Soil Geochemistry and Normative Mineralogy across Canada

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Abstract

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Soils play a crucial role in ecosystem functioning, for example, soil minerals provide important provisioning and regulate ecosystem services. This study used major soil oxides from the North American Soil Geochemical Landscapes Project (n=560) to assess elemental associations and infer soil minerals through exploratory data analysis and to determined quantitative soil mineralogy using a normative method, Analysis to Mineralogy (n=1170). Results showed elemental variability of oxides across the provinces of Canada and strong correlations occurred between elements indicative of soil mineral composition (e.g., Silicon and Aluminium). Principal component analysis inferred soil minerals from soil oxides trends on biplots and classified minerals, generally, as carbonates, silicates, and weathered secondary oxides. Spatial variability in minerals (quartz, plagioclase, potassium feldspar, chlorite, and muscovite) was related to the underlying bedrock geology. The use of Analysis to Mineralogy led to a reliable method of quantifying soil minerals at a large scale.

Keywords: soil geochemistry, soil mineralogy, exploratory data analysis, normative procedures, North American Soil Geochemical Landscapes Project, Analysis to Mineralogy

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1. General Introduction

1.1 Soil formation

Soil is a thin layer (up to 1.5 m in depth) of organic and inorganic material that covers the earth's surface; it is an integral component of the biogeochemical cycle, where elements (e.g., carbon, nitrogen, phosphorous, etc.) cycle through biological, chemical, and geological pathways. Biological organisms in soil contribute to the decomposition of organic material. Climate factors, for example precipitation, infiltrates soil to support a chemical mechanism of altering (weathering) inorganic material. Geology also affects the composition of soil as it is the parent material, which has been weathered and influences the minerals present in the soil. These factors contribute to the breakdown of organic and inorganic material to generate nutrients that are cycled through the environment. Soil systems are an integral part of their surroundings as the alteration of soil properties allows for the contribution of mass and energy over varied timescales to the environment (Amundson, 2005).

The process of soil formation, known as pedogenesis, depends on bedrock geology or parent material and environmental conditions (Heimsath et al., 1997). During soil formation, weathering of bedrock geology occurs through physical or chemical processes. Physical weathering is the breakdown of parent rock material through actions such as frost wedging or mechanical weathering. These actions cause disintegration of rock fragments into different size fractions. Chemical weathering is the alteration of rocks and minerals by reactions of hydrolysis, leaching, oxidation, dehydration, or complete dissolution. These reactions occur due to the interaction with water, weak acids, or lack of solution (e.g., dehydration). For example, hydrolysis involves adding a hydrogen ion to a mineral:

$$4KAlSi_3O_8 + 4H^+ + 2H_2O \rightarrow 4K^+ + Al_4Si_4O_{10}(OH)_8 + 8SiO_2$$

Orthoclase + hydrogen ions + water → potassium ions + kaolinite + quartz

where potassium and silicon dioxide (quartz) are released from orthoclase and the clay mineral, kaolinite, forms.

Soil genesis (or formation) leads to the development of a soil profile consisting of different soil horizons that display unique characteristics. Major soil horizons from surface to subsurface before encountering bedrock are divided into organic and mineral soils. Organic soils contain more than 30% organic matter and are identified as L, F, H and O horizons with L, F, and H developed from the accumulation of leaves, twigs, and woody matter, while the Organic (O) horizon is associated with peat materials, consisting of mosses, rushes and woody materials (Singer, 2008). Mineral soils are classified into A, B, and C horizons with the A horizon containing leached organic matter as it is directly below the O horizon. The B horizon contains a portion of organic matter but is comprised of primary and secondary minerals. The C horizon has little to no organic matter, relatively unaffected by pedogenic processes, and with minerals that, may, resemble the underlying bedrock geology (Singer, 2008). Soil horizon characteristics, also, may not reflect the local environment as transport of mineral matter can cover large distances depending on the transport vehicle. Transport processes can include wind, water, and glacial ice.

Soil texture and colour are two of the most common distinguishing properties in soil horizons. The texture of a soil depends on the parent material and environmental conditions that break down soil particles. Soil texture is predominantly described using three size fractions (based on the diameter), the largest particles between 0.05 and 2 mm are classified as sand. The next fraction is silt between 0.05 and 0.002 mm in size and the smallest size fraction is defined as clay which is less than 0.002 mm (Foth, 1990). Particle size distribution affects nutrient availability and the ability of soil to retain water. In addition, minerals break down into smaller

particles over time and certain minerals are more susceptible than others. As a consequence, e.g., quartz is more resistant to weathering, which causes the allocation of minerals to be skewed with respect to the size fraction. The colour of a soil horizon varies due to soil mineralogy, microbial activity, and the moisture content. The soil minerals present influence the soil colour depending on chemical and biological reactions that have occurred. For example, iron minerals (e.g., hematite, magnetite) undergo oxidation and the soil has a distinctive rusty, red colour. The amount of organic matter will cause the soil to be varying shades of brown while the presence of water causes the soil to appear darker.

Soils across Canada are classified into different soil orders based on distinguishing features, such as texture, colour, or the type of drainage. For example, soils with permafrost within 1 m of the surface, found throughout northern Canada, are classified as Cryosolic (CSSC, 1998). These soil orders are generalized, which causes a degree of uncertainty with respect to knowing specific soil details within a certain region. The soil orders also provide little to no information on mineral composition. For example, orders such as Luvisolic characterize the illuvial B horizon as silicate clay that has accumulated (CSSC, 1998), which does not define the type of silicate mineral and it may not be a realistic representation of the mineral content. The soil orders describe detailed features of the A and B horizons, but the description of the C horizon is lacking. The C horizon has the least amount of organic matter, as such, it is difficult to acknowledge distinct C horizon features across all the soil orders. An additional factor that contributes to characterizing soil orders is based on location and the environmental conditions in Canada.

The landscape of Canada impacts soil horizons and is categorised into differing ecological regions with common features, such as soil type, landforms, vegetation, and climate,

known as ecozones (CEC, 1997). These diverse ecosystems impact the near-surface soil geochemistry, such as the rate of weathering. For example, the Atlantic Maritime ecozone has high precipitation owing to its proximity to the ocean, which creates chemical weathering of primary minerals to release ions into the soil (CEC, 1997). In comparison, the Prairie ecozone of Western Canada has high winds and is very dry due to limited precipitation, meaning less ability to weather minerals that contribute to nutrient cycling (CEC, 1997).

1.2 Bedrock Geology and Mineralogy

The bedrock geology in Canada is diverse with the age of the geology spanning in excess of 3.0 Ga. Geological processes are varied, to form igneous, metamorphic, and sedimentary rock types. Areas across Canada are distinctive due to their rock type, for example the Precambrian Shield or the Western Canadian Sedimentary Basin (Figure 1.1). Rocks are composed of minerals, which can be defined as "a naturally occurring homogeneous solid with a definite (but generally not fixed) chemical composition and a highly ordered atomic arrangement" (Klein and Hurlbut, 1993).

Bedrock minerals can be primary or secondary where primary minerals are formed under the chemical and physical conditions when magma solidifies at either the earth's surface or at depth or as carbonate precipitates (calcium carbonate) from organic or inorganic material. Igneous primary minerals follow an idealized description of crystallization known as Bowen's reaction series where silicate minerals form under high to low temperature. At high temperatures, two different reactions begin, known as continuous or discontinuous, where the continuous branch crystallization begins with calcium-rich plagioclase (anorthite) and as the magma cools it reaches the sodium-rich endmember (albite). The discontinuous series forms the minerals

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olivine, pyroxene, amphiboles, and biotite. These series meet when the magma has cooled to where felsic rocks form (orthoclase and muscovite) and the crystallization of quartz, the lowest temperature mineral. Primary minerals can be altered by hydrothermal or weathering processes to form metamorphic or secondary minerals. Secondary minerals include, but are not limited to, clay minerals (kaolinite, illite), iron oxyhydroxides (goethite), and secondary carbonate precipitates (calcrete).

The stability of minerals at the earth's surface follow the Goldich dissolution series, which is similar to Bowen's reaction series. The primary minerals that form at high temperatures and pressures (e.g. olivine, pyroxene, anorthite) are less stable at the earth's surface and are more prone to chemical weathering as they are composed of cations with ionic bonds compared with the more stable minerals, which have more silica with covalent bonds. In contrast, primary minerals that are more resistant to weathering are formed at lower temperatures (e.g. muscovite, quartz). Secondary minerals are, typically, stable as they have formed at the earth's surface.
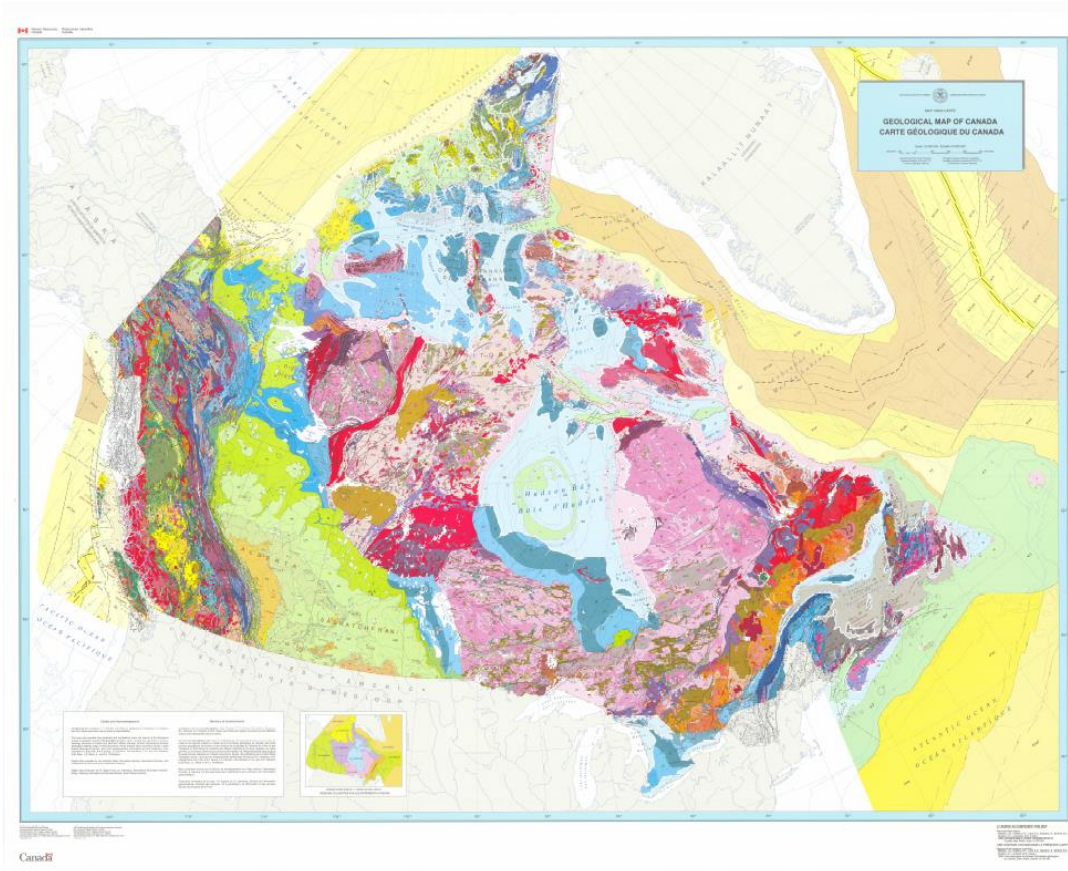
Figure 1.1. Geological map of Canada at a scale of 1:5 000 000 showing the principal bedrock geology (igneous, metamorphic, and sedimentary rock types) across Canada (Wheeler et al., 1996; legend in Appendix A).

1.3 Soil Mineralogy

Soil mineralogy is the study of the soil mineral phase (Feldman et al., 2008). In addition, soil minerals are essential in biotic and abiotic factors of ecosystems as they create environments to store water, provide nutrients for plant growth, regulate the chemistry of natural waters, and neutralize the effects of pesticides or atmospheric pollutant deposition. Soil mineralogy is widely employed in the exploration of precious elements, agriculture, or environmentally to understand the occurrence and distribution of minerals in soil. The knowledge of soil minerals can be used to determine weathering rates of surficial material, the age of soils, and paleoenvironmental conditions (White, 1995).

Soil minerals are arranged in a crystallographic matrix dominated by oxygen and silicon. The other components are major elements that include aluminum, iron, calcium, sodium, magnesium, and potassium. These elements and their stoichiometric arrangement are dependent on the minerals, which occurs during formation of primary or secondary minerals. Chemical weathering of soil minerals impacts the release of elements, in particular base cations (i.e., calcium, sodium, magnesium, and potassium), which are important nutrients for plant growth and the buffering capacity of soils. Determining quantitatively the soil minerals present is key to interpretation of chemical sources (Eberl and Smith, 2009).

1.4 Normative Procedures

Quantitative soil mineralogy can be estimated by X-Ray Diffraction, a technique used to identify minerals by the atomic and molecular structure of a crystal. However, this procedure requires specialized equipment, skilled analysts, and is time consuming, and as such it may not be feasible for all projects. Alternatively, quantitative soil mineralogy can be estimated by normative mineral calculations from geochemical analysis, such as whole rock analysis using X-Ray Fluorescence or Inductively Coupled Plasmas-Mass Spectrometry. Early normative procedures, such as Cross, Iddings, Pirsson, and Washington (CIPW) in the 1900s, were developed to estimate the mineralogy of a rock sample based on Bowen's reaction series and the crystallization sequence of mineral formation of igneous rocks (Cross et al., 1902). Other normative calculations have been developed based on the geological environment of metamorphic (Barth, 1959, 1962) and sedimentary rocks (Cohen and Ward, 1991) with additional procedures reflecting specific geological settings, such as greenschist facies meta-volcanic rocks from the Abitibi Greenstone Belt (Piché and Jébrak, 2004).

The aid of computers has greatly enhanced the ability to estimate mineralogy as normative calculations are no longer computed manually and numerous software packages utilize algorithms and matrix algebra to solve for mineralogy. For example, SEDNORM (Cohen and Ward, 1991) establishes mineral abundance for sedimentary rock types by applying a series of linear equations under a best-fit solution. NORMA (Raisanen et al., 1995) is another program to calculate mineralogy of glacial tills from the (additional) geochemical analysis using aqua regia; MINSQ computes least-square solutions of mineral compositions from whole rock analysis (Herrmann & Berry, 2002); and MODAN uses Gaussian elimination and linear regression to estimate mineral quantities from bulk compositions (Paktunc, 1998; 2001). The program, Analysis to Mineralogy (A2M), uses soil oxides to identify all possible mineral modes from a pre-determined mineral list, where the solutions form a finite convex polyhedron, the dimension of which is "number of minerals minus number of elements" (Posch and Kurz, 2007). This normative method is effective with either small or large datasets, regardless of the geology. A Swedish study evaluated A2M at two sites by comparison with X-Ray Diffraction (XRD) mineralogy and found a close agreement between the modeled (A2M) and measured (XRD) mineralogy (Casetou-Gustafson et al., 2018). A number of studies have used A2M in conjunction with the PROFILE model to investigate weathering rates as one of the PROFILE inputs is soil mineralogy and the use of A2M allows for the selection at sites of specific minerals associated with weathering (Sverdrup and Warfvinge, 1993; Akselsson et al., 2004; Whitfield et al., 2011; Koseva et al., 2010, Stendahl et al., 2013).

1.5 Soil Geochemistry

Soil geochemistry involves identifying appropriate chemical principles to explain the element concentrations (Sverdrup, 1996). The elements found in soil have been weathered from bedrock geology, which have implications to human and ecosystem health (Rencz et al., 2011). Major elements are the abundant soil chemicals, whereas minor, also known as trace, elements constitute the rest of soil mineral composition. Investigation of trace elements, e.g., environmental impact assessments, are typically given more attention when they could affect human health due to exceeding toxicity levels.

The type of minerals in the soil impact its geochemistry and depending on the mineral, a dissolution reaction can cause weathering and the process of altering a primary mineral to a secondary mineral occurs. Potentially, secondary minerals could be dissolved further. This change in soil geochemistry can have consequences in the environment by changing the pH-buffering mechanism of the soil. An additional effect is the weathering of silicate minerals, which can act as an important CO_2 sink and part of the global carbon cycle and ultimately impacts climate change (Appelo and Postma, 2005).

1.6 Soil Geochemical Surveys

Soil surveys and sample collection are typically conducted for a single purpose, such as conservation, permit planning, and mineral exploration. However, recently surveys have become more systematic in the investigation, description, and mapping of soils, and in general are carried out in collaboration with multiple agencies (Wilson et al., 2008). Depending on the scale of a survey, a large amount of data can be generated, where the assemblage and interpretation can be difficult. The addition of geochemical analysis to surveys has allowed for the study of pedogenic processes such as mineral weathering, podzolization, or illuvation (Wilson et al., 2008). For

example, in Europe, one study examined the total element concentrations in agricultural soils and found soils were influenced by the main bedrock geology (Reimann et al., 2012). Governments have undertaken nation-wide surveys to provide a consistent database of geochemical information, for example, a Geochemical Atlas of Australia was published, which covers approximately 81% of Australia and provides a continent-wide dataset of 59 chemical elements (Caritat and Cooper, 2011). This has allowed for the determination of geochemical background variation to distinguish between natural concentrations and potentially toxic elements (Reimann and de Caritat, 2017).

During the 2000s in North America, a tri-national collaboration between the United States, Canada, and Mexico formed the North American Soil Geochemical Landscapes Project (NASGLP). The continent-wide project aimed to provide a consistent database of soil geochemical and soil mineralogical data and an archive of soil samples for future use (Smith et al., 2009). Field sampling included soil samples, soil gas radon and natural radioactivity (Friske et al., 2014). The United States completed the project in 2010, whereas Canada withdrew from the project in 2009 before all the sampling had been accomplished. Canada sampled 577 sites and released data for 560 sites to the public domain (Friske et al., 2013). A plethora of information is available including field data, horizon data, and laboratory analysis, which involved geochemical analysis of 55 elements by Inductively Coupled Plasma-Mass Spectrometry and Inductively Coupled Plasma-Atomic Emission Spectrometry. However, soil mineralogy was not analysed for the majority of the Canadian portion of NASGLP.

1.7 Compositional Data and Exploratory Data Analysis

Geochemical data, expressed in wt %, ppm, ppb, is considered to be compositional as it sums to a constant (e.g., 1, or 100). This causes statistical techniques, for example correlation matrices, to potentially provide misleading results and erroneous interpretation of the data. This spurious statistical behaviour of compositional data was first reported by Karl Pearson (1897) and subsequently geologist Felix Chayes (1960) raised concerns of interpreting results after applying multivariate statistical analysis to compositional data due to a negative bias. John Aitchison (1986) introduced a technique of transforming compositional data using log-ratios which allows for statistical methods to be reliable and defensible.

Analysis of soil geochemical results includes exploring relationships within the dataset by statistical techniques. Exploratory Data Analysis (EDA) is beneficial when examining geochemical data as it can help to reveal patterns, outliers, missing data, and ultimately it is an essential step to really understanding and knowing the data (Grunsky, 2010). EDA typically includes statistical analysis via numerical or visual methods applied to a dataset. Statistical summaries may involve the mean, median, standard deviation, or coefficient of variation. Graphical methods could be univariate such as boxplots, histograms, or quantile-quantile plots, bivariate with scatter plot matrices, or multivariate with use of principal component analysis or clustering procedures. Principal component analysis is a prominent exploratory technique that transforms the variables (in this case, chemical composition) in a dataset into components, which project the results in a graphical manner (Grunsky, 2010). EDA typically uses untransformed and transformed log-ratio data depending on the statistical method.

1.8 Objectives

The objectives of this study were to assess whether geochemical data can be used to infer qualitative soil mineralogy and to predict quantitative soil mineralogy by a normative procedure at sampling sites across Canada. This thesis is written in manuscript style, with a general introduction (Chapter 1) and two research (manuscript style) chapters (Chapter 2 and Chapter 3). The data used in Chapter 2 is also used in Chapter 3, thus some portions of the methods are repeated. A general conclusion and summary are presented in the final chapter (Chapter 4).

Chapter 2 (Exploratory Analysis of Geochemical Data and Inference of Soil Minerals at sites across Canada) utilized soil geochemical data collected from the North American Soil Geochemical Landscapes Project, i.e., 560 sites sampled across Canada. The chapter examined major element soil oxide data by exploratory statistical methods to determine if the oxide data revealed information about site-specific element associations of the soil mineralogy. Principal component analysis was used to visually assess the soil oxides and to determine if soil minerals can be inferred at sites across Canada. Geospatial mapping of the principal components was used to visualize the distribution of soil minerals, also in relation with regional bedrock geology.

Chapter 3 (Determination of Normative Soil Mineralogy at 1170 sites across Canada) focused on the prediction of quantitative soil mineralogy from geochemical data at sites across Canada. Normative prediction using the solver program Analysis to Mineralogy (A2M) provided quantitative soil mineralogy, with A2M using soil oxides and qualitative soil mineral data to create a list of all possible mineral modes for each site. The objective was to evaluate A2M predictions compared to XRD mineralogy estimates and subsequently determine soil mineralogy at 1170 sites with A2M.

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2. Exploratory Analysis of Geochemical Data and Inference of Soil Minerals at sites across Canada

2.1 Abstract

Soil plays a crucial role in ecosystem functioning; e.g., soil minerals provide important provisioning and regulating ecosystem services. The determination of soil mineral composition can help to link geochemical processes to underlying bedrock and surficial geology, however analysing quantitative soil mineralogy by X-Ray Diffraction can be expensive. This study used data from the North American Soil Geochemical Landscapes Project sampled at sites (n=560) across Canada; exploratory analysis of major elements from the C-horizon, <2 mm size fraction, was carried out to determine if geochemical data can infer site-specific qualitative soil minerals. Results indicated variability of major elements across Canadian provinces with noticeable differences of the elements silicon and calcium. Geochemical data are compositional, as such their statistical assessment is subject to the problem of closure. In the current study, all raw geochemical data were centred log-ratio transformed prior to statistical analysis to overcome closure. Graphical measures indicated skewed element data prior to centred log-ratio transformation, which produced a more normal distribution. Strong correlations between elements indicated soil mineral composition, such as silicon and aluminum from aluminosilicates minerals. Principal Component Analysis of transformed geochemical data revealed three distinct groups of calcium, magnesium; iron, titanium, manganese; and aluminum, potassium, silicon, sodium, while phosphorous had smaller variability independent of these groups. The interpretation of these groups was based on soil minerals and identified as carbonates, silicates, and weathered secondary oxides. These minerals corresponded geospatially to the regional bedrock geology of the sites across Canada, such as the sedimentary rock types from Western Canada to more variable minerals from igneous, metamorphic, or sedimentary rocks in Eastern Canada.

2.2 Introduction

Soil is defined as a thin layer of material at the Earth's surface composed of organic and inorganic matter, formed from a combination of bedrock geology (known as parent material), climate, topography, biological organisms, and time (Amundson, 2005; Jenny, 1941). With respect to parent material, geochemistry is the study of the chemical composition of rocks and minerals, and soil geochemistry provides an estimate of the distribution of chemical elements and minerals in soils. Identifying the minerals in soil is essential to understanding nutrient management, resource exploration and is often a key to solving environmental problems.

Bedrock geology across Canada encompasses a broad spectrum of stratigraphic rock formations (Wheeler et al., 1996; Appendix A1). Eastern Canada encompasses a combination of Paleozoic aged sedimentary, igneous, and metamorphic rocks. Further, an expansive region of Precambrian igneous and metamorphic rock, known as the Canadian Shield, extends across much of eastern, central, and northern Canada. Western Canada is dominated by the Western Canadian Sedimentary basin of Cretaceous aged sedimentary rocks plus multiple terranes of igneous, metamorphic, and sedimentary rocks. In addition, glacial till was deposited across large areas of Canada during the last glacial period, approximately 100,000 to 10,000 years ago.

This diverse bedrock landscape is associated with an equally diverse spectrum of soil minerals (Klassen, 2009). Minerals can be primary or secondary, where primary minerals reflect the composition of the parent material. Secondary minerals consist of altered primary minerals that have undergone physical or chemical weathering. The composition of minerals and their stoichiometric arrangement, is dependent on the chemical interactions of the elements involved and their crystallographic structure. Soil mineralogy is central to interpreting geochemical patterns and elemental variability released into the environment by weathering (Eberl and Smith, 2009).

Identification of quantitative soil minerals is generally conducted by X-Ray Diffraction (XRD), which provides information on the crystallographic arrangement of minerals. However, XRD analyses can be expensive, which may be a limiting factor for assessments with large number of samples. Further, it may also be inaccurate owning to uncertainty in mineral phase distinction and the amount of amorphous material that cannot be attributed to any specific mineral phase.

Alternative cost-effective methods of analyses are required to provide information about environmental, geological, or even anthropogenic processes. Soil geochemistry can be measured either by X-Ray Fluorescence, which identifies atoms by their fluorescent x-ray emissions, or by Inductively Coupled Plasma, which ionizes a sample then separates and measures the ions with mass spectrometry (ICP-MS) or the absorption of radiation with atomic absorption spectrometry (ICP-AAS). Subsequent analysis of soil geochemical composition data typically involves the statistical exploration of relationships within the elements. Principal component analysis (PCA) is a prominent exploratory data technique that can reduce the number of variables (in this case, chemical composition) in a dataset (Grunsky, 2010). These principal components may reveal element associations (i.e., mineral stoichiometry) that reflect geological origins and as such, be used to infer soil minerals (de Caritat et al., 2017).

Soil geochemical surveys provide quantitative site-specific measures of chemical composition, typically in parts per million, parts per billion, or weight percent. However, these results are compositional in nature, i.e., they sum to a constant (100%), which limits the ability to perform statistical analysis (Chayes, 1960). To solve this issue, Aitchison (1986) proposed that compositional data be transformed by log-ratios to avoid misleading negative components in correlation matrices. Common log-ratio transformations include centred log-ratio (clr), additive log-ratio (alr), and isometric log-ratio (ilr); the clr transformation is widely used with geochemical

data (e.g. Grunsky, 2010; Dmitrijeva et al., 2018; Martín-Fernández et al., 2018; Tolosana-Delgado et al., 2018), as the ilr transformation has the disadvantage that resulting new variables are no longer directly interpretable in terms of the original variables. Soil geochemical survey data are used in multiple industries such as mineral exploration or environmental investigations. The scale of a geochemical survey may be relatively localized, regional, or at a national level depending on the study objectives. National surveys have been recently completed in United States, Australia, and Northern Ireland, providing consistent databases of information (United States: Smith et al., 2011; Australia: de Caritat and Cooper, 2011a, 2011b; Northern Ireland: Young et al., 2013). These databases contain chemical analysis from thousands of sites and allow for country-wide interpretations of geological processes in broad landscape environments.

