Environmental and Nutritional Chemistry of Wild Harvested Blueberries vs. Commercial Blueberries: Depositional and Uptake Chemistry and Human Health Assessment

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Contents

LIST OF ABBREVIATIONS

ABS - Athabasca Bituminous Sands Region

Bq – becquerel

CCME – Canadian Council of Ministers of the Environment

CNSC – Canadian Nuclear Safety Commission

COPCs - contaminants of potential concern

DW – dry weight

EPA – Environmental Protection Agency

FW – fresh weight

IAEA – International Atomic Energy Agency

ICRP - International Commission on Radiological Protection

LOD – limit of detection

MDL – minimum detection limit

mSv - millisievert

NORM – naturally occurring radioactive materials

PTFE – polytetrafluoroethylene

SRM – Standard Reference Materials

TF – Transfer Factor

TOC – total organic carbon

ABSTRACT

In northern Saskatchewan, Canada, there are several active and decommissioned uranium mines and mills licensed by Canada's nuclear regulator, the Canadian Nuclear Safety Commission (CNSC). In these areas, Indigenous communities harvest traditional foods and Canadian diet studies have identified wild berries as an important part of their diet (Furgal, Powell, & Myers, 2005), (Roseanne C. Schuster, 2011), (Health Canada, 2010). Food ingestion is recognized as an exposure pathway of anthropogenic and naturally occurring radioactive materials and trace metals (Kuhnlein & Chan, 2000) and some communities may be concerned their traditional foods are contaminated from facility operations.

Wild blueberries and the soil the plant roots grew in were sampled approximately 10-25 kms away from CNSC-licensed facilities in northern Saskatchewan. As a comparison, commercially-available blueberries and soil were collected from Ontario farms and blueberries were obtained from grocery stores. Samples were analyzed for trace elemental concentrations by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and radionuclide activity concentrations were measured. Annual ingestion dose for blueberry consumption was conservatively estimated to be 0.0079 mSv/a. The blueberry results were compared to international guidelines and published literature and were not found to pose an ingestion health risk. The activity concentrations in blueberries ranged between 0.001-0.006 Bq/g d.w. for ^{210}Po and 0.003-0.005 Bq/g d.w. for ^{210}Pb and the concentrations of cadmium and arsenic in blueberries ranged between 0.002-0.07 µg/g and 0.0002-0.007 µg/g, respectively. This research project identifies geochemical relationships between radionuclides and trace elements in blueberries, examines the uptake chemistry, environmental cycling of radionuclides and trace elements, and the soil mineralogy and composition, helps inform CNSC's regulatory decision-making process, and supports future human health risk communication with Indigenous communities.

KEY WORDS

Wild Blueberries

Radionuclides

Trace Elements

Ingestion Dose

Atmospheric Deposition

Soil Uptake Chemistry

Traditional food

Indigenous

COPC

NORM

Chemical analogue

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CHAPTER 1: INTRODUCTION

1.1 Importance of Traditional Foods to Canadian Indigenous Communities

Indigenous peoples share a deep, spiritual relationship with all living things and with the land on which they live. For thousands of years, these communities have lived off the land, hunted and gathered traditional or country foods, have unique uses for wild plants and animals, and hold a wealth of knowledge about their traditional lands and the life these lands support (Kuhnlein & Chan, 2000). Having a diet rich in Indigenous traditional foods contributes to the personal and physical well-being of Indigenous people (Furgal, Powell, & Myers, 2005), (Roseanne C. Schuster, 2011) and numerous studies show that supplying oneself with food is culturally important to Canadian Indigenous people (Health Canada, 2010), (Furgal, Powell, & Myers, 2005). Indeed, traditional foods provide essential nutrients, better nutrient density than packaged foods, and physical activity for the harvester (Roseanne C. Schuster, 2011), (Furgal, Powell, & Myers, 2005). Despite this, there have been changes to consumption patterns of traditional foods due to the availability of low cost market food alternatives and in the perceptions of the health risks from ingesting traditional foods (Furgal, Powell, & Myers, 2005). Studies of changing diet patterns in Indigenous communities show that replacing traditional foods with market foods, which have high levels of sodium, saturated fats, and carbohydrates, is a risk factor in the rise of cardiovascular disease, obesity, and diabetes among Indigenous peoples (Furgal, Powell, & Myers, 2005), (Roseanne C. Schuster, 2011).

Food ingestion is a pathway of exposure of anthropogenic and naturally occurring radioactive materials (NORM), especially when chemicals may bioaccumulate in the food chain and when foods consumed are largely garden-grown produce and traditionally harvested foods (Gwynn, 2013), (Health Canada, 2010). There are challenges in communicating information concerning metals and radionuclides in traditional foods to Indigenous communities residing in Canada's north since the perception of health risks in ingesting their traditional foods may affect the physical and mental well-being of Indigenous people. Fishing, hunting, and harvesting foods are physical activities that positively contribute to better

fitness and better general health (Kuhnlein & Chan, 2000) and can reduce stress although stress levels may increase with lower amounts of traditional foods consumed. Mental well-being may also be affected with feelings of mistrust, scepticism, and confusion arising from scientists explaining concepts about "invisible" contaminants in their vitally important foods (Furgal, Powell, & Myers, 2005).

Traditional foods consumption varies regionally due to ecosystems and cultural preferences and there are many publications examining the quantities and preferences of Canadian Indigenous communities. Traditional or country foods represent between 6-40% of Indigenous diets in Canada with >250 different country foods identified from community surveys (L. Chan, 2018), (McGill University, 2008), (Roseanne C. Schuster, 2011), (Doyle, 2012), (Canada North Environmental Services, 2014), (M. Batal, 2017). The amounts consumed and types of traditional foods ingested is seasonally dependent. From Canadian diet surveys, over half of the Indigenous participants reported eating foraged foods (Health Canada, 2010) and wild berries have been identified as an important part of the traditional diets of Indigenous communities in Canada (Country Foods Study Year 1 - Uranium City, Saskatchewan, 2011; (Canada North Environmental Services, 2014); (Roseanne C. Schuster, 2011), (Chan, 2018).

1.2 CNSC Regulation of Licensed Uranium Mines and Mills in Northern Saskatchewan

The Canadian Nuclear Safety Commission (CNSC) regulates and licenses all nuclear activity in Canada, which includes proposed, existing, and decommissioned uranium mines and mills. All licensees must comply with the *Nuclear Safety and Control Act* and its regulations and they must comply with conditions set out in their licenses, which are issued by the Commission. There are both operating and decommissioned uranium mines and mills in Saskatchewan and the CNSC issues licences throughout a facility's lifecycle, enabling them to operate. Compliance activities are conducted by CNSC staff for mines and mills that are operating and decommissioned (Canadian Nuclear Safety Commission, 2021).

There are decommissioned uranium mines and mills in Northern Saskatchewan managed by federal, provincial or territorial government, or the former owners and are subject to regulation through verification activities, such as inspections, to ensure compliance with their license conditions (Canadian Nuclear Safety Commission, 2021). Uranium mines and mills must comply with the *Uranium Mines and Mills Regulations*, SOR/2000-206, which requires licensees to have an environmental protection policy and program, must have an environmental monitoring program, to have measures in place to control releases of nuclear substances and hazardous substances in the environment, and to have measures to prevent or mitigate the effects of accidental releases of nuclear and hazardous substances on the environment and the health and safety of persons (Uranium Mines and Mills Regulations, SOR/2000-206, Nuclear Safety and Control Act, 2000).

1.3 Studies of Trace Elements and Radionuclides in Foods

There have been many studies published on radionuclides in foods and trace elements in foods, whereas few studies consider both radionuclides and trace elements together.

Studies of Trace Elements in Foods:

A wild foods study was conducted in Saskatchewan near the Lac La Ronge Indian Band communities that included a diet survey with community members to gain information about the wild foods they consume. Blueberries, soil, sediment, and water were among the sample types collected and analyzed for elements and nutrients to establish a study area baseline. The elemental analysis results for blueberries showed the concentrations were similar to or lower than commercially available blueberries and were often below the laboratory's detection limits. The research concluded there are health benefits in consuming traditional foods and the contaminants of potential concern (COPCs) analyzed in wild foods from this area were among regional norms (Canada North Environmental Services, 2014).

Dr. William Shotyk has published several studies analyzing trace elements in berries in regions potentially impacted by industrial activities, such as oil sands development. Trace elements were studied in wild cranberries growing in peat bogs from northern Alberta, Canada, where sphagnum moss acted as the rooting medium. Trace elements in wild berries were compared to berries available commercially and from remote locations. The plant's elemental uptake, the natural elemental concentrations in cranberries, and the inputs from atmospheric dust were quantified. It was found that elements such as Ag, Al, Be, Co, Cr, Pb, and U appear to be from soil-derived dust and that elements such as Ba, Cd, Cu, Fe, Mn, Ni, and Zn were supplied by root uptake from soil (Shotyk W. , 2019). Figure 1.1 below shows concentrations of Al, Rb, Mn, Cu, Cd, and Pb in wild berries from reclaimed sites (RS berries) compared to commercial berries and berries from remote locations (Shotyk W. , 2020).

In 2020, Shotyk published a study on trace elements in wild berries growing on former open-pit bitumen mining areas, which included blueberries. Figure 1.1 shows elemental concentrations of Al, Rb, Mn, Cu, Cd, and Pb for berries from reclaimed sites, remote locations, in-house references, and blueberries obtained commercially. Shotyk found that micronutrients (Cu, Zn, Ni, and Mo) in the berries were supplied from plant uptake from their growing medium and that berries growing in remote and rural areas had higher concentrations of Mn, Cd, Ni, and Mo when compared to berries available commercially (Shotyk W. , 2020).

In 2019, Stachiw, et al. studied trace elements in wild berries growing near open pit mines in Alberta, Canada and compared the concentrations to berries from remote locations. It was found that essential elements for plants such as Cu, Mo, Ni, Zn and chemically mobile non-essential elements in the soil such as Rb, Sr, Ba, and Cd were independent of Y and were found to be taken up through roots into the berries. Contrasting this, elements such as Al, Cr, Pb, U, and V, were strongly correlated to Y, were found to be in higher concentrations in berries sampled from the open pit mines, and were largely

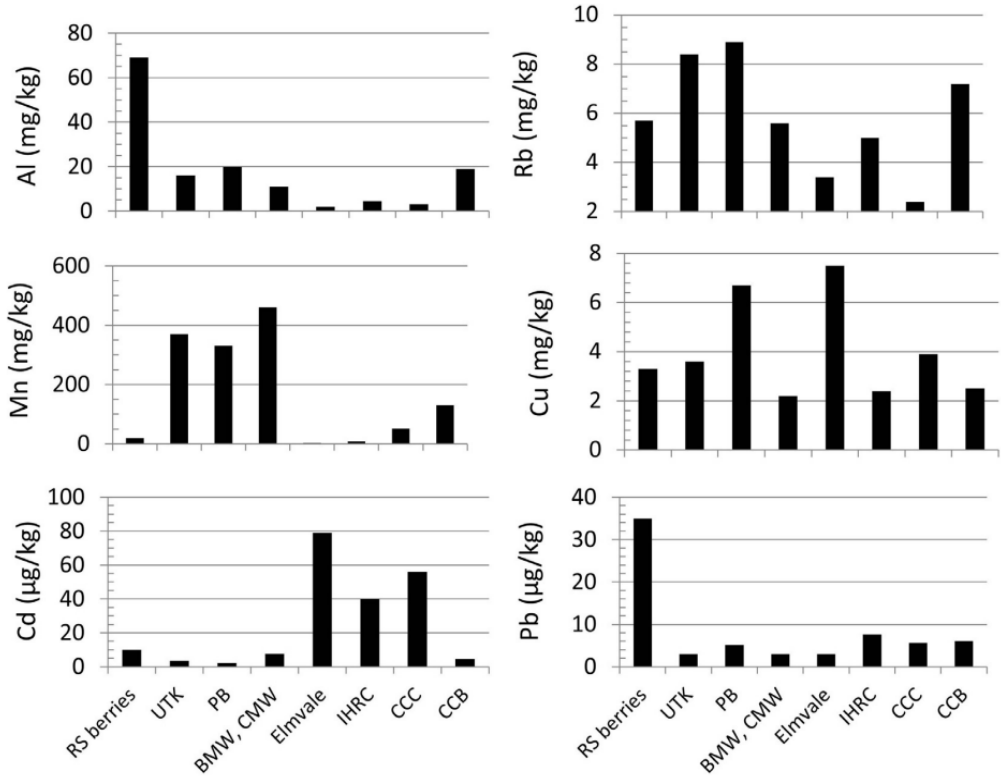

Figure 1.1: Concentrations of Al, Rb, Mn, Cu, Cd, and Pb (mg/kg or µg/kg) in wild berries sampled from reclaimed sites (RS berries), berries from remote locations (UTK, PB, BMW, and CMW), in-house reference cranberries (IHRC), and commercial berries (Elmvale, CCC, and CCB). Modified from (Shotyk W. , 2020).

deposited on the berry's surface from atmospheric dust, thus could be removed from the berries by washing. Figure 1.2 below shows the Y concentrations for berries sampled in the Athabasca Bituminous Sands Region before and after washing with water (Stachiw, 2019).

Trace elements have a natural crustal abundance, undergo geochemical cycling, and may also be supplied to the environment from anthropogenic activities. The research conducted on trace elements in wild berries from reclaimed bitumen mining sites in Alberta show that the elevated concentrations found in berries were largely from atmospheric dust inputs (ie. Al, Cr, Fe, Pb, Sc, Th, V, and Y). Figure 1.2 shows the Y concentrations in unwashed and washed berries from the Athabasca Bituminous Sands Region (ABS). The essential elements for plants (ie. Cu, Mo, Ni, and Zn) found in berries are taken into the plant

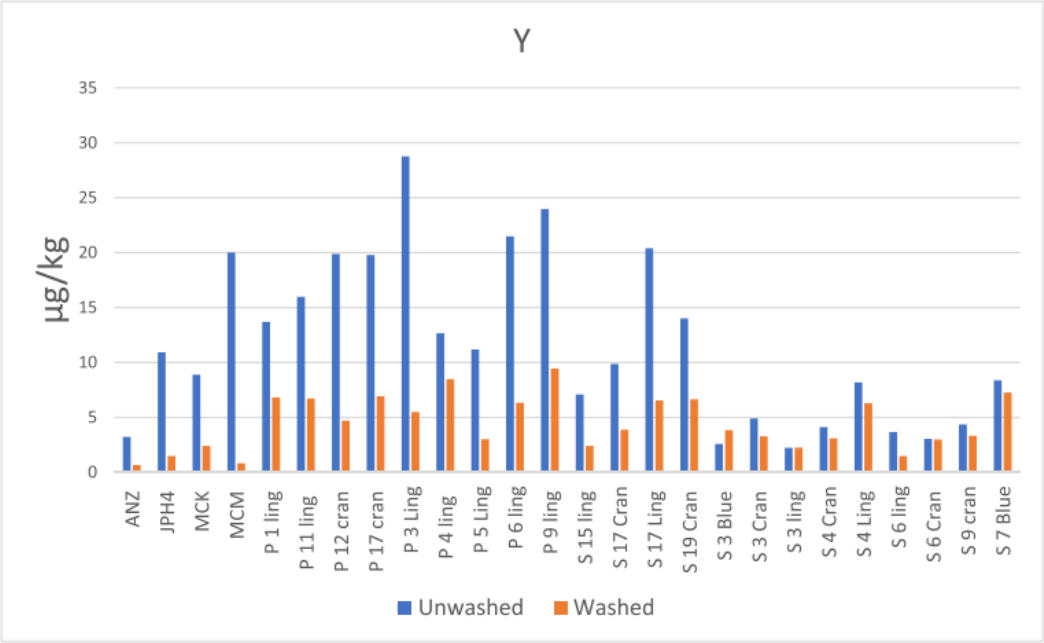

Figure 1.2: Y concentrations (µg/kg) in unwashed berries and berries washed with water, which were sampled from the Athabasca Bituminous Sands Region. Modified from (Stachiw, 2019).

through their roots and were only marginally more elevated, with a concentration factor between 2-4 times higher, or were similar to concentrations of berries from other locations (Shotyk W. , 2020), (Stachiw, 2019), (Shotyk W. , 2019).

Studies of Radionuclides in Foods:

Research on food-chain pathways and the uptake of trace elements and radionuclides in foods has been conducted worldwide and experiments have been done to determine the soil-to-plant concentration ratios for radionuclides (Napier, 2012). Transfer factors (TF) are used to describe the radionuclide uptake into plants from the soil compartment and is represented as a concentration ratio per mass unit of the plant's radionuclide concentration divided by the soil's radionuclide concentration. There are several factors that affect the TF value: soil mineralogy, soil composition, soil pH, amount of organic material in soil, the radionuclide's chemical form, the season, and time after contamination (Al-Masri, 2008), (Carini, 1999).

In 2002, the IAEA conducted habit surveys research and analyzed wild food samples that included berries in the United Kingdom. Concentrations of naturally occurring radionuclides, ^{210}Po, ^{210}Pb, ^{234}U, ^{235}U, ^{238}U, ^{230}Th, ^{232}Th, and ^{226}Ra were determined to estimate ingestion doses for high consumers. It was found that ^{210}Po and ^{210}Pb were the highest contributors to total dose for all foods measured in this study and were responsible for greater than 95% of the ingestion dose (Green, 2002). The IAEA recently published a guidance document based on extensive literature research which found that four radionuclides contribute approximately 78% of the ingestion dose from foods, namely ^{210}Po, ^{210}Pb, ^{228}Ra, and ^{226}Ra (IAEA, 2022).

Gwynn, et al. studied ^{210}Po, ^{210}Pb, ^{40}K, and ^{137}Cs in wild berries and mushrooms in Norway and estimated ingestion dose. It was found that for berries, the dose was mainly from ^{40}K. Using a high consumption rate, it was estimated that wild berries contributed a dose of 0.05 mSv/year while mushrooms contributed a dose of 0.5 mSv/year since mushrooms had higher concentrations of ^{210}Po (Gwynn, 2013).

Lehto, et al. studied ^{137}Cs, ^{239,240}Pu, and ^{241}Am in soil from Finland at different depths to determine the radionuclide transfer to different plant parts of wild berry plants and found that ^{137}Cs accumulated more in the edible berry than in other plant parts. Figure 1.3 shows activity concentrations for ^{137}Cs in berries from the Parkano site and their distribution through different plant tissues (Lehto & Vaaramaa, 2013).

Another study in Finland analyzed ^{210}Po and ^{210}Pb in mushrooms and wild berries growing in forests to determine their activity concentrations and distribution in the plant. Figure 1.4 that shows the distribution of ^{210}Po and ^{210}Pb activity in the different plant parts of berries. Vaaramaa, et al. found that the activity concentrations of ^{210}Po and ^{210}Pb were lowest in the fruit and highest in the plant stems and that the ^{210}Po/^{210}Pb activity concentration for wild berries showed the ^{210}Po activity concentration was elevated (Vaaramaa, 2009).

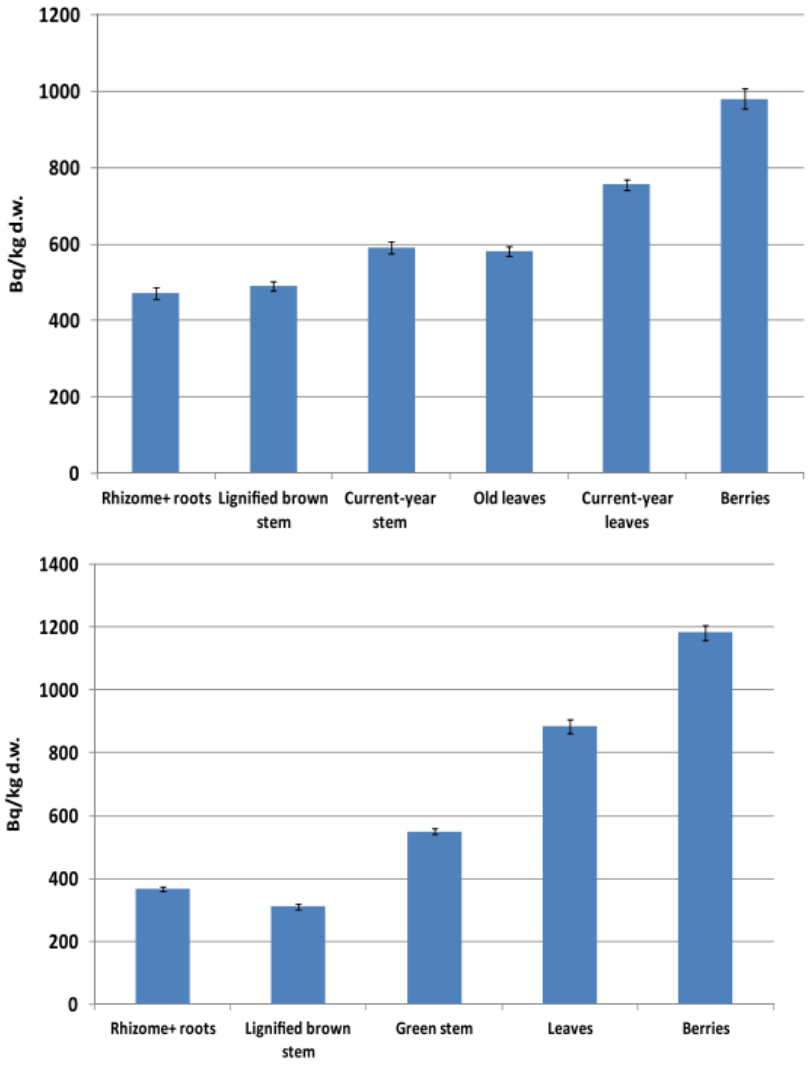

Figure 1.3: ^{137}Cs activity concentration (Bq/kg d.w.) distribution in lingonberry (left) and in billberry (right). Berries were sampled from the Parkano site in 2006. Modified from (Lehto & Vaaramaa, 2013).

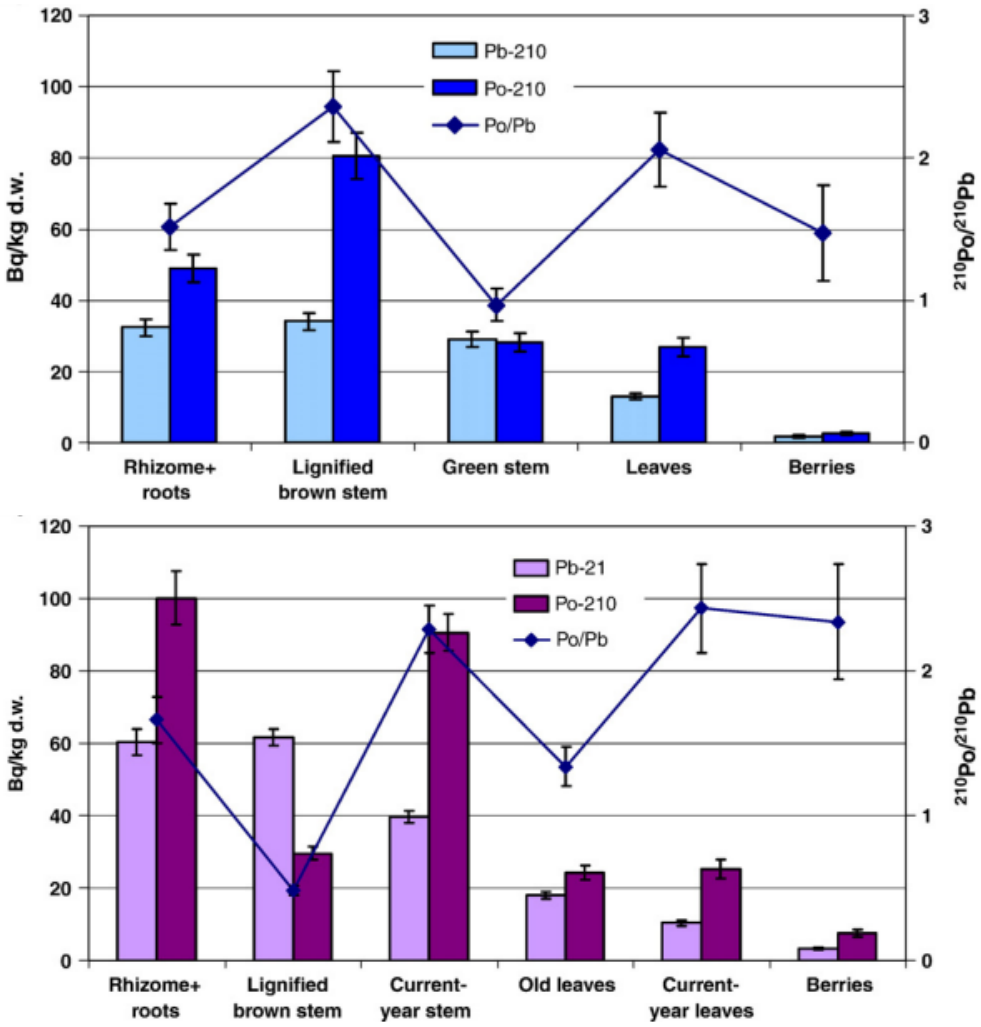

Figure 1.4: ^{210}Po and ^{210}Pb activity concentration (Bq/kg d.w.) distribution in blueberry from the southern Finland site, 2006 (above) and ^{210}Po and ^{210}Pb activity concentration (Bq/kg d.w.) distribution in lingonberry from the southern Finland site, 2006 (below). Modified from (Vaaramaa, 2009).

In the United Kingdom, McDonald, et al. studied several different foods, including blackberries, from 11 sites and analyzed for ^{210}Po and ^{210}Pb activity concentrations since these radionuclides contribute significantly to radiation dose from the diet. They found that cereals and offal had the highest concentrations and that the highest fruit, blackberries, had a ^{210}Po concentration of 0.4 Bq/kg (McDonald, 1999).

In Belarus, Sokolik, et al. studied the behaviour, bioavailability parameters, and soil to plant transfer of ^{238}U, ^{234}U, and ^{226}Ra in wild berries. Figure 1.5 shows activity concentration ratios of ^{238}U, ^{234}U,

and ^{226}Ra in wild berries. Sokolik, et al. found that soil characteristics were a factor in the uptake of these radionuclides from the soil into the berries. The concentration ratios for uranium and radium were higher in berries growing in sandy soils (sampling locations SPS2 and SPS3) when compared to the same berry species growing in loamy soils (sampling locations SPL3-1 and SPL4) (Sokolik, 2014).

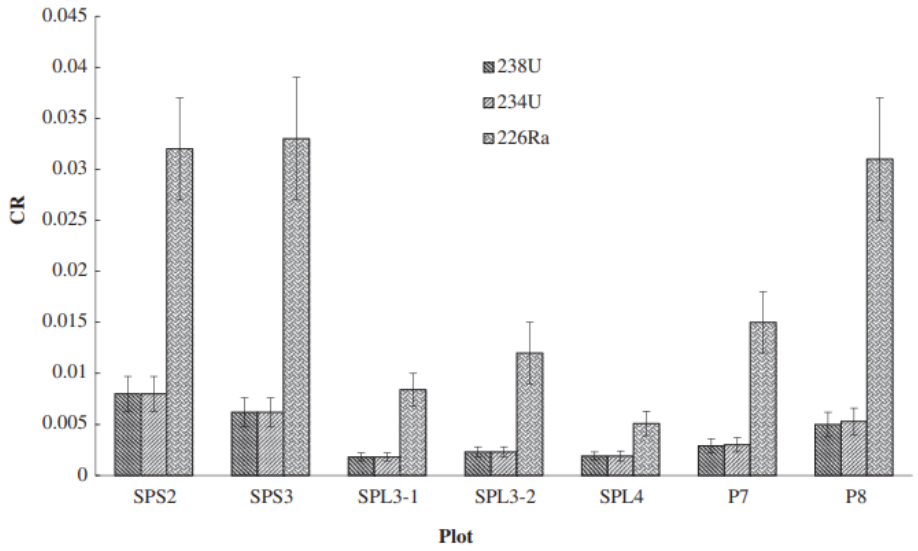

Figure 1.5: ^{238}U, ^{234}U, and ^{226}Ra activity concentration ratios for wild berries. Figure values are expressed as concentration ratios of specific activities with units Bq/kg d.w. Sampling location SPS2 and SPS3 had sandy soil whereas sampling locations SPL3-1 and SPL4 had loamy soil with the same berry species growing at each location. Modified from (Sokolik, 2014).

Wild food studies in Canada have identified berries as an important part of Indigenous diets and studies of radionuclides in berries have identified different factors that influence the uptake into different plant parts. Four radionuclides, ^{210}Po, ^{210}Pb, ^{228}Ra, and ^{226}Ra, have been shown to contribute approximately 78% of the ingestion dose from foods. In wild berries, ^{210}Po and ^{210}Pb were shown to have the lowest activities in fruit and ^{137}Cs was found to have the highest activities in fruit when compared to other plant parts (Canada North Environmental Services, 2014), (Al-Masri, 2008), (Carini, 1999), (Green, 2002), (IAEA, 2022), (Lehto & Vaaramaa, 2013), (Vaaramaa, 2009), (Sokolik, 2014).

1.4 Elements of Interest to Human Health Through Ingestion

There are both natural and anthropogenic sources of elements that can impact human health through ingestion and information about some elements of interest are provided below.

Element	Sources and Significance	Human Health Risk
Beryllium[1]	• Aircraft components (brakes, inertial guidance systems and gyroscopes, windshield frames) • Neutron moderators in nuclear reactors • Springs, switches, and connectors in radar and telecommunications equipment	• Carcinogen (lungs) • Berylliosis • Lung disease (chronic Beryllium disease)
Arsenic[2,3]	• Occurs naturally in the environment and the earth's crust • May enter waterways from dissolved rock and mineral deposits, industrial waste discharges, and atmospheric deposition • Can enter environment from burning waste and fossil fuels (ie. coal), producing metals (ie. Gold), and agricultural practices (ie. spreading pesticides and feed additives) • Introduced to food chain from water, soil, air, and food • Inorganic chemical form is more toxic than organic chemical form • Organic Arsenic in fish and shellfish; inorganic Arsenic in fruit juice and rice	Exposure (years or decades) to high levels in drinking water: • Risk of bladder, liver, and lung cancer • Thickening and discoloration of skin • Nausea and diarrhea • Decreased blood cell production • Abnormal heart rhythm and blood vessel damage • Numbness in hands and feet • Fetus or child: exposure to high concentrations of inorganic Arsenic may pose increased risk to adult cancer and may affect development
Selenium[4,5]	• Occurs naturally in the environment and the earth's crust • Essential nutrient • Natural sources: weathering of rocks and soils, volcanic activity, and wildfires • In crude oil and coal deposits • Can enter environment from fossil fuel combustion, mining, metal smelting and refining, agriculture, and wastewater treatment • In foods (nuts, fish and seafood, cereal products, marine mammals, and organ meats)	• Selenosis can result from elevated exposures • Hair loss • Muscle weakness • Reduced brain function • Nail loss and deformities • Stomach and intestinal disorders • Tolerable upper intake level = 400 µg/day (total intake from food, water, and supplements)
Cadmium[6]	• Occurs naturally in the environment • From industrial processes and can accumulate over time • Major source for cigarette smokers via inhalation • Major source for non-smokers via food ingestion with potential exposure from ambient air, drinking water, dust, and soil	• Carcinogen • Can affect kidneys, lungs, and gastrointestinal tract

Lead[7,8,9,10]	• Ubiquitous in the environment and occurs naturally in earth's crust • Leaded gasoline, lead-based paint, lead-acid batteries, and plumbing • Air travel, commercial and consumer products, and industry (ie. pulp and paper, iron and steel, mining, and metal smelting) • Can enter food chain from the uptake from soil by plants, deposition from airborne lead on plant surfaces, absorption of lead from water and sediments by fish, and in game shot with lead bullets	• Harmful effects to brain, heart, kidneys, and reproductive organs • Infants, children, and developing feus are the most susceptible due to their developing brains • Added to List of Toxic Substances in Schedule 1 of CEPA 1988
Uranium[11,12, 13, 14]	• Occurs naturally in soil and rock • Found in large deposits in Canada, which is one of the world's largest uranium producers • Natural uranium contains three main isotopes as a percent by mass: ^{238}U (99.27%), ^{235}U (0.72%), and ^{234}U (0.0054%) • Uranium ore is mined, milled, enriched to increase the ^{235}U concentration, and processed into fuel bundles to be used in nuclear power reactors • Uranium decay produces long-lived radionuclides ^{230}Th and ^{226}Ra and its final form after decay is stable lead • Depleted uranium metal is used as aircraft counterweight, shielding material, and as the container material for transporting radioactive substances	• Affects kidney function • Inhalation of large quantities of uranium for a long time increases lung cancer risk • Heavy metal with similar health effects to Pb, Cd, Ni, Co, and W • Toxic when taken internally (no chemical toxicity from external exposure) • Chemical toxicity is more of a human health risk than its radiological toxicity

Table 1.1: Sources, Significance, and Human Health Risk of Elements

References:

[1] (Government of Canada, 2013), [2] (Government of Canada, 2022), [3] (Government of Canada, 2006), [4] (Government of Canada, 2019), [5] (Government of Canada, 2021), [6] (Government of Canada, 2021), [7] (Government of Canada, 2020), [8] (Government of Canada, 2020), [9] (Government of Canada, 2021), [10] (Government of Canada, 2013), [11] (Rachel Lane, n.d.), [12] (Government of Canada, 2008), [13] (Government of Canada, 2021), [14] (Government of Canada, 2009).

1.4.1 Cycling, Reservoirs, and Levels of Trace Elements in the Environment

Beryllium

Burning fossil fuels, mining, metallurgy, and increases in anthropogenic activities that disturb the land has contributed to increases in beryllium in our environment and its transport within ecosystems. (J. Vesely, 2002).

Beryllium is a lightweight, strong metal, commonly mined from beryllium-containing silicate rocks such as beryl, $Al_2Be_3Si_6O_{18}$, and bertrandite, $Be_4(OH)_2Si_2O_7$ and there are around 50 naturally occurring minerals that contain beryllium. The most commonly occurring beryllium-containing silicates are not readily affected by chemical weathering due to their insolubility in aqueous environments. In acidic and highly organic rivers, beryllium is readily mobile, whereas in oceans, beryllium is found at much lower concentrations. Beryllium tends to react similarly to zinc (Zn^{2+}) due to its small size and ability to bond covalently although it forms mainly oxides and is more lithophilic than zinc (T. P. Taylor, 2003).

In the soil compartment, beryllium's concentration is not uniform and ranges worldwide between 0.1 - 40 mg/kg. In acidic soils (pH <4) and in the presence of fulvic and humic acids, Beryllium complexes with phenol and carboxyl species. In environments with acidic soil (pH <5.5) without humic acid, beryllium will adsorb to silica and kaolinite minerals and it was found that the presence of humic acid dramatically increased beryllium's solubility in acidic environments (T. P. Taylor, 2003).

The primary source of beryllium in the atmosphere is from burning coal. In the atmosphere, there are ^{9}Be and soil dust particles from anthropogenic emissions and also ^{7}Be and ^{10}Be from cosmogenic production. Wet precipitation will deposit these beryllium isotopes back to the earth's surface. The concentrations of beryllium measured in precipitation are correlate with the quantities of emissions from coal combustion operations in that area (J. Vesely, 2002).

It is estimated there is 80,000 tons of beryllium worldwide with between 1.9 ppm beryllium in the upper continental crust (Z. Hu, 2008) (T. P. Taylor, 2003).

Arsenic

Arsenic accumulates in ocean sediments from runoff from the earth's surface, upwelling of the ocean floor, and weathering of rocks that contain arsenic, such as shales. Shales are formed in areas with particles the size of clays and silt and arsenic in these environments tends to adsorb to their surfaces.

The earth's dominant arsenic reservoir has been found to be in the ocean's carbonaceous shales due to the sorption of arsenic on shale-forming particles (Nordstrom, 2012).

Anthropogenic activities worldwide are responsible for producing an estimated 82,000 metric tons of arsenic annually. With the knowledge of arsenic toxicity to humans through ingestion and its affects on the environment, there has been a decrease since the 1960's in using arsenic rich compounds in agricultural practices (Nordstrom, 2012).

Studies on the As(V) cycling have shown this process is facilitated by microorganisms capable of arsenic respiration to reduce As(V) to the mobile As(III) species below the earth's surface. In a mining community in Sweden, where there were high concentrations of arsenic in soil, sediments, groundwater, and surface water, the predominant arsenic species in the groundwater and surface water was As(III). In studying the microorganisms living in the sediment, it was found that in an aqueous environment, *Arsenicicoccus bolidensis* was able to reduce As(V) to As(III) and this microorganism may play an important role in the biogeochemical cycling of arsenic (P. Bhattacharya, 2007).

It is estimated there is between 4.8-5.7 ppm of arsenic in the upper continental crust. Its distribution in the earth is not uniform and it has been found that its concentration decreases with increasing depth toward the earth's mantle (Z. Hu, 2008) (Nordstrom, 2012).

Selenium

Selenium is largely found in limestone, quartzite, and sandstone rocks and is supplied to other earth compartments through interactions between rocks and water, weathering, and other biological processes. The average concentration of selenium in soil is estimated to be between 0.01 to 2 ppm. Soils from parent rocks such as Cretaceous shales and Precambrian carbonates tend to have elevated selenium concentrations. Of selenium's five oxidation states, its oxyanions selenite (SeO_3^{2-}) and selenate (SeO_4^{2-}) are found in the aqueous phase within alkaline soils that are well-aerated due to their solubility. Elemental

selenium and its insoluble forms tend to be found in soils that are reducing, acidic, not well-aerated, and organic-rich (Fernández-Martínez, 2009).

Agricultural irrigation and the use of phosphate pesticides and phosphate fertilizers has mobilized selenium in the environment due to higher concentrations of selenium in some phosphate rock. In soils, selenium cycling involves bio-methylation by microorganisms. Bio-methylation involves several redox reactions that convert Se^{+4} and Se^{+6} to Se^{-2} and then the Se^{-2} species undergoes methylation. There are volatile and non-volatile selenium-containing compounds produced from bacterial and microbial methylation and the volatile products are able to enter the atmosphere from the Earth (Fernández-Martínez, 2009).

Coal combustion and industrial processes are key contributors of atmospheric selenium. Selenium also enters the atmosphere from volcanic activity since the high temperature environments of volcanoes causes selenium to volatilize and escapes as a gas, which reduces the selenium concentration found in volcanic soils. Other sources of atmospheric selenium come from suspended sea salts and from wind erosion of the Earth's surface that contributes selenium-containing dusts to the atmosphere (Fernández-Martínez, 2009).

In the earth's crust, selenium is a trace element with an averaged estimated concentration between 0.05 to 0.09 mg/kg. Its compounds are found worldwide in air, water, soil, and rocks. (Fernández-Martínez, 2009).

Cadmium

Cadmium occurs naturally in the Earth's crust and flows to different compartments through a number of processes that include volcanism, uplift, weathering, sedimentation, biological mobilization, atmospheric transport and deposition, and ice, groundwater flows, and streams (National Academy of Sciences, 1997).

Coal combustion, burning household wastes, metal mining, and metal refining releases cadmium to the atmosphere and the highest atmospheric concentrations will correspond to anthropogenic activities that produce cadmium in that area such as coal combustion facilities, smelting facilities, and municipal incinerators (National Academy of Sciences, 1997) (B. O. Otunola, 2020).

In the soil compartment, cadmium and other heavy metals have been found to adsorb to the charged surfaces of clay minerals in acidic aqueous solution, which can transfer cadmium and other heavy metals to other environmental compartments via clay transport. Clay minerals have been successfully used in soil remediation activities. The addition of clay minerals to amend cadmium-polluted, acidic rice paddy soils in some agricultural areas in China was able to reduce cadmium's bioavailability, increase soil pH, immobilize and stabilize cadmium, and reduce the heavy metal fraction overall that was phytoavailable, which resulted in a decrease in cadmium concentration in brown rice grown in these soils. Clay mineral's ability to increase soil pH is the key to remediation activities of soil polluted with heavy metals (National Academy of Sciences, 1997) (B. O. Otunola, 2020) (Y. Xu, 2017).

Cadmium is mobile in soils. It is not an essential nutrient but it can be taken up by plant roots as a chemical analogue of zinc (Stachiw, 2019).

Cadmium can enter surface water and groundwater through leaching from rocks, atmospheric deposition, and industrial discharge. Freshwater burial is an important sink for cadmium that enters active compartments such as lakes, rivers, ocean pools, soils and the atmosphere (National Academy of Sciences, 1997).

There is estimated to be, on average, 0.06 ppm Cd in the upper continental crust (Z. Hu, 2008).

Lead

Lead occurs naturally in the earth's crust and is one of the world's major heavy metal, environmental contaminants and its persistence in the environment and toxic effects on all living things

is concerning. Natural environmental lead sources are from erosion of rock containing lead deposits, volcanic eruptions, fires, and salt spray from the sea. Lead exists primarily in the inorganic Pb(II) oxidative state but can also exist as inorganic Pb(0) and Pb(IV). The organic forms of lead are triethyl lead, $Pb(CH_3)_3$, and tetraethyl lead, $Pb(CH_3)_4$ which are more toxic and more volatile than its inorganic forms (B. O. Otunola, 2020) (Rahman, 2019) (Rauch, 2009).

Over the last 5000 years, anthropogenic sources of lead have entered the atmosphere through fossil fuel combustion of coal and leaded gasoline, metals smelting, and incinerating waste. Isotopic analysis of Pb has been used to trace the sources of Pb in the environment. Research has found that Pb aerosols in the atmosphere can transport over long distances and that atmospheric lead in typically in the following forms: $PbSO_4$, $PbCO_3$, $Pb(CH_3)_3$, and $Pb(CH_3)_4$ (Komarek, 2008) (Rahman, 2019) (Rauch, 2009). Leaded gasoline was a significant source of atmospheric lead in the 20th century until it was banned in the USA in the 1980's although some uses of leaded gasoline were exempt from the ban. According to the EPA's 2020 National Emission Inventory, leaded gasoline from the aviation industry is currently the largest Pb source in the USA (R. Levin, 2021).

Currently, recycling of lead-acid batteries, lead mining, and processing lead ore are the main pathways of mobilizing lead in the environment. Dumping leaded waste in areas such as India, Kenya, and Indonesia, where hazardous waste is uncontrolled, has had environmental consequences to people living nearby. Soil is the primary reservoir for lead introduced into the environment from leaded gasoline and lead-based paints (Rahman, 2019), (R. Levin, 2021).

In the soil compartment, water and soil pH affects Pb's solubility and mobility. Pb tends to form complexes with organic ligands and inorganic ions and can adsorb onto the surface of clay minerals, which have been used in remediation activities. Lake sediments and aqueous solutions polluted with heavy metals such as Pb have been successfully remediated with the addition of clay minerals such as

attapulgite. Bentonite clay has also been shown to reduce the Pb concentrations in brown rice grown in heavy metal polluted soils due to its ability to decrease the mobility of heavy metals (Rahman, 2019), (B. O. Otunola, 2020).

Rauch, et al. estimated the global mean metal concentrations for lead to be 17 ppm in the upper continental crust, 27 ppm in soil, 0.000001 ppm in the atmosphere, and 17 ppm in continental sediment (Rauch, 2009).

Uranium

Uranium is a long-lived radioisotope with a half-life of 4.5 billion years, which is in the same range as that of the earth's age, and it is an actinide with the highest natural abundance. This mineral has been found in sedimentary-type and sandstone-type deposits worldwide, is a non-renewable resource, and is globally important to energy production. Starting about 2.4 billion years from the present, with the increase in oxygen concentrations in the atmosphere, the uranium that was concentrated in the continental crust became oxidized. This promoted its mobility in aqueous solutions on the earth's surface and lead to its considerable deposits to the oceans where it could be subducted and recycled

back to the earth's mantle (Mortvedt, 1994), (Clark, 2015), (Finch, 1999), (F. Wang, 2017), (M. B. Andersen, 2015).

The oxidation states of uranium in the natural environment are most commonly Uranium(VI) and Uranium(IV) and its oxidation state depends on if its environment is oxidizing or reducing. Weathering of primary mineral rocks containing uranium by oxidizing waters can change uranium's oxidation state from its highly immobile, tetravalent U(IV) oxidative state to the highly mobile, hexavalent U(VI) oxidative state, which forms soluble uranyl cations (UO_2^{2+}) or uranium-carbonate complexes, which can be deposited again when waters reach reducing zones (Napier, 2012), (Clark, 2015), (Walther C. , 2015) (Finch, 1999).

Bacteria species have been found to be important in uranium bioremediation activities since they influence uranium's oxidation state and increase its mobility in the environment. Chao et al. studied uranium remediation using hydroponically grown plants (*Syngonium podophyllum*) in the presence of the fungus *Aspergillus niger*. They found that *A. niger* changed uranium's chemical form and decreased its root cell phytotoxicity (Finch, 1999), (Chao, 2019).

There is estimated to be, on average, 2.6 ppm of uranium in the upper continental crust, 120 ppm in phosphate rocks, and 1.2 ppm in sedimentary rocks (Clark, 2015), (Z. Hu, 2008), (Finch, 1999).

1.5 Radionuclides of Interest to Human Health Through Ingestion

Both natural and artificial sources of radionuclides can impact human health through ingestion. Information about some radionuclides of interest is provided below.

Radionuclide	Sources and Significance	Human Health Risk
^{137}Cs References: 1,2,3,4,5, 11, 20	• Half-life of 30.17 years • Long lived, artificial radionuclide • Decays to stable barium, ^{137}Ba; both are used to sterilize medical equipment • Sources: Fission fallout pollutant from Chernobyl in Ukraine (1986), Fukushima Daiichi in Japan (2011), released following a graphite fire from Windscale facility in the UK (1957), and released from nuclear weapons testing (1950's, 1960's, 2016, 2017) • Gamma radiation emitter • Exposure: ingestion of ^{137}Cs in food and water and inhalation of ^{137}Cs in air	• Leukemia and cancer risk from long-term exposure • ^{137}Cs distributes uniformly in the body • Homologue to potassium (essential plant nutrient); can be passively taken up by plants • Contributes ~1% of ingestion dose from food
^{210}Pb References: 4, 6, 7, 8, 9, 10, 11, 12, 16	• Half-life of 22.3 years • Naturally occurring radionuclide; virtually all ^{210}Pb is from the ^{238}U decay series • Daughter nuclide of ^{222}Rn gas (atmospheric deposition) and from the decay of ^{238}U in soil (in situ) • Decays to stable lead, ^{208}Pb • Beta radiation emitter • Sources: Produced from thermonuclear detonations where Soviet bomb material was ^{208}Pb (1959-1962), emitted to air from the phosphate fertilizer, iron, and	• Leukemia and cancer risk • Highest internal dose from ^{210}Pb is in bone surfaces; intermediate dose to soft tissues (red marrow, kidneys, liver, and spleen); lower dose to radiosensitive organs (brain, breast, thyroid, gonad) • High chemical toxicity and high radiological toxicity • Air quality may be affected by seasonality and presence of aerosol

	steel industries, metal smelting, and from burning fossil fuels and vegetation • Exposure: food ingestion (cereal, meat, vegetables, reindeer/caribou tissues, such as liver and kidneys, and alcoholic beverages), drinking untreated mineral water, and inhalation when smoking tobacco and from ^{210}Pb in air (inhalation of ^{222}Rn gas will also decay into ^{210}Pb in the body)	particles; higher ^{210}Pb activity concentrations in winter and ^{210}Pb adsorbs to sub-micron sized particles • Contributes ~ 19% of ingestion dose from food
^{210}Po References: 7, 8, 10, 11, 12, 13, 14, 16	• Half-life of 138.4 days • Naturally occurring radionuclide; virtually all ^{210}Po is from ^{238}U decay series • Daughter nuclide of ^{210}Pb • Decays to stable lead, ^{206}Pb • Alpha radiation emitter • Sources: emissions from cement industry, phosphate fertilizers • Uses: Alloyed with beryllium for neutron sources, removes static in industrial settings, removes dust from camera lenses and film, and heat source for satellites • Exposure: food ingestion (fish, shellfish, seafood, reindeer/caribou tissues including liver and kidneys, and alcoholic beverages) and inhalation of ^{210}Po when smoking tobacco and from inhaling smoke from vegetation fires	• Leukemia and cancer risk • Highly radioactive and chemically toxic • Elevated concentrations in lungs of smokers • Very low natural concentrations so large ^{210}Po radiation dose is extremely unlikely • Cannot penetrate skin (not an external dose concern) • Distributes uniformly in soft tissues; tissues can be damaged by alpha particle absorption • More harmful to tissues than ^{210}Pb • Most ^{210}Po is excreted through feces but can concentrate in kidneys, liver and spleen • Contributes ~52% of ingestion dose from food
^{226}Ra References: 1, 4, 6, 8, 11, 15, 16, 17, 18, 19	• Half-life of 1620 years • Naturally occurring radionuclide; decay product from ^{238}U decay series • Decays to stable lead, ^{206}Pb • Alpha radiation emitter • Ingredient in luminescent paint (early 1900's) • Sources: Production and processing water and in wastes from oil and gas extraction, phosphate fertilizers (found in phosphogypsum waste), iron and steel industries, and mine wastes (tailings) • Exposure: Radium can be inhaled (ore dust from uranium processing), can enter the food chain through streams and underground waters, and can then enter soil, be taken up by plants and animals	• Lung, bronchi, lymphoma, leukaemia, liver, kidney, and bone cancer risk • Risk of non-malignant respiratory, renal, and cardiovascular disease • Found primarily in bone (long retention in bone and 1/10th of bone activity compared to ^{210}Pb) • Chemical analogue of calcium; can be taken up from soil into plants and transferred to animals and humans through ingestion • Contributes ~6% of ingestion dose from food

Table 1.2: Sources, Significance, and Human Health Risk of Radionuclides

References:

[1] (IAEA, 2014), [2] (Chatterjee, 2017), [3] (Al-Masri, 2008), [4] (Walther C. , 2015), [5] (UNSCEAR, 2017), [6] (IAEA, 2022), [7] (Gwynn, 2013), [8] (IAEA, 2017), [9] (Clark, 2015), [10] (Salmon, 1998), [11] (UNSCEAR, 2000), [12] (Pang, 2019), [13] (Canadian Nuclear Safety Commission, 2012), [14] (IAEA, 2006), [15] (Madruga, 1998), [16] (Gupta, 2014), [17] (Salmon, 1998), [18] (Zablotska, 2013), [19] (IAEA, 2014), [20] (United States EPA, 2002).

1.5.1 Cycling, Reservoirs, and Levels of Radionuclides in the Environment

^{137}Cs

^{137}Cs is a fission product (half-life: 30.2 years) found on the earth's surface as fallout from nuclear accidents and from weapons testing. Fallout has been unevenly distributed and has predominately deposited Northern Hemisphere, where nuclear testing originated (IAEA, 2014), (Walther C. , 2015), (Chatterjee, 2017).

Radionuclides in the atmosphere can adsorb to particles and can then be deposited on the earth's surface through wet and/or dry deposition. ^{137}Cs is volatile and can be released to the atmosphere from explosions, fires, and heating, as was the case during the Chernobyl accident in 1986, which was a major atmospheric contributor of ^{137}Cs. Chernobyl released an estimated 85 x 10^{15} Bq of aerosol and gaseous emissions of ^{137}Cs following the accident. Another major contributor of ^{137}Cs was nuclear weapons testing in the 1950's and 1960's, which peaked in 1963, and released an estimated 948 x 10^{15} Bq of ^{137}Cs. With a half-life of 30.2 years, ^{137}Cs from these sources has undergone significant decay. More recently, ^{137}Cs has been released to the atmosphere from the Fukushima Daiichi Nuclear Power Plant's 2011 accident, which released an estimated 2.7 x 10^{15} Bq, and from North Korea's underground nuclear weapons testing in 2016 and 2017 (Walther C. , 2015), (IAEA, 2014), (Lehto & Vaaramaa, 2013), (Nanba, 2022), (Russell, 2015), (Onda, 2020), (UNSCEAR, 2000).

In soils, ^{137}Cs can adhere to the surface of mineral particles (especially to clay minerals), which can lower its bioavailability to be taken up and absorbed into plant roots. There are several factors that affect the immobilization of ^{137}Cs in soil: the type and amount of clay minerals present, soil pH, organic carbon, and the ammonia and potassium content. Plants can uptake ^{137}Cs from soil, although the amount is considered negligible, and ^{137}Cs will be returned to the soil through vegetation decay. ^{137}Cs can also be

redistributed in the environment from the soil compartment via processes such as erosion (UNSCEAR, 2000), (IAEA, 2014), (Lehto & Vaaramaa, 2013), (Nanba, 2022), (Russell, 2015).

Cesium is not an essential element in the body but is taken into tissues since it is a chemically related homologue of potassium. In body fluids, cesium is soluble and evenly distributes in body tissues; it primarily accumulates in soft tissues, has a half-time retention of ~100 days, and is excreted via the kidneys (Al-Masri, 2008), (Walther C. , 2015), (Chatterjee, 2017), (IAEA - International Advisory Committee, 1991), (UNSCEAR, 2000).

^{210}Pb

^{210}Pb has a half-life of 22.3 year. It is naturally occurring and virtually all ^{210}Pb comes from within the ^{238}U decay series in the earth's crust. It is considered a continuous fallout radionuclide since it continually deposits on the earth's surface from the decay of ^{222}Rn gas in the atmosphere; a relatively small amount of ^{222}Rn can escape to the atmosphere from the decay of ^{238}U in soil. After ^{222}Rn gas decays in the atmosphere, ^{210}Pb adsorbs to atmospheric dust particles and aerosols and falls back to the surface via wet and dry deposition. ^{210}Pb decays by beta decay and eventually decays to stable lead, ^{206}Pb (IAEA, 2017), (Walther C. , 2015).

Anthropogenic activities also release ^{210}Pb into the environment. ^{210}Pb is released to the atmosphere from processing phosphate rocks for fertilizer, burning vegetation and fossil fuels, and from the iron, steel, and metal smelting industries. Between 1959-1962, Soviet bombs made of ^{208}Pb material contributed to environmental ^{210}Pb after thermonuclear detonations. In the northern hemisphere, the average atmospheric activity concentration of ^{210}Pb is estimated to be 0.5 mBq/m^3 (Walther C. , 2015), (IAEA, 2022), (Gwynn, 2013), (IAEA, 2017), (Clark, 2015), (Salmon, 1998), (UNSCEAR, 2000), (Pang, 2019), (Gupta, 2014), (Pang, 2019), (IAEA, 2014).

In soil, ^{210}Pb adsorbs strongly to fine particles accumulates at the soil and sediment surface. In the

environment, ^{210}Pb behaves similarly to ^{137}Cs since it forms complexes with clay minerals, oxides, and organic matter, and is strongly held in soils. ^{210}Pb can enter the environment from industrial activities and physical processes such as erosion and can be distributed throughout the environment through sediment transport processes. Precipitation can also deliver ^{210}Pb-containing sediment, soil, fertilizer, and industrial process materials from the surface into waterways (IAEA, 2014).

Studies have shown that ^{210}Pb varies spatially on a global scale with higher ^{210}Pb fallout in the eastern parts of continents, which is due to air masses predominantly moving from west to east: the air masses moving from over the ocean have picked up very little ^{210}Pb from over the continental crust but will pick up and deposit more ^{210}Pb as they travel over the continent. ^{210}Pb also exhibits seasonal variations and environmental monitoring programs have shown higher ^{210}Pb activity concentrations in air in the winter and fall, which have been attributed to increases in wet precipitation that deposit greater quantities of atmospheric ^{210}Pb to the surface (IAEA, 2014).

Once in soils, plants can take up ^{210}Pb via their roots. Natural lead is not an essential nutrient for Plant growth so its uptake into plants is relatively low and the uptake of ^{210}Pb into plants is similar. Radionuclide transport and plant bioavailability research has shown that ^{210}Pb's bioavailability is enhanced in acidic conditions and that uptake is related to the plant species' tolerance for lead. Forest fires and burning vegetation can subsequently release radionuclides, such as ^{210}Pb held in plant material, to the atmosphere (Madruga, 1998), (Carvalho, 2012).

^{210}Po

^{210}Po has a half-life of 138 days and is found in the earth's crust at very low concentrations. Virtually all ^{210}Po is produced in the earth's crust from within the ^{238}U decay chain. Its parent radionuclide is ^{210}Pb, which comes from the decay of ^{222}Ra in rocks and soils. ^{210}Po undergoes alpha decays to eventually become stable lead, ^{206}Pb, and it emits a multitude of alpha particles as it decays: 140 watts of energy is

released per gram every second (IAEA, 2006), (IAEA, 2017), (Green, 2002).

