Management of Sterilant Impacted Sites: Literature Synthesis

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EXECUTIVE SUMMARY

Soil sterilants are non-selective residual herbicides that render the treated soil unfit for plant growth for relatively long periods of time. Sterilants were commonly used in Alberta from the 1960s to late 1990s for non-selective vegetation control on oil and gas wells, gas processing plants, rights-of-way, railways, saw mills, pulp mills, and electrical utility sites; residues may also be found at agrochemical dealer sites. Sterilant treated areas can remain devoid of vegetation for many years, depending upon the type, rate and frequency of application of soil sterilant and the climatic conditions. Soils treated with sterilant can be a source of contamination through leaching, surface runoff and wind dispersion of the sterilants to adjacent land and waterbodies. Reclamation and remediation issues arise when a treated site is no longer needed for industrial use and the site must be returned to equivalent land capability. At present, many of these sites either remain as liabilities for industry, or impacted soil is excavated and disposed at a landfill.

In Alberta, awareness of the issues associated with soil sterilants is on the rise as more legacy oil and gas sites (constructed prior to 1970), where sterilants were typically used, are abandoned and slated for remediation and reclamation. Cotton and Sharma ([1]) estimated the number of oil and gas sites in Alberta with soil sterilant residues to be as many as 61,750 sites. As of 2018, many of these sites, as well as numerous industrial facilities, are still in the queue for reclamation and remediation due to the recalcitrant nature of the contaminants that have impacted soil and groundwater.

While a considerable amount of literature review and experimentation has occurred over the past 20 years on this topic in Alberta, sterilant-impacted sites in many cases remain as liabilities for their owners. An opportunity was identified to synthesize past learnings and partner with those who are interested in and/or impacted by soil sterilants to gain a clear understanding of the size and scope of the issues and specific challenges associated with sites impacted by soil sterilants in Alberta. The long term goal of the project is to develop strategies and best management practices to effectively manage these sites. The purpose of this document is to provide a high level summary of available information related to remediation of soil sterilants. An overview of sterilant physical and chemical properties, persistence and fate in the environment, ecotoxicological information, regulatory guidelines, applicable remediation technologies, and operational challenges associated with residual sterilants is provided. The references were also input into a companion Excel database which identifies the type of information contained within each document. The information herein is intended to be used to identify knowledge gaps and a path forward for best management practices for industry to address issues associated with sterilants on their sites.

This review identified that a considerable body of knowledge exists regarding residual herbicide properties and their use in agricultural settings at low rates; however, limited knowledge is available on industrial uses, and in particular, on field-scale remediation of sites affected by the sterilants historically used in Alberta. Several major challenges were identified associated with management of sterilant impacted sites in Alberta through this literature review, industry consultation and personal communication, including 1) the research and demonstration trials that have been undertaken have limited applicability to Alberta conditions and/or have mostly been done in the laboratory or greenhouse, 2) information on the effects of sterilants on Alberta-specific native plants is very limited, and 3) the majority of remediation information found in the literature focuses on soils rather than surface water or groundwater which is a significant problem for Alberta sites where highly mobile sterilants such as bromacil have been used.

There are considerable differences between sterilants in terms of persistence and fate in the environment which depend on several factors related to the sterilant itself and to the soil and climatic conditions, resulting in unique challenges associated with each of them. The two main sterilants found impacting soil and groundwater on or near industrial sites in Alberta include bromacil and tebuthiuron. Several technologies have been utilized to treat sterilant-contaminated soils, both in-situ and ex-situ. The most common treatment technique previously used in Alberta has been sterilant-immobilization, utilizing activated carbon, however several gaps were identified with utilizing this technique for long term management of sterilant impacted sites. Additional knowledge gaps were identified related to the effective management of sterilant impacted sites in Alberta (and have been substantiated through conversations with Alberta practitioners in recent workshops sponsored by InnoTech Alberta):

1. Uncertainty in the number and size of industrial sites impacted by soil sterilants in Alberta leading to uncertainty in identifying impacted sites.
2. Analytical methods currently used in Alberta to characterize sterilants found in soil and/or groundwater have variable detection limits, sometimes higher than guideline levels, and only provide total concentrations, rather than bioavailable.
3. Comparison of laboratory and field derived soil and water half-life data for the common sterilants to be used in risk assessment modeling.
4. Ecological contact pathways for the protection of irrigation water and freshwater aquatic life are below analytical detection limits for bromacil and tebuthiuron.
5. Lack of an ecological direct soil contact pathway for sterilants other than bromacil and tebuthiuron.
6. Incomplete or missing data for Alberta species toxicity to assist in establishing site-specific remediation objectives.
7. Lack of long-term evaluations of remediation treatment longevity, particularly relevant for treatments that rely on the sterilant being adsorbed to organic matter, clays or amendments.
8. Lack of detailed, publicly accessible data on field-scale treatment trials in Alberta – target sterilant(s) and concentrations, co-contaminants, methods, rates, costs.
9. Lack of information on the potential for, and value of, combining treatments technologies to increase remediation success.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF TERMS AND ACRONYMS

Terms

Activated carbon / charcoal
Finely ground charcoal which has been electrically charged to attract oppositely charged molecules or ions.

Adsorption
Physical or chemical binding of an herbicide to soil or an amendment.

Bioaccessibility
Sterilants that are immediately available for microbial degradation plus those which may become available.

Bioaugmentation
Inoculation of enriched/acclimated consortia or single pollutant degrading strains of microbes or fungi to enhance degradation of contaminants.

Bioavailability
Sterilants that are immediately available for microbial degradation.

Biogenic
Produced or brought about by living organisms.

Biostimulation
Addition of appropriate nutrients (nitrogen, phosphorus, trace elements) and/or small amounts of secondary carbon sources to provide microorganisms with an environment which favors the development of metabolic pathways for contaminant biodegradation.

Biosurfactant
Surfactants that are synthesized by living cells or organisms, including microorganisms such as bacteria and yeasts.

Cyclodextrins
A family of compounds made up of sugar molecules bound together in a ring (cyclic oligosaccharides).

Degradation
Chemical, photochemical or biological breakdown of an herbicide.

Dissipation
Removal of an herbicide through leaching, runoff, volatilization, plant uptake, photodecomposition, microbial decomposition or adsorption ([2], [3]). Also called transfer.

EC_{50} (Half Maximal Effect Concentration)
In ecotoxicity, EC_{50} (median effective concentration) is the concentration of test substance which results in a 50% reduction in either algae, daphnia or plants. They are often obtained from acute toxicity studies.

Fenton Process (Reaction)
Use of metals that have oxygen transfer properties which improve the use of hydrogen peroxide.

Glycolipid
Lipids with a carbohydrate attached by a glycosidic bond or covalently bonded.

Herbicide Carry Over
The amount of active ingredient present in the soil after all breakdown and physical loss has occurred throughout the season (depends largely on local weather and soil characteristics) ([4]).

Inhibition Concentration (IC_{25})
Dose inhibiting 25% of the test organisms; IC_{50} - Dose inhibiting 50% of the test organisms.

Lethal Concentration (LC_{50})
Toxicity to aquatic organisms is quantified with LC_{50} (Lethal Concentration 50%), which is the concentration of the herbicide in water that is required to kill half of the study organisms (measured in µg a.i./L).

Lethal Dose (LD_{50})
Toxicity to mammals and birds is described by its LD_{50} (Lethal Dose 50%), which is the dose of herbicide received either orally or dermally that kills half the population of study animals (reported as g a.i/kg body weight) ([5])

Lowest Observed Adverse Effect Level (LOAEL)
Lowest exposure level at which there are biologically significant increases in frequency or severity of adverse effects between the exposed population and its appropriate control group.

Mobility
Ability of an herbicide to move or be moved. Mainly influenced by adsorption coefficient and water solubility ([3]).
Oregon State University has developed a *pesticide movement rating* derived from soil half-life and Koc values ([6]).

No Observed Adverse Effect Level (NOAEL)
Highest exposure level at which there are no biologically significant increases in the frequency or severity of adverse effect between the exposed population and its appropriate control. NOAEL are typically obtained from repeated dose toxicity studies.

Non-Selective Herbicide (Broad Spectrum Herbicide)
An herbicide that kills all actively growing vegetation by contact or by a systemic mode of action (chemical transported throughout plant).

Persistence
Continued or prolonged existence of a herbicide; related to half-life which depends on application rate, soil moisture, pH, temperature, OM content, structure, chemistry, physical properties, composition and microbial content ([3]).
Persistent is defined in the 1999 Canadian Environmental Protection Act as any chemical that has a soil half-life of greater than or equal to 182 days ([6]).

Photocatalysis
The acceleration of a chemical reaction by light.

Polymixin
Any of a group of polypeptide antibiotics that are active chiefly against Gram-negative bacteria.

Residual Herbicide
An herbicide that persists in the soil and kills regrowth and/or germinating seedlings. It can be selective or non-selective.

Rhamnolipid
A class of glycolipid produced by *Pseudomonas aeruginosa*, amongst other organisms, frequently cited as the best characterised of the bacterial surfactants.

Selective Herbicide
Herbicide formulated to control specific weeds or weed categories. A material that is toxic to some plant species but less toxic to others.

Sophorolipid
A surface-active glycolipid compound that can be synthesized by a selected number of non-pathogenic yeast species.

Sorption
The retention process with no distinction between the specific processes of adsorption, absorption and precipitation.

Sterilant
A chemical that temporarily or permanently prevents the growth of all plants and animals. Soil sterilants are a type of non-selective herbicides generally restricted to industrial site use.

Tensioactive
Chemical substances with a polar-non polar structure that affect surface tension.

Total Vegetation Control
The suppression or control of all vegetation to maintain a vegetation-free or barren area.

Acronyms

The following acronyms are used in this report or the cited references.

AC	Activated Carbon / Activated Charcoal
AEP	Alberta Environment and Parks
AENV	Alberta Environment
a.i.	Active Ingredient
AGTD	Alberta Gas Transmission Division
AOP	Advanced Oxidation Processes
ARC	Alberta Research Council
BDL	Below Detection Limit
CCME	Canadian Council of Ministers of the Environment
DUA	Drinking Use Aquifer
EC	Electrical Conductivity
EKSF	Electrokinetic Soil Flushing

ELISA	Enzyme-Linked Immunosorbent Assays
ERH	Electrical Resistivity Heating
FRTR	Federal Remediation Technologies Roundtable
GAC	Granular Activated Carbon
GC/MS	Gas Chromatography/Mass Spectrometry
HPBCD	Hydroxypropyl-β-cyclodextrin
HPLC/MS	High Performance Liquid Chromatography/Mass Spectrometry
ISTR	In-situ Thermal Remediation
LOAEL	Lowest Observable Adverse Effect Level
MNA	Monitored Natural Attenuation
MRE	Molecular Recognition Element
NOAEL	No Observable Adverse Effect Level
nZVI	Nano-scale Zero-Valent Iron
OM	Organic Matter
PAC	Powdered Activated Carbon
SEE	Steam Enhanced Extraction
ssDNA	Single Stranded DNA
TEC	Threshold Effects Concentration
TCH	Thermal Conductive Heating
US EPA	United States Environmental Protection Agency
UV	Ultraviolet
WHC	Water Holding Capacity

MANAGEMENT OF STERILANT IMPACTED SITES: LITERATURE SYNTHESIS

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1.0 INTRODUCTION

1.1 PROJECT BACKGROUND

Soil sterilants are non-selective residual herbicides that render the treated soil unfit for plant growth for relatively long periods of time. Sterilants, were commonly used in Alberta from the 1960s to late 1990s for non-selective vegetation control on oil and gas wells, gas processing plants, rights-of-way, railways, saw mills, pulp mills, and electrical utility sites ([1], [2], [7]); residues may also be found at agrochemical dealer sites ([8]). Sterilant treated areas can remain devoid of vegetation for many years, depending upon the type, rate and frequency of application of soil sterilant and the climatic conditions. Soils treated with sterilant can be a source of contamination through leaching, surface runoff and wind dispersion of the sterilants to adjacent land and waterbodies. Reclamation and remediation issues arise when a treated site is no longer needed for industrial use and the site must be returned to equivalent land capability. At present, many of these sites either remain as liabilities for industry, or impacted soil is excavated and disposed at a landfill.

In Alberta, awareness of the issues associated with soil sterilants is on the rise as more legacy oil and gas sites (constructed prior to 1970; operational prior to 1990), where sterilants were typically used, are abandoned and slated for remediation and reclamation. Cotton and Sharma ([1]) estimated the number of oil and gas sites in Alberta with soil sterilant residues to be as many as 61,750 sites. Historical work has focused on upstream oil and gas sites, however there are many others in the province. It's estimated that there are well over 3,000 additional sites associated with distribution sites, pipelines and electric metering stations and many other industrial facilities not yet identified. While a considerable amount of literature review, experimentation and operational activities have occurred over the past 20 years on this topic in Alberta, as of 2018, many of these sites are still in the queue for reclamation and remediation due to the recalcitrant nature of the contaminants that have impacted soil and groundwater and remain as liabilities for their owners.

