The Soil Sterilants Program: Collaboration and Engagement Key to Addressing Challenging Contaminants

Canadian Land Reclamation Association – 2022 Conference and AGM

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SSP Soil Sterilants Program

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What are Soil Sterilants?

Non-selective, persistent, residual herbicides that render treated soil unfit for plant growth

- Selective vs non-selective
  - Selective herbicides control specific types of vegetation
  - Non-selective herbicides used for total vegetation control
- Residual and Persistent
  - Continued or prolonged existence of herbicides (beyond one growing season)
  - Related to half life which depends on:
    - Application rate, soil moisture, pH, temperature, OM content, microbial content, etc.
    - Chemical and physical properties, composition, etc.

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Soil Sterilant Application

- Applied historically at wellsites, transmission lines, oil and gas distribution and industrial facilities, pipelines and electric substations, railways
- Program participants halted use in 1990s based on **persistence** and **mobility**
- **Secondary impacts** through leaching, runoff or wind dispersion
- Best estimate - **>60,000** sites in Alberta

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Sterilants – Management Challenges

- Identification and Delineation
- Risk Assessment and Management
- Remediation

Considerable effort over past 20 years, however knowledge gaps remain

Sterilants – Collaboration Opportunity

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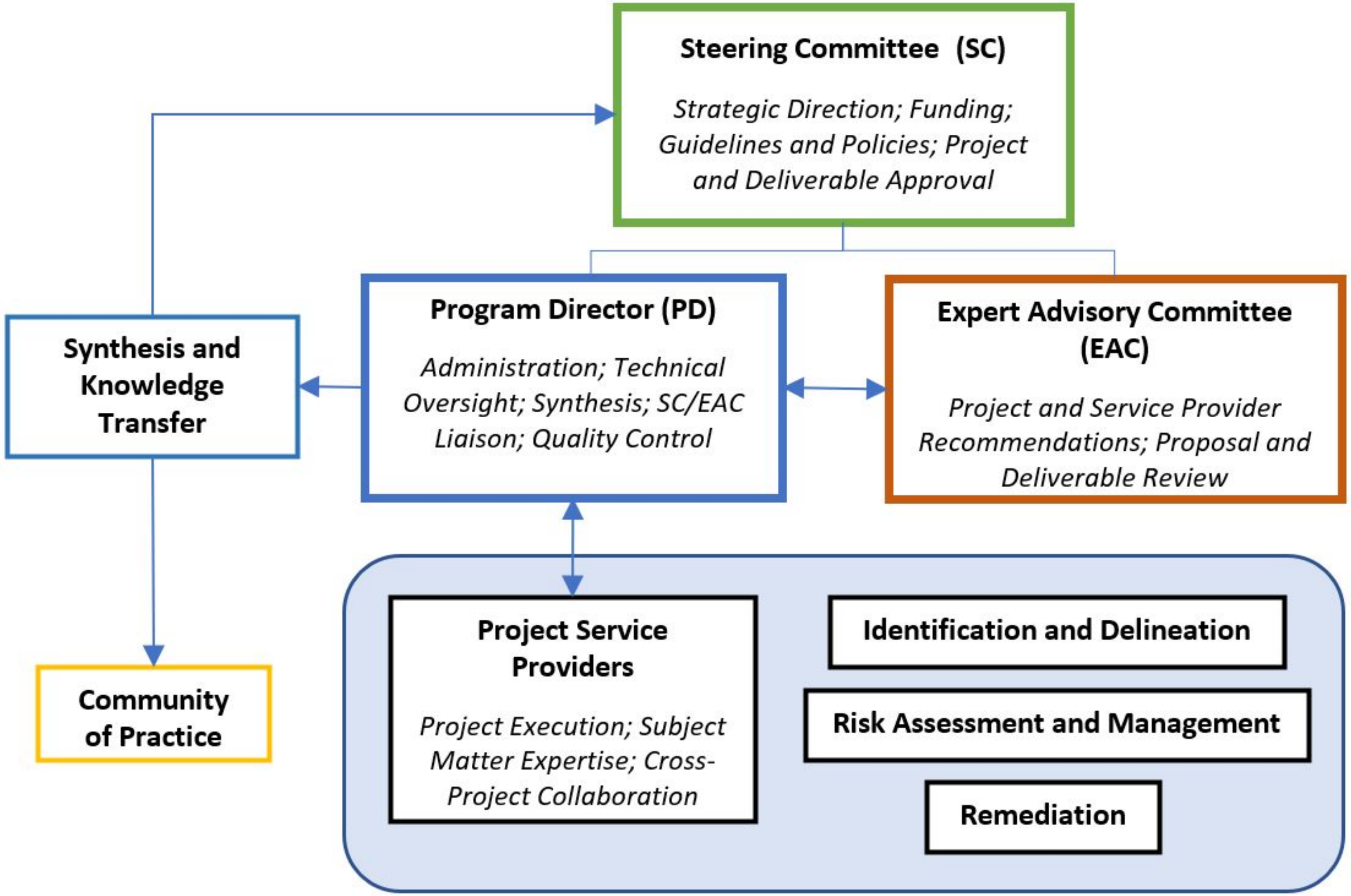
OBJECTIVE:

To establish **proven, technical,** and **cost-effective** strategies and best management practices for **effective management** of sites impacted by residual soil sterilants, with the goal of supporting regulatory site closure.

