Rare earth and trace element geochemistry in Ontario agricultural soils

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ABSTRACT

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Agriculture may result in soil disturbances, including contamination by rare earth elements (REE) and trace elements (TEs) from agricultural inputs (e.g. fertilizers, pesticides). Regulations concerning agricultural inputs currently do not consider TE background concentrations, concurrent use of inputs, and emerging contaminants. Therefore, they may not sufficiently protect against TE contamination, including that of REEs as emerging contaminants. The objective of this work was to assess the concentration and distribution of TEs and REEs in agricultural soil and whether agricultural management alters soil geochemistry. Fourteen farms were sampled in southeastern Ontario, and the geochemistry of soils was analysed using ICP-MS and ED-XRF. Trace element concentrations exceeded environmental safety standards in some sites, including those characterized by historical contamination or elevated background concentrations. Concentrations of REEs are reported in Ontario agricultural soils, and the normalized REE values indicated enrichment of the middle REEs. Geographic location drives site geochemistry more than agricultural management.

Keywords: Rare earth elements, agriculture, soil geochemistry, trace elements, phosphate fertilizer

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1 Introduction

Soils are the basis for global agricultural production, and soil fertility is one of the most common aspects of soil quality assessed by agricultural producers. Soil fertility is the availability of macro- and micro-nutrients necessary for plant growth, which is influenced by soil chemical, biological, and physical characteristics (FAO, 2019). Soil fertility may be degraded by contamination arising from agricultural management, through direct or indirect routes (Rojas et al., 2016). Soil contamination with trace elements (TEs) is of particular concern due to their ubiquity in natural environments, the occurrence and proximity to various point and non-point sources, potential negative impacts on plant growth and development, and human health risks through crop consumption.

Trace elements are metals, metalloids, and non-metals that make up a small portion of the earth's crust, defined previously as quantities less than 0.1% of the mass (Shaheen et al., 2013). Some TEs are essential micro-nutrients for plant or animal growth, e.g. copper or selenium, while others are nonessential elements, such as lead. In excess, soil TEs may diminish soil fertility and cause phytotoxic effects to crops, impacting crop growth and quality (Pagano, 2017; Reboredo et al., 2019). Agricultural inputs, which includes fertilizers, pesticides, or wastewater irrigation can act as direct sources of TEs, along with non-point sources of TE contamination, like atmospheric deposition (Rojas et al., 2016).

In some cases, agricultural soil contamination can result in negative human health outcomes through the consumption of crops with elevated concentrations of TEs (Alengebawy et al., 2021). This concern is not new, as analysis for TE content in Ontario agricultural soils has been occurring for decades (Whitby et al., 1978). As an example, the toxic effects of Pb have been a part of the public consciousness for centuries, with references to its toxicity documented as early as the 19th century (Jonasson & Afshari, 2018). Efforts to eliminate Pb exposure from many household products (e.g. paint, plumbing, gasoline) have been carried out, and aside from legacy contamination or occupational exposure, the main route of Pb exposure is now through diet (European Food Safety Authority, 2012; Kasowski & Kasowski, 1976; O'Grady & Perron, 2011). Soils contaminated with Pb may result in elevated levels of Pb in food, presenting increased risk to consumers. Some TEs have been the subject of extensive study over the past few decades (e.g. Cd, Zn, Cu, Pb), leading to a comprehensive understanding of their environmental behaviour, geochemical background and reactivity, and associated risks. Nevertheless, there are new elements of concern associated with the continued use of agricultural inputs (e.g. mineral fertilizers) that require in-depth investigation.

Rare earth elements (REEs) are emerging TE contaminants of concern in agricultural soils (Balaram, 2019; Silva et al., 2019). Considerable interest has been devoted to the potential benefit of REEs for crop production because of demonstrated increases in crop yield when used as an agricultural input (Tommasi et al., 2021, 2023). However, at high concentrations, REEs can cause environmental degradation and loss of productivity through toxic effects to crops (El-Ramady, 2010; Pagano, 2017). Rare earth elements are a common contaminant of mineral phosphorus fertilizers that are applied at high rates in the Canadian agricultural system (Abdel-Haleem et al., 2001; Otero et al., 2005; Ramos et al., 2016; Reid & Schneider, 2019; Silva et al., 2019). To date, a comprehensive survey of REE concentrations in Canadian agricultural soils has not been conducted, and REEs are not included in standard soil health assessments. Furthermore, fertilizers used in Canada are not monitored for their REE content, and only a limited number of TEs are monitored (e.g., As, Cd, Cu, Cr, Co, Pb, Hg, Mo, Ni, Se, Tl, V, Zn; Canadian Food Inspection Agency, 2023).

The aim of this work was to first assess the status of TEs and REEs in Ontario agricultural soils. Trace elements of concern were related to environmental safety guidelines, and REE content was compared to previously reported values in Canadian soils and fractionation patterns examined. Finally, the impact of agricultural management on soil geochemistry was assessed based on reported agricultural management practices.

2 Literature Review: Rare earth elements and agricultural management

2.1 Introduction

Trace elements exist in small quantities in the environment and constitute less than 0.1% of soil mass (Shaheen et al., 2013). Some TEs are essential micro-nutrients at low doses but can become toxic at elevated levels. Their contamination in agricultural systems is of great concern because of TE exposure through the diet (El Hosry et al., 2023; European Food Safety Authority, 2012). Agricultural inputs can act as a source of TE contamination, as the primary materials used in their manufacture can be enriched in TEs (Otero et al., 2005). A model estimating the risk of TE accumulation in Canadian soils indicated that areas of intensive agriculture may have significant accumulation based on current threshold values set by the Canadian Council of Ministers of the Environment within a century (Sheppard et al., 2009a). In Ontario agricultural soils, surface soil (0-15 cm) concentrations of Sb, Cd, Pb, Nb, Se, U, and Zn were 1.4 to 2.2 times higher than subsoil concentration (30-60 cm), for which the authors attributed anthropogenic disturbance and agricultural management (Sheppard et al., 2009b). Conventional TEs, sometimes referred to as 'heavy metals' (Cd, Pb, Cu, etc.) have extensive bodies of research on their distribution, fate, and toxicity in the environment, and therefore are outside of the purview of this review. This review introduces the issue of REE enrichment in agricultural soils, as they are an emerging contaminant in agricultural systems.

2.2 Rare Earth Elements

2.2.1 Overview and Global Significance

The REEs are a group of elements that encompasses the lanthanide series (La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu), along with the non-lanthanides scandium (Sc) and yttrium (Y). Promethium is often excluded because of its infinitesimal natural abundance and its occurrence as short-lived radioactive isotopes. These elements are grouped because of the similarities in their chemical and physical properties, a shared single oxidation state of +III, of which only Ce^{+IV} and Eu^{+II} have additional oxidation states (Tyler, 2004). The REEs have a strong preference to bind with negatively charged carrier phases (e.g. clay minerals), and because their similar chemical characteristics are found enriched as a group mainly in a mineral form (Balaram, 2019; Tyler, 2004).

The REEs are lithophilic and do not form concentrated ore deposits. Instead, they exist as a minor constituent of rocks (Balaram, 2019; Lipin & Boynton, 1989). This group of elements can become concentrated in primary minerals such as acidic igneous rocks, and secondary weathered minerals that contain clay sediments (Silva et al., 2019). Deposits rich in REE are uncommon, and the major areas of extraction are located in China, the United States, Myanmar, and Australia (Dang et al., 2024; Du & Graedel, 2013).

In particular, the REEs are critical for modern manufacturing as they are incorporated into low-emission green technology, communications technology, medical imaging, along with having uses as industrial catalysts (Du & Graedel, 2013). The REEs feature prominently in Canada’s list of 31 critical minerals, which are defined as having none or poor substitutes for their use and being limited in their production (Government of Canada, 2022). Their invaluable role in the global economy is due to their unique chemical properties which are applied for their magnetic, catalytic, and fluorescent properties (Balaram, 2019; Dushyantha et al., 2020). Because of this, Canada is prioritizing creating stronger supply chains for the REEs due to their potential contributions to economic growth.

2.2.2 Rare Earth Element Fractionation

Although represented as a homogeneous group, it is useful to further divide the REEs based on their electrochemical properties. Throughout the lanthanide series, an increase in atomic number corresponds to an increase in nuclear charge, which results in gradually smaller atomic radii (Tyler, 2004). The smaller ionic radii can result in more stable complexation between the metals and ligands, altering the mobility of REEs through soil and water systems (Tyler, 2004). Due to these electrochemical differences, the REEs are often divided into the light REEs (LREE; La to Sm) and heavy REEs (HREE; Gd to Lu). Studies that describe REE fractionation patterns also sometimes define a third group: the middle REEs (MREE; Auer et al., 2017; Dang et al., 2021; Ding et al., 2005). This group is comprised of the lanthanides with an intermediate atomic mass and often includes Sm, Eu, Gd, Tb, and Dy, but is variously defined from study to study. Comparisons between the relative enrichment of these subgroups allows for a better understanding of the role of REEs in biogeochemical processes.

A common technique of REE analysis is a qualitative examination of the pattern of enrichment or depletion between LREE, HREE, and MREE (Bispo et al., 2021; Ding et al., 2005; Liu et al., 2022; Piper & Bau, 2013). However, comparisons among the REE are complicated by their variable natural abundances. As the atomic numbers of the elements increases, their abundance decreases. This trend is further complicated by the Oddo-Harkins effect, by which even atomic numbers will have higher abundances than neighbouring odd numbered elements (Harkins, 1917; Winter, 2014). This leads to a characteristic "zig-zag" pattern of elemental abundance (Harkins, 1917).

To overcome the challenge presented by the variable natural abundances within the REE group, each element concentration must be normalized before comparison. Normalization is the ratio between the measured concentration of an element and a known standard reference value of the same element (Equation 2.1). This is useful because a value greater than 1 indicates an enrichment of REEs compared to the reference material, while a value less than 1 indicates a depletion of REEs (Piper & Bau, 2013). This normalization approach allows for easier comparisons within the lanthanide group by eliminating the challenges posed by variable abundance and the Oddo-Harkins effect. To qualitatively examine the relationships between the REEs, the normalized values of each element are plotted by atomic number (Piper & Bau, 2013). The normalized curve is important for the assessment of enrichment or depletion of specific REEs (e.g., redox-sensitive anomalies in the concentration patterns of Eu or Ce) or fractionation between the LREEs, MREEs, and HREEs (Aide & Aide, 2012; Ding et al., 2005; Emsbo et al., 2015; Liang et al., 2005; Liu et al., 2022; Piper & Bau, 2013; Pourmand et al., 2012; Silva et al., 2019; Wang et al., 2011)

Equation 2.1.

$$RE_N = RE_s / RE_{ref}$$

Where:
RE_N is the normalized value of the element (mg kg^{-1}),
RE_S is the measured value of the element in a sample (mg kg^{-1}), and
RE_{ref} is the concentration of the element reported in the reference material.

Multiple reference materials used for REE normalization exist and may be selected based on the research goals (Piper & Bau, 2013). Chondrites represent meteorites and are used to normalize REE values from both lunar and terrestrial samples (Masuda & Nakamura, 1973; Pourmand et al., 2012). Chondrites, considered the earliest rocks, are believed to have similar elemental concentrations as the nebulas which form planetary materials (Winter, 2014).

Chondrite normalization is not ideal for many environmental samples, as these reference materials do not reflect any environmental weathering of the REEs that is characteristic of the upper crust or of ecological samples (Piper & Bau, 2013). A second set of reference vales is comprised of the estimated concentrations of elements from the upper continental crust (UCC; Rudnick & Gao, 2003). When UCC REE values are normalized by chondrite values, a distinctive fractionation can be seen between the LREEs and HREEs with an enrichment of 1-2 orders of magnitude (Piper & Bau, 2013). Normalizing soil or mineral sample values by chondrite reference values may reveal artificial enrichments, when the REE concentrations would be near the expected background values of the Earth's continental crust. Other reference materials are based on shale deposits which include the World Shale Average, the North American Shale Composite, and the Post Archean Australian Shale (PAAS; Piper & Bau, 2013; Taylor & McLennan, 1985). Each shale sample has slightly differing concentrations of the REEs, but have similar normalized patterns and are employed in environmental studies (Piper & Bau, 2013).

2.3 Rare Earth Elements in Agriculture

2.3.1 Rare Earth Elements in Agriculture

In addition to their industrial applications, REEs are also associated with agricultural production. For over forty years, REEs have been used as micronutrient fertilizers, representing a direct REE input into agricultural systems (Pang et al., 2001). Rare earth nitrates and chlorides are most often used as seed treatments and foliar sprays to promote plant growth, and they have also been used as feed supplements in the poultry and meat sectors (Pang et al., 2001; Tommasi et al., 2021, 2023; Wen et al., 2001). Nevertheless, this practice of REE fertilization is not global, largely due to the conflicting results obtained in studies on the effects of REEs on plant growth (Agathokleous et al., 2019; Tommasi et al., 2021). Further, unintentional routes of REE input into agricultural soils is also of concern. The REEs often exist at high concentrations in phosphate rocks, which are the primary materials for the manufacture of mineral phosphorus fertilizers (Kabata-Pendias & Mukherjee, 2007; Silva et al., 2019).

Phosphorus is one of the major growth-limiting nutrients in agricultural production as it is crucial for the synthesis of lipids, DNA, and ATP molecules in organisms. Phosphorus fertility must be carefully managed in agricultural systems to ensure that low P levels will not limit crop growth while also ensuring that there is not an over-abundance of P that will contribute to environmental degradation (Reid & Schneider, 2019). However, this is a difficult balance because many agricultural systems have less than a 25% P use efficiency (Zhang et al., 2004). Accumulation of P is an unfortunate consequence of standard fertilization methods, as P fertilizers are often applied in excess of crop requirements. In Ontario, a large percentage of agricultural areas have a cumulative P balance of greater than 100 kg P ha^{-1} over 30 years, with some areas reaching > 600 kg P ha^{-1} (Reid & Schneider, 2019). There is noted accumulation of soil P in agricultural areas across Canada, with severe accumulation in areas of Southern Ontario that reflects high rates of P fertilization and manure use. With long term fertilization, P becomes enriched in agricultural soils due to low mobility and its quick transformation into non-available forms for plant uptake (Reid & Schneider, 2019). Trace element contaminants of P fertilizers, e.g. U, can have similar fates of accumulation (Sun et al., 2022). The risk of REE accumulation in agricultural soils associated with high P fertilizer use must be assessed for Ontario agricultural soils.

2.3.2 Rare Earth Elements and Phosphorus Fertilizers

As noted previously, P fertilizers may be enriched with REEs if the parent mineral from which they are derived had high concentrations of REEs. Phosphate and carbonate rocks, both sedimentary and igneous in origin, are widely exploited for fertilizer manufacturing (Silva et al., 2019). During the manufacturing of P fertilizers, some of the total REE content is removed from the raw material through the process of acid leaching. It is estimated that 50-60% of the initial REE content is maintained through the production process of superphosphates, and 29% is maintained through the production of mono-ammonium phosphates (MAP; Ramos et al., 2016).

Multiple studies have characterized REE content in P fertilizers and primary materials such as phosphate rock, limestone, gypsum, and sulfur (Abdel-Haleem et al., 2001; Ramos et al., 2016; Silva et al., 2019; Volokh et al., 1990). In 27 samples of commercial fertilizers sourced from Spanish suppliers, La concentrations ranged from 6.2 to 619 mg kg^{-1} and Ce concentrations ranged from 7 to 744 mg kg^{-1} (Otero et al., 2005). From Brazil, single superphosphates (SSP; $Ca(H_2PO_4)_2 \cdot 2H_2O$) and organic-mineral rock phosphate fertilizers had large ranges in REE concentrations, with La concentrations ranging from 8 to 450 mg kg^{-1} (Silva et al., 2019). Ramos et al. (2016) also reported high REE concentrations in SSP fertilizers, with a total REE content of 8365 mg REE kg^{-1}. Even at the lower end of the range of reported REE contamination in Egyptian-sourced fertilizers, inputs of 18.09 mg La kg^{-1} and 8.55 mg Ce kg^{-1} were predicted to lead to high annual inputs of the REEs in treated fields (Abdel-Haleem et al., 2001). Overall, P fertilizers can be found to have high total REE content and concentrations of the REEs are highly variable.

Importantly, P fertilizers have their own distinct normalized REE patterns based on their parent source. According to Silva et al. (2019), some P fertilizers derived from igneous sources show distinctive LREE enrichment, often with a positive Eu anomaly when normalized with PAAS values. Sedimentary sources of P fertilizer show quite different patterns, often with HREE or MREE enrichment (“hat-shaped” pattern) and a negative Ce anomaly (Auer et al., 2017; Silva et al., 2019). In biogenic phosphate sources, often found in sedimentary P mineral deposits, there can be clear levels of MREE enrichment (Auer et al., 2017). Normalized patterns of the REEs may be important when studying REE signatures in agricultural soils to determine the REE source.

2.3.3 Rare Earth Element Mobility

The movement of REEs through soil is complex, but there are seven distinct processes by which REEs could be removed from the soil, including erosion, leaching of inorganic complexes, association with clay particles in suspension, plant uptake, microbial immobilization, chemical precipitation, and adsorption of the REEs (Aide & Aide, 2012). Research focusing on the movement of the REEs through soil is limited, and base soil characteristics like soil texture or mineralogy will alter the predominance of the processes listed here.

In soil profiles, vertical transport and leaching of REEs plays a minor role in overall REE transport. In general, REEs have low solubility and prefer to exist in mineral forms associated with fluorides, carbonates, phosphates, and hydroxides. Therefore, REEs associated with P fertilizers may have low solubility in soils (Silva et al., 2019). In one leaching experiment conducted over 14 days, the leachable fraction of amended chloride salts of REEs (Ce, Dy, Sm, La, Nd) reached background levels in the leachate after approximately 10 days in four of the tested soils (Wang et al., 2011). One soil which was characterized by the lowest clay content and highest soil test phosphorus levels had slower release of REEs, and REEs were still decreasing in the leachate after the 14-day mark (Wang et al., 2011). In the same experiment, a soil characterized by the highest sand content (61%) had the greatest loss of both exogeneous REE and soil P. Soils with high silt and clay fractions bind more strongly to REEs than soils with low silt and clay. Similarly, another leaching study evaluating REEs as tracers for soil erosion found that REE oxides (La, Pr, Nd, Sm, Gd) were associated with silt sized particles, had low mobility through the soil profile, and became concentrated in the surface layers of the soil (Zhang et al., 2001). Similarly, Wang et al. (2011) reported that the highest concentrations of amended REEs was found in the top 2 cm of the soil columns, and below 4 cm REE concentrations were not significantly different from background levels. The vertical enrichment of REE is mirrored by the distribution of leached P, which also significantly decreases below 6 cm of soil depth (Wang et al., 2011). It is likely that along with soil P, a majority of REE loss is due to surface runoff of particulate matter associated with bound REE rather than soluble runoff (Wang et al., 2011). It is thought than less than 10% of the total REE content is water soluble (Pang et al., 2001).

2.4 Effects of Rare Earth Elements on Plant Growth

There is a common opinion that amendment with the REEs produces hormetic effects on plant growth. A hormetic response is when low concentrations of REEs improve plant response, and high concentrations induce phytotoxic effects (Agathokleous et al., 2019; El-Ramady, 2010; Nascarella & Calabrese, 2017; Tommasi et al., 2021, 2023). For example, maximum growth responses to La amendment in a meta-analysis of growth-response experiments was determined to occur at concentrations of 7.8 mg L^{-1} (geometric mean, n = 666), while the lowest observed adverse effect level (LOAEL) was at concentrations of 77 mg L^{-1} (geometric mean, n = 259; Agathokleous et al., 2019). However, the process and the extent of this response pattern is not clear (d'Aquino et al., 2009; Dang et al., 2024; El-Ramady, 2010). Experimental exposure trials are a valuable resource to determine toxic thresholds of REE exposure and both positive and negative impacts on plant response have been recorded with the amendments of REEs. One major challenge for interpreting the results of available REE exposure studies is the variability between experiments.

First, there is no consistency in the investigated element or combination of elements. It is common that a single element of the LREEs is chosen (e.g. La, Ce, or Nd), while there are also studies combining several LREEs, MREEs, and HREEs in their experimental designs (El-Ramady, 2010). Furthermore, the chemical form of the REE applied also varies; studies examining the phytotoxic effects of separate REEs have found that plant responses vary depending on element bioavailability (Pellegrino et al., 2022). For example, La nitrates, chlorides, and oxides have all been reported in the literature, along with a small number of studies that do not report the chemical form of La at all (Agathokleous et al., 2019). If not properly controlled for, the anions in rare earth salts may mask the true impact of the rare earth cations on plant growth and development. Chloride, for example, is a necessary micronutrient for plants and it is also well known for its phytotoxic impact on plants at high concentrations (Xu et al., 1999). Accounting for this, an ecological risk assessment for Ce included controls of Cl concentrations equal to the four highest test concentrations of $CeCl_3$, which indicated that there were significant decreases in plant response associated with the high Cl concentrations (Moreira et al., 2019). Therefore, the release of anions could confound the results of RE amendment studies.

Second, the dose ranges of REEs assessed in exposure experiments varies considerably. The dose ranges assessed are often linked to study objectives, for instance establishing toxic thresholds versus determining low-level hormetic effects (El-Ramady, 2010). In a review of 666 instances of La-exposure hormetic responses, only 39% of trials included a range of doses that produced both hormetic effects and the LOAEL (Agathokleous et al., 2019). To properly describe a hormetic dose-response relationship, the width and amplitude of the range in which a stimulated response occurs must be properly described, requiring experiments designed with multiple doses below the LOAEL (Nascarella & Calabrese, 2017).

Finally, inconsistency in the endpoints of exposure studies renders the results from literature difficult to compare. The studied endpoints of REE exposure on plants was summarized into three main categories by El-Ramady (2010), outlining general parameters that covers physical properties (e.g. overall biomass production and germination rate), physiological properties (e.g. photosynthetic rate and nutrient metabolism), and finally enzyme activity (e.g. antioxidant response and chlorophyll synthesis). When general parameters are measured, the results may indicate the overall impact of REE amendment on plant productivity but reveals little of the mechanism producing this effect. Due to the demonstrated toxicity of REEs, it is believed that REEs improve plant response in indirect ways (El-Ramady, 2010).

Of particular interest are REE exposure experiments which are conducted in soil systems, of which there are few. The toxicity of the REEs to plants is far lower in soil systems than when plants are grown hydroponically or in a non-soil medium (e.g., vermiculite) with the REEs added in solution (Kotelnikova et al., 2019; von Tucher & Schmidhalter, 2005). Soils reduce the bioavailability of REEs compared to dissolved REEs in solution. This calls into question the application of results derived from non-soil experiments to predict growth outcomes in soil systems. Bioavailability impacts REE toxicity, as demonstrated by Moreira et al. (2019) and Zeng et al. (2006), both of whom compared two or more soils in REE exposure experiments. The prominent difference in the soils by tested by Zeng et al. (2006) was the organic matter concentrations, 27.7 g kg^{-1} in a cambisol and 7.7 g kg^{-1} in a haplic acrisol (World reference base (WRB); FAO, 1998). The haplic acrisol induced growth inhibition at lower concentrations of La and Ce amendments than the cambisol (Zeng et al., 2006). Moreira et al. (2019) compared plant response in two tropical soils (oxisol and inceptisol, WRB) and a tropical artificial soil (10% coconut fiber, 20% kaolinite clay, and 70% fine sand) with the addition of $CeCl_3$. Plant response, measured as percent germination and shoot dry matter was found to be more sensitive to Ce amendment in the natural soils than in the artificial soil, indicating that results obtained from artificial soil experiments may not be representative of in-field processes (Moreira et al., 2019).

Not only does substrate strongly affect the bioavailability and therefore the toxicity of the REEs, but plant response is also species dependent. In general, soil REE exposure studies have focused on agricultural crop response (Moreira et al., 2019), but wild species, and some even native to Canada, have been tested (Carpenter et al., 2015; Dang et al., 2024; Thomas et al., 2014). Native wild species (milkweed, *Asclepias syriaca*; showy ticktrefoil, *Desmodium canadense*; and switchgrass, *Panicum virgatum)* were more sensitive to phytotoxic effects from REE amendment into soils (La, Ce, Y, Pr, Nd, Sm, Tb, Dy, Er) than crop species tested (radish, *Raphanus sativus* and tomato, *Solanum lycopersicum*) in experiments conducted by Thomas et al. (2014) and the follow up by Carpenter et al. (2015). In Brazilian soils, eight crop species were exposed to Ce concentrations ranging from 50 to 2051 mg Ce kg^{-1} dry soil, to which sunflower and radish were the most sensitive (Moreira et al., 2019). Of note perhaps is the fact that sunflower and radish were the only two non-grass and non-leguminous species tested (Moreira et al., 2019).

The only studies showing positive effects of REE amendment into soils are by Dang et al. (2024), Cheng et al. (2015), and Zeng et al. (2006). Cheng et al. (2015) only report significant correlations (R-values of < 0.6) of navel orange quality with increasing La concentration, which does not address questions of plant growth or production. Zeng et al. (2006) report phytotoxic effects of $LaCl_3$ (0 – 1200 mg kg^{-1}) when amended to rice (*Oryza sativa* L.). Potential benefits are reported as there was a significant increase in plant height in haplic acrisol at the 30 mg La kg^{-1} level. Dang et al. (2024) assessed plant response in ferns and tomatoes (*Osmunda cinnamomea* and *S. lycopersicum*) to a mixture of REEs (La, Gd, Yb). Increased photosynthetic potential and increased juvenile biomass was reported in tomatoes at REE concentrations 31 times greater than found in the upper continental crust, while there was no response for ferns.

2.5 Conclusion

To date, the link between exogeneous REEs in agricultural soils and the potential for adverse or beneficial effects on crop production is unclear. Multiple studies performed in solution point to potential benefits of low REE concentrations, signaling that there may be a hormetic effect of REE amendments. However, the phytotoxic effects of the REEs and their potential to bind soil P is well known, and the assessment of their risk in Ontario agricultural soils is long overdue. A large gap exists around understanding the potential range of REE concentrations in currently applied P fertilizers, along with estimates of annual REE enrichment in agricultural soils. In addition, agricultural management practices which can alter the soil system, soil fertility and the fate of trace elements may help to understand the mobility and transport of REEs in agricultural soils. Overall, this work will assess to what extent current concentrations of REEs in agricultural soils represent a risk of toxic effects to plant production and whether current levels of REEs could potentially impact soil fertility and will provide a first look at the status of REEs in Ontario agricultural soils.

3 Geochemical survey and status of trace element concentrations across farm types in southeastern Ontario

3.1 Abstract

Agricultural soils are subject to considerable impacts of anthropogenic activity, including the loading of trace element (TE) contaminants added through fertilizer and pesticide use. To determine whether there is an association between agricultural management and TE geochemistry, a geochemical survey of 14 farms in Southeastern Ontario was conducted. Trace element concentrations in agricultural soils were determined using ICP-MS and ED-XRF. Principal components analysis and hierarchical clustering were used to determine if on-farm management influenced TE concentrations. Multiple surface soils exceed the environmental standards of total metal concentrations set by the Canadian Council of Ministers of the Environment (V, Cr, As, Pb). Chromium levels exceeded environmental safety standards on all farms (> 64 mg kg^{-1}), indicating high background levels of chromium. Management practices on farm were not associated with how observations clustered, indicating that agricultural management may have a lesser impact on site geochemistry than background geochemical variation. The use of agricultural inputs warrants consideration of baseline TE concentrations to avoid unintended TE contamination at sites where background element concentrations are elevated, or past contamination has occurred.

