DEVELOPMENT OF AN EXTRACTION METHOD FOR ESTIMATING PHYTOACCESSIBLE FRACTIONS OF BROMACIL AND TEBUTHIURON

by

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Abstract

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

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

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

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

Dedication

I started planning for a graduate degree January 2019. Navigating the obstacles of graduate application four months postpartum was difficult. Acceptance into the U of A did not happen until June 2020. Those eighteen months brought another pregnancy and a global pandemic. I wrote a research proposal between the sixth and ninth months of pregnancy. Two weeks after birth, I attended online classes with a newborn in my arms. Online learning proved to be a silver lining of the pandemic. Sleepless nights do not lend themselves to hustling to university every morning.

Laboratory work began in January 2021, at InnoTech Alberta. I enjoyed solitude 8 hours a day as my partner took over newborn patrol. Between weighing soil samples and preparing herbicide solutions, I pumped breast milk peacefully in a private room at the nursing station. Thank you forever, to the three people who helped me secure this arrangement. Prior, I was pumping in a bathroom.

As lab work progressed, my partner started a new job with a better salary. We decided our family of four no longer suited a two-bedroom condo. Searching for a home was added to an already full list of responsibilities. Upon securing a new home in June 2021, our then two-year-old son contracted COVID. Under isolation, movers were canceled. My partner and I moved the entire household in turns. One cared for the children, the other brought loads of boxes and furniture; then we would switch.

The summer of 2021 passed swiftly as everyone rescheduled all the postponed events from summer 2020. We enjoyed the socialization and our new home. Peace was shattered on August 31, 2021, when the basement flooded. The months that followed were a parade of contractors in and money out. I taught two labs for extra income, took two advanced statistic classes, and was on the phone with the bank for more loans. The furnace failed. The washing machine broke. In-laws arrived from France for Christmas.

I completed a graduate degree through a global pandemic, pregnancy, birth, nursing, parenting a willful toddler, selling a condo, buying a house, a basement flood along with all the other unplanned events like furnace and washing machine failure, a child with COVID…on and on. In a fantastically vain moment, I dedicate this work to my effort. Obviously, this effort could not have been sustained without the love of my partner, the joy of my children, all my amazing friends, Sylvie, Bonnie, Simone, Sarah, Twyla, Miles D., Christie, Carol, Tariq, and Steve. Through the challenges I had support from an empathetic network of good and honest people. Thank you.

Acknowledgements

Dr. Sylvie Quideau provided supervisory support before she had any obligation to me as a student. She is why I had a graduate program at all, reaching out to InnoTech Alberta for a project. Thank you for meeting with me out of the blue, continuing efforts to find a project and funding; and for weathering with me the most difficult years many of us have experienced.

Thank you to Bonnie Drozdowski for meeting with me on the recommendation of Dr. Quideau and believing in what I could contribute to the Herbicides Program at InnoTech Alberta. Bonnie provided the industry partner monetary support for a Mitacs grant. She rose to another position, placing me in the calm, kind care of Simone Levy. Thank you for everything Simone! I cannot thank InnoTech Alberta enough for the funding; laboratory and office space; and the help of InnoTech staff.

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Chapter II: Calcium Chloride Extraction of Bromacil and Tebuthiuron

Chapter III: Effect of Organic Matter and Clay Content on Adsorption

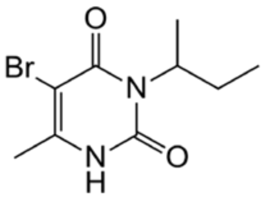
Chapter I: Introduction

1. Background

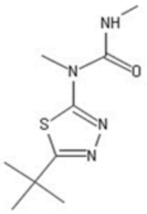
InnoTech Alberta, as part of their Herbicides Program, conducted an extensive literature review which found that bromacil and tebuthiuron are present at industrial sites throughout Alberta (Drozdowski et al., 2018). Bromacil and tebuthiuron are a class of non-selective herbicides (i.e., herbicides) meant to render soil unfit for plant growth for months to years (Chang & Stritzke, 1977; Drozdowski et al., 2018; Duncan & Scifres, 1983; Grover, 1975; Helbert, 1990; Kim et al., 2007; Koskinen et al., 1996; Landsburg and Dwyer, 1995; Matallo et al., 2005; Ting et al., 1980; Turin & Bowman, 1997; Weber, 1980). These 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, sawmills, pulp mills, and electrical utility sites; affecting an estimated 61,750 sites (Drozdowski et al., 2018).

Studies have found variable results under different environmental conditions for soil adsorption and mobility of bromacil and tebuthiuron (Drozdowski et al., 2018). Behaviour of bromacil and tebuthiuron in soil depends greatly on soil characteristics. Adsorption of both herbicides is expected to increase with increasing soil organic matter and secondly, possibly increased by clay content (results are mixed). Bromacil and tebuthiuron can persist in soil from months to years, depending on the rate and number of applications. Chemical formulae and characteristics (Table 1) are presented below.

Bromacil



Tebuthiuron



https://oehha.ca.gov/chemicals/bromacil

Tebuthiuron | C9H16N4OS | 673910 | 34014-18-1 (hpc-standards.com)

Table 1. Properties of Bromacil and Tebuthiuron

Property	**Bromacil**	**Tebuthiuron**
Solubility in water (mg/L @ 25oC)	815	2500
Vapour Pressure (mm Hg @ 25oC)	Negligible	2x10-6
Henry's Law Constant	1.50x10-5	2.47x10-5
	Non-volatile	Non-volatile
Abiotic hydrolysis as a function of pH	Stable at all relevant pHs	Not sensitive to pH
	---	64 days
Kow	2.11	1.79
Biodegradability	60 days to 5-6 months	1300 days
pKa of ionisable substances	Very weakly acidic	Non-ionisable
pKa @ 25oC	9.27	Non-ionisable
Direct photolysis in water	Stable at all relevant pHs	Not sensitive to pH
Solubility in acetone (mg/L @ 25oC)	167000	70000
Solubility in methanol (mg/L @ 25oC)	14000	170000
Linear Koc	32 mg/L	80 mg/L
Notes and Range	log Koc 1.51; gen lit Koc 2.3 to 289	Log Koc 2.1

(Drozdowski et al., 2018).

Reviewed literature indicated that both bromacil and tebuthiuron molecules are very stable. Adsorptive mechanisms are generally not described, nor which characteristics of each molecule make these more strongly adsorbed to soil organic matter. It is assumed that adsorption occurs and resulting phytoaccessible or soluble herbicide concentration is reduced below the total herbicide concentration, which consists of both the solid, adsorbed phase and the soluble, phytoaccessible phase. Whether adsorption significantly reduces the herbicide concentration to which receptors can be vulnerable is not reported nor compared to remediation guidelines.

For environmental site assessments in Alberta, substance concentrations in soil (mg/kg) are initially compared to *Alberta Tier 1 Soil and Groundwater Remediation Guidelines* (Tier 1 guidelines, Alberta Environment and Parks, 2019a). If a substance is included in the Tier 1 guidelines, and its concentration in soil is above the guideline, the site is considered contaminated. Further assessment of a contaminated site should proceed to comparison against *Alberta Tier 2 Soil and Groundwater Remediation Guidelines* (Tier 2 guidelines, Alberta Environment and Parks, 2019b), for consideration of site-specific conditions. Upon completion of assessment to site-specific conditions, contamination can be risk managed and/or remediated.

Following this framework in Alberta, herbicides are first assessed as meeting (below or at) or exceeding (above) Tier 1 guidelines. The 61,750 sites above are considered contaminated as herbicides exceed Tier 1 and/or Tier 2 guidelines. Ninety-nine percent methanol is used to estimate all the bromacil and tebuthiuron present in the soil (Alexander, 2000; Cotterill, 1980; Element Laboratory, 2020). Herbicide concentrations extracted by 99 percent methanol, assumed to represent the total herbicide concentration in soil, are used for comparison against Alberta's guidelines. Methanol extraction is not expected to discriminate between adsorbed and water-soluble fractions. Bromacil and tebuthiuron exhibit adsorption to:

1) Organic matter (Farenhorst et al., 2010; Parolo, María Eugenia; Savini, Mónica Claudia; Loewy, 2017).
2) Soil particles (i.e., sand, silt, or clay) (Bonfleur et al., 2016; Singh et al., 2014); and/or
3) Remedial amendments (e.g., powdered activated carbon) (Drozdowski et al., 2018; Kim et al., 2007).

The portion of bromacil and tebuthiuron that is adsorbed is not accessible to plants; in other words, it is not *phytoaccessible* (Feng et al., 2016; Xiao et al., 2015). Substances are accessible to plants when dissolved in soil pore water (Shaner et al., 2012). Phytoaccessibility is defined here as:

the amount of herbicide that is desorbed from the solid phase
and dissolved in soil pore water.

Using phytoaccessibility for bromacil and tebuthiuron is applicable as plants are the most sensitive receptor (Stantec Consulting Ltd., 2008, 2012).

Remediation guidelines in Alberta do not consider that the total herbicide concentration is comprised of

$$Adsorbed\ Sterilant + Phytoaccessible\ Sterilant = Total\ Sterilant$$

and that the adsorbed herbicide concentration could significantly reduce the concentration which is phytoaccessible. Immobilization could then be used as a remediation strategy. Common remediation techniques include landfilling or sterilizing soil through thermal desorption. Although useful in areas of high herbicide concentrations in soil, marginal exceedances of Alberta Tier 1 or 2 guidelines could be managed through increasing adsorption by applying immobilizing agents such as activated carbon. Such an approach would leave healthy soil in place preserving soil organic matter and structure to provide resiliency against current and future challenges to soil ecosystems.

2. Literature Review

2.1 Immobilizing Contaminants in Soil

Current remedial methods for removing contamination from soil which involve removing and processing a large amount of soil are costly and time-consuming (J. Ehlers & G. Luthy, 2003; Khorram et al., 2016; Morillo et al., 2017; Semple, K.T., 2004). Immobilizing contaminants, by in-situ application of an adsorbent amendment, is a cost-effective remedial solution that: 1) reduces further land disturbances following decommissioning of industrial sites; 2) keeps potentially healthy and productive soil from being landfilled; 3) eliminates the need for clean backfill material to be sourced and trucked to site; and 4) reduces soil erosion, fertility loss and nutrient leaching (Khorram et al., 2016; Morillo et al., 2017).

Analyzing soil samples for the total herbicide concentration in soil (mg/kg) precludes immobilization as a remedial method. Currently in Alberta, there is not an accepted methodology by which to immobilize contaminants and then analyze for phytoaccessible concentration. Bromacil or tebuthiuron are considered by the provincial regulations to be 100 percent accessible to receptors, under all conditions and always (Alberta Environment and Parks, 2019a).

Bromacil and tebuthiuron are good candidates for phytoaccessibility assessments at sites where: 1) these are and remain the main risk drivers, and 2) default assumptions of risk assessment are not applicable at a site (e.g., greater than 300 m from a surface water body, see Section 2.2.1), (Ehlers and Luthy, 2003).

2.2 Regulatory Framework

2.2.1 Bromacil

Alberta Environment and Parks (AEP) 2019 *Alberta Tier 1 Soil and Groundwater Remediation Guidelines* (Tier 1) sets a management limit of 0.009 mg/kg of bromacil in soil, regardless of land use, to mitigate its impact to Freshwater Aquatic Life (Alberta Environment and Parks, 2019a). If the site is greater than 300 m from surface water, the next most protective guideline is the Direct Soil Contact pathway (fine-grained soils – 0.20 mg/kg; coarse – 0.12 mg/kg). Direct Soil Contact is considered applicable under all site conditions. Invertebrate survival and progeny production were the least sensitive endpoints relative to bromacil contamination (Alberta Environment and Parks, 2019a; Stantec Consulting Ltd., 2012). Vegetation is the intended target of the herbicides and therefore the most sensitive receptor in the scenario of bromacil contamination.