Program Structure

- 5-year Program
  - Initiated in 2019
- Scope
  - Address challenges specific to AB
  - *Applied* research
  - Bromacil and tebuthiuron focus
- Structure
  - Program management and delivery agent – InnoTech
  - Steering Committee
  - Expert Advisory Committee



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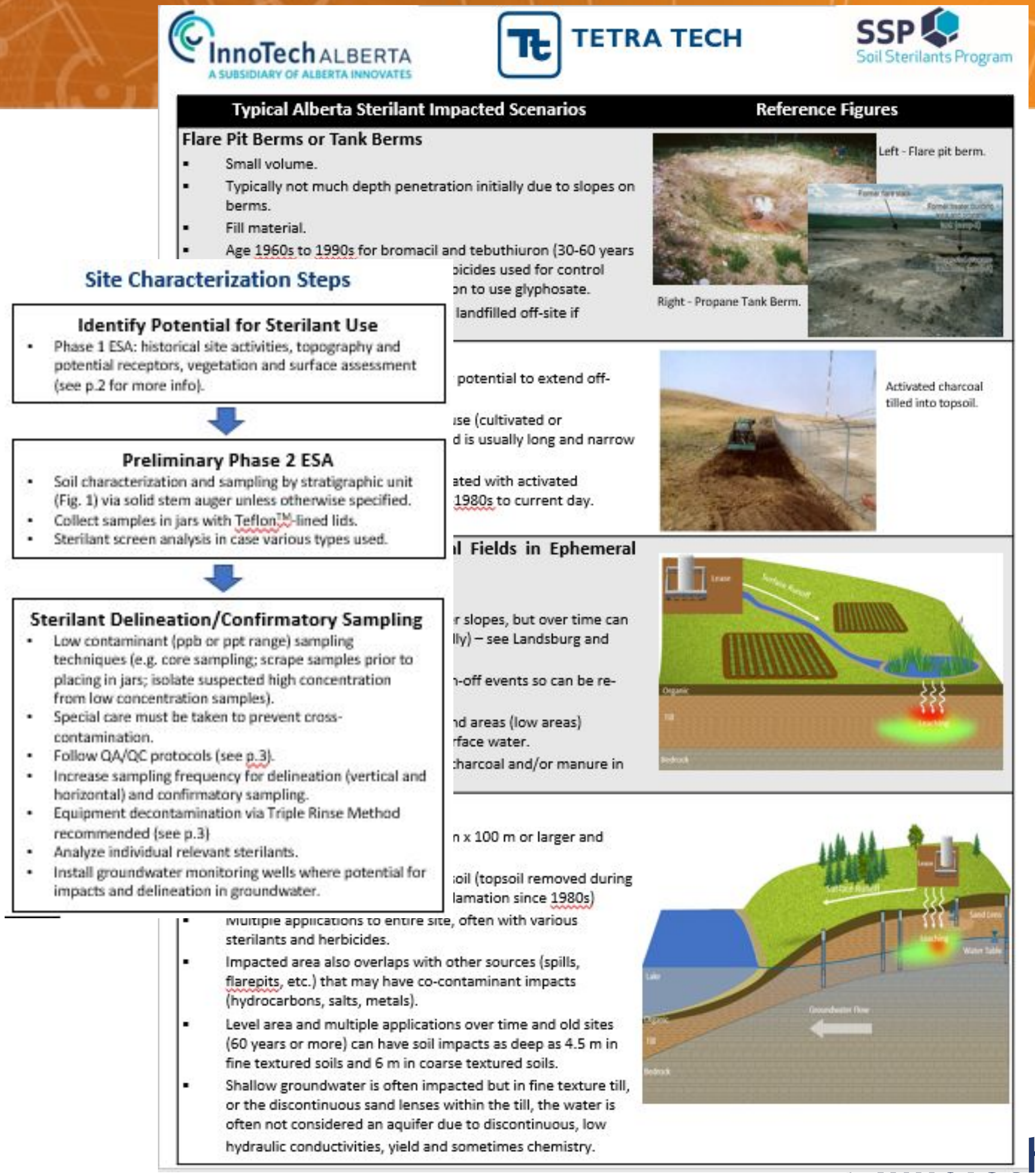
Identification and Delineation

#2. Sampling Best Management Practices



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Typical Alberta Sterilant Impacted Scenarios	Reference Figures

Flare Pit Berms or Tank Berms

- Small volume.
- Typically not much depth penetration initially due to slopes on berms.
- Fill material.
- Age 1960s to 1990s for bromacil and tebuthiuron (30-60 years

…picides used for control
…on to use glyphosate.
…landfilled off-site if

Left - Flare pit berm.
Right - Propane Tank Berm.

