# Trace elements in berries collected near upgraders and open pit mines in the Athabasca Bituminous Sands Region (ABSR): distinguishing atmospheric dust deposition from plant uptake

**by**

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# Abstract

Bitumen mining and upgrading operations in the Athabasca Bituminous Sands Region (ABSR) may lead to increased concentrations of trace elements in the surrounding environment. Elevated concentrations of potentially toxic trace elements could pose a risk to local indigenous communities through the contamination of native berries that are an important part of their traditional diet. The objective of this study was to determine the magnitude of trace element enrichment in cranberries, lingonberries, and blueberries growing in the ABSR. To quantify the extent of enrichment, the same species of berries were also collected from remote areas, for comparison. The concentrations of 19 trace elements were measured using ICP-MS in the ultraclean metal-free SWAMP lab at the University of Alberta. Berries collected from the ABSR contain similar concentrations of Ba, Cd, Cu, Mn, Mo, Rb, Sr, and Zn compared to berries grown in remote locations (ie within a factor of two). In contrast, concentrations of Cr, Li, Pb, U, V, and Y were 2-24 times greater in ABSR berries compared to those grown in remote locations. The concentrations of these elements decreased after the berries were washed, suggesting that the trace elements were present in the form of dust. The presence of dust particles on the surface of the berries grown near open pit mines and upgraders was confirmed using SEM. In addition, the concentrations of Al, Cr, Pb, U, and V were strongly correlated with Y, a conservative, lithophile element which is not taken up by plants via their roots. Using Y as an indicator of the abundance of dust particles, we can distinguish between trace elements supplied primarily by aerial deposition

of dust (e.g., Cr, Pb, V) from those that are primarily obtained by absorption through root uptake (e.g., Cu, Mn, Zn).

# Preface

The following thesis is composed of original data generated and analyzed by Samantha Stachiw and includes one published paper and one paper accepted for publication. The contribution made by the candidate and the co-authors to the completion of the work are described here. The first published paper, "A geochemical perspective on the natural abundance and predominant sources of trace elements in cranberries (*Vaccinium oxycoccus*) from remote bogs in the Boreal region of northern Alberta, Canada" (located in Appendix 1) was published in *Science of the Total Environment*. The candidate co-authored this chapter with William Shotyk, Iain Grant-Weaver, and Beatriz Bicalho. In this chapter the candidate was responsible for sample preparation and sample and data analysis. Dr. Shotyk generated the Figures and Tables and wrote the entirety of the publication. Dr. Bicalho helped with analytical results, and Iain Grant-Weaver assisted in sample analysis.

Chapter 2 of this thesis was co-authored by the candidate and Beatriz Bicalho, Iain Grant-Weaver, Tommy Noernberg, and William Shotyk. The publication entitled "Trace elements in berries collected near upgraders and open pit mines in the Athabasca Bituminous Sands Region (ABSR): distinguishing contribution from atmospheric dust deposition versus plant uptake" has been submitted to the *Science of the Total Environment* Special Issue on Forest Health and Atmospheric Deposition and is currently in press. In this publication the candidate was responsible for the sample preparation, data analysis, statistical analysis, and manuscript writing. Dr. Shotyk contributed revisions of Figures, Tables and content. Dr. Bicalho gave analytical advice and confirmed the results. Iain

Grant-Weaver assisted in the analysis of the samples, and Tommy Noernberg assisted in sample collection.

# Acknowledgments

I would like to thank the SWAMP lab team for analyzing samples and funding the Berries to Beavers project: the Alberta Conservation Association for additional funding for analyzing trace elements in berries though Grants in Biodiversity; Dr. Beatriz Bichalho and Iain Grant Weaver for helping with the analysis of samples on the ICP-MS, providing excellent QA/QC and helping with endless questions about chemistry, and Tommy Noernberg, Gillian Mullan-Boudreau and Mark Donner for collecting the berry samples. Big thanks to Karen Lund and Tracy Gartner for assisting with daily tasks and providing support throughout my Master project, everyone else in the SWAMP laboratory for providing constant support, positive feedback and helpful advice, and Rick Pelletier for producing GIS maps for all the different trace elements in berries. Finally, I would like to thank my supervisor William Shotyk for all the support throughout the project and for allowing me to pursue a Master of Science degree and providing edits for this thesis.

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# 1 Chapter 1

## 1.1 INTRODUCTION

Native lingonberries, cranberries, and blueberries are commonly consumed by Canadians and more specifically by Aboriginal community members (Parlee, Berkes, and Gwich'In 2005). Unfortunately, bitumen mining in the Athabasca Bituminous Sands Region (ABSR) is believed to have increased trace element contamination in the surrounding environment (Kelly et al. 2010), possibly affecting these traditional foods.

One possible source of trace element contamination is dust deposition produced from open-pit bitumen mining (Shotyk et al. 2016). The removal of overburden in open-pit mining to access the underlying bitumen generates a significant amount of dust (Jain et al. 2016). Dust contamination can increase trace element concentrations associated with terrestrial plants because of the mineral fraction present in the dust (Perlwitz et al. 2015).

It is crucial for human health and Aboriginal traditions to understand the full effect of dust contamination on traditional foods. In berries, essential micronutrients (Mn, Fe, Zn) are found in trace amounts (Kabata-Pendias 2011). Due the abundance of essential trace elements in berries (Rodushkin et al.1999), it is reasonable to hypothesize that dust deposition will not affect the concentrations of these essential trace elements. In other words, that dust will contribute these elements in insignificant amounts compared to the mass absorbed naturally by the plants via the roots. Elements which are not essential for plants (e.g. Cr, Pb, U), however, could be profoundly impacted by dust deposition simply because plant uptake via the roots is negligible (Rodushkin et al.1999). These trace elements should decrease in concentration with distance from industry (Kelly et al. 2010).

Lithophile elements (Al, Th, Y), which are contained in silicate minerals found in the earths crust, are common in soil and therefore in the mineral matter of dust. Continental crust (Rudnick and Gao 2014), soil (Bowen 1979) and dust (Perkins 2011) contain approximately the same ratios of lithophile elements (Perkins 2011). By comparing a conservative lithophile element to micronutrients or to potentially toxic trace elements, it is possible to determine whether dust significantly contributes these trace elements to native berries collected in northern Alberta.  Berries will not naturally absorb conservative lithophile elements (Kabata-Pendias 2011), therefore, dust deposition is probably the main contribution of trace elements to the environment around open pit mines.

## 1.2 BACKGROUND

### 1.2.1 The importance of bitumen mining in Alberta

Alberta's oil industry started growing rapidly in the 1950s.  In recent years bitumen mining in Alberta has been recognized as Canada's leading natural resource (Alberta Energy and Utilities Board 2000). The bitumen deposits, located in Alberta, contains the third largest reservoir of oil after Saudi Arabia and Venezuela (Government of Alberta 2016), and Alberta is estimated to have 27 billion $m^3$ of crude oil in reserve. The technology to extract the bitumen and recover oil is becoming more efficient, thereby increasing the proportion that is recoverable (Gosselin et al. 2010).

Bitumen mining in Alberta is fundamental to the provincial and national economy of Canada. The oil industry directly employed 140,300 people in Alberta in 2018 (Alberta Government 2018) and produced $12.7 billion in capital investment for Alberta in 2017 (Government of Canada 2018). Canada has approximately 10,000,000 km$^2$ of land, while the area of bituminous sand resources was calculated at approximately 142, 200 km$^2$ in 2017. In Alberta only 4,800 km$^2$ of the land is suitable to open pit mining (ie. shallow bitumen deposits which can be mined by excavating large amounts of overburden) and only 901 km$^2$ is currently being mined (Government of Canada 2018). The tailings ponds, representing mining by-products, are responsible for a total area of approximately 220 km$^2$ of the total mined area (Government of Canada 2018).

The range of environmental impacts caused by bitumen mining and upgrading were listed by Giesy et al. (2010), Kelly et al. (2010), and Schindler (2010, 2014). The tailings generated by bitumen extraction are quite toxic, containing polycyclic aromatic compounds and heavy metals (Ni and V) ( (Nesbitt et al. 2017; Rodríguez-Estival and Smits 2016) which could affect the environment. Aboriginal communities and scientists have expressed concerns about heavy metal contamination from open pit mining and upgraders (McLachlan 2014). During bitumen mining, particulate matter (PM) is released to the atmosphere: from overburden removal, drilling, blasting, loading, unloading, transportation, wind erosion, and vehicle exhaust (Jain et al. 2016).

In Alberta there are two possible ways to extract bitumen: open pit mining and *in-situ* mining. Open pit mining is the surface extraction of bitumen from large open pits. The raw bitumen is first removed from the earth. At this point the bitumen ore is crushed and mixed with hot water to separate the mineral and organic fractions (Gosselin et al. 2010). The collected bitumen is further treated at a froth-cleaning plant before the bitumen fraction is sent to upgraders (Gosselin et al. 2010). The upgraders remove any further impurities such as N, S Ni, and V creating synthetic crude oil which can then be sent through pipelines to refineries (Gosselin et al. 2010). *In-situ* extraction is used when bitumen is below 60 m and surface mining is not economically feasible. There are multiple ways of extracting bitumen through *in-situ* mining. Some of the common methods used in Alberta include SAGD (steam assisted gravity drainage), conventional, and CSS (cyclic steam stimulation) (Ramp-Alberta 2018). Typically, heat and pressure are applied down a well to decrease the viscosity of the bitumen, allowing it to flow to the surface effortlessly. *In-situ* mining decreases disturbance to the land, but is not efficient in recovering bitumen (Gosselin et al. 2010). Twenty percent of bitumen in northern Alberta is economically recoverable by surface mining, while the remaining 80% requires *in-situ* recovery. Although 90% of bitumen today is recovered by open-pit mining, *in-situ* mining recovers only 50% of total bitumen (Gosselin et al. 2010).

### 1.2.2 Geological sources of trace elements

Most trace elements are naturally present in soil systems due to weathering of exposed bedrock. Trace elements such as Mn, Cr, Co, Ni, Cu, and Zn are weathered from igneous rocks, which account for 95% of the earth's crust (Ross 1994), and generally contain higher quantities of metals than are found in sedimentary rocks. Some trace elements occur as sulfide minerals. The weathering of these sulfide minerals could potentially allow toxic elements, such as Pb and Hg, into the environment. Minerals such as galena (PbS), cinnabar (HgS), chalcopyrite, ($CuFeS_2$), sphalerite (ZnS) and pentlandite ($(NiFe)_9S_8$) contain toxic trace elements and if they weather can contribute trace elements to the environment (Ross 1994).

However, toxic elements that are bound up in minerals tend to be insoluble and stable, and therefore unavailable to plants (Adriano 2001).

### 1.2.3 Dust particles produced by bitumen mining

There are two major classes of contaminants which may be found in Alberta berries growing close to open pit mines and upgraders: organic and inorganic contaminants. This thesis will focus on inorganic contamination in berries located near open pit mines and upgraders in Alberta.

A point source is a known location where a contaminant is released into the environment (Kloke et al. 1984). A few point sources associated with bitumen mining include upgraders, open-pit mines and mining products (tailings and petroleum coke). The extent of contamination from these point sources on the surrounding environment is still being studied (Donner et al. 2017). These dust particles contain naturally occurring trace elements including those considered to be toxic at low concentrations (As, Cd, Hg, Pd) (Kloke et al. 1984). Since trace elements are found in mineral matter such as dust, an increase in dust will also increase concentrations of trace elements (Perkins 2011).

Another point source associated with bitumen mining is the upgrading process. Once the bitumen is extracted and separated, it is sent to the upgraders which turn it into synthetic crude oil (Government of Canada 2018). After the upgrading process, the bitumen which is now considered synthetic crude oil, can be sent to the refineries (Government of Canada 2018). The large stacks which release $CO_2$ (Shahandeh and Li 2017) may also release a fraction of S, N, Ni, and V which was removed during the process. Therefore, it is believed that upgraders may therefore contribute trace elements to the surrounding environment (Kelly et al. 2010).

### 1.2.4 Trace elements present in dust particles

Dust is typically composed of both organic matter and mineral matter. The mineral matter which is derived from the earth's crust is composed of major, minor, and trace elements. Each mineral has a specific solubility, which will cause the elements bound in chemical form to be released into solution (Kabata-Pendias 2011). Changes in pH, temperature or redox potential could increase or decrease the solubility of these minerals and, therefore, affect the concentrations of trace elements in solution (Kabata-Pendias 2011). The release of trace elements (e.g. Mo, Mn, Zn) could be beneficial if, for example, they are essential to plants. Conversely they could have negative effects at low concentrations (e.g. As, Pb, Cd) (Stiles 2013). Each element becomes toxic to organisms at different concentrations (Ross 1994). Both acute and chronic symptoms can occur in organisms if the dose is high enough. Acute toxicity is defined as a large dose of poison for a short duration and is usually lethal. Chronic toxicity is a low dose of poison over an extended period, which can be lethal or sublethal (Ross 1994). Both chronic and acute toxicity is concerning for all organisms.

### 1.2.5 Atmospheric transportation of dust particles

Dust that is generated by bitumen mining in the Athabasca region shows limited atmospheric transport: increasing distance from the source results in a decrease in deposition of trace elements and PAHs. For example, Bari et al. (2014) found that atmospheric deposition of both metals and PAHs decrease rapidly beyond 45 Km from the source.

The following figures illustrates how dust on plants varies with proximity to a duct source. The plant on the left side has no visible dust particles. The plant on the right is covered with dust (Figure1-1). When the plants are dried, milled, digested and analyzed for trace elements, the dusty plant (right) will have a significantly higher concentrations of trace elements.

Figure 1-1: Dust-free (left) and dust-containing (right) berries (Shotyk 2018)

### 1.2.6 Natural abundance of trace elements in the earth's crust and mineral dust

The earth's crust and the soils which are derived from it, are mainly composed of major elements (i.e. O, Si, Al, Fe, Ca, Na, K, and Mg): these make up over 95% of the earth's crust (Figure 1-2). Trace elements are found at much lower concentrations: either parts per million as seen in Figure 1-3 or in parts per billion as seen in Figure 1-4 (Rudnick and Gao 2014). The trace elements that are found in the earth's crust are also found in the mineral fraction of soil due to weathering of the crust. Therefore, mineral dust particles that are derived from the soil also contain similar trace element concentrations.

Using the baseline trace element concentrations found in the earth's crust, it is possible to infer the source of trace elements that are associated with the berries. Trace elements can be associated with the berry either by absorption through plant roots or by mineral dust deposition on the surface of the leaves and berry.

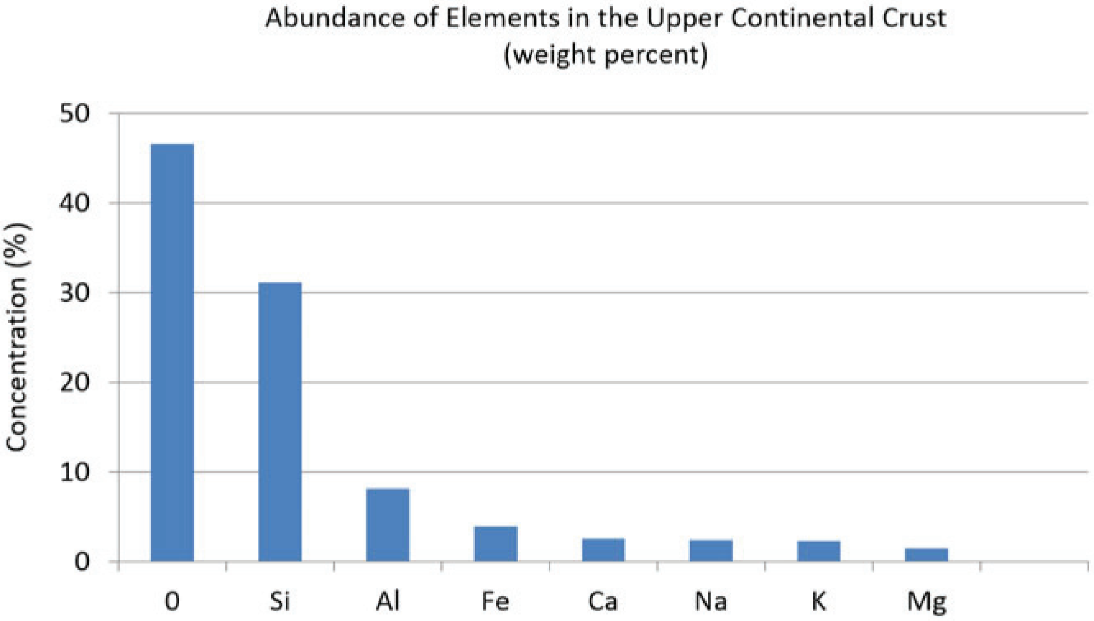

Figure 1-2:The most abundant elements in the earth's crust (Shotyk 2018)

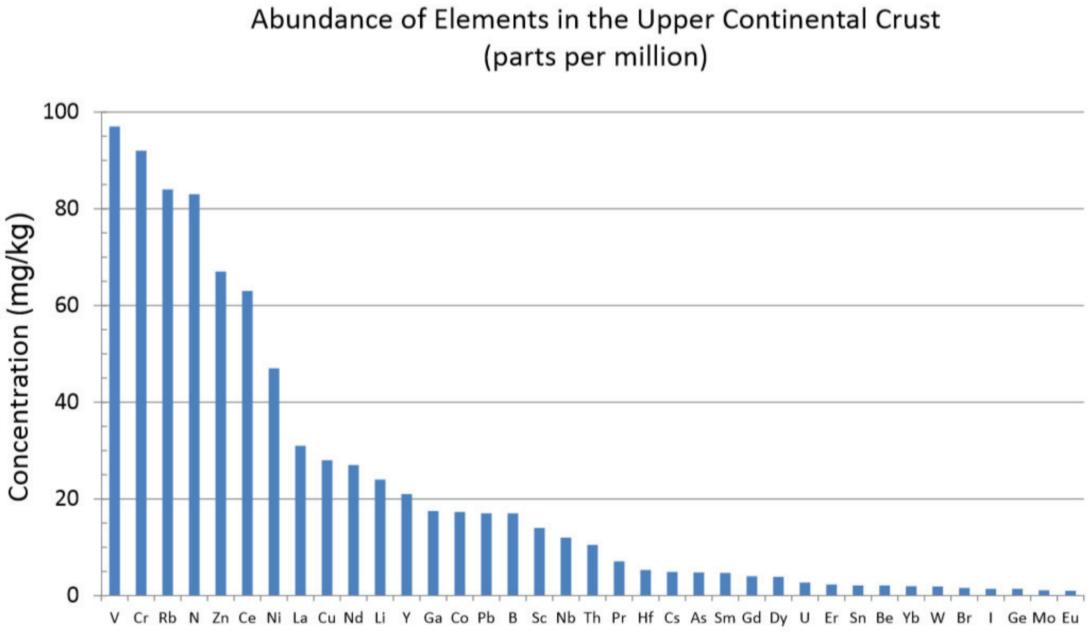

Figure 1-3: Trace elements that are abundant in the earth's crust at the parts per million level (Shotyk 2018)

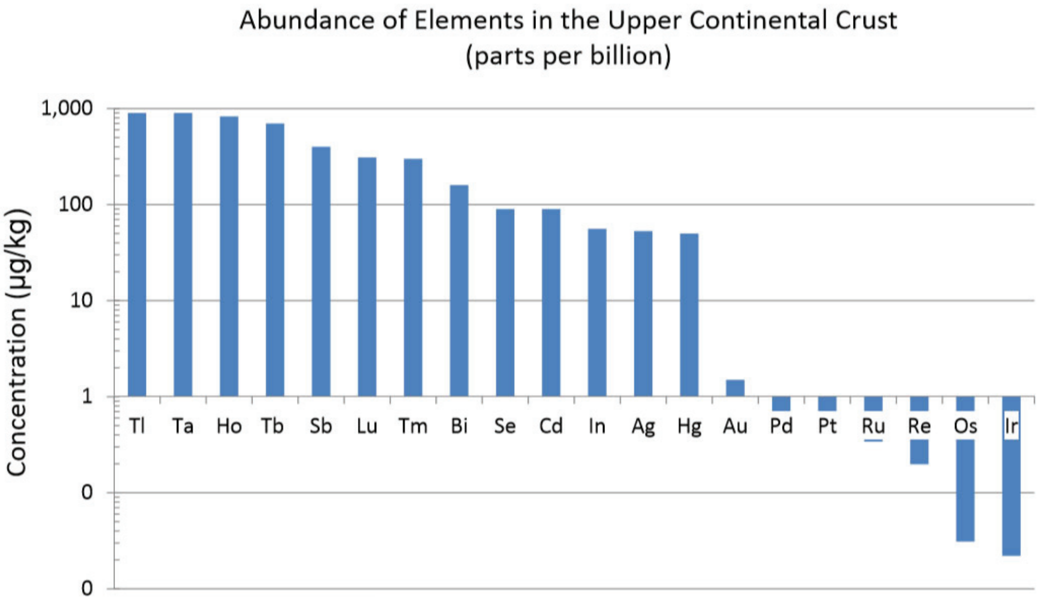

Figure 1-4: Trace elements that are abundant in the earth's crust at the parts per billion level (Shotyk 2018)

Using Rahn's approach (1976), it is possible to determine if the trace elements associated with a berry are derived mainly from mineral dust or through absorption via roots. The enrichment factor (EF) in a berry sample is calculated using the following equation:

$$\text{Enrichment Factor} = (Pb/Y)_{\text{Berry}} / (Pb/Y)_{\text{Earths Crust}}$$

Here, the element lead (Pb) is used as an example, but the same approach can be used for any other trace element. Assuming that Y is not absorbed via the roots by the plant and that 100% of the Y is obtained from dust deposition, then it is possible to also determine if other elements are obtained by absorption or by dust deposition on the berry surface. In the above example, if the Pb/Y ratio in the berry is equal to the Pb/Y ratio in the earth's crust then the Pb in the berry can be explained by dust deposition alone. However, if the Pb/Y ratio in the berry is significantly larger than the Pb/Y ratio in the earth's crust (i.e. greater than a factor of two) then the berry must have an additional source of Pb other than purely dust inputs. This enrichment is most likely due to the plant absorbing the Pb through the soil solution via root uptake. A Pb enrichment might also be due to anthropogenic inputs, which may be quantified by comparing trace elements concentrations in berries collected around the ABSR to berries which were collected from a remote area.

To determine which of these processes dominates, Pb concentrations in the berries are plotted against Y concentrations. If the slope of the regression line for the berries is similar to the ratio found in the earth's crust then Pb is from mineral dust deposition. If there is no correlation, then Pb is enriched in the berries, relative to the earth's crust, due to plant uptake. If there is a strong, positive linear correlation between Pb and Y, but if the slope exceeds that of the earth's crust then the dust on the berry is enriched in Pb.

Yttrium is used as a reference element for the following reasons;

- it behaves conservatively during chemical weathering (Shotyk et al. 2001),
- it is not significantly absorbed by plants from the soil (Pospiech et al. 2019), and
- it can be accurately measured in berries using quadrupole ICP-MS (Shotyk et al. 2019).

### 1.2.7 Trace element accumulation and interactions with plants

Trace elements in living organisms are generally defined as elements that do not exceed concentrations of 0.01% dry weight of material (Bertoldi et al. 2011). The term "trace elements" however is not consistently used in the literature. In some cases, trace elements only refer to elements that are not beneficial to organisms (Bertoldi et al. 2011). However, the present Thesis will define a trace element as one which has a concentration lower than 0.01% dry weight of the berry. Manganese will also be classified as a trace element even though many berries contain over 0.01% of Mn dry weight (Rodushkin et al. 1999). This definition, however, differs depending on the context. For example, the trace element concentrations found in the earth's crust (e.g. Al and Fe) have concentrations over 1% (Rudnick and Gao 2014).

The most common route of metal uptake into plants is through the root/ mycorrhizae system. Trace elements can either be beneficial to plants (where they are used for biological plant functions), or they can have no beneficial effects and are typically stored in organs (roots). Some trace elements which do not benefit the plant are quite toxic at low concentrations (e.g. As, Hg). Other trace elements which do not benefit plants but are also not toxic at low concentrations may not be toxic (e.g. Sr, Rb). All elements can be toxic to plants depending on the concentrations present in the soil. Plants can be either hyper- or non-accumulating plants (Mustafa and Komatsu 2016). Hyper-accumulating plants can store high levels of metals in their tissues and yet experience little to no stress on their ability to grow (Jamal et al. 2002). These plants can be used in phytoremediation (Jamal et al. 2002). However, most plants are sensitive to an abundance of heavy metals in the soil. Heavy metals will bind onto chelating sites and chaperones inside the cell, which can block other important ions. This will harm the plant because the essential micronutrients cannot be transferred to the designated location (Mustafa and Komatsu 2016). When heavy metals bind to proteins, this can cause inactivation of enzymes and generate reactive oxygen species, which in turn can cause the proteins, lipids and nucleic acid to be damaged (Mustafa and Komatsu 2016). The soil solution is extremely complex containing all naturally-occurring trace elements (Mustafa and Komatsu 2016). Plants mitigate the effects of high concentrations of toxic trace elements by creating metal-binding constituents such as amino acids which bind to the toxic trace elements and reduce their harmful effects (Mustafa and Komatsu 2016). Plants will also isolate a toxic element by removing it from a general location in the cell and accumulate it in a certain part of the cell such as the vacuole. Excreting metals from the roots is also a mechanism used by plants to detoxify trace elements. Root exudates, which are produced by the roots and mycorrhizae, can chelate trace elements to decrease or increase their absorption into the plant (Ross 1994).

Foliar transfer is the process which transfers particulate trace elements which land on the surface of the plant to the internal organs. Essential elements such as Fe, Cu, Mn and Zn and non-essential elements such as As, Cd, Cr and Pb can enter the plant through foliar transfer (Shahid et al. 2017). Two main steps in foliar transfer are adsorption and internalization via the cuticle and penetration of metals via stomatal pores (Shahid et al. 2017). Interactions between the plant and the trace elements vary with the size of the particle and the composition of the plant. Smaller particles can penetrate the leaves while larger dust particles get trapped in the epicuticular wax and are then absorbed into the leaves. The hydrophobic waxy layer contains multiple functional groups which interact with the trace elements (Shahid et al. 2017). Therefore, in highly contaminated areas, it is possible to have higher concentrations of trace elements in the organs of plants due to adsorption through the soil or foliar transfer.

For the purpose of this thesis, 18 trace elements have been divided into 5 groups to best classify each element. The first group is the conservative lithophile elements (Al, Cr, Co, Ga, U, Y) which are trace elements that are not essential for plant growth. The second group is the micronutrients (Cu, Fe, Mn, Zn), which are trace elements essential for plant growth. The third group includes soluble (mobile) lithophile elements (Li, Rb, Sr). These elements are common in the earth's crust, but their solubility and mobility make them more abundant in water and therefore more available to plants. The fourth group is made up of the potentially toxic, elements (Cd, Pb). The last group consists of elements enriched in bitumen (Mo, Ni, V). These trace elements are therefore the most likely to be emitted to the surrounding environment from industrial activities. It is important to understand how each class of these trace elements interacts with plants to help determine their predominant source (dust deposition or root uptake).

#### 1.2.7.1 Conservative lithophile elements (Al, Cr, Co, Ga, U, and Y)

Conservative lithophile elements tend to be insoluble and non-mobile, which makes them unavailable for plants to absorb (Kabata-Pendias 2011). Lithophile elements have an affinity for oxygen- rich minerals and are enriched in the earth's crust, relative to the bulk composition of the earth. The classification of lithophile elements comes from Goldschmidt's geochemical classification of elements. The report created by Dr. Shotyk (2018) provided a summary of the trace elements that are lithophile (green), siderophile (blue), chalcophile (tan), and atmophile (yellow) (Figure1-5).

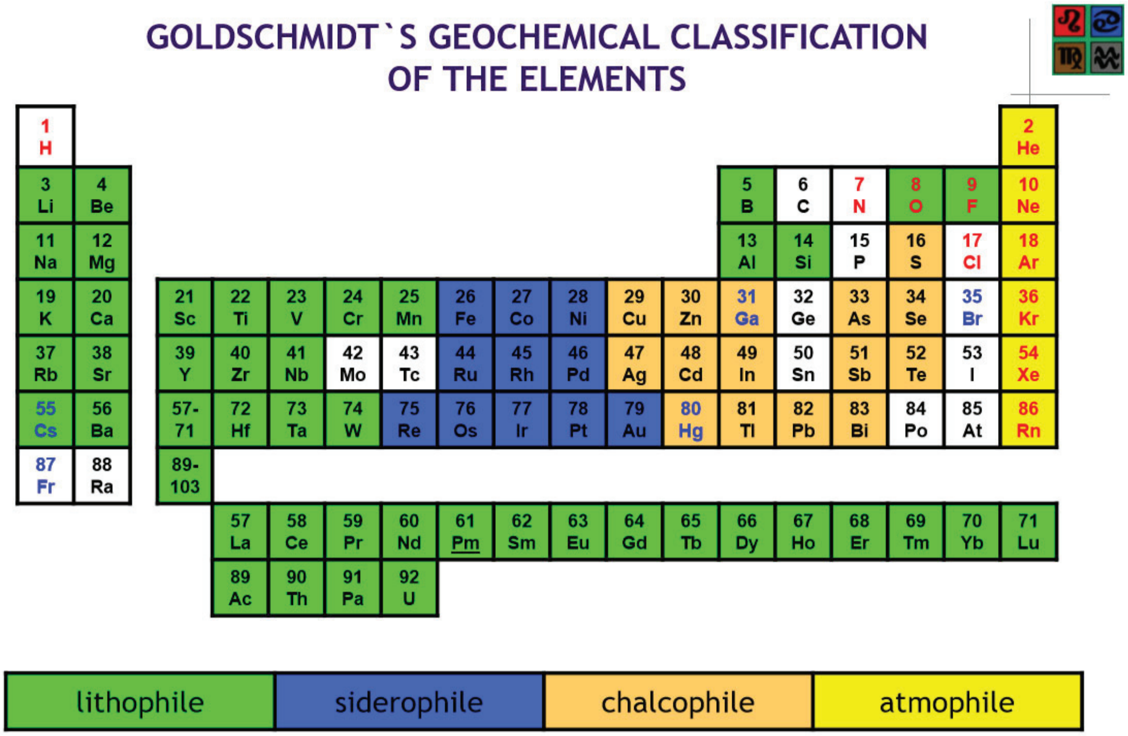

Figure 1-5: Goldschmidt's geochemical classification of the elements (Shotyk 2018)

Aluminum (Al)

Aluminum can be toxic at low concentrations to plants when it is in the form $Al^{3+}$ (Mustafa and Komatsu 2016). Aluminum may migrate into a plant and bind to phosphate, sulfate, and carbonyl functional groups, which cause growth defects in the plant. Plants have formed two distinct ways of limiting $Al^{3+}$ a) by limiting the amount migrating through the mycorrhizae and roots and b) detoxifying cellular Al through the formation of harmless complexes with organic ligands (Mustafa and Komatsu 2016).

### Chromium (Cr)

Chromium is not essential to plants but is essential for human and animal nutrition. Chromium toxicity in plants can create the following physical deformations: wilting, root abnormities, chlorosis in young leaves, and discolored leaves (brown/red) (Kabata-Pendias 2011).

### Cobalt (Co)

The role that cobalt plays in plant nutrition is controversial, as some studies suggest it is necessary for plant function (Kloke et al. 1984), while others disagree. It is well known that it plays a significant role in $N_2$ fixation for blue-green algae (Kabata-Pendias 2011). A lack of Co in the soil tends to stunt plant growth, while high concentrations are toxic (Kabata-Pendias 2011).

Cobalt bound to organic matter or Fe/ Mn oxides has a higher bioavailability (Kabata-Pendias 2011). There is a strong correlation between the soluble Co in soil solution and Co concentrations found in plants (Kabata-Pendias 2011).

### Gallium (Ga)

Gallium is not essential for plant growth (Kabata-Pendias 2011).

### Uranium (U)

Uranium is not essential for plant growth and can become toxic at low concentrations (Kabata-Pendias 2011).

### Yttrium (Y)

Yttrium has no function in plants, but concentrations have been reported to be as high as 700 mg/kg (fresh weight) in cabbage (Emsley 2001).

#### 1.2.7.2 Micronutrients (Cu, Fe, Mn, and Zn)

Micronutrients are essential for the healthy growth of plants (Kabata-Pendias 2011). When micronutrients in soil are deficient, plants are likely to express stress in their growth (Emsley 2001). These micronutrients are also common in the earth's crust and are typically dissolved in soil solution. Plants tend to seek out these key nutrients with their roots. The following is a list of micronutrients that are important for this Thesis, with a brief description of their behaviour. In Figure 1-6, dark green indicates the major elements that are necessary for plant growth and function. The light green represents the micronutrients that are essential for plant growth. Elements in yellow are considered beneficial. However, all elements, even those that are essential to plants, may become toxic when concentrations are elevated.

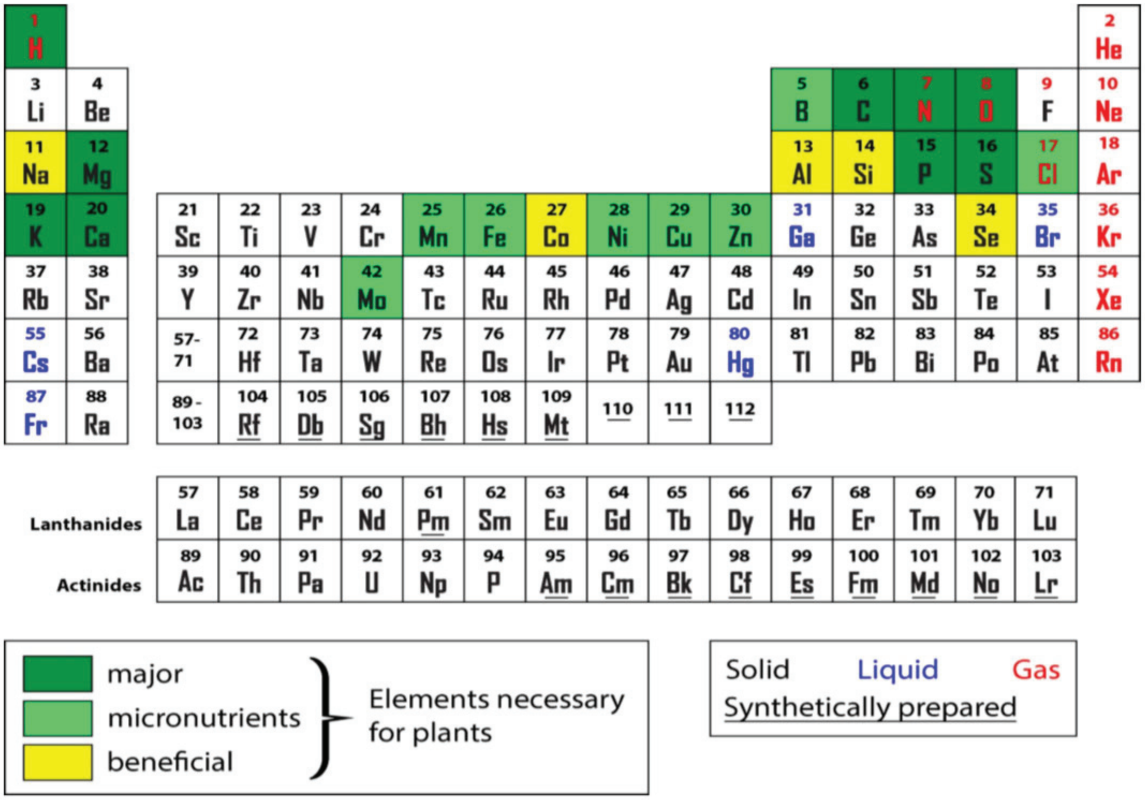

Figure 1-6: Elements that are essential for plants (Shotyk 2018)

Copper (Cu)

Copper is required for physiological processes in plants such as photosynthesis, respiration, $N_2$ reduction and fixation, protein metabolism, the production of DNA/RNA, and cell wall metabolism (Kabata-Pendias 2011). The phyto-availability and toxicity of Cu depends primarily on the pH, redox potential, soil organic matter content, soil texture, mineral composition, and temperature of the soil (Kabata-Pendias 2011). Copper may become toxic at higher concentrations because it can compete with another essential element, Zn. Excess Cu may damage tissue cells/DNA, create abnormal root growth, and inhibit photosynthetic processes (Kabata-Pendias 2011). An increase in Cu can alter mineral nutrition, enzyme activity, photosynthesis, and leaf chlorophyll content, which can result in a decrease in plant growth (Mustafa and Komatsu 2016).