In 2002, the United States Geological Survey (USGS), the Mexican Geological Survey (MGS) and the Geological Survey of Canada (GSC) formed the North American Soil Geochemical Landscapes Project (NASGLP) and initiated a tri-national geochemical survey to mitigate the limited knowledge of soil geochemistry and mineralogy in North America (Smith et al., 2009; Friske et al., 2013a). The goals of the project were to generate a continental scale inventory (and baseline level) of soil geochemical data, and depending on the country, soil mineralogical data, and to form an archive of soil samples for future use (Smith et al., 2009). The NASGLP established common sampling protocols to ensure consistent soil geochemical and mineralogical data across the entire study domain. The USGS and MGS completed sampling in 2010 (Chipres et al., 2009; Smith et al., 2011). Canada sampled 577 sites of their intended 6,018 sampling sites, approximately 10%, but did not finish the project due to a change of priorities at the GSC (Friske et al., 2013a).

The objectives of this study were to assess element associations and spatial variability in soil geochemical data through exploratory data analysis, and to determine if geochemical data can

infer qualitative soil mineralogy at sites across Canada. To accomplish this, the study used the Canadian soil geochemical data from NASGLP as it provided a consistent set of observations.

2.3 Methods

2.3.1 Data acquisition

Site selection under the NASGLP was based on a 40 km × 40 km grid system (or one site per 1600 km^2) using a study design that was spatially balanced and allowed for consistent sample site density (Garrett and Kettles, 2009). This resulted in 13,487 sites across North America with 6,018 sites in Canada (Friske et al., 2013a). Final field site locations were decided by the pre-determined coordinates and field conditions (Friske et al., 2010). Site selection allowed for estimates of background soil element concentrations to be statistically defensible owing to the spatially random sample design (for further details see Friske et al., 2013a).

Consistent field sampling, chemical, and physical analysis protocols were developed across the NASGLP (Friske et al., 2013b, 2014). Pilot studies comprising two continental-scale transects across the United States and Canada were carried to guide the development of these protocols. The two transects, an East–West and a North–South, were sampled in 2004 (Smith et al. 2005). The North–South transect went from southern New Mexico, United States into northern Manitoba, Canada, where 29 sites were sampled (Smith et al., 2005).

In Canada, systematic sampling under the NASGLP was conducted by the GCS, provincial Geological Surveys, and soil scientists from Agriculture and Agri-food Canada (AAFC). Field sampling began in 2007 throughout the Maritime Provinces (New Brunswick, Nova Scotia, and Prince Edward Island) and further field sampling occurred during 2008 and 2009 across the remaining provinces (Grunsky et al., 2013; Friske et al., 2014). Sampling was completed in the Maritime Provinces; however, only a limited number of sites were sampled in the other provinces

(Newfoundland, Quebec, Ontario, Manitoba, Saskatchewan, Alberta, and British Columbia), owing to changing priorities in GSC (Friske et al., 2013b). In total, 577 sites were sampled, however data were released for only 541 sites (Friske et al., 2013a). Based on available data from the Manitoba transect (n = 29) and the Canadian portion of NASGLP, data from 560 sites was used in this project (Figure 2.1).
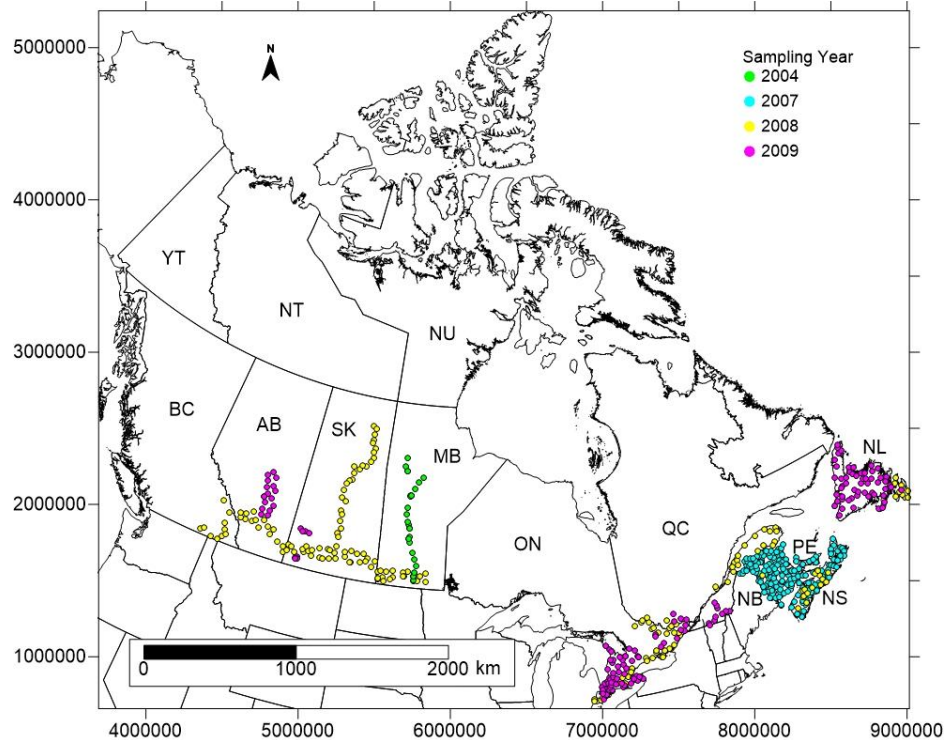
Figure 2.1. Sampling sites locations (n=560) and year of sampling from the North American Soil Geochemical Landscapes Project (Map projection: Lambert Conformal Conic).

Field sampling comprised of excavating a 60 cm wide by 70 cm long soil pit at each site (Friske et al., 2014). Soil samples were collected from the Public Health layer (0–5 cm), 0–30 cm (2009 field season only), and the A, B, and C horizons. Other information collected included site ID, location coordinates, elevation, and a site description of the surface material, mode of surface deposition, local surface expression, bedrock type, slope, drainage, contamination potential, and vegetation cover.

Laboratory methods are described in detail by Friske et al. (2014). In general, soil samples were air dried and split into two size fractions of <2 mm and <0.63 µm. A split of the <2 mm was ball milled before a 4-acid digestion. This 'near-total' digestion method consists of a mixed ratio of 2:2:1:1 using HCl, HNO_3, $HClO_4$ and HF. The acid digestion breaks down most of the insoluble elements, with exceptions of Ca and Mg. Analysis of 58 major and trace elements was carried out using ICP-MS. The remaining <2 mm sample was analysed for total carbon by combustion (in %) using a Leco CR-412 Carbon Analyser. Organic matter was estimated by loss on ignition (LOI) at 500°C (Friske et al., 2013b). Particle size analysis for grain size greater than 63 µm was determined by wet sieving and grain size less than 63 µm was determined using a Lecotrac LT-100 Particle Size Analyser (Friske et al., 2014). Further details on sampling procedures are described by GCS (Open Files 6433, 7334) and the USGS (Open File 2005-1253).

2.3.2 Data selection

The current study focused only on the C horizon data, <2 mm size fraction that underwent 4-acid digestion, as this horizon most closely resembles the parent material (Friske et al., 2013a). In addition, the <2 mm size fraction has better element detection (Klassen, 2009). A total of 560 sites across the 10 Canadian provinces were available for the study (Figure 1): British Columbia had 10 survey sites, Alberta 32, Saskatchewan 65, Manitoba 49, Ontario 108, Quebec 39, New Brunswick 115, Nova Scotia 67, Prince Edward Island 9, and Newfoundland 66.

Major elements, e.g. Al, Ca, Fe, K, Mg, Mn, Na, P and Si, represent the dominant proportion of the soil mineralogy composition; these elements were the focus of this study. In the current study, elements were presented as oxide weight percent for comparison with published data; conversions from element concentrations requires the molecular weights of the individual

oxides. For example, to convert 1.19 wt% Mg to MgO wt% the atomic mass of Mg (24.305 g/mol) and O (15.994 g/mol) are required:

$$1.19 \text{ wt\% Mg} \times (24.305 + 15.994) \div 24.305 = 1.97 \text{ wt\% MgO} \qquad \text{Eq. 1}$$

This calculation was applied to the individual major element; however, Si was not analyzed, as such it was calculated as follows:

$$100\% - \text{sum of major element oxides (\%)} - \text{loss on ignition (\%)} = \% \text{ SiO}_2 \qquad \text{Eq. 2}$$

It is important to note that calculated-Si did not account for trace elements or elements that do not completely dissolve under 4-acid digestion, i.e., Ca and Mg. As such, calculated-Si is a simplified estimate of Si, as it also includes the sum of unmeasured elements (other than Si) and analytical errors.

The Manitoba transect data (n = 29) did not contain LOI measurements but did provide Total Organic Carbon (TOC). Further, the dataset from the 2007–2009 field seasons also had a small proportion of samples (n=24 or 4.3%) missing LOI data but with TOC data available. To convert TOC to LOI, the Van Bemmelen conversion factor of 1.724 (Pribyl, 2010) was utilized (i.e., LOI (%) = TOC (%) × 1.72). In addition, there were 8 (1.4%) samples from the 2007–2009 dataset that did not have LOI or TOC data for the <2 mm fraction. In order to avoid removing these samples, LOI for the <2 mm fraction was estimated from observations of TOC for the <63 µm size fraction using simple linear regression to define the relationship between LOI (<2 mm) and TOC (<63 µm) at sites where both observations were available. It should be noted that the estimation of Si (as 100 – sum of the elements – LOI (%)), and the estimation of LOI (from TOC), are based on simple assumed relationships that cannot be tested and, therefore, may introduce uncertainties in the analysis.

2.3.3 Exploratory Data Analysis

Numerical and graphical methods were used to explore the distribution of the major element data. For example, mean and median summaries and coefficient of variation (CV), i.e., the ratio of the standard deviation to the mean, provide information on data dispersion. Similarly, univariate graphical measures, such as boxplots, histograms, density plots, quantile-quantile (Q-Q) plots, and scatter plot matrices, help visualise data distribution. Furthermore, Q-Q plots can compare observed frequency distributions against an expected frequency distribution, typically a normal distribution. Bivariate graphical measures, such as scatter plot matrices (SPLOM), can be used to visually evaluate linear correlations between variables.

In this study, intra- and inter-associations between elements were used as an indicator of soil geochemical processes and to identify potential mineral groups. Summary statistics, specifically mean, median, and CV, provided quantitative measures of the data distribution. Graphical measures were applied to reveal outliers or to further evaluate oxide distributions; Q-Q plots were the most beneficial in describing the distribution characteristics of a specific oxide. SPLOM were used to assess positive and negative correlations between oxides as an indication of their potential soil mineralogical composition.

Principal component analysis is a multivariate data analysis technique that reduces the number of variables in a data set (Joliffe, 2002). The technique describes the variability in a dataset by establishing linear combinations as principal components from a measure of association, either a correlation or covariance matrix (Joliffe, 2002). The matrix contains eigenvectors that correspond to the highest variability in the dataset. A scree plot is generally used to visualise the variance explained by each principal component; components with total eigenvalues above 1.0 are generally assumed to have the most influence on the data. However, it should be noted that

components with eigenvalues < 1.0 may represent important process that have been under sampled. The principal components and eigenvectors can be presented on a biplot (Gabriel, 1971), which visually displays the relationships between the variables and the observations.

In this study, eigenvectors represent the oxides, and their sign indicates positive or negative association between oxides within a component. The combination of principal components and eigenvectors from the biplots were used to infer the likelihood of specific minerals at a site. The site-specific principal component scores were also mapped to evaluate the spatial variability of likely minerals across Canada.

2.3.4 Compositional Data

Chayes (1960) identified the spurious, or false, behaviour of statistical testing of compositional data due to the closed sum on the correlation coefficient as a negative bias. To circumvent this issue, Aitchison (1986) developed a method to transform compositional data using log-ratios. The transformation allows compositional data to be projected into real number space for robust statistical analysis. The transformation chosen for this study was centered log-ratio (clr) as it has been shown to provide more interpretable results than other log-ratio transformations (Grunsky, 2010):

$$clr(x) = \left[\ln \frac{x_1}{g(x)}, \ln \frac{x_2}{g(x)}, \dots, \ln \frac{x_D}{g(x)}\right] \qquad \text{Eq. 3}$$

where x is the composition of D elements measured from a sample and g is the geometric mean of all the components (McKinley et al. 2015). This transformation allows for the graphical representation of the principal components by preserving the relative scale of the data (Pawlowsky-Glahn et al., 2015).

In the current study, it was recognized that statistical analysis of raw data may be subject to the effect of closure, as such the clr transformation was applied to the raw data prior to data analysis. In general, the ilr transformation is widely promoted as the mathematically correct way to express a compositional data set (e.g., Egozcue and Pawlowsky-Glahn, 2006; Mateu-Figueras et al., 2011). However, the utility of the ilr transformation has been recently debated (Greenacre et al., 2019). In the current study, we chose to use the clr transformation for consistency with previous work carried out in Canada (Grunsky et al., 2013); moreover, clr provides a simpler, more intuitive and more interpretable alternative to ilr. All statistical analysis was conducted with the statistical program R and the following packages: compositions, devtools, ggfortify, ggplot2, and graphics (The R Foundation, 2018).

2.4 Results

2.4.1 General Survey Site Characteristics

Ecosystems across Canada are categorised into distinctive ecozones based on common biotic and abiotic characteristics across broad geographical regions (CEC, 1997). Survey sites from NASGLP encompassed six ecozones, the proportion of sites in the Atlantic Maritime ecozone was 38%, Boreal Plains 4%, Boreal Shield 21%, Mixedwood Plains 18%, Montane Cordillera 2%, and Prairies 18%. Land cover at survey sites was classified as deciduous forest, mixed forest, coniferous forest, agriculture crop, grassland, and shrubland (Friske, 2013b). The dominant bedrock geology underlying the sampling sites was sedimentary (clastic and carbonate rocks) at 79%, igneous geology at 16%, and metamorphic geology at 5% (Wheeler et al., 1996).

2.4.2 Oxide Data

The dominant oxide in the soil C horizon was calculated-SiO_2 (Table 2.1); Manitoba had the lowest mean amount (65%) and Prince Edward Island had the highest mean value of SiO_2 (78%). The oxide that contributed the least to soil composition was MnO (mean <0.1%). Calcium oxide content varied widely across the study sites as evidenced by a high coefficient of variation (CV = 1.42), suggesting a large dispersion in the data. Average CaO content was <1% in Prince Edward Island, Nova Scotia, and New Brunswick (full provincial surveys); in contrast, values up to 8% were observed in Manitoba and Ontario. A distinctive variation in CaO and calculated-SiO_2 values was noticeable between provinces west of Quebec (i.e., Ontario, Manitoba, Saskatchewan, Alberta, and British Columbia) compared with provinces to the east (New Brunswick, Nova Scotia, Prince Edward Island, and Newfoundland). Average CaO to the west are predominantly high with a range of 4.24 to 8.66 wt% compared with low CaO values of 0.12 to 1.75 wt% in the east. In contrast, average calculated-SiO_2 in the west ranged from 64.57 to 72.20 wt% compared with higher calculated-SiO_2 values of 69.29 to 78.08 wt% in the east. The observed difference between the median and mean values for CaO, LOI, and MgO indicated skewed data, suggesting outliers or strong regional variation (Table 2.1). A few atypical values in the dataset such as calculated-SiO_2 at 29.02% (in Manitoba) appeared to be outliers but after log-centred transformation the values fit a normal distribution and were not removed from the dataset. This highlights the need to transform compositional data; any statistical measures, e.g., average, coefficient of variation, variance, on raw compositional data should be interpreted with caution as they are subject to the effect of closure.

Quantile-quantile plots were advantageous in identifying unique aspects of the oxide data distributions, e.g., untransformed quantile-quantile plots indicated normal (e.g., calculated-SiO_2) or skewed (e.g., MnO, MgO, CaO) oxide distribution data (Figure 2.2); however, following

transformation, the skewed data were more normally distributed (Figure 2.3). The other graphical data techniques (i.e., boxplots and histograms) showed similar results (i.e., skewed distribution prior to log-centred transformation, see Appendix A2). The log-centred MgO and CaO had tails at the ends of their distributions (Figure 2.3), which suggests strong regional variation in bedrock geology, i.e., a regional contrast between carbonate sediments and silicates (as noted in Table 2.1).

Strong positive correlations (i.e., coefficients of the Variation Matrix) of log-centred major oxides were observed between Si-Al, Si-K, Ti-Al, Ti-Fe, Al-Fe, Al-K, and Fe-Mn oxides (Figure 2.4). The positive associations are strong indicators of soil mineral composition, for example the correlation between calculated-SiO_2 and Al_2O_3 (r = 0.61) could indicate aluminosilicate minerals. Aluminosilicate minerals are major components of clay minerals such as kaolinite from chemical weathering of feldspars or the metamorphic polymorphs andulasite, kyanite, and sillimanite. Similarly, the correlation between calculated-SiO_2 and K_2O are indicators of potassium-feldspar minerals. The other strong positive element associations may suggest minerals that are typically found in soil together but may not be composed of those elements, e.g., TiO_2 could be from the mineral rutile and Al_2O_3 from clay minerals such as kaolinite, indicating highly weathered soils or minerals. Strong negative associations occurred between Al-Mg, Al-Ca, Fe-Ca, and Ca-K oxides, which suggests that minerals composed of these elements are rarely found in association. The MgO-CaO scatter plot showed a unique curved (boomerang) pattern that could be attributed to regional differences in bedrock geology (Figure 2.4), i.e., high positive correlations in CaO-MgO content from central and western Canada is dominated by sedimentary formations, especially in Manitoba with carbonate (or dolomite) bedrock geology, whereas in eastern Canada carbonate minerals are not as prominent or calcium and magnesium may be a smaller component of silicate

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minerals. The weak oxide (or inverse) associations have less influence on soil mineral composition and generally soil minerals are not composed of those oxides.

2.4.3 Soil Mineral Identification

Principal component analysis conducted on the log-centred oxide data was limited to the first three principal components (PC) based on the scree plot (Figure 2.5) and eigenvalues (Table 2.2; all eleven eigenvectors are presented in Appendix A3). The first three components accounted for 70.34% of the variation in the dataset with the proportion of the first PC at 39.28%, the second at 21.26%, and the third at 9.81% (Table 2.2). Previous studies have suggested that in geological systems a total variance > 65% (for all eigenvalues > 1) reflects real structure in a dataset, which allows for interpretations from the biplot (Tolosana-Delgado and McKinley, 2016). The additional principal components were not examined but may represent under sampled processes. In this study, inferences regarding site-specific soil mineralogy were based on the biplots of the oxide eigenvectors for the first three PCs (Figure 2.6 and 2.7). Principal component 1 (PC1) was dominated by the Al_2O_3 eigenvector at 0.89 and almost completely opposite was CaO at –0.90. The eigenvector loading of PC2 was dominated by LOI at 0.66 and Na_2O at –0.70. Principal component 3 eigenvectors had P_2O_5 at 0.68 and MnO at 0.41 (Table 2.2).

Table 2.1. Statistical summary of untransformed major oxides (%) for the soil C-horizon (<2 mm size fraction), and mean content by province (n=560) from the North American Soil Geochemical Landscapes Project.

	Min	25%	Median	Mean	75%	Max	CV	AB	BC	MB	NB	NL	NS	ON	PE	QC	SK
SiO_2	29.09	65.75	70.84	70.06	75.20	90.43	0.11	71.57	69.96	64.57	72.03	69.29	73.24	66.50	78.08	70.25	72.20
TiO_2	0.06	0.42	0.57	0.58	0.72	2.60	0.43	0.49	0.43	0.33	0.65	0.84	0.58	0.57	0.64	0.74	0.35
Al_2O_3	2.96	9.78	11.55	11.52	13.26	19.02	0.23	11.02	10.65	10.01	12.34	12.11	12.43	11.12	10.49	12.24	10.39
Fe_2O_3	0.61	2.97	4.22	4.34	5.57	10.87	0.41	3.57	3.69	3.19	4.98	5.24	4.52	4.20	3.73	5.71	2.97
MnO	0.01	0.05	0.07	0.08	0.10	0.74	0.68	0.07	0.06	0.06	0.07	0.11	0.11	0.09	0.09	0.09	0.05
MgO	0.12	1.06	1.58	2.19	2.56	19.83	0.92	1.73	3.08	4.77	1.59	1.97	1.07	2.69	1.07	2.09	2.14
CaO	0.03	0.35	1.39	3.70	4.39	29.41	1.42	4.24	5.85	8.66	0.47	1.75	0.41	8.18	0.12	1.30	4.96
K_2O	0.67	1.81	2.14	2.27	2.74	4.64	0.29	1.89	2.68	1.91	2.19	2.17	2.45	2.46	3.08	2.68	2.03
Na_2O	0.18	1.10	1.49	1.66	2.06	4.15	0.49	1.16	1.49	1.57	1.51	2.34	1.46	1.67	0.98	1.93	1.69
P_2O_5	0.02	0.08	0.12	0.12	0.14	1.15	0.59	0.13	0.14	0.11	0.10	0.12	0.10	0.16	0.07	0.15	0.12
LOI	0.03	1.93	2.86	3.48	4.26	18.10	0.76	4.12	1.98	4.83	4.07	4.07	3.63	2.36	1.65	2.83	3.09

Note: SiO_2 (%) was calculated as 100% – sum of major elements (%) – loss on ignition (%), CV = Coefficient of Variation, AB = Alberta, BC = British Columbia, MB = Manitoba, NB = New Brunswick, NL = Newfoundland, NS = Nova Scotia, ON = Ontario, PE = Prince Edward Island, QC = Quebec, SK = Saskatchewan
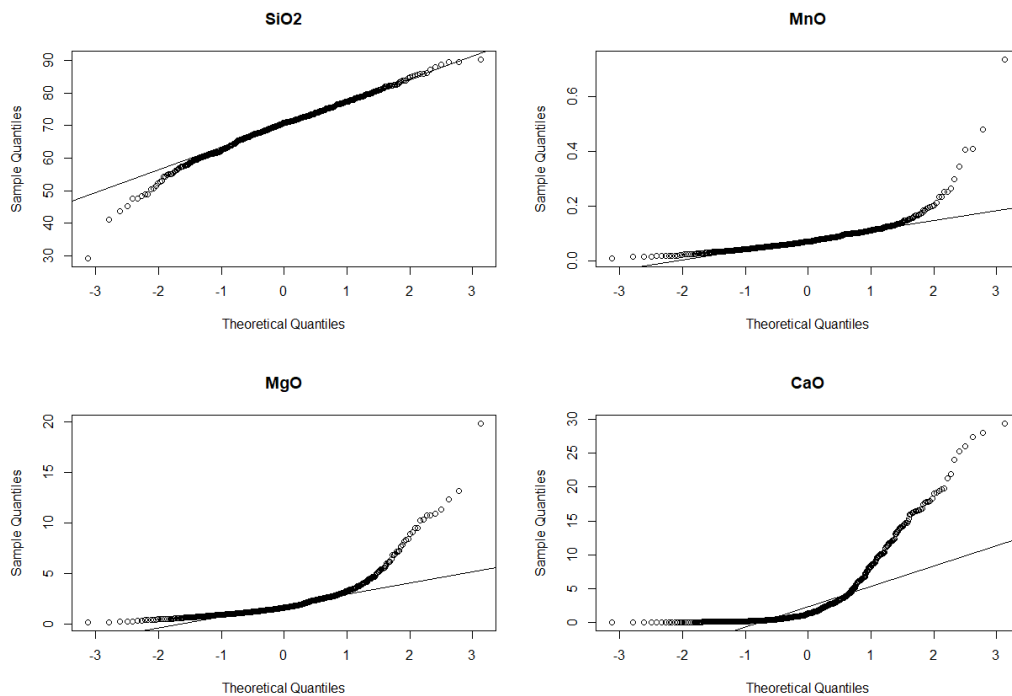
Figure 2.2. Quantile-quantile plots of untransformed major oxide data (SiO$_2$, MnO, MgO, and CaO) for the soil C-horizon, <2 mm size fraction, from the North American Soil Geochemical Landscapes Project (n=560).

Figure 2.3. Quantile-quantile plots of log-centred major oxide data (SiO$_2$, MnO, MgO, and CaO) for the soil C-horizon, <2 mm size fraction, from the North American Soil Geochemical Landscapes Project (n=560).