2.2.2 Tebuthiuron

AEP Tier 1 Guidelines identify two management limits for tebuthiuron in soil: 0.046 mg/kg for natural, agricultural, and residential/parkland land uses; and 0.60 mg/kg for commercial and industrial land uses. These management limits are driven by the Ecological Direct Soil Contact pathway considered applicable under all site conditions. Plant species have been observed to more sensitive to tebuthiuron than invertebrate species, as expected as tebuthiuron is a nonselective herbicide that specifically inhibits photosynthesis (Stantec Consulting Ltd., 2008). Vegetation is the intended target and most sensitive receptor in the scenario of tebuthiuron contamination.

2.3 Risk Assessment for Bromacil and Tebuthiuron

Alberta's regulatory framework assumes that bromacil and tebuthiuron are 100 percent phytoaccessible under all conditions, always. "The vast heterogeneity of soil characteristics at contaminated sites has precluded adoption of [phyto]accessibility in risk assessment" (Alexander, 2000; National Research Council, 2003). "Measurement of [phyto]accessible fractions would focus remedial efforts where environmental degradation [from herbicides] is most acute and allow risk management of the rest" (Fisher et al., 2020; Rapport et al., 1998). To be able to implement risk management plans for herbicide impacted sites, the disparity between science and regulatory practice in terms of explicitly incorporating methods to assess phytoaccessibility of contaminants must be addressed (Anderson et al., 2013).

2.4 Behaviour in Soil

Bromacil and tebuthiuron can have limited phytoaccessibility in soil due to a combination of the following: 1) adsorption to soil organic matter (Bonfleur et al., 2016; Chang & Stritzke, 1977; Duncan & Scifres, 1983; Eriksson et al., 2004; Farenhorst et al., 2010; Frankki et al., 2007; Grover, 1975; Helbert, 1990; Kim et al., 2007; Koskinen et al., 1996; Obrigawitch et al., 1981; Parolo, 2017); 2) adsorption to clay particles (Chang & Stritzke, 1977; Duncan & Scifres, 1983; Suyal et al., 2013; Weber, 1980); 3) limited (bromacil) to moderate (tebuthiuron) solubility (Grover, 1975; Kim et al., 2007; Landsburg and Dwyer, 1995; Schreiber et al., 1975); and 4) micro-pore sequestration (B Gevao et al., 2000; Odukkathil & Vasudevan, 2013; Semple, K.T., 2004). Adsorption to organic matter and clay affects to a large degree the extent of the other processes above (Bailey, G.W.; White, 1970; B Gevao et al., 2000; Bondi Gevao et al., 2003).

2.4.1 Soil Factors that Affect Phytoaccessibility

Adsorption of herbicides by soil colloids influences phytotoxicity (and on the flip side, phytoaccessibility) to plants, degradability by microorganisms, mobility in soil, and loss by vaporization (Weber, 1980). Reviewed literature suggests that soil factors affecting phytoaccessibility, from most to least important, are: 1) soil moisture, 2) soil organic matter and soil organic carbon, 3) organo-mineral interactions, particularly in the 2-53 μm size range, and, lastly, 4) soil particles and aggregates (Bailey, G.W.; White, 1970; Bonfleur et al., 2016; Chang & Stritzke, 1977; Duncan & Scifres, 1983; B Gevao et al., 2000; Grover, 1975; Kim et al., 2007;

Landsburg and Dwyer, 1995; Matallo et al., 2005; Odukkathil & Vasudevan, 2013; Ortiz-Hernández et al., 2014; Parolo, 2017; Schaffer, 2011; Suyal et al., 2013; USEPA, 2000).

2.4.1.1 Soil Moisture

For model soil ecosystems, soil moisture content was identified as the most important soil property (Schaffer, 2011). Bromacil dissipation is closely related to movement of soil water (Landsburg and Dwyer, 1995), and its movement with soil water can be slowed by increasing organic carbon content in soils (Kim et al., 2007; Landsburg and Dwyer, 1995). Soil moisture, in combination with temperature, affected persistence of tebuthiuron (Chang & Stritzke, 1977). Greater dissipation occurred at 15 percent soil moisture and 30ºC than at lower moisture and temperature levels (Chang & Stritzke, 1977).

2.4.1.2 Soil Organic Matter / Carbon

The chemical composition of soil organic matter is known to have a substantial effect on the sorption of organic pollutants and pesticides (Parolo, 2017). Among the estimated molecular components, lignin and charcoal contents correlated best with the sorption of carbaryl and phosalone (Parolo, 2017). Grover (1975) found that herbicides could be readily desorbed by water from soils with low to medium organic matter content but not from loam soils with a high level of organic matter.

Bromacil is generally not strongly adsorbed to soil and is more likely to leach through the soil profile. Adsorption of bromacil is higher in a Chernozemic soil with greater clay and organic matter content compared to a Luvisolic soil with lower clay and organic matter content (Landsburg and Dwyer, 1995). In experimental designs powdered activated carbon (PAC) is added as a proxy for soil organic carbon; and bromacil transport through sandy soils was slowed by increasing PAC content (Kim et al., 2007). Powdered activated charcoal or carbon reduces phytotoxicity of bromacil as it lowers its phytoaccessibility (Landsburg and Dwyer, 1995). Ecotoxicity tests with three plant and two invertebrate species found plant species were more sensitive to bromacil in both fine and coarse textured soils, which is expected as bromacil inhibits photosynthesis (Stantec Consulting Ltd., 2012).

Tebuthiuron is generally expected to be more strongly adsorbed to soil organic matter and less likely to leach through the soil profile, despite its 2,500 mg/L solubility in water. Tebuthiuron dissipation is closely related to organic matter, moisture, temperature, and clay content (Chang & Stritzke, 1977; Duncan & Scifres, 1983; Helbert, 1990; Johnsen & Morton, 1991; Koskinen et al., 1996; Weber, 1980). Greater soil organic matter and clay content correlate to less movement of tebuthiuron (Chang & Stritzke, 1977; Duncan & Scifres, 1983; Helbert, 1990; Johnsen & Morton, 1991; Koskinen et al., 1996; Weber, 1980). The further downward tebuthiuron leaches, the less it is adsorbed as organic matter content typically decreases with increasing soil depth (Matallo et al., 2005). Soil mobility of tebuthiuron is greater in soil with low organic matter and low clay content (Matallo et al., 2005). The organic LF horizon is a very important residue sink with a high buffering capacity: for tebuthiuron the mean percentage of residue detected in each respective LF horizon was approximately 93% (Helbert, 1990).

2.4.1.3 Organo-Mineral Complexes

Organo-mineral complexes affect adsorption as clay occupies sites on organic matter that could be available for other substances adsorption. Farenhorst et al. (2010) found that organic-C that is not-complexed with clay minerals had a higher adsorptive capacity for atrazine than organic-C complexed with clay minerals (organo-mineral complexes). Bonfleur et al (2016) showed that soil organic carbon cannot be used as the sole indicator of pesticide sorption affinity to soils; quality of soil organic matter and organo-mineral interactions play significant roles.

2.4.1.4 Soil Particles and Aggregates

Clay and silt/clay aggregates can adsorb herbicides and lower phytoaccessibility (Bonfleur et al., 2016; Duncan & Scifres, 1983; Grover, 1975; Koskinen et al., 1996; Obrigawitch et al., 1981; Singh et al., 2014; Suyal et al., 2013; Weber, 1980). The type and amount of clay could affect adsorption due to surface area and surface charge (Obrigawitch et al., 1981). Pesticides studied in Bonfleur et al (2016) exhibited more adsorption on clay-containing, silt-sized aggregates in the 2-53 μm size range. Adsorption on clay-sized aggregates less than 2 μm was lower than larger aggregates (Bonfleur et al., 2016).

2.5 Phytoaccessibility of Nutrients, Herbicides, and Other Contaminants

2.5.1 Nutrients

Agricultural studies have long looked at plant-available (a.k.a., phytoaccessible) macro-and micronutrients in soil to determine application rates of chemical fertilizers for optimal crop growth.

Several 'classical' extractants for measuring phytoaccessible macro-or-micronutrients include water or a weak calcium chloride solution as these neither destroy soil structure nor change the pH (Grzebisz and Oertli, 1992). 'Universal' extractants include 0.073 M sodium acetate, Mehlich No.1, Mehlich No.3, ammonium acetate-EDTA, 0.01 M calcium chloride, EDTA or DTPA, modified Kelowna (ammonium fluoride, ammonium acetate and acetic acid) or Olsen (sodium bicarbonate), which are effective in a range of soils for determining phytoaccessible plant nutrients (Grzebisz & Oertli, 1992; McKenzie, 2016; Zikeli et al., 2013).

2.5.2 Herbicide Application Rates

Application rates of bromacil and tebuthiuron have been adjusted over the years to account for soil moisture, or adsorption to soil organic matter and clay particles (Chang & Stritzke, 1977; Duncan & Scifres, 1983; Schreiber et al., 1975). Growth of corn in soil spiked with two parts per million of weight of tebuthiuron was significantly influenced by soil type due to differences in adsorption (Chang & Stritzke, 1977). These considerations are rarely extended to risk assessment of contaminants (Ehlers & Luthy, 2003). All this research could be mined for indications of bromacil and tebuthiuron phytoaccessibility.

2.5.3 Contamination

Phytoaccessibility in contaminant fate and transport is often studied under the banner of bioavailability, bioaccessibility, or within adsorption/desorption studies.

2.5.3.1 Bioavailability

The Canadian Council of Ministers for the Environment (CCME, 2006) defines bioavailability as the amount of chemical available to the target tissues following exposure. They recommend that soil contact guidelines be developed based on data reflective of Canadian soils; and the toxicity studies on which soil contact guideline is developed should be assessed for site-specific conditions (Canadian Council of Ministers of the Environment, 2006). Most environmental site assessments do not have budget for gathering enough site-specific information for independent derivation of soil contact guidelines. Bioavailability is usually assumed to be 100 percent to provide the most protection for land uses and ecological receptors (Alberta Environment and Parks, 2019a; Canadian Council of Ministers of the Environment, 2006).

2.5.3.2 Bioaccessibility

The Canadian Council of Ministers for the Environment (CCME, 2006) defines bioaccessibility as that fraction of chemical that is bioavailable plus that which may become bioavailable; it is the chemical pool plus that which may be replenished as uptake occurs. It is influenced by soil and groundwater conditions in which the chemical is present, and how changes in soil or groundwater conditions may change bioaccessibility. If, as is suggested with bromacil and tebuthiuron, the major conditions which affect bioaccessibility are resilient ones like soil organic matter and texture, it may be possible to use bioaccessibility as an estimate of toxicity to the target plant tissues. Remediation scientists are probably more interested in the bioaccessible rather than the bioavailable chemical fraction, as it is difficult to estimate the bioavailable fraction as it is time-and-space dependent. The bioaccessible fraction can be estimated in adsorption/desorption studies, many of which have been conducted for various contaminants.

2.5.3.3 Adsorption/Desorption

Adsorption/desorption studies for various chemicals provide information on:

- the mobility of chemicals
- partitioning in soil, air, and water
- availability for degradation, transformation, and uptake by organisms
- leaching through the soil profile
- volatility in the soil profile
- run-off potential from land surfaces

All of which can be used for comparative and modeling purposes (USEPA, 2000). Despite being unable to cover all environmentally possible phenomena, valuable information is still obtained through simplified laboratory models of adsorption/desorption (USEPA, 2000). Maintaining in-situ soil characteristics could a be a way to maintain the environmental conditions in which the chemical is observed.

Batch equilibrium tests using a weak (0.01 M or similar) calcium chloride solution are used to estimate adsorption and desorption of various substances in soil (Abernathy & Davidson, 1971; Alva & Singh, 1991; Bailey, G.W.; White, 1970; Bonfleur et al., 2016; Chang & Stritzke, 1977; Duncan & Scifres, 1983; Eriksson et al., 2004; Farenhorst et al., 2010; Frankki et al., 2007; Gaultier et al., 2008; Grover, 1975; Houba et al., 2000; Kim et al., 2007; Koskinen et al., 1996; Matallo et al., 2005; Obrigawitch et al., 1981; Shaner et al., 2012; Singh et al., 2014; Suyal et al., 2013; Turin & Bowman, 1997; Weber, 1980). A 0.01 N or 0.01 M calcium chloride solution is commonly used in adsorption and desorption studies, for metals, organic pollutants, and nutrients (Abernathy & Davidson, 1971; Bonfleur et al., 2016; Farenhorst et al., 2010; Fu et al., 1994; Gaultier et al., 2008; Houba et al., 2000; Singh et al., 2014; USEPA, 2000). It is chosen because 1) the pH of the solution is determined by the soil itself, 2) it maintains the appropriate charge balance against negatively charged clay particles to prevent deflocculation of clay sheets and 3) it has similar ionic strength as the average salt content in many soil solutions (Houba et al., 2000). Combined with not drying, grinding, or burning off organic matter, factors responsible for adsorption and desorption in soil may be maintained close to in-situ.