### Iron (Fe)

When iron enters a plant, it may be involved in any number of biochemical processes within cells. Iron may be needed as a component of cytochromes, which are used in electron transport and are important for oxidative stress and enzyme activation, and have a role in chlorophyll synthesis (Soetan et al. 2010).  A deficiency in Fe may result in plant stress, causing chlorosis (Soetan et al. 2010)).

### Manganese (Mn)

Manganese plays a role in a few major functions in plants, including amino acid formation, the activation of enzymes, hydrolysis reactions in photosynthesis, and chlorophyll synthesis (Soetan et al. 2010). A deficiency in Mn can lead to the leaves of the plant becoming discoloured and then dying (Soetan et al. 2010).

### Zinc (Zn)

Zinc is involved in the production of energy and protein synthesis (Kloke et al. 1984), the formation of chlorophyll, enzyme activation, and the formation of auxins, chloroplasts, and starch (Soetan et al. 2010). If the concentration of Zn is too high, it may replace other similar essential metals, resulting in growth defects, such as shorter and thicker roots (Mustafa and Komatsu 2016). A defiency in Zn will result in abnormal roots and bronzed leaves (Soetan et al. 2010).

#### 1.2.7.3 Other lithophile elements (Li, Rb, and Sr)

These “other” lithophile elements are more soluble in the soil solution rendering them available to plants.

Lithium (Li)

Lithium has been reported to have positive effects on plant growth (Bertoldi et al. 2011) but has not been classified as essential.

Rubidium (Rb)

Rubidium is not an essential element to plants, however, neither is it very toxic. Rubidium will likely substitute for K in plant function, and stress to the plant will be minimal (Soetan, Olaiya, and Oyewole 2010).

Strontium (Sr)

No reliable evidence supports an essential role for Sr in plants. Researchers have found a close relationship between Sr and Ca uptake in plants. Strontium can compete with Ca, and both can be absorbed into a plant, but Sr cannot replace Ca in biological functions; therefore, it enters the plant but does not cause toxicity (Kabata-Pendias 2011).

#### 1.2.7.4 Potentially toxic elements (Cd and Pb)

Some elements, such as Cd and Pb, do not benefit plants at any concentrations. Figure 1-7 shows the toxicity of essential elements versus non-essential elements.

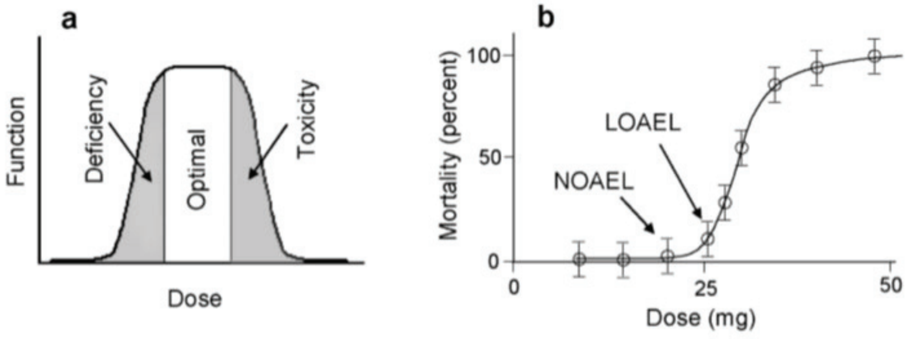

Fig 1. Schematic dose-response curves for (a) and essential metal and (b) a non-essential toxic metal. NOAEL and LOAEL are *no observed adverse effect level and lowest observed adverse effect level* (see Table 1).

Reeder et al. (2006). Reviews in Mineralogy & Geochemistry

Figure 1-7: Illustration of essential and non-essential trace element toxicity

Cadmium (Cd)

Plants can rapidly uptake $Cd^{2+}$ through their roots and transfer it throughout their cells and organs. The uptake of Cd can lead to oxidative stress because of its strong affinity with protein sulfhydryl groups. Cadmium behaves similarly to Zn, Fe, and Ca and thus can replace these necessary elements (Ca, Fe, Mn, P) in protein, rendering them inactive (Kabata-Pendias 2011). Cadmium and zinc affect photosynthesis and reduce the amount of energy a plant receives overall, decreasing the growth and health of the plant (Mustafa and Komatsu 2016).

Lead (Pb)

The presence of toxic levels of Pb in a plant can cause a decrease in water potential, and electron transport, and it can affect hormonal imbalance, and the cell membrane structure and can increase/decrease enzyme activity (Sharma and Dubey 2005). Lead uptake by the roots depends on the availability of $Pb^{2+}$ in the soil solution which, in turn depends on soil pH, particle size, CEC, the surface area of roots, mycorrhizal transpiration, and the availability of Pb. Visual toxicity of Pb can include stunted growth, chlorosis, and blackening of the root system (Sharma and Dubey 2005).

#### 1.2.7.5 Elements enriched in bitumen (Mo, Ni, and V)

Four metals are known to be enriched in bitumen: molybdenum (Mo), nickel (Ni), vanadium (V), and rhenium (Re). For this thesis, I focus on three: Mo, Ni, and V. Rhenium is extremely difficult to analyze accurately in berries and it is likely to be found in such low concentrations that it would not be relevant. The following list depicts the important trace elements that are enriched in bitumen and their interactions with plants.

Molybdenum (Mo)

Molybdenum is essential for plants. Plants absorb Mo through the soil solution and as the pH of the soil solution decreases Mo becomes more soluble/ available for plants (Kabata-Pendias 2011). Molybdenum is essential for many components of enzyme function. Molybdenum primarily acts as a carrier in redox reactions; Mo (VI) acts as an electron acceptor (Kabata-Pendias 2011). However an increase in Mo in soil solutions can be problematic to plants, affecting RNA and DNA production and in turn causing growth defects (Kabata-Pendias 2011) .

### Nickel (Ni)

Older research suggests that Ni is essential for microbes, which in turn directly benefit plant growth (Kabata-Pendias 2011). A review article on nickel in the environment suggest it directly benefits for plant growth, and is therefore essential for plant growth (Shahzad et al. 2018). However, it is also known that Ni can become quite toxic if the concentration increases (Shahzad et al. 2018). Nickel is bioavailable when it is in the free ion form ($Ni^{2+}$) and may be absorbed through plant roots. The uptake of Ni into the plant is strongly correlated to the concentration of soluble Ni in the soil solution (Kabata-Pendias 2011) and therefore can become toxic to the plant if there is excessive Ni enrichment in the soil.

### Vanadium (V)

The role of vanadium in plants is still undetermined. In some cases, it has been suggested that V is essential for plants in small quantities (Bertoldi et al. 2011). This is because V is essential for microbes that influence the growth of plants (Imtiaz et al. 2015). Increased concentrations of V in the soil, however, can cause toxicity to plants resulting in alterations in metabolism, such as water retention, element uptake, reductions in enzymatic activity, and interference with membrane integrity, photosynthesis, and biological yield (Imtiaz et al. 2015).

### 1.2.8 Previous research on trace elements in berries around open-pit bitumen mines and upgraders in Alberta

Previous research on berries in the Athabasca region has been limited. A report by Hopkins and colleagues determined trace element concentrations in berries in the region north of Fort McMurray in Alberta. The report presented concentrations of both inorganic and organic contaminants (Hopkins et al. 2014). However, the study had a few deficiencies that weaken its effectiveness, such as the lack of peer review, inappropriate analytical methods, and the lack of a discussion (Hopkins et al. 2014): the data was simply presented in Tables with no conclusions drawn. The method used for determining trace elements was ICP-OES (Hopkins et al. 2014), which is appropriate for naturally abundant elements, such as K, Zn, P, Mn, Mg, Fe, Na, and Al, but is less accurate for trace elements such as Sn, U, Tl, Mo, Pb, Li, Sb, Ba, Cr, and Co. An ICP-MS can more accurately detect less abundant trace elements and produce more accurate values (Khan et al. 2013). The work by Hopkins et al. (2014), however, is important as a starting point and helped raise awareness regarding contaminants in country foods in the ABSR.

### 1.2.9 Berry picking traditions of Aboriginal peoples in Canada

Aboriginal women consider berries to be both nutritious and an important part of their traditions and culture. Aboriginal women believe that berries are placed on the land by the "Creator" so that they will never go hungry. Berry gathering within Aboriginal groups was not a tradition that was passed on for mere recreational use. In the past, it was important to collect enough berries during the summer and fall to last through the winter (Parlee et al. 2005). The berries were stored in jars or deep under-ground to preserve them during the winter. In 2003, it was estimated that approximately 10% of a given Aboriginal community picked berries (cloudberries, blueberries, cranberries), and the estimated number of berries picked annually was 5000 liters in Fort McPherson, Northwest Territories. In years where berries were scant, due to poor growing conditions, the native people valued the berries they found, more so than in standard growing years when berries were plentiful (Parlee et al. 2005). In Fort McPherson, Northwest Territories, berries are essential to keep over the winter provideing a food source enriched with vitamins and minerals, which are difficult to obtain during the winter months. It was also essential to ensure that every family had enough berries throughout the winter. If berries remained in the home until the end of the winter, it was considered impolite, because they could have been shared with families who had run out. There is a strong sense of support within the community (Parlee et al. 2005). In recent years there has been an increasing concern about environmental change and its effects on berry, human health and Aboriginal traditions.

## 1.3 OBJECTIVES

The primary objective of this study was to determine to what extent berries in northern Alberta are contaminated with trace elements from open-pit bitumen mining and upgrading. To achieve this objective, it is important to determine the natural abundance of trace elements in berries. The specific objectives in this Thesis are:

1. To quantify the extent of trace element contamination in berries collected in the vicinity of open pit bitumen mines and upgraders.

2. To distinguish between atmospheric dust contributions to trace element inventories from plant uptake via roots.

3. To determine how much of the trace element inventory contributed by dusts can be removed simply by washing the berries in water.

# 2 CHAPTER 2 -TRACE ELEMENTS IN BERRIES COLLECTED NEAR UPGRADERS AND OPEN PIT MINES IN THE ATHABASCA BITUMINOUS SANDS REGION (ABSR): DISTINGUISHING ATMOSPHERIC DUST DEPOSITION FROM PLANT UPTAKE

## 2.1 ABSTRACT

There are ongoing concerns regarding environmental emissions of trace elements (TEs) from bitumen mining and upgrading in the Athabasca Bituminous Sands Region (ABSR). Depending on their physical and chemical forms, elevated concentrations of potentially toxic TEs in berries could pose a health risk to local indigenous communities because native fruits are an important part of their traditional diet. The objective of this study was to distinguish between aerial deposition of TEs versus plant uptake, in cranberries, lingonberries, and blueberries growing in the ABSR. The concentrations of TEs were determined using ICP-MS in the metal-free, ultraclean SWAMP lab at the University of Alberta. The spatial variation in abundance of conservative, lithophile elements such as Y in berries resembles the published map of dust deposition rates obtained using *Sphagnum* moss. The presence of dust particles on the surface of the berries near open pit mines and upgraders was confirmed using SEM. Elements which show strong, positive correlation with Y include Al, Cr, Pb, U, and V; these are supplied mainly by dust. Elements which are largely independent of Y concentrations include Ba, Cd, Cu, Mn, Mo, Ni, Rb, Sr, and Zn; these are obtained primarily by plant uptake from soil. The concentrations of elements associated with dust were considerably reduced after washing with water, but the elements independent of dust inputs were unaffected.

Elements which are supplied almost exclusively by dust (e.g. Y) are more abundant in berries from the ABS region (2 to 24 times), compared to berries from remote locations.

#### 2.1.1.1 Key words

Bituminous sands; native berries; mineral dust; atmospheric aerosols; trace elements; micronutrients

#### 2.1.1.2 Bullet points

- native berries were collected from peat bogs near open pit bitumen and upgraders

- Al, Cr, Pb, U, V and Y occur on the surface of the berries as dust particles

- Ba, Cd, Cu, Mn, Mo, Ni, Rb, Sr, and Zn occur in the berries due to plant uptake

- elements which are associated with dust particles can be removed by washing

- elements taken up by plants via roots are not removed by washing

## 2.2 INTRODUCTION

Bitumen mining, upgrading and refining in Alberta benefits the Canadian economy, employing more than 130,000 people and generating more than \$5 billion CAD in revenue for Alberta in 2013 (Government of Alberta 2016). With an estimated 27 billion $m^3$ of crude oil still in reserve (Gosselin et al. 2010), it is crucial to study the impacts of this growing industry on the environment. Concern has been expressed regarding contamination by trace elements (TEs) of air and water (Kelly et al. 2010) as well as biota (Rodríguez-Estival & Smits 2016; Pilote et al., 2018). Studies of atmospheric metal deposition using *Sphagnum* moss from peat bogs, however, have found that moss samples from the Athabasca bituminous sands region (ABSR) yield concentrations of many TEs (e.g. Ag, As, Bi, Cd, Cu, Mo, Ni, Pb, Sb, Tl, and Zn) that are at or below the levels found in mosses collected from other regions of Canada and Europe (Shotyk et al., 2014, 2016). Moreover, the predominant source of TEs appears to be dust deposition (Shotyk et al. 2016).

Dust is composed of both organic and inorganic material and, in the ABS region, is derived from both natural sources such as soil and sediment as well as anthropogenic sources including open pit mines, quarries, gravel roads, and dry tailings (Wang et al. 2015; Watson etal.et. 2014). All naturally-occurring TEs, including the potentially toxic "heavy metals" (such as Cd and Pb), are found in atmospheric mineral dusts derived from weathering of crustal rocks and wind erosion of soils. The mineral fraction of these dusts include silicates such as quartz, feldspars and micas, carbonates such as calcite, sulphates such as gypsum, phosphates such as apatite, and iron-oxides such as hematite (Green et al. 1990). Dust particles such as these are dominated by major elements such as Si, Al, Fe, Ca, Mg, Na, and K, but also contain all of the TEs, albeit at much lower concentrations (Perkins 2011).

Trace elements in the form of dust particles can affect human health (Brimblecombe, 1995), either via inhalation or ingestion. Once inhaled or ingested, elements may become liberated from their mineral hosts, depending on the physical and chemical form of the particles, their chemical reactivity in biological fluids, and the behaviour of the elements in solution (Nordberg et al. 2014). Some of the elements found in the mineral components of dusts are essential for plants (e.g. Mg, P, K, and Ca, as well as the TEs Mn, Fe, Cu, Ni, Zn and Mo), whereas others are not essential (Ag, As, Cd, Pb, Sb, Tl) and potentially toxic (Kabata-Pendias 2011). The bioaccessibility of TEs in soil-derived dusts will depend on particle size, and their mineralogical and chemical composition. Elements found in the more refractory silicate minerals should be inaccessible to living organisms, even when ingested, because of the chemical stability of these phases and their resistance to dissolution (Shotyk et al., 2001). In contrast, elements hosted in comparatively unstable carbonates, sulphates and phosphates (e.g. Ca, Mg, Sr, P, S) tend to form ionic species which can easily cross cell membranes. Trace elements such as Cd and Pb, when present in ionic form, are also potentially toxic.

One way to determine whether or not an element is in mineral form on a plant leaf surface is to compare its abundance to that of a conservative lithophile element (Shotyk et al. 2016). Conservative lithophile elements such as Al, Sc, Th, Ti and Y, are found in chemically stable silicate minerals (Shotyk et al., 2001), and the concentrations of these elements reflect the abundance of dust particles on the plant surface (Ram et al. 2014). Moreover, because conservative, lithophile elements have very low solubilities in water and are not required by plants, uptake from the soil via root systems is negligible (Kabata-Pendias 2011).

Here we examine TEs in cranberries, blueberries, and lingonberries which are common, native berries in Alberta and important components of the traditional diet for many First Nations communities (Kuhnlein and Turner, 1991). Previous work on berries in the ABS region is limited to the report by Hopkins et al. (2014). These authors reported an average of approximately 1.5 mg/kg Tl in blueberries (Hopkins et al. 2014) which exceeds the crustal abundance of the element (Rudnick and Gao, 2014). The report by Hopkins et al. (2014), however, employed ICP-OES which has inadequate sensitivity for most TEs (Khan et al. 2013). Thus, there is uncertainty regarding the validity of some of the data reported to date for berries in this region.

The main objective of this study is to better understand the impact of open-pit mining and upgrading on concentrations of TEs in berries collected in the ABSR. Specifically, we wish to distinguish between TEs on the surface of the berries and found mainly in the form of dust particles, versus elements contained within the berries and having been derived from uptake via roots. Also, we wish to determine the extent to which TEs may be removed after the berries are washed in water. Cranberries and lingonberries from remote bogs in northern Alberta (Shotyk et al., 2019) are used for comparison.

## 2.3 MATERIALS AND METHODS

### 2.3.1 Sample collection

Cranberries (*Vaccinium oxycoccus*), Lingonberries (*Vaccinium vitis-idaea*), and Blueberries (*Vaccinium myrtilloides*) were collected by hand from ombrotrophic *Sphagnum* bogs in the vicinity of open pit bitumen mines and upgraders (Figure 1). Berry collection took place during the autumn of 2015, as part of the *Sphagnum* moss sample collection campaign described in detail elsewhere (Mullan-Boudreau et al., 2017). Access to remote sites was provided by helicopter. The focus of the campaign was the collection of moss, but the presence of berries presented an additional scientific opportunity. The availability of berries at each bog was variable. The berries were removed from the plants by hand while wearing polyethylene (PE) gloves and a hair net, and placed in a PE bag. The berries were brought back to the University of Alberta and were placed in a freezer (-20 ºC) until analysis.

### 2.3.2 Washing

If sufficient material was available, a portion of the sample was washed before drying and milling. Berries were rinsed four times in 18.2 MΩ•cm water, soaking for three minutes the first three times, and five minutes on the final rinse before the samples were drained and placed in a drying oven.

### 2.3.3 Drying and milling

Samples were placed in an oven at 105 ºC until constant weight (48-72 h). The dried berries were then ground by hand using an agate mortar and pestle. The berry samples were then removed from the mortar using a disposable PP spatula, and placed in polypropylene (PP) jars. The mortar and pestle were cleaned with methanol and wiped with Kimwipes between each sample.

### 2.3.4 Sample digestion and analysis

#### 2.3.4.1 Reagents and materials

After drying and milling, all further handling of the samples was done in the metal-free, ultraclean SWAMP laboratory at the University of Alberta (Shotyk et al. 2017). All sample handling was performed within metal-free, Class 100, clean air cabinets. High-purity water (18.2 MΩ•cm, Element, Millipore) or double-distilled nitric acid was used for sample dilution.

### 2.3.4.2 Microwave Digestion

Berry samples were digested, along with selected certified, standard reference materials (NIST 1547 Peach Leaves, NIST 1515 Apple Leaves, and IEEA 336-Lichen), plus appropriate blanks. A complete description of the digestion procedure is given elsewhere (Shotyk et al. 2014). In essence, approximately 0.2 g of sample was combined with 3 mL $HNO_3$ and 0.1 mL HBF4 and digested in a high-pressure microwave (Ultraclave, MLS, Leutkirch, Germany). The digested samples were transferred to PP tubes, diluted with water to 10 mL and refrigerated.

### *2.3.4.3* Inductively coupled plasma mass spectrometry (ICP-MS*)*

Samples were diluted either 100 or 50 times with 2% $HNO_3$ before being run on the ICP-MS (ICAP Qc, Thermo Fisher) as described in detail elsewhere (Shotyk et al. 2017) and analyzed along with the SRMs and blanks. Indium and Bi were used as internal standards. The accuracy of the measurements, based on the analyses of the SRMs, is presented in Table 1.

### 2.3.4.4 Estimating the contributions of dust to TE inventories

The relative importance of dust deposition to TE inventories can be estimated by calculating the ratio of each TE to that of a conservative, reference element, and then comparing this ratio to the estimated “background” ratio. This approach was described in detailed by Rahn (1976) who distinguished natural and industrial Pb in aerosols by normalizing the Pb/Al ratio in aerosol samples to the corresponding ratio in the Earth’s Crust (EC). The calculation is based on the assumption that, if there is no significant contribution of anthropogenic Pb, the Pb/Al ratio in the aerosols should be similar to the ratio in the EC. To evaluate the assumption, Rahn (1976) included in his study aerosol samples from the most remote locations on earth. Using this approach, an Enrichment Factor is calculated as:

$$(\mathrm{Pb/Al})_{\mathrm{sample}} / (\mathrm{Pb/Al})_{\mathrm{UCC}}$$

The Enrichment Factor is simply the magnitude of the enrichment of Pb (or any other element), relative to its crustal abundance. Rahn (1976) used Al as a reference element because it behaves conservatively during chemical weathering of soils, is abundant, readily measured reliably using a number of analytical methods, and industrial contributions to the atmosphere are insignificant, relative to natural sources. Other conservative, lithophile elements, such as Sc, Ti, Th and Y, behave similarly and can be used for the same calculation.

Here, Y was used as the reference element to determine the origin of TEs in berries, as we have done before (Shotyk et al., 2019). Yttrium was used for the following reasons: 1) it behaves conservatively during chemical weathering; 2) it is not taken up from the soil by plants to any significant extent; and 3) it can be measured accurately using ICP-MS. Moreover, Y concentrations in berries are typically well above the limit of detection (LOD): in this study, the LOD was 0.088 ng/g and the lowest Y concentration found in the samples was 0.7 ng/g.

Here, we used an analogous approach to that of Rahn (1976), based on similar assumptions: taking Y concentrations to represent the abundance of dust particles on the plant surface, the concentrations of individual elements in the samples were plotted against those of Y. To place these data in perspective, the corresponding ratios representing “natural background” values are also shown. The natural background, or “reference” values used here are taken from the compilation for the Earth’s Crust from Krauskopf (1979), the Upper

Continental Crust of Rudnick and Gao (2014), as well as the values for “typical soil” presented by Bowen (1979). There are three possible outcomes of this comparison. First, if the element under investigation shows a strong, positive, correlation with Y, then that element has been supplied to the berries primarily by dust. Second, if there is no significant, positive correlation between the element and Y, then dust is not a significant source of the element to the berry, and the presence of the element is due mainly to plant uptake via the roots. Third, if the element of interest shows a strong positive correlation with Y, but the berries yield significantly greater metal/Y ratios than the estimated background values, then the dust in the ABS region is enriched, relative to crustal rocks and typical soils.

It is important to acknowledge and to recognize that all trace elements, whether or not they are essential, may be taken up by plants via the roots, if the element is present in an ionic form in the soil solution.  For example, in recent experimental studies, Y was found to be taken up by plants from solutions containing Y salts ((Maksimovic et al., 2014; Saatz et al., 2015). In the soils of northern Alberta, we assume that concentrations of ionic forms of Y in soil solutions are extremely low, based on chemical analyses of surface waters of the region. First, concentrations of dissolved (<0.45 µm) Y in the Athabasca River are low: approximately 70 ng/l (Shotyk et al., 2017).

Second, within the dissolved fraction, 70 to 90 % of the Y is colloidal (Cuss et al., 2018), bound mainly to dissolved organic matter (approximately 10 nm in size) and ferric hydroxide (approximately 100 nm in size). Based on these two studies, concentrations of ionic Y species in soil solutions may be on the order of 10 to 20 ng/l: these concentrations are as much as four orders of magnitude below the lowest concentrations employed by Maksimovic et al. (2014)

and Saatz et al. (2015). While we do not doubt that Y may be taken up by plants from soil solutions via roots, in our case, we question the significance of this process, given the low concentrations expected for ionic forms of the element.

It is also important to recognize and acknowledge that plants can absorb elements through their leaves. But again, the chemical form of the element is the key to this process. If the elements being supplied to the berry plants are mainly in the form of dust, the dust particles would either have to be small enough to pass directly through the stomata, or they would have to dissolve on the surface of the leaf to liberate individual elements in ionic forms. The stomata in the leaves of commercially-grown cranberry plants are approximately 2 microns wide and 7 microns long (Sawyer, 1932). The dusts being deposited on the surface of Sphagnum moss in the ABS region are commonly in the range 10 to 50 microns (Mullan-Boudreau et al., 2017), and particles in this size range would not be able to directly enter the stomata. Morever, the dust particles are primarily aluminosilicates, and these are resistant to chemical weathering in the cirumneutral pH range. In consequence, very little dissolution of the dusts on the plants is expected. Thus, we assume that Y being deposited on the leaves of the berry plants is essentially inaccessible and unavailable.

#### 2.3.4.5 Scanning electron microscopy

The concentrations of Y in the berries is assumed to provide an estimate of the abundance of dust particles on the surface of the berries. As an independent check on this assumption, the surfaces of berries from selected locations was examined using Scanning Electron Microscopy (SEM). Specifically, berry samples from JPH4, one of the peat bogs closest to the open pit bitumen mines and upgraders (Figure 1), and berry samples from UTK, the control site, were washed in the lab using 18.2 MΩ•cm water. The wash water was then collected and filtered through a 0.45µm filter which was dried and then analyzed using the SEM.

#### 2.3.4.6 Statistical analysis

Significant differences between washed and unwashed berries were determined by the Permutational T-Test. The Permutational T-test is used because the number of washed and unwashed berries is not the same. Sample variances differ from element to element, and there are a few outliers that could skew the data.

#### 2.3.4.7 Estimating plant uptake of TEs

Plant uptake of TEs was determined by assuming that uptake of Y from the rooting medium is insignificant ie that all of the measured Y found in the berries is due to dust deposition. The concentrations of individual elements are then plotted against those of Y, and a linear regression calculated for each element. The Y intercept of the regression equation yields the concentration of that element attributable to plant uptake via the roots.

## 2.4 RESULTS

The average, median and range in concentrations of TEs in washed and unwashed berries, are presented in Tables 2 and 3.

### 3.1 Conservative, lithophile elements (Al, Cr, Co, Ga, U, Y)

The spatial distribution of Y concentrations in berries from the ABS region (Fig. 2) strongly resembles the variation in dust deposition rates determined using *Sphagnum* moss from the same bogs (Fig. 3). Cranberries typically contain higher concentrations of Y than lingonberries collected from the same bog (Fig. 2). This could potentially be due to the growth habit of the plants: cranberries lie directly on the moss carpet of the bog unlike the lingonberries which are suspended in the air by the stems of the plants (Fig. 4). The median concentration of Y in unwashed berries from the ABS region is 10 μg/kg (Table 2) which is an order of magnitude greater than the corresponding value (0.91 μg/kg) for Y in berries from remote locations (Table 4). The minimum concentration of Y in berries from the ABS region (2.2 μg/kg) is roughly double that of the remote berries which suggests that all of the berries in the ABS region are to some extent affected by anthropogenic dusts. The maximum concentration of Y in berries from the ABS region (29 μg/kg) is 26 times that of the remote berries which reveals the extent to which berries in the ABS region may be impacted by anthropogenic dusts. A significant amount of Y was removed when the berries were washed ($p=0.029$), with the berries containing the most Y also losing the most Y after washing (Fig. 5): the large losses of Y upon washing confirms that most of the Y occurs on the surfaces of the berries as dust. An independent confirmation of this interpretation was obtained using the SEM: berries from JPH4, one of the peat bog sampling locations which is closest to industry, revealed abundant dust particles adhering to the surfaces of the berries (Fig. 6). Based on the morphology and chemical composition of the individual particles, obtained using energy-dispersive X-ray analyses, the dusts consist of minerals such as quartz and aluminosilicates (Fig. 6), and they are generally rather large (e.g. 50 to 100 μm). In contrast, the berries from UTK, the control location, yielded fewer dust particles, and they were much smaller (data not shown).

For comparison with Y, the spatial variation in Al, Co, Cr, Ga, and U show similar distributions (Supporting Information), and each was strongly correlated with Y: the correlation coefficients ($R^2$) were Al 0.726, Co 0.592, Cr 0.893, Ga 0.687, U 0.891.

### 2.4.1 Micronutrients (Cu, Fe, Mn, Zn)

Manganese, Cu, and Zn concentrations are independent of Y concentrations ($R^2 < 0.06$). Unlike the conservative lithophile elements, the linear regressions of Mn, Cu, and Zn against Y do not pass through the origin. Manganese is representative of this type of behaviour: the Y intercept corresponds to a Mn concentration of 248 mg/kg which shows that the Mn content of the berries is independent of the amount of dust they contain (Fig. 7). Washing did not remove significant amounts of Mn (p=0.088), Cu (p=0.24), or Zn (p= 0.74) which supports the suggestion that these elements are mainly found within the fruits themselves.

Iron, however, revealed a different behaviour compared to the other micronutrients. Since Fe is very abundant in the earth's crust (approximately 5 % by weight), it shows a strong correlation to Y ($R^2=0.90$), and the regression line for Fe against Y yields a slope which is similar to that of the Fe/Y ratio of the EC and soil (Fig. 8). Washing, however, removes a significant amount of Fe (p=0.013) in many, but not all samples (Fig 8).

### 2.4.2 Other lithophile elements (Li, Rb, Sr)

Similarly to elements which are essential to plants such as K and Ca. The behaviour of these elements (Li, Rb, Sr) in respect to Y is similar to that of the micronutrients (Supporting Information): there is no significant, positive correlation between these elements and Y, and washing does not remove significant amounts of Li (p=0.99), Rb (p=0.38) and Sr (p=1.0).

### 2.4.3 Potentially toxic TEs (Cd, Pb)

The potentially toxic TEs Cd and Pb reveal contrasting behaviours in respect to the abundance of dust particles, as reflected by their relationship to Y. Comparing Cd with Y (Fig. 9) reveals features similar to those of the mobile lithophile elements and the micronutrients.

Cadmium concentrations are independent of those of Y (ie it yields a low $R^2$ value of 0.051) and has a non-zero y-intercept. Washing does not remove a significant amount of Cd from the berries (Fig. 9).

Unlike Cd, Pb shows a strong, positive correlation to Y (Fig. 10) similar to graphs for the conservative lithophile elements such as Al, Cr, and U (Supporting Information). There is a strong, positive, linear correlation between Pb and Y ($R^2$=0.826) and the y-intercept approaches zero. Lead, therefore, is mainly supplied by dust deposition and its concentration reflects the abundance of dust particles on the berry surface. Washing the berries (Fig. 10) removed a significant amount of Pb (p=0.011) simply because washing removes a considerable portion of the dust. The Pb to Y ratios in the berries correspond to the same ratio for soil (Bowen, 1979), but these exceed the crustal values (Fig. 10); the difference between the two sets of reference values most likely reflects the modest (factor of two), natural enrichment of Pb in soils, relative to crustal rocks, during chemical weathering (Shotyk et al., 2001).

### 2.4.4 Elements enriched in bitumen (V, Ni, Mo)

Five TEs are enriched in bitumen, including V, Ni, Mo and Re (Bicalho et al., 2017), plus Se (Donner et al., 2018a). Of these, V, Ni and Mo were successfully determined in the berry samples. Comparing Mo, Ni, and V with Y in the berries, Mo and Ni are not significantly correlated with Y ($R^2$<0.06) and show trends similar to the micronutrients (Cu, Fe, Mn, Zn). These observations (Supporting Information) are consistent with the fact that both Mo and Ni are essential TE for plants (Kabata-Pendias 2011), and both are comparatively mobile in soils and therefore available for plant uptake (Kabata-Pendias 2011). There is no significant difference in Mo and Ni concentrations between washed and unwashed berries (p=1.0 and 0.95, respectively), so both elements are found almost exclusively within the fruits themselves.

Vanadium shows a different trend, compared to Ni and Mo: V yields a strong, positive, linear correlation to Y ($R^2$=0.89), which suggests that it is mainly deposited on the surface of the berries in the form of dust (Fig. 11). The map showing the spatial variation in V concentrations (Fig. 11) is similar to the corresponding map for Y concentrations (Fig. 2), and both of these resemble the map showing dust deposition rates (Fig. 3). There is a significant difference in V concentrations between washed and unwashed berries (p=0.001) which confirms that most of the V is found in the form of dust particles.

### 2.4.5 Other elements (Ag, Re, Sb, Sc, Se, Th, Tl)

Of the 56 samples analyzed (51 from the ABS region and 5 from the control sites UTK, BMW and CMW), Ag was always < LOD and Tl was determined in only one sample; this sample contained 2 ng/g of Tl which is far below (ca. 750 times) the average value for Tl (1.5 mg/kg) reported by Hopkins et al. (2014) for blueberries in the ABS region. Antimony was determined in only 4 samples, Se in 6 and Sc in 9; Re and Th were commonly below the LOD and Be mainly below the LOD. Elements such as As and Se present several challenges for ICP-MS instruments with a single quadrupole mass analyzer, and hydride generation - atomic fluorescence spectroscopy (HG-AFS) is recommended for both elements (Donner et al., 2017, 2018b). Given that Ag, Be, Re, Sb, Sc, Se, Th and Tl were mainly, almost always, or always < LOD, these data are neither presented nor discussed. For the elements which were reliably determined in all or almost all berry samples, a summary of the concentration data is presented in Supporting Information Table 2 (unwashed) and Table 3 (washed).

## 2.5 DISCUSSION

### 2.5.1 Conservative, lithophile elements (Al, Co, Cr, Ga, U, Y)

Conservative lithophile elements occur primarily in the dust fraction found on the surfaces of the berries (Shotyk et al., 2019 and this study): their concentrations in soil solutions are low because they tend to be hosted by stable minerals, and because of their tendency to hydrolyze in aqueous solution (Goldschmidt, 1954); moreover, they are not readily taken up through the roots of plants. Comparing Al, Co, Cr, Ga, and U to Y results in strong, positive correlations, and their ratios to Y resemble crustal values. Aluminum presents a slightly different case in that the ratio of Al to Y in the berries is less than the assumed background values (Supporting Information). Given that Al is enriched in phyllosilicate clay minerals, it may be that the locally-derived dust particles are poor in clay, compared to background ie that local dusts are dominated by comparatively large particles of quartz and feldspars (Fig. 6).