Figure 2.4. Scatter plot matrix (SPLOM) of log-centred major oxide data for the soil C-horizon, <2 mm size fraction, from the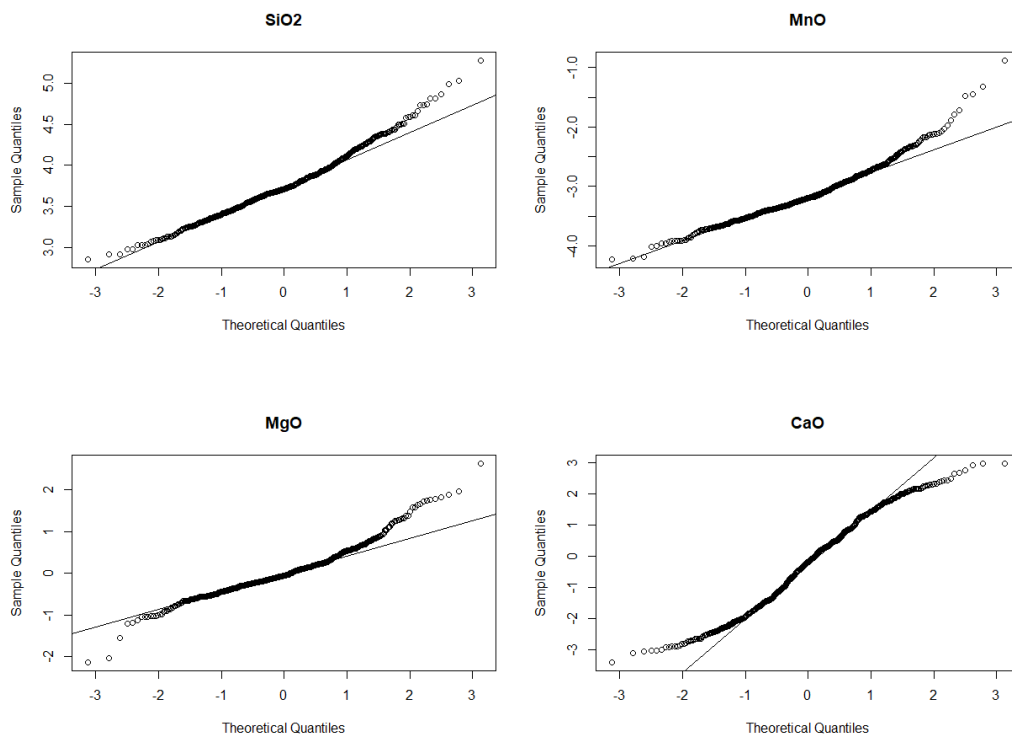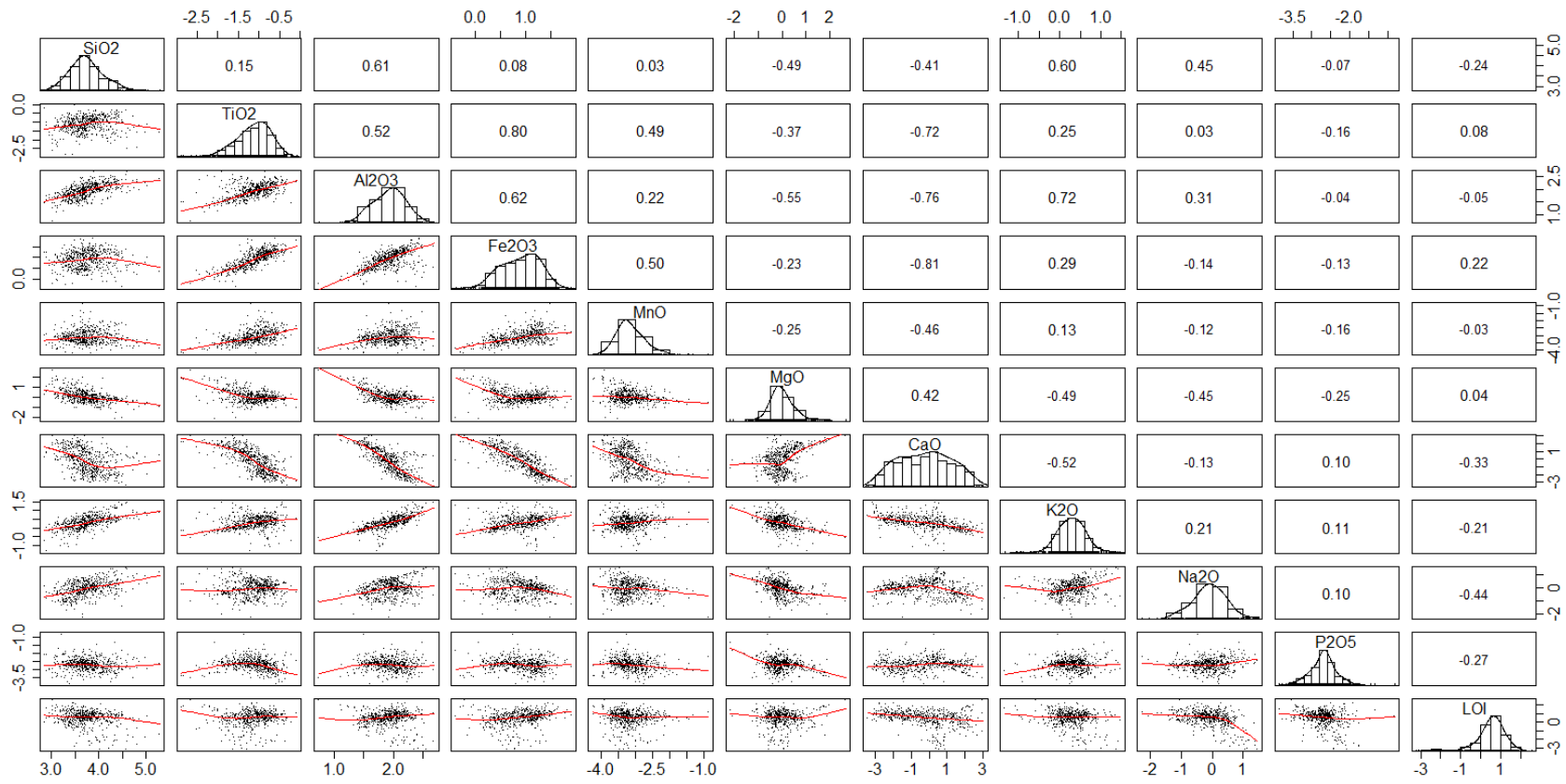 North American Soil Geochemical Landscapes Project (n=560). The scatter plot matrix includes histograms for each oxide, and pairwise correlation coefficients for each scatter plot variable.
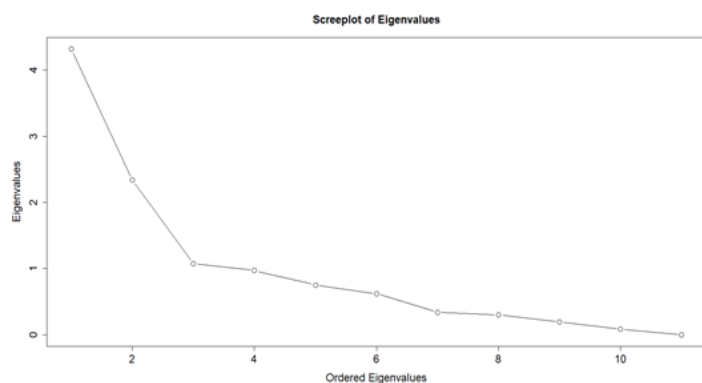
Figure 2.5. Scree plot of eigenvalues from the log-centred, C horizon, <2 mm size fraction, major oxide data from the North American Soil Geochemical Landscapes Project.

Table 2.2. Principal component eigenvectors, eigenvalues (λ), percent variance (%), and cumulative percent variance (Σ%).

	PC1	PC2	PC3	PC4
SiO_2	0.59	–0.54	–0.39	0.09
TiO_2	0.75	0.39	0.21	0.15
Al_2O_3	0.89	–0.15	–0.16	–0.09
Fe_2O_3	0.75	0.53	0.16	–0.01
MnO	0.48	0.39	0.41	0.43
MgO	–0.66	0.37	–0.16	0.21
CaO	–0.90	–0.28	0.08	0.14
K_2O	0.70	–0.37	–0.12	–0.17
Na_2O	0.29	–0.70	–0.04	0.25
P_2O_5	–0.06	–0.41	0.68	–0.56
LOI	0.01	0.66	–0.40	–0.52
λ	4.32	2.34	1.08	0.97
%	39.28	21.26	9.81	8.82
Σ%	39.28	60.53	70.34	79.16

Iron oxide, MnO, and TiO_2 were plotted in the positive x- and y-axes of PC1 and PC2 (Figure 2.6); these oxides could be associated with igneous and metamorphic geology (e.g., TiO_2 mineral rutile) or additionally the sites could have undergone weathering to form secondary minerals (e.g., iron oxides such as magnetite) (Figure 2.6). A second pattern in the positive x-axis and negative y-axis grouped the Si, Al, K, and Na oxides eigenvectors, which could indicate minerals of the feldspar family (plagioclase and K-feldspar). In addition, the Al_2O_3 could also represent the secondary mineral gibbsite as the Al oxide eigenvector was aligned with other possible secondary minerals (Fe, Ti, Mn). In contrast, CaO and MgO were plotted (in isolation) on the negative x-axis of PC1, suggesting carbonate minerals. These sites are distinctly different in mineral composition from the other survey sites as shown on the biplot (Figure 2.6). The phosphorous oxide had a small eigenvector loading in PC1, suggesting it had less influence on the soil mineralogy. Similarly, LOI plotted directly along the positive x-axis of PC1 and had an

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eigenvector coefficient of 0.01, therefore, it did not directly influence the soil mineralogy of PC1. In PC2, the phosphorous oxide had a larger eigenvector indicating the presence of soil minerals with phosphorous (e.g., apatite). Similarly, LOI had more influence in PC2 indicating the presence of organic matter in the C horizon or alternatively the presence of carbonate minerals from the release of volatile material during combustion. The high loading of LOI may also be due to the presence of clays, sheet silicates and other hydrous-bearing minerals.

The PC1 and PC3 biplot (Figure 2.7) showed similar relationships, with the exception of MgO, P_2O_5, and LOI. Magnesium oxide switched from the positive component to negative along the x-axis, and had a smaller eigenvector indicating that the soil minerals containing MgO were less prominent than in PC2. The phosphorous oxide and LOI essentially exchanged places on the PC1 and PC3 biplot with P_2O_5 having more variability in the dataset and LOI having less on the PC3 axis based on the eigenvectors. This could indicate survey sites that had phosphorous soil minerals (e.g., apatite) or sites with less organic matter or less carbonate minerals. The sites with low LOI seemed to occur in Manitoba and Saskatchewan (Figure 2.6 and 2.7), which may suggest a geological association, such as the Precambrian Shield. However, it is important to note that the oxide content represent the C horizon, which generally has smaller amounts of organic matter compared with other soil horizons.

Figure 2.6. Biplot of principal component (PC) 1 versus PC2 of the log-centred major oxide data for the soil C horizon, <2 mm size fraction, from the North American Soil Geochemical Landscapes Project (n=560). Points are coloured by province.
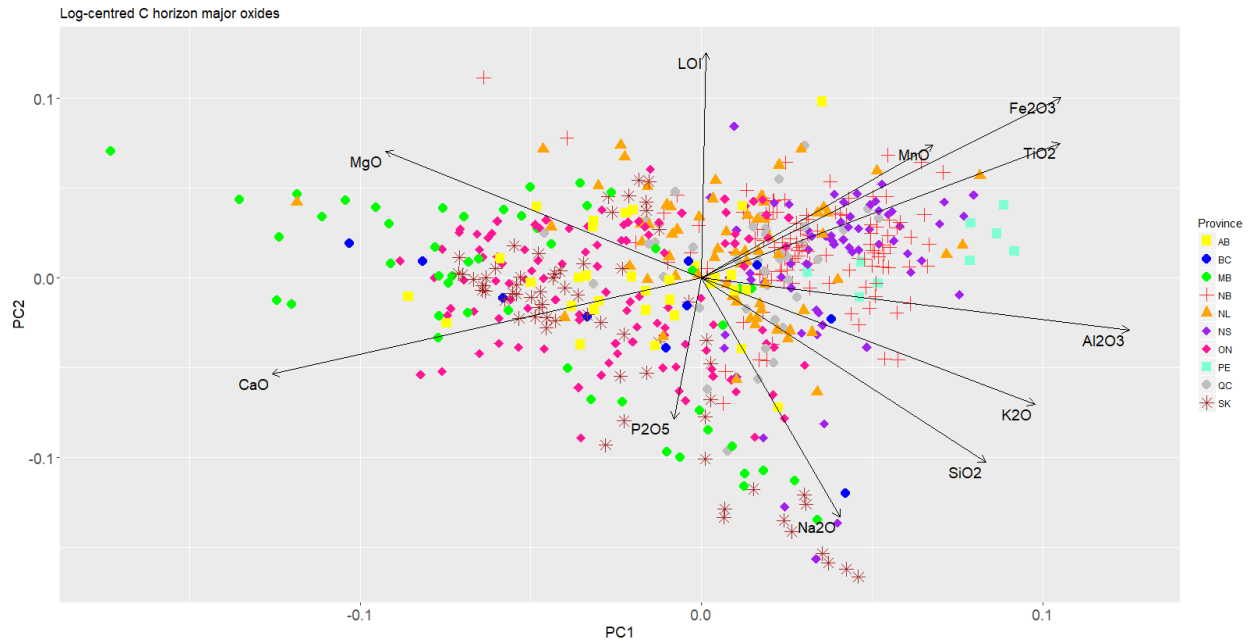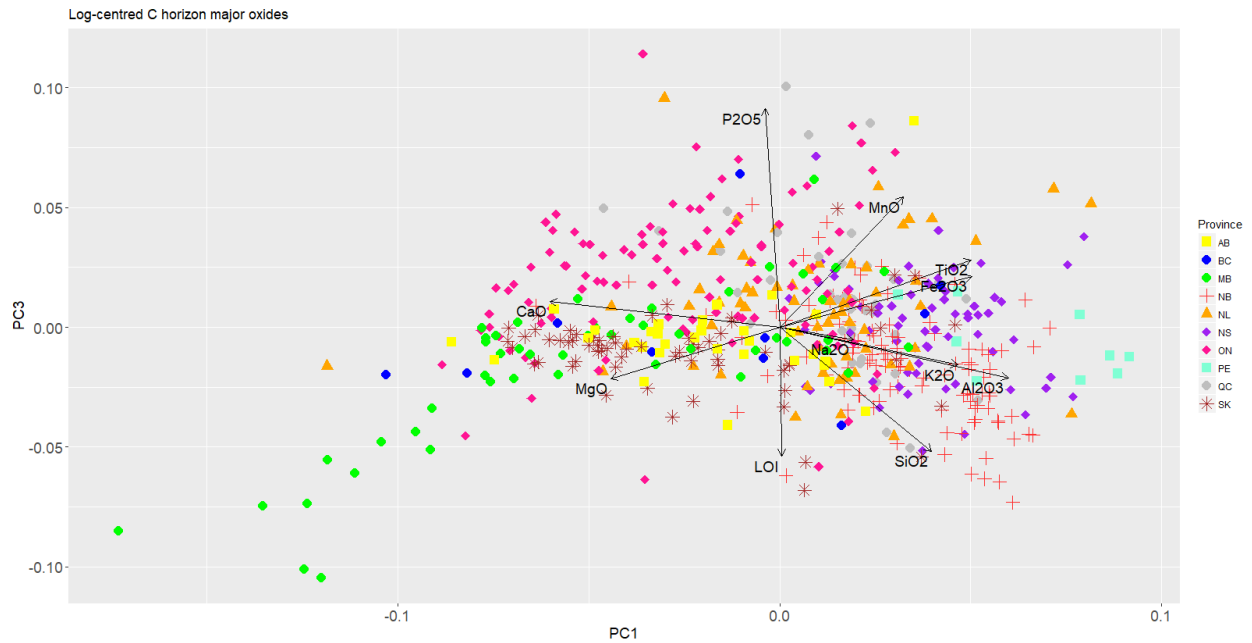

Figure 2.7. Biplot of principal component (PC) 1 versus PC3 of the log-centred major oxide data for the soil C horizon, <2 mm size fraction, from the North American Soil Geochemical Landscapes Project (n=560). Points are coloured by province.

2.4.4 Geospatial Analysis

Study sites with strong negative eigenvalue scores on PC1 (see green filled-circles in Figure 2.8), which corresponded to the CaO and MgO eigenvectors, were located in the provinces of Saskatchewan, Manitoba, and Ontario on the geospatial map (Figure 2.8). These sites were correlated to areas with sedimentary bedrock geology and minerals containing Ca and Mg (e.g., calcite and dolomite). Positive PC1 scores (pink and yellow filled-circles in Figure 2.8) reflect more diverse bedrock geology consisting of mainly igneous and metamorphic rocks. These regions include a large number of silicate minerals (e.g., feldspar, micas) across the Maritime Provinces (New Brunswick, Newfoundland, Nova Scotia, and Prince Edward Island) and the Precambrian Shield (northern region in Saskatchewan).

Principal component 2 showed distinctive negative scores in central to northern regions of Saskatchewan (see green filled-circles in Figure 2.9). The lowest PC2 score was Na_2O which indicated silicate minerals rich in Na (e.g., plagioclase end-member albite). The strong positive PC2 score (yellow) represented LOI as shown in Manitoba, Newfoundland, and New Brunswick. As LOI denotes the loss of volatile material (e.g., water and carbon dioxide) from organic or inorganic carbon matter, this corresponds to carbonate minerals and most evident in Manitoba.

The map of PC3 showed high positive scores that correlated to P_2O_5, which is most apparent in Manitoba (see yellow in Figure 2.10). This is unique as it could indicate phosphorous minerals (e.g., apatite); however, the plausibility of a high quantity of phosphorous minerals is not realistic due to the carbonate bedrock geology. Alternatively, the high values may be indicative of agricultural (fertilizer) contamination. The negative scores were related to LOI and occurred mainly in southern Ontario and Quebec (see green in Figure 2.10). It is possible that these samples had higher amounts of volatile material released from organic carbon matter. However, given that

PC3 only accounted for 9.81% of the variance in the dataset, this implies that the geological

processes are not as substantial.

Figure 2.8. Map of principal component 1 scores at sampling sites for log-centred C-horizon, <2
mm size fraction, major oxide data (n=560) from the North American Soil Geochemical
Landscapes Project (Map projection: Lambert Conformal Conic).
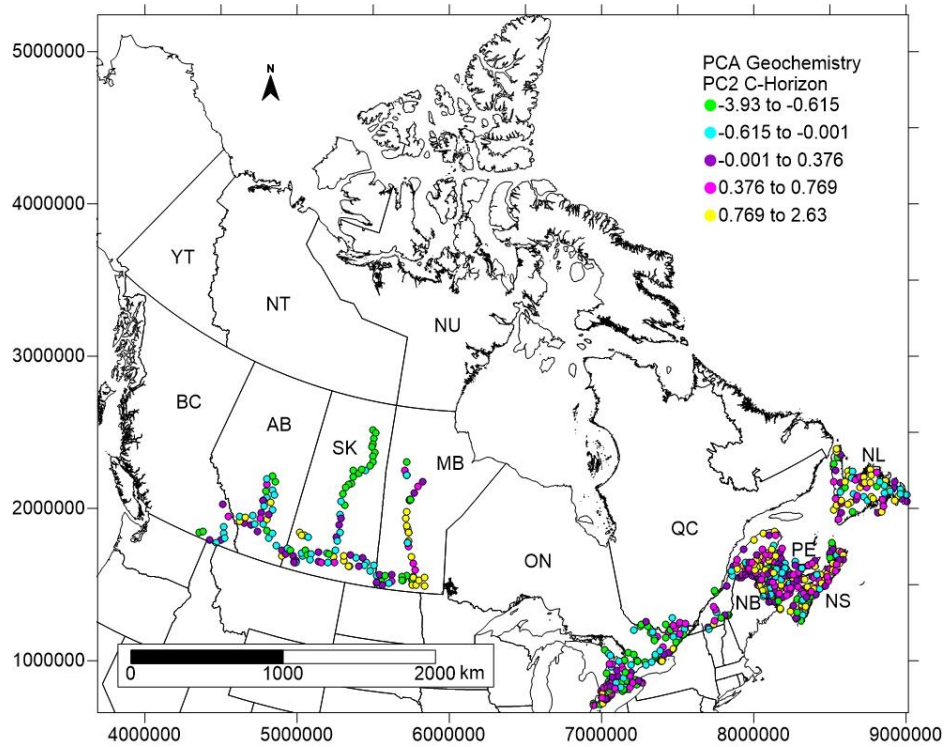
Figure 2.9. Map of principal component 2 scores at sampling sites for log-centred C-horizon, <2 mm size fraction, major oxide data (n=560) from the North American Soil Geochemical Landscapes Project (Map projection: Lambert Conformal Conic).
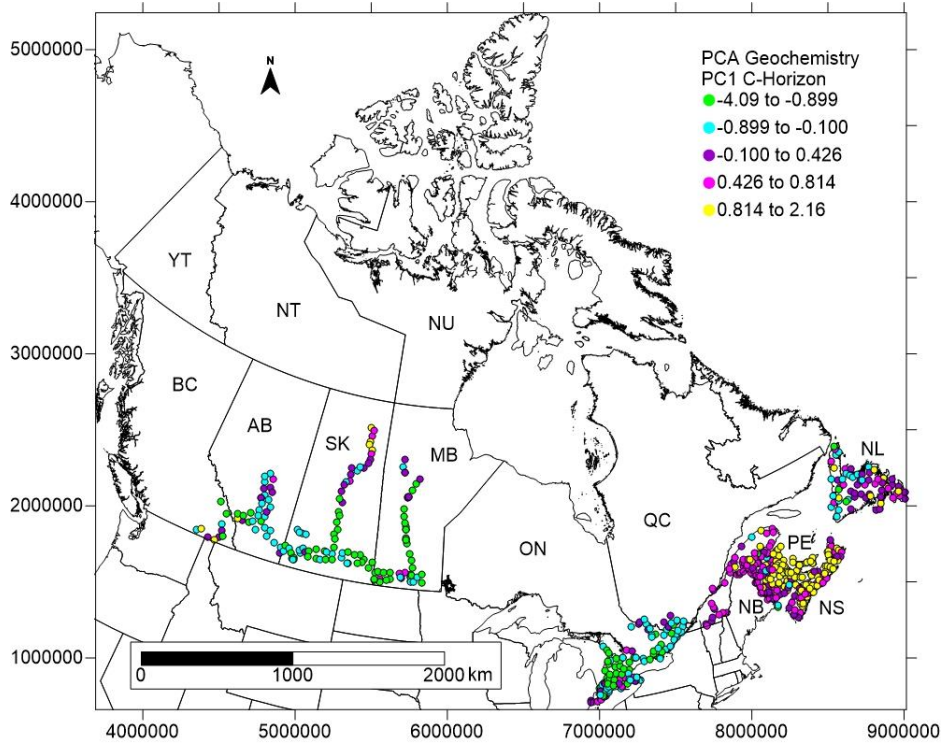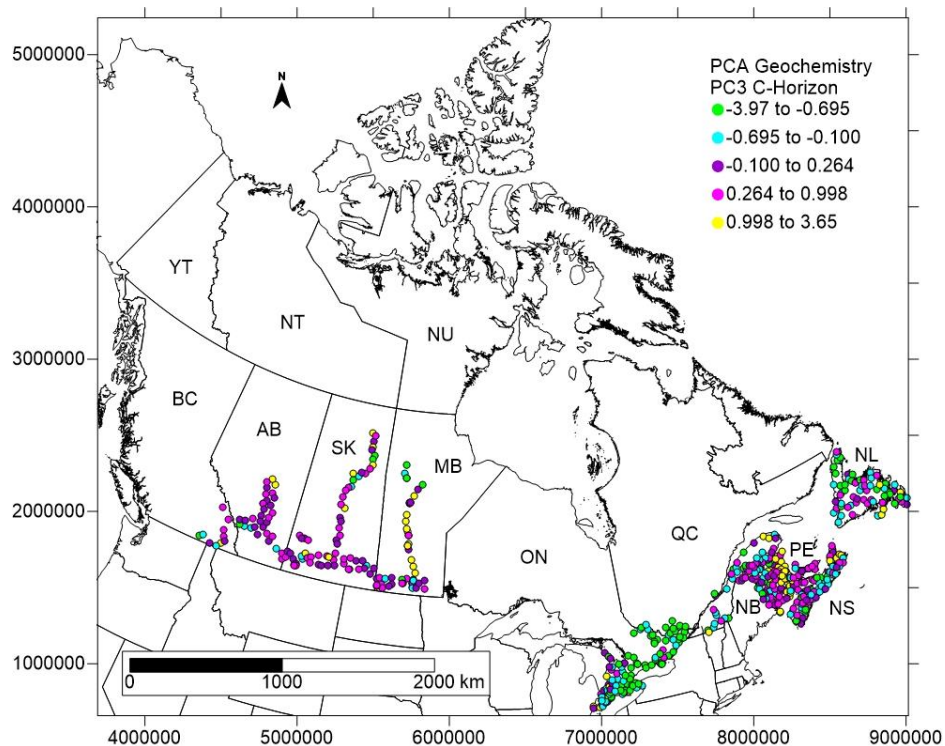
Figure 2.10. Map of principal component 3 scores at sampling sites for log-centred C-horizon, <2 mm size fraction, major oxide data (n=560) from the North American Soil Geochemical Landscapes Project (Map projection: Lambert Conformal Conic).

2.5 Discussion

Previous multivariate analysis of the north-south continental transect from the NASGLP showed that the northern most sites were characterized by soil geochemistry from Paleozoic platform carbonate minerals (Drew et al., 2010). In the current study, the biplot of PC1 and PC2 of the major soil oxides similarly suggested carbonate mineralogy (Figure 2.6). In addition, soil oxides (Figure 2.8–2.10) indicated a change in soil mineral composition associated with Precambrian Shield bedrock geology terrain in northern Manitoba and sedimentary bedrock geology, specifically the Paleozoic platform carbonates, in central and southern Manitoba (Klassen, 2009). The sedimentary bedrock geology of Manitoba typically produces soils with lower amounts of Si and also accounts for higher amounts of Ca and Mg. This pattern is also

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observed in southern Ontario, where the regional bedrock geology is sedimentary, predominantly carbonates, and the sampling sites corresponded to Ca and Mg oxides on the PC1 biplot.

In the Maritime Provinces (New Brunswick, Nova Scotia, and Prince Edward Island), Grunsky et al. (2013) conducted principal component analysis of the C horizon and found that Mg and Fe along with trace elements, Ni, Cr, Co, V, and Sc, in the negative quadrant of the biplot were related to shale or mafic igneous parent material. The study also confirmed the elements that were correlated to bedrock geology by plotting the first principal component on a map of the Maritime Provinces (Grunsky et al., 2013). Similarly, in the current study the Maritime Provinces plotted in proximity to silicates and secondary oxides on the biplot (Figure 6), which corresponds well to the greater diversity of bedrock geology in the Maritime Provinces.

Studies in other countries have used soil geochemical data and exploratory data analysis to show associations between elements and bedrock geology. For example, the Tellus soil geochemical survey in Northern Ireland, UK, used principal component analysis biplots (after centred-log transformation) to evaluate contrasting lithologies of mafic or felsic affinities (Tolosana-Delgado and McKinley, 2016). In Australia, principal component interpretations from an Australia-wide geochemical dataset determined element associations based on weathering of different geology (de Caritat and Grunsky, 2013).

Soil minerals can weather via chemical weathering and release elements during reactions that can precipitate into secondary minerals, such as iron oxides or clays, or used as nutrients in the ecosystem (Sverdrup, 2009). Elements, such as Fe, Mn, Ti, and Mg, can be substituted during mineral formation of silicates or weathering to secondary minerals (see the PCA biplot in Figure 2.6). In the Maritime Provinces, climate factors such as precipitation could influence the weathering of minerals to a greater degree compared with other regions in Canada, e.g., the Prairies

of Alberta, Saskatchewan, and Manitoba. In general, the degree of weathering depends on the type of parent material as the mineral composition may be more susceptible or more resistant to weathering.