A small amount of ^{222}Rn gas produced is exhaled from the earth's surface and can enter the atmosphere where it undergoes alpha decay to produce ^{210}Pb and then ^{210}Pb's daughter, ^{210}Po, is produced. ^{210}Po is volatile and has a positive charge in the gas phase so it can adhere to the surface of aerosol particles and can be delivered to the surface through wet and dry deposition. Once in soil, the movement of ^{210}Po is influenced by water. In soil, ^{210}Po can be resuspended in the atmosphere on coarse particles from mechanical processes such as wind (IAEA, 2017) (Carvalho, F., et al., 2017) (Gwynn, 2013), (Walther C. , 2015), (Green, 2002).

After ^{210}Po is produced in soil, interactions between rocks, soil and sediments with rainwater can carry ^{210}Po to surface water and groundwaters. In surface waters, the in situ decay of ^{226}Ra in sediments contributes to ^{210}Po concentrations and the concentrations of ^{210}Po in drinking water can reflect the area's geological variability of ^{230}Th and ^{226}Ra (IAEA, 2017).

Anthropogenic activities contribute to environmental ^{210}Po and sources include combusting fossil fuels (especially coal), cement industry emissions, and the phosphate fertilizer industry. Discharging, landfilling, and land spreading wastes such as scale and sludge from the petroleum industry also contribute to ^{210}Po in the environment. Approximately 100 g of ^{210}Po is produced annually; it is alloyed with beryllium for neutron sources, used as a satellite heat source, used to remove static in industrial settings, and is used to remove dust from camera lenses and film (IAEA, 2006), (IAEA, 2017).

Plants can accumulate ^{210}Po via root uptake from soil and from foliar uptake following atmospheric deposition, with foliar uptake being a dominant accumulation pathway for ^{210}Po. ^{210}Po can then be transferred to animals and humans through ingestion. Burning vegetation and forest fires can then release ^{210}Po to the atmosphere (Madruga, 1998), (Carvalho, 2012), (IAEA, 2017).

^{226}Ra

^{226}Ra is a naturally occurring radionuclide from the ^{238}U decay series. It has a half-life of ~1600 years and produces ^{222}Rn gas through alpha decay. It can be released from the earth's crust and transferred to other compartments by natural means such as weathering rocks that contain ^{226}Ra, groundwater dissolving and leaching it from rocks, volcanic eruptions, forest fires, and the exhalation of ^{222}Rn gas (IAEA, 2017), (IAEA, 2014), (Walther C. , 2015).

^{226}Ra is mobile in the environment and can adsorb onto mineral particle surfaces, which can carry it to other environmental compartments. This radionuclide is a chemical analogue to calcium, which is an essential macronutrient for plant growth, and the uptake of ^{226}Ra is similar to that of calcium (Madruga, 1998), (Gupta, 2014).

Anthropogenic activities from industry can release ^{226}Ra to the environment so it is important to properly manage these wastes. ^{226}Ra is found in the residues, tailings, waste rock, and wastewater from the uranium ore mining and milling industries. Petroleum industry wastes such as processing water, coal ash, scale, and sludge can have high concentrations of radium that can enter the environment through

discharge, landfilling, and land spreading and the phosphate industry also contributes to environmental ^{226}Ra (IAEA, 2017), (Walther C. , 2015).

Human exposure to radium can be through inhalation if a source exists or it can enter the food chain through water or in soil and be taken up by plants and animals.

1.6 Uptake of Trace Elements and Radionuclides in Plants

Many factors influence nutrient, trace element, and radionuclide uptake to different plant tissues (Al-Masri, 2008) and the bioavailability, solubility, and the nutritional requirements of plants are

important considerations. This is an important area of study since the decay products of primordial radionuclides, ^{232}Th and ^{238}U, are the main internal radiation dose contributors from the natural environment and a pathway of ingestion exposure (Gwynn, 2013) (Al-Masri, 2008) (Thorring, 2020).

For radionuclides and trace elements in the environment, some factors that affect bioavailability in the soil include physico-chemical characteristics, the soil's organic matter content, the amount of water in the soil, soil pH, the concentration of elements in the soil, and the soil solution's composition. Radionuclides can move from the soil's top later down to deeper soil layers with the passage of time and the amount of precipitation. The depths the radionuclide reaches depends on its half-life, the rate at which the radionuclide is deposited to the soil's top layer (if applicable), and land use, which is an important consideration since uptake via plant roots from the soil occurs at a depth of approximately 10-20cm from the soil surface where the bulk of plant root density is found. In discussing bioavailability, Walther, C., et al. provided information about the readily available and potentially available radionuclides:

Readily available: $^{90}Sr >> ^{137}Cs, ^{226}Ra, ^{239+240}Pu > ^{238}U, ^{241}Am > ^{40}K > ^{210}Pb > ^{232}Th$

Potentially available: $^{90}Sr >> ^{241}Am > ^{210}Pb; ^{239+240}Pu > ^{226}Ra > ^{137}Cs > ^{238}U > ^{40}K > ^{232}Th$

In soil, uranium can complex with organic matter and in the absence of organic matter, uranium is considered mobile and can be transported throughout the environment in different solution pH as a divalent uranyl ion, UO_2^{2+}. In soil, thorium is generally much less mobile than uranium and, in the presence of clays, their mobilities can be reduced since they can adsorb to charged clay surfaces (Greger, 2004) (Al-Masri, 2008) (Walther C. , 2015).

Solubility is a key factor for the uptake of trace elements and radionuclides into plants since highly mobile and water-soluble fractions in soil are considered readily available for uptake. An element's reactivity, chemical nature, and availability in the soil pore water in the plant root's rhizosphere affects uptake. The oxidation state of an element also affects its adsorption and precipitation behaviour, which

influences its solubility and mobility in the environment. Studies have shown that temperature and precipitation can affect the mobility of radionuclides: in environments with reduced temperatures and high humidity, radionuclide mobility is increased since the organic matter degradation is low and this increases the absorption of radionuclides in the fraction of organic soil, which increases the bioavailability of radionuclides for root uptake. Additionally, elemental and radionuclide mobility increases with soil biological activity since microorganisms can change an element's oxidation state through redox reactions with actinides (Gupta, 2014), (Napier, B. A., et al, 2011), (Walther C. , 2015).

Plants obtain essential elements from the soil that are needed for growth and their nutritional requirements are important when examining the uptake of trace elements and radionuclides. A plant species' nutrient needs and an element's chemically similarity to a required nutrient are important uptake factors. An example of this is ^{226}Ra: this highly soluble, highly mobile radionuclide in the environment is a chemical analogue of Ca, Ba, and Sr since it has been shown that in the periodic table, elements in the same group have similar chemical characteristics although their ionic radii increase as you move down a group. It has been found that plants will uptake more ^{226}Ra in environments with less exchangeable Ca, which is an important nutrient for growth. Another example is ^{137}Cs: cesium is a chemical analogue to potassium, which is an essential plant macronutrient. Annually, trees obtain significant amounts of potassium from the decomposed litter and will also obtain ^{137}Cs via root uptake when it is present in soil. In the absence of potassium-rich fertilization, trees may be in a state of potassium starvation, which may inadvertently increase their ^{137}Cs uptake while boosting their uptake processes to obtain potassium. Al-Masri et al. found that of the radionuclides studied, ^{40}K had one of the highest transfer factor ratios from soil to plant tissues since ^{40}K was taken up with stable potassium. In addition to soil uptake, plants can obtain elements through foliar uptake after deposition on their leaves (ie. ^{40}K, ^{210}Pb, ^{210}Po, and Cd), although foliar absorption varies between plant species due to physiological habits such as their individual metabolism rates as well as their leaf characteristics; large leaves with higher surface areas with hair or

trichomes present will intercept and retain more radioactivity than small, smooth leaves. Interestingly, there have been studies on the transfer of radionuclides and elements between different plant tissues and there are literature values for different plant types for translocation factors, which capture the transfer of elements deposited on foliage and distributed to different plant tissues. There are also soil to plant transfer factors, which can be used in radiological assessments. For some radionuclides (ie. ^{137}Cs), root uptake is the dominant pathway into the plant whereas for other radionuclides (ie. ^{210}Pb and ^{210}Po), foliar uptake may be dominant. There are also some elements (ie. Cd and Rb) that are not required for growth but are passively taken up by plants from soil (Napier, 2012), (Al-Masri, 2008) (Walther C. , 2015) (Carvalho, F., et al., 2017), (IAEA, 2014), (Gupta, 2014), (National Academy of Sciences, 1997), (IAEA, 2010), (Shotyk W. , 2020), (Carini, 1999).

1.6.1 Plant Nutrition and Uptake Science

Plant nutrient and uptake is a complex process influenced by the nutritional requirements of the plant, the plant's characteristics, and the soil composition.

A plant's nutritional requirements are important factors when examining the uptake of elements (Walther C. , 2015). Plants primarily obtain elements required for growth from the soil and, if essential nutrient concentrations are low, chemical analogues or elements with similar chemical properties may be taken up into the plant as a substitute (Walther C. , 2015), (Madruga, 1998), (IAEA, 2014), (P. C. Nagajyoti, 2010), (Greger, 2004). Examples of chemical analogues in plants include ^{137}Cs for potassium (Carini, 1999) and ^{226}Ra for calcium (Madruga, 1998). It has also been found that the transfer of radionuclides throughout plant tissues and organs after uptake will generally follow a radionuclide's chemical similarity to essential elements needed for growth (Walther C. , 2015).

Uptake is also influenced by leaf and fruit characteristics as well as the plant's age. Carini et al. found that when studying radionuclide leaf-to-fruit translocation and foliar absorption rates, there were significant differences between plant species and plants with higher metabolisms may translocate more radionuclides from contaminated leaves to their fruit. Leaf characteristics such as the presence of hair, waxes, trichomes, and the surface cuticle affect radionuclide retention. When studying leaves after the Chernobyl disaster, higher radioactivity was found in hairy leaves of fruit-bearing plants due to their larger surface area that received radionuclide deposition. Radionuclide uptake and plant cell distribution studies have shown that age is a factor since higher ^{137}Cs activities were found in newer branches of orange and olive plants (Carini, 1999). Contrasting this, a berry study from Finland found higher ^{137}Cs, ^{210}Pb, and ^{210}Po activities in lignified brown stems and lowest in berries (Lehto & Vaaramaa, 2013), (IAEA, 2017).

Soil characteristics are important factors in plant uptake. For ^{238}U and ^{232}Th, for example, the amount of organic matter in soil can increase their mobilities through the formation of organic complexes with soil colloids (Walther C. , 2015). The presence of microorganisms in soil can influence uptake by changing an element's chemical form through complexation and redox reactions (Chao, 2019). The soil pH can also influence an element's solubility and mobility, which affects uptake (Rahman, 2019). Research in Canada, for example, has shown that low pH in uranium mine tailings increased the bioavailability of radionuclides (Madruga, 1998).

1.7 Objectives

Indigenous communities living in northern Saskatchewan may harvest traditional foods near Canadian Nuclear Safety Commission licensed facilities such as active and decommissioned uranium mines and mills. Plants obtain nutrients for growth from the soil compartment via their roots (Stachiw, 2019) and radionuclides and trace elements can be transferred from roots, stems, and leaves into edible

portions of plants (Sokolik, 2014), (Lehto & Vaaramaa, 2013), (Shotyk W. , 2019). These elements in edible plant portions can be transferred to humans through ingestion, which is a significant exposure pathway when harvesting foods such as vegetation, mushrooms, and berries (Health Canada, 2010).

The primary research objectives of this thesis are to identify geochemical relationships between radionuclides and trace elements in blueberries and explore the cycling and environmental reservoirs of radionuclides and trace elements. Two additional research objectives are to quantify the human health risk through blueberry consumption to support future human health risk communication with Indigenous communities. These goals will:

- Help inform CNSC's regulatory decision-making process
- Build future scientific networks through collaboration between CNSC, University of Ottawa, University of Alberta

1.8 Scope of Work

This research aims to study the uptake of radionuclides and trace elements from soil into blueberries. Soil and blueberries from northern Saskatchewan, Canada were sampled, samples from 2 Ontario blueberry farms were obtained, and commercially available blueberries that were products of Argentina and Peru were obtained. All samples were analyzed for a range of radionuclides and trace elements. Portions of washed berries and unwashed berries were analyzed separately to determine the atmospheric deposition component and soil characterization work was completed to help explain some uptake factors of radionuclides and trace elements from soil into the plant. The following radionuclides and trace elements were analyzed:

- 6 Radionuclides: Cs-137, I-131, Po-210, Pb-210, Ra-226, K-40

- 45 Trace elements: Li, Be, Mg, Ca, Al, As, Se, V, Cr, Mn, Ba, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Mo, Ag, Cd, Sb, Cs, Ba, W, Tl, Pb, Th, U + several Lanthanides

Soil pH and total organic carbon (TOC) work was completed to characterize the soil.

1.9 Collaborators

There were several collaborators on this research project who provided most of the sampling and much of the data collection and were key to this project's success. Some of the sampling, some of the laboratory work and data collection, and the majority of the interpretation was completed by the author (CM).

Chapter 2 includes the analysis of radionuclides and trace elements in blueberries and soil.

The sample collection in Saskatchewan was conducted by the East Athabasca Regional Monitoring Program staff. The Ontario and Grocery Store sampling was conducted by the author and thesis supervisor (CM and MH).

The sample washing and portion separation was conducted by Dr. William Shotyk, Professor and Bocock Chair for Agriculture and the Environment, University of Alberta, Canada and lab staff at the SWAMP Lab in Alberta. Dr. William Shotyk and staff at the SWAMP lab dried, milled, digested and analyzed the blueberries and soil for many of the trace elements presented in this chapter.

Additional analysis for trace elements was conducted at the CNSC laboratory in collaboration with Dr. Slobodan Jovanovic and Niall Crawley. Method validation work for the analysis of trace elements in vegetation was completed, digestions were conducted using the samples that were processed at the SWAMP lab, and additional trace elements were analyzed.

The analysis of Total Organic Carbon for soils was done collaboratively between Dr. Slobodan

Jovanovic and the author (CM) and the analysis of soil pH was done by the author (CM) at the CNSC laboratory.

The Saskatchewan Research Council conducted the analysis of radionuclides for blueberries and soil.

Dr. Matt Herod completed editorial reviews on all chapters and there were contributions from Dr. Ian Clark and Dr. Richard Amos who were thesis examiners.

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Chapter 2: Trace Elements and Radionuclides in Soil and Blueberries

2.1 Abstract

Canadian diet studies have identified wild berries as important components of traditional Indigenous diets and an exposure pathway of anthropogenic and naturally occurring radionuclides and trace metals is food ingestion (Health Canada, 2010), (Kuhnlein & Chan, 2000). Plants primarily obtain what they need for growth from the soil compartment (R. Moodley, 2013), (Walther C. , 2015) but can also accumulate radionuclides and trace elements through uptake and foliar absorption after deposition on leaves. Soil factors such as pH and the amount of organic matter and clays can influence the uptake of radionuclides and elements into plants to contribute to their solubility, mobility and bioavailability (Napier, 2012), (Al-Masri, 2008), (Walther C. , 2015), (Madruga, 1998), (Carvalho, F., et al., 2017), (IAEA, 2014), (Gupta, 2014), (IAEA, 2010), (Shotyk W. , Trace elements in wild berries from reclaimed lands: Biomonitors of contamination by atmospheric dust, 2020), (Carini, 1999). If the concentrations of essential nutrients in soil are inadequate, plants will uptake chemical analogues of and elements with similar chemical properties to elements that are required for growth and there are some elements and radionuclides that have been shown to be able to passively transfer to plants (Walther C. , 2015), (Madruga, 1998), (IAEA, 2014), (P. C. Nagajyoti, 2010), (Greger, 2004). The use of fertilizers and pesticides can contribute to elevated heavy metal concentrations in soil, which may transfer to edible plant parts, and this is a concern for consumers (P. C. Nagajyoti, 2010). Blueberries and soil were sampled from areas near CNSC-licensed nuclear facilities in Northern Saskatchewan, Canada where Indigenous communities gather traditional foods, from two Ontario blueberry farms, and from grocery stores to compare commercial blueberries with wild blueberries. Blueberries and the soil they were growing in were analyzed for radionuclides and trace elements and relationships were drawn between the natural underlying geochemistry, soil properties, and plant uptake chemistry.

2.2 Introduction

The human health implications from ingesting foods containing contaminants and artificial and naturally occurring radioactive materials continue to be studied. Dietary habits, food types, agricultural practices, and the soil's physical and chemical characteristics are important factors that influence the transfer of radionuclides and elements from food into humans (IAEA, 2021). The soil compartment is the primary reservoir in which plant roots uptake radionuclides and elements such as essential nutrients required for growth (Walther C. , 2015). Foliar uptake from dry and wet deposition can also deliver radionuclides and elements to soil and vegetation. Dry deposition involves the removal of atmospheric pollutants by vegetative surfaces through the absorption of gases or particles whereas wet deposition is the removal of atmospheric pollutants by transport to the ground as rain, snow, or hail (IAEA, 2010). The roughness of the surface of the edible portion of the plant (ie. berry) can affect its ability to retain atmospherically deposited particles and the amount and presence of leaves can shield the berry. Additionally, the berry's distance from the soil are factors to consider when studying trace elements in different berry species (Shotyk W. , 2020).

This paper considers these factors and aims to bring together the data for radionuclides and trace elements to discuss the cycling and uptake into blueberries.

2.3 Objectives

The research objectives in this section of the thesis include the following:

- Quantify the trace elements and radionuclides in blueberries and soil
- Identify geochemical differences between sampling locations
- Explore how soil mineralogy, soil composition, and mineral solubility of the different locations are reflected in the blueberries

- Determine if there is a human health risk through blueberry consumption

2.4 Materials and Methods

2.4.1 Sample Collection

Blueberries and soil were collected from East and West Athabasca in Saskatchewan, from two blueberry farms in Ontario, and from grocery stores. Figure 2.1 shows the sampling locations in Saskatchewan, Canada and Ontario, Canada.

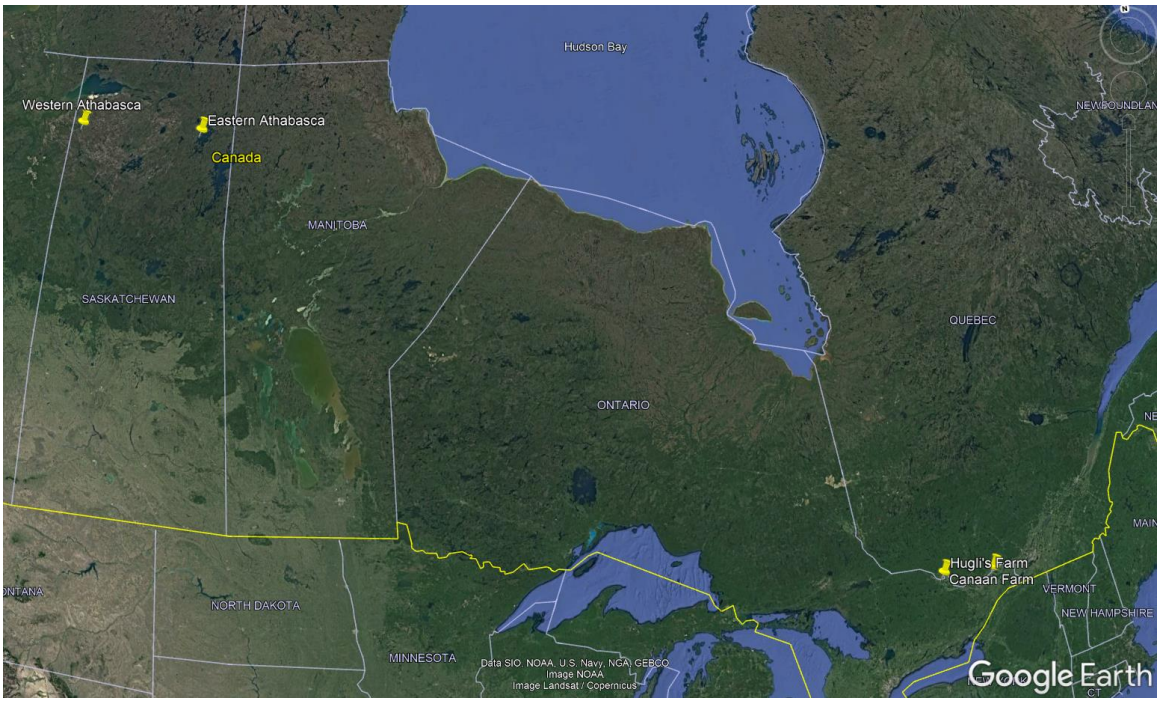

Figure 2.1: Map Showing Sampling Locations in Saskatchewan and Ontario.

2.4.1.1 Field Sampling in Northern Saskatchewan, Canada

Field sampling in Northern Saskatchewan, Canada was conducted by the Eastern Athabasca Regional Monitoring Program's field staff. Field sampling was conducted away from roadways, motor

vehicles, and no smoking was done during sampling to ensure they were free from metal contamination. GPS coordinates, notes, and photographs of samples collected were recorded by field staff.

In West Athabasca, five blueberry and five corresponding soil samples were collected on August 8 and 28, 2019. In East Athabasca, three blueberry and three corresponding soil samples were collected on September 12 and 16, 2019.

Blueberry samples were collected by hand while wearing polyethylene hair nets, polyethylene gloves, and samples were collected in polyethylene ziplock bags to ensure they were free from metal contaminants. Care was taken to not crush the blueberries and samples were stored in coolers with ice to keep samples cool during sampling. Long term storage of blueberries was done in a -20 ^{o}C freezer upon receipt at the laboratory. Blueberry leaves were collected along with the fruit for identification.

Soil samples were collected using polypropylene scoops in polypropylene bags. The scoops were rinsed with 18.2 MΩ·cm water and cleaned with ethanol and kimwipes between samples to ensure there was no cross-contamination. Soil samples were taken from around the blueberry plant roots at a depth of 10-20cm from the soil surface and were co-located with blueberry samples taken. Samples were stored in coolers with ice to keep samples cool during sampling. Long term storage of fresh soils was done in a cold room <10 ^{o}C.

2.4.1.2 Field Sampling in Pembroke, Ontario and Sarsfield, Ontario

In Pembroke, Ontario, one blueberry and one corresponding soil sample were collected on August 8, 2019 by the author (CM).

In Sarsfield, Ontario, one blueberry and one corresponding soil sample were collected on August 9, 2019 by the author (CM) and the author's thesis supervisor (MH).

Blueberry samples were collected by hand while wearing polyethylene hair nets, polyethylene gloves, and samples were collected in polyethylene ziplock bags to ensure they were free from metal contaminants. Care was taken to not crush the blueberries and samples were stored in coolers with ice to keep samples cool during sampling. Long term storage of blueberries was done in a -20 ^{o}C freezer upon receipt at the laboratory. Blueberry leaves were collected along with the fruit for identification.

Soil samples were collected using polypropylene scoops in polypropylene bags. The scoops were rinsed with 18.2 MΩ·cm water and cleaned with ethanol and kimwipes between samples to ensure there was no cross-contamination. Soil samples were taken from around the blueberry plant roots at a depth of 10-20cm from the soil surface and were co-located with blueberry samples taken. Samples were stored in coolers with ice to keep samples cool during sampling. Long term storage of fresh soils was done in a cold room <10 ^{o}C.

2.4.1.3 Grocery Store Blueberries Obtained

Commercial blueberries, products of Peru and Argentina, were obtained in Ottawa, Ontario on November 7 and 8, 2019. One sample of each were obtained.

2.4.2 Washing, Drying, and Milling Blueberries and Soil

Each blueberry sample had a portion removed for washing using 18.2 MΩ·cm water. For the first three rinses, the blueberry portions were soaked for three minutes in 18.2 MΩ·cm water and for the fourth rinse, they were soaked for five minutes in 18.2 MΩ·cm water before being drained and put in the drying oven.

Both blueberry sample portions (unwashed and washed) were dried in a 105°C oven for 48-72 h

until they reached constant weight. Using an agate mortar and pestle, the dried blueberries were ground by hand and put in polypropylene jars using a disposable polypropylene spatula.

Soil samples were dried in a 105°C oven for 48-72 h until they reached constant weight. Using an agate ball mill, the soils were milled and put in polypropylene jars using a disposable polypropylene spatula.

2.4.3 Sample Digestion and Elemental Analysis

Sample digestions and elemental analysis were conducted at the SWAMP Labs at the University of Alberta in Edmonton, Alberta, Canada and some additional digestions and elemental analysis for the blueberries and soils were conducted at the CNSC laboratory in Ottawa, Ontario, Canada.

2.4.3.1 SWAMP Laboratory

After washing, drying and milling, blueberry samples were processed in a metal-free, ultraclean lab in a Class 100 laminar flow cabinet made of polypropylene. Blueberry samples were digested on May 4, 2020 in double distilled nitric acid in polytetrafluoroethylene (PTFE) vessels using a high pressure Ultraclave microwave. Soil samples were digested on May 5, 2020 in double distilled nitric acid in polytetrafluoroethylene (PTFE) vessels using a high pressure Ultraclave microwave. A quartz still was used to twice distill the nitric acid. Several certified, Standard Reference Materials (SRMs) were digested along with blueberry and soil samples: NIST 1547 Peach Leaves, NIST 3281 Cranberries, NIST 3287 Blueberries, and NIST 2710 Montana Soil, as well as blank samples. Sample digests were diluted using deionized/reverse osmosis water and analyzed using an ICP-QMS.

2.4.3.2 CNSC Laboratory

Some additional elements in blueberries and soils were analyzed at the CNSC laboratory. Digestions were performed by the author (CM) with Niall Crawley, the laboratory's Laboratory Technical Officer. The elemental analysis using an ICP-MS was conducted by the laboratory's Chief Analyst, Dr. Slobodan Jovanovic. Blueberries and soils that were previously processed, washed, dried and milled at SWAMP labs were used to analyze elemental concentrations at the CNSC laboratory.

Soils were digested on March 15, 2022 using Optima grade nitric acid and Optima grade hydrochloric acid in Teflon cups and sample holders using a high pressure Milestone UP Microwave. Blueberries were digested on March 7-8, 9-10, and 14-15, 2022 in Optima grade aqua regia (3:1 solution of hydrochloric acid and nitric acid) with Optima grade hydrogen peroxide in Teflon cups and sample holders using a high pressure Milestone UP Microwave. Blanks and SRMs were digested along with blueberry and soil samples. SRMs for the blueberry samples included NIST 1570a, trace elements in spinach leaves, and NIST 1566b, trace elements in oyster tissue. SRMs for the soil samples included NIST 2706, New Jersey Soil. After digestion, soil digests were analyzed using an Agilent 8900 triple-quadrupole ICP-MS on March 16, 2022. After digestion, blueberry digests were prepared further using an evaporation and reconstitution method with an EZ2 Plus Evaporator ahead of analysis using an Agilent 8900 triple-quadrupole ICP-MS on March 8, 10, and 15, 2022.

2.4.4 Sample Preparation and Radionuclide Analysis

Radionuclide preparations and analyses were performed at the Saskatchewan Research Council (SRC) laboratory.

2.4.4.1 ^{137}Cs, ^{131}I, and ^{40}K Analysis for Blueberries and Soil

For gamma-emitting radionuclides, gamma activity was analyzed at the SRC laboratory (Standard Operating Procedure number Rad-300) using an HPGe Solid-state Photon Detector with a digital spectrometer, which follows the Standard Methods for the Examination of Water and Wastewater, Part 7120, APHA-AWWA-WEF procedure.

2.4.4.2 ^{210}Pb Analysis for Blueberries and Soil

The ^{210}Pb activity was analyzed at the SRC laboratory (Standard Operating Procedure number Rad-101) using a precipitation method with indirect ^{210}Bismuth counting using a gas-flow proportional detector, which follows ASTM Method D7535-09 procedure.

2.4.4.3 ^{210}Po Analysis for Blueberries and Soil

The ^{210}Po activity was analyzed at the SRC laboratory (Standard Operating Procedure number Rad-103) using a nickel disk method and counting using alpha spectroscopy, which follows ASTM Method D7535-09 procedure.

2.4.4.4 ^{226}Ra Analysis for Blueberries and Soil

The ^{226}Ra activity was analyzed at the SRC laboratory (Standard Operating Procedure number Rad-105) using a lead sulfate coprecipitation method and counting using an alpha spectrometer, which follows the National Uranium Tailings Program Radioanalytical Methods Manual procedure.

2.4.5 Soil Characterization

Soil characterization was conducted at the CNSC laboratory by the author (CM) for pH and by the author (CM) with the laboratory's Chief Analyst, Dr. Slobodan Jovanovic, for Total Organic Carbon (TOC). Soils were analyzed for pH on February 9, 2022 using the Environmental Protection Agency's (EPA)

Method 9045D for Soil and Waste procedure, a Mettler AT240 balance, 18.2 MΩ·cm water, and a Thermo Scientific Orion 2 Star pH meter with an Orion triode pH/ATC electrode. The balance used was within its calibration due date of March 22, 2022. Ahead of use, the pH meter was internally calibrated using buffer standards, as per the manufacturer's manual, and the pH meter was within calibration its calibration due date of March 22, 2022. The pH probe with a glass electrode and temperature compensation was used and the probe was calibrated with standard solutions. 20 mL of deionized water was added to a 20 g sample of soil. The soil suspension was covered and stirred using a Teflon stir bar for 5 min and was then allowed to stand for 1 h. The water portion was then decanted and the pH was measured in three sample aliquots. The soil pH was determined for corresponding blueberry samples and is presented in Table 2.18.

Soil was analyzed for TOC on April 5-6, 2022 using a Shimadzu TOC-L Total Organic Carbon Analyzer with SSM-5000A Solid Sample Module using the manufacturer's manual. First, the total carbon content in soils was measured and then the inorganic carbon content was measured. The measurements were obtained using the procedure in the instrument manual and are presented in Table 2.19.

2.4.6 Statistical Analysis

Pearson correlation and principle component analysis (PCA) were used in XLSTAT to try to analyze the data and identify relationships. Many of the trace elemental and radionuclide values were close to the limit of detection and this made it difficult to reliably interpret relationships among the radionuclide and trace elements since there was an overwhelmingly high correlation within the dataset. Steps were taken to attempt to overcome these issues by reducing the number of samples and focus on trace elements and radionuclides of interest that are chemical analogues of each other yet the results showed there were still only high correlation so it wasn't possible to reliably interpret relationships using statistical analysis.

2.5 Results and Discussion

2.5.1 Radionuclide Activity Concentrations in Blueberries and Soil

Radionuclides were analyzed in blueberry and soil samples from East and West Athabasca in Saskatchewan, two Ontario blueberry farms, and in blueberry samples obtained from grocery stores that were products of Peru and Argentina. The radionuclide data is presented below along with a discussion of the results.

The decay corrected radionuclide activities were used where appropriate and were calculated using the following formula from IAEA (IAEA, 2014):

$$A = A_o \times e^{-\lambda t}$$

Where A is the activity (in Bq);

Where A_o is the initial activity

Where $\lambda = \ln 2 / T_{1/2}$ and $T_{1/2}$ is the radionuclide half-life (in seconds);

And where t is the time elapsed between sampling and analysis (in seconds)

2.5.1.1 Washed Blueberries

Table 2.1 presents the decay corrected radionuclide activities for unwashed and washed blueberries and Figures 2.2, 2.3, and 2.4 present the decay corrected radionuclide activities for the washed blueberry samples.

East and West Athabasca

Radionuclide activity concentrations for washed blueberries from East and West Athabasca show there are distinct geochemical differences between these sampling locations. ^{137}Cs ranged between

Sample ID (MDL)	^{137}Cs (Bq/g dw)	^{131}I (Bq/g dw)	^{210}Pb (Bq/g dw) (0.002)	^{210}Po (Bq/g dw) (0.0005)	^{226}Ra (Bq/g dw)	^{40}K (Bq/g dw)	^{232}Th (Bq/g dw) (1.18E-07)	^{238}U (Bq/g dw) (5.44E-07)
East Atha Blueberry 01 Unwashed	<0.005	<0.002	0.00303	0.00187	0.004 (0.0005)	0.28 (0.03)	3.72E-07	7.01E-07
Eat Atha Blueberry 01 Washed	<0.004	<0.002	0.00303	0.00562	0.004 (0.001)	0.37 (0.02)	3.68E-07	<5.44E-07
East Atha Blueberry 02 Unwashed	0.00906 (0.004)	<0.001	0.00404	0.00551	0.007 (0.0005)	0.44 (0.03)	1.90E-05	5.61E-05
East Atha Blueberry 02 Washed	<0.002	<0.004	0.00404	0.00367	0.01 (0.001)	<0.1	1.15E-05	4.57E-05
East Atha Blueberry 03 Unwashed	0.00806 (0.003)	<0.002	0.00404	0.00367	0.006 (0.0005)	0.37 (0.04)	4.89E-07	2.85E-06
East Atha Blueberry 03 Washed	<0.005	<0.002	0.00303	0.00367	0.006 (0.001)	0.32 (0.01)	3.74E-07	2.53E-06
West Atha Blueberry 01 Unwashed	0.00808 (0.004)	<0.002	<0.002	0.00223	0.002 (0.0005)	0.31 (0.0005)	1.66E-06	<5.44E-07
West Atha Blueberry 01 Washed	<0.005	<0.007	0.00304	0.00223	<0.001	0.28 (0.03)	1.04E-06	<5.44E-07
West Atha Blueberry 02 Unwashed	0.00807 (0.003)	<0.001	0.00402	0.00202	0.002 (0.0005)	0.29 (0.02)	1.39E-06	<5.44E-07
West Atha Blueberry 02 Washed	0.00807 (0.004)	<0.005	0.00405	0.00202	0.004 (0.001)	0.36 (0.02)	9.17E-07	<5.44E-07
West Atha Blueberry 03 Unwashed	0.00605 (0.004)	<0.003	<0.002	0.00202	0.002 (0.0005)	0.2 (0.05)	9.69E-06	9.96E-07
West Atha Blueberry 03 Washed	<0.002	<0.005	0.00506	0.00404	0.002 (0.001)	<0.03	1.93E-05	3.76E-06
West Atha Blueberry 04 Unwashed	0.02924 (0.003)	<0.003	<0.002	0.00404	0.0009 (0.0005)	0.41 (0.01)	8.35E-07	<5.44E-07
West Atha Blueberry 04 Washed	0.02723 (0.004)	<0.006	<0.002	0.00404	0.001 (0.001)	0.24 (0.04)	7.88E-07	<5.44E-07
West Atha Blueberry 05 Unwashed	<0.007	<0.002	<0.002	0.00182	<0.0005	<0.09	8.74E-07	<5.44E-07
West Atha Blueberry 05 Washed	0.02522 (0.004)	<0.004	<0.002	0.00202	0.002 (0.001)	0.3 (0.02)	1.26E-06	<5.44E-07
Grocery Store Blueberry (Arg) Unwashed	<0.003	<0.7	0.00402	0.00141	<0.0005	0.33 (0.02)	4.89E-06	1.19E-06
Grocery Store Blueberry (Arg) Washed	<0.003	<0.006	<0.002	0.00113	<0.001	0.44 (0.02)	1.06E-05	1.48E-06
Grocery Store Blueberry (Peru) Unwashed	<0.003	<0.6	<0.002	<0.0005	0.001 (0.0005)	0.29 (0.03)	2.43E-05	1.77E-05
Grocery Store Blueberry (Peru) Washed	0.00603 (0.002)	<0.004	0.00402	0.00099	<0.001	<0.03	1.09E-05	7.98E-06
Sarsfield, ON Blueberry Unwashed	<0.002	<0.002	<0.002	0.00156	0.0006 (0.0005)	0.33 (0.02)	7.64E-07	<5.44E-07
Sarsfield, ON Blueberry Washed	<0.003	5931.6416 (0.005)	<0.002	0.00111	<0.001	0.33 (0.03)	8.71E-07	<5.44E-07
Pembroke, ON Blueberry Unwashed	<0.005	<0.002	<0.002	0.00134	<0.0005	0.34 (0.01)	5.53E-06	1.13E-06
Pembroke, ON Blueberry Washed	<0.004	<0.005	<0.002	<0.0005	0.002 (0.001)	0.34 (0.03)	4.78E-06	9.38E-07

Table 2.1: Decay Corrected Radionuclide Measurement Results for ^{137}Cs, ^{131}I, ^{210}Pb, ^{210}Po, ^{226}Ra, ^{40}K, ^{232}Th, and ^{238}U for Blueberry Samples

Note: Symbol "<" denotes "less than" and is followed by the MDL value; values in brackets are the MDL; the short form "dw" denotes "dry weight"

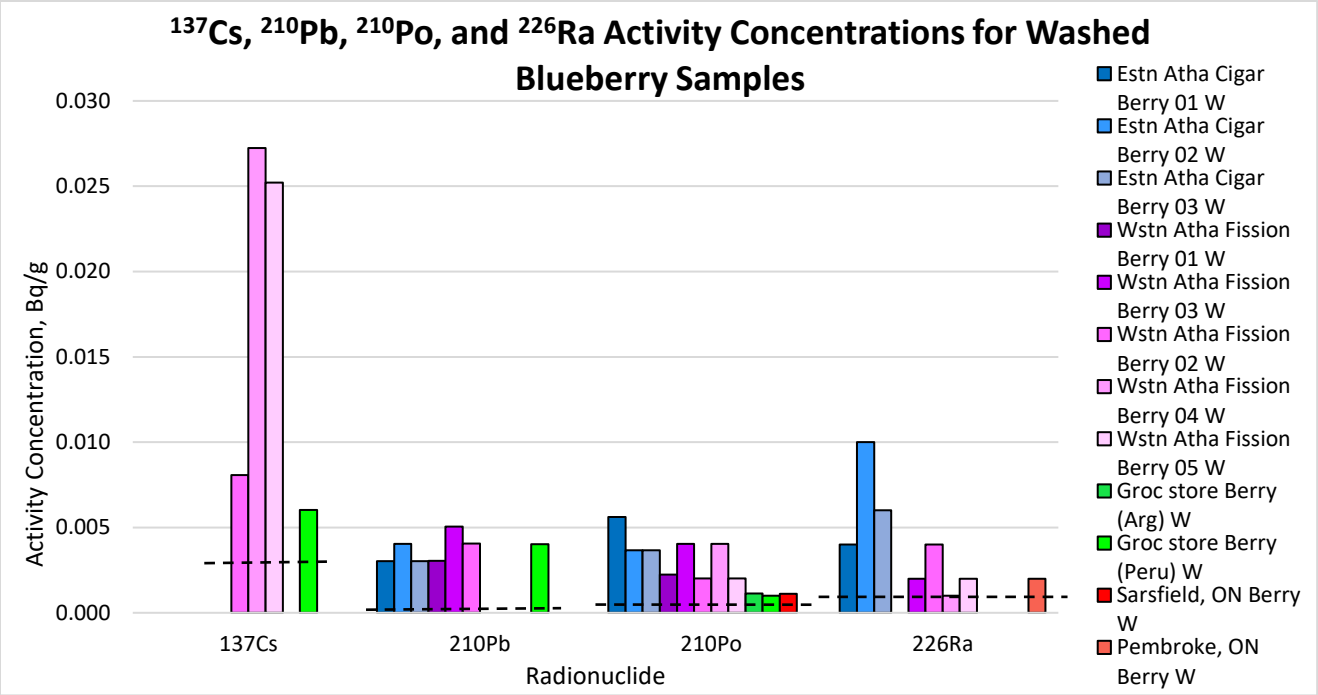

Figure 2.2: Decay corrected radionuclide activity concentrations in Bq/g DW for all washed blueberry samples.

Notes:

-There were no detectable ^{131}I concentrations in washed blueberries and this radionuclide was not included in this figure.

-^{40}K was not included in this figure since the values were an order of magnitude higher than the highest values in this figure and would impede distinguishing small differences among the other samples for different radionuclide concentrations.

- ^{232}Th and ^{238}U activity concentrations were very low and are included in a separate figure below.

-The vertical dashed lines represent the MDL. Where there was a range of MDL values, the vertical dashed line represents the average MDL.

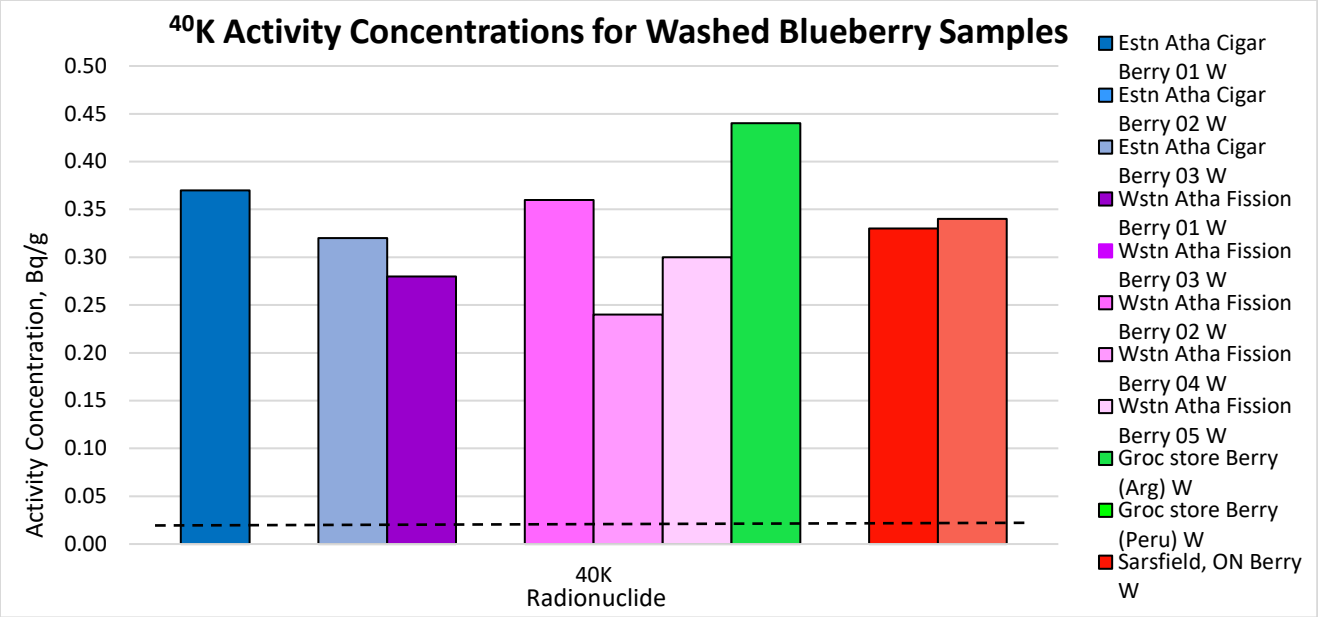

Figure 2.3: ^{40}K activity concentrations in Bq/g for all washed blueberry samples.

Note: The vertical dashed line represents the average MDL.

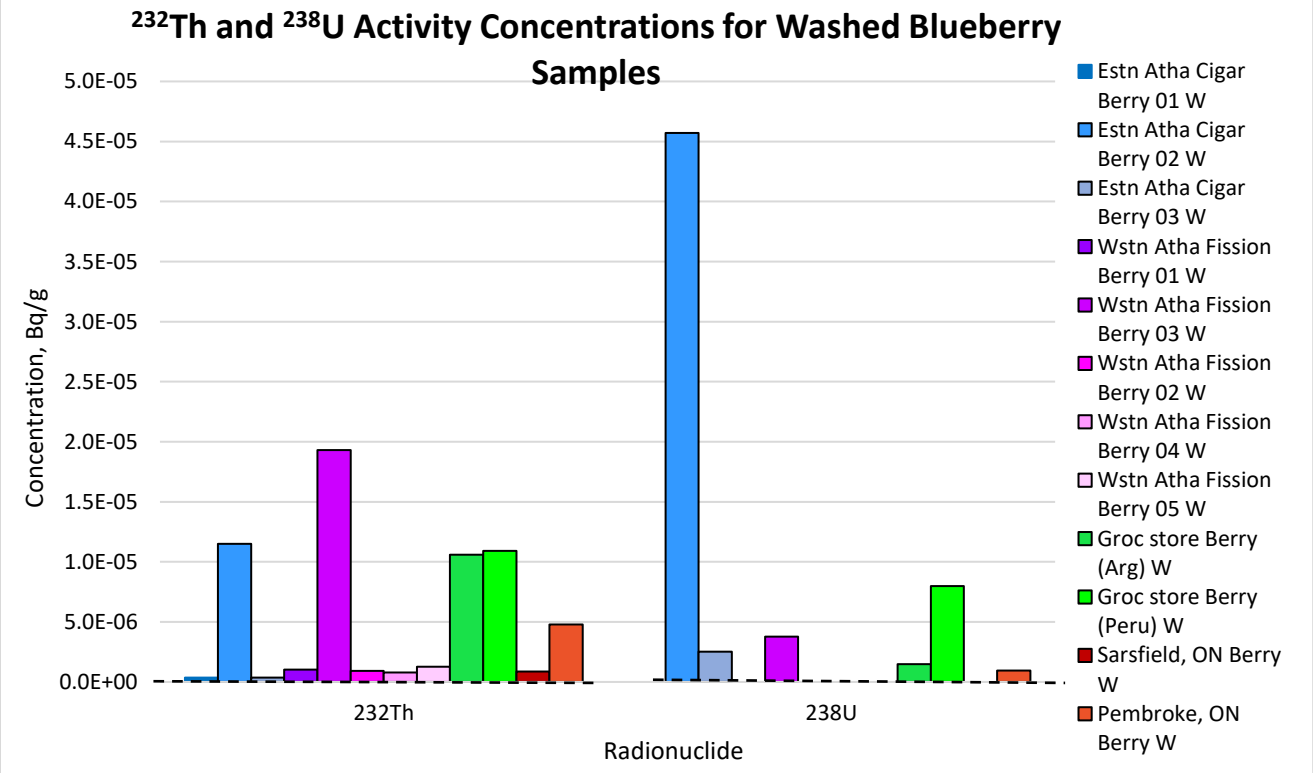

Figure 2.4: ^{232}Th and ^{238}U activity concentrations in Bq/g for all washed blueberry samples.

Note: The vertical dashed line represents the average MDL.

<0.002 Bq/g and 0.02723 Bq/g, DW, with the West Athabasca samples having considerably higher activities, although the values were within the same range as wild berries studied in Northern Norway (0.0058 Bq/g to 0.0351 Bq/g, DW) (Gwynn, 2013). The ^{137}Cs activity concentrations in soil from East and West Athabasca were very similar and may originate from nuclear weapons testing, Chernobyl, and from being liberated from vegetation after area forest fires. Elevated ^{137}Cs activities in the West Athabasca blueberries may be from potassium depletion in the corresponding soils since the potassium concentrations were much lower than in East Athabasca soils; the West Athabasca plants could have taken up higher amounts of ^{137}Cs in the absence of potassium, which is an essential nutrient for growth, since cesium is a chemical analogue to potassium. Additionally, the West Athabasca soils had no organic matter content and this tends to increase the uptake of ^{137}Cs by preventing ^{137}Cs from adsorbing to clay particles, which reduces radionuclide mobility (Walther C. , 2015).

For ^{210}Pb, ^{210}Po, and ^{40}K, the activity concentrations for washed blueberries from East and West Athabasca were quite comparable: the activities ranged between <0.002 and 0.00506 Bq/g, DW for ^{210}Pb, 0.00202 and 0.00562 Bq/g, DW for ^{210}Po, and <0.03 and 0.37 Bq/g, DW for ^{40}K. The ^{210}Pb and ^{210}Po activity concentrations in Athabasca blueberries were within the same magnitude as wild blueberries studied in Finland (0.0017 Bq/g, DW for ^{210}Pb and 0.0025 Bq/g, DW, for ^{210}Po). Additionally, the ^{210}Po activities in East and West Athabasca blueberries were an order of magnitude lower than in blueberries from Germany (0.034 Bq/g, DW) (IAEA, 2017). The ^{40}K activities in East and West Athabasca blueberries were found to be within the same range as wild berries studied in Northern Norway (0.221 Bq/g to 0.525 Bq/g, DW) (Gwynn, 2013). The ^{226}Ra activities ranged from <0.001 Bq/g to 0.01 Bq/g, DW with slightly elevated activities found in East Athabasca blueberries when compared to West Athabasca blueberries. ^{226}Ra is a chemical analogue of Ca and the slightly elevated activities in the East Athabasca blueberries may be due to the lower soil pore Ca concentrations found in the corresponding soil, which prompted an uptake of

^{226}Ra as a Ca substitute. In addition to this, the soil pH in East Athabasca was more acidic than in West Athabasca, which helps to increase the radionuclide mobility and root uptake.

The ^{232}Th and ^{238}U activities ranged between 3.72E-07 and 1.93E-05 Bq/g, DW and <5.44E-07 and 4.57E-05 Bq/g, DW, respectively. For ^{232}Th, the activities in washed blueberries from East and West Athabasca were similar in magnitude, although for ^{238}U, one sample from East Athabasca was elevated. This elevated ^{238}U activity could be due to the relative bioavailability between these radionuclides since ^{238}U is more readily available than ^{232}Th for uptake from the soil. The corresponding soil also had a much higher ^{238}U activity and the lower pH of East Athabasca soils helps to increase the mobility and root uptake of radionuclides (Walther C. , 2015).

Ontario

The washed blueberries results from Ontario showed there were differences between sampling locations. The ^{137}Cs and ^{210}Pb activities were below detection for both Ontario locations. Only the Sarsfield, Ontario sample had a detectable ^{210}Po activity (0.00111 Bq/g, DW) which could be due to root uptake since its corresponding soil had twice the ^{210}Po activity as the Pembroke, Ontario soil and its acidic soil could have increased the availability of radionuclides for uptake (Walther C. , 2015). Only the Pembroke sample had a detectable ^{226}Ra activity (0.002 Bq/g, DW) which could be due to its corresponding soil's low calcium concentration: radium is a known chemical analogue for calcium, which is an essential nutrient for plants. The Pembroke soil's calcium concentration was an order of magnitude lower than that of the Sarsfield soil so the ^{226}Ra found in Pembroke's washed blueberries indicates it was taken from the soil substrate as a chemical analogue of calcium (IAEA, 2014). The ^{232}Th and ^{238}U detected in Ontario samples showed the activities were among the lowest detected for all locations.

Grocery Store

The grocery store washed blueberries from Peru and Argentina showed differences in their chemistry as well. There were ^{137}Cs and ^{210}Pb activities measured in only the Peru sample. It is possible

that Peruvian soils may have received more ^{137}Cs fallout from nuclear weapons testing and Chernobyl than Argentinan soils, given its closer proximity to the Northern Hemisphere where studies have shown fallout has predominately deposited (IAEA, 2014). The higher ^{210}Pb activity found in Peru blueberries could be from higher ^{238}U activity in the growing region when compared to that of Argentina since ^{210}Pb is deposited from the decay of ^{222}Ra in the atmosphere, which is a daughter radionuclide of ^{238}U in soils (IAEA, 2017). The slightly elevated ^{40}K activity detected in Argentina blueberries indicates the potential use of potassium-based fertilizers and pesticides since ^{40}K is typically found with naturally occurring, non-radioactive potassium (Commodore, 2012).

Summary For Radionuclides in Athabasca Washed Blueberries:

- West Athabasca washed blueberries had higher ^{137}Cs activity concentrations than East Athabasca; K depletion in West Athabasca soils contributed to ^{137}Cs uptake as a chemical analogue to K and the absence of organic matter in West Athabasca soils increased ^{137}Cs availability
- East and West Athabasca had comparable ^{210}Pb, ^{210}Po, ^{40}K, and ^{232}Th activity concentrations in washed blueberries
- East Athabasca washed blueberries had slightly higher ^{226}Ra activity concentrations when compared to West Athabasca; Ca depletion in East Athabasca soils contributed to ^{226}Ra uptake as a chemical analogue of Ca and East Athabasca's low soil pH increased the radionuclide mobility and root uptake
- One East Athabasca washed blueberry had an elevated ^{238}U activity concentration when compared to all other sampling locations; reflects the East Athabasca's naturally higher soil ^{238}U activity and the lower soil pH that helps increase radionuclide mobility and root uptake
- Radionuclide activities in washed blueberries from Athabasca were generally within or lower than literature values

- Radionuclide activities in washed blueberries reflect geochemical differences between East and Athabasca

Summary For Radionuclides in Ontario Washed Blueberries:

- ^{137}Cs and ^{210}Pb activity concentrations were below detection and ^{232}Th and ^{238}U activity concentrations were low in Ontario washed blueberries
- Washed blueberries from Sarsfield had a detectable ^{210}Po activity; its corresponding soil had twice the ^{210}Po activity as the Pembroke soil and its acidic soil increased the availability of radionuclides for uptake
- Washed blueberries from Pembroke had a detectable ^{226}Ra activity concentration; its corresponding soil had low Ca concentration and took up ^{226}Ra as a chemical analogue

Summary For Radionuclides in Grocery Store Washed Blueberries:

- Only Peru washed blueberries had detectable ^{137}Cs activity; there may be more ^{137}Cs in Peru soil over Argentina soil from nuclear weapons testing and Chernobyl which predominantly deposited in the Northern Hemisphere
- Only Peru washed blueberries had detectable ^{210}Pb activity; higher ^{210}Pb activity could reflect higher ^{238}U activity in Peru soil
- Argentina washed blueberries had slightly elevated ^{40}K activity when compared to Peru washed blueberries; this indicates the potential use of potassium-based fertilizers and pesticides in Argentina

2.5.1.2 Washed and Unwashed Blueberries

Radionuclide activity concentrations for unwashed and washed blueberry samples were analyzed and compared and are presented in Figures 2.5 – 2.11.

East and West Athabasca

Overall, after taking into account the measurement uncertainties, there were no dramatic differences between the washed and unwashed blueberry activity concentrations for radionuclides in East and West Athabasca samples. This showed the radionuclide activities in the dust were very low and suggests that the dominant contribution of radionuclides in the blueberries was from root uptake. This was surprising in the case of ^{210}Pb since this daughter of ^{222}Ra gas can deposit as dust on the earth's surface via wet and dry deposition (IAEA, 2017). For ^{137}Cs, many of the unwashed blueberry activities were close to the detection limit although there was evidence of a small amount of activity in the dust: ^{137}Cs was detected in some the unwashed blueberries although ^{137}Cs was below detection in the washed sample. For ^{40}K, there were two unwashed blueberry samples with an activity reliably above the detection limit but the corresponding washed sample was below detection. It is possible that radionuclide dust was intercepted by leaves or did not adhere well to the smooth blueberry surface. Historical weather data for 10 days leading up to sampling in East and West Athabasca showed there was 21mm and between 9 and 30mm (sampling in West Athabasca took place on two different days) of rain, respectively, that could have washed dust from the blueberries (Carini, 1999), (Shotyk W. , 2020), (Government of Canada, 2023). There were also some samples with absent or lower unwashed activity results which were unexpected and could be due to errors during washing and processing.