An opportunity was identified to synthesize past learnings and partner with those who are interested in and/or impacted by soil sterilants to gain a clear understanding of the size and scope of the issues and specific challenges associated with sites impacted by soil sterilants in Alberta. The long term goal of the project is to develop strategies and best management practices to effectively manage these sites. This will be accomplished by establishing a network of collaborators including industry, environmental service providers, technology providers, and researchers to identify proven technical and cost effective solutions for risk management, remediation and reclamation of industrial sites impacted by residual soil sterilants.

1.2 LITERATURE SYNTHESIS SCOPE AND OBJECTIVE

The purpose of this document is to provide a high-level summary of available information related to remediation of soil sterilants commonly found in Alberta. An overview of sterilant physical and chemical properties, persistence and fate in the environment, ecotoxicological information, regulatory guidelines, applicable remediation technologies, and operational challenges associated with residual sterilants is provided. The review focuses on the sterilants most commonly encountered on industrial sites in Alberta (bromacil and tebuthiuron), however relevant information for sterilants identified as priorities in Alberta is provided where available. The information herein is intended to be used to identify knowledge gaps and a path forward for best management practices for industry to address issues associated with sterilants on their sites.

1.3 LITERATURE REVIEW METHODOLOGY AND DATABASE

For this review, searches through multiple resources including books; conference proceedings; databases; peer reviewed journals; industry, government and public reports; and, the Internet were completed to find literature related to the themes within the scope of the project. Once collected, the references were reviewed and input into a companion Excel database which identifies the type of information contained within each document. A high level summary of the relevant topic areas related to sterilant remediation was then prepared and is provided herein.

2.0 STERILANT OVERVIEW

A review conducted by Intrinsik Environmental Sciences ([6]) identified a list of 25 priority pesticides which are routinely detected in environmental monitoring programs, are either persistent or mobile in soil, and have been identified as being of concern in various jurisdictions of Canada. A subset of those contaminants are generally screened for by commercial laboratories in Alberta, including: bromacil, tebuthiuron, atrazine, simazine, diuron, and linuron (not on the priority list)[1] ([7], [9], [10]). These sterilants have different modes of action ([11]), soil and water half-life, physical and chemical characteristics and environmental fate and behaviour ([7]), but are all considered to persist in soils, especially in arid areas. This section reviews the properties of these common sterilants; however emphasis is placed on the two most commonly found sterilants in Alberta; bromacil and tebuthiuron.

2.1 STERILANT PROPERTIES

A description of the physical and chemical properties of sterilants commonly screened for on legacy industrial sites in Alberta is provided in Table 1. These sterilants can be categorized within 3 main herbicide classes: uracils (bromacil), ureas (tebuthiuron, diuron, and linuron), and trizines (atrazine and simazine) ([12]).

2.2 STERILANT USAGE

For most sites, historical pesticide use or storage data are generally not available until the phased environmental site assessment process is undertaken ([13]). Information relevant to pesticide use or likely environmental concentrations for industrial sites can sometimes be estimated through personal communication, however the accuracy and relevance of the information is often unknown. Rakewich and Bakker ([3]) indicated there are three sources of sterilant contamination: spills (very rare); migration (runoff and spray drift); and industrial sites (arising from high application rates over many years; can be >45 cm deep). In 1982, the Pesticides Management Branch of Alberta Environment instituted a method for monitoring the types of sterilants used on forested regions within the province. A form was completed prior to sterilant application and the data showed atrazine (Primatol), followed by bromacil (Hyvar X, Calmix, Krovar), diuron (Karmex) and tebuthiuron (Spike) to be the four most commonly used active ingredients in sterilant products ([2]). It is reasonable to assume that the same sterilants would have been used in similar proportions for vegetation control on industrial sites in the agricultural areas of Alberta. In 1990, 36,000 kg of bromacil were sold in Canada for commercial uses; most of which was sold in Alberta (12,300 kg), Manitoba (9,600 kg), and Ontario (9,500 kg) ([13]).

Total vegetation control through use of sterilants (mostly bromacil) was practiced by Alberta Gas Transmission Division (AGTD) of NOVA Corporation of Alberta prior to 1987 within the fence lines of 36 compressor stations, 850 meter stations, off-line sales stations, yards of maintenance and storage facilities, most valve sites and some rectifiers ([14]). Bromacil was typically used at rates up to 27 kg a.i./ha for non-selective vegetation control outside of agricultural land ([14]). Due to problems with off-site migration, AGTD suspended use of soil sterilants in 1987.

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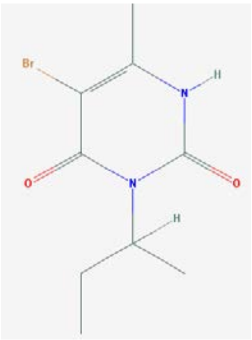
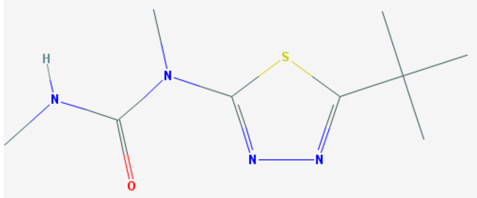
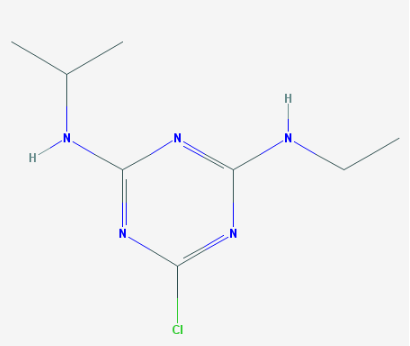
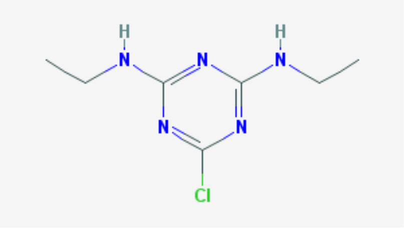
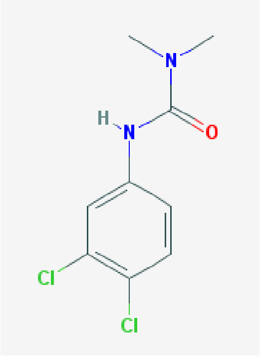
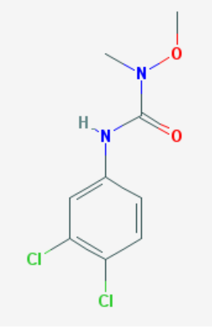
[1] This report focuses primarily on these six sterilants, however information on other sterilants is also provided.

Although bromacil and tebuthiuron are the most commonly found sterilants on legacy industrial sites in Alberta, other herbicides identified that create challenges with remediation and reclamation (often in combination with bromacil and tebuthiuron) include amitrole, borax, hexazinone, imazapyr, sodium chlorate, sodium metaborate octahydrate, and sodium metaborate tetrahydrate (G. Byrtus, B. Lambert, V. Servant, Personal Communication, 2018). In addition, selective products have also been used on industrial sites and rights of way (dicamba and picloram) and have caused issues with off-site movement, however they do not persist as long as sterilants. Selective products that have started to replace picloram which may pose similar challenges for remediation in the future include aminopyralid and aminocyclopyrachlor.

Table 1. Physical and chemical properties of sterilants commonly found on legacy industrial sites in Alberta.

Soil Sterilant*	**Relevant Physical and Chemical Characteristics***	**Structure**	**Mode of Action/Historical Use**
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** (spary), Calmix (combinded with 2,4-D as pellets), **Krovar** (combined with diuron)	Appearance: Colourless to white crystalline solid Available as wettable powder, soluble concentrate or granular Molecular Formula: $C_9H_{13}BrN_2O_2$ Molecular weight: 261.119 g/mol Melting point: 158-160°C Solubility in water: 815 mg/L @25°C Vapour pressure: negligible @ 25°C		Powerful and selective inhibitor of photosynthesis by blocking a step in the electron transport chain of photosystem II ([2], [15]); used on non-cropland areas for non-selective control of a wide range of annual and perennial grasses, broadleaf weeds and certain woody species ([12]); used at lower rates for selective control of annual and perennial weeds ([2]); industrial application rates varied: 10.7 – 21.5 kg a.i./ha ([1]); 4.5 – 13.5 kg a.i./ha ([16])
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	Appearance: Colourless crystals Non corrosive Molecular Formula: $C_9H_{16}N_4OS$ Molecular weight: 228.314 g/mol Melting point: 164°C Solubility in water: 2,500 mg/L @25°C Vapour pressure: 2.0 x 10^{-6} mm Hg @ 25°C		Typically applied for total vegetation control ([12]); inhibition of photosynthesis ([10]); prevention of lipid and RNA synthesis by disruption of photosynthesis ([17]); industrial application rates varied: 4.4-11.25 kg a.i./ha ([1]); 0.6 and 11.2 kg a.i./ha which corresponds to concentrations in soil between 0.3 and 5.0 mg a.i./kg soil ([17])

Soil Sterilant*	Relevant Physical and Chemical Characteristics*	Structure	Mode of Action/Historical Use
Atrazine Chemical name: 6-chloro-N2-ethyl-N4-(propan-2-yl)-1,3,5-triazine-2,4-diamine Commonly used product names: 1912-24-9, fenatrol, gesaprim, **aatrex,** atred, chromozin, and more	Appearance: White crystalline solid Molecular Formula: $C_8H_{14}N_5Cl$ Molecular weight: 215.69 g/mol Melting point: 176°C Solubility in water: 34.7 mg/L @26°C Vapour pressure: 1.5 x 10^{-7} mm Hg @ 25°C		Inhibits Hill reaction of photosynthesis ([18]); foliar and soil applied for selective and nonselective weed control ([12]); typically used for weed control in corn and general vegetation control; industrial application rates varied from 11.25 – 22.5 kg a.i./ha ([1]); commonly applied annually for total vegetation control from 1959 to 1978 at rates between 1.4 and 4.5 kg/ha ([4]); approximately 35 Mg a.i./year in US and number one herbicide for US corn crops in 2001 ([8]); #1 a.i. in US in 1987, 1997, and 1999 then #2 in 2001 ([19])
Simazine Chemical name: 6-Chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine Commonly used product names: 122-34-9, Gesatop, **Princep**, Simanex, Aquazine, Batazina, Herbazin, Primatol and others	Appearance: White to off-white crystalline powder Molecular Formula: $C_7H_{12}ClN_5$ or $CH_3CH_2NH(C_3N_3Cl)NHCH_2CH_3$ Molecular weight: 201.658 g/mol Melting point: 225-227°C Solubility in water: 6.2 mg/L @20°C Vapour pressure: 6.1 x 10^{-9} mm Hg @ 20°C		Inhibits the photosynthetic electron transport process ([20]); foliar and soil applied for selective and nonselective weed control ([12]); 0.5 – 2.0 mg a.i./kg soil application rate as a pre-emergence herbicide ([9]); typically used for total vegetation control on non-crop lands; commonly applied annually for total vegetation control from 1963 to 1976 at a rate of 4.5 kg/ha ([4]); #13 a.i. in the US in 2001 ([19])

Soil Sterilant*	Relevant Physical and Chemical Characteristics*	Structure	Mode of Action/Historical Use
Diuron Chemical name: 3-(3,4-dichlorophenyl)-1,1-dimethylurea Commonly used product names: **Karmex**, 330-54-1, DCMU, Duran, Dynex, Dichlorfenidim, Herbatox, Vondurон, Dailon and others	Appearance: White crystalline solid Wettable powder Molecular Formula: $C_9H_{10}Cl_2N_2O$ Molecular weight: 233.092 g/mol Melting point: 158-159°C Solubility in water: 42.0 mg/L @25°C Vapour pressure: 6.9 x 10^{-8} mm Hg @ 25°C		Non-selective herbicide; used at high rates as a general vegetation control in non-crop areas and lower rates in irrigation and drainage ditches ([12]) or in combination with bromacil (Krovar); blocks electron transport in photosynthesis ([21]); Strongly inhibits photosynthesis II system via the Hill reaction ([22]); industrial application rates varied from 11.2 – 44 kg a.i./ha ([1]); commonly applied annually for total vegetation control from 1963 to 1976 at rates around 4.5 kg/ha ([4]); used in US at 2 – 4 million pounds/yr ([21]); more than 2,000 tonnes/yr in Australia ([22]); applied at rates of 4 – 36 kg a.i./ha on Australian ROW and commercial/industrial areas; 3.1 – 16 kg a.i./ha for re-treatment ([22])
Linuron Chemical name: 3-(3,4-Dichlorophenyl)-1-methoxy-1-methylurea Product names: 330-55-2, Methoxydiuron, Afalon F, Cephalon, Linurex, Lorox L and others	Appearance: Colourless crystals. Non corrosive. Molecular Formula: $C_9H_{10}Cl_2N_2O_2$ Molecular weight: 249.091 g/mol Melting point: 93-94°C Solubility in water: 75 mg/L @25°C Vapour pressure: 1.4 x 10^{-6} mm Hg @ 25°C		Commonly used in agriculture for selective control of annual grassy and broadleaf weeds ([12]); Commonly applied annually from 1963 to 1971 at rates around 4.5 kg/ha ([4]); Soil or foliar applied; readily absorbed by roots and rapidly translocated to upper plant parts to accumulate in leaves and inhibit photosynthesis ([12]).

*PubChem, 2018 – https://pubchem.ncbi.nlm.nih.gov/; Product names in **bold** are trade names for products commonly used in Alberta ([4]).