### 2.5.2 Micronutrients (Cu, Fe, Mn, Zn)

Micronutrients are essential for plant growth and should be elevated in the berries, relative to the soil, because of natural enrichment processes: these elements are taken up from the soil by roots and then they accumulate in plant tissues such as fruits. Dust deposition is a minor contribution to the inventory of these elements, as Mn demonstrates (Fig. 7). Washing the berries removes a significant proportion of the dust particles, as demonstrated by losses of Y (which is therefore found mainly on the berry surface) but does not significantly impact Mn (which is found mainly in the fruit) or other micronutrients (Cu, Zn). Given that Mn concentrations are independent of those of Y (Fig. 7), Mn (as well as Cu and Zn) are predominantly supplied by uptake from the substrate. While Y concentrations clearly demonstrate the impact of dust on the berries of the ABS region, the median concentrations of

Cu (3.2 mg/kg) and Zn (7.5 mg/kg) in the ABS region (Table 2) are similar to the abundance of Cu (3.6 mg/kg) and Zn (9.2 mg/kg) in berries from remote sites (Table 4).

Iron is unlike the other micronutrients in that it is not only essential to plants but is also abundant in silicate minerals. Iron is the 4th most abundant element in the earth's crust and the second most abundant metal, following Al (Krauskopf, 1979). The non-zero intercept obtained when Fe is plotted against Y (Fig. 8) reveals the amount of Fe which is present in the berries, independent of dust; at the same time, however, the positive linear correlation between the two elements (Fig. 8) shows that dust is also an important contributor to the Fe inventories. Washing the berries in water provides additional evidence of the importance of dust to the Fe inventories: notice that the berries nearest industrial activities show large differences in Fe concentrations in washed versus unwashed berries (Fig. 8). In contrast, berries that were collected to the west, and primarily upwind of industry (sites S3, S4 and S6 in Fig. 1), show remarkably little difference in Fe concentrations between washed and unwashed berries (Fig. 8); virtually the same trend in spatial variation was seen for Y (Fig. 5).

### 2.5.3 Other lithophile elements (Li, Rb, Sr)

These elements follow a trend similar to that exhibited by the essential micronutrients, such as Mn (Fig. 7): they all have regression lines with a low $R^2$ value, a broad range in confidence intervals, and plot well above the soil and EC reference levels (Supporting Information). These elements are mobile in soil solutions (Goldschmidt 1954) easily taken up through plant roots. Washing the berries does not remove a significant amount of Li, Rb, or Sr, which suggests that these elements are mainly in the berries rather than on their surfaces.

### 2.5.4 Potentially toxic TEs (Cd, Pb)

Cadmium is not an essential element, but is easily taken up by roots because of its mobility in soil environments combined with its chemical behaviour being so similar to that of Zn (Adriano 2001). As seen in Figure 9, Cd concentrations are independent of Y, much like the pattern seen for micronutrients such as Mn (Fig. 7) and Zn (Supporting Information). Cadmium can replace Ca, Fe, Mn, and Zn in proteins, rendering them inactive (Kabata-Pendias 2011). Cadmium can also affect photosynthesis, which reduces the amount of energy a plant receives and decreases the growth and health of the plant (Mustafa and Komatsu 2016). Clearly, Cd is potentially toxic to plants. Having said this, the Cd concentrations found in the ABS berries are similar to the Cd levels found in the berries from remote sites (Shotyk et al., 2019). Specifically, the median Cd concentration in the berries of the ABS region is 6.2 µg/kg (Table 2), compared to 7.6 µg/kg in the berries from remote locations (Table 4).

Unlike Cd, Pb is not mobile and is not taken up by the roots of the plant (Shotyk et al., 2019). Lead shows a distribution similar to that of the conservative lithophile elements: Pb strongly correlates with Y (Fig. 10), which suggests that the Pb in berries is primarily related to dust deposition. The y-intercept for Pb against Y is relatively close to zero, which suggests that a minimal amount of lead is naturally taken up through the roots of the plants. Ratios of Pb to Y in the berries (Fig. 10) are similar to those reported for the Earth's Crust (Krauskopf, 1979) and soil (Bowen, 1979), suggesting that the main source of Pb is related to dust deposition. Lead is present in many silicates due to isomorphic substitution by $Pb^{2+}$ for $Ca^{2+}$ and $K^{+}$ (Shotyk et al., 2001). The median Pb concentration in the berries of the ABS region is 8.0 µg/kg (Table 2), compared to 2.1 µg/kg in the berries from remote locations (Table 4).

### 2.5.5 Elements enriched in bitumen (V, Ni, Mo)

Molybdenum, Ni, and V are enriched in bitumen (Bicalho et al. 2017), relative to crustal abundance, so these are the TEs that are most likely to be enriched in the berries from the ABSR. Upgraders that are located in the ABSR produce large amounts of petroleum coke which is even more enriched in V, Ni and Mo than the bitumen itself (Al-Haj-Ibrahim and Morsi 1992; Nesbitt, Lindsay, and Chen 2017); coke is piled in huge deposits and contributes to the generation of dust.

Molybdenum is essential to plants, and is readily taken up by roots and accumulates in tissues (Emsley 2001). The independence of Mo concentrations on Y in berries (Supporting Information) is evidence of Mo uptake. The accumulation of Mo from roots dominates to such an extent that it is difficult to discern an impact of dust deposition on the overall Mo concentrations found in the berries. Molybdenum shows trends similar to other essential elements such as Mn and Zn. The median Mo concentration in the berries of the ABS region is 37 µg/kg (Table 2), compared to 13 µg/kg in the berries from remote locations (Table 4). Thus, it would appear that berries in the ABS region may be receiving additional Mo which is in a plant-available form, but much more sampling of berries from background locations are needed to be able to draw firm conclusions.

Nickel is another element that is readily taken up by plant roots: this is evident from the y-intercept obtained from the linear regression of Ni against Y (Supporting Information). While the role of Ni in plant nutrition remains uncertain (Cempel and Nikel 2006; Emsley 2001; Bertoldi et al. 2011), recent studies have concluded that Ni is essential to plants (White and Brown, 2010; Klein and Costa 2015; Shahzad et al., 2018). In the soil solution, Ni is mainly found in relatively mobile, ionic forms and for this reason, Ni concentrations in plants tend to correlate with Ni concentrations in soils (Kabata-Pendias 2011). In the berries from the ABS region, the correlation between Ni and Y is poor (low $R^2$ value) which shows that the Ni inventory in the berries is independent of dust deposition, and dominated by plant uptake. The median Ni concentration in the berries of the ABS region is 0.38 mg/kg (Table 2), compared to 0.24 mg/kg in the berries from remote locations (Table 4).  Again, there is insufficient data for berries from remote locations to decide whether berries in the ABS region may be receiving additional Ni in a plant-available form.

Vanadium has a y-intercept close to zero (Fig. 11), which indicates that the berry plants do not take up this element from the substrate, and that the V contents of the berries in the region are a reflection of dust deposition. The slope of the regression equation is comparable to the V/Y ratio of the Upper Continental Crust (Fig. 11), which shows that any enrichment of V in the local dusts is difficult to discern from background values. The median V concentration in the berries of the ABS region is 66 µg/kg (Table 2), compared to 5.9 µg/kg in the berries from remote locations (Table 4) which demonstrates the impact of dust deposition in the ABS region. Like Y and the other elements found primarily in the dust fraction, much if not most of this V can be removed from the berries by washing in water: the median V concentration after washing was 29 µg/kg (Table 3), with berries containing the highest V concentrations most affected (Fig. 11).

## 2.6 CONCLUSIONS

Elements which are essential for plants such as Cu, Mo, Ni and Zn, accumulate in the berries because of uptake via roots. Elements which are not essential but chemically mobile in soil environments, including benign elements such as Rb and Sr, as well as potentially toxic elements such as Cd, are similarly affected. In contrast, elements such as Al, Cr, Pb, U, V and Y are supplied to the berries almost exclusively from dust deposition: the variation in abundance of these elements in the berries reflects differences in dust inputs. However, the dust particles themselves are not enriched in these elements, relative to background values (ie soils and rocks).

Washing the berries removed a significant amount of the elements associated with the dust particles (Al, Cr, Pb, U, V, Y) which supports our interpretation that these elements are contributed mainly by dusts. Future studies should examine the bioaccessibility and bioavailability of the TEs associated with these dusts. Dust deposition does not significantly affect the concentrations of TEs that are supplied mainly by uptake via roots (Cd, Cu, Mn, Mo, Ni, and Zn), and washing does not reduce their concentrations. Of this list of elements, only Mo and Ni appear to be more abundant in berries from the ABS region, compared to background sites, but only by 2 to 3 times.

## 2.7 ACKNOWLEDGEMENTS

We are grateful to the Alberta Conservation Association for their support of this study, through the Grants in Biodiversity program. The graduate student assistantship to S.S. was provided by the SWAMP laboratory. Sincere thanks to Rick Pelletier for creating the maps.

## 2.8 SUPPORTING INFORMATION – APPENDIX 2

The Supporting Information includes the GPS coordinates of the sites investigated (SI Table 1), the concentrations of TE determined (and the limits of detection) for unwashed berries (SI Table 2), and the washed berries (SI Table 3). Also included in the Supporting Information are the maps showing the spatial distribution in concentrations, and the linear regressions versus Y, for the following elements: Al, Ba, Co, Cr, Ga, Li, Mo, Ni, Rb, Sr, U and Zn

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## 2.10 FIGURES

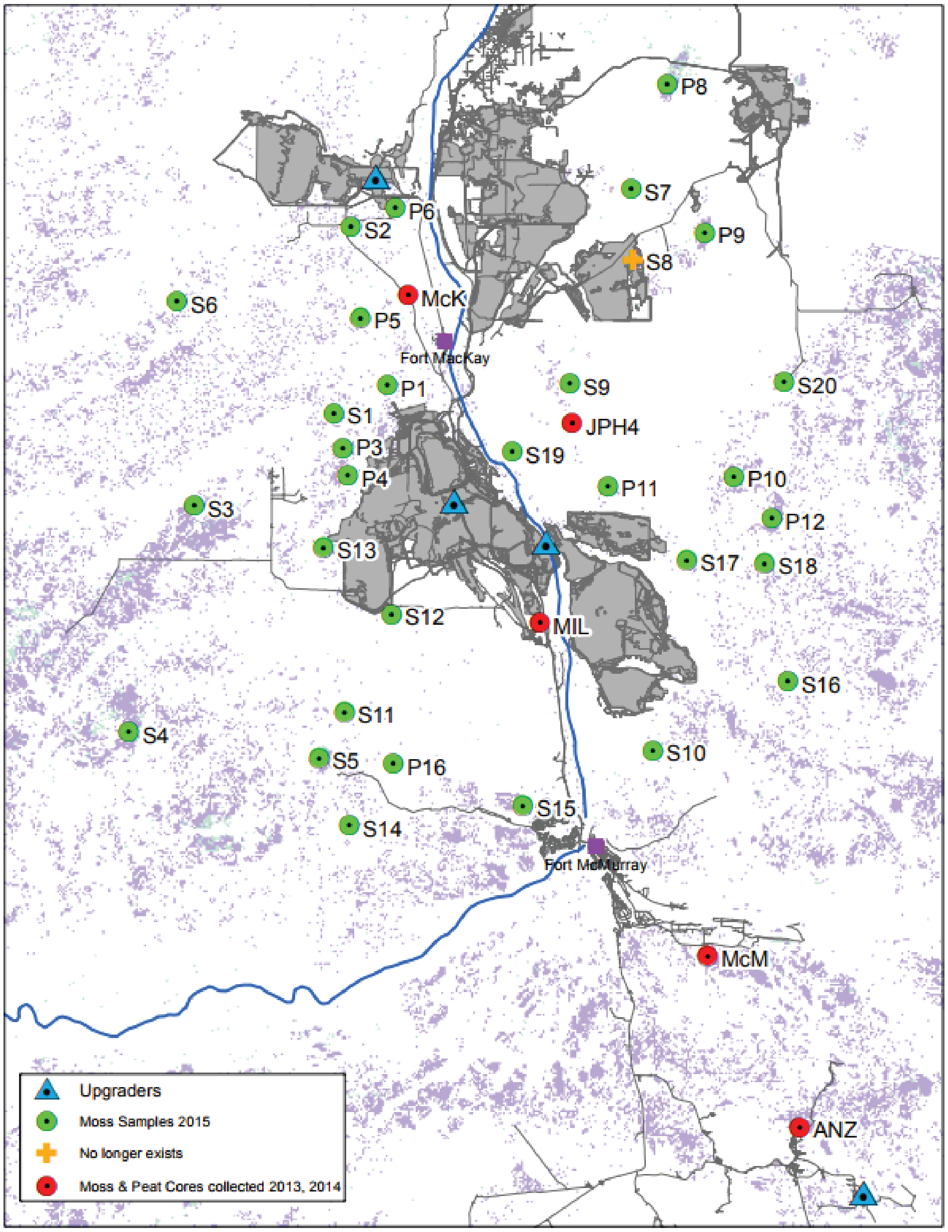

Figure 2-1: Sampling locations. Berries were collected at the sites sampled for moss in September of 2015 (green circles), but also from the bogs that had been sampled for moss and peat in 2013 and 2014 (red circles). Also shown in gray are the areas disturbed by industrial activities (open pit mines, upgraders, tailings ponds and dry tailings) and the locations of the four bitumen upgraders (blue triangles). From Mullan-Boudreau et al., (2017).

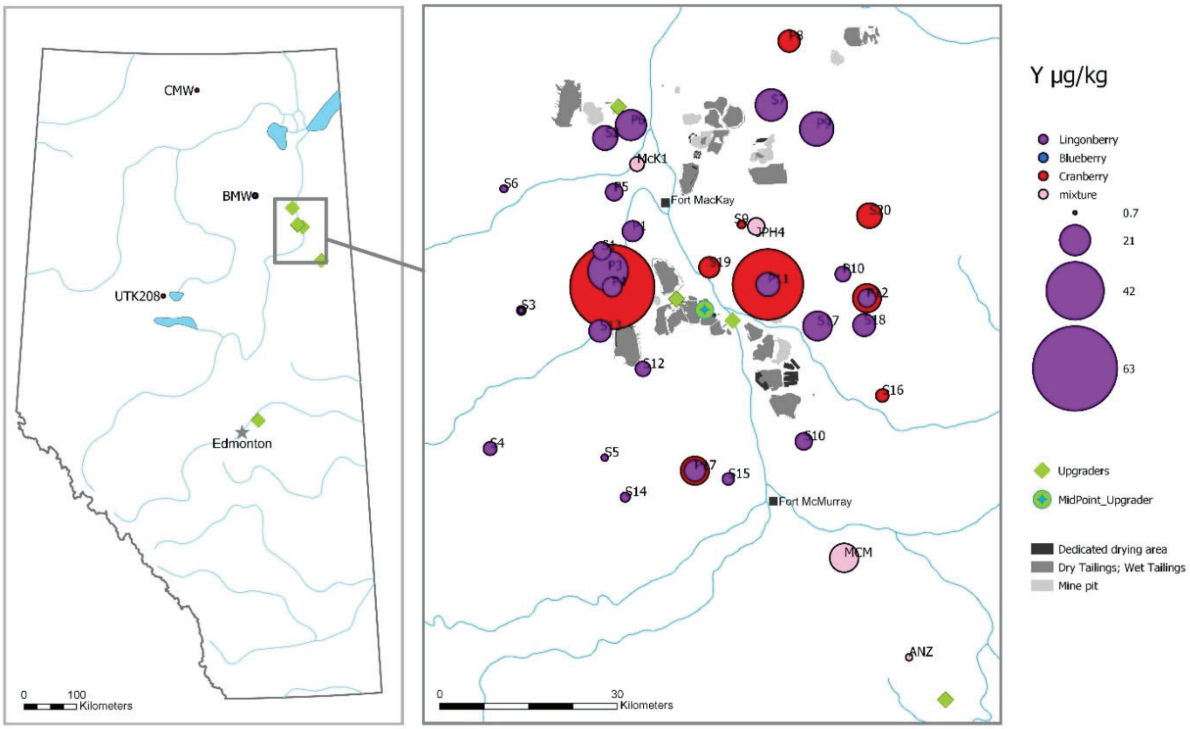

Figure 2-2: Map showing the spatial variation in Y concentrations (µg/kg) in berries for the ABS region (right hand side) and the remote sampling locations, UTK, BMW and CMW (left hand side).

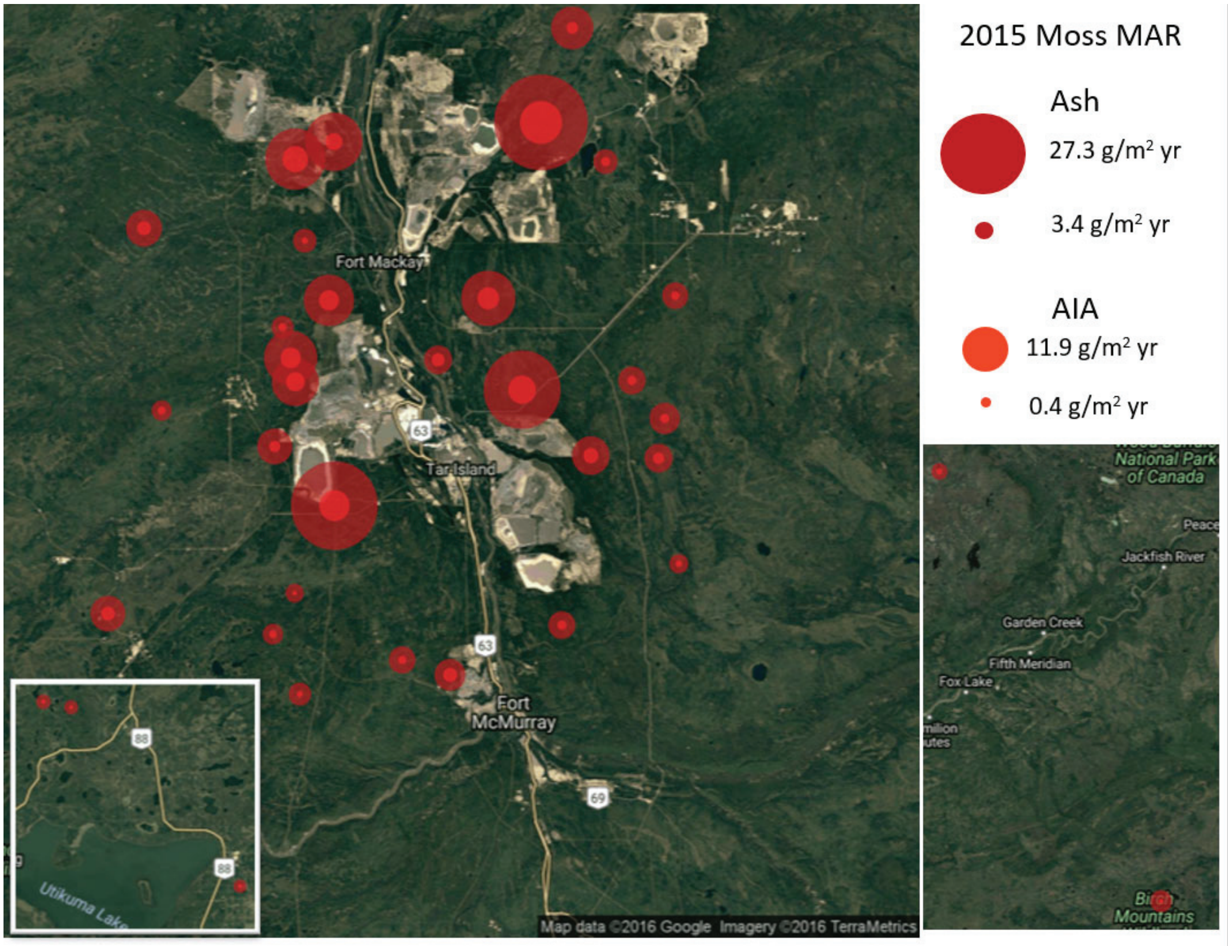

Figure 2-3: Deposition rates (g/m$^2$/yr) of ash and acid-insoluble ash (ie mineral matter) in the ABS region, and at the control sites, determined using Sphagnum moss (from Mullan-Boudreau et al., 2017).

Figure 2-4: Bog cranberry, *Vaccinium oxycoccus* (top), and Lingonberry, *Vaccinium vitis-idaea* (bottom). Photos by W.S.

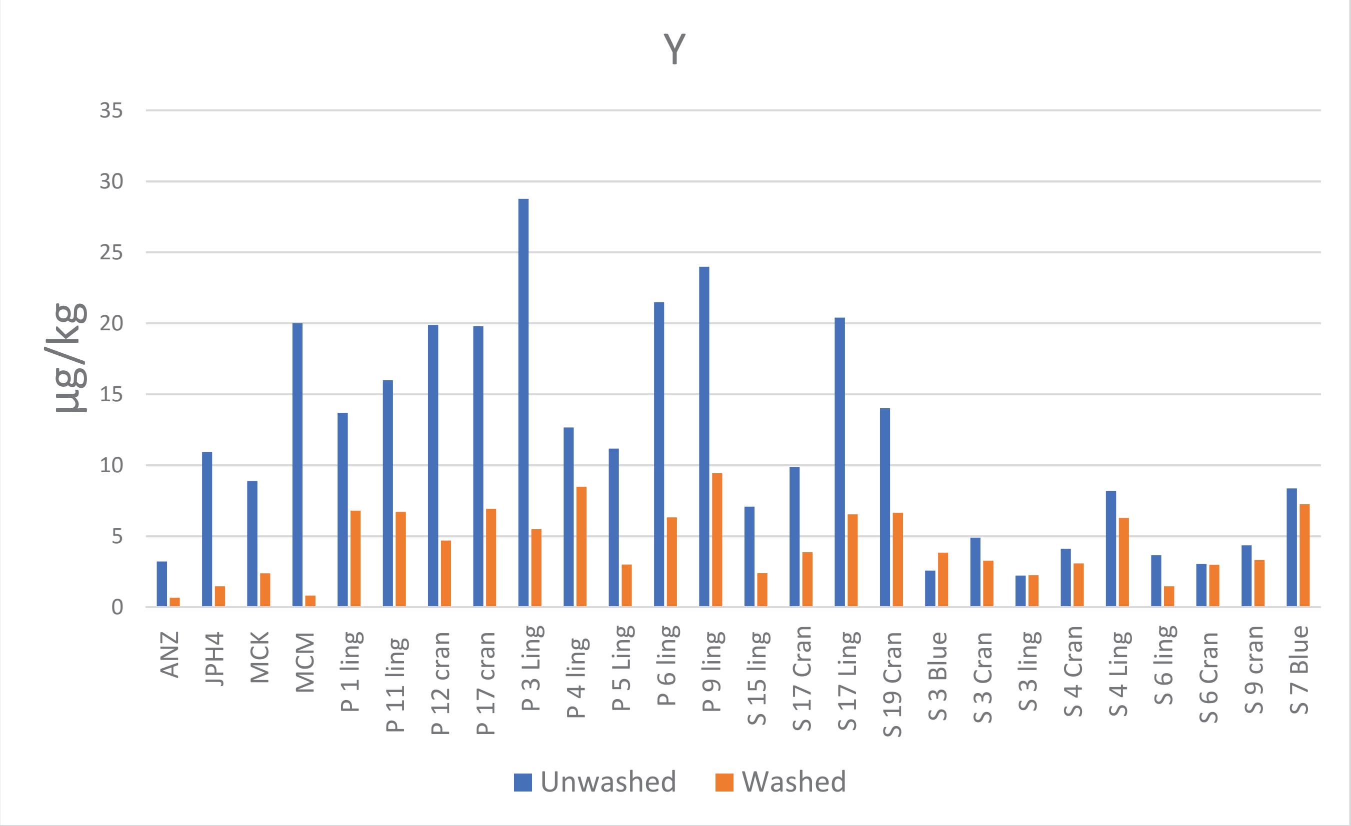

Figure 2-5: A comparison of Y concentrations (µg/kg) in berries from the ABS region, before and after washing in water. The sites yielding the lowest Y concentrations (S3, S4, and S6) are to the west of the industrial area (see Fig. 1) and tend generally to be upwind.

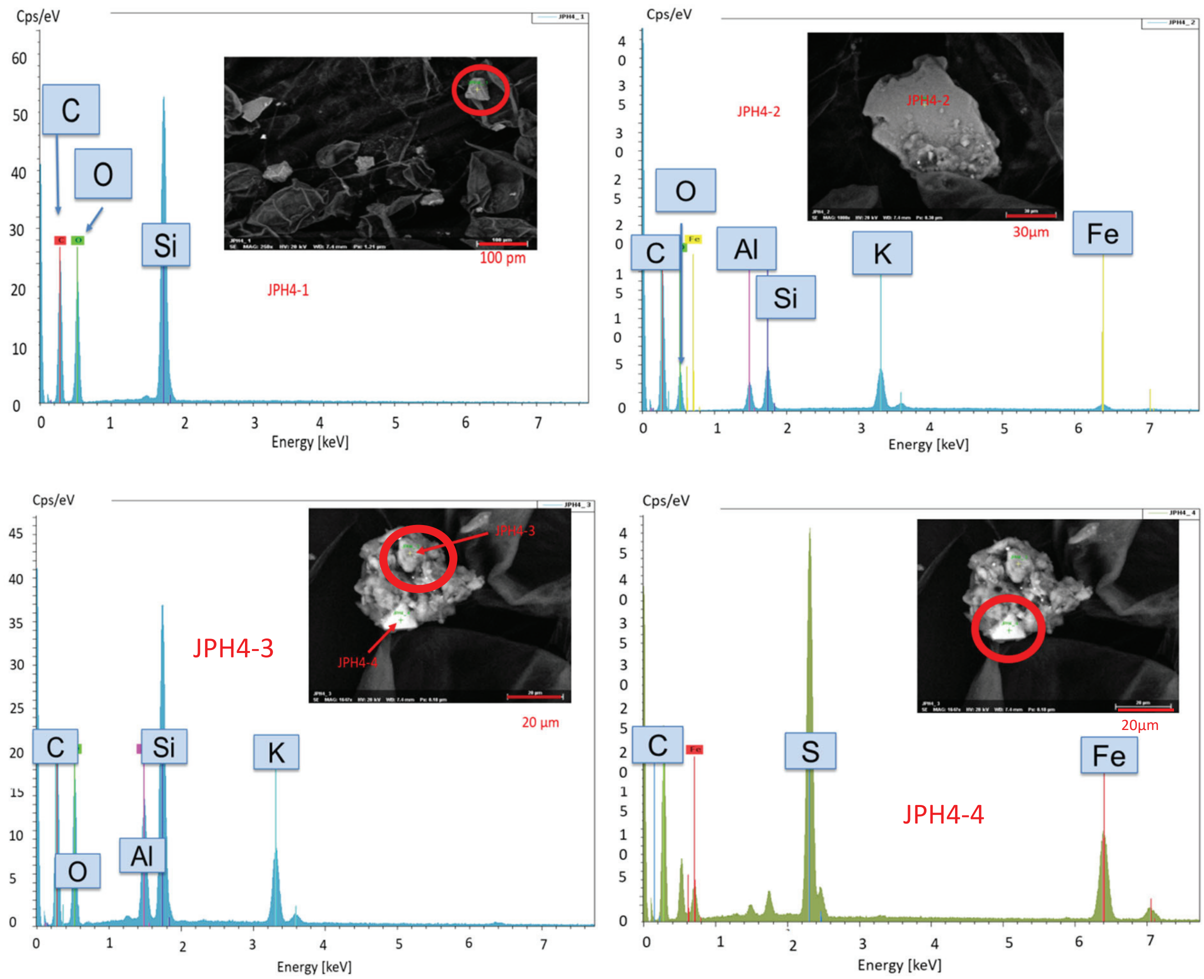

Figure 2-6: SEM images of particles removed from the surface of berries from JPH4, after washing in water. JPH4 is approximately 12 km from the mid-point between the two central bitumen upgraders shown in Figure 1. The images show the size and morphology of the particles, and the energy dispersive X-ray spectra provide the relative abundance of major elements. Upper left, quartz; upper right, potassium feldspar; lower right, potassium feldspar within an aggregate of particles; lower right, pyrite within the same aggregate.

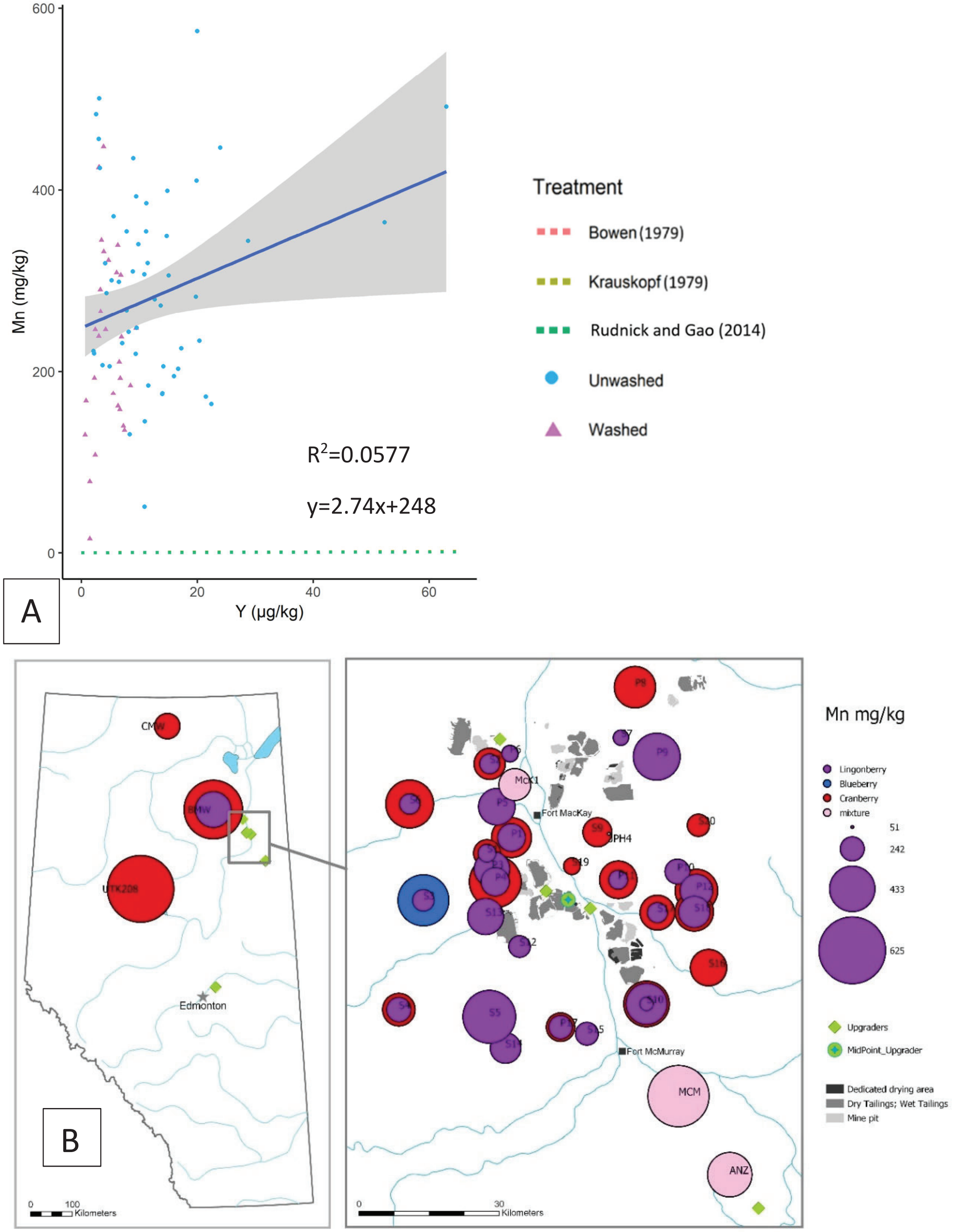

Figure 2-7: Top: linear regression of Mn concentrations (mg/kg) versus Y (µg/kg) in washed and unwashed berries collected from the ABS region. Bottom: Spatial variation in Mn concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). Notice that the Mn concentrations in berries collected near industry are sometimes at or below the concentrations obtained from samples collected at control sites.

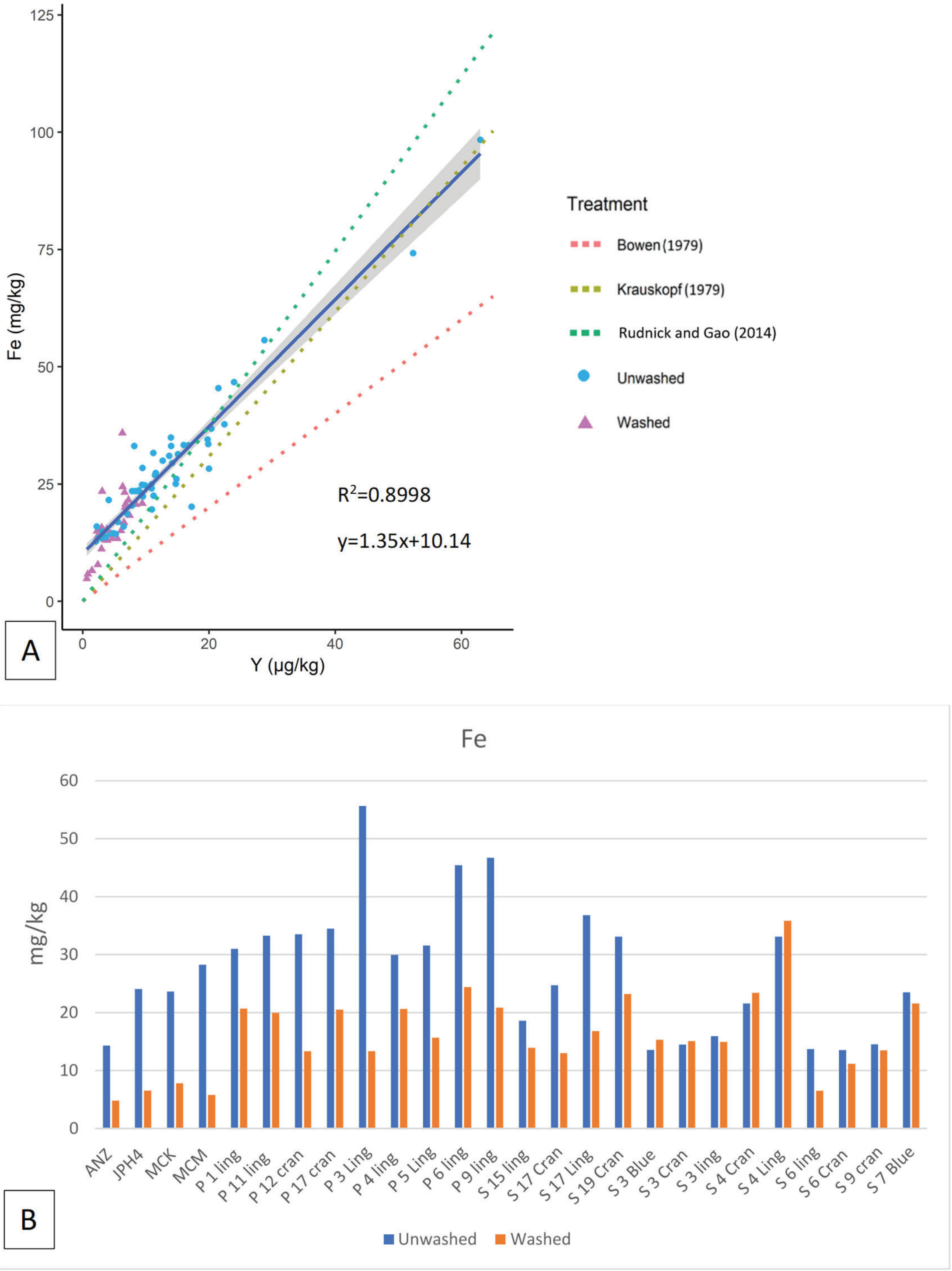

Figure 2-8: Top: linear regression of Fe concentrations (mg/kg) versus Y (µg/kg) in washed and unwashed berries. Bottom: concentrations of Fe in washed and unwashed berries, listed by sample name.