2.6 Conclusion

In the current study, soil mineralogy was inferred through exploratory analysis of the C-horizon major oxides data (<2 mm size fraction) from the North American Soil Geochemical Landscapes Project. Statistical analysis identified provincial differences in the distribution of the major soil oxides, especially between Eastern and Western Canada. Inference of soil minerals came from principal component analysis, as oxide associations reflected mineralogy relationships driven by their bedrock geology of sedimentary, igneous, and metamorphic rocks. Soil minerals were generally classified as carbonates, silicates, and weathered oxides. Mapping the principal component scores confirmed the spatial influence of regional bedrock geology on the predicted soil minerals. This study demonstrated that the use of soil geochemistry from the C-horizon can be used to generate mineralogy at a regional scale and in accordance to bedrock lithology.

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3. Determination of Normative Soil Mineralogy at 1170 sites across Canada

3.1 Abstract

Weathering of soil minerals provides base cations that buffer against acidity and support plant growth. Direct observations of soil minerals are rare and infrequent, given analytical time and costs, however, the abundance of minerals in soil can be determined indirectly through soil geochemistry using chemical analyses, such as X-Ray Fluorescence. This study complied a data set of major oxide content averaged over the soil profile (horizons A, B, and C, weighted by depth and bulk density), using published/existing Canadian soil geochemical observations. A determination of quantitative soil mineralogy using the normative method, Analysis to Mineralogy (A2M) was carried out at sites across Canada (n=1170) after the approach was evaluated by a comparison of X-Ray Diffraction (XRD) mineralogy of 85 sites throughout New Brunswick, Nova Scotia and Prince Edward Island. Predicted A2M mineralogy was comparable with XRD estimates for minerals, quartz, plagioclase, and muscovite, whereas potassium feldspar and chlorite had significant statistical differences. Predicted quantitative soil mineralogy was consistent with the underlying bedrock geology, such as northwestern Saskatchewan and northeastern Alberta, which had high amounts of quartz due to the Western Canadian Sedimentary Basin. Other minerals (plagioclase, potassium feldspar, chlorite, and muscovite) had more variable amounts in the soil depending on the bedrock geology across Canada. This research led to a reliable approach for regional-scale determination of soil mineralogy.

Key words: soil mineralogy, soil geochemistry, normative procedures, Analysis to Mineralogy

3.2 Introduction

Chemical weathering results in the release of soil nutrients such as base cations – e.g., calcium (Ca), potassium (K), magnesium (Mg), and sodium (Na) – from primary or secondary minerals. Primary minerals form during the solidification and crystallization of magma. Igneous minerals that form under high temperature and pressure are olivine, pyroxene, amphibole, and calcium rich plagioclase. Orthoclase, muscovite, and quartz form under lower temperature and pressure conditions. Secondary minerals (e.g., clay minerals) form when pre-existing primary minerals undergo chemical weathering, for example muscovite weathers to illite.

The determination of soil weathering rates is important when assessing anthropogenic environmental impacts, for example, sustainable forest management or the buffering capacity of soils against acidic deposition, and for an understanding of the ability of soil minerals to replenish (base cation) nutrients (Casetou-Gustafson et al., 2018). Direct determination of base cation weathering rates is difficult; various methods have been used, such as the calculation of mass-balances or watershed budgets (Ouimet et al., 2006). A widely used soil chemical model is PROFILE, which requires physical and chemical input data (Sverdrup and Warfvinge, 1993). A challenge in using PROFILE is the availability of quantitative mineralogy. X-Ray Diffraction (XRD), which is based on the crystallographic structure of minerals and is widely used to estimate soil mineralogy, however, it can be an expensive procedure, especially if a large number of samples are required and detection limits hinder the ability to identify minerals in low amounts.

Normative procedures, which incorporate bulk soil geochemical compositions, are an indirect technique to estimate soil mineralogy and are more widely applicable owing to cost effectiveness. Originally developed to calculate mineral percentages of igneous rocks with the

CIPW (Cross, Iddings, Pirsson, and Washington) method (Cross et al., 1902), normative procedures have expanded to include different rock types. One program, SEDNORM, was developed to calculate normative mineralogy for clastic sedimentary rocks and coal ash (Cohen and Ward, 1991). Other programs to determine mineralogy include MINLITH, an experience-based algorithm to predict likely mineral compositions of sedimentary rocks from bulk chemical analyses, MINSQ, a least squares spreadsheet method to quantitatively estimate the mineral proportions of a rock from whole rock analyses, or MODAN that uses Gaussian elimination and linear regression to estimate mineral quantities from bulk composition (Rosen et al., 2004; Herrmann & Berry, 2002; Paktunc, 1998, 2001).

Analysis to Mineralogy (A2M) is a solver program developed to estimate all possible mineral modes across all geology types by using total chemical analyses and a pre-determined mineral stoichiometry list (Posch and Kurz, 2007). The program determines all extreme mineral modes, since the solution is not unique, the solution space is a finite convex polyhedron with the dimension "number of minerals minus number of elements". As such, A2M has been used to provide quantitative soil minerals at a regional scale and in particular to provide data for PROFILE, which is a soil chemical model to calculate base cation weathering rates (Koseva et al., 2010; Johnson et al., 2015; Casetou-Gustafson et al., 2018).

The objective of this study was to evaluate the performance of A2M using sites with paired soil total element and XRD mineralogy data (n=85) and to determine quantitative soil mineralogy for more than 1100 sites across Canada from the North American Soil Geochemical Landscapes Project and the Trent University Soil Archive.

3.3 Methodology

3.3.1 Study Area and Study Sites

The study primarily focused on provincial Canada (British Columbia, Alberta, Saskatchewan, Manitoba, Ontario, Quebec, New Brunswick, Nova Scotia, Prince Edward Island, and Newfoundland). Study sites included locations with observations of soil geochemistry, with an emphasis on consistent (or comparable) soil horizon sampling and analysis. All sites generally had multiple observations per soil profile, either measured by soil horizon or at a fixed depth representing A, upper and lower B, and C horizons. Depending on soil depth, all horizon (or depth) data were averaged to a maximum depth of 50 cm of mineral soil. Data for this research was primarily obtained from two sources, the North American Soil Geochemical Landscapes Project (NASGLP) and from the Trent University's Soil Archive (TUSA) housed within the School of the Environment.

The NASGLP was an initiative between the United States Geological Survey (USGS), the Geological Survey of Canada (GCS), and the Mexican Geological Survey (MGS) to co-ordinate a comparable tri-national survey for the purpose of collecting soil samples to analyze the soil geochemistry and mineralogy (Woodruff et al., 2009). An initial pilot project was conducted in 2004 and comprised two transects, north-south and east-west of North America with 29 sites located in Manitoba (Smith et al., 2005). The USGS finished sampling and analysis in 2010, while Canada sampled 577 sites between 2007–2009 and released physical and geochemical data for 541 sites, but did not complete the project (Friske et al., 2014). Additional examination of the soil geochemistry and mineralogy took place in the Maritime Provinces (New Brunswick, Nova Scotia, and Prince Edward Island) of Canada (Grunsky et al., 2013). The Maritime Provinces had 85 site locations (Figure 3.1) that included XRD mineralogy from the A

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and C soil horizons (data obtained from the United States Geological Survey; Cannon, unpublished data).

The second set of data was primarily obtained from Trent University's School of the Environment, where soil oxide data were available from research projects conducted across many provinces in Canada (Whitfield et al., 2006; Whitfield et al., 2011; Whitfield and Watmough, 2012; Koseva et al., 2010). These sites were sampled between 2005 and 2016 and analysed for soil oxides. In addition, published soil oxide data of the B-Horizon from 21 catchment sites in Quebec (Houle et al., 2012) were included in the TUSA data. Additional mineralogy analyses by XRD occurred at 10 sites in Ontario and Alberta, and 46 in Saskatchewan.

The total number of sites from NASGLP was 570, which included British Columbia with 10 sites, Alberta 32, Saskatchewan 65, Manitoba 49, Ontario 110, Quebec 39, New Brunswick 115, Nova Scotia 69, Prince Edward Island 9, and Newfoundland 72 (Figure 3.1). The TUSA total number of sites was 600; British Columbia 80 sites, Alberta 141, Northwest Territories 22, Saskatchewan 192, Ontario 139, Quebec 21, and Nova Scotia 5. The study sites from the two sources cover all 10 provinces and 1 territory.

3.3.2 Sampling and Analysis

Uniform field sampling as well as chemical and physical analysis methods were established for the NASGLP (Friske et al., 2013, 2014). In Canada, site selection was based on a spatially balanced and consistent sample site density, which was a 40 km × 40 km grid system (Garrett and Kettles, 2009). The proposed number of sites in Canada was 6,018; however, only sampled 577 sites from 2007 to 2009 as the GSC changed priorities (Friske et al., 2013). At the

sites, a pit of 60 cm wide by 70 cm long was excavated and soil samples were collected from the Public Health layer (0–5 cm), 0–30 cm (2009 field season only), and the A, B, and C horizons (Friske et al., 2014), and, in addition, soil bulk density samples were obtained. Laboratory protocols included air drying prior to a 4-acid digestion on two different size fractions (<2 mm and <0.63 µm). The 4-acid digestion method consists of a mixed ratio of 2:2:1:1 using HCl, HNO_3, $HClO_4$ and HF and this 'near-total' digestion helps to breakdown most insoluble elements, with the exception of Ca and Mg (Friske et al., 2014). Inductively coupled plasma-mass spectrometry was used to determine 58 major and trace elements. Total carbon was analysed by combustion (in %) with a Leco CR-412 Carbon Analyser and organic matter was estimated by loss on ignition (LOI) at 500°C (Friske et al. 2014). Further details on sampling procedures and laboratory methods are described by GCS (Open Files 6433, 7334) and the USGS (Open File 2005-1253).

Regional-specific research methods for TUSA were used for site sampling, which included sampling of excavated soil pits at the approximate depths of the A, B, and C horizons or at fixed depths of 0-10, 25-35, and 40-50 cm; in addition, sites were sampled for soil bulk density using a volumetric sampling ring and hammer corer. All samples underwent consistent laboratory methods, i.e., air-drying samples, and sieving to a <2 mm size fraction prior to X-Ray Fluorescence (XRF) to generate total soil oxide content (Whitefield and Watmough, 2012; Whitefield et al., 2006). Additional laboratory analyses typically included estimating organic matter from loss on ignition measurement by heating soil in a muffle furnace at 375°C for 16 hours.

In general, the two datasets had similar field sampling and laboratory protocols, where sampling was conducted at multiple soil horizon depths from an excavated soil pit. The

laboratory procedures included air drying prior to sieving at <2 mm. The significant difference between the two datasets is the analytical method for element detection, where the NASGLP used ICP-MS to determine the major and trace elements (converted to oxides in the current study). In contrast, the TUSA soils were analysed by XRF to produce total soil oxide content.

3.3.3 Soil Total Oxide Database

Major oxides, SiO_2, Al_2O_3, Fe_2O_3, MnO, CaO, MgO, Na_2O, and K_2O, represent the dominant elements that compose soil minerals. Oxide weight percent are widely used, and the TUSA data were already generated as soil oxides. However, the NASGLP data were presented as major elements and required conversion from element concentrations, which entailed converting to oxides based on the molecular weights of the individual elements. In addition, NASGLP did not include data for silicon, as such it was calculated from the subtraction of the sum of the major element oxides and loss on ignition from 100%.

Observations (by profile) from 1170 sites were summarised into a consistent database to represent average oxide content in the top 50 cm of the soil profile, which was a maximum as not all profiles reached a depth of 50 cm. The database included soil horizon depth (cm), bulk density (g/m^3), and weighted average soil oxide content. Soil oxide data was averaged for each soil profile, weighted by depth (to a maximum of 50 cm) and bulk density for both the NASGLP and TUSA data. For example, the NASGLP weighted average soil oxide content was calculated from the A, B, C soil horizons for each survey site (n=570) data:

$$\frac{\sum\left(\text{depth(cm)} \times \text{bulk density (g/m}^3) \times \text{soil oxide (wt\%)}\right)}{\sum(\text{depth (cm)} \times \text{bulk density (g/m}^3))} \qquad \text{Eq. 1}$$

where the sum runs over the soil layers. In instances where only two soil horizons were available, the weighted average was based on two horizons. A number of survey sites (n=262)

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did not have soil horizon depth information and thus average soil horizon depths for A, B, and C

horizons (0-15 cm, 15-40 cm, 40-75 cm) were derived from the existing soil horizon depth

information. Further, for sites with missing bulk densities, a predictive relationship based on

observed bulk density and LOI was developed, following De Vos et al. (2005):

$$\text{Bulk density} = -0.716558 \times \log_{10}(\text{loss on ignition}) + 1.57989 \qquad \text{Eq. 2}$$

where the coefficients were derived from the best fit to observation ($R^2 = 71.5$).

A comparison of soil oxides between NASGLP and TUSA was carried out to determine

if the datasets were statistically different. Soil oxide data from 16 areas in Ontario were selected

for analysis based on proximity of NASGLP and TUSA sites with the same bedrock geology.

The results indicate that the soil oxides from NASGLP and TUSA had no statistical differences

and the two datasets can be unified (Appendix B1).

3.3.4 Analysis to Mineralogy

Analysis to Mineralogy is a solver program used to predict quantitative soil minerals

from soil geochemical data (Posch and Kurz, 2007). The model determines all possible minerals

combinations which form a convex polyhedron solution space, characterised by the so-called

extreme modes. Every possible solution (i.e., mineral combination) is a linear combination (with

the sum of coefficients equal to 1) of these extreme modes, a special case of which is the

arithmetic mean. It is best suited when the number of minerals is greater than the number of

oxides (which is a typical constraint of other normative procedures). Inputs required for A2M are

the weight percentages of soil oxides (e.g., SiO_2, CaO, etc.) and a list of potential minerals and

their stoichiometry. Minerals such as quartz and feldspars (e.g., plagioclase or potassium

feldspar) can generally be expected in the soil compositions, whereas other minor amounts of

minerals may also be present (e.g., chlorite). Minerals have a fixed stoichiometry based on their chemical formula (e.g., SiO_2), whereas some have numerous stoichiometric possibilities. Clay minerals, e.g., vermiculite, montmorillonite, and illite, have multiple endmembers due to compositional variation of elements that form in solid solution. In the case of multiple endmember possibilities, either an average of the elements involved was used (e.g., muscovite and illite) or the specific endmembers (e.g., albite and anorthite minerals of the plagioclase group).

Analysis to Mineralogy was applied using a consistent list of minerals that focused on dominant minerals (i.e., quartz, plagioclase, K-feldspar, chlorite, and muscovite/illite) across all study sites (Table 3.1). Depending on the mineral, it may be classified under a general mineral category, for example, albite and anorthite grouped as plagioclase minerals. For sites where A2M was not able to create mineral percentages, additional minerals were used. Knowledge of the site location and bedrock geology influenced which other (additional) minerals were include in the site-specific analysis. In general, the other (additional) minerals used were hornblende, kaolinite, calcite and biotite.

The list of minerals and their associated stoichiometry are generalized which is a limitation. However, for the purpose of this study, the minerals and stoichiometry were intended to be broad to encompass the large study area and the varied bedrock geology. The basis of utilizing A2M in the current study was to generate mineral compositions at sites with the intention to provide the compositions to calculate base cation weathering rates.

Table 3.1. List of minerals used in Analysis to Mineralogy (A2M), the general mineral category, and their chemical formula.

Mineral	Category	Chemical Formula
Quartz	Quartz	SiO_2
Albite	Plagioclase	$NaAlSi_3O_8$
Anorthite	Plagioclase	$CaAl_2Si_2O_8$
K-feldspar	K-feldspar	$KAlSi_3O_8$
Chamosite	Chlorite	$(Fe_5Al)(AlSi_3)O_{10}(OH)_8$
Clinochlore	Chlorite	$(Mg_5Al)(AlSi_3)O_{10}(OH)_8$
Pennantite	Chlorite	$(Mn_5Al)(Si_3Al)O_{10}(OH)_8$
Muscovite	Muscovite	$KAl_2(AlSi_3O_{10})(F,OH)_2$
Illite	Muscovite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$
Hornblende*	Hornblende	$Ca_2(Mg, Fe, Al)_5 (Al, Si)_8O_{22}(OH)_2$
Kaolinite*	Kaolinite	$Al_2Si_2O_5(OH)_4$
Calcite*	Calcite	$CaCO_3$
Biotite*	Biotite	$K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$

* not used at every site

3.3.5 Evaluation of Analysis to Mineralogy

Sites with observations of both XRD and soil oxides were used to compare the predicted mineralogy from A2M with estimated mineralogy from XRD. These XRD data presented quantitative estimates of the major minerals at 85 sites from the C-Horizon and the locations coincided with available soil oxide data, which consisted of 52 sites in New Brunswick, 28 in Nova Scotia, and 5 in Prince Edward Island (Figure 3.1). The evaluation was conducted by generating A2M mineralogy from the soil oxide data (using a common mineral list) and comparing to the XRD mineral weight percentages.

The common mineral list was compared against the XRD mineralogy results. The major minerals are present in both however the mineral input list did not contain unique, or trace, minerals that may be abundant at a site – those minerals should be determined at a site-specific level. Minor minerals that may be present at sites but were not in the XRD results as levels may

have been below detection limits or not quantified, for example, the minerals apatite or rutile. In contrast, soil oxides for all the research sites from NASGLP and TUSA contained phosphorous and titanium but were not included in the A2M analysis as amounts would be minor, especially rutile which is not a mineral that contributes to base cation weathering capabilities.

The evaluation of A2M to XRD estimates involved numerical and graphical statistical methods, for example, mean, maximum, minimum, and coefficient of variation (CV), i.e., the ratio of the standard deviation to the mean. Univariate graphical measures, such as boxplots, were used to visualise the data distribution. While bivariate graphical measures, such as scatter plot matrices, were used to assess the linear correlations between A2M and XRD results, and in addition, the coefficient of determination provided the proportion of variance between the variables. The predictions of A2M mineralogy versus XRD estimates were assessed by a paired t-test ($p < 0.01$) to determine the statistical difference.

An evaluation of A2M results on the wider application of the 1170 sites was conducted using XRD mineralogy from TUSA; 10 sites in Ontario had XRD analysis and soil oxide data, 46 in Saskatchewan, and 10 in Alberta. The evaluation also involved the comparison of A2M and XRD predictions by paired t-tests.
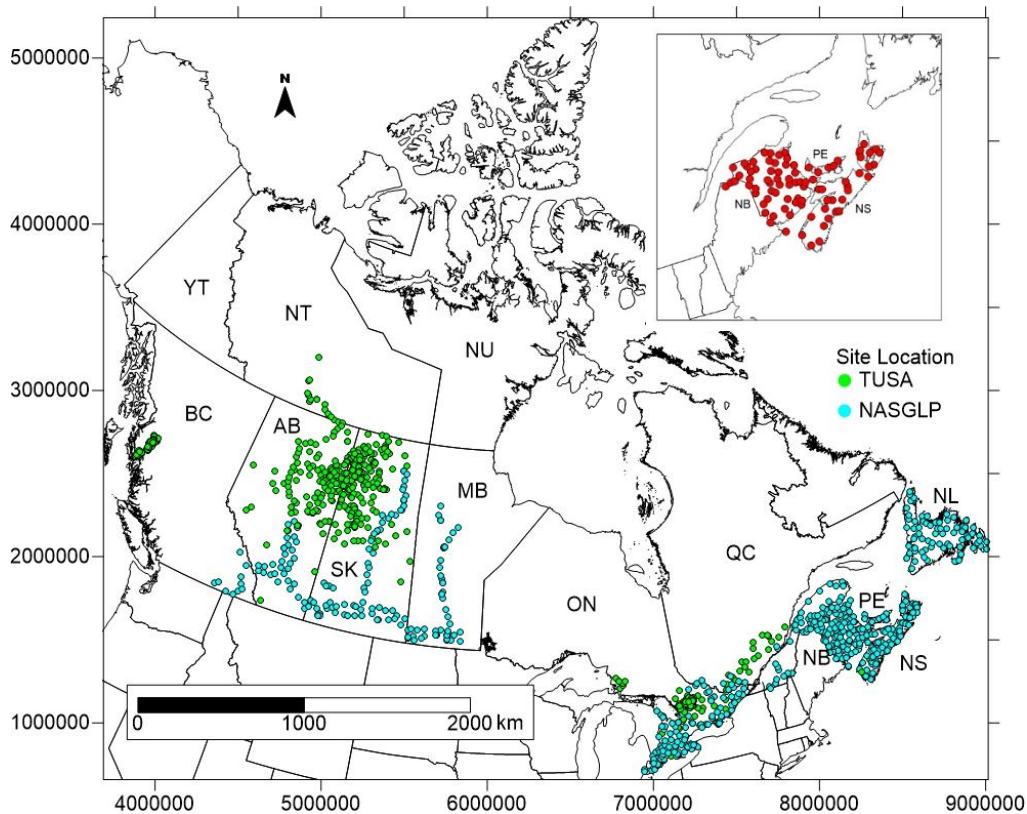
Figure 3.1. Location of study sites with soil oxide data from Trent University (TUSA) and the North American Soil Geochemical Landscape Project (NASGLP) across Canada (n=1170). Inset of NASGLP sites (n=85) with paired soil oxide data and XRD mineralogy data (Map projection: Lambert Conformal Conic).

3.4 Results

3.4.1 Distribution of Observed Soil Oxides, Bulk Density, and Loss on Ignition

The distribution of sites covered the entirety of the Maritime Provinces (Nova Scotia, New Brunswick, Prince Edward Island), whereas sites in Ontario and Quebec were in the southern areas of the provinces only. Alberta, Saskatchewan, and Manitoba had moderate site distribution across the provinces whereas British Columbia (BC) and Northwest Territories only had coverage in select areas (the region of Kitimat in western BC and the southeast corner of BC, and 22 sites in the southern Northwest Territories) (Figure 3.1).

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Average SiO$_2$ had high concentrations (>80 wt%) in Saskatchewan and into Alberta, whereas British Columbia had the lowest amount (<60 wt%) (Table 3.2). Visual representation of SiO$_2$ highlighted the higher concentrations in the central to northwestern part of Saskatchewan and into Alberta, which is associated with the Athabasca basin (Figure 3.2). Other oxides, CaO and K$_2$O, were mapped to spatially identify where the base cations Ca and K have the greatest potential to be released into the environment (Figure 3.2). Calcium oxide was, generally, less than 0.62 wt% in the Maritime Provinces and northern Saskatchewan and greater than 1.70 wt% in the southern regions of Ontario, Quebec, Manitoba, and southern Saskatchewan. Potassium oxide showed amounts less than 1.10 wt% in northern Saskatchewan and Alberta and greater than 2.40 wt% in Ontario and Quebec and a region in southern Nova Scotia.

The weighted soil profile oxides included depth at sampling sites, which varied across the province, with a minimum depth of 4 cm in Saskatchewan and a maximum depth of 135 cm in Nova Scotia and Ontario (Figure 3.3), but – where possible – depths were limited to 50 cm. The average sampling depth was 54 cm for the majority of provinces, the exceptions were Nova Scotia at 65 cm and Prince Edward Island at 74 cm. Loss on ignition showed less than 1.68 % organic matter in northern Saskatchewan and Alberta, but sites in New Brunswick and Newfoundland had amounts greater than 7.06 % (Figure 3.4). Average bulk density for sites in British Columbia, New Brunswick, and Newfoundland was <0.82 g/cm^3, whereas Alberta and Saskatchewan were >1.20 g/cm^3 (Figure 3.5).

Table 3.2. The number of sites per province (n), mean soil oxides (in wt%) and loss on ignition (LOI in %) per province from the North American Soil Geochemical Landscapes Project and Trent University Soil Archive (n=1170).