3. Research Objectives and Thesis Organization

The experimental design described herein is first focused on whether total herbicide concentrations estimated by 99 percent methanol extraction, or a total herbicide concentration yields information about soluble / phytoaccessible concentrations. In another way:

$$Phytoacessible\ Sterilant \neq Total\,Sterilant,\ as$$

$$Adsorbed\ Sterilant \gg 0$$

Second, the experimental design tests the partial effects of soil clay and organic matter content on apparently adsorbed herbicide, and whether there is an interaction between the two characteristics. The method estimated the adsorbed fraction of bromacil or tebuthiuron on different soil types with a varying range of organic matter and clay contents (USEPA, 2000). Bromacil and tebuthiuron can be tightly adsorbed to organic matter, soil particles, or activated carbon. Relying on the herbicide concentration estimated by 99 percent methanol extraction rather han only the soluble / phytoaccessible herbicide concentration in soil for environmental assessment could result in an overestimation of bromacil and tebuthiuron risk to receptors.

Hypothesis: Adsorption to soil organic matter and/or soil particles reduces what remains soluble or phytoaccessible of bromacil or tebuthiuron concentrations; this soluble or phytoaccessible portion is less than the bromacil or tebuthiuron concentration estimated by 99 percent methanol extraction conducted at commercial laboratories.

Research questions:

1. How can the soluble / phytoaccessible portion of bromacil and tebuthiuron be measured?
2. Do higher percentages of clay and organic matter significantly increase adsorption of bromacil or tebuthiuron?

Chapter II: Calcium Chloride Extraction of Bromacil and Tebuthiuron

1. Introduction

Commercial laboratories use 99 percent methanol extraction of herbicide herbicides from solid matrices by wrist action shaker / paint shaker, followed by concentration, filtration and analysis by reverse phase high-pressure liquid chromatography using mass-selective detection (Cotterill, 1980; Element Laboratory, 2020; National Research Council, 2003). Solubility of bromacil in methanol is 14,000 mg/L at 25ºC; and solubility of tebuthiuron in methanol is 170,000 mg/L at 25ºC (Table 1). Methanol will dissolve approximately 17 times more bromacil and 68 times more tebuthiuron than water. Extraction with water, or a weak calcium chloride solution, should reflect that portion most likely to be mobile under ambient conditions (Garrett et al., 2009; Houba et al., 2000), or the phytoaccessible portion.

Mechanisms involved in bromacil- or tebuthiuron-specific adsorption in soil are not well studied. More common is a description of the amount of soil organic matter or clay which increase adsorption, and how to overcome adsorption with increasing the application rate (Duncan & Scifres, 1983). Speculative discussion suggests possible ionic, covalent or hydrogen bonding; charge transfer bonds between electron deficient herbicide aromatic rings and electron rich organic matter rings of organic matter; molecular surface area; weak-and-short-ranged van der Waals forces; ligand exchange; hydrophobic bonding or partitioning; and/or pH dependent reactions (Bailey, G.W.; White, 1970; B Gevao et al., 2000; Texeira et al., 2018; Weber, 1980).

Calcium chloride is a common extractant to assess soluble phases of various compounds in soil (Bonfleur et al., 2016; Farenhorst et al., 2010; USEPA, 2000), in other words, the phytoaccessible portion. Calcium chloride maintains in-situ soil conditions that influence phytoaccessibility. Several ionic strengths of calcium chloride have been tested and there is not a significance difference between 0.01 M and 0.1 M solutions in extraction capacity (Abernathy & Davidson, 1971; Alva & Singh, 1991). A 0.01 M calcium chloride solution was chosen as an extractant to minimize disruption to the soil mineral environment and allow reactions to occur at a constant ionic strength (Farenhorst et al., 2010).

2. Research Objectives

The first objective of this study was to measure recovery of bromacil or tebuthiuron from soil samples extracted with calcium chloride. Soil samples were spiked with one or the other herbicide and aged for eight weeks, aged for one year, or aged for decades from previous field applications. Spiked soil samples were not duplicated and analyzed by methanol extraction because it was assumed that the methanol extraction would recover most of the applied herbicide. Soil sample and budget limitations influenced the decision to make this assumption. It was also assumed that the difference between assumed total herbicide concentration and calcium chloride-extractable concentrations were due to adsorption. Commercial labs require at least 100 g of soil and charge upwards of $185 per sample. Based on discussions with the herbicide committee and graduate supervisors, the herbicide concentration in the spiking solutions was considered representative of that herbicide concentration estimated by 99 percent methanol extraction at a commercial laboratory.

3. Materials and Methods

3.1 Sources of Soil

As COVID-19 restrictions limited soil sampling opportunities, most soil samples were selected from stores at InnoTech (Brooks) and from extra soil samples I had collected for training personnel in soil classification (Fort McMurray and Mildred Lake). Two soil sampling events were conducted. One was for soil contaminated with a decades-old application of tebuthiuron in an agricultural field near Westlock, Alberta in October 2020. The other was conducted near Huxley, Alberta in April 2021 at a second agricultural site with a variety of soil types. Two samples were obtained by others from Lac La Biche and Shaw Lake. An attempt was made to choose samples from these sources with a wide variety of characteristics (Table 1).

Table 1. Soil Sample Sources and Characteristics

Location	Legal Site Description(s)	Soil Orders	Textures	Samples
Brooks	10-20-018-14 W4M	Brown Solodized Solonetz	Silt Loam and Sandy Loam	B01 to B12; and T01 to T11
Huxley	9 to 16-21-034-24 W4M	Orthic Black Chernozem, Rego Black Chernozem	Sandy Loam	21-01 to 21-08
Fort McMurray	30, 31, 35 and 36-088-09 W4M	Dark Grey Luvisol, Eluviated Melanic Brunisol, Hemic Folisol, Typic Mesisol	Loam, Sandy Loam and Loamy Sand; Organic	Select Samples from TH19-100 to TH19-228
Fort McMurray	02, 10 and 11-089-09 W4M	Dark Grey Luvisol, Eluviated Melanic Brunisol, Hemic Folisol, Typic Mesisol	Loam, Sandy Loam and Loamy Sand; Organic	Select Samples from TH19-100 to TH19-228
Lac La Biche	23-069-14 W4M	Typic Mesisol, Orthic Humic Gleysol, Orthic Dark Grey Chernozem	Loamy Sand	21-09
Shaw Lake	SE-07-067-11 W4M	Typic Mesisol, Orthic Humic Gleysol, Orthic Dark Grey Chernozem	Silt Loam	21-10
Mildred Lake	07-13-093-12 W4M	Organic Soils and Regosols	Peat, Sandy Loam, Loamy Sand	BH10, BH22, BH25, BH30, BH32, BH35, BH42, BH52, BH53, BH60A, BH60B, PH06, PH011, PH111
Westlock	07-15-060-02 W5M	Solonetzic Dark Grey Chernozem	Loam to Clay Loam	BH20-2, BH20-3, SS19-6, SS20-2, SS20-4, SS20-7, SS20-8, SS20-9

3.1.1 Description of Soil Samples

Soil from Brooks were previously spiked in 2020 with varying levels of bromacil (B01 to B12) or tebuthiuron (T01 to T11) in 2020 for a separate project within InnoTech's Soil Herbicide Program. Bromacil concentration in soil estimated by 99 percent methanol extraction conducted by a commercial laboratory ranged from 0.01 mg/kg to 8.9 mg/kg. Tebuthiuron concentration in soil as determined by 99 percent methanol extraction conducted by a commercial laboratory ranged from 0.073 mg/kg to 14.87 mg/kg. These are labeled total concentrations. Samples were very uniform with a loam texture, mean organic matter of 3.44 percent +/- 0.55 and moisture content between 10 and 15 percent.

Soil samples from Westlock (SS19-6, SS20-2, SS20-4, SS20-7, SS20-8, and SS20-9) were impacted with tebuthiuron from applications of the herbicide in the 1980s. Total tebuthiuron concentration in soil was determined by 99 percent methanol extraction at a commercial laboratory and ranged from 0.017 mg/kg to 0.282 mg/kg. The site was available for sampling through collaboration between InnoTech, a consultant and an industry partner. Samples were very uniform as well, with a silt loam or loam texture, mean organic matter of 6.88 percent +/- 0.65, and moisture content between 7 and 12 percent.

All other soil samples were chosen to increase variety in soil characteristics, as the above samples were relatively uniform. These samples did not contain any bromacil or tebuthiuron and were spiked with one or the other. The herbicide concentration applied in a spike was assumed like the concentration that would be obtained by 99 percent methanol extraction by a commercial laboratory. Spiked samples were aged for eight weeks on recommendation from another project within InnoTech's Soil Herbicide Program.

3.1.2 Spiking Procedure

Spiking consisted of preparing solutions of bromacil and tebuthiuron from commercial herbicide formulations. Bromacil is the active ingredient in the commercial liquid herbicide Hyvar. It contains 240 mg/L bromacil in its liquid formulation and a stock solution with water was prepared to maintain this concentration. Tebuthiuron is the active ingredient in the commercial granular herbicide Spike. A solution was prepared from the granules by dissolving 500 mg in one liter of water.

Stock solutions were diluted using the following equation:

$$C1V1 = C2V2$$

Each prepared stock solution was serially diluted to prepare concentrations from 0.01 mg/L up to 12 mg/L. Spiking consisted of measuring 1 mL stock solution and applying that to 1.0 g of soil. The soil and herbicide mixtures were vortexed to increase contact between the liquid and solid. To allow adsorptive processes to reach equilibrium, mixtures were 'aged' for eight weeks. Eight weeks was a recommendation from another project within InnoTech's herbicide program.

3.2 Extraction Procedure

The extraction procedure is based on the following formula:

$$Total\ Sterilant - Adsorbed\ Sterilant = Phytoaccessible\ Sterilant$$

where:

Total Herbicide: total concentration of herbicide in soil

Adsorbed Herbicide: the apparent portion of herbicide concentration in solid phase with soil

Phytoaccessible Herbicide: the portion of herbicide concentration extracted with 0.01 M calcium chloride, i.e., that portion is solubilized and not in solid phase with soil.

The total herbicide concentration in soil is either the spiked herbicide concentration or the herbicide concentration estimated by 99 percent methanol extraction at a commercial laboratory (see Section 3.1.1). Adapted from Garrett et al. (2009), the following modified procedure was used to estimate phytoaccessible / soluble herbicide concentration:

1) Use 1 g soil to 40 mL extractant. A sample weight to extractant ratio of 1 g soil per 40 mL extractant was selected. Less volume of extractant per gram of soil tended to create a less efficient extraction, and a larger volume of extractant impairs detection limits. The soil is extracted with a solution which has similar ionic strength as the average salt content in many soil solutions.
2) Decant soil into a 50-mL polypropylene (PP) centrifuge tube, with 40-mL calcium chloride solution. Use brief (less than 10 seconds), vigorous handshaking to break-up and suspend soil in calcium chloride.

3) Shake the soil-calcium chloride solution in the PP tube for 50 minutes on mechanical shaker at 385 oscillations or shakes per minute.
4) Centrifuge samples for 10 min at a Relative Centrifugal Force (RCF) of 3200.
5) Decant supernatant into a new pre-cleaned 50-mL PP tube.
6) Re-centrifuge the supernatant for 20 min at a RCF of 3200.
7) Pipette 5 mL of the supernatant into a new, clean 15-mL PP centrifuge tube
8) Dilute the sample twofold (add 5 mL) with two percent HNO_3 into a 15-mL PP centrifuge tube, mix by vortex, and centrifuge immediately for 20 min at a RCF of 3600.
    a. Acidification of the drawn supernatant is done to prevent elemental adsorption to reaction vessel and to prevent growth of bacteria.
    b. The acidified supernatant can be stored without a change in composition.