3.0 PERSISTENCE AND FATE IN THE ENVIRONMENT

When a residual herbicide enters the soil it is subjected to a variety of natural processes ([11]). These processes are physical, chemical and biological in nature. They result in either physical removal of the herbicide or its breakdown into non-toxic compounds ([4]). In the case of industrial lands there may be additional operational practices that affect sterilant concentrations, in addition to any remediation and reclamation steps taken on the site.

Persistence of an herbicide in soil depends on several factors related to the herbicide itself, and to the soil and climatic conditions. The type of herbicide used, its formulation (granular vs. emulsified concentrate), and its rate, time and method of application influence the length of time a herbicide remains active in a soil ([4]). Residual herbicides differ in their physical and chemical properties, such as water solubility, volatility, and susceptibility to breakdown by sunlight and biological and chemical processes. Persistent herbicides (sterilants) generally have one or more of the following properties: low water solubility (simazine, linuron); moderate degree of adsorption (some more than others); low volatility (bromacil, tebuthiuron, simazine, diuron); low susceptibility to decomposition by light (bromacil, tebuthiuron, atrazine, linuron); low susceptibility to chemical degradation (bromacil, tebuthiuron, diuron, linuron); and low susceptibility to microbial decomposition (bromacil, tebuthiuron, linuron).

3.1 ENVIRONMENTAL FATE

Herbicide activity, movement and persistence in the environment depend on solubility, volatility and the interaction of the herbicide molecule with the adsorption capacity of the soil's colloids ([5]). The six sterilants investigated in this review are considerably different in the way they interact with the environment, thus have different levels of soil sorption and mobility, influencing the fate and transport of the various products. The parameters influencing the environmental fate of the most commonly found sterilants in Alberta, bromacil and tebuthiuron, are provided in Table 2. Similar information, although less detailed, is provided for atrazine, simazine, diuron and linuron in Table 3.

Studies have found variable results under different environmental conditions in terms of soil sorption, mobility, and leaching potential for the various sterilants evaluated (Tables 2 and 3). For example, the soil/organic matter sorption coefficient (Kd/Koc) values for bromacil in the literature ranged from 2.3 to 289 (average 57) from several different studies conducted in soils ranging from sandy soils to mucky peats ([16]). The Koc measures the affinity of a chemical to organic carbon, relative to water. The lower the Koc, the more soluble in water and the lower the affinity for organic carbon (thus higher mobility). Generally, a Koc value less than 100 indicates that a pesticide is mobile in soils ([5]).

The range of Koc and soil/organic matter sorption coefficient values obtained for bromacil in the literature indicate that under a variety of environmental conditions the herbicide is likely to react differently. Bromacil moves quite readily through the soil due to low soil adsorption and high water solubility and is highly likely to leach into the groundwater and/or move offsite to aquatic ecosystems. It is more strongly adsorbed by organic matter than clay, therefore is more likely to be found at the surface where the soils have higher organic matter. Tebuthiuron has a high solubility and is weakly adsorbed to soil particles therefore has a very high leaching potential, particularly in areas receiving high amounts of precipitation. Mobility of tebuthiuron is influenced by soil texture and is highest in sandy soils with low organic matter content and lowest in clay loam soils or highly organic soils ([17]). Similar variability in terms of mobility and fate in the environment can be found in the literature for atrazine, simazine, diuron and linuron depending on water solubility, and adsorption and desorption from soil particles and organic matter (Table 3). In a study conducted by de Paz and Rubio ([23]) the leaching potential of herbicides was ranked from highest to lowest potential as follows: bromacil>simazine>diuron>linuron. Atrazine and tebuthiuron were not included in the study.

Alberta Environment provided a summary of pesticide monitoring data of 3,055 samples from 326 surface water bodies throughout Alberta ((i.e., rivers, creeks, lakes, wetlands, irrigation canals and returns, and urban streams) from 1995 to 2002 ([24]). Four of the five sterilants included in the investigation were identified in surface waterbodies in Alberta (tebuthiuron was not included):

- atrazine in 115 of 3,054 samples – detection limit = 0.005 µg/L; median concentration 0.20 µg/L; maximum concentration 2.617 µg/L. atrazine detections in Crowfoot Creek were traced back to urban use of a sterilant in the Calgary area.
- bromacil in 32 of 3,052 samples – detection limit = 0.03 µg/L; median concentration 0.25 µg/L; maximum concentration 2.70 µg/L.
- diuron in 24 of 3,052 samples – detection limit = 0.02 µg/L; median concentration 0.03 µg/L; maximum concentration 2.80 µg/L.
- linuron was not found in any the 42 samples – detection limit = 0.02 µg/L.
- simazine in 117 of 3,052 samples – detection limit = 0.01 µg/L; median concentration 0.011 µg/L; maximum concentration 0.464 µg/L.

Table 2. Environmental fate of bromacil and tebuthiuron.

Parameter	**Sterilant**	
	Bromacil*	**Tebuthiuron****
Water Solubility	815 mg/L at 25°C; increases with higher pH [16])	2,500 mg/L at 25°C
Soil/organic matter sorption coefficient (Kd/Koc); Octanol-water partition coefficient (log Kow)	Koc: 32 g/mL ([5]); Kd/Koc: variable from 2.3 to 289 in soils ranging from sand to peat ([16]); Log (Koc): 1.86 (average) for soil; 1.61 (average for sediments) ([16]) Log Kow: 2.11	Koc: 80 mg/L ([25]); Kd: 0.2-10.0 ([25]); Log Kow: 1.79 ([17], [25])
Mobility	Highly likely to be mobile in soils low in organic matter ([5]); Moves horizontally on surface and vertically with water ([14]); Moderate mobility in soils high in OM and clay content ([3])	Influenced by soil texture and organic matter content (higher mobility in sandy soils and soils low in OM; lower in clay loams soils or highly organic soils) High ([3]); Yes ([6])
Leaching Potential	Restricted by high water table ([2]); High ([1], [5]); An important dissipation process ([14]); Readily leached ([12])	Medium ([1]); High solubility in water, weak adsorption to soil particles and is highly persistent therefore has high potential to leach ([17])
Adsorption/ Desorption	Lower than other herbicides ([14]); Sorption to soils increases with clay and OM content ([5], [10]); Will not partition to suspended particles or sediments in aquatic systems (remain dissolved in water column) ([9]); Relatively low ([26])	Relatively poor soil sorption; Sorption to soils highest in soils high in OM content followed by clay content ([17], [27]); <1% at soil OM of 0.3% and 40% with soil OM of 4.8% ([17])
Volatilization	Minor importance ([12], [14])	Not volatile ([17])

* A full review of the physical and chemical properties of bromacil described in the literature to 2005 is provided in ([16]) and additional information can be found in US EPA ([28]);

**An extensive review of the fate of tebuthiuron in the environment is provided in Stantec ([17]);

K_{OC} value < 100 indicates that a pesticide is mobile in soils ([5]).

Table 3. Environmental fate of atrazine, simazine, diuron and linuron.

*Soil/organic matter sorption coefficient; **Octanol-water partition coefficient

Parameter	Sterilant			
	Atrazine	Simazine	Diuron	Linuron
Water Solubility	Moderately soluble in water: 33 ug/mL ([29]); 34.7 mg/L at 26°C	Low water solubility: 5 mg/L ([29]); 6.2 mg/L (pH 7, 20°C)	Slightly to moderately soluble in water: 42.0 mg/L at 25°C ([30]); Moderately soluble ([22])	Slightly to moderately soluble in water: 75.0 mg/L at 25°C ([31])
Koc; Kd; Kd/Koc*; log Kow**	Koc (average from multiple sources) – ranges from 122-163 (but has been reported between 39 and 13,600 in the literature) ([32]); Koc: 100 g/mL ([33]); log Kow: 2.61	Koc: 138 g/ml ([29]) Log Kow: 2.18 Kd: 0.3 mL/g in sand to 21.5 mL/g in montmorillonite clay amended with organic matter (([20])	Log Kow: 2.77 ([30]) Koc: range from 418 – 574 in soils low in OM indicating moderate sorption to soil particles and major dependence on OM content ([22]); 366 – 1,750 for five Australian soils ([22]).	Log Kow: 3.2 Kd: nonionic Koc: 860 ([31])
Mobility	Yes ([6]); Moderately to high; especially where soils have low clay or OM content ([9], [32], [33]);	Yes ([6]); Low water solubility (less mobile) ([9])	Yes, dependent on organic matter and degree of degradation ([6], [9]) (metabolites less mobile than parents); Ranges from very high to low mobility in soils; correlated with soil OM ([34])	Moderately soluble; Moderately persistent; does not move freely (mobility decreases as OM increase) ([9])
Leaching Potential	Medium ([1]); Commonly found in groundwater and DUA ([9]); Negligible ([4])	Limited leaching potential due to low solubility, however will concentrate in groundwater when it does leach ([9]); with repeated applications over time, likelihood of leaching is higher (([35])	Limited leaching potential ([1]);	Limited leaching potential ([9]); Negligible ([4])
Adsorption/ Desorption	Strongly adsorbed to OM ([4]) (particularly at low soil pH); Does not strongly adsorb to inorganic sediments ([32]); Degree of adsorption varies with soil texture, OM, water content and pH ([12])	Does not adsorb strongly to soil particles ([29]); Moderately to poorly bound to soils (does adsorb to clay; particularly montmorillonite) ([9], [20], [26]); Strongly adsorbed to OM ([4]) (particularly at low soil pH)	Strongly adsorbed to OM ([4], [36]) (no effect of soil pH); High ([26]); Metabolites have different adsorption and desorption than the parent product ([22]).	Sorption to soils increases with clay and OM content ([9]); Very strongly adsorbed to OM ([4])
Volatilization	Yes ([9])	No ([9]); Low ([20])	Unlikely to volatilize ([9], [32]); Very slightly volatile ([22])	Unlikely based on the herbicide class

3.2 DEGRADATION PATHWAYS AND HALF-LIVES

A herbicide's persistence in soils is generally described by its half-life, defined as the time it takes for half of the herbicide applied to the soil to be dissipated. Large differences are reported in the literature for herbicide half-lives within lab or field conditions making it very problematic to accurately predict the fate of the contaminants in the environment. Sterilants typically have lengthy half-lives which are influenced by environmental parameters (Tables 4 and 5).

Landsburg and Fedkenheuer ([14]) found persistence values in the literature ranging from six months to a year for bromacil depending on application rate and soil type. Sanders et al. (([37]) found bromacil degradation in soil was significantly impacted by the number of applications within a season, and over time, and concluded that bromacil applications caused stress on the soil microflora contributing to retarded degradation with repeated bromacil use. Shea reported persistence of various herbicides in Nebraska soils, including: 6 – 30 months for simazine and 6 – 24 months for atrazine ([38]). Persistence may be increased by the application of other pesticides ([38]). Gerstl ([39]) found that temperature and soil moisture content affected persistence in Israeli soils more than soil type or initial bromacil concentration. Bromacil can be degraded by microorganisms, however degradation is very slow and it has been noted by other authors that co-metabolism may be a more important microbial degradation pathway than degradation of a specific sterilant ([17]).

Stantec conducted a laboratory microcosm study to determine half-life for tebuthiuron in subsoils from a site near Brooks ([17]). Tebuthiuron levels in the soils were as high as 0.6 mg/kg. After 256 days the tebuthiuron degradation varied from 26% to 67% depending on water holding capacity (WHC) and whether or not alfalfa hay had been added to the sample, translating to half-lives ranging from 4 to 13.5 months. The most rapid degradation occurred when soils were amended with alfalfa hay and maintained at 1.0 x WHC. Qureshi ([4]) reported herbicide residues ranging from 0.102 to 0.473 mg/kg for atrazine; 0.952 to 2.4 mg/kg for diuron; 1.38 mg/kg for linuron; and 0.016 to 0.473 mg/kg for simazine and its metabolites years after multiple annual herbicide applications.

Table 4. Degradation pathways and half-lives of bromacil and tebuthiuron.

Parameter	Sterilant	
	Bromacil	**Tebuthiuron**
Degradation	• Biodegradation important dissipation process ([12], [14]); however it is very slow ([9]); • Co-metabolism may be a more important microbial degradation pathway than direct bio-degradation ([17]); • Stable in aquatic environments (stable to hydrolysis and photodegradation only occurs under alkaline conditions) ([9]); • May degrade in natural waters through microbial and photo-sensitized degradation ([5]); • Aerobic and anaerobic metabolites listed in US EPA ([28]).	• Variable results for rate and importance of microbial degradation are reported ([17]); • Relatively resistant to abiotic and biotic degradation ([17]); • Photodegradation occurs, although it is of limited importance in soil; • Microbial degradation is influenced by soil moisture and temperature (lower at lower moisture and temperature); • Degradation pathways are further explored in Stantec ([17]) which also investigated microbial organisms with the capacity to degrade tebuthiuron.
Half-Life	• Field derived soil dissipation half-life – 349 days (average from the literature) ([16]); • Soil dissipation half-life – 132 days (average from the literature (aerobic) ([16]); • 140 – 1,494 days in soil ([3]) • 140 – 168 days ([1]); • 60 – 240 days ([5]); • soil biodegradation half-life – 275 to 350 days ([16]); • Variable depending on number of applications in a season and over time ([37]) [4-6 months with a single application]	• Highly persistent in soils; soil half-life increases in arid and semi-arid environments with low annual precipitation and in soils high in organic matter; • soil half-life: 360 days; 12 – 15 months ([3]) (in areas receiving high annual rainfall (takes longer in areas receiving less rainfall); • 52 – 60 weeks ([1]); • 1 to 7 years ([17])

Table 5. Degradation pathways and half-lives for atrazine, simazine, diuron and linuron.