3.2 Introduction

Soil classification systems group and order soils based on their shared characteristics and distinct soil horizons with the rationale of determining their suitability for human needs, such as food and fibre production (Warren et al., 2022). Since the retreat of the Laurentide ice sheet over

1200 years ago, the process of soil formation has been transforming the unsorted mixture of glacial sediment left behind over the much of southern Ontario (Barnett et al., 1998). Natural factors that are understood to influence the soil formation process include parent material, climate, time, relief, and organisms, including humans (Jenny, 1941). Anthropogenic activity is a noted factor in the development of some soils, denoted with a subclass "*p*" when identifying disturbed soil horizons (Soil Classification Working Group, 1998). However, this classification of disturbed soils does not differentiate between types of soil disturbances or the varying impact of anthropogenic activity on soil development. To ensure the continued health and productivity of agricultural soils, greater detail is required in documenting the impact of anthropogenic disturbances.

Agricultural soils have a long history of degradation through cultivation, as conventional practices can cause soil erosion, nutrient loading or runoff, and the accumulation of contaminants in soils (Alengebawy et al., 2021; Bergen et al., 2022; Reboredo et al., 2019). Contamination of agricultural soils with TEs is of concern when using agricultural inputs such as fertilizers or pesticides, because of elevated TE concentrations often found in these products (Abdel-Haleem et al., 2001; Otero et al., 2005; Sun et al., 2022). In some cases, the active ingredients of the agricultural input may be of concern, for instance the pesticides copper sulfate ($CuSO_4$) or lead arsenate ($PbHAsO_4$). In other cases, fertilizers derived from natural mineral sources can have elevated concentrations of background TEs, which are transferred to the agricultural system when applied. The use of fertilizers as agricultural inputs is linked with the accumulation of potentially harmful TEs including Cd, Cu, Zn, Pb, and U in soils (Bergen et al., 2022; Bispo et al., 2021; Mann et al., 2002; Reboredo et al., 2019; Sun et al., 2022). Not only does total TE content increase in soils, but long-term fertilization increases fractions of plant-available TEs, e.g. Cd ($CaCl_2$ and EDTA extractable; Mann et al., 2002). The risk of long-term fertilization using mineral fertilizers is nonetheless still unclear, as TEs content varies according to the fertilizer primary materials and fertilizer application rates, which are dependant on soil nutrient status, type of crop grown, and local climate (Jiao et al., 2012).

In Canada, fertilizers are regulated by the Canadian Food Inspection Agency (CFIA) for the accumulation of thirteen TEs in agricultural soils and do not take soil TE baseline values into account (Canadian Food Inspection Agency, 2023). Even in recent notable amendments to the Fertilizer Act, regulations do not account for farm history, the presence of legacy contaminants, or concurrent use of agricultural amendments in assessing the risk of TE contamination. Instead, the regulations limit agricultural input use by the potential for accumulation of TEs over a period of 45 years (Fertilizers Regulations, SOR/2020-232, 2020). Furthermore, emerging contaminants found in fertilizers, such as the REEs, are currently not monitored in the fertilizer supply (Bispo et al., 2021; Canadian Food Inspection Agency, 2023). There is a potential risk of TE contamination from the overuse of agricultural inputs, which may be observable in the geochemical signature of sites.

In Canada, a national database of baseline geochemical and compositional data of soil is critically needed; the lack of this database is a large oversight for determining baseline values for TE contaminants (Sheppard, et al., 2009a). In a pilot study for a national geochemical database in North America, significant differences were found in the composition of soils at the smallest measured scale of 40 km (Garrett, 2009). Local and anthropogenic factors will likely affect the geochemical composition of agricultural soils at even finer resolutions. Geochemical analyses may also be a precise tool to classify soils affected by anthropogenic activity by detecting contamination or enrichment of potentially harmful elements.

This study aims to examine the geochemical composition of agricultural soils in southeastern Ontario using multivariate principal component analysis and clustering approaches to identify how soil geochemical composition is related to on-farm management practices. The objectives of this study are to (1) characterize the status of TE concentrations in agricultural soils and compare concentrations of elements of concern to CCME environmental safety thresholds, (2) using clustering algorithms, determine if base soil characteristics and soil geochemistry differentiates agricultural sites in ways that align with agricultural management, and (3) determine if on-farm management practices influence the geochemical composition of agricultural soils.

3.3 Methods

3.3.1 Study area

Soil sampling was conducted on fourteen farms in southeastern Ontario, located between 43 51’ 55” – 44 32’ 05” N and 76 49’ 35” – 78 49’ 06” W (Figure 3.1). The sampled farms are located in ecoregion 6E of Southern Ontario, which is characterized by moist and temperate climate (Crins et al., 2009). All farms were within 35 km of the nearest weather station (Table 3.1). Agricultural land use accounts for 57% of the ecoregion, 78% of which is dedicated to crop production, while the remaining 22% is pasture or left fallow (Crins et al., 2009).

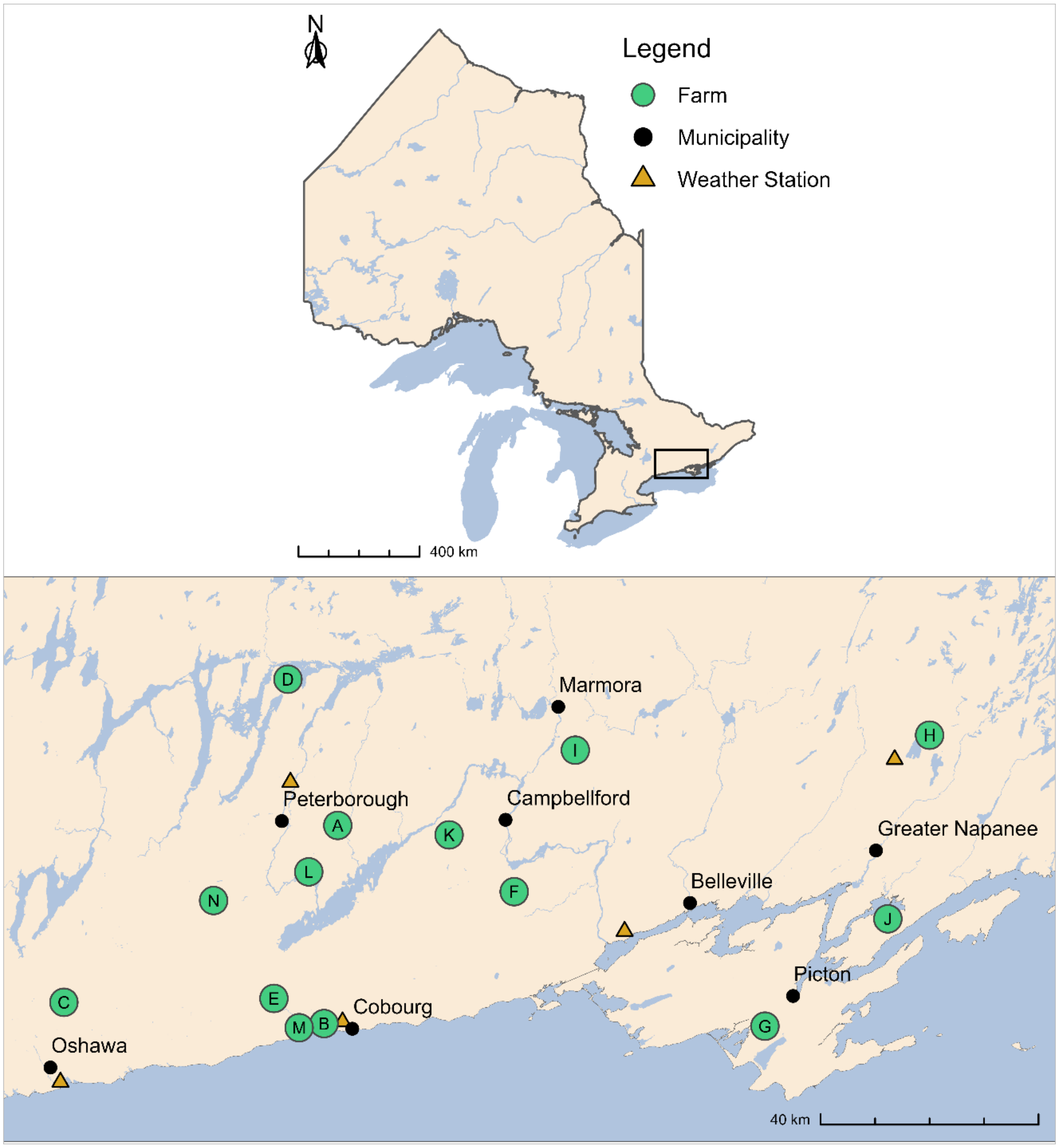


Figure 3.1. Farm locations in Southern Ontario, with notable municipalities included, along with the location of climate monitoring stations (Table 3.1).

Table 3.1. Weather station summaries of Canadian climate normals, 1991-2020 (Government of Canada, 2025).

	Oshawa		**Peterborough**		**Cobourg**		**Trenton**		**Centreville**	
	Mean	*sd*	*Mean*	*sd*	*Mean*	*sd*	*Mean*	*sd*	*Mean*	*sd*
Annual temperature (°C)	8.1	2.6	6.5	1.6	7.7	2.8	7.6	1.0	7.3	1.2
Precipitation (mm)	906.3		839.6		-		940.5		983.8	

The underlying bedrock is sedimentary, primarily composed of limestone, dolostone, and shale (Figure 3.2; Ontario Geological Survey, 2011). These sedimentary rocks were formed during the middle and upper Ordovician (434 to 470 million years ago; Ontario Geological Survey, 2011). However, the surficial geology of the area is composed of deposited glacial sediments, arising from the retreat of the Laurentide ice sheet, with a majority of the deposited surficial sediments being an unsorted glacial till (see also Figure 4.1; Barnett et al., 1998).

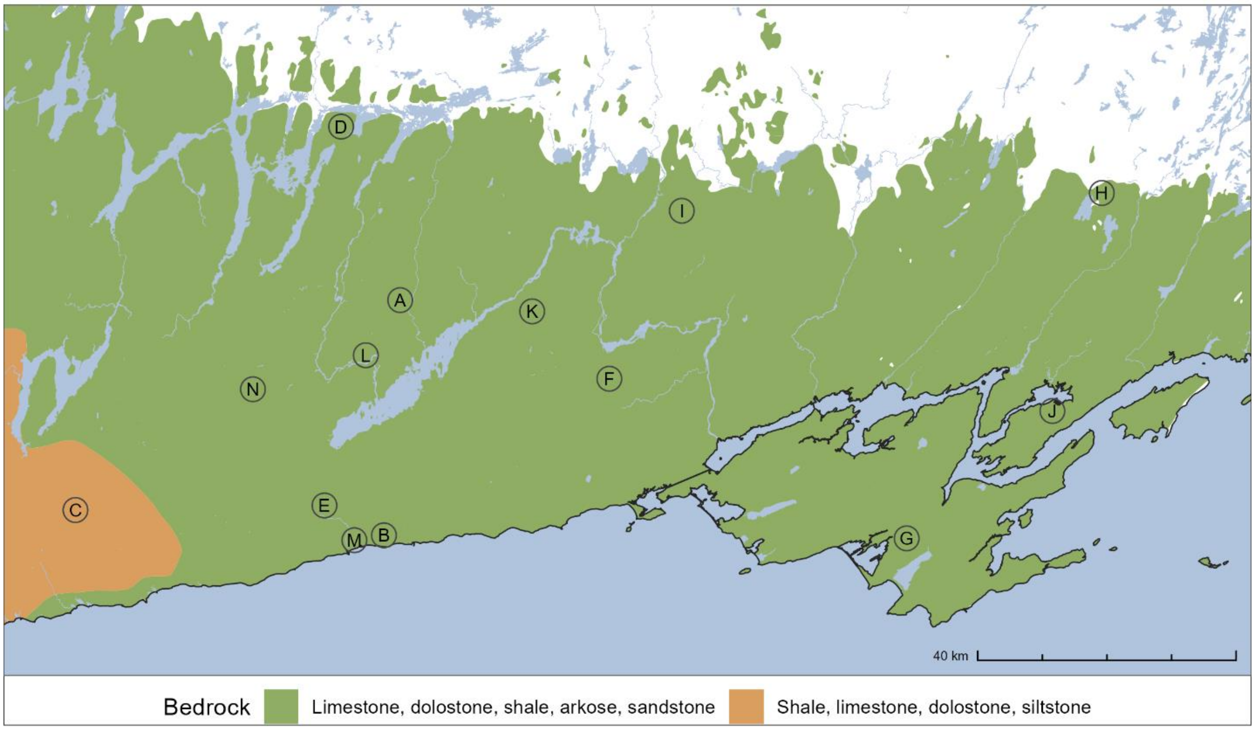


Figure 3.2. Bedrock geology of sampling area with farm locations indicated (Ontario Geological Survey, 2011).

Permission for sampling on private land was obtained through professional relationships with farmers, many of whom agreed to participate through collaboration with Trent University via the Quinte Farm Research and Stewardship Collaborative (*Quinte Soil and Crop Improvement Association*, 2023). Farms were selected to maximize diversity of field use and management strategies at the time of sampling. From the fourteen farms, fifty-two fields were chosen for sampling. Study farms were assigned an identifying letter from A-N, with numbers following the letter identifier denoting a study field.

Field use was categorized into four main agricultural production types: hay production, cattle pasture, field crop production, and apple orchards (Table 3.2). Both fertility management and crop type differed between the four field uses. In addition to crop history, information on soil fertility management and farm history was collected when available, including the incorporation of animal manures (supplementary Table 3.S1).

Table 3.2. Cropping systems in fields from farms A-N.

Farm	Field Crop	Hay	Pasture	Orchard
A	A.1	A.2, A.3		
B	B.1, B.2			B.3
C	C.1	C.2	C.3	
D				D.1
E	E.1			
F	F.3, F.4, F.5, F.6	F.1, F.2		
G	G.1, G.2, G.3, G.4, G.5, G.6			
H	H.3	H.1, H.2		
I	I.1, I.4, I.5	I.3	I.2	
J	J.1, J.2, J.3, J.4, J.5, J.6			
K	K.1, K.5, K.6	K.2, K.3, K.4		
L	L.2	L.1		
M	M.1, M.2, M.3, M.4			
N	N.1, N.3		N.2	

Field crop (Fc) production (n = 35) was usually managed using cash crop rotation, which often consisted of corn (*Zea mays*), soybean (*Glycine max*), and winter wheat (*Triticum aestivum*). A three-crop rotation consisting of maize, a leguminous crop, and a cereal is common in Ontario and considered part of agricultural best management practice (Agriculture Canada, 2008). Substitutions on the standard rotation exist; for example, farm B incorporated adzuki beans (*Vigna angularis*) as the leguminous stage in the rotation. Some of the study farms also incorporated cover crops (CC) as an additional stage in their crop rotation. Cover crops are an added phase of vegetative growth used to protect and improve the soil but not harvested for profit.

Hay (Hy) fields (n = 12) were comprised of both seeded and non-seeded perennial cropping systems that produce forage, which is cut and baled multiple times during the growing season. Similarly, pasture (Pa) fields (n = 3) are similar to hay production systems because they are also perennial grass systems. However, Pa fields directly incorporate grazing cattle, which inputs animal manure directly from the source. Grazing management systems can have variable impacts on soil water infiltration, soil organic matter content, soil biota, and greenhouse gas release (Bork et al., 2020; Khatri-Chhetri et al., 2024; Russell & Bisinger, 2015). Fruit orchards (Or, n = 2) had the fewest number of fields out of the four production types. Despite this, orchards were included because of their unique agricultural management when compared to the other three production types. In comparison to perennial orchards, Hy, Pa, and Fc fields are more likely to undergo tillage, reseeding, and other soil disturbances more frequently.

3.3.2 Soil sampling

Soil sampling was completed from May to October 2021, prior to crop removal. A systematic sampling design was used for each field and four parallel transects were established within a representative 100 m by 100 m plot (Pennock et al., 2007). Representative plots were chosen as the field area varied considerably within and between farms, and were determined based on a visual assessment of field conditions, taking slope and edge effects into account (Pennock et al., 2007). For the orchard fields, transects were taken parallel to the tree line, equidistant between the trunks. Soils were sampled using a stainless-steel soil probe (2.5 cm diameter, 0-20 cm depth), and along each transect, 10-12 cores were collected and placed into re-sealable Ziploc® bags to form a composite sample. The composite soil samples were then thoroughly mixed and stored at 4°C for transport. Between transects, the soil probe was washed and sanitized using a 70% ethanol solution.

Three bulk density samples were additionally collected along each transect. Tin cylinders with a known volume (151 cm^3) were driven into the soil with force to avoid soil compression (Hao et al., 2007). When the top of the cylinder was flush with the soil surface, they were dug out with a trowel to prevent soil loss from either end. Extra soil protruding from the bottom of the core was levelled off before transferring the sample into separate Ziploc® bags. Bulk density samples were not used for chemical analysis and were stored at ambient temperature during transport.

3.3.3 Soil characteristics

Base soil characteristics, including soil pH and electrical conductivity, soil organic matter (SOM), soil inorganic carbon (SIC), and soil particle size were determined for the composite soil samples. Soils were prepared by air drying (48 h) and sieving to 2 mm for all physical and chemical analysis. Water-extractable soil pH and electrical conductivity were conducted on a soil slurry where reverse osmosis (RO) water was added to dried and sieved soil in a 2:1 ratio in 50 mL Falcon tubes. The samples were then shaken for 30 minutes on a shaker table at 200 oscillations min^{-1} before the suspended particles were allowed to settle out of the overlying water for one hour. The supernatant was then measured with a combination pH and electrical conductivity (EC) meter (Fisherbrand Accumet AB200).

Soil organic matter and soil inorganic carbon contents were determined by loss on ignition (LOI). Ceramic crucibles were oven-dried to a constant weight and 2 g of oven-dried soil was added. The soils were ignited at 550°C for four hours, after which the mass lost can be interpreted as the loss of SOM, represented by LOI_{550} (equation 3.1.; Heiri et al., 2001). Soils and crucibles were kept at 105°C between ignition and weighing to prevent atmospheric moisture from being absorbed by either the soil or crucible. After the initial firing, soils and crucibles were re-weighed and then ignited at 950°C for two hours (Heiri et al., 2001). In this second firing, carbonate materials in the soil are burned and the percent inorganic carbon present in the soil (LOI_{950}) can be estimated (Equation 3.2.; Heiri et al., 2001). Soil organic matter and soil inorganic carbon are both expressed as a percent of the total soil volume.

Equation 3.1.

$$\mathrm{LOI}_{550} = \left(\frac{W_{105} - W_{550}}{W_{105}}\right) \times 100$$

Where:

LOI_{550} is the soil organic matter (%) as a percentage of the original soil weight,
W_{550} is the weight of the soil (g) after ignition at 550°C, and
W_{105} is the original weight of the oven-dried soil (g).

Equation 3.2.

$$\mathrm{LOI}_{950} = \left(\frac{W_{550} - W_{950}}{W_{105}}\right) \times 100$$

Where:

LOI_{950} is the soil inorganic carbon (%) as a percentage of the original soil weight,
W_{950} is the weight of the soil (g) after ignition at 950°C,
W_{550} is the weight of the soil (g) after ignition at 550°C, and
W_{105} is the original weight of the oven-dried soil (g).

Soil particle size analysis was determined using the hydrometer method. Approximately 25 g of soil was dispersed using an electric mixer into 100 mL of 5% sodium hexametaphosphate ($Na_6(PO_3)_6$), commonly known as Calgon. The Calgon was used as a dispersing solution for the clay within the soil (Kroetsch & Wang, 2007). The soil and Calgon mixture was then placed in a 1000-mL graduated cylinder and filled to 1000 mL with RO water. To measure the particle size distribution, the soil at the bottom of the graduated cylinder was mixed thoroughly with a plunging apparatus for one minute, to disperse all the soil equally through the column of water. After 40 seconds, the hydrometer was inserted into the graduated cylinder to measure the density of the liquid after the sand fraction of the soil had settled out of suspension. Another measurement was taken at 7 h, at which point the silt fraction had also settled out of suspension. Percentages of sand, silt, and clay in the soil were calculated using equation 3.3 (Kroetsch & Wang, 2007). A blank column of 100 mL of 5% Calgon and 900 mL of RO water was used to measure the temperature and background water density at each time interval to correct for temperature fluctuations. For each field, three replicates were analysed. Soil textural class was determined from particle size fractions using the soil textural triangle as seen in the Canadian System of Soil Classification (Soil Classification Working Group, 1998).

Equation 3.3.

$$\text{Clay (\%)} = R_{7h} \times \left(\frac{100}{w}\right)$$

$$\text{Silt (\%)} = R_{40s} \times \left(\frac{100}{w}\right) - \text{Clay \%}$$

$$\text{Sand (\%)} = 100 - (\text{Clay \%} + \text{Silt \%})$$

Where:
R_{7h} is the temperature-corrected hydrometer reading (g L^{-1}) at the 7-hour mark,
R_{40s} is the temperature-corrected hydrometer reading (g L^{-1}) at 40 seconds, and
w is the original weight of soil (g).

Soil bulk density was determined by oven drying (105°C) the soil core until a constant weight was obtained, and the mean dry weight from the three transect replicates was taken. Measurements of BD are the mass of the dry solids (m) by the volume of the sampling core (V), as depicted in Equation 3.4. Gravels were removed and the cylinder volume was corrected.

Equation 3.4.

$$D_b = \frac{m}{V}$$

Where:

D_b is the bulk density (g cm^{-3}),

m is mass of the soil (g), and

V is the volume of the sampling core (cm^3).

3.3.4 Total element analyses with x-ray fluorescence

Dried and sieved soil samples were ground to a fine powder using a planetary ball mill (Retsch PM 100). Ground samples were mixed in a 2:1 ratio of soil to a binding agent (X-Ray Mix, SCP Science) before pelletizing. The samples were pelletized using an evacuating die cast and a hydraulic press at 11 metric tons. Along with a visual assessment, sample pellets were placed in a vacuum chamber at -20 bar for one minute to assess the stability of the pellet surface and to determine if there was any instability or material crumbling from the edges. If the surface of the pellet was not homogenous and stable, a new pellet was prepared following the same procedure.

Total element analysis was conducted using energy dispersive X-ray fluorescence (ED-XRF, Thermo Scientific ARL Quant'X) on pelletized soil samples for major oxides (Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_3) and trace elements (tTE; S, Cl, V, Cr, Ni, Cu, Zn, As, Br, Rb, Sr, Y, Zr, Nb).

3.3.5 Acid-leachable trace element analyses

Dried and sieved composite soil samples were ground to a fine powder using a ceramic mortar and pestle, which was cleaned between samples using high-purity water (18.2 MΩ cm) from a Millipore Milli-Q water system. Sample grinding was later switched to a bead beater for reduced sample preparation time and less potential for cross contamination as a new 2 mL sample tube and two 3 mm glass beads were used per samples. In 15-mL digestion tubes, 0.2 g of soil was transferred and combined with 4 mL of *aqua regia*, a 3:1 mixture of Trace Metal Grade hydrochloric acid (HCl) and nitric acid (HNO_3). The digestion tubes were allowed to rest overnight before being capped tightly and heated to 120°C for eight hours. After cooling, the supernatant was collected by pipette and diluted 100x in 2% HNO_3.

Triple quadrupole inductively coupled plasma mass spectrometry (Agilent 8800 ICP-MS) was used for acid-leachable trace element (aTE) analysis in this study. The aTEs include: Li, Co, Ga, Ge, Cd, Cs, Pb, Th, U, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Indium (In; final concentrations of 10 ppb) was added to each sample as an internal standard to monitor instrument drift throughout the run. An acid blank was included in each leaching batch to determine background TE concentrations in *aqua regia*. Calibration of the instrument was performed daily using a 14-point standard curve of a multi-element solution comprised of 60 elements.

3.3.6 Quality assurance and quality control

Total element analyses were calibrated using five soil and sediment CRMs from the National Research Council of Canada (HISS-1, PACS-3 and MESS-4) and Natural Resources Canada (TILL-2 and TILL-3; Dang et al., 2024). A pelletized CRM of a similar matrix to the soil samples (i.e., TILL-2 or TILL-3, or both) was included daily to the analytical sequence to assess the accuracy of the ED-XRF. The measured concentrations and error terms of the total elements (major oxides and total trace elements) alongside the respective certified values are reported in supplementary Table 3.S2. The linear relationship between the results of the ED-XRF measured values and certified values of TILL-2 and TILL-3 are shown in Figure 3.S1.

Two marine sediment CRMs from the National Research Council of Canada (HISS-1 and MESS-4) were included in each leaching batch to measure the element recovery of the *aqua regia* leaching method following the same workflow as for the analysed soil samples (Berman et al., 1997; Willie et al., 2014). A river water CRM (SLRS-6) was used to validate the accuracy and precision of elemental analyses using ICP-MS (Yang et al., 2015; Yeghicheyan et al., 2019). The measured concentrations and certified values of the marine sediment CRMs are provided in supplementary Table 3.S3, and the elemental recovery of SLRS-6 is reported in supplementary Table 3.S4.

Complete digestion was not accomplished by *aqua regia* leaching on the soil samples. The percent recovery of the acid-leached elements was determined by taking the concentrations of the aTE concentrations as a percentage of the tTE concentrations measured by ED-XRF (Table 3.3). The percent recovery of the seven elements is better represented by the median and inter-quantile range due to the presence of outliers, a visual representation of which can be seen in supplementary Figure 3.S3. The median *aqua regia* extraction yield ranged from 33% (As) to 124% (Cu). For seven elements (V, Ni, Cu, As, Rb, Y, and Nb) with both total and acid-leachable concentrations, the tTE concentrations were used in the multivariate data analyses.

Table 3.3. Summary (median and interquartile range) of the percent recovery (%) of acid-leached trace elements in unknown samples taken as a percentage of total trace element concentrations determined by ED-XRF.

	V	**Ni**	**Cu**	**As**	**Rb**	**Y**	**Nb**
Median	65	87	124	33	41	72	84
1st Q	55	73	102	28	33	63	65
3rd Q	85	106	150	41	51	85	108

3.3.7 Data analysis

Calculation of summary statistics and all statistical analyses were carried out in R Studio (R version 4.4.1; R Core Team, 2024). Concentrations of the elements of concern (As, Cd, Cr, Co, Cu, Ni, Pb, Zn) were compared to the upper environmental safety limits for agricultural soils using one-sample Student's t-tests ($\alpha = 0.05$). All values for the environmental safety standards for trace element contaminants are retrieved from the Canadian Council of Ministers of the Environment ecotoxicology database (CCME; Canadian Council of Ministers of the Environment, 2024). It is important to note that the CCME guideline concentrations are reported for the acid leachable fractions using *aqua regia.* For some elements of this study, the total concentration (tTE) may not be methodologically comparable to these guideline values. However, concentrations of trace metals leached with *aqua regia* tend to approximate the total concentration with an average recovery of ~ 75% in soil certified reference materials (Chen & Ma, 2001). To determine if elevated levels of TEs differed between farms, element means were compared between farms using a multivariate non-parametric Kruskal-Wallis test, using two transects per field as replicates.