Eighty-four bromacil-containing and sixty-five tebuthiuron-containing soil samples were extracted using the above method. Prepared liquid sample extracts were submitted to Element Laboratory for analysis by high pressure liquid chromatography using mass-selective detection (HPLC/MSD) for bromacil and tebuthiuron concentration. Element filters the liquid sample through a syringe filter. The extract was injected into the HPLC/MSD.

3.3 Preparation of Solutions

Preparation of 0.01 M $CaCl_2$ Solution

1. 1.1130 g of anhydrous $CaCl_2$ pellets on Mettler Toledo scale.
2. Grind in mortar and pestle.
3. Place in 1 L of H_2O in an amber bottle.
4. Invert 10 - 20 times to mix.

Preparation of Nitric Acid Solution

29.21 mL 67-70 percent HNO3 into 1,000 mL of H20 to make 2 percent nitric acid solution

$$\text{A) } 2\, percent\ v/v\ HNO3\ = \frac{20\ mL\ of\ 100\ percent\ HNO3}{1000\ mL\ of\ H2O}$$

$$\text{B) } 2\, percent\ v/v\ HNO3\ = \frac{20\ mL\ 100\ percent\ HNO3}{1000\ mL\ H2O} = \frac{x\ mL\ \ 67\ percent\ HNO3}{1000\ mL\ H2O}$$

$$\text{C) } 2\, percent\ v/v\ HNO3\ = \frac{20\ mL\ 100\ percent\ HNO3}{x\ mL\ 67\ percent\ HNO3} = \frac{1000\ mL\ H2O}{1000\ mL\ H2O}$$

$$\text{D) } 2\, percent\ v/v\ HNO3\ = \frac{20\ mL\ 100\ percent\ HNO3}{67\ percent\ HNO3} = (1)(x\ mL)$$

$$\text{E) } 2\, percent\ v/v\ HNO3\ = 29.9\ mL\ of\ 60\ percent\ HNO3\ into\ 1000\ mL\ of\ H2O$$

F) Same process for 70 percent HNO3; which equals 28.6 mL of 70 percent HNO3 into 1000 mL of H2O

Average volume = 29.2 mL into 1000 mL of H_2O to make two percent HNO_3

3.4 Calibration of Wrist Action Shaker Oscillations / Minute

Original method suggested 2 hours (120 minutes) at 160 oscillations per minute. Available equipment had one speed of 385 oscillations per minute. Minutes of shaking was adjusted using the following equation:

$$120\ minutes\ \times \frac{160\ oscillations}{1\ minute} \times \frac{1\ minute}{385\ oscillations} = 49.87013\ minutes$$

3.5 Calculating the Dry Soil Weight and Total Herbicide Concentration (mg/kg)

Dry soil weight was estimated using the following formula:

$$\text{A) } Moisture\ Content = \frac{(Mass\ of\ Wet\ Soil - Mass\ of\ Dry\ Soil)}{Mass\ of\ Dry\ Soil}$$

$$\text{B) } Moisture = \frac{Mass\ of\ Wet\ Soil}{Mass\ of\ Dry\ Soil} - \frac{Mass\ of\ Dry\ Soil}{Mass\ of\ Dry\ Soil}$$

$$\text{C) } Moisture = \frac{Mass\ of\ Wet\ Soil}{Mass\ of\ Dry\ Soil} - 1$$

$$\text{D) } Moisture + 1 = \frac{Mass\ of\ Wet\ Soil}{Mass\ of\ Dry\ Soil}$$

Once the values for the moisture and wet mass are substituted, the dry mass can be estimated. From there, the resulting total herbicide concentration in mg/kg was estimated from the total solution concentration in mg/L using the following formula:

$$Total\ concentration\ in\ mg/kg = \frac{0.24\,mg}{1\,L} = \frac{0.00024\,mg}{1\,mL} = \frac{0.00024\,mg}{1\,g} = \frac{0.24\,mg}{1\,kg}$$

For the final herbicide concentration, the following formula was used:

$$Dry\ Soil\ Concentration\ mg/kg = \frac{\text{Amount of sterilant in mg}}{\text{Dry soil weight in kg}}$$

3.6 Statistical Test Selection

Data were assessed for normality and homogeneity of variances. Analysis was conducted in RStudio. Total and phytoaccessible concentrations in soil were non-normally distributed with homogeneous variances. A Wilcoxon Ranked Sum Test was used to statistically test if median total herbicide concentration in mg/kg was significantly different from median phytoaccessible herbicide concentration in mg/kg.

3.7 Duplicates, Solution Blanks and Soil Blanks

Duplicates were included for reproducibility of the extraction method results. For bromacil, 10 duplicate pairs were systematically prepared at a rate of one for approximately every eight samples. For tebuthiuron, 11 duplicate pairs were systematically prepared at a rate of one for approximately every six samples. Relative Percent Difference (RPD) was estimated for each duplicate pair. It is the absolute value of difference between two results divided by the mean of the two results:

$$Relative\ Percent\ Difference = \frac{|X_2 - X_1|}{((X_2 + X_1)/2)}\ x\ 100\ percent$$

For environmental consultants, RPDs less than 50 percent are not considered to affect the interpretation of the results and are representative of the soil conditions at the site. A one-tailed t-test was run on the estimated RPDs to assess whether these were significantly greater than 50 percent.

Solution (no soil) and soil blanks (no herbicide) were included for assessment of cross contamination or other errors during extraction. A sandy soil with low adsorptive capacity was chosen to limit masking of cross-contamination. Due to budgetary constraints, limited blanks were prepared. For bromacil, three solution blanks (1BLANK, 2BLANK, 3BLANK) and three soil blanks (1SOIL, 2SOIL, 3SOIL) were included at a rate of one in approximately thirty samples. For tebuthiuron, three solution blanks (4BLANK, 5BLANK, 6BLANK) and three soil blanks (4SOIL, 5SOIL, 6SOIL) were included at a rate of one in approximately twenty samples. A rate of one solution and soil blank for every ten samples would have been ideal.

4. Results

4.1 Solution and Soil Blanks

Solution blanks were included in the same glass vials containing only the stock solution without soil. These were prepared at the same time soil samples were spiked and all were aged for eight weeks. After eight weeks, the solution blanks without soil underwent the same extraction procedure to assess:

1) That the same herbicide concentration remained after eight weeks of aging.
2) If there were any losses of herbicide concentration because of non-soil processes

4.1.1 Bromacil

Solution blanks (no soil) for bromacil showed that the same total herbicide concentration was more-or-less returned by the extraction procedure.

Table 2. Solution Blanks Analyzed for Total Bromacil Concentration after Aging

Solution Blank	Total Bromacil Concentration (mg/kg)	Extracted Bromacil Concentration (mg/kg)
1BLANK	0.24	0.24
2BLANK	0.24	0.21
3BLANK	0.24	0.22

The soil blanks were not spiked with bromacil. Cross-contamination was not observed in soil blanks as bromacil was not detected.

Table 3. Soil Blanks Analyzed for Possible Cross-Contamination During Extraction

Soil Blank	Total Bromacil Concentration (mg/kg)	Extracted Bromacil Concentration (mg/kg)	Organic Matter (%)	Sand (%)
1SOIL	0	0	0.63	88
2SOIL	0	0	0.63	88
3SOIL	0	0	0.63	88

4.1.2 Tebuthiuron

Solution blanks for tebuthiuron showed that approximately half total herbicide concentration was estimated by the extraction procedure after aging. Other projects in InnoTech's Soil Herbicide Program have noted issues with spiking soil samples with tebuthiuron and obtaining the same herbicide concentration of spiked soil samples even with 99 percent methanol extraction. These issues were identified after the conclusion of the lab portion of this study. Therefore, total herbicide concentration was adjusted to account for possible losses of tebuthiuron to factors other than adsorption to soil.

Table 4. Solution Blanks Analyzed for Total Tebuthiuron Concentration after Aging

Solution Blank	Total Tebuthiuron Concentration (mg/kg)	Extracted Tebuthiuron Concentration (mg/kg)
4BLANK	0.50	0.27
5BLANK	0.50	0.26
6BLANK	0.50	0.24

A correction factor was estimated by dividing the total tebuthiuron concentration by the phytoaccessible concentration and taking an average of the three values.

$$Tebuthiuron\ Correction\ Factor = \frac{(0.50 \div 0.27) + (0.50 \div 0.26) + (0.50 \div 0.24)}{3} = 1.95$$

Each total tebuthiuron concentration applied as a spike was divided by 1.95 to account for factors other than soil adsorption which may contribute to losses of herbicide during the extraction procedure. Tebuthiuron concentration in soil determined by a commercial laboratory was not corrected, as these longer aged samples were considered to have reached an adsorptive equilibrium in the all-soil environment from which these were sampled.

The soil blanks were not spiked with tebuthiuron. Cross-contamination was not observed in soil blanks as tebuthiuron was not detected.

Table 5. Soil Blanks Analyzed for Possible Cross-Contamination During Extraction

Soil Blank	Total Tebuthiuron Concentration (mg/kg)	Extracted Tebuthiuron Concentration (mg/kg)	Organic Matter (%)	Sand (%)
4SOIL	0	0	0.63	88
5SOIL	0	0	0.63	88
6SOIL	0	0	0.63	88

4.3 Duplicates

See Section 3.7 for an explanation on how duplicates were chosen.

Bromacil duplicate pair RPD values ranged from 13 percent to 47 percent with a median of 31 percent. A one-tailed t-test conducted on the bromacil duplicates indicates that the mean is not significantly greater than 50 percent (t = -3.4899, p = 0.999).

Table 6. Duplicate Samples Analyzed for Reproducibility of $CaCl_2$ Extraction of Bromacil

Sample	DUP1	DUP2	MDL	RPD
TH19-112B	0.16	0.14	0.008	13%
TH19-128	0.16	0.14	0.008	13%
B10	1.2	1.03	0.008	15%
BH42	0.19	0.16	0.008	17%
PH011	0.2	0.15	0.008	29%
0.5 MG/KG	0.252	0.18	0.008	33%
B08	0.38	0.27	0.008	34%
BH30	0.11	0.17	0.008	43%
B11	3.54	2.28	0.008	43%
TH19-137B	0.21	0.13	0.008	47%

Tebuthiuron duplicate pair RPD values ranged from 16 percent to 32 percent with a mean of 24 percent. A one-tailed t-test conducted on the tebuthiuron duplicates indicates that the mean is not significantly greater than 50 percent (t = -7.1866, p = 1).

Table 7. Duplicate Samples Analyzed for Reproducibility of $CaCl_2$ Extraction of Tebuthiuron

Sample	DUP1	DUP2	MDL	RPD
T03	6.537	5.02	0.005	26%
T10	1.86	1.588	0.005	16%
T11	2.308	1.82	0.005	24%
TH19-122B	1.92	1.39	0.005	32%
TH19-123	1.74	1.42	0.005	20%
TH19-127	2.65	2.09	0.005	24%
TH19-131	3.34	2.57	0.005	26%
TH19-137B	3.97	3.11	0.005	24%
TH19-144A	1.49	1.21	0.005	21%
TH19-144B	5.48	4.13	0.005	28%
TH19-163A	5.7	4.43	0.005	25%

4.2 Total versus Phytoaccessible Herbicide Concentration

4.2.1 Bromacil

Eighty-four soil samples were assessed for the apparent adsorbed concentration of bromacil in soil after an aging period of eight weeks up to one year. Median phytoaccessible bromacil concentration of 0.190 mg/kg was significantly less than median total bromacil concentration of 0.300 mg/kg ($W = 5131$, $p < 0.001$). Visual representation of this difference is presented in Figure 1.