Parameter	Sterilant			
	Atrazine	**Simazine**	**Diuron**	**Linuron**
Degradation	• s-triazine ring fairly resistant to degradation ([32]); • Biodegradation important for removal from terrestrial ([40]) and aquatic environments ([9]); • Hydrolysis important degradation pathway in acidic or basic environments (resistant at neutral pH) ([32], [33]); • Highly influenced by pH	• Degrades by ultraviolet radiation; • Microbial degradation is significant (particularly in high pH soils) ([9]); • Hydrolysis will occur at low pH in soil ([9]); • Persistent (up to eight months) and not easily degraded by microbes; however, biotic degradation seems to be the most effective method of simazine degradation compared to the abiotic processes ([20]); • Limited to slow bacterial biodegradation ([41])	• Biodegradation and photodegradation important loss mechanism in aquatic and terrestrial systems ([9], [32]); • Stable to hydrolysis ([9]) (both in terrestrial and aquatic systems) degradation occurs faster in aerobic soils; • Limited biodegradation in water ([42])	• Not readily broken down in the soil ([9])
Half-Life	• 2 – 742 days ([18]); • Soil half-life: 60 – 100+ days ([33]); • 24 – 32+ weeks ([1]); • Significantly impacted by OM in the field ([32]) (e.g., 244 days at 25°C and pH 4 with no organics and 1.73 days with 2% humic acid); • Aqueous half-life of 3 – 120 days ([19])	• Soil half-lives reported vary from 16.3 to 25.5 weeks in loamy sand and silt loam ([29]); • 28 – 149 days ([9]); 36-234 days in sandy loams ([43]); • Varies based on single vs. repeated applications, temperature and soil moisture ([41])	• 52 – 78 weeks ([1]); • 73 – 330 days ([9], [32]); • 20 – 546 days depending on soil type and temperature and metabolite ([22]); • 90 days ([21]); 372 days (aerobic soils); • >1,000 days (anaerobic soils) ([9]); • Hydrolysis 1,240-2,020 days based on pH; • aqueous photolysis 43.1 – 2,180 days; soil photolysis 173 days; field dissipation 99.9 – 134 days ([34]) • aerobic soil degradation 372 days; anaerobic soil degradation 995 days;	• 75 – 230 days (aerobic conditions) ([9])

4.0 ECOTOXICOLOGICAL INFORMATION

In toxicology and eco-toxicology, dose descriptor is the term used to identify the relationship between a specific effect of a chemical substance and the dose at which it takes place. Toxicity data for studies completed on terrestrial, aquatic and invertebrate organisms and concentrations affecting plant growth for bromacil, tebuthiuron, simazine, atrazine, diuron and linuron are provided where available in Table 6. Variable results have been reported in the literature for toxicity to mammals, birds, reptiles, aquatic organisms and plants at variable concentrations, particularly for bromacil, tebuthiuron and atrazine.

Environment Canada and CCME have established specific guidelines and test methods to assess toxicity for development of soil eco-contact guidelines ([10]):

- Tests for Toxicity of Contaminated Soil to Earthworms. EPS1/RM/32 (2004)
- Test Measuring Emergence and Growth of Terrestrial Plants Exposed to Contaminants in Soil EPS1/RM/45 (2005; updated 2007)
- Guidance Document on Statistical Methods for Environmental Toxicity Tests. EPS1/RM/46 (2005)
- Test for Measuring Survival and Reproduction of Springtails Exposed to Contaminants in Soil. EPS1/RM/47 (2007; updated 2014)
- A Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines. PN1332 (2006)

Toxicity of tebuthiuron from a native prairie battery site in southeastern Alberta was assessed (subsoil levels 0.03258 mg/kg ± 0.001027 ([44])) to aid in the development of an ecological direct contact pathway ([10], [45]). Chronic (invertebrates) and definitive (plants) screening tests were conducted with tebuthiuron in 2008 ([44], [45]) on multiple species (soil organism (springtail (*Folsomia candida*), soil invertebrate (earthworm (*Eisenia andrei*)), and plants (blue grama grass (*Bouteloua gracilis*), western wheatgrass (*Pascopyrum smithii*), silver sage (*Artemisia cana*), Durum Wheat (*Triticum durum*)) and resulted in a recommendation for a site-specific guideline for tebuthiuron of 0.020 mg/kg based on the plant species being more sensitive than the invertebrates (0.046 mg/kg).

A similar ecotoxicity assessment of bromacil was conducted in 2012 and evaluated multiple species (soil organisms, plants and soil invertebrates) ([15]) and found that plants are more sensitive to bromacil than invertebrates even at low concentrations and that plant toxicity varies between species with durum wheat being more sensitive than blue grama grass and alfalfa. The assessment, which was conducted using fine and coarse textured soils containing from 0.005 mg/kg to 2,000 mg/kg bromacil resulted in site-specific guideline recommendations for agricultural/residential uses of 0.25 mg/kg for fine textured soil and 0.11 mg/kg for coarse textured soil, and for commercial/industrial uses of 0.93 mg/kg for fine textured soil and 0.30 mg/kg for coarse textured soil ([10], [15], [46]). When only considering plant screening tests, the values were lower at 0.20 mg/kg (fine) and 0.12 mg/kg (coarse) for agricultural/residential uses and 0.49 (fine) and 0.20 (coarse) mg/kg for commercial/industrial uses ([15]).

There are not many toxicity data for native prairie or boreal forest species and very few data for naturally occurring invertebrates ([7]). Bessie et al. ([45], [47]) assessed toxicity of tebuthiuron to native prairie grass species (June grass (*Koeleria macrantha*) and needle and thread grass (*Hesperostipa comata*)) and confirmed they were not suitable for ecotoxicity testing. McKelvey et al. ([48]) investigated the effectiveness of regulatory non-target plants testing using crop species in the US to predict phytotoxicity of herbicides to non-crop species and found that for pre-emergence and post-emergence exposure only one non-crop species was more sensitive than the most sensitive crop species evaluated which indicated that crop species sensitivity to bromacil was likely to be representative of non-crop herbaceous species response.

Fairchild ([19]) reviewed the toxic effects of herbicides, with an emphasis on atrazine, on aquatic ecosystems. Van den Brink et al. ([49]) found that chronic low concentrations of atrazine (5 µg/L) applied in aquatic microcosms had no effect on zooplankton or macroinvertebrates. Sura ([11]) described the toxicity of various herbicides, including atrazine, on algae, cyanobacteria and duckweed in prairie pothole wetlands. Cuppen et al. ([50]) studied effects of a chronic application of five dosage rates of linuron and found no effects on plant litter decomposition, and varying effects on densities of zooplankton and macroinvertebrates in mesocosms.

Table 6. Ecotoxicity and related environmental impacts of soil sterilants.

Soil Sterilant	Bioaccumulation	Ecotoxicity			Concentrations Affecting Plant Growth
		Mammalian/Bird	**Aquatic**	**Invertebrates**	
Bromacil	Unlikely ([9], [16])	Developmental toxin to mice, rats, dogs and sheep upon consumption ([9]); skin and mucosal irritant; possible carcinogen ([9]); Non-toxic to mammals (LD_{50} – 3,998 mg/kg), birds (LD_{50} – 2,250 mg/kg) and reptiles ([5]); Low toxicity hazard to terrestrial animals ([16])	Growth inhibition (EC_{50}) ranges from 5 to 500 µg/L (various aquatic algae, plants, and invertebrate animals species) ([51]); Slightly toxic to non-toxic to most organisms ([5], [16]); Algae adversely impacted at low concentrations ([9])	Acute adverse effect concentrations occurred at 65 mg ai/L ([9], [16])	0.1 ppm ([14]); NOAEL ranged from 0.094 – 0.00585 mg/kg ([7]); Trees and shrubs are often more tolerant to bromacil than grasses ([2]); Effects have been noted at an order of magnitude lower than the direct eco-contact pathway for agricultural use ([10]); Terrestrial plants sensitive to concentrations as low as 0.0012 ppm ([16])
Tebuthiuron	Unlikely ([9])	Moderate toxicity ([9]); Moderately toxic by the oral route for rats, rabbits and cats and only slightly toxic to mice and dogs ([52]); practically non-toxic by the dermal route and not considered a dermal irritant	Low toxicity to fish and amphibians ([52]); High toxicity to aquatic plants (EC_{50} = 0.05 mg/L) ([9])	Low to slight toxicity to [aquatic] invertebrates ([52])	0.015 – 0.0402 mg/kg ([7]) Wheat (most sensitive crop) 0.0201 mg/kg NOAEL and 0.0402 mg/kg LOAEL ([27]); Weeds controlled at levels as low as 0.015 mg/kg ([27]); Seed emergence most sensitive indicator of toxicity at low application rates
Atrazine	Low levels of bioaccumulation ([9], [32])	Chronic effects on dogs and acute effects in rats ([18]); Slightly toxic to birds ([9]); Oral LD_{50} for rats = 5,100 mg/kg ([38])	Chronic effects on frogs; acute effects on fish and shellfish ([9], [18]); 96 hr LC_{50} for bluegill sunfish >24 ppm ([38]); EC_{50} for bluegill 28.3 mg/L ([19])		0.01 – 0.02 mg/kg ([7], [9])

Simazine	Human carcinogen	No acute toxicity information available for reptiles or amphibians ([9]); oral LD_{50} for rats >5,000 mg/kg ([38])	Variable (moderately toxic) ([9]); 96 hr LC_{50} for bluegill sunfish = 16.0 ppm ([38]) or >100 mg/L ([20]); Fish and higher order mammals are generally tolerant ([20]); Algae are sensitive at concentrations less than the US maximum concentration level of 4 µg/L ([20]); Toxicity, measured as % inhibition of ^{14}C uptake in algae (96 – 99), cyanobacteria (65 – 97), and 7-day growth of duckweed (95) ([11])	Moderate toxicity to invertebrates and earthworms ([9]); Reduction in mites, springtails, millipedes and enchytraid worms ([41])	0.5 mg/kg ([7]); Mortality increased in presence of mycorrhizae ([41])
Diuron	Low to moderate tendency ([9]); Low potential ([42])	Not highly toxic to terrestrial species; Causes genetic damage in developing embryos and bone marrow in mice ([19]) Impacts to fungi and nitrogen fixing nodules and bacteria ([19]); Increased the incidence of urinary bladder carcinomas in both male and female Wistar rats; mammary gland adenocarcinomas noted in NMRI mice; negative genotoxicity ([42])	Moderately toxic to fish and highly toxic to aquatic plants ([9]) ([21]); Approximately 50 times more toxic to fish than bromacil ([53]); Has the potential to cause acute harm to sensitive aquatic organisms at low concentrations (i.e., acute LC_{50} values are ≤1.0 mg/L)([42]); Amphibians less sensitive	Highly toxic to aquatic invertebrates (0.71 mg/L) ([9]);	0.01 – 0.02 mg/kg ([7]); vegetation vigour most sensitive indicator to assess toxicity ([9])
Linuron	Unlikely to slightly likely (low levels in aquatic organisms) ([9])	Toxic/irritant to animals at high doses ([9])	Slightly toxic	n/a	0.25 – 3.0 mg/kg ([7], [9])

5.0 REGULATORY GUIDELINES AND ANALYSIS

5.1 REGULATORY GUIDELINES

The Alberta Tier 1 guidelines for bromacil, tebuthiuron, atrazine, simazine, diuron and linuron are provided in Table 7 for fine and coarse-textured soils and human and ecological exposure pathways.

A Canadian Water Quality Guideline for bromacil for the protection of agriculture water uses was developed based on CCME protocols and first introduced in 1993 ([13]). Research suggested that bromacil was toxic to a variety of non-target species, particularly in agriculture and the effects of bromacil on fruits and vegetables was variable from beneficial (soybeans), to tolerant (plum trees), to harmful (apple trees) ([13]). The most sensitive species to bromacil treatment was cucumber. The guideline derivation for the irrigation pathway was then calculated according to the CCME protocol for species which had sufficient data and the lowest value was adopted in 1997. It was stated in the CCME fact sheet for protection of agriculture water uses for bromacil that "*the guideline value may be modified for areas that do not grow the most sensitive species (upon which the guideline was derived) or for areas with sources of the contaminant other than irrigation water* ([13])". ENSR International ([16]) conducted an ecological risk assessment on bromacil for the Bureau of Land Management in the US in 2005 and summarized the majority of research related to ecotoxicity of bromacil. Much of this information was later used as the basis for ecotoxicity evaluations in Canada.