To determine whether on-farm management impacted soil geochemistry, principal components analysis (PCA) was conducted using 51 variables. The retained variables included the base soil characteristics of pH, EC, SOM, and SIC, and 47 major oxides and trace elements that were validated using the CRMs. The number of principal components (PCs) to retain was assessed visually using the scree plot method. Simplification of the PCA biplot was done by grouping positively correlated variables using Pearson's correlation coefficient (> 0.6). Associations between the grouped variables and individual observations (differentiated by field use, farm, and agricultural best management practices) were qualitatively assessed. Agricultural best management practices (BMP) included (a) incorporation of manures, (b) the use of cover crops, and (c) tillage. Cover crop use and the use of manures were limited to the fields under Fc cultivation, as cover crops exist as a stage in crop rotation and the information on the use of manures was not complete in Ha, Pa, and Or fields. For the use of tillage, all field types were included, other than orchards, which did not undergo tillage.

To assess whether soil composition differentiates agricultural sites independent of human classification and aligns with agricultural management, agglomerative hierarchical clustering analysis was performed using Ward's method in conjunction with the PCA (Murtagh & Legendre, 2014). Clustering tendency and the number of clusters retained was validated using the average silhouette method.

3.4 Results

3.4.1 Soil characteristics

The average soil pH was approximately neutral, with a range of 5.6 to 8.6 (Table 3.4). Electrical conductivity was highly variable, i.e. from 9 to 391 µS cm^{-1}. Soil organic matter was a larger fraction of the soil carbon pool than SIC and had a lower relative standard deviation (RSD) than SIC (33% vs 79%). Additional bar graphs displaying the mean values for all base characteristics by farm are provided in supplementary Figure 3.S2.

Table 3.4. Summary statistics of the base soil characteristics for all samples (n = 104).

	pH	**EC (µS cm^{-1})**	**SOM (%)**	**SIC (%)**
Mean	7.1	120	4.6	1.2
SD	0.7	92.4	1.5	1.0
Median	7.0	94.1	4.5	1.0
1st Q	6.5	42.0	3.7	0.6
3rd Q	7.8	179	5.3	1.4

Most farms had soil textural classes of loam, sandy loam, or clay loam. Sand was generally the largest fraction of the soil texture, ranging from 20% to 85%, with a mean of 45 ± 14% (Table 3.5). Following sand in abundance was silt which ranged from 4-60%, with a mean of 36 ± 13%. Finally, clay content comprised the smallest textural proportion and ranged from 3-47% with an average of 19 ± 11%.

Table 3.5. Summary of soil texture (%) and bulk density for farms A-N. The overall soil textural class is reported as determined from the average particle size composition on each farm.

Farm		**Sand**		**Silt**		**Clay**		**Soil texture class**	**Bulk Density (g cm^{-3})**	
		Mean	*sd*	*Mean*	*sd*	*Mean*	*Sd*		*Mean*	*sd*
A	6	47	5.2	43	3.9	9.7	2.0	Loam	1.31	0.05
B	6	36	3.2	51	1.7	13	2.4	Loam	1.30	0.1
C	6	40	5.1	43	4.3	18	2.9	Loam	1.17	0.1
D	2	58	0	38	0	4	0	Sandy loam	1.36	0.01
E	2	69	1.4	26	0.01	5	1.4	Sandy loam	1.31	0.02
F	9	52	18	35	14	13	8.7	Loam	1.41	0.1
G	12	60	14	24	10	16	6.2	Sandy loam	1.51	0.14
H	6	47	7.8	9.5	4.7	43	4.4	Sandy clay	0.88	0.14
I	7	32	13	50	9.2	19	6.0	Loam	1.28	0.14
J	7	35	12	34	3.9	31	10	Clay loam	1.31	0.15
K	4	39	6.8	39	11	22	4.0	Loam	1.26	0.12
L	4	32	5.9	38	3.4	31	4.1	Clay loam	1.18	0.05
M	7	48	12	36	6.2	16	6.3	Loam	NA*	NA*
N	6	36	4.4	50	6.5	16	7.1	Loam	1.32	0.18

*Bulk density values are not available for farm M due to data loss.

3.4.2 Distribution of major oxides

The distribution of major oxides follows the conventional abundance in soils, with SiO_2 as the major component, followed by A_2O_3, Fe_2O_3, CaO, K_2O, MgO, and Na_2O (Table 3.6). Titanium oxide and P_2O_5 represent less than 1% of soil weight. It is also important to note that despite the large number of samples (n = 104), most of the major oxide distributions have an RSD that is below 10%, except for Na_2O, Fe_2O_3, and CaO. The major oxide concentrations that have the largest potential to be affected by agricultural inputs are CaO, MgO, K_2O, and P_2O_5, as these are often applied directly as agricultural amendments. Of the major oxides, CaO concentrations had the greatest variability, with an RSD of 45%. In addition, CaO was not normally distributed and was instead positively skewed (Figure 3.3).

Table 3.6. Summary statistics of the major oxides (%) for the entire data set (n = 104).

Element	**Mean**	**sd**	**Median**	**1st Q**	**3rd Q**
SiO_2	64.8	2.8	65	63.3	66.2
Al_2O_3	13.4	1.0	13.2	12.8	13.8
Fe_2O_3	5.0	0.9	4.8	4.5	5.0
CaO	3.4	1.6	3.0	2.4	3.8
MgO	2.0	0.4	1.9	1.7	2.2
Na_2O	1.5	0.6	1.7	1.2	2.0
K_2O	2.6	0.4	2.6	2.3	2.8
TiO_2	0.81	0.08	0.79	0.75	0.83
P_2O_5	0.3	0.1	0.3	0.25	0.34
MnO	0.13	0.03	0.12	0.1	0.14
LOI	5.9	1.9	5.7	4.7	7

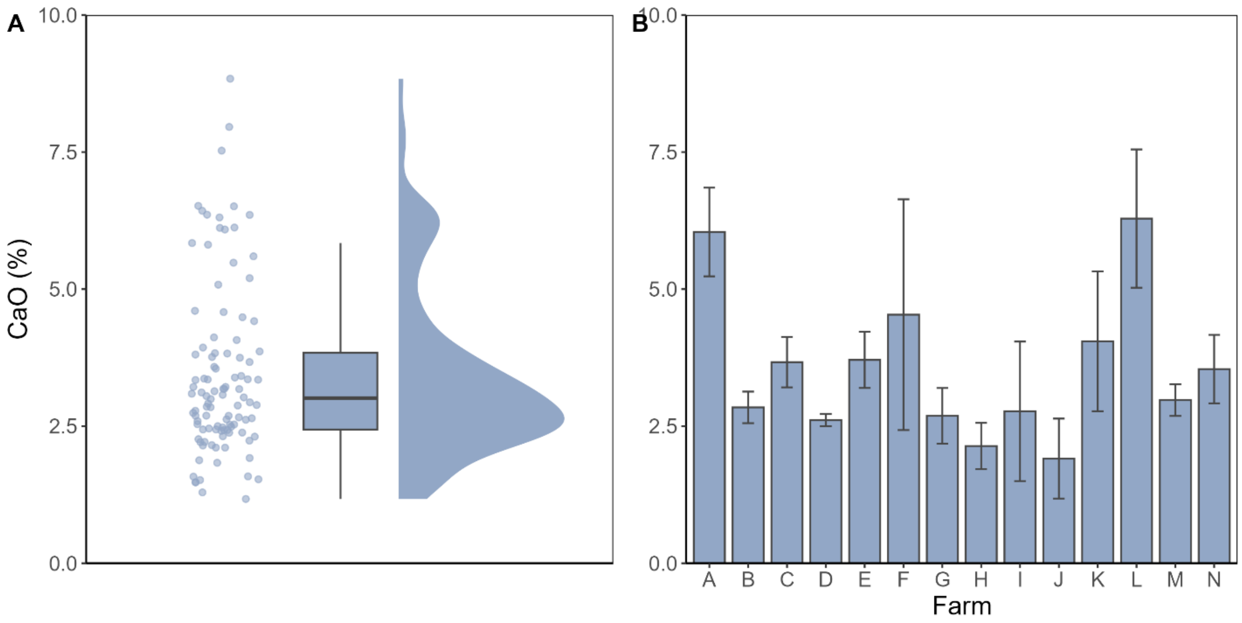


Figure 3.3. Calcium oxide (CaO %), where (A) is the distribution of the entire data set (n = 104) with a density plot, boxplot, and jittered points of raw data. (B) shows the mean (± sd) of the CaO content for each farm.

3.4.3 Trace element content and environmental safety thresholds

The tTE concentrations followed a decreasing order of abundance of: S > Zr > Sr > Cl > V > Zn > Rb > Cr > Y > Ni > Cu > Nb > As > Br (Table 3.S6). Total TE concentrations had greater variation than the major oxides, with the average RSD of 22% for the major oxides and 30% for the tTEs. Unlike the major oxides, none of the tTEs displayed < 10% RSD for all observations. Copper and arsenic have the greatest variability of the tTEs (69% and 57% RSD, respectively).

Of the tTEs that are noted environmental contaminants, some fields exceeded environmental safety thresholds set by the CCME. The TEs that were enriched beyond the respective safety thresholds included V, Cr, Ni, Cu, and As. For Ni and Cu, less than 2% of all samples exceeded their respective safety standards. No farms had mean V concentrations that were significantly higher than the safety standard, but concentrations exceeded the guideline on farms E, H, and J (Figure 3.4). Arsenic concentrations were consistent in most of the farms, with levels approaching or exceeding the CCME threshold value. However, the arsenic levels measured in field B3 were four times greater than the arsenic safety guideline. Finally, the mean chromium values were enriched beyond the CCME safety level (64 mg kg^{-1}) for nearly all farms other than farms A, I, and L (Figure 3.4), and the overall mean concentration of Cr was significantly greater than the upper safety limit ($t = 4.89$, $df = 103$, $p = < 0.001$). However, the concentration of Cr was not significantly different between farms ($X^2(13) = 20.5$, $p = 0.08$).

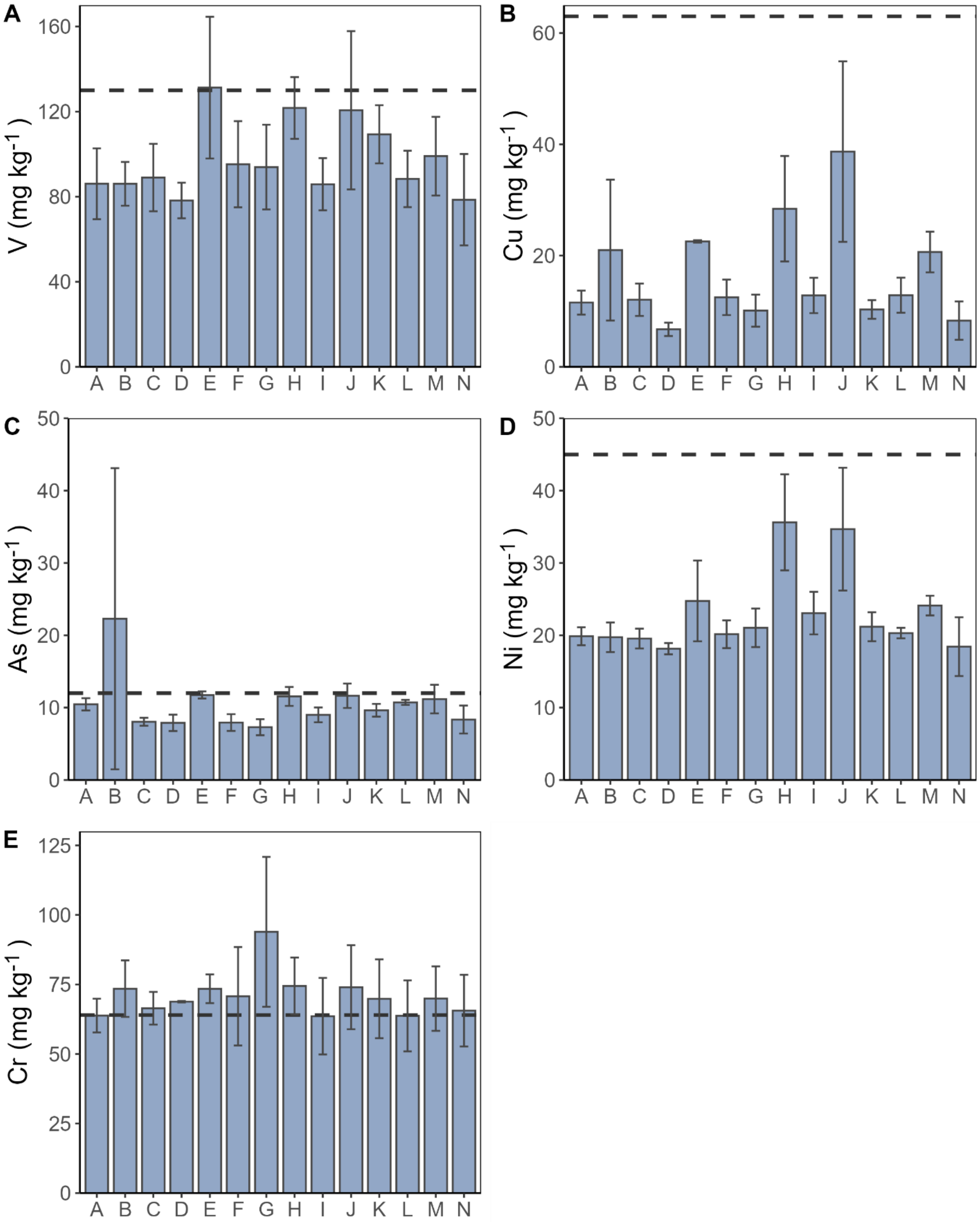


Figure 3.4. Mean values by farm of total trace elements (A) vanadium, (B) copper, (C) arsenic, (D) nickel, and (E) chromium. Note that the y-axes are not generally comparable between the plots. The upper environmental safety limit for agricultural soils for each trace element is denoted by a horizontal dashed line (CCME, 2024).

For the aTEs, the variation in the entire data set was greater than the variation in the tTEs, with a mean of 43% RSD, with a maximum of 114% RSD for Pb (Table 3.7). The elements of concern identified for potential harmful effects on the environment were Cd, Pb, and U. Of the three, only Pb exceeded the upper safety limit of 70 mg kg^{-1} for field B3, like the high total arsenic concentrations (Figure 3.5). The REEs were included in the acid-leached trace elements and are a more chemically homogenous group. The REEs had lower levels of variation (RSD) than the other aTEs, ranging from 29-41 %.

Table 3.7. Summary statistics of the acid-leachable trace elements (mg kg-1) for the entire data set (n = 104). Mean values and standard deviation by farm can be found in supplementary Table 3.S8. Environmental safety standards for agricultural soils are included when available (Canadian Council of Ministers of the Environment, 2024).

Element	Mean	SD	Median	1st Q	3rd Q	CCME Guidelines
Li	12.1	5.3	11.2	8.3	15	-
Co	11.7	6.5	9.9	7.8	12.4	40
Ga	10.8	4.4	9.7	8.1	12.3	-
Ge	1.7	0.8	1.5	1.2	2.2	-
Cd	0.4	0.2	0.4	0.3	0.5	1.4
Cs	2.1	1.1	1.7	1.4	2.3	-
Pb	21.2	24.1	16	12.9	19.1	70
Th	6.1	3.6	5.0	3.8	7.1	-
U	1.4	0.9	1.1	0.9	1.7	23
La	38.3	15.4	34.1	27.7	43.6	-
Ce	90	36.8	77.6	66	102	-
Pr	10.2	3.8	9.1	7.7	11.4	-
Nd	40.5	15.0	36.6	30.8	45.9	-
Sm	7.9	2.8	7.1	6	8.9	-
Eu	1.5	0.5	1.4	1.2	1.7	-
Gd	7.0	2.3	6.4	5.5	7.9	-
Tb	1.0	0.3	0.9	0.8	1.1	-
Dy	5.8	1.8	5.3	4.6	6.6	-
Ho	1.1	0.4	1.1	0.9	1.3	-
Er	3.2	1.0	3.0	2.5	3.6	-

Tm	0.4	0.1	0.4	0.4	0.5	-
Yb	2.9	0.9	2.7	2.3	3.3	-
Lu	0.4	0.1	0.4	0.3	0.5	-

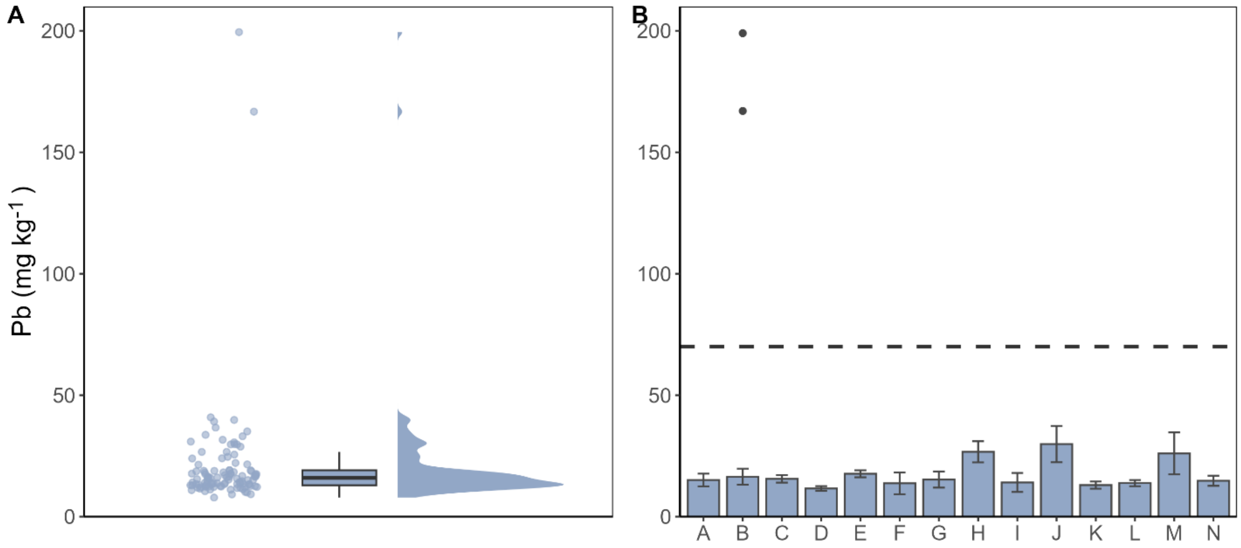


Figure 3.5. Lead concentrations (mg kg^{-1}) where (A) represents the distribution of the entire data set (n = 104), with a density plot, boxplot, and jittered points of raw data. Note the two values > 150 mg kg^{-1}. Plot (B) shows the mean (± sd) of the Pb content for each farm.

3.4.4 Principal components analysis and impact of agricultural management

The first two PCs were retained and represented 59.9% of the variation within the data. Supplementary Table 3.S9 includes the variable loadings for PC1 and PC2. The position of the loadings along the x-axis (PC1) or the y-axis (PC2), combined with the distance from the origin indicates the degree to which the variable influences the principal component (Figure 3.6). Interpreting the impact of all 51 variables on the PCs would be exhaustively detailed. To simplify interpretation, a single variable was chosen to visually represent a group of loadings that are associated with one another. For example, the variables pH, CaO, and SIC were positively correlated (R > 0.6) and can be best represented by the largest loading of CaO (Figure 3.7).

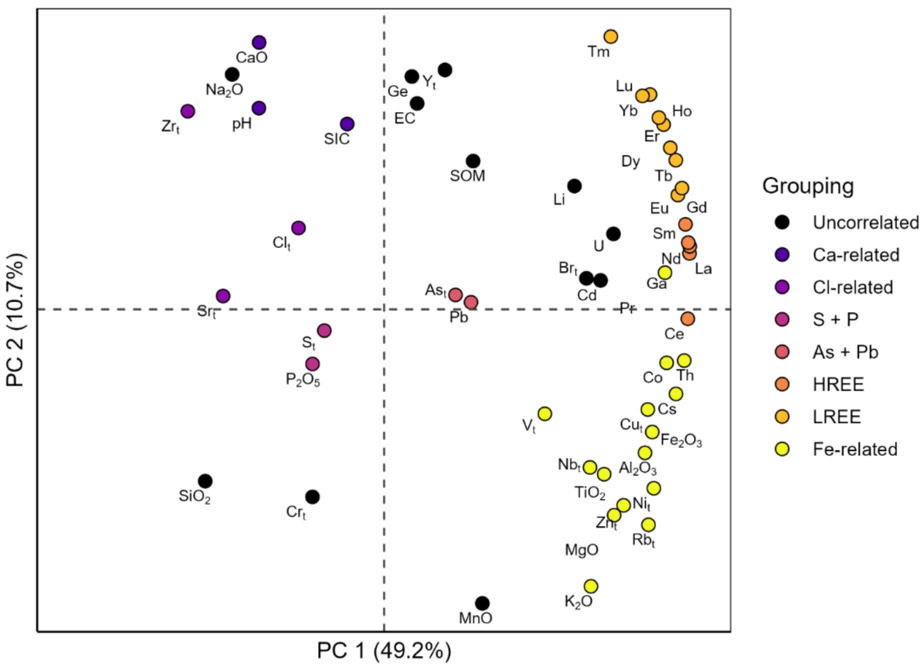


Figure 3.6. Variable loadings of the PCA. Loadings with correlations > 0.6 were grouped and are represented by the same colour points. Loadings in black are uncorrelated to the other variables.

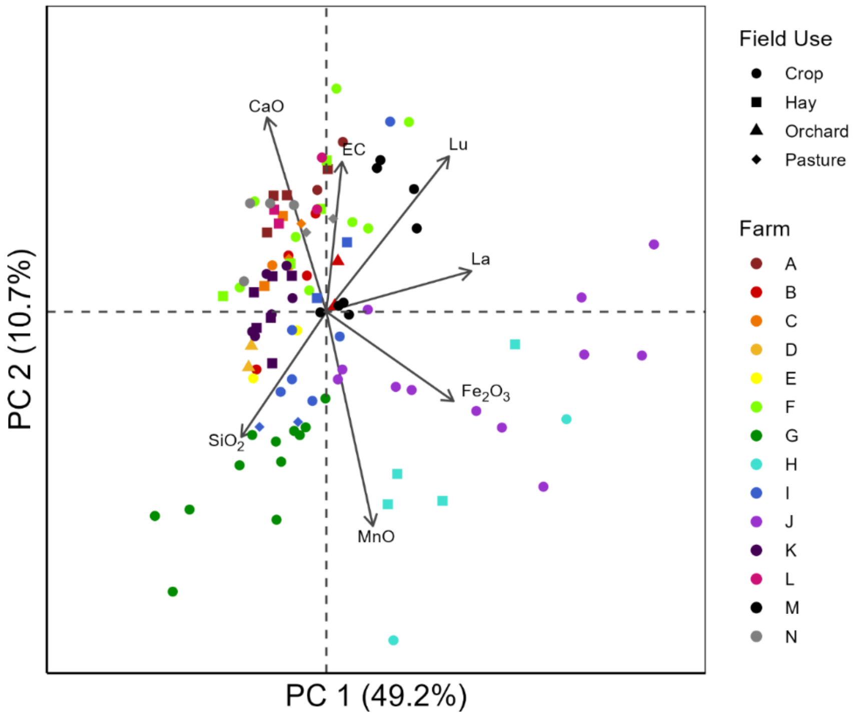


Figure 3.7. Simplified biplot of major identified loadings, along with data scores that are grouped by farm and field use type.

Agricultural management reported by producers were best summarized by field use and the adoption of agricultural BMPs. When the observations are categorized by field use on the simplified biplot (Figure 3.8), there is no clear separation of one field use type from another. There are large amounts of overlap between the four categories, and no distinct relationships with any of the major loading groups. For the agricultural BMPs, 51% of the Fc fields used cover crops in their rotation to some extent, and manure use was less widely adopted, at 31% of fields. Finally, 34% of the relevant fields incorporated tillage into their farm management. However, the agricultural BMPs did not create any distinct partitioning in the observations (supplementary Figure 3.S4).

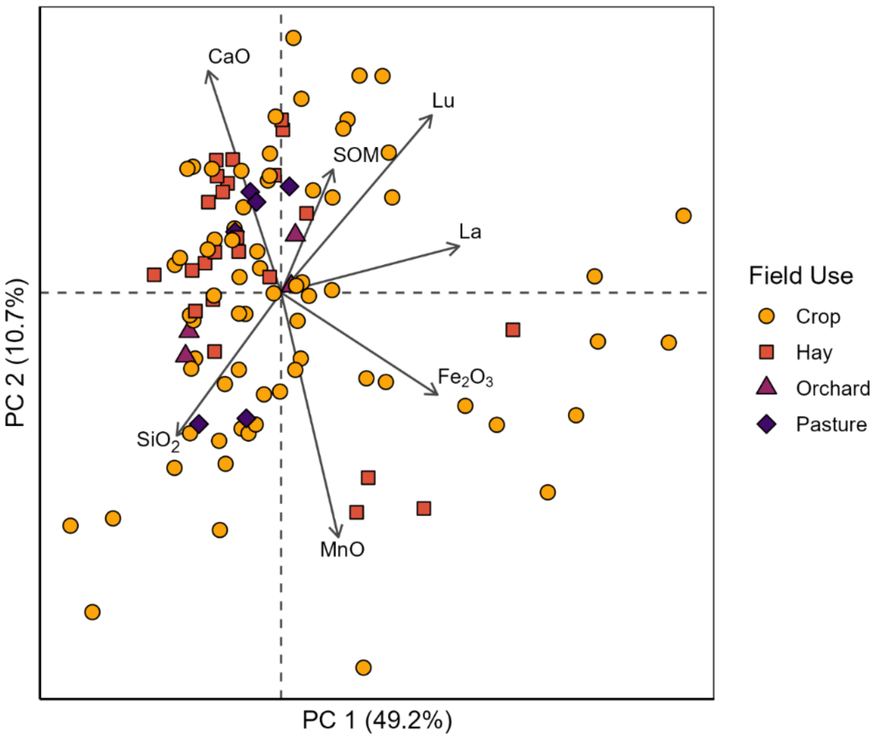


Figure 3.8. Simplified biplot with observations divided into the four field use categories.