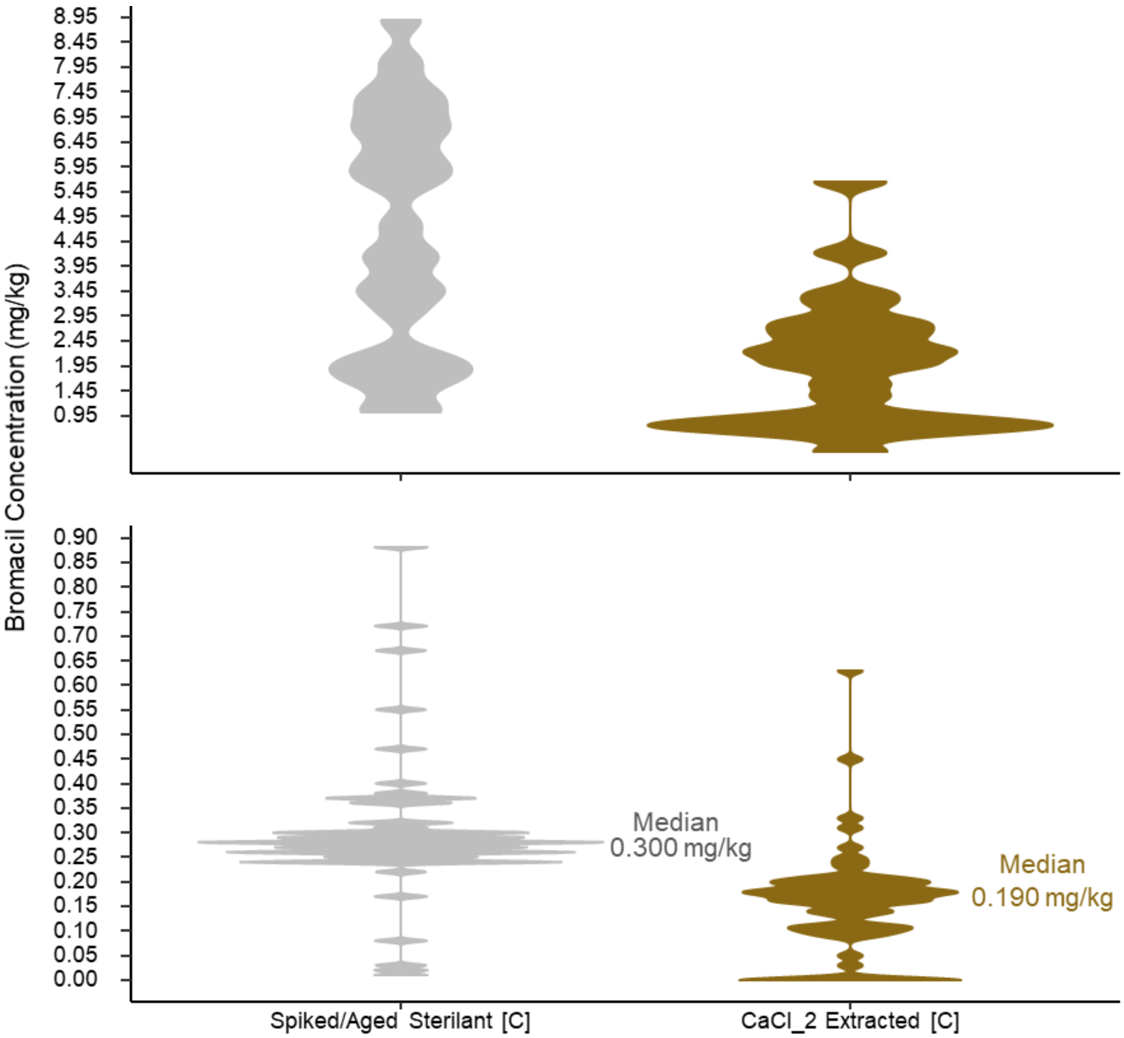


Figure 1. Median bromacil concentration in soil shown are for the entire dataset of 84 samples. Median concentration of estimated phytoaccessible bromacil by calcium chloride extraction is significantly less than median concentration of total bromacil (W = 5131, $p < 0.001$).

4.2.2 Tebuthiuron

Sixty-five soil samples were assessed for apparent adsorbed concentration of tebuthiuron in soil after an aging period of eight weeks up to decades. Median phytoaccessible tebuthiuron concentration was significantly less than the median total concentration, indicating adsorption does contribute to a reduction in phytoaccessibility of tebuthiuron (W = 2694, p = 0.003). Visual representation of this difference is presented in Figure 2.

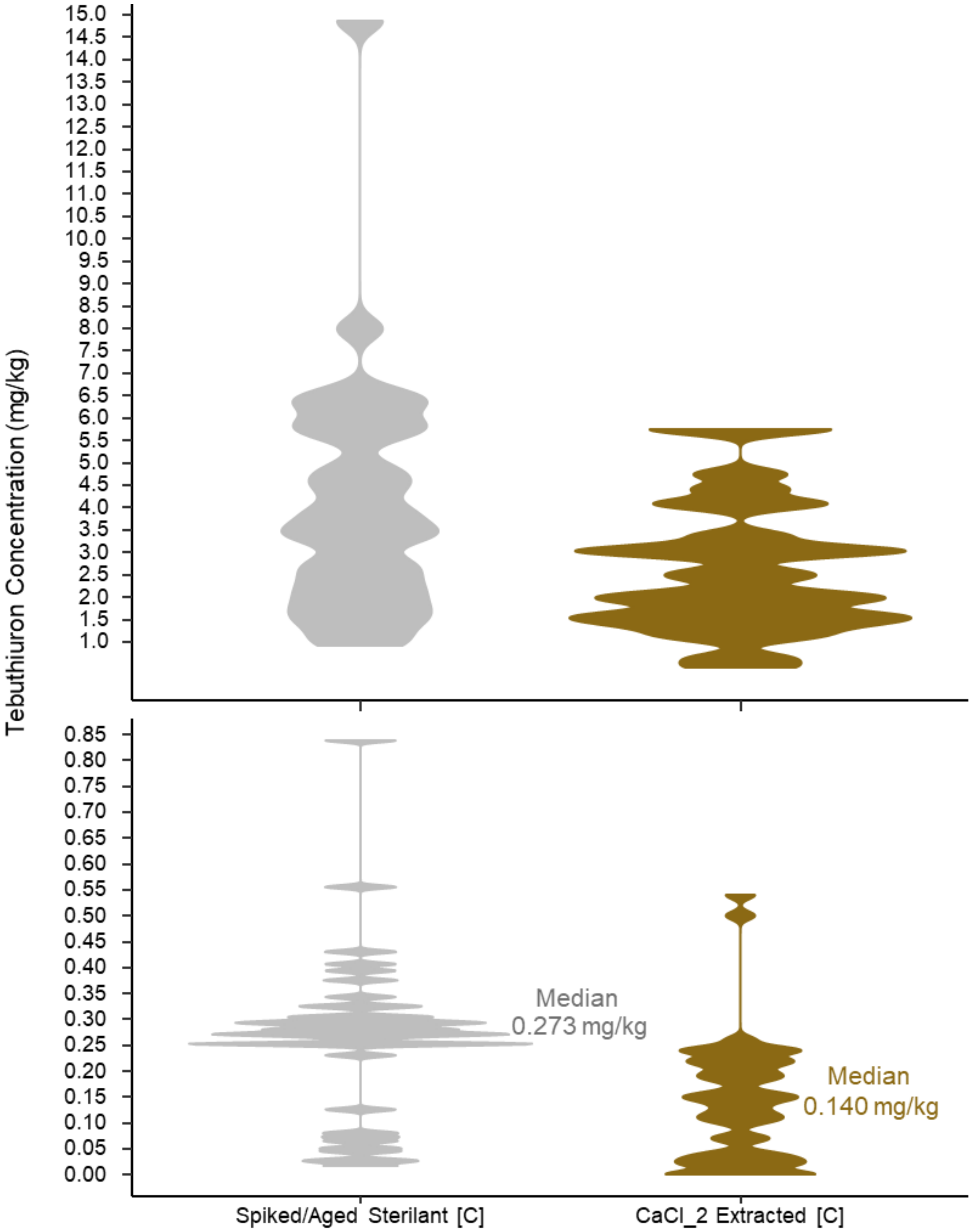


Figure 2. Median tebuthiuron concentration in soil for all 66 samples. Median concentration of the estimated phytoaccessible tebuthiuron by calcium chloride extraction is significantly less than median concentration of total tebuthiuron (W = 2694, p = 0.003).

5. Discussion

Adsorption possibly lowers phytoaccessibility of bromacil and tebuthiuron (Drozdowski et al., 2018). Whether a significant concentration ends up adsorbed by soil resulting in a true difference between the total and phytoaccessible concentration is not reported and site-specific studies are required to determine risk from herbicides (Bresee, 2019). Using 0.01 M calcium chloride to estimate phytoaccessibility of a contaminant is a well-studied and accepted method in other jurisdictions outside Alberta (USEPA, 2000). Combining these studies (USEPA, 2000) with a procedure developed for water extraction of metals from soil (Garrett et al., 2009) was chosen to assess that the soluble, or phytoaccessible, concentration is actually less than the total herbicide concentration in soil.

Calcium chloride extraction is an easy and inexpensive way to extract non-or-weakly-adsorbed substances in soil (USEPA, 2000). It makes it possible to use immobilization technology such as activated carbon to control phytoaccessibility of bromacil and tebuthiuron in risk management, or even remediation (Morillo et al., 2017). As soil contamination from bromacil or tebuthiuron is often diffuse over a large area and marginally exceeds guidelines, immobilization preserves the characteristics of otherwise healthy soils (Khorram et al., 2016).

Results from this experiment show calcium chloride recovers approximately 50 percent of bromacil or tebuthiuron. Phytoaccessible or soluble bromacil concentration (median 0.190 mg/kg bromacil) was close to phytoaccessible tebuthiuron concentration (0.140 mg/kg tebuthiuron). Although tebuthiuron is more soluble (2,500 mg/L in water) it has a higher adsorption coefficient Koc of 80 mg/L (Drozdowski et al., 2018). Bromacil is less soluble (815 mg/L in water) and has a lower adsorption coefficient Koc of 32 mg/L (Drozdowski et al., 2018). Competing characteristics seem to make bromacil and tebuthiuron have similar phytoaccessibility.

Adsorptive capacity in soil depends mostly on clay and organic matter content (Centofanti et al., 2016; Parolo, 2017; Singh et al., 2014; Texeira et al., 2018). Soils available for the study varied in their characteristics: 1) organic matter content ranged from 0 percent to 66 percent with an average of 6 percent, 2) clay content varied from 0 percent to 64.6 percent with an average of 18 percent. Surveyed areas in Alberta show that the Grey soil zone covers approximately 45 percent of the land mass. The Black soil zone covers approximately 20 percent. Dark Brown and Brown soil zones cover approximately 25 percent. The remainder is the Dark Grey soil zone. Available samples were primarily from the Grey, Black, Dark Brown and Brown soil zones.

Chapter III: Effect of Organic Matter and Clay Content on Adsorption

1. Introduction

Soil organic matter is the principal sorbent for tebuthiuron particularly when clay content is low (Koskinen et al., 1996). Bromacil adsorption increases as soil organic matter increases (Landsburg and Dwyer, 1995). Clay content is sometimes observed to increase adsorptive capacity in soils, yet significant interaction between soil organic matter and clay content has not been found in the reviewed literature. Even if clay alone is insignificant in adsorption (Grover, 1975), there may a significant interactive effect between organic matter and clay that increases adsorption.

2. Research Objectives

Objective of this research is examining effect of soil organic matter content, clay content and their possible interactive effect on increasing adsorption of bromacil or tebuthiuron.

3. Materials and Methods

3.1 Parameter and Statistical Test Selection

Exploratory data analysis in R for regression was checked for potential relationships between clay and organic matter, and the estimated adsorbed herbicide fractions. Available ranges of organic matter and clay percentages compared to estimated adsorbed herbicide fractions did not meet assumptions for regression analysis. Transformation of data using common techniques (log, square root, inverse or reciprocal, inverse square root, power, or arcsine) did not change data non-normality or heterogeneity of variances. Confidence in any conclusions from regression analysis would be low and would have to be interpreted with caution.