When sterilants were added to the Alberta Tier 1 Guidelines in 2007 there was no guideline for the Direct Soil Contact pathway for the six primary sterilants ([7]). In 2012, Intrinsik reviewed the literature related to 25 high priority pesticides, including several soil sterilants, in support of potentially developing CCME direct ecological contact soil quality guidelines ([6]). For many of the pesticides there were few data that expressed ecotoxicity values as soil bulk concentrations (i.e., mass a.i./mass soil) which is required for soil guideline development. Only atrazine, tebuthiuron and trifluralin had sufficient plant and/or soil data to be used for general soil quality guideline development. Risk-based soil eco-contact remediation guidelines have since been developed and adopted by Alberta Environment and Parks (AEP) for tebuthiuron and bromacil through CCME procedures ([10]). Soil eco-contact guidelines are not available for atrazine, diuron, simazine, or linuron in Alberta.

Table 7. Regulatory soil guidelines for soil sterilants in Alberta.

	Alberta Tier 1 Guidelines (Agricultural and Natural Area Land Uses)*											
Soil Sterilant	**Soil (Coarse-grained; mg/kg)**						**Soil (Fine-grained; mg/kg)**					
	Ecological				**Human**		**Ecological**				**Human**	
	Protection of Irrigation Water	**Protection of Freshwater Aquatic Life**	**Direct soil contact**	**Protection of Livestock Water**	**Protection of Domestic Use Aquifer**	**Direct Soil Contact**	**Protection of Irrigation Water**	**Protection of Freshwater Aquatic Life**	**Direct soil contact**	**Protection of Livestock Water**	**Protection of Domestic Use Aquifer**	**Direct Soil Contact**
Bromacil	BDL	**0.009**	0.12	2.0	10.0	2,000	BDL	**0.009**	0.20	2.0	7.0	2,000
Tebuthiuron	BDL	BDL	0.046	0.11	3.7	1600	BDL	BDL	0.046	0.12	2.5	1600
Atrazine	0.057	**0.010**	--	0.028	0.19	11	0.049	**0.0088**	--	0.025	0.10	11
Simazine	--	0.022	--	**0.038**	0.25	29	--	**0.033**	--	0.033	0.14	29
Diuron	--	--	--	--	**3.5**	350	--	--	--	--	**1.9**	350
Linuron	BDL	0.059	--	--	**0.56**	44	BDL	0.051	--	--	**1.1**	44

***bold** is lowest applicable guideline; no differences exist between agricultural and natural area land uses
BDL = below detection limit (groundwater assessment and comparison to groundwater remediation guidelines is required)
Adapted from *Alberta Tier 1 Soil and Groundwater Remediation Guidelines* ([54])

5.2 ANALYSIS OF SOIL STERILANTS

Accurately sampling soil for sterilant analysis can be problematic. Sterilant concentrations in soil can easily be diluted to less than guideline levels if samples are not taken appropriately. Previous recommended sampling methods ([55]) may not be adequate to properly characterize soil sterilant concentrations in the parts per billion range. Environmental analysis labs provide sampling instructions in terms of materials, sampling handling and preparation, however there is little information available on appropriate field sampling procedures.

Current detection of soil sterilants is costly, time consuming and labour intensive. Chromatographic methods (gas and high pressure liquid) are historically used for sterilant detection, and quantification in complex matrices ([32]). There also have been mass spectrometry methods developed for bromacil and metabolite detection ([56]). Laboratory detection limits have improved significantly for all sterilants since 1998 (0.01 mg/kg in 1998 to 0.005 mg/kg in 2008) leading to more “hits” in samples but were still above the guideline values for linuron, simazine and tebuthiuron ([7]). Detection limits vary between methods and the number and type of sterilants being screened for. Analytical labs in Alberta typically use Gas Chromatography/Mass Spectrometry (GC/MS) or High Performance Liquid Chromatography/Mass Spectrometry (HPLC/MS) to analyze for sterilants. Methods are modified depending on the lab conducting the analysis, however methanol is the extractant typically used to remove the sterilants from soil in sample preparation. Analysis of soil sterilants requires multiple steps, therefore is quite expensive. Screening for a variety of pesticides simultaneously during an environmental site assessment can become extremely expensive if it is unknown what products were previously used on a site. In addition, detection limits are generally higher during screening tests rather than sterilant-specific analysis which could result in false negatives and the wrong remedial action plans developed.

There were antibody-based enzyme-linked immunosorbent assays (ELISA) developed for bromacil detection in the 1990's ([57]), however they were not widely adopted mainly because the techniques suffered from lack of reusability, cost of use and production, and time to obtain results as well as inherent lack of specificity in typical antibody production ([51]). Williams et al. ([51]) investigated the selection of a stable single stranded DNA (ssDNA) molecular recognition element (MRE) with high affinity and specificity for the herbicide bromacil to be incorporated into a device to allow rapid, portable, cost-efficient, and reusable monitoring of bromacil. Potential disadvantages of this technique include nuclease degradation of the sensing element, sensitivity, and specificity compared to conventional methods, however the potential advantages of an ssDNA MRE device are noteworthy when compared to existing bromacil detection methods, such as chromatography, mass spectrometry, and ELISAs with antibodies. Additional research is required for the development of a sensor incorporating this technique.

Bioavailability of pesticides and other organic contaminants is a major limitation to complete bioremediation of contaminated soils. It affects the clean-up time, cost, and the end-point of the process ([58]). From a biodegradation point of view, bioavailability is defined as the accessibility of a chemical for assimilation by microorganisms ([59]). The term "bioaccessibility" encompasses what is immediately available plus that which may become available, whereas bioavailability refers to what is available immediately. Studies have been conducted to examine the bioaccessible fraction of the contaminant after different aging periods. Recently, Villaverde et al. ([60]) used different non- exhaustive extraction techniques to determine whether their extraction abilities correlated with the bioaccessible fraction of the sterilant diuron in an aged contaminated soil. Diuron bioaccessibility was evaluated through diuron extracted by a biomimetic extraction using a 50 mM hydroxypropyl-β-cyclodextrin (HPBCD) solution, 10 mM $CaCl_2$, hexane, or butanol. The authors concluded that the aqueous HPBCD extraction technique has potential to become a valuable tool for estimating the bioaccessible fraction of soil-associated diuron at different aging times, and this could be applicable in the assessment of risk and contaminated land bioremediation potential. Further investigation is required to determine if this technique could be applicable to other sterilants found in Alberta.

6.0 SOIL REMEDIATION TECHNOLOGIES

Technologies used to deal with pesticide-contaminated soils generally fall into two categories: containment-immobilization or treatment. Treatment technologies fall into two different categories: separation and destruction. To reduce, eliminate, isolate or stabilize a sterilant, soil remediation technologies use physical, chemical, or biological processes. The selection of appropriate technologies depends on several factors, such as site characteristics, concentration and type of sterilant to be removed, and the end use of the contaminated media ([61]). Depending on the technology used, techniques for soil remediation can be applied in three ways ([62]): (1) In-situ – the remediation method is applied without excavating the soil and the contaminants are treated on the place the contamination occurred; (2) on site – contaminated soil is excavated, treated on site and returned to the original location; (3) ex-situ – contaminated soil is excavated and transported to another location for its treatment and/or disposal ([61]).

Caliman et al. ([62]) and Marican and Duran-Lara ([63]) summarized the benefits and limits of remedial technologies for a variety of contaminants, including pesticides. Shea ([38]) suggested that focusing on managing the soil water content, temperature and aeration are key to successful remediation – more complex treatment technologies should only be considered when these efforts are not successful. As most of pesticide-contaminated soils contain complex mixtures of different compounds rather than one single contaminant, their remediation can be a complicated process ([61]). A summary of the technologies applicable to remediation of residual soil sterilants evaluated in this review is provided in Tables 8, 10 and 11. Technologies have been reviewed previously by others; Bessie ([7]) listed remedial options for soil applicable to the six primary sterilants based on a review of the literature, and Cotton and Sharma ([1]) provide a literature review supporting the use of specific amendments tested in a laboratory study.

6.1 IMMOBILIZATION TECHNOLOGIES

Given the nature of the contaminants and the sites impacted by sterilants, removing contaminated soil and transporting it for treatment or disposal is relatively undesirable. Economical remediation approaches which reduce the risks associated with the sterilants and meet the requirements to protect human and ecological health are needed. Such risks can be mitigated by reducing the bioavailability of the contaminant and, thereby, a higher contaminant mass could be left in place, reducing the need for more expensive remediation actions ([64]). Morillo and Villaverde ([61]) provided a review of the recent literature evaluating various immobilization technologies for a number of organic pesticides and found a wide range of results depending on the pesticide compound, type and age of amendment and source of amendment feedstock. They concluded that the in-situ application of an adsorbent amendment in contaminated soils is a cost-effective technique for remediation of sterilant impacted soils ([61], [65]). A list of immobilization technologies available for treatment of soil sterilants is provided in Table 8.

Table 8. Summary of immobilization remediation technologies proposed for or applied to soil sterilants.

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages
Activated Carbon	Bromacil, diuron, linuron, simazine, tebuthiuron ([7]) atrazine, diuron, bromacil, tebuthiuron ([1]) bromacil ([14])	Adsorption ([1]) Assists in the rehabilitation of bromacil contaminated soils by first adsorbing the bromacil and second, providing conditions conducive to the microbial growth which is responsible for degrading bromacil ([14])	Requires mechanical mixing into soil ([27]); Only effective in the zone that AC is physically mixed into ([9]); No evidence to verify that release from charcoal is less than degradation rate	Effective in field trials at rates of 200:1 activated carbon to herbicide a.i; increased activated carbon rates had no effect
Humates / Humic Acid	Atrazine, diuron, bromacil, tebuthiuron ([1])	Adsorbent that decreases biological availability in soil and the potential for environmental pollution ([1])	Not a permanent solution	Low cost
Ash / Fly Ash	Bromacil, tebuthiuron ([1])	Adsorbent ([1])	Potential to elevate boron and selenium levels ([1])	Large surface area for adsorption ([1]) Large volumes near coal-fired power plants
Biochar	Diuron, atrazine, ([66]), linuron ([61])	Adsorbent ([67])	No evidence to verify that biochar will react similarly to AC in soil or that the release from biochar is less than degradation rate.	Adsorbent that decreases biological availability of herbicides to plants, however may still allow microbial degradation([67])

A considerable amount of literature review and experimentation has occurred over the past 20 years on this topic in Alberta. Researchers have investigated the use of a variety of amendments for their effectiveness in remediating herbicide residues in soil ([1], [14], [65]) to varying degrees of success. Activated carbon was applied in the field and greenhouse by Landsburg and Fedkenheuer in combination with manure and fertilizers to both promote adsorption and microbial degradation of bromacil [9]. Cotton and Sharma ([1]) and Shea ([38]) indicate that activated charcoal is probably the most widely investigated adsorbent for herbicide detoxification. Activated charcoal was also used for inactivation of bromacil and tebuthiuron in the greenhouse by Sharma ([65]) and in the field ([1]). The ratio of herbicide:active charcoal concentrations, influence of soil texture, organic matter content and moisture content were taken into consideration when evaluating the effectiveness for inactivation and degradation of the herbicides. However, no follow up studies have been conducted to evaluate the long term effects of activated charcoal application to inactivate herbicides. The amount of activated charcoal required to inactivate herbicides in soil is described in Qureshi ([4]) and the field manual for rehabilitating soils affected by residual herbicides ([55]) and is provided Table 9. Shea noted that approximately 100 kg/ha of activated carbon would be required to detoxify about 1 kg atrazine a.i./ha ([38]) and reported that activated carbon has a significant potential drawback in that immobilization retards degradation and has the potential to bind future herbicide applications. He recommended using activated carbon only for localized spills ([38]).

Table 9. Amount of activated charcoal required to inactivate herbicides in soil.

Active Ingredient in Soil (Based on 15 cm Sampling Depth)		**Charcoal Required*** ([55])	**Charcoal Required**** ([4])
ppm (mg/kg)	**kg/ha**	**kg/ha**	**kg/ha**
0.045	0.1	n/a	10 – 20
0.09	0.2	n/a	20 – 30
0.2	0.5	n/a	50 – 100
0.5	1.12	168 – 224	100 – 200
1.0	2.24	336 – 448	200 – 400
1.5	3.36	504 – 672	300 – 600
2.5	5.60	840 – 1,120	500 – 1,000
5.0	11.20	1,680 – 2,240	n/a
10.0	22.40	3,360 – 4,480	n/a

n/a – indicates data were unavailable; *Adapted from the field manual for rehabilitating soils affected by residual herbicides ([55]); **Adapted from herbicide carry-over information in Qureshi ([4]).

Biochar is a carbon-rich solid made from agricultural crop residues, wood or waste via pyrolysis in the absence of oxygen. Although biochar was primarily introduced as a soil amendment for carbon sequestration, reductions of greenhouse gas emissions, and improvement of soil fertility, it has more recently attracted attention for its ability to reduce the bioavailability of pesticides ([67]). Studies have shown varying results depending on the age of the biochar ([66]), feedstock ([67]), and length of time in the soil. The characteristics of biochar vary widely with the use of different biomass materials and pyrolysis conditions, therefore research in Alberta on soil sterilants such as bromacil and tebuthiuron would be required to confirm the ability of biochar to adsorb the compounds, the duration of effectiveness and the best materials and rate of application required to achieve optimal remediation.

Researchers have also trialed green wastes and composts from various origins to remediate pesticides with varying results. These techniques are considered less permanent given that the products can be altered due to aging, and the environmental fate of retained pesticides would need to be evaluated over years. Morillo and Villaverde ([61]) concluded that the applications of biochar and organic green wastes for the remediation of contaminated soil have mainly been conducted in the laboratory, greenhouses or small plot experiments and large-scale field trials would be needed before operational scale re-mediation projects could be implemented.