3.4.5 Agglomerative hierarchical clustering

The agglomerative clustering results were divided into three clusters (supplementary Figure 3.S4). Of the three clusters, cluster 1 is the largest, containing 75% of the samples, while clusters 2 and 3 contain 16% and 9% of the samples, respectively (Figure 3.9). Clusters 1 and 2 exhibit greater similarity to each other than to cluster 3. Generally, samples from the same farms tended to cluster together, however, farms F, H, J, and M showed a split distribution with fields divided between at least two clusters (supplementary Figure 3.S4). Specifically, farms H and J had samples in both clusters 2 and 3, which shows greater difference in the characteristics of those samples, as opposed to being split between clusters 1 and 2. The three clusters are strongly influenced by PC1, indicating that the variable loadings associated with Fe and the LREE are driving the distribution of the observed clusters.

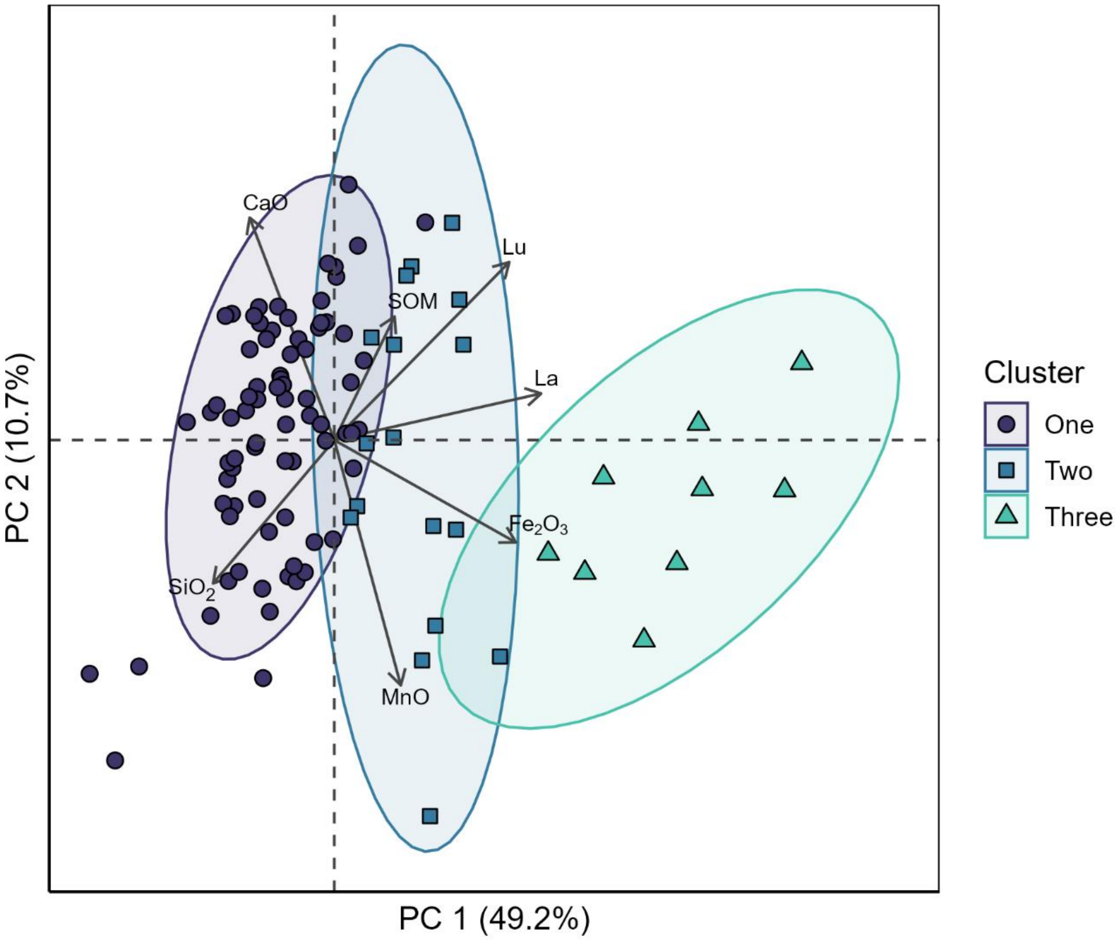


Figure 3.9. Simplified biplot of major identified loadings, along with data scores that are grouped by cluster. Note the generally undefined characteristics of cluster One, the cluster group with the greatest number of observations.

3.5 Discussion

3.5.1 Loading variable relationships

The associative relationship between element variables in the PCA, represented by the position of the loadings, can reveal geochemical trends that may be influenced by agricultural management. For example, one group of related loadings was the correlation between soil pH, CaO content, and SIC. Soil inorganic carbon is present in soils as carbonate minerals, a majority of which are calcium carbonates (An et al., 2019; Tan et al., 2014). Alkaline soils have been shown to have greater SIC content due to the greater concentrations of Ca and Mg (Tan et al., 2014). Calcium (and Mg) carbonates are linked to pH because as these minerals dissolve, they neutralize free H^+, altering the soil pH. The three-way relationship between SIC, CaO, and pH supports grouping them together in a representative loading, shown with CaO in the simplified biplot. In soils under intensive agriculture, the use of inputs may alter soil pH (e.g. elemental S, agricultural lime), which may differentiate intensively cultivated soils from soils not receiving these inputs. The position of the sample observations in relation to the variable loadings can help add context to the main drivers of the geochemical signature at the site. Taking the example of CaO again, the average Ca content of Ontario soils has been reported as 3.8 % (Aldis et al., 2023), which is comparable to this study (3.4 % ± 1.6). Farms A and L had the highest Ca concentrations out of all farms (6.0 ± 0.8 % and 6.3 ± 1.3 %, respectively). The position of the A and L observations in proximity to the CaO variable group indicates that high Ca content is a shared characteristic of these farms, which is related to both SIC and pH.

Inverse to the CaO and pH loadings, Fe_2O_3, Al_2O_3, MgO, K_2O, TiO_2, and multiple trace elements formed a large group of positively correlated elements that were a strongly associated with farms H and J. These elements are not applied as agricultural amendments (other than K), and it is unlikely that a group containing soil major oxides that are not amended to agricultural soils is influenced by anthropogenic agricultural activity. The positive correlation of major oxide concentrations according to Aldis et al. (2023) indicated that Fe_2O_3, Al_2O_3, and K_2O were derived from the same source mineralogy. The association of the trace elements with clays and soil oxy-hydroxides (often Fe- or Al-) indicates that this loading grouping may represent the clay-associated fraction of the soil (Aide & Aide, 2012; Shaheen et al., 2013). The trace elements associated with this grouping also support this, as elements like Rb and Cs are strongly associated with clay content in soils (Wampler et al., 2012).

Another main explanatory variable was SiO_2 (%) content, which is a major component of soil mineralogy and was uncorrelated with other loadings. The mean SiO_2 values reported in this study (64 ± 3 %) are comparable to the previously reported average values for Ontario (63.7 %; Aldis et al., 2023). In silicon rich soils, soil SiO_2 is not believed to be impacted by anthropogenic activity or agricultural management. Only in highly weathered soils can agricultural production reduce the pool of plant-available silica (Haynes, 2014). Therefore, the differences observed in SiO_2 content between farms are likely pedogenic. Observations from farm G were associated with the SiO_2 loading in the simplified biplot, and farm G had the highest SiO_2 content when compared to the other farms (69 ± 3; supplementary Table 3.S5). The high value of SiO_2 in farm G is likely reflective of natural variation in the soil texture.

Phosphorus and sulfur were positively correlated, but did not represent a group of major loadings as they were close to the origin of the simplified biplot. This group is of interest as P and S are both agricultural soil amendments and therefore may be related to anthropogenic activity. Total P is difficult to relate to soil geochemical background as multiple forms of P are amended to agricultural soils, e.g. organic manures and inorganic P fertilizers, and becomes enriched on farms relative to background (Blake et al., 2000; Reid & Schneider, 2019). Sulfur, in contrast does not accumulate in soils in the long term, due to the uptake by crops and losses from agricultural systems (Feinberg et al., 2021). The grouping of P and S, although potentially anthropogenic in nature, does not strongly influence the PCs or clustering results. Phosphorus and sulfur are not largely influencing the geochemistry of farms in this study and were not included on the simplified biplot.

The REEs separated into two loadings groups, one for the heavy rare earth elements (HREE) and one for the light rare earths (LREE). In the simplified biplot, the HREEs were indicated with Lu, while the LREEs were represented by the loading for La. The REEs were generally correlated with one another, but the LREEs were also correlated with the grouping of transition metal variables indicated by Fe content and together formed a strong predictor for PC1. The REEs were also negatively correlated with P content, indicating that P and REE concentrations may have different drivers in agricultural soils. Thought to be an avenue for the emerging contamination of the REEs, mineral phosphate fertilizers have been shown to have high REE content (Abdel-Haleem et al., 2001; Bergen et al., 2022; Ramos et al., 2016). The REEs then may be pedogenic in origin, and are known to be good tracers of pedogenic processes (Aide & Aide, 2012; Laveuf & Cornu, 2009). None of the farms or identified clusters were particularly enriched in REEs, and therefore it is unlikely then that HREEs or LREEs were a major determinants of soil geochemistry in this study.

Additionally, some variable loadings did not group with other variable loadings at all. Chromium concentrations, which were elevated on farm G, were not correlated with any other variables. Similarly, MnO, Y, Na, EC, and SOM did not correlate with other variables.

3.5.2 Clustering

The results of the clustering algorithm divided the observations into three clusters that were highly influenced by PC1. Overall, it is likely that the clustering is influenced by the trace element content in the Fe-related element grouping or the element grouping containing the LREEs, both of which are pedogenic in origin, not anthropogenic. In particular, cluster three contains observations of only farms J and H. These farms were noted previously to have high levels of Fe_2O_3 and were highly influenced by the Fe-related and LREE variables. Compared to cluster three, the observations in cluster one were notably undifferentiated and individual farms did not separate out from the cluster. Cluster one contained most of the observations in this study, which indicates that the clustering results did not differentiate farm geochemistry well at such a small spatial scale. Previous results by Garrett (2009) found that at a scale of 40 km^2 there existed significant differences in the geochemistry of sites. The clustering results separated farms H and J from the other farms, which were the farms located furthest to the east from the other farms.

The clustering results also had no association with agricultural management practices examined in this study. The loadings of the PCA which were identified as being most likely to be anthropogenic in nature (P and S, As and Pb), were not strongly associated with any clusters of observations. Potentially, agricultural management has a homogenizing effect on the natural variability of soil, with soil amendments reducing the heterogeneity of soils. In future work, clustering analysis for agricultural soil composition should be assessed on a smaller geographic scale, focusing on specific differences in agricultural input use (fertilizers and pesticides) to determine the impact on TE geochemistry.

3.5.3 Impact of farm management

No differentiation of the geochemical signature of sites was observed between different farm management practices. The indicators chosen for this study, field use and agricultural BMPs were not associated with geochemical partitioning of the observations. Major loading groups were not associated with the categorical BMPs. Therefore, there were no observable differences in the geochemical signature of fields based on agricultural management in this study.

The categorical indicators chosen were likely too broad to indicate clustering tendencies in the multivariate space. Since one main source of trace element contamination in agricultural soils is long-term fertilizer application to agricultural soils, accurate and detailed information about specific fertilizer application rates and formulations is needed. However, detailed histories of fertilization regimes are difficult to obtain as fertilization rates change annually and fertilizer formulations change to best address crop needs. Additionally, management history was only available for the length of time the current landholder was managing the farm. Furthermore, for those farms where detailed records could be obtained, extra fertilizer or manures were not available, barring the possibility that the amendment could be analysed for TE content. Documenting the relationship between fertilizer application and trace element accumulation in agricultural soils must therefore be founded on analyses of trace element content in agricultural amendments (Reboredo et al., 2019; Silva et al., 2019; Sun et al., 2022).

3.5.4 Trace metal concentrations

Legacy contamination on farms has implications for the continued use of fertilizers and pesticides containing TEs. In general, most of the elements of concern in fertilizers were below the environmental safety standards set by the CCME. Notable exceptions to this are the concentrations of As, Pb, and Cr. On farm B, As and Pb were both heavily enriched and far exceeded the guidelines in field B3, an apple orchard that has had a long-term history (50 years) of lead arsenate application as a foliar pesticide ($PbHAsO_4$). The soil concentrations of lead and arsenic are twice and four times greater than the Canadian soil quality standards, respectively. This shows the importance of geochemical analyses of soils, as past agricultural practices may have legacies of contamination that go unaddressed. Additional uses of fertilizers or pesticides on the site are only regulated for the potential of future accumulation, effectively ignoring what is already present and increasing the contaminant load. Additionally, the use of multiple fertilizers or pesticides is not regulated for the potential TE accumulation when amendments are used together. Although the enrichment of Pb and As is dramatic, it is isolated to a single field, indicating that As and Pb are not natural to the geochemical background of the site.

Also of note is the enrichment of Cr in the studied soils, where over half of the fields were above the Cr guidelines set by the CCME of 64 mg kg^{-1}. The concentrations of Cr in this study are not comparable to other concentrations previously reported in Ontario. A survey of 59 soils on southern Ontario farms found that the median *aqua regia* extractable Cr concentration in the 0-15 cm depth was 31 mg kg^{-1}, with a maximum of 70 mg kg^{-1} (Sheppard et al. , 2009b). However, most of the sampling done by Sheppard et al. (2009b) did not overlap with the current study area and represents an acid-extractable fraction of the total Cr. Whitby et al. (1978) determined the total Cr by atomic absorption spectro-photometry in southwestern Ontario, reporting a mean of 53 ± 19 mg kg^{-1}, with a maximum of 88 mg kg^{-1}. This is slightly lower than the mean total Cr in this study (72.1 ± 16.9), and lower than the maximum reported values of 154 mg kg^{-1}.

Since the concentrations of Cr are consistently high across all farms, it appears that the elevated Cr concentrations are a natural byproduct of pedogenesis. However, diffuse contamination from agricultural inputs cannot be ruled out. In studies on the concentration of Cr in agricultural amendments, fertilizer precursors (magmatic and sedimentary phosphatic rocks) had Cr content (Krüger et al., 2017). Whether anthropogenic in nature or not, the elevated Cr concentrations are one example of how a geochemical database of TE concentrations would be of great importance for determining levels of TEs that constitute contamination or reflect background variation.

3.6 Conclusion

This study highlights the importance of creating a baseline geochemical database for Canadian soils to understand the anthropogenic impacts of agriculture on soils. The samples collected in Southeastern Ontario contained elevated levels of trace element contaminants related to site history and agricultural inputs, as in the case of As and Pb. Additionally, throughout the studied region total chromium was significantly higher than the recommended environmental upper safety limit set by the CCME. Overall, soil geochemistry did not differ based on agricultural management practices, which included field use type, manure use, cover crop use, and tillage. The use of agricultural amendments such as phosphate fertilizers may have a homogenizing effect on soil geochemical characteristics, as seen in the cluster analysis. Natural soil heterogeneity is a greater driver of soil geochemistry than agricultural management at the studied scale. Therefore, geochemical analyses may be more suited to determining contamination in agricultural soils rather than assessing how soil composition is related to anthropogenic activity.

3.7 Supplementary Materials

3.7.1 3.6.1 Supplementary Figures

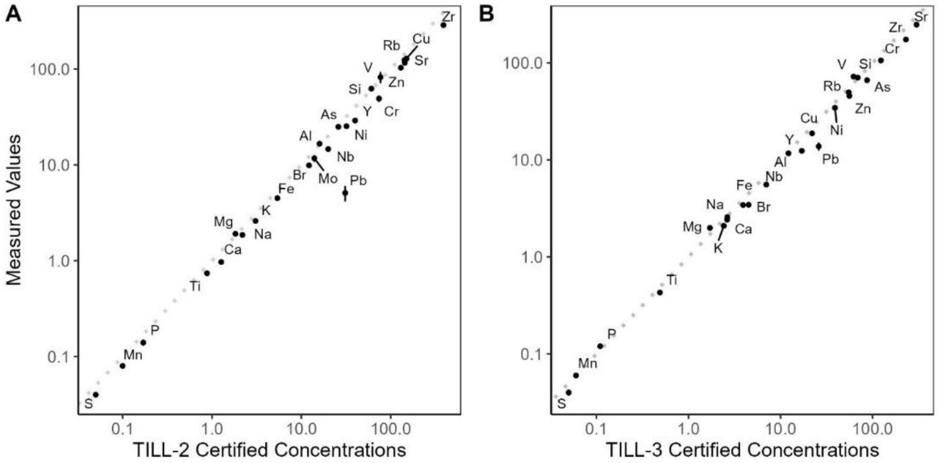


Figure 3.S1. Relationships between the measured values by ED-XRF and certified values of elements in (A) TILL-2 and (B) TILL-3 certified reference materials (Lynch, 1990). Note the low recovery of Pb in both reference materials when compared to the other elements. A perfect linear relationship between certified and reference values is represented by the dotted gray line.

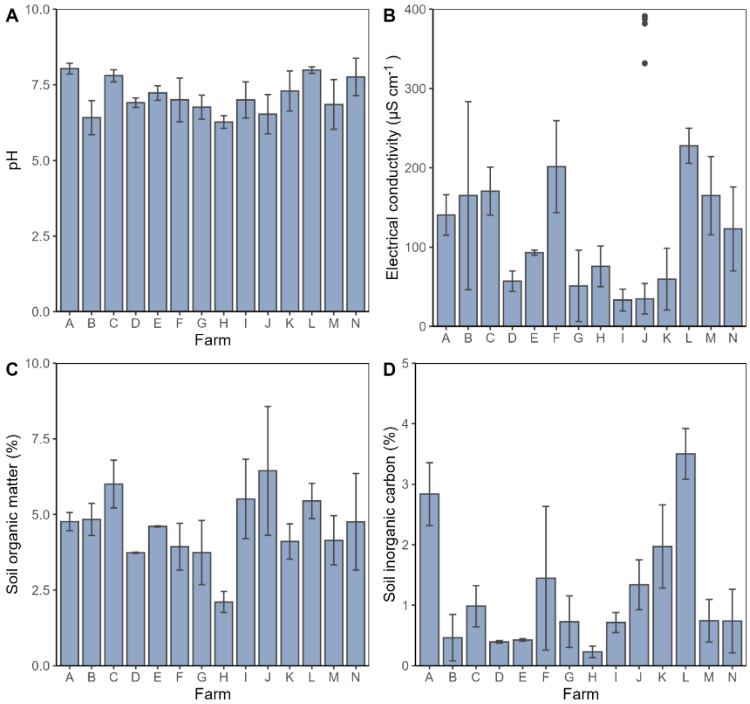


Figure 3.S2. Mean values (± sd) by farm of basic soil characteristics including (A) pH, (B) electrical conductivity, (C) soil organic matter, (D) and soil inorganic carbon.

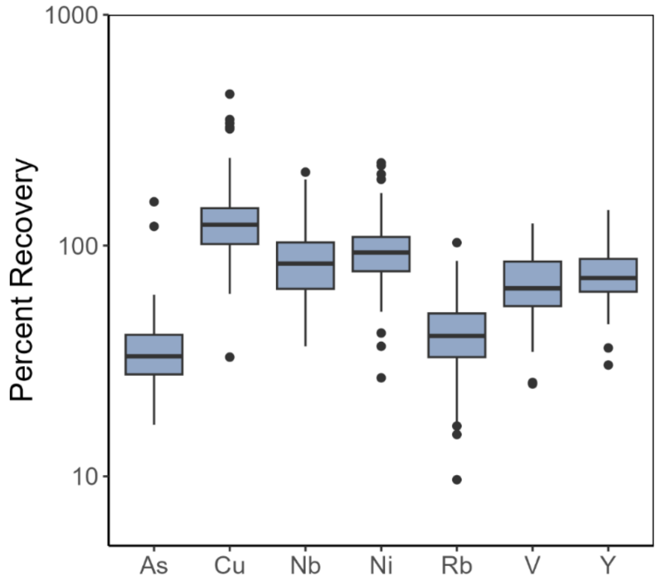


Figure 3.S3. Distribution of the percent recovery acid-leached V, Ni, Cu, As, Rb, Y, and Nb; taken as a percentage of total element concentrations determined by ED-XRF. Three outliers were excluded from the percent recovery distribution of copper.

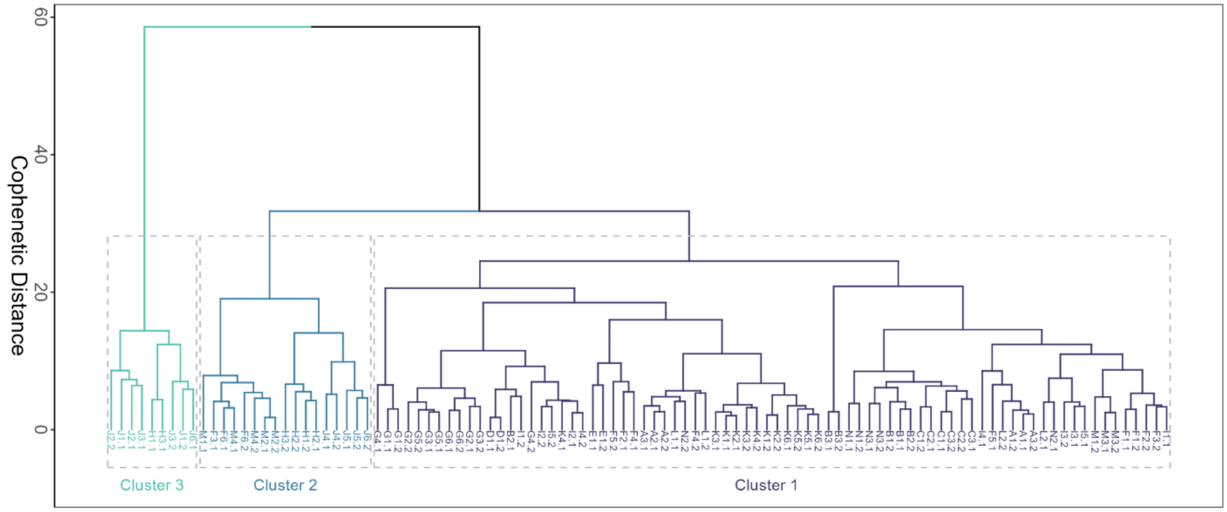


Figure 3.S4. Dendrogram of hierarchical clustering results, grouped into three clusters.

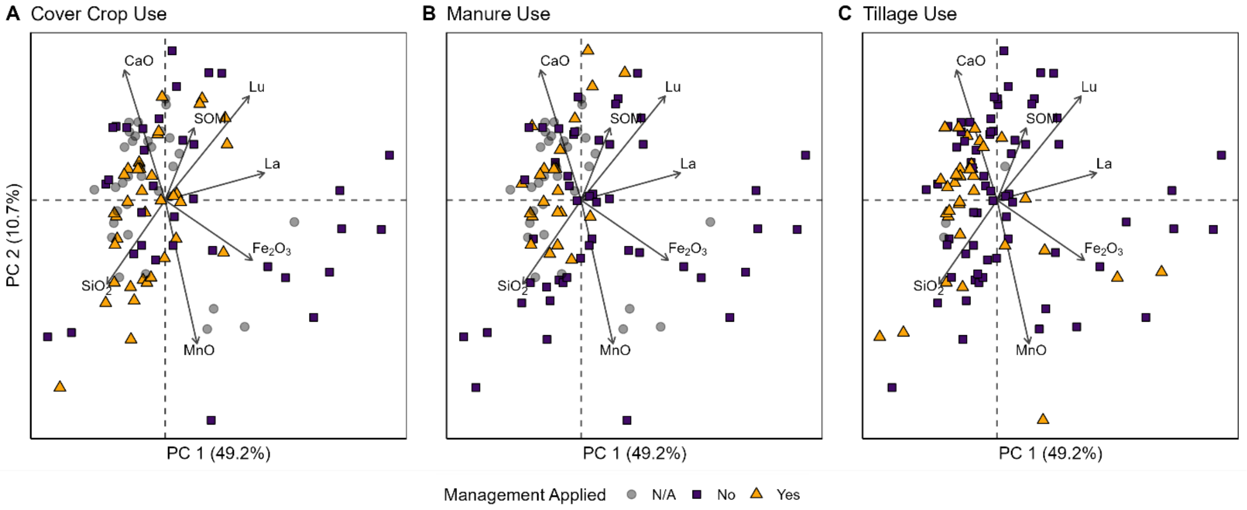


Figure 3.S5. Simplified biplots indicating the adoption of the agricultural management practices of (A) cover crops, (B) manure applications, and (C) tillage use. The management practices of cover crop use and manure application are not applicable for pasture, hay, and orchard cultivation. Tillage was not applicable only for orchard fields.

3.7.2 Supplementary Tables

Table 3.S1. Summary of field sites from farms A-N, including gathered information on tillage use, agricultural input summaries, and crop rotation pattern (or current stage).