Ontario

The Ontario blueberry samples also showed no dramatic differences in radionuclide activity concentrations when comparing the washed and unwashed samples and taking into consideration the

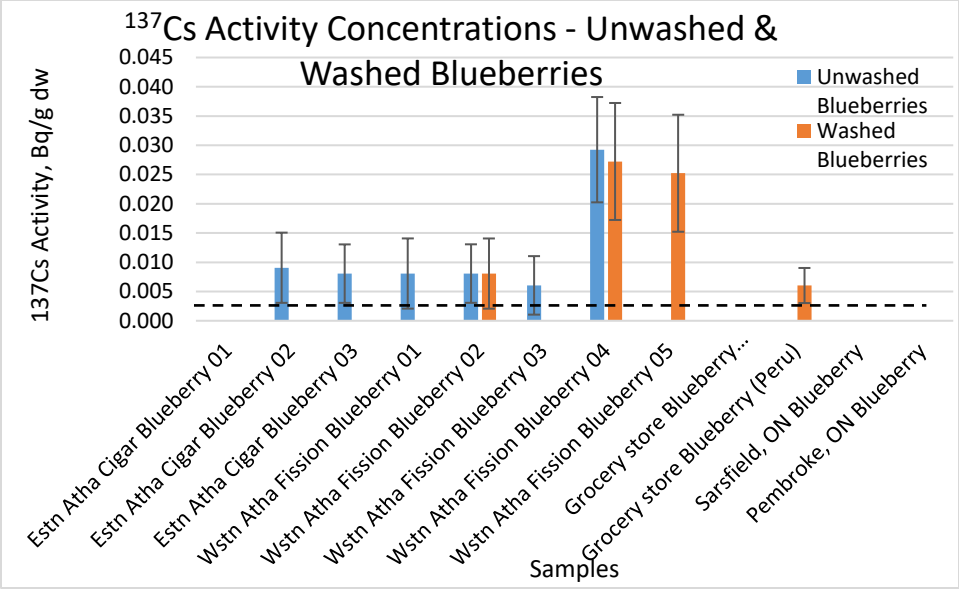

Figure 2.5: ^{137}Cs activities for unwashed and washed blueberries

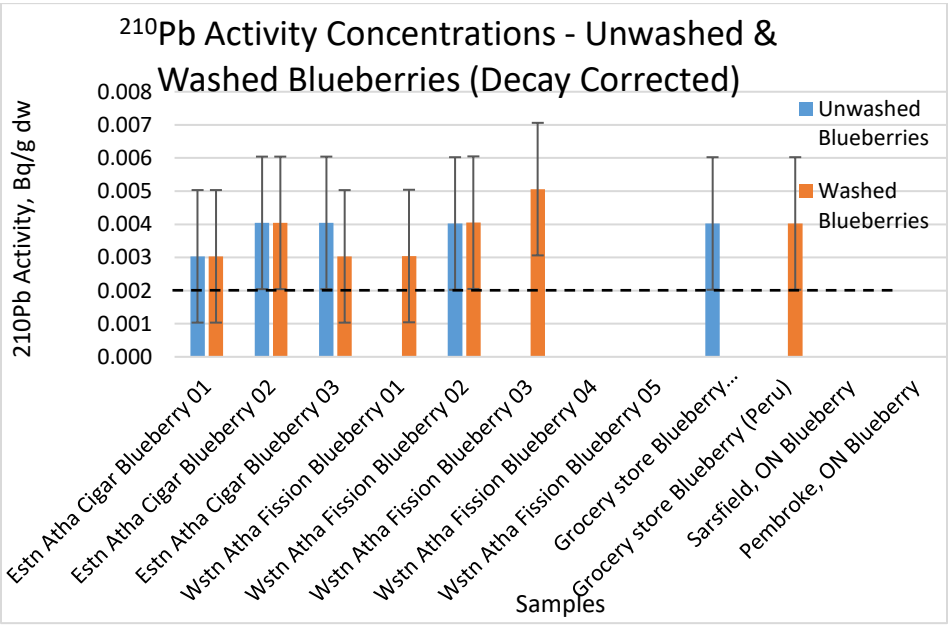

Figure 2.6: ^{210}Pb activities for unwashed and washed blueberries

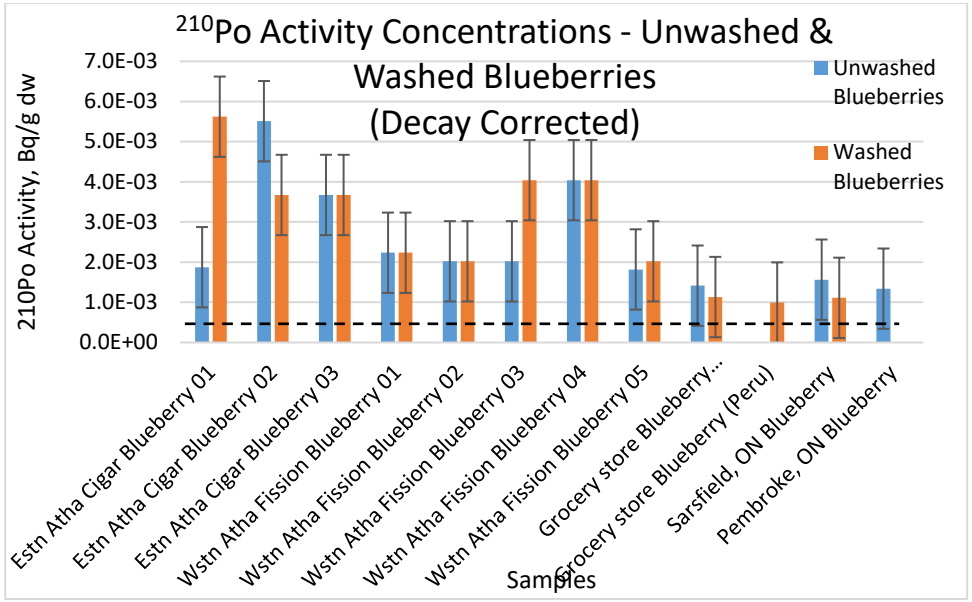

Figure 2.7: ^{210}Po activities for unwashed and washed blueberries

Note: dashed lined indicate the MDL

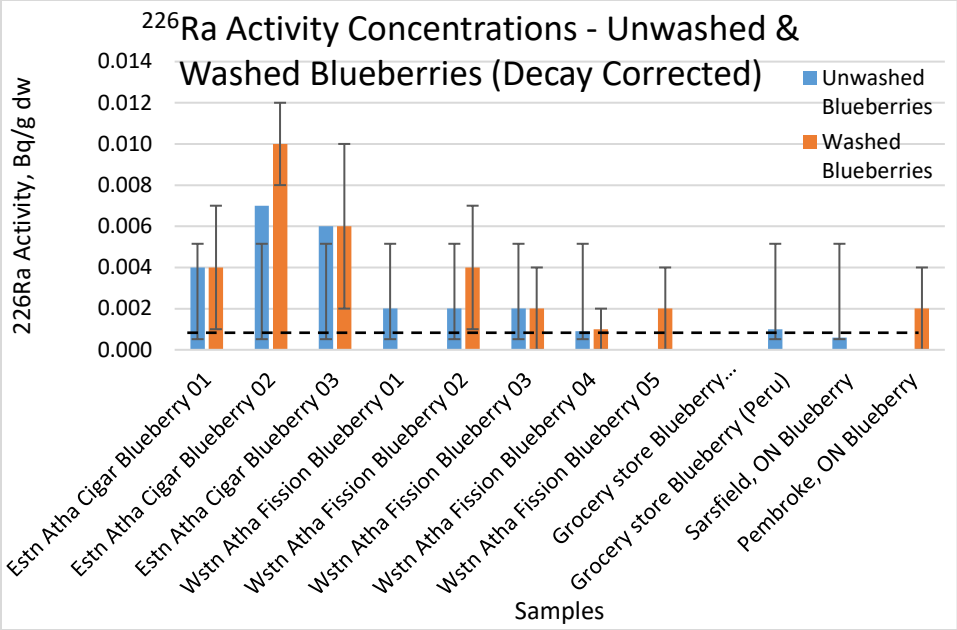

Figure 2.8: ^{226}Ra activities for unwashed and washed blueberries

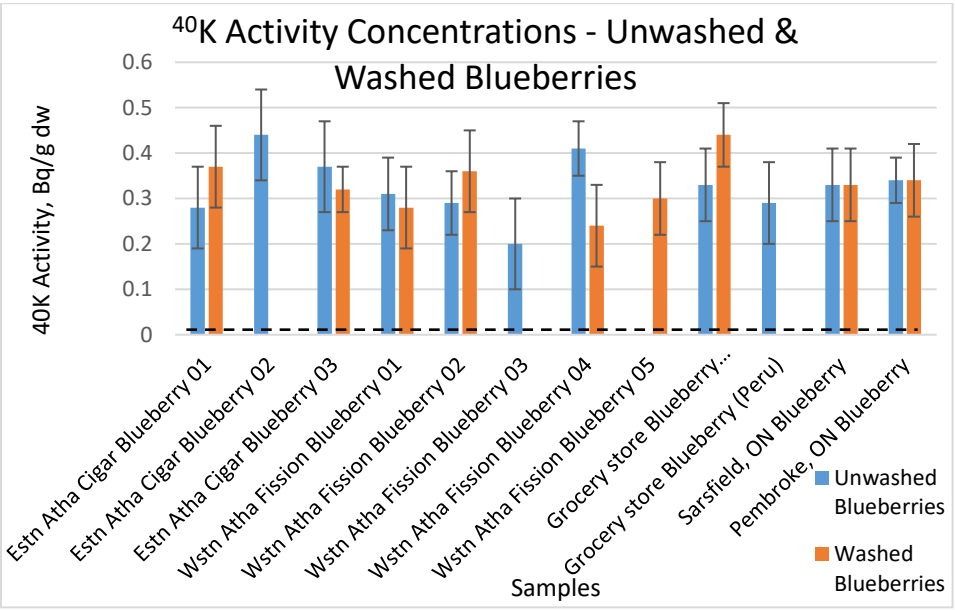

Figure 2.9: ^{40}K activities for unwashed and washed blueberries

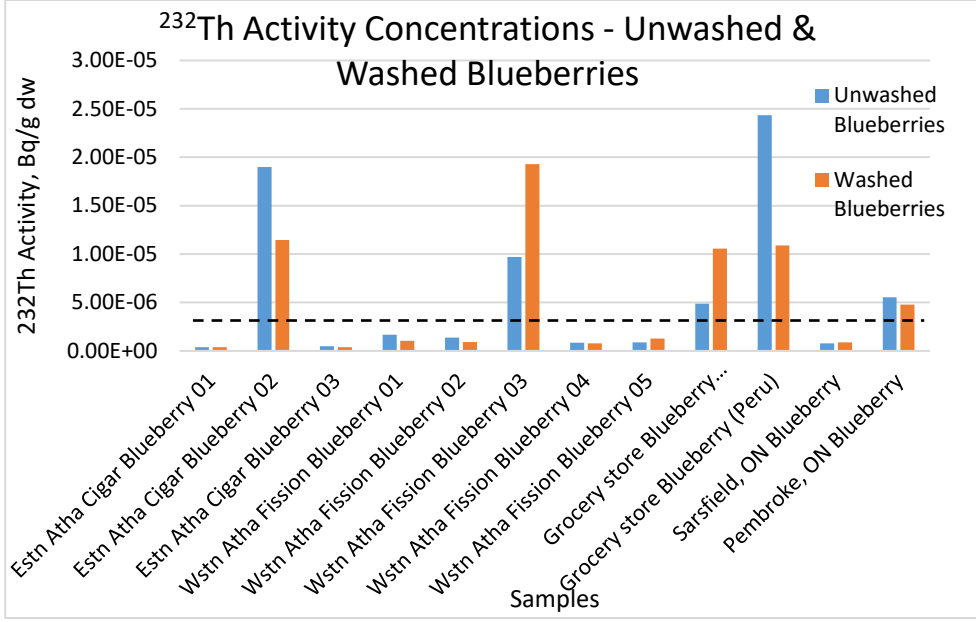

Figure 2.10: ^{232}Th activities for unwashed and washed blueberries

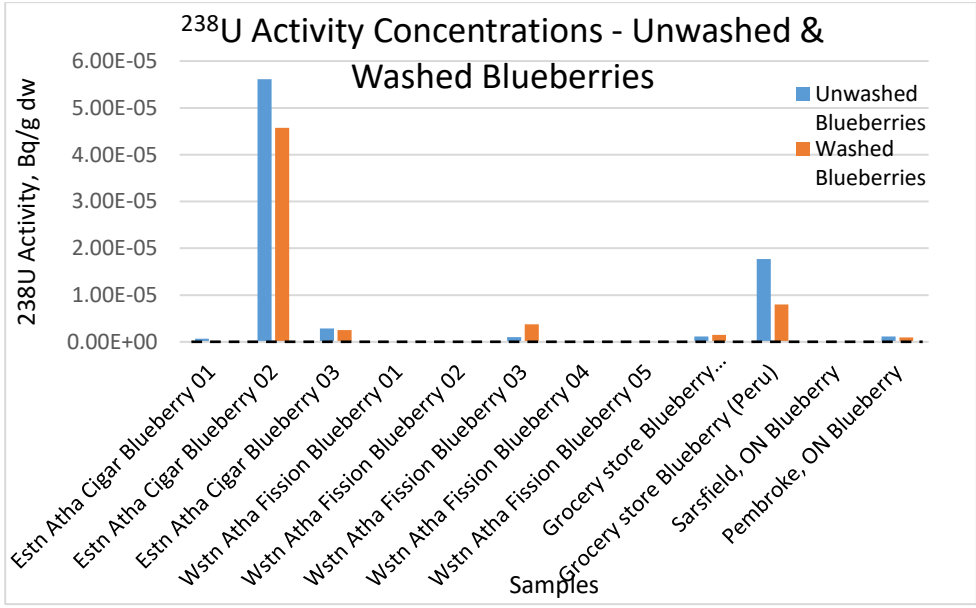

Fig 2.11: ^{238}U activities for unwashed and washed blueberries

measurement uncertainties, although there appears to be some ^{210}Po in the dust fraction of the Pembroke blueberries. Historical weather data for the 10 days leading up to sampling in Sarsfield, Ontario and Pembroke, Ontario showed there were 26mm and 9mm of precipitation, respectively, that could have washed dust off of the blueberries (Government of Canada, 2023), (Government of Canada, 2023).

Grocery Store

The unwashed and washed blueberries from Argentina and Peru showed some differences in the radionuclide content of the dust. ^{210}Pb was found in the dust of the Argentina blueberries since only the unwashed portion had a detectable activity. This is an indication the growing region in Argentina has ^{238}U in the soil although one would need to obtain and analyze the corresponding soil for this sample (IAEA, 2017). For ^{210}Pb in Peru blueberries, only the washed portion had a detectable activity, which was unexpected and could be due to errors during washing and processing. In the unwashed Peru blueberries, there was a ^{40}K activity in the dust. Since only the unwashed portion had a detectable activity, this suggests the use of potassium-based fertilizers and pesticides in this growing region (Commodore, 2012).

2.5.1.3 Estimating the Contributions of Dust to Radionuclide Inventories

Decay-corrected radionuclide inventories for the blueberry dust were estimated from the difference between the unwashed and washed activity concentrations measured and are presented in Table 2.2. Where either the unwashed or washed sample was below the MDL, the difference was not calculated and negative values were not included in the table. The percentage of activity contribution was calculated to show how much the dust fraction contributed to each radionuclide's total activity. This was done by taking the dust's activity, dividing by the unwashed blueberry activity, and multiplying by 100 to represent percentage. Overall, there were few values for the calculated dust fraction from which to draw conclusions. This was likely due to rain events, which were discussed earlier, which washed off dust that

Sample ID	^{137}Cs (Bq/g dw)	^{131}I (Bq/g dw)	^{210}Pb (Bq/g dw)	^{210}Po (Bq/g dw)	^{226}Ra (Bq/g dw)	^{40}K (Bq/g dw)	^{232}Th (Bq/g dw)	^{238}U (Bq/g dw)
Estn Atha Cigar Blueberry 01								
Estn Atha Cigar Blueberry 02				1.84E-03 (33%)			7.5E-06 (40%)	1.0E-05 (18%)
Estn Atha Cigar Blueberry 03			1.01E-03 (25%)			5.00E-02 (14%)		
Wstn Atha Fission Blueberry 01						3.00E-02 (10%)		
Wstn Atha Fission Blueberry 02								
Wstn Atha Fission Blueberry 03								
Wstn Atha Fission Blueberry 04	2.01E-03 (7%)					1.70E-01 (42%)		
Wstn Atha Fission Blueberry 05								
Grocery store Blueberry (Arg)				2.83E-04 (20%)				
Grocery store Blueberry (Peru)							1.3E-05 (55%)	9.7E-06 (55%)
Sarsfield, ON Blueberry				4.52E-04 (29%)				
Pembroke, ON Blueberry							7.5E-07 (14%)	

Table 2.2: The contribution of radionuclides in the dust on blueberries. The percentage value in the brackets indicates the amount of dust the value represents to the total activity from the unwashed blueberries.

Note: Decay corrected radionuclide activities in Bq/g dw values were used this table. Where either the unwashed sample or the washed sample was below the MDL, the difference between the unwashed and washed concentration was not calculated and negative values were not included in the table.

was atmospherically deposited prior to sampling. Additionally, foliar retention studies for radionuclides have found that hair on the surface increased retention (Carini, 1999) so the relatively smooth surface of blueberries may naturally inhibit dust adherence.

East and West Athabasca

For the radionuclide activities in the dust fraction of East and West Athabasca blueberries that could be calculated, a range of activity percentage contributions were observed relative to the total radionuclide activities.

The Chernobyl disaster in 1986 was a major atmospheric contributor of ^{137}Cs fallout which was dispersed in the atmosphere with wind and deposited to the earth's surface through dry and wet deposition. Another major contributor of radioactive cesium was from nuclear weapons testing that occurred during the 1950's and 1960's. ^{137}Cs from these sources has undergone significant decay due to its 30.2 year half-life. In recent years, ^{137}Cs fallout was released to the atmosphere from the Fukushima Daiichi Nuclear Power Plant's 2011 accident and also from North Korea's underground nuclear weapons testing in 2016 and 2017. For ^{137}Cs, only one sample from Athabasca (a West Athabasca sample) had a calculated dust fraction value which accounted for only 7% of the total ^{137}Cs radioactivity. This was amongst the lowest contribution from dust calculated for all blueberry samples and may be a result of the partly decayed ^{137}Cs's environmental redistribution from the soil compartment via processes such as erosion, transport, and deposition and also from the more recent atmospheric fallout inputs in 2011, 2016, and 2017 (Lehto & Vaaramaa, 2013) (Nanba, 2022) (Russell, 2015).

^{210}Po and ^{210}Pb in the terrestrial environment occur naturally from the decay of ^{238}U in soil and from the decay of ^{222}Rn gas in the atmosphere. These radionuclides can adhere to the surface of aerosol particles in the atmosphere and can then be transferred to the earth's surface via dry and wet deposition. It is also possible for ^{210}Po and ^{210}Pb present in the soil to became resuspended into the atmosphere on

coarse particles from mechanical process such as wind (Carvalho, F., et al., 2017), (Gwynn, 2013), (IAEA, 2017). The ^{210}Pb contribution from dust was calculated to be 1.01E-03 Bq/g, DW for only one Athabasca blueberry sample (an East Athabasca sample) and this accounted for 25% of the total ^{210}Pb radioactivity. There was also only one ^{210}Po dust value (for a different East Athabasca sample) and it was calculated to be 1.84E-03 Bq/g, DW, which accounted for 33% of its total ^{210}Po radioactivity. Looking at the ^{210}Po and ^{210}Pb activities in West Athabasca soils, many activities were below the MDL, whereas there were some activities measured in East Athabasca soils. Because of this, it is possible that ^{210}Po and ^{210}Pb activities found in the blueberry's dust fraction are from the decay of ^{222}Rn gas in the soil and the resuspension from wind (Carvalho, F., et al., 2017), (Gwynn, 2013), (Green, 2002).

^{40}K is a naturally occurring radionuclide and an essential plant growth nutrient which is obtained via root uptake from soil. ^{40}K can enter the atmosphere from burning coal and can be released from plant material during vegetation fires. Once in the atmosphere, ^{40}K can then fall back to the surface and deposit on plant surfaces (Chatterjee, 2017) (Carvalho, F., et al., 2017) (Commodore, 2012), which is likely the case for the samples in this study. The ^{40}K contribution from dust was calculated for only one East Athabasca blueberry sample (5.0E-02 Bq/g, DW) and two West Athabasca blueberry samples, 3.0E-02 Bq/g, DW, and 1.7E-01 Bq/g, DW, which accounted for 14%, 10%, and 42% of the total ^{40}K radioactivity, respectively. There was a significant contribution of ^{40}K in the dust from one of the West Athabasca samples, which corresponds to only 9mm of rain in the area in the 10 days ahead of sampling (Government of Canada, 2023).

^{232}Th and ^{238}U are released to the environment from weathering of thorium-rich and uranium-rich rocks, from uranium mining, and they can be released to the atmosphere as smoke particle aerosols from the oil and gas industry and from burning vegetation which liberate these radionuclides from plant tissues. Once in the atmosphere, ^{232}Th and ^{238}U can be returned to the surface via wet and dry deposition (Walther C. , 2015), (Carvalho, F., et al., 2017). Since 1967, there has been open-pit mining operations in the

Athabasca Bituminous Sands area. To produce one crude oil barrel, two tons of sand is processed (NASA, 2016) and this can generate atmospheric dust which may be transferred and deposited thousands of kilometers away (Shotyk W. , 2019). Studies of trace element concentrations in the mineral fraction of bituminous sand show the presence of thorium and uranium as well as other trace elements although the concentrations were depleted when compared to concentrations in the Upper Continental Crust (Shotyk W. , 2021). Together, these are the likely sources contributing to ^{232}Th and ^{238}U in dust for the Athabasca samples. For the ^{232}Th and ^{238}U contributions from dust, one East Athabasca blueberry sample had values of 7.5E-06 Bq/g, DW and 1.0E-05 Bq/g, DW, which accounted for 40% and 18% of the total ^{232}Th and ^{238}U radioactivity, respectively.

Ontario

For Sarsfield, Ontario, there was only a calculated value for ^{210}Po activity in the dust (4.52E-04 Bq/g, DW), which accounted for 29% of the total ^{210}Po activity. Similarly to the Athabasca blueberries, the most likely ^{210}Po source in this dust is from the decay of ^{222}Ra in the atmosphere depositing on the blueberries (Carvalho, F., et al., 2017) (Gwynn, 2013)(Green, 2002).

For Pembroke, Ontario samples, only a ^{232}Th activity in the dust was calculated (7.5E-07 Bq/g, DW), which accounted for 29% of the total ^{232}Th activity. It is possible that the ^{232}Th activity in the dust may be from weathering thorium-rich rocks and from recent vegetation fires (Walther C. , 2015) (Carvalho, F., et al., 2017).

Grocery Store

Argentina blueberries had a calculated dust contribution for ^{210}Po of 2.83E-04 Bq/g, DW, which accounted for 20% of the total ^{210}Po activity. The ^{210}Po in dust likely came from atmospheric ^{222}Ra that decayed to ^{210}Po and fell back to the earth's surface (Carvalho, F., et al., 2017), (Gwynn, 2013), (Green, 2002).

Only the blueberries from Peru had a ^{232}Th and ^{238}U contribution from dust and each accounted for 55% of the total activity for each radionuclide, respectively. The ^{232}Th and ^{238}U dust likely came from uranium mining in the area or from releases to the atmosphere from vegetation fires (Walther C. , 2015) (Carvalho, F., et al., 2017).

Summary For Radionuclides in Blueberry Dust for East and West Athabasca Samples:

- No dramatic differences between radionuclide activities between washed and unwashed Athabasca blueberries; suggests root uptake of radionuclides was dominant and precipitation prior to sampling could have washed off the dust or the dust was intercepted by leaves
- Very few radionuclide dust fraction values were able to be calculated; smooth blueberry surface could have inhibited dust adherence and rain could have washed dust away
- One West Athabasca blueberry sample had a detectable ^{137}Cs activity in the dust (7% total ^{137}Cs contribution); may be from soil redistribution containing ^{137}Cs from nuclear weapons testing (from the 1950's, 1960's, and recently in 2011, 2016, and 2017), Chernobyl, and Fukushima
- Only East Athabasca blueberries had a ^{210}Pb activity in the dust (25% total ^{210}Pb contribution) and a ^{210}Po activity in the dust (33% total ^{210}Po contribution); may be from the decay of ^{222}Rn gas in the soil and resuspension from wind
- One West Athabasca blueberry sample had a significant ^{40}K activity in the dust (42% total ^{40}K contribution); may be from the deposition of atmospheric ^{40}K released from burning coal or from vegetation fires
- One East Athabasca blueberry sample had 40% and 18% total activity contributions from ^{232}Th and ^{238}U, respectively, in the dust; may be from mining, the oil and gas industry, or from burning vegetation

Summary For Radionuclides in Blueberry Dust for Ontario Samples:

- No dramatic differences between radionuclide activities for washed and unwashed Ontario blueberries
- Very few radionuclide dust fraction values were able to be calculated; smooth blueberry surface could have inhibited dust adherence and rain could have washed dust away
- Only the Sarsfield blueberries had a ^{210}Po activity in the dust (29% total ^{210}Po contribution); may be from the decay of atmospheric ^{222}Ra and the deposition on blueberries
- Only Pembroke blueberries had a ^{232}Th activity in the dust (29% total ^{232}Th contribution); may be from weathering of thorium-rich rocks or from vegetation fires

Summary For Radionuclides in Blueberry Dust for Grocery Store Samples:

- Very few radionuclide dust fraction values were able to be calculated; smooth blueberry surface could have inhibited dust adherence and rain could have washed dust away
- Argentina blueberries had a ^{210}Po activity in the dust (20% total ^{210}Po contribution); likely from the atmospheric decay of ^{222}Ra
- Peru blueberries had a 55% total activity contribution of both ^{232}Th and ^{238}U in the dust; may be from mining in the area or from vegetation fires

2.5.1.4 Activity Concentrations in Soil

Activity concentrations were measured in soil for the corresponding blueberry samples for the different sampling locations. A data table and figures are presented in Table 2.3 and in Figures 2.12-2.17 with a discussion of the results.

Sample ID	^{137}Cs (Bq/g dw)	^{131}I (Bq/g dw)	^{210}Pb (Bq/g dw)	^{210}Po (Bq/g dw)	^{226}Ra (Bq/g dw)	^{40}K (Bq/g dw)	^{232}Th (Bq/g dw)	^{238}U (Bq/g dw)
MDL			0.04	0.01	0.01		1.18E-07	5.44E-07
East Atha Soil 1	0.00403 (0.003)	<0.0008	<MDL	0.07419	0.04	0.8 (0.01)	0.04	0.02
East Atha Soil 2	0.00605 (0.002)	<0.001	0.04042	0.03636	0.03	0.44 (0.03)	0.02	0.01
East Atha Soil 3	0.00403 (0.002)	<0.002	<MDL	0.03636	0.01	0.88 (0.01)	0.04	0.01
West Atha Soil 1	0.00404 (0.001)	<0.0008	<MDL	<MDL	0.03	0.05 (0.03)	3.47E-03	1.17E-03
West Atha Soil 2	0.00303 (0.001)	<0.0009	<MDL	0.02	<MDL	<0.03	2.62E-03	1.06E-03
West Atha Soil 3	0.00303 (0.001)	<0.0006	<MDL	<MDL	0.02	0.07 (0.006)	2.20E-03	8.35E-04
West Atha Soil 4	0.00303 (0.001)	<0.0005	<MDL	<MDL	0.02	0.08 (0.006)	2.43E-03	1.07E-03
West Atha Soil 5	<0.002	<0.0006	<MDL	0.01883	0.02	0.04 (0.006)	2.61E-03	9.69E-04
Sarsfield, ON Soil	0.00404 (0.002)	<0.0005	0.06083	0.22003	0.02	0.6 (0.02)	0.01	0.02
Pembroke, ON Soil	0.00707 (0.002)	<0.001	<MDL	0.11057	0.03	<0.06	0.01	6.70E-03

Table 2.3: Decay Corrected Radionuclide Measurement Results for ^{137}Cs, ^{131}I, ^{210}Pb, ^{210}Po, ^{226}Ra, ^{40}K, ^{232}Th, and ^{238}U for Soil Samples

Note: Symbol "<" denotes "less than" and is followed by the MDL value; values in brackets are the MDL; the short form "dw" denotes "dry weight". There were no soil samples with detectable ^{131}I activities so there is no corresponding figure for ^{131}I below.

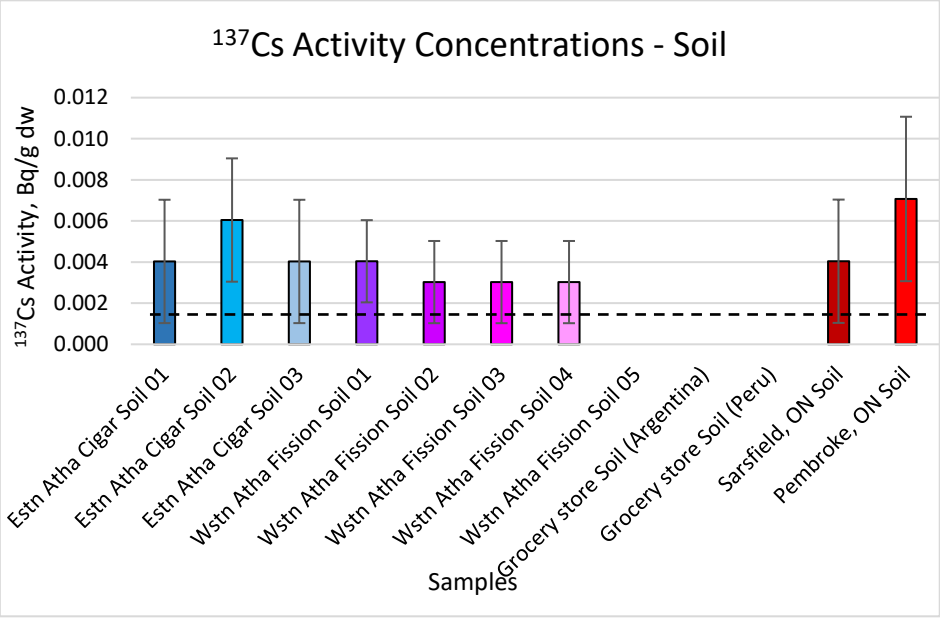

Figure 2.12: ^{137}Cs activity concentrations for soil

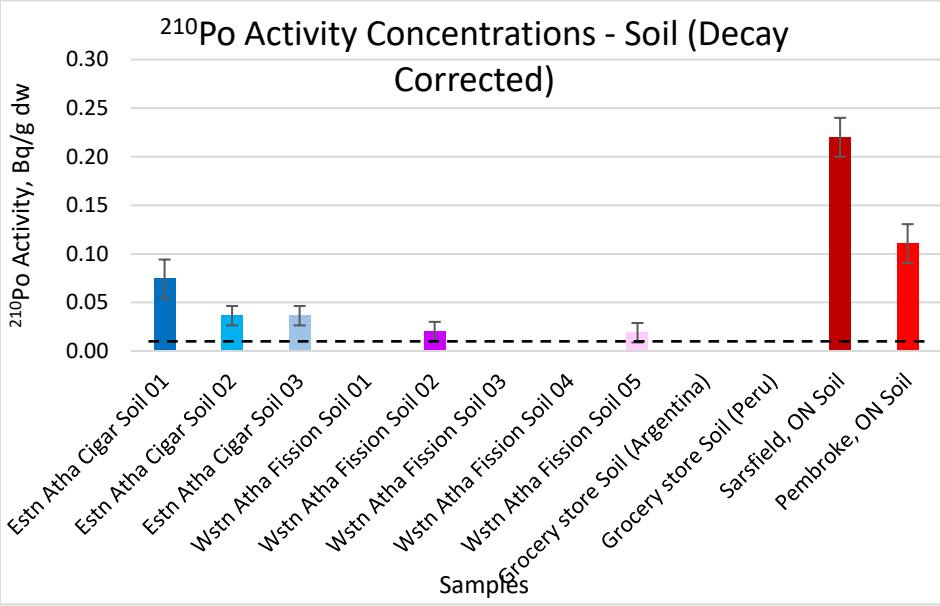

Figure 2.13: ^{210}Po activity concentrations for soil

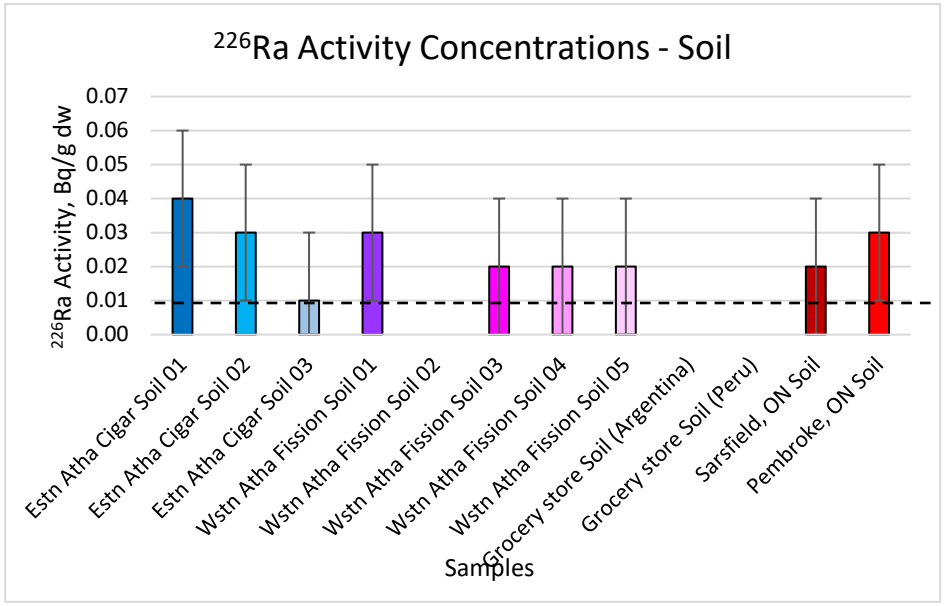

Figure 2.14: ^{226}Ra activity concentrations for soil

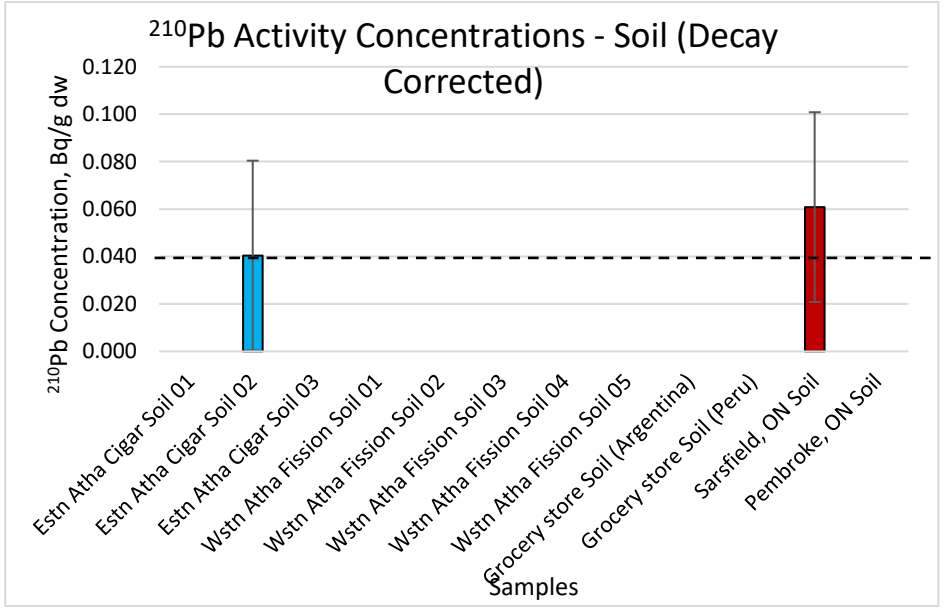

Figure 2.15: ^{210}Pb activity concentrations for soil

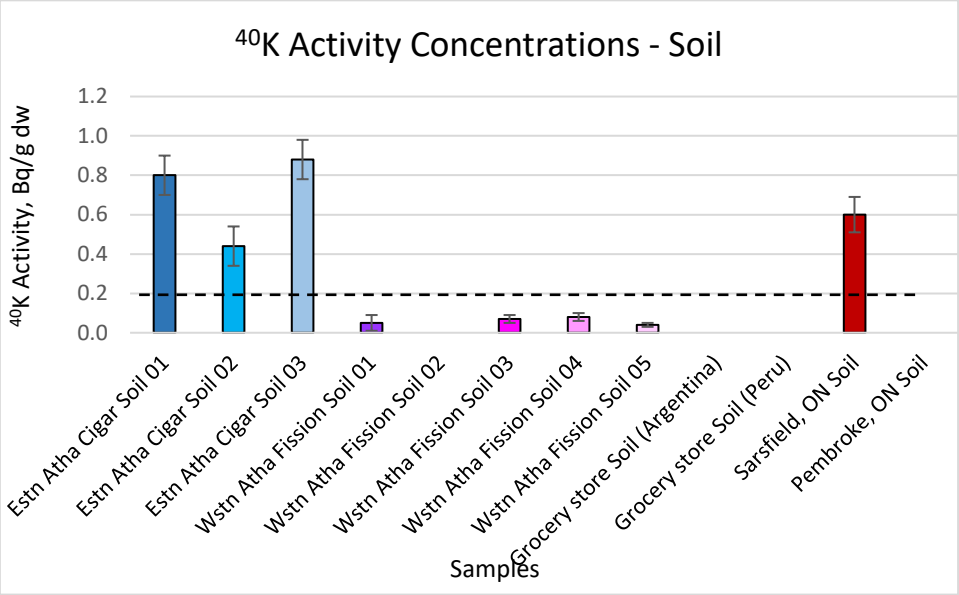

Figure 2.16: ^{40}K activity concentrations for soil

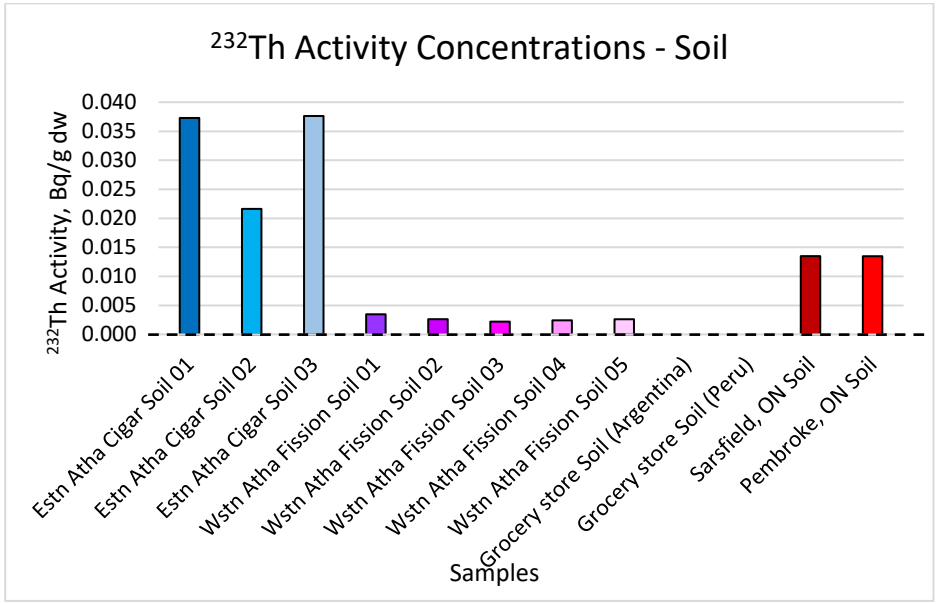

Figure 2.18: ^{232}Th activity concentrations for soil

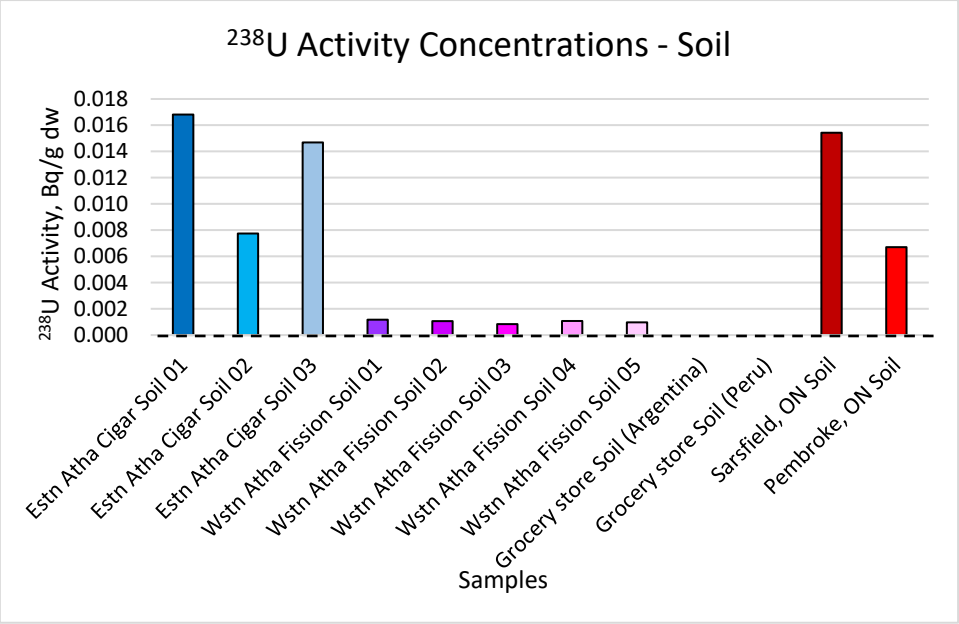

Figure 2.17: ^{238}U activity concentrations for soil

East and West Athabasca

Samples from East and West Athabasca showed distinct geochemistry in their soil. Overall, soil samples from East Athabasca were much more elevated in ^{232}Th and ^{238}U, with average activity concentrations of 0.033 Bq/g, DW and 0.013 Bq/g, DW, respectively, when compared to soils from West Athabasca, which had average activity concentrations of 2.7E-03 Bq/g, DW and 1.0E-03 Bq/g, DW for ^{232}Th and ^{238}U, respectively. To compare, soil from Syrian agricultural areas ranged between 0.011 and 0.033 Bq/g, DW for ^{238}U activity and shows East Athabasca soils are within this range and West Athabasca soils are a magnitude lower (Al-Masri, 2008). ^{238}U is a naturally occurring, long-lived radionuclide that is ubiquitous in the earth's crust and ^{226}Ra, ^{210}Pb, and ^{210}Po are progeny produced within the ^{238}U decay chain (IAEA, 2017), (Clark, 2015). The presence of elevated ^{238}U in the East Athabasca soils explains their relatively elevated ^{210}Po values (average activity concentration of 0.045 Bq/g, DW), although it is surprising to find these soils had only one detectable ^{210}Pb activity, 0.040 Bq/g, DW, which was at the detection limit. When analyzing the West Athabasca soils, the low ^{238}U activities correspond to the low ^{210}Pb and ^{210}Po activities observed: all ^{210}Pb activities were below detection and only two of five soils had a detectable ^{210}Po activity concentration of 0.02 and 0.019 Bq/g, DW. For comparison, soil from Syrian agricultural areas ranged between 0.015 and 0.043 Bq/g, DW for ^{210}Pb activity and shows Athabasca soils are within the same magnitude (Al-Masri, 2008). When averaged, the East Athabasca soils had only a slightly higher ^{226}Ra activity concentration (0.027 Bq/g, DW) when compared to West Athabasca soils (average for four of five soils above detection was 0.023 Bq/g, DW), which was surprising given that the ^{238}U in East Athabasca soils was an order of magnitude higher than in soils from West Athabasca. To compare, ^{226}Ra activities in soils from Syrian agricultural areas ranged between 0.013 and 0.036 Bq/g, DW, which shows the ^{226}Ra activities in Athabasca soils are within the same range (Al-Masri, 2008). Additionally, the West Athabasca soils were depleted in ^{40}K (average activity of 0.06 Bq/g, DW, for four of five samples above detection) when compared to East Athabasca (average activity concentration of 0.71 Bq/g, DW). For

comparison, soil from Syrian agricultural areas ranged between 0.214 and 0.540 Bq/g, DW for ^{40}K activity and shows Athabasca soils have much lower ^{40}K activities (Al-Masri, 2008), which make sense since this area is not fertilized with potassium-based fertilizers whereas the Syrian sampling locations likely are.

Ontario

There were also differences noted in the geochemistry of Ontario soils. Overall, the Sarsfield, Ontario soil was elevated in ^{238}U, with an activity concentration of 0.02 Bq/g, DW, when compared to the Pembroke, Ontario soil, which had an activity concentration of 6.7E-03 Bq/g, DW. The Sarsfield soil was very similar in ^{238}U activity to East Athabasca soils. Since the decay products of ^{238}U include ^{226}Ra, ^{210}Pb, and ^{210}Po, and the Sarsfield soil had an elevated ^{238}U activity, it is expected the Sarsfield soil would also be elevated in these radionuclide activities, which is indeed the case, with activity concentrations of 0.02 Bq/g, DW for ^{226}Ra, 0.061 Bq/g, DW for ^{210}Pb, and 0.220 Bq/g, DW for ^{210}Po. The ^{210}Po activity in Sarsfield soil was the highest for all sampling locations. The Pembroke soil had a low ^{238}U activity and a correspondingly low ^{210}Pb activity that was below detection. Curiously, the Pembroke soil had a relatively high ^{210}Po activity (0.111 Bq/g, DW), which was half that of Sarsfield soil but was an order of magnitude higher than the East Athabasca soils. Another surprise was that the Pembroke soil also had a ^{226}Ra activity (0.03 Bq/g, DW) similar to Sarsfield's soil, despite having a lower ^{238}U activity. Additionally, the Sarsfield soil had an elevated ^{40}K activity of 0.6 Bq/g, DW, which was similar in magnitude to East Athabasca soils and indicates the use of potassium-based fertilizers at this farm, whereas the Pembroke soil was quite depleted and was below detection for ^{40}K.

Grocery Store

There were no soil samples to analyze that corresponded to the grocery store blueberry samples.

Summary For Radionuclides in East and West Athabasca Soil Samples:

- Distinct geochemical differences between East and West Athabasca soils

- Overall, East Athabasca soil was elevated in ^{232}Th, ^{238}U, and ^{40}K activity when compared to West Athabasca and was comparable in ^{238}U and ^{40}K activity to Sarsfield, Ontario soil
- East Athabasca soil also had low but detectable ^{226}Ra and ^{210}Po activities whereas these radionuclides were not reliably above detection for West Athabasca soils; these are progeny produced within the ^{238}U decay chain and activities are explained by East Athabasca soil's elevated ^{238}U activity although it is surprising there was no ^{210}Pb activity reliably above detection
- When compared to literature, Athabasca soils were comparable to or a magnitude lower in ^{238}U, ^{210}Pb, ^{226}Ra, and ^{40}K activities

Summary For Radionuclides in Ontario Soil Samples:

- Distinct geochemical differences between Ontario soils
- Sarsfield soil was elevated in ^{238}U, ^{226}Ra, ^{210}Pb, and ^{210}Po activities when compared to Pembroke soil; ^{226}Ra, ^{210}Pb, and ^{210}Po are progeny produced within the ^{238}U decay chain and elevated activities are explained by Sarsfield soil's elevated ^{238}U
- Sarsfield soil had the highest ^{210}Po activity for all sampling locations and an elevated ^{40}K activity; the elevated ^{40}K activity indicates the use of potassium-based fertilizer
- Pembroke soil had higher than expected ^{210}Po and ^{226}Ra activities, given its correspondingly low ^{238}U activity

2.5.1.5 Soil to Plant Transfer Factors for Radionuclides

The IAEA has compiled data from research publications worldwide for the transfer of radionuclides and elements from soil to many different plants in terrestrial environments in its *Technical Report Series no. 472*. Specifically for fruit, values for fresh weight activities (since consumption data is typically provided with fresh weights) and dry soil activities values were used in calculations. This IAEA

Sample ID	^{137}Cs	^{131}I	^{210}Pb	^{210}Po	^{226}Ra	^{40}K	^{232}Th	^{238}U
Estn Atha Cigar Blueberry 01				1.0E-02	1.3E-02	6.1E-02	1.3E-06	
Estn Atha Cigar Blueberry 02			1.3E-02	1.3E-02	4.4E-02		7.0E-05	7.8E-04
Estn Atha Cigar Blueberry 03				1.3E-02	7.9E-02	4.8E-02	1.3E-06	2.3E-05
Wstn Atha Fission Blueberry 01						7.4E-01	4.0E-05	
Wstn Atha Fission Blueberry 02	3.5E-01			1.3E-02			4.6E-05	
Wstn Atha Fission Blueberry 03					1.3E-02		1.2E-03	5.9E-04
Wstn Atha Fission Blueberry 04	1.2E+00					4.0E-01	4.3E-05	
Wstn Atha Fission Blueberry 05				1.4E-02	1.3E-02	9.9E-01	6.4E-05	
Sarsfield ON Blueberry				6.7E-04		7.3E-02	8.5E-06	
Pembroke, ON Blueberry					8.8E-03		4.7E-05	1.8E-05
Mean East:				**1.2E-02**	**4.5E-02**	**5.5E-02**	**2.4E-05**	**4.0E-04**
Median East:				**1.3E-02**	**4.4E-02**		**1.3E-06**	
Mean West:	**7.7E-01**			**1.4E-02**	**1.3E-02**	**7.1E-01**	**2.7E-04**	
Median West:						**7.4E-01**	**4.6E-05**	
Mean Ontario:							**2.8E-05**	
Median Ontario:								

Table 2.4: Soil to Plant Activity Ratios of Washed Blueberries:Soil for All Radionuclides

Note: Decay corrected radionuclide activities in Bq/g fw were used for the blueberries and Bq/g dw were used for soils in this table. Where either the washed blueberry sample or the soil sample was below the MDL, the ratio was not calculated.

publication includes data on the dry matter content of wild blueberries, which provides a mean of 13.2% (IAEA, 2010). Soil to plant transfer factors were calculated for samples analyzed and are presented in Table 2.4. The radionuclide transfer efficiency from soil into blueberries was determined by taking the radionuclide activity in the washed blueberry (Bq/g, dry weight), multiplying by 0.132 to account for the dry matter content, and dividing by the corresponding radionuclide activity in the soil (Bq/g, dry weight). In cases where one value was below the MDL, the calculation was not performed. The radionuclide transfer efficiency for grocery store blueberries could not be determined since the corresponding soils were not obtained.

East and West Athabasca

Radioecologists have studied soil-to-fruit transfer factors for different radionuclides and soil properties are largely responsible for the transfer factor variability for fruit. Radioecologists have shown that plant uptake is complex and that radionuclide concentrations in fruit tissues are not similar to the radionuclide concentrations in soil. Transfer factors can be used in radiological risk assessments when estimating ingestion doses (IAEA, 2010). Overall, the West Athabasca blueberries were efficient in the uptake of ^{137}Cs and ^{40}K from soil with values of 7.7E-01 (two samples averaged) and 7.4E-01 (median of three values), respectively, which correspond to efficiencies of over 74%. Potassium is important in plant metabolism and cesium and potassium are analogue element pairs with similar chemical behaviour. Plants will obtain the potassium needed for growth from the soil and will uptake cesium as a chemical analogue (Walther C. , 2015), (IAEA, 2010) so it is not surprising that the West Athabasca blueberries were efficient in obtaining both ^{137}Cs and ^{40}K from soil, considering these soils were depleted in potassium.

Contrasting this, the East Athabasca soils had a higher potassium concentration and the soil to plant transfer for ^{40}K was calculated to be 5.5E-02 (two samples averaged), which is an order of magnitude lower than the value for West Athabasca samples. There were no ^{137}Cs transfer factors calculated for East Athabasca. In literature, the soil to fruit transfer values for Cs for shrubs growing in temperate

environments ranged between 6.9E-01 to 5.7E+00 and shows the West Athabasca's soil to fruit values were within this range (IAEA, 2010). For ^{232}Th, the West Athabasca samples were also more efficient in uptake with a calculated transfer factor of 4.6E-05 (median of five samples) when compared to 1.3E-06 (median of three samples) for East Athabasca samples.

Other soil to plant transfer factors for ^{210}Po, ^{226}Ra, and ^{238}U were reasonably similar in magnitude between East and West Athabasca samples and showed a <5% transfer factor. For comparison, the literature values for the soil to plant transfer for Po in non-leafy vegetables growing in temperate environments ranged between 1.6E-02 to 3.7E-01, which corresponds to a transfer of between 1.6-37% and shows the Athabasca soil to fruit transfer values were within this range. The literature also provided a soil to plant (berries) transfer range of 2.4E-01 to 6.3E+03 for Ra, 6.2E-02 to 1.6E+01 for Th, and 5.2E-01 to 2.0E+02 for U, which shows the transfer of Ra, Th, and U can very considerably and the values in Athabasca fall within the literature ranges (IAEA, 2010).

Ontario

There was limited data to calculate and compare each soil to plant transfer factor for Ontario samples. For the values that were calculated, they were generally similar in magnitude or slightly lower than values calculated for the Athabasca samples and within the literature ranges (IAEA, 2010).

Grocery Store

Soil to plant transfer activity ratios could not be calculated for grocery store samples since the corresponding soils for these blueberries were not obtained and analyzed.

Summary For Radionuclide Soil to Plant Transfer for East and West Athabasca Samples:

- West Athabasca samples were more efficient in the uptake of ^{137}Cs and ^{40}K from soil when compared to East Athabasca; West Athabasca soils were depleted in potassium and obtained ^{137}Cs and ^{40}K as chemical analogues

- The soil to fruit transfer value for Cs was in the same range as the value found for West Athabasca samples
- West Athabasca samples were more efficient in the uptake of ^{232}Th when compared to East Athabasca
- East Athabasca soil to plant transfer of ^{40}K was low and there was no ^{137}Cs transfer factors calculated; East Athabasca soil had an adequate concentration of K available for plant uptake
- There were similar soil to plant transfer factors for Athabasca samples for ^{210}Po, ^{226}Ra, ^{238}U, and ^{232}Th; values for Athabasca samples were comparable to literature ranges

Summary For Radionuclide Soil to Plant Transfer for Ontario Samples:

- Limited data for Ontario samples
- Generally, Ontario soil to plant transfer values for radionuclides were similar in magnitude or slightly lower than Athabasca samples and were within literature ranges

2.5.2 Trace Elemental Concentrations in Blueberries and Soil

Trace elements were analyzed in blueberries and soil from several sites in East and West Athabasca in Saskatchewan, two Ontario blueberry farms, and in blueberries from grocery stores that were products of Peru and Argentina.

2.5.2.1 Concentrations in Washed Blueberries

The trace element concentrations in washed and unwashed blueberries are presented in Tables 2.5-2.9 and in Figures 2.19-2.41. Overall, there were similar trends for all elemental concentrations measured in washed blueberry samples. Some of the highest concentrations in blueberries were magnesium, calcium, potassium, manganese, iron, zinc, rubidium, strontium, and barium, which correlate

Sample ID	Li (µg/g)	Be (µg/g)	Mg (µg/g)	Al (µg/g)	K (µg/g)	Ca (µg/g)	V (µg/g)	Cr (µg/g)	Mn (µg/g)	Fe (µg/g)
MDL	**2.5E-02**	**3.5E-04**	**2.4E-01**	**6.5E-02**	**1.5E+00**	**2.2E+00**	**1.1E-03**	**4.7E-03**	**1.9E-03**	**6.5E-02**
East Atha Blueberry 01 Unwashed	< MDL	< MDL	4.8E+02	6.5E+00	6309.42	1.0E+03	6.7E-04	< MDL	1.9E+02	1.0E+01
East Atha Blueberry 01 Washed	< MDL	< MDL	4.0E+02	8.5E+00	5245.58	9.6E+02	6.3E-04	< MDL	1.6E+02	9.4E+00
East Atha Blueberry 02 Unwashed	< MDL	< MDL	8.7E+02	2.0E+01	6579.61	1.8E+03	1.3E-02	1.8E-02	2.1E+02	1.8E+01
East Atha Blueberry 02 Washed	< MDL	< MDL	8.6E+02	1.7E+01	7340.45	1.9E+03	9.0E-03	1.2E-02	1.7E+02	1.8E+01
East Atha Blueberry 03 Unwashed	3.2E-02	< MDL	7.4E+02	1.1E+01	7545.82	1.8E+03	1.4E-03	1.4E-02	1.8E+02	1.2E+01
East Atha Blueberry 03 Washed	< MDL	< MDL	7.1E+02	9.6E+00	7340.86	1.7E+03	1.4E-03	1.2E-02	2.2E+02	1.3E+01
West Atha Blueberry 01 Unwashed	< MDL	< MDL	5.0E+02	7.9E+00	5015.55	1.1E+03	2.8E-03	5.5E-03	3.3E+02	1.1E+01
West Atha Blueberry 01 Washed	< MDL	< MDL	5.6E+02	7.7E+00	4864.70	1.3E+03	3.2E-03	< MDL	3.3E+02	1.1E+01
West Atha Blueberry 02 Unwashed	< MDL	< MDL	4.9E+02	7.3E+00	5024.16	1.2E+03	2.9E-03	< MDL	3.8E+02	9.8E+00
West Atha Blueberry 02 Washed	< MDL	< MDL	5.3E+02	8.3E+00	4814.85	1.2E+03	2.2E-03	4.6E-03	4.4E+02	1.0E+01
West Atha Blueberry 03 Unwashed	< MDL	< MDL	4.0E+02	9.4E+00	5096.45	1.0E+03	5.0E-03	8.8E-03	2.3E+02	1.0E+01
West Atha Blueberry 03 Washed	< MDL	< MDL	4.1E+02	9.8E+00	4940.83	1.2E+03	3.5E-03	1.5E-02	2.0E+02	1.1E+01
West Atha Blueberry 04 Unwashed	< MDL	< MDL	6.2E+02	1.0E+01	5245.00	1.4E+03	4.4E-03	5.8E-02	6.6E+02	1.3E+01
West Atha Blueberry 04 Washed	< MDL	< MDL	8.1E+02	1.3E+01	5846.01	1.9E+03	3.0E-03	1.5E-02	6.1E+02	1.6E+01
West Atha Blueberry 05 Unwashed	< MDL	< MDL	7.8E+02	5.2E+00	5760.75	1.4E+03	2.9E-03	4.2E-03	4.3E+02	1.3E+01
West Atha Blueberry 05 Washed	< MDL	< MDL	8.4E+02	5.5E+00	5173.96	1.6E+03	2.7E-03	5.1E-03	4.1E+02	1.4E+01
Groc store Blueberry (Arg) Unwashed	1.8E-01	< MDL	5.8E+02	1.0E+01	6617.30	7.3E+02	1.7E-02	2.0E-02	3.5E+01	1.6E+01
Groc store Blueberry (Arg) Washed	1.3E-01	< MDL	5.2E+02	9.1E+00	6467.85	5.5E+02	1.8E-02	1.4E-02	3.0E+01	1.6E+01
Groc store Blueberry (Peru) Unwashed	3.8E-01	< MDL	4.9E+02	5.0E-05	65581.00	1.3E+03	9.9E-02	1.3E-01	2.2E+01	5.3E+01
Groc store Blueberry (Peru) Washed	3.6E-01	< MDL	4.6E+02	2.6E-05	4598.30	1.3E+03	4.4E-02	8.3E-02	1.8E+01	2.3E+01
Sarsfield, ON Blueberry Unwashed	1.5E-02	< MDL	5.1E+02	1.3E+01	6843.20	3.4E+02	4.9E-03	5.9E-03	1.3E+01	2.0E+01
Sarsfield, ON Blueberry Washed	3.3E-02	< MDL	5.0E+02	1.4E+01	6538.07	4.6E+02	3.8E-03	1.3E-02	1.4E+01	2.1E+01
Pembroke, ON Blueberry Unwashed	< MDL	< MDL	3.4E+02	1.7E+01	5730.30	4.2E+02	2.0E-02	5.0E-02	3.0E+01	1.8E+01
Pembroke, ON Blueberry Washed	< MDL	< MDL	3.7E+02	1.5E+01	5286.55	4.3E+02	1.8E-02	4.1E-02	2.8E+01	1.8E+01

Table 2.5: Trace Element Concentrations in µg/g for Li, Be, Mg, Al, K, Ca, V, Cr, Mn, and Fe for Washed and Unwashed Blueberries. Note: Symbol "<" denotes "less than" and is followed by the MDL value; values in brackets are the MDL; the short form "dw" denotes "dry weight".