6.2 TREATMENT TECHNOLOGIES

Remediation treatment technologies investigated or considered for removal or degradation of sterilants primarily include soil washing and/or flushing, chemical oxidation and reduction, thermal desorption, bioremediation, and phytoremediation ([9]). Several of these technologies, in addition to several newer technologies that have not been widely tested for remediation of sterilants (e.g., in-situ thermal, electrokinetic, enzymatic) can be applied either ex-situ (soil washing and/or flushing, chemical oxidation and reduction, thermal desorption) (Table 10), or in-situ (soil flushing, chemical oxidation and reduction, bioremediation and phytoremediation) (Table 11). A brief description of several of the technologies previously used to treat pesticide-impacted soils is provided below.

6.2.1 Soil Washing and Flushing

Soil washing is an ex-situ remediation technique that uses liquids, usually aqueous solutions of different kinds of extractants (organic compounds, acids, tensioactives, etc.), to remove chemical pollutants from soils. The excavated contaminated soil is mixed with water containing extractants in an extractive unit and agitated. After washing, soil particles are allowed to settle out, and the washing solution can be separated and regenerated or sent to a landfill. The extraction of pesticides from soils has been studied in a wide variety of papers, which are summarized in Morillo and Villaverde ([61]). Soil washing is most appropriate for soils that contain at least 50% sand and gravel and successful application of the technology is highly dependent on the appropriate selection of the solvent/surfactant to extract or solubilize the pollutant of interest, which in turn is influenced by factors such as solvent/surfactant concentration, contact time and temperature, mixing speed, or solution to soil ratio.

Organic solvents and many synthetic surfactants have the disadvantage of being toxic to resident microbial populations, therefore if it is desirable to return the soil to the site an alternative is the use of biogenic compounds such as biosurfactants ([68]) or cyclodextrins. The biosurfactants commonly used for soil remediation include glycolipid (e.g., rhamnolipids, fructose lipids, sophorolipids) and lipopeptide (e.g., surfactin, polymyxin) compounds. In particular, the feasibility of rhamnolipid biosurfactants, mostly produced by *Pseudomonas aeruginosa*, to remove pesticides from soil has been studied ([69]). Further research is required on the behaviour of biosurfactants in fate and transport of pesticides in soil, however the technology may be a feasible choice for surfactant-based soil remediation ([61]). Cyclodextrins have been approved as non-toxic compounds – due to their glucose-based composition – that do not harm resident microbial populations and have been used to improve the remediation efficiency of contaminated soil, because they can increase the apparent water solubility of low-polarity organic compounds ([70]), reducing their sorption to soil ([71], [72]).

The use of biosurfactants and/or cyclodextrins is an important step to transfer the residual contaminants into the soil solution ([73], [74]) which is essential to increase the subsequent efficiency of soil remediation by phytoremediation ([69]), oxidation ([74], [75]) or biodegradation ([75]–[77]). Although no studies were found where cyclodextrins were used in the remediation of bromacil or tebuthiuron, studies have shown successful remediation of 2,4-D, alachlor, metolachlor, acetochlor, dimethenamid, and dicamba ([78]); the majority of the studies were completed at the laboratory scale. Field-level research would be required to confirm the efficacy of these techniques, however sterilant mobilization risks would need to be considered on a case by case basis.

In-situ soil flushing using extractant eluents with additives that enhance contaminant solubility is another potential strategy for remediation of soil sterilants. Flushing solutions are injected into the area of contamination via injection wells. Similar surfactants or solvents used for soil washing are frequently used as additives. After passing through the contamination zone, the contaminant-bearing fluid is collected and brought to the surface for disposal, recirculation, or on-site treatment and reinjection. The effectiveness of this process is dependent on hydrogeologic variables (e.g., type of soil, soil moisture) and the type of contaminant. This technique has not been widely used for remediation of pesticides and the only soil sterilants applicable include atrazine ([61]).

Electrokinetic soil flushing (EKSF) is a promising new technology for remediation of soils impacted by pesticides. In EKSF, an electric field is applied across the soil using electrodes located in the subsurface. This current simultaneously initiates many physical processes (heating, changes in viscosity, etc.), electrochemical processes (water oxidation and reduction, etc.), chemical processes (ion exchange, dissolution of precipitates, etc.), and electrokinetic transport processes (electro-osmosis, electromigration, electrophoresis, etc.), which significantly change the soil ([79], [80]) and cause favourable transport and subsequent removal of contaminants from soils. This technology may be highly effective in Alberta because it has been shown to be particularly useful for fine-grained soils with low hydraulic conductivities and large specific surface areas, and is capable of treating fine and low-permeability materials. The integration of EKSF with chemical oxidation, especially Fenton's process, is predicted to be highly effective, however, most of the research has been conducted on artificially contaminated soil in laboratory settings and the successful results cannot always be transferred to soils at contaminated sites. Further research is needed since technical and environmental issues will require a careful evaluation for further full-scale implementation.

6.2.2 Chemical Oxidation and Reduction

In chemical oxidation and reduction reactions, one reactant loses electrons (is oxidized) and the other gains electrons (is reduced). Reducing conditions are typically more favourable for degradation of pesticides persistent in aerobic environments. Nano-scale zero-valent iron (nZVI) is usually used as a chemical reductant for cost-efficient degradation of chlorinated pollutants in soil. Depending on the contaminants, the effectiveness of this technology can be increased by combining it with other amendments, such as aluminum sulfate to decrease the pH and remediation options, such as biodegradation ([61]). Shea et al. ([81]) tested nZVI, in combination with acetic acid or aluminum sulphate or both on windrowed soils in Nebraska contaminated with metolachlor, alachlor, atrazine, pendimethalin, and chlorpyrifos and found the technique to be successful. Atrazine concentration was reduced by 91% with nZVI plus aluminum sulphate, compared to 63% with nZVI alone and 42% with all three amendments.

The purpose of chemical oxidation in contaminated soils is to mineralize the pollutants to CO_2, water and inorganics, or transform them into biodegradable or harmless products. The most commonly used oxidizing agents (ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide ([82])) are not effective enough to degrade pesticides, however, when combined with iron salts, semiconductors (such as TiO_2) and/or ultraviolet-visible light irradiation (advanced oxidation processes (AOPs)) the results are more promising for remediation of soils contaminated with pesticides ([83]). Fenton processes, TiO_2 photocatalysis, plasma oxidation, ozonation and electrochemical oxidation processes are the most common AOP techniques ([79]), however their application to the remediation of soil sterilants is scarce in the literature for studies other than in the laboratory. An alternative to using AOPs as single treatment technologies is to combine AOPs with other technologies to minimize cost or enhance efficiency by exploiting complementarities or synergies between technologies. Innovations such as the use of chelating agents or surfactants on the traditional AOPs and the combined utilization with bioremediation or soil washing have been documented ([61]).

Over 20 years ago, a pilot scale demonstration of the DARAMEND® process was conducted ([84]) to remediate metolachlor, 2,4-D, dinoseb, and atrazine. Approximately 200 tons of soil was remediated in a 1 year time frame utilizing this ex-situ soil bioremediation technology that treats chlorinated organics which typically degrade slowly under aerobic conditions. The process uses organic (DARAMEND®) and inorganic (multivalent metal) amendments to promote the indigenous microorganisms in the soil to degrade contaminants. The demonstration was designed to cycle between anaerobic and aerobic conditions to promote reductive dechlorination and subsequent aerobic degradation of chlorinated pesticides. After 10 complete aerobic and anaerobic cycles, amendment addition, mixing (twice a week during aerobic cycle) and irrigation 2,4-D was reduced from initial concentration of 3.7 mg/kg to below detection limits, atrazine was reduced from initial concentrations of 17.0 mg/kg to below detection limits and metolachlor was reduced from 48 – 84 mg/kg to below the detection level of 1.0 mg/kg, indicating a 99% removal of contaminants. Key learnings from this case study included: effective and complete tillage is required to achieve desired reduction rates, limiting the depth of treatment cells; use of alternating aerobic and anaerobic cycles promotes effective bioremediation of chlorinated pesticides without the use of inoculum; time and number of cycles is site-dependent. The technology (combined with other products such as EHC®) has subsequently been widely applied to soil environments to successfully treat a variety of residual herbicides ([85]). Other studies have shown that simazine is resistant to ozone degradation, however when used in a fluidized bed reactor the concentration of simazine was reduced 80% after 144 hours ([43]).

6.2.3 Thermal Desorption

Thermal desorption is a process by which contaminants are vapourized by heating wastes to moderate temperatures. These temperatures range from 93°C to 540°C depending on the contaminant to be vaporized. Case studies in Alberta have shown thermal desorption to reduce tebuthiuron concentrations, (maximum 0.029 mg/kg) and bromacil concentrations (maximum 0.015 mg/kg) in soils to below laboratory detection limits (<0.0016 mg/kg tebuthiuron, <0.005 mg/kg bromacil) ([9]). Lin ([27]) reported on a field pilot of thermal desorption of 15,136 tonnes of native prairie battery site soil from southeastern Alberta contaminated with tebuthiuron which was successfully remediated and the soil was then used as backfill on the site.

6.2.4 Bioremediation

The main biological agents used in bioremediation of pesticide-impacted soils are bacteria and fungi which use the contaminants as a nutrient or energy source. The microbial diversity of the site is one of the most important parameters for bioremediation, together with the nature of the pollutants, and some properties of the soil (pH, moisture content, nutritional state, temperature, oxidation-reduction potential) ([86]). In natural soil bioremediation, the native microflora already present in the contaminated soil is used to degrade the target contaminants. In situations in which microbial populations are not believed to be large or diverse enough to efficiently degrade the target contaminants, soils can be bioaugmented or inoculated with enriched/acclimated consortia or single contaminant-degrading strains ([61]). The inoculant can be obtained from the indigenous soil flora by isolating strains from the contaminated site and selecting them under laboratory conditions according to the contaminant (enrichment cultures). Chaudhry and Cortez ([87]) isolated a *Pseudomonas* sp. in 1988 from soil by using bromacil as the sole source of carbon and energy and concluded that the microorganism showed potential to decontaminate soil samples contaminated with bromacil under laboratory conditions. Gunasekara ([20]) summarized results of a study showing a gram-positive bacterium, *Arthrobacter aurescens* strain TC1, capable of consuming 3,000 mg/L of atrazine in liquid as a sole carbon and nitrogen source via catabolism to supplement its growth. This bacterium is also capable of degrading 23 other s-triazines, including simazine. Strandberg and Scott-Fordsmand ([41]) noted previous researchers had isolated bacteria and a fungi which could breakdown and use simazine.

A number of fungal strains belonging to different genera have also been isolated and characterized for degradation of various pesticides. No studies were found which successfully bioremediated bromacil or tebuthiuron using these methods, however several other pesticides have been successfully degraded using these techniques ([8], [61]). Alternatively, researchers have studied the addition of appropriate nutrients (nitrogen, phosphorus, trace elements) and/or small amounts of secondary carbon sources to provide the microorganisms with an environment which favors the development of metabolic pathways for contaminant biodegradation (biostimulation). Research has shown this technique to be effective for removal of DDT and its metabolites ([88]), pentachlorophenol ([89]), and Arazine ([90]). Bioavailability of soil sterilants is a major limitation to complete bioremediation of contaminated soils. Surfactants can be used as bioremediation promoters, accelerating pesticide mineralization through increasing the amount of the pollutant present in the soil solution.

Composting is a treatment technology which consists of mixing contaminated soil with non-hazardous organic amendments, generally other solid wastes (e.g., manure, agricultural wastes) suitable for composting applications, to encourage the development of bacterial populations or other organisms, such as fungi, earthworms, etc., which can degrade contaminants in the soil via co-metabolic pathways. Researchers have used various organic amendments (e.g., compost, corn fermentation byproduct, corn stalks, manure, peat, sawdust, sewage sludge, pruning wastes, urban solid residues) to improve the removal of herbicides atrazine, trifluralin, metolachlor ([91]) and diuron ([92]) from contaminated soils. Grover ([93]) found that addition of peat moss to a heavy clay soil from Regina reduced simazine toxicity to oats. Other researchers found the addition of organic amendments (vermicompost and olive cake) did not increase the removal of different pesticides in soil, including simazine, cyanazine, terbuthylazine and prometryn ([94]). Shea ([38]) reported a study comparing sewage sludge and manure treatments of atrazine and diuron – in both cases manure was more effective. Various nutrient solutions have also been added to enhance mineralization. This approach is generally more effective when applied as an ex-situ technique through landfarming and biopiles or slurry bioreactors. The process and level of engineering for these technologies differ, however the principles of mixing amendments with contaminated soil and allowing natural biodegradation to occur are common among them. Research results have been variable, and relatively ineffective for heavily contaminated soils or products strongly adsorbed to soil.

The results obtained from many of these studies revealed that the use of amendments (compost, activated carbon, biochar, inoculants, chemicals, etc.) to remediate pesticides in soils requires a preliminary study to evaluate the environmental specific persistence of these compounds and the effectiveness of amended soils to enhance pesticide biodegradation ([61]). The success of composting in the bio-remediation of contaminated soils depends on a number of physical, chemical and biological characteristics of the reaction environment. A key factor is the microbial bioaccessibility to the pollutants, which is determined both by the mechanical conditions (mixing, moisture contents, soil composition), and by the properties of the applied amendment.