Field	Tillage Use	Agricultural and Nutrient Input History	Crop rotation
A.1	No tillage	Chicken manure and compost (1:25 N:C ratio), early addition of urea ammonium nitrate (UAN) (45 lbs ac^{-1}), Mid-June applications of 120 lbs urea, additional 200g ac^{-1} micronutrients (150K:1Mg:1B)	Oat and barley, no CC
A.2	No tillage	-	Hay cultivation
A.3	No tillage	-	Hay cultivation
B.1	No tillage	Unknown subsurface fertilizer inputs	Corn, adzuki bean, winter wheat, with variety CC
B.2	No tillage	Unknown subsurface fertilizer inputs	Corn, adzuki bean, winter wheat, with variety CC
B.3	No tillage	50-year historical use of lead arsenate ($PbHAsO_4$) as foliar pesticide.	Apple Orchard
C.1	Tillage	Organic production, spring use of liquid urea, use of pellet N source in the fall (55-26-30), horse, chicken, and cattle	Unknown rotation, Corn with multi-species CC is in use.

		manure were also applied at unknown rates	
C.2	Tillage	Organic production	Hay cultivation
C.3	Tillage	Organic production	Pasture
D.1	No tillage	-	Apple Orchard
E.1	No tillage (2017)	Chicken manure, previous use of compost, humates, biostimulants, chemical fertilizer use of urea (UAN 28), ammonium thiosulfate (ATS), potassium, boron,	Corn, soybean, and winter wheat with variety CC
F.1	No tillage (40 years)	-	Hay cultivation
F.2	No tillage (40 years)	-	Hay cultivation
F.3	No tillage (40 years)	Unknown N-P-K, 300 lbs ac^{-1}	Corn, soybean, and winter wheat, followed by hay for three years
F.4	No tillage (40 years)	Manure applications	Corn, soybean, and winter wheat, followed by hay for three years
F.5	No tillage (40 years)	Manure applications	Corn, soybean, and winter wheat, followed by hay for three years
F.6	No tillage (40 years)	Unknown N-P-K, 300 lbs ac^{-1}	Corn, soybean, and winter wheat, followed by hay for three years
G.1	Tilled	Unknown chemical fertilizer use	Corn, soybean, and winter wheat
G.2	No tillage	Unknown chemical fertilizer use	Corn, soybean, and winter wheat, with oats and peas as CC
G.3	No tillage	Unknown chemical fertilizer use	Corn, soybean, and winter wheat with sorghum CC
G.4	No tillage	Unknown chemical fertilizer use	Corn, soybean, and winter wheat with cereal rye CC
G.5	No tillage	Unknown chemical fertilizer use	Corn, soybean, and winter wheat, with oats and buckwheat as CC
G.6	Minimal tillage	Unknown chemical fertilizer use	Corn, soybean, and winter wheat with cereal rye CC
H.1	No tillage (50 years)	-	Hay cultivation
H.2	No tillage (50 years)	-	Hay cultivation
H.3	Tillage	Unknown chemical fertilizer use	Corn and soybeans were observed

I.1	No tillage	Manure inputs, unknown chemical fertilizer use	Wheat or rye, CC of volunteer oats
I.2	No tillage	-	Pasture
I.3	No tillage	-	Hay cultivation
I.4	No tillage	Manure inputs, unknown chemical fertilizer use	Corn silage, wheat, or rye
I.5	No tillage	Manure inputs, unknown chemical fertilizer use	Wheat or rye, CC of volunteer oats
J.1	No tillage	Unknown chemical fertilizer use	Corn, soybean, winter wheat, with CC (barley, oats, cereal rye)
J.2	No tillage	Unknown chemical fertilizer use	Corn, soybean, winter wheat, with CC (barley, oats, cereal rye)
J.3	No tillage	Unknown chemical fertilizer use	Corn, soybean, winter wheat, with CC (barley, oats, cereal rye)
J.4	No tillage	Unknown chemical fertilizer use	Corn, soybean, winter wheat, with CC (barley, oats, cereal rye)
J.5	Tillage	Unknown chemical fertilizer use	Wheat and soybeans
J.6	Tillage	Unknown chemical fertilizer use	Wheat and soybeans
K.1	Tillage	Cattle manure (3 years)	Oats and red clover CC
K.2	Tillage	-	Hay cultivation
K.3	Tillage	-	Hay cultivation
K.4	Tillage	-	Hay cultivation
K.5	Tillage	Cattle manure (3 years)	Oats and red clover CC
K.6	Tillage	Cattle manure (3 years)	Wheat and red clover CC
L.1	No tillage (14 years)	-	Hay
L.2	No tillage (14 years)	No Manure use, 9-9-25 NPK with 3% Mg at 175 lbs ac^{-1}	Wheat and soy, red clover CC
M.1	No tillage	Unknown chemical fertilizer use	Corn, soy, and wheat rotation with a year of fallow with mixed CC
M.2	No tillage	Unknown chemical fertilizer use	Corn, soy, and wheat rotation with a year of fallow with mixed CC
M.3	No tillage	Unknown chemical fertilizer use	Corn, soy, and wheat rotation with a year of fallow with mixed CC
M.4	No tillage	Unknown chemical fertilizer use	Corn, soy, and wheat rotation with a year of fallow with mixed CC
N.1	Tillage	150 lbs ac^{-1} of ½ MAP and ½ MEZ with 10 lbs of Sulfur	Continuous corn

N.2			Pasture field
N.3	Tillage	200 lbs ac^{-1} of ½ MAP and ½ MEZ with 10 lbs of Sulfur	Corn cultivation

Table 3.S2. Measured concentrations of 26 major elements by ED-XRF in reference materials TILL-2 (n = 4) and TILL-3 (n = 3) compared to certified values (Lynch, 1990).

		TILL-2			**TILL-3**		
Element	Unit	Mean	SD	Certified Values	Mean	SD	Certified Values
Na_2O	%	1.86	0.05	2.19	2.57	0.06	2.64
MgO	%	1.91	0.03	1.83	1.99	0.03	1.71
Al_2O	%	16.6	0.04	16	11.7	0.10	12.2
SiO_2	%	62.3	0.07	60.8	70.5	0.03	69.1
P_2O_5	%	0.14	0.01	0.17	0.12	0.004	0.11
S	%	0.04	0.001	<0.05	0.04	0.003	<0.05
Cl	ppm	85.7	9.53		107	9.02	
K_2O	%	2.60	0.003	3.07	2.09	0.01	2.42
CaO	%	0.97	0.01	1.27	2.42	0.13	2.63
TiO_2	%	0.74	0.003	0.88	0.43	0.004	0.49
V	ppm	82.0	10.8	77	72.3	3.30	62
Cr	ppm	49.1	3.79	74	106	2.80	123
MnO	%	0.08	0.001	0.1	0.06	0.0004	0.06
Fe_2O_3	%	4.49	0.02	5.39	3.43	0.02	3.92
Ni	ppm	25.3	0.45	32	34.4	0.43	39
Cu	ppm	128	1.31	150	18.8	0.46	22
Zn	ppm	103	0.86	130	45.7	0.66	56
As	ppm	24.9	0.60	26	66.2	1.15	87
Br	ppm	9.87	0.13	12.2	3.45	0.03	4.5
Rb	ppm	124	1.80	143	49.7	0.38	55
Sr	ppm	116	1.26	144	248	3.11	300
Y	ppm	29.0	1.18	40	12.4	0.23	17
Zr	ppm	287	6.77	390	174	3.24	230
Nb	ppm	14.6	0.70	20	5.56	0.22	7
Mo	ppm	11.7	0.93	14	n.d.	n.d.	2
Pb	ppm	5.09	0.93	31	13.8	1.33	26
Carbon	%			8.1			4.6

Table 3.S3. Measured concentrations of trace elements in *aqua regia* leached soils from certified reference materials MESS-4 and HISS-1 (n = 3; ref; Berman et al., 1997; Willie et al., 2014).

	MESS-4					**HISS-1**				
Element	Mean	SD	Certified Values			Mean	SD	Certified Values		
Sb	1.71	1.37	1.07	±	0.2	0.05	0.03	0.13	±	
As	28.3	2.66	21.7	±	2.8	1.19	0.67	0.801	±	0.099

Be	1.32	0.54	2.09	±	0.3	0.04	0.05	0.129	±	0.023
Bi	1.37	2.16	2.7							
Cs	7.62	1.46	10							
Cd	0.40	0.06	0.28	±	0	0.15	0.29	0.024	±	0.009
Ce	59.1	10.9	72							
Cr	68.4	12.0	94.3	±	1.8	6.16	0.69	30	±	6.8
Co	16.1	1.54	13	±	0.8	0.57	0.13	0.65		
Cu	46.6	8.33	32.9	±	1.8	4.50	3.91	2.29	±	0.37
Eu	1.44	0.27	1.3							
Ga	14.1	2.43	18							
Ge	1.22	0.39	0.16							
Hf	1.02	1.74	3							
La	29.3	5.13	35							
Pb	32.2	5.03	21.5	±	1.2	3.38	1.46	3.13	±	0.4
Li	38.9	15.2	65.3	±	6.8	0.89	1.00	2.83	±	0.54
Lu	0.22	0.05	0.11							
Mo	4.21	1.86	2.53	±	0.1					
Nd	29.5	5.24	42							
Ni	53.0	4.83	42.8	±	1.6	4.36	4.29	2.16	±	0.29
Nb	2.78	3.94	12							
Re	0.07	0.17	0.004							
Rb	88.0	17.0	180							
Sm	6.44	1.08	5.5							
Se	4.48	9.02	1.5			0.42	1.17	0.05	±	0.007
Ag	0.13	0.32				0.86	2.27	0.016	±	0.016
Ta	2.43	4.96	1							
Tl	12.3	1.89	0.85	±	0.1					
Th	3.43	8.55	12							
W	2.26	0.34	1.3							
U	168	31.3	3.4	±	0.4	0.36	0.27	0.26		
V	1.43	0.26	216	±	8	6.42	0.99	6.8	±	0.78
Yb	18.2	1.82	2							
Y	185	42.6	20							
Zn	17.3	7.13	147	±	6	8.32	9.90	4.94	±	0.79
Zr	1.71	1.37	96							

Table 3.S4. Average measured concentrations (n = 3) of 40 elements by ICP-MS in SLRS-6 compared to certified concentrations (Yang et al., 2015). Certified values marked with an * are reported in Yeghicheyan et al. (2019).

	Measured Concentrations (ppb)			**Certified Values (ppb)**		
Sb	0.341	±	0.065	0.34	±	0.006
As	0.59	±	0.07	0.57	±	0.08
Be	0.007	±	0.004	0.0066	±	0.0022
B	5.92	±	2.8	7.39*	±	1.2

Cd	0.013	±	0.005	0.0063	±	0.0014
Ce	0.299	±	0.006	0.2927*	±	0.0151
Cs	0.008	±	0.003	0.0046*	±	0.0005
Cr	1.24	±	1.7	0.25	±	0.012
Co	0.078	±	0.05	0.053	±	0.012
Cu	25.1	±	2.1	24	±	1.8
Dy	0.024	±	0.001	0.0219*	±	0.0011
Er	0.013	±	0.0002	0.0124*	±	0.0007
Eu	0.009	±	0.0004	0.0073*	±	0.00035
Gd	0.031	±	0.001	0.0316*	±	0.0025
Ga	0.024	±	0.008	0.011*	±	0.007
Ge	0.032	±	0.02	0.01*	±	0.007
Hf	0.128	±	0.08	0.0095*	±	0.0004
Ho	0.005	±	0.001	0.0043*	±	0.0003
La	0.261	±	0.02	0.2483*	±	0.0121
Pb	0.206	±	0.05	0.17	±	0.026
Li	0.402	±	0.15	0.53*	±	0.025
Lu	0.003	±	0.0003	0.00191*	±	0.00023
Mo	0.230	±	0.14	0.215	±	0.018
Nd	0.235	±	0.009	0.2278*	±	0.0094
Ni	3.87	±	5.7	0.617	±	0.02
Nb	0.071	±	0.06	0.0081*	±	0.0057
Pr	0.061	±	0.001	0.0591*	±	0.0019
Re	0.017	±	0.003	0.0135*	±	0.0002
Rh	0.003	±	0.001	0.00069*	±	0.00017
Rb	1.41	±	0.1	1.41*	±	0.05
Sm	0.039	±	0.0005	0.0395*	±	0.0017
Sc	0.108	±	0.16	0.33*	±	0.015
Tb	0.005	±	0.001	0.00407*	±	0.00027
Tl	0.134	±	0.11	0.0085*	±	0.0029
Th	0.003	±	0.0005	0.00179*	±	0.0002
U	0.075	±	0.002	0.07	±	0.0034
V	0.352	±	0.04	0.35	±	0.006
Yb	0.012	±	0.001	0.0112*	±	0.0007
Y	0.127	±	0.009	0.128*	±	0.006
Zn	2.36	±	0.7	1.76	±	0.12
Zr	0.261	±	0.10	0.062*	±	0.011

Table 3.S5. Mean and standard deviation of major element concentrations (%) presented by farm. Note the inclusion of LOI, which is just the sum of the SOM and SIC values for each sample. The mean LOI is presented by farm to represent the carbon fraction of the soil that cannot be analysed by ED-XRF.

	n		**SiO_2**	**Al_2O_3**	**Fe_2O_3**	**CaO**	**MgO**	**Na_2O**	**K_2O**	**TiO_2**	**P_2O_5**	**MnO**	**LOI**
A	6	mean	61.9	12.7	4.86	6.04	1.78	1.48	2.22	0.74	0.29	0.12	7.6
		sd	0.84	0.24	0.23	0.81	0.05	0.15	0.04	0.02	0.03	0.012	0.38
B	6		66.2	13.3	4.59	2.84	1.82	1.97	2.56	0.79	0.35	0.10	5.3
			0.63	0.18	0.31	0.29	0.08	0.12	0.07	0.03	0.03	0.008	0.54
C	6		65.1	12.7	4.39	3.67	1.62	1.58	2.36	0.74	0.41	0.12	7.0
			0.69	0.04	0.20	0.46	0.07	0.07	0.04	0.01	0.06	0.012	0.48
D	2		67.5	13.6	4.71	2.61	1.35	2.10	2.52	0.80	0.33	0.15	4.1
			0.02	0.21	0.01	0.11	0.01	0.06	0.09	0.01	0.02	0.001	0.0
E	2		65.6	12.7	5.57	3.71	1.48	1.52	2.19	0.90	0.81	0.14	5.0
			0.72	0.34	0.81	0.51	0.01	0.34	0.06	0.01	0.04	0.004	0.0
F	12		64.9	13.0	4.60	4.53	1.79	2.04	2.44	0.78	0.28	0.10	5.4
			2.23	0.83	0.40	2.10	0.24	0.22	0.21	0.05	0.09	0.013	1.4
G	12		68.8	12.8	4.31	2.69	1.91	0.97	2.66	0.75	0.38	0.14	4.5
			2.79	0.87	0.45	0.51	0.29	0.29	0.10	0.03	0.14	0.023	1.4
H	6		64.7	15.3	6.75	2.14	3.00	0.92	3.27	1.00	0.22	0.19	2.3
			1.52	0.57	0.81	0.42	0.29	0.27	0.16	0.05	0.06	0.032	0.36
I	10		64.5	13.6	4.84	2.77	2.09	1.97	2.67	0.80	0.23	0.12	6.2
			1.18	0.32	0.32	1.27	0.18	0.20	0.17	0.03	0.03	0.018	1.4
J	12		61.7	14.5	6.34	1.91	2.53	0.53	3.22	0.88	0.30	0.16	7.8
			3.01	1.25	1.33	0.73	0.19	0.13	0.14	0.12	0.12	0.029	1.9
K	12		64.6	13.1	4.9	4.05	1.76	1.83	2.25	0.82	0.25	0.13	6.1

		1.38	0.39	0.24	1.28	0.14	0.17	0.12	0.03	0.05	0.015	1.0
L	4	60.7	12.5	4.84	6.29	1.81	1.29	2.30	0.76	0.27	0.13	8.9
		1.40	0.53	0.04	1.26	0.15	0.08	0.05	0.07	0.04	0.011	0.74
M	8	65.3	13.8	4.99	2.98	2.14	1.78	2.64	0.81	0.30	0.11	4.9
		0.88	0.43	0.36	0.29	0.18	0.23	0.11	0.02	0.04	0.007	0.80
N	6	66.6	12.8	4.41	3.54	1.48	1.87	2.38	0.76	0.33	0.12	5.5
		2.79	0.27	0.57	0.62	0.26	0.40	0.10	0.06	0.08	0.013	1.8

Table 3.S6. Summary statistics of the total TEs (mg kg^{-1}) for the entire data set (n = 104), measured with XRF. Mean values and standard deviation by farm can be found in supplementary Table 3.S7. Environmental safety standards for agricultural soils are included when available (Canadian Council of Ministers of the Environment, 2024).

Element	**Mean**	**SD**	**Median**	**1st Q**	**3rd Q**	**CCME Guideline**
S	646	135	634	563	705	-
Zr	376	85.7	385	334	434	-
Sr	335	65.5	331	300	358	-
Cl	248	40.4	247	221	269	-
V	98.3	23.9	95	80.6	115	130
Zn	94.9	27.9	86.7	76.7	108	250
Rb	86.4	25.9	78.1	71.5	88.7	-
Cr	72.1	16.9	69.3	60.4	79.8	64
Y	36.2	5.7	36.3	32.3	40	-
Ni	23.4	6.7	21.4	19.5	24.2	45
Cu	16.8	11.7	12.9	10.1	18.3	63
Nb	10.3	1.9	10.1	9.08	10.7	-
As	10.2	5.8	9.3	8.1	11.1	12
Br	7.74	3.8	6.9	5.7	8.73	-

Table 3.S7. Summary of the mean and standard deviation of total trace element concentrations (mg kg^{-1}), presented by farm.

	n		**S**	**Zr**	**Sr**	**Cl**	**V**	**Zn**	**Rb**	**Cr**	**Y**	**Ni**	**Cu**	**Nb**	**As**	**Br**
A	6	mean	685	406	359	249	86.1	80.8	75.1	63.8	39.6	19.9	11.6	9.47	10.5	7.85
		sd	36	33	20	14	17	6.5	4.2	6.1	2.1	1.2	2.2	1.1	0.84	0.57

B	6	663	424	342	284	86.1	92.1	75.6	73.5	38.5	19.7	21.0	10.0	22.3	8.55
		66	16	24	25	10	16	5.3	10	4.7	2.0	13	0.51	21	1.9
C	6	847	431	337	253	89	86.5	72.3	66.5	37.3	19.6	12.1	9.67	8.05	7.87
		98	20	12	17	16	5.5	3.3	5.9	2.6	1.4	2.9	0.72	0.55	1.8
D	2	699	513	413	262	78.2	79.4	78.7	68.8	38.9	18.2	6.75	11.8	7.9	5.9
		25	3.5	3.3	24	8.3	0.21	2.7	0.28	3.7	0.78	1.2	0.71	1.1	0.14
E	2	1081	564	481	290	131	130	78.2	73.5	46.2	24.8	22.6	13.0	11.8	9.75
		73	115	125	49	33	19	16	5.2	11	5.6	0.21	2.4	0.49	1.1
F	12	629	404	369	278	95.2	74.0	71.0	70.7	36.3	20.2	12.5	9.86	7.94	6.92
		214	65	63	37	20	7.2	6.3	18	3.5	1.9	3.2	1.3	1.2	2.4
G	12	668	354	358	225	93.9	103	84.2	93.9	29.2	21.0	10.1	9.72	7.29	5.27
		117	45	88	55	20	21	10	27	3.6	2.7	2.9	1.2	1.1	1.1
H	6	663	247	357	273	122	133	136	74.4	35.1	35.6	28.4	13.3	11.6	8.37
		80	37	78	38	15	29	25	10	8.7	6.6	9.5	1.9	1.3	2.4
I	10	560	340	307	249	85.8	87.8	82.6	63.6	31.0	23.1	12.8	10.2	9.00	5.63
		85	52	33	22	12	12	9.9	14	4.3	2.9	3.2	0.74	1.0	1.1
J	12	611	252	233	194	121	130	130	74.0	35.3	34.7	38.7	12.1	11.6	14.1
		66	66	29	24	37	42	35	15	4.9	8.5	16	3.3	1.7	7.4
K	12	557	417	339	224	109	76.3	70.5	69.8	38.6	21.2	10.3	8.90	9.64	5.51
		51	46	31	16	14	6.4	5.2	14	4.4	2.0	1.7	1.1	0.88	0.92
L	4	612	373	334	239	88.4	83.5	80.9	63.7	40.9	20.3	12.9	9.78	10.7	7.73
		71	72	32	8.8	13	9.4	3.9	13	2.4	0.73	3.2	0.97	0.35	0.64
M	8	614	398	339	290	99.1	107	82.9	69.9	39.0	24.1	20.7	10.3	11.2	8.74
		105	36	31	16	18	15	8.9	12	3.5	1.4	3.7	0.73	2.0	1.3
N	6	655	452	335	246	78.6	70.6	72.5	65.6	38.8	18.4	8.32	9.77	8.35	6.68
		85	67	38	11	21	13	13	13	6.6	4.1	3.4	1.0	1.9	1.7

Table 3.S8. Summary of the mean and sd of acid-leachable TE concentrations (mg kg^{-1}), presented by farm.

		Farm													
		A	B	C	D	E	F	G	H	I	J	K	L	M	N
n		6	6	6	2	2	12	12	6	10	12	12	4	8	6
Li	*mean*	11.2	15.2	13.6	6.2	8.3	10.7	5.7	14.3	17.2	16.6	10.7	17.5	7.6	13.1
	sd	2.8	1.6	1.0	0.2	0.4	3.9	2.3	3.2	5.9	6.7	1.0	3.8	1.2	4.9
Co	*mean*	9.1	9.5	8.4	6.6	7.0	10.4	6.5	20.5	15.5	22.3	9.0	9.3	10.3	8.0
	sd	1.6	2.3	1.5	0.2	1.1	3.3	2.3	3.7	4.8	9.5	0.9	2.0	1.7	2.2
Ga	*mean*	9.8	10.5	11.9	8.1	8.3	9.2	6.6	16.0	12.4	17.6	8.0	12.4	9.1	10.2
	sd	1.6	2.1	1.2	0.7	1.0	2.5	2.2	3.5	3.4	6.3	0.8	1.9	1.1	2.8
Ge	*mean*	2.2	2.5	2.4	1.7	2.0	1.4	0.7	1.4	2.1	1.6	1.4	2.4	1.1	2.8
	sd	0.4	0.3	1.4	0.0	0.4	0.4	0.2	0.2	0.4	0.4	0.1	1.0	0.2	0.8
Cd	*mean*	0.3	0.5	0.6	0.2	0.3	0.3	0.3	0.6	0.3	0.7	0.2	0.3	0.5	0.5
	sd	0.1	0.2	0.3	0.0	0.0	0.1	0.1	0.1	0.1	0.2	0.0	0.3	0.1	0.2
Cs	*mean*	1.8	1.4	1.8	0.9	1.0	1.5	1.9	3.6	2.0	4.1	1.4	1.9	2.0	1.6
	sd	0.3	0.2	0.3	0.0	0.1	0.4	0.9	0.8	0.4	1.6	0.1	0.6	0.3	0.5
Pb	*mean*	15.1	72.0	15.6	11.6	17.7	13.7	15.3	26.7	14.1	29.9	13.0	13.8	26.0	14.8
	sd	2.6	86.7	1.6	1.0	1.4	4.5	3.3	4.3	3.9	7.5	1.5	1.3	8.6	2.1
Th	*mean*	5.0	4.4	3.7	4.1	2.0	5.7	4.4	11.0	5.9	12.4	3.9	4.4	7.5	4.1
	sd	0.6	0.8	0.3	0.0	1.0	2.4	1.8	2.5	2.1	4.8	0.8	0.3	1.6	0.7
U	*mean*	1.0	1.8	1.3	0.9	1.3	1.4	0.9	1.4	1.1	2.5	0.8	1.1	3.1	1.0
	sd	0.1	0.2	0.1	0.0	0.2	0.3	0.2	0.3	0.3	1.2	0.1	0.1	1.1	0.0
La	*mean*	40.5	35.7	28.9	28.3	30.2	38.5	26.3	55.4	35.3	64.5	26.6	31.5	47.1	29.9
	sd	5.4	7.7	3.2	0.3	6.1	10.9	7.8	15.0	7.8	18.7	3.2	4.9	9.0	5.1
Ce	*mean*	82.1	74.7	67.2	67.9	64.7	90.1	65.8	137.8	86.1	157.7	63.1	71.7	103.9	70.3
	sd	11.1	11.5	5.8	3.0	10.9	24.4	17.2	23.9	23.9	43.0	6.4	11.7	15.1	8.8
Pr	*mean*	10.2	9.1	8.2	6.9	7.7	10.4	7.4	14.4	8.9	16.6	7.4	9.1	12.6	8.4
	sd	1.3	1.5	0.7	0.1	1.6	2.8	2.2	3.7	2.1	4.4	0.8	1.3	2.1	1.3
Nd	*mean*	39.6	35.5	32.8	26.4	30.1	41.7	30.0	57.2	34.4	65.7	29.7	36.4	50.9	33.8
	sd	4.9	5.3	2.8	0.2	6.1	10.9	8.8	15.1	8.8	16.9	3.1	4.7	8.5	5.0
Sm	*mean*	7.8	6.8	6.9	5.3	6.0	8.2	5.7	10.9	6.8	12.5	6.0	6.7	9.9	6.8
	sd	1.0	1.2	0.7	0.1	1.2	2.2	1.7	2.9	1.7	3.1	0.6	0.9	1.6	1.2
Eu	*mean*	1.5	1.4	1.3	1.0	1.2	1.6	1.1	2.1	1.3	2.3	1.2	1.4	1.9	1.4
	sd	0.2	0.2	0.1	0.0	0.2	0.4	0.3	0.6	0.3	0.5	0.1	0.2	0.3	0.2
Gd	*mean*	7.1	6.3	6.0	4.8	5.5	7.3	4.9	9.2	6.1	10.6	5.6	6.5	8.7	6.2
	sd	1.0	1.0	0.4	0.2	1.1	1.9	1.5	2.5	1.6	2.6	0.6	0.9	1.4	0.8
Tb	*mean*	1.0	0.9	0.9	0.7	0.8	1.1	0.7	1.3	0.9	1.4	0.8	1.0	1.2	0.9
	sd	0.1	0.1	0.1	0.0	0.1	0.3	0.2	0.4	0.2	0.4	0.1	0.2	0.2	0.1
Dy	*mean*	6.0	5.2	4.8	4.3	4.7	6.3	3.9	7.3	5.2	8.2	4.8	5.2	7.3	5.2
	sd	1.0	1.0	0.2	0.2	0.9	1.6	1.1	2.1	1.3	2.0	0.5	0.4	1.2	0.6
Ho	*mean*	1.2	1.1	1.0	0.9	0.9	1.3	0.8	1.4	1.0	1.6	1.0	1.1	1.5	1.1
	sd	0.2	0.2	0.0	0.1	0.2	0.3	0.2	0.4	0.3	0.4	0.1	0.2	0.2	0.1
Er	*mean*	3.4	2.9	2.6	2.5	2.6	3.5	2.1	3.9	2.9	4.3	2.7	2.8	4.1	2.8
	sd	0.6	0.5	0.3	0.2	0.4	0.9	0.6	1.1	0.8	1.0	0.3	0.5	0.7	0.3
Tm	*mean*	0.5	0.4	0.5	0.3	0.3	0.5	0.3	0.5	0.4	0.6	0.4	0.4	0.5	0.6
	sd	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.1	0.1	0.1	0.0	0.1	0.1	0.1
Yb	*mean*	3.0	2.6	2.5	2.2	2.2	3.3	1.8	3.5	2.6	3.8	2.4	2.7	3.8	2.7
	sd	0.5	0.4	0.1	0.1	0.3	0.9	0.5	1.0	0.7	0.9	0.3	0.4	0.6	0.3
Lu	*mean*	0.4	0.4	0.3	0.3	0.3	0.5	0.3	0.5	0.4	0.6	0.3	0.4	0.5	0.4
	sd	0.1	0.1	0.1	0.0	0.0	0.1	0.1	0.2	0.1	0.1	0.0	0.0	0.1	0.1

Table 3.S9. Variable loadings for PC1 and PC2. Loadings with values closer to 1 or -1 have a greater impact on the principal component as they represent the correlation between the original variables and the PCs.