Sample ID	Co (µg/g)	Ni (µg/g)	Cu (µg/g)	Zn (µg/g)	Ga (µg/g)	As (µg/g)	Se (µg/g)	Rb (µg/g)	Sr (µg/g)	Y (µg/g)
MDL	**1.4E-04**	**5.2E-03**	**3.9E-03**	**9.2E-02**	**1.3E-03**	**2.4E-01**	**2.6E-01**	**2.9E-03**	**2.4E-03**	**2.4E-04**
East Atha Blueberry 01 Unwashed	1.6E-02	9.8E-01	2.4E+00	4.8E+00	2.7E-03	3.1E-03	4.6E-03	1.9E+01	1.8E+00	3.3E-04
East Atha Blueberry 01 Washed	1.6E-02	9.7E-01	2.4E+00	4.4E+00	2.2E-03	5.4E-03	2.8E-03	1.9E+01	2.1E+00	< MDL
East Atha Blueberry 02 Unwashed	2.2E-02	8.7E-01	4.7E+00	6.7E+00	6.4E-03	3.4E-03	1.3E-02	3.5E+01	2.8E+00	6.2E-03
East Atha Blueberry 02 Washed	1.7E-02	7.8E-01	4.7E+00	6.7E+00	4.1E-03	5.0E-03	9.6E-03	2.8E+01	1.8E+00	3.9E-03
East Atha Blueberry 03 Unwashed	1.8E-02	1.2E+00	3.8E+00	6.9E+00	4.4E-04	3.0E-03	1.3E-02	2.0E+01	1.1E+01	4.6E-04
East Atha Blueberry 03 Washed	1.7E-02	1.1E+00	4.2E+00	7.0E+00	4.1E-03	3.9E-03	1.2E-02	2.0E+01	7.6E+00	< MDL
West Atha Blueberry 01 Unwashed	2.2E-03	2.6E-01	3.0E+00	5.4E+00	1.0E-03	2.0E-03	4.8E-03	1.2E+01	9.5E-01	8.6E-04
West Atha Blueberry 01 Washed	2.2E-03	3.1E-01	2.9E+00	5.5E+00	9.5E-03	5.8E-03	2.3E-03	1.1E+01	9.4E-01	6.3E-04
West Atha Blueberry 02 Unwashed	3.0E-03	4.2E-01	2.6E+00	5.4E+00	1.3E-03	8.6E-04	6.9E-03	1.2E+01	1.8E+00	8.2E-04
West Atha Blueberry 02 Washed	3.0E-03	3.8E-01	2.5E+00	5.6E+00	3.8E-03	3.0E-03	7.0E-03	1.2E+01	1.4E+00	7.1E-04
West Atha Blueberry 03 Unwashed	1.9E-03	3.7E-01	2.1E+00	4.8E+00	1.0E-02	2.0E-03	4.9E-03	8.8E+00	1.5E+00	2.4E-03
West Atha Blueberry 03 Washed	3.6E-03	4.5E-01	2.4E+00	5.7E+00	2.2E-03	2.6E-03	3.4E-03	8.6E+00	2.0E+00	1.1E-03
West Atha Blueberry 04 Unwashed	3.1E-03	7.9E-01	4.3E+00	8.1E+00	1.5E-02	< MDL	1.3E-02	1.6E+01	5.1E+00	5.5E-04
West Atha Blueberry 04 Washed	4.2E-03	9.4E-01	4.9E+00	9.1E+00	9.5E-03	2.2E-03	2.0E-02	1.7E+01	8.1E+00	3.0E-04
West Atha Blueberry 05 Unwashed	3.6E-03	1.8E-01	3.6E+00	8.5E+00	3.2E-03	6.3E-03	5.0E-03	1.3E+01	3.4E+00	7.9E-04
West Atha Blueberry 05 Washed	2.7E-03	1.8E-01	3.6E+00	9.2E+00	2.2E-03	7.8E-03	6.7E-03	1.3E+01	3.9E+00	4.8E-04
Groc store Blueberry (Arg) Unwashed	1.2E-02	4.1E-01	5.3E+00	7.0E+00	2.8E-03	6.3E-02	2.1E-03	4.9E+00	6.5E+00	3.7E-03
Groc store Blueberry (Arg) Washed	8.9E-03	3.3E-01	5.0E+00	7.0E+00	< MDL	6.7E-02	2.8E-04	4.6E+00	5.7E+00	5.5E-03
Groc store Blueberry (Peru) Unwashed	2.5E-02	4.4E-01	2.4E+00	3.8E+00	1.4E-02	8.5E-02	1.5E-03	3.2E+00	3.0E+00	1.2E-02
Groc store Blueberry (Peru) Washed	2.3E-02	3.9E-01	2.1E+00	2.6E+00	3.6E-03	5.8E-02	1.8E-03	2.2E+00	3.0E+00	5.7E-03
Sarsfield, ON Blueberry Unwashed	2.4E-02	1.2E+00	2.5E+00	7.3E+00	< MDL	1.7E-02	< MDL	4.0E+00	6.2E-01	2.6E-03
Sarsfield, ON Blueberry Washed	3.7E-02	9.3E-01	2.1E+00	6.2E+00	< MDL	1.7E-02	8.1E-04	3.9E+00	8.4E-01	2.1E-03
Pembroke, ON Blueberry Unwashed	4.7E-03	5.0E-01	3.8E+00	4.1E+00	1.1E-02	4.7E-03	3.6E-03	3.0E+00	1.0E+00	8.2E-03
Pembroke, ON Blueberry Washed	4.4E-03	3.4E-01	3.9E+00	4.5E+00	3.1E-03	3.8E-03	7.5E-03	3.5E+00	1.2E+00	7.0E-03

Table 2.6: Trace Element Concentrations in µg/g for Co, Ni, Cu, Zn, Ga, As, Se, Rb, Sr, and Y for Washed and Unwashed Blueberries. Note: Symbol "<" denotes "less than"; MDL = method detection limit.

Sample ID	Mo (µg/g)	Ag (µg/g)	Cd (µg/g)	Sb (µg/g)	Cs (µg/g)	Ba (µg/g)	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)
MDL	**7.6E-04**	**4.4E-04**	**3.7E-04**	**6.5E-04**	**8.7E-04**	**4.0E-03**	**4.4E-05**	**7.9E-05**	**2.5E-04**	**8.9E-05**
East Atha Blueberry 01 Unwashed	7.1E-02	< MDL	8.0E-04	< MDL	2.4E-02	1.8E+01	6.1E-04	9.9E-04	5.3E-05	1.0E-04
East Atha Blueberry 01 Washed	4.9E-02	< MDL	1.9E-03	< MDL	2.7E-02	2.1E+01	4.2E-04	4.6E-04	3.5E-04	3.6E-04
East Atha Blueberry 02 Unwashed	2.6E-01	< MDL	5.8E-04	9.5E-04	1.0E-01	3.1E+01	9.7E-03	1.9E-02	2.1E-03	7.0E-03
East Atha Blueberry 02 Washed	3.1E-01	< MDL	1.4E-03	8.9E-04	7.6E-02	2.2E+01	6.6E-03	1.2E-02	1.4E-03	5.7E-03
East Atha Blueberry 03 Unwashed	1.3E-01	< MDL	2.0E-03	< MDL	2.5E-02	3.2E+01	6.9E-04	1.4E-03	1.4E-04	6.4E-05
East Atha Blueberry 03 Washed	1.7E-01	< MDL	1.0E-03	< MDL	2.6E-02	3.3E+01	6.1E-04	8.8E-04	< MDL	3.9E-04
West Atha Blueberry 01 Unwashed	1.3E-01	< MDL	1.6E-03	< MDL	2.2E-02	2.0E+01	3.1E-03	5.4E-03	5.2E-04	1.8E-03
West Atha Blueberry 01 Washed	1.3E-01	< MDL	2.2E-03	< MDL	2.3E-02	2.1E+01	1.9E-03	3.0E-03	2.8E-04	5.5E-04
West Atha Blueberry 02 Unwashed	5.7E-02	< MDL	1.4E-04	< MDL	2.3E-02	1.7E+01	1.5E-03	3.3E-03	2.7E-04	1.0E-03
West Atha Blueberry 02 Washed	9.6E-02	< MDL	8.1E-04	< MDL	2.6E-02	1.9E+01	1.6E-03	2.6E-03	2.8E-04	8.5E-04
West Atha Blueberry 03 Unwashed	1.0E-01	< MDL	6.1E-04	< MDL	1.9E-02	1.6E+01	1.8E-02	2.8E-02	5.3E-03	2.3E-02
West Atha Blueberry 03 Washed	1.2E-01	< MDL	7.6E-04	< MDL	2.3E-02	1.5E+01	7.4E-03	1.4E-02	1.5E-03	4.7E-03
West Atha Blueberry 04 Unwashed	4.3E-02	< MDL	< MDL	< MDL	1.3E-01	2.5E+01	1.0E-03	1.7E-03	2.8E-04	8.7E-04
West Atha Blueberry 04 Washed	3.3E-02	< MDL	2.8E-04	< MDL	1.1E-01	2.5E+01	1.3E-03	2.1E-03	3.6E-04	8.5E-04
West Atha Blueberry 05 Unwashed	2.88.0E-02	< MDL	8.1E-04	< MDL	5.6E-02	2.1E+01	1.3E-03	2.4E-03	1.8E-04	1.4E-03
West Atha Blueberry 05 Washed	8.6E-02	< MDL	2.4E-04	< MDL	7.9E-02	2.4E+01	1.7E-03	3.2E-03	2.6E-04	1.3E-03
Groc store Blueberry (Arg) Unwashed	1.5E-02	< MDL	1.5E-03	3.1E-03	8.8E-03	4.7E+00	5.4E-03	1.1E-02	1.0E-03	4.3E-03
Groc store Blueberry (Arg) Washed	6.1E-02	< MDL	5.9E-03	5.4E-03	2.2E-02	4.3E+00	8.6E-03	1.9E-02	2.0E-03	7.2E-03
Groc store Blueberry (Peru) Unwashed	1.7E-01	< MDL	4.3E-03	4.4E-03	1.3E-01	1.3E+00	3.6E-02	7.1E-02	7.4E-03	2.6E-02
Groc store Blueberry (Peru) Washed	1.7E-01	< MDL	2.6E-03	3.2E-03	8.6E-02	1.4E+00	7.1E-03	1.5E-02	1.7E-03	5.8E-03
Sarsfield, ON Blueberry Unwashed	4.4E-04	< MDL	7.5E-03	< MDL	1.8E-03	1.6E+00	1.6E-03	2.8E-03	1.5E-04	1.3E-03
Sarsfield, ON Blueberry Washed	< MDL	< MDL	7.2E-03	< MDL	2.9E-03	2.5E+00	1.9E-03	2.9E-03	4.0E-04	1.4E-03
Pembroke, ON Blueberry Unwashed	2.2E-01	< MDL	8.1E-03	< MDL	< MDL	2.9E+00	3.5E-02	7.5E-02	7.9E-03	2.4E-02
Pembroke, ON Blueberry Washed	5.1E-02	< MDL	2.7E-03	< MDL	< MDL	3.0E+00	7.5E-03	1.7E-02	1.9E-03	7.1E-03

Table 2.7: Trace Element Concentrations in µg/g for Mo, Ag, Cd, Sb, Cs, Ba, La, Ce, Pr, and Nd for Washed and Unwashed Blueberries. Note: Symbol "<" denotes "less than"; MDL = method detection limit.

Sample ID	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (µg/g)	Dy (µg/g)	Ho (µg/g)	Er (µg/g)	Tm (µg/g)	Yb (µg/g)	Lu (µg/g)
MDL	**7.3E-05**	**2.4E-05**	**1.0E-04**	**5.7E-05**	**9.0E-05**	**1.5E-05**	**3.0E-05**	**6.5E-06**	**3.5E-05**	**1.5E-05**
East Atha Blueberry 01 Unwashed	1.2E-04	5.2E-04	< MDL	< MDL	< MDL	< MDL	3.0E-05	< MDL	4.6E-05	< MDL
East Atha Blueberry 01 Washed	< MDL	4.5E-04	< MDL	< MDL	< MDL	< MDL	6.6E-05	< MDL	< MDL	9.2E-06
East Atha Blueberry 02 Unwashed	9.2E-04	1.1E-03	1.2E-03	2.7E-04	1.4E-03	1.4E-04	6.5E-04	1.4E-04	4.6E-04	5.3E-05
East Atha Blueberry 02 Washed	7.0E-04	9.1E-04	8.7E-04	1.6E-04	7.3E-04	8.9E-05	4.2E-04	2.8E-05	4.2E-04	2.0E-05
East Atha Blueberry 03 Unwashed	< MDL	9.3E-04	1.4E-04	< MDL	1.5E-04	< MDL	< MDL	< MDL	8.7E-05	< MDL
East Atha Blueberry 03 Washed	< MDL	7.0E-04	< MDL	2.3E-05	< MDL	< MDL	< MDL	< MDL	< MDL	< MDL
West Atha Blueberry 01 Unwashed	2.4E-04	6.6E-04	3.1E-04	2.4E-05	3.2E-04	1.2E-05	8.5E-05	1.1E-05	1.2E-04	< MDL
West Atha Blueberry 01 Washed	3.6E-04	6.8E-04	1.1E-04	1.7E-05	1.9E-04	2.9E-05	1.0E-04	1.6E-05	4.6E-05	< MDL
West Atha Blueberry 02 Unwashed	3.8E-04	5.2E-04	1.2E-04	2.5E-05	< MDL	< MDL	5.1E-05	< MDL	1.5E-07	9.5E-09
West Atha Blueberry 02 Washed	1.6E-04	5.3E-04	9.6E-05	< MDL	1.9E-05	2.0E-05	7.3E-05	9.1E-06	1.6E-07	< MDL
West Atha Blueberry 03 Unwashed	4.9E-03	6.2E-04	2.3E-03	2.0E-04	4.7E-04	8.1E-05	1.1E-04	1.9E-05	1.3E-04	< MDL
West Atha Blueberry 03 Washed	1.2E-03	5.1E-04	5.4E-04	4.4E-05	1.9E-04	3.3E-05	3.4E-05	1.2E-05	< MDL	1.1E-05
West Atha Blueberry 04 Unwashed	1.1E-04	7.0E-04	1.7E-04	8.8E-05	1.4E-04	6.1E-05	1.3E-04	2.5E-05	8.7E-05	1.8E-05
West Atha Blueberry 04 Washed	1.3E-04	6.3E-04	1.2E-04	3.2E-05	1.8E-04	5.0E-05	8.8E-05	< MDL	4.8E-05	1.0E-05
West Atha Blueberry 05 Unwashed	1.3E-04	5.4E-04	< MDL	9.7E-06	1.3E-04	4.3E-05	8.7E-05	2.2E-05	7.2E-05	< MDL
West Atha Blueberry 05 Washed	2.3E-04	8.3E-04	1.7E-04	1.5E-05	2.5E-04	< MDL	8.0E-05	1.0E-05	< MDL	8.6E-06
Groc store Blueberry (Arg) Unwashed	7.2E-04	2.3E-04	4.2E-04	1.3E-04	6.5E-04	1.0E-04	3.0E-04	1.9E-05	2.2E-04	5.8E-05
Groc store Blueberry (Arg) Washed	1.1E-03	4.5E-04	1.1E-03	2.0E-04	1.2E-03	2.1E-04	6.3E-04	1.1E-04	4.7E-04	6.7E-05
Groc store Blueberry (Peru) Unwashed	4.4E-03	6.9E-04	3.8E-03	4.2E-04	2.5E-03	4.0E-04	2.6E-04	1.4E-04	1.0E-03	1.4E-04
Groc store Blueberry (Peru) Washed	1.3E-03	2.9E-04	1.5E-03	1.8E-04	1.2E-03	1.7E-04	4.0E-04	6.1E-05	7.0E-04	4.6E-05
Sarsfield, ON Blueberry Unwashed	2.7E-04	7.7E-05	2.8E-04	8.1E-05	2.7E-04	3.8E-05	2.3E-04	3.8E-05	1.7E-04	8.5E-06
Sarsfield, ON Blueberry Washed	3.5E-04	9.9E-05	< MDL	9.0E-05	1.4E-04	3.5E-05	1.6E-04	4.3E-05	2.7E-04	< MDL
Pembroke, ON Blueberry Unwashed	3.4E-03	6.5E-04	2.1E-03	3.3E-04	1.9E-02	2.5E-04	8.4E-04	1.2E-04	6.8E-04	1.2E-04
Pembroke, ON Blueberry Washed	1.7E-03	4.0E-04	1.6E-03	1.7E-04	1.0E-03	2.2E-04	6.2E-04	1.1E-04	6.1E-04	8.8E-05

Table 2.8: Trace Element Concentrations in µg/g for Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu for Washed and Unwashed Blueberries. Note: Symbol "<" denotes "less than"; MDL = method detection limit.

Sample ID	W (µg/g)	Re (µg/g)	Tl (µg/g)	Pb (µg/g)	Th (µg/g)	U (µg/g)
MDL	**1.8E-04**	**4.3E-05**	**1.1E-04**	**1.6E-04**	**2.9E-05**	**4.4E-05**
East Atha Blueberry 01 Unwashed	3.3E-03	< MDL	3.6E-04	2.4E-02	9.2E-05	5.6E-05
East Atha Blueberry 01 Washed	7.2E-03	< MDL	< MDL	4.5E-02	9.1E-05	< MDL
East Atha Blueberry 02 Unwashed	2.9E-02	4.3E-05	5.9E-04	7.9E-03	4.7E-03	4.5E-03
East Atha Blueberry 02 Washed	2.8E-02	5.6E-05	8.0E-04	1.9E-02	2.8E-03	3.7E-03
East Atha Blueberry 03 Unwashed	6.0E-04	< MDL	2.0E-02	2.3E-03	1.2E-04	2.3E-04
East Atha Blueberry 03 Washed	9.8E-04	< MDL	5.7E-03	2.6E-03	9.2E-05	2.0E-04
West Atha Blueberry 01 Unwashed	7.0E-04	< MDL	1.0E-02	2.0E-03	4.1E-04	< MDL
West Atha Blueberry 01 Washed	7.5E-04	< MDL	1.1E-02	2.3E-03	2.6E-04	< MDL
West Atha Blueberry 02 Unwashed	1.6E-03	< MDL	5.1E-03	3.9E-03	3.4E-04	< MDL
West Atha Blueberry 02 Washed	1.1E-03	< MDL	8.7E-04	3.0E-03	2.3E-04	< MDL
West Atha Blueberry 03 Unwashed	1.3E-03	2.3E-05	5.8E-04	9.7E-03	2.4E-03	8.0E-05
West Atha Blueberry 03 Washed	2.7E-03	< MDL	6.5E-04	2.7E-03	4.8E-03	3.0E-04
West Atha Blueberry 04 Unwashed	3.9E-04	5.0E-05	8.4E-03	2.7E-03	2.1E-04	< MDL
West Atha Blueberry 04 Washed	6.1E-04	2.5E-05	1.1E-02	1.5E-03	1.9E-04	< MDL
West Atha Blueberry 05 Unwashed	8.0E-04	< MDL	6.5E-04	3.4E-03	2.2E-04	< MDL
West Atha Blueberry 05 Washed	2.5E-03	< MDL	2.0E-03	2.8E-03	3.1E-04	< MDL
Groc store Blueberry (Arg) Unwashed	5.6E-04	3.1E-05	8.6E-04	1.1E-02	1.2E-03	9.5E-05
Groc store Blueberry (Arg) Washed	6.0E-04	< MDL	4.6E-04	2.8E-02	2.6E-03	1.2E-04
Groc store Blueberry (Peru) Unwashed	2.3E-03	5.0E-05	< MDL	4.7E-02	6.0E-03	1.4E-03
Groc store Blueberry (Peru) Washed	8.0E-02	< MDL	< MDL	2.2E-02	2.7E-03	6.4E-04
Sarsfield, ON Blueberry Unwashed	2.7E-03	< MDL	< MDL	4.2E-03	1.9E-04	< MDL
Sarsfield, ON Blueberry Washed	5.2E-04	< MDL	< MDL	8.6E-03	2.1E-04	< MDL
Pembroke, ON Blueberry Unwashed	4.4E-04	< MDL	< MDL	7.5E-03	1.4E-03	9.1E-05
Pembroke, ON Blueberry Washed	1.2E-03	< MDL	< MDL	6.8E-03	1.2E-03	7.5E-05

Table 2.9: Trace Element Concentrations in µg/g for W, Re, Tl, Pb, Th, and U for Washed and Unwashed Blueberries. Note: Symbol "<" denotes "less than"; MDL = method detection limit.

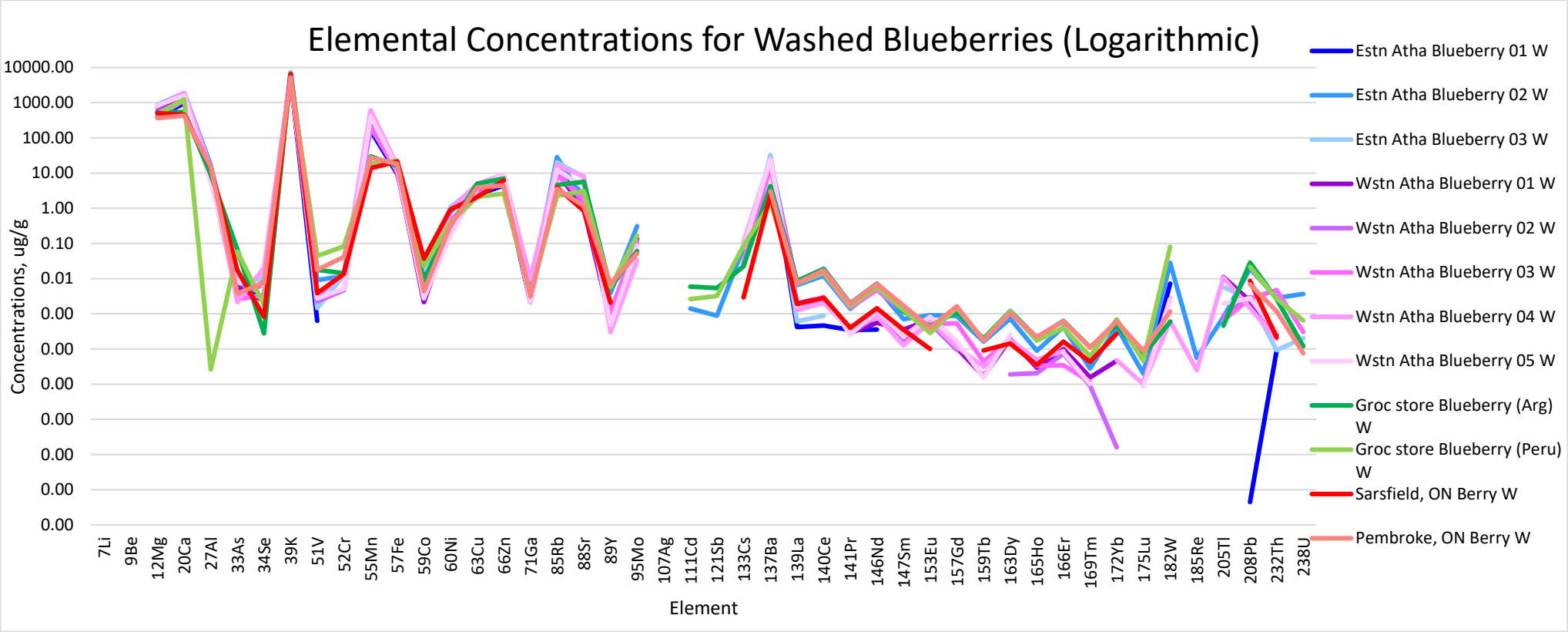

Figure 2.19: Elemental Concentrations for Washed Blueberries. A logarithmic scale was used for this figure in order to display the data more compactly since the data covers a large range. Generally, the elemental concentrations measured in all blueberry samples for the different sample locations follow similar trends. Some of the highest elemental concentrations in the washed blueberries were magnesium, calcium, potassium, manganese, iron, zinc, rubidium, strontium, and barium. This speaks to the nutritional requirements of the blueberry plant since plant roots will take essential macro- and micronutrients that are needed for growth and are available in the soil.

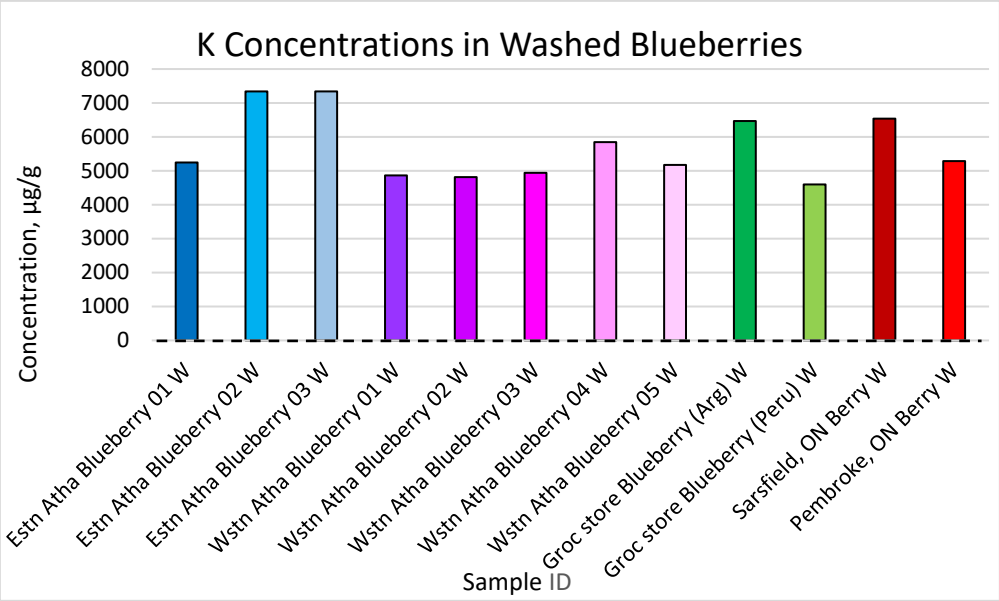

Figure 2.20: Concentration of K in Washed Blueberries, µg/g

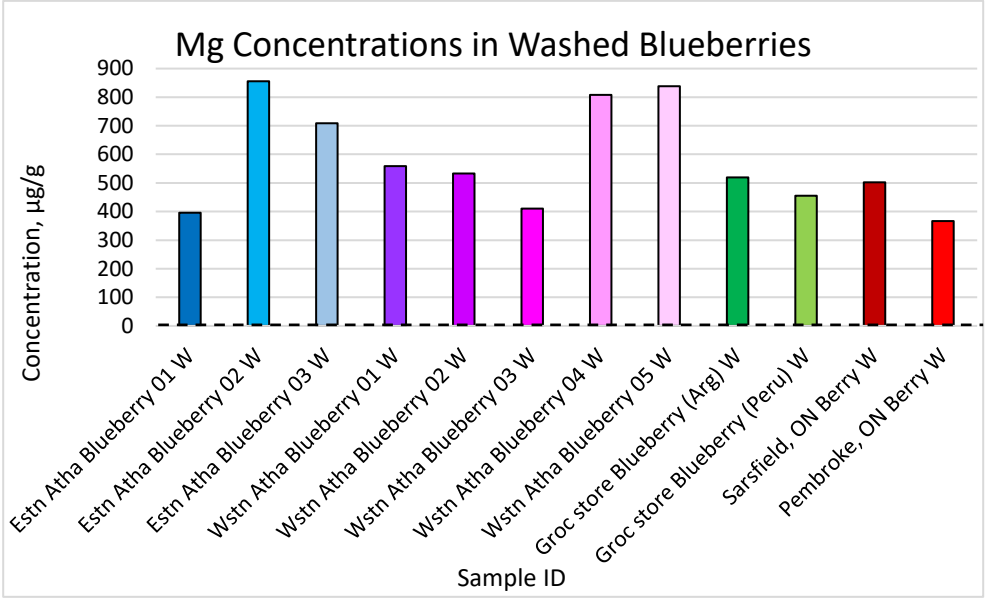

Figure 2.22: Concentration of Mg in Washed Blueberries, µg/g

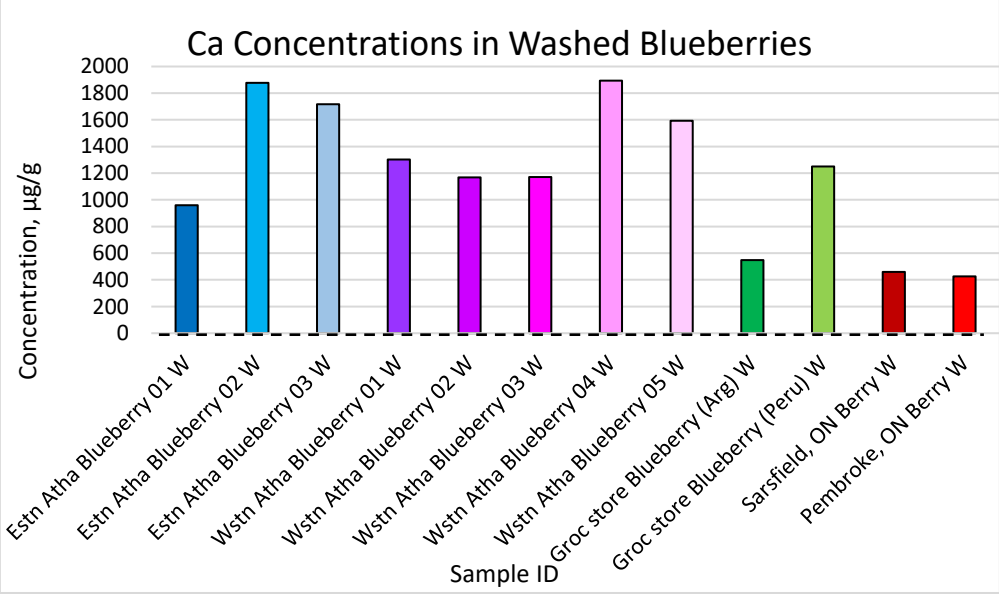

Figure 2.21: Concentration of K in Washed Blueberries, µg/g

Figures 2.20-2.22:

Essential Macronutrients for Plant Growth

to the blueberry plant's nutritional requirements in which roots, primarily, obtain nutrients from the soil and that are needed for growth (R. Moodley, 2013), (Walther C. , 2015).

2.5.2.1.1 Essential Macronutrients (K, Ca, and Mg)

Figures 2.20-2.22 present the essential macronutrients in washed blueberries.

East and West Athabasca

Plants obtain essential macronutrients from soil, sediment, water, and air. The uptake of elements from soil varies with the soil pH, the presence of organic matter and clays, and the solubility and availability of elements in the rhizosphere around the plant roots. Plants secrete and release substances from their roots to help bind elements for uptake or to help prevent the uptake of other elements. Once elements are taken into the roots cell membranes, there are many different biochemical processes that control their transport into the xylem, passage across different plant cell membranes, and elemental distribution to different plant parts such as fruit (Greger, 2004). All of the blueberries analyzed had considerable concentrations of the essential nutrients. Some of the highest concentrations were found in East Athabasca washed blueberries with values of 7341 µg/g dw of K, 960 µg/g dw of Ca, and 860 µg/g dw of Mg. These amounts are comparable to wild blueberry concentrations in a study from Latvia* with ranges of 5015-7424 µg/g dw for K, 500-1152 µg/g dw for Ca, and 341-765 µg/g dw for Mg (A. Karlsons, 2018). The elevated concentrations of essential macronutrients in East Athabasca blueberries when compared to the West Athabasca blueberries may correspond to the growth stage of its fruit because as the fruit grows, it increases the water content and organic matter content, which dilute the concentration of elements in the fruit (Carini, 1999). Vegetables and fruit are good sources dietary nutrients and the East Athabasca blueberries, especially, were shown to be good sources of dietary calcium and magnesium when compared to many other fruit analyzed in a comprehensive total diet study conducted by the

United States Food and Drug Administration (Pennington, 1995).

*Literature concentrations were presented as mg in 100g of fresh weight blueberries. Concentrations were converted to per gram by dividing by 100 and then converted to µg/g by multiplying by 1000. Using the IAEA dry matter content for wild blueberries of 13.2% (IAEA, 2010), the µg/g concentrations were divided by 0.132 to convert to a dry weight.

Ontario

The Sarsfield blueberries had elevated K and Mg concentrations when compared to Pembroke blueberries, whereas the Ca concentrations in both Ontario blueberry samples were comparable. When compared to berries from the Athabasca basin, Peru, and Argentina, the Ontario blueberries were among the samples with higher K concentrations and lower Ca and Mg concentrations. Strontium is a chemical analogue to Ca because of their similar chemical properties (Gupta, 2014), (Guillén, 2017). Due to the relatively low Ca concentrations in Ontario blueberries, elevated Sr concentrations were expected; however, this was not the case, as these samples had among the lowest Sr concentrations of all samples analyzed. When analyzing the corresponding soils, the Pembroke soil had similar Sr concentrations and had much higher K, Ca, and Mg concentrations than the Sarsfield soil, although the uptake of these essential macronutrients into the blueberries was similar. This speaks to the plant species' metabolic needs since it is known that plants will take what is needed for growth from the soil (R. Moodley, 2013).

Grocery Store

Overall, the grocery store washed blueberries had among the lowest concentrations of essential macronutrients when compared to all other sampling locations. The Argentina blueberries had higher K and Mg concentrations when compared to blueberries from Peru, whereas the opposite was found for Ca. When comparing the mineral composition between wild and cultivated blueberries in Latvia, Karlsons, et al. also found that wild berries had higher concentrations of Ca and Mg, although both wild and cultivated blueberries were considered good nutritional sources of dietary minerals (A. Karlsons, 2018).

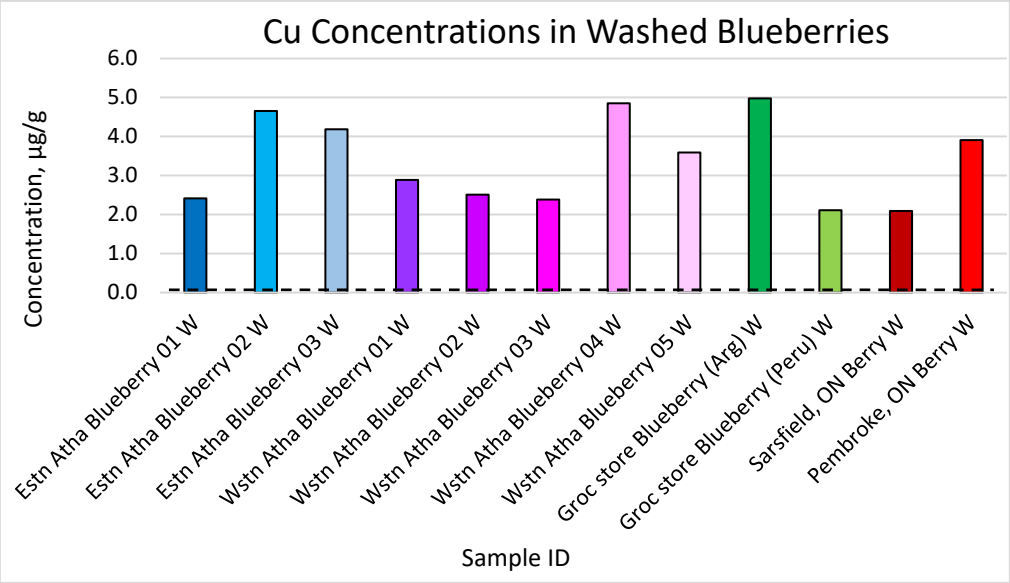

Figure 2.23: Concentration of Cu in Washed Blueberries, µg/g

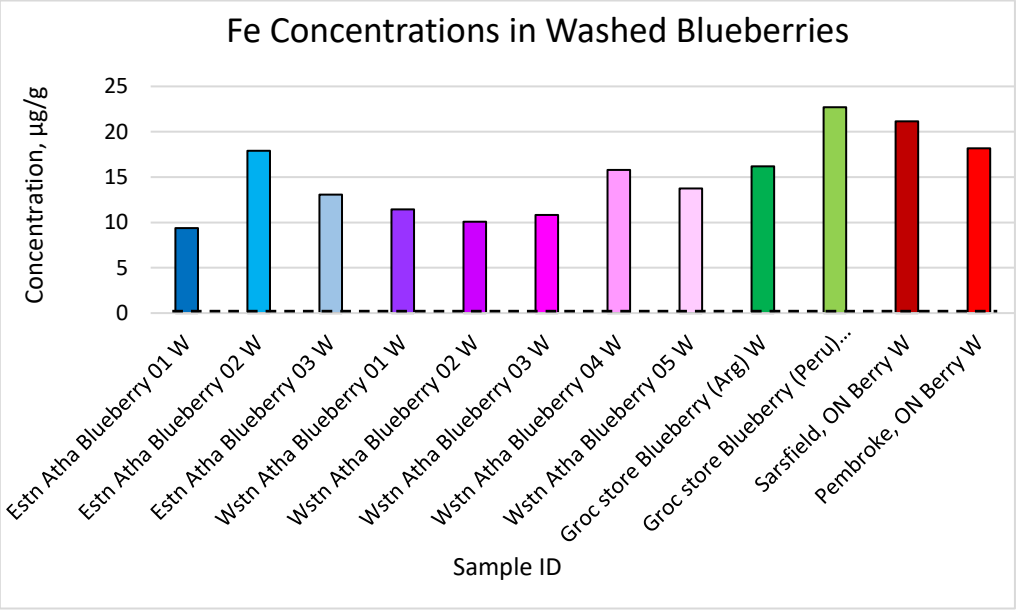

Figure 2.24: Concentration of Fe in Washed Blueberries, µg/g

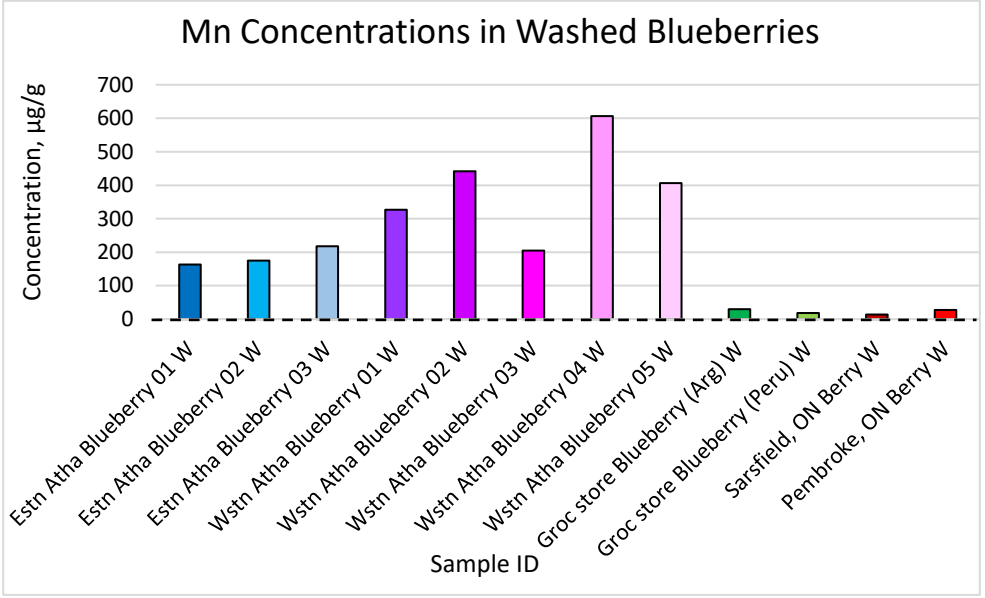

Figure 2.25: Concentration of Mn in Washed Blueberries, µg/g

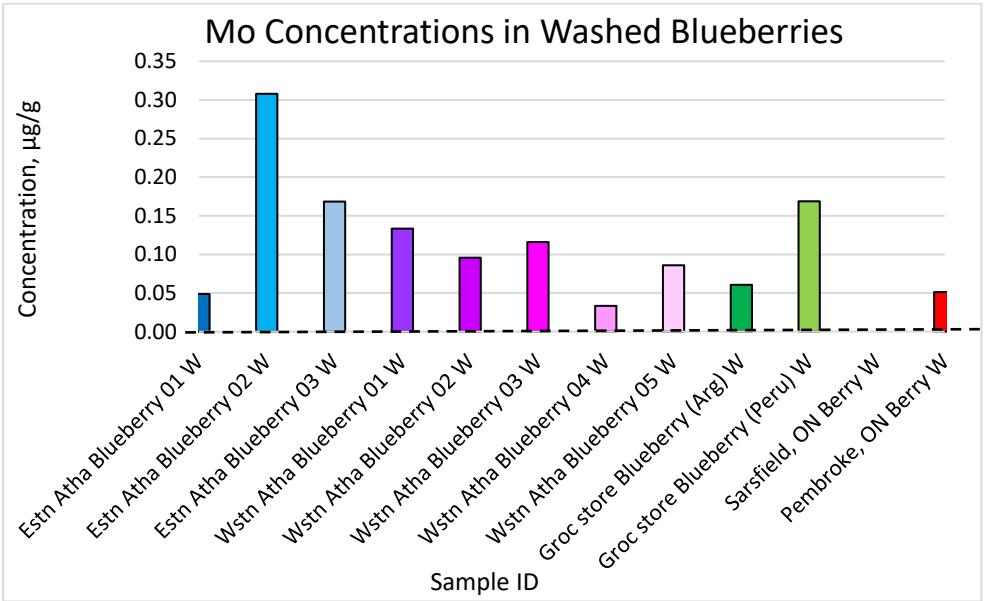

Figure 2.26: Concentration of Mo in Washed Blueberries, µg/g

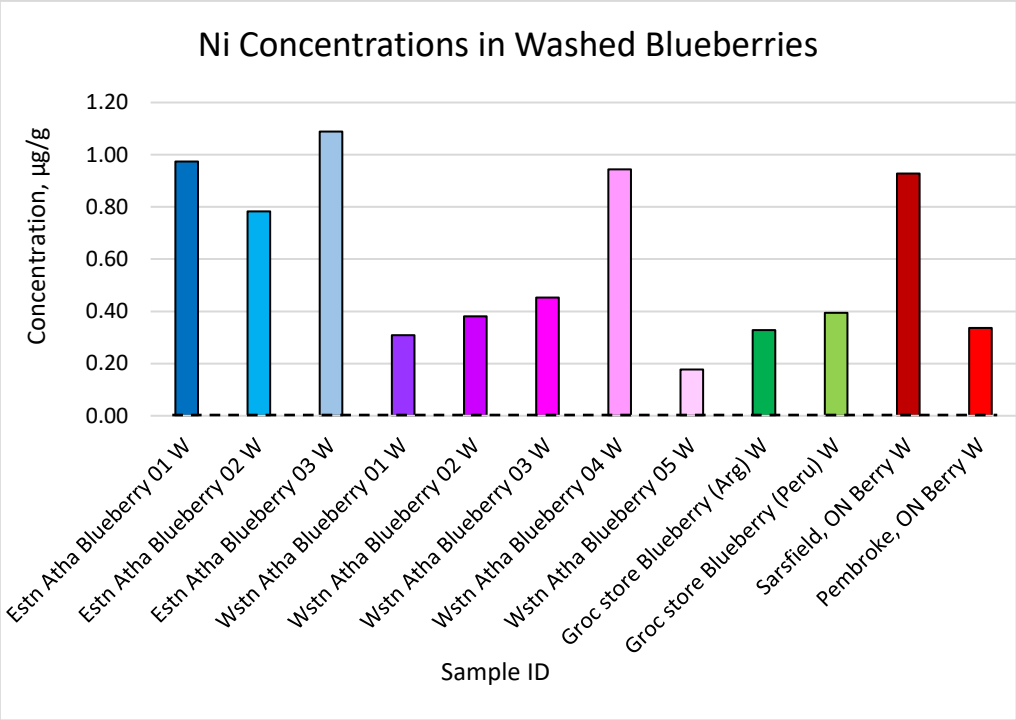

Figure 2.27: Concentration of Ni in Washed Blueberries, µg/g

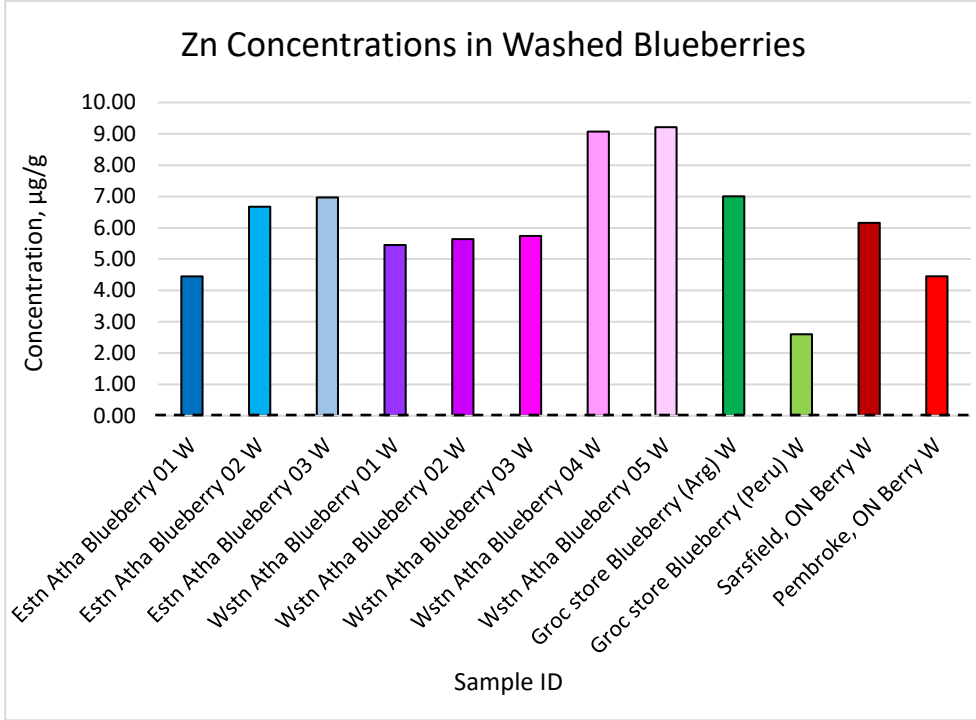

Figure 2.28: Concentration of Zn in Washed Blueberries, µg/g

Figures 2.23-2.28: Essential Micronutrients for Plant Growth

2.5.2.1.2 Essential Micronutrients (Cu, Fe, Mn, Mo, Ni, and Zn)

Figures 2.23-2.28 present the essential macronutrients in washed blueberries.

East and West Athabasca

For essential micronutrient concentrations in washed blueberries, there was considerable variation when comparing East and West Athabasca samples. Generally, for elements other than Fe, Athabasca blueberries had some of the highest essential micronutrient concentrations for all sampling locations. Mn was elevated in West Athabasca blueberries (average concentration of 398 µg/g, dw) when compared to East Athabasca (average concentration of 183 µg/g, dw), although the elevated Mn concentration was comparable to berries studied from Alberta, Canada (370 and 330 µg/g for Mn, dw) (Shotyk W. , 2020), to blueberries from Latvia (73 and 317 µg/g for Mn, dw*) (A. Karlsons, 2018), and to berries studied from Northern Alberta (577 and 378 µg/g for Mn, dw) (Shotyk W. , 2019). Research has shown that some essential micronutrients such as Cu, Mn, Mo, Ni, and Zn are primarily taken up by plant roots from the soil (Shotyk W. , 2020). The Mn concentrations in West Athabasca soils were higher than in East Athabasca soils, which could have contributed to the elevated Mn concentrations found in West Athabasca blueberries. The Mo concentrations were also slightly higher in East Athabasca blueberries (average concentration of 0.176 µg/g, dw), which was similar in magnitude to berries from Alberta, Canada (0.240 and 0.306 µg/g, dw for Mo) (Shotyk W. , 2020), and corresponded to slightly higher Mo concentrations in East Athabasca soils. Additionally, the essential nutrient concentrations for Cu, Fe, Mo, Ni, and Zn measured in Athabasca blueberries were within the same concentration ranges as berries studied from Alberta, Canada (Shotyk W. , 2020).

*Literature concentrations were presented as mg in 100g fresh weight blueberries. Concentrations were converted to per gram by dividing by 100 and then converted to µg/g by multiplying by 1000. Using the IAEA dry matter content for wild blueberries of 13.2% (IAEA, 2010), the µg/g concentrations were divided by 0.132 to convert to a dry weight.

Ontario

The Ontario washed blueberry samples were depleted in Mn and Mo. They were also among the highest concentrations for Fe (average concentration of 19.5 µg/g, dw) so were shown to be a good source of dietary Fe when compared to other sample locations in this study and also when compared to literature values for Alberta, Canada berries (Fe concentrations of 13 and 12 µg/g, dw (Shotyk W. , 2020) and 12.9 and 9.3 µg/g, dw (Shotyk W. , 2019)). The higher Fe concentrations in the Ontario blueberries coincided with Fe-rich and acidic soil, which appears to have increased the availability and solubility of metals (P. C. Nagajyoti, 2010), (Walther C. , 2015). The Sarsfield blueberries likely had a higher Fe concentration when compared to the Pembroke blueberries because the Sarsfield soil's pH was more acidic, enabling the uptake of Fe, despite both soils having the similar Fe concentrations.

Grocery Store

For the essential micronutrients in grocery store washed blueberries, Mn was depleted when compared to Athabasca samples but was similar to concentrations in Ontario blueberries. Blueberries from Argentina were elevated in Cu and Zn (5 µg/g, dw and 7 µg/g, dw, respectively) when compared to blueberries from Peru, although the elevated Cu and Zn concentrations were within the same magnitude as blueberries from Alberta, Canada (2.1 and 3.6 µg/g, dw for Cu; 9.2 and 9.7 µg/g, dw for Zn) (Shotyk W. , 2019). The Peru blueberries could be considered as an excellent source of dietary Fe. The relative elevated Cu, Zn, and Fe concentrations suggest the likely addition of fertilizers, pesticides, fungicides, manure, sewage sludge to these crops and soils since these are sources of metals in agriculture (P. C. Nagajyoti, 2010).

2.5.2.1.3 Potentially Toxic Trace Elements (Be, As, Se, Cd, Pb, and U)

Figures 2.29-2.33 present the essential macronutrients in washed blueberries.