PROV	n	SiO_2	Al_2O_3	Fe_2O_3	MnO	CaO	MgO	Na_2O	K_2O	LOI
AB	173	83.06	6.46	2.41	0.04	1.01	0.69	0.66	1.25	3.96
BC	90	56.10	13.17	5.50	0.08	2.31	1.59	2.31	1.56	16.52
MB	49	64.85	9.96	3.20	0.06	7.61	4.43	1.55	1.92	5.97
NB	115	66.78	11.95	5.19	0.07	0.43	1.30	1.26	1.85	10.40
NL	72	60.31	10.97	5.46	0.10	1.32	1.55	1.95	1.84	15.60
NS	74	71.03	12.36	4.68	0.12	0.38	0.92	1.31	2.26	6.17
NT	22	68.84	8.13	3.05	0.04	5.48	2.18	1.16	1.79	8.84
ON	249	63.66	12.09	5.00	0.09	3.80	1.65	2.18	2.30	8.43
PE	9	76.64	9.65	3.41	0.09	0.12	0.90	0.88	2.78	4.83
QC	60	67.19	12.68	5.68	0.09	1.86	1.71	2.10	2.64	5.06
SK	257	85.49	5.55	1.69	0.03	1.38	0.79	0.96	1.17	2.64
Mean	1170	71.74	9.69	3.86	0.07	2.10	1.35	1.48	1.76	7.32
Max	1170	99.28	18.11	12.80	0.84	27.42	19.83	5.87	4.94	74.95
Min	1170	18.22	0.18	0.20	0.00	0.00	0.02	0.00	0.03	0.00
CV	1170	0.20	0.45	0.58	0.92	1.44	1.08	0.65	0.47	1.01

Note: PROV = Provinces, AB = Alberta, BC = British Columbia, MB = Manitoba, NB = New Brunswick, NL = Newfoundland, NS = Nova Scotia, NT = Northwest Territories, ON = Ontario, PE = Prince Edward Island, QC = Quebec, SK = Saskatchewan, CV = Coefficient of Variation;
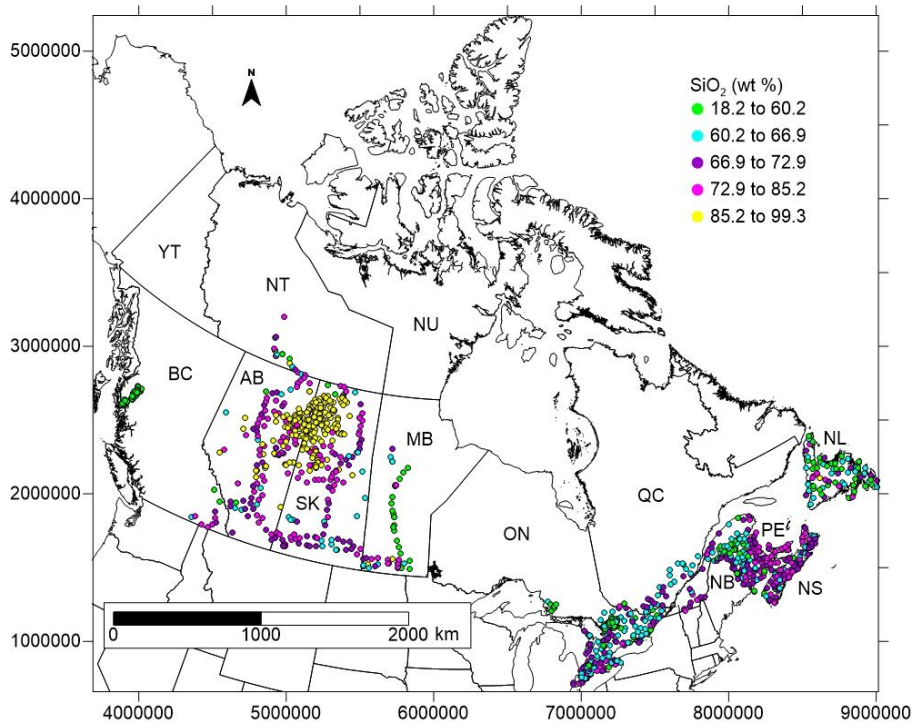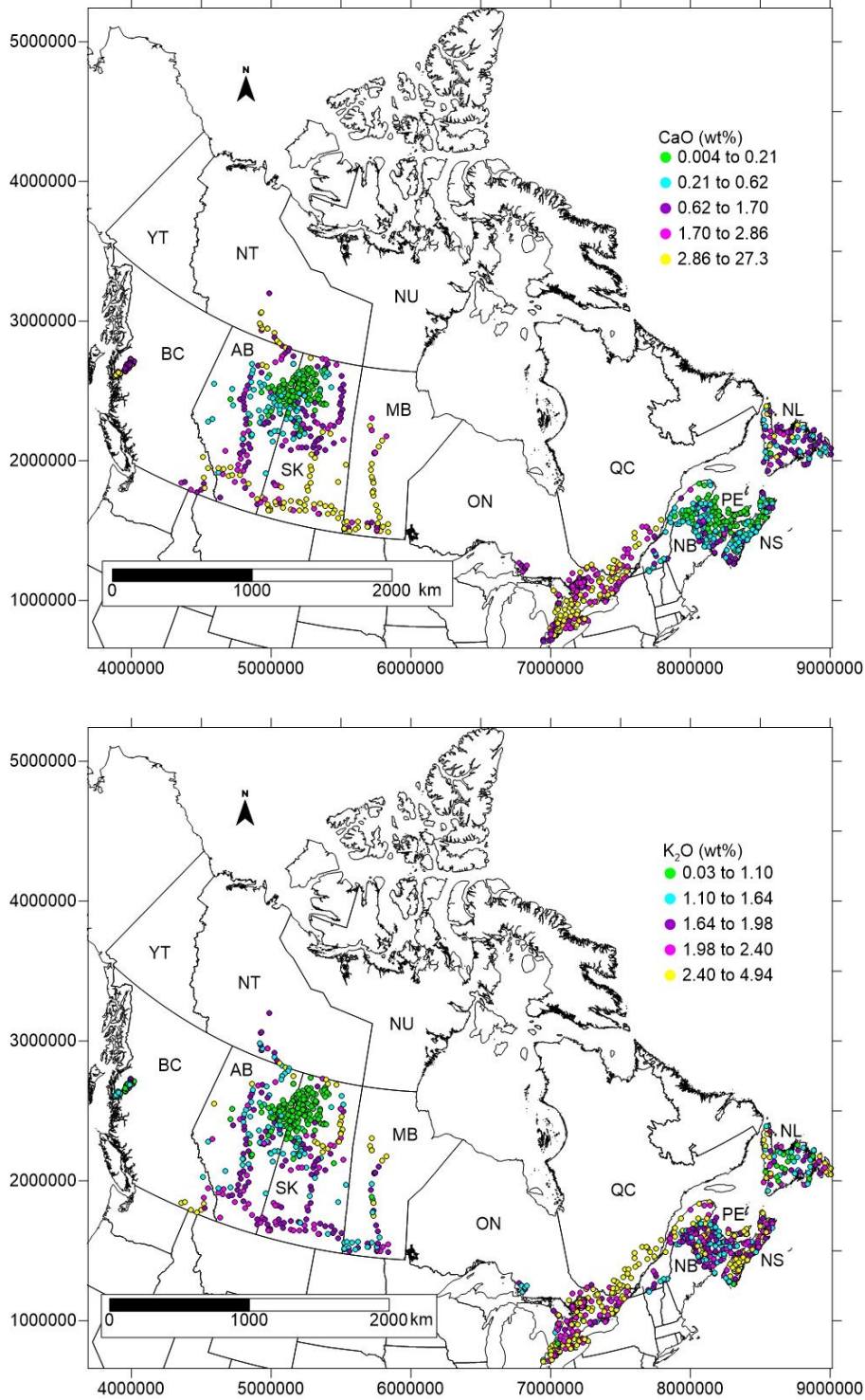
Figure 3.2. Distribution of selected average soil oxide data (to a maximum depth of 50 cm) weighted by depth and bulk density (wt %) across Canada (n=1170) from the North American Soil Geochemical Landscapes Project and Trent University Soil Archive (top to bottom: silicon dioxide, calcium oxide, potassium oxide). Legends were set at an equal distribution of sites among five categories (Map projection: Lambert Conformal Conic).
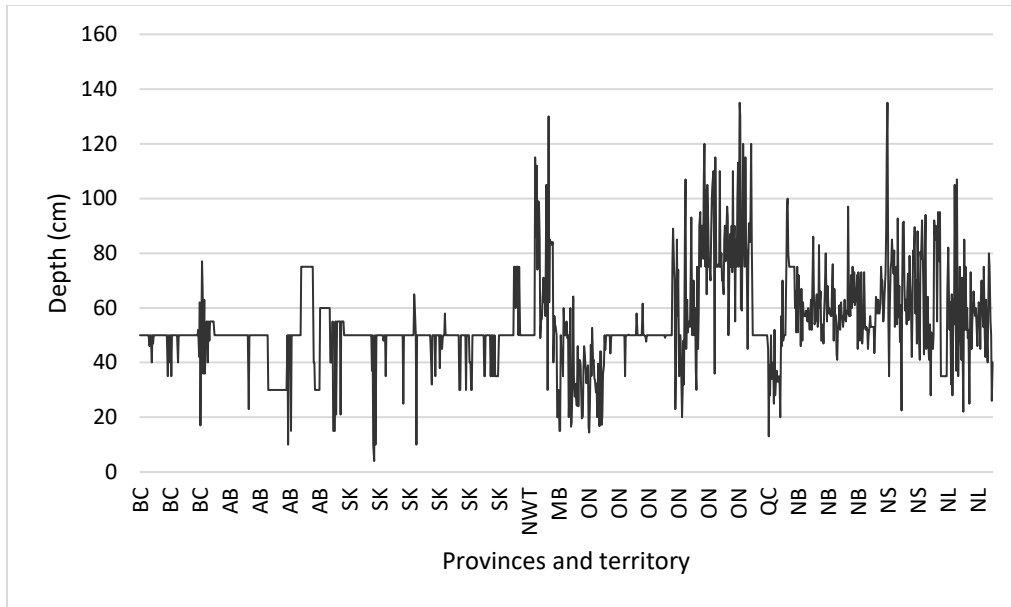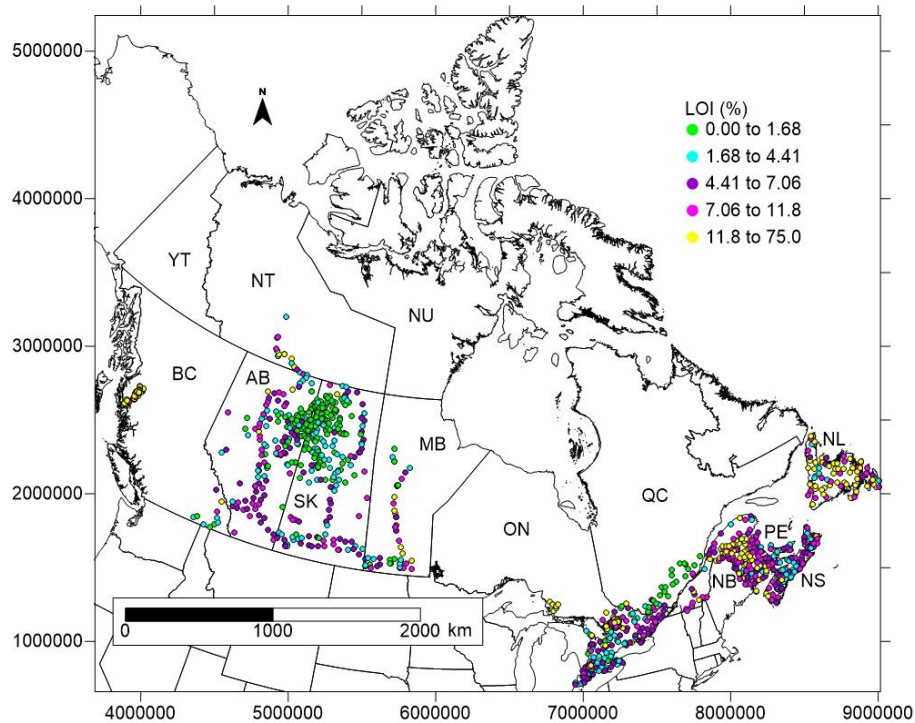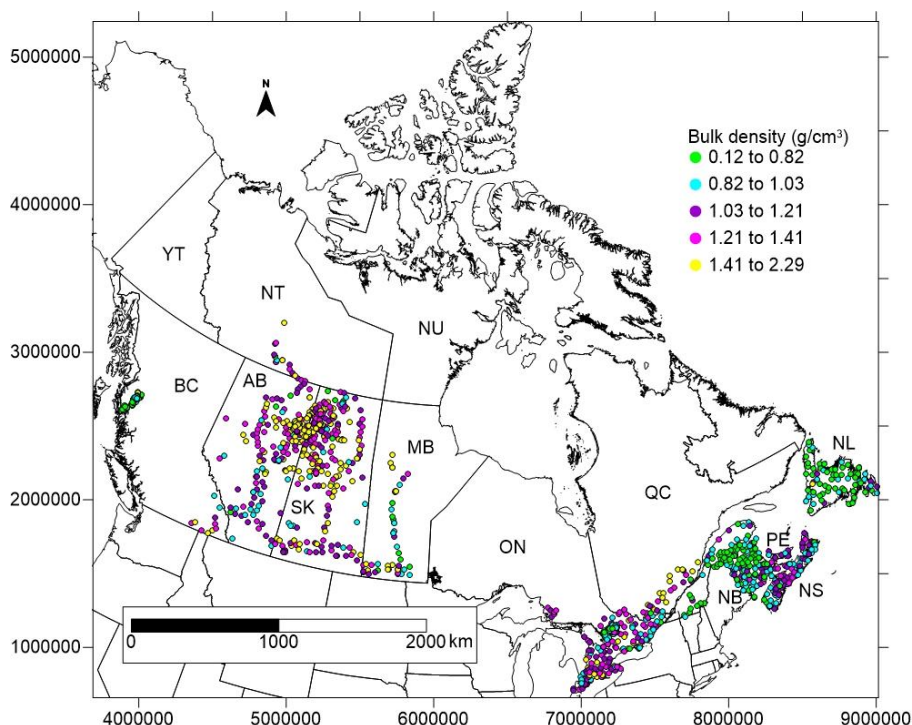
Figure 3.3. Distribution of the depth (cm) at sampling sites across Canada from the North American Soil Geochemical Landscapes Project and Trent University Soil Archive data (n=1170).

Figure 3.4. Average loss on ignition (LOI, in %) across Canada from the North American Soil Geochemical Landscapes Project and Trent University Soil Archive (n=1170). The legend was set at an equal distribution of sites among five categories (Map projection: Lambert Conformal Conic).

Figure 3.5. Average soil bulk density at sampling sites (g/cm^3) across Canada from the North American Soil Geochemical Landscapes Project and Trent University Soil Archive (n=1170). The legend was set at equal distribution of sites among five categories (Map projection: Lambert Conformal Conic).

3.4.2 Evaluation of Predicted Quantitative Soil Mineralogy

The evaluation of predicted soil mineralogy obtained by A2M from observed soil oxides against estimated soil mineralogy from XRD at co-located sites allowed for a paired comparison of the selected minerals (quartz, plagioclase, potassium feldspar, chlorite, and muscovite). Plagioclase had comparable averages between A2M versus XRD mineralogy (15.48 to 15.12 wt%, respectively) in contrast to quartz, which had the greatest difference between averages (50.19 vs. 57.18 wt%, respectively) (Table 3.3). The distribution of minerals from A2M and XRD showed the greatest differences in quartz, chlorite, and muscovite (Figure 3.6). Plagioclase A2M and XRD mineralogy were strongly related ($R^2 = 0.83$), whereas potassium feldspar had the lowest coefficient of determination ($R^2 = 0.40$). The minerals with more dispersion of A2M

results versus XRD mineralogy were potassium feldspar ($R^2 = 0.40$), chlorite ($R^2 = 0.63$), and

muscovite (R^2 of 0.43) at the sites (Figure 3.7). The results of the paired t-test between A2M and

XRD showed quartz and chlorite as statistically different from a p-value of 0.01 while

plagioclase, K-feldspar, and chlorite were not statistically different (Table 3.3). Based on the

high coefficients of determination for quartz and chlorite, the statistical differences are not as

significant.
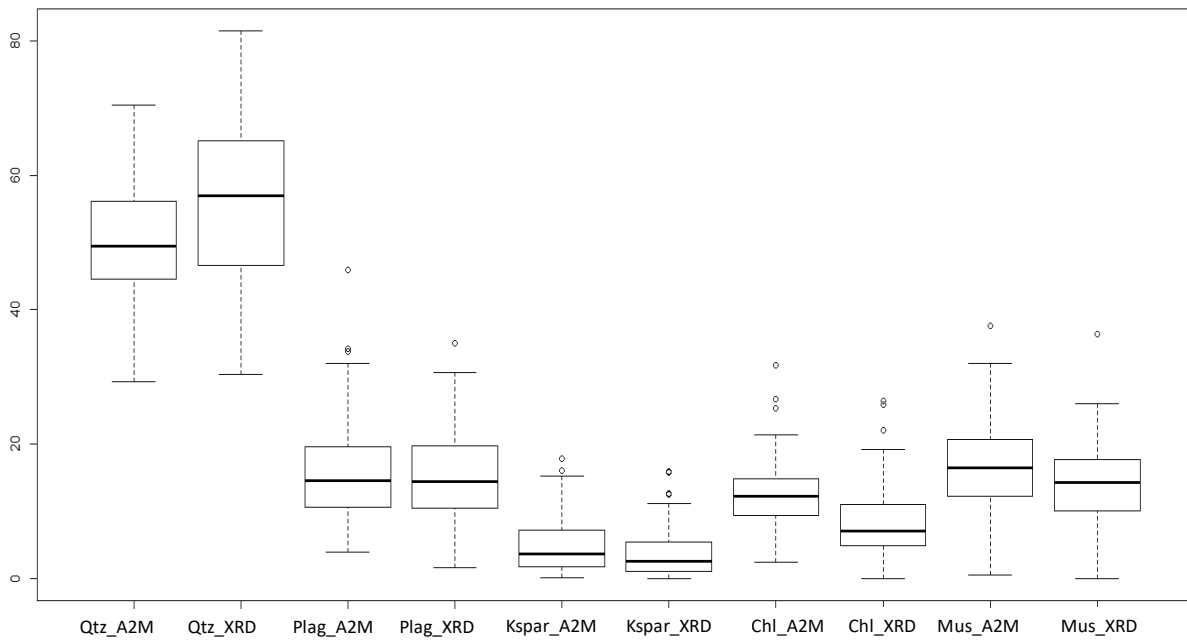
Figure 3.6. Boxplots of A2M and XRD results (n=85) of selected minerals (Qtz = Quartz, Plag = Plagioclase, Kspar = Potassium feldspar, Chl = Chlorite, Mus = Muscovite).
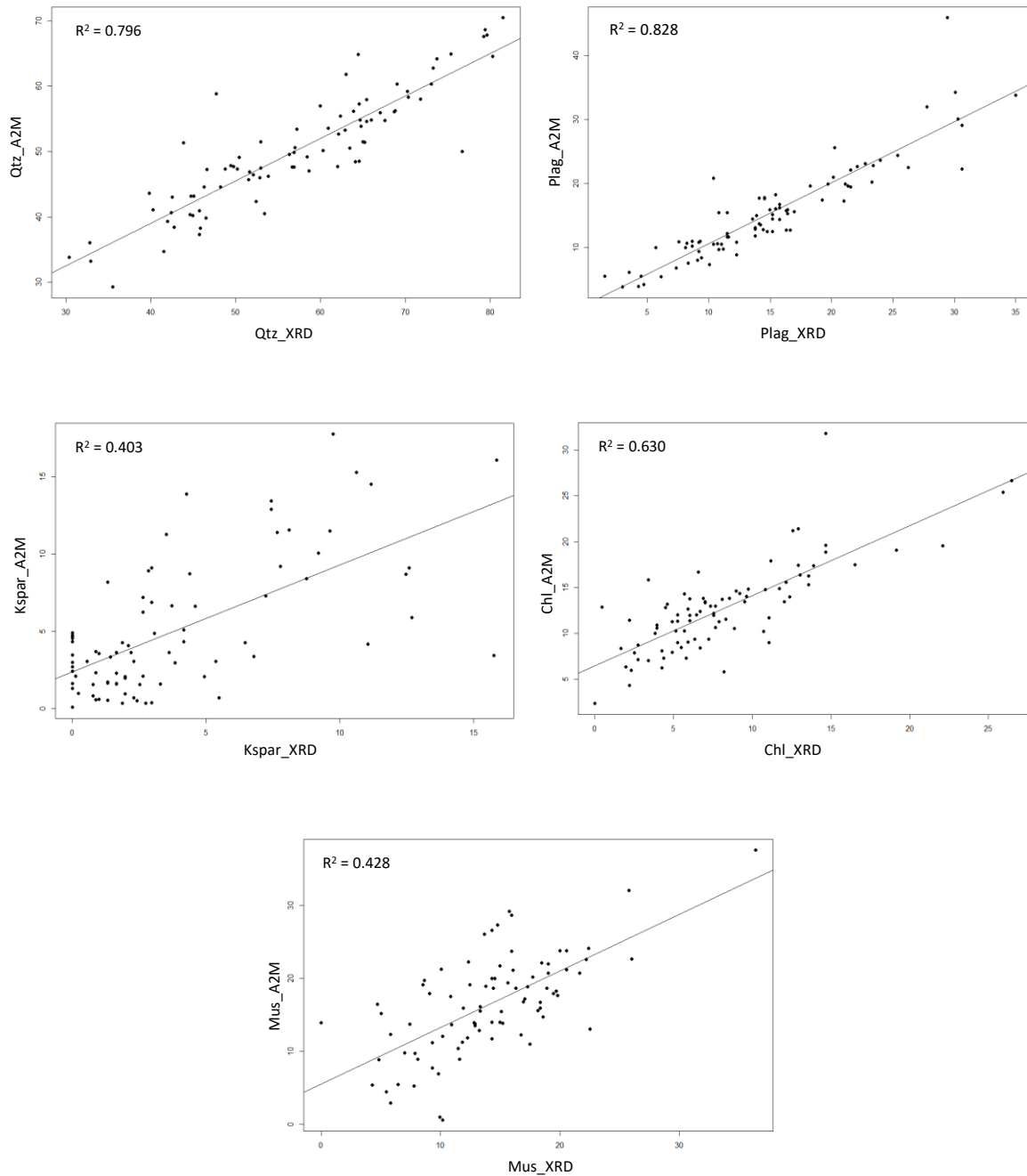
Figure 3.7. Scatter plots with linear regression of estimated X-Ray Diffraction (XRD) versus predicted Analysis to Mineralogy (A2M) quantitative soil mineralogy at 85 sites across New Brunswick, Nova Scotia, and Prince Edward Island (Qtz = Quartz, Plag = Plagioclase, Kspar = Potassium feldspar, Chl = Chlorite, Mus = Muscovite).

3.4.4 Canada-Wide Prediction of Soil Mineralogy

The predicted average bulk mineralogy for the soil profile ranked in order of quartz > plagioclase > potassium feldspar > chlorite > muscovite, which is typically the order of abundance of these minerals in soil. Average predicted quartz mineralogy had the least variation (coefficient of variation of 0.42) among the provinces, with 30.53 wt% in British Columbia to 73.04 wt % in Saskatchewan (Table 3.4). The sites with lower quartz percentages, typically less than 40 wt%, are in regions with variable bedrock geology, such as the Precambrian Shield in Ontario and Quebec, and therefore these sites have higher amounts of other minerals (e.g., plagioclase, potassium feldspar) in the soil (Figure 3.9). Portions of Saskatchewan and Alberta have high quantities of quartz in the soil due, in part, to the Western Canadian Sedimentary Basin bedrock geology and the high weathering resistance of quartz (Figure 3.8).

In general, average predicted plagioclase was lowest in Prince Edward Island at <9 wt% in Prince Edward Island and highest in British Columbia at 31 wt% (Table 3.4). Areas of northeastern Saskatchewan, Ontario, and Quebec show elevated plagioclase amounts (>30 wt%) due to the underlying Precambrian Shield bedrock geology (Figure 3.8). The Precambrian Shield geology of igneous and metamorphic rock types correlate with the higher amounts of plagioclase in the soil (see the yellow-filled circles in Figure 3.8). Plagioclase stoichiometric endmembers, albite and anorthite, had varying ratios of sodium and calcium across Canada (Figure 3.9). In general, albite was the dominant endmember, particularly in New Brunswick with the stoichiometric amount at 0.88 and Nova Scotia at 0.87, while anorthite had increased amounts in multiple provinces, such as Alberta at 0.31, Saskatchewan 0.25, and Ontario 0.26 (Figure 3.9).

Potassium-feldspar (K-feldspar) had the greatest variation between provinces in the data (coefficient of variation of 0.78). New Brunswick had the lowest mean of 2.73 wt% and Quebec

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had the highest mean of 10.94 wt%. The sites in Quebec are located on the Precambrian Shield, which explains the higher K-feldspar amounts, whereas New Brunswick is composed of sedimentary and igneous rocks. This highlights the different bedrock geology across Canada, regardless of the fact the two provinces are next two each other. In addition, New Brunswick had more site coverage than Quebec. Similarly, higher K-feldspar from the Precambrian Shield is shown on the transect in central to northern Saskatchewan. Sites with lower amounts of K-feldspar in northern Saskatchewan are on the cusp of the Precambrian Shield but are mostly located on the Western Canadian Sedimentary Basin where the geology is typically low in K-feldspar (Figure 3.8).

The mineral muscovite/illite had higher average amounts in Nova Scotia and New Brunswick (>17 wt%) which could be due to elevated weathering and the breakdown of muscovite to illite (clay minerals) (Table 3.4). Muscovite minerals are formed in igneous and metamorphic rock types and these rock types are found throughout New Brunswick and Nova Scotia. Saskatchewan had the lowest average muscovite at <4 wt% which was visible in the northern part of the province due to the geology of the Western Canadian Sedimentary Basin, which is not associated with muscovite (Figure 3.8).

The provinces of Newfoundland and New Brunswick had higher amounts (>14 wt%) of chlorite while Saskatchewan had lower amounts (<4 wt%) throughout the province (Table 3.4; Figure 3.8). Chlorite is an abundant mineral and commonly associated with igneous, metamorphic, and sedimentary geology.

All provinces and territory, with the exception of Prince Edward Island, needed additional minerals in the A2M mineral inputs to generate site compositions. These minerals included hornblende (approximately 30% of the sites), calcite (approximately 21% of the sites),

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and kaolinite (approximately 7% of the sites). Hornblende had higher occurrences of >12 wt% in provinces and territory associated with the Precambrian Shield (Quebec, Ontario, Newfoundland). Calcite had greater amounts where sedimentary, specifically carbonate, bedrock geology occurred (Manitoba at >12 wt%). Kaolinite was only used in 92 sites and the majority were in British Columbia and the Maritime Provinces (>10 wt%); these areas have higher levels of precipitation, which generates more weathering to produce an abundance of clay minerals in the soil.

In addition to the evaluation of predicted A2M versus XRD estimated mineralogy in the Maritime Provinces, paired comparison was carried out with TUSA data for Ontario, Saskatchewan and Alberta. Ontario results showed quartz, plagioclase, and hornblende to have no statistical differences in the means; however, potassium feldspar, chlorite, and were significantly different (Appendix B2). In Saskatchewan, quartz, plagioclase, potassium feldspar, and muscovite had no statistical difference while chlorite did. The paired t-test in Alberta indicated that quartz, plagioclase, and potassium feldspar were not significantly different; however, chlorite and muscovite were different (Appendix B2).

Table 3.3. Statistical summary of mineral results (n=85) generated by A2M versus the XRD results from USGS (in wt %).

	Qtz_A2M	Qtz_XRD	Plag_A2M	Plag_XRD	Kspar_A2M	Kspar_XRD	Chl_A2M	Chl_XRD	Mus_A2M	Mus_XRD
Mean	50.19	57.18	15.48	15.12	5.00	3.80	12.68	8.12	16.39	14.05
Max	70.45	81.51	45.88	35.01	17.76	15.86	31.79	26.48	37.57	36.43
Min	29.25	30.42	3.86	1.53	0.09	0.00	2.35	0.00	0.54	0.00
CV	0.18	0.21	0.48	0.47	0.84	1.03	0.39	0.63	0.41	0.41
p-value	<0.001		0.74		<0.05		<0.001		0.02	

Note: CV = Coefficient of Variation; Qtz = Quartz, Plag = Plagioclase, Kspar = Potassium feldspar, Chl = Chlorite, Mus = Muscovite

Table 3.4. Statistical summary of mineral results (n=1170) from A2M by Canadian provinces and territory (in wt %).