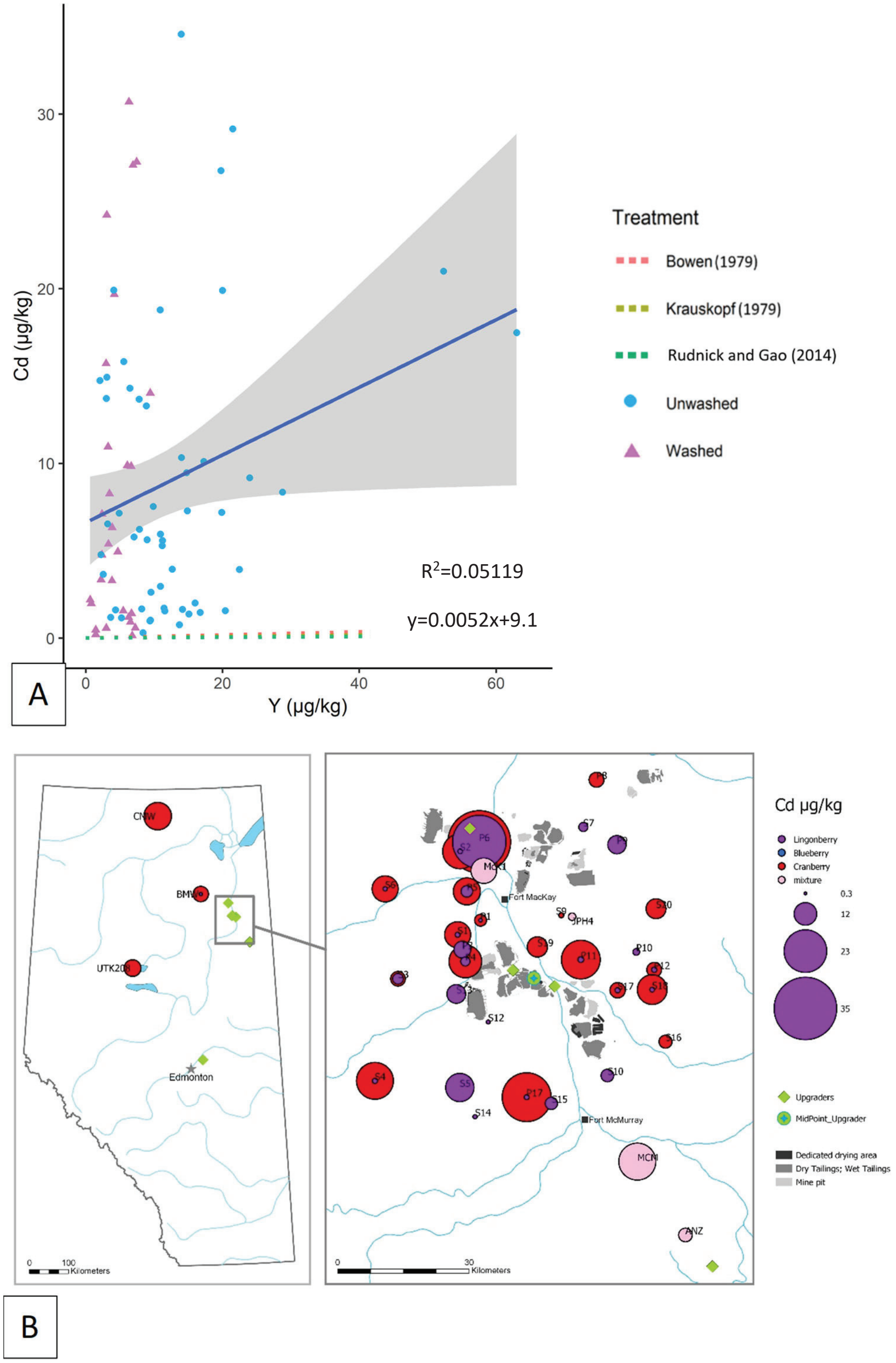

Figure 2-9: Top: linear regression of Cd versus Y concentrations (both in units of μg/kg) in washed and unwashed berries collected from the ABS region. Bottom: spatial variation in Cd concentrations (μg/kg) in berries from the ABS region (right hand side) and the control sites (left hand side).

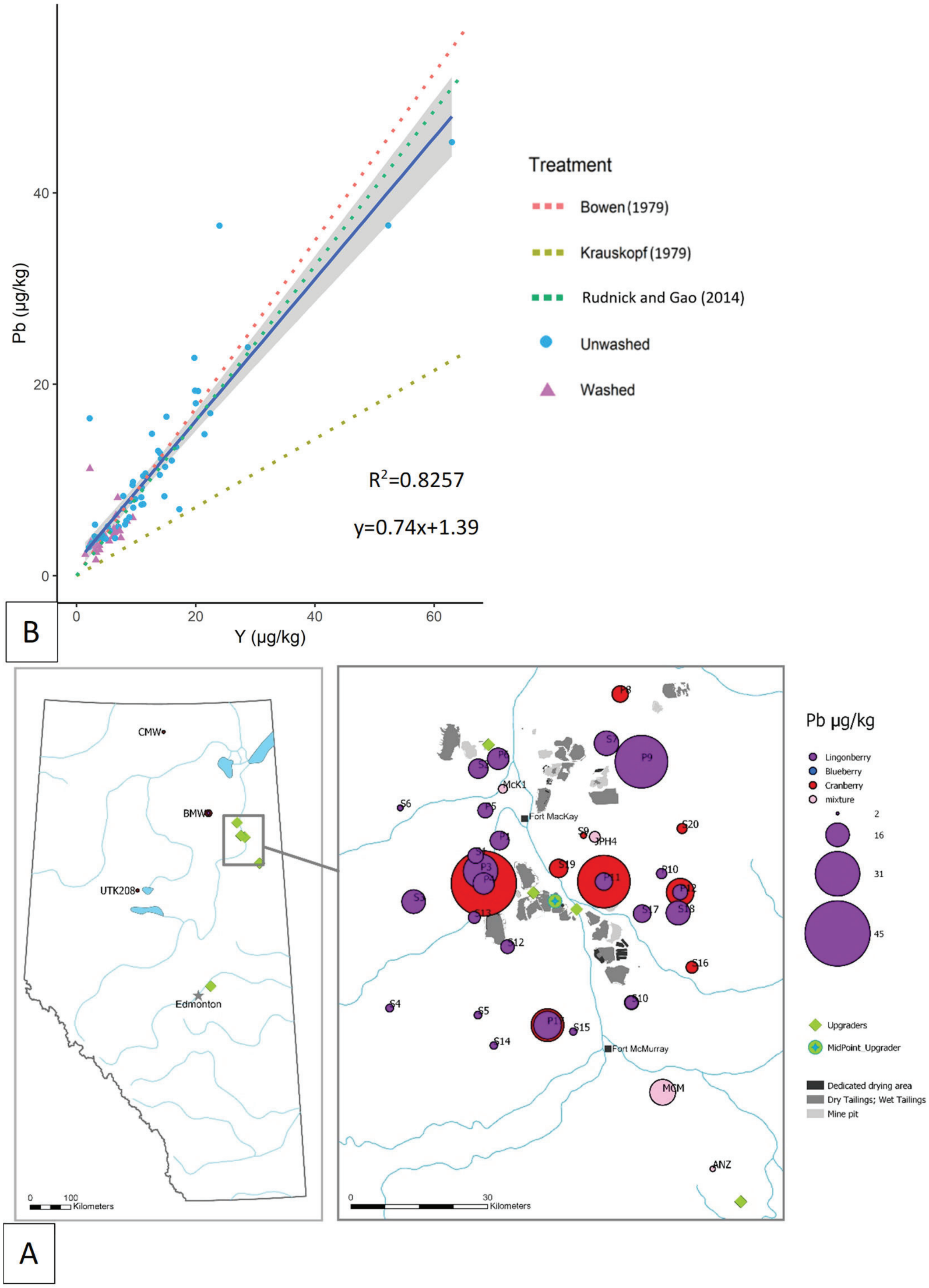

Figure 2-10: Top: linear regression of Pb concentrations versus Y (both in units of µg/kg) in washed and unwashed berries collected from the ABS region. Bottom: spatial variation in Pb concentrations (µg/kg) in berries from the ABS region (right hand side) and the control sites (left hand side)

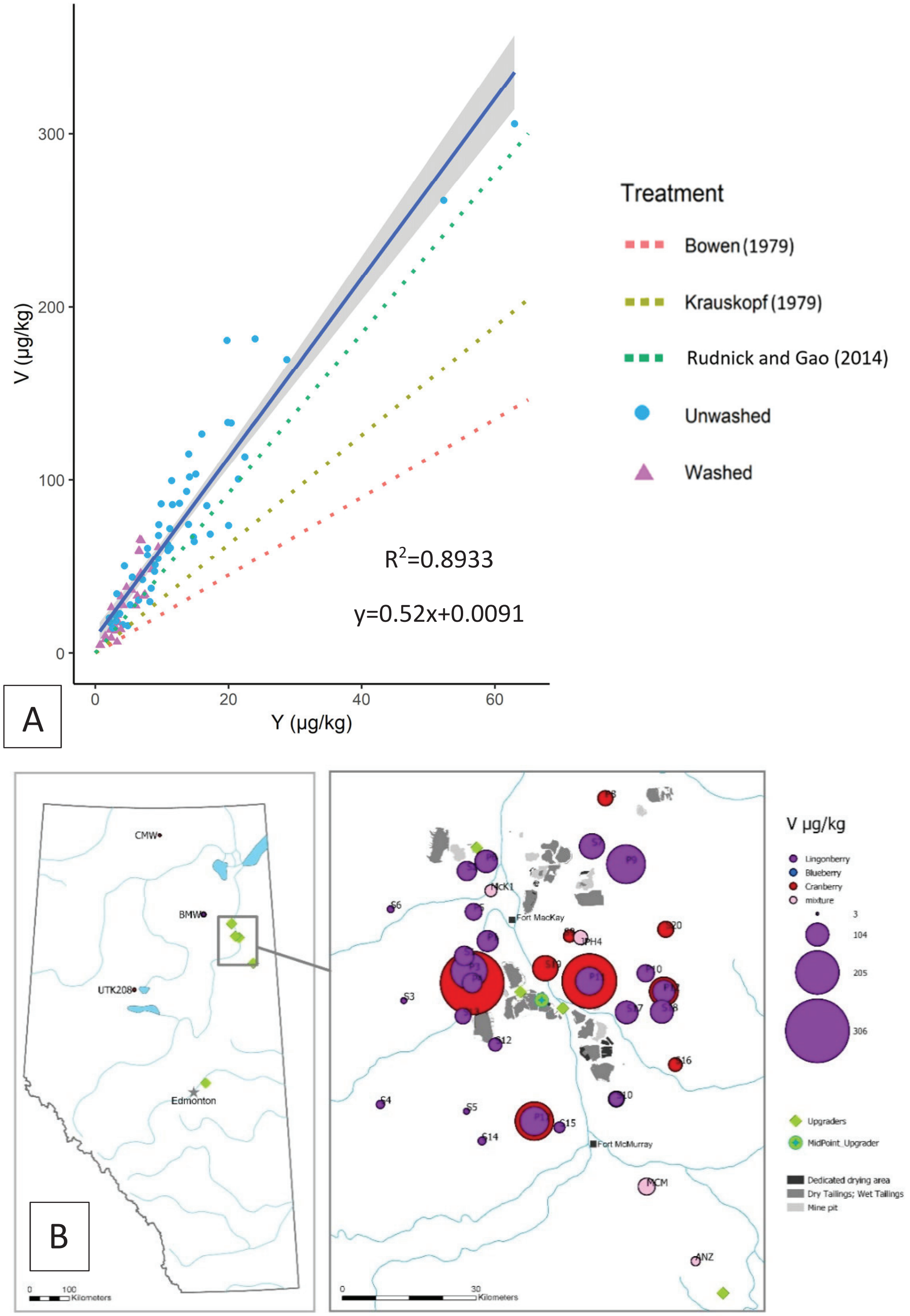

Figure 2-11: Top: linear regression of V concentrations versus Y (both in units of µg/kg) in washed and unwashed berries collected from the ABS region. Bottom: spatial variation in V concentrations (µg/kg) in berries from the ABS region (right hand side) and the control sites (left hand side).

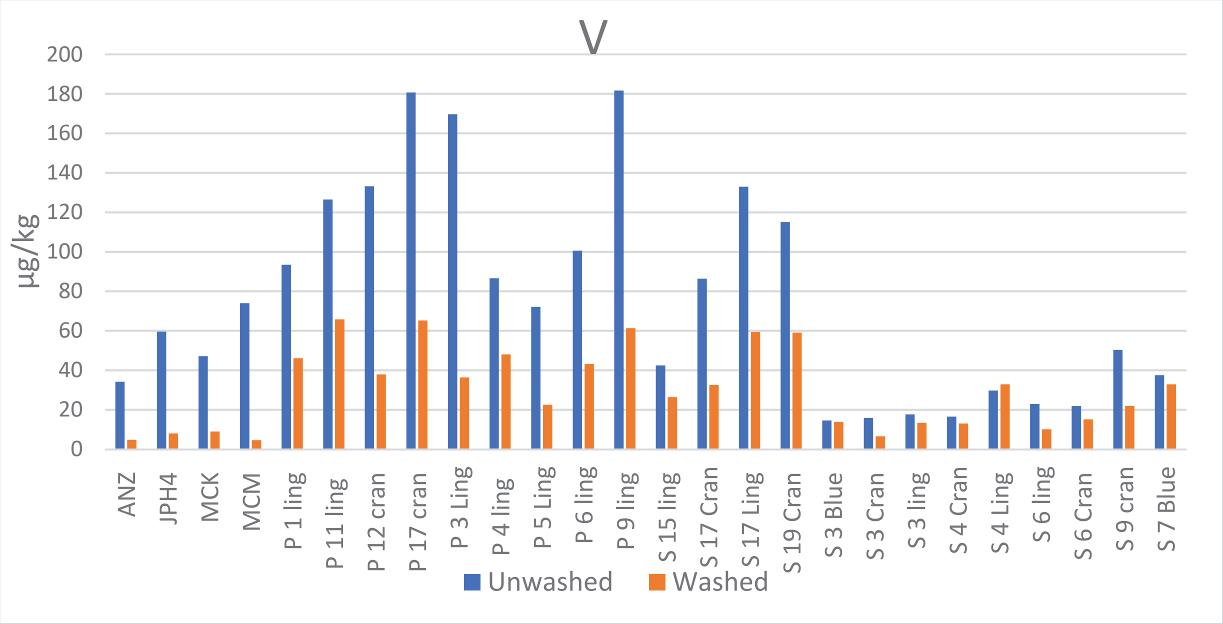

Figure 2-12: Concentrations of V (µg/kg) in washed and unwashed berries, listed by sample name. The sites yielding the lowest V concentrations (S3, S4, and S6) are to the west of the industrial area (see Fig. 1), and tend generally to be upwind.

## 2.11 TABLES

| **Average Accuracy of SRMs** | **Al** | **Ba** | **Cd** | **Co** | **Cr** | **Cu** | **Fe** | **Ga** | **Mn** | **Mo** | **Ni** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Moss HB 36-Trace elements in moss (Pleurozium schreberi) | | | | | | | | | | | |
| Average Accuracy(%) n=2 | 144 | 94 | 90 | 90 | 138 | 82 | 100 | 132 | 87 | 82 | 86 |
| NIST 1547 - Trace Elements in Peach Leaves | | | | | | | | | | | |
| Average Accuracy(%) n=3 | 91 | 96 | 90 | 97 | 122 | 92 | 94 | | 96 | 82 | 104 |
| NIST 1515-Trace elements in Apple Leaves | | | | | | | | | | | |
| Average Accuracy(%) n=5 | 92 | 90 | 95 | 102 | 120 | 93 | 93 | | 100 | 92 | 164 |

| | **Pb** | **Rb** | **Sb** | **Sc** | **Sr** | **Th** | **Tl** | **U** | **V** | **Y** | **Zn** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Moss HB 36-Trace elements in moss (Pleurozium schreberi) | | | | | | | | | | | |
| Average Accuracy(%) n=2 | 98 | 92 | 96 | | 88 | 99 | 78 | 94 | 95 | 116 | 84 |
| NIST 1547 - Trace Elements in Peach Leaves | | | | | | | | | | | |
| Average Accuracy(%) n=3 | 95 | 78 | 98 | 110 | 101 | 117 | | 104 | 99 | | 92 |
| NIST 1515-Trace elements in Apple Leaves | | | | | | | | | | | |
| Average Accuracy(%) n=5 | 91 | 92 | 98 | 108 | 96 | 98 | | 126 | 100 | | 91 |

Table 2-1: Accuracy of the trace element determinations, based on certified, Standard Reference Materials. Accuracy is expressed as the percentage of the certified value.

| Element | Al (mg/kg) | Ba (mg/kg) | Cd (µg/kg) | Co (µg/kg) | Cr (µg/kg) | Cu (mg/kg) | Fe (mg/kg) | Ga (µg/kg) | Li (µg/kg) | Mn (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|---|
| Average | 35 | 11 | 8.3 | 14 | 40 | 3.1 | 27 | 17 | 81 | 294 |
| Standard Deviation | 21 | 4.8 | 7.9 | 7.0 | 24 | 0.9 | 11 | 7.5 | 97 | 120 |
| RSD (%) | 59 | 45 | 95 | 49 | 60 | 28 | 41 | 45 | 119 | 41 |
| Median | 32 | 10 | 6.2 | 15 | 46 | 3.2 | 26 | 14 | 55 | 281 |
| Maximum | 83 | 22 | 29 | 33 | 86 | 4.8 | 56 | 34 | 462 | 575 |
| Minimum | 7.7 | 3.2 | 0.3 | 3.7 | 9.3 | 0.9 | 14 | 6.9 | 13 | 51 |

| Element | Mo (µg/kg) | Ni (mg/kg) | Pb (µg/kg) | Rb (mg/kg) | Sr (mg/kg) | U (µg/kg) | V (µg/kg) | Y (µg/kg) | Zn (mg/kg) |
|---|---|---|---|---|---|---|---|---|---|
| Average | 46 | 0.51 | 11 | 8.2 | 2.1 | 1.1 | 75 | 12 | 7.8 |
| Standard Deviation | 36 | 0.44 | 8.4 | 3.1 | 2.0 | 0.69 | 53 | 7.6 | 1.9 |
| RSD (%) | 77 | 85 | 74 | 38 | 96 | 63 | 71 | 65 | 24 |
| Median | 37 | 0.38 | 8.0 | 8.4 | 1.1 | 1.0 | 66 | 10 | 7.5 |
| Maximum | 181 | 1.73 | 36.57 | 16.95 | 8.3 | 2.93 | 182 | 29 | 12 |
| Minimum | 9.0 | 0.08 | 3.4 | 2.5 | 0.42 | 0.24 | 15 | 2.2 | 4.5 |

Table 2-2: Trace elements in unwashed berries from the ABS region: average, standard deviation, relative standard deviation, median, minimum, and maximum concentrations. Note differences in units of concentration.

| **Element** | **Al (mg/kg)** | **Ba (mg/kg)** | **Cd (µg/kg)** | **Co (µg/kg)** | **Cr (µg/kg)** | **Cu (mg/kg)** | **Fe (mg/kg)** | **Ga (µg/kg)** | **Li (µg/kg)** | **Mn (mg/kg)** |
|---|---|---|---|---|---|---|---|---|---|---|
| Average | 19 | 8.4 | 7.2 | 9.4 | 23 | 2.7 | 16 | 9 | 70 | 232 |
| Standard Deviation | 13 | 5.1 | 8.8 | 5.3 | 11 | 1.1 | 7.1 | 4.2 | 90 | 108 |
| RSD (%) | 68 | 61 | 123 | 56 | 48 | 40 | 44 | 44 | 129 | 46 |
| Median | 16 | 7.4 | 3.3 | 8.5 | 25 | 3.0 | 15 | 10 | 45 | 224 |
| Maximum | 47 | 21 | 31 | 23 | 51 | 4.4 | 36 | 15 | 427 | 448 |
| Minimum | 3.9 | 2.0 | 0.14 | 2.6 | 2.1 | 1.0 | 4.8 | 1.7 | 12 | 16 |

| **Element** | **Mo (µg/kg)** | **Ni (mg/kg)** | **Pb (µg/kg)** | **Rb (mg/kg)** | **Sr (mg/kg)** | **U (µg/kg)** | **V (µg/kg)** | **Y (µg/kg)** | **Zn (mg/kg)** |
|---|---|---|---|---|---|---|---|---|---|
| Average | 42 | 0.41 | 4.5 | 7.0 | 1.7 | 0.5 | 30 | 4.5 | 7.0 |
| Standard Deviation | 41 | 0.40 | 2.2 | 3.4 | 1.8 | 0.2 | 20 | 2.5 | 4.2 |
| RSD (%) | 96 | 96 | 48 | 48 | 104 | 44 | 67 | 55 | 61 |
| Median | 22 | 0.31 | 4.4 | 6.7 | 1.1 | 0.5 | 29 | 3.9 | 6.7 |
| Maximum | 171 | 1.9 | 11 | 16 | 8.8 | 1.0 | 66 | 9.4 | 24 |
| Minimum | 9.2 | 0.059 | 1.6 | 1.5 | 0.31 | 0.20 | 4.6 | 0.7 | 2.4 |

Table 2-3: Trace elements in washed berries from the ABS region: average, standard deviation, relative standard deviation, median, minimum, and maximum concentrations. Note differences in units of concentration.

| **Element** | **Al (mg/kg)** | **Ba (mg/kg)** | **Cd (µg/kg)** | **Co (µg/kg)** | **Cr (µg/kg)** | **Cu (mg/kg)** | **Fe (mg/kg)** | **Ga (µg/kg)** | **Li (µg/kg)** | **Mn (mg/kg)** |
|---|---|---|---|---|---|---|---|---|---|---|
| Average | 10.5 | 9.9 | 6.3 | 2.0 | 6.6 | 2.9 | 11.6 | 5.7 | 12.1 | 452.0 |
| Standard Deviation | 8.7 | 5.5 | 5.9 | 0.6 | 2.4 | 1.3 | 1.4 | 5.3 | 7.5 | 154.4 |
| RSD (%) | 83.1 | 55.5 | 93.5 | 32.3 | 36.4 | 45.7 | 12.0 | 94.3 | 62.3 | 34.2 |
| Median | 6.5 | 8.5 | 7.6 | 1.8 | 7.4 | 3.6 | 12.0 | 4.7 | 10.5 | 437.9 |
| Max | 23.1 | 19.1 | 14.6 | 2.8 | 8.3 | 4.3 | 12.9 | 14.6 | 24.4 | 625.2 |
| Min | 2.4 | 4.3 | 0.5 | 1.3 | 3.1 | 1.0 | 9.3 | 0.8 | 4.0 | 241.9 |

| **Element** | **Mo (µg/kg)** | **Ni (mg/kg)** | **Pb (µg/kg)** | **Rb (mg/kg)** | **Sr (mg/kg)** | **U (µg/kg)** | **V (µg/kg)** | **Y (µg/kg)** | **Zn (mg/kg)** |
|---|---|---|---|---|---|---|---|---|---|
| Average | 149.2 | 0.2 | 2.6 | 7.0 | 1.0 | 0.1 | 7.3 | 1.1 | 8.9 |
| Standard Deviation | 308.9 | 0.1 | 1.2 | 3.4 | 1.1 | 0.1 | 4.4 | 0.6 | 1.8 |
| RSD (%) | 207.1 | 61.0 | 43.8 | 48.2 | 112.7 | 69.2 | 60.5 | 51.8 | 19.8 |
| Median | 13.0 | 0.2 | 2.1 | 5.8 | 0.5 | 0.1 | 5.9 | 0.9 | 9.2 |
| Max | 701.5 | 0.5 | 4.7 | 13.0 | 3.0 | 0.2 | 14.5 | 2.2 | 11.3 |
| Min | 2.2 | 0.1 | 2.0 | 5.0 | 0.4 | 0.0 | 2.7 | 0.7 | 6.7 |

Table 2-4: Trace elements in berries from remote areas: average, standard deviation, relative standard deviation, median, minimum, and maximum concentrations. Note differences in units of concentration.

# 3 CHAPTER 3 – CONCLUSIONS

## 3.1 LIMITATIONS OF THE STUDY

This study could have been improved through the following:

1) The analytical methods used during the study were conducted at a very high standard. However, due to time constraints and sample size the analyses were restricted to quadrupole ICP-MS which is very sensitive, but is unable to detect elements such as Ag, Be, Re, Sb, Sc, Th, and Tl. Using the sector field ICP-MS would decrease the limit of detection (LOD), allowing these elements to be determined. However, sector field IPC-MS is not only expensive and time consuming, but it is also a much more complex analysis. Elements such as Hg and As could have been analysed using HG-AFS, but this was not possible because of time limitations.
2) The number of berry samples collected was purely based on opportunistic sampling, which limits the locations sampled. The study could have been improved if there was prior research done on the berries and their growing environment, allowing for better chances of collecting larger quantity of samples and more sites with berries present.

## 3.2 FUTURE WORK AND RECOMMENDATIONS

Possible future studies include:

A) Sampling other berries. Increasing the number of berry species studies would increase the knowledge of trace element concentrations in berries.

B) Working closely with with Aboriginal communities would likely have the greatest impact, since they have their own food preferences.

C) Studying other traditional food sources including mammals, fish, and other vegetation, such as medicinal plants.

D) Determining the effects of organic contaminants on a wide range of traditional food sources. It is important to understand both inorganic and organic contamination of traditional foods that grow in the ABSR.

E) Conducting toxicology studies, which would help to further understand the possible impacts of consuming berries contaminated by dust.

## 3.3 IMPLICATIONS

The combined results from Chapter 2 and the published paper in Appendix 1 show that dust contamination is impacting trace element concentrations of berries growing in the ABSR. The concentrations of conservative lithophile elements are elevated in berries located near upgraders and open pit mines compared to berries grown in remote locations. This is mainly due to the increase in dust deposition associated with the berries. The increased dust deposition also increases human exposure to trace elements such as U, V, Y, and Pb. To fully understand the implications of the findings, toxicology testing should be conducted to better determine how ingested mineral matter affects human health.

The results provided in this Thesis should be used to inform future toxicology studies. Specifically, it would be important to discover whether there is an increased risk to human health associated with consuming berries grown in the ABSR. Even though washing the berries removes a significant amount of Al, Cr, Pb, U, V, and Y it would be useful to know whether washing is needed or not. From the findings presented in this Thesis it is recommended that the berries collected in the ABSR should be washed before consumption, because the interaction of these dust particles within the human body remains unclear.

It would also be important for the information presented here to be communicated to Aboriginal communities in the area. This Thesis presents data on trace elements in berries, a traditional food for Aboriginal peoples, and could assist local Aboriginal groups to better understand the impact of the bitumen mining industry on their traditional diet.

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# APPENDIX 1: A GEOCHEMICAL PERSPECTIVE ON THE NATURAL ABUNDANCE AND PREDOMINANT SOURCES OF TRACE ELEMENTS IN CRANBERRIES (*VACCINIUM OXYCOCCUS*) FROM REMOTE BOGS IN THE BOREAL REGION OF NORTHERN ALBERTA, CANADA

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# A geochemical perspective on the natural abundance and predominant sources of trace elements in cranberries (*Vaccinium oxycoccus*) from remote bogs in the Boreal region of northern Alberta, Canada☆

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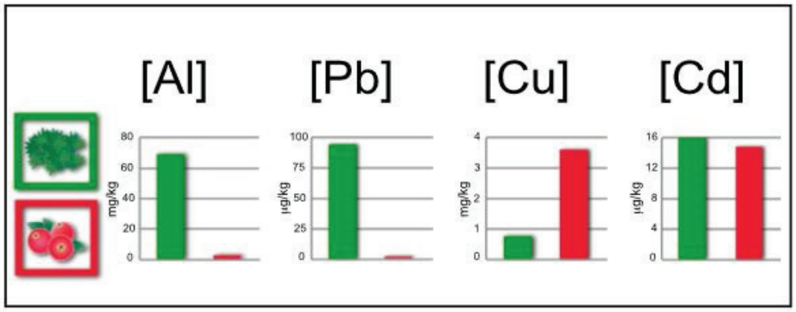
## GRAPHICAL ABSTRACT



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## ABSTRACT

Trace elements in native cranberry (*Vaccinium oxycoccus*) were compared with the underlying *Sphagnum* moss on which it grows, from two remote ombrotrophic (rain-fed) peat bogs in northern Alberta, Canada. The purpose of the comparison was to distinguish between dust inputs to the berries versus plant uptake from the substrate, and to determine the natural abundance of trace elements in native berries. Using Al as an indicator of the abundance of soil-derived mineral particles, the abundance of dust on the surface of the berries is 20 to 29× lower than that of the substrate (moss). Other lithophile elements (V, Cr, Co, Ga, Li and Y) show similar differences between moss and berry. The concentrations of Rb and Ba in berries were similar to moss and Sr within a factor of 3 to 4×, probably reflecting passive uptake of these lithophile elements by the plants, even though they have no known physiological function. Of the micronutrients examined (Mn, Fe, Ni, Cu, Zn and Mo), Cu and Mn were more abundant in berries than moss, Ni and Zn yielded similar concentrations in both whereas Fe followed by Mo showed the greatest concentration difference. For these micronutrients, uptake by the plants through their roots via the substrate (moss and peat) outweighs contributions from atmospheric dusts.

In respect to potentially toxic "heavy metals", Pb concentrations in the moss (BMW, 89 ± 7.3 µg/kg; CMW, 93 ± 27 µg/kg) are below the natural, "background" values reported for ancient layers of Swiss peat from the mid-Holocene (>6000 years old). The Pb concentrations in the berries, however, are 19 to 47× lower than in the underlying moss indicating that Pb in the berries, like Al, is exclusively supplied by dust. Cadmium in the berries is at or above the level found in moss due to active uptake by the plants from the substrate, most likely because of the chemical similarity of this element to Zn. Silver, Sb and Tl in the berries were <LOD, but assuming that they are

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supplied exclusively by dust inputs, their concentrations in the berries can be estimated from the Al concentrations. Taken together, these data provide an estimate of the natural abundance of these elements in berries, based on measured (Cd, Pb) and calculated (Ag, Sb, Tl) values.

## 1. Introduction

Trace elements such as Ni, Cu and Zn are, on the one hand, potentially toxic "heavy metals" (Duffus, 2002) which are released to the environment from industrial activities such as mining and smelting of base metal ores, coal combustion, waste incineration, and cement manufacturing (Nriagu, 1990; Rauch and Pacyna, 2009). At the same time, however, these same elements are essential micronutrients for all plants and animals and there are diverse, complex, biological processes which give rise to their natural enrichment in biota (Fraústo da Silva and Williams, 2001). In studies of environmental contamination of terrestrial plants, it can be difficult to discern how much of any given element may be due to environmental contamination from human activities and how much due to plant uptake from the substrate (Martin and Coughtrey, 1982). In addition to atmospheric contamination and biological uptake from soils, a third potentially important source of these metals to plants is atmospheric deposition of soil-derived mineral dusts. Fortunately, there are elements known to be essentially unavailable to plants (e.g. Al, Sc, Y, Th), due largely to the insolubility of their host minerals (Jackson and Sherman, 1953), their tendency to hydrolyze in aqueous solution (Chesworth, 1992) combined with the low solubility of their hydroxides (Baes and Mesmer, 1976) plus their lack of physiological role (White and Brown, 2010). Elements such as these (Al, Sc, Y, Th), therefore can be used to quantify aerial inputs to plants from dust (Mitchell, 1960; Bargagli et al., 1995; Pospiech et al., 2017). By comparing the abundance of these two types of elements, namely those that are essential versus those that are unavailable, in plants from remote locations where anthropogenic inputs are negligible, it should be possible to provide insight into the natural abundance of micronutrients such as Ni, Cu and Zn.

This same approach - comparing the abundance of essential trace elements with elements which are effectively unavailable to plants except from aerial deposition - might also provide insight into the sources of potentially toxic elements such as Ag, Cd, Pb, Sb and Tl. These elements serve no physiological roles in plants, and their geochemical cycles have been profoundly affected by human activities since the dawn of mining and metallurgy (Nriagu, 1985). Although they are not required by plants, plant uptake of Cd from soil, for example, is well known (Adriano, 2001). By comparing the abundance of potentially toxic elements in plants from remote areas with elements which are unavailable to plants (Al, Sc, Th, Y), it should be possible to determine the extent to which Ag, Cd, Pb, Sb and Tl are taken up by the plant from the soil. In addition, knowledge of the natural abundance of these elements in plant materials from remote locations would yield natural, "background" values against which plant samples from impacted regions could be compared. The wilderness regions of northern Alberta provide unique opportunities for these types of investigations. To date, there are very few studies of the natural abundance of trace elements in wild berries (Rodushkin et al., 1999), and we know of no studies of trace elements in bog cranberries from remote locations.

The purpose of this study of native berries is threefold: first, to determine which lithophile elements (Al, Ba, Be, Li, Rb, Sc, Sr, Th, U, Y) are most representative of dust inputs to the berries selected for study. Second, to then estimate the contribution of soil-derived dust particles to the contents of plant micronutrients (Cu, Fe, Mn, Mo, Ni, Zn) in berries. Third, to estimate the contribution of soil-derived dust particles to the contents of potentially toxic "heavy metals" (Ag, Cd, Pb, Sb and Tl). The berries examined here were collected from two remote locations in northern Alberta which leads to a fourth objective, namely, to estimate the natural abundance of all these elements in berries from regions largely unaffected by atmospheric contamination. The Pb concentrations in moss samples from these areas, presented below, provide original and independent evidence of the lack of trace metal contamination from human activities.

The focus of this study is the native cranberry (*Vaccinium oxycoccus*) which is found in *Sphagnum*-dominated, ombrotrophic (i.e. rain-fed) peat bogs throughout the Boreal zone of the northern hemisphere. Four species of these berries are recognized in Canada, and all are important foods for First Nations peoples across northern North America (Kuhnlein and Turner, 1991). The surface layers of ombrotrophic bogs are hydrologically isolated from surface waters and groundwaters, and receive inputs exclusively from the atmosphere (Shotyk, 1996). *Sphagnum* moss, having no roots, is completely dependent on the air for its mineral nutrition: rain and snow, plus dust. In contrast, the cranberry plants have roots, and therefore receive nutrients both from the atmosphere as well as the substrate which, in the case of bogs, consists mainly of moss and peat (Shotyk, 1988). Peat represents an accumulation of fossil plant matter in various stages of decay, and, in the case of bogs of the northern hemisphere, is dominated by *Sphagnum*. By comparing the concentrations of trace elements in berries (inputs from air + substrate) with the data for moss (inputs only from air), we are able to quantify the contribution of the substrate to the trace element inventory of the berries.