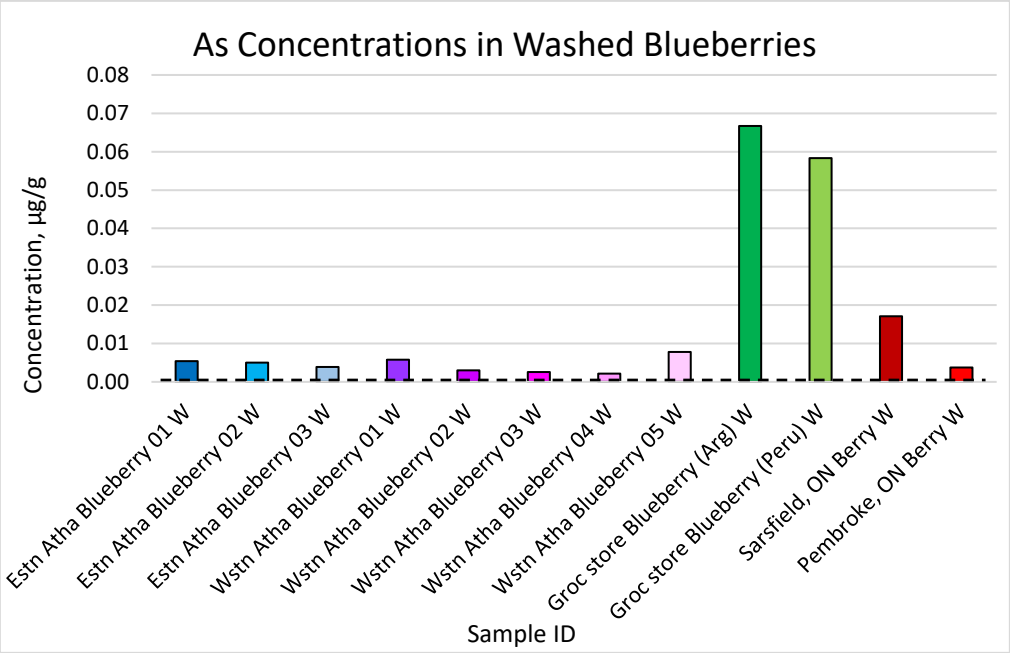

Figure 2.29: Concentration of As in Washed Blueberries, µg/g

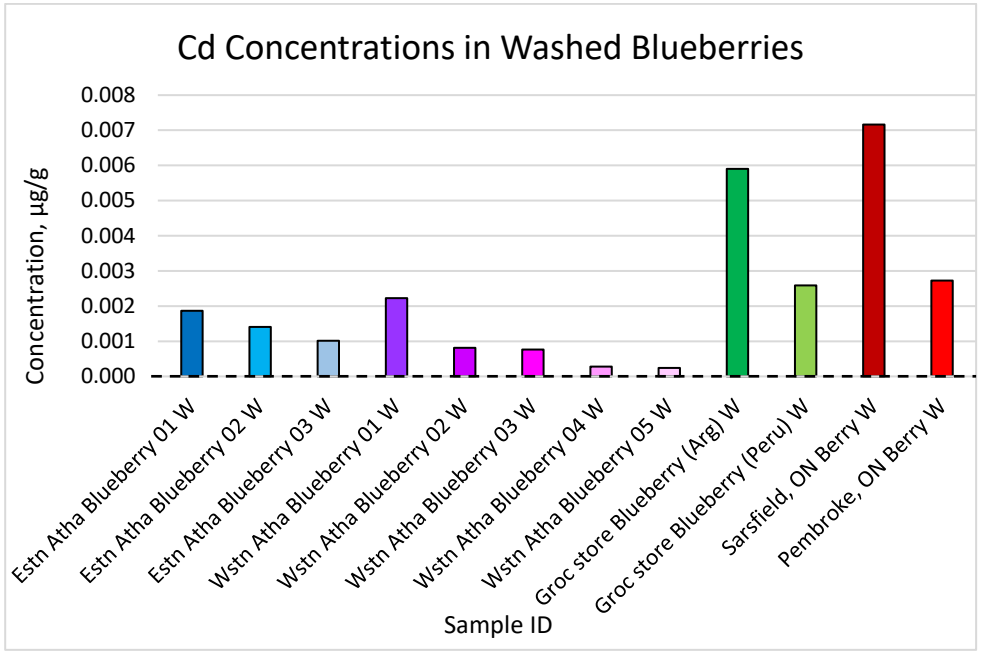

Figure 2.31: Concentration of Cd in Washed Blueberries, µg/g

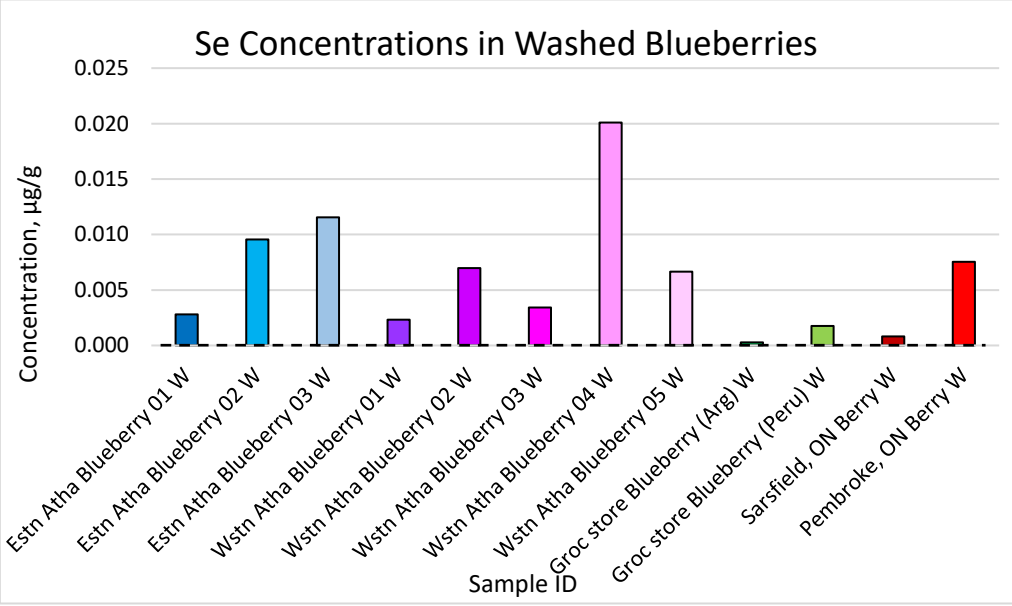

Figure 2.30: Concentration of Se in Washed Blueberries, µg/g

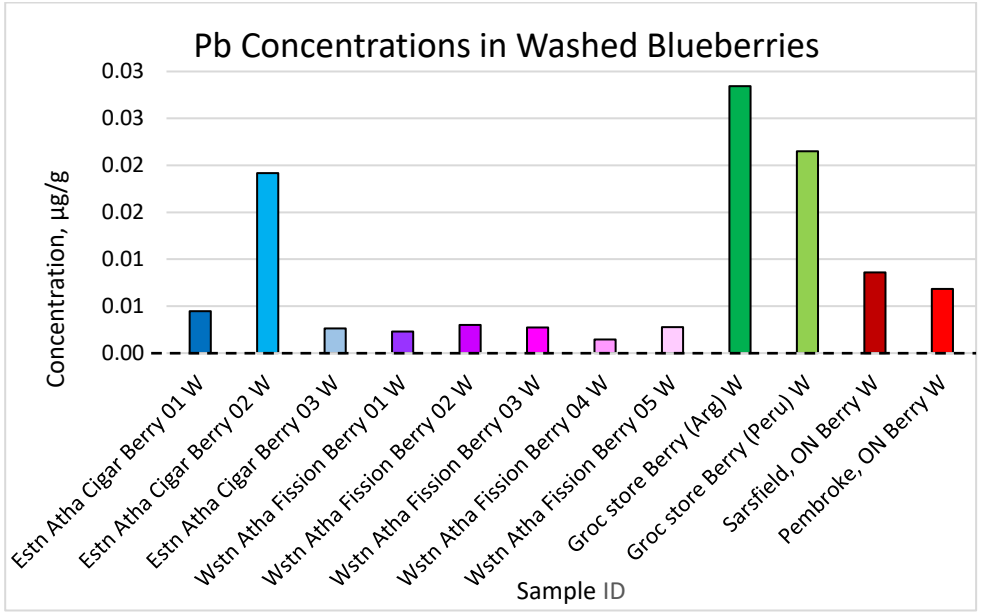

Figure 2.32: Concentration of Pb in Washed Blueberries, µg/g

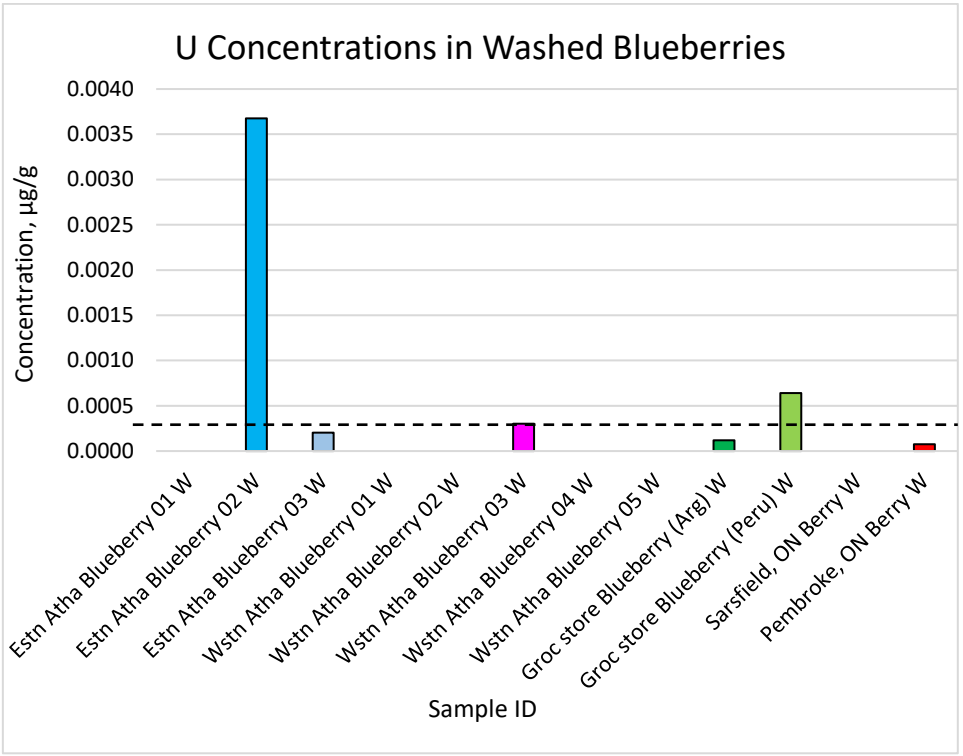

Figure 2.33: Concentration of U in Washed Blueberries, µg/g

Figures 2.29-2.33: Potentially Toxic Trace Elements

East and West Athabasca

Overall, washed blueberries from Athabasca had relatively low concentrations of potentially toxic trace elements and had the lowest concentrations of As and Cd for all blueberries analyzed in this study. When comparing the Athabasca blueberries to all others sampled, all but one Athabasca blueberry sample (East Athabasca 02) had the lowest Pb and U concentrations of all blueberries analyzed. The East Athabasca 02 blueberry sample had elevated Pb and U concentrations (3.7E-03 µg/g, dw and 1.9E-02 µg/g, dw, respectively); its U concentration indicates the underlying natural geochemistry of this area, which is geochemically distinct from other sampling locations, and the Pb is likely from the decay of naturally occurring ^{238}U in this area which decayed to stable lead, ^{206}Pb (Clark, 2015). The East Athabasca 02 blueberries had higher U and Pb concentrations than blueberries from one Alberta, Canada study (2.3E-04 and 8E-05 µg/g, dw for U; 4.7E-03 and 2E-03 µg/g, dw for Pb) (Shotyk W. , 2019) and higher U and Pb concentration than berries from another Alberta, Canada study (2E-04 µg/g, dw for U; 3E-03 and 5.1E-03 µg/g, dw for Pb) (Shotyk W. , 2020). Selenium is largely found in sandstone, limestone, and quartzite rocks (Fernández-Martínez, 2009). It is likely that the uranium deposits in Saskatchewan, such as around the Cigar Lake deposit in East Athabasca, have sandstone nearby (Clark, 2015) since the waste rock in this area of Athabasca contains Se (Kaczowka, 2021), (Campbell, 2007). This may be the source of Se for one West Athabasca blueberry sample that had a slightly elevated Se concentration when compared to East Athabasca and all other sampling locations.

Ontario

Cadmium can be found in phosphate rock fertilizers derived from sedimentary rock. Due to its potential to accumulate in soil and its negative effects on human health, there has been a movement by the European Commission to reduce the cadmium in phosphate fertilizers (Bradl, 2005), (Gilbert, 2018). For the Ontario washed blueberry samples, the most notable observation was that Cd was slightly more elevated in Sarsfield blueberries (7.2E-03 µg/g, dw) when compared to Pembroke blueberries and all other

sampling locations. It is known that plant roots and leaves readily uptake Cd, roots can passively uptake Cd, and that a low soil pH increases the mobility, solubility, and availability of metals (P. C. Nagajyoti, 2010), (Greger, 2004). When comparing the soil's Cd concentrations, the Sarsfield and Pembroke soils had similar Cd concentrations, although the much more acidic Sarsfield soil (pH 3.82 for Sarsfield's soil and pH 6.60 for Pembroke's soil) appears to have increased the availability of this metal cation for uptake through cation exchange with negatively charged colloids in the vicinity of the plant roots (Greger, 2004). The elevated Cd concentration and elevated ^{40}K activity in Sarsfield blueberries indicates the use of phosphate fertilizers in this area, although, when compared to berries studied in Alberta (3.4E-03 and 2.2 µg/g, dw for Cd) (Shotyk W. , 2020), the Sarsfield blueberry's Cd concentration was within the same magnitude.

Grocery Store

Our current intensive land use practices to produce food has necessitated the use of fertilizers and pesticides that contain heavy metals. Metal-based pesticides of the past contained As and Pb that persist in the environment today (Bradl, 2005). Arsenic rich compounds are still being used in agricultural practices, despite their environmental effects and the potential for human toxicity, although their use has been decreasing since the 1960's (Nordstrom, 2012). The Argentina and Peru blueberries had the highest concentrations of As and Pb (6.7E-02 and 5.8E-02 µg/g, dw, respectively, for As; 2.8E-02 and 2.2E-02 µg/g, dw, respectively, for Pb) when compared to other samples and this suggests the use of fertilizers and pesticides. The Argentina blueberries also had an elevated Cd concentration (5.9E-03 µg/g, dw), which further suggests the use of phosphate fertilizers in this growing region since Cd is known to be elevated in phosphate fertilizers from sedimentary rocks (Bradl, 2005).

2.5.2.1.4 Conservative, Lithophilic Elements (Al, Co, Cr, Ga, and Y)

Figures 2.34-2.38 present the essential macronutrients in washed blueberries.

East and West Athabasca

Overall, the washed blueberries from East and West Athabasca had variable concentrations of conservative, lithophilic elements with concentrations that were largely within the same magnitude, making it difficult to compare and contrast differences between these sampling locations.

Ontario

Co is essential to plant metabolism (P. C. Nagajyoti, 2010). Blueberries from Sarsfield were enriched in Co (3.7E-02 µg/g, dw) when compared to blueberries from other locations, although this concentration was within the same magnitude as berry samples from Alberta, Canada (2.8E-03 and 1.1E-02 µg/g, dw for Co) (Shotyk W. , 2020). The availability of Co in soil determines its uptake into plants and the mobility, solubility, and availability of metals can be increased with an acidic soil pH (P. C. Nagajyoti, 2010). It was found that the Sarsfield soil was quite acidic and this appears to have increased the availability of Co for uptake since Sarsfield blueberries had one of the highest Co concentrations in this study (P. C. Nagajyoti, 2010), (Greger, 2004).

Grocery Store

Cr is an essential metal in plant metabolism (P. C. Nagajyoti, 2010). A study from northern Alberta, Canada found that conservative, lithophilic elements such as Y and Cr in cranberries can be from soil-derived atmospheric dust (Shotyk W. , 2019). The grocery store washed blueberries in this study had Y and Cr concentrations (5.5E-03 and 1.4E-02 µg/g, dw, respectively, for Argentina; 5.7E-03 and 8.3E-02 µg/g, dw, respectively, for Peru) within the same magnitude as cranberries from Alberta, Canada (2.2E-03 and 7E-04 µg/g, dw for Y; 6.7E-03 and 3.1E-03 µg/g, dw for Cr) (Shotyk W. , 2019). Cr is also found in fertilizers, fungicides, manure, and sewage sludge that is added to agricultural crops and soils (P. C. Nagajyoti, 2010). Blueberries from Peru had the highest concentration of Cr and, overall, both grocery store blueberry samples had higher concentrations of conservative, lithophilic elements when compared to other samples, which indicates the use fertilizers.

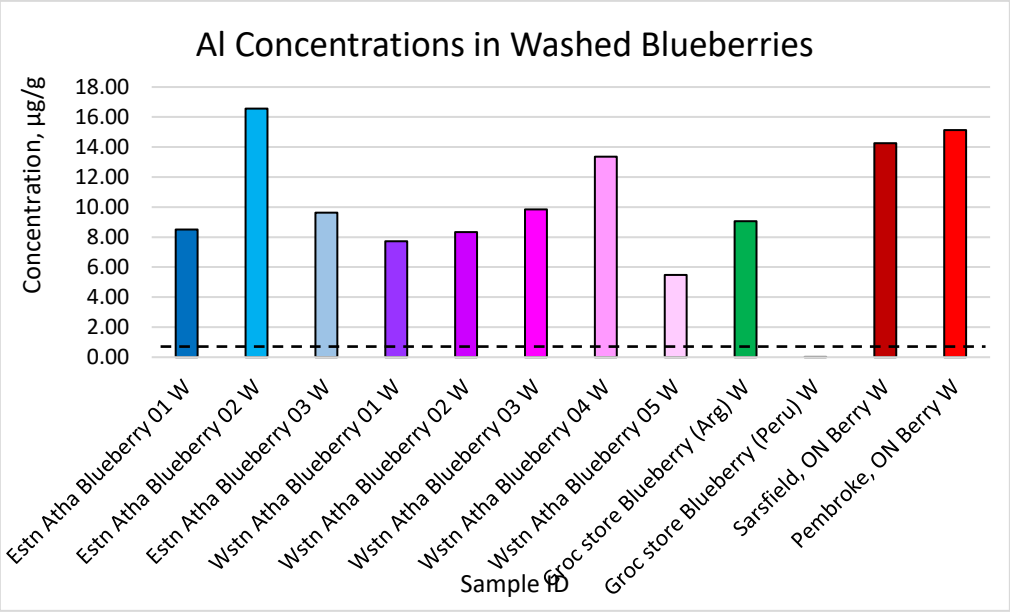

Figure 2.34: Concentration of Al in Washed Blueberries, µg/g

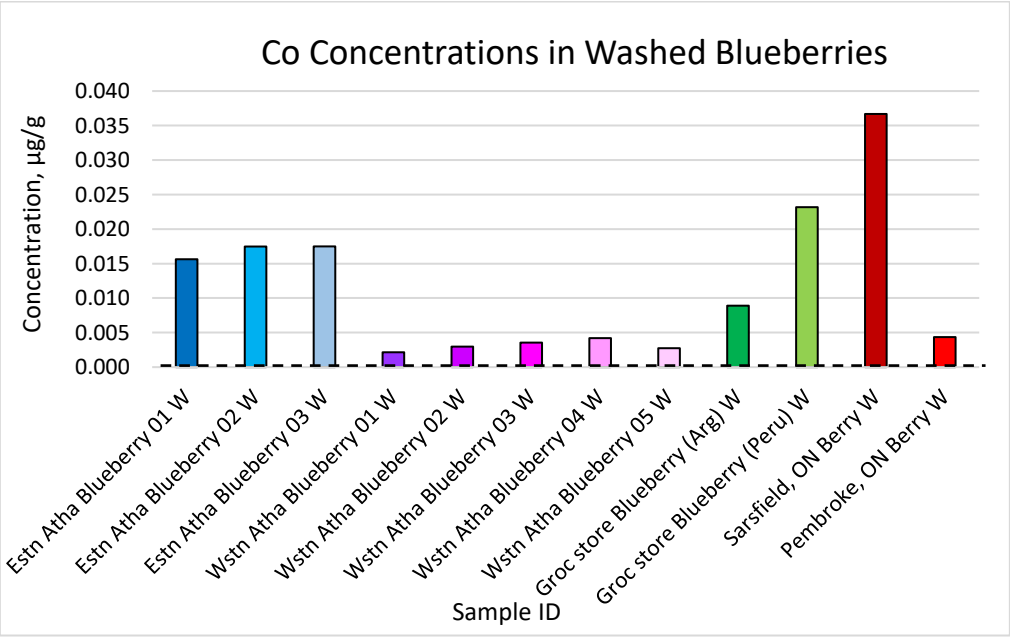

Figure 2.35: Concentration of Co in Washed Blueberries, µg/g

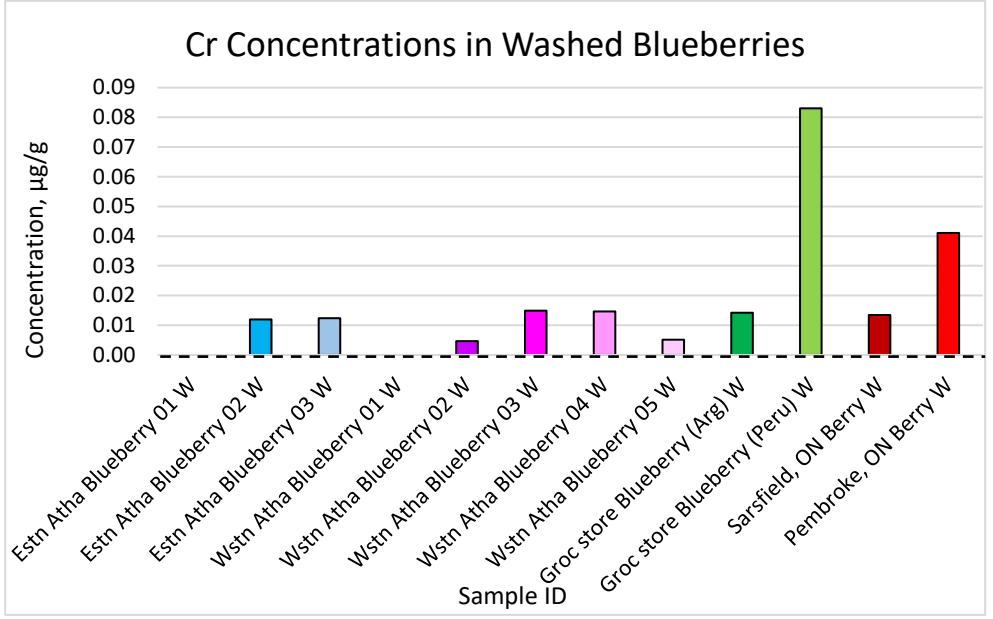

Figure 2.36: Concentration of Cr in Washed Blueberries, µg/g

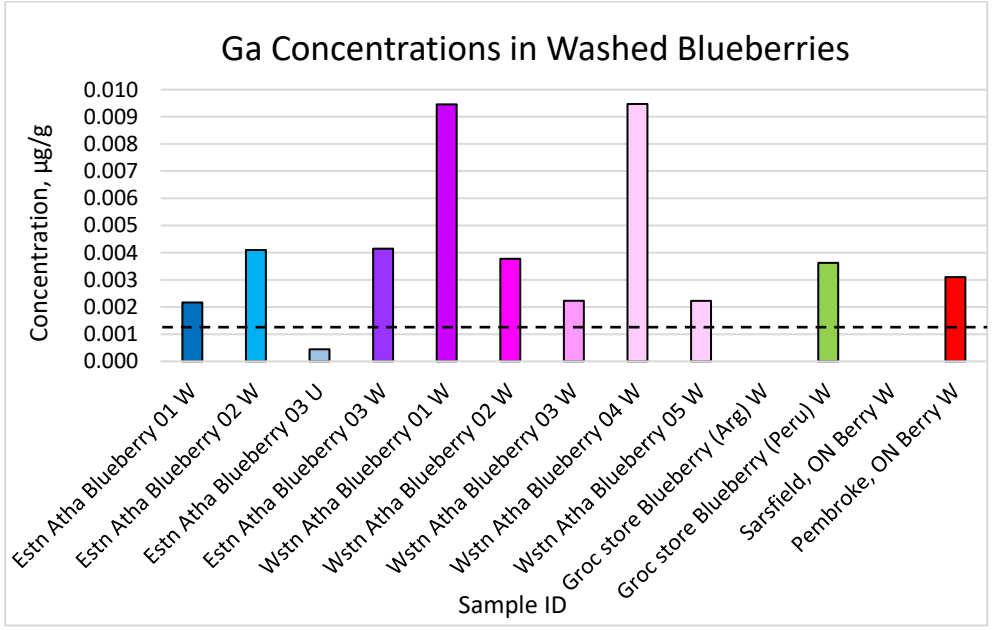

Figure 2.37: Concentration of Ga in Washed Blueberries, µg/g

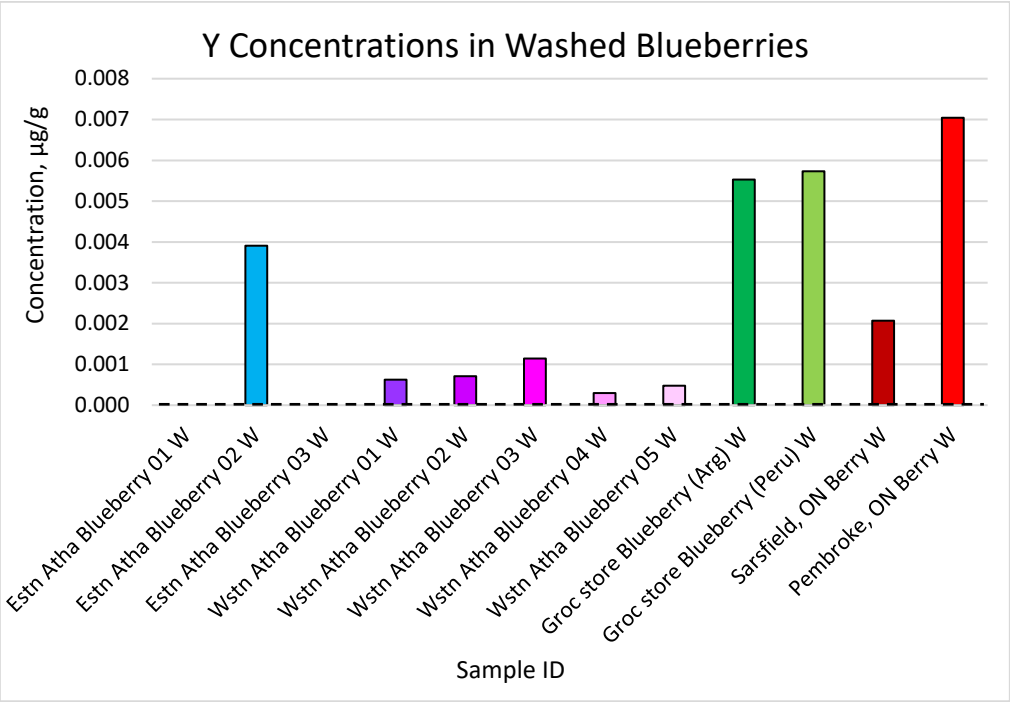

Figure 2.38: Concentration of Y in Washed Blueberries, µg/g

Figures 2.34-2.38: Conservative, Lithophilic Elements

2.5.2.1.5 Other Lithophilic Elements (Ba, Rb, and Sr)

Figures 2.39-2.41 present the essential macronutrients in washed blueberries.

East and West Athabasca

Overall, the Athabasca washed blueberries were enriched in Ba, Rb, and Sr when compared to other sampling locations. It is known that elements in the same periodic table group have similar chemical characteristics and behaviours but have different ionic radii (IAEA, 2014). After reviewing the essential macronutrient concentrations of K, Mg, and Ca in East Athabasca blueberries and soil, there were no clear correlations between these and the variable concentrations of other lithophilic elements found in these blueberries. The West Athabasca soils were certainly depleted in K, Mg, and Ca concentrations, which reflect the different geochemistry of this area, and this explains the uptake of Ba, Rb, and Sr into the blueberries as chemical substitutes for these essential nutrients (Guillén, 2017). Perhaps the low soil pH for these areas could have influenced the metal uptake of Ba, Rb, and Sr by increasing their solubility and availability (P. C. Nagajyoti, 2010).

Ontario

It is known that a plant's nutritional requirements are important when examining the uptake of trace elements (Walther C. , 2015). The Ontario blueberries were depleted in Ba, Rb, and Sr when compared to all samples analyzed. It was observed that the Ontario blueberries had lower Ca and Mg concentrations, despite having elevated soil concentrations of Ca and Mg, so perhaps the blueberry plant species growing in Ontario have a lower metabolism, which is controlled by its genes (Greger, 2004), when compared to the Athabasca plant species.

Grocery Store

Blueberries from Argentina were elevated in Ba, Rb and Sr when compared to the Peru blueberries

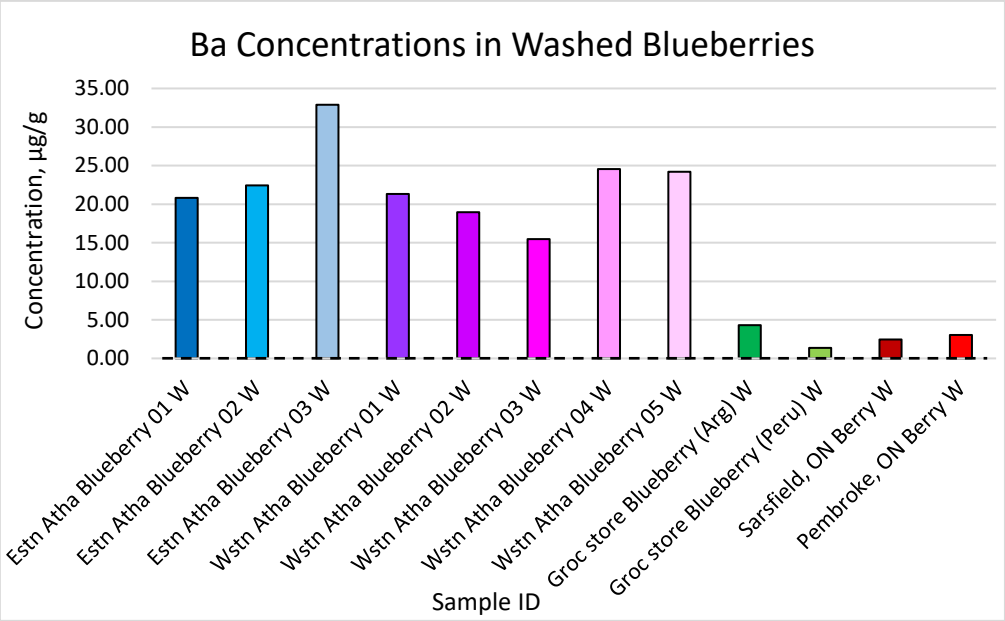

Figure 2.39: Concentration of Ba in Washed Blueberries, µg/g

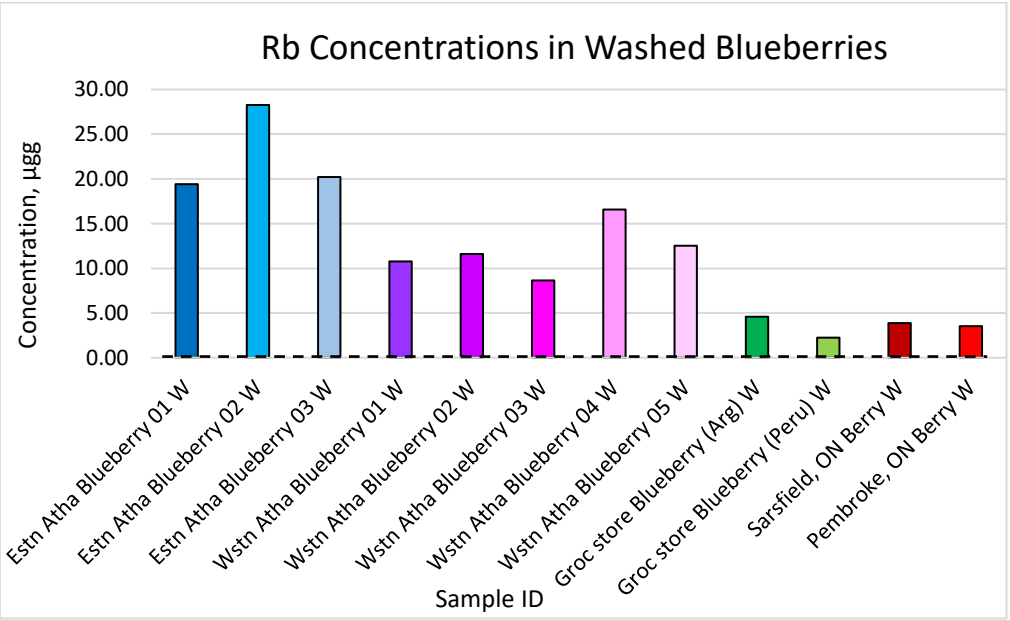

Figure 2.40: Concentration of Rb in Washed Blueberries, µg/g

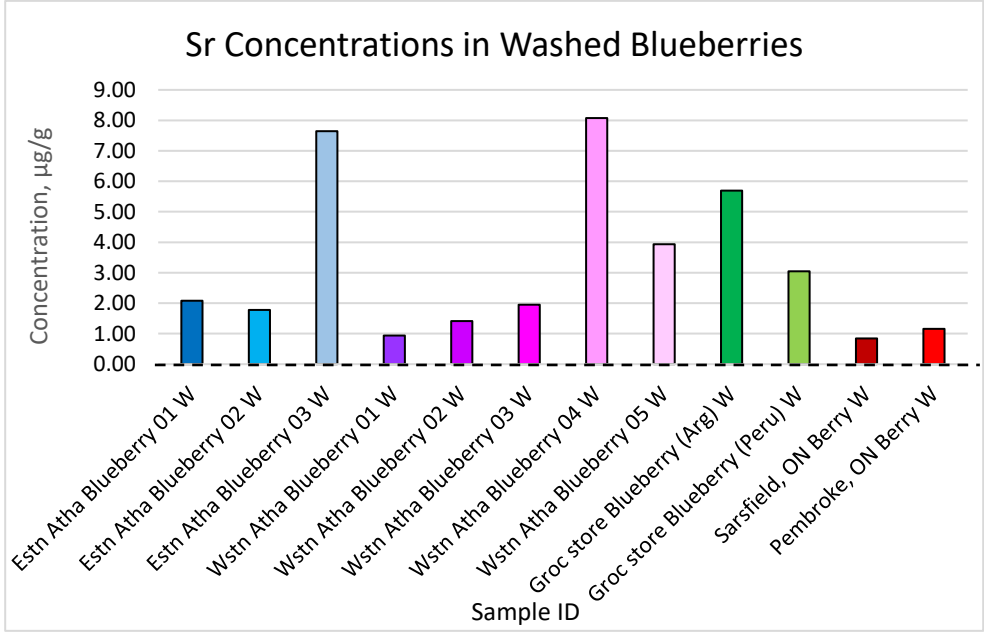

Figure 2.41: Concentration of Sr in Washed Blueberries, µg/g

Figures 2.39-2.41: Other Lithophilic Elements

although only the Sr concentration was clearly higher than that of the Peru blueberries. The differences may reflect the underlying geochemistry of these growing regions and soil factors such as pH could have influenced uptake. For example, if the Argentina soil was much more acidic than the Peru soil, the mobility, solubility, and availability of metals would have increased and resulted in elevated blueberry concentrations (P. C. Nagajyoti, 2010).

In summary, the uptake of elements into washed berries showed that the main driver for uptake is the plant's nutritional requirements. A summary of the trace elemental concentrations in washed blueberries is provided below.

Summary For Trace Elements in Athabasca Blueberries:

- Highest essential macronutrient concentrations (K, Ca, and Mg) of all samples in this study and good sources of dietary Ca and Mg when compared to other fruit in literature studies
- Highest essential micronutrient concentrations when compared to Ontario and grocery store blueberries; higher Mn (West Athabasca) and Mo (East Athabasca) concentrations in blueberries corresponded to higher soil concentrations for these elements and concentrations in blueberries were comparable to literature values and reflects differences in the geochemistry of these areas
- Generally low concentrations of potentially toxic trace elements although East Athabasca 02 blueberry sample had elevated Pb and U concentrations, which is likely due to the underlying natural geochemistry of this area
- Variable concentrations of conservative lithophilic elements
- Athabasca blueberries were enriched in Ba, Rb, and Sr when compared to other sampling locations; uptake of Ba, Rb, and Sr into West Athabasca blueberries due to soils with depleted K, Mg, and Ca concentrations (chemical substitutes for these essential nutrients)

Summary For Trace Elements in Ontario Blueberries:

- Higher K and lower Ca and Mg concentrations when compared to Athabasca and grocery store blueberries; similar uptake of essential macronutrients from the soil, despite much higher concentrations in Pembroke soil speaks to the plant's metabolic needs for growth
- Highest Fe concentrations when compared to Athabasca and grocery store blueberries and good source of dietary Fe when compared to literature values; lower pH of Sarsfield's soil increased the uptake into the blueberries
- Slightly elevated Cd concentration in Sarsfield blueberries when compared to Pembroke blueberries and was comparable to literature values, despite similar Cd concentrations in their corresponding soils; Sarsfield's more acidic soil increased the Cd availability and uptake into blueberries and indicates use of phosphate fertilizers
- Sarsfield blueberries were enriched in Co when compared to Athabasca and grocery store blueberries but was similar in magnitude to literature values; acidic soil pH increased the Co availability for uptake
- Depleted in Ba, Rb, and Sr when compared to all samples analyzed; Ontario blueberries had lower Ca and Mg concentrations despite having elevated Ca and Mg soil concentrations and is perhaps due to the species' lower metabolism

Summary For Trace Elements in Grocery Store Blueberries:

- lowest concentrations of K, Ca, and Mg when compared to Athabasca and Ontario blueberries
- elevated concentrations of Cu, Zn, and Fe suggests the use of fertilizers and pesticides
- highest concentrations of As Pb (Argentina and Peru blueberries) when compared to Athabasca and Ontario blueberries and elevated Cd concentrations (Argentina blueberries) suggests the use of fertilizers and pesticides

- Peru blueberries had highest Cr concentrations when compared to Athabasca and Ontario blueberries and suggests the use of fertilizers, fungicides, manure, and sewage sludge on crops
- Argentina blueberries were elevated in Sr when compared to the Peru blueberries; this may reflect the underlying geochemistry and differences in soil pH that affects solubility and availability

2.5.2.2 Estimating the Contributions of Dust to Trace Element Inventories

The trace element inventories in blueberry dust were estimated from the difference between the unwashed and washed concentrations measured in blueberries and are presented in Tables 2.10 and 2.11. Where either the unwashed sample or washed sample was below the MDL, the difference was not calculated and where the difference was a negative value, the value was not included in the table. The percentage of concentration contribution was also calculated to show how much the dust fraction contributed to the total concentration for each element. This was done by taking the elemental concentration in the dust, dividing by the unwashed blueberry elemental concentration and multiplying by 100 to represent it as a percentage.

For several elements, there were few values for the calculated dust fraction from which to draw conclusions from and this was likely due to rain events washing off the dust that was atmospherically deposited prior to sampling. Studies of plant uptake from roots have found that hair on the berry or leaf surface increased the radionuclide retention (Carini, 1999) so the relatively smooth blueberry surface may naturally inhibit the dust adherence to the surface. Additionally, leaves can intercept and reduce the amount of dust that reaches the fruit. The distance between the fruit and soil can also affect the amount of dust that deposits on the fruit since fruit close to the ground has a higher potential to receive more dust from the soil (Shotyk W. , 2020).

	Essential Macronutrients			Essential Micronutrients						Other Lithophilic Elements		
Sample ID	**K (µg/g)**	**Ca (µg/g)**	**Mg (µg/g)**	**Cu (µg/g)**	**Fe (µg/g)**	**Mn (µg/g)**	**Mo (µg/g)**	**Ni (µg/g)**	**Zn (µg/g)**	**Ba (µg/g)**	**Rb (µg/g)**	**Sr (µg/g)**
MDL	**1.5155**	**2.2204**	**0.2405**	**0.0039**	**0.0651**	**0.0019**	**0.0008**	**0.0052**	**0.0918**	**0.0040**	**0.0029**	**0.0024**
East Atha Blueberry 01	1.1E+03 (17%)	3.7E+01 (4%)	8.8E+01 (18%)	1.4E-02 (1%)	7.1E-01 (7%)	2.8E+01 (14%)	2.2E-02 (31%)	4.3E-03 (<1%)	3.4E-01 (7%)			
East Atha Blueberry 02			1.2E+01 (1%)	5.3E-02 (1%)	6.0E-01 (3%)	3.2E+01 (15%)		8.9E-02 (10%)	6.3E-02 (1%)	8.6E+00 (28%)	6.5E+00 (19%)	1.0E+00 (36%)
East Atha Blueberry 03	2.0E+02 (3%)	1.1E+02 (6%)	2.8E+01 (4%)					1.5E-01 (12%)			1.7E-01 (1%)	3.3E+00 (30%)
West Atha Blueberry 01	1.5E+02 (3%)			9.4E-02 (3%)		1.7E+00 (1%)					1.7E+00 (14%)	9.3E-03 (1%)
West Atha Blueberry 02	2.1E+02 (4%)	8.1E+00 (1%)		4.9E-02 (2%)				3.7E-02 (9%)			3.9E-01 (3%)	4.2E-01 (23%)
West Atha Blueberry 03	1.6E+02 (3%)					2.2E+01 (10%)				9.4E-01 (6%)	1.2E-01 (1%)	
West Atha Blueberry 04						4.9E+01 (78%)	9.7E-03 (23%)			1.7E-01 (1%)		
West Atha Blueberry 05	5.9E+02 (10%)					2.3E+01 (5%)		5.9E-03 (3%)			2.9E-01 (2%)	
Grocery Store Blueberry (Arg)	1.5E+02 (2%)	1.8E+02 (25%)	6.5E+01 (11%)	2.8E-01 (5%)	7.8E-02 (1%)	5.3E+00 (15%)		7.7E-02 (19%)		4.4E-01 (9%)	3.2E-01 (7%)	8.0E-01 (12%)
Grocery Store Blueberry (Peru)	6.1E+04 (93%)	5.3E+01 (4%)	3.3E+01 (7%)	2.7E-01 (12%)	3.0E+01 (57%)	3.1E+00 (15%)		5.0E-02 (11%)	1.2E+00 (31%)		9.2E-01 (29%)	
Sarsfield, ON Blueberry	3.1E+02 (5%)		9.3E+00 (2%)	4.0E-01 (16%)				2.5E-01 (21%)	1.1E+00 (15%)		1.3E-01 (3%)	
Pembroke, ON Blueberry	4.4E+02 (8%)					2.8E+00 (9%)	1.7E-01 (77%)	1.6E-01 (33%)				

Table 2.10: Trace Elements in Blueberry Dust: Essential Macronutrients, Essential Micronutrients, and Other Lithophilic Elements. The percentage value in the brackets indicates the amount of dust the value represents to the total activity from the unwashed blueberries. Note: Where either the unwashed sample or the washed sample was below the MDL, the difference between the unwashed and washed concentration was not calculated and negative values were not included in the table.

	Potentially Toxic Trace Elements						Conservative, Lithophilic Elements				
Sample ID	**Be (µg/g)**	**As (µg/g)**	**Se (µg/g)**	**Cd (µg/g)**	**Pb (µg/g)**	**U (µg/g)**	**Al (µg/g)**	**Co (µg/g)**	**Cr (µg/g)**	**Ga (µg/g)**	**Y (µg/g)**
MDL	**0.0004**	**0.2396**	**0.2590**	**0.0004**	**0.0002**	**0.0000**	**0.0654**	**0.0001**	**0.0047**	**0.0014**	**0.0002**
East Atha Blueberry 01			1.8E-03 (39%)		1.9E-02 (81%)			3.1E-04 (2%)		5.0E-04 (19%)	
East Atha Blueberry 02			3.7E-03 (28%)			8.3E-04 (18%)	3.8E+00 (19%)	5.0E-03 (22%)	6.1E-03 (34%)	2.3E-03 (36%)	2.3E-03 (37%)
East Atha Blueberry 03			1.2E-03 (9%)	9.6E-04 (49%)		2.6E-05 (11%)	1.5E+00 (14%)	6.8E-04 (4%)	2.1E-03 (15%)		
West Atha Blueberry 01			2.5E-03 (52%)				1.7E-01 (2%)	7.8E-05 (4%)			2.4E-04 (28%)
West Atha Blueberry 02					9.3E-04 (24%)			1.9E-05 (1%)			1.1E-04 (13%)
West Atha Blueberry 03			1.5E-03 (31%)		6.9E-03 (72%)					8.1E-03 (78%)	1.3E-03 (52%)
West Atha Blueberry 04					1.3E-03 (47%)				4.3E-02 (75%)	5.5E-03 (37%)	2.6E-04 (46%)
West Atha Blueberry 05				5.7E-04 (70%)	6.7E-04 (20%)			8.5E-04 (24%)		1.0E-03 (31%)	3.1E-04 (39%)
Grocery Store Blueberry (Arg)			1.8E-03 (87%)				9.2E-01 (9%)	3.3E-03 (27%)	5.4E-03 (28%)		
Grocery Store Blueberry (Peru)		2.7E-02 (31%)		1.7E-03 (40%)	2.6E-02 (55%)	7.8E-04 (55%)	2.4E-05 (48%)	1.8E-03 (7%)	4.5E-02 (35%)	1.1E-02 (75%)	6.7E-03 (54%)
Sarsfield, ON Blueberry				3.3E-04 (4%)							4.9E-04 (19%)
Pembroke, ON Blueberry		9.1E-04 (19%)		5.4E-03 (67%)	6.5E-04 (9%)	1.5E-05 (17%)	1.5E+00 (9%)	3.6E-04 (8%)	9.3E-03 (18%)	7.7E-03 (71%)	1.1E-03 (14%)

Table 2.11: Trace Elements in Blueberry Dust: Potentially Toxic Trace Elements and Conservative, Lithophilic Elements. The percentage value in the brackets indicates the amount of dust the value represents to the total activity from the unwashed blueberries. Note: Where either the unwashed sample or the washed sample was below the MDL, the difference between the unwashed and washed concentration was not calculated and negative values were not included in the table.

2.5.2.2.1 Essential Macronutrients (K, Ca, and Mg)

East and West Athabasca

For the essential macronutrient concentrations in the dust fraction of Athabasca blueberries that could be calculated, the elemental contributions were fairly low; between 1-18%. The smooth berry surface might have hindered the retention of dust (Shotyk W. , 2020) or perhaps rain events prior to sampling washed the dust from the blueberries since in the 10 days leading up to sampling in East and West Athabasca, there was 21mm and between 9 and 30mm of rain, respectively (there are two precipitation values since sampling in West Athabasca took place on two different days) (Carini, 1999), (Shotyk W. , 2020), (Government of Canada, 2023).

Ontario

The Ontario blueberries also had low amounts of essential macronutrients in the dust which contributed between 2-8% of the total concentration of these elements. In the 10 days leading up to sampling in Sarsfield and Pembroke, Ontario there were 26mm and 9mm of precipitation, respectively, that might have washed dust off of the blueberries (Government of Canada, 2023), (Government of Canada, 2023).

Grocery Store

Interestingly, there was a huge range of essential macronutrients as a percentage contribution in the dust for the grocery store blueberries, which represented between 2-93%. The Peru blueberries had a high dust contribution value of 93% for K, which perhaps indicates the use of potassium-based fertilizers sprayed onto crops to increase yield (Melo, 2012) and perhaps little rain in this area to wash off the dust before harvest.

2.5.2.2.2 Essential Micronutrients (Cu, Fe, Mn, Mo, Ni, and Zn)

East and West Athabasca

Overall, the concentrations of essential macronutrients in the dust fraction of Athabasca blueberries were low. A notable exception was a West Athabasca sample with a 78% dust contribution of Mn, which may speak to the natural geochemistry of this area, reflects the geochemical differences between these sampling areas, points to industrial activities that could contribute to dust deposition (Canada-Saskatchewan Agriculture Green Plan Agreement, 2021), and perhaps low amounts of rain did not wash the dust off the blueberries before sampling.

Ontario

Overall, the Ontario blueberries had low essential micronutrient concentrations in dust although the Pembroke blueberries had a dust contribution of 77% for Mo. Molybdenum, as molybdenite, is part of the natural geology in this area and reflects the geochemical differences in these sampling areas so disturbing the soil by mechanical means could have contributed to Mo in dust (Ontario Geological Survey, 2022). Pembroke had only 9mm of precipitation in the 10 days leading up to sampling (Government of Canada, 2023), (Government of Canada, 2023) so this low amount of rain may not have washed off the dust from the blueberries.

Grocery Store

The grocery store blueberries had a range of dust contribution values for essential micronutrients. One notable value was a 57% Fe contribution in the dust of the Peru blueberries. Fe is an element that has mainly been linked to dust particles (Shotyk W. , 2020) and this may point to the use of heavy-metal based pesticides since Fe is found in some sprays used to control crop pests (P. C. Nagajyoti, 2010).

2.5.2.2.3 Potentially Toxic Trace Elements (Be, As, Se, Cd, Pb, and U)

East and West Athabasca

Only Se, Cd, Pb and U were detected in the dust of some Athabasca blueberries with a wide range of percentage contributions, although there was no Be or As detected. An interesting finding was that for one East Athabasca sample, 81% of the Pb analyzed was in the dust fraction. There were also higher contributions of Cd (70%) and Pb (72%) found in West Athabasca samples. The dust sources may be from mechanically disturbing area soils through industrial activities such as mining, quarries, gravel roads, and soil piles (Shotyk W. , 2020) and coupled with a low amount of rain leading up to sampling.

Ontario

More dust fractions were calculated for the Pembroke blueberries than for the Sarsfield blueberries. For the Pembroke blueberries, Cd had a notable percentage contribution of 67%, which may be from gravel roads and quarry activities that disturbed soils in this area (Shotyk W. , 2020) and from the addition of fertilizers that are a known source of heavy metals such as Cd (P. C. Nagajyoti, 2010).

Grocery Store

More dust fractions were calculated for the Peru blueberries and there were reasonable dust contributions of 55% for both Pb and U, which may be from the use of fertilizers since they are a source of heavy metals (P. C. Nagajyoti, 2010). For Argentina blueberries, there was a high contribution of Se in dust (87%), which indicates the use of phosphate-based pesticides and phosphate-based fertilizers in this growing area since higher concentrations of selenium have been found in some phosphate rock (Fernández-Martínez, 2009).

2.5.2.2.4 Conservative, Lithophilic Elements (Al, Co, Cr, Ga, and Y)

East and West Athabasca

The concentrations of conservative, lithophilic elements can correspond to the amounts of soil derived dust particles. Aluminum is a key trace element to analyze since it is not actively taken up from the soil by plants and can be an indicator of the dust abundance (Shotyk W. , 2019), (Shotyk W. , 2020). Many Athabasca blueberries had relatively small amounts of conservative, lithophilic elements in the dust fraction, which included low amounts of Al. Among the higher amounts were two West Athabasca samples with a dust contribution of 75% for Cr and 78% for Ga, which may reflect the distinct, natural geochemistry of this area and the industrial activities in this area to mechanically disturb the soil (Shotyk W. , 2020).

Ontario

Overall, Ontario blueberries had low amounts of conservative, lithophilic elements, with the exception of Ga in Pembroke blueberries with a dust contribution of 71%, which could reflect this area's natural geochemistry since conservative, lithophilic elements have been found to correspond with soil derived dust (Shotyk W. , 2019), (Shotyk W. , 2020).

Grocery Store

The grocery store blueberries had a range of values for conservative, lithophilic elements in the dust. Ga was notably high in the dust of Peru blueberries with a 75% contribution. Generally, the Peru blueberries had higher contributions of elements in dust when compared to the Argentina blueberries and this may correspond to increased industrial activity to disturb soil in this area (Shotyk W. , 2020).

2.5.2.2.5 Other Lithophilic Elements (Ba, Rb, and Sr)

East and West Athabasca

Overall, the other lithophilic elements were not present in high amounts in the Athabasca blueberry dust, although the contributions for these elements in East Athabasca were slightly higher than in West Athabasca. This may be due to increased industrial activity in East Athabasca that disturbs soil (Shotyk W. , 2020).

Ontario

There were very little values for the other lithophilic elements in the dust for Ontario blueberries in which to analyze.

Grocery Store

The contributions of other lithophilic elements in the dust for the grocery store blueberries were too close to the MDL for reliable calculations or were not able to be calculated.

2.5.2.3 Trace Elemental Concentrations in Soil

Elemental concentrations were measured in soil for the samples from different locations and are presented in Tables 2.12-2.15 and Figures 2.32-2.54 with a discussion of the results. Overall, there were similar trends followed for all elemental concentrations measured in soil samples, as seen in Figure 2.32, although there are distinct geochemical differences between the different sampling locations. Some of the most elevated concentrations were magnesium, calcium, aluminum, potassium, and iron, which reflect the natural geochemical composition and natural abundance of soil elements.

All of the trace elemental concentrations in soil were compared to relevant Canadian soil quality guidelines which are based on scientific research and the values within the guidelines are set considerably lower than levels that are expected to pose health risks to humans or to the environment (CCME, 2023), (MECP, 2011). All of the elemental concentrations in soil in this research study that have guideline values were considerably lower than the Canadian soil quality guidelines.

2.5.2.3.1 Essential Macronutrients (K, Ca, and Mg)

East and West Athabasca

Sample ID	Li (µg/g)	Be (µg/g)	Mg (µg/g)	Al (µg/g)	K (µg/g)	Ca (µg/g)	V (µg/g)	Cr (µg/g)	Mn (µg/g)	Fe (µg/g)	Co (µg/g)	Ni (µg/g)
MDL	**2.5E-02**	**3.5E-04**	**2.4E-01**	**6.5E-02**	**1.5E+00**	**2.2E+00**	**1.1E-03**	**4.7E-03**	**1.9E-03**	**6.5E-02**	**1.4E-04**	**5.2E+03**
East Atha Soil 1	5.0E+00	1.9E-01	5.8E+02	8.5E+03	472.97	4.8E+02	1.3E+01	1.0E+01	3.4E+01	4.6E+03	8.0E-01	2.5E+00
East Atha Soil 2	3.6E+00	1.0E-01	4.0E+02	5.1E+03	94.95	1.4E+02	5.9E+00	6.3E+00	1.6E+01	3.7E+03	2.4E-01	1.2E+00
East Atha Soil 3	3.8E+00	1.2E-01	4.7E+02	5.5E+03	258.38	4.5E+02	9.6E+00	8.6E+00	2.8E+01	4.4E+03	4.2E-01	1.3E+00
West Atha Soil 1	2.5E-01	1.8E-02	2.1E+01	4.8E+02	0.00	4.0E+01	1.2E+00	9.9E-01	5.0E+00	3.7E+02	3.2E-02	1.0E+00
West Atha Soil 2	3.6E-01	1.5E-02	1.2E+01	4.0E+02	0.00	1.6E+01	1.0E+00	9.6E-01	6.1E+00	4.0E+02	3.6E-02	1.9E+01
West Atha Soil 3	2.2E-01	1.4E-02	1.4E+01	2.7E+02	0.00	1.5E+01	5.4E-01	5.7E-01	3.3E+00	1.6E+02	1.9E-02	1.5E+01
West Atha Soil 4	2.9E-01	1.3E-02	7.8E+00	3.6E+02	0.00	1.8E+00	6.0E-01	7.6E-01	7.3E+00	2.0E+02	2.5E-02	1.7E+01
West Atha Soil 5	2.4E-01	1.6E-02	1.4E+01	3.5E+02	0.00	2.4E+01	4.9E-01	7.8E-01	2.9E+00	1.8E+02	1.5E-02	6.8E+02
Sarsfield, ON Soil	4.0E+00	1.3E-01	1.1E+03	7.8E+03	426.35	9.9E+02	2.7E+01	2.8E+01	1.8E+02	1.4E+04	2.5E+00	5.3E+00
Pembroke, ON Soil	7.2E+00	2.6E-01	3.2E+03	1.1E+04	1464.06	4.9E+03	2.6E+01	2.3E+01	7.0E+02	1.5E+04	4.5E+00	1.0E+01

Sample ID	Cu (µg/g)	Zn (µg/g)	Ga (µg/g)	As (µg/g)	Se (µg/g)	Rb (µg/g)	Sr (µg/g)	Y (µg/g)	Mo (µg/g)	Ag (µg/g)	Cd (µg/g)	Sb (µg/g)
MDL	**3.9E-03**	**9.2E-02**	**1.3E-03**	**2.4E-01**	**2.6E-01**	**2.9E-03**	**2.4E-03**	**2.4E-04**	**7.6E-04**	**4.4E-04**	**3.7E-04**	**6.5E-04**
East Atha Soil 1	5.1E+00	4.9E+00	8.5E+00	7.7E-01	5.3E-02	9.2E+00	1.1E+01	6.3E+00	7.7E-02	4.9E-02	3.8E-02	7.0E-03
East Atha Soil 2	1.1E+00	2.0E+00	4.5E+00	5.2E-01	< MDL	3.0E+00	1.4E+01	3.7E+00	4.1E-02	6.3E-03	2.1E-02	4.8E-03
East Atha Soil 3	2.6E+00	3.1E+00	7.2E+00	6.9E-01	< MDL	6.7E+00	1.2E+01	5.1E+00	1.3E-01	3.1E-02	1.5E-02	4.3E-03
West Atha Soil 1	1.6E-01	5.5E-01	1.1E+00	2.0E-01	< MDL	3.5E-01	1.5E+01	1.6E+00	1.2E-02	4.2E-03	3.5E-03	1.4E-03
West Atha Soil 2	6.4E-01	5.1E-01	9.4E-01	2.5E-01	< MDL	2.5E-01	1.5E+01	1.1E+00	1.4E-02	2.9E-03	4.9E-03	2.7E-03
West Atha Soil 3	1.8E-01	5.2E-01	8.0E-01	2.0E-01	< MDL	2.1E-01	1.3E+01	8.3E-01	2.3E-02	4.2E-03	5.6E-03	5.3E-03
West Atha Soil 4	1.8E-01	4.1E-01	8.4E-01	7.5E-02	< MDL	3.2E-01	1.5E+01	1.1E+00	1.3E-02	3.9E-03	7.0E-03	2.8E-03
West Atha Soil 5	8.8E-02	1.4E+00	1.0E+00	2.5E-01	< MDL	1.7E-01	2.0E+01	1.3E+00	7.2E-03	5.2E-03	1.8E-03	2.9E-03
Sarsfield, ON Soil	4.3E+00	1.9E+01	7.4E+00	2.0E+00	2.7E-01	4.9E+00	3.4E+01	1.2E+01	2.2E-01	4.7E-02	9.5E-02	1.0E-01
Pembroke, ON Soil	7.8E+00	4.5E+01	7.6E+00	1.5E+00	1.2E-01	1.2E+01	3.1E+01	1.1E+01	1.3E-01	6.4E-02	2.2E-01	1.9E-02

Tables 2.12 and 2.13: Elemental Concentrations in Soil (µg/g) for Li, Be, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co and Ni (top) and Cu, Zn, Ga, As, Se, Rb, Sr, Y, Mo, Ag, Cd and Sb (bottom).