Mineral	Quartz	Plagioclase	K-spar	Chlorite	Muscovite	Hornblende	Calcite	Kaolinite
Mean	52.65	18.39	6.12	9.06	8.92	9.88	6.07	8.58
Max	98.89	62.34	28.39	51.08	40.98	48.09	56.87	17.58
Min	7.26	0.05	0.00	0.07	0.00	0.02	0.00	0.01
CV	0.42	0.65	0.78	0.67	0.79	0.70	1.20	0.59
AB	72.76	9.35	3.65	6.05	7.15	5.05	5.05	4.71
BC	30.54	31.74	5.73	13.42	9.00	9.38	1.50	13.24
MB	44.62	17.36	5.76	8.84	10.31	13.18	12.34	2.85
NB	49.21	14.15	2.73	14.03	17.10	1.66	0.08	9.63
NL	40.08	24.82	7.61	14.50	9.19	14.87	3.72	9.89
NS	50.80	13.80	3.94	11.55	18.17	1.07	0.06	10.51
NT	50.11	15.76	7.38	5.74	7.05	11.54	7.32	--
ON	36.54	27.34	9.58	10.28	8.78	13.85	7.91	1.65
PE	59.82	8.56	9.04	8.92	13.67	--	--	--
QC	37.71	24.88	10.94	11.53	9.17	15.07	--	--
SK	73.05	11.80	5.04	3.64	3.51	7.89	4.48	0.78

Note: CV = Coefficient of Variation; AB = Alberta, BC = British Columbia, MB = Manitoba, NB = New Brunswick, NL = Newfoundland, NS = Nova Scotia, NT = Northwest Territories, ON = Ontario, PE = Prince Edward Island, QC = Quebec, SK = Saskatchewan
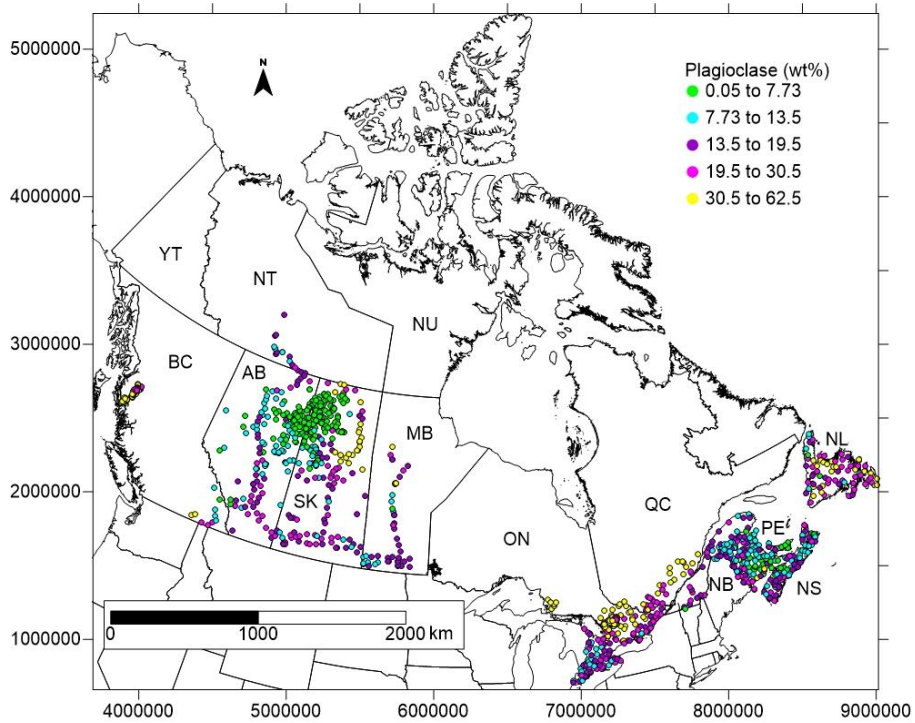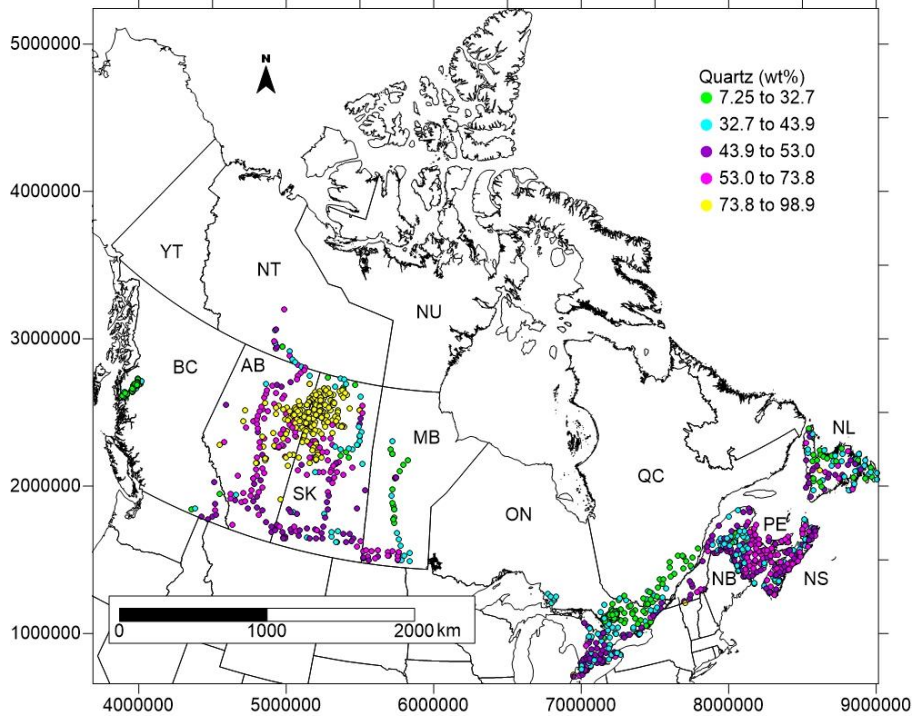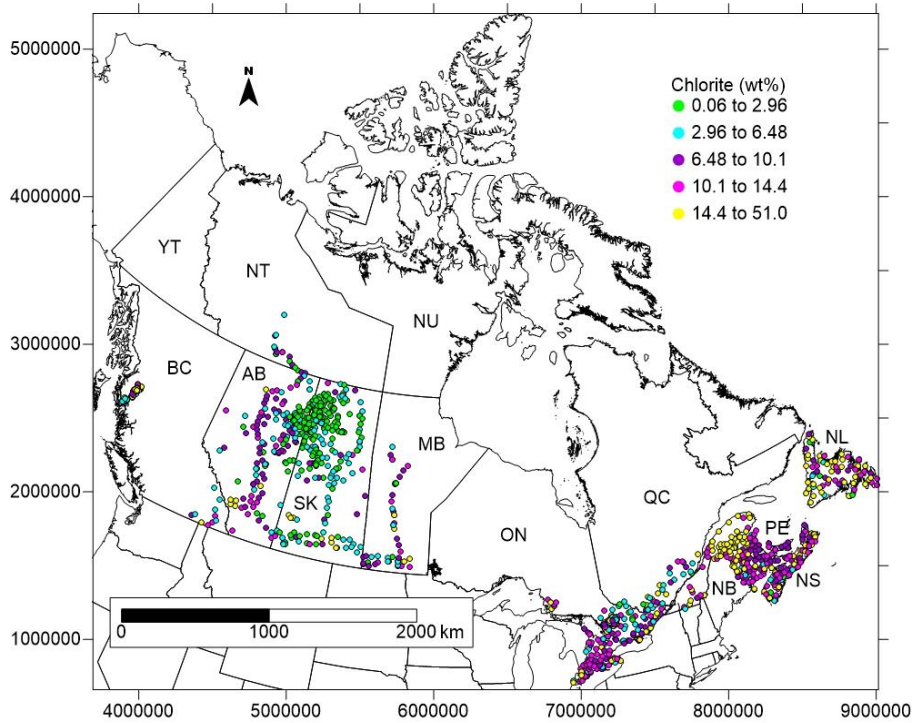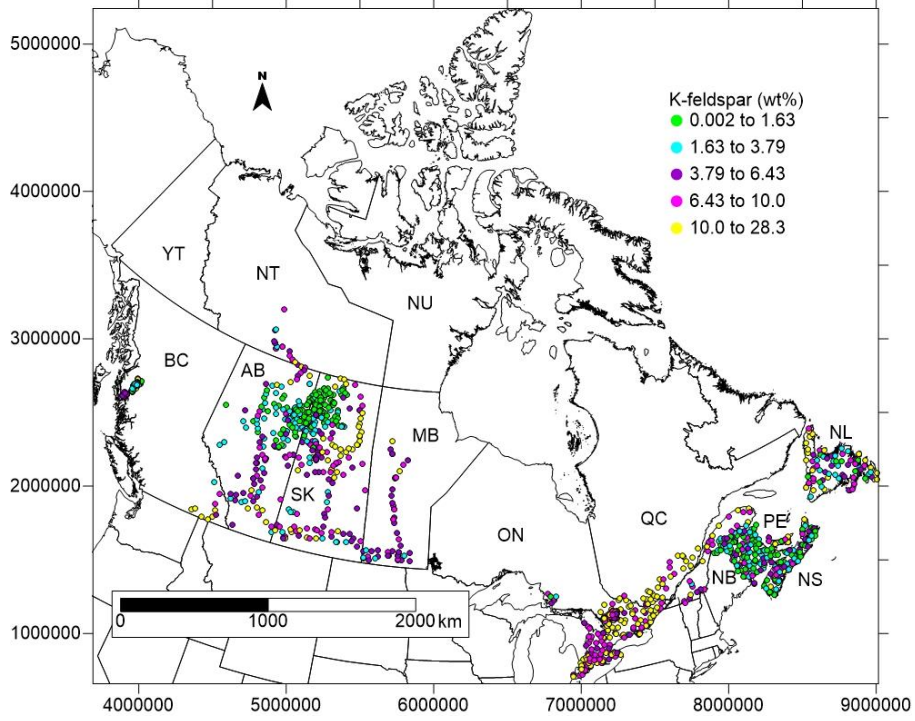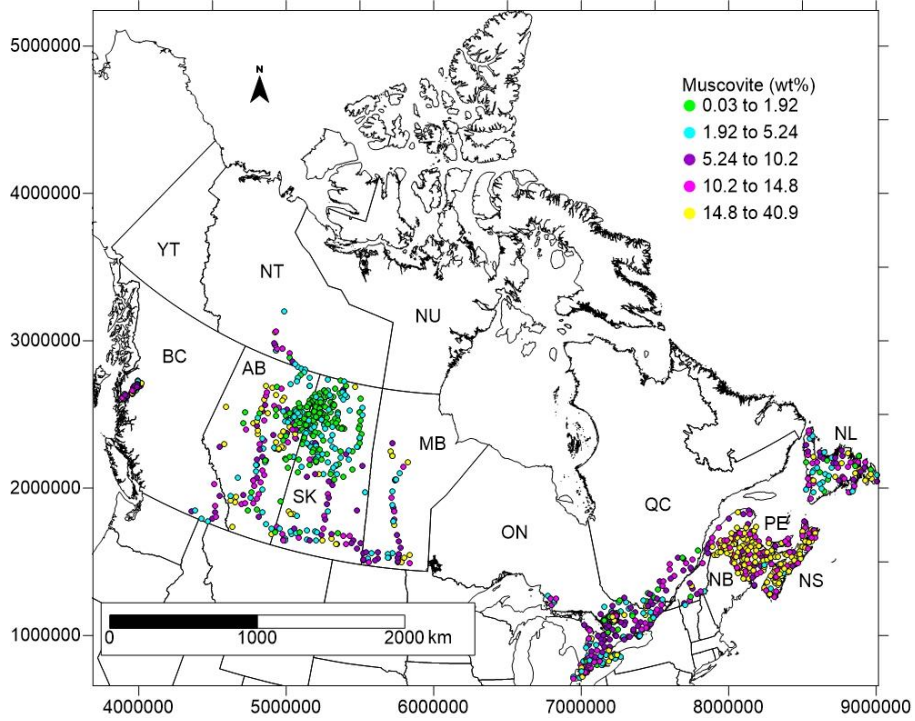
Figure 3.8. Mineral results in weight percentages from A2M (top to bottom: quartz, plagioclase, k-feldspar, muscovite, chlorite) across Canada from the North America Soil Geochemical Landscapes Project and Trent University Soil Archive (n=1170). Legends were set at equal distribution of sites among five categories (Map projection: Lambert Conformal Conic).
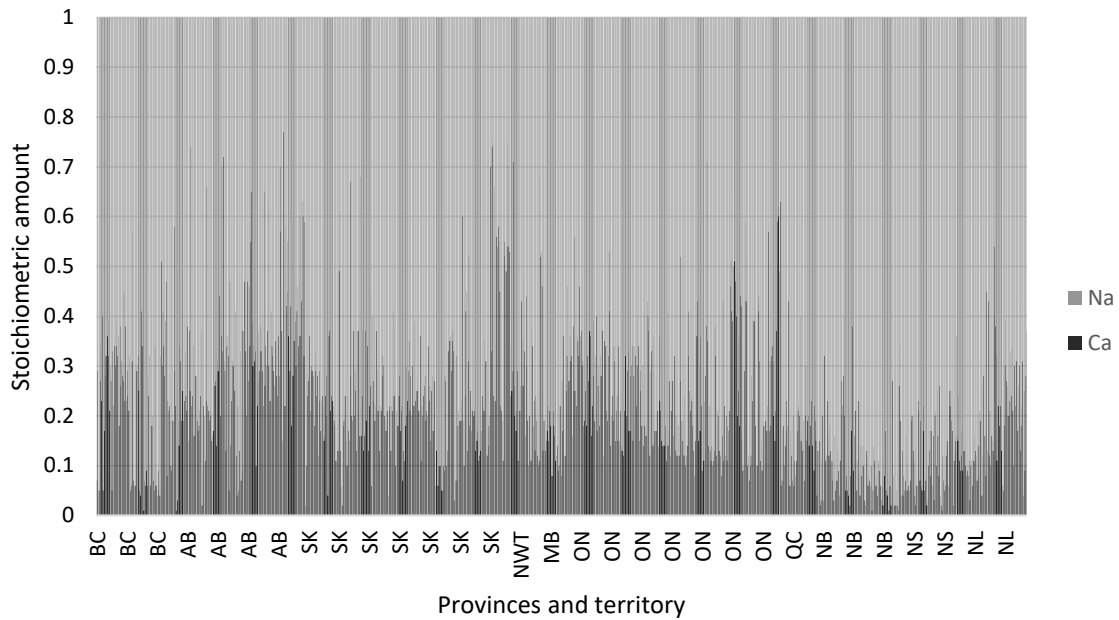
Figure 3.9. Distribution of plagioclase stoichiometric ratio for sodium (Na) and calcium (Ca), from West to East across Canada from the North American Soil Geochemical Landscapes Project and Trent University Soil Archive (n = 1170).

3.5 Discussion

The use of A2M in previous studies has primarily supported the determination of weathering rates, i.e., the prediction of quantitative mineralogy for the PROFILE model. As well, previous studies have typically focused on a regional scale, for example, Koseva et al. (2010) used A2M at 41 sites in southern Ontario and Casetou-Gustafson et al. (2018) used A2M at 8 sites in two different regions of Sweden. Koseva et al. (2010) applied A2M in conjunction with XRD mineralogy for 10 additional sites in Ontario, which were used to optimise A2M. The minerals from the XRD results at these sites were condensed into a mineral list, which was concentrated on the weathering capacities of minerals. Koseva et al. (2010) observed significant differences between A2M and XRD, however, the differences were <10% and the predicted mineralogy from A2M was in general agreement with the XRD observations. The study found

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that the A2M mineral list provided a broad coverage of southern Ontario geology and reliable estimates of soil mineral compositions to determine weathering rates. In general, the current study is consistent with results of the Koseva et al. (2010) study, i.e., the evaluation and application of A2M. The mineral list used in this study was similar and the predicted A2M mineralogy for quartz, plagioclase, and hornblende had comparable results to the XRD mineralogy and were not statistically different, while potassium feldspar, chlorite, and muscovite had statistical differences, but the differences were <8% which is relatively minor and could be accounted for by different stoichiometric ratios.

In Sweden, Casetou-Gustafson et al. (2018) evaluated approaches to predicted A2M mineralogy, where a regional investigation used a mineral list based on common soil minerals and knowledge of the local geology, versus site-specific A2M mineralogy which had mineral lists that were tailored based on X-Ray Diffraction and electron microprobe data. Results showed site-specific mineral lists had better A2M outputs in contrast to the regional approach. The Swedish results had significant differences in potassium feldspar and dioctahedral mica (known as muscovite in this study). This is consistent with the current study A2M results that had statistical differences of potassium feldspar and muscovite but were dependent on province. For example, Ontario had significant differences in potassium feldspar and muscovite, with A2M underestimating potassium feldspar and overestimated in muscovite. However, this study used a common mineral list and if a site-specific mineral list was applied, it could reduce the statistical differences.

Determination of soil minerals at a national scale is lacking worldwide, with the exception of United States following their completion of the North American Soil Geochemical Landscapes Project. Their dataset provides a unique insight and baseline on the abundance and

distribution of soil geochemistry and mineralogy (Smith et al., 2013). The predicted minerals in this study could be used as a baseline in the future, especially as inputs for the determination of weathering rates and the replenishment of base cations to the ecosystem via nutrient cycling.

3.6 Conclusion

The current study used soil oxide data from the North American Soil Geochemical Landscapes Project and Trent University Soil Archive to determine quantitative soil mineralogy using the normative model, A2M. The evaluation of A2M by comparison with XRD estimates showed strong correlations for quartz, plagioclase, and muscovite and therefore A2M. Predicted soil mineralogy was influenced by underlying bedrock geology of igneous, metamorphic, or sedimentary origins. This study demonstrated that quantitative soil minerals can be determined successfully with A2M at a large scale.

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4. Conclusion

4.1 General Conclusions

Soil geochemical analyses are widely carried out to determine the elemental composition of a soil, which supports different industries such as mineral exploration or environmental impact assessments. This research examined soil geochemical data from sites across Canada to infer qualitative soil mineralogy (Chapter 2) and to predict quantitative soil mineralogy by a normative method (Chapter 3).

Major soil oxides were assessed for elemental associations by exploratory data analysis and to determine if qualitative soil mineralogy could be inferred. Data were obtained from the North American Soil Geochemical Landscapes Project (NASGLP), which was a trinational survey between United States, Mexico and Canada, to analyze soil geochemistry and mineralogy and to collect and archive soil samples with consistent sampling and laboratory protocols. While the United States and Mexico completed the project, Canada did not, however, 560 sites across all provinces (British Columbia, Alberta, Saskatchewan, Manitoba, Ontario, Quebec, New Brunswick, Nova Scotia, Prince Edward Island, and Newfoundland) were sampled and analyzed for soil geochemistry. In this study, the major element soil oxides from <2 mm size fraction of the C-horizon were used to infer soil mineralogy as the C-horizon contains less organic matter and is more representative of the bedrock geology.

Exploratory data analysis included quantitative statistical summaries of the raw data and graphical measures to indicate oxide distributions. It is recognized that the raw soil geochemical data is compositional in nature and could be subject to the closure effect. Therefore, log-centred transformation of the data was applied prior to further analysis. Scatter plot matrices of log-centred data observed positive and negative correlations between the oxides, where the

associations of the oxides indicated or did not indicate a soil mineral composition. For example, SiO_2 and Al_2O_3 had a correlation ($R^2 = 0.61$), which suggested aluminosilicate minerals. Alternatively, Fe-Ca oxides had a negative correlation that implied minerals associated with these elements are rarely found together. Principal component analysis of the soil oxides was conducted to determine if soil minerals could be identified. The first three components accounted for 70.34% of the variation in the data, which allowed for interpretations from the biplots. For instance, TiO_2 could be identified as the mineral rutile or Fe_2O_3 could have weathered to a secondary mineral (e.g., magnetite). The soil minerals were generally classified as silicates, carbonates, and weathered oxides. These minerals reflected the bedrock geology types of igneous, metamorphic, or sedimentary. Regions with silicate minerals indicated igneous rock types and were noticeably located on the geospatial map in the Maritime Provinces (New Brunswick, Nova Scotia, Prince Edward Island, and Newfoundland) and the Precambrian Shield (northern region of Saskatchewan). Sedimentary geology, specifically carbonates, corresponded strongly to CaO and MgO and in areas of southern Saskatchewan, Manitoba, and Ontario. These results highlighted that multivariate analysis of soil oxide data can provide site-specific information in relation to the bedrock geology.

Chapter 3 predicted soil mineralogy at a national scale (n>1100) with the normative method, Analysis to Mineralogy (A2M). In addition to the NASGLP data, data from the Trent University Soil Archive was used. The soil horizons (A, B, C) at each site were combined into a weighted soil profile average for the top 50 cm of mineral soil based on bulk density and depth. Quantitative soil mineralogy was determined from a specified mineral list with a defined stoichiometry, that included quartz, plagioclase, potassium feldspar, chlorite, and muscovite, with hornblende, calcite, kaolinite, and biotite used as needed. An evaluation of A2M was

conducted with a sub-set of data (n=85) by comparing of A2M results and XRD mineralogy with the XRD data obtained from the United States Geological Survey. A2M results were not statistically different for plagioclase, potassium feldspar, and muscovite minerals. Further, strong correlations were shown for quartz, plagioclase, and muscovite. This indicated that the A2M method could be reliable approach for a national assessment.

Application of A2M across Canada showed variations for each mineral and of interest are the minerals with the potential to release base cations through chemical weathering into the environment (plagioclase, potassium feldspar, chlorite, muscovite, hornblende, and calcite). Soil containing plagioclase and potassium feldspar is highest (>30 wt% and >10 wt%, respectively) where the bedrock geology is the Precambrian Shield. Chlorite and muscovite have higher amounts (both >14 wt%) in areas with higher degree of weathering (Maritime Provinces). Calcite has greater quantities (>5 wt%) when the bedrock geology is sedimentary (Southern Ontario, Western Canadian Sedimentary Basin). These mineralogy results are useful to the prediction of soil weathering rates and to the indication of the areas that could provide base cations.

The results from Chapters 2 and 3 concluded that soil mineralogy could be inferred through statistical analysis or quantitatively by normative procedure. The majority of the Canadian data from NASGLP (exception being the Manitoba transect and the Maritime Provinces) had not been analysed before and this research gives an insight into the distribution of the major elements. In addition, the soil geochemistry of the C-Horizon was able to infer soil mineralogy at a regional scale from principal component analysis. Chapter 3 conducted a large-scale prediction of soil mineralogy by a normative method, which has not been done before.

4.2 Recommendations for Further Work

Further exploratory analysis of the NASGLP Canadian data could include the A and B soil horizons, which would provide a better understanding of the soil oxide variation in the soil profile. This project used soil oxides as is commonly reported, however, the use of elements for statistical analysis could be considered because not all elements form as oxides in soil, which could lead to under-reporting of elements.

In addition, completion of the NASGLP Canadian portion would be beneficial as it would allow for an understanding of the soil geochemical distribution across North America, as the project had initially intended. Furthermore, it would provide consistent database of soil geochemical information and a baseline for future research.

This study showed normative methods provide a reasonably inexpensive way to generate soil mineralogy at a national scale from available oxide data. Any available soil oxide data could be used to predict soil minerals at sites across Canada. This would be beneficial as weathering rates could then be calculated, which would help to deliver a more complete estimation of the base cation potential, especially in areas of known pollution and acidic deposition as well as natural resource management with regards to harvesting of biomass.

Appendix A

A1

Geological Map of Canada
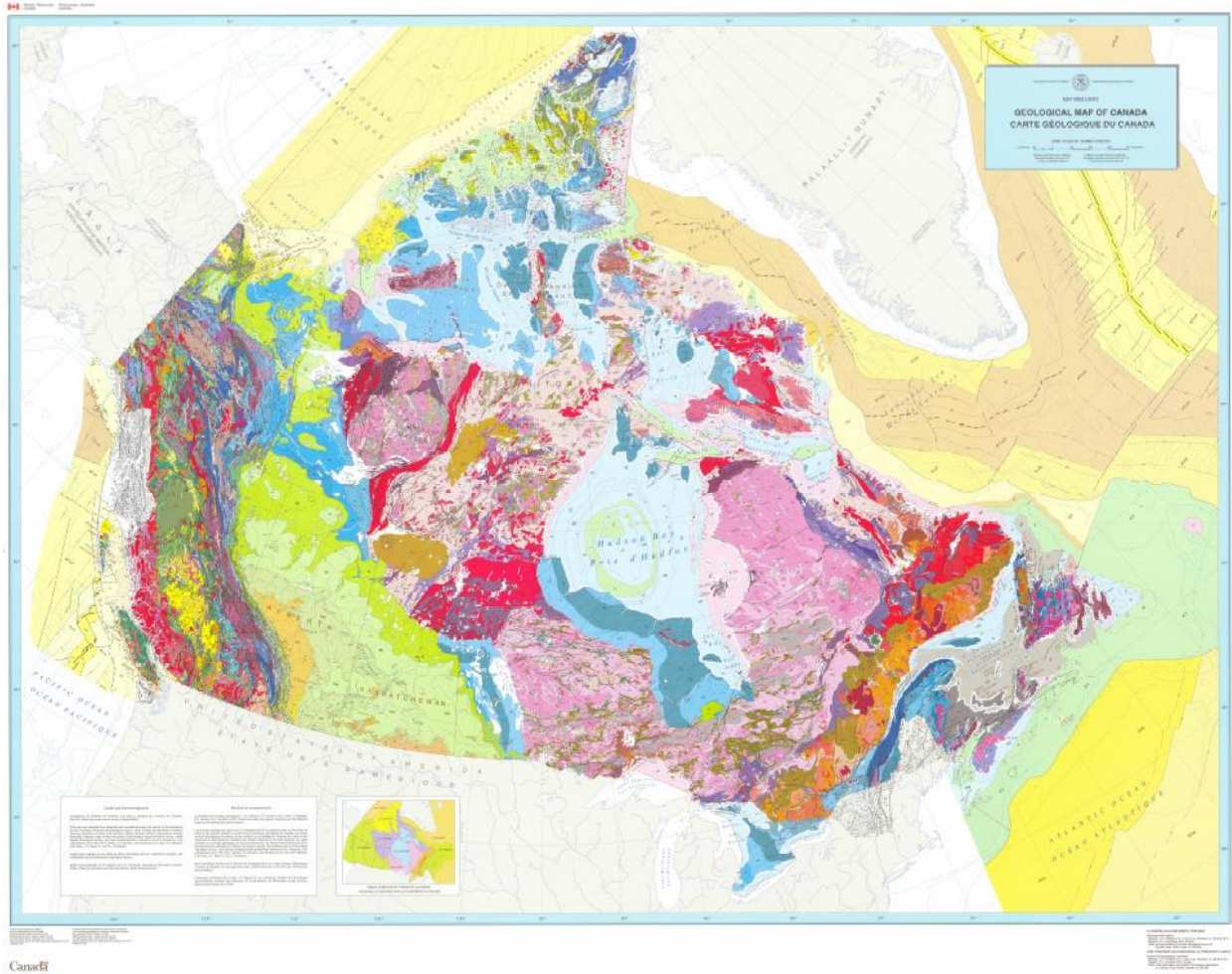
Wheeler J, Hoffman P, Card K, Davidson A, Sanford B, Okulitch A, Roest W (1996) Geological map of Canada. Geological Survey of Canada, Map 1860A, scale 1:5000000. Legend below.