…potential to extend off-
…ise (cultivated or
…d is usually long and narrow
…ated with activated
…1980s to current day.

Activated charcoal tilled into topsoil.

…l Fields in Ephemeral

…r slopes, but over time can
…lly) – see Landsburg and
…-off events so can be re-
…nd areas (low areas)
…rface water.
…harcoal and/or manure in

…n x 100 m or larger and
…oil (topsoil removed during
…lamation since 1980s)

- Multiple applications to entire site, often with various sterilants and herbicides.
- Impacted area also overlaps with other sources (spills, flarepits, etc.) that may have co-contaminant impacts (hydrocarbons, salts, metals).
- Level area and multiple applications over time and old sites (60 years or more) can have soil impacts as deep as 4.5 m in fine textured soils and 6 m in coarse textured soils.
- Shallow groundwater is often impacted but in fine texture till, or the discontinuous sand lenses within the till, the water is often not considered an aquifer due to discontinuous, low hydraulic conductivities, yield and sometimes chemistry.

Site Characterization Steps

Identify Potential for Sterilant Use

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

Preliminary Phase 2 ESA

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

Sterilant Delineation/Confirmatory Sampling

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

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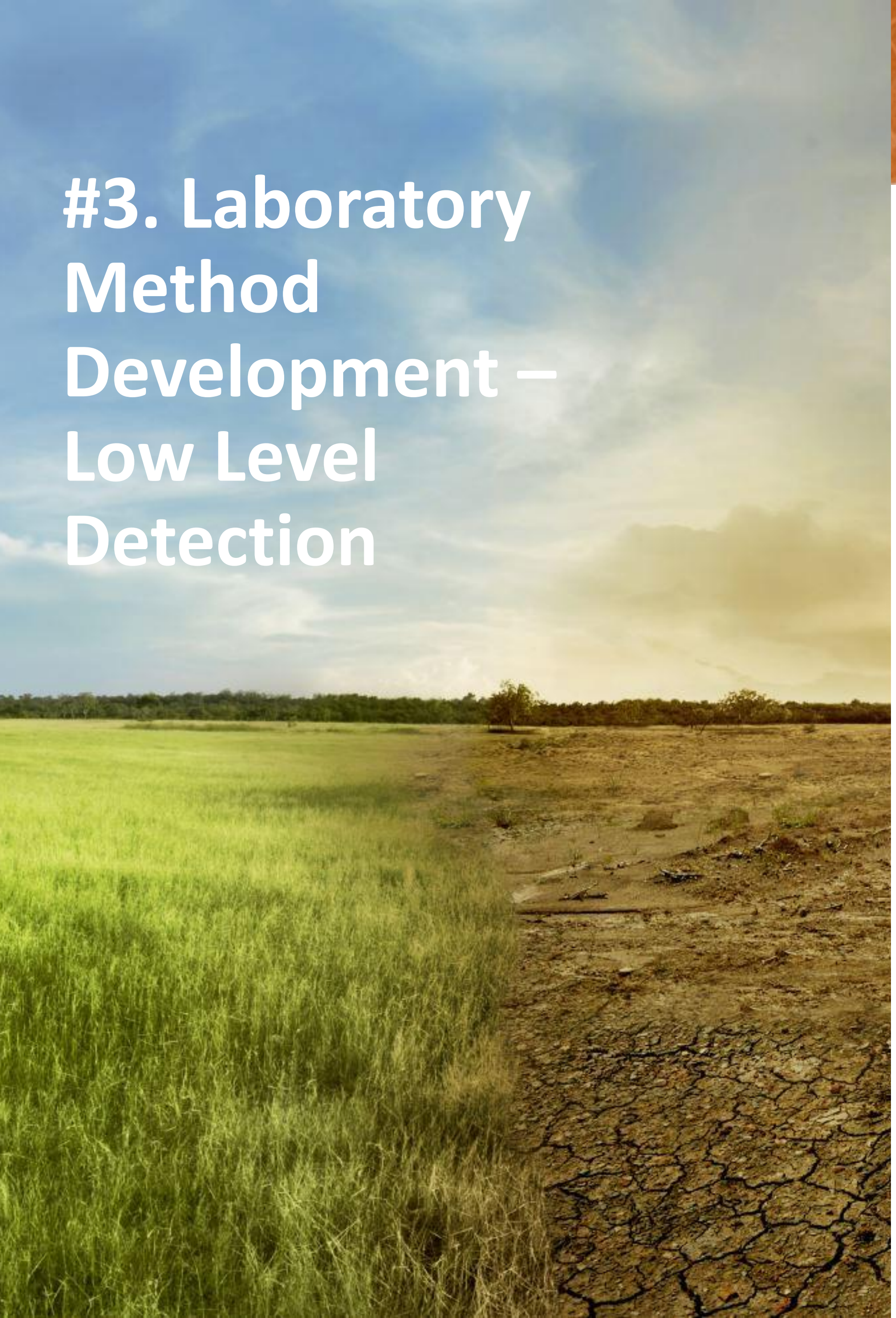
#5. Field Screening Technologies

