta Tier 1 target of 0.009 mg/kg, though increased bromide levels indicated bromacil destruction was 		
	A community of practice consisting of practitioners, industry, and government representatives is developed and retained.	 Occurring. Approximately 45 people joined the Community of Practice and participated in the Annual Sharing Events. 		
Knowledge Transfer	Technical information is disseminated through annual workshops and external presentations.	 Four Annual Sharing Events were held, with presentations on the overall program, and on each of the active projects. 13 external presentations were given in a variety of 		
		forums by the Program Manager and individual researchers.		

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APPENDIX A: Bromacil and Tebuthiuron Physical and Chemical Characteristics

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 in the form of a wettable powder or	Appearance: Colourless to white crystalline solid Available as wettable powder, soluble concentrate or granular Molecular Formula: C ₉ H ₁₃ BrN ₂ O ₂ Molecular weight: 261.119 g/mol Melting point: 158-160°C Solubility in water: 815 mg/L @25°C		
a liquid	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: C9H16N4OS Molecular weight: 228.314 g/mol Melting point: 164°C Solubility in water: 2,500 mg/L @25°C Vapour pressure: 2.0 x 10-6 mm Hg @25°C		

Common physical and chemical characteristics of bromacil and tebuthiuron.

APPENDIX B: Bromacil and Tebuthiuron Metabolites and Degradation Processes

Bromacil

Chemical Name	Molecular Weight	Suspected Process/Mechanism
Bromacil (parent compound)	261.12	
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
3-sec-butyl-6-methyluracil (Metabolite F)	182.22	Biodegradation, Debromination, Photodecomposition in aqueous solutions
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
Debromobromacil Radical Dimer	362.43	Sensitized Sunlight Photodegradation

Tebuthiuron

Chemical Name	Molecular Weight	Suspected Process/Mechanism
Tebuthiuron (parent compound)	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
N-(5-(1,1-dimethylethyl)-1,3,4-thiadiazol-2-yl)-N'- hydroxymethyl-N-methylurea (Metabolite 109)	244.32	Mammal Metabolism, Plant Metabolism

Chemical Name	Molecular Weight	Suspected Process/Mechanism
N-(5-(2-hydroxy-1,1-dimethylethyl)-1,3,4- thiadiazol-2-yl)-N'-hydroxymethyl-N-methylurea (Metabolite 109[OH])	260.32	Mammal Metabolism