STRATIFIED SEQUENCES

VOLCANIC ROCKS

INTRUSIVE ROCKS

METAMORPHIC ROCKS

COMPOSITION

EXPLANATORY NOTES

Era	Period
CENOZOIC	QUATERNARY
	TERTIARY
MESOZOIC	CRETACEOUS
	JURASSIC
	TRIASSIC
PALEOZOIC	PERMIAN
	PENNSYLVANIAN
	CARBONIFEROUS
	MISSISSIPPIAN
	DEVONIAN
	SILURIAN
	ORDOVICIAN
	CAMBRIAN
PRECAMBRIAN	NEOPROTEROZOIC (1000–541 Ma)
	MESOPROTEROZOIC (1600–1000 Ma)
	PALEOPROTEROZOIC (2500–1600 Ma)
	NEOARCHEAN (2800–2500 Ma)
	MESOARCHEAN (3200–2800 Ma)
	PALEOARCHEAN (3600–3200 Ma)
	EOARCHEAN (>3600–4000 Ma)

ONSHORE FEATURES

OFFSHORE FEATURES

REFERENCES

Canada

1860A Legend

A2

Untransformed Histograms
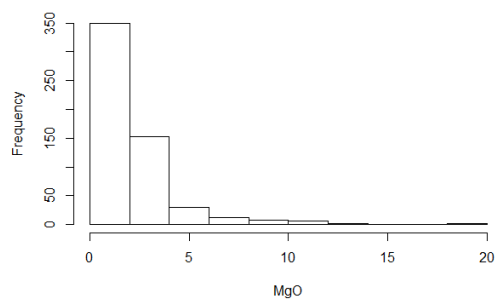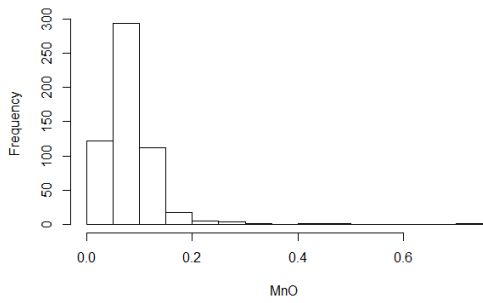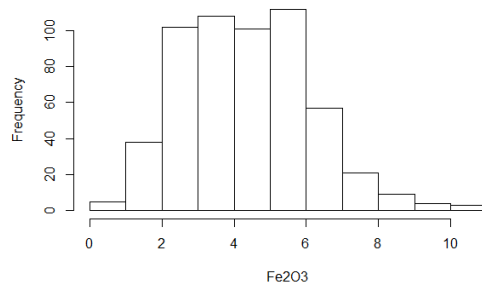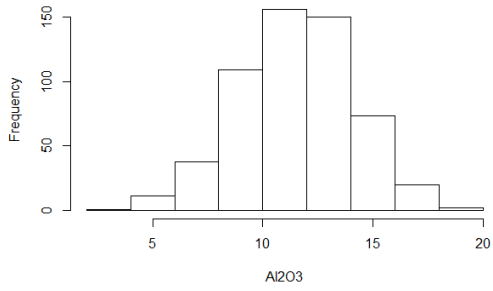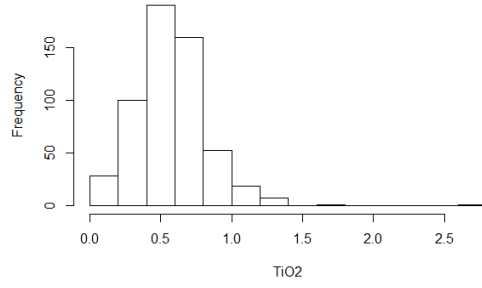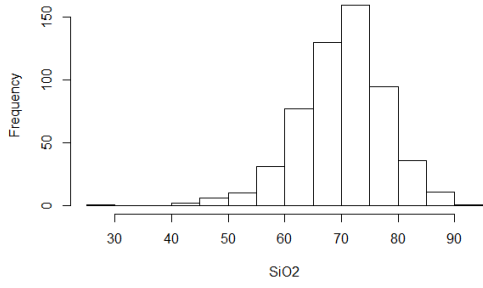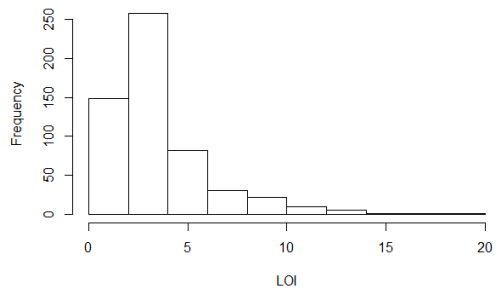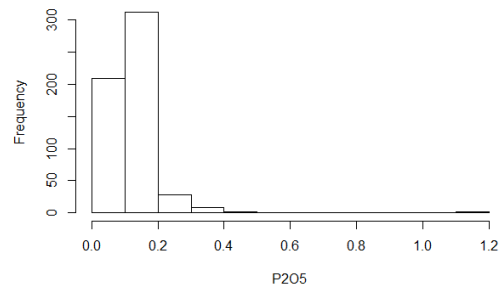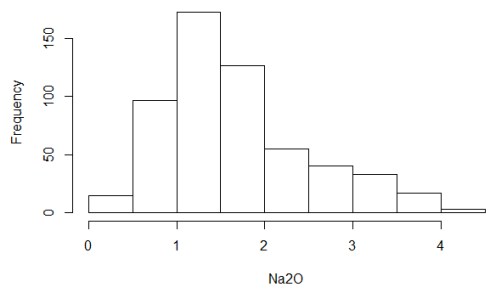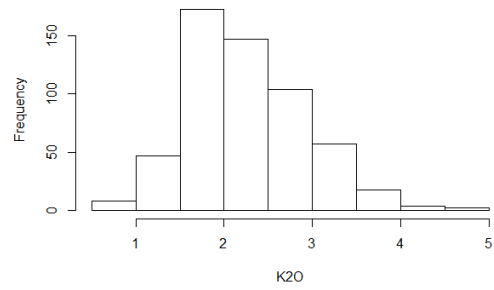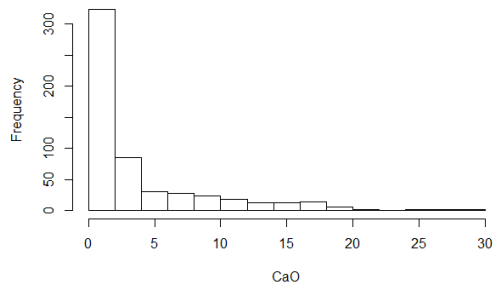
Logcentred histograms

Untransformed Quantile-Quantile plots

CaO

K2O

Na2O

P2O5

LOI
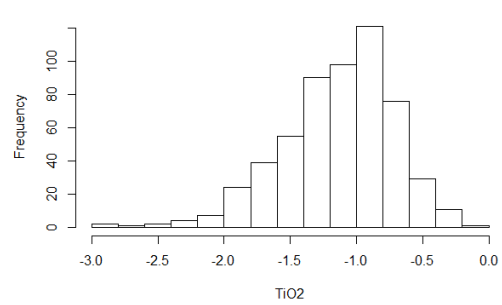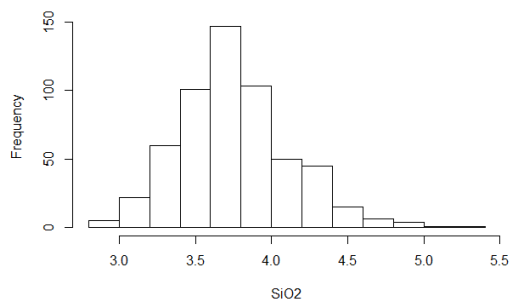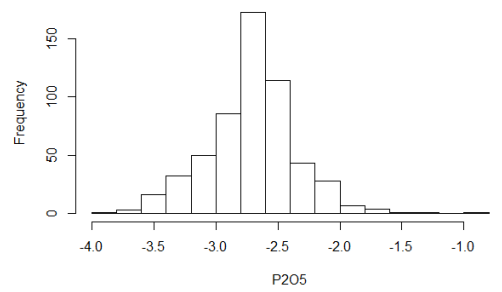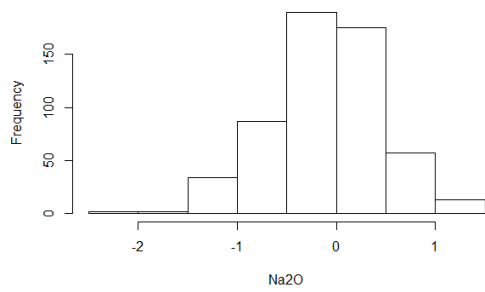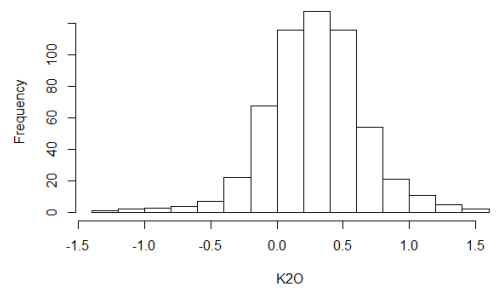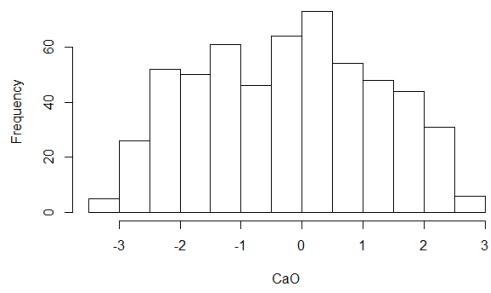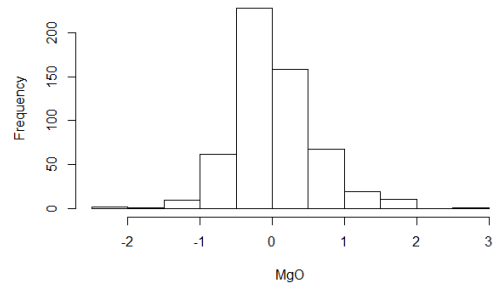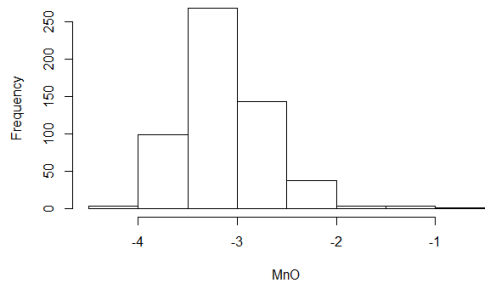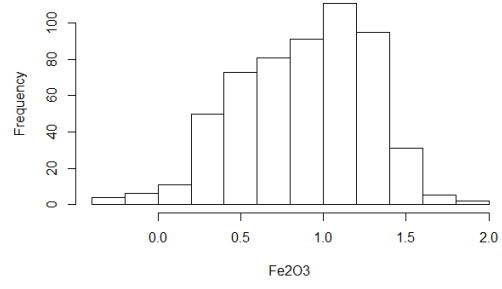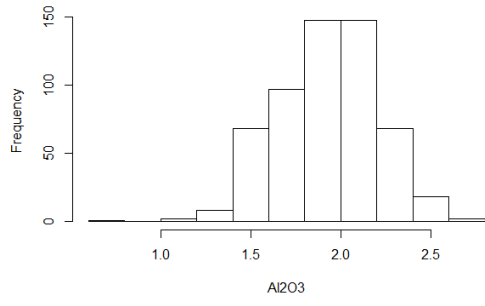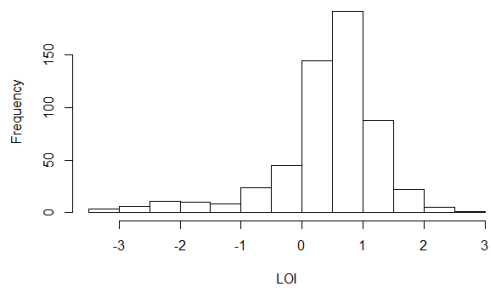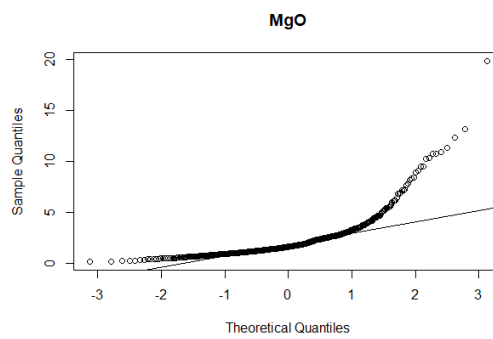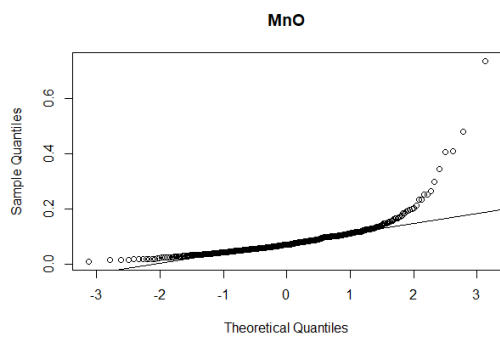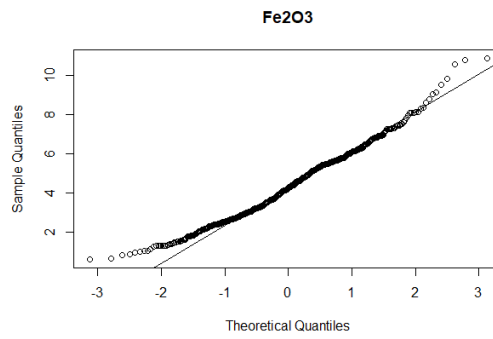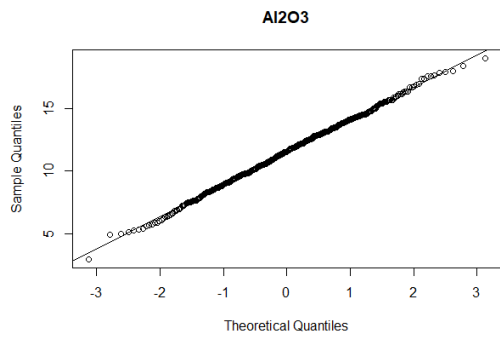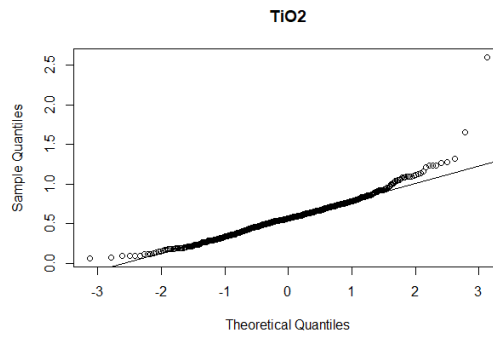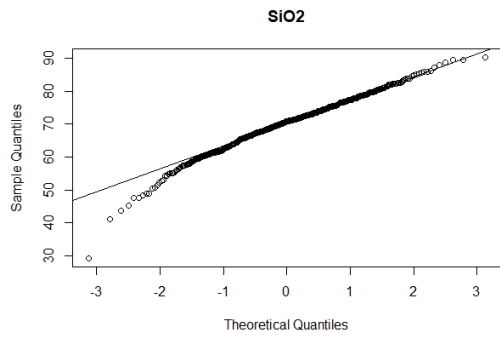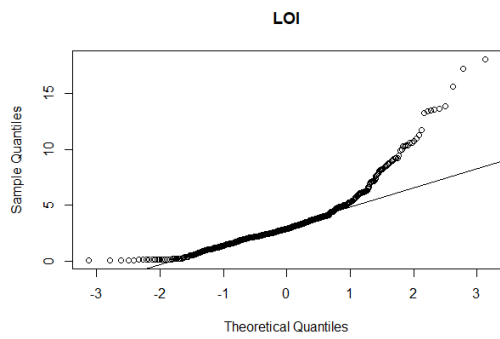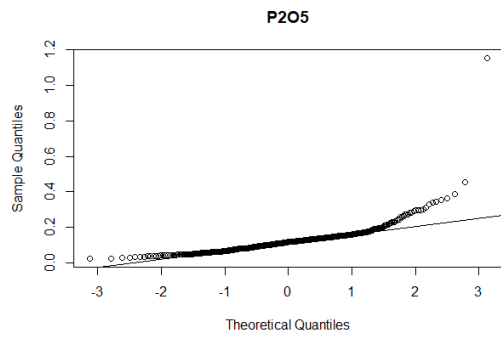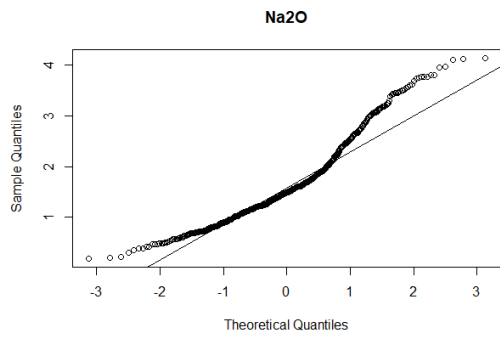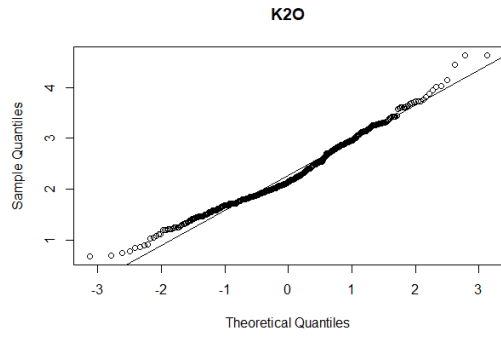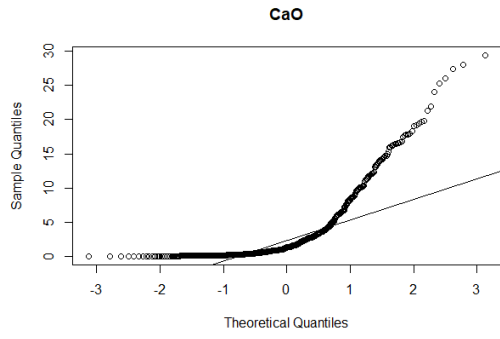
Logcentred Quantile-Quantile plots

SiO2

TiO2

LOI
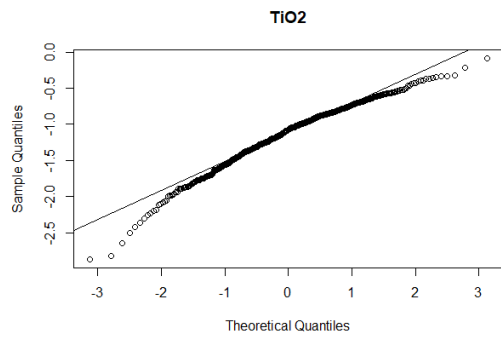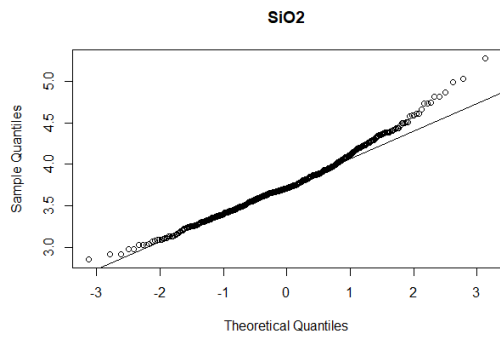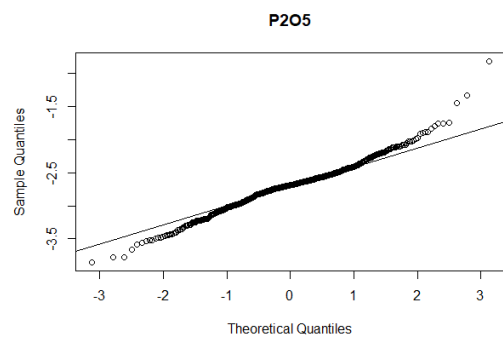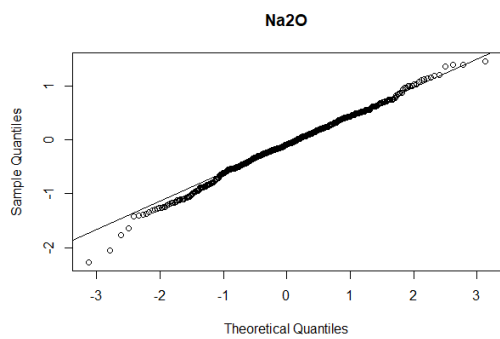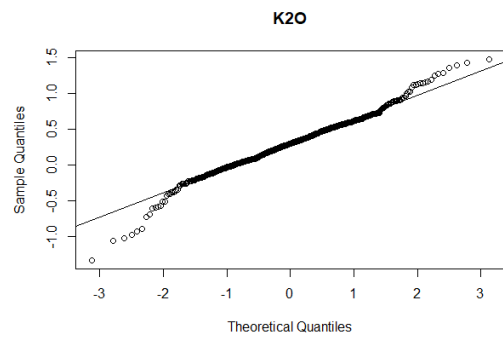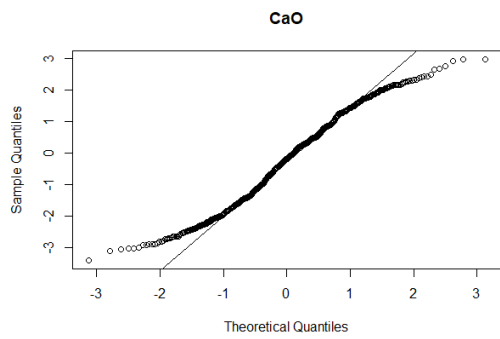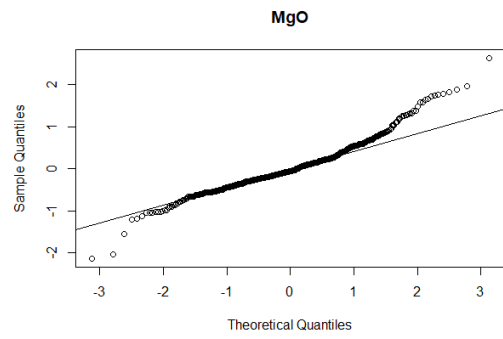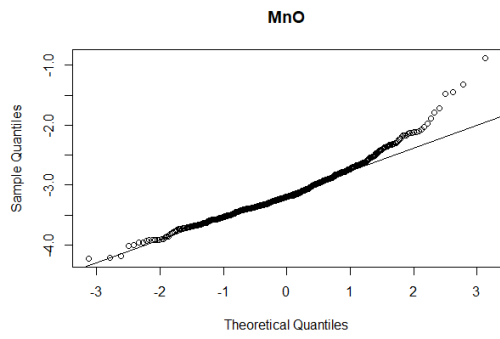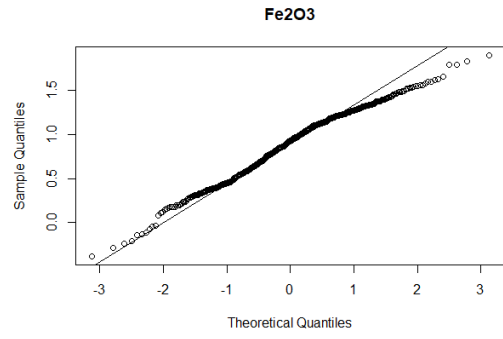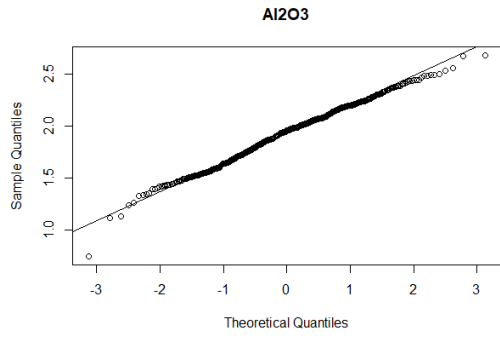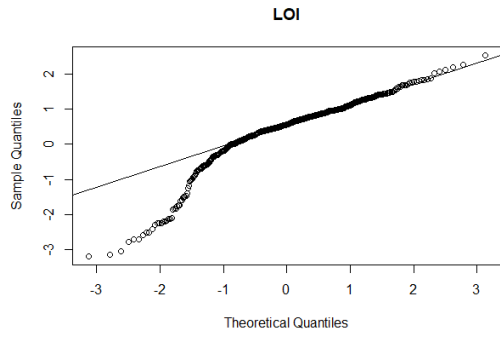
Untransformed boxplots