Sample ID	Cs (µg/g)	Ba (µg/g)	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (µg/g)	Dy (µg/g)	Ho (µg/g)
MDL	**8.7E-04**	**4.0E-03**	**4.4E-05**	**7.9E-05**	**2.5E-04**	**8.9E-05**	**7.3E-05**	**2.4E-05**	**1.0E-04**	**5.7E-05**	**9.0E-05**	**1.5E-05**
East Atha Soil 1	9.5E-01	3.7E+01	2.4E+01	4.5E+01	5.3E+00	1.9E+01	3.0E+00	2.9E-01	2.3E+00	2.9E-01	1.4E+00	2.5E-01
East Atha Soil 2	4.0E-01	1.7E+01	1.1E+01	2.2E+01	2.5E+00	8.5E+00	1.4E+00	1.4E-01	1.1E+00	1.4E-01	7.4E-01	1.4E-01
East Atha Soil 3	8.2E-01	1.6E+01	2.2E+01	4.0E+01	4.8E+00	1.6E+01	2.6E+00	2.2E-01	1.9E+00	2.5E-01	1.1E+00	2.0E-01
West Atha Soil 1	3.7E-02	5.5E+00	4.8E+00	9.9E+00	1.1E+00	3.8E+00	6.3E-01	9.7E-02	4.7E-01	6.4E-02	3.3E-01	6.3E-02
West Atha Soil 2	1.8E-02	5.9E+00	4.5E+00	9.0E+00	1.0E+00	3.5E+00	5.8E-01	9.3E-02	4.1E-01	5.1E-02	2.4E-01	4.6E-02
West Atha Soil 3	1.9E-02	4.8E+00	3.7E+00	7.8E+00	8.3E-01	3.0E+00	5.0E-01	8.1E-02	3.5E-01	4.1E-02	1.9E-01	3.5E-02
West Atha Soil 4	2.5E-02	4.9E+00	3.9E+00	8.2E+00	8.9E-01	3.1E+00	5.3E-01	8.2E-02	3.9E-01	4.8E-02	2.3E-01	4.3E-02
West Atha Soil 5	1.3E-02	5.4E+00	4.3E+00	9.1E+00	9.8E-01	3.4E+00	5.9E-01	9.8E-02	4.5E-01	5.8E-02	2.7E-01	5.0E-02
Sarsfield, ON Soil	3.4E-01	3.4E+01	1.3E+01	3.1E+01	3.5E+00	1.4E+01	2.9E+00	6.4E-01	2.7E+00	4.1E-01	2.4E+00	4.9E-01
Pembroke, ON Soil	6.0E-01	7.1E+01	1.5E+01	3.6E+01	3.9E+00	1.5E+01	2.8E+00	5.9E-01	2.5E+00	3.7E-01	2.0E+00	4.1E-01

Sample ID	Er (µg/g)	Tm (µg/g)	Yb (µg/g)	Lu (µg/g)	W (µg/g)	Re (µg/g)	Tl (µg/g)	Pb (µg/g)	Th (µg/g)	U (µg/g)
MDL	**3.0E-05**	**6.5E-06**	**3.5E-05**	**1.5E-05**	**1.8E-04**	**4.3E-05**	**1.1E-04**	**1.6E-04**	**2.9E-05**	**4.4E-05**
East Atha Soil 1	6.6E-01	8.1E-02	5.2E-01	7.2E-02	4.2E-02	2.8E-04	8.8E-02	3.8E+00	9.2E+00	1.4E+00
East Atha Soil 2	4.1E-01	5.4E-02	3.6E-01	5.2E-02	4.9E-02	1.9E-04	3.9E-02	1.7E+00	5.3E+00	6.2E-01
East Atha Soil 3	5.5E-01	6.8E-02	4.4E-01	6.3E-02	4.7E-02	2.4E-04	5.7E-02	2.9E+00	9.3E+00	1.2E+00
West Atha Soil 1	1.8E-01	2.4E-02	1.5E-01	2.1E-02	1.2E-02	1.1E-04	5.5E-03	9.9E-01	8.5E-01	9.4E-02
West Atha Soil 2	1.3E-01	1.7E-02	1.2E-01	1.6E-02	4.7E-03	5.4E-05	4.8E-03	1.1E+00	6.5E-01	8.5E-02
West Atha Soil 3	9.8E-02	1.3E-02	7.9E-02	1.1E-02	4.4E-03	3.0E-05	4.7E-03	1.1E+00	5.4E-01	6.7E-02
West Atha Soil 4	1.2E-01	1.6E-02	1.1E-01	1.6E-02	1.3E-02	3.3E-06	4.0E-03	9.5E-01	6.0E-01	8.6E-02
West Atha Soil 5	1.4E-01	1.8E-02	1.1E-01	1.6E-02	9.7E-03	6.2E-05	2.2E-03	1.0E+00	6.4E-01	7.8E-02
Sarsfield, ON Soil	1.6E+00	2.2E-01	1.5E+00	2.1E-01	5.6E-02	9.2E-04	4.3E-02	1.6E+01	3.3E+00	1.2E+00
Pembroke, ON Soil	1.2E+00	1.7E-01	1.1E+00	1.5E-01	7.2E-02	7.5E-04	1.2E-01	8.4E+00	3.3E+00	5.4E-01

Tables 2.14 and 2.15: Elemental Concentrations in Soil (µg/g) for Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Ho (top) and Er, Tm, Yb, Lu, W, Re, Tl, Pb, Th, and U (bottom).

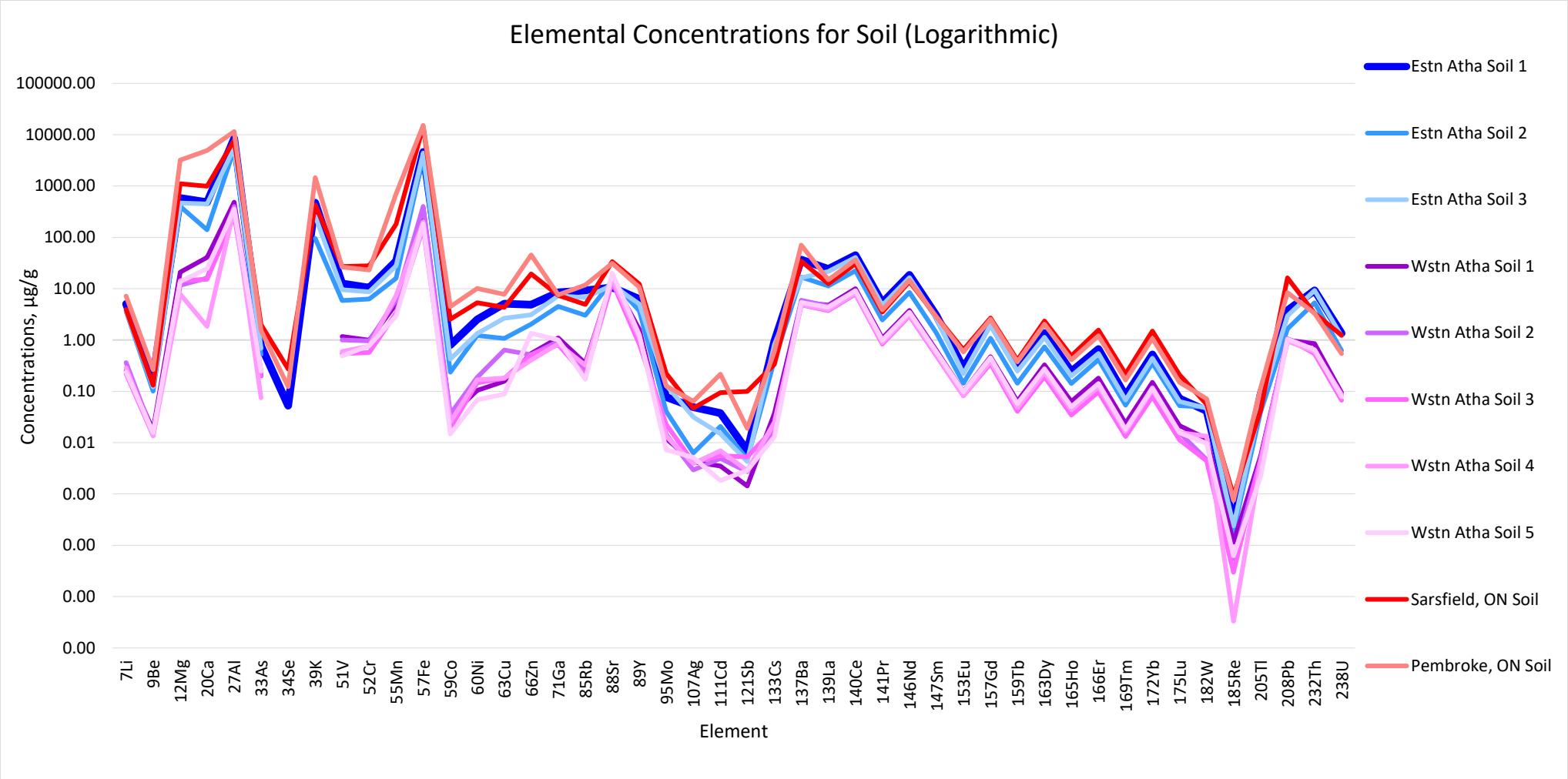

Figure 2.32: Elemental Concentrations for Soil. A logarithmic scale was used for this figure in order to display the data more compactly since the data covers a large range. Generally, the elemental concentrations measured in all soil samples for the different sample locations follow similar trends. Some of the highest elemental concentrations in the soils were magnesium, calcium, aluminum, potassium, and iron. This speaks to the geochemical composition of the soil

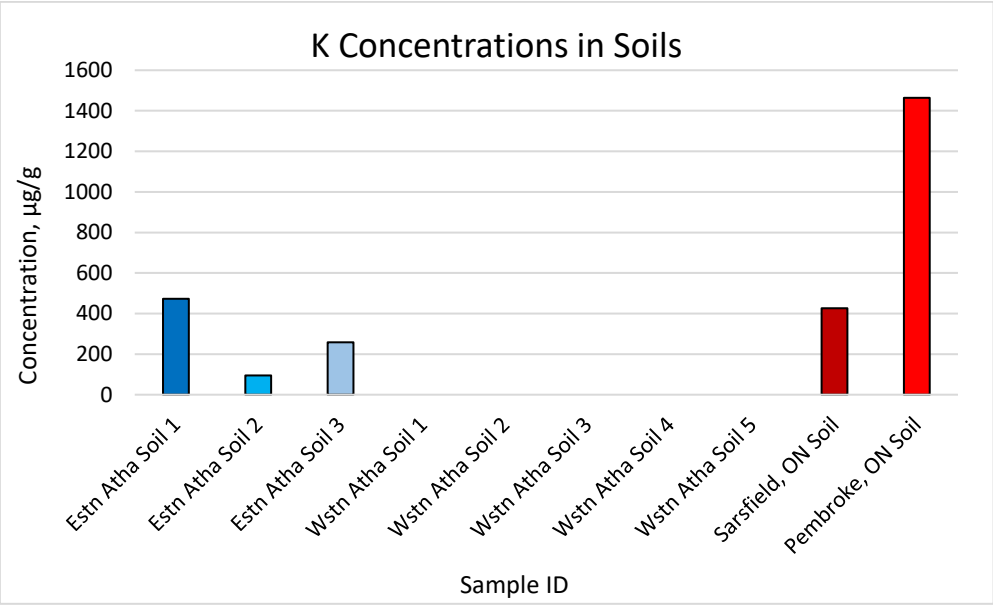

Figure 2.33: Concentrations in µg of K in Soils.

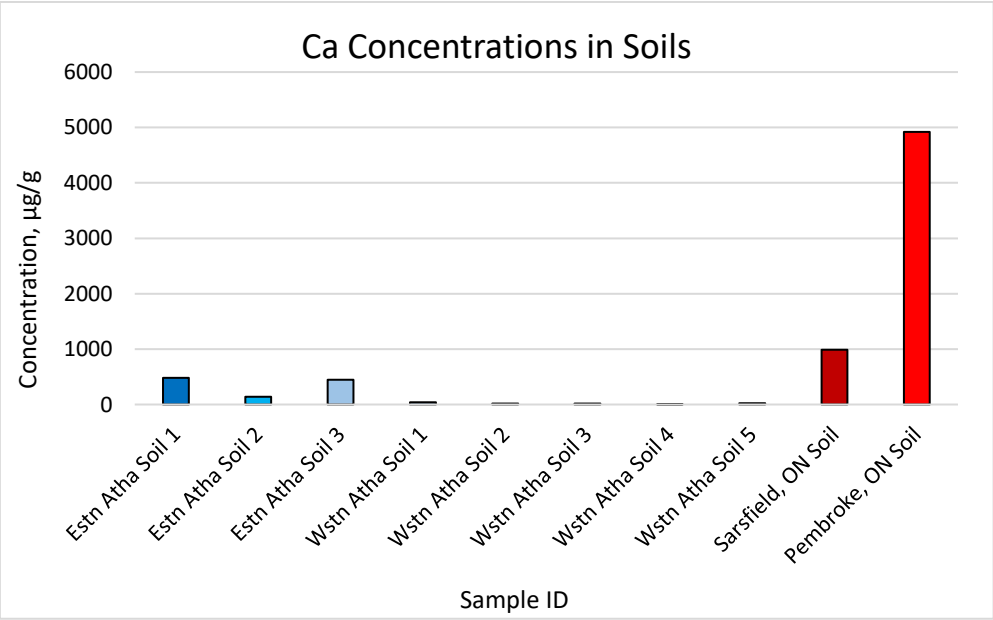

Figure 2.34: Concentrations in µg of Ca in Soils.

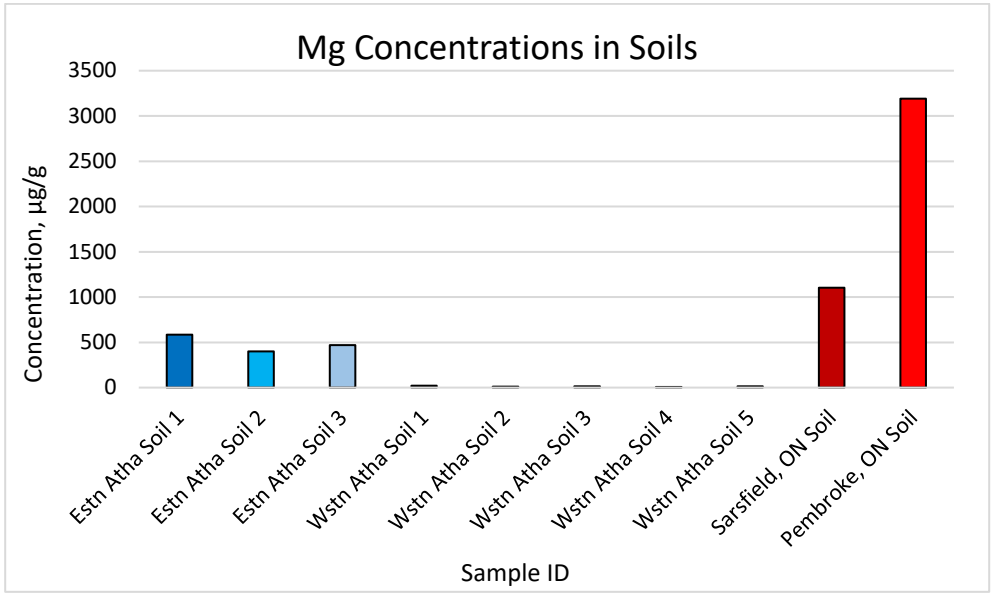

Figure 2.35: Concentrations in µg of Mg in Soils.

Figures 2.33-2.35: Essential Macronutrients for Plant Growth

Plants need large amounts of essential macronutrients for growth and they obtain them primarily from soil (Greger, 2004). It was found there are distinct geochemical differences between East and West Athabasca soils. All East Athabasca soils were enriched in essential macronutrients when compared to the West Athabasca soils although the Athabasca soils were not as enriched in these elements as Ontario farm soils, which are likely amended by the addition of fertilizers and pesticides (Commodore, 2012).

Ontario

The Ontario soils were much more enriched in essential macronutrients when compared to Athabasca soils and the Pembroke soil was particularly enriched in essential macronutrients when compared to the Sarsfield soil. Most notably, the Pembroke soil had a K concentration that was an order of magnitude higher than the Sarsfield soil, which likely indicates the use of potassium-based fertilizers and pesticides (Commodore, 2012).

Grocery Store

Elemental soil data was not obtained for the grocery store samples.

2.5.2.3.2 Essential Micronutrients (Cu, Fe, Mn, Mo, Ni, and Zn)

East and West Athabasca

Essential micronutrients needed for plant growth are primarily taken up by plant roots from the soil (Shotyk W. , 2020) and it was found that the West Athabasca soils were depleted in all essential micronutrients when compared to East Athabasca soils. This is likely due to the natural geochemistry of the area and also the absence of fertilization to replenish nutrients obtained by plants from the soil. When compared to the Ontario farm soils, the East Athabasca soils were depleted in all essential micronutrients, which reflects the geochemical differences between these sampling locations.

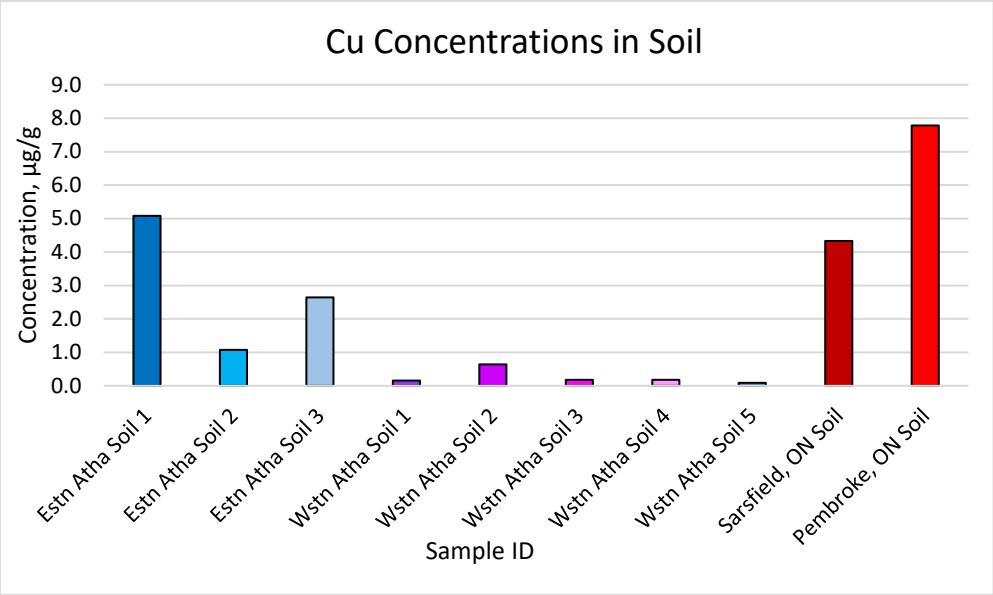

Figure 2.36: Concentrations in µg of Cu in Soils.

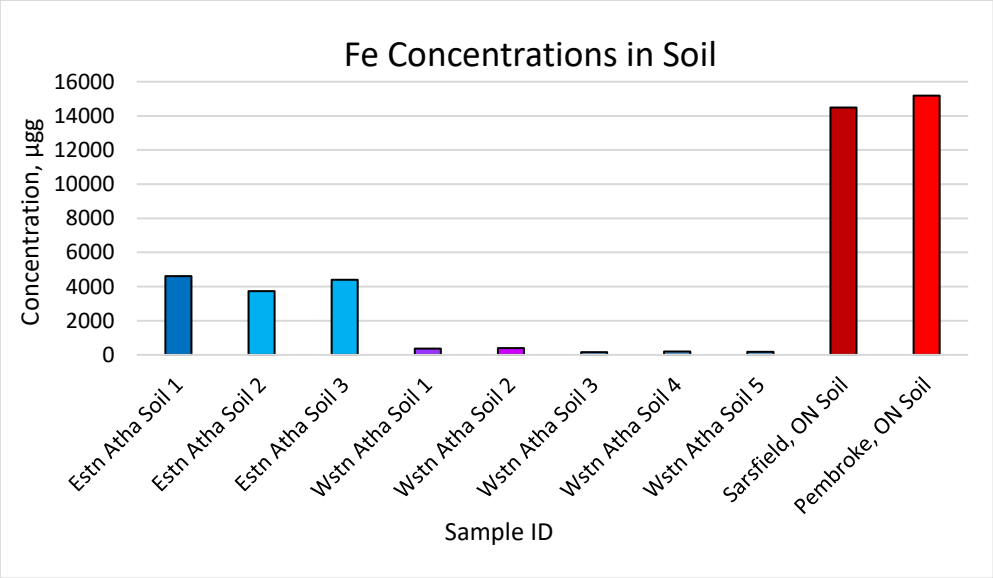

Figure 2.37: Concentrations in µg of Fe in Soils.

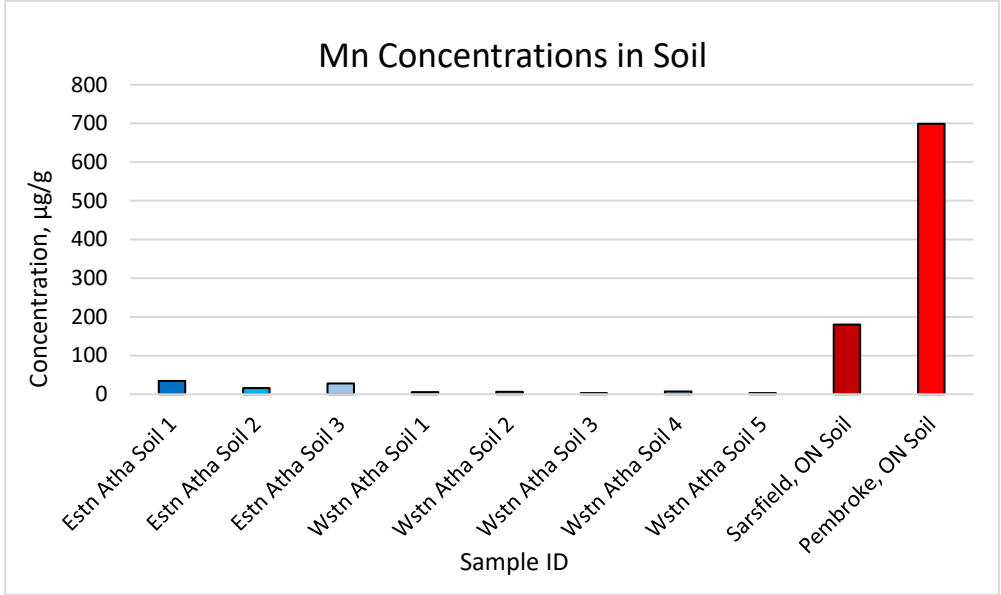

Figure 2.38: Concentrations in µg of Mn in Soils.

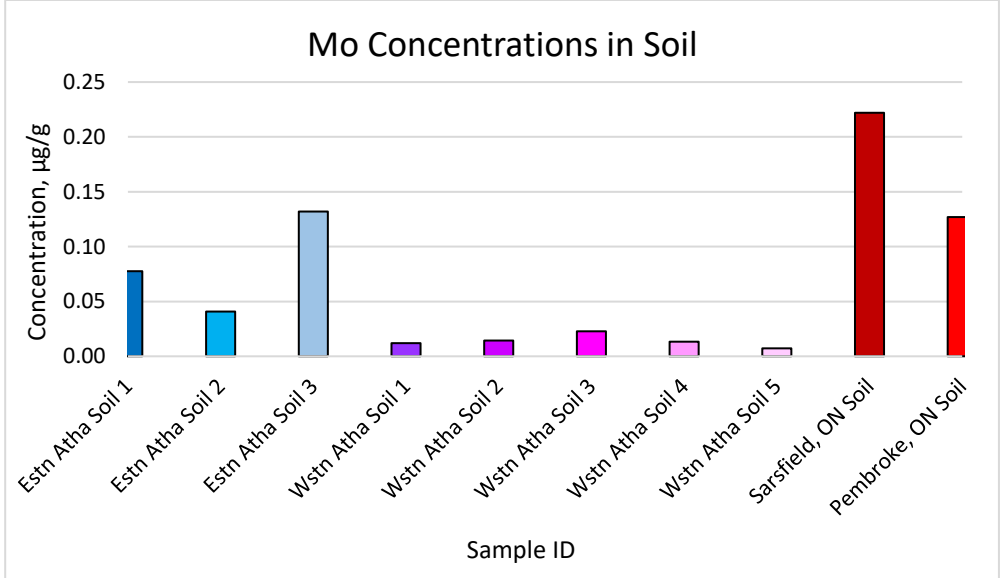

Figure 2.39: Concentrations in µg of Mo in Soils.

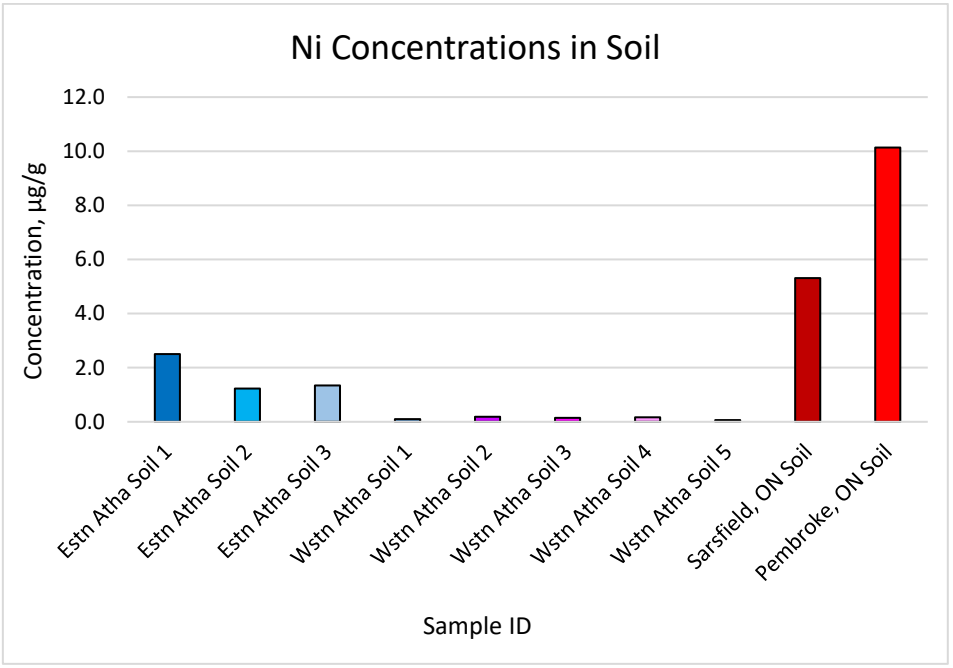

Figure 2.40: Concentrations in µg of Ni in Soils.

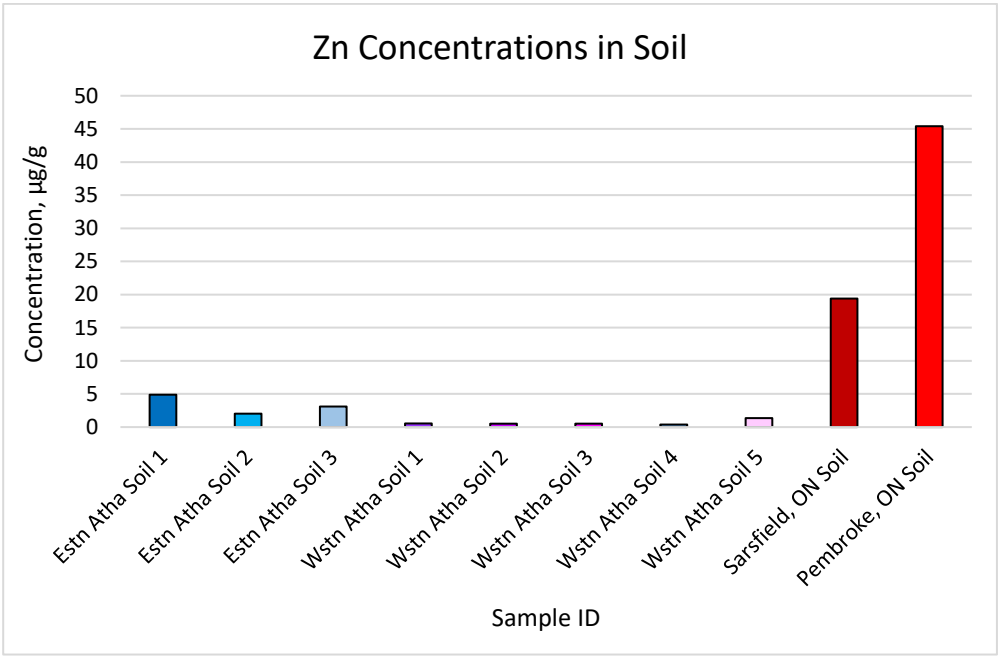

Figure 2.41: Concentrations in µg of Zn in Soils.

Figures 2.36-2.41: Essential Micronutrients for Plant Growth

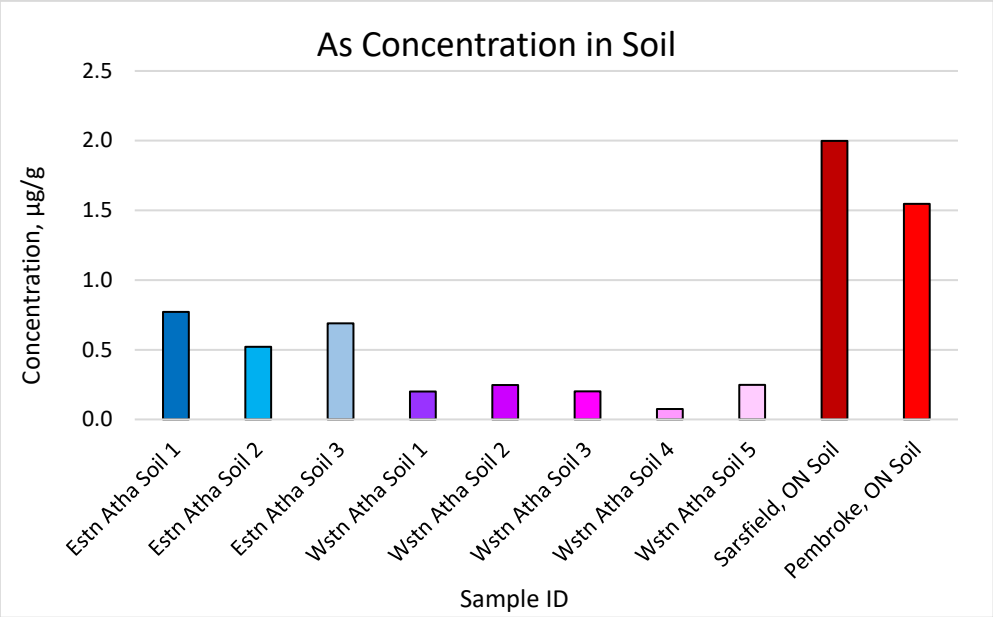

Figure 2.42: Concentrations in µg of As in Soils.

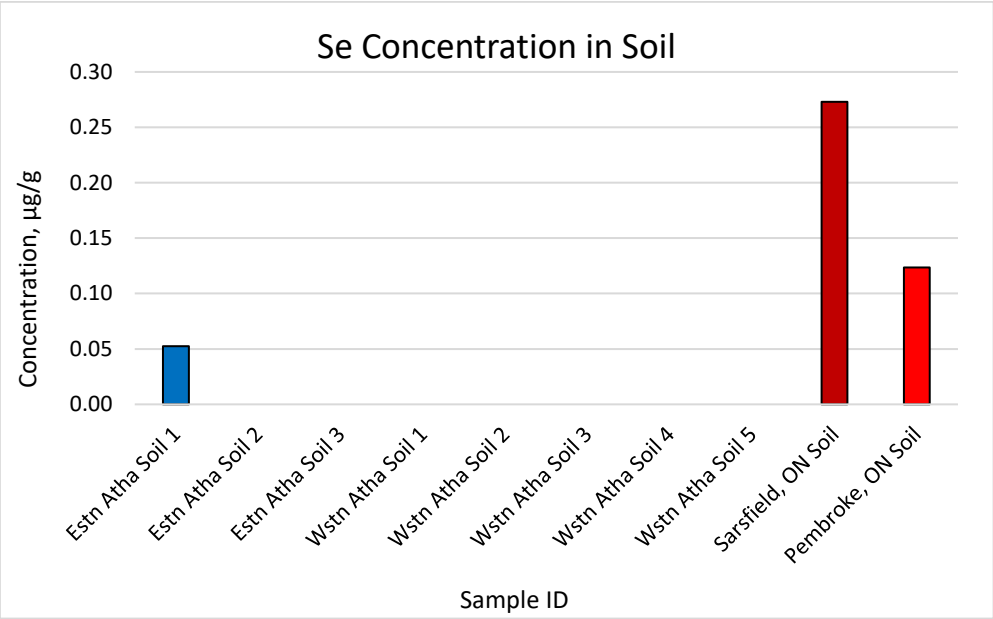

Figure 2.43: Concentrations in µg of Se in Soils.

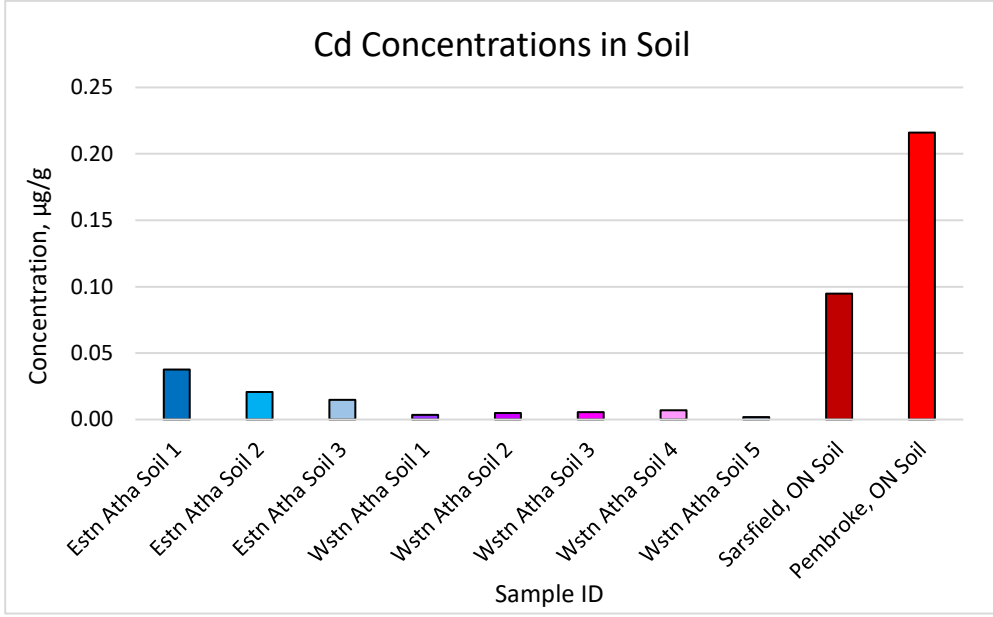

Figure 2.44: Concentrations in µg of Cd in Soils.

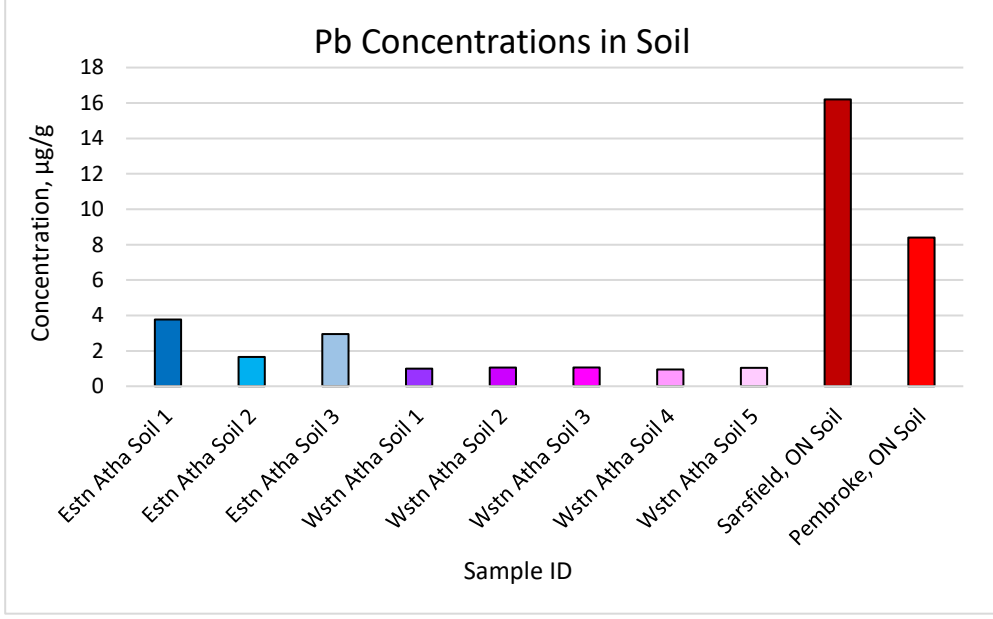

Figure 2.45: Concentrations in µg of Pb in Soils.

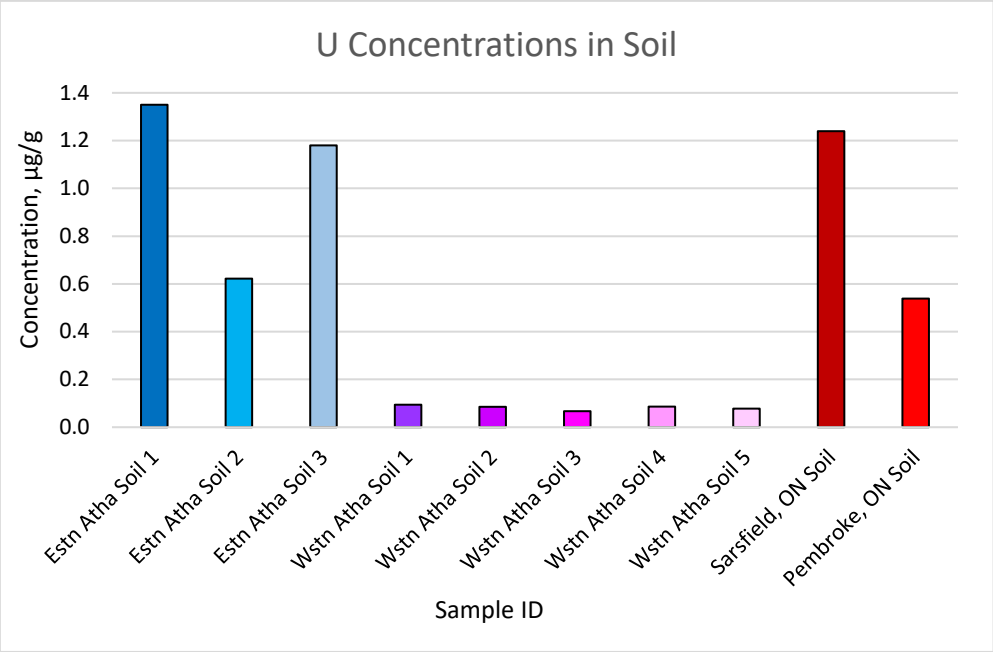

Figure 2.46: Concentrations in µg of U in Soils.

Figures 2.42-2.46: Potentially Toxic Trace Elements.

Note: Concentrations of As, Se, Cd, Pb and U in Soils, µg/g. Be was not included in these figures since its concentrations were below the MDL.

Ontario

Both Ontario farm soils were enriched in all essential micronutrients when compared to Athabasca soils. Overall, the Pembroke soil was much more enriched in essential micronutrients when compared to the Sarsfield soil and this could be due to the addition of fertilizers and pesticides (Commodore, 2012), (P. C. Nagajyoti, 2010).

Grocery Store

Elemental soil data was not obtained for the grocery store sample.

2.5.2.3.3 Potentially Toxic Trace Elements (Be, As, Se, Cd, Pb, and U)

Potentially toxic trace element such as Be, As, Se, Cd, Pb, and U may pose a particular health concern to humans. The concentrations of potentially toxic trace elements in soil from this research were compared to Canadian Soil Quality Guidelines in Table 2.16 to be able to put into context the results and it was found that none of the concentrations exceeded the CCME's Soil Quality Guidelines values and were orders of magnitude lower than the guideline values (CCME, 2023).

Element	Maximum Concentration - East Athabasca Soil, mg/kg	Maximum Concentration - West Athabasca Soil, mg/kg	Maximum Concentration - Ontario Soil, mg/kg	CCME Soil Quality Guidelines for Agricultural Land Use, mg/kg
Be	0.00019	0.000018	0.00026	**4**
As	0.00077	0.00025	0.002	**12**
Se	0.000052	< MDL	0.00027	**1**
Cd	0.000038	0.000007	0.00022	**1.4**
Pb	0.0038	0.0011	0.0084	**70**

U	0.0014	0.000094	0.0012	**23**

Table 2.16: Maximum Elemental Concentrations Measured in Soils and Compared to CCME Soil Quality Guidelines (CCME, 2023)

East and West Athabasca

Some metals in the environment pose potential health effects to humans. Many of the potentially toxic trace elements are heavy metals that come from both natural and anthropogenic sources. Heavy metal s exist naturally in the earth's crust and their concentrations vary in rocks. Weathering of rocks such as shale during soil formation can contribute to environmental concentrations of Cd and Pb (P. C. Nagajyoti, 2010). All East Athabasca soils were enriched in many of the potentially toxic trace elements when compared to the West Athabasca soils, although the Ontario farm soils were more enriched, and many of these metals in Ontario soils likely come from the use of pesticides and fertilizers (P. C. Nagajyoti, 2010). The exception was that East Athabasca soils generally had the highest U concentrations, which is likely due to the natural geochemistry of this area. This shows there are distinct geochemical differences between these sampling locations. When compared to Canadian soil quality guidelines, all of the potentially toxic trace element concentrations that have guidelines were well below the Canadian Council of Ministers of the Environment's Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (CCME, 2023).

Ontario

Fertilizers added to soil and crops are the principal sources of heavy metals that can accumulate in agricultural soil since fertilizers, fungicides, pesticides, sewage sludge, manure, and limes can contain elevated concentrations of metals such as As, Cd, Pb, Cr, Ni, Zn, Co, and Cu. Plant leaves can accumulate elevated amounts of Cd, which poses a special human health concern since it can accumulate in the food chain and be ingested by humans (P. C. Nagajyoti, 2010). There was evidence of the use of fertilizers and pesticides in the Ontario soils since there were elevated concentrations of all the potentially toxic trace

elements when compared to the Athabasca soils. The Sarsfield soil had higher concentrations of all potentially toxic trace elements when compared to the Pembroke soil, although the Pembroke soil was elevated in Cd. Despite the relatively elevated concentrations, all of the potentially toxic trace element concentrations with guideline values were well below both the Ministry of the Environment's Soil, Groundwater, and Sediment Standards for Use Under Part XV.1 of the Environmental Protection Act (MECP, 2011) and the Canadian Council of Ministers of the Environment's Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (CCME, 2023).

Grocery Store

Elemental soil data was not obtained for the grocery store samples.

2.5.2.3.4 Conservative, Lithophilic Elements (Al, Co, Cr, Ga, and Y)

East and West Athabasca

The West Athabasca soils were depleted in all conservative, lithophilic elements when compared to East Athabasca soils, which is likely due to the natural geochemistry of these areas. When compared to the Ontario farm soils, the East Athabasca soils had lower concentrations in all conservative, lithophilic elements, although the exception was that the Ga concentrations were comparable. When compared to Canadian soil quality guidelines, all of the conservative, lithophilic elemental concentrations that have guidance values were well below the Canadian Council of Ministers of the Environment's Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (CCME, 2023).

Ontario

Some conservative, lithophilic elements such as Co and Cr are found in fertilizers, fungicides, animal manure, and sewage sludge that are added to crops and can accumulate in agricultural soil (P. C. Nagajyoti, 2010). The Ontario farm soils generally had higher concentrations of the conservative, lithophilic elements when compared to the Athabasca soils. When compared to the Ontario soils, the

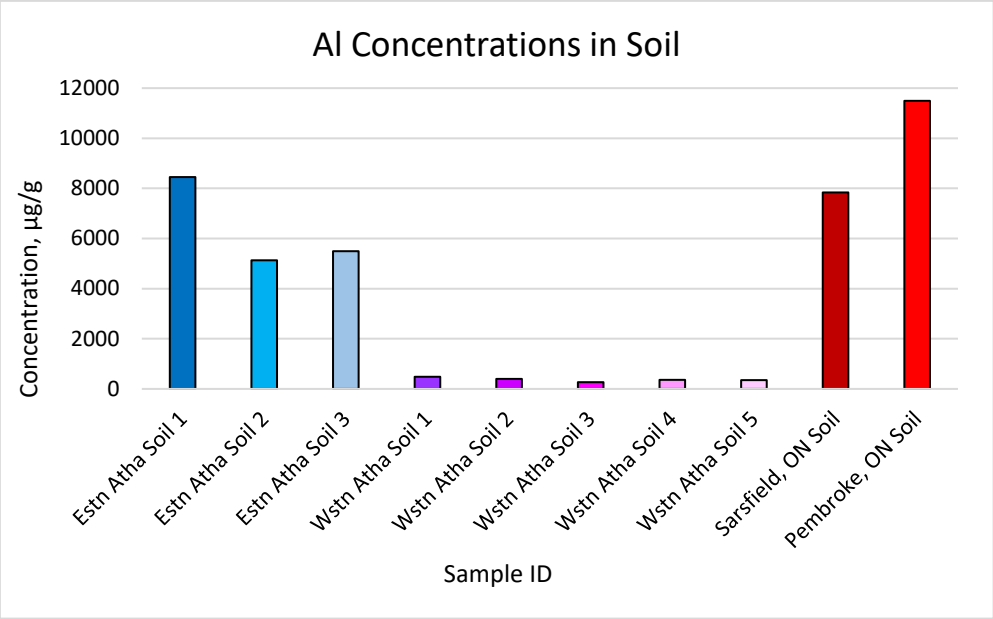

Figure 2.47: Concentrations in µg of Al in Soils.

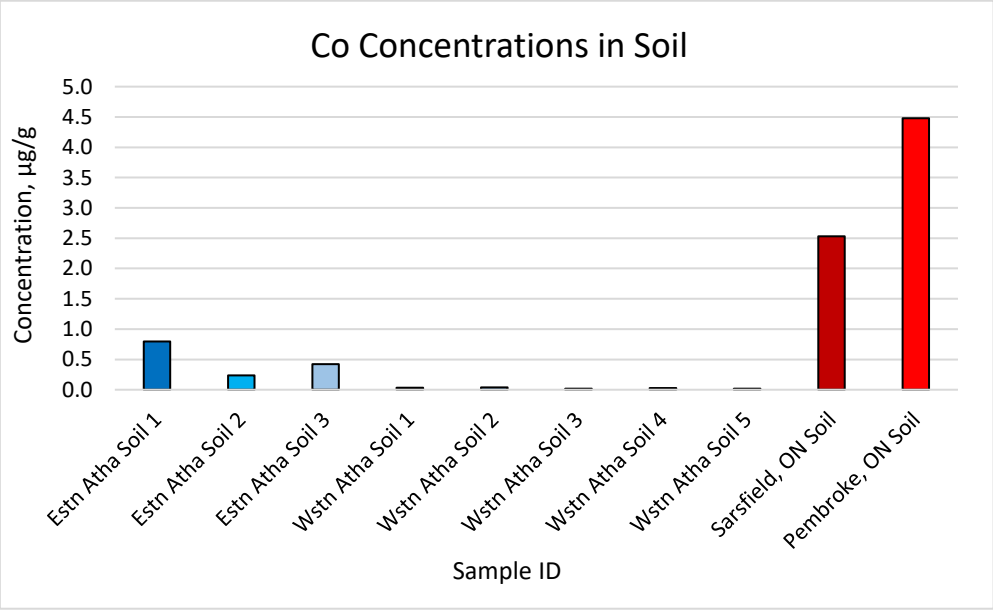

Figure 2.48: Concentrations in µg of Co in Soils.

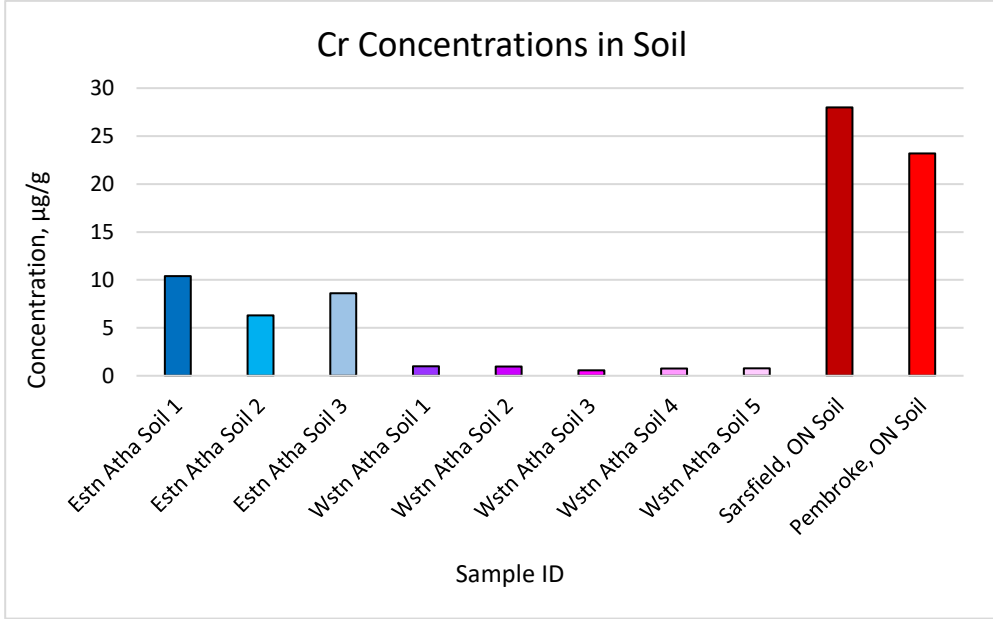

Figure 2.49: Concentrations in µg of Cr in Soils.

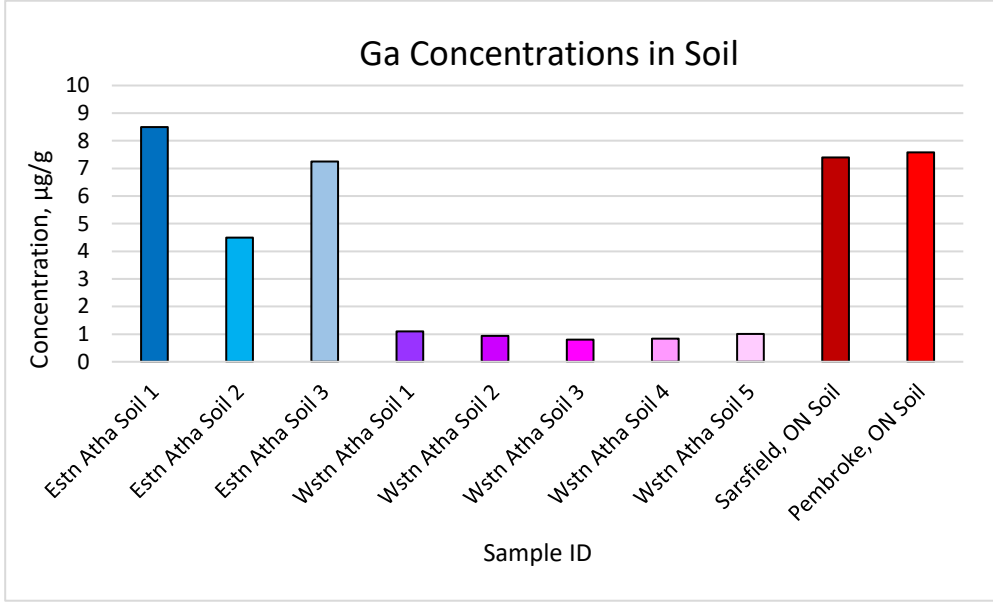

Figure 2.50: Concentrations in µg of Ga in Soils.

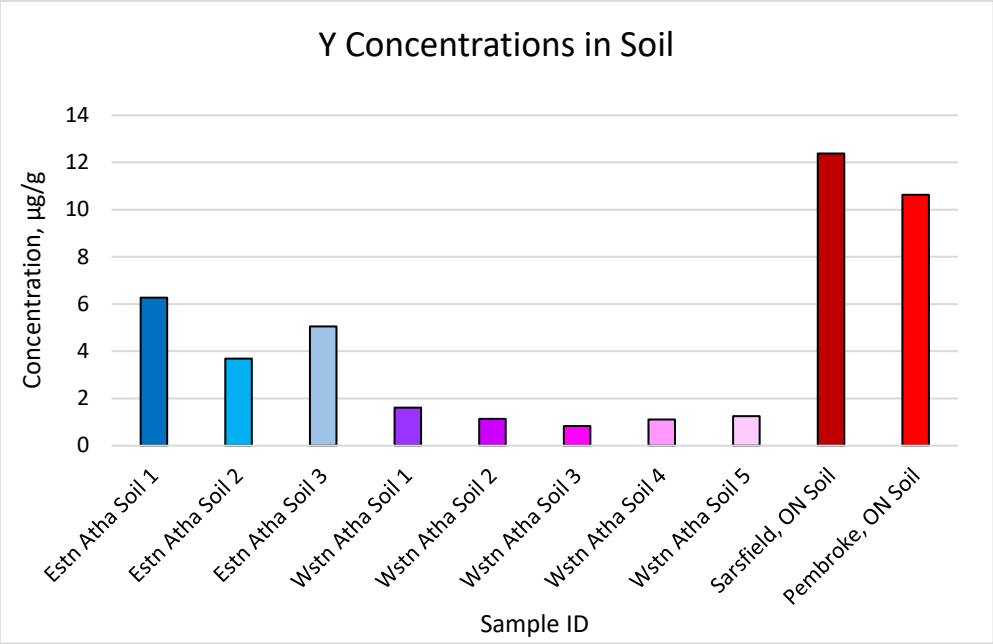

Figure 2.51: Concentrations in µg of Y in Soils.

Figures 2.47-2.51: Conservative, Lithophilic Elements

Pembroke soil was enriched in Al and Co, whereas the Pembroke soil was depleted in Cr and Y. For Ga, the two Ontario farm soils were comparable. All of the conservative, lithophilic elemental concentrations that have guidance values were well below both the Ministry of the Environment's Soil, Groundwater, and Sediment Standards for Use Under Part XV.1 of the Environmental Protection Act (MECP, 2011) and the Canadian Council of Ministers of the Environment's Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health (CCME, 2023).

Grocery Store

Elemental soil data was not obtained for the grocery store samples.

2.5.2.3.5 Other Lithophilic Elements (Ba, Rb, and Sr)

East and West Athabasca

For the other lithophilic elements, the East Athabasca soils were enriched in Ba and Rb when compared to West Athabasca soils and the Sr concentrations were slightly higher in West Athabasca soils. When compared to the Ontario farm soils, the East and West Athabasca soils were generally more depleted in Ba, Rb, and Sr, which reflects the natural geochemistry of these sampling locations.

Ontario

Generally, the Ontario farm soils were more enriched in all of the other lithophilic elements when compared to the Athabasca soils. The Pembroke soil was more enriched in Ba and Rb than Sarsfield soil although the Sarsfield soil was slightly more enriched in Sr.

Grocery Store

Elemental soil data was not obtained for the grocery store samples.

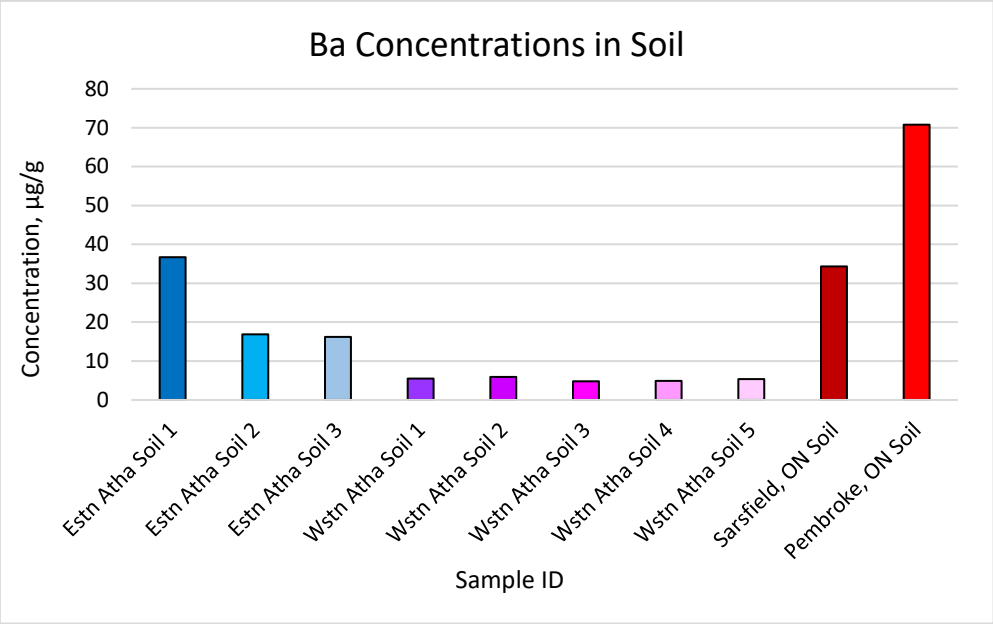

Figure 2.52: Concentrations in µg of Ba in Soils.