## 2. Materials and methods

### 2.1. Locations of sites investigated

The bogs are located in the Birch Mountain Wildlands and the Caribou Mountain Wildlands, approximately 135 and 365 km, respectively, NW of the Town of Fort McMurray in northern Alberta (Fig. 1). These areas are part of the Lower Boreal Highlands (Natural Regions Committee, 2006) which are characterized by an average annual temperature of −1 °C, with 97 frost-free days per year and 495 mm of mean annual precipitation (334 mm during the growing season). Both sites were accessed using helicopter.

### 2.2. Birch Mountain Wildlands

The Birch Mountain Wildlands (1445 km$^2$) are located within the Birch Mountains of northern Alberta. A wilderness region accessible only by air and in winter by snowmobile, it is known for one of Canada's few remaining herds of free-roaming wood bison (*Bison bison athabascae*). Sampling was undertaken on September 6, 2015, within an area of open, dwarf shrub *Sphagnum* bog, ca. 100 m wide and 300 m long, underlain by at least 3.5 m of peat, and part of a huge peatland complex. Samples were collected at least 300 m from the landing area of the helicopter. The site where the samples were collected (N 57° 34.866′, W 112° 55.992′) is 59 km from the nearest road. The species of *Sphagnum* harvested included *S. fuscum, magellanicum, angustifolium and Warnstorffi* (Mullan-Boudreau et al., 2017). The ash contents of the moss samples ranged from 1.6 to 1.8% and the dry matter accumulation rates were 373 ± 78 g/m$^2$/yr (Mullan-Boudreau et al., 2017).

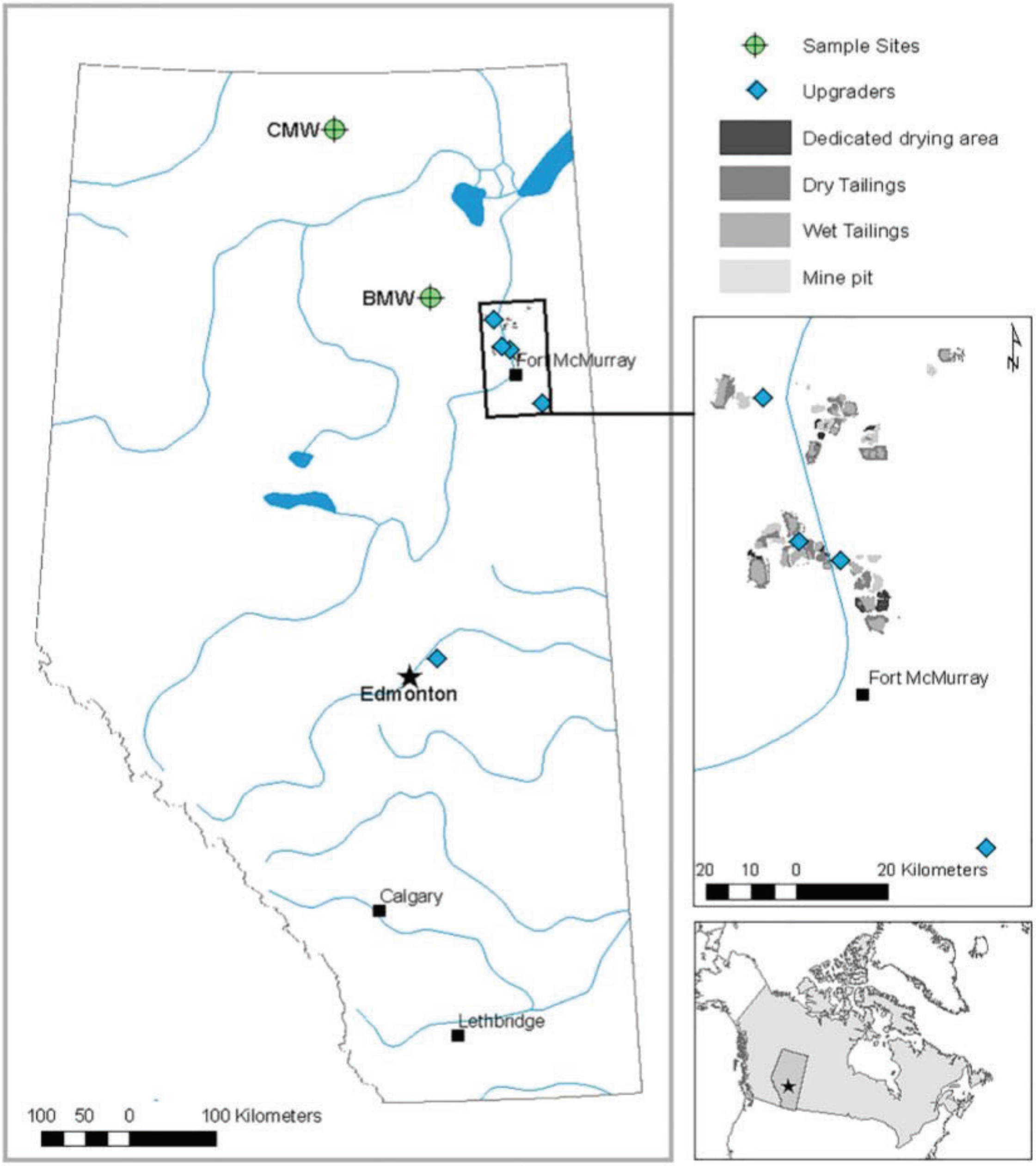

**Fig. 1.** Locations of the sampling sites within the Birch Mountain Wildlands and Caribou Mountain Wildlands Parks. Inset: location of open pit bitumen mines and upgraders in the vicinity of Fort McMurray.

### 2.3. Caribou Mountain Wildlands

The Caribou Mountain Wildlands (5900 km$^2$) are located in the Caribou Mountains, west of Wood Buffalo National Park. An even more remote wilderness region than Birch Mountains, it is known for providing core habitat for Canada's threatened boreal woodland caribou (*Rangifer tarandus caribou*). Sampling was undertaken on September 5, 2015, within a small, circular peat bog, ca. 35 m in diameter, again part of a much larger complex surrounded by lichen covered peatlands with abundant black spruce (*Picea mariana*). Samples were collected ca. 350 m from the landing area of the helicopter, in an area underlain by at least 1.5 m of peat. The site where the samples were collected (N 59° 23.413′, W 114° 45.087′) is 89 km from the nearest road. The samples consisted exclusively of *Sphagnum fuscum* with ash contents ranging from 1.1 to 1.4% and the dry matter accumulation rates were 378 ± 103 g/m$^2$/yr (Mullan-Boudreau et al., 2017).

### 2.4. Moss and berries

Triplicate samples of *Sphagnum* moss along with samples of native cranberries (*Vaccinium oxycoccus macrocarpum* and *Vaccinium oxycoccus microcarpum*) were collected from each site. Volumetric samples of

*Sphagnum* were collected in polypropylene boxes from three locations in each bog using the procedure described in detail elsewhere (Mullan-Boudreau et al., 2017). Cranberries were harvested by hand while wearing polyethylene gloves, but the two types of berries were combined into a single, composite sample from each bog, and no effort was made to distinguish any possible differences between the berries from the two plant species. Cranberry plants are very small and occupy a very small part of the bog surface (Fig. 2). In addition, the berries themselves are small (*macrocarpum*) or tiny (*microcarpum*). To obtain sufficient material for chemical analyses, berries were picked at random from within an area of approximately 1 ha of the bog to form one bulk sample from each site.

### 2.5. Peat and porewater

To confirm that the bogs are ombrotrophic, peat cores were collected from each bog to allow pH and electrical conductivity (EC) to be determined in the porewaters. Peat cores were collected using a modified Wardenaar monolith sampler (Wardenaar, 1987) as described in detail elsewhere (Shotyk et al., 2016, 2017). The peat cores (ca. 15 × 15 × 100 cm long) were extracted from the corer, photographed, wrapped in polyethylene cling film, then packed into wooden boxes in the field. In the lab, the cores were frozen at −18 °C. The living (green) layer at the top of the peat core is removed first: although this material represents the first sample in each peat bog profile, this is living plant material and not peat. The remainder of each core was then cut precisely into 1 cm slices, while frozen, using a stainless steel band saw and polypropylene cutting table. The edges (1 cm) were trimmed away from each slice and, after warming the samples to room temperature over 24 h, the porewaters were extracted from i) the living layer, ii) every odd-numbered slice, and iii) the last layer of each core. Porewaters were extracted from the moss and peat samples using luer-slip plastic syringes (10 mL), then filtered through a syringe filter (0.45 μm, PTFE, 30 mm) into microcentrifuge tubes (1.5 mL) The pH and EC were determined using a combination electrode (Mettler Toledo Seven Excellence pH/ORP/Ion/Conductivity/DO Meter). The instrument was calibrated before each core was analyzed using relevant standards.

### 2.6. Analytical methods

Moss and berries were kept cool during transport and frozen (−20 °C) immediately upon arrival in the lab. Prior to analysis, the moss samples were thawed, cleaned by hand-picking using surgical stainless steel (316) tweezers to remove foreign plant materials, and the living layer corresponding to annual growth during the year of collection, removed for analysis (approximately top 2 cm of each stem). Moss was oven dried (at 105 °C to constant weight), milled in an agate centrifugal ball mill (Retsch PM 400, Haan, Germany) and digested in nitric acid in a high pressure microwave autoclave (Ultraclave, MLS, Leutkirch, Germany) as described in detail elsewhere (Shotyk et al., 2014). The nitric acid used for acid-digestion was purified by sub-boiling distillation, twice, in a quartz still (MLS Duopur, Leutkirch, Germany). The berry samples were also oven dried, but ground by hand using an agate mortar and pestle; the berries were digested using the same procedure as the moss.

Once the samples had been dried and milled, all of the subsequent work was undertaken in the metal-free, ultraclean SWAMP lab (www.swamp.ualberta.ca) within polypropylene, Class 100, laminar flow clean air cabinets. Trace elements were determined using quadrupole ICP-MS (ICAP Qc, Thermo Fisher) as described in detail elsewhere (Shotyk et al., 2017). For QA/QC, the following certified, Standard Reference Materials (SRMs) were analyzed: NIST 1515 Apple Leaves, NIST 1547 Peach Leaves, and Moss HB 36. The list of elements analyzed, the lower limits of detection obtained, and the accuracy and precision of the measurements (based on the measurements of the SRMs), are listed in Supporting information Table 1.

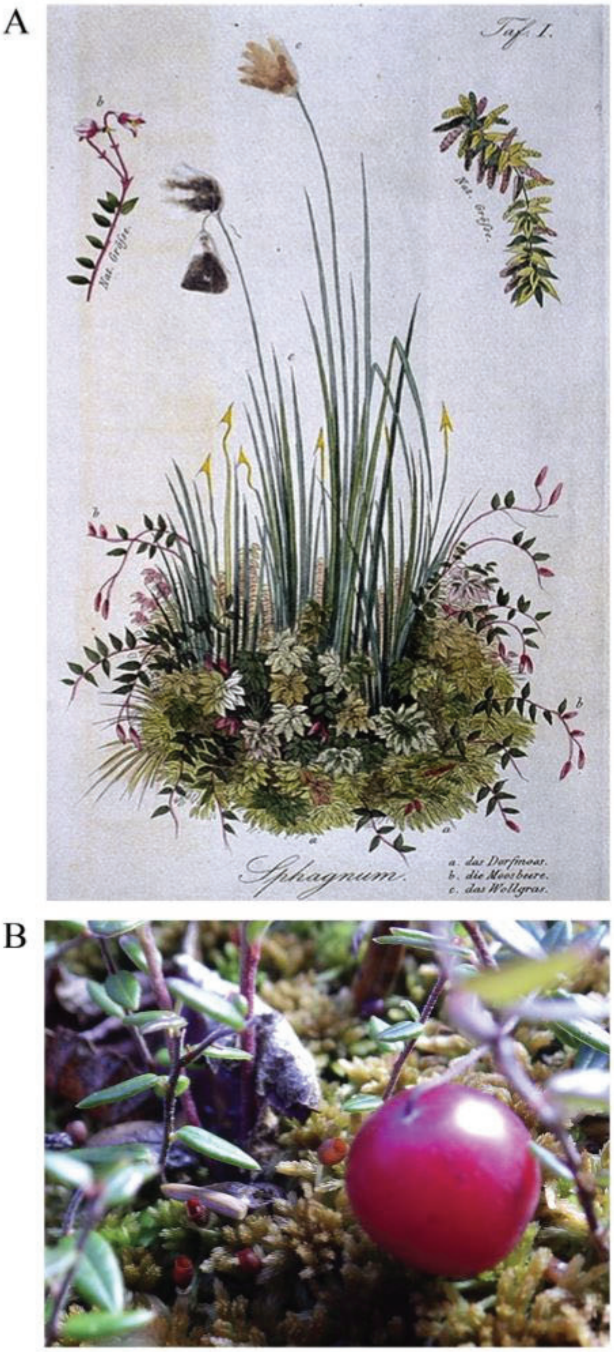

**Fig. 2.** A) Illustration of bog surface vegetation, comparing the relative sizes of *Sphagnum* moss and the cranberry plant (*Vaccinium oxycoccus*), drawn at the same scale (from Moser, 1840). B) Photograph of a cranberry fruit growing on a carpet of *Sphagnum* moss; notice the size of the fruit compared to the leaf of the same plant.

## 3. Results

### 3.1. The ombrotrophic condition of the bogs

The pH and EC of the porewaters confirm are well within the range presented elsewhere for ombrotrophic bogs (Gorham et al., 1985;

Shotyk, 1989). The EC of the porewaters extracted from the living layer and near-surface peat layers is elevated relative to underlying waters (Fig. 3), and this is attributed to efficient uptake and recycling of nutrients (e.g. K, Mg, Ca, P, S) from precipitation by the bog plants (Damman, 1978). Below a depth of 25 cm, the EC values are 55 ± 11 μS/cm at BMW (n = 36) and 68 ± 11 μS/cm at CMW (n = 36) which are in the range reported for continental rainwater (Krämer et al., 1996). Again, below a depth of 25 cm, the pH values average 4.1 ± 0.1 at BMW and 4.0 ± 0.1 at CMW which are characteristic of bog waters from around the world, and diagnostic of their ombrotrophic condition (Shotyk, 1988). Taken together, the pH and EC values presented here support the view that trace elements in the *Sphagnum* moss collected from these bogs were supplied exclusively from the atmosphere.

### 3.2. Anthropogenic, atmospheric inputs of trace elements to the bogs

The average Pb concentrations in the moss samples from BMW and CMW are 89 ± 7.3 μg/kg and 93 ± 27 μg/kg, respectively (Supporting information, Table 2). For perspective, these Pb concentrations are below those reported for ancient layers of Swiss peat from the mid-Holocene (Shotyk et al., 1998). Specifically, peat samples between ca 6000 and 9000 years old yielded 280 ± 50 μg/kg of Pb (n = 17) which represents the lowest Pb concentrations thus far reported for peat in the northern hemisphere (Shotyk et al., 1998). The average concentrations of Pb in the moss samples combined with the average dry matter accumulation rates presented earlier, yield the following rates of atmospheric Pb deposition: BMW, 33 μg/m$^2$/yr and CMW, 35 μg/m$^2$/yr. For perspective, the lowest rates of atmospheric Pb deposition reported for the Swiss peat bog was 10 μg/m$^2$/yr. The lower, pre-anthropogenic Pb accumulation rate at the Swiss bog may be related to differences in climate: with an average annual temperature of 5.5 °C and 1300 mm of precipitation (Steinmann and Shotyk, 1997), the Swiss site is in a region which is much warmer and far wetter than BMW and CMW (−1 °C and 495 mm of mean annual precipitation) and therefore the importance of wet deposition may be very different between the two regions. Perhaps a more relevant comparison is the Pb to Sc ratio, where Pb is taken to represent natural plus anthropogenic metal inputs whereas Sc in peat is exclusively from natural sources (see Shotyk et al., 2001, for discussion). The natural background ratio of Pb to Sc ratio of the Swiss peat samples was 4 (Shotyk et al., 1998); for comparison, the Pb to Sc ratio in the moss samples studied here ranges from 4 (BMW) to 9 (CMW). For additional perspective, the Pb/Sc ratio of Arctic ice dating from the mid-Holocene is 6.3 ± 1.8 (Zheng et al., 2007). Thus, the Pb/Sc ratio in the moss from BMW and CMW is similar to the pre-industrial, background value for the mid-Holocene from continental Europe as well as the Arctic. Lead is probably the single most representative tracer of atmospheric metal inputs from industrial activities (Shotyk and Le Roux, 2005). Thus, the moss samples from BMW and CMW, with their low i) Pb concentrations, ii) Pb accumulation rates, and iii) Pb to Sc ratios, indicate that Pb inputs to these bogs today are comparable to, or at least approaching natural, "background" values; we assume that this is the case for other trace elements. Following this interpretation, given that the cranberry plants are growing on the moss carpet of these bogs, we further assume that the concentrations of trace elements in the berries are also comparable to, or at least approaching, natural, background levels.

### 3.3. Conservative, lithophile elements

Aluminum concentrations are greater in the moss from BMW (129 ± 6 mg/kg) compared to CMW (69 ± 16 mg/kg) and, given that moss receives metals exclusively from the air, these differences are assumed to reflect differences in the abundance of soil-derived dust particles (Rahn, 1976). Compared to moss, the concentrations of Al in the berries are far lower at both sites: 6.5 mg/kg at BMW and 2.4 mg/kg at CMW (Fig. 4). The large ratio of Al in moss to berry (20 and 29 at BMW and

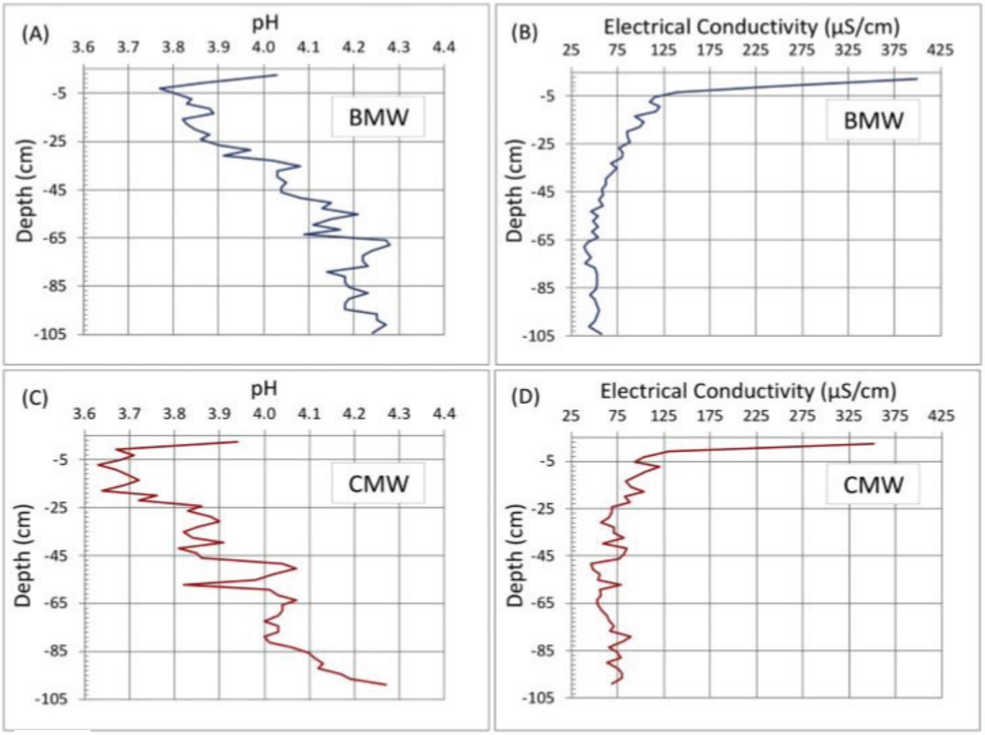

**Fig. 3.** pH and electrical conductivity (μS/cm) of the porewaters from the peat core collected at BMW (A, B) and CMW (C, D).

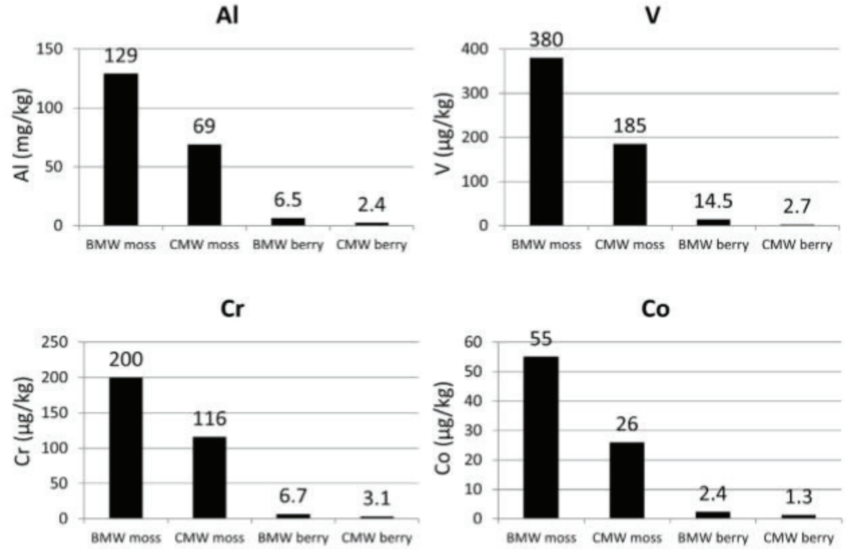

**Fig. 4.** Concentrations of Al (mg/kg) and V, Cr and Co (µg/kg) in moss from BMW and CMW versus cranberries from these two bogs.

CMW, respectively; see Table 1) suggests that either uptake of Al by the plants via their roots is neglible, retention of dust particles on the berry surface is inefficient, or both. The conservative behavior of Al during the weathering cycle is firmly established: during chemical weathering of primary minerals in soils, by far the majority of Al becomes incorporated into phyllosilicate clays (Chesworth, 1992), and the small amounts released to aqueous solution become hydrolyzed and precipitate as insoluble hydroxides such as gibbsite ($Al(OH)_3$, loq $K_{sp} = -34$; Singh, 1974) or amorphous aluminum hydroxides (Driscoll and Schecher, 1990). Because plants do not actively take up Al from the soil solution to any significant extent (Hutchinson, 1943; Adriano, 2001), the Al content of plant leaves is a reflection of the abundance of atmospheric dust particles (Mitchell, 1960; Bargagli et al., 1995; Pospiech et al., 2017). Given that *Sphagnum* has no roots, we assume that the Al content of this moss is a direct reflection of the concentration of soil-derived mineral particles. Moreover, given that both of these bogs are in remote wilderness locations, the source of the Al is assumed to consist mainly of clay-size mineral particles i.e. <2 µm supplied by long-range atmospheric transport (Schütz, 1989; Schütz and Rahn, 1982). Because the rate of moss growth is virtually identical at the two locations (373 and 378 g/m$^2$/yr at BMW and CMW, respectively), it appears that dust deposition at BMW is greater than that seen at CMW; this is consistent with the slightly greater ash contents of the moss from BMW (1.6 to 1.8%) compared to CMW (1.1 to 1.4%).

**Table 1**
Ratios of trace element concentrations in Sphagnum moss to cranberry.

| Element | BMW | CMW |
|---|---|---|
| *Conservative, lithophile elements* | | |
| Al | 20 | 29 |
| Co | 23 | 20 |
| Cr | 30 | 37 |
| Ga | 9 | 40 |
| Li | 19 | 5 |
| U | 34 | 56 |
| V | 26 | 69 |
| Y | 25 | 40 |
| *Other lithophile elements* | | |
| Rb | 0.8 | 0.5 |
| Sr | 3.9 | 2.6 |
| Ba | 1.3 | 1.1 |
| *Micronutrients* | | |
| Cu | 0.4 | 0.2 |
| Fe | 7.8 | 5.9 |
| Mn | 0.7 | 0.7 |
| Mo | 9 | 12 |
| Ni | 0.9 | 1.0 |
| Zn | 1.0 | 0.9 |
| *Potentially toxic "heavy metals"* | | |
| Ag | NA | NA |
| Cd | 1.6 | 1.1 |
| Pb | 19 | 47 |
| Sb | NA | NA |
| Tl | NA | NA |

NA = not available.

Other elements which show similar differences in concentration between moss and berry include V, Cr, Co (Fig. 4) as well as Ga, Li, Y and U (Fig. 5). It can reasonably be expected that Be may, and certainly Sc and Th should exhibit comparable differences between moss and berry, based on the geochemical behavior of these elements in weathering environments (Chesworth, 1992). However, the abundance of these elements in the berries is below our abilities to measure them (Fig. 6). Assuming that the ratio of Al in moss to berry applies also to these elements, we estimate the following concentrations (µg/kg) in berries from BMW and CMW: Be, 0.15, 0.06; Sc, 1.2, 0.34; Th, 1.2, 0.42. The Th concentrations in the berries were <LOD (0.06 µg/kg) which is well below the predicted values, perhaps due to winnowing of Th-bearing heavy minerals such as monazite and zircon during atmospheric transport, or poor retention of these minerals on the surface of the berries.

### 3.4. Other lithophile elements (Ba, Rb, Sr)

Rubidium, Sr, and Ba are also lithophile elements, but the differences in concentration between moss and berry are small (Fig. 7). In fact, Rb is more abundant in the berries than in the moss. Either the host minerals of these elements are dissolving in the acidic peat bog environment, or there is active uptake of these elements by the berry plants from the aqueous phase (snowmelt plus rain), or both. There is very little evidence of significant dissolution of silicate and aluminosilicates in acidic peat bogs: even after thousands of years of burial, quartz, plagioclase, potassium feldspar, micas, amphiboles and pyroxenes are well preserved (Sapkota et al., 2007). In contrast to the silicates, carbonate

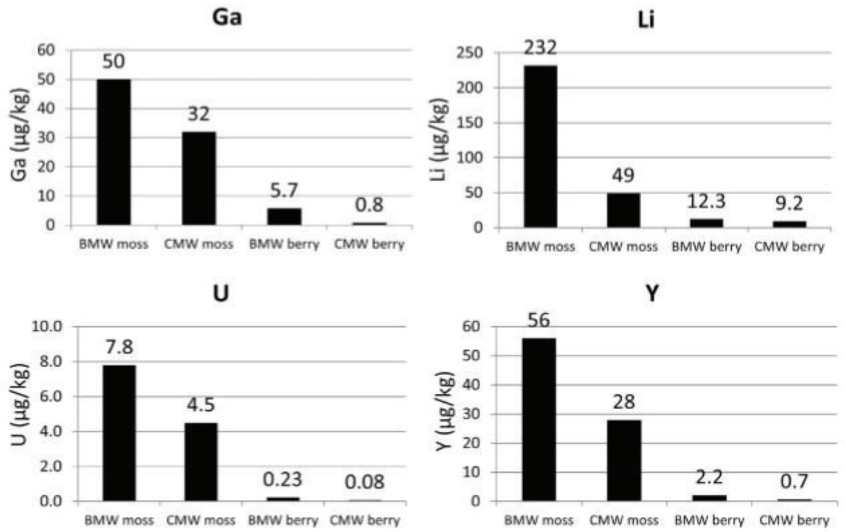

**Fig. 5.** Concentrations of Ga, Li, U, and Y (μg/kg) in moss from BMW and CMW versus cranberries from these two bogs.

and phosphate minerals dissolve readily in acidic bog waters (Le Roux et al., 2006), and these are the obvious sources of Sr and Ba. Thus, uptake of these elements by the plants from the substrate is a more likely explanation of the relative abundance of these elements in the berries. Although these elements are not essential for plants (White and Brown, 2010), K, Mg and Ca are efficiently recycled by bog plants, and enriched in the surface layers of peat profiles (Damman, 1978). Given that K/Rb and Mg/Ca/Sr/Ba have the same ionic charge and similar ionic radii (Chesworth, 1992), it seems reasonable to suggest that the plants may be inadvertently taking up Rb in place of K, plus Sr and Ba in place of Mg and Ca.

### 3.5. Micronutrients (Cu, Fe, Mn, Mo, Ni, Zn)

These elements are essential for all plants (White and Brown, 2010). The concentrations of Mn in the berries exceed the values found in moss whereas Fe is 6 to 8 x more abundant in moss compared to the berries (Fig. 8). Recalling that dust concentrations, as indicated by Al (Fig. 3), are 20 to 29 times greater in moss compared to berries, Mn is strongly enriched in the berries, compared to dust. We note further that Mn is four or five times more abundant in moss compared to Fe which is remarkable, considering the fact that the abundance of Fe in the Upper Continental Crust is approximately 50 times that of Mn (Rudnick and Gao, 2014), and that there is a comparable concentration difference between the two elements in soil-derived mineral dusts (Schütz and Rahn, 1982). The chemical composition of moss and berry, therefore, reveal profound biogeochemical transformations of both elements at the surface of the bogs. It is well known that Fe-bearing silicates are rapidly attacked in acidic, organic-rich, anoxic bog waters because of reductive dissolution (Shotyk, 1992; Le Roux and Shotyk, 2007), and the same should happen to Mn-bearing solids: evidence for this comes from the elevated concentrations of dissolved Mn in bog waters (Robinson, 1930). In acidic, anoxic, ombrotrophic peat, both Fe and Mn become depleted over time, relative to their crustal abundance (Shotyk et al.,

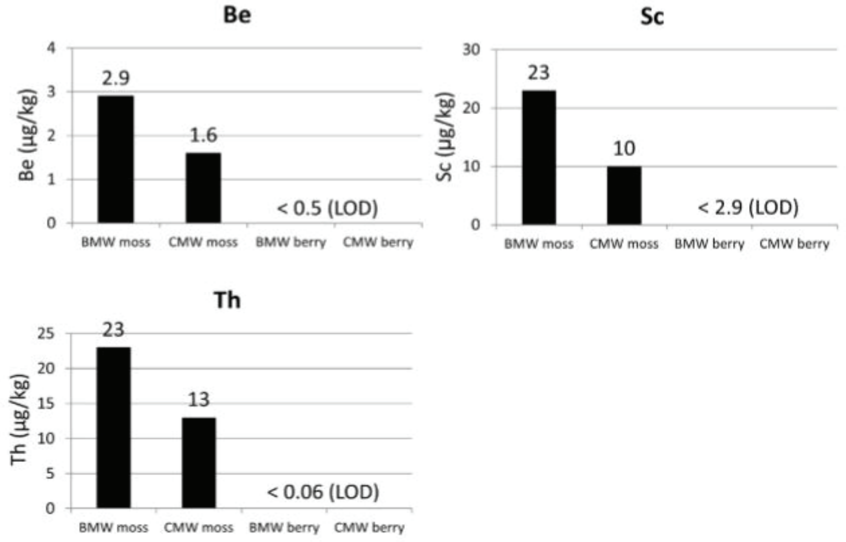

**Fig. 6.** Concentrations of Be, Sc and Th (μg/kg) in moss from BMW and CMW. The concentrations in the berries were below the LODs which were 0.5, 2.9 and 0.06 μg/kg, respectively.

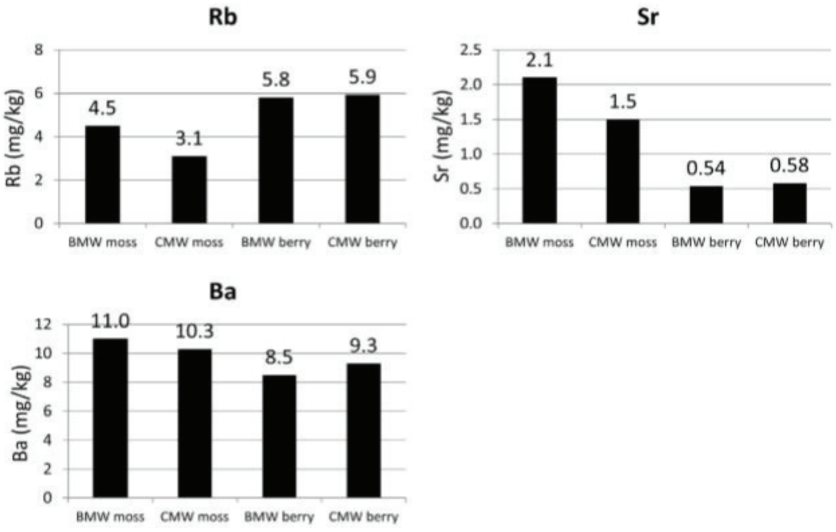

**Fig. 7.** Concentrations of Rb, Sr, and Ba (mg/kg) in moss from BMW and CMW versus cranberries from these two bogs.

1990). Manganese, however, is enriched in the surface peat layers of bogs (Feustel and Byers, 1930) whereas Fe is not (Shotyk et al., 1992). Atmospheric dusts supplied to the bogs contain far more Fe than Mn, and it appears that both elements are liberated by the reductive dissolution of solids in the anoxic peat because bog waters are enriched in both elements. The berries, however, clearly indicate a strong preference for Mn over Fe. Regardless of how the concentrations are viewed, Mn is highly enriched in the berries.

Nickel and Zn concentrations in the berries are similar to the values for moss (Fig. 9), so both of these elements, like Mn, must be readily bioavailable to the berry plants. Like Mn, it is well known that Ni and Zn are both mobile in acidic bog waters (Rausch et al., 2005) and their relative abundance in the berries is consistent with their geochemical behavior in bog environments.

Copper is unique in that it is 3 to 4× more abundant in the berries than in the moss (Fig. 9). This circumstance suggests that either Cu is readily available to the plants, or that the plants have a mechanism for actively obtaining this element. It seems very unlikely that Cu is readily bioavailable in bog ecosystems, for several reasons. First, because Cu is supplied exclusively from the atmosphere, the amount of dissolved Cu being supplied to the bog must be very small. Second, most of Cu deposited from the air will be in the form of soil-derived silicate minerals which will dissolve only very slowly, if at all, in the peat (Sapkota et al., 2007). Third, Cu is strongly complexed by natural organic matter, especially by peat (Tummavuori and Aho, 1980) which is one of the reasons it is effectively immobile in peat profiles (Jones and Hao, 1993; Rausch et al., 2005). In fact, Cu is one of the least available micronutrients in peatlands drained for agriculture, and invariably has to be added to fertilizers for vegetable production on organic soils (Mathur et al., 1984). The more likely possible explanations for the strong Cu enrichment in the berries are that 1) the cranberry plant actively stores Cu in its tissue and creates a reservoir of this element (Oregon State University, 2015), 2) the cranberry plant is assisted in nutrient uptake by mycorrhizae (Marschner and Dell, 1994), or some combination of these. Whatever the underlying cause of the Cu enrichment in the berries, from a biogeochemical perspective, it is remarkable.

Molybdenum is more enigmatic than the other micronutrients, because the concentrations in the berries are so low compared to the moss. Recently it was found that *Sphagnum* moss receives assistance in satisfying its nitrogen needs by virtue of $N_2$-fixing prokaryotes (Vile et al., 2014). Given that nitrogen fixation involves Mo as catalyst (Fraústo da Silva and Williams, 2001), it may be that there is competition for Mo between plant and microbial communities in bog ecosystems.