6.2.5 Phytoremediation

The use of plants to remediate contaminants is called phytoremediation. Low molecular weight compounds such as some pesticides can be transported across plant membranes and removed from the soil. They can be released through leaves via evapotranspiration processes (phytovolatilization). Non-volatile compounds can be degraded (phytodegradation) or become non-toxic via enzymatic modification and sequestration in plants (phytoextraction), or are degraded by microorganisms present in the rhizosphere (rhizodegradation) ([95]). The majority of the research to date, which is summarized in Morillo and Villaverde ([61]), has been on DDT and its metabolites. Researchers have shown rhizodegradation to be the most effective form of phytoremediation ([96]–[98]), however phytoremediation can be enhanced by the addition of organic acids ([99]) or surfactants ([100], [101]). The potential use of non-target plants such as trees, shrubs and grasses in remediating pesticide-contaminated soil has been investigated ([102], [103]) and demonstrated that plants can survive in soil moderately contaminated with pesticides, and their presence increases the degradation rate. Russell reported on several studies using *Kochia spp*., cattails, corn or hybrid poplars to degrade atrazine ([104]), and Henderson reported on phytoremediation trials on atrazine using grasses native to the US Midwest ([8]). Researchers in Iowa investigated combinations of deep-rooted perennial plants with long growing seasons that have previously shown phytoremediation potential (yellow indiangrass, switchgrass, big bluestem, mulberry trees) and found varying degrees of recoverable herbicide depending on the type ([102]); successful remediation of atrazine and metolachlor was achieved. Other herbicides caused root inhibition and treatments did not reduce herbicide concentrations. Previous research has shown potential for remediation of atrazine and bromacil using hybrid poplar and soybean plants, respectively ([105]). However, no information is available on native Alberta plants and sterilants commonly impacting sites in Alberta, and given the fact that plant species selection is essential ([102]), more work is required to effectively use this technique. Furthermore, there have been many challenges in translating phytoremediation research from the lab to the field ([95]) and numerous inconclusive and unsuccessful attempts at remediation utilizing this technology have been made.

A more recent advance in phytoremediation is the development of transgenic plants expressing pesticide-degrading enzymes ([106], [107]). The overexpression of genes involved in metabolism, uptake or transport of specific pollutants in transgenic plants enable them to overcome some of the disadvantages of phytoremediation, such as high concentrations of pesticides or the disposal of plants that accumulate organic pollutants ([108]), however field applications have not yet been trialed or regulated in Canada due to their possible impacts on the environment and biodiversity.

Table 10. **Summary of ex-situ soil remediation technologies proposed for or applied to soil sterilants.**

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages
Remedial Excavation and Disposal	All	Physically excavate and haul contaminated soil to appropriate landfill facility	Landfill acceptance ([14]) Difficult to ensure contaminant delineation due to mobility and length of time in the environment; destructive; Requires fill material	Complete removal of contaminant
Soil Washing	All (dependent on solvent, surfactant)	Excavated contaminated soil is mixed with water containing extractants (solvent, (bio or synthetic) surfactant, and/or cyclodextrin) and agitated. After washing, soil particles settle out, and washing solutions are separated and regenerated or disposed of ([61])	Only works effectively in soils containing at least 50% sand and gravel ([61]); Solvent extraction is typically low on very high molecular weight pesticides ([61]); Solvents can be toxic to soil microbial populations ([82])	Proven to work effectively if applied appropriately
Soil Flushing	Atrazine, bromacil, tebuthiuron ([7])	Extraction eluents with additives that enhance contaminant solubility are injected in the ground to dissolve soluble contaminants and then physically move the contaminants to an area where they may be extracted from the ground and treated or disposed of ([27])	Requires water source and recovery/treatment system ([27])	Proven to work effectively if applied appropriately
Thermal Desorption	Atrazine, tebuthiuron, bromacil ([7], [9])	Contaminants are destroyed by heating wastes to moderate temperatures – ranging from 200°F to 1,000°F depending on the contaminant ([27])	Dewatering may be necessary to excavate soils for treatment ([7]) Cost effective at volumes greater than 5,000 m^3; OM and clay rich soils bind contaminants and increase reaction time required for processing ([9])	Highly effective
Enhanced Thermal Conduction	Unknown – All	Ex-situ thermal process that heats stationary contaminated soil either through infrared heating elements or conducting rods, volatilizes the contaminants, and destroys the off-gases	Effectiveness yet to be determined for soil sterilant remediation	Can be applied to smaller volumes; doesn't require homogenization

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages
Landfarming, biopiles and composting	Atrazine (and other similar compounds) ([61]); bromacil, diuron, simazine (high pH conditions), linuron ([9])	Mixing of contaminated soil with non-hazardous organic amendments and nutrient solutions to encourage the development of bacterial populations or other organisms, which can degrade pollutants via co-metabolic pathways ([86], [88], [90], [92])	Success is influenced by microbial bioaccessibility to the pollutants, which is determined both by the mechanical conditions (mixing, moisture contents, soil composition), the properties of the applied amendment and contaminant properties; length of time required to remediate soil is years to decades; leaching concerns; may result in less uniform treatment	Can be performed in-situ or ex-situ; most applicable when time is not a limiting factor; easy to implement; does not require heavy infrastructure; cost-efficient; utilizes naturally occurring microbes, stimulated by natural (and synthetic) amendments and mechanical aeration
Slurry bioreactors	Unknown (chlorinated pesticides) ([61])	Wastewater residue is mixed with contaminated soil to obtain a slurry of a predetermined consistency; an aqueous suspension in the range of 10 – 30% w/v. The system can work under aerobic or anaerobic conditions and in different feed modes: continuous, semi-continuous, and batch ([61])	High cost, which has to be justified for each application; lack of good medium- to full-scale successful demonstration ([61])	Accurate control of bioremediation process, which can be optimized by setting and monitoring the most critical parameters ([61])

Table 11. Summary of in-situ soil remediation technologies proposed for or applied to soil sterilants.

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages
Soil Flushing	Atrazine, bromacil, tebuthiuron, diuron ([7], [9])	Solution is injected in the ground to dissolve soluble contaminants and then physically move the contaminants to an area where they may be extracted from the ground and treated or disposed of ([27])	Requires water source and recovery/treatment system ([27]); Effectiveness of process is dependent on hydrogeologic variables (e.g., type of soil, soil moisture) and the type of contaminant ([61]); Only applicable for more soluble sterilants (or solvent/surfactant required); not applicable for low permeability soils ([9])	Can be combined with multiple technologies for better effectiveness; works on multiple contaminants simultaneously
Chemical Oxidation/ Reduction	Diuron ([109]); atrazine ([81]); simazine ([20])	Advanced oxidation processes (Fenton processes, TiO_2 photocatalysis) produce strong oxidizing intermediates (mainly OH• radicals) and their reaction with organic contaminants (pesticides/sterilants) leads to their destruction and mineralization	nZVI and surfactants can be toxic to resident microbial populations, plants or earthworms; a portion of nZVI is lost due to reaction with dissolved oxygen, oxide minerals and organic matter, which needs to be compensated for in application rates; adsorption of surfactant onto soils is sometimes high; success is dependent on solvent/surfactant concentration, contact time and effectiveness and temperature; Fenton process can lead to losses in soil organic matter; difficulties of diffusion through heterogeneous soil matrices	Can be done both in-situ and ex-situ
In-situ Thermal Remediation (ISTR)	Unknown – All	Various methods where heat can be transferred to the subsurface including: 1) direct conduction of heat away from heaters placed in trenches or wells (thermal conductive heating or TCH), 2) electrical resistivity heating (ERH) of the subsurface by passing electrical currents through the soil, and 3) steam injection or steam enhanced extraction (SEE). Often paired with both vapour and liquid recovery for contaminant removal ([110])	Some of the ISTR methods may not be appropriate for remediation of very low volatility organics, such as pesticides; requires full site characterization	Thermal conductivity of media within the vadose and non-vadose zones vary less than permeability which allows much more uniform heating and treatment within a contaminated zone when compared to delivery of reagents

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages
Electrokinetic Remediation	All (very little information available)	Electric field is applied across the soil using electrodes initiating physical, chemical and electrokinetic processes in the soil causing favorable transport and removal of contaminants	No field-scale data to verify effectiveness; may require integration of other technologies (chemical oxidation) to work effectively; requires full site characterization	Applicable in fine grained soils with low hydraulic conductivities and large specific surface areas; capable of treating fine and low permeability materials
Manure / Organic Amendments	Atrazine, diuron, bromacil, tebuthiuron ([1]) bromacil ([14]) atrazine and diuron ([38]), simazine ([93]) ([41])	Improve soil structure, cation exchange, nutrients and enhance biodegradation; amendments include peat and sawdust ([1]), green wastes and compost ([61]); Large amounts can retard degradation by providing more readily degradable carbon sources ([38])	Increases pH and EC ([14]); Not effective alone or with activated carbon at high sterilant levels in lab study ([1]); Manure age has an impact of effectiveness – older is better ([1])	Large volumes commercially available ([1]); Some amendments will require fertilizer (N) addition to maintain appropriate C:N ratios ([1]); Adding manure or peat and fertilizer improved plant productivity ([1]) and subsequent degradation
Fertilizers	Bromacil, tebuthiuron ([1]) bromacil ([14])	Enhance microbial degradation ([1])	Not a permanent solution	Low cost
Bioremediation and natural attenuation	Atrazine, bromacil, diuron ([61]), linuron, simazine ([7]); tebuthiuron ([1]); atrazine ([8]); simazine ([20])	Natural bioremediation – Existing native microflora (microbes or fungi) degrade the target contaminants; bioaugmentation – inoculation of enriched/acclimated consortia or single pollutant degrading strains of microbes or fungi to enhance degradation of contaminants ([1]); biostimulation – addition of appropriate nutrients (nitrogen, phosphorus, trace elements) and/or small amounts of secondary carbon sources to provide microorganisms with an environment which favors the development of metabolic pathways for contaminant biodegradation	Limited control; not proven to be effective for many contaminants under field conditions	Low cost; can be completed in-situ

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages
Phyto-remediation	Atrazine, linuron ([7], [9]) atrazine ([8], [104])	Compounds are transported across plant membranes and removed from the soil. Compounds can be released through leaves via evapotranspiration processes (phytovolatilization); degraded (phytodegradation) or become non-toxic via enzymatic modification and sequestration in plants (phytoextraction); or are degraded by microorganisms in the rhizosphere (rhizodegradation)	Long durations to effective remediation ([102]) (may never reach remedial endpoints); Highly dependent on climatic conditions, contaminant concentration and bioavailability, plant tolerance to contaminants, contamination areal extent and depth (limited by the rhizosphere or the root zone) or the disposal of plant wastes ([9], [61]); Plant selection is crucial, and little information is known about Alberta species; limited ability to measure "bioavailable" concentrations of herbicide residue to determine if this technology is applicable	Low cost; reduced erosion rates, improved chemical, physical and biological soil properties which may stabilize herbicide residues, decreasing potential for leaching and uptake ([102]); Land esthetic improvement
Enzymatic Remediation	Atrazine ([8]) – All (unknown)	Enzymes and enzymatic proteins are added to soil to facilitate the breakdown of organic contaminants	Enzymes for specific contaminants or by products may not be identified; incomplete conversion can create undesirable or hazardous by-products; sourcing enzymes may be difficult and/or costly; relatively new and unproven at field scale	Can be used to target specific contaminants or broad range of contaminants; can be used where microbial activity would be limited either by environment or high toxicity; can completely convert contaminants to harmless inorganic by-products

6.3 COSTS

Cost assessment and comparative cost evaluation of the potential technological alternatives may be some of the most important considerations in the decision-making process. Costs associated with soil remediation are highly variable and depend on the contaminant, soil properties, site location and conditions, and the volume of material to be remediated (Table 12). Morillo and Villaverde ([61]) provided a recent assessment of the costs associated with various technologies for remediation of pesticide-contaminated soil. They based the assessment on the costs for remediation of organic pollutants with similar characteristics as pesticides because they found no reports in the literature about the costs of remediation techniques applied to pesticide contaminated soil.

Table 12. Soil remediation treatments costs.