VERTEX Environmental Inc.

Instruments assessed:	Results:
Ultraviolet laser induced fluorescence (UVOST® or OIP®)	Potentially viable but likely not practical
Visible light laser induced fluorescence (TarGOST® or OIP-G®)	Not viable
Near infrared reflectance spectroscopy (NIRS)	Potentially viable but likely not practical
X-ray fluorescence (XRF)	**Potentially viable (elemental)**
Portable gas chromatography/photoionization detector (GC/PID)	Not viable; not tested
Raman spectroscopy	**Potentially viable (molecular)**
Laser-induced breakdown spectroscopy (LIBS)	Not viable
Gas Chromatography/Thermionic Ionization Detector (GC/TID)	Not tested; not available

Biosensors assessed:	Results:
Single-stranded DNA molecular recognition element (ssDNA MRE)	**Potentially viable; not tested**
Enzyme-linked immunosorbent assays (ELISA)	**Potentially viable; not tested**



#3. Laboratory Method Development – Low Level Detection

Sample	Depth	Bromacil	
		InnoTech EAS (LC-MS/MS)	Commercial Lab (GC-MS)
	m	µg/kg	µg/kg
Tier 1 Agricultural Guidelines for Fine and Coarse-Grained Soil *		*9*	*9*
Detection Limit		*0.02*	*8*
BH1	0.5	0.08	<8
BH1	2.5	0.81	<8
BH2	0.5	0.04	<8
BH2	2.5	2.1	<8
BH3	0.5	0.19	<8
BH3	2.5	3.33	<8
BH3	3.5	**86.8**	**64**
BH3	4.8	4.93	<8

***Applicable Guidelines**

Alberta Environment and Parks (AEP). 2019. Alberta Tier 1 Soil and Groundwater Remediation Guidelines. Land Policy Branch, Policy and Planning Division. 198 pp.

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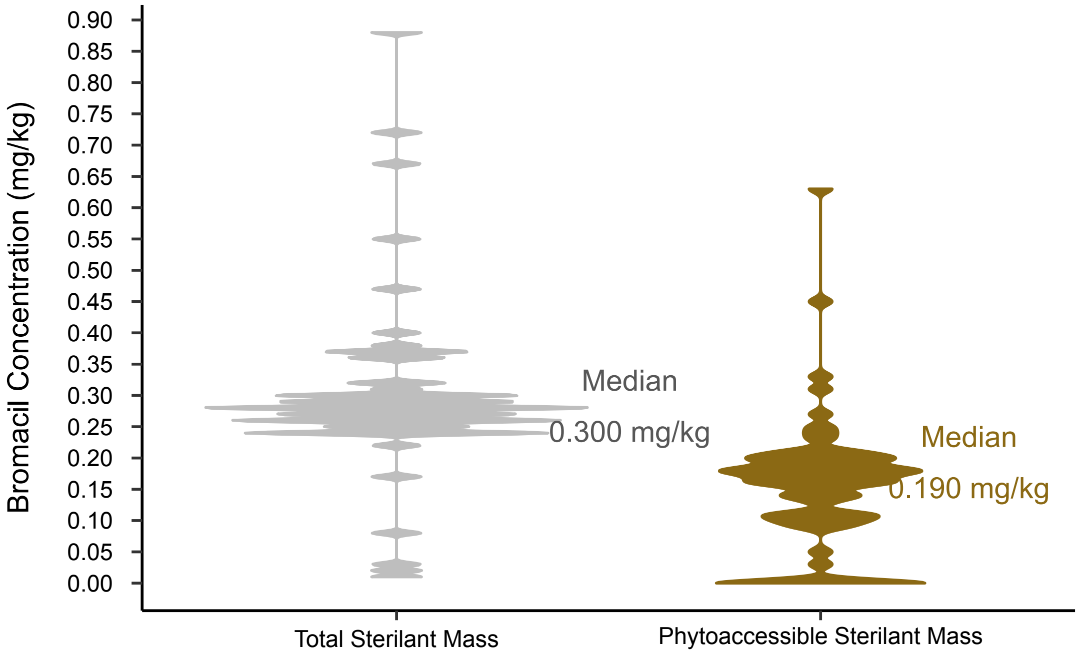
#4. Total vs. Phytoaccessible Concentrations of Bromacil and Tebuthiuron