### 3.6. Potentially toxic, chalcophile elements (Ag, Cd, Pb, Sb, Tl)

Of the potentially toxic chalcophile elements, only Cd and Pb could be measured in both moss and berries; Ag, Sb and Tl could be measured in moss only (Fig. 10). Concentrations of Cd in the berries are within a factor of 2 of the moss which suggests active uptake by plants, even though this metal has no physiological role. In this respect, the behavior of Cd is similar to that of Zn, and the biogeochemical similarity of these two elements in soil-plant systems is well known (Adriano, 2001). In contrast, Pb in the berries is far less abundant than in the moss: the ratio of Pb in moss to berry at BMW (19:1) and CMW (47:1); these ratios are similar to those found for conservative, lithophile elements such as Al, Cr, Co, Ga, U, V and Y (Table 1), suggesting that Pb is supplied to the berries almost exclusively by atmospheric deposition of soil-derived dust, with little or no

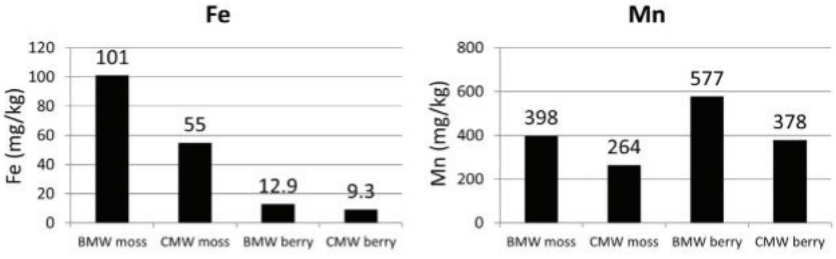

**Fig. 8.** Concentrations of Fe and Mn (mg/kg) in moss from BMW and CMW versus cranberries from these two bogs.

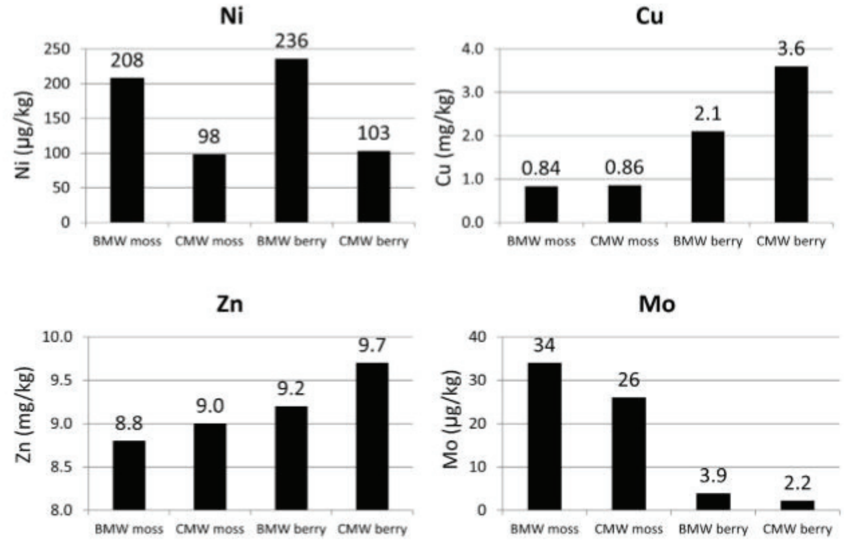

**Fig. 9.** Concentrations of Ni, Cu, Zn and Mo in moss from BMW and CMW versus cranberries from these two bogs. Note that Cu and Zn are in units of mg/kg whereas Ni and Mo are in units of µg/kg.

uptake of Pb by plants. In fact, there is very little, if any, documented evidence of Pb uptake by plants via roots (Shotyk and Le Roux, 2005). The ratio of Pb to Cd in the Upper Continental Crust is 189 to 1 (Rudnick and Gao, 2014), and we assume it is similar in soil-derived aerosols. The ratio of Pb to Cd in the berries, however, is far smaller: 7.4 at BMW and 5.8 at CMW. Clearly, there is a strong preference for Cd uptake by the plant, compared to Pb.

## 4. Discussion

### 4.1. Atmospheric dust deposition rates at BMW versus CMW

The Caribou Mountain Wildlands are far more remote than the Birch Mountain Wildlands, and the moss samples contain less ash (1.1 to 1.4% at CMW versus 1.6 to 1.8% at BMW) and lower concentrations of conservative, lithophile elements (Figs. 4-6). Given the similar rates of moss growth, the data suggests that atmospheric dust deposition rates are lower at CMW than at BMW. For example, considering the Al concentrations (69 ± 16 mg/kg at CMW versus 129 ± 6 mg/kg at BMW) and the rates of moss growth (378 $g/m^2/yr$ at CMW versus 373 $g/m^2/yr$ at BMW), the following Al accumulation rates are obtained: 26 $mg/m^2/yr$ at CMW and 48 $mg/m^2/yr$ and BMW. For trace elements that are supplied to the bog mainly in the form of particulate matter, inputs of these elements to the bog at BMW are approximately twice that of the bog at CMW. Elevated Al inputs to the BMW bog may be related to dusts generated from open-pit mining of the Athabasca Bituminous Sands (Mullan-Boudreau et al., 2017); these ores contain clays such as kaolinite and illite (Gosselin et al., 2010) which can be transported in the atmosphere thousands of kilometers (Schütz, 1989). Regardless of the source of the dust, the

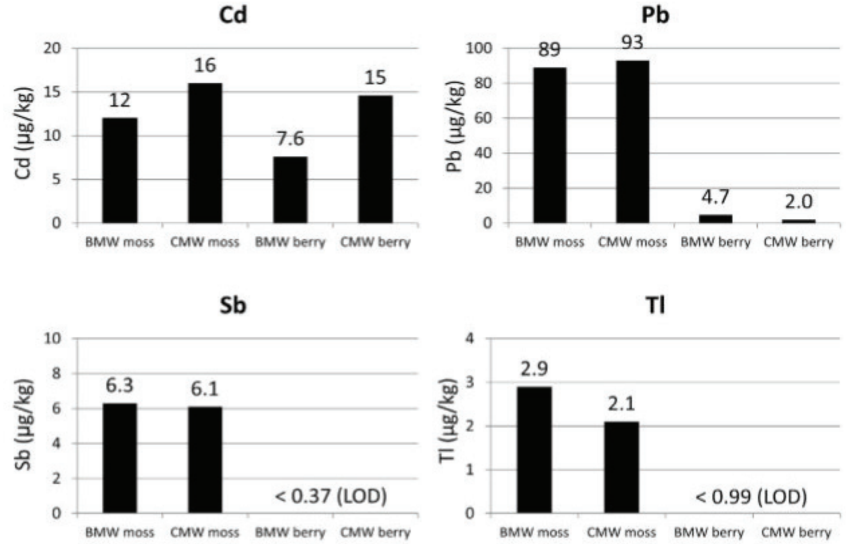

**Fig. 10.** Concentrations of Cd and Pb (µg/kg) in moss and berries from BMW and CMW, and concentrations of Sb and Tl in moss from these sites. The concentrations of Sb and Tl in the berries were below the LODs which were 0.37 and 0.99 µg/kg, respectively.

berries from CMW provide a better estimate of the natural composition of the wild cranberry.

### 4.2. Natural abundance of Ag, Cd, Pb, Sb, and Tl in moss

As noted earlier, the Pb concentrations in the moss are below the levels found in ancient peat from a Swiss bog, suggesting that contamination by heavy metals is insignificant at both sites. For additional perspective, we note that the average concentrations of Cd, Pb, Sb and Tl in BMW and CMW moss samples are 32×, 70×, 34× and 20×, respectively, lower than the corresponding values for the reference moss (Supporting information, Table 1). The reference moss (M2), however, was collected near the Harjavalta smelter in Finland (Steinnes et al., 1997) which has an established record of environmental contamination by trace elements (Rausch et al., 2005). Lead concentrations in the moss from BMW and CMW are 20 to 34× lower than the range in Pb values recently reported for forest moss (*Hypnum cupressiforme*) from a "presumably unpolluted region" of northern Spain (Boquete et al., 2016), and the Cd values in the Canadian moss are one-quarter the concentration of the Spanish moss. Moreover, if we compare the metal concentrations in the moss from BMW and CMW with moss from Antarctica (*Bryum psuedotriquetrum* and *Sarconeurum glaciale*), the Alberta moss samples are lower in respect to Ba (ca. 4×), Cd (ca. 6–10×), Cr (ca. 16×), Cu (ca. 8×), Ni (ca. 18×), Pb (ca. 18×) and Zn (ca. 4×). Thus, to the best of our ability, it would appear that the concentrations of potentially toxic trace elements (Ag, Cd, Pb, Sb, Tl) reported here for moss from BMW and CMW represent the natural abundance of these elements, or at least closely resemble the natural abundance of these elements. Given this circumstance, and given that the moss represents the rooting medium for the berries, the concentrations of these elements in the berries would appear to either represent, or at least approach, their natural abundance. With very few exceptions, the abundance of trace elements in bog cranberries from the CMW site are comparable to the data for published for lingonberries from remote locations in northern Sweden (Rodushkin et al., 1999).

### 4.3. The natural abundance of trace elements in cranberries

To the list of elements which were measured in the berries, the concentrations of Ag, Be, Re, Sb, Sc, Th and Tl were estimated (Supporting information, Table 3). The estimated concentrations are calculated using the abundances of these elements measured in moss, divided by the ratio of Al in moss to berry i.e.:

$$\begin{aligned}&(\text{Estimated element concentration in berry})\\&\quad=(\text{Measured element concentration in moss})\\&\qquad\div(\text{Ratio of Al in moss to berry})\end{aligned}$$

These estimated values may prove helpful in future studies, first and foremost to the analyst, to have some idea of the anticipated concentration of an element in uncontaminated berries, and to help design an appropriate analytical program. Some past studies of trace elements in wild berries have employed analytical methods and procedures which are inadequate for measuring potentially toxic trace elements such as Tl in wild berries (Hopkins et al., 2014), given their low natural abundance (e.g. Tl, <1 μg/kg). Second, they should be helpful to scientists engaged in the studies of berries as biomonitors of environmental contamination (Ward and Savage, 1994: Pöykiö et al., 2005) to have some idea of the natural abundance of the element, against which berries from impacted sites may be compared. To date berries have been used to study impacts from long-range atmospheric transport (Sheppard and Sheppard, 1991), contamination from smelters (Shaw, 1981; Barcan et al., 1998), roadside dusts (Fowles, 1976), and the effectiveness of land reclamation (Shorthouse and Bagatto, 1995), as well as to help estimate the effects of soil amendments on berry composition (Levula et al., 2000; Moilanen et al., 2006). For all of these studies, the natural composition of wild berries provides an essential point of reference.

### 4.4. The predominant sources of trace elements in cranberries

In the remote regions of northern Alberta, there are two principal sources of trace elements to the bog cranberry: atmospheric dust, and root uptake from the substrate. Based on the concentration differences between moss and berry, the following elements appear to be supplied to berries exclusively by soil-derived atmospheric dusts: Ag, Al, Be, Co, Cr, Ga, Li, Pb, Re, Sb, Sc, Th, Tl, U, V and Y. The berries from BMW yielded greater concentrations of Al, V, Cr, Co, Ga, Li, U, and Y than the berries from CMW; this is consistent with the greater rates of dust deposition at BMW as noted above. Thus, in the absence of anthropogenic inputs of specific elements, the abundance these elements in berries reflect the amount of dust they receive. In contrast to the conservative, lithophile elements, the following elements are to a lesser or greater extent, supplied to the berries by uptake from the roots: Ba, Cd, Cu, Fe, Mn, Ni, Rb, Sr, and Zn. Molybdenum appears to behave in a way which is intermediate between these two groups of elements and may have an independent biogeochemical cycle. Using the ratio of nutrient elements in berry to moss as a guide to the uptake efficiency by the plant from the substrate, this efficiency decreases in the order $\mathrm{Cu} > \mathrm{Mn} > \mathrm{Ni} = \mathrm{Zn} \gg \mathrm{Fe} > \mathrm{Mo}$.

### 4.5. The analytical challenges presented by trace elements in berries

We wish to emphasize the fact that, even with metal-free, ultraclean lab procedures and protocols, and state-of-the-art ICP-MS with quadrupole mass analyzer, the following elements could not be measured directly in the acid digests of the berries: Ag, Be, Re, Sb, Sc, Th and Tl. Given the estimated concentrations of these elements in the wild cranberries (Supporting information, Table 3), larger samples would have to be digested and/or pre-concentrated, to permit the determination of these elements. Any data being reported for these elements in berries from remote locations, should be viewed with caution. While berries from contaminated regions may contain elevated concentrations of elements such as Ag, Sb and Tl, depending on the source of the elements and many other factors, the extent of contamination will be difficult to quantify, until the natural abundance of these elements in berries from pristine regions is known.

### 4.6. Climate, atmospheric dust and the natural abundance of trace elements in berries

As noted above, many trace elements in berries are supplied exclusively from atmospheric dusts. Thus, for these elements, their abundance in the berries will reflect the rate of dust deposition in the region where the berries are collected. The rate of supply and the predominant sources of atmospheric dusts to ombrotrophic bogs have varied with climate change during the Holocene. For example, during the mid-Holocene climate optimum, the rate of dust supply to the Swiss peat bog EGR mentioned earlier, was 0.12 g/m$^2$/yr (Shotyk et al., 2001). Assuming that these dusts had the same abundance of Al as the UCC (i.e. 8.2% Al), this corresponds to an Al flux of 9.8 mg/m$^2$/yr. For comparison, the rates of Al deposition today at BMW and CMW are 26 mg/m$^2$/yr and 48 mg/m$^2$/yr, respectively. Thus, the dust deposition rates at BMW and CMW today are 2.5 to 5 times greater than the mid-Holocene values for central Europe. While it is tempting to suggest that these differences in dust deposition rates may be due to anthropogenic dust inputs to the BMW and CMW bogs, the differences might simply be a reflection of the differences in climate regime. For example, the average rate of dust deposition in the Oreste Bog from Patagonia, for the past 6000 years, was $0.43 \pm 0.12$ g/m$^2$/yr ($n = 145$; Sapkota et al., 2007) which 3× greater than that obtained from the Swiss bog. To determine whether or not dust deposition rates to the bogs at BMW and CMW are elevated today, compared to the past, detailed studies of past rates of dust deposition using peat cores could be very helpful. An understanding of past rates of dust deposition to these two remote regions, using the peat cores as archives of dust accumulation rates in the past, will provide a clearer picture of the natural abundance of many trace elements in wild berries.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.06.248.

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# APPENDIX 2 : SUPPORTING INFORMATION

| Sample Name | GPS Latitude | GPS Longitude |
|---|---|---|
| ANZ | 56.479388 | -111.030545 |
| JPH 4 | 57.144061 | -111.386934 |
| McK | 57.247627 | -111.710795 |
| MCM | 56.634969 | -111.193034 |
| P1 | 57.14609 | -111.73227 |
| P10 | 57.06467 | -111.15269 |
| P11 | 57.05528 | -111.36288 |
| P12 | 57.02599 | -111.08999 |
| P17 | 56.77908 | -111.59211 |
| P3 | 57.08775 | -111.80556 |
| P4 | 57.06323 | -111.79662 |
| P5 | 57.20668 | -111.77855 |
| P6 | 57.3069 | -111.72284 |
| P8 | 57.42187 | -111.26675 |
| P9 | 57.28675 | -111.20317 |
| S 12 | 56.93714 | -111.72176 |
| S 16 | 56.87767 | -111.06291 |
| S1 | 57.11879 | -111.82107 |
| S10 | 56.8148 | -111.2867 |
| S13 | 56.99745 | -111.83602 |
| S14 | 56.74397 | -111.78785 |
| S15 | 56.76378 | -111.50061 |
| S17 | 56.98812 | -111.23141 |
| S18 | 56.98551 | -111.10171 |
| S18 | 56.98551 | -111.10171 |
| S19 | 57.08565 | -111.52352 |
| S2 | 57.28937 | -111.79685 |
| S2 | 57.28937 | -111.79685 |
| S20 | 56.8148 | -111.2867 |
| S3 | 57.03401 | -112.05236 |
| S4 | 56.8266 | -112.15509 |
| S5 | 56.80544 | -111.83947 |
| S6 | 57.21935 | -112.08611 |
| S7 | 57.32645 | -111.32666 |
| S9 | 57.14824 | -111.42753 |
| UTK | 55.87381 | -115.798383 |
| CMW | 59.38345 | -114.75002 |
| BMW | 57.56691 | -112.91694 |

Table A2-1: GPS coordinates of all sampling locations

Unwashed

| Sample ID | Ag (ng/g) | Al (ug/g) | Ba(ug/g) | Be (ng/g) | Cd(ng/g) | Co (ng/g) | Cr (ng/g) | Cu(ug/g) | Fe (ug/g) | Ga (ng/g) | Li (ng/g) | Mn (ug/g) | Mo (ng/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **MDL** | **2.62** | **0.089** | **0.0015** | **0.12** | **0.18** | **0.54** | **2.9** | **0.0093** | **0.069** | **0.56** | **2.17** | **0.0042** | **0.48** |
| ANZ sept 2016 | <MDL | 14 | 9.6 | <MDL | 6.5 | 7.3 | 21 | 3.8 | 14 | 14.2 | 42 | 424 | 37 |
| JPH 4 sept 2016 | <MDL | 28 | 16.1 | 2.5 | 3.0 | 33 | 48 | 2.6 | 24 | 11.7 | 30 | 51.0 | 40 |
| McK-1 sept 2016 | <MDL | 22 | 10 | <MDL | 13 | 19 | 48 | 4.2 | 24 | 16.6 | 67 | 310 | 65 |
| MCM sept 28 2016 | <MDL | 30 | 14 | 1.3 | 20 | 10 | 46 | 4.5 | 28 | 25.9 | 44 | 575 | 44 |
| P1 cranberry | <MDL | 32 | 12 | <MDL | 5.6 | 16 | 35 | 3.0 | 23 | 20.0 | 40 | 385 | 16 |
| P1 Lingonberry | <MDL | 55 | 6.3 | <MDL | 0.8 | 13 | 51 | 2.6 | 31 | 21.7 | 42 | 272 | 17 |
| P10 Lingonberry | <MDL | 34 | 9.2 | <MDL | 2.6 | 8 | 47 | 2.2 | 22 | 17.5 | 83 | 248 | 36 |
| P11 Cranberry | <MDL | 91 | 15.7 | 1.6 | 21.0 | 51 | 105 | 3.5 | 74 | 39.0 | 89 | 364 | 29 |
| P11 Lingonberry | <MDL | 65 | 5.6 | <MDL | 2.0 | 17 | 69 | 3.6 | 33 | 22.4 | 66 | 195 | 22 |
| P12 Cranberry | <MDL | 47 | 11 | <MDL | 7.2 | 16 | 58 | 2.7 | 34 | 28.8 | 39 | 410 | 34 |
| P12 Lingonberry | <MDL | 55 | 5.2 | <MDL | 1.7 | 10 | 52 | 2.7 | 27 | 23.7 | 36 | 319 | 26 |
| P17 Cranberry | <MDL | 35 | 10 | <MDL | 27 | 15 | 54 | 3.1 | 34 | 12.8 | 79 | 282 | 60 |
| P17 Lingonberry | <MDL | 83 | 3.8 | 1.4 | 1.6 | 14 | 61 | 4.8 | 37 | 23.3 | 53 | 234 | 26 |
| P3 Lingonberry | <MDL | 74 | 8.6 | 1.6 | 8.4 | 22 | 85 | 2.8 | 56 | 31.2 | 315 | 344 | 19 |
| P4 Cranberry | <MDL | 131 | 21 | 3.9 | 17 | 51 | 173 | 4.4 | 98 | 59.7 | 127 | 491 | 29 |
| P4 Lingonberry | <MDL | 52 | 11 | <MDL | 4.0 | 15 | 55 | 3.6 | 30 | 21.6 | 97 | 279 | 29 |
| P5 Cranberry | <MDL | 17 | 11 | <MDL | 14.3 | 10 | 28 | 2.8 | 16 | 13.5 | 36 | 298 | 46 |
| P5 Lingonberry | <MDL | 42 | 12 | 0.6 | 5.3 | 16 | 40 | 3.8 | 32 | 15.5 | 62 | 354 | 22 |
| P6 Cranberry | <MDL | 31 | 17 | <MDL | 35 | 13 | 39 | 2.1 | 35 | 7.1 | 496 | 175 | 200 |
| P6 Lingonberry | <MDL | 48 | 17 | 1.6 | 29 | 16 | 67 | 1.9 | 45 | 19.3 | 462 | 172 | 181 |
| P8 Cranberry | <MDL | 36 | 11 | <MDL | 7.3 | 15 | 45 | 2.9 | 26 | 23.4 | 47 | 399 | 26 |
| P9 Lingonberry | <MDL | 63 | 15 | <MDL | 9.2 | 21 | 86 | 2.9 | 47 | 33.6 | 68 | 447 | 37 |
| S 12 Lingonberry | <MDL | 42 | 5.6 | <MDL | 1.0 | 10 | 31 | 4.4 | 25 | 8.8 | 40 | 219 | 22 |
| S 16 Cranberry | <MDL | 42 | 4.9 | <MDL | 6.2 | 7.6 | 32 | 2.2 | 20 | 11.5 | 32 | 354 | 120 |
| S1 Cranberry | <MDL | 23 | 11 | <MDL | 13.7 | 17 | 32 | 3.6 | 24 | 6.7 | 31 | 267 | 39 |
| S1 Lingonberry | <MDL | 48 | 5.5 | <MDL | 1.6 | 11 | 37 | 3.5 | 27 | 6.7 | 39 | 185 | 15 |
| S10 Cranberry | <MDL | 22 | 14 | <MDL | 5.6 | 15 | 23 | 3.5 | 23 | 11.9 | 39 | 435 | 38 |
| S10 Lignoberry | <MDL | 56 | 3.6 | <MDL | 1.0 | 8.4 | 35 | 3.3 | 28 | 11.3 | 36 | 393 | 39 |
| S13 Lingonberry | <MDL | 42 | 7.7 | <MDL | 9.5 | 10 | 29 | 4.0 | 25 | 9.7 | 43 | 349 | 25 |
| S14 Lingonberry | <MDL | 33 | 3.9 | <MDL | 1.2 | 5.9 | 10 | 2.6 | 14 | 1.7 | 13 | 300 | 22 |
| S15 Lingonberry | <MDL | 18 | 11 | 0.3 | 5.8 | 14 | 21 | 3.4 | 19 | 11.3 | 58 | 231 | 55 |
| S17 Cranberry | <MDL | 35 | 11 | 0.3 | 7.5 | 19 | 31 | 3.2 | 25 | 18.4 | 46 | 340 | 20 |
| S17 Lingonberry | <MDL | 64 | 3.8 | <MDL | 1.6 | 12 | 46 | 4.1 | 29 | 12.0 | 40 | 206 | 21 |
| S18 Cranberry | <MDL | 16 | 8.6 | <MDL | 16 | 14 | 22 | 3.3 | 17 | 4.5 | 24 | 371 | 35 |
| S18 Lingonberry | <MDL | 55 | 5.1 | 1.3 | 1.4 | 12 | 48 | 3.4 | 31 | 16.4 | 42 | 306 | 33 |
| S19 Cranberry | <MDL | 33 | 22 | 0.7 | 10 | 23 | 48 | 3.5 | 33 | 14.3 | 91 | 176 | 77 |
| S2 Cranberry | <MDL | 29 | 12 | 1.3 | 19 | 20 | 32 | 3.3 | 25 | 10.3 | 60 | 307 | 13 |
| S2 Lingonberry | <MDL | 53 | 6.4 | 1.4 | 1.5 | 11 | 41 | 3.9 | 33 | 11.6 | 58 | 203 | 17 |
| S20 Cranberry | <MDL | 14 | 14 | <MDL | 10 | 6.4 | 25 | 1.5 | 20 | 1.2 | 107 | 226 | 52 |
| S20 Lingonberry | <MDL | 29 | 5.7 | <MDL | 6.0 | 5.3 | 22 | 0.4 | 20 | 1.2 | 79 | 145 | 139 |
| S3 Blueberry | <MDL | 9 | 21 | <MDL | 3.6 | 20 | <MDL | 3.7 | 14 | 13.4 | 19 | 483 | 88 |
| S3 Cranberry | <MDL | 8 | 7.1 | <MDL | 7.2 | 8.7 | 12 | 0.9 | 14 | 7.3 | 121 | 206 | 22 |
| S3 Lingonberry | <MDL | 17 | 6.7 | 0.4 | 4.8 | 3.7 | 16 | 1.4 | 16 | 6.9 | 75 | 220 | 78 |
| S4 Cranberry | <MDL | 10 | 8.7 | <MDL | 19.9 | 7.0 | 9.3 | 3.2 | 22 | 11.6 | 92 | 319 | 61 |
| S4 Lingonberry | <MDL | 34 | 3.2 | <MDL | 1.7 | 5.5 | 12 | 2.3 | 33 | 12.6 | 28 | 244 | 18 |
| S5 Lingonberry | <MDL | 8 | 9.2 | <MDL | 14.9 | 10 | 14 | 3.7 | 15 | 6.3 | 15 | 500 | 32 |
| S6 Cranberry | <MDL | 9 | 9.5 | <MDL | 13.7 | 8.1 | 12 | 3.2 | 14 | 12.5 | 29 | 456 | 9 |
| S6 lingonberry | <MDL | 30 | 5.4 | <MDL | 1.2 | 3.9 | 12 | 3.4 | 14 | 8.8 | 13 | 207 | 15 |
| S7 Blueberry | <MDL | 27 | 14 | 1.0 | 0.30 | 12 | 24 | 3.6 | 23 | 7.5 | 16 | 131 | 57 |
| S7 Lingonberry | <MDL | 61 | 6.4 | 1.8 | 3.9 | 18 | 60 | 5.3 | 38 | 17.8 | 66 | 164 | 38 |
| S9 Cranberry | <MDL | 25 | 5.3 | <MDL | 1.6 | 6.1 | 12 | 2.8 | 15 | 10.1 | 50 | 286 | 72 |
| Utk site 208 blueberry | <MDL | 16 | 19 | <MDL | 0.54 | 2.8 | 8.2 | 3.6 | 12 | 4.7 | 4 | 2.4E+02 | 7.0E+02 |
| Utk 208 cranberry | <MDL | 4.6 | 8.4 | 0.40 | 8.3 | 1.8 | <MDL | 4.3 | 12 | 14.6 | 24 | 6.3E+02 | 25 |
| CMW Cranberry | <MDL | 2.4 | 9.3 | <MDL | 14.6 | 1.3 | 3.1 | 3.6 | 9.3 | 0.8 | 9.2 | 3.8E+02 | 2.2 |
| BMW Cranberry | <MDL | 6.5 | 8.5 | <MDL | 7.6 | 2.4 | 6.7 | 2.1 | 13 | 5.7 | 12 | 5.8E+02 | 3.9 |
| BMW Lingonberry | <MDL | 23 | 4.3 | <MDL | 0.60 | 1.5 | 8.3 | 1.0 | 12 | 2.5 | 11 | 4.4E+02 | 13 |

Table A2-2: Trace element (Ag-Mo) concentrations of all unwashed berry samples analyzed (including berries from remote locations).

Unwashed

| Sample ID | Ni (ug/g) | Pb (ng/g) | Rb (ug/g) | Re (ng/g) | Sb (ng/g) | Sc (ng/g) | Se (ng/g) | Sr (ug/g) | Th (ng/g) | Tl (ug/g) | U (ng/g) | V (ng/g) | Y (ng/g) | Zn (ug/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | **0.016** | **0.30** | **0.0030** | **0.0091** | **0.90** | **9.1** | **7.1** | **0.0011** | **0.045** | **0.0016** | **0.031** | **2.4** | **0.088** | **0.043** |
| ANZ sept 2016 | 0.57 | 3.8 | 8.8 | 0.006 | <MDL | <MDL | <MDL | 0.76 | <MDL | <MDL | 0.24 | 34 | 3.2 | 9.1 |
| JPH 4 sept 2016 | 1.6 | 7.4 | 11 | <MDL | <MDL | <MDL | <MDL | 8.3 | 2.2 | <MDL | 1.0 | 60 | 11 | 7.7 |
| McK-1 sept 2016 | 0.68 | 6.1 | 17 | 0.22 | <MDL | <MDL | <MDL | 1.1 | 2.0 | <MDL | 0.79 | 47 | 8.9 | 10.2 |
| MCM sept 28 2016 | 0.38 | 18 | 11 | 0.039 | <MDL | <MDL | <MDL | 1.0 | 3.3 | <MDL | 1.6 | 74 | 20 | 11.3 |
| P1 cranberry | 0.55 | 7.5 | 6.5 | <MDL | <MDL | <MDL | <MDL | 1.3 | <MDL | <MDL | 0.36 | 61 | 11 | 5.6 |
| P1 Lingonberry | 0.19 | 13 | 4.2 | <MDL | <MDL | <MDL | <MDL | 1.0 | <MDL | <MDL | 1.1 | 93 | 14 | 4.5 |
| P10 Lingonberry | 1.7 | 7.1 | 6.0 | <MDL | <MDL | <MDL | <MDL | 1.5 | <MDL | <MDL | 0.76 | 74 | 9.5 | 6.5 |
| P11 Cranberry | 1.1 | 37 | 9.7 | 0.11 | <MDL | 24.1 | 64 | 1.6 | 18.1 | <MDL | 4.1 | 261 | 52 | 7.7 |
| P11 Lingonberry | 0.26 | 12 | 8.2 | <MDL | <MDL | 9.5 | <MDL | 0.71 | <MDL | <MDL | 1.3 | 126 | 16 | 5.5 |
| P12 Cranberry | 0.49 | 19 | 6.7 | 0.11 | <MDL | <MDL | <MDL | 0.83 | <MDL | <MDL | 1.2 | 133 | 20 | 6.0 |
| P12 Lingonberry | 0.11 | 10 | 5.4 | <MDL | <MDL | <MDL | <MDL | 0.45 | <MDL | <MDL | 0.67 | 100 | 11 | 5.1 |
| P17 Cranberry | 0.34 | 23 | 8.7 | <MDL | <MDL | <MDL | <MDL | 2.8 | 4.9 | <MDL | 1.8 | 181 | 20 | 11.7 |
| P17 Lingonberry | 0.47 | 19 | 9.3 | <MDL | <MDL | <MDL | <MDL | 0.61 | <MDL | <MDL | 2.0 | 133 | 20 | 6.6 |
| P3 Lingonberry | 0.20 | 24 | 6.1 | 0.10 | <MDL | 15.8 | 59 | 4.2 | 11 | <MDL | 2.9 | 170 | 29 | 9.1 |
| P4 Cranberry | 0.91 | 45 | 12 | 0.10 | <MDL | 26.6 | 128 | 2.5 | 25 | 0.0028 | 5.9 | 306 | 63 | 8.4 |
| P4 Lingonberry | 0.39 | 15 | 6.9 | 0.12 | <MDL | 13.7 | <MDL | 1.5 | 45 | <MDL | 1.09 | 87 | 12.7 | 7.9 |
| P5 Cranberry | 0.18 | 3.9 | 5.1 | <MDL | <MDL | <MDL | <MDL | 2.2 | <MDL | <MDL | <MDL | 31 | 6.5 | 7.6 |
| P5 Lingonberry | 0.19 | 10 | 2.5 | 0.066 | <MDL | <MDL | 29.0 | 4.4 | <MDL | <MDL | 1.4 | 72 | 11 | 8.9 |
| P6 Cranberry | 0.2 | 11 | 6.1 | <MDL | <MDL | <MDL | <MDL | 2.4 | 4.6 | <MDL | 1.3 | 75 | 14 | 11 |
| P6 Lingonberry | 0.19 | 14.8 | 5.3 | 0.034 | <MDL | 11.9 | <MDL | 2.6 | 7.8 | <MDL | 2.2 | 101 | 21 | 9.2 |
| P8 Cranberry | 1.0 | 11.4 | 7.3 | <MDL | <MDL | <MDL | <MDL | 0.8 | <MDL | <MDL | 1.1 | 65 | 15 | 7.0 |
| P9 Lingonberry | 1.1 | 37 | 7.8 | <MDL | <MDL | 10.5 | <MDL | 1.2 | <MDL | <MDL | 2.0 | 182 | 24 | 8.7 |
| S 12 Lingonberry | 0.44 | 9.5 | 7.8 | 0.020 | <MDL | <MDL | <MDL | 1.2 | 7.3 | <MDL | 1.1 | 54 | 9.4 | 7.3 |
| S 16 Cranberry | 0.25 | 8.3 | 9.8 | <MDL | <MDL | <MDL | <MDL | 0.73 | 4.7 | <MDL | 1.2 | 57 | 7.8 | 7.3 |
| S1 Cranberry | 0.60 | 7.0 | 9.3 | 0.0 | <MDL | <MDL | <MDL | 1.6 | 2.7 | <MDL | 1.1 | 61 | 7.8 | 9.1 |
| S1 Lingonberry | 0.32 | 11 | 4.5 | <MDL | <MDL | <MDL | <MDL | 1.0 | 3.4 | <MDL | 1.4 | 86 | 12 | 7.0 |
| S10 Cranberry | 1.0 | 7.8 | 9.1 | 0.022 | <MDL | <MDL | <MDL | 1.0 | 2.0 | <MDL | 0.87 | 51 | 9.0 | 8.8 |
| S10 Lignoberry | 0.34 | 9.8 | 6.9 | 0.054 | <MDL | <MDL | <MDL | 0.41 | 2.9 | <MDL | 1.1 | 68 | 9.5 | 7.0 |
| S13 Lingonberry | 0.30 | 8.3 | 7.0 | 0.040 | <MDL | <MDL | <MDL | 1.0 | 2.8 | <MDL | 1.2 | 67 | 14.7 | 7.4 |
| S14 Lingonberry | 0.17 | 5.2 | 9.7 | <MDL | <MDL | <MDL | <MDL | 0.44 | 0.23 | <MDL | 0.46 | 28 | 5.2 | 5.3 |
| S15 Lingonberry | 0.84 | 5.1 | 9.0 | <MDL | <MDL | <MDL | <MDL | 1.1 | <MDL | <MDL | 0.67 | 42 | 7.1 | 7.4 |
| S17 Cranberry | 0.95 | 8.0 | 9.0 | <MDL | <MDL | <MDL | <MDL | 1.0 | <MDL | <MDL | 0.94 | 86 | 9.9 | 7.3 |
| S17 Lingonberry | 0.41 | 12.2 | 8.8 | 0.030 | <MDL | <MDL | <MDL | 0.56 | 5.8 | <MDL | 1.6 | 102 | 14 | 6.2 |
| S18 Cranberry | 0.64 | 4.7 | 11 | 0.026 | <MDL | <MDL | <MDL | 0.74 | 1.5 | <MDL | 0.60 | 44 | 5.6 | 7.6 |
| S18 Lingonberry | 0.40 | 17 | 6.3 | 0.028 | <MDL | <MDL | <MDL | 0.63 | 4.4 | <MDL | 1.6 | 103 | 15 | 6.9 |
| S19 Cranberry | 0.89 | 13 | 9.3 | <MDL | <MDL | <MDL | <MDL | 1.9 | <MDL | <MDL | 1.5 | 115 | 14 | 9.8 |
| S2 Cranberry | 0.63 | 8.2 | 12.3 | 0.047 | 6.4 | <MDL | <MDL | 1.2 | 9.2 | <MDL | 1.2 | 63 | 11 | 6.9 |
| S2 Lingonberry | 0.35 | 13 | 8.5 | 0.010 | <MDL | <MDL | <MDL | 0.75 | 5.3 | <MDL | 1.8 | 85 | 17 | 8.1 |
| S20 Cranberry | 0.31 | 6.9 | 13.5 | <MDL | <MDL | <MDL | <MDL | 3.4 | 1.4 | <MDL | 0.84 | 69 | 17 | 13 |
| S20 Lingonberry | 0.19 | 9.2 | 8.8 | <MDL | <MDL | <MDL | <MDL | 1.4 | 1.5 | <MDL | 0.77 | 61 | 11 | 6.5 |
| S3 Blueberry | 0.18 | 3.4 | 6.5 | <MDL | <MDL | <MDL | <MDL | 3.3 | <MDL | <MDL | 0.08 | 15 | 2.6 | 6.1 |
| S3 Cranberry | 0.08 | 3.9 | 11 | <MDL | 8.5 | 6.7 | <MDL | 2.7 | 16.4 | <MDL | 0.45 | 16 | 4.9 | 9.7 |
| S3 Lingonberry | 0.09 | 16 | 9.6 | <MDL | <MDL | <MDL | 3.8 | 2.8 | <MDL | <MDL | 0.41 | 18 | 2.2 | 7.3 |
| S4 Cranberry | 0.41 | 3.8 | 9.5 | <MDL | <MDL | <MDL | <MDL | 0.78 | <MDL | <MDL | 0.33 | 17 | 4.1 | 8.2 |
| S4 Lingonberry | 0.09 | 5.4 | 6.8 | <MDL | <MDL | <MDL | <MDL | 0.42 | <MDL | <MDL | 0.55 | 30 | 8.2 | 6.0 |
| S5 Lingonberry | 0.59 | 5.3 | 12 | 0.028 | 1.9 | <MDL | <MDL | 0.64 | 1.7 | <MDL | 0.34 | 19 | 3.1 | 7.6 |
| S6 Cranberry | 0.43 | 4.1 | 7.1 | <MDL | <MDL | <MDL | <MDL | 0.93 | <MDL | <MDL | 0.41 | 22 | 3.0 | 7.2 |
| S6 lingonberry | 0.26 | 4.0 | 4.1 | <MDL | <MDL | <MDL | <MDL | 0.7 | <MDL | <MDL | 0.38 | 23 | 3.7 | 6.3 |
| S7 Blueberry | 1.7 | 5.7 | 14 | 0.14 | <MDL | <MDL | 16 | 7.5 | 2.6 | <MDL | 0.86 | 37 | 8.4 | 5.3 |
| S7 Lingonberry | 1.4 | 17 | 13 | <MDL | 3.9 | <MDL | 76 | 1.2 | 7.9 | <MDL | 2.7 | 113 | 22 | 8.4 |
| S9 Cranberry | 0.31 | 4.2 | 4.7 | <MDL | <MDL | <MDL | <MDL | 1.2 | <MDL | <MDL | 0.51 | 50 | 4.4 | 6.0 |
| Utk site 208 blueberry | 0.46 | 2.1 | 13 | <MDL | <MDL | <MDL | <MDL | 3.0 | <MDL | <MDL | <MDL | 5.9 | 0.9 | 6.7 |
| Utk 208 cranberry | 0.31 | 2.1 | 5.2 | <MDL | <MDL | <MDL | <MDL | 0.53 | <MDL | <MDL | 0.04 | 5.7 | 1.0 | 11 |
| CMW Cranberry | 0.10 | 2.0 | 5.9 | <MDL | <MDL | <MDL | <MDL | 0.58 | <MDL | <MDL | 0.08 | 2.7 | 0.7 | 9.7 |
| BMW Cranberry | 0.24 | 4.7 | 5.8 | <MDL | <MDL | <MDL | <MDL | 0.54 | <MDL | <MDL | 0.23 | 14 | 2.2 | 9.2 |
| BMW Lingonberry | 0.11 | 2.3 | 5.0 | <MDL | <MDL | <MDL | <MDL | 0.36 | <MDL | <MDL | 0.14 | 7.6 | 0.9 | 7.7 |

Table A2-3: Trace element (Ni-Zn) concentrations of all unwashed berry samples analyzed (including berries from remote locations).