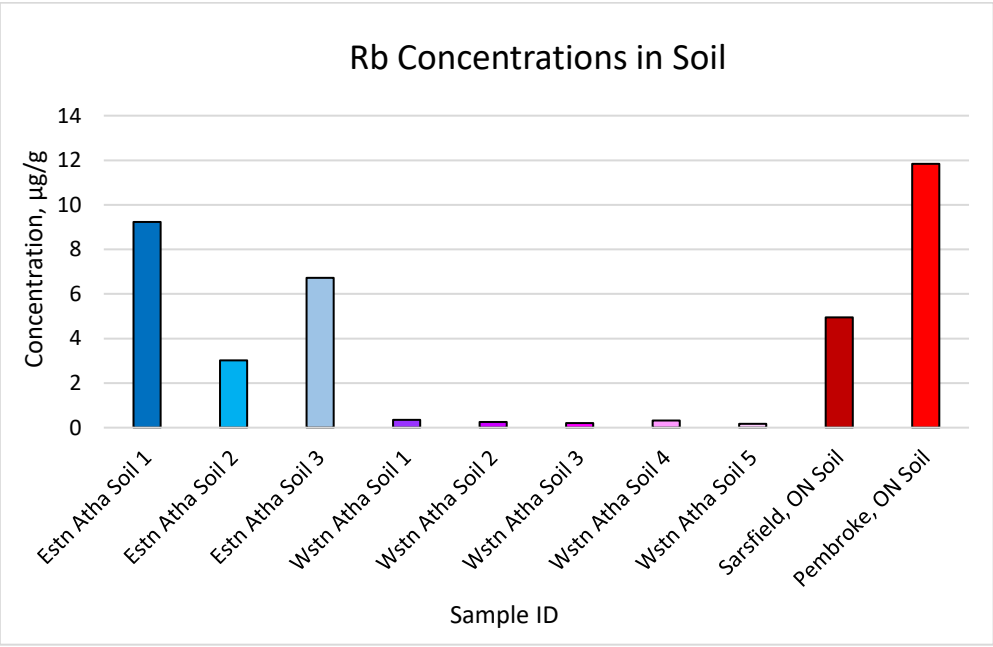

Figure 2.53: Concentrations in µg of Rb in Soils.

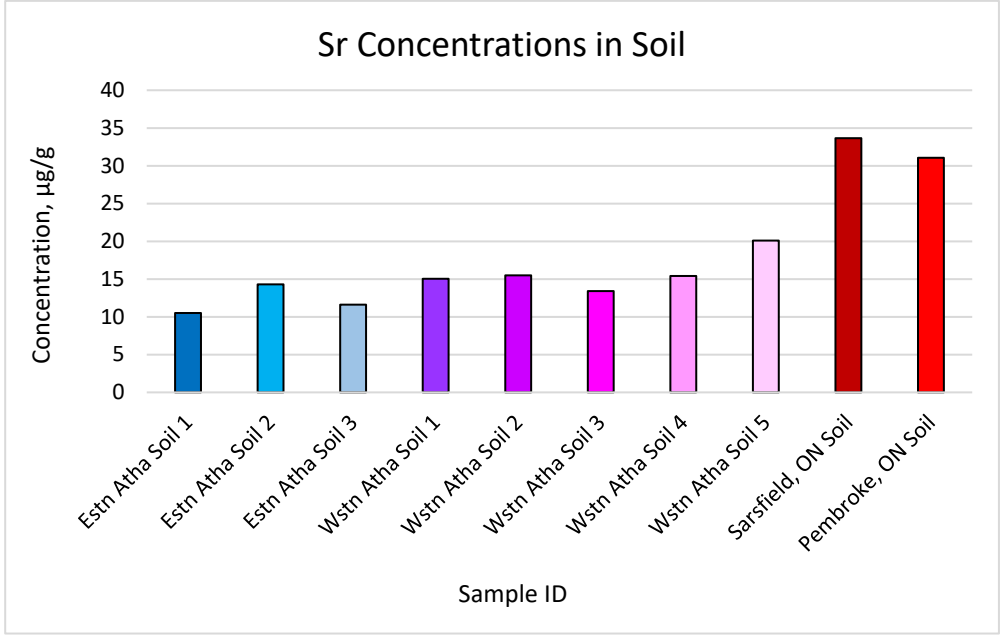

Figure 2.54: Concentrations in µg of Sr in Soils.

Figures 2.52-2.54: Other Lithophilic Elements

In summary, the determination of trace elemental concentrations in soil is key when studying the uptake of elements from soil into plants and showed that the main driver for uptake is the plant's nutritional requirements and that uptake is influenced by soil factors such as pH. In general, the elemental concentrations measured in all soil samples followed similar trends. Some of the highest elemental concentrations in the soils were magnesium, calcium, aluminum, potassium, and iron, which speaks to the geochemical composition of soil. A summary of the trace elemental concentrations in soil is provided below. All of the trace elemental concentrations in soil were compared to Canadian soil quality guideline values and none of the guideline values were exceeded.

Summary For Trace Elements in Athabasca Soils:

- West Athabasca soils were depleted in essential macronutrients and micronutrients when compared to all other soils; likely due to the absence of fertilization to replenish nutrients and reflects the differences in geochemistry between East and West Athabasca
- East Athabasca soils were enriched in potentially toxic trace elements compared to West Athabasca soils and had the highest U concentrations; likely due to the natural geochemistry of this area; concentrations of potentially toxic trace elements were below CCME's Canadian soil quality guidelines
- West Athabasca soils were depleted in conservative, lithophilic elements when compared to Athabasca soils; likely due to the distinct natural geochemistry of the area
- Athabasca soils were generally more depleted in other lithophilic elements when compared to Ontario soils

Summary For Trace Elements in Ontario Soils:

- Ontario soils were enriched in essential macronutrients and micronutrients when compared to

Athabasca soils; the Pembroke soil was particularly more enriched than the Sarsfield soil and likely indicates the use of fertilizers and pesticides

- Ontario soils had elevated concentrations of potentially toxic trace elements when compared to Athabasca soils and likely indicates the use of fertilizers and pesticides; concentrations were below CCME's Canadian soil quality guidelines and below the MOE's standards for soil, groundwater, and sediment
- Ontario soils generally had higher concentrations of conservative lithophilic elements when compared to Athabasca soils; concentrations were below CCME's Canadian soil quality guidelines and below the MOE's soil, groundwater, and sediment standards
- Ontario soils were generally more enriched in other lithophilic elements when compared to Athabasca soils

2.5.2.4 Soil to Plant Transfer Factors for Trace Elements

Soil to plant transfer factors were calculated and are presented in Tables 2.17 and 2.18. The efficiency of elemental transfer from the soil into the edible plant portion (blueberry) was determined by taking the elemental concentration in the washed blueberry (µg/g, dry weight) and dividing it by the corresponding elemental concentration (µg/g, dry weight) in the soil. In cases where one of the values were below the MDL, the calculation was not performed.

Note: The elemental transfer efficiency for grocery store blueberries could not be determined since the corresponding soils were not obtained.

	Essential Macronutrients			Essential Micronutrients						Other Lithophilic Elements		
Sample ID	**K (µg/g)**	**Ca (µg/g)**	**Mg (µg/g)**	**Cu (µg/g)**	**Fe (µg/g)**	**Mn (µg/g)**	**Mo (µg/g)**	**Ni (µg/g)**	**Zn (µg/g)**	**Ba (µg/g)**	**Rb (µg/g)**	**Sr (µg/g)**
MDL	**1.5155**	**2.2204**	**0.2405**	**0.0039**	**0.0651**	**0.0019**	**0.0008**	**0.0052**	**0.0918**	**0.0040**	**0.0029**	**0.0024**
East Atha Blueberry 01	11.09	1.99	0.68	0.48	2.0E-03	4.75	0.63	0.39	0.91	0.57	2.10	0.20
East Atha Blueberry 02	77.31	13.42	2.14	4.33	4.8E-03	10.95	7.55	0.64	3.29	1.33	9.36	0.12
East Atha Blueberry 03	28.41	3.84	1.51	1.58	3.0E-03	7.82	1.28	0.81	2.25	2.03	3.01	0.66
West Atha Blueberry 01		32.22	26.82	18.41	0.03	64.84	11.14	2.96	9.95	3.88	30.80	0.06
West Atha Blueberry 02		72.58	45.95	3.92	0.03	72.51	6.67	2.04	10.95	3.20	45.53	0.09
West Atha Blueberry 03		77.20	28.44	13.32	0.07	61.30	5.09	3.10	11.07	3.23	42.07	0.15
West Atha Blueberry 04		1032.27	103.37	26.95	0.08	83.13	2.51	5.66	22.31	5.01	51.79	0.52
West Atha Blueberry 05		65.42	60.76	40.90	0.08	139.16	11.86	2.59	6.79	4.51	73.01	0.20
Sarsfield, ON Blueberry	15.33	0.47	0.46	0.48	1.5E-03	0.08		0.17	0.32	0.07	0.78	0.03
Pembroke, ON Blueberry	3.61	0.09	0.11	0.50	1.2E-03	0.04	0.40	0.03	0.10	0.04	0.30	0.04
Mean East	**38.94**	**6.42**	**1.44**	**2.13**	**0.00**	**7.84**	**3.15**	**0.61**	**2.15**	**1.31**	**4.82**	**0.33**
Median East	**28.41**	**3.84**	**1.51**	**1.58**	**0.00**	**7.82**	**1.28**	**0.64**	**2.25**	**1.33**	**3.01**	**0.20**
Mean West		**255.94**	**53.06**	**20.70**	**0.06**	**84.19**	**7.45**	**3.27**	**12.21**	**3.96**	**48.64**	**0.20**
Median West		**72.58**	**45.95**	**18.41**	**0.07**	**72.51**	**6.67**	**2.96**	**10.95**	**3.88**	**45.53**	**0.15**
Mean Ontario	**9.47**	**0.28**	**0.29**	**0.49**	**0.00**	**0.06**		**0.10**	**0.21**	**0.06**	**0.54**	**0.03**
Median Ontario												

Table 2.17: Soil to Plant Transfer Concentration Ratios for Essential Macronutients (K, Ca, and Mg), Essential Micronutrients (Cu, Fe, Mn, Mo, Ni, and Zn), and Other Lithophilic Elements (Ba, Rb, and Sr). Note: Where either the washed blueberry concentration or the soil concentration was below the MDL, the ratio was not calculated.

	Potentially Toxic Trace Elements						Conservative, Lithophilic Elements				
Sample ID	**Be (µg/g)**	**As (µg/g)**	**Se (µg/g)**	**Cd (µg/g)**	**Pb (µg/g)**	**U (µg/g)**	**Al (µg/g)**	**Co (µg/g)**	**Cr (µg/g)**	**Ga (µg/g)**	**Y (µg/g)**
MDL	**0.0004**	**0.2396**	**0.2586**	**0.0004**	**0.0002**	**0.0000**	**0.0654**	**0.0001**	**0.0047**	**0.0014**	**0.0002**
East Atha Blueberry 01		0.01	0.05	0.05	2.3E-01		1.0E-03	0.02		2.6E-04	
East Atha Blueberry 02		0.01		0.07	1.2E-02	0.01	3.2E-03	0.07	1.9E-03	9.1E-04	1.1E-03
East Atha Blueberry 03		0.01		0.07	8.9E-04	1.7E-04	1.8E-03	0.04	1.4E-03	5.7E-04	
West Atha Blueberry 01		0.03		0.63	2.3E-03		0.02	0.07		8.6E-03	3.9E-04
West Atha Blueberry 02		0.01		0.17	2.8E-03		0.02	0.08	4.8E-03	4.0E-03	6.3E-04
West Atha Blueberry 03		0.01		0.14	2.6E-03	4.5E-03	0.04	0.18	0.03	2.8E-03	1.4E-03
West Atha Blueberry 04		0.03		0.04	1.5E-03		0.04	0.17	0.02	0.01	2.7E-04
West Atha Blueberry 05		0.03		0.13	2.7E-03		0.02	0.19	0.01	2.2E-03	3.8E-04
Sarsfield, ON Blueberry		0.01	3.0E-03	0.08	5.3E-04		1.8E-03	0.01	4.8E-04		1.7E-04
Pembroke, ON Blueberry		2.4E-03	0.06	0.01	8.1E-04	1.4E-04	1.3E-03	9.7E-04	1.8E-03	4.1E-04	6.6E-04
Mean East		**0.01**		**0.06**	**0.08**		**0.00**	**0.05**	**0.00**	**0.00**	
Median East		**0.01**		**0.07**	**0.01**		**0.00**	**0.04**		**0.00**	
Mean West		**0.02**		**0.22**	**0.00**		**0.03**	**0.14**	**0.01**	**0.01**	**0.00**
Median West		**0.03**		**0.14**	**0.00**		**0.02**	**0.17**	**0.01**	**0.00**	**0.00**
Mean Ontario		**0.01**	**0.03**	**0.04**	**0.00**		**0.00**	**0.01**	**0.00**		**0.00**
Median Ontario											

Table 2.18: Soil to Plant Transfer Concentration Ratios for Potentially Toxic Trace Elements (Be, As, Se, Cd, Pb, and U) and Conservative, Lithophilic Elements (Al, Co, Cr, Ga, and Y).

Note: Where either the washed blueberry concentration or the soil concentration was below the MDL, the ratio was not calculated

2.5.2.4.1 Essential Macronutrients (K, Ca, and Mg)

East and West Athabasca

The soil to plant transfer concentration ratio for K was not able to be calculated for West Athabasca due to the low concentrations in washed blueberries. For the other soil to plant transfer concentration ratios for the essential macronutrients, the median soil to plant transfer efficiency was high (>1). The median transfer efficiency was especially high for K in East Athabasca blueberries and for Ca and Mg in West Athabasca blueberries, which is expected since plants will obtain essential elements from the soil that are needed for growth (Napier, 2012).

Ontario

For Ontario blueberries, only the soil to plant transfer concentration ratio for K was highly efficient (>1) and the soil to plant transfer efficiency for Ca and Mg was lower (<1), which may be due to the nutritional requirements of the blueberry variety in Ontario (Napier, 2012).

Grocery Store

Elemental soil data was not obtained for the grocery store samples and the soil to plant concentration ratio could not be calculated.

2.5.2.4.2 Essential Micronutrients (Cu, Fe, Mn, Mo, Ni, and Zn)

East and West Athabasca

Blueberries from West Athabasca had high soil to plant transfer efficiency for several essential micronutrients: Mn was especially efficient, followed by Cu, Zn, Mo and Ni. Fe was not efficiently transferred from the soil compartment into West Athabasca blueberries since this concentration ratio was <1. The East Athabasca blueberries efficiently transferred the essential nutrients Mn, Cu, Zn and Mo from

the soil to the blueberries and, overall, the concentration ratio values were lower than the West Athabasca values. In neutral or alkaline soils, Fe solubility is low. To overcome this, higher plants have developed different strategies to mobilize iron from the soil compartment although the capability of iron uptake in higher plants varies considerably. Studies have shown that one strategy used by higher plants includes the release of protons, reducing enzymes, and chelating chemicals to acidify the rhizosphere and reduce the insoluble Fe^{3+} to more soluble Fe^{2+} to increase its availability for uptake. Another higher plant strategy involves the release of complexation compounds to mobilize Fe from the soil and increase its availability for uptake (Marshner, 1986). The difficulty for higher plants to mobilize Fe from soil is known and the analysis results show that Fe was not efficiently transferred from the soil into East Athabasca blueberries since their concentration ratios were <1.

Ontario

All of the essential micronutrients in Ontario blueberries had low transfer efficiencies from the soil to the plant and Fe had an especially low concentration ratio for both Ontario blueberry samples. It appears the plants obtained what they needed from the soil for growth (Napier, 2012) even though there were higher concentrations available for soil uptake.

Grocery Store

Elemental soil data was not obtained for the grocery store samples and the soil to plant concentration ratio could not be calculated.

2.5.2.4.3 Potentially Toxic Trace Elements (Be, As, Se, Cd, Pb, and U)

East and West Athabasca

Overall, the transfer efficiency for the potentially toxic trace elements for Athabasca blueberries were very low or were not able to be calculated. This shows that the plant did not need these elements

for growth (Napier, 2012). For East Athabasca blueberries, there was no Be data and very little data for Se and U, which showed very low transfer efficiencies. For West Athabasca blueberries, there was no data for Be or Se, there was only one concentration ratio value for U, which was very low, and the median values for As, Cd, and Pb were also very low, although the values were marginally higher than those from East Athabasca.

Ontario

The Ontario blueberries also had very low transfer efficiencies for all potentially toxic trace elements that could be calculated. The Sarsfield blueberries had a slightly higher transfer efficiency for As and this could be due to its highly acidic soil, which could have increased its uptake by increasing its solubility and availability (P. C. Nagajyoti, 2010).

Grocery Store

Elemental soil data was not obtained for the grocery store samples and the soil to plant concentration ratio could not be calculated.

2.5.2.4.4 Conservative, Lithophilic Elements (Al, Co, Cr, Ga, and Y)

East and West Athabasca

Overall, the transfer efficiency for the conservative, lithophilic elements (Al, Co, Cr, Ga, and Y) for Athabasca blueberries were very low. There was a noticeably higher Co transfer efficiency for West Athabasca blueberries although the efficiency is still very low, which could reflect the plant's nutritional requirements (Napier, 2012).

Ontario

The transfer efficiencies were also very low for Ontario blueberries for the conservative, lithophilic elements, although the Sarsfield blueberries had a noticeably higher Co transfer efficiency when

compared to the Pembroke blueberries. This could be due to the highly acidic Sarsfield soil which could have increased the solubility and availability of Co (P. C. Nagajyoti, 2010).

Grocery Store

Elemental soil data was not obtained for the grocery store samples and the soil to plant concentration ratio could not be calculated.

2.5.2.4.5 Other Lithophilic Elements (Ba, Rb, and Sr)

East and West Athabasca

The Athabasca blueberries had high transfer efficiencies for other lithophilic elements, Ba and Rb, although the West Athabasca blueberries were significantly more efficient at transferring these elements from the soil to plant tissues when compared to East Athabasca blueberries. Elements in the same periodic table group have similar chemical characteristics and behaviours (IAEA, 2014). When looking at essential nutrient concentrations in soil, the West Athabasca soils were significantly depleted in Ca and Mg so it is likely the blueberry plants obtained Ba and Rb as chemical analogue substitutes.

Ontario

The Ontario blueberries had low transfer efficiencies for all other lithophilic elements (Ba, Rb, and Sr). When comparing the two Ontario sampling location, which shows they had adequate essential nutrient concentrations in the soil for growth and did not require to uptake these elements as chemical analogues (IAEA, 2014).

Grocery Store

Elemental soil data was not obtained for the grocery store samples and the soil to plant concentration ratio could not be calculate.

In summary, the soil to plant transfer factors were determined for trace elements and show that the transfer efficiency was dictated by the plant's nutritional requirements and the availability of the element in the soil compartment.

Summary For the Soil to Plant Transfer Factors for Trace Elements in Athabasca Samples:

- Athabasca soil to plant transfer ratios for essential macronutrients and micronutrients generally showed high efficiency although Fe was not as efficiently transferred; the difficulty for higher plants to mobilize Fe from soil is known, despite the plant strategies to release substances into soils to help increase Fe availability
- Low transfer efficiency for potentially toxic trace elements and conservative, lithophilic elements; plants did not require these elements for growth
- Athabasca samples had high transfer efficiencies for other lithophilic elements and West Athabasca samples were particularly efficient; West Athabasca soils were significantly depleted in Ca and Mg and obtained Ba and Rb as chemical analogues

Summary For the Soil to Plant Transfer Factors for Trace Elements in Ontario Samples:

- Ontario soil to plant transfer ratios were especially efficient for K
- Ontario samples had low relative transfer efficiencies of essential macronutrients; the plants obtained what was needed for growth despite higher concentrations of essential macronutrients available in the soil
- Low transfer efficiency for potentially toxic trace elements, conservative, lithophilic elements, and other lithophilic elements; plants did not require these elements for growth
- Sarsfield blueberries had a slightly higher transfer efficiency for As and Co when compared to Pembroke blueberries; highly acidic Sarsfield soil could have increased As solubility and availability

2.5.3 Soil Composition and Mineralogy

Examining the soil's composition and mineralogy are important to understand why the soil from different sampling locations are distinct and why the different soil compositions are reflected in the co-located blueberry samples. Knowing what minerals are in the soil will be helpful in determining mineral solubility, which is known to increase the availability for uptake into plants (P. C. Nagajyoti, 2010), (Walther C. , 2015). Additionally, the soil composition and mineralogy could provide insight into the sources of radionuclides and trace elements found in the blueberries.

East and West Athabasca

Due to several glaciation periods and the advance and retreat of ice sheets during the last glacial maximum, Northern Saskatchewan's cover is both extensive and complex with glacial sediments. This area receives a low amount of annual precipitation (between 270-350 mm) and the Athabasca Basin has less than a 5% bedrock outcrop. Since the 1970's, East Athabasca's geology has been studied through extensive mapping, surficial geochemical and geological surveys, and overburden drilling studies. The sandstone bedrock-derived till in the Eastern Athabasca basin was found to be enriched in K, U, and Th (Pennock, 2021), (Campbell, 2007). In West Athabasca, the bedrock was also found to be sandstone with sandstone-derived till although this area was characterized by moderate K levels, a slight enrichment of U, and low Th levels (Campbell J. E., 2006). The analysis of East Athabasca soil in this blueberry study reflects the enrichment of K, U, and Th from the literature publications since these soils were found to be enriched in these elements when compared to West Athabasca soils. The geochemical signature of the Athabasca Basin's till reflects the different amounts of detritus from basement rocks: K-feldspar and K-mica are the sources of radioactive K and zircon monazite and apatite are the sources of radioactive U and Th. Additionally, uranite and pitchblende are reported in the literature in these areas as sources of U. Campbell, et al. reported elevated concentrations of MgO in the Northern and Eastern Athabasca Basin, which reflects the phyllosilicate and mafic minerals of the basement rocks (Campbell J. E., 2006). Minerals

such as Ni, Co, As, Mo, and Zn were found in literature studies to frequently accompany uranium minerals (Ruzicka, 1997) and the presence of faults and fractures in rocks can allow for the upward movement of these elements into vegetation, soil, and till at the surface (Carlson, 2016). Research on East Athabasca's Cigar Lake U deposit found both polymetallic and monometallic mineralization which contain complexes of U-Ni-Co-As, U-Cu, and U alone (Ruzicka, 1997) as well as an enrichment of Fe, Zn, and Pb, which is consistent with the results from this research since East Athabasca soils were found to be enriched in U as well as in elements such as Ni, Co, As, Mo, Zn, Fe, and Pb when compared to West Athabasca soils. One East Athabasca soil had a particularly elevated concentration of Se, which is not surprising since Se enrichment was found in studies of East Athabasca's waste rock around the Cigar Lake deposit and its source is likely the nearby sandstone (Clark, 2015), (Kaczowka, 2021), (Campbell, 2007).

Studies of the transfer of radionuclides from soils to plants have generally found that higher radionuclide activities in plants result from soils with higher radionuclide activities. Variability in uptake can arise due to the physiology of plant species and to the sorption of radionuclides onto soil particles, which can reduce the availability for uptake (Walther C. , 2015). Soil geology of different wine producing regions has been studied and researchers have found there are many factors that contribute to the overall quality of wine. They found that in some regions, the bedrock geology directly influences the fruit quality by influencing the soil type and, in other regions, the bedrock geology indirectly influences the fruit quality (Huggett, 2006).

The soil composition and mineralogy in the Athabasca Basin and the differences between East and West Athabasca soils are linked to the levels of radionuclides and trace elements found in the blueberries. It is known that Ni and Mo are essential plant nutrients, are mobile in soils, and are available for plant uptake (Stachiw, 2019). When compared to West Athabasca soils, the East Athabasca soils were found to be enriched in Ni, Mo, and U, and this is reflected in the relatively enriched concentrations of these elements in corresponding blueberry samples. The Ni and Mo enrichment in East Athabasca soils in

this research is consistent with the literature in that these minerals tend to accompany U (Ruzicka, 1997) and East Athabasca soils were found to be enriched in U when compared to West Athabasca soils. In soil, ^{238}U is insoluble and immobile in its reduced tetravalent state, U(IV), but its mobility can increase after forming colloids of organic complexes (Walther C. , 2015) and it becomes soluble in water in oxidating environments up to pH 5.8 where it is found in its hexavalent state as uranyl, UO_2^{2+} (Clark, 2015). The East Athabasca 02 blueberry sample had an elevated U activity when compared to all other blueberry samples and its the low soil pH (pH 4.28; the lowest pH found for all Athabasca soils) increased the solubility of U that was present in the soil solution. The presence of soil organic carbon (TOC 0.7530) in this sample further allowed organic complexes to form with U to increase its availability for uptake by the plant roots into the blueberries. This shows the different mineralogy and soil compositions were reflected in the different soils and blueberries in these areas.

Ontario

The Ontario soils are distinct in composition and mineralogy when compared to Athabasca soils. The soil in Eastern Ontario and the Ottawa Valley has been characterized in the literature as consisting of a variety of clays with an overlay of sand, silt, organic material deposits, and gravel (Fransham, 1977). The Ontario sampling locations in this research are within the Ottawa embayment area where the retreat of the Laurentide Ice Sheet during the last glacial maximum resulted in the Champlain Sea, which is the source of the glaciomarine silt and clay deposits (Foubister, 2023). This study area of Ontario is classified as part of the Mixedwoods Plains Ecozone with carbonate rich limestone, sandstone, and dolostone bedrock and Precambrian basement rock. The till in this area of Ontario is from the advance and retreat of the parent material of glaciers and from the carbonate bedrock's physical and chemical weathering (Foubister, 2023), (Fransham, 1977), (Baldwin, 2000), (Saurette, 2021). Studies have found that precipitation and temperature affect element leaching and soil weathering of parent rocks (Woodruff,

2009), (Saurette, 2021). This area of Ontario receives the highest amount of annual precipitation in Ontario (between 770-1202 mm), which is significantly higher than that of Athabasca (Saurette, 2021).

The Ontario soil composition and mineralogy reflect the levels of radionuclides and trace elements in the blueberries although this research found evidence of the use of fertilizers and pesticides due to elevated concentrations of potentially toxic trace elements such as As, Cd, Pb, Cr, Ni, Zn, Co, and Cu. Soluble uranyl, UO_2^{2+}, is the dominant U species in well-aerated, dryer soils. The mobility of U in soils has been shown to increase with the presence of carbonate and increases with acidic soil environments (pH <6) since U sorption by soils peaks between pH 5-7 and sorption reduces U's mobility. The presence of clays also reduces U mobility since clay can adsorb metals on their charged surfaces (Walther C. , 2015). The Sarsfield, Ontario soil had a similar U concentration to East Athabasca soils in this study although the much dryer East Athabasca soils likely had more soluble U and these soils had a much lower clay component when compared to Sarsfield, Ontario soil, which helped to increase the availability of U for uptake. The East Athabasca blueberries had higher concentrations of U and this shows the composition and mineralogy of these different soils are reflected in different U concentrations in blueberries.

2.5.3.1 Soil pH

Soil pH characterization work was conducted for all soils since soil pH can explain the mobility or immobility of elements in the soil. The soil pH can change an element's speciation, charge, and influence its solubility and mobility, which will affect its uptake into plants (Rahman, 2019). Highly acidic soil pH can increase an element's mobility, solubility, and availability (P. C. Nagajyoti, 2010) and is useful when analyzing the uptake of elements from different locations. Soil pH results are presented in Table 2.19.

East and West Athabasca

The East and West Athabasca soils were all quite acidic and were between pH 4.28-5.42. The East Athabasca soils were lower in pH with a median of 4.68 than the West Athabasca soils, which had a median pH of 5.01. The soil pH results helped explain the radionuclide and trace element uptake results in the blueberries since an acidic pH increased the uptake from the soil compartment into the blueberries. The pH was fairly similar in these sampling locations and would have contributed roughly equally in making elements in the soil more soluble, mobile, and available for uptake (Rahman, 2019), (P. C. Nagajyoti, 2010).

Ontario

The Ontario soils were also acidic. The Sarsfield, ON soil was the most acidic soil of all the samples obtained and had an average pH of 3.82, whereas the Pembroke, ON soil had the highest pH with an average of 6.60. The Sarsfield blueberries showed elevated concentrations of some radionuclides and elements when compared to the Pembroke blueberries and the differences in uptake can be explained by the differences in soil pH for these sampling locations: the highly acidic Sarsfield soil helped increase the solubility, mobility, and availability of elements (Rahman, 2019), (P. C. Nagajyoti, 2010).

2.5.3.2 Total Organic Carbon – Soil

Soil total organic carbon characterization work was conducted for all soils since it can help explain the mobility or immobility of elements in the soil solution, which can affect uptake. Studies of metal mobility and availability in soils have shown that soil properties and characteristics such as organic carbon can influence metal adsorption and desorption. After soil pH, the amount of organic carbon in soil is important to determine since organic matter can reduce bioavailability of metals through complexation and retention to prevent the uptake by plants or may provide chelating agents to the soil solution to increase the availability of elements for uptake (Zeng, 2011). The total organic carbon in soils was found

Sample IDs:	East Atha Soil 01	East Atha Soil 02	East Atha Soil 03	West Atha Soil 01	West Atha Soil 02	West Atha Soil 03	West Atha Soil 04	West Atha Soil 05	Sarsfield, ON Soil	Pembroke, ON Soil
Soil pH (Average of 3 Aliquots)	4.68	4.28	4.71	4.85	5.16	5.42	4.37	5.01	3.82	6.60
Mean Soil pH		**4.56**				**4.96**				**5.21**
Median Soil pH		**4.68**				**5.01**				

Table 2.19: Averaged Soil pH Measurements.

Sample IDs:	East Atha Soil 01	East Atha Soil 02	East Atha Soil 03	West Atha Soil 01	West Atha Soil 02	West Atha Soil 03	West Atha Soil 04	West Atha Soil 05	Sarsfield, ON Soil	Pembroke, ON Soil
Total Organic Carbon (Mass %)	1.9516	0.7530	0.5530						3.9985	5.3818
Mean Total Organic Carbon (Mass %)		**1.0859**								**4.6902**
Median Total Organic Carbon (Mass %)		**0.7530**								

Table 2.20: Total Organic Carbon Measurements in Soil. Note: During analysis, the West Athabasca soils had a negative Total Carbon measurement and could not be analyzed further, thus had no Total Organic Carbon result since these samples were depleted in organic carbon

by subtracting the inorganic carbon value from the total carbon value and the soil TOC results are presented in Table 2.20.

East and West Athabasca

The East and West Athabasca soils had low total organic carbon content. The mean total organic carbon (mass %) for East Athabasca soils was 0.7530. The total organic carbon in all West Athabasca soils was depleted and the values were not obtained since, during the analysis, the measurement for total carbon was a negative value so the samples were not analyzed further. The absence of organic carbon in the West Athabasca soils influenced the availability of some radionuclides and trace elements for uptake. An example of this is that ^{137}Cs was available for uptake in West Athabasca soils since it was not immobilized by organic carbon in the soil.

Ontario

The Ontario soils both had more organic carbon than the Athabasca soils. The Pembroke, ON soil had the highest total organic carbon content (mass %) at 5.3818 and the Sarsfield, ON soil had a total organic carbon value (mass %) of 3.0095.

2.5.4 Food Ingestion and Effective Dose

The general public is exposed to radiation from natural and artificial radionuclides with approximately 79% from natural sources, 19% from medical therapies, and 2% from nuclear power and the fallout from nuclear weapons testing (Walther C. , 2015). In Canada, specifically, the annual average effective dose from natural background radiation is approximately 1.8 mSv/yr and approximately 2.4 mSv/yr worldwide. There are trace amounts of radioactivity in food and drinking water and ingestion accounts for an annual average effective dose of approximately 0.3 mSv (Canadian Nuclear Safety Commission, 2020). An exposure pathway of anthropogenic and naturally occurring radioactive materials

and trace metals is food ingestion (Kuhnlein & Chan, 2000) and there have been an increasing number of research publications determining human exposure from radionuclide ingestion. In their study of northern indigenous people's traditional food systems, Kuhnlein and Chan found indigenous foods were high in nutritional quality, were economically and socially beneficial to the community, and were the best food options for the communities when compared to poor-quality market foods, despite the findings that these foods contained heavy metals, radionuclide contaminants, and organochlorine species (Kuhnlein & Chan, 2000).

The IAEA conducted an extensive worldwide literature review in conjunction with the Food and Agriculture Organization of the United Nations (FAO), the World Health Organization (WHO), and consulted with Member States before publishing TECDOC-2011, which provides guidance and an approach for managing radionuclide exposures from food in non-emergency situations. TECDOC-2011 discusses both natural and human-made radionuclides in foods and outlines relevant requirements in the IAEA Safety Standard Series No. GSR Part 3: the regulatory body or other relevant authority is to establish reference levels for radionuclide exposures from commodities and this includes radionuclides in food and drinking water. From the IAEA's literature review, it was found that four radionuclides, ^{210}Po, ^{210}Pb, ^{228}Ra, and ^{226}Ra, contribute approximately 89% of the annual ingestion dose from food. This IAEA guidance document considers an individual's annual dose reference level of about 1 mSv per year, which is based on a representative person's annual effective dose from food and this value is not normally exceeded. The IAEA recommends that Member States establish radionuclide reference levels for foods, and recommends Member States establish comprehensive monitoring programs for radionuclides in food (IAEA, 2022).

In Canada, health and nutrition studies have been conducted across all provinces which focused on Indigenous diets. Through diet surveys, the types, quantities, and ingestion frequencies of traditional foods and store bought foods were identified. Traditional foods continue to be pivotal to the diets of First Nation communities and berries are routinely identified on diet surveys. In these diet studies, it was found

that blueberries were one of the most frequently eaten traditional foods and, for all three ecozones, blueberries were the most commonly eaten berry from the 2015 Saskatchewan report. Blueberry samples were analyzed for potentially toxic elements and the mean concentrations in blueberries were 0.0152 µg/g dry weight for As*, 0.0015 µg/g dry weight for Cd*, and 0.0227 µg/g dry weight for Pb*. One of the conclusions from this study was that traditional foods had higher nutrient values when compared to store bought foods (First Nations Food, Nutrition & Environment Study, 2023). This study's potentially toxic elemental concentrations in blueberries were within the same magnitude as concentrations found in Athabasca washed blueberries (see Tables 2.6, 2.7, and 2.9).

*Literature concentrations were presented as 0.002 µg/g fresh weight for As, 0.0002 µg/g fresh weight for Cd, and 0.003 µg/g fresh weight for Pb concentrations in blueberries. Using the IAEA dry matter content for wild blueberries of 13.2% (IAEA, 2010), the µg/g concentrations were divided by 0.132 to convert to a dry weight to compare the results.

In Saskatchewan, Canada, the Eastern Athabasca Regional Monitoring Program (EARMP) has established a technical environmental monitoring program in the Eastern Athabasca region of northern Saskatchewan which includes the analysis of wild blueberries for radionuclide activities and elemental concentrations. Blueberry samples were analyzed from Fond Du Lac (5 samples), Stony Rapids (1 sample), and Uranium City (2 samples) for radionuclide activities that included ^{210}Pb, ^{210}Po, ^{226}Ra, and ^{232}Th and they were analyzed for elemental concentrations that included elements of interest to human health such as Be, As, Se, Cd, Pb, and U (Eastern Athabasca Regional Monitoring Program, 2023). When comparing the individual radionuclide activities and elemental concentrations for wild blueberries from the 2019 EARMP study to blueberry results from Athabasca, Ontario, and the Grocery Store, the results were all within the same magnitude as the radionuclide and elemental results from this research, although this research study did not include the analysis of ^{232}Th activity in blueberries. In comparing the EARMP blueberry data to data obtained for blueberries from East and West Athabasca, the average activities for the three different sampling location from the EARMP study ranged between 0.002 to 0.00525 Bq/g dw for ^{210}Pb,

0.00086 to 0.0015 Bq/g dw for ^{210}Po, and 0.0005 to 0.00456 Bq/g dw for ^{226}Ra, which is comparable to the average activities of 0.00371 Bq/g dw for ^{210}Pb, 0.00342 Bq/g dw for ^{210}Po, and 0.00414 Bq/g dw for ^{226}Ra found in washed blueberries from East and West Athabasca. The radionuclide and elemental data for blueberries from this EARMP study shows the values obtained here are comparable to what was found in blueberries from Athabasca.

The data from this research was used to conservatively estimate an annual ingestion dose of 0.0079 mSv/a to an adult Indigenous consumer, which is significantly lower than the estimate of ingestion dose from natural background radiation of 0.3 mSv/a (Canadian Nuclear Safety Commission, 2020). The blueberry sample with the highest detectable ^{210}Po, ^{210}Pb, and ^{226}Ra activities was selected for this estimate since these radionuclides together contribute ~77% of the ingestion dose from food (IAEA, 2022). When compared to Athabasca blueberries, the Ontario blueberries and Grocery Store blueberries generally had lower detectable radionuclide activities with one or more ^{210}Po, ^{210}Pb, or ^{226}Ra values below detection and were thus not used to calculate a conservative ingestion dose estimate. This estimate was calculated using a washed blueberry sample from East Athabasca with the highest ^{210}Po, ^{210}Pb, and ^{226}Ra activities, the dose coefficients for each radionuclide from the International Commission on Radiological Protection (ICRP) 119 publication, a high blueberry consumption rate of 21.3 g of berries per day from a diet survey publication from Saskatchewan that detailed Indigenous diets from residents of the Boreal Shield ecozone (First Nations Food, Nutrition & Environment Study, 2023), which is in the same area as this blueberry sample was taken, a blueberry water content of 85% (Brown, 1995), and the following ICRP equation (ICRP, 2019):

$$\textit{Effective dose (mSv)} = \textit{intake (Bq)} \times \textit{dose coefficient (mSv/Bq)}$$

It is important to put into context the intake of metals of particular interest to human health from ingesting blueberries. For the ingestion of elements of importance to human health, guidance from the

Codex Alimentarius, International Food Standards and Health Canada was used. Se is an element that can be toxic if ingested in large quantities and the Government of Canada provides a tolerable upper intake level = 400 µg/day (total intake from food, water, and supplements) (Government of Canada, 2021). The highest Se concentration in washed blueberries was 0.02 µg/g dw. After converting this value to a fresh weight* of 0.00264 µg/g, it would require a person to consume an impossible serving of over 151,000 g of blueberries in a day to approach this maximum daily intake value for Se. The Codex Alimentarius is a partnership between the Food and Agriculture Organization of the United Nations and the World Health Organization that provides internationally adopted food standards, guidelines, and food safety information based on international experts and scientific research (Codex Alimentarius International Food Standards, 2019). In Table 2.21, all of the elements available in the Codex Alimentarius for maximum concentrations in foods are presented and compared to blueberry concentration data from Athabasca, Ontario, and Grocery Stores. In Table 2.22, all of the elements available in a Health Canada publication for tolerable daily intakes (Health Canada, 2006) are presented and compared to blueberry concentration data from Athabasca, Ontario, and Grocery Stores. For these daily intakes, a high consumer value of 21.3 g of berries per day was used (First Nations Food, Nutrition & Environment Study, 2023). The comparison of values in both tables show that concentrations measured in Athabasca, Ontario, and Grocery Store blueberries were all well below the maximum guidance values and ingestion of these blueberries does not pose a health concern.

*Concentration was converted to fresh weight. Using the IAEA dry matter content for wild blueberries of 13.2% (IAEA, 2010), the dw concentration was multiplied by 0.132 to convert to fresh weight.

Element	Maximum Concentration - East Athabasca Washed Blueberries, mg/kg fw*	Maximum Concentration - West Athabasca Washed Blueberries, mg/kg fw*	Maximum Concentration - Ontario Washed Blueberries, mg/kg fw*	Maximum Concentration – Grocery Store Washed Blueberries, mg/kg fw*	Codex Alimentarius – Maximum Concentration, mg/kg fw*
Cd	0.00025	0.00029	0.00095	0.00078	**0.05** (for fruiting vegetables)
Pb	0.00594	0.00037	0.00114	0.00370	**0.1** (for berries and other small fruit)

Table 2.21: Comparison of Elemental Concentrations in Washed Blueberries to the Codex Alimentarius – General Standard for Contaminants and Toxins in Food and Feed (Codex Alimentarius International Food Standards, 2019)

Notes:

-There were no guidance values in the Codex Alimentarius for Cd specifically for fruit or berries so the value for fruiting vegetables was used as the closest approximation to berries.

Element	Maximum Concentration - East Athabasca Washed Blueberries	Maximum Concentration - West Athabasca Washed Blueberries	Maximum Concentration - Ontario Washed Blueberries	Maximum Concentration – Grocery Store Washed Blueberries	Health Canada's Tolerable Upper Intake Levels (for 31 year old male)
Ca, mg/day	0.00027	0.00001	0.00013	0.00015	2500
Cu, µg/day	13.21452	13.77684	10.96524	14.058	10,000
Fe, mg/day	0.26429	0.44986	0.50609	0.64667	45
Mg, mg/day	0.00024	0.00024	0.00015	0.00014	350
Mn, mg/day	0.61855	1.71508	0.07872	0.08435	11
Mo, µg/day	0.87160	0.36551	0.14339	0.47797	2000
Ni, mg/day	0.00309	0.00264	0.00261	0.00110	1
Se, µg/day	0.03373	0.05623	0.02109	0.00506	400
V, mg/day	0.00003	0.00001	0.00001	0.00012	1.8
Zn, mg/day	0.01968	0.02587	0.01743	0.01968	40

Table 2.22: Comparison of Elemental Concentrations in Washed Blueberries to Health Canada's Tolerable Upper Intake Levels in the Dietary Reference Intakes Tables (Health Canada, 2006)

*Concentration was first converted to fresh weight using the IAEA dry matter content for wild blueberries of 13.2% (IAEA, 2010). The dry weight concentration was multiplied by 0.132 to convert to fresh weight. A high blueberry consumption rate of 21.3 g of berries per day was used from a diet survey publication from Saskatchewan that detailed Indigenous diets from residents of the Boreal Shield ecozone (First Nations Food, Nutrition & Environment Study, 2023). Fresh weight concentrations were multiplied by 21.3 g and were converted from µg, where needed, to mg values by dividing by 1000 to be able to compare with the units from the Health Canada tables. For example, converting the highest Ca value in East Athabasca blueberries: (0.096 µg/g x 0.132 x 21.3 g/day)/1000 = 0.00027 mg per day

2.6 CONCLUSIONS

This research is one of few berry studies that has analyzed both radionuclides and trace elements together to better understand plant uptake and the factors that influence this. There are distinct geochemical differences between the different sampling locations in this study, as was evident in analyzing the radionuclides and trace elements in blueberries, soil, and in the dust on the blueberries. It was found that the uptake of radionuclides and trace elements into plant tissues is primarily controlled by the plant's nutritional requirements for growth. The blueberries primarily obtained essential nutrients from the soil and obtained chemical analogues (both radionuclides and trace elements) in the absence of essential nutrients as substitutes. The uptake was influenced by soil factors including pH, which helped increase the solubility, mobility, and availability of radionuclides and trace elements. The radionuclide activities and elemental concentrations of interest in blueberries and soils were compared to other relevant research publications and it was generally found that the radionuclide activities and elemental concentration values for blueberries in this study were within the same magnitudes and ranges. Additionally, when compared to Canadian soil quality guidelines, none of the soil element concentrations in this research exceeded guidelines to pose any health concerns.

Overall, soils from Athabasca were depleted in some essential nutrients such as K and Ca. The concentrations of K in soil were below detection for all five West Athabasca samples and the East and Athabasca soils were orders of magnitude lower for Ca concentrations when compared to the Ontario soils. The depletion of K and Ca appears to have influenced the uptake of chemical analogues such as ^{137}Cs and ^{226}Ra, respectively, into blueberries and their acidic soils increased the solubility, mobility, and availability of radionuclides and trace elements for uptake. West Athabasca soils were especially depleted in essential nutrients and obtained ^{137}Cs as a chemical substitute for growth. Three of the five West Athabasca washed blueberry samples had detectable ^{137}Cs measurements which ranged between 0.008

and 0.027 Bq/g d.w, whereas there was only one other washed blueberry sample with a detectable ^{137}Cs activity concentration: a grocery store (Peru) blueberry sample, at 0.006 Bq/g d.w. East Athabasca soils showed elevated ^{238}U and ^{232}Th activities when compared to soils from the other sampling locations, which speaks to the distinct natural geochemistry of this area. The East Athabasca washed blueberry activity concentrations ranged between 2.53E-06 and 4.57E-05 Bq/g d.w. for ^{238}U and between 3.68E-07 and 1.15E-05 Bq/g d.w for ^{232}Th. The West Athabasca washed blueberries had one ^{238}U value above the detection limit which measured 3.76E-06 Bq/g d.w. for ^{238}U and ranged between 7.88E-07 and 1.93E-05 Bq/g d.w. for ^{232}Th. The distinctly higher concentrations of naturally occurring ^{238}U in East Athabasca soils (0.62-1.35 μg/g ^{238}U in East Athabasca soil vs 0.07-0.09 μg/g ^{238}U in West Athabasca soil) produces more ^{232}Th in the soil as a daughter nuclide of ^{238}U decay and results in naturally higher ^{238}U and ^{232}Th soil activities when compared to West Athabasca soils. This resulted in slightly higher ^{238}U activity in one East Athabasca blueberry sample (0.004 μg/g for ^{238}U). Overall, the Athabasca blueberries were efficient in obtaining essential nutrients for growth from the soil compartment and blueberries and soils did not have significantly elevated concentrations of potentially toxic trace elements when compared to other research, literature, and Canadian soil quality guidelines. Athabasca blueberries had the lowest concentrations of As and Cd (between 0.002-0.008 μg/g for As and between 0.0002-0.0022 μg/g for Cd) when compared to all blueberries analyzed in this study and were found to be good sources of dietary minerals such as Mg and Ca with concentrations as high as 856 μg/g for Mg and 1877 μg/g for Ca.

Generally, the soils and blueberries from Ontario blueberry farms showed evidence of the use of fertilizers and pesticides since the soils were elevated in many essential nutrients but were also elevated in some potentially toxic trace elements such as As, Se, Cd, Pb and U. This translated to blueberries that were among the best sources of dietary iron (21 μg/g Fe for Sarsfield, Ontario's washed blueberries) when compared to other samples in this research study but also to blueberries with slightly higher Cd concentrations (0.007 μg/g Cd for Sarsfield, Ontario's washed blueberries). Their acidic soils at the plant

roots influenced the uptake of metals and radionuclides into plant tissues by increasing the solubility, mobility, and availability of these elements. Despite the slightly elevated concentrations of potentially toxic trace elements found in the Ontario soils and blueberries, none of the Ontario sample measurement results exceeded Canadian guidelines or the ranges of values in literature publications for berry research.

Overall, grocery store blueberries also showed evidence of the use of fertilizers and pesticides with elevated concentrations of heavy metals such as As, Cd, and Pb and slightly elevated activity concentrations for ^{40}K. The highest values of As, Cd, and Pb measured in the grocery store washed blueberries were 0.067 µg/g, 0.006 µg/g, and 0.028 µg/g, respectively. Overall, these blueberry samples were good sources of essential minerals such as K, Mg, Ca, and Fe. Additionally, none of the blueberry measurement values for grocery store samples exceeded the ranges published in the literature for other berry research and values did not exceed Canadian guidelines.

An annual blueberry ingestion dose of 0.0079 mSv/a was estimated for an adult Indigenous consumer (high consumer), which is significantly lower than the estimate of ingestion dose from natural background radiation of 0.3 mSv/a (Canadian Nuclear Safety Commission, 2020). Additionally, the concentrations of elements of human health interest measured in blueberries were compared to Canadian dietary intake guidance values from Health Canada and international food safety guidance in the Codex Alimentarius. The radionuclide activities and elemental concentration data shows that blueberries from all sampling areas are safe to eat and can be good sources of dietary nutrients.

Finally, the differences in composition and mineralogy of soils from Athabasca and Ontario were explored to understand why these soils are distinct, why the soil compositions are reflected in the corresponding blueberry samples, and what are the potential sources of radionuclides and trace elements found in the blueberries. The solubility of minerals in soils was also explored to help determine the availability for uptake into plants. East Athabasca soil was found to be enriched in K, U, and Th as well as

in elements such as Ni, Co, As, Mo, Zn, and Fe. East Athabasca soil was distinct from West Athabasca soil and the West Athabasca soil was generally depleted in metals. The low pH of East Athabasca's soil (average pH of 4.56 for East Athabasca's soil vs average pH of 4.96 for West Athabasca's soil) also increased the solubility of metals. The soil in Eastern Ontario and the Ottawa Valley was distinct from Athabasca's soil due to its clay deposits and the higher amount of annual precipitation it receives. The dryer soils and low clay content of East Athabasca's soils helped to increase the solubility and availability of U for uptake into blueberries.

The objectives set out in this research study were met. The geochemical relationships between radionuclides and trace elements in blueberries were identified and discussed. By using the radionuclide activities and trace element concentrations together, a better understanding of the geochemical relationships surrounding plant uptake was possible. The cycling and environmental reservoirs of radionuclides and trace elements were explored and this information was valuable in analyzing and discussing the measurement data. The human health risk of blueberry consumption was conservatively estimated to be 0.0079 mSv/a and the blueberry and soil data was compared to Canadian and international guidelines as well as relevant literature studies. This information will be useful in communicating human health risk with Indigenous communities and the public and will help inform future regulatory decisions at the CNSC. Finally, this collaborative project helped build scientific relationships between Canadian scientists that could lead to fruitful future work.

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CHAPTER 3: CONCLUSIONS

Chapter 1, section 7 outlines the objectives of this thesis, which were to Identify geochemical relationships between radionuclides and trace elements in berries, explore the cycling and environmental reservoirs of radionuclides and trace elements, quantify human health risk through blueberry consumption, to help inform CNSC's regulatory decision-making process, and build future scientific networks through collaboration. Geochemical relationships between radionuclides and trace elements were identified in berries through examining the uptake of essential nutrients from soil and atmospheric deposition, identifying chemical analogues (both trace elements and radionuclides) for essential nutrients, and using soil characterization factors to explain uptake. The cycling and environmental reservoirs of radionuclides and trace elements were explored and summarized in this research from literature in Chapter 1, sections 1.4 and 1.5. The human health risk of ingesting blueberries from Athabasca were estimated in Chapter 2, section 2.3.4, and was found to be 0.0079 mSv/a, which is significantly lower than the annual public dose limit of 1 mSv/a. The information that resulted from this work will be used to help inform CNSC's regulatory decision-making process. Finally, this research collaboration has contributed to strengthening scientific networks to lead to future, fruitful work.

In summary, a better understanding of the geochemical relationships and interconnectivity between radionuclides and trace elements and the factors affecting uptake has resulted from this research and can be used to communicate that there does not appear to pose any human health risks in ingesting Indigenous traditional foods (blueberries) in the Athabasca area.

3.1 Future work

There remains to be many research opportunities for future studies that would benefit from considering both trace elements and radionuclides together since this research on blueberries and soil

has shown there are geochemical relationships between trace elements and radionuclides and there is an interconnectivity with respect to uptake. Soil factors and how they influence the uptake of radionuclides and elements would be a valuable study area. Additionally, there is much to be learned from continuing radionuclide activity and trace element concentration research in the area of Indigenous traditional foods in Canada since this information is a very important human health risk communication tool that can be used to inform the Canadian Federal Government's regulatory decision-making process.

APPENDIX – Additional Data Complimentary to Chapter 2

This addendum contains additional data that supports the information, results, and discussions presented in Chapter 2.

Concentration Ratios for Elements

Concentration ratios for washed:unwashed blueberries were calculated for each element (selected elements of interest were previously presented in Chapter 2) and the results for additional elements are presented in Tables A1-A4 below. The ratios are used to distinguish between the elemental input from atmospheric deposition on the blueberries and the input from soil uptake into the blueberries. The concentration ratios for washed:unwashed blueberries were calculated by dividing each elemental concentration in a washed blueberry sample by the corresponding elemental concentration in the unwashed blueberry sample. In cases where one of the values were below the MDL, the calculation was not performed. Overall, the blueberries from the grocery store (products of Peru and Argentina) had more dust inputs from elements when compared to blueberries from Ontario and Athabasca. The Peru blueberries, especially, had notable dust inputs from Al, K, Ga, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm, and Lu as well as a number of heavy metals previously discussed since the concentration ratios were considerably >1 and this points to the use of fertilizers and pesticides (P. C. Nagajyoti, 2010).

Transfer Factors for Elements

Tables A5-A8 below present data for soil to plant transfer factors for additional elements. Which provides the efficiency of the transfer of elements from the soil into the blueberries. This was determined by taking the elemental concentration in the washed blueberry (µg/g, dry weight) and dividing it by the

corresponding elemental concentration (μg/g, dry weight) in the soil. In cases where one of the values were below the MDL, the calculation was not performed. Overall, the plants were most efficient at transferring essential nutrients from the soil compartment into edible plant tissues, which is logical since plants predominantly obtain elements needed for growth from the soil (Napier, 2012), (Al-Masri, 2008) (Walther C. , 2015). The West Athabasca blueberries were notably efficient at transferring Rb from the soil into the blueberries. Rb is in the same group as K on the periodic table and shares similar chemical properties. Studies have shown that plants may uptake Rb as a chemical analogue for K, an essential plant nutrient (U. Drobner, 1998), and it appears that the West Athabasca have taken up Rb as a chemical analogue since their soils were quite depleted in K.

Soil Characterization – pH and Total Organic Carbon

Soil characterization work was done to help better explain the uptake of radionuclides and trace elements from the soil into plant tissues.

The soil pH results along with temperatures and QC data from the measurements are presented in Table A9. The US EPA's SW-846 Test Method 9045D: Soil and Waste pH procedure was followed to measure soil pH. The soils were acidic and has been shown to increase the uptake of some elements and radionuclides into plants by increasing solubility, mobility, and availability (P. C. Nagajyoti, 2010), (Greger, 2004).

Table A10 presents the Total Organic Carbon (TOC) data for all soils. The amount of organic carbon in soil can affect the immobilization of some radionuclides and elements (IAEA, 2014). It was found that the West Athabasca soils were depleted in TOC.

Decay Correcting Radionuclide Activities

Table A11-A13 presents the data for decay correcting radionuclide activities from the date of laboratory measurements back to the activities at the time of sampling. The following equation from IAEA was used to find A_0 for ^{137}Cs, ^{210}Pb, and ^{210}Po since these radionuclides have relatively short half-lives and their activities were affected by the elapsed time in between sampling and measurement (IAEA, 2014):

$$A = A_0 \times e^{-\lambda t}$$

Where A is the activity (in Bq);

Where A_o is the initial activity;

Where $\lambda = \ln 2 / T_{1/2}$ and $T_{1/2}$ is the radionuclide half-life (in seconds);

And where t is the time elapsed between sampling and analysis (in seconds)

The following half-life values for radionuclides were used in the decay correction calculations: ^{137}Cs, $T_{1/2}$ = 30.17 years (IAEA, 2014); ^{210}Pb, $T_{1/2}$ = 22.1 years (IAEA, 2014); and ^{210}Po, $T_{1/2}$ = 138 days (IAEA, 2014). Decay corrected values for these radionuclides were used to perform calculations throughout this research paper.

Elemental Analysis Using ICP-MS

The ICP-MS instrument parameters, settings, and standard reference material are presented in Tables A14-A28 for the elements analyzed at SWAMP labs.

The ICP-MS acquisition methods for blueberry and soil analysis conducted at the CNSC lab are presented in Tables A29-A36. Figures A9-A20 present the certificates of analysis for standard reference

materials NIST 1570a Trace Elements in Spinach Leaves and NIST 1566b Oyster Tissue that were used at the CNSC lab when analyzing trace elements in blueberries.