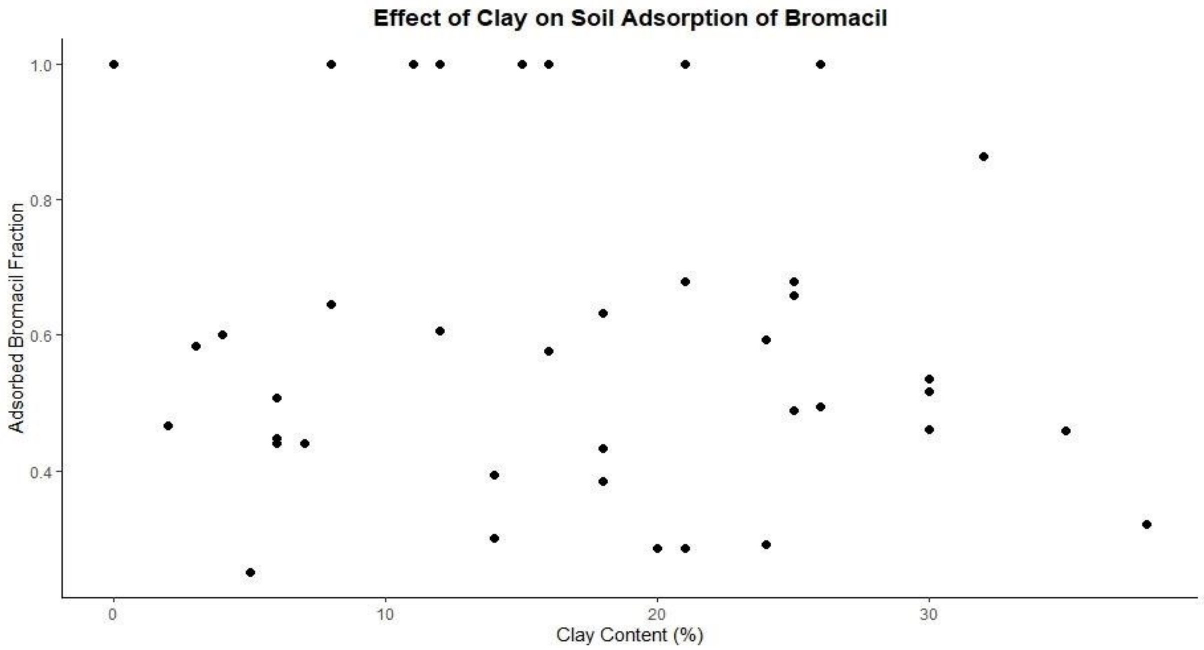


Figure 1. Exploratory data visualization of percent clay content in soil against the estimated adsorbed bromacil fraction. A visual relationship between these two is not apparent.

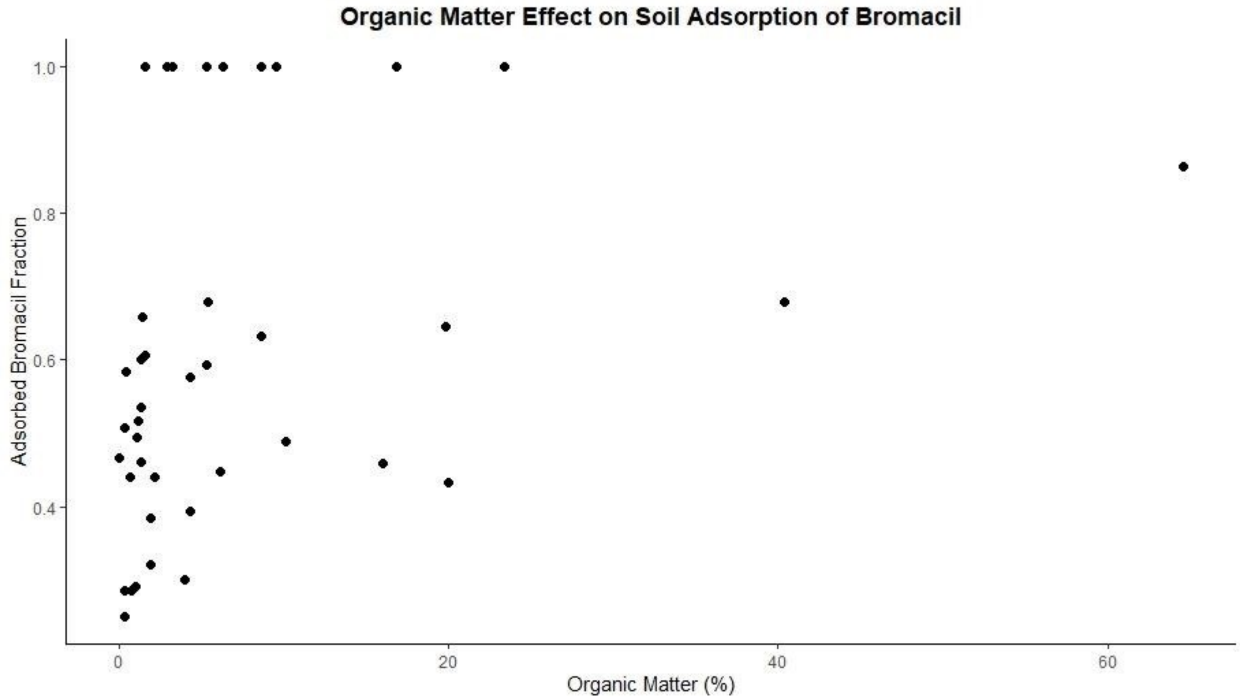


Figure 2. Exploratory data visualization of percent organic matter content in soil against the estimated adsorbed bromacil fraction. An increase in organic matter generally corresponds to an increase in the adsorbed bromacil fraction.

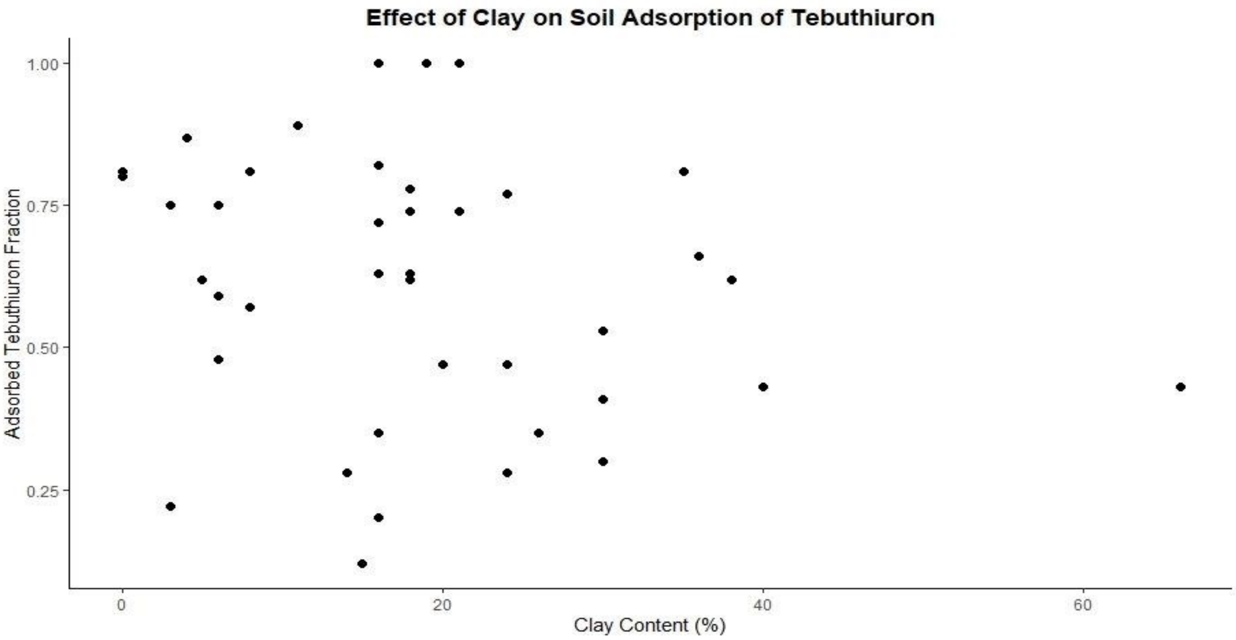


Figure 3. Exploratory data visualization of percent clay content in soil against the estimated adsorbed tebuthiuron fraction. A visual relationship between these two is not apparent.

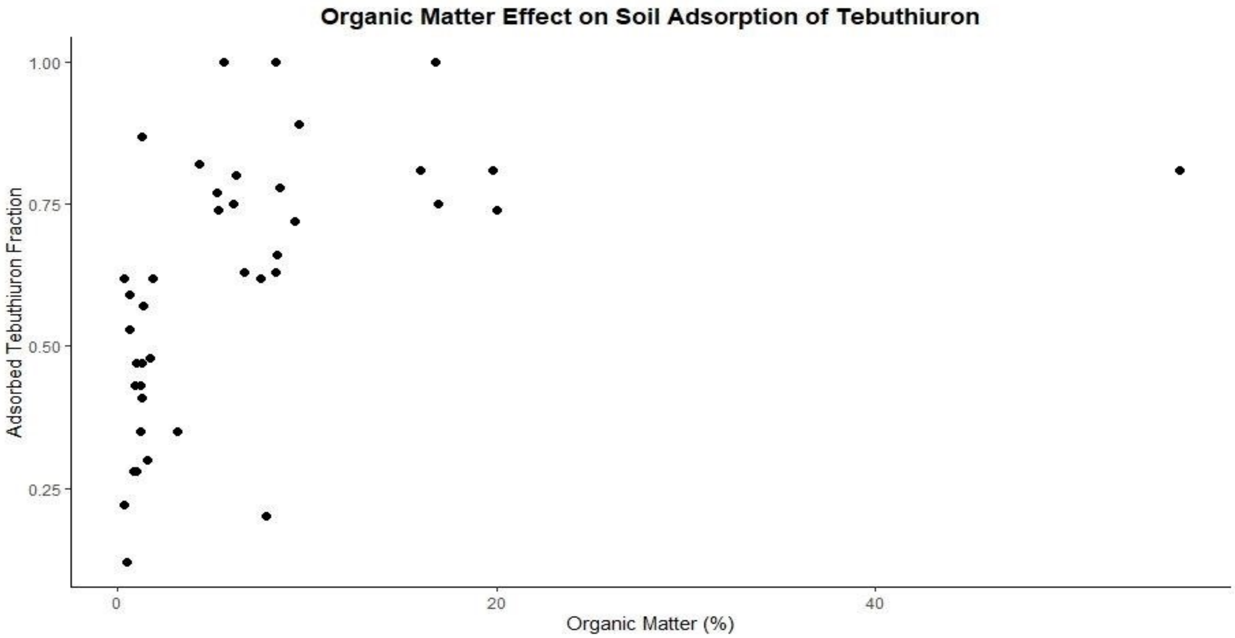


Figure 4. Exploratory data visualization of percent organic matter content in soil against the estimated adsorbed tebuthiuron fraction. An increase in organic matter generally corresponds to an increase in the adsorbed tebuthiuron fraction.

Use of categorical predictors, rather than the continuous data, for high or low clay or organic matter were selected to define four groups of equal size (n = 10). These produced a model which met assumptions of parametric data for use of two-by-two Analysis of Variance (ANOVA).

Several ANOVA models were run in R to determine contribution of soil organic matter, soil organic carbon, moisture, and clay, to adsorption of bromacil or tebuthiuron. Available literature indicated these soil characteristics contribute most to adsorption. In the tested ANOVA model in R, neither moisture nor clay alone contributed significantly to adsorption in available soil samples. Organic carbon and organic matter contributed the same weight in the model, with organic matter being slightly more significant. Organic matter was chosen as it is assumed to be more inclusive of possible adsorptive capacity.

A two-by-two ANOVA was selected to test if 1) if organic matter significantly increases adsorption, 2) if clay significantly increases adsorption, and 3) if there is an interactive effect between organic matter and clay in increasing adsorption of either herbicide. Each cell in the design included n = 10 to 1) increase confidence in the statistical results, 2) 10 samples were the maximum with appropriate criteria in certain cells and 3) sample size *n* had to match in each cell. Sample data were organized in R for specific percentages of soil organic matter and clay content to obtain these 10 replicates. The categories in Table 1 were identified for bromacil or tebuthiuron samples.