Washed

| Sample ID | Ag (ug/g) | Al (ug/g) | Ba (ug/g) | Be (ng/g) | Cd(ng/g) | Co (ng/g) | Cr (ng/g) | Cu (ug/g) | Fe (ug/g) | Ga (ng/g) | Li (ng/g) | Mn(ug/g) | Mo (ng/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **MDL** | **2.62** | **0.089** | **0.0015** | **0.12** | **0.18** | **0.54** | **2.9** | **0.0093** | **0.069** | **0.56** | **2.17** | **0.0042** | **0.48** |
| ANZ | <MDL | 4.1 | 3.0 | 0.94 | 2.2 | 2.6 | 22 | 1.3 | 4.8 | 2.6 | 25 | 130 | 15 |
| JPH4 | <MDL | 6.3 | 4.9 | 1.3 | 0.21 | 12 | 26 | 1.0 | 6.5 | 1.7 | 18 | 15.8 | 11 |
| MCK | <MDL | 6.5 | 3.5 | 1.0 | 4.8 | 6.3 | 27 | 1.6 | 7.8 | 3.6 | 35 | 108 | 23 |
| MCM | <MDL | 5.6 | 4.1 | 1.2 | 2.0 | 3.2 | 23 | 1.3 | 5.8 | 3.9 | 23 | 167 | 12 |
| P1 lingonberry | <MDL | 36 | 5.3 | 0.88 | 0.14 | 6.8 | 26 | 3.2 | 21 | 12.2 | 25 | 306 | 21 |
| P11 Cranberry | <MDL | 9.5 | 9.5 | <MDL | 8.3 | 7.3 | 18 | 3.0 | 13 | 13.8 | 23 | 344 | 32 |
| P11 Lingonberry | <MDL | 43 | 4.9 | <MDL | 1.4 | 12 | 51 | 3.5 | 20 | 13.4 | 45 | 193 | 19 |
| P12 Lingonberry | <MDL | 14 | 8.1 | <MDL | 4.9 | 7.4 | 11 | 2.6 | 13 | 12.9 | 12 | 322 | 35 |
| P17 Cranberry | <MDL | 22 | 8.0 | <MDL | 27.1 | 8.9 | 28 | 2.7 | 21 | 12.6 | 45 | 238 | 42 |
| P3 Cranberry | <MDL | 13 | 12 | 0.18 | 19.7 | 15 | 22 | 2.9 | 14 | 10.7 | 174 | 246 | 17 |
| P3 Lingonberry | <MDL | 22 | 5.0 | <MDL | 1.6 | 4.9 | 9.1 | 1.8 | 13 | 11.0 | 230 | 176 | 21 |
| P4 Cranberry | <MDL | 16 | 15 | <MDL | 9.9 | 19 | 16 | 3.4 | 15 | 14.2 | 46 | 309 | 24 |
| P4 lingonberry | <MDL | 36 | 7.5 | <MDL | <MDL | 11 | 28 | 3.3 | 21 | 12.4 | 93 | 185 | 13 |
| P5 lingonberry | <MDL | 23 | 7.4 | 0.77 | 0.6 | 5.2 | 24 | 3.8 | 16 | 6.3 | 35 | 239 | 21 |
| P6 Lingonberry | <MDL | 19 | 15 | 0.59 | 31 | 8.5 | 30 | 1.8 | 24 | 9.7 | 427 | 162 | 171 |
| P6 Lingonberry | <MDL | 18 | 14 | <MDL | 27 | 8.0 | 22 | 1.4 | 18 | 8.0 | 437 | 135 | 150 |
| P9 lingonberry | <MDL | 29 | 13 | <MDL | 14 | 23 | 31 | 2.7 | 21 | 15.3 | 46 | 247 | 21 |
| S17 Lingonberry | <MDL | 47 | 3.1 | <MDL | 0.92 | 3.7 | <MDL | 4.2 | 17 | 14.4 | <MDL | 211 | 15 |
| S19 Cranberry | <MDL | 19 | 20 | <MDL | 9.8 | 16 | 25 | 3.4 | 23 | 13.2 | 98 | 158 | 85 |
| S15 Lingonberry | <MDL | 18 | 4.6 | <MDL | 7.1 | 8.4 | 15 | 3.0 | 14 | 8.1 | 52 | 246 | 62 |
| S17 Cranberry | <MDL | 11 | 11 | <MDL | 6.3 | 13.4 | <MDL | 3.5 | 13 | 14.8 | <MDL | 332 | 16 |
| S3 Cranberry | <MDL | 3.9 | 10 | <MDL | 10.9 | 9.8 | 27 | 1.0 | 15 | 7.3 | 134 | 290 | 28 |
| S3 Blueberry | <MDL | 8.4 | 21 | <MDL | 3.3 | 23 | 12 | 4.2 | 15 | 5.2 | 20 | 448 | 108 |
| S3 Lingonberry | <MDL | 14 | 7.2 | <MDL | 3.3 | 9.5 | 8.0 | 1.7 | 15 | 8.1 | 64 | 193 | 126 |
| S4 Cranberry | <MDL | 10 | 11 | 0.7 | 24.2 | 7.5 | 34 | 4.4 | 23 | 10.7 | 97 | 425 | 70 |
| S4 Lingonberry | <MDL | 43 | 3.9 | <MDL | 1.2 | 6.6 | 39 | 2.9 | 36 | 14.2 | 47 | 339 | 29 |
| S6 Cranberry | <MDL | 5.8 | 8.8 | 0.17 | 15.7 | 8.3 | 2.1 | 3.2 | 11 | 11.7 | 22 | 425 | 12 |
| S7 Blueberry | <MDL | 25 | 15 | 0.033 | 0.59 | 12 | 16 | 3.8 | 22 | 9.2 | 17 | 140 | 61 |
| S9 Cranberry | <MDL | 10 | 12 | 0.30 | 5.4 | 12 | 12 | 3.4 | 14 | 8.4 | 46 | 266 | 53 |

Table A2-4: Trace element (Ag-Mo) concentrations of all washed berry samples analyzed.

Washed

| Sample ID | Ni (ug/g) | Pb (ng/g) | Rb (ug/g) | Re (ng/g) | Sb (ng/g) | Sc (ng/g) | Se (ng/g) | Sr (ug/g) | Th (ng/g) | Tl (ug/g) | U (ng/g) | V (ng/g) | Y (ng/g) | Zn (ug/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **0.016** | **0.30** | **0.0030** | **0.0091** | **0.90** | **9.1** | **7.1** | **0.0011** | **0.045** | **0.0016** | **0.031** | **2.4** | **0.088** | **0.043** |
| ANZ | 0.20 | <MDL | 2.8 | 0.064 | <MDL | <MDL | <MDL | 0.33 | 0.30 | <MDL | 0.60 | 4.8 | 0.7 | 2.8 |
| JPH4 | 0.57 | <MDL | 3.2 | 0.039 | <MDL | <MDL | 25.8 | 2.8 | 0.64 | <MDL | 0.63 | 8.0 | 1.5 | 2.9 |
| MCK | 0.23 | <MDL | 5.2 | <MDL | <MDL | <MDL | 34.6 | 0.47 | 0.85 | <MDL | 0.74 | 9.0 | 2.4 | 3.3 |
| MCM | 0.10 | <MDL | 2.8 | 0.1 | <MDL | <MDL | 39.0 | 0.40 | 0.34 | <MDL | 0.54 | 4.6 | 0.8 | 3.0 |
| P1 lingonberry | 0.30 | 4.9 | 4.3 | <MDL | <MDL | <MDL | <MDL | 0.92 | 2.4 | <MDL | 0.84 | 46 | 6.8 | 5.5 |
| P11 Cranberry | 0.31 | 3.1 | 8.1 | <MDL | <MDL | <MDL | <MDL | 0.61 | <MDL | <MDL | <MDL | 18 | 3.5 | 6.0 |
| P11 Lingonberry | 0.34 | 5.0 | 7.9 | <MDL | <MDL | <MDL | <MDL | 0.59 | <MDL | <MDL | 0.35 | 66 | 6.7 | 5.1 |
| P12 Lingonberry | 0.33 | 4.3 | 6.8 | <MDL | <MDL | <MDL | <MDL | 0.49 | <MDL | <MDL | <MDL | 38 | 4.7 | 4.6 |
| P17 Cranberry | 0.06 | 8.1 | 5.6 | <MDL | <MDL | <MDL | <MDL | 2.1 | <MDL | <MDL | 0.22 | 65 | 6.9 | 7.8 |
| P3 Cranberry | 1.7 | 4.2 | 8.3 | 0.069 | <MDL | <MDL | <MDL | 2.4 | <MDL | <MDL | 0.38 | 27 | 4.2 | 8.3 |
| P3 Lingonberry | 0.47 | 3.6 | 5.2 | <MDL | 51 | <MDL | <MDL | 2.2 | 52.9 | <MDL | <MDL | 36 | 5.5 | 3.8 |
| P4 Cranberry | 0.57 | 4.1 | 11 | <MDL | 5.3 | <MDL | <MDL | 1.5 | 7.5 | <MDL | 0.12 | 27 | 6.1 | 5.7 |
| P4 lingonberry | 0.09 | 5.7 | 6.6 | <MDL | <MDL | <MDL | <MDL | 1.3 | <MDL | <MDL | 0.39 | 48 | 8.5 | 5.5 |
| P5 lingonberry | 0.17 | 3.1 | 2.8 | 0.014 | <MDL | <MDL | 16 | 2.7 | 0.66 | <MDL | 0.39 | 23 | 3.0 | 6.9 |
| P6 Lingonberry | 0.17 | 4.5 | 5.2 | 0.005 | <MDL | <MDL | <MDL | 2.1 | 2.1 | <MDL | 0.79 | 43 | 6.3 | 9.1 |
| P6 Lingonberry | 5.14 | 3.9 | 5.0 | <MDL | <MDL | <MDL | <MDL | 1.9 | <MDL | <MDL | 0.27 | 34 | 7.4 | 7.4 |
| P9 lingonberry | 0.63 | 6.0 | 8.8 | 0.1 | <MDL | <MDL | <MDL | 1.1 | <MDL | <MDL | 0.41 | 61 | 9.4 | 5.2 |
| S17 Lingonberry | 0.34 | 4.6 | 8.4 | <MDL | <MDL | <MDL | <MDL | 0.3 | <MDL | <MDL | <MDL | 59 | 6.5 | 5.8 |
| S19 Cranberry | 0.95 | 6.3 | 8.5 | <MDL | <MDL | <MDL | <MDL | 1.7 | <MDL | <MDL | 0.75 | 59 | 6.6 | 9.9 |
| S15 Lingonberry | 0.38 | 3.5 | 5.6 | <MDL | <MDL | <MDL | <MDL | 1.1 | <MDL | <MDL | 0.39 | 26 | 2.4 | 7.1 |
| S17 Cranberry | 0.90 | 2.7 | 9.4 | <MDL | <MDL | <MDL | <MDL | 0.81 | <MDL | <MDL | <MDL | 33 | 3.9 | 7.5 |
| S3 Cranberry | 0.12 | 1.6 | 13 | <MDL | <MDL | <MDL | <MDL | 3.8 | <MDL | <MDL | 0.50 | 6.6 | 3.3 | 12 |
| S3 Blueberry | 0.22 | 3.2 | 6.2 | <MDL | <MDL | <MDL | <MDL | 3.4 | <MDL | <MDL | 0.26 | 14 | 3.8 | 7.0 |
| S3 Lingonberry | 0.13 | 11 | 8.7 | <MDL | <MDL | <MDL | <MDL | 2.9 | <MDL | <MDL | 0.22 | 13 | 2.2 | 24 |
| S4 Cranberry | 0.56 | 2.6 | 12 | <MDL | <MDL | <MDL | <MDL | 1.1 | <MDL | <MDL | 0.63 | 13 | 3.1 | 11 |
| S4 Lingonberry | 0.16 | 4.9 | 8.3 | <MDL | <MDL | <MDL | <MDL | 0.6 | <MDL | <MDL | 1.05 | 33 | 6.3 | 8.5 |
| S6 Cranberry | 0.42 | 3.1 | 7.6 | <MDL | <MDL | <MDL | <MDL | 0.8 | <MDL | <MDL | 0.20 | 15 | 3.0 | 6.9 |
| S7 Blueberry | 1.9 | 4.7 | 16 | <MDL | <MDL | <MDL | <MDL | 8.8 | <MDL | <MDL | 0.69 | 33 | 7.3 | 6.5 |
| S9 Cranberry | 0.83 | 2.4 | 9.2 | <MDL | <MDL | <MDL | <MDL | 1.1 | <MDL | <MDL | 0.32 | 22 | 3.3 | 7.6 |

Table A2-5: Trace element (Ni-Zn) concentrations of all washed berry samples analyzed.

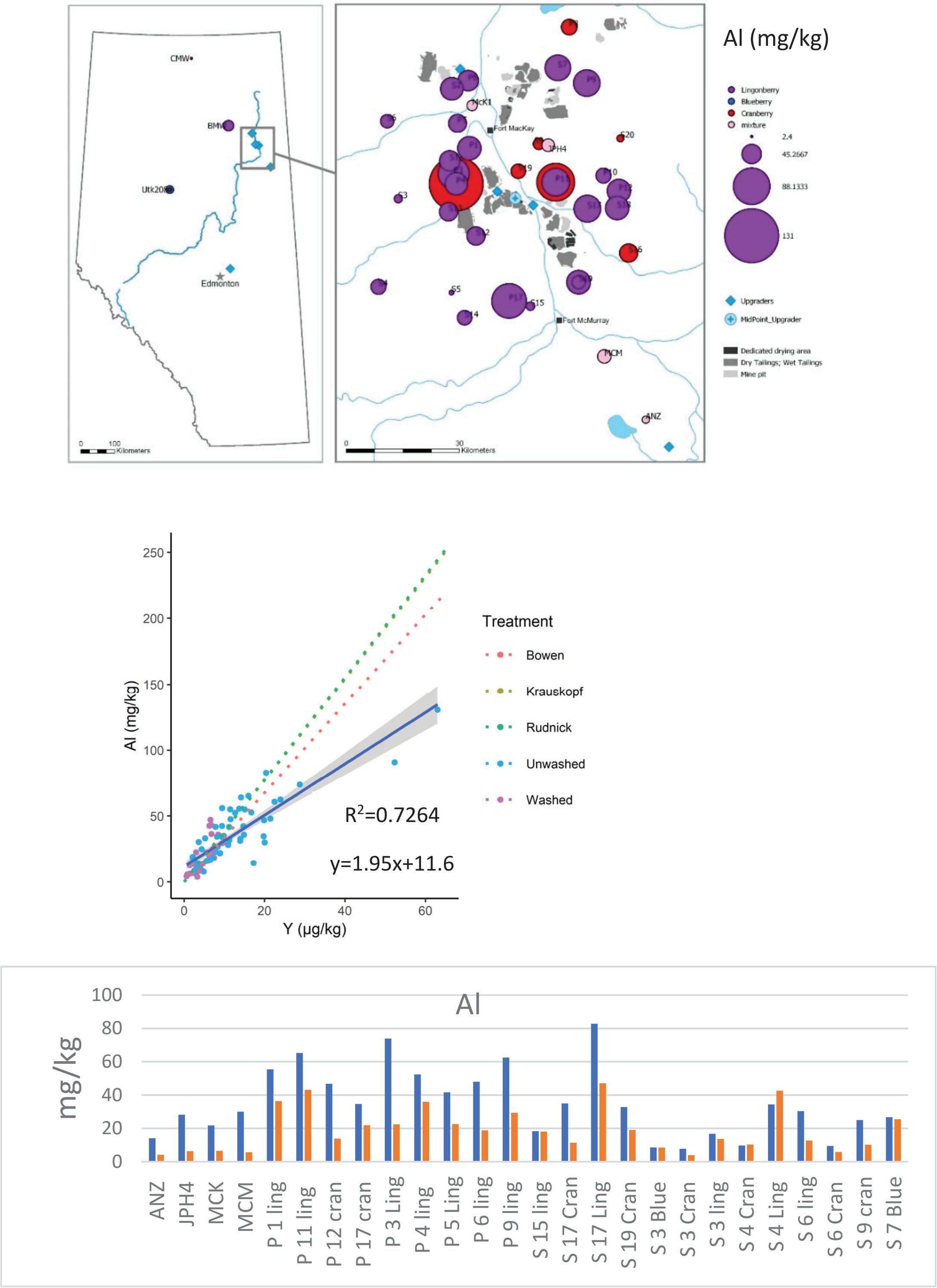

Figure A2-1: A) Spatial distribution of Al concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Al concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Al in washed and unwashed berries, listed by sample name.

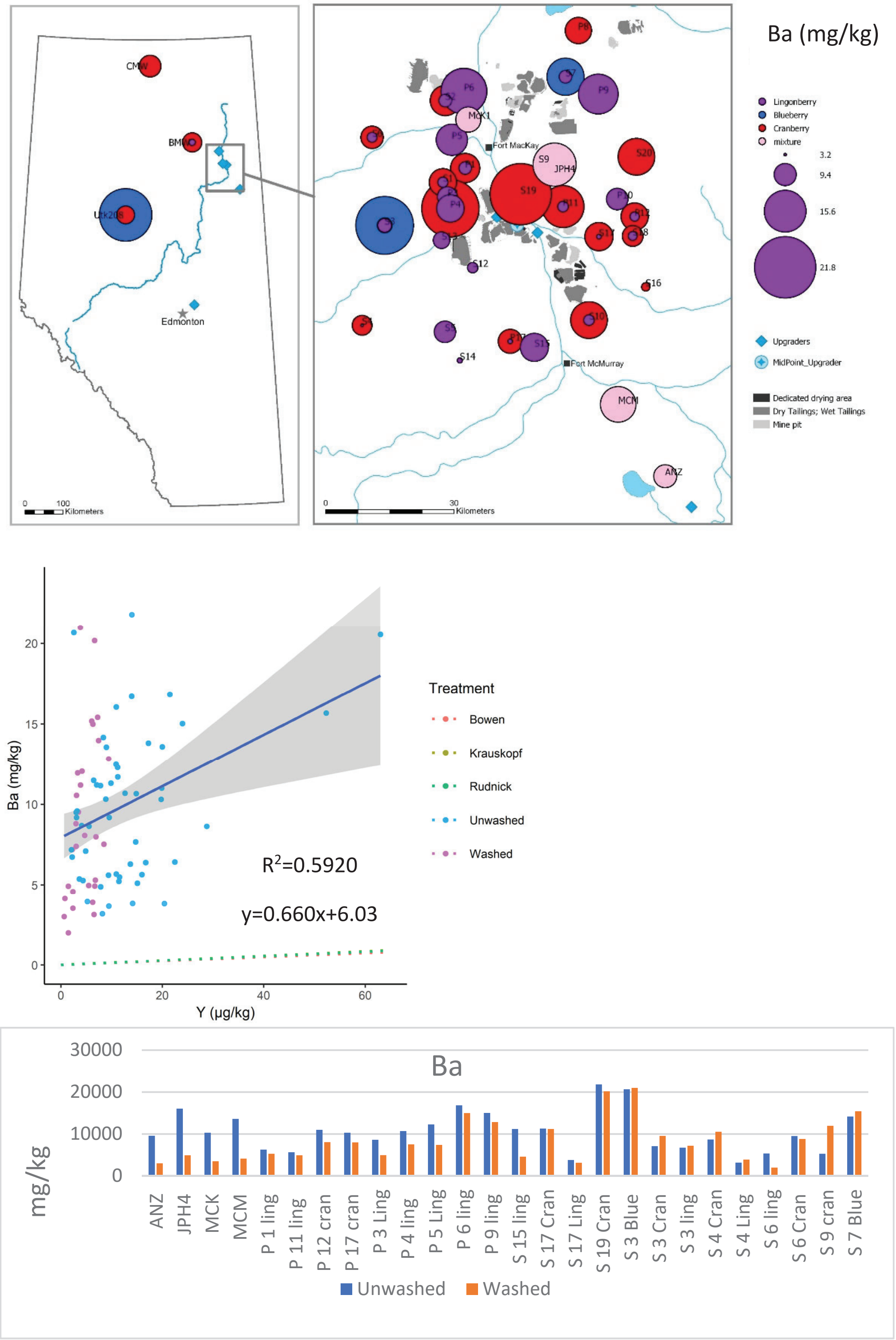

Figure A2-2:A) Spatial distribution of Ba concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Ba concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Ba in washed and unwashed berries, listed by sample name.

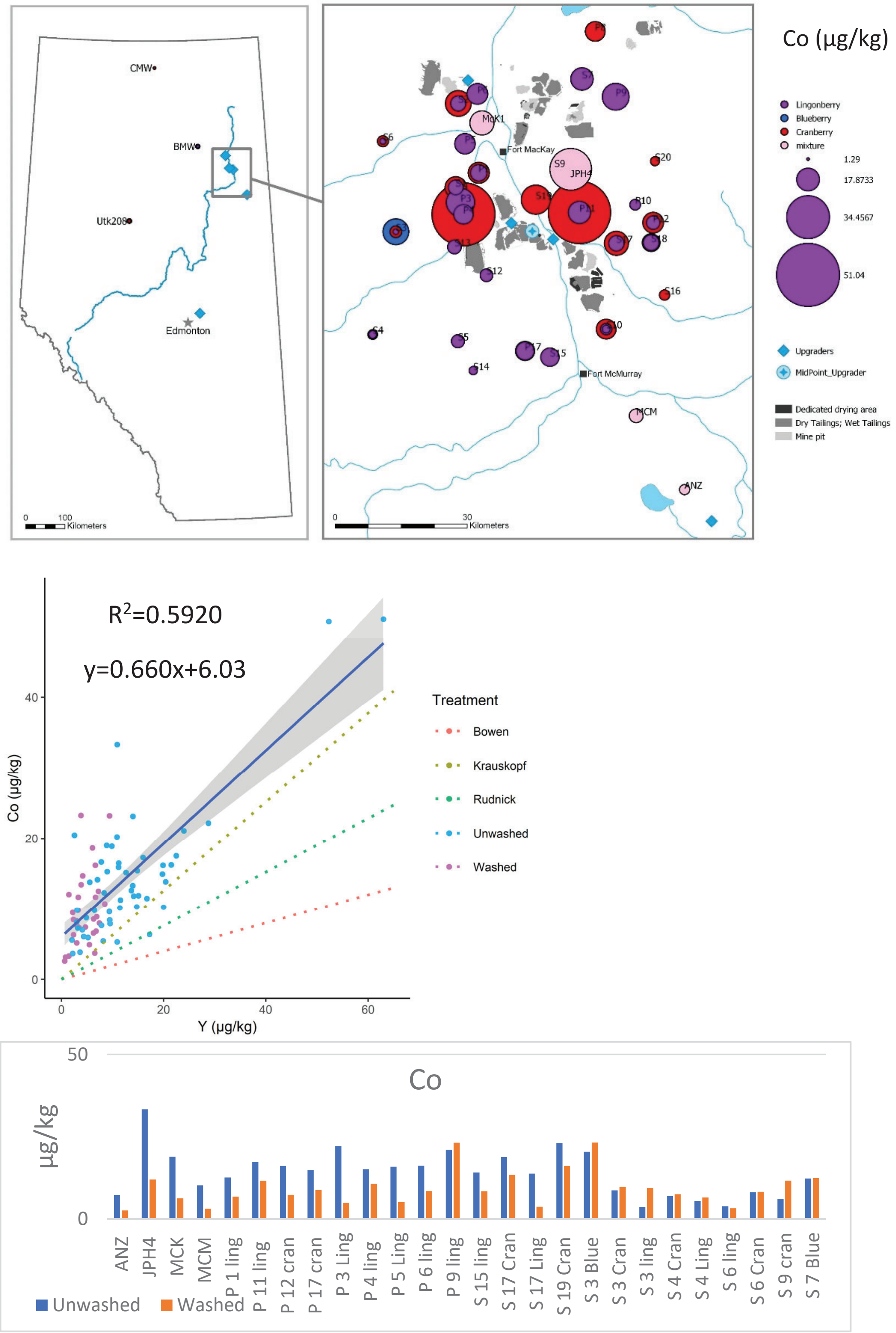

Figure A2-3: A) Spatial distribution of Co concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Co concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Co in washed and unwashed berries, listed by sample name.

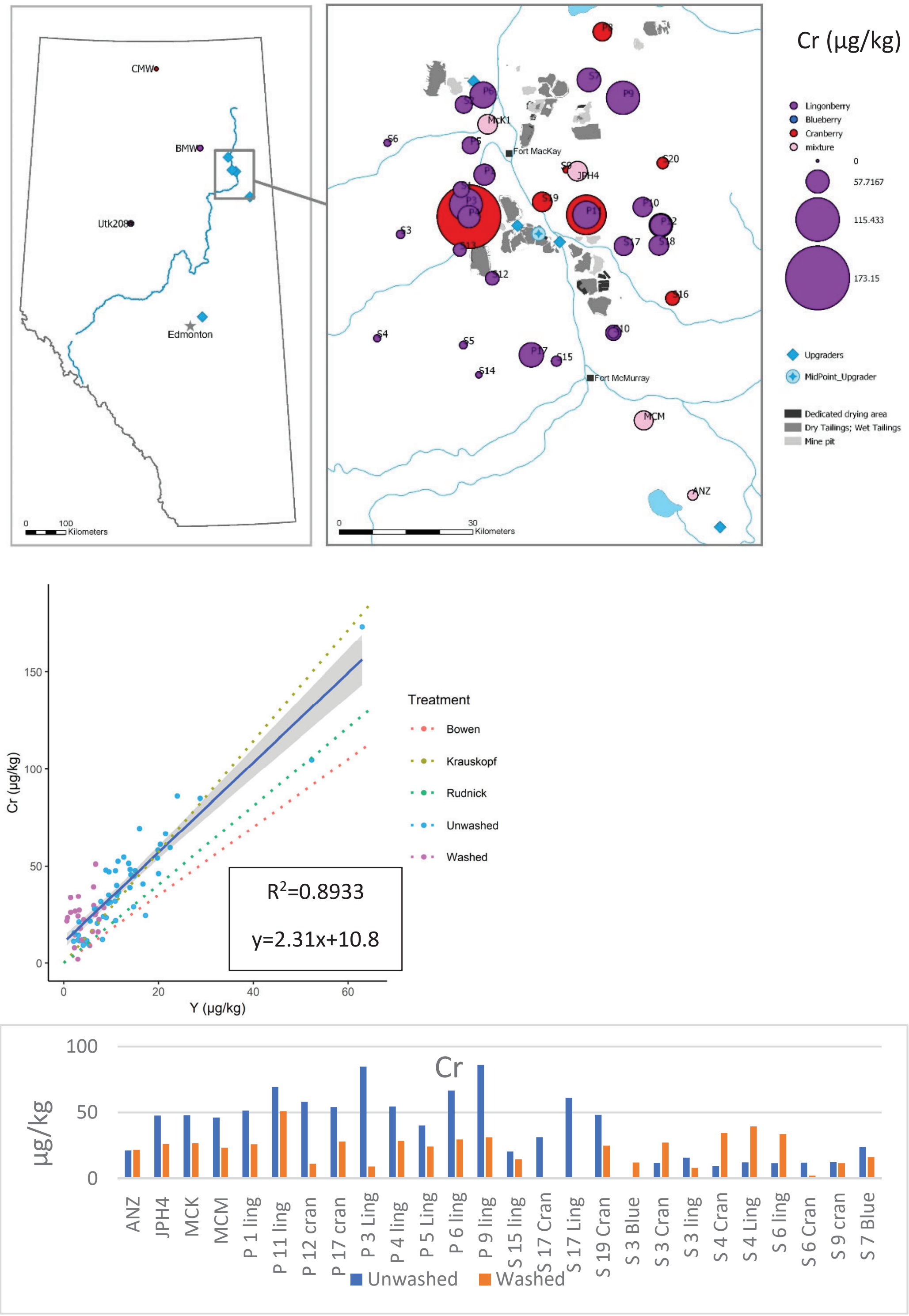

Figure A2-4: A) Spatial distribution of Cr concentrations in berries from the ABS region (right hand side) and the control sites (left hand side) B) Linear regression of Cr concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Cr in washed and unwashed berries, listed by sample name.

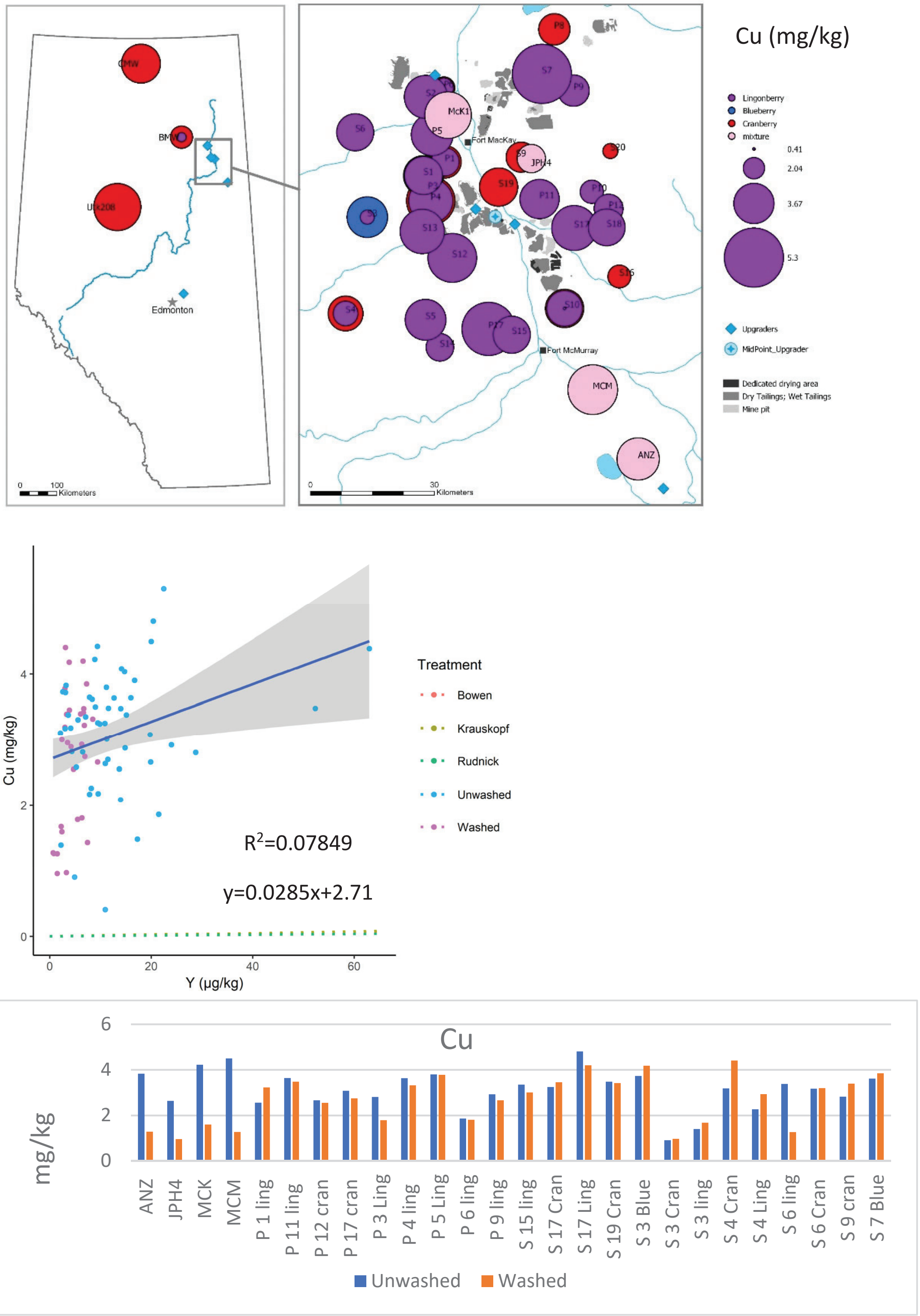

Figure A2-5:A) Spatial distribution of Cu concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Cu concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Cu in washed and unwashed berries, listed by sample name.