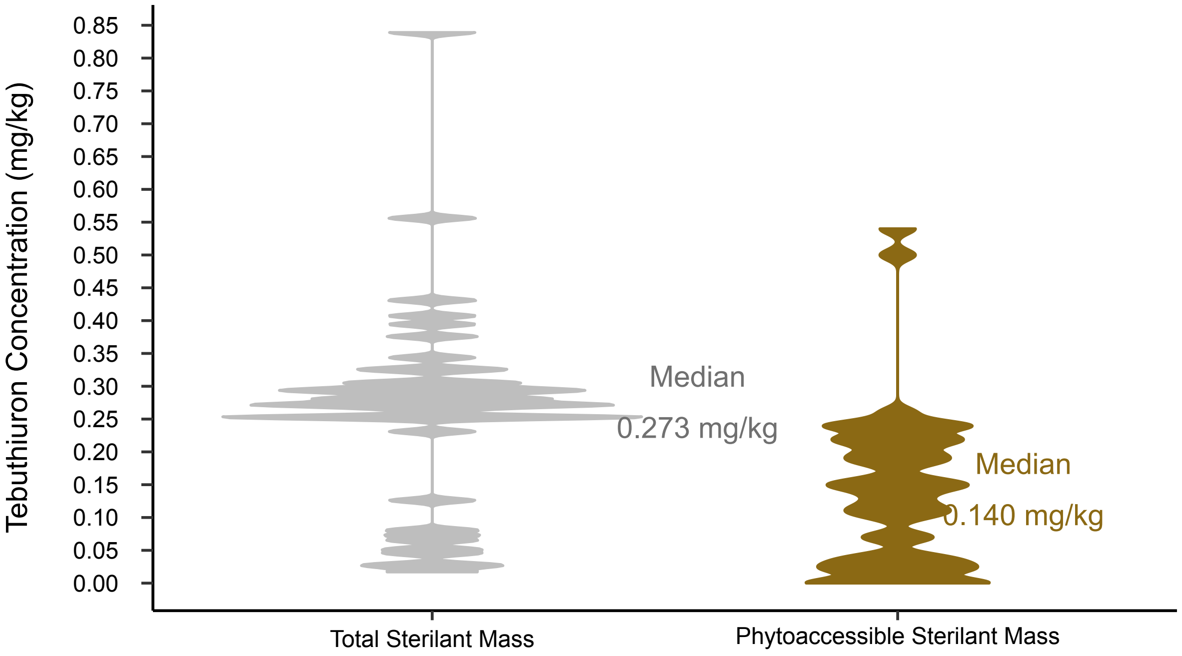
RESEARCH QUESTION

Does adsorption of bromacil or tebuthiuron to soil result in a significant difference between the total sterilant mass in soil and the phytoaccessible sterilant mass?

Bromacil: Adsorption Reduces Phytoaccessibility of Total Sterilant Mass



Tebuthiuron: Adsorption Reduces Phytoaccessibility of Total Sterilant Mass



Risk Assessment and Management

#6/8. Sterilant-Specific Model Input Data and Bromacil Mobility

GOAL

Refine input parameters for sterilant fate, mobility & degradation

- AB-specific (field conditions & receptors)
- Applicable within AB Tier 1 and 2 guideline framework

Task	Status
Sensitivity analysis	Complete
Summarize Impacted Site Characteristics	Complete
Metabolite Review Memo	Complete
Laboratory Experimental Design	Complete
Laboratory Experiment – Half-life (bromacil & tebuthiuron)	Ongoing
Laboratory Experiment – Koc	Complete
Summary Report and Information Matrix (combined with project #8)	Pending lab experiment results

#7. Risk Assessment for Protection of Irrigation Water and Freshwater Aquatic Life

MILLENNIUM EMS Solutions Ltd.