Untransformed C horizon major oxides

Logcentred boxplots
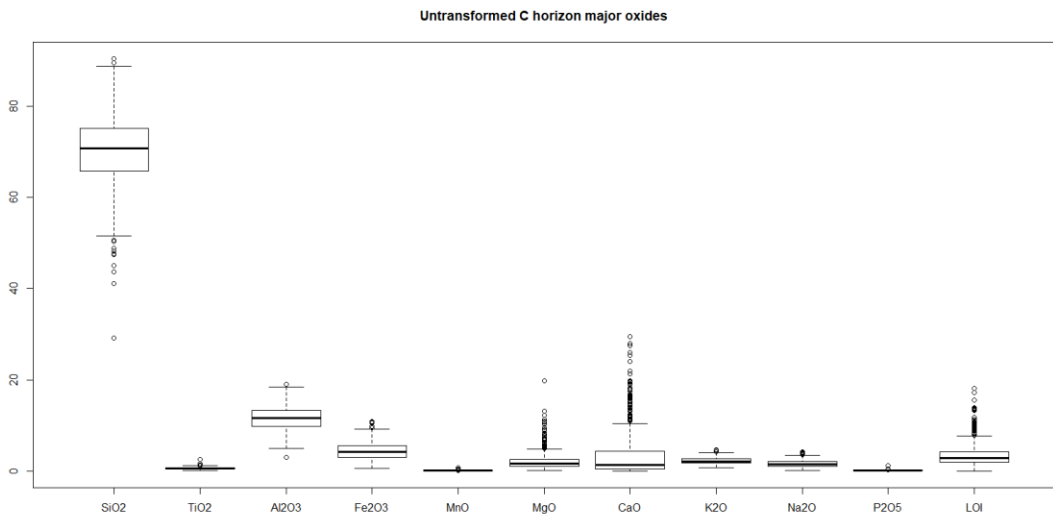
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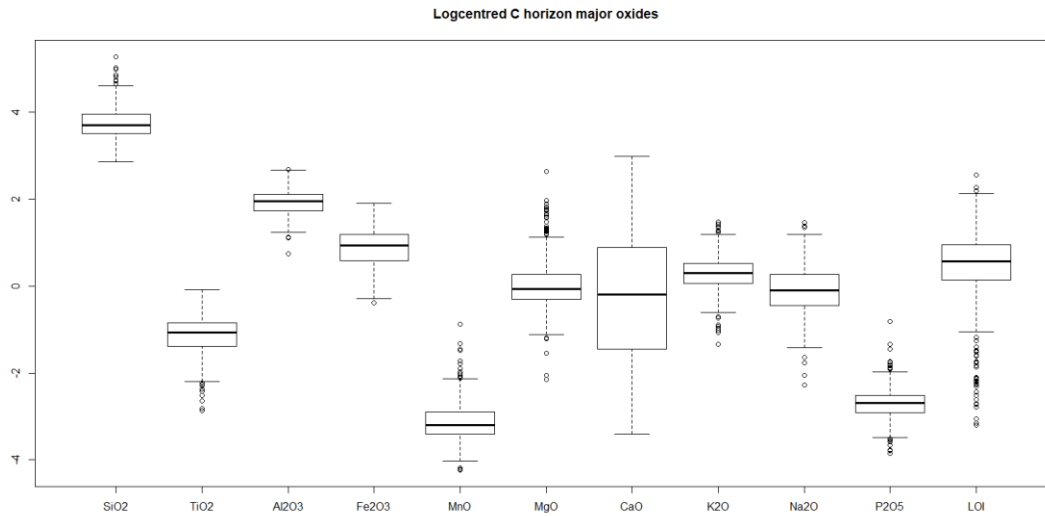
A3

Principal components (all)

	PC1	PC2	PC3	PC4	PC5	PC6	PC7	PC8	PC9	PC10	PC11
SiO_2	0.593	-0.539	-0.386	0.085	-0.102	0.156	-0.062	0.402	0.005	-0.033	0.000
TiO_2	0.748	0.393	0.210	0.151	0.153	-0.225	0.288	0.140	-0.182	0.095	0.000
Al_2O_3	0.893	-0.153	-0.158	-0.087	-0.122	-0.150	-0.027	-0.116	0.263	0.158	0.000
Fe_2O_3	0.751	0.527	0.158	-0.012	-0.052	-0.267	-0.022	0.013	0.140	-0.198	0.000
MnO	0.484	0.389	0.405	0.430	-0.052	0.468	-0.202	-0.040	0.005	0.034	0.000
MgO	-0.660	0.370	-0.160	0.212	-0.366	-0.365	-0.275	0.053	-0.095	0.052	0.000
CaO	-0.898	-0.281	0.081	0.144	-0.061	0.077	0.252	-0.027	0.119	-0.019	0.000
K_2O	0.696	-0.370	-0.117	-0.167	-0.470	0.093	0.075	-0.241	-0.204	-0.048	0.000
Na_2O	0.289	-0.698	-0.038	0.250	0.505	-0.203	-0.194	-0.153	-0.082	-0.028	0.000
P_2O_5	-0.058	-0.412	0.681	-0.563	-0.052	-0.069	-0.149	0.128	-0.021	0.028	0.000
LOI	0.008	0.657	-0.401	-0.524	0.288	0.196	-0.087	-0.027	-0.052	0.015	0.000

B1

Comparison results of 16 soil oxide sites from NASGLP vs TUSA in Ontario

| Site	SiO$_2$_NASGLP	SiO$_2$_TUSA	TiO$_2$_NASGLP	TiO$_2$_TUSA	Al$_2$O$_3$_NASGLP	Al$_2$O$_3$_TUSA	Fe$_2$O$_3$_NASGLP	Fe$_2$O$_3$_TUSA	MnO_NASGLP	MnO_TUSA
1	64.94	72.59	0.60	0.45	11.41	10.98	4.01	3.74	0.07	0.08
2	72.38	70.07	0.70	0.72	9.56	11.81	5.07	4.47	0.11	0.10
3	67.65	58.71	0.57	0.14	10.58	4.50	3.85	2.04	0.06	0.05
4	72.66	65.15	0.47	0.73	10.10	13.92	5.22	5.75	0.17	0.12
5	73.93	68.46	0.51	0.72	9.53	12.36	4.37	5.42	0.07	0.12
6	74.37	73.85	0.48	0.48	11.33	11.25	2.80	4.01	0.07	0.11
7	58.06	65.57	0.43	0.88	7.31	12.42	2.96	6.76	0.06	0.12
8	65.46	72.09	0.51	0.50	9.47	11.26	3.44	3.73	0.09	0.09
9	68.58	60.39	0.60	0.68	12.41	14.49	4.52	6.18	0.11	0.12
10	74.38	68.06	0.41	0.45	9.52	12.13	2.42	3.84	0.05	0.06
11	70.28	66.68	0.62	0.61	10.85	12.47	3.52	4.72	0.05	0.09
12	65.98	61.45	0.57	0.61	11.05	12.09	4.12	4.30	0.13	0.06
13	69.23	67.78	0.23	0.51	5.96	10.64	1.29	3.94	0.03	0.10
14	62.69	73.75	0.49	0.59	9.65	10.98	3.51	4.32	0.08	0.10
15	65.94	62.14	0.68	0.58	13.03	14.30	5.28	5.25	0.09	0.08
16	70.53	60.83	0.55	0.69	12.80	13.51	4.02	6.30	0.07	0.12
p-value	0.28		0.27		0.03		0.02		0.2	

Site	MgO_NASGLP	MgO_TUSA	CaO_NASGLP	CaO_TUSA	K$_2$O_NASGLP	K$_2$O_TUSA	Na$_2$O_NASGLP	Na$_2$O_TUSA	P$_2$O$_5$_NASGLP	P$_2$O$_5$_TUSA	LOI_NASGLP	LOI_TUSA
1	3.61	0.64	6.55	1.70	2.65	2.28	1.20	2.35	0.13	0.11	4.82	5.08
2	1.00	1.10	2.46	1.27	1.97	2.53	2.13	1.71	0.17	0.10	4.44	6.12
3	3.13	2.83	5.29	13.97	2.79	0.92	0.82	0.67	0.09	0.05	5.17	16.12
4	1.14	1.54	1.64	0.97	2.14	3.22	1.45	1.01	0.11	0.10	4.88	7.49
5	0.98	1.24	3.78	1.75	1.88	2.55	2.53	1.79	0.15	0.15	2.26	5.44
6	1.07	0.83	2.94	2.09	2.32	2.27	3.12	2.81	0.19	0.11	1.31	2.21
7	1.10	1.69	11.73	2.71	1.35	1.86	1.60	2.37	0.14	0.20	15.24	5.42
8	1.43	1.26	9.48	1.70	2.02	2.31	1.17	1.49	0.24	0.10	6.69	5.47
9	1.55	2.08	3.32	2.99	2.37	2.04	3.06	2.47	0.19	0.27	3.30	8.29
10	0.81	0.88	2.21	2.28	2.02	2.28	2.68	2.34	0.12	0.11	5.39	7.57
11	0.91	1.26	2.06	2.82	2.31	2.52	2.47	1.85	0.17	0.26	6.76	6.72
12	3.99	1.23	5.72	1.92	2.39	2.41	1.79	1.34	0.17	0.16	4.09	14.43
13	5.69	1.98	13.49	3.02	1.37	2.32	1.27	1.19	0.07	0.10	1.37	8.42
14	2.62	0.90	14.37	1.86	2.19	2.15	1.31	1.88	0.15	0.13	2.93	3.34
15	2.30	1.05	2.80	2.44	3.22	2.56	2.97	2.49	0.23	0.17	3.47	8.97
16	1.00	1.55	2.72	2.76	3.10	2.26	3.57	2.57	0.15	0.20	1.48	9.21
p-value	0.09		0.05		0.9		0.25		0.48		0.03	

Location of the 16 areas to compare NASGLP (red) vs TUSA (green) soil oxides

Boxplots of soil oxides from NASGLP vs TUSA in Ontario
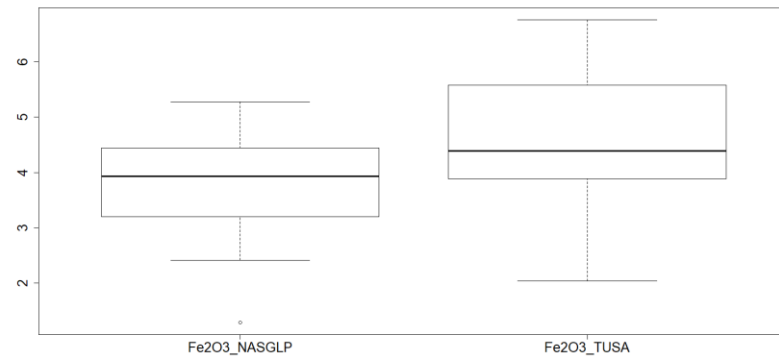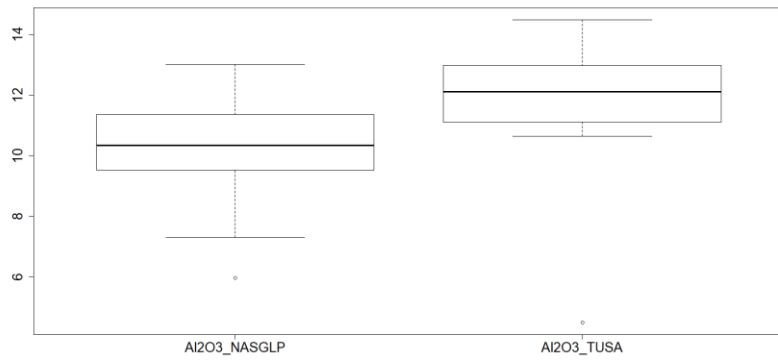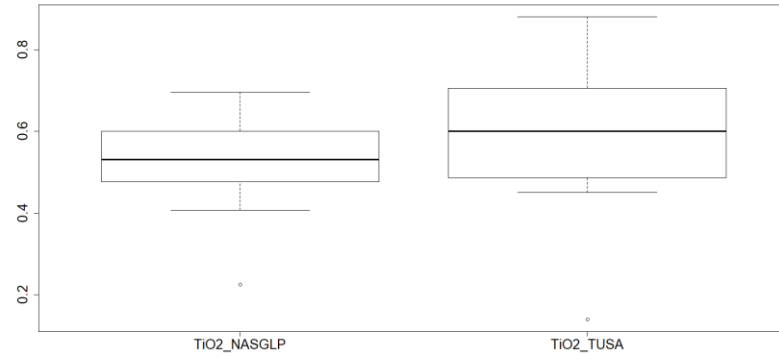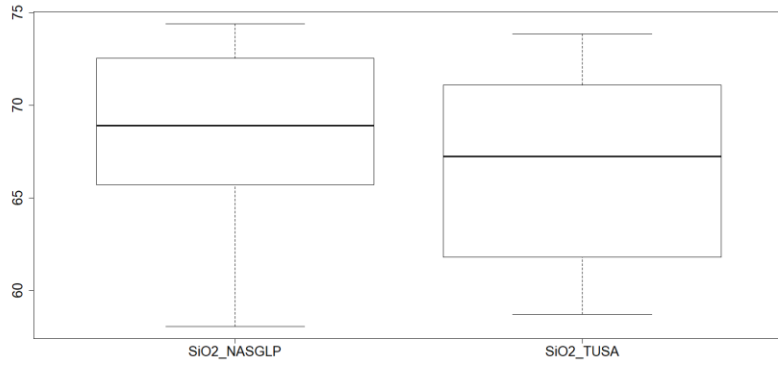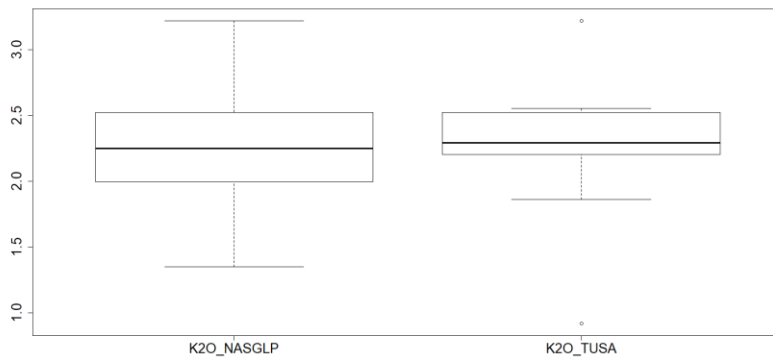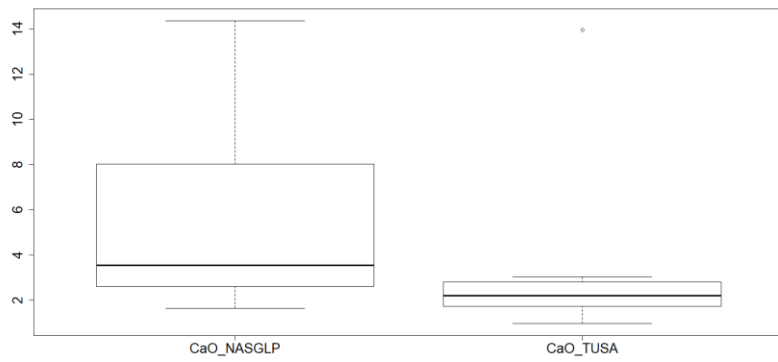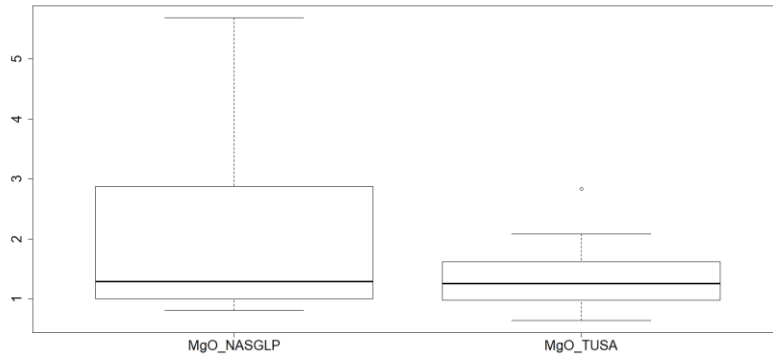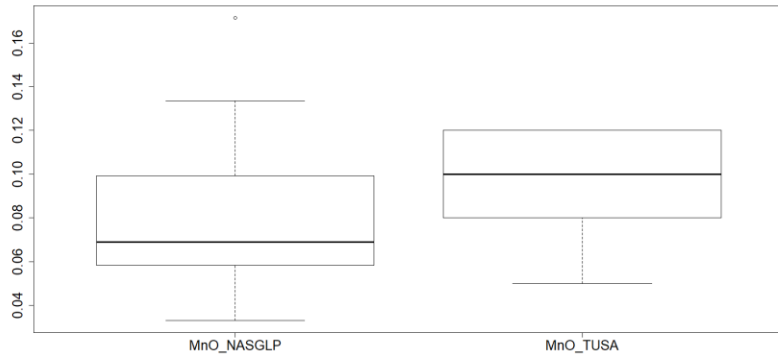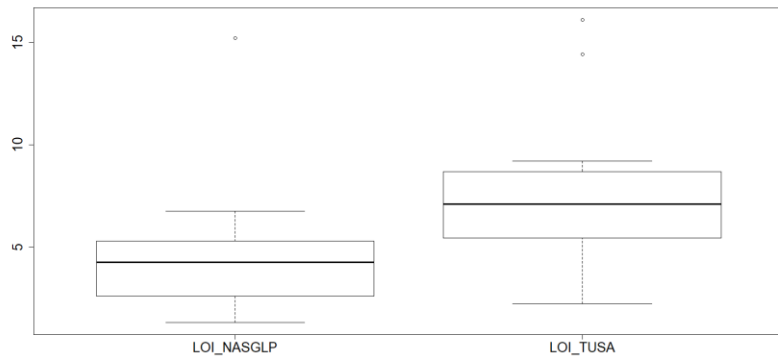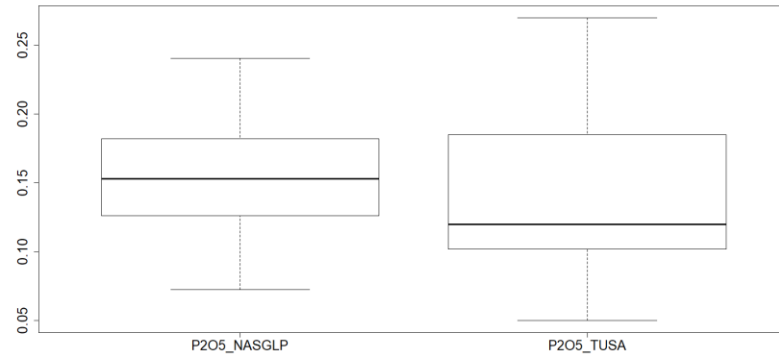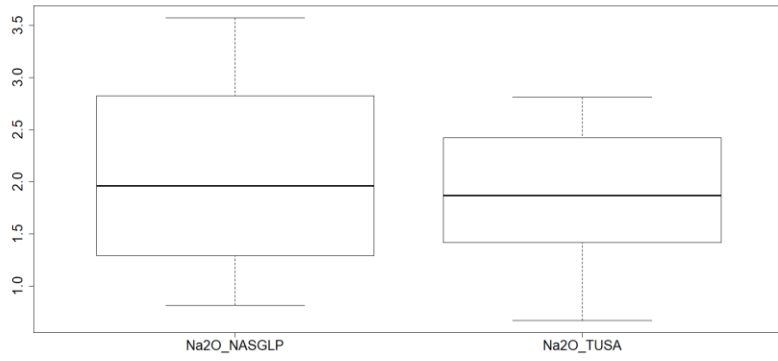
B2: Additional A2M vs XRD results at sites in Ontario, Saskatchewan, and Alberta

Prov	Site ID	Qtz_XRD	Qtz_A2M	Plag_XRD	Plag_A2M	Kspar_XRD	Kspar_A2M	Chl_XRD	Chl_A2M	Mus_XRD	Mus_A2M	Hbl_XRD	Hbl_A2M
ON	11	34.23	26.46	33.38	31.43	13.91	4.09	0.00	9.56	3.32	15.69	12.47	12.77
ON	14	43.38	37.98	27.52	24.92	10.47	7.75	1.91	4.98	6.80	12.78	4.63	11.59
ON	22	45.52	37.57	32.87	33.44	12.47	10.74	0.00	4.33	0.40	6.33	6.42	7.59
ON	42	51.38	44.14	19.39	20.45	10.45	9.93	2.57	5.93	9.52	8.37	2.65	11.18
ON	61	34.61	28.43	34.03	33.40	17.83	11.25	0.00	6.39	1.44	9.01	10.04	11.51
ON	79	36.97	26.20	32.63	33.84	17.37	7.70	2.64	5.76	1.29	13.01	7.91	13.49
ON	83	43.17	36.63	21.08	18.99	16.63	9.32	3.15	8.82	5.00	12.28	5.54	13.97
ON	101	44.91	36.50	28.88	32.76	18.29	12.88	0.00	13.60	2.03	4.25	5.45	0.00
ON	9-3	50.64	38.56	30.74	32.69	9.99	2.39	2.08	12.43	0.86	13.92	4.45	0.00
ON	1132	30.93	26.76	35.49	28.84	14.04	4.64	0.00	9.90	2.54	16.27	15.39	13.59
SK	A01-02	39.00	37.11	40.69	40.43	14.50	13.96	0.62	1.36	2.02	2.59	---	---
SK	A03-02	34.99	29.71	31.40	25.59	17.10	6.51	3.19	6.77	4.30	17.30	---	---
SK	B02-01	13.54	7.26	20.94	28.52	0.00	1.30	4.01	10.44	9.67	4.40	---	---
SK	C01-02	94.68	92.29	3.63	4.05	1.29	1.33	0.00	1.32	0.00	1.01	---	---
SK	C01-04	96.96	96.05	1.78	0.72	0.83	0.02	0.00	1.37	0.00	1.83	---	---
SK	C02-02	97.73	97.47	1.27	0.07	1.01	0.07	0.00	1.71	0.00	0.69	---	---
SK	C02-03	98.89	97.89	0.47	0.07	0.00	0.02	0.00	1.19	0.00	0.84	---	---
SK	C02-07	99.73	97.96	0.00	0.07	0.00	0.07	0.00	1.24	0.00	0.66	---	---
SK	C03-03	100.00	97.96	0.00	0.07	0.00	0.03	0.00	1.36	0.00	0.60	---	---
SK	C03-06	93.56	94.38	3.00	1.00	1.70	0.99	0.51	1.88	0.71	1.76	---	---
SK	C04-04	95.68	94.35	1.13	1.12	1.00	0.02	0.87	1.75	0.98	2.77	---	---
SK	C05-03	96.51	92.97	1.67	2.53	1.27	0.86	0.00	1.73	0.00	1.92	---	---
SK	C06-01	95.72	95.86	2.30	1.29	1.31	0.59	0.00	1.37	0.00	0.89	---	---
SK	C06-04	89.96	91.28	5.29	3.23	2.08	0.73	0.00	1.52	0.76	3.23	---	---
SK	C07-05	90.64	88.13	4.89	4.60	1.97	0.17	0.29	3.12	0.81	3.98	---	---
SK	C08-02	46.14	43.30	43.44	42.61	9.17	9.89	0.00	3.88	0.00	0.32	---	---
SK	C09-05	80.50	79.77	11.30	10.21	5.84	5.38	0.00	2.57	0.76	2.08	---	---
SK	C10-02	88.04	88.00	5.61	5.29	3.25	2.02	0.89	2.04	1.62	2.64	---	---
SK	C11-01	96.88	95.56	1.51	0.23	1.52	0.33	0.00	1.48	0.00	1.11	---	---
SK	C12-02	59.00	52.86	26.73	26.20	10.52	8.51	1.02	5.73	0.41	6.71	---	---
SK	C12-05	66.97	63.35	21.70	20.77	9.28	7.10	0.38	5.00	0.00	3.78	---	---
SK	D01-01	96.63	95.81	1.94	0.89	1.43	0.17	0.00	1.52	0.00	1.61	---	---
SK	D01-02	87.68	84.28	8.47	7.20	2.88	2.08	0.00	3.32	0.22	3.11	---	---
SK	D01-03	86.42	97.70	8.56	0.07	3.17	0.32	0.56	1.16	0.00	0.75	---	---
SK	D01-04	98.58	97.53	0.60	0.25	0.82	0.08	0.00	1.13	0.00	1.02	---	---
SK	D03-02	68.68	63.94	16.40	16.88	7.78	9.83	2.24	6.12	3.08	3.22	---	---
SK	D04-09	36.81	33.06	32.90	33.45	18.70	18.15	0.57	3.66	4.17	4.76	---	---
SK	D05-03	96.70	94.55	1.76	1.03	1.33	0.39	0.00	2.78	0.00	1.25	---	---
SK	D05-05	92.69	89.18	4.56	4.69	2.24	2.56	0.00	2.81	0.00	0.77	---	---
SK	D08-03	43.06	39.21	33.29	35.03	15.43	14.72	1.62	7.23	2.38	3.81	---	---
SK	D09-02	28.43	26.22	36.04	39.51	16.49	18.81	3.18	15.31	8.46	0.15	---	---
SK	D09-08	35.46	31.64	43.40	42.27	5.63	8.10	0.60	3.30	1.60	3.70	---	---
SK	D10-03	35.04	34.93	33.44	34.47	12.43	8.12	2.19	14.06	8.70	8.43	---	---
SK	E01-02	95.08	93.11	1.92	7.07	2.05	1.26	0.00	1.90	1.02	11.29	---	---
SK	E02-02	80.26	77.26	8.78	8.21	4.32	4.71	0.00	4.93	4.72	4.90	---	---
SK	E03-01	85.59	87.44	7.39	5.64	2.40	3.10	1.12	2.44	1.81	1.38	---	---
SK	E05-03	72.65	69.62	12.54	13.39	6.75	7.31	1.75	5.00	4.33	4.67	---	---
SK	E07-02	82.52	92.60	9.17	2.24	5.28	1.01	0.00	2.04	3.12	0.98	---	---
SK	E12-03	70.03	66.08	14.61	16.71	6.70	9.22	0.36	0.74	2.98	1.39	---	---
SK	E14-02	81.33	80.37	9.18	8.77	5.14	6.05	0.00	2.96	2.44	1.85	---	---
SK	E16-01	57.63	58.07	13.58	13.55	7.76	3.90	0.00	8.69	12.18	15.79	---	---
SK	E17-02	57.21	42.29	22.50	28.38	8.43	6.13	0.00	3.93	5.41	9.12	---	---
SK	E24-01	62.46	60.03	22.08	22.36	7.87	9.82	0.00	6.04	3.58	1.75	---	---
SK	E26-01	61.61	59.03	17.10	16.61	6.89	6.36	0.00	8.20	9.08	9.81	---	---
SK	E27-02	59.86	48.83	18.38	14.58	6.41	8.08	0.00	6.59	3.81	2.40	---	---
SK	E29-01	54.99	46.61	18.97	13.99	7.05	5.60	0.00	6.71	6.35	7.55	---	---
AB	FIR	87.46	84.74	3.86	2.23	4.68	0.30	0.39	3.97	2.50	8.76	---	---
AB	JP205	95.48	96.16	1.60	0.35	2.25	0.32	0.67	0.86	0.00	1.10	---	---
AB	JP210	91.35	87.38	4.11	5.18	4.15	3.61	0.00	2.41	0.00	1.42	---	---
AB	JP212	92.94	91.15	4.00	2.35	2.36	2.23	0.00	3.31	0.11	0.97	---	---
AB	JPH1	95.03	92.07	2.66	1.80	2.31	0.69	0.00	1.97	0.00	3.46	---	---
AB	KIN	85.43	78.13	6.27	7.06	4.41	2.60	1.69	4.59	1.35	7.63	---	---
AB	MAR	92.96	90.25	2.95	3.24	2.37	1.75	0.42	2.33	0.77	2.44	---	---
AB	MIL	83.49	82.81	6.94	7.33	6.29	3.08	1.20	2.79	1.61	4.00	---	---
AB	NE07	82.00	81.97	7.21	7.40	4.33	3.18	0.00	3.25	2.35	4.20	---	---
AB	NE11	95.58	91.73	1.94	2.25	2.02	0.93	0.45	1.92	0.00	3.17	---	---