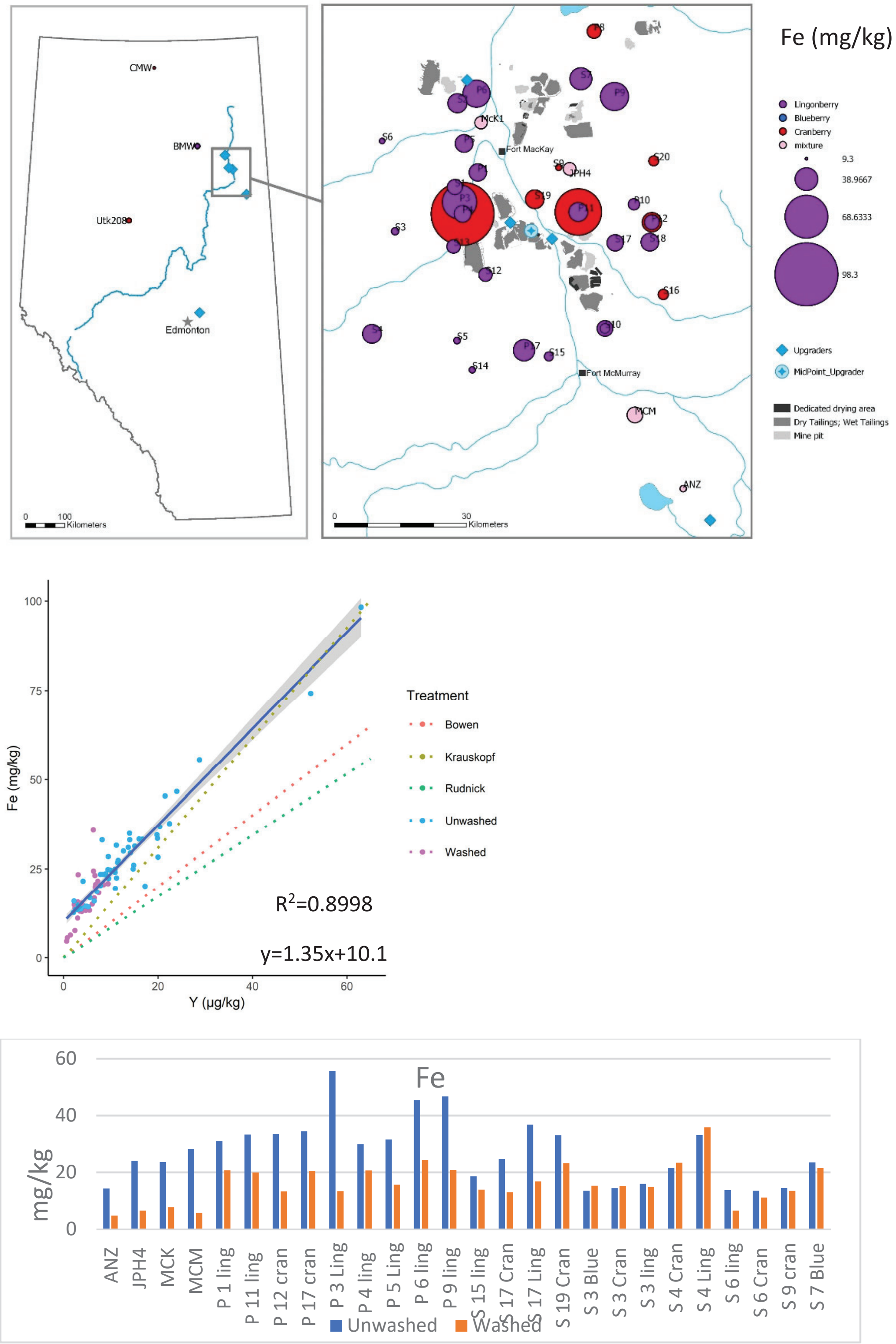

Figure A2-6: A) Spatial distribution of Fe concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Fe concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Fe in washed and unwashed berries, listed by sample name.

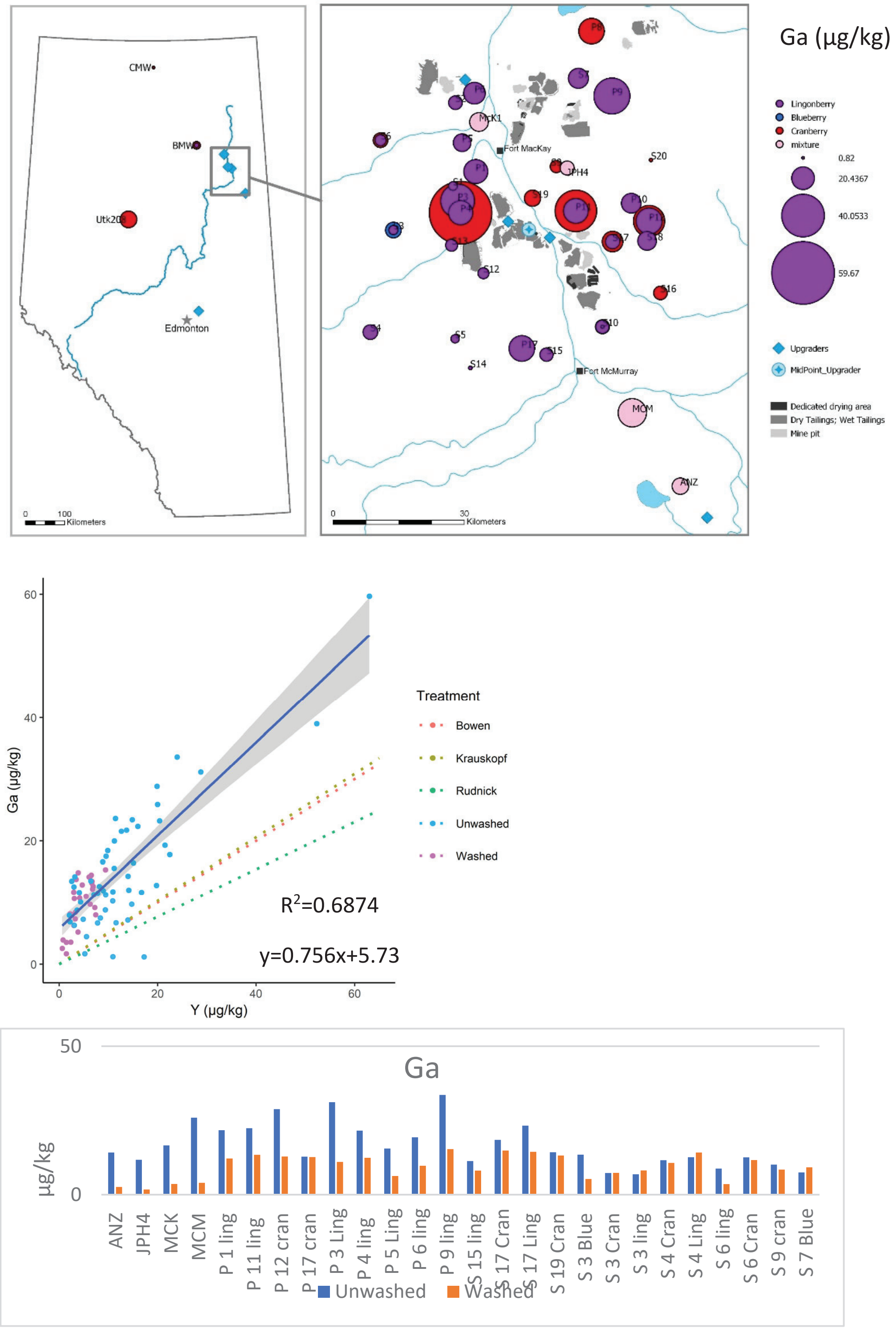

Figure A2-7:A) Spatial distribution of Ga concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Ga concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Ga in washed and unwashed berries, listed by sample name.

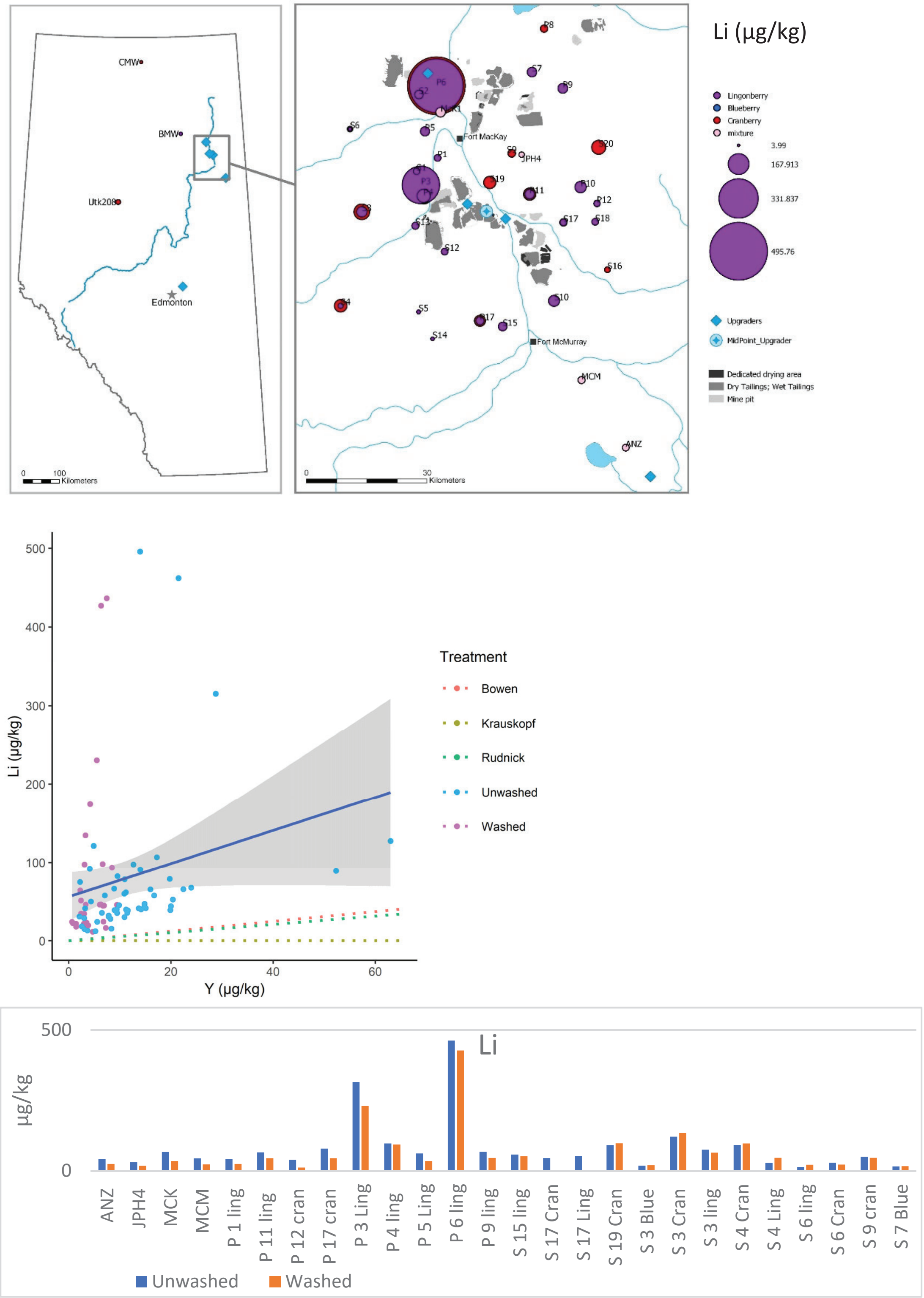

Figure A2-8: A) Spatial distribution of Li concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Li concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Li in washed and unwashed berries, listed by sample name.

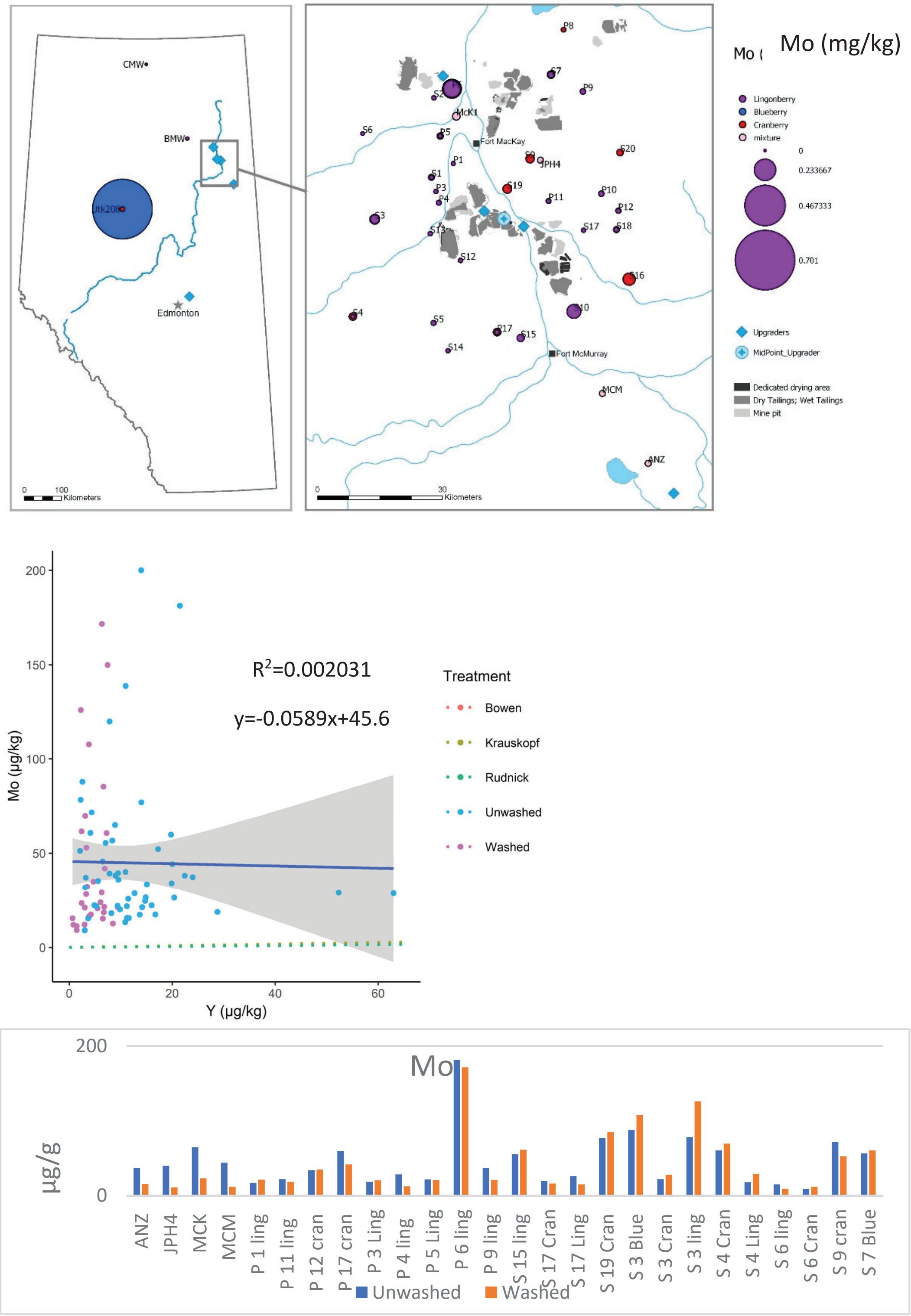

Figure A2-9:A) Spatial distribution of Mo concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Mo concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Mo in washed and unwashed berries, listed by sample name.

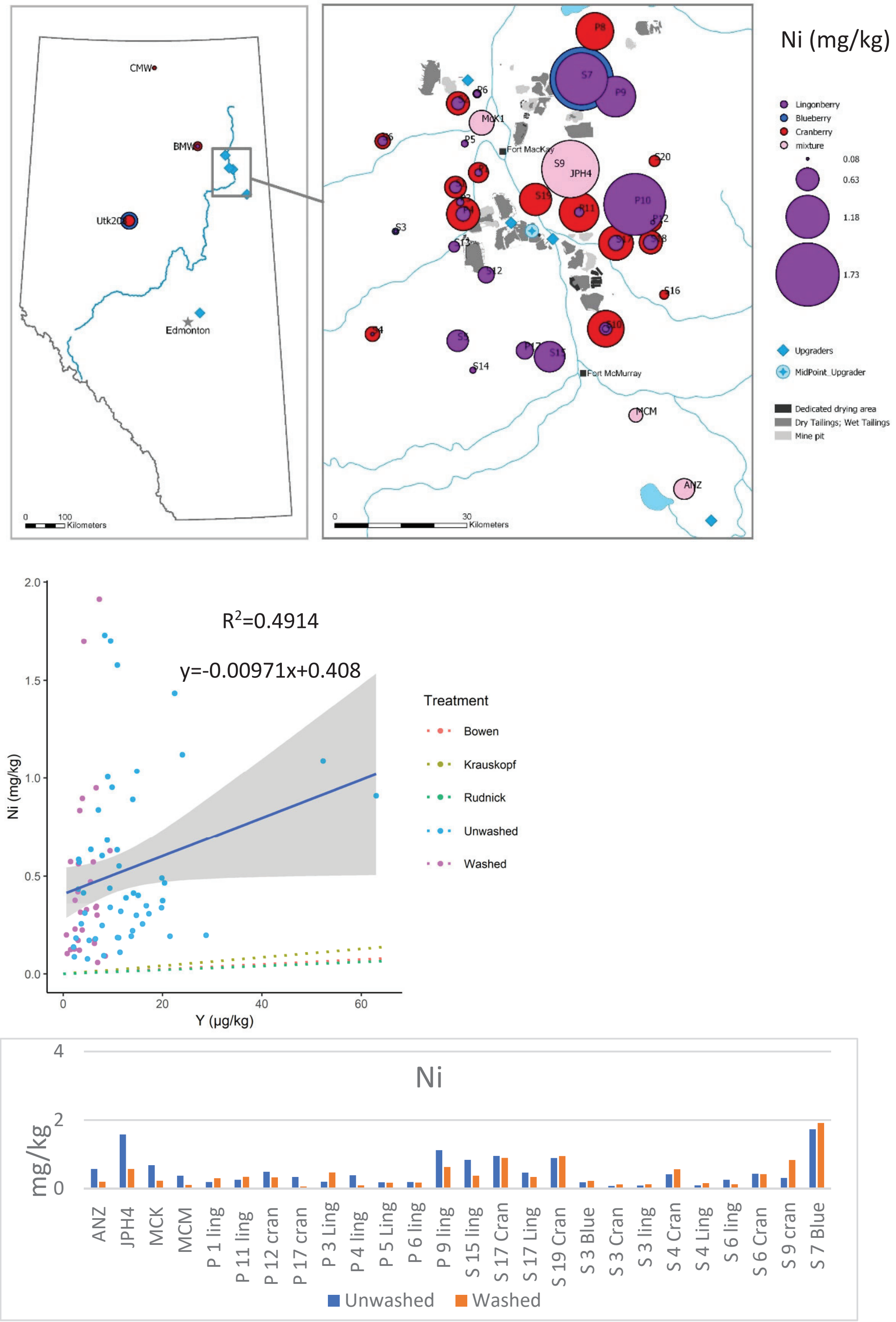

Figure A2-10:A) Spatial distribution of Ni concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Ni concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Ni in washed and unwashed berries, listed by sample name.

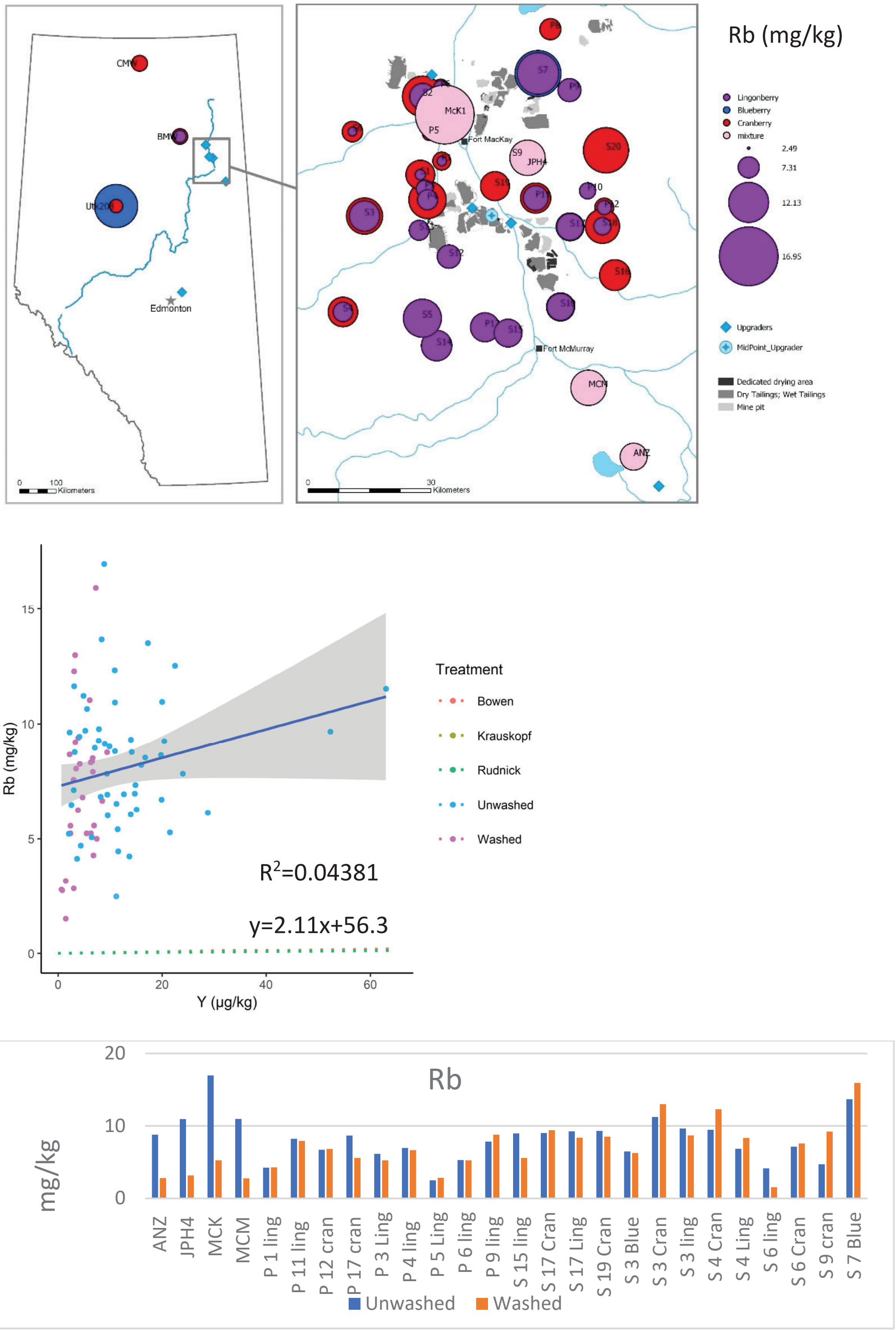

Figure A2-11:A) Spatial distribution of Rb concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Rb concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Rb in washed and unwashed berries, listed by sample name.

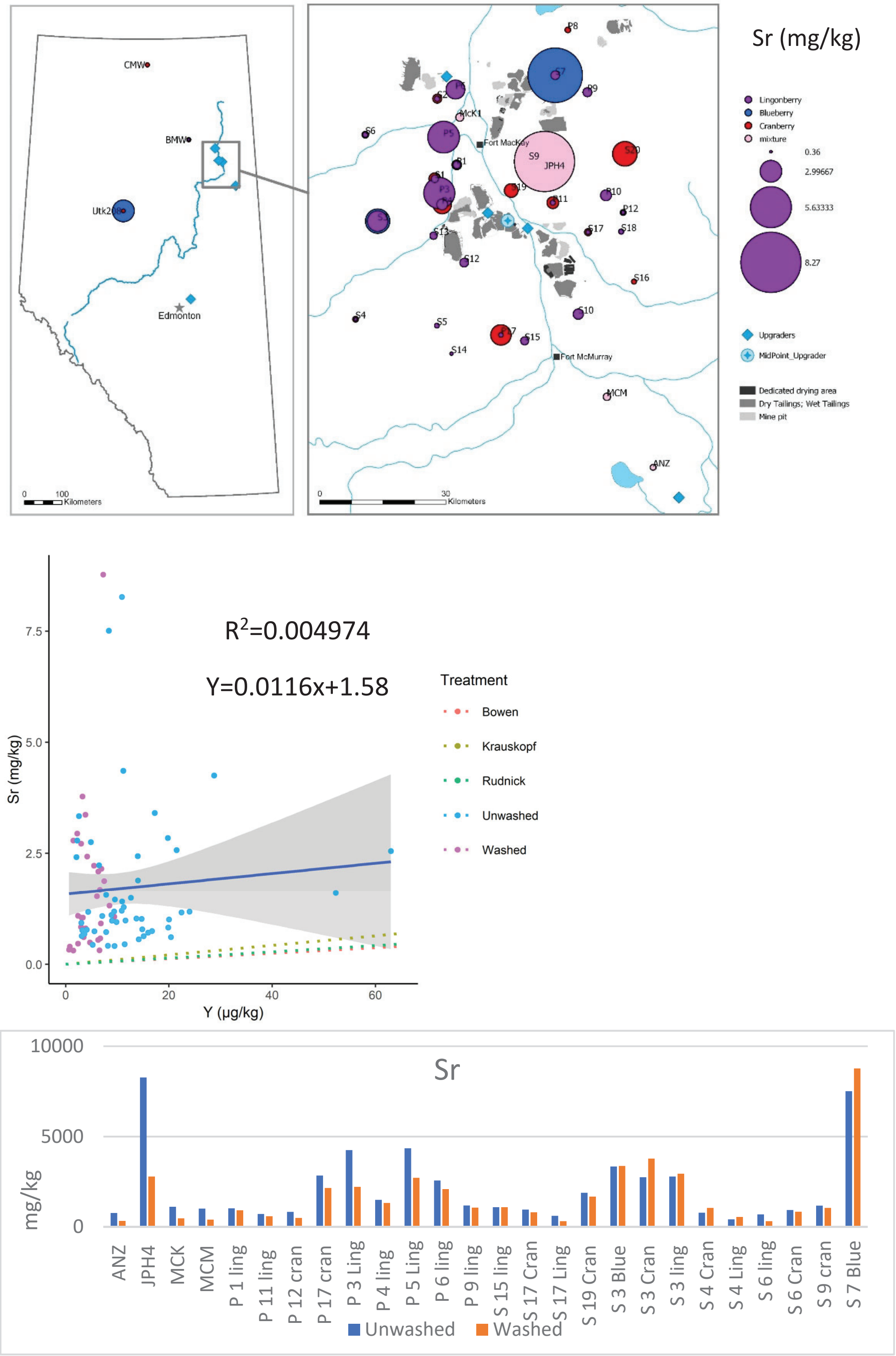

Figure A2-12:A) Spatial distribution of Sr concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Sr concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Sr in washed and unwashed berries, listed by sample name.

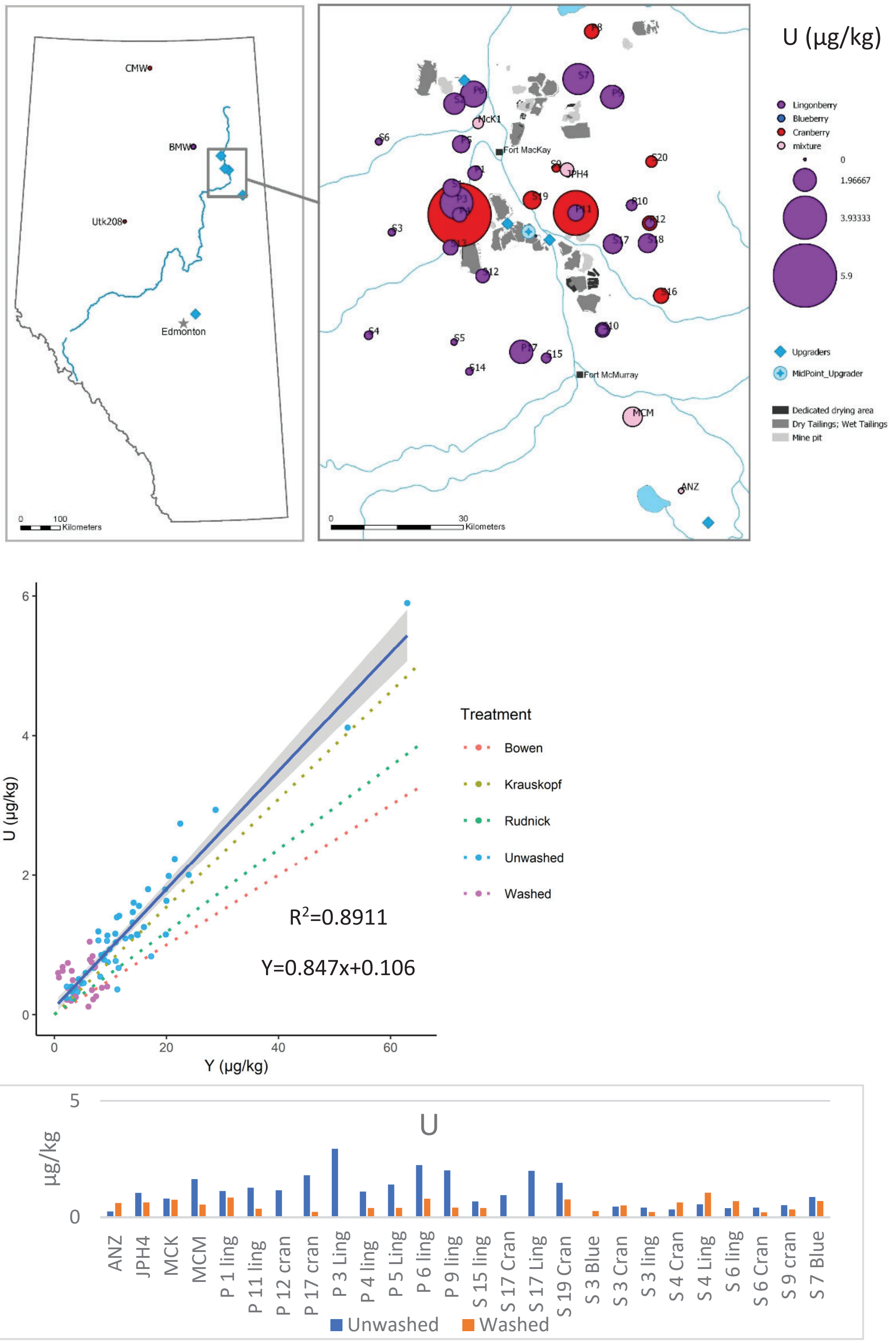

Figure A2-13:A) Spatial distribution of U concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of U concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of U in washed and unwashed berries, listed by sample name.

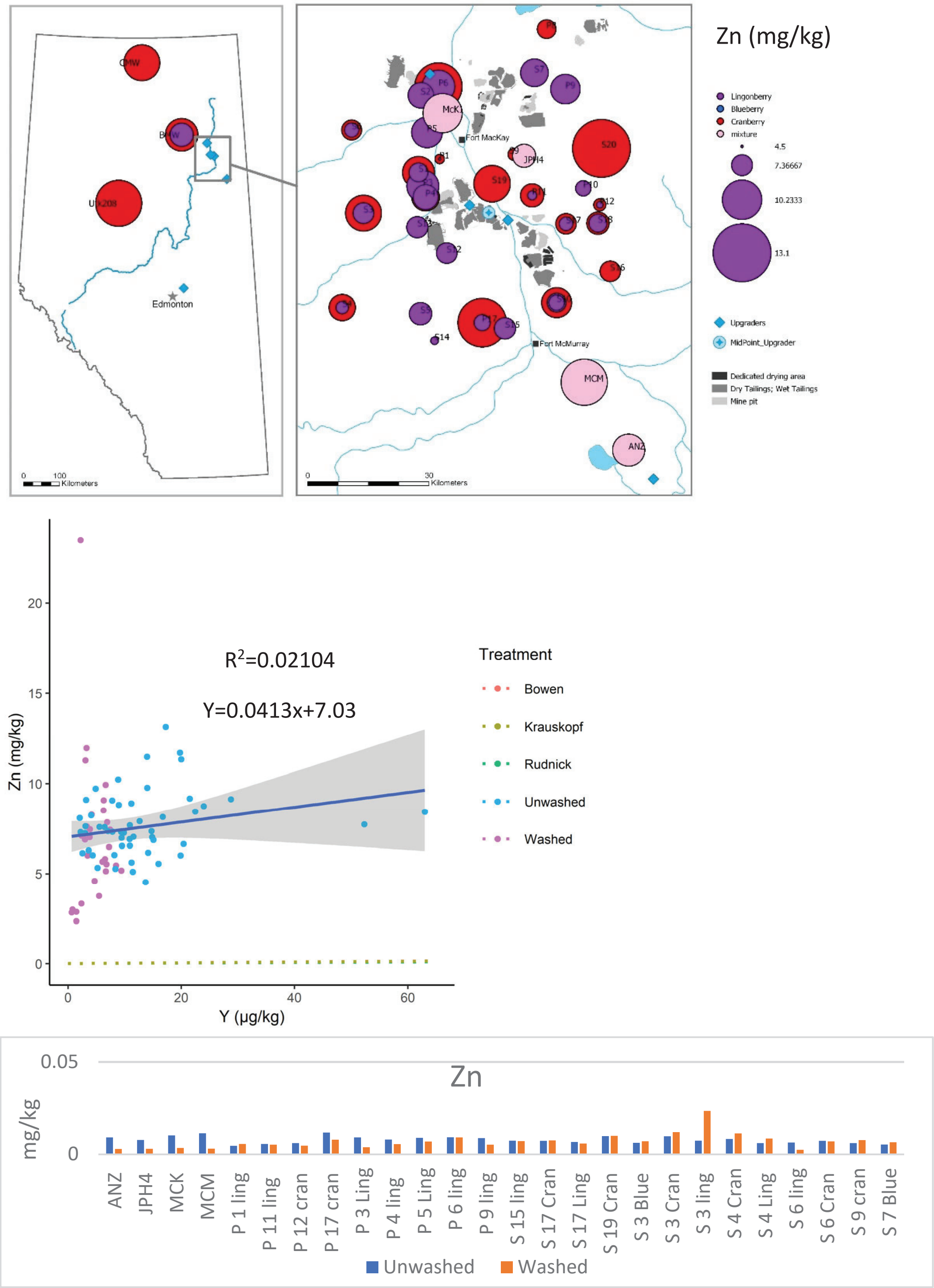

Figure A2-14: A) Spatial distribution of Zn concentrations in berries from the ABS region (right hand side) and the control sites (left hand side). B) Linear regression of Zn concentrations versus Y in washed and unwashed berries collected from the Athabasca bituminous sands region. C) Concentrations of Zn in washed and unwashed berries, listed by sample name.