TASKS

1. Current Tier 1 model evaluation for irrigation and freshwater aquatic life pathways for bromacil and tebuthiuron (Complete)
2. Alternative model evaluation to adjust irrigation and freshwater aquatic life pathways for bromacil and tebuthiuron (Complete)
3. Sterilant-pathway risk matrix development (In progress)
4. Guideline development considering source depletion and varying Alberta field conditions (In progress)

		Range of Values	Most Cited Value	Current AB Tier 1 Input
Bromacil	Koc*	2.3 – 1,768	30 – 40	66.6
	T1/2 (days)	12 – 1,494	180 – 275 (0.5-0.75 yrs)	n/a
Tebuthiuron	Koc	1.7 - 92	80	23
	T1/2 (days)	12 – 2,920	365 – 730 (1-2 yrs)	n/a

*Koc = octanol-water partitioning coefficient (no units); measure of mobility of substance in soil with higher values indicating strong adsorption

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#9. Native Species Ecotoxicity Evaluation

CHALLENGE

- Evaluate the toxicity of bromacil and tebuthiuron to Alberta native species
- Develop potential alternative limits for direct soil eco-contact endpoints for areas of the province with dominant native species

	Endpoint	Land Use – Natural (fine-grained soil; mg/kg)
Bromacil	Current AB Tier 1	0.20
	Native species-specific*	0.028
Tebuthiuron	Current AB Tier 1	0.046
	Native species-specific*	0.018

*Not intended to replace existing guidelines for agricultural land or urban areas; endpoints based on research in fine-grained soil with select native vegetation species and modified protocol

Remediation

#10: Investigation of Long-term Effects of Activated Carbon

PROJECT GOAL

Assess the long-term ability of activated carbon (AC) to immobilize bromacil and tebuthiuron in soil to evaluate AC as a valid remediation technology

RESEARCH QUESTIONS

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

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#10: Investigation of Long-term Effects of Activated Carbon (II)

METHODS

1. Desorption Assessment

- Modified SPLP (non-acidified) method desorption experiments with coarse- and fine-grained soils