Variable	**PC1**	**PC2**
pH	-0.079	0.177
EC	0.021	0.181
SOM	0.056	0.130
SIC	-0.023	0.163
Li	0.121	0.108
Co	0.179	0.047
Ga	0.178	0.032
Ge	0.018	0.205
Cd	0.137	0.025
Cs	0.185	-0.075
La	0.194	0.049
Ce	0.193	-0.008
Pr	0.194	0.055
Nd	0.193	0.059
Sm	0.191	0.075
Eu	0.186	0.101
Gd	0.189	0.107
Tb	0.185	0.131
Dy	0.181	0.142
Ho	0.177	0.163
Er	0.174	0.169
Tm	0.144	0.240
Yb	0.169	0.189
Lu	0.164	0.188
Pb	0.055	0.006
Th	0.190	-0.045
U	0.145	0.066
Na_2O	-0.096	0.207
MgO	0.152	-0.173
Al_2O_3	0.165	-0.126
SiO_2	-0.113	-0.151
P_2O_5	-0.045	-0.048
S	-0.038	-0.019
Cl	-0.054	0.072
K_2O	0.131	-0.244
CaO	-0.079	0.235
TiO_2	0.139	-0.145
V	0.102	-0.092
Cr	-0.045	-0.165

MnO	0.062	-0.259
Fe_2O_3	0.170	-0.108
Ni	0.171	-0.157
Cu	0.167	-0.088
Zn	0.146	-0.181
As	0.045	0.013
Br	0.128	0.027
Rb	0.168	-0.190
Sr	-0.102	0.012
Y	0.039	0.211
Zr	-0.125	0.174
Nb	0.130	-0.139

4 Rare earth element concentration, fractionation, and association with agricultural management in Ontario agricultural soils

4.1 Abstract

Despite the increasing use of rare earth elements (REEs) in technological and agricultural applications, their background concentrations in Canadian soils remain effectively unknown. To describe the concentrations and fractionation patterns of the REEs in agricultural soils, soil REE concentrations were determined from fourteen farms in Southeastern Ontario. The measured REE concentrations did not show significant differences from the Post Archaean Australian Shale reference material (PAAS); their concentrations varied between 30% to 300% of the PAAS abundance. We also observed typical REE fractionation patterns in soils with an enrichment of the middle REEs (Sm, Eu, Gd, Tb, Dy), representing significantly different fractionation patterns than those measured in fertilizers. The variation in REE concentrations were therefore associated with soil lithology and retention on clay particles rather than enrichment related to mineral fertilizer amendment. Background geochemistry had a greater impact on REE concentrations than did agricultural management. Overall, REE concentrations in soils may be representative of background concentrations, which may open avenues to incorporate these elements as plant growth promoters.

4.2 Introduction

Rare earth elements are an emerging area of research for agricultural production due to their potential for plant growth promotion (Tommasi et al., 2021; Tyler, 2004). Environmental studies concerning REEs often focus on their role as TE contaminants due to the release of REEs to the environment from their use in high-tech industries (Bispo et al., 2021; Tyler, 2004; Volokh et al., 1990). Yet, REEs have also been applied as an exogenous fertilizers in China for over 30 years with demonstrable plant growth-promoting effects at low concentrations (Agathokleous et al., 2019; Pang et al., 2001; Tommasi et al., 2021). Because of a potential dose-dependent relationship that may stimulate plant growth and other biological functions, REE amendments may be a novel inclusion in the Canadian and global agricultural systems. However, the adoption of REE fertilizers should proceed with caution, as the background concentrations of REEs in agricultural soils are not known and the addition of REEs may have unknown impacts on the soil environment.

Positive impacts of REE amendments can be seen on multiple growth endpoints including cellular growth, germination, biomass production, physiological indicators, and metabolic indicators (Agathokleous et al., 2019; Tommasi et al., 2023). At low doses of La, plant growth moderately increases independent from the response endpoint studied (149%, geometric mean; Agathokleous et al., 2019). While bioavailability of TEs in plant-soil systems complicates the interpretation of these results, concentrations of 34.6 mg La L^{-1} showed increased plant growth with no negative effects, while concentrations above 77.4 mg La L^{-1} showed negative impacts (geometric means; Agathokleous et al., 2019; Pellegrino et al., 2022). It is therefore important to determine the status of REE concentrations in Canadian agricultural soils to consider the feasibility of introducing REE amendments.

Canada lacks a comprehensive national geochemical database, which extends to the REE content in soils. In the UCC, the most abundant REEs (La, Ce, Nd, Y) have comparable concentrations to other trace metals such as copper and lead (Rudnick & Gao, 2003). Underlying geology, weathering rates, and anthropogenic activity can impact the accumulation and soil content of REEs (Aide & Aide, 2012; Bispo et al., 2021; Laveuf & Cornu, 2009; Loell et al., 2011). Furthermore, the REEs are divided into two major groupings that differ in how they persist in soils: the LREEs and HREEs. Due to a gradual contraction of their atomic radius from La to Lu, environmental factors can lead to a relative enrichment of LREEs or HREEs. A third group, the MREEs, is emerging in the literature as another distinct stage often associated with organic matter, biogenic phosphate, or fertilizers (Auer et al., 2017). The MREEs are variously defined, but often consist of Sm, Eu, Gd, Tb, and Dy (Bispo et al., 2021). On cultivated soils, the impact of anthropogenic activity on REE accumulation and fractionation patterns between the LREEs, MREEs, and HREEs is unknown.

Inorganic fertilizers can be a major source of REEs, as these elements often co-exist in phosphate and carbonate rocks (Bispo et al., 2021; Kabata-Pendias & Mukherjee, 2007; Silva et al., 2019). Elevated and highly variable levels of REEs have been detected in the raw materials (limestone, gypsum, phosphate rock) and finished products (superphosphates, phosphogypsum, monoammonium phosphate) of agricultural fertilizers (Abdel-Haleem et al., 2001; Otero et al., 2005; Ramos et al., 2016; Silva et al., 2019). Canada, which regulates some TE content allowable in agricultural fertilizers, does not regulate or test for REE content (Canadian Food Inspection Agency, 2023). Due to the regular application of mineral P fertilizers, there may be an unintended accumulation of REEs in Canadian agricultural soils due to the current and historical use of agricultural inputs.

Unknown background levels of REEs and the uncertain impact of agricultural management on REE content in soils limits the possibility of using REEs as agricultural inputs without exceeding the range in which positive crop growth effects are seen. This study aims to determine the status of REEs for the first time in agricultural soils of southeastern Ontario. The objectives of this study are to (1) report concentrations and fractionation patterns of the REEs in agricultural soils, (2) compare the REE content and fractionation patterns in commercially available mineral fertilizers to soil concentrations, and (3) determine if base soil characteristics or on-farm management practices are related to soil concentrations of the REEs.

4.3 Methods

4.3.1 Study area and soil sampling

Soils were collected from fourteen farms in southeastern Ontario, as described in the previous chapter. In this area, average annual rainfall ranges from 882.1 to 911.4 mm, and the average annual temperature is 6.9 to 7.5°C (Government of Canada, 2023). Soil sampling was arranged through the Quinte Farm Research and Stewardship Collaborative along with professional relationships with farmers. Agricultural management was considered and cropping system diversity was prioritized when selecting study farms. From the fourteen farms, fifty-two fields were sampled that fell under the categories of field crop production (Fc, n = 35), hay production (Hy, n = 12), cattle pasture (Pa, n = 3), and orchards (Or, n = 2). Full site descriptions and management practices can be found in the previous chapter and supplementary Table 3.S1. The underlying parent material was consistent throughout all sites (sedimentary, primarily limestone), while the surficial geology is comprised of deposited glacial sediments (Figure 4.1).

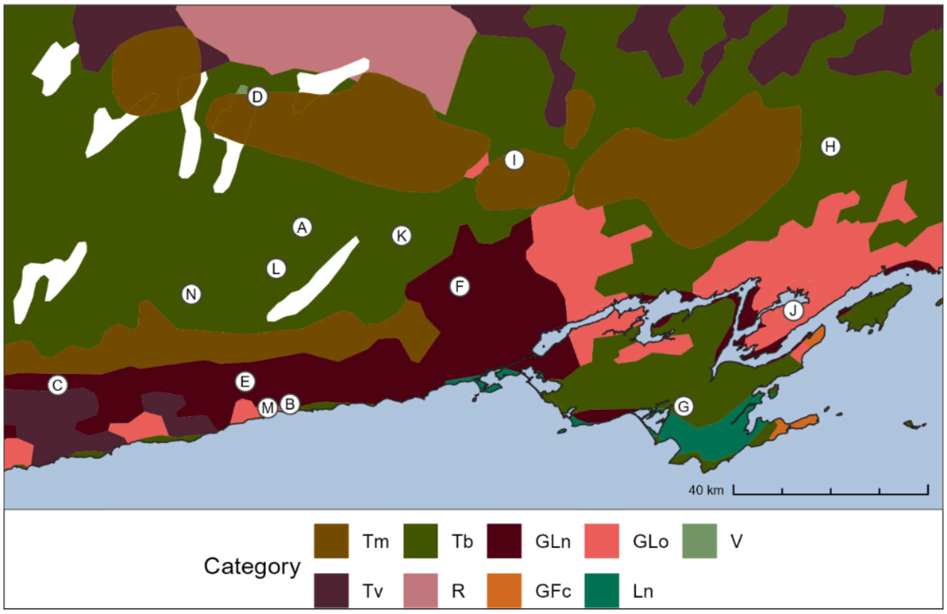


Figure 4.1. Surficial geology of the sampling area with farm sites indicated. Refer to Table 4.1for category descriptions.

Table 4.1. Code identification and descriptions of the surficial geology of the study area. Names and descriptions are from Natural Resources Canada (2025). Note the potential confusion between the geological description of Tm, Tb, and V and the elements thulium, terbium, and vanadium.

Code	Type	Sub-Category	Description
Tm	Glacial sediments	Moraine complex	Diamicton variable thickness end and interlobate moraines may include glaciofluvial sediments.
Tb	Glacial sediments	Till blanket	Diamicton thick and continuous may include fluted landforms, drumlins and morainal deposits.
GLn	Glaciolacustrine sediments	Littoral and nearshore sediments	Sand, silt, and gravel variable thickness deposited as deltas, sheet sands, and lag deposits.
GLo	Glaciolacustrine sediments	Offshore sediments	Silt and clay, locally containing stones variable thickness deposited in quiet water environments.
Tv	Glacial sediments	Till veneer	Diamicton thin and discontinuous may include extensive areas of rock outcrop.
R	Bedrock	Undifferentiated	Bedrock area of abundant (greater than 75%) rock outcrop alpine and non-alpine settings may include colluvial deposits, till, and other minor surficial sediments.

GFc	Glaciofluvial sediments	Ice-Contact sediments	Sand and gravel and locally diamicton variable thickness complex of ice-contact stratified drift, and outwash locally includes till and bedrock.
Ln	Lacustrine sediments	Littoral and nearshore sediments	Sand and locally gravel variable thickness deposited as sheet sands, lags, and beaches.
V	Volcanic deposits	Quaternary volcanic rocks and deposits, undifferentiated.	Consolidated lava, breccia and tephra variable thickness quaternary igneous dominantly basaltic and andesitic in composition includes flows, volcanic piles and cinder cones.

A systematic sampling design was implemented from May to October 2021. In each sampled field, 10-12 soil cores were collected along four parallel transects within a 10 000 m^2 area that was representative of the sampled field (Pennock et al., 2007). Soil sampling was completed using a stainless-steel soil probe (2.5 cm diameter, 0-20 cm depth) that was cleaned with 70% ethanol solution between samples. Collected samples were placed into re-sealable Ziploc® bags and mixed before being stored at 4°C for transport. Three bulk density samples (4.4 cm diameter, 10 cm depth) were collected from each transect along with the transect composite soil samples. Methods for maintaining a known volume of soil while sampling for bulk density can be reviewed in the previous chapter. Bulk density samples were stored in Ziploc® bags at ambient temperature during transport, as they were not used for chemical analyses.

4.3.2 Soil characteristics

Base soil characteristics including soil pH, electrical conductivity, soil texture, soil organic matter, and soil inorganic carbon content were determined for three replicates of each field. Soils were prepared by air drying and sieving to < 2 mm for all physical and chemical analyses. To determine water-extractable soil pH and EC, a 1:2 soil slurry with RO water was shaken for 30 minutes and allowed to settle before measurement. Soil organic matter was determined using the LOI method which measures mass loss after 4 hours at 550°C (Heiri et al., 2001). Similarly, SIC was determined by mass loss after 2 hours at 950°C. Soil particle size analysis was determined using the hydrometer method and soil bulk density was determined using the collected bulk density cores. For each transect, the mean oven-dried weight of the three cores was obtained and divided by the volume of the sampling core (Hao et al., 2007). Full descriptions of the procedures and equations used were provided in Chapter 3.

4.3.3 Elemental analyses

Triple quadrupole inductively coupled plasma mass spectrometry (Agilent 8800 ICP-MS-QQQ) was used for acid-leachable TE analysis. Dried and ground composite soil samples were digested in *aqua regia*, a 3:1 v:v solution of Trace Metal Grade HCl and HNO_3. The digestion supernatant was collected and diluted 100 times in double-distilled Trace Metal Grade 2% HNO_3. Indium was added to each sample as an internal standard (final concentrations of 10 ppb) and an *aqua regia* acid blank was included in each leaching batch to measure background element concentrations in the acid. Calibration of the instrument was performed daily using a 14-point standard curve of a multi-element solution comprised of 60 elements.

Major oxides and total TEs were analyzed using energy dispersive X-ray fluorescence (ED-XRF, Thermo Scientific ARL Quant'x) on pelletized soil samples. A 2:1 ratio of soil to binding agent (X-Ray Mix®, Chemplex) was used and samples were compressed at 11 metric tons in an evacuating die cast. To ensure the pellets' stability, the pellets were assessed for rough or crumbling edges along with placing them in a vacuum chamber at -20 Bar for one minute. If the surface was not stable, a new pellet was prepared. Full details regarding sample preparation for the elemental analyses are provided in the previous chapter.

4.3.4 Fertilizer analysis

To assess the potential contribution from commercial mineral fertilizers to the REE concentrations in soils, elemental concentrations of four commercially available fertilizers were analysed using ICP-MS. The fertilizers were analysed in duplicate following the same acid-leaching protocol and QA/QC measures as the soil samples. The fertilizers chosen were derived from mineral sources, as the REEs are not considered contaminants of synthetic fertilizers, e.g. urea (Table 4.2).

Table 4.2. Summary of analysed mineral fertilizer composition.

ID	Common name	Composition
F1	Potash	(KCl); ~N/P/K = 0/0/60
F2	Monoammonium Phosphate	($NH_4H_2PO_4$); N/P/K = 11/52/0
F3	Micronutrient - Zinc	N/P/K = 12/40/10, 1% Zn
F4	Micronutrient – Magnesium and Sulfur	N/P/K = 0/0/22, 11% Mg, 22% S

4.3.5 Quality assurance and quality control

Analytical recovery of the ICP analyses was validated with a water CRM for trace metals (SLRS-6) which was diluted to 50% using 2% HNO_3, with the addition of the internal In standard (Yang et al., 2015; Yeghicheyan et al., 2019). To assess the recovery of the digestion procedure with *aqua regia*, two marine sediment CRMs, HISS-1 and MESS-4, from the National Research Council of Canada were included in each leaching batch (Berman et al., 1997; Willie et al., 2014). Approximately 0.2 g of each sediment CRM was added to 4 mL *aqua regia* and was heated alongside the unknown samples, as reported above. The leached material was allowed to cool to room temperature before being diluted into 2% HNO_3 and adding the In internal standard. To ensure analysis of the total soil sample by ED-XRF, a pelletized soil CRM was included daily. The agricultural soil CRMs TILL-2 and TILL-3 (Lynch, 1990) were used, which were of a similar matrix to the unknown samples. Results of the CRM recovery are provided in chapter 3.

4.3.6 Data analysis

Summary statistics were calculated and statistical analyses were performed using the R statistical environment (R version 4.4.1; R Core Team, 2024). To assess the fractionation of the LREEs, MREEs, and HREEs, the normalized REE patterns between farms were compared visually. REE concentrations were normalized using Post-Archaean Australian Shale values (Equation 4.2) and plotted against atomic number.

Equation 4.1.

$$RE_N = \frac{RE_S}{RE_{ref}}$$

Where:
RE_S is the measured value of the rare earth (La – Lu) in the sample (mg kg^{-1}),
RE_{ref} is reported value of the same rare earth (mg kg^{-1}) in the reference material being used.

Ratios between La_N/Gd_N and La_N/Yb_N were calculated to determine the enrichment of the LREEs over MREEs and HREEs. Similar to the interpretation of RE_N values, a ratio > 1 indicated enrichment of the LREE over HREE or MREE, while < 1 indicates a similar depletion. The REE content in the commercial fertilizers was also normalized with PAAS values to compare to soil normalized patterns and REE concentrations in previously reported fertilizers.

To determine if on-farm management impacted REE distributions, a Kruskal-Wallis rank-sum test was used to determine if La concentrations differed between farms, and a post-hoc Dunn's test with p-value adjustments using the Benjamini-Hochberg method was used to distinguish which of the farms were significantly different. To further assess if differences in REE distribution between farms was a result of geochemical variation or anthropogenic activity, normalization by soil aluminum concentrations was calculated, as Al is highly immobile in the environment and its concentrations can be interpreted as representing pedogenic processes (Ho et al., 2012). See supplementary Figure 4.S1. for a map of mean Al concentrations on each farm, which shows the low variability in Al concentrations in the sampling region.

To determine if base soil characteristics were related to REE concentrations, Spearman's rank correlation was performed against La concentrations in soils ($\alpha = 0.05$). Lanthanum concentrations are used for the statistical analyses as a proxy for the REEs, as the REEs act as a homogenous group. When assessing if the response of the MREEs differs from the LREEs, Gd concentrations are used as a proxy element in stead. Agricultural management was summarized into three BMPs: cover crop use, manure use, and tillage use. Univariate comparisons of REE concentrations were conducted between the presence or absence of the agricultural BMPs using Student's and Welch's *t*-tests. Levene's test was used to assess the homogeneity of variance to determine if a Student's or Welch's test would be appropriate. Both the multivariate Kruskal-Wallis test and the univariate *t*-tests assessing cover crop and manure use were run on a subset of only the Fc samples, as the management-related variables would not apply to Hy, Pa, or Or fields. For tests comparing the use of tillage as a management practice, all fields were included other than the Or fields.

4.4 Results

4.4.1 Rare earth element concentrations and normalization

The recovery of the REEs from the acid-leached soils was 75 ± 19 % (median 72%) for Y, the only REE with overlap between the ICP-MS and ED-XRF analysis. This indicates a good level of recovery for the determination of REEs in soil using *aqua regia* leaching, while the remaining REEs would exist in the refractory fraction. Refractory REEs are unlikely to be biologically significant for agricultural production because of their bio-unavailability. Hereafter, the concentrations of REEs reported are acid-leached REEs.

The normalized patterns of REEs allow for qualitative assessment of trends seen in the enrichment of LREEs, MREEs, and HREEs both within and between farms. The range of REE_{PAAS} across the study farms spanned from 0.5 to 3.0 times the concentrations of the reference geological material, with a general enrichment of MREEs (Figure 4.2). The normalized patterns for all farms can be seen in supplementary Figure 4.S2. Between farms, there is variation in the level of enrichment of the REEs and farms J, H, and M have the highest mean REE concentrations. The mean PAAS-normalized concentrations of the REEs from this study are presented alongside other reported soil REE values from Nunavut and a LREE-enriched area in Quebec (Figure 4.3; Butler & Dawson, 2018; Romero-Freire et al., 2019). Compared to the previously reported soil REE values, the normalized pattern from this study shows greater HREE content and enrichment of the MREEs.

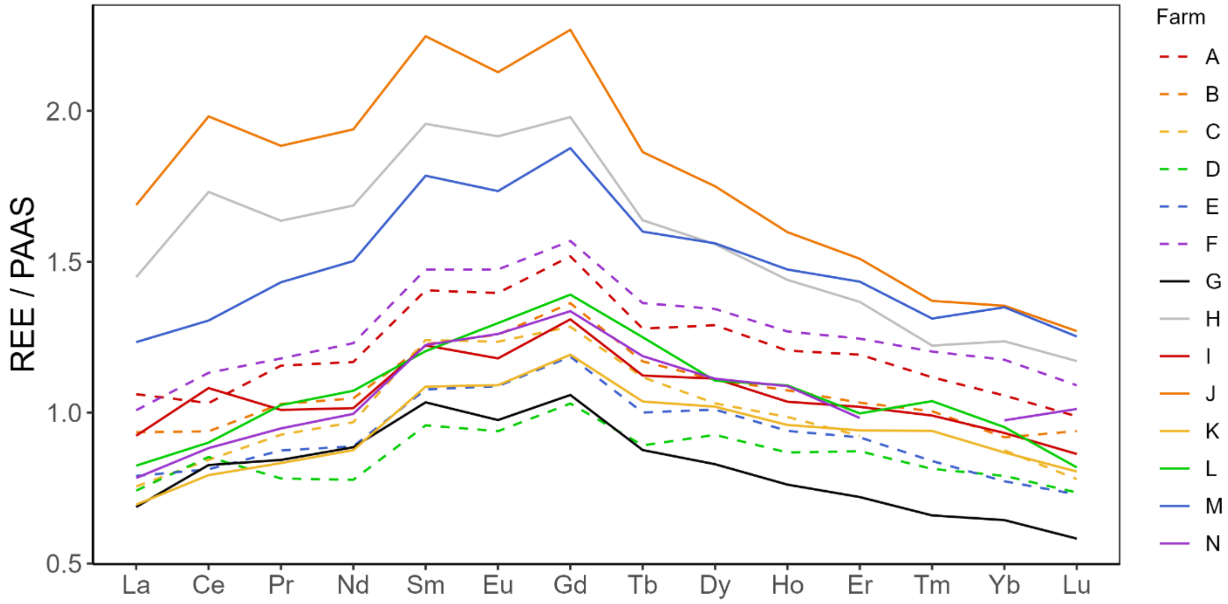


Figure 4.2. Mean normalized REE values by PAAS per farm, plotted against atomic number. Normalized values > 1 indicate enrichment compared to the reference material, and < 1 indicates depletion.

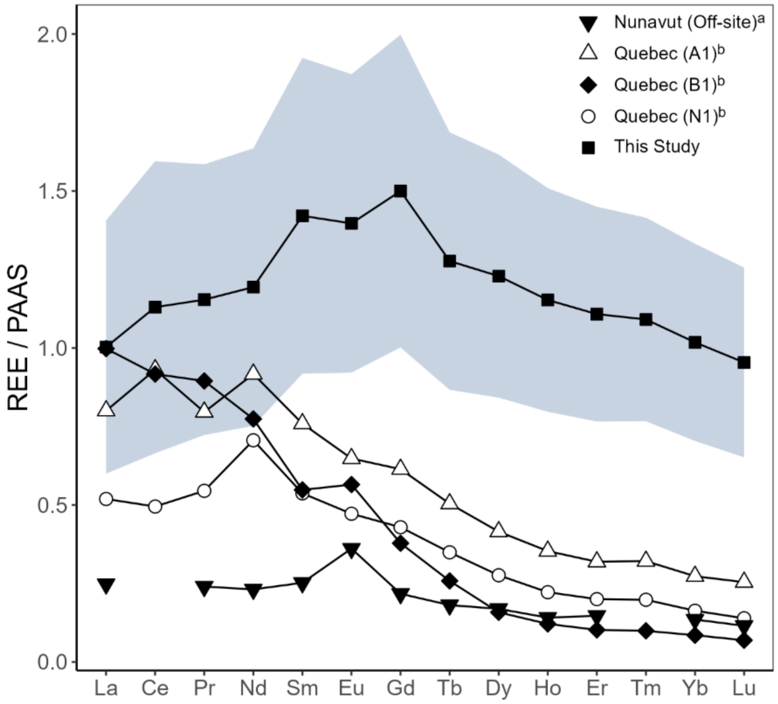


Figure 4.3. Mean (± sd) of normalized REE concentrations in the study compared to reported concentrations in soils from Nunavut [a](Butler & Dawson, 2018), and Quebec [b](Romero-Freire et al., 2019). Original site names are in brackets.

For all farms, the La_N/Gd_N ratio was < 1, with a range of 0.54 to 0.86, while the La_N/Yb_N ratio ranged from 0.8 to 1.24. There was no significant enrichment ($t(103) = -1.5$, $p = 0.06$) or depletion of the HREEs, which was represented by the mean La_N/Yb_N ratio close to 1 (Figure 4.4). The mean La_N/Gd_N ratio (0.66 ± 0.07), indicated that there is a significant enrichment of the MREEs for all farms ($t(103) = -48$, $p < 0.001$).

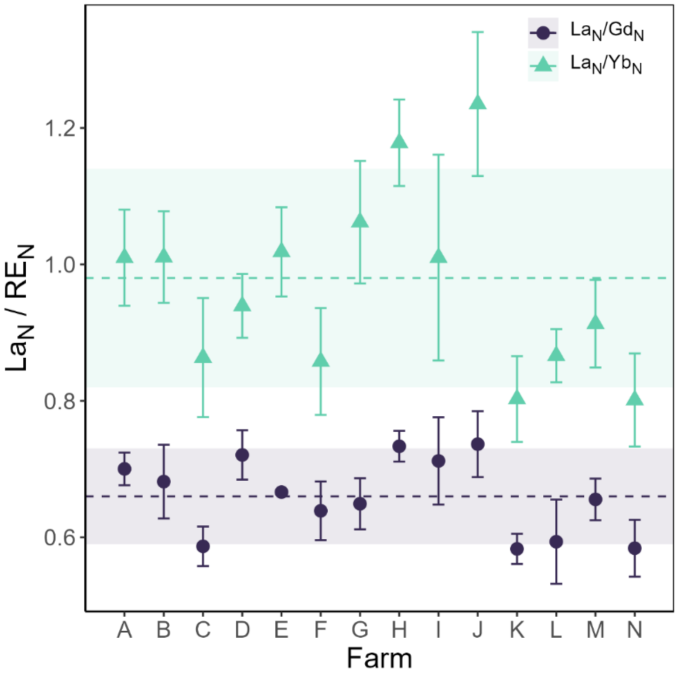


Figure 4.4. Mean (± sd) of the La_N/Gd_N and La_N/Yb_N ratios by farm. The dotted lines indicate the overall mean of each ratio for all samples, and the shaded area represents the overall standard deviation for each ratio.

4.4.2 Fertilizer REE content

The REE content was higher in the mineral P fertilizers (F2 and F3) than in the mineral-K based fertilizers (Table 4.3). All the fertilizers had similar or lower LREE content than reported in the agricultural soils, as the soils had minimum values of 10.3 mg La kg^{-1} and 30.6 mg Ce kg^{-1}, the most abundant LREEs. However, the mineral P derived fertilizer HREE concentrations were greater than observed in the soil samples. For example, the mean concentration of Lu in this study was 0.41 ± 0.1 mg kg^{-1}, compared with the nearly 2 mg Lu kg^{-1} from fertilizer F2. This difference can be seen in the normalized patterns of the fertilizers when compared with the soil concentrations (Figure 4.5). Observation of the normalized curves indicates large differences in enrichment patterns of the REEs between the soil and fertilizer samples. Normalized REE concentrations of the analysed fertilizers are compared to previously reported REE concentrations of MAP fertilizers originating in Brazil (Figure 4.6; Ramos et al., 2016; Silva et al., 2019). The fertilizer values reported in the literature have overall higher content of the REEs, and particularly higher LREE content with significant positive Eu anomalies when compared to the fertilizers in this study.