Table 1. Selected Categories for Organic Matter and Clay Content

Bromacil	High Clay Content (18 - 38%)	Low Clay Content (0 - 16%)
High Organic Matter (3.24 - 64.6%)	10	10
Low Organic Matter (0.00 - 2.92%)	10	10

Tebuthiuron	High Clay Content (18 - 66%)	Low Clay Content (0 - 16%)
High Organic Matter (5.29 - 56%)	10	10
Low Organic Matter (0.28 - 4.34%)	10	10

3.2 Estimation of Adsorbed Fraction

The apparent adsorbed fraction was estimated using this formula:

$$Adsorbed\ Fraction = \frac{Spiked/Aged - Extract}{Spiked/Aaged}$$

where:

Total = total herbicide concentration (mg/kg)

Extract = herbicide extracted by 0.01 M calcium chloride (mg/kg)

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

3.3 Selected Soil Samples

Soil samples came from the same sources as identified in Chapter II – Section 3.1. Six soil samples were added: one from Saddle Lake Cree Nation in Central Alberta (TH21-05B), one from the U of A Woodbend research area south of Leduc (WB), and four from an undisclosed site included for increasing range of clay and organic matter content (ADV series).

3.3.1 Bromacil Soil Samples

Bromacil soil samples were inclusive of locations from which soil samples were collected. Four categories of clay and organic matter content were identified, labeled as high or low. To the extent possible given limited sampling opportunities during COVID, samples from around Alberta were represented in each category. Tables 2 through 5 show samples, locations, organic matter and clay content, adsorbed fraction, and texture of included samples.

Table 2. Category 1: High Organic Matter (3.24-64.6%) and High Clay Content (18-38%)

Sample	Location	High Organic Matter Content	High Clay Content	Bromacil Adsorbed Fraction	Texture
BH10	Mildred Lake	10.1	25	0.49	Loam
BH32	Mildred Lake	40.4	25	0.68	Sandy Clay Loam
BH35	Mildred Lake	64.6	32	0.86	Clay Loam
BH60A	Mildred Lake	16	35	0.46	Clay Loam
BH60B	Mildred Lake	5.29	24	0.59	Loam
F21-01	Huxley	23.4	26	1.00	Loam
F21-05	Huxley	20	18	0.43	Loam
F21-06	Huxley	5.35	21	0.68	Sandy Clay Loam
PH006	Mildred Lake	16.8	21	1.00	Silt Loam
PH011	Mildred Lake	8.59	18	0.63	Sandy Loam

Table 3. Category 2: High Organic Matter (3.24-64.6%) and Low Clay Content (0-16%)

Sample	Location	High Organic Matter Content	Low Clay Content	Bromacil Adsorbed Fraction	Texture
B02	Brooks	3.24	15	1.00	Loam
BH20-2	Westlock	4.01	14	0.30	Loam
BH30	Mildred Lake	4.34	16	0.58	Loam
BH41	Mildred Lake	6.14	6	0.45	Loamy Sand
F21-02	Huxley	8.64	15	1.00	Sandy Loam
F21-03	Huxley	5.33	8	1.00	Sandy Loam
F21-08	Huxley	19.8	8	0.65	Sandy Loam
F21-10	Huxley	4.35	14	0.39	Silt Loam
TH19-137A	Fort McMurray	9.56	11	1.00	Sandy Loam
TH19-144A	Fort McMurray	6.27	0	1.00	Sandy Loam

Table 4. Category 3: Low Organic Matter (0-2.92%) and High Clay Content (18-38%)

Sample	Location	Low Organic Matter Content	High Clay Content	Bromacil Adsorbed Fraction	Texture
ADV16CI#1	Undisclosed	0.74	20	0.29	Sandy Clay Loam
ADV16CI#2	Undisclosed	0.37	21	0.29	Sandy Clay Loam
BH25	Mildred Lake	1.1	26	0.49	Sandy Clay Loam
F21-07	Huxley	1.9	18	0.38	Sandy Loam
TH19-103	Fort McMurray	1.4	25	0.66	Loam
TH19-110	Fort McMurray	1.2	30	0.52	Sandy Clay Loam
TH19-112B	Fort McMurray	1.3	30	0.46	Sandy Clay Loam
TH19-137B	Fort McMurray	1.3	30	0.54	Sandy Clay Loam
TH19-144B	Fort McMurray	0.99	24	0.29	Sandy Clay Loam
TH21-05B	Saddle Lake	1.9	38	0.32	Clay Loam

Table 5. Category 4: Low Organic Matter (0-2.92%) and Low Clay Content (0-16%)

Sample	Location	Low Organic Matter Content	Low Clay Content	Bromacil Adsorbed Fraction	Texture
ADV22CC#1	Undisclosed	0	2	0.47	Sand
ADV25FC#1	Undisclosed	0.35	6	0.51	Sand
B03	Brooks	2.92	16	1.00	Loam
F21-04	Huxley	1.6	12	1.00	Sandy Loam
F21-09	Huxley	1.3	4	0.60	Loamy Sand
TH19-105	Fort McMurray	1.6	12	0.61	Sandy Loam
TH19-112A	Fort McMurray	2.17	7	0.44	Sandy Loam
TH19-128	Fort McMurray	0.63	6	0.44	Sand
TH19-131	Fort McMurray	0.39	3	0.58	Sand
WB	Woodbend	0.34	5	0.25	Sand

3.3.2 Tebuthiuron Soil Samples

Tebuthiuron soil samples were inclusive of locations from which soil samples were collected. Four categories of clay and organic matter content were identified, labeled as high or low. To the extent possible given limited sampling opportunities during COVID, samples from around Alberta were represented in each category. Tables 5 through 9 show samples, locations, organic matter and clay content, adsorbed fraction, and texture of included samples.

Table 6. Category 1: High Organic Matter (5.29-56%) and High Clay Content (18-66%)

Sample	Location	High Organic Matter Content	High Clay Content	Tebuthiuron Adsorbed Fraction	Texture
21-05F	Huxley	20	18	0.74	Loam
21-06F	Huxley	5.35	21	0.74	Sandy Clay Loam
BH60A	Mildred Lake	16	35	0.81	Clay Loam
BH60B	Mildred Lake	5.29	24	0.77	Loam
PH006	Mildred Lake	16.8	21	1.00	Silt Loam
PH011	Mildred Lake	8.59	18	0.78	Sandy Loam
SS19-6	Westlock	7.58	18	0.62	Silt Loam
SS20-9	Westlock	8.37	19	1.00	Loam
TH19-149	Fort McMurray	8.44	36	0.66	Silty Clay Loam
TH19-181	Fort McMurray	8.39	18	0.63	Loam

Table 7. Category 2: High Organic Matter (5.29-56%) and Low Clay Content (0-16%)

Sample	Location	High Organic Matter Content	Low Clay Content	Tebuthiuron Adsorbed Fraction	Texture
21-08F	Huxley	19.8	8	0.81	Sandy Loam
BH22	Mildred Lake	9.33	16	0.72	Sandy Loam
BH42	Mildred Lake	6.14	6	0.75	Loamy Sand
SS20-4	Westlock	5.62	16	1.00	Loam
SS20-7	Westlock	7.88	16	0.20	Loam
SS20-8	Westlock	6.67	16	0.63	Loam
TH19-137A	Fort McMurray	9.56	11	0.89	Sandy Loam
TH19-142	Fort McMurray	16.9	3	0.75	Sandy Loam
TH19-144A	Fort McMurray	6.27	0	0.80	Sandy Loam
TH19-179	Fort McMurray	56	0	0.81	Peat

Table 8. Category 3: Low Organic Matter (0.28-4.34%) and High Clay Content (18-66%)

Sample	Location	Low Organic Matter Content	High Clay Content	Tebuthiuron Adsorbed Fraction	Texture
ADV25FI#1	Undisclosed	0.99	24	0.47	Silt Loam
ADV25FI#2	Undisclosed	0.68	30	0.53	Clay Loam
TH19-123	Fort McMurray	0.91	40	0.43	Sandy Clay
TH19-127	Fort McMurray	1.2	66	0.43	Heavy Clay
TH19-136	Fort McMurray	1.2	26	0.35	Sandy Clay Loam
TH19-137B	Fort McMurray	1.3	30	0.41	Sandy Clay Loam
TH19-141	Fort McMurray	1.3	20	0.47	Loam
TH19-144B	Fort McMurray	0.99	24	0.28	Sandy Clay Loam
TH19-147	Fort McMurray	1.6	30	0.30	Sandy Clay Loam
TH21-05B	Saddle Lake	1.9	38	0.62	Clay Loam

Table 9. Category 4: Low Organic Matter (0.28-4.34%) and Low Clay Content (0-16%)

Sample	Location	Low Organic Matter Content	Low Clay Content	Tebuthiuron Adsorbed Fraction	Texture
21-09F	Huxley	1.3	4	0.87	Loamy Sand
BH30	Mildred Lake	4.34	16	0.82	Loam
T07	Brooks	3.16	16	0.35	Loam
TH19-120	Fort McMurray	0.87	14	0.28	Loam
TH19-122B	Fort McMurray	0.48	15	0.12	Sandy Loam
TH19-124	Fort McMurray	1.7	6	0.48	Loamy Sand
TH19-128	Fort McMurray	0.63	6	0.59	Sand
TH19-131	Fort McMurray	0.39	3	0.22	Sand
TH19-207	Fort McMurray	1.4	8	0.57	Sandy Loam
WB	Woodbend	0.34	5	0.62	Sand

4. Results

For bromacil the mean adsorbed fraction was significantly higher for high organic matter compared to low organic matter (bromacil: $F = 8.09$, $p < 0.01$). Clay did not significantly increase adsorption (bromacil: $F = 2.36$, $p = 0.133$). A significant interaction of organic matter and clay increasing adsorption was not observed (bromacil: $F = 0.62$, $p = 0.437$). Figures 1 plots mean adsorbed bromacil fraction for each category: 1) high organic matter (3.24-64.6 percent) and high clay (18-38 percent), 2) high organic matter (3.24-64.6 percent) and low clay (0-16 percent), 3) low organic matter (0-2.92 percent) and high clay (18-38 percent), and 4) low organic matter (02.92 percent) and low clay (0-16 percent).

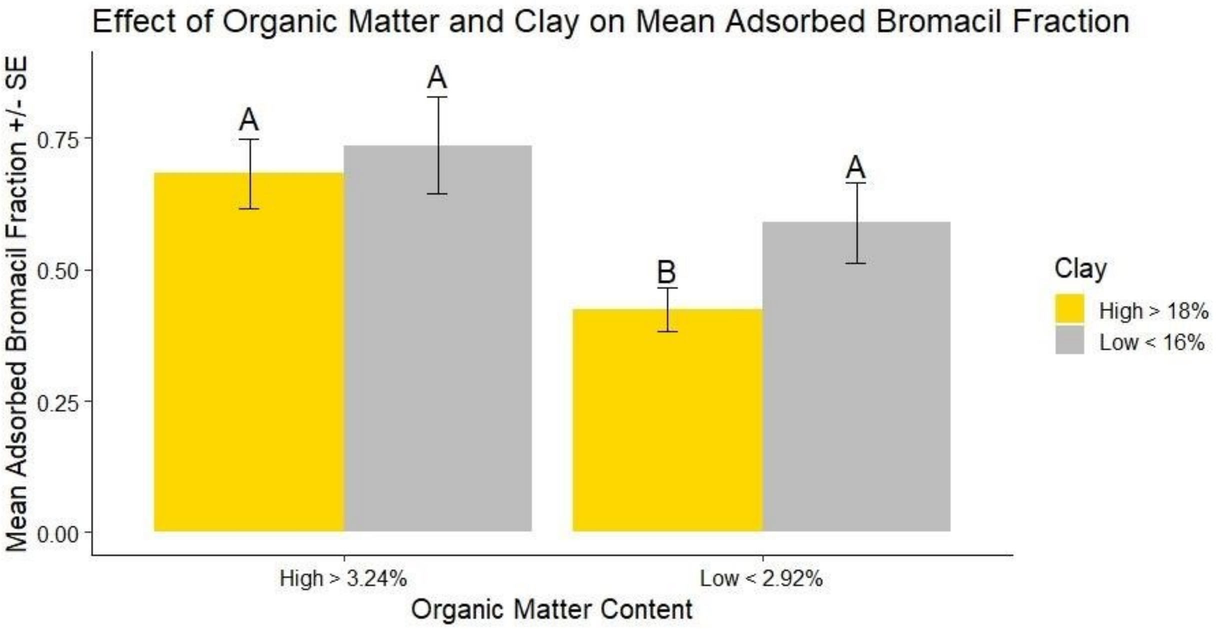


Figure 5. Organic matter significantly increases adsorption of bromacil (F = 8.09, $p < 0.01$). Clay does not significantly increase adsorption of bromacil (F = 2.36, p = 0.133). There is not a significant interaction between organic matter and clay to increase adsorption of bromacil (F = 0.62, p = 0.437). Error bars represent the standard error of the mean.