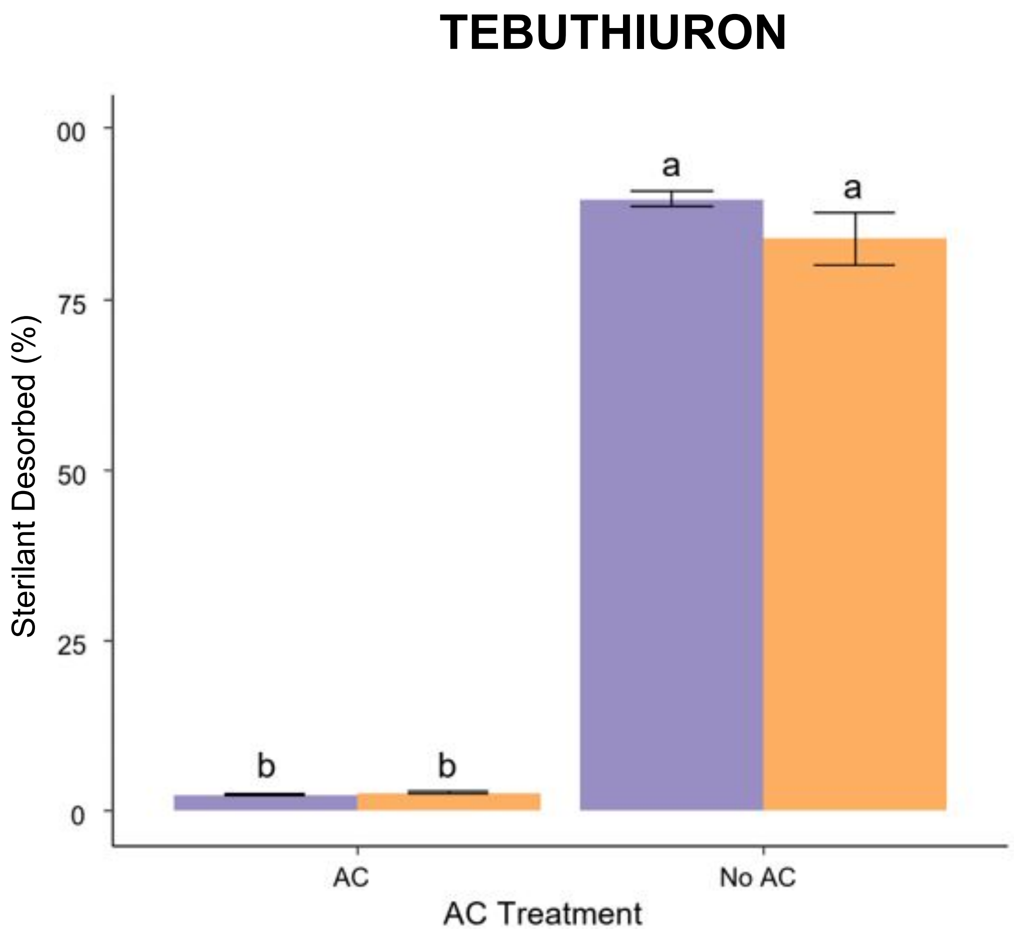
2. Literature Review

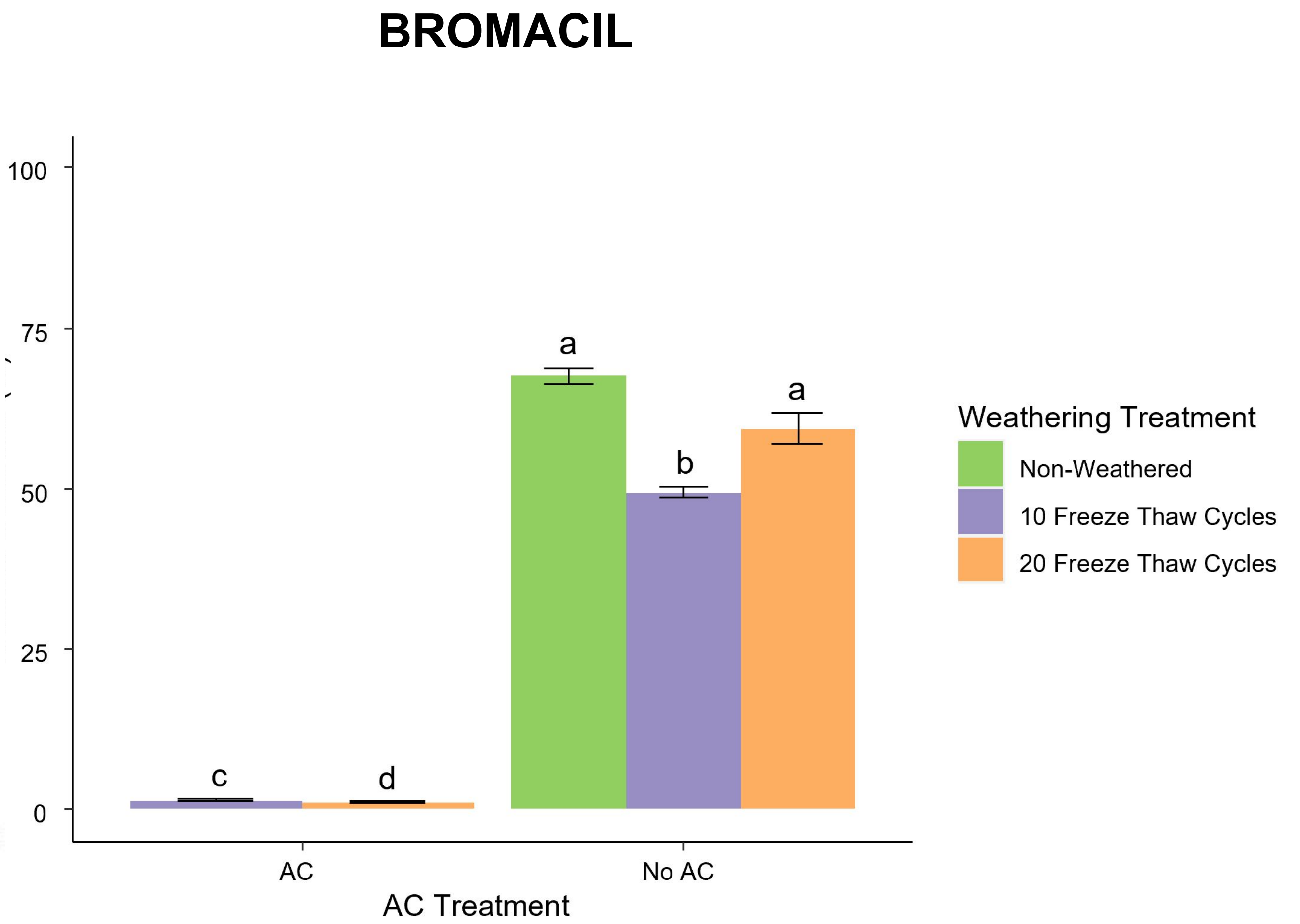
- Could AC to degrade over time?
- What factors potentially influence desorption of sterilants from AC?
- How to simulate in-soil conditions over time (artificial weathering)?

3. Artificial Weathering

- 0, 10 and 20 freeze-thaw cycles
- Assess total vs. phytoaccessible fractions

#10: Investigation of Long-term Effects of Activated Carbon (II)





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Bench-Scale Testing of Remediation Technologies

Technology identification

Applicable media	Feasibility	In/Ex-situ

Validation

Establish effectiveness limits and influential factors	Evaluate costs and logistics