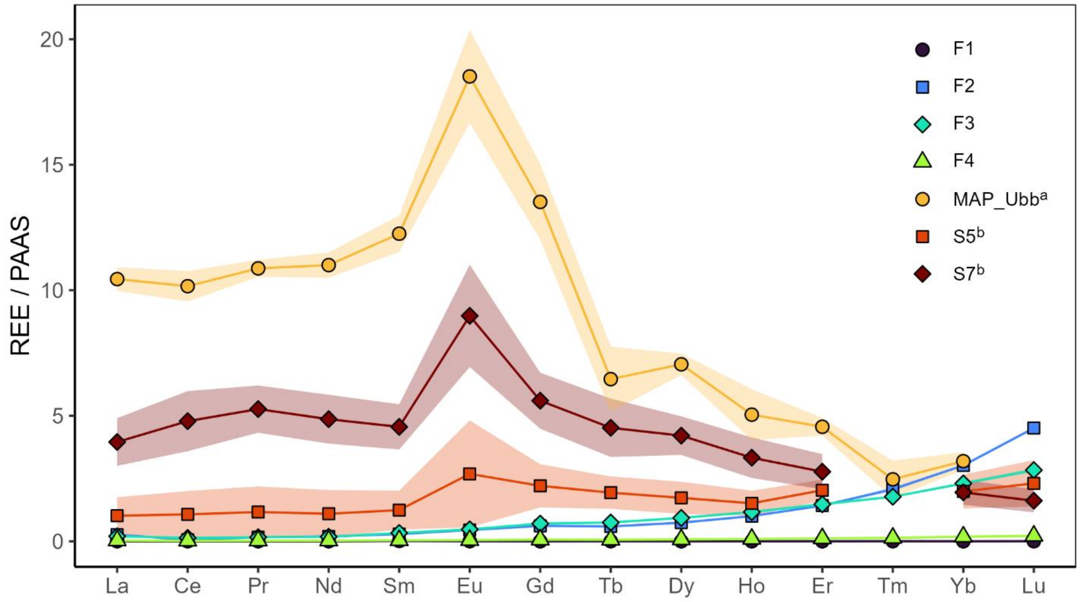


Table 4.3. Mean (± sd) of REE content (mg kg^{-1}) in fertilizer samples F1-F4.

	Fertilizers (mg kg^{-1})							
Element	F1		F2		F3		F4	
	mean	*sd*	*mean*	*sd*	*mean*	*sd*	*mean*	*sd*
La	0.14	0.04	10.1	1.1	7.71	0.03	1.08	0.06
Ce	0.29	0.06	4.86	0.48	10.8	0.13	1.63	0.17
Pr	0.03	0.01	1.46	0.14	1.43	0.02	0.21	0.02
Nd	0.10	0.02	6.52	0.56	6.19	0.08	0.83	0.09
Sm	0.08	0.003	1.61	0.05	1.85	0.01	0.22	0.01
Eu	0.006	0	0.49	0.04	0.51	0.02	0.05	0.008
Gd	0.01	0.001	2.87	0.11	3.28	0.01	0.32	0.06
Tb	0.004	0	0.46	0.03	0.58	0.01	0.05	0.006
Dy	0.01	0.003	3.50	0.17	4.36	0.08	0.352	0.06
Ho	0.003	0.001	1.00	0.04	1.16	0.03	0.09	0.01
Er	0.007	0.004	4.06	0.06	4.21	0.18	0.33	0.06
Tm	0.002	0	0.84	0.03	0.72	0.01	0.06	0.007
Yb	0.006	0.003	8.52	0.08	6.50	0.17	0.52	0.06
Lu	0.002	0	1.95	0.01	1.23	0.03	0.09	0.02

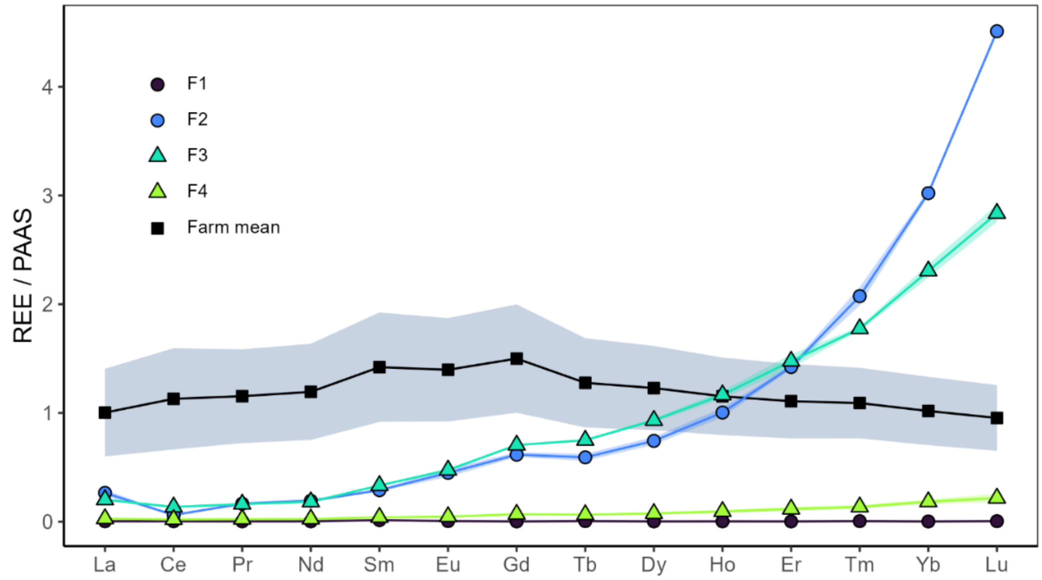


Figure 4.5. Mean normalized REE concentrations in analysed fertilizers (F1-F4) compared to mean REE concentrations in agricultural soils. The shaded area represents their respective standard deviations.

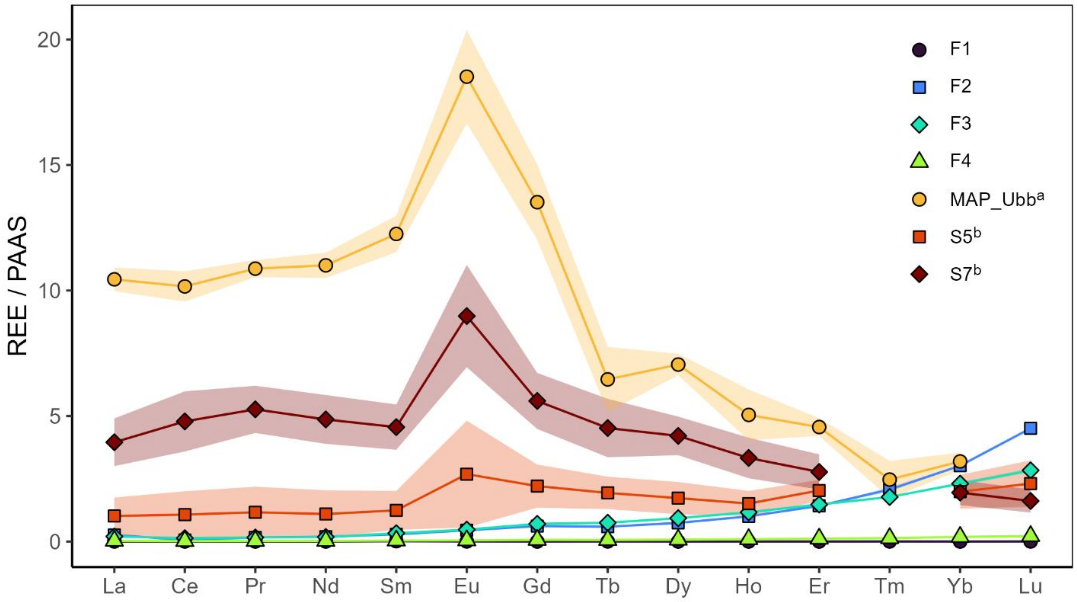


Figure 4.6. Mean normalized REE concentrations in analysed fertilizers (F1-F4) compared to reported total REE concentrations in MAP fertilizers, all originating in Brazil. Fertilizers S5 and S7 are sedimentary and igneous in origin, respectively [b](Silva et al., 2019), while the origin of the final fertilizer is unknown [a](Ramos et al., 2016). Original sample names are retained. The shaded area represents the standard deviation as reported.

4.4.3 Rare earth elements and farm-level differences

There was a significant difference in the distributions of La concentrations between farms (χ^2 (12, $N = 70$) = 46.9, $p < .001$). A post-hoc Dunn test showed that the distributions of farms G, J, K, N, and M were significantly different from certain other farms, with the distribution of farm J being higher compared to farms G, K, and N (Figure 4.7). Farm J had the highest overall values of REEs when compared to the other farms. The ratio of Al-normalized La is also significantly different between farms (χ^2 (12, $N = 70$) = 44.3, $p < .001$; Figure 4.8) and follows the same distribution between farms as the raw concentrations of La. This indicates that while REE concentrations varies between farms, the variation in REE content can be attributed to natural geochemical variation rather than a significant differences in farm-level management. A map of the sample region indicates the highest concentrations of La (Farms H, J) are furthest to the east of the sampling region (Figure 4.9).

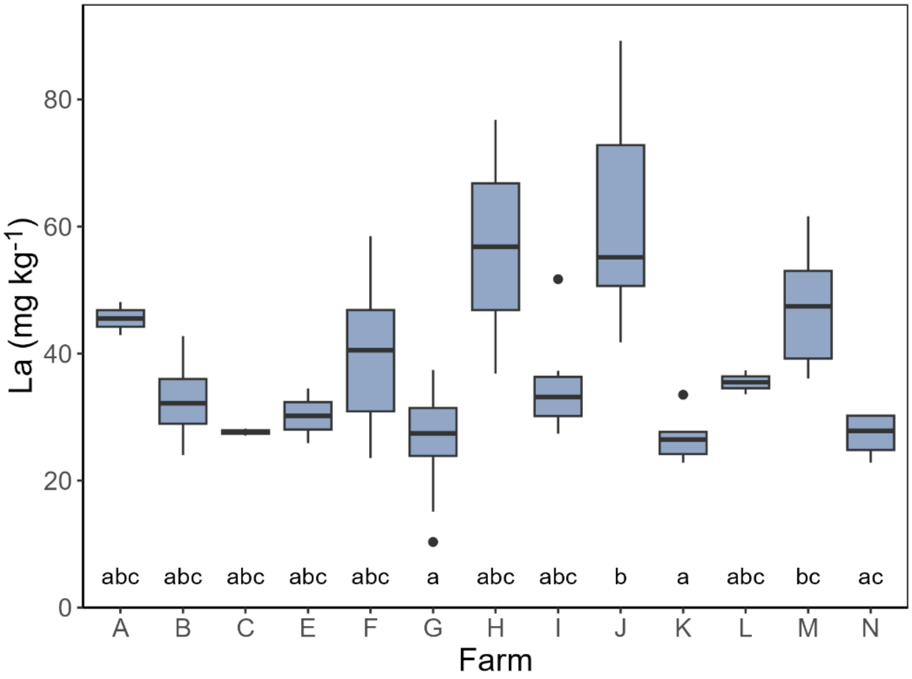


Figure 4.7. La concentrations between farms (including Fc sites only), using letter signifiers to denote significant differences between groups (p = < .001).

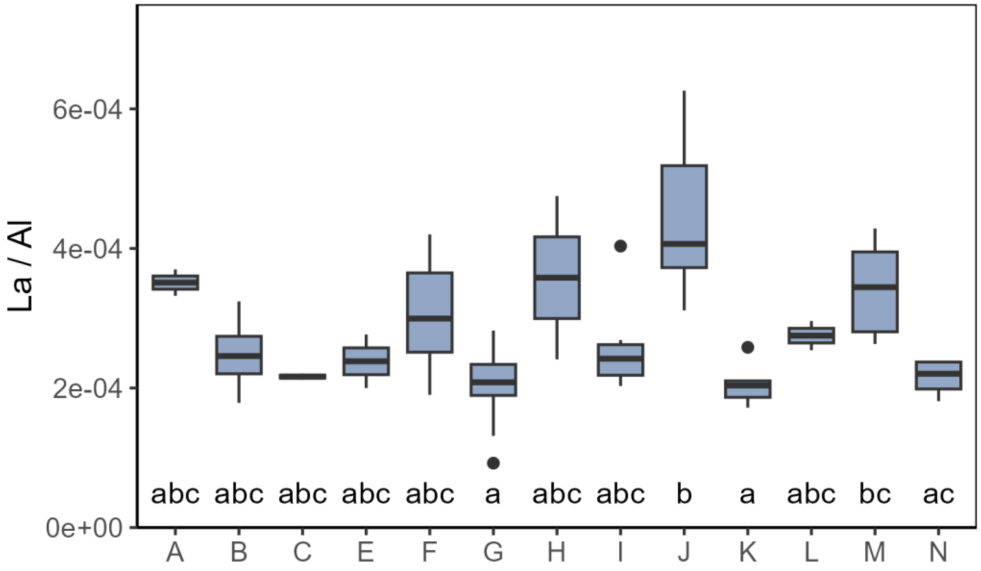


Figure 4.8. Al – normalized values of La between farms (including Fc sites only), using letter signifiers to denote significant differences between groups ($p = < .001$).

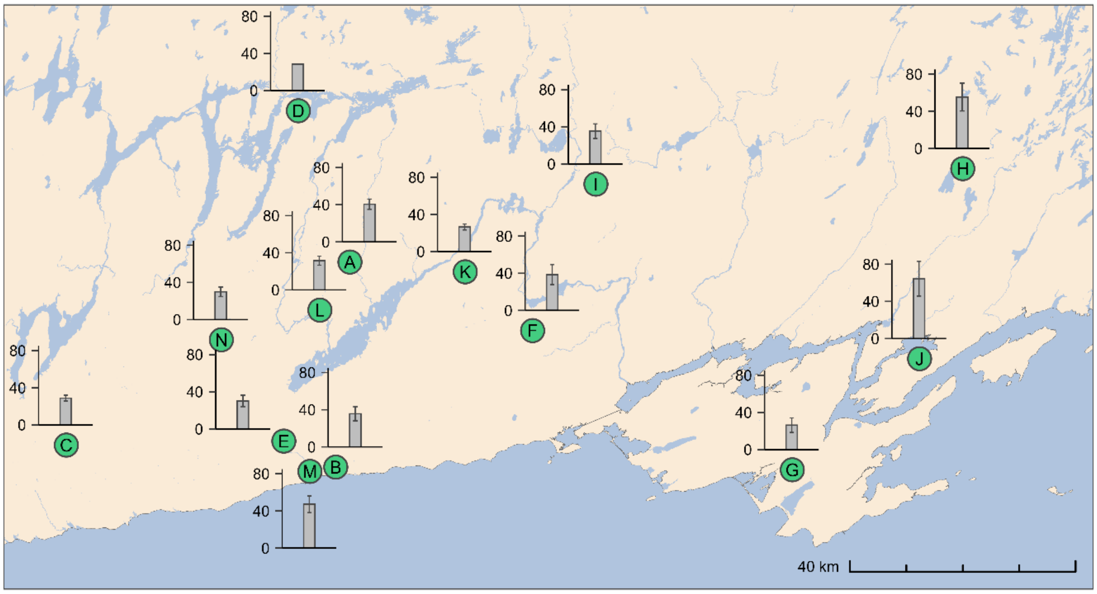


Figure 4.9. Map of farm sites with La concentrations (mg kg^{-1}).

4.4.4 Soil characteristics and relationship to agricultural management

A statistical summary of the base soil characteristics of pH, EC, SOM, SIC, soil texture, and soil bulk density for all farms was provided in the previous chapter. Of the soil characteristics, only pH, SOM, sand %, clay %, and BD were significantly correlated ($p < 0.05$)

with La concentrations (Figure 4.10). There was no significant correlation between La concentrations and EC, SIC, or silt content. Soil pH, sand %, and BD had weak negative relationships with La concentrations in soils, while SOM and clay % were positively correlated. Lanthanum was also positively correlated with other trace element cations (Th, Cs, Rb) that are retained by clay in soils (Figure 4.11).

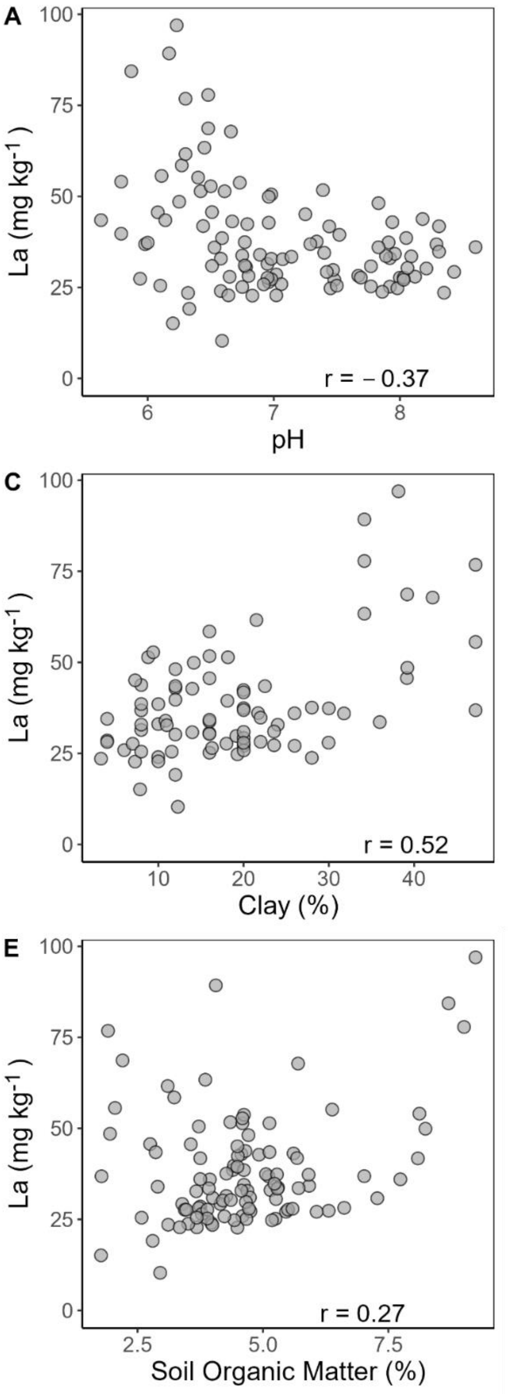


Figure 4.10. Significant correlations (*a* = 0.05) between La concentrations (mg kg^{-1}) and selected soil characteristics presented with *r* values for: (A) soil pH, (B) bulk density, (C) clay percentage, (D) sand percentage, and (E) soil organic matter.

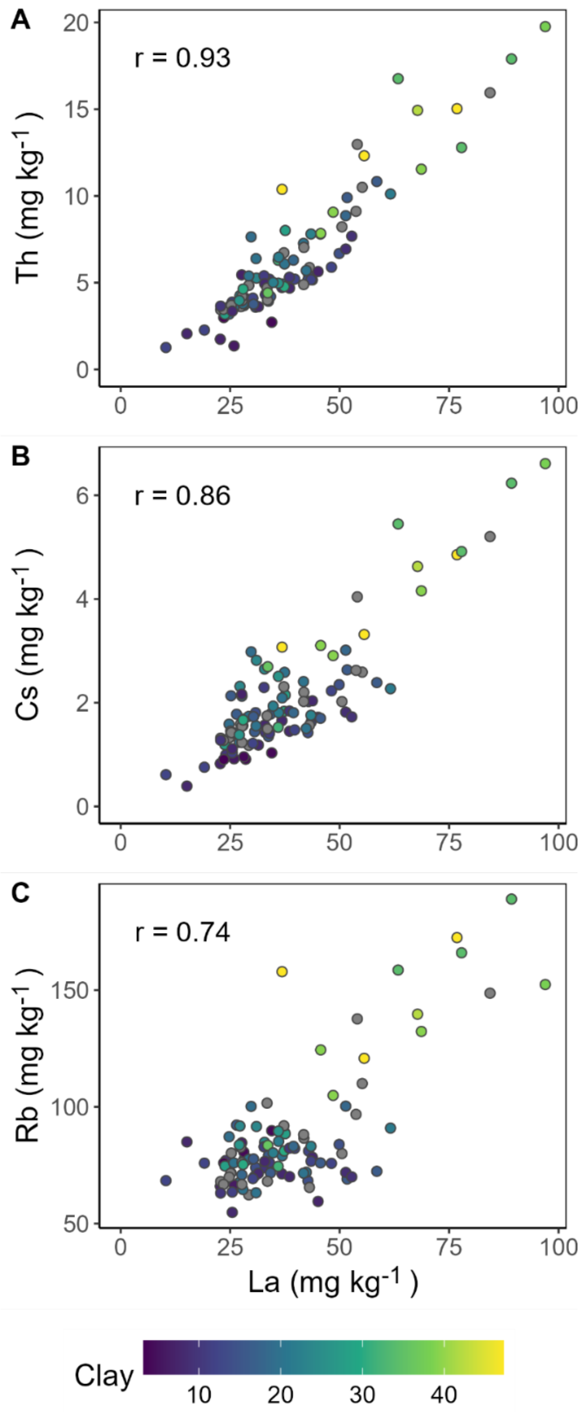


Figure 4.11. Correlation between La concentrations and (A) Th, (B) Cs, and (C) Rb concentrations, with clay percentage indicated by colour. Grey points (n = 20) had missing clay data.

Multivariate comparison of the La distribution between Fc, Hy, Pa, and Or fields was not conducted as the similarities between group means and the large difference in variance between the field use invalidated test parameters (Figure 4.12). However, the agricultural BMPs were assessed for their impact on REE concentrations (Figure 4.13). The distribution of La concentrations was significantly different between the presence and absence of each BMP, manure use ($t(67.8) = -3.4$, $p = 0.001$), cover crop use ($t(47.6) = -2.8$, $p = 0.007$), and tillage ($t(98) = -3.1$, $p = 0.002$). Since there was a noted enrichment of the MREEs on all farms, the above tests were repeated using Gd as a proxy REE to determine if agricultural management practices had a differing impact on the MREE. All agricultural BMPs showed significant differences between the Gd distributions and followed the same pattern as La (supplementary Figure 4.S3). Full *t*-test results for Gd can be found in supplementary Table 4.S1.

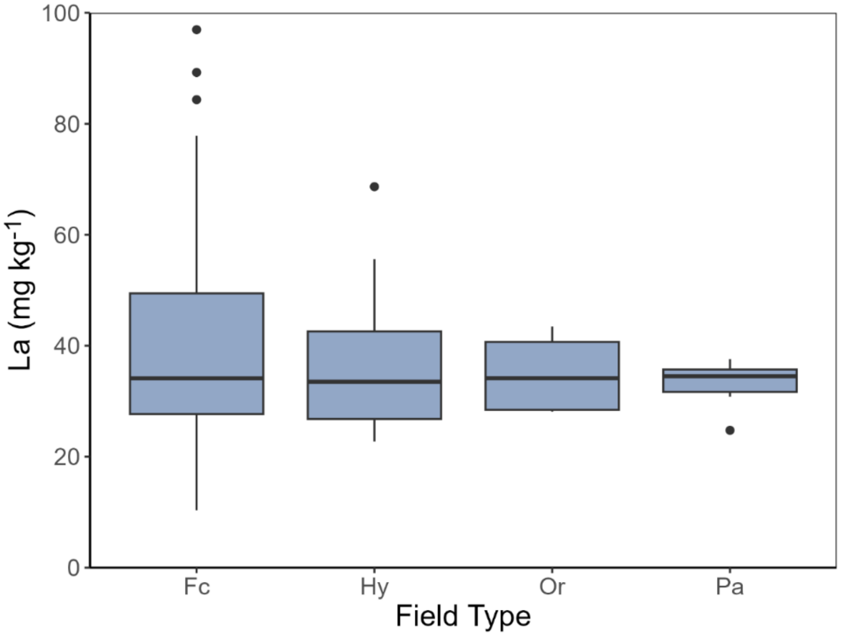


Figure 4.12. Distribution of La concentrations between field use categories, field crop (n = 35), hay (n = 12), orchard (n = 2), and pasture (n = 3).

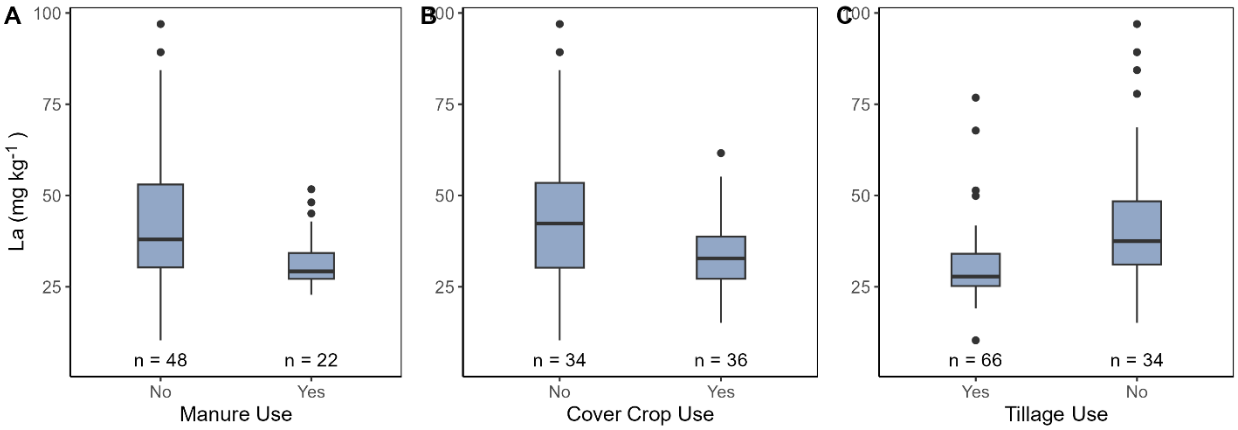


Figure 4.13. Boxplot comparison of La concentrations in Fc sites for (A) manure use and (B) cover crop use. Tillage use (C) represents all observations other than orchard fields.

4.5 Discussion

4.5.1 Rare earth element normalization

For all farms, the average normalized values of the REEs differ by less than one order of magnitude than the average concentrations in PAAS. In all farms there was no significant enrichment or depletion of the HREEs, which was represented by La_N/Yb_N ratios close to 1 (Butler & Dawson, 2018; Liang et al., 2005; Zhang et al., 2021). Preferential leaching of the HREEs and retention of the LREEs in soils can indicate a highly weathered soil (Lara et al., 2018; Laveuf & Cornu, 2009) , which was not observed in this study. The MREE concentrations of the studied farms are significantly enriched compared to PAAS values, to a maximum of 3 times the PAAS concentrations. Enrichment of the MREEs is often associated with biogenic carbonates or phosphates (Auer et al., 2017), along with soil colloids such as clay content, Fe-oxyhydroxides, and soil organic matter (Laveuf & Cornu, 2009).

Very few studies exist in which concentrations of REEs in Canadian soils are reported. Compositional data or analysis of the REEs are reported more frequently for underlying parent material, often for mining exploration. Rare earth element content in bedrock and parent material samples does not reflect the weathering process and surface inputs that that soil REEs are subject to, and should not be compared to the values measured in the current study (Aide & Aide, 2012; Zhou et al., 2020). The mean normalized REE patterns from this study differed when compared to previously reported REE concentrations in Canadian soils. From norther Quebec the REE values reported by Romero-Freire et al. (2019) and show a distinct pattern of LREE enrichment. This pattern in the Quebec sites is due to the natural enrichment of the bedrock, which influences the soil REE normalized patterns. The normalized patterns out of Nunavut showed almost no LREE/HREE enrichment, and very low concentrations of REEs (Butler & Dawson, 2019). This indicates that the drivers of REE content in soils (e.g. sources, weathering rates) differs between the southern, agricultural soils and northern soils.