Remediation Technology	**Cost Associated with Remediation Literature** ([9], [61])*** (US$ and/or CAD$)**
Excavation and landfilling	US$2,200 – 2,400/ton ([111]) CAD$$100 – 200/ton depending on distance to landfill ([9])
Immobilization (w/ Activated Charcoal)	CAD$15 – 35/m^3 ([9])
Land treatment	Biopiles CAD$35 – 260/m^3 Landspreading US$39/m^3 ([81]) Composting CAD$45 – 180/m^3 ([9]) Landfarming CAD$5 – 100/m^3 ([9])
Biosurfactants and surfactants	US$1 – 60/kg US$1 – 2/kg surfactant ([112])
EKSF	Unavailable
Phytoremediation	$10 and $50/ton; $12 – 60/m^3 ([95]) CAD$50 – 147/m^3 ([9])
Chemical Oxidation (DARAMEND® and EHC®)	$17/m^3 ($12.5/yd^3)([85]) $29 – 63/ton ([85]) US$77 – S94/m^3; nZVI alone, nZVI + acetic acid, nZVI + aluminum sulphate or nZVI + acetic acid + aluminum sulphate ([81])
Soil washing and flushing	$50 – 104/m^3 for in situ treatments, and $150 – 200/m^3 for ex-situ treatments ([113], [114]) CAD$19 – 191/m^3 ([9])
Bioremediation (using microorganisms)	$6.4 – $150/m^3 ([114], [115]) ($50 – 100/m^3 for in situ or $150 – 500/m^3 for ex-situ)
w/ use of Cyclodextrin	$220/ton ([73])
Thermal desorption	CAD$44 – 252/m^3 ([9])
Removal and incineration	US$261 –1,961/m^3 ([81])

7.0 WATER REMEDIATION TECHNOLOGIES

7.1 TREATMENT TECHNOLOGIES

Water remediation technologies fall into two broad categories: (1) pump-and-treat, where surface water or groundwater water is removed from a contaminated source and treated ex-situ and then either returned to the source or is used/disposed elsewhere; and, (2) in-situ by injection of various treatment chemicals.

Lazorko-Connon ([18]) noted that conventional water treatment technologies are not effective for atrazine; granular activated carbon is the recommended best available technology. Rakewich and Bakker ([3]) reported use of sodium persulphate solution injected into groundwater at a compressor site contaminated with bromacil (successful) and dicamba (unsuccessful) and use of granular activated carbon to successfully treat recovered groundwater contaminated with bromacil and dicamba. Seech et al. ([85]) evaluated remediation of organochlorine pesticides in groundwater using DARAMEND® and EHC® (which contain patented combinations of organic carbon and zero-valent iron) bioremediation amendments at both the bench- and field-scale and found significant reductions (99.7%) in tetrachloride and TCE after six months. The applicability to sterilants commonly found in groundwater in Alberta is speculative, however researchers believe the products would effectively remediate bromacil and tebuthiuron (Seech Personal Communication, February 2018).

A summary of the technologies applicable to remediation of residual sterilants in water evaluated in this review is provided in Table 13. Technologies have been reviewed previously by others; Bessie ([7]) listed remedial options for water applicable to the six primary sterilants in this report based on a review of the literature.

Table 13. **Summary of water remediation technologies proposed for or applied to soil sterilants.**

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages
Deep Well Injection	All ([7])	Contaminants are injected below DUA	Requires aquifer characterization	Injected into saline zones below DUA zone; permanent storage in the subsurface
Monitored Natural Attenuation (dissipation)	Atrazine, diuron, tebuthiuron ([7])	All contaminants to remain in place and naturally remediate	Requires longer time frames compared to active procedures; requires modelling and evaluation of degradation rates to ensure feasibility	Low cost
Nanofiltration	Atrazine ([18])		Interference from natural organic matter ([18])	Not concentration dependent ([18])
Photolysis	Atrazine, bromacil, diuron ([7])			
Chemical Oxidation and Reduction	Atrazine ([18]); simazine (photo-Fenton reaction) ([20])	Water is pumped out and treated in a reaction chamber using UV catalyzed hydrogen peroxide (or other oxidizing chemical) oxidation and sterilization; Oxidizing chemicals (peroxides, ozone, permanganates) are injected into the contaminated zone and contaminants are rapidly oxidized.	Forms bromate in high bromide waters ([18]); atrazine difficult to oxidize ([18]); inefficient without surfactants and solvents; Contaminants can/will be sorbed on soil, even after repeated pump and treat cycles; not effective for contaminants that are not soluble in water or adsorb strongly to soil; chemicals involved can be highly toxic to environment, public, workers; incomplete oxidation can create hazardous by-products	Used in pump and treatment. Can remediate a wide range of contaminants; can be applied both in-situ and ex-situ depending on site characteristics

Technology	Applicable Sterilants	Contaminant Removal Process	Limitations	Advantages
Hydrolysis	Atrazine (if followed by biodegradation) ([7])			
Activated Carbon	Atrazine ([18]); linuron ([9])	Adsorbed ([18]); water is pumped through vessels containing activated carbon; Sorption to organo-zeolites ([18])	Interference from natural organic matter and suspended solids (>50 mg/L); multiple contaminants can influence performance (oil and grease >10 mg/L); not effective for highly water soluble contaminants ([9])	Effective for low concentrations of contaminants ([9]); Increased adsorption with increased adsorbent concentration ([18]); may be applicable both in-situ and ex-situ
Bioremediation	Atrazine, diuron, simazine ([7])			Aerobic or anaerobic conditions and in-situ or ex-situ ([7])
Phytoremediation	Linuron, simazine ([7], [9])	Sterilants absorbed through the roots	Limited to shallow groundwater and surface water ([9]); Seasonal process	Poplar trees have been shown to be effective given the large amount of water they draw ([9])
Enhanced Biodegradation (in situ); bioreactors and/or constructed wetlands) (ex-situ)	Diuron, atrazine (aerobic or anaerobic), simazine ([9])	Oxygen is introduced by air sparging below the water table or dilute hydrogen peroxide solutions; nitrate solutions are added for anaerobic conditions	Solutions are difficult to deliver in heterogeneous systems; peroxide solutions must be <100 to 200 ppm; nitrate injections can have impacts on DUA; ex-situ requires removal from aquifers so compounds must be soluble; dilute concentrations of contaminants often will not support microbial populations in bioreactors; influenced by climate (constructed wetlands) ([9])	Low cost

*Largely adapted from Sterilants Literature Review conducted by EBA Engineering in 2007 ([9]) which predominantly used the Federal Remediation Technologies Roundtable (FRTR) Remediation Technologies Screening Matrix V. 4.0 (http://www.frtr.gov/matrix2.section4/)

7.2 COSTS

Costs associated with remediation of groundwater impacted by residual herbicides are reported less frequently in the literature and were more difficult to obtain (Table 14).

Table 14. Water remediation treatment costs.

Remediation Technology	**Cost Associated with Remediation Literature** ([9])* **(US$)**
ChemOx (EHC®)	US$6.0/m^3 of treated aquifer ([85])
Enhanced biodegradation (aerobic) – air sparging	US$10 to 20/m^3
Enhanced biodegradation (anaerobic) – chemical hydrolysis and nitrate enhanced	US$40 to 60/L
Enhanced biodegradation (ex-situ)	US$6.1 to 8.6/m^3 bioreactor unit
Adsorption by activated carbon	US$0.32 to 1.7/m^3 (flow rate of 0.4 M L/day)

*Unless otherwise referenced, value was adapted from Sterilants Literature Review conducted by EBA Engineering in 2007 ([9]) which predominantly used the Federal Remediation Technologies Roundtable (FRTR) Remediation Technologies Screening Matrix V. 4.0 (http://www.frtr.gov/matrix2.section4/)

8.0 SUMMARY AND KNOWLEDGE GAPS

This review identified that a considerable body of knowledge exists regarding residual herbicide properties and their use in agricultural settings at low rates; however, limited knowledge is available on industrial uses, and in particular, on field-scale remediation of sites affected by the sterilants historically used in Alberta. Several major challenges were identified associated with management of sterilant impacted sites in Alberta through this literature review, industry consultation and personal communication, including 1) the research and demonstration trials that have been undertaken have limited applicability to Alberta conditions and/or have mostly been done in the laboratory or greenhouse, 2) information on the effects of sterilants on Alberta-specific native plants is very limited, and 3) the majority of remediation information found in the literature focuses on soils rather than surface water or groundwater which is a significant problem for Alberta sites where highly mobile sterilants such as bromacil have been used.

There are considerable differences between sterilants in terms of persistence and fate in the environment which depend on several factors related to the sterilant itself and to the soil and climatic conditions, resulting in unique challenges associated with each of them (Table 15). The two main sterilants found impacting soil and groundwater on or near industrial sites in Alberta are bromacil and tebuthiuron. Atrazine, simazine, and diuron pose significant challenges in other parts of the world, including the U.S., Australia and parts of Europe; however, they are not commonly found impacting soils on legacy industrial sites in Alberta. Groundwater and surface impacts have been identified in Alberta, however there is far less information readily available for historical use, presence and treatment of these products in Alberta. Linuron does not appear to be a concern on industrial sites in Alberta.

Table 15. Challenges associated with sterilants and their relevance in Alberta.

Soil Sterilant	Major Challenges Associated with Sterilant
Bromacil	• Most commonly found sterilant on industrial sites in Alberta; • Variable effects to vegetation in coarse vs. fine soils; variable effects depending on moisture content; • Not historically analyzed for unless vegetation issues obvious; variable plant tolerance levels; • Low concentration guidelines with limiting pathways for protection of aquatic life and irrigation water; • Degradation half-life 60 to >1,400 days – variable in different soil conditions, moisture and temperature conditions ([2]); • Biodegradation in soils is slow; leaches readily and contaminates groundwater; stable in aquatic environments (resistant to hydrolysis).
Tebuthiuron	• Second most commonly found sterilant on industrial sites in Alberta; • Resistant to abiotic and biotic degradation; • Highly mobile (high probability of groundwater contamination); • Negligible volatilization from soil; • Soil half-life increases in abiotic environments and with increasing OM

Soil Sterilant	Major Challenges Associated with Sterilant
Atrazine	• Not commonly found on industrial sites in Alberta; • Identified in surface waters in Alberta; however, source of contamination was not identified; • Widespread contamination of groundwater in the U.S., Australia and Europe; persistent in groundwater and surface water – half-life in Lake Michigan est. at 13.9 years ([18]); found in 100% of the samples from 12 monitoring sites in Iowa and northern Missouri from 1991-1998 ([19]).
Simazine	• Occasionally found on industrial sites in Alberta in groundwater and/or neighboring surface waters; • Contaminant commonly found in California surface waters and groundwater, in some cases approaching the US maximum concentration level of 4 µg/L ([20]).
Diuron	• Often used in combination with bromacil and tebuthiuron, therefore can be found on the same sites in Alberta; • Identified in surface waters in Alberta; however, source of contamination was not identified; • Widespread contamination of surface water in the US; ([21]); frequent groundwater and surface water contaminant in California ([34]); • Toxic to non-target plants at very low concentrations; Cox ([21]) reports significant growth inhibition of aquatic plants at concentrations as low as 5 ppb; • Moderate to high persistence; longer in dry soils than wet ([21]); persistent in water and aerobic soil and sediment ([42]).
Linuron	• Not commonly found on industrial sites in Alberta; • Wide-scale use in the U.S. in many agricultural crops such as corn, wheat, barley, carrots, potatoes and soybeans.

Several technologies have been utilized to treat pesticide-contaminated soils, both in-situ (soil flushing, chemical oxidation and reduction, bioremediation and phytoremediation) and ex-situ (soil washing and/or flushing, chemical oxidation and reduction, thermal desorption). In addition, several newer contaminant remediation technologies have not been widely tested on sterilants (in-situ thermal, electrokinetic, and enzymatic remediation); they may potentially provide effective treatment of contaminated soils. There are limitations associated with each of the technologies and their application for a specific site is dependent on a number of factors including the site conditions (topography, geology, soils, moisture, vegetation, etc.) and contaminant characteristics. Costs associated with treatment of a site vary widely depending on the technology, size of the impacts, accessibility, location and concentration of the contaminant. The most common treatment technique previously used in Alberta has been sterilant-immobilization utilizing activated carbon, however several gaps were identified with this technique for long term management of sterilant impacted sites.

On the positive side, sterilant-impacted sites require the same standard physical, chemical and biological site characterization information that other contaminated sites do, and Alberta practitioners are well versed in collecting those data. In addition, knowledge gained from remediating hydrocarbon contaminated sites appears to provide useful guidance for development of sterilant remediation technologies.

Several knowledge gaps were identified related to the effective management of sterilant impacted sites in Alberta (and have been substantiated through conversations with Alberta practitioners in recent workshops sponsored by InnoTech Alberta):

1. Uncertainty in the number and size of industrial sites impacted by soil sterilants in Alberta leading to uncertainty in identifying impacted sites.
2. Analytical methods currently used in Alberta to characterize sterilants found in soil and/or groundwater have variable detection limits, sometimes higher than guideline levels, and only provide total concentrations, rather than bioavailable.
3. Comparison of laboratory- and field-derived soil and water half-life data for the common sterilants to be used in risk assessment modeling.
4. Ecological contact pathways for the protection of irrigation water and freshwater aquatic life are below analytical detection limits for bromacil and tebuthiuron.
5. Lack of an ecological direct soil contact pathway for sterilants other than bromacil and tebuthiuron.
6. Incomplete or missing data for Alberta species toxicity to assist in establishing site-specific remediation objectives.
7. Lack of long-term evaluations of remediation treatment longevity, particularly relevant for treatments that rely on the sterilant being adsorbed to organic matter, clays or amendments.
8. Lack of detailed, publicly accessible data on field-scale treatment trials in Alberta – target sterilant(s) and concentrations, co-contaminants, methods, rates, costs.
9. Lack of information on the potential for, and value of, combining treatments technologies to increase remediation success.

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9.1 PERSONAL COMMUNICATION

G. Byrtus, B. Lambert, V. Servant, Alberta Environment and Parks, 2018
A. Seech, PeroxyChem, February 2018