Scaled testing

Decision support for potential users	Information for providers/developers

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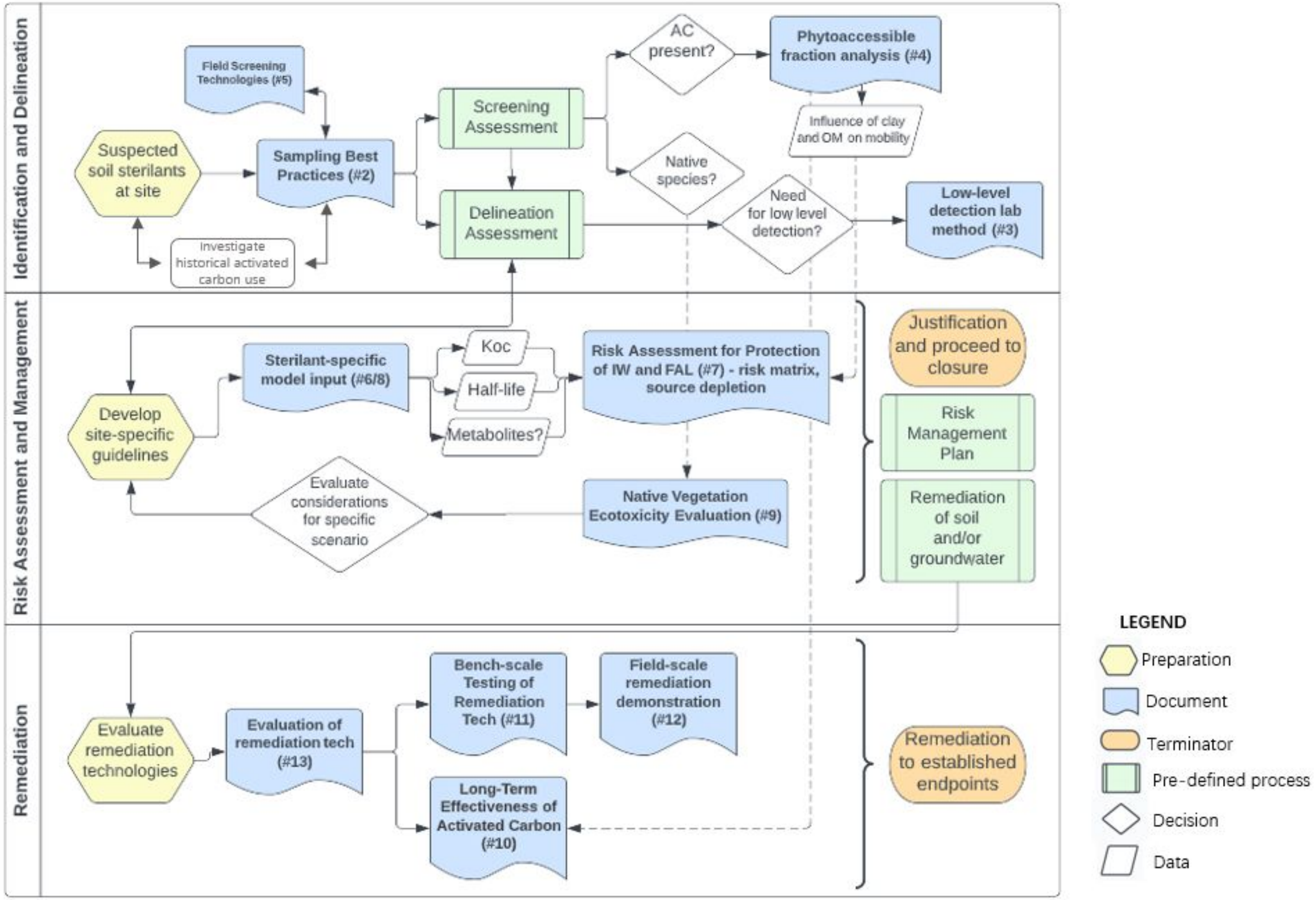
#13/11. Screening and Bench-Scale Testing of Remediation Technologies

Key Challenge	Bench-Scale Testing
1) Treatment of sterilants at depths greater than 50 cm bgs in unsaturated soil, thus inaccessible to treatment at surface (ideally treated *in situ*)	Chemical oxidation and reduction approach, with and without surfactants
2) Sterilant destruction in soil where immobilization is not considered an acceptable option (in situ or ex situ)	In situ Biostimulation, with and without surfactants
3) In situ treatment of saturated fine-grained till soils and groundwater	In situ Biostimulation, with and without surfactants AND Electrocoagulation (ex situ) trial

Project Synergies



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Synthesis and Collaboration

Program Outputs:

- Synthesize past learnings
- Partner to develop strategies and methods to effectively manage sterilant impacted sites
- Publicly available reports and fact sheets (post-program)
- Established community of practice

Drozdowski, B., C.B. Powter, S. Levy, 2018. Management of Sterilant Impacted Sites: Literature Synthesis. InnoTech Alberta, Edmonton, Alberta. 49 pp.

Drozdowski, B., S. Levy and C.B. Powter, 2018. Remediating Soil Sterilant-Affected Lands: Summary of Stakeholder Discussions. InnoTech Alberta, Edmonton, Alberta. 42 pp.

THANK YOU

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