4.5.2 Fertilizer REE content

Of the four fertilizers analysed in this study, the mineral K fertilizers (F1 and F4) had lower REE content than the mineral P fertilizers (F2 and F3). The mineral P fertilizers show high HREE concentrations and substantial fractionation between the LREE and HREE groups. The normalized curve of the mean REEs in the farm soils displays a very different pattern than the analysed mineral P fertilizers. As stated previously, the agricultural soils have an enrichment of the MREEs which does not match the normalized pattern of the mineral P fertilizers. This could indicate that these fertilizers are not influencing the REE signature of sites. However, although these mineral P fertilizers are procured from a local commercial depot, there samples may not represent all mineral P fertilizers distributed in Ontario, as their geographic origins remain unknown.

Multiple fertilizer REE concentrations have been reported previously in the literature and are variable in the raw materials and manufactured end products (Abdel-Haleem et al., 2001; Hu et al., 1998; Otero et al., 2005; Ramos et al., 2016; Silva et al., 2019). Previously reported REE concentrations of MAP fertilizers, originating in Brazil, have much higher overall REE content and specifically, LREE content when compared to the fertilizers in this study (Ramos et al., 2016; Silva et al., 2019). It should be noted that the methods employed by Ramos et al. (2016) and Silva et al. (2019) would result in a more complete digestion of the fertilizers, potentially resulting in a slightly greater recovery than the *aqua regia* leached fertilizers reported in this study. Despite the methodological dissimilarities, the fraction of the REE content that may be refractory (25%, see section 4.4.1) in the acid-leached samples would not account for the large differences in REE content between the fertilizers.

The greatest influence on REE content in mineral P fertilizers is the origin of the raw materials. The concentrations of the REEs in MAP fertilizers varies considerably when the source of the rock phosphate is sedimentary or igneous (Otero et al., 2005; Silva et al., 2019). Igneous sources of rock phosphate, mainly carbonatites, are some of the greatest REE-bearing minerals in the world (e.g. bastnaesite and monazite; Richardson & Birkett, 1996). Manufacture of the phosphate fertilizer does decrease the end concentration of the REEs, with an estimated 29% of REE content maintained through the manufacture of MAP (Ramos et al., 2016). Other mineral-P fertilizers, e.g. superphosphates, may retain approximately 50 – 60% of their original REE content (Ramos et al., 2016). Due to the variability of REE content in mineral-P fertilizers, the uncertainty around annual inputs of REEs to agricultural soils remains. Future work should increase the number and variety of fertilizers analysed for REE content available in Ontario to monitor if the REE values remain low, or if fertilizers with elevated REE concentrations are available for use.

4.5.3 Geographic distribution of the rare earth elements

While the distribution of La varied significantly between farms, the Al-normalized values reflected the same pattern of distribution between farms. As Al is not impacted by agricultural management, the similarities between the La distribution and Al-normalized values indicate that La is related to the surficial geology of the sample area, rather than agricultural management. The surficial geology is mainly comprised of glacial tills, an unsorted or semi-sorted mixture of sediments deposited after the retreat of the Laurentide ice sheet (Barnett et al., 1998). Near the shore of Lake Ontario, the surficial geology is comprised of lakebed sediments from when it was a larger lake, known as Glacial Lake Iroquois (Barnett et al., 1998). Of note is the placement of farm J, the farm with the highest mean La concentrations, is the sole farm located on Ln coded sediments, which are littoral and near-shore sediments not of glacial origin (Natural Resources Canada, 2025). Particle size distribution in the deposition of the lacustrine sediments in the surficial geology of farm J may provide an explanation for the elevated La concentrations compared to the other farms.

4.5.4 Base soil characteristics and rare earth element content

Although statistically significant, many of the relationships between the base soil characteristics and La concentrations are very weak. Clay content had the strongest correlation to La, which supports previous studies linking soil texture and clay content to REE retention in soils (Aide & Aide, 2012; Cao et al., 2001; Dushyantha et al., 2020; Fang et al., 2007; Laveuf & Cornu, 2009; Loell et al., 2011; Nisti et al., 2015; Saueia et al., 2020; Yan et al., 1999). Lanthanum was also positively correlated with other trace element cations (Th, Cs, Rb) that are retained by clay in soils (Figure 4.10; Wampler et al., 2012). In German agricultural soils, concentrations of REEs (excluding Ce) were found to be positively correlated with clay content ($r > 0.54$) and Fe and Mn oxides ($r = 0.6$-0.7; Loell et al., 2011). Positive correlations between La, Ce, Gd, and Y with Fe and Mn oxides were also reported by Cao et al. (2001) and Fang et al. (2007), showing that clay content and clay type are strongly related to the REE content in soils.

When separated by size, soil particles < 75 µm carried 99% of the water-soluble REE content of the entire soil (Yan et al., 1999). Out of the < 75 µm fraction, an estimated 15-20 % was assumed to be clay which had a majority of the REE contents loosely adsorbed to the surface. When hydroxylamine hydrochloride ($NH_2OH \cdot HCl$) leaching was applied to the < 75 µm fraction, the greatest content of REEs was released (25-30% total REE) which the authors attributed to REEs bound to amorphous Fe and Mn oxy-hydroxides, which can coat other minerals or exist as very fine particles (Yan et al., 1999). This relationship was also seen in a leaching experiment that used sandy soil (15% clay) and clay soil (58% clay) and found that background concentrations of REEs in the clay soil were approximately one order of magnitude larger than the sandy soil (Nisti et al., 2015; Saueia et al., 2020).

Soil pH and La concentrations were significantly negatively correlated, and mobility of La and other LREEs from soils is strongly related to soil pH (Cao et al., 2001; Fang et al., 2007; Loell et al., 2011; Sadeghi et al., 2013; Tyler & Olsson, 2001). Previous studies have found similar negative correlations between La concentrations and pH ($r = -0.73$; Fang et al., 2007). This study had a relatively large range in pH, although the mean value was approximately neutral, indicating that the range in soil pH may represent areas with greater mobilization of soil REEs.

4.5.5 Relationship to agricultural management

As there were so few orchard or pasture fields, the level of variance between field use types made it difficult to compare La concentrations based on field use type alone. Instead, differences in agricultural BMPs were characterized to explore the differences in La concentrations based on agricultural management. The impact of the agricultural management practices was consistent between the MREEs and the LREEs (represented by Gd and La, respectively).

Lanthanum concentrations were lower in fields that incorporated manure into the agricultural system. Manure use associated with lower La concentrations was unanticipated, as the use of manures has been demonstrated to increase or slow the loss of SOM (Rayne & Aula, 2020), and as previously discussed, SOM % is weakly positively correlated with La concentrations. However, in a study that compared REE concentrations in mineral fertilizers to pig and cattle slurry, the animal manures were found to have far lower REE concentrations than mineral P fertilizers (Hu et al., 1998). If applied manures had significantly lower concentrations of REEs than soils, an argument could be made for the dilution of REE concentrations through addition. The only reported values of REEs in manures is by Hu et al. (1998), but the REE content excreted in the manure is likely tied to the diet and diet supplements. It is uncertain whether the reported concentrations would be relevant to current Ontario agricultural systems. Although commercially available fertilizers were analysed in this study for REE content, no manures were assessed. Without information on REE content in applied manures, there mechanism behind this result remains unclear.

Cover crop (CC) use as a rotational stage had lower La concentrations in the studied fields. While also introducing soil organic matter, cover crops reduce surface-level erosion by stabilizing the soil with living roots. Since REEs are associated with soil colloids and clay particles, a dominant pathway of REE loss from soil systems is through surface runoff of clay-sized particles (Aide & Aide, 2012; Wang et al., 2011). In this way the results of this study are also unexpected, as one of the major benefits of CC use is to reduce surface erosion, which theoretically would increase the retention of REEs (Agriculture Canada, 2008). Uptake of REEs by CC biomass may reduce plant-available REE concentrations over time, but most conventional CC management includes returning the CC residue to the soil without removing the biomass (Agriculture Canada, 2008). In this way, uptake of REEs by CC biomass would not be considered a pathway of removal unless the CCs were consistently removed from the system.

Finally, the use of tillage was also associated with lower La concentrations in soils, which could be due to increased REE mobilization associated with soil instability. Runoff is a major form of REE transportation due to the association with clay particles, and the percent clay was positively correlated with La content (Wang et al., 2011). Dilution effects are also a possibility as soil samples were taken from the 0-20 cm depth. Any deep tillage may have introduced underlying material into the sampled cores. Unfortunately, tillage depth was often not reported by the producers, and tillage data had to be generalized to presence or absence. Since the concentrations of REEs in the underlying material is unknown, it is possible tillage practices diluted the REE concentration in the soils if the tillage depth was greater than 20 cm. Further work to identify the transport of REEs off-site by over-land transport or infiltration is required to assess the full impact of agricultural management on REE concentrations.

It is possible that a confounding factor associated with the three management practices is obscuring the relationship between REE concentrations and agricultural management. The adoption of sustainable agricultural practices, such as cover crop use, incorporation of manures, and no-till agriculture are not binary decisions for producers. These are complex decisions in which knowledge of practices, environmental and social values, communication, and perceived risks and benefits all play a part in the decision to adopt new agricultural practices (Han & Niles, 2023). In their framework of adoption of sustainable agricultural practices, Han and Niles (2023) identify a previously unspoken of type of producer: the innovative new adopters of sustainable agricultural practices. Innovative new adopters are more likely to practice sophisticated sustainable management practices. In the case of CC, this may include species mixtures, interseeding, or planting a cash crop directly into a living cover crop (Han & Niles, 2023). Not only that, but the decision to use CC by the innovative new adopters is significantly influenced by the number of other conservation practices already used by these producers. Therefore, the adoption of individual best management practices may not be independent, confounding the univariate comparisons against REE concentrations.

4.6 Conclusion

The current status of REEs in Ontario agricultural soils indicates that geochemical variation is a stronger driver than agricultural management of REE concentrations. Agricultural BMPs, such as tillage, cover crop use, and manure use have a significant impact on La concentrations in soil, however, the process behind this impact is unclear. Rare earth element concentrations were at most three times the concentration of reference values, and normalized patterns for all farms indicated no significant fractionation between the LREE and HREE. Fractionation patterns did show MREE enrichment, potentially associated with the colloidal fraction of soil. Future work must focus on assessing the REE content in multiple mineral fertilizers that are currently applied to Canadian agricultural soils to determine annual inputs of REEs. It is important is to determine REE concentrations for additional soils in Ontario and Canada in order to create a baseline for determining potential future REE accumulation.

4.7 Supplementary Materials

4.7.1 Supplementary figures

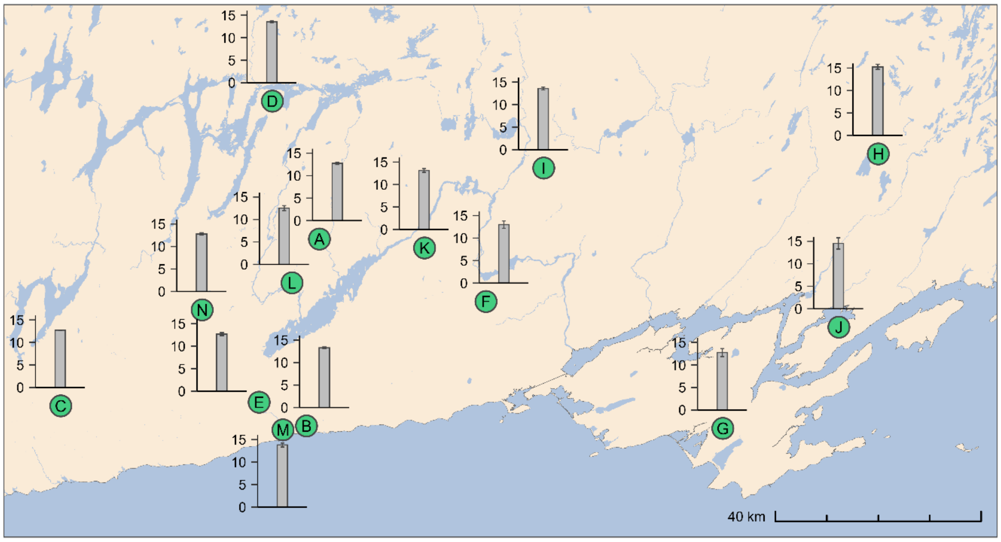
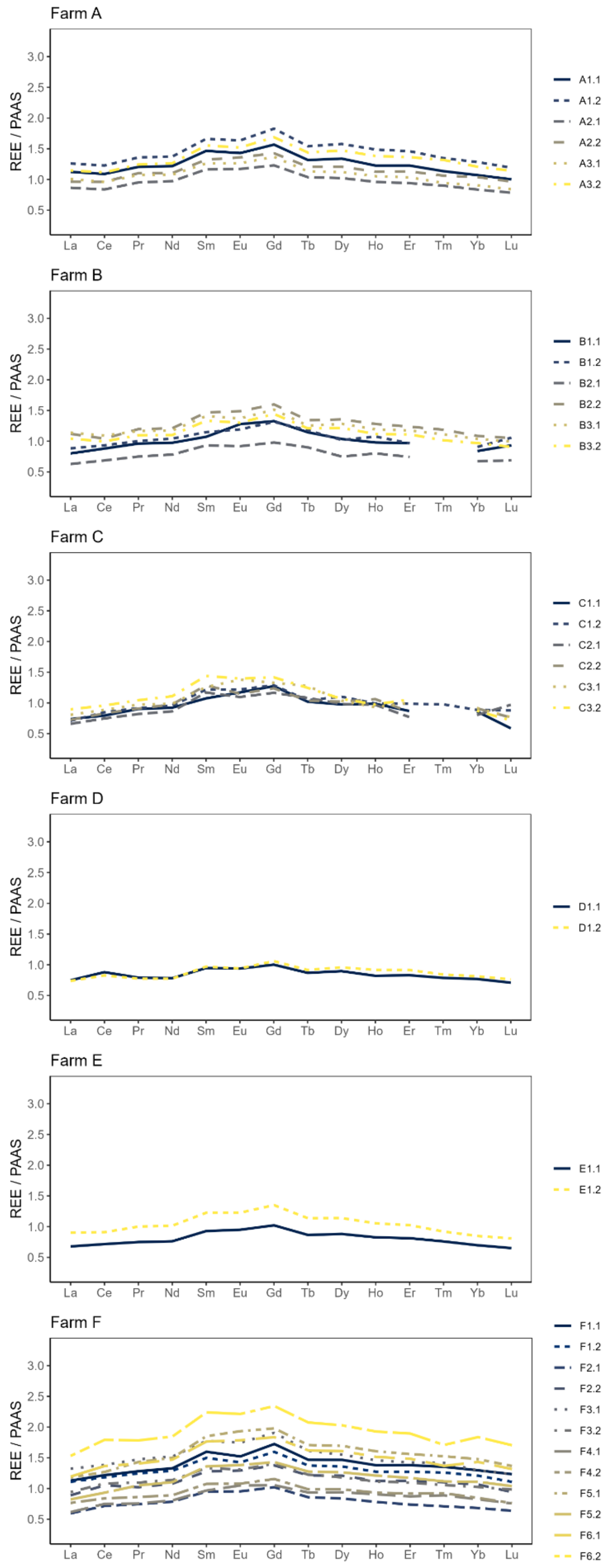


Figure 4.S1. Map of mean Al oxide concentrations (%) for each farm in the sampling region.


Farm A
REE / PAAS
3.0
2.5
2.0
1.5
1.0
0.5
La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
A1.1
A1.2
A2.1
A2.2
A3.1
A3.2
Farm B
B1.1
B1.2
B2.1
B2.2
B3.1
B3.2
Farm C
C1.1
C1.2
C2.1
C2.2
C3.1
C3.2
Farm D
D1.1
D1.2
Farm E
E1.1
E1.2
Farm F
F1.1
F1.2
F2.1
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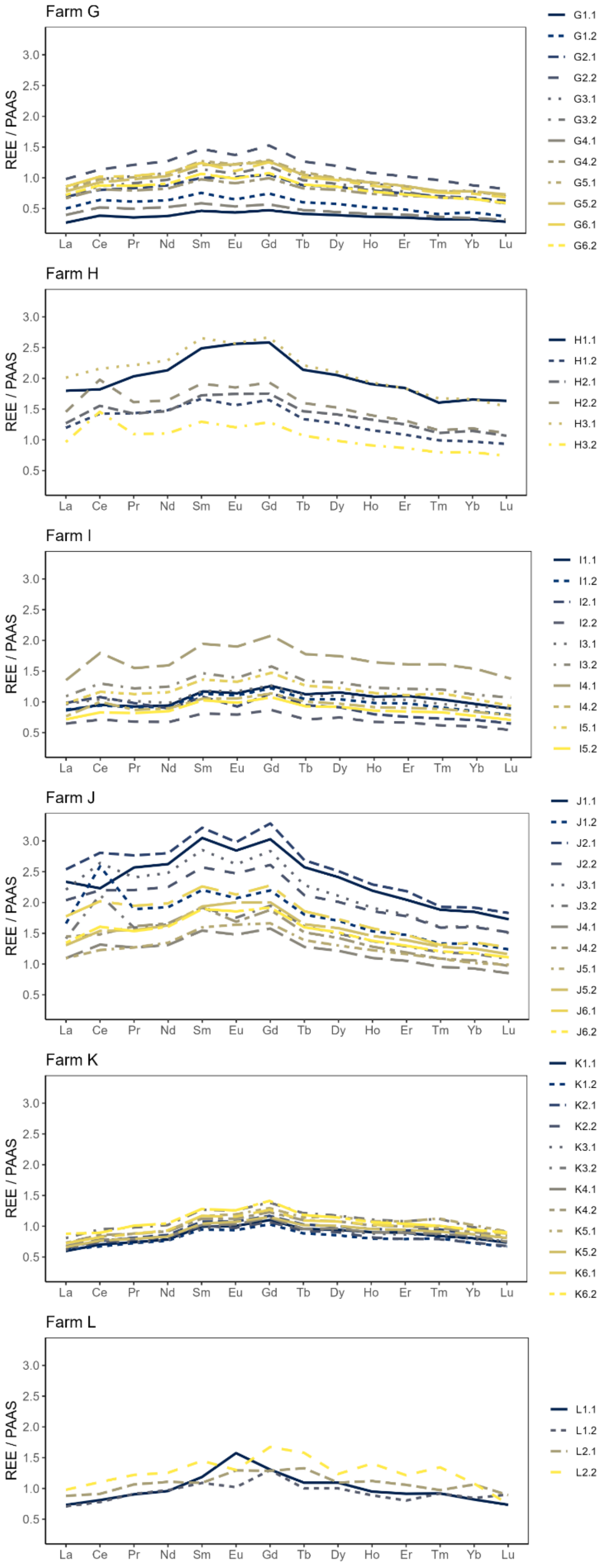
F3.1
F3.2
F4.1
F4.2
F5.1
F5.2
F6.1
F6.2


Farm G
Farm H
Farm I
Farm J
Farm K
Farm L
REE / PAAS
0.5
1.0
1.5
2.0
2.5
3.0
La
Ce
Pr
Nd
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
G1.1
G1.2
G2.1
G2.2
G3.1
G3.2
G4.1
G4.2
G5.1
G5.2
G6.1
G6.2
H1.1
H1.2
H2.1
H2.2
H3.1
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I1.1
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I4.1
I4.2
I5.1
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J1.1
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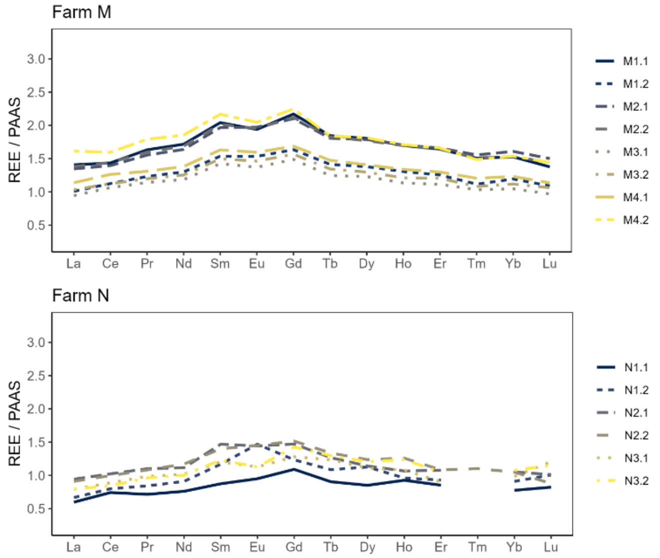
L2.2



Figures 4.S2. Normalized REE patterns for all fields, by farm (14 Figures).

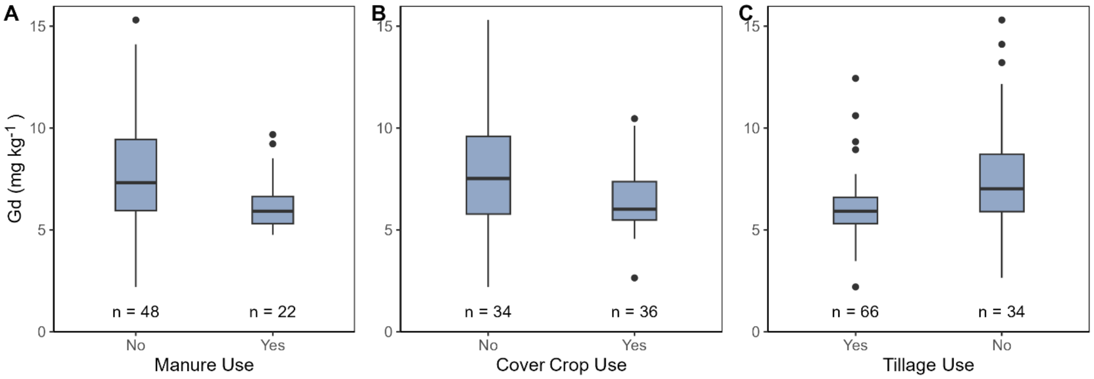


Figure 4.S3. Boxplot comparison of Gd concentrations in Fc sites for (A) manure use and (B) cover crop use. Tillage use (C) represents all observations other than orchards.

4.7.2 Supplementary tables

Table 4.S1. *t*-test results comparing the mean Gd concentrations (mg kg^{-1}) between farm management practices of manure use, cover crop use, and tillage use. Note that manure use and cover crop use tests were conducted on a subset of only field crop sites, while tillage tests were conducted on all observations other than orchard sites.

	Use	**n**	**Mean**	**sd**	**Method**	**df**	***t*-statistic**	***P***
Manure	No	48	7.7	2.9	Welch's	67.8	-2.95	0.004
	Yes	22	6.2	1.4				
Cover Crop	No	34	8.0	3.1	Welch's	51.3	-2.56	0.01
	Yes	36	6.5	1.7				
Tillage	No	66	7.5	2.4	Student's	98	-2.59	0.01
	Yes	34	6.2	1.9				

5 Discussion and conclusion

The results of the multivariate analyses from this work indicate that the geochemical signature of agricultural soils in Ontario does not vary significantly in response to agricultural management as assessed. The results of the TEs and REEs indicate that farm- and landscape-level drivers, as opposed to field-level drivers, have a greater influence on site geochemistry. This is attributed to the geographic distance between farms, as farms that were further apart had distinct patterns in multivariate space. In particular, farms J, H, and G were divergent when assessed visually using PCA and hierarchical clustering, reflecting how they were the only three farms assessed from the Napanee and Prince Edward county regions. This trend is also reflected in the significant differences in La concentrations between farms, while there was no significant difference found for field use. When mapped, a pattern of greater REE concentrations is displayed to the East of the sampling region. Geographic variability of the REEs outweighs management-related impacts, despite the many disturbances implicit in agricultural management, particularly with the use of agricultural inputs which have the potential to contribute to TE contamination.

Most TEs for which agricultural environmental safety standards exist and that are regulated in agricultural inputs (elements of concern) are not enriched beyond the environmental safety standard set by the CCME. However, legacy contamination led to high TE contents in certain fields. This was clearly seen in field B3, where As and Pb were enriched due to the long-term use of the pesticide lead arsenate. Although most sites did not display abnormal patterns in TE content, individual sites like B3 demonstrate that site history cannot be disregarded when considering future site management, as is the current standard in agricultural input management. Elevated concentrations of harmful TEs may result in future environmental or human health hazards if TEs continue to accumulate. In cases where contamination is suspect, determination of TE concentrations should be a priority.

An interesting aspect of TE geochemistry revealed that Cr is enriched above the environmental safety standard in the majority of the soils in the sample region, which has not been previously reported in Ontario. Previously reported values of trace metals, including Cr, have been primarily focused in southwestern Ontario. Since the elevated Cr concentrations are widespread across all farms, it is likely that Cr concentrations are associated with the background geochemical variation of the region than with the use of agricultural inputs. Results like the elevated Cr concentrations in this sampling region indicate that lack of a provincial- or national-level geochemical database is a large oversight. Without an understanding of the natural variability of TEs in soils, it may be challenging to distinguish contamination from natural background concentrations. A greater knowledge of soil geochemistry in agricultural areas can serve as a precise tool for tailoring agricultural management. In areas where Cr is naturally enriched, fertilizer regulations concerning the addition of Cr should be far more protective than other areas. A geochemical database would go a long way in solving some of these problems.

Rare earth element concentrations in Ontario agricultural soils are presented here, which have not been reported previously, and are indicative of background concentrations. Agricultural management had less of an impact on variations in REE concentrations than the geographic area. When compared to other published concentrations of REEs in Canadian soils, the REEs are in the same order of magnitude, but display a significantly different fractionation pattern. Instead of light REE enrichment or a flat pattern, southern agricultural soils have a domed pattern that indicates the enrichment of the MREEs. As the other Canadian soils were located in the far north (Northern Quebec, Nunavut; Butler & Dawson, 2018; Romero-Freire et al., 2019), which are quite different in characteristics and geology to agricultural soils, it is likely that soil characteristics influenced the apparent MREE enrichment and heavy REE retention. As reporting the REE concentrations and detailed TE composition is untapped work in Canada, the values presented should be used in future work as a starting point and expanded to include a greater area. The creation of a Canadian geochemical database should be seen as a goal, similar to the GEMAS program in European soils (Sadeghi et al., 2013).

Finally, although these results showed that agricultural BMPs may be linked with La and Gd concentrations, there was no association between field use and soil geochemical composition. However, outliers like field B3 and studies on long term fertilization trials (Bergen et al., 2022; Sun et al., 2022) indicate that agricultural inputs can have a significant impact on trace element and soil composition. Agricultural management should therefore be studied at in greater detail to determine the impacts of mineral fertilizers and pesticides on TE and REE loading in soil. This would include sourcing and analysing agricultural inputs with a known provenance, particularly those derived from mineral sources to determine the TE and REE load. This is complicated when using BMPs for fertilizer use, as fertilization should be tailored to soil test values and crop needs of the nutrient in question. Therefore, annual fertilizer inputs may not be the same between farms and may change by year. Detailed records of agricultural input type, source, and application rate should be considered in future work in conjunction with TE and REE soil concentrations to assess the risk of soil contamination.

6 References

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