For tebuthiuron mean adsorbed fraction was significantly higher for high organic matter compared to low organic matter (tebuthiuron: F = 25.89, $p < 0.001$). Clay did not significantly increase adsorption (tebuthiuron: F = 0.03, p = 0.858). A significant interaction of organic matter and clay increasing adsorption was not observed (tebuthiuron: F = 0.75, p = 0.391). Figure 2 plots mean adsorbed fraction of tebuthiuron for each category: 1) high organic matter (5.29-56 percent) and high clay (18-66 percent), 2) high organic matter (5.29-56 percent) and low clay (0-16 percent), 3) low organic matter (0.28-4.34 percent) and high clay (18-66 percent), and 4) low organic matter (0.28-4.34 percent) and low clay (0-16 percent).

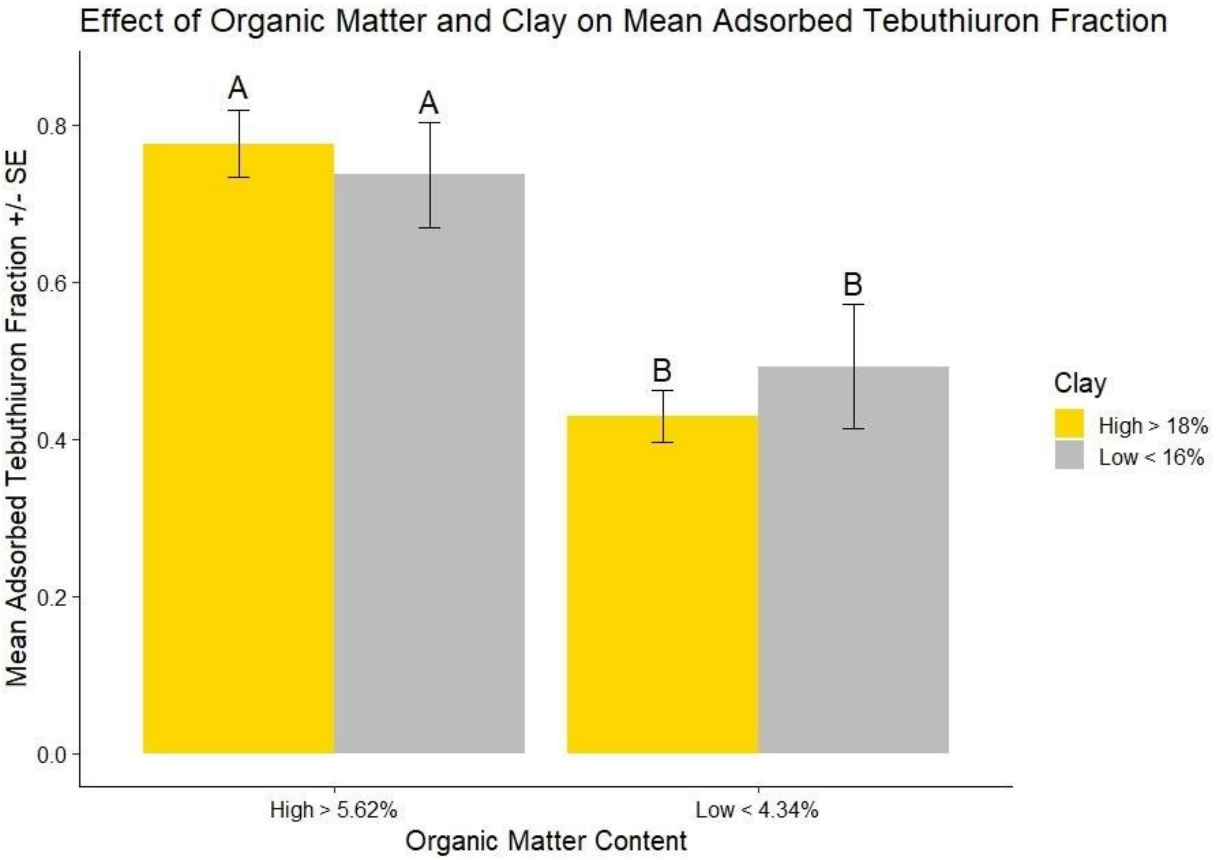


Figure 6. Organic matter significantly increases adsorption of tebuthiuron (F = 25.65, p < 0.001). Clay does not significantly increase adsorption of tebuthiuron (F = 0.03, p = 0.858). There is not a significant interaction between organic matter and clay to increase adsorption of tebuthiuron (F = 0.75, p = 0.391). Error bars represent the standard error of the mean.

5. Discussion

Clay in this experiment did not have a significant effect on adsorption, yet an interesting depression was observed when clay contents were high in the selected soil samples. It is possible that clay particles occupy adsorptive sites on organic matter in organo-mineral interactions. Farenhorst et al., 2010 observed organic-C not-complexed with clay minerals had a higher adsorptive capacity for atrazine than organic-C complexed with clay minerals (organo-mineral complexes). In another paper, organo-mineral interactions in Oxisols of Brazil were thought to block adsorptive surfaces on soil organic carbon which resulted in lower adsorption of studied pesticides including bromacil (Bonfleur et al., 2016).

A depressive effect of increased clay content on herbicide adsorption was not expected. Clay was assumed to have adsorptive sites of its own and provide increased adsorptive capacity. Bromacil, to an insignificant extent, had a lower adsorbed fraction for high clay content in both high and low organic matter categories. Adsorbed tebuthiuron fraction also showed the (not significant) depressive effect of high clay when organic matter was low. But tebuthiuron showed slight increase in its adsorbed fraction with high clay and organic matter over low clay and high organic matter. Perhaps the organic matter percent (5.62) was high enough to accommodate both organo-mineral complexation and adsorption of tebuthiuron. A study with an expanded set of samples with greater range of clay contents may show organo-mineral complexes mask adsorption sites up to a certain threshold of organic matter content.

In the case of bromacil and tebuthiuron contaminated soils reducing phytoaccessibility can minimize human and ecological risks (Centofanti et al., 2016). High organic matter increased adsorbed fraction of bromacil and tebuthiuron in this study. Amendment of herbicide-impacted soils with immobilizing agents would increase adsorption and lower risk (Dean, 2007; Interstate Technology & Regulatory Council, 2017). There are several readily available and inexpensive immobilizing agents that are variations on activated carbon (Drozdowski et al., 2018; Khorram et al., 2016; Morillo et al., 2017). Using immobilization to remediate requires regulators recognize that total herbicide concentration is not necessarily phytoaccessible herbicide concentration. These can be evaluated by separate methods to inform a Conceptual Site Model, risk management and/or remediation.

Chapter IV: Synthesis

1. Research Summary

Phytoaccessible concentration of bromacil and tebuthiuron is less than total herbicide concentration due to adsorption on organic matter. Where there are large areas of marginal bromacil or tebuthiuron contamination, economical approaches are needed to reduce risk, meet regulatory requirements, and protect soil health (Centofanti et al., 2016). Aged applications of bromacil and tebuthiuron spread from target areas through wind and water erosion, as these herbicides are adsorbed to eroding soil. Small tebuthiuron soil concentrations (from 0.017 mg/kg to 0.282 mg/kg) of tebuthiuron have been observed over hectares in an agricultural field, which I will call Field W, in north-central Alberta. Removal of soil which, marginally, does not meet the provincial guideline of 0.046 mg/kg would affect the productivity of the agricultural land more than the risk posed by the total tebuthiuron concentration.

Soil samples collected from the above-mentioned Field W had the following total and phytoaccessible tebuthiuron concentrations (mg/kg):

Table 1. Field W Total and Phytoaccessible Tebuthiuron Concentration

Sample	Total (MeOH Extract) Tebuthiuron (mg/kg)	Phytoaccessible (CaCl2 Extract) Tebuthiuron (mg/kg)
SS19-6	0.052	0.020
SS20-2	0.065	0.030
SS20-4	0.282	<0.008
SS20-7	0.025	0.020
SS20-8	0.081	0.030
SS20-9	0.017	<0.008

Several total soil concentrations do not meet the Tier 1 criterion of 0.046 mg/kg for agricultural land use. Further assessment with more site-specific criteria might find that the phytoaccessible tebuthiuron concentration can be compared to Tier 2 guidelines. Immobilization technologies, such as activated carbon, could be applied to the field to further reduce phytoaccessibility. Calcium chloride extracted tebuthiuron concentration could be measured as part of a risk management plan (RAP) to monitor how phytoaccessibility changes over time (decreases, is stable, or increases). Monitoring could cease after so many years of the RAP if phytoaccessible tebuthiuron concentration remains stable or decreases. Eventually, if regulatory authorities consider phytoaccessibility legitimate in environment assessment, regulatory closure could be achieved without affect to soil fertility, structure, or organic matter content or a farmer's bottom line.

2. Research Limitations

Calcium chloride-extractable concentrations were not correlated to any plant measurements or bioassay. Correlating this study with a bioassay would make the results more reliable. It is unclear whether a bioassay or calcium chloride-extractable would be preferable for estimating phytoaccessibility.

Soil samples included in the study were obtained from a variety of sources and not screened for clay and organic matter content. Lack of a significant contribution of clay on adsorption is possibly due to the minimal difference between the high (18 percent and higher) and low (16 percent and lower) clay categories for both herbicides. Testing soil samples with a greater difference of clay content may show clay does have a significant influence on sorption.

Phytoaccessibility is meant to be considered as part of a robust Conceptual Site Model (CSM). It should not be compared against Alberta Tier 1 criteria to maintain appropriate protection for human and ecological health. Total herbicide concentration should be compared to Tier 1 criteria. If there is an exceedance, the fate and transport of the total herbicide concentration should further be studied in a CSM and under purview of Tier 2 criteria to remain protective of public health and the environment.

Spiked soil samples were not comparatively extracted with methanol to compare with calcium chloride extraction. The total herbicide concentration present in the stock solution was considered potentially extractable. Issues with spiking of tebuthiuron to achieve a target concentration, and subsequent extraction by methanol or calcium chloride were identified within the Soil Herbicide Program and are without resolution at this time.

3. Research Applications

As reviewed in available literature, calcium chloride is a common extractant to determine phytoaccessible nutrients. It has also been used for accessible portions of metals. Organic contaminants are assessed in adsorption/desorption studies using calcium chloride as well. Using 0.01 M calcium chloride to represent accessible portions for marginal contamination over a large area could allow cost-effective immobilization remediation technologies to be employed.

Phytoaccessibility determined by calcium chloride extraction can be used by consultants and regulatory authorities to determine risk from contaminants using site-specific information to achieve protection of human and ecological health.

4. Future Research

Narrowing the scope of work in a bioaccessibility or phytoaccessibility study is a graduate program itself. Comparative extraction between methanol and calcium chloride would make the results in this analysis robust. It could answer why only half the total tebuthiuron stock concentration was extracted by calcium chloride.

Micro-pore sequestration was not explored in this study. Visualizing molecular-sized space in which bromacil or tebuthiuron could be sequestered may require computer modeling with well selected parameters. Investigation of the physical organic matter structure of soil may be a clue to quantify adsorptive capacity for contaminants.

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