Food Ingestion and Effective Dose Calculation

The effective dose was calculated for an adult indigenous consumer (high consumer) and the data is found in Table A37. This was conservatively calculated using the following ICRP equation (ICRP, 2019):

Effective dose (mSv) = intake (Bq) × dose coefficient (mSv/Bq)

For each radionuclide, the effective dose was calculated with a blueberry intake of 21.3 g of berries per day (this high blueberry consumption rate is from a diet survey publication from Saskatchewan that detailed Indigenous diets from residents of the Boreal Shield ecozone (First Nations Food, Nutrition & Environment Study, 2023), which is in the same area as this blueberry sample was taken), using activities from a washed blueberry sample from East Athabasca with the highest ^{210}Po, ^{210}Pb, and ^{226}Ra activities (which together contribute ~77% of the ingestion dose from food) (IAEA, 2022), the dose coefficients for each radionuclide from the International Commission on Radiological Protection (ICRP) 119 publication, and a blueberry water content of 85% (Brown, 1995). The annual effective doses calculated for each radionuclide were summed and, to account for the blueberry water content, the sum was multiplied by 0.15 since these were dry weight activities used in the calculation and represent only 15% of the activity by weight. The annual effective dose of ingesting these blueberries was conservatively estimated to be 0.0072 mSv/a, which is significantly lower than the annual public dose limit of 1 mSv/a, and shows that consuming these berries does not pose a human health risk.

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Sample ID MDL	Li (µg/g) 0.0251	Be (µg/g) 0.0004	Mg (µg/g) 0.2405	Al (µg/g) 0.0654	K (µg/g) 1.5515	Ca (µg/g) 2.2204	V (µg/g) 0.001	Cr (µg/g) 0.0047	Mn (µg/g) 0.0019	Fe (µg/g) 0.0651	Co (µg/g) 0.0001	Ni (µg/g) 0.0052
East Atha Blueberry 01			0.82	1.31	0.83	0.96	0.94		0.86	0.93	0.98	1.00
East Atha Blueberry 02			0.99	0.81	1.12	1.05	0.67	0.66	0.85	0.97	0.78	0.90
East Atha Blueberry 03			0.96	0.86	0.97	0.94	1.00	0.85	1.18	1.10	0.96	0.88
West Atha Blueberry 01			1.11	0.98	0.97	1.14	1.12		0.99	1.09	0.96	1.17
West Atha Blueberry 02			1.08	1.15	0.96	0.99	0.78		1.16	1.03	0.99	0.91
West Atha Blueberry 03			1.03	1.05	0.97	1.12	0.70	1.69	0.90	1.07	1.84	1.22
West Atha Blueberry 04			1.31	1.33	1.11	1.36	0.67	0.25	0.93	1.20	1.37	1.20
West Atha Blueberry 05			1.08	1.06	0.90	1.11	0.95	1.21	0.95	1.04	0.76	0.97
Grocery Store Blueberry (Arg)	0.72		0.89	0.91	0.98	0.75	1.05	0.72	0.85	1.00	0.73	0.81
Grocery Store Blueberry (Peru)	0.93		0.93	0.52	0.07	0.96	0.44	0.65	0.85	0.43	0.93	0.89
Sarsfield, ON Blueberry	2.23		0.98	1.10	0.96	1.35	0.78	2.28	1.04	1.07	1.54	0.79
Pembroke, ON Blueberry			1.07	0.91	0.92	1.02	0.88	0.82	0.91	1.04	0.92	0.67
Mean East			**0.92**	**1.00**	**0.97**	**0.98**	**0.87**	**0.76**	**0.96**	**1.00**	**0.91**	**0.92**
Median East			**0.96**	**0.86**	**0.97**	**0.96**	**0.94**		**0.86**	**0.97**	**0.96**	**0.90**
Mean West			**1.12**	**1.11**	**0.98**	**1.15**	**0.84**	**1.05**	**0.99**	**1.08**	**1.19**	**1.09**
Median West			**1.08**	**1.06**	**0.97**	**1.12**	**0.78**	**1.21**	**0.95**	**1.07**	**0.99**	**1.17**
Mean Ontario	**0.82**		**1.03**	**1.01**	**0.94**	**1.18**	**0.83**	**1.55**	**0.98**	**1.06**	**1.23**	**0.73**
Median Ontario												
Mean Grocery Store			**0.91**	**0.71**	**0.52**	**0.86**	**0.75**	**0.69**	**0.85**	**0.71**	**0.83**	**0.85**
Median Grocery Store												

Table A1: Washed:Unwashed Blueberry Concentration Ratios for Li, Be, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, and Ni. Note: Where either the unwashed or washed blueberry sample was below the MDL, the ratio was not calculated.

Sample ID MDL	Cu (µg/g) 0.0039	Zn (µg/g) 0.0918	Ga (µg/g) 0.0014	As (µg/g) 0.2396	Se (µg/g) 0.2590	Rb (µg/g) 0.0029	Sr (µg/g) 0.0024	Y (µg/g) 0.0002	Mo (µg/g) 0.0008	Ag (µg/g) 0.0004	Cd (µg/g) 0.0004	Sb (µg/g) 0.0007
East Atha Blueberry 01	0.99	0.93	0.81	1.74	0.61	1.01	1.17		0.69		2.34	
East Atha Blueberry 02	0.99	0.99	0.64	1.49	0.72	0.81	0.64	0.63	1.20		2.41	0.93
East Atha Blueberry 03	1.09	1.02	9.36	1.30	0.91	0.99	0.70		1.25		0.51	
West Atha Blueberry 01	0.97	1.00	9.28	2.86	0.48	0.86	0.99	0.72	1.04		1.37	
West Atha Blueberry 02	0.98	1.04	2.99	3.51	1.02	0.97	0.77	0.87	1.67		5.86	
West Atha Blueberry 03	1.15	1.19	0.22	1.28	0.69	0.99	1.29	0.48	1.14		1.25	
West Atha Blueberry 04	1.13	1.11	0.63		1.58	1.02	1.59	0.54	0.77			
West Atha Blueberry 05	1.01	1.08	0.69	1.25	1.33	0.98	1.16	0.61	1.07		0.30	
Grocery Store Blueberry (Arg)	0.95	1.01		1.06	0.13	0.93	0.88	1.48	3.94		4.05	1.72
Grocery Store Blueberry (Peru)	0.89	0.69	0.25	0.69	1.14	0.71	1.02	0.46	1.02		0.60	0.72
Sarsfield, ON Blueberry	0.84	0.85		1.01		0.97	1.37	0.81			0.96	
Pembroke, ON Blueberry	1.03	1.10	0.29	0.81	2.11	1.16	1.15	0.86	0.23		0.33	
Mean East	**1.03**	**0.98**	**3.60**	**1.51**	**0.75**	**0.94**	**0.84**		**1.04**		**1.76**	
Median East	**0.99**	**0.99**	**0.81**	**1.49**	**0.72**	**0.99**	**0.70**		**1.20**		**2.34**	
Mean West	**1.05**	**1.09**	**2.76**	**2.23**	**1.02**	**0.96**	**1.16**	**0.64**	**1.14**		**2.20**	
Median West	**1.01**	**1.08**	**0.69**	**2.07**	**1.02**	**0.98**	**1.16**	**0.61**	**1.07**		**1.31**	
Mean Ontario	**0.93**	**0.97**		**0.91**		**1.06**	**1.26**	**0.84**			**0.65**	
Median Ontario												
Mean Grocery Store	**0.92**	**0.85**		**0.87**	**0.63**	**0.82**	**0.95**	**0.97**	**2.48**		**2.32**	**1.22**
Median Grocery Store												

Table A2: Washed:Unwashed Blueberry Concentration Ratios for Cu, Zn, Ga, As, Se, Rb, Sr, Y, Mo, Ag, Cd, and Sb. Note: Where either the unwashed or washed blueberry sample was below the MDL, the ratio was not calculated.

Sample ID	Cs (µg/g)	Ba (µg/g)	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (µg/g)	Dy (µg/g)	Ho (µg/g)
MDL	**0.0009**	**0.0040**	**0.0000**	**0.0001**	**0.0003**	**0.0001**	**0.0001**	**0.0000**	**0.0001**	**0.0001**	**0.0001**	**0.0000**
East Atha Blueberry 01	1.10	1.16	0.70	0.47	6.49	3.56		0.85				
East Atha Blueberry 02	0.73	0.72	0.68	0.65	0.65	0.81	0.77	0.80	0.73	0.59	0.52	0.65
East Atha Blueberry 03	1.04	1.02	0.88	0.65		6.06		0.76				
West Atha Blueberry 01	1.04	1.07	0.63	0.55	0.55	0.30	1.48	1.02	0.35	0.68	0.60	2.48
West Atha Blueberry 02	1.09	1.09	1.03	0.80	1.04	0.83	0.41	1.03	0.82			
West Atha Blueberry 03	1.25	0.94	0.42	0.52	0.28	0.21	0.24	0.82	0.23	0.22	0.41	0.41
West Atha Blueberry 04	0.85	0.99	1.25	1.18	1.29	0.98	1.12	0.90	0.70	0.36	1.29	0.81
West Atha Blueberry 05	1.41	1.13	1.29	1.32	1.41	0.88	1.80	1.55		1.58	2.02	
Grocery Store Blueberry (Arg)	2.53	0.91	1.58	1.74	1.92	1.65	1.59	1.95	2.66	1.49	1.85	2.07
Grocery Store Blueberry (Peru)	0.68	1.09	0.20	0.21	0.22	0.22	0.29	0.41	0.40	0.43	0.47	0.43
Sarsfield, ON Blueberry	1.59	1.55	1.20	1.02	2.63	1.14	1.28	1.29		1.12	0.54	0.93
Pembroke, ON Blueberry		1.04	0.22	0.23	0.24	0.29	0.50	0.62	0.77	0.53	0.05	0.90
Mean East	**0.95**	**0.97**	**0.75**	**0.59**	**3.57**	**3.48**		**0.80**				
Median East	**1.04**	**1.02**	**0.70**	**0.65**		**3.56**		**0.80**				
Mean West	**1.13**	**1.05**	**0.92**	**0.87**	**0.91**	**0.64**	**1.01**	**1.07**	**0.52**	**0.71**	**1.08**	**1.23**
Median West	**1.09**	**1.07**	**1.03**	**0.80**	**1.04**	**0.83**	**1.12**	**1.02**	**0.52**	**0.52**	**0.95**	**0.81**
Mean Ontario		**1.29**	**0.71**	**0.62**	**1.44**	**0.71**	**0.89**	**0.96**		**0.82**	**0.30**	**0.91**
Median Ontario												
Mean Grocery Store	**1.60**	**1.00**	**0.89**	**0.98**	**1.07**	**0.94**	**0.94**	**1.18**	**1.53**	**0.96**	**1.16**	**1.25**
Median Grocery Store												

Table A3: Washed:Unwashed Blueberry Concentration Ratios for Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho. Note: Where either the unwashed or washed blueberry sample was below the MDL, the ratio was not calculated.

Sample ID MDL	Er (µg/g) 0.0000	Tm (µg/g) 0.0000	Yb (µg/g) 0.0000	Lu (µg/g) 0.0000	W (µg/g) 0.0002	Re (µg/g) 0.0000	Tl (µg/g) 0.0001	Pb (µg/g) 0.0002	Th (µg/g) 0.0000	U (µg/g) 0.0000
East Atha Blueberry 01	2.22				2.16			0.00	0.99	
East Atha Blueberry 02	0.65	0.19	0.92	0.38	0.97	1.31	1.36	2.43	0.60	0.82
East Atha Blueberry 03					1.63		0.29	1.15	0.77	0.89
West Atha Blueberry 01	1.19	1.47	0.39		1.06		1.06	1.18	0.63	
West Atha Blueberry 02	1.44		1.10		0.72		0.17	0.76	0.66	
West Atha Blueberry 03	0.31	0.61			2.04		1.11	0.28	1.99	3.78
West Atha Blueberry 04	0.67		0.56	0.56	1.55	0.50	1.28	0.53	0.94	
West Atha Blueberry 05	0.92	0.46			3.20		2.99	0.81	1.45	
Grocery Store Blueberry (Arg)	2.12	5.75	2.08	1.17	1.06		0.53	2.67	2.16	1.25
Grocery Store Blueberry (Peru)	1.52	0.44	0.69	0.34	34.71			0.45	0.45	0.45
Sarsfield, ON Blueberry	0.72	1.13	1.62		0.20			2.02	1.14	
Pembroke, ON Blueberry	0.74	0.95	0.90	0.76	2.65			0.91	0.86	0.83
Mean East	**1.43**				**1.59**		**0.82**	**1.19**	**0.79**	**0.85**
Median East					**1.63**			**1.15**	**0.77**	
Mean West	**0.91**	**0.85**	**0.68**		**1.71**		**1.32**	**0.71**	**1.13**	
Median West	**0.92**	**0.61**	**0.56**		**1.55**		**1.11**	**0.76**	**0.94**	
Mean Ontario	**0.73**	**1.04**	**1.26**		**1.42**			**1.47**	**1.00**	
Median Ontario										
Mean Grocery Store	**1.82**	**3.09**	**1.39**	**0.75**	**17.89**			**1.56**	**1.31**	**0.85**
Median Grocery Store										

Table A4: Washed:Unwashed Blueberry Concentration Ratios for Er, Tm, Yb, Lu, W, Re, Tl, Pb, Th, and U. Note: Where either the unwashed or washed blueberry sample was below the MDL, the ratio was not calculated.

Sample ID	Li (µg/g)	Be (µg/g)	Mg (µg/g)	Al (µg/g)	K (µg/g)	Ca (µg/g)	V (µg/g)	Cr (µg/g)	Mn (µg/g)	Fe (µg/g)	Co (µg/g)	Ni (µg/g)
MDL	**0.0251**	**0.0004**	**0.2405**	**0.0654**	**1.5515**	**2.2204**	**0.0011**	**0.0047**	**0.0019**	**0.0651**	**0.0001**	**0.0052**
East Atha Blueberry 01			0.68	1.0E-03	11.09	1.99	5.0E-05		4.75	2.0E-03	0.02	0.39
East Atha Blueberry 02			2.14	3.2E-03	77.31	13.42	1.5E-03	1.9E-03	10.95	4.8E-03	0.07	0.64
East Atha Blueberry 03			1.51	1.8E-03	28.41	3.84	1.5E-04	1.4E-03	7.82	3.0E-03	0.04	0.81
West Atha Blueberry 01			26.82	0.02		32.22	2.7E-03		64.84	0.03	0.07	2.96
West Atha Blueberry 02			45.95	0.02		72.58	2.2E-03	4.8E-03	72.51	0.03	0.08	2.04
West Atha Blueberry 03			28.44	0.04		77.20	0.01	0.03	61.30	0.07	0.18	3.10
West Atha Blueberry 04			103.37	0.04		1032.27	5.0E-03	0.02	83.13	0.08	0.17	5.66
West Atha Blueberry 05			60.76	0.02		65.42	5.6E-03	0.01	139.16	0.08	0.19	2.59
Sarsfield, ON Blueberry	0.01		0.46	1.8E-03	15.33	0.47	1.4E-04	4.8E-04	0.08	1.5E-03	0.01	0.17
Pembroke, ON Blueberry			0.11	1.3E-03	3.61	0.09	6.8E-04	1.8E-03	0.04	1.2E-03	9.7E-04	0.03
Mean East			**1.44**	**0.00**	**38.94**	**6.42**	**0.00**	**0.00**	**7.84**	**0.00**	**0.05**	**0.61**
Median East			**1.51**	**0.00**	**28.41**	**3.84**	**0.00**		**7.82**	**0.00**	**0.04**	**0.64**
Mean West			**53.06**	**0.03**		**255.94**	**0.00**	**0.01**	**84.19**	**0.06**	**0.14**	**3.27**
Median West			**45.95**	**0.02**		**72.58**	**0.00**	**0.01**	**72.51**	**0.07**	**0.17**	**2.96**
Mean Ontario			**0.29**	**0.00**	**9.47**	**0.28**	**0.00**	**0.00**	**0.06**	**0.00**	**0.01**	**0.10**
Median Ontario												

Table A5: Soil to Plant Transfer Factors for elements Li, Be, Mg, Al, K, Ca, V, Cr, Mn, Fe, Co, and Ni. Washed blueberry elemental concentrations/soil elemental concentrations.

Sample ID	Cu (µg/g)	Zn (µg/g)	Ga (µg/g)	As (µg/g)	Se (µg/g)	Rb (µg/g)	Sr (µg/g)	Y (µg/g)	Mo (µg/g)	Ag (µg/g)	Cd (µg/g)	Sb (µg/g)
MDL	**0.00392**	**0.09178**	**0.00135**	**0.23960**	**0.25860**	**0.00292**	**0.00236**	**0.00024**	**0.00076**	**0.00044**	**0.00037**	**0.00065**
East Atha Blueberry 01	0.48	0.91	2.6E-04	0.01	0.05	2.10	0.20		0.63		0.05	
East Atha Blueberry 02	4.33	3.29	9.1E-04	0.01		9.36	0.12	1.1E-03	7.55		0.07	0.19
East Atha Blueberry 03	1.58	2.25	5.7E-04	0.01		3.01	0.66		1.28		0.07	
West Atha Blueberry 01	18.41	9.95	8.6E-03	0.03		30.80	0.06	3.9E-04	11.14		0.63	
West Atha Blueberry 02	3.92	10.95	4.0E-03	0.01		45.53	0.09	6.3E-04	6.67		0.17	
West Atha Blueberry 03	13.32	11.07	2.8E-03	0.01		42.07	0.15	1.4E-03	5.09		0.14	
West Atha Blueberry 04	26.95	22.31	0.01	0.03		51.79	0.52	2.7E-04	2.51		0.04	
West Atha Blueberry 05	40.90	6.79	2.2E-03	0.03		73.01	0.20	3.8E-04	11.86		0.13	
Sarsfield, ON Blueberry	0.48	0.32		0.01	3.0E-03	0.78	0.03	1.7E-04			0.08	
Pembroke, ON Blueberry	0.50	0.10	4.1E-04	2.4E-03	0.06	0.30	0.04	6.6E-04	0.40		0.01	
Mean East	**2.13**	**2.15**	**0.00**	**0.01**		**4.82**	**0.33**		**3.15**		**0.06**	
Median East	**1.58**	**2.25**	**0.00**	**0.01**		**3.01**	**0.20**		**1.28**		**0.07**	
Mean West	**20.70**	**12.21**	**0.01**	**0.02**		**48.64**	**0.20**	**0.00**	**7.45**		**0.22**	
Median West	**18.41**	**10.95**	**0.00**	**0.03**		**45.53**	**0.15**	**0.00**	**6.67**		**0.14**	
Mean Ontario	**0.49**	**0.21**		**0.01**	**0.03**	**0.54**	**0.03**	**0.00**			**0.04**	
Median Ontario												

Table A6: Soil to Plant Transfer Factors for elements Cu, Zn, Ga, As, Se, Rb, Sr, Y, Mo, Ag, Cd, and Sb. Washed blueberry elemental concentrations/soil elemental concentrations.

Sample ID	Cs (µg/g)	Ba (µg/g)	La (µg/g)	Ce (µg/g)	Pr (µg/g)	Nd (µg/g)	Sm (µg/g)	Eu (µg/g)	Gd (µg/g)	Tb (µg/g)	Dy (µg/g)	Ho (µg/g)
MDL	**0.00087**	**0.00404**	**0.00004**	**0.00008**	**0.00025**	**0.00009**	**0.00007**	**0.00002**	**0.00010**	**0.00006**	**0.00009**	**0.00002**
East Atha Blueberry 01	0.03	0.57	1.7E-05	1.0E-05	6.5E-05	1.9E-05		1.6E-03				
East Atha Blueberry 02	0.19	1.33	5.8E-04	5.4E-04	5.7E-04	6.7E-04	5.1E-04	0.01	8.0E-04	1.1E-03	9.9E-04	6.2E-04
East Atha Blueberry 03	0.03	2.03	2.8E-05	2.2E-05		2.4E-05		3.2E-03		9.4E-05		
West Atha Blueberry 01	0.62	3.88	4.1E-04	3.0E-04	2.6E-04	1.5E-04	5.6E-04	0.01	2.3E-04	2.6E-04	5.9E-04	4.6E-04
West Atha Blueberry 02	1.41	3.20	3.5E-04	2.9E-04	2.8E-04	2.5E-04	2.7E-04	0.01	2.3E-04		8.0E-05	4.5E-04
West Atha Blueberry 03	1.21	3.23	2.0E-03	1.8E-03	1.8E-03	1.6E-03	2.4E-03	0.01	1.5E-03	1.1E-03	9.8E-04	9.6E-04
West Atha Blueberry 04	4.36	5.01	3.2E-04	2.5E-04	4.0E-04	2.8E-04	2.4E-04	0.01	3.0E-04	6.6E-04	7.7E-04	1.1E-03
West Atha Blueberry 05	6.09	4.51	3.9E-04	3.5E-04	2.6E-04	3.7E-04	3.8E-04	0.01	3.7E-04	2.7E-04	9.2E-04	
Sarsfield, ON Blueberry	0.01	0.07	1.5E-04	9.4E-05	1.1E-04	1.0E-04	1.2E-04	1.5E-04		2.2E-04	6.1E-05	7.1E-05
Pembroke, ON Blueberry		0.04	5.0E-04	4.7E-04	5.0E-04	4.8E-04	6.1E-04	6.9E-04	6.4E-04	4.7E-04	5.1E-04	5.4E-04
Mean East	**0.08**	**1.31**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**		**0.00**		
Median East	**0.03**	**1.33**	**0.00**	**0.00**		**0.00**		**0.00**				
Mean West	**2.74**	**3.96**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**
Median West	**1.41**	**3.88**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.01**	**0.00**	**0.00**	**0.00**	**0.00**
Mean Ontario		**0.06**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**	**0.00**		**0.00**	**0.00**	**0.00**
Median Ontario												

Table A7: Soil to Plant Transfer Factors for elements Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, and Ho. Washed blueberry elemental concentrations/soil elemental concentrations.

Sample ID	Er (µg/g)	Tm (µg/g)	Yb (µg/g)	Lu (µg/g)	W (µg/g)	Re (µg/g)	Tl (µg/g)	Pb (µg/g)	Th (µg/g)	U (µg/g)
MDL	**0.0000**	**0.0000**	**0.0000**	**0.0000**	**0.0002**	**0.0000**	**0.0001**	**0.0002**	**0.0000**	**0.0000**
East Atha Blueberry 01	1.0E-04			1.3E-04	0.17			1.2E-09	9.9E-06	
East Atha Blueberry 02	1.0E-03	5.2E-04	1.2E-03	3.8E-04	0.57	0.30	0.02	1.2E-02	5.3E-04	0.01
East Atha Blueberry 03					0.02		0.10	8.9E-04	9.9E-06	1.7E-04
West Atha Blueberry 01	5.5E-04	6.6E-04	3.1E-04		0.06		2.01	2.3E-03	3.0E-04	
West Atha Blueberry 02	5.5E-04	5.3E-04	1.4E-06		0.24		0.18	2.8E-03	3.5E-04	
West Atha Blueberry 03	3.5E-04	8.9E-04		9.8E-04	0.61		0.14	2.6E-03	0.01	4.5E-03
West Atha Blueberry 04	7.2E-04		4.5E-04	6.4E-04	0.05	7.57	2.69	1.5E-03	3.2E-04	
West Atha Blueberry 05	5.7E-04	5.5E-04		5.5E-04	0.26		0.88	2.7E-03	4.8E-04	
Sarsfield, ON Blueberry	1.0E-04	2.0E-04	1.8E-04		0.01			5.3E-04	6.5E-05	
Pembroke, ON Blueberry	5.1E-04	6.6E-04	5.7E-04	5.9E-04	0.02			8.1E-04	3.5E-04	1.4E-04
Mean East	**0.00**			**0.00**	**0.26**		**0.06**	**0.00**	**0.00**	
Median East					**0.17**			**0.00**	**0.00**	
Mean West	**0.00**	**0.00**	**0.00**	**0.00**	**0.24**		**1.18**	**0.00**	**0.00**	
Median West	**0.00**	**0.00**	**0.00**	**0.00**	**0.24**		**0.88**	**0.00**	**0.00**	
Mean Ontario	**0.00**	**0.00**	**0.00**		**0.01**			**0.00**	**0.00**	
Median Ontario										

Table A8: Soil to Plant Transfer Factors for elements Er, Tm, Yb, Lu, W, Re, Tl, Pb, Th, and U. Washed blueberry elemental concentrations/soil elemental concentrations.

Sample ID	Mass Fresh Soil (g)	Vol deionized H20 Added (mL)	pH 1	Temp 1, C	pH 2	Temp 2, C	pH 3	Temp 3, C	pH 4	Temp 4, C	Avg pH
West Atha 01	20.0024	20	4.97	19.8	4.87	19.8	4.86	19.8	4.82	19.8	4.85
West Atha 02	20.0518	20	5.19	20.3	5.16	20.4	5.14	20.7			5.16
West Atha 03	20.0176	20	5.56	19.5	5.44	19.8	5.41	20.0	5.41	20.2	5.42
West Atha 04	20.0128	20	4.49	19.8	4.35	20.1	4.37	20.2	4.39	20.3	4.37
West Atha 05	20.0205	20	5.03	20.3	5.02	20.3	4.99	20.3			5.01
QC Sample pH 4			4.01	20.9	4.03	20.8	4.04	20.8			
QC Sample pH 7			7.04	20.9	7.02	20.9	7.02	20.8			
East Atha 01	20.0146	20	4.70	20.1	4.68	20.2	4.67	20.3			4.68
East Atha 02	20.0183	20	4.29	19.5	4.26	19.7	4.28	19.8			4.28
East Atha 03	20.0404	20	4.70	19.5	4.71	19.7	4.71	19.8			4.71
Pembroke, ON Soil	20.0113	20	6.59	19.8	6.59	19.8	6.62	19.9			6.60
Sarsfield, ON Soil	20.0033	20	3.81	20.1	3.83	20.1	3.83	20.1			3.82
QC Sample pH 4			4.03	20.8	4.04	20.8	4.04	20.8			
QC Sample pH 7			7.01	20.9	7.02	20.9	7.02	20.8			

QC Buffer 4	Lot # 212704	Expiry Date: 05/2023
QC Buffer 7	Lot # 215003	Expiry Date: 07/2023

Table A9: Soil pH results.

Sample ID	Mass Dry Soil for TC Measurement (mg)	Total Carbon (mg)	Mass Dry Soil for IC Measurement (mg)	Inorganic Carbon (mg)	Total Organic Carbon (mg)	Total Organic Carbon (Mass %)	Notes
Sarsfield, ON Soil	114.2	5.7480	86.90	0.0000	0.0400	3.9985	
Sarsfield, ON Soil duplicate	102	3.0230	n/a	n/a	n/a	n/a	
Pembroke, ON Soil	102.1	5.5020	105.30	0.0074	0.0538	5.3818	
East Atha 01 Soil	115.6	2.2560	84.50	0.0000	0.0195	1.9516	
East Atha 02 Soil	118.6	0.8969	88.70	0.0028	0.0075	0.7530	
East Atha 03 Soil	80.1	0.4551	90.10	0.0137	0.0055	0.5530	
West Atha 01 Soil	119.2	n/a					negative TC value, did not proceed further
West Atha 02 Soil	116	n/a					negative TC value, did not proceed further
West Atha 03 Soil	95.6	n/a					negative TC value, did not proceed further
West Atha 04 Soil	102	n/a					negative TC value, did not proceed further
West Atha 05 Soil	96.4	n/a					negative TC value, did not proceed further

Table A10: Total Organic Carbon in Soil Measurements.

Sample ID	Activity Bq/g	Number of Days from Sampling to Analysis	Decay-Corrected Activity Bq/g
Estn Atha Blueberry 01 Unwashed	<MDL	117	
Estn Atha Blueberry 01 Washed	<MDL	119	
Estn Atha Soil 1	0.004	126	0.00403
Estn Atha Blueberry 02 Unwashed	0.009	113	0.00906
Estn Atha Blueberry 02 Washed	<MDL	115	
Estn Atha Soil 2	0.006	122	0.00605
Estn Atha Blueberry 03 Unwashed	0.008	113	0.00806
Estn Atha Blueberry 03 Washed	<MDL	116	
Estn Atha Soil 3	0.004	122	0.00403
Wstn Atha Blueberry 01 Unwashed	0.008	153	0.00808
Wstn Atha Blueberry 01 Washed	<MDL	155	
Wstn Atha Soil 1	0.004	160	0.00404
Wstn Atha Blueberry 02 Unwashed	0.008	133	0.00807
Wstn Atha Blueberry 02 Washed	0.008	135	0.00807
Wstn Atha Soil 2	0.003	140	0.00303
Wstn Atha Blueberry 03 Unwashed	0.006	133	0.00605
Wstn Atha Blueberry 03 Washed	<MDL	135	
Wstn Atha Soil 3	0.003	140	0.00303
Wstn Atha Blueberry 04 Unwashed	0.029	133	0.02924
Wstn Atha Blueberry 04 Washed	0.027	135	0.02723
Wstn Atha Soil 4	0.003	140	0.00303
Wstn Atha Blueberry 05 Unwashed	<MDL	133	
Wstn Atha Blueberry 05 Washed	0.025	137	0.02522
Wstn Atha Soil 5	<MDL	140	
Groc store Blueberry (Arg) Unwashed	<MDL	62	
Groc store Blueberry (Arg) Washed	<MDL	66	
Groc store Blueberry (Peru) Unwashed	<MDL	64	
Groc store Blueberry (Peru) Washed	0.006	67	0.00603
Sarsfield, ON Blueberry Unwashed	<MDL	153	
Sarsfield, ON Blueberry Washed	<MDL	156	
Sarsfield, ON Soil	0.004	160	0.00404
Pembroke, ON Blueberry Unwashed	<MDL	154	
Pembroke, ON Blueberry Washed	<MDL	155	
Pembroke, ON Soil	0.007	161	0.00707

Table A11: Decay Correcting Activities for ^{137}Cs.

Sample ID	Activity Bq/g	Number of Days from Sampling to Analysis	Decay-Corrected Activity Bq/g
Estn Atha Blueberry 01 Unwashed	0.003	126	0.00303
Estn Atha Blueberry 01 Washed	0.003	126	0.00303
Estn Atha Soil 1	<MDL	125	
Estn Atha Blueberry 02 Unwashed	0.004	122	0.00404
Estn Atha Blueberry 02 Washed	0.004	122	0.00404
Estn Atha Soil 2	0.04	121	0.04042
Estn Atha Blueberry 03 Unwashed	0.004	122	0.00404
Estn Atha Blueberry 03 Washed	0.003	122	0.00303
Estn Atha Soil 3	<MDL	121	
Wstn Atha Blueberry 01 Unwashed	<MDL	161	
Wstn Atha Blueberry 01 Washed	0.003	162	0.00304
Wstn Atha Soil 1	<MDL	160	
Wstn Atha Blueberry 02 Unwashed	0.004	141	0.00402
Wstn Atha Blueberry 02 Washed	0.004	142	0.00405
Wstn Atha Soil 2	<MDL	140	
Wstn Atha Blueberry 03 Unwashed	<MDL	141	
Wstn Atha Blueberry 03 Washed	0.005	142	0.00506
Wstn Atha Soil 3	<MDL	140	
Wstn Atha Blueberry 04 Unwashed	<MDL	141	
Wstn Atha Blueberry 04 Washed	<MDL	142	
Wstn Atha Soil 4	<MDL	140	
Wstn Atha Blueberry 05 Unwashed	<MDL	141	
Wstn Atha Blueberry 05 Washed	<MDL	142	
Wstn Atha Soil 5	<MDL	140	
Groc store Blueberry (Arg) Unwashed	0.004	70	0.00402
Groc store Blueberry (Arg) Washed	<MDL	71	
Groc store Blueberry (Peru) Unwashed	<MDL	71	
Groc store Blueberry (Peru) Washed	0.004	72	0.00402
Sarsfield, ON Blueberry Unwashed	<MDL	160	
Sarsfield, ON Blueberry Washed	<MDL	161	
Sarsfield, ON Soil	0.06	159	0.06083
Pembroke, ON Blueberry Unwashed	<MDL	161	
Pembroke, ON Blueberry Washed	<MDL	162	
Pembroke, ON Soil	<MDL	160	

Table A12: Decay Correcting Activities for ^{210}Pb.

Sample ID	Activity Bq/g	Number of Days from Sampling to Analysis	Decay-Corrected Activity Bq/g
Estn Atha Blueberry 01 Unwashed	0.001	125	0.00187
Estn Atha Blueberry 01 Washed	0.003	125	0.00562
Estn Atha Soil 1	0.04	123	0.07419
Estn Atha Blueberry 02 Unwashed	0.003	121	0.00551
Estn Atha Blueberry 02 Washed	0.002	121	0.00367
Estn Atha Soil 2	0.02	119	0.03636
Estn Atha Blueberry 03 Unwashed	0.002	121	0.00367
Estn Atha Blueberry 03 Washed	0.002	121	0.00367
Estn Atha Soil 3	0.02	119	0.03636
Wstn Atha Blueberry 01 Unwashed	0.001	160	0.00223
Wstn Atha Blueberry 01 Washed	0.001	160	0.00223
Wstn Atha Soil 1	<MDL	158	
Wstn Atha Blueberry 02 Unwashed	0.001	140	0.00202
Wstn Atha Blueberry 02 Washed	0.001	140	0.00202
Wstn Atha Soil 2	0.01	138	0.02000
Wstn Atha Blueberry 03 Unwashed	0.001	140	0.00202
Wstn Atha Blueberry 03 Washed	0.002	140	0.00404
Wstn Atha Soil 3	<MDL	138	
Wstn Atha Blueberry 04 Unwashed	0.002	140	0.00404
Wstn Atha Blueberry 04 Washed	0.002	140	0.00404
Wstn Atha Soil 4	<MDL	138	
Wstn Atha Blueberry 05 Unwashed	0.0009	140	0.00182
Wstn Atha Blueberry 05 Washed	0.001	140	0.00202
Wstn Atha Soil 5	0.01	126	0.01883
Groc store Blueberry (Arg) Unwashed	0.001	69	0.00141
Groc store Blueberry (Arg) Washed	0.0008	69	0.00113
Groc store Blueberry (Peru) Unwashed	<MDL	70	
Groc store Blueberry (Peru) Washed	0.0007	70	0.00099
Sarsfield, ON Blueberry Unwashed	0.0007	159	0.00156
Sarsfield, ON Blueberry Washed	0.0005	159	0.00111
Sarsfield, ON Soil	0.10	157	0.22003
Pembroke, ON Blueberry Unwashed	0.0006	160	0.00134
Pembroke, ON Blueberry Washed	<MDL	160	
Pembroke, ON Soil	0.05	158	0.11057

Table A13: Decay Correcting Activities for ^{210}Po.

Instrument Parameter (Thermo iCAP Qc)	Setting
Spray Chamber Temperature	2.7 ˚C
Peristaltic Pump Speed	40 RPM
Cool Flow	14 L/min
Plasma Power	1550 W
Auxilliary Flow	0.8 L/min
Nebulizer Flow	1.03 L/min
He (Collision Cell) Gas Flow	5 mL/min
Sweeps per run	40
Runs per sample*	3

Table A14: ICP-MS Instrument Parameters.

*The reported sample concentration is the average value of the 3 main runs

Isotope	Acquisition Mode	Internal Standard
7Li	Collision Gas (He)	115In
9Be	Standard Mode	115In
27Al	Collision Gas (He)	115In
51V	Collision Gas (He)	115In
52Cr	Collision Gas (He)	115In
55Mn	Collision Gas (He)	115In
57Fe	Collision Gas (He)	115In
59Co	Collision Gas (He)	115In
60Ni	Collision Gas (He)	115In
63Cu	Collision Gas (He)	115In
66Zn	Collision Gas (He)	115In
71Ga	Collision Gas (He)	115In
75As	Collision Gas (He)	115In
78Se	Collision Gas (He)	115In
85Rb	Collision Gas (He)	115In
88Sr	Collision Gas (He)	115In
89Y	Collision Gas (He)	115In
95Mo	Collision Gas (He)	115In
107Ag	Collision Gas (He)	115In
111Cd	Collision Gas (He)	115In
121Sb	Collision Gas (He)	115In
133Cs	Collision Gas (He)	115In - 209Bi Interpolation
137Ba	Collision Gas (He)	115In - 209Bi Interpolation
139La	Collision Gas (He)	115In - 209Bi Interpolation
140Ce	Collision Gas (He)	115In - 209Bi Interpolation
141Pr	Collision Gas (He)	115In - 209Bi Interpolation
146Nd	Collision Gas (He)	115In - 209Bi Interpolation
147Sm	Collision Gas (He)	115In - 209Bi Interpolation

153Eu	Collision Gas (He)	115In - 209Bi Interpolation
157Gd	Collision Gas (He)	115In - 209Bi Interpolation
159Tb	Collision Gas (He)	115In - 209Bi Interpolation
163Dy	Collision Gas (He)	115In - 209Bi Interpolation
165Ho	Collision Gas (He)	115In - 209Bi Interpolation
166Er	Collision Gas (He)	115In - 209Bi Interpolation
169Tm	Collision Gas (He)	115In - 209Bi Interpolation
172Yb	Collision Gas (He)	115In - 209Bi Interpolation
175Lu	Collision Gas (He)	115In - 209Bi Interpolation
182W	Collision Gas (He)	115In - 209Bi Interpolation
185Re	Collision Gas (He)	115In - 209Bi Interpolation
205Tl	Collision Gas (He)	209Bi
208Pb	Collision Gas (He)	209Bi
232Th	Collision Gas (He)	209Bi
238U	Collision Gas (He)	209Bi

Table A15: ICP-MS Instrument Settings.

NIST 1640a - Elements in Natural Surface Water											
Certified Reference Material	7Li ug/L	9Be ug/L	27Al ug/L	51V ug/L	52Cr ug/L	55Mn ug/L	57Fe ug/L	59Co ug/L	60Ni ug/L	63Cu ug/L	66Zn ug/L
*Certified values (ug/L)**	0.41	3.03	53.00	15.10	40.50	40.40	36.80	20.20	25.30	86.00	55.60
SD	0.01	0.03	1.80	0.25	0.30	0.36	1.80	0.24	0.14	0.51	0.35
Instrument LOD (ug/L)	0.013	0.00	0.03	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.05
1:10 Dilution Factor											
Average Concentration (n = 8)	0.40	2.95	59.77	14.05	37.99	38.00	41.93	19.05	23.92	83.74	52.89
SD	0.06	0.41	6.63	0.95	2.24	3.10	3.10	0.73	0.77	2.16	2.41
RSD	15	14	11	7	6	8	7	4	3	3	5
Accuracy (%)	98	97	113	93	94	94	114	94	95	97	95
1:100 Dilution Factor											
Average Concentration (n = 8)	< LOD	3.244	61.688	14.513	39.200	39.648	43.158	19.577	25.071	86.351	57.638
SD		0.49	7.81	1.02	2.43	3.39	4.95	0.77	1.56	2.16	4.43
RSD		15	13	7	6	9	11	4	6	3	8
Accuracy (%)	243	107	116	96	97	98	117	97	99	100	104

Table A16: Standard Reference Material Analysis for Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn - NIST 1640a Elements in Natural Surface Water for ICP-MS.

NIST 1640a - Elements in Natural Surface Water											
Certified Reference Material	71Ga ug/L	85Rb ug/L	88Sr ug/L	89Y ug/L	95Mo ug/L	107Ag ug/L	111Cd ug/L	121Sb ug/L	133Cs ug/L	137Ba ug/L	139La ug/L
*Certified values (ug/L)**		1.19	126.00		45.60	8.08	3.99	5.11		151.80	
SD		0.10	0.91		0.61	0.05	0.07	0.05		0.83	
Instrument LOD (ug/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1:10 Dilution Factor											
Average Concentration (n = 8)		1.13	122.82		43.54	7.47	3.80	5.37		163.96	
SD		0.04	6.34		0.43	0.12	0.04	0.18		2.62	
RSD		4	5		1	2	1	3		2	
Accuracy (%)		95	97		95	92	95	105		108	
1:100 Dilution Factor											
Average Concentration (n = 8)		1.259	126.127		45.786	7.796	4.019	5.592		168.881	
SD		0.21	7.35		0.64	0.16	0.23	0.24		2.78	
RSD		17	6		1	2	6	4		2	
Accuracy (%)		106	100		100	96	101	110		111	

Table A17: Standard Reference Material Analysis for Ga, Rb, Sr, Y, Mo, Ag, Cd, Sb, Cs, Ba, and La - NIST 1640a Elements in Natural Surface Water for ICP-MS.

NIST 1640a - Elements in Natural Surface Water											
Certified Reference Material	140Ce ug/L	141Pr ug/L	146Nd ug/L	147Sm ug/L	153Eu ug/L	157Gd ug/L	159Tb ug/L	163Dy ug/L	165Ho ug/L	166Er ug/L	169Tm ug/L
*Certified values (ug/L)**											
SD											
Instrument LOD (ug/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1:10 Dilution Factor											
Average Concentration (n = 8)											
SD											
RSD											
Accuracy (%)											
1:100 Dilution Factor											
Average Concentration (n = 8)											
SD											
RSD											
Accuracy (%)											

Table A18: Standard Reference Material Analysis for Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm - NIST 1640a Elements in Natural Surface Water for ICP-MS.

NIST 1640a - Elements in Natural Surface Water								
Certified Reference Material	172Yb ug/L	175Lu ug/L	182W ug/L	185Re ug/L	205Tl ug/L	208Pb ug/L	232Th ug/L	238U ug/L
*Certified values (ug/L)**					1.619	12.10		25.35
SD					0.02	0.05		0.27
Instrument LOD (ug/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1:10 Dilution Factor								
Average Concentration (n = 8)					1.56	11.50		22.59
SD					0.03	0.21		0.49
RSD					2	2		2
Accuracy (%)					97	95		89
1:100 Dilution Factor								
Average Concentration (n = 8)					1.621	12.102		23.525
SD					0.02	0.62		0.27
RSD					1	5		1
Accuracy (%)					100	100		93

Table A19: Standard Reference Material Analysis for Yb, Lu, W, Re, Tl, Pb, Th, and U - NIST 1640a Elements in Natural Surface Water for ICP-MS.

SPS-SW2 Elements in Surface Water											
Certified Reference Material	7Li	9Be	27Al	51V	52Cr	55Mn	57Fe	59Co	60Ni	63Cu	66Zn
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Certified values (ug/L)			250.00	50.00	10.00	50.00	100.00	10.00	50.00	100.00	100.00
SD			1.00	0.30	0.05	0.30	1.00	0.05	0.30	1.00	1.00
Instrument LOD (ug/L)	0.013	0.00	0.03	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.05
1:100 Dilution Factor											
Average Concentration (n = 8)			255.27	45.07	9.06	46.30	107.01	9.22	47.13	95.30	94.20
SD			33.73	3.30	0.57	3.89	11.26	0.55	1.95	4.60	5.55
RSD			13	7	6	8	11	6	4	5	6
Accuracy (%)			102	90	91	93	107	92	94	95	94
1:500 Dilution Factor											
Average Concentration (n = 8)			253.84	47.37	9.43	51.08	125.96	9.61	52.38	96.11	99.40
SD			40.13	3.21	0.89	3.05	25.23	0.60	7.34	3.52	14.91
RSD			16	7	9	6	20	6	14	4	15
Accuracy (%)			102	95	94	102	126	96	105	96	99

Table A20: Standard Reference Material Analysis for Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn – SPS-SW2 Elements in Surface Water for ICP-MS.

SPS-SW2 Elements in Surface Water											
Certified Reference Material	71Ga ug/L	85Rb ug/L	88Sr ug/L	89Y ug/L	95Mo ug/L	107Ag ug/L	111Cd ug/L	121Sb ug/L	133Cs ug/L	137Ba ug/L	139La ug/L
Certified values (ug/L)		50.00	250.00	2.50	50.00		2.50		10.00	250.00	2.50
SD		0.30	1.00	0.02	0.30		0.02		0.10	1.00	0.02
Instrument LOD (ug/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1:100 Dilution Factor											
Average Concentration (n = 8)		45.20	237.69	2.54	46.34		2.43		8.96	260.36	2.52
SD		2.12	10.69	0.13	1.78		0.12		0.37	5.42	0.07
RSD		5	4	5	4		5		4	2	3
Accuracy (%)		90	95	102	93		97		90	104	101
1:500 Dilution Factor											
Average Concentration (n = 8)		47.02	245.87	2.68	47.83		2.53		9.34	264.42	2.60
SD		2.92	14.98	0.26	1.12		0.31		0.51	10.81	0.08
RSD		6	6	10	2		12		5	4	3
Accuracy (%)		94	98	107	96		101		93	106	104

Table A21: Standard Reference Material Analysis for Ga, Rb, Sr, Y, Mo, Ag, Cd, Sb, Cs, Ba, and La – SPS-SW2 Elements in Surface Water for ICP-MS.

SPS-SW2 Elements in Surface Water											
Certified Reference Material	140Ce	141Pr	146Nd	147Sm	153Eu	157Gd	159Tb	163Dy	165Ho	166Er	169Tm
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Certified values (ug/L)	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50	2.50
SD	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Instrument LOD (ug/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1:100 Dilution Factor											
Average Concentration (n = 8)	2.57	2.60	2.47	2.50	2.55	2.59	2.62	2.45	2.54	2.65	2.52
SD	0.09	0.08	0.08	0.10	0.10	0.12	0.08	0.09	0.09	0.09	0.08
RSD	3	3	3	4	4	5	3	4	3	3	3
Accuracy (%)	103	104	99	100	102	104	105	98	102	106	101
1:500 Dilution Factor											
Average Concentration (n = 8)	2.64	2.82	2.64	2.58	2.62	2.64	2.64	2.50	2.60	2.74	2.54
SD	0.08	0.13	0.17	0.19	0.11	0.16	0.07	0.15	0.07	0.15	0.09
RSD	3	4	6	7	4	6	3	6	3	5	3
Accuracy (%)	106	113	106	103	105	106	105	100	104	110	102

Table A22: Standard Reference Material Analysis for Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm – SPS-SW2 Elements in Surface Water for ICP-MS.

SPS-SW2 Elements in Surface Water								
Certified Reference Material	172Yb	175Lu	182W	185Re	205Tl	208Pb	232Th	238U
	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L	ug/L
Certified values (ug/L)	2.50	2.50			2.500	25.00	2.50	2.50
SD	0.02	0.02			0.02	0.10	0.02	0.02
Instrument LOD (ug/L)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1:100 Dilution Factor								
Average Concentration (n = 8)	2.64	2.55			2.40	23.16	2.58	2.24
SD	0.09	0.09			0.07	0.55	0.06	0.09
RSD	3	3			3	2	2	4
Accuracy (%)	106	102			96	93	103	90
1:500 Dilution Factor								
Average Concentration (n = 8)	2.66	2.57			2.47	24.10	2.59	2.24
SD	0.24	0.12			0.09	2.00	0.09	0.08
RSD	9	5			4	8	3	3
Accuracy (%)	106	103			99	96	104	90

Table A23: Standard Reference Material Analysis for Yb, Lu, W, Re, Tl, Pb, Th, and U – SPS-SW2 Elements in Surface Water for ICP-MS.

NIST 2710 - Montana Soil Reference Material	7Li	9Be	27Al	51V	52Cr	55Mn	57Fe	59Co	60Ni	63Cu	66Zn
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
Certified Value (mg/kg)*			64400	76.6	**39**	10100.0	33800	**10**	14.3	2950	6952
SD			800	2.3		400	1000		1.0	130	91
Avg. Conc.			30987.06	54.01	24.75	7486.88	29661.76	8.04	12.26	2579.49	5782.48
SD			937.43	1.28	0.52	143.89	589.91	0.14	0.21	47.61	72.39
RSD			3	2	2	2	2	2	2	2	1
Accuracy (%)			48	71	63	74	88	80	86	87	83

NIST 1547 - Trace Elements in Peach Leaves	7Li	9Be	27Al	51V	52Cr	55Mn	57Fe	59Co	60Ni	63Cu	66Zn
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
Certified Value (mg/kg)*			248.90	0.367	**1**	97.8	219.8	**0.07**	0.689	3.75	17.97
SD			6.50	0.038		1.8	6.8		0.095	0.37	0.53
Avg. Conc.	0.06	0.01	226.40	0.29	0.92	80.74	207.87	0.06	0.55	3.28	14.98
SD	0.04	0.00	10.92	0.01	0.05	2.28	7.01	0.00	0.05	0.15	0.45
RSD	57	15	5	2	5	3	3	5	9	5	3
Accuracy (%)			91	78	92	83	95	80	79	88	83

Notes:

1. Bold font indicates a reference concentration with informational value only, not certified.

Table A24: Standard Reference Material Analysis for Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn – NIST 2710 Montana Soil Reference Material and NIST 1547 Trace Elements in Peach Leaves for ICP-MS.

NIST 2710 - Montana Soil Reference Material	71Ga	85Rb	88Sr	89Y	95Mo	107Ag	111Cd	121Sb	133Cs	137Ba	139La
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
Certified Value (mg/kg)*	**34**	**120**	**330**	**23**	**19**	35.3	21.8	38.4	**107**	707	**34**
SD						1.5	0.2	3.0		51	
Avg. Conc.	32.02	80.18	102.56	18.24	5.73	24.89	20.04	4.16	97.42	353.24	26.15
SD	0.66	2.92	2.37	0.35	0.75	6.11	0.27	0.72	5.79	7.33	0.61
RSD	2	4	2	2	13	25	1	17	6	2	2
Accuracy (%)	94	67	31	79	30	70	92	11	91	50	77

NIST 1547 - Trace Elements in Peach Leaves	71Ga	85Rb	88Sr	89Y	95Mo	107Ag	111Cd	121Sb	133Cs	137Ba	139La
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
Certified Value (mg/kg)*		19.65	53.0		0.0603		0.026	**0.02**		123.7	**9**
SD		0.89	5.0		0.0068		0.002			5.5	
Avg. Conc.		16.14	50.91		0.06		0.02	0.02		127.38	9.20
SD		0.24	1.30		0.05		0.00	0.00		3.92	0.36
RSD		2	3		86		12	12		3	4
Accuracy (%)		82	96		105		89	87		103	102

Notes:

1. Bold font indicates a reference concentration with informational value only, not certified.

Table A25: Standard Reference Material Analysis for Ga, Rb, Sr, Y, Mo, Ag, Cd, Sb, Cs, Ba, and La – NIST 2710 Montana Soil Reference Material and NIST 1547 Trace Elements in Peach Leaves for ICP-MS.

NIST 2710 - Montana Soil Reference Material	140Ce ug/g	141Pr ug/g	146Nd ug/g	147Sm ug/g	153Eu ug/g	157Gd ug/g	159Tb ug/g	163Dy ug/g	165Ho ug/g	166Er ug/g	169Tm ug/g
Certified Value (mg/kg)*	**57**		**23**	**7.80**	**1**			**5.4**	**0.6**		
SD											
Avg. Conc.	50.32		22.38	4.32	0.84			3.25	0.67		
SD	1.07		0.61	0.11	0.03			0.08	0.03		
RSD	2		3	3	3			3	4		
Accuracy (%)	88		97	55	84			60	111		

NIST 1547 - Trace Elements in Peach Leaves	140Ce ug/g	141Pr ug/g	146Nd ug/g	147Sm ug/g	153Eu ug/g	157Gd ug/g	159Tb ug/g	163Dy ug/g	165Ho ug/g	166Er ug/g	169Tm ug/g
Certified Value (mg/kg)*	**10**		**7**	**1**	**0.17**	**1**	**0.1**				
SD											
Avg. Conc.	10.30		6.91	1.11	0.19	0.99	0.12				
SD	0.37		0.25	0.02	0.01	0.05	0.01				
RSD	4		4	2	4	5	5				
Accuracy (%)	103		99	111	115	99	118				

Notes:

1. Bold font indicates a reference concentration with informational value only, not certified.

Table A26: Standard Reference Material Analysis for Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, and Tm – NIST 2710 Montana Soil Reference Material and NIST 1547 Trace Elements in Peach Leaves for ICP-MS.

NIST 2710 - Montana Soil Reference Material	172Yb ug/g	175Lu ug/g	182W ug/g	185Re ug/g	205Tl ug/g	208Pb ug/g	232Th ug/g	238U ug/g
Certified Value (mg/kg)*	**1.3**		**93**		**1.3**	5532	**13**	**25**
SD						80		
Avg. Conc.	1.93		11.95		0.91	4936.13	13.18	21.64
SD	0.08		1.68		0.04	203.13	0.54	1.11
RSD	4		14		5	4	4	5
Accuracy (%)	148		13		70	89	101	87

NIST 1547 - Trace Elements in Peach Leaves	172Yb ug/g	175Lu ug/g	182W ug/g	185Re ug/g	205Tl ug/g	208Pb ug/g	232Th ug/g	238U ug/g
Certified Value (mg/kg)*	**0.2**					0.869	**0.05**	**0.015**
SD						0.018		
Avg. Conc.	0.14					0.78	0.05	0.01
SD	0.01					0.02	0.00	0.00
RSD	5					3	5	4
Accuracy (%)	69					89	103	74

Notes:

1. Bold font indicates a reference concentration with informational value only, not certified.

Table A27: Standard Reference Material Analysis for Yb, Lu, W, Re, Tl, Pb, Th, and U – NIST 2710 Montana Soil Reference Material and NIST 1547 Trace Elements in Peach Leaves for ICP-MS.

NIST 3281 - Elements in Cranberries	7Li	9Be	27Al	51V	52Cr	55Mn	57Fe	59Co	60Ni	63Cu	66Zn
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
Certified Value (mg/kg)			**14.14**			21.59	26.30			3.65	6.69
SD			**0.66**			0.44	1.50			0.15	0.51
Avg. Conc.			9.58			18.70	26.26			3.56	5.68
SD			0.78			0.64	1.60			0.46	0.38
RSD			8			3	6			13	7
Accuracy (%)			68			87	100			98	85

NIST 3287 - Elements in Blueberries	7Li	9Be	27Al	51V	52Cr	55Mn	57Fe	59Co	60Ni	63Cu	66Zn
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
Certified Value (mg/kg)						8.47	12.20			2.22	6.49
SD						0.59	0.74			0.16	0.61
Avg. Conc.						7.45	11.94			2.04	5.57
SD						0.25	0.52			0.09	0.64
RSD						3	4			4	11
Accuracy (%)						88	98			92	86

Notes:

1. Bold font indicates a reference concentration with informational value only, not certified.
2. There were no certified values for NIST 3281 or NIST 3287 for the remaining elements

Table A28: Standard Reference Material Analysis for Li, Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn – NIST 3281 Elements in Cranberries and NIST 3287 Elements in Blueberries for ICP-MS.

Blueberries

Acq Method

Data File Name	CalBlk.d
Acq/Data Batch	D:\Agilent\ICPMH\1\DATA\MAR162201.b
[ACQ PARAMETERS]	
Acq Mode	Spectrum
Q2 Peak Pattern	3 points
Replicates	3
Sweeps/Replicate	10
Monitored Mass Pairs:	
Element Name	Q1 -> Q2
Li	7 -> 7
Be	9 -> 9
Na	23 -> 23
Mg	24 -> 24
Rh	103 -> 103
Tune Mode #1:	No Gas
Quick Scan	OFF
Independent P/A Factors	ON
Stabilization Time	10 sec
Scan Type	MS/MS
Number of Masses	7

Element Name	Q1 -> Q2	+0.5 u	IntegTime/Mass [sec]	Detector Mode
Li	7 -> 7	OFF	0.9999	Auto
Be	9 -> 9	OFF	9.9999	Auto
B	11 -> 11	OFF	0.9999	Auto
Na	23 -> 23	OFF	0.9999	Auto
Mg	24 -> 24	OFF	0.5100	Auto
Al	27 -> 27	OFF	0.0999	Auto
Rh	103 -> 103	OFF	0.3000	Auto

Tune Mode #2:	He
Quick Scan	OFF
Independent P/A Factors	ON
Stabilization Time	10 sec
Scan Type	MS/MS
Number of Masses	36

Element Name	Q1 -> Q2	+0.5 u	IntegTime/Mass [sec]	Detector Mode
Al	27 -> 27	OFF	2.0001	Auto
K	39 -> 39	OFF	5.0001	Auto
V	51 -> 51	OFF	0.9999	Auto
Cr	52 -> 52	OFF	0.9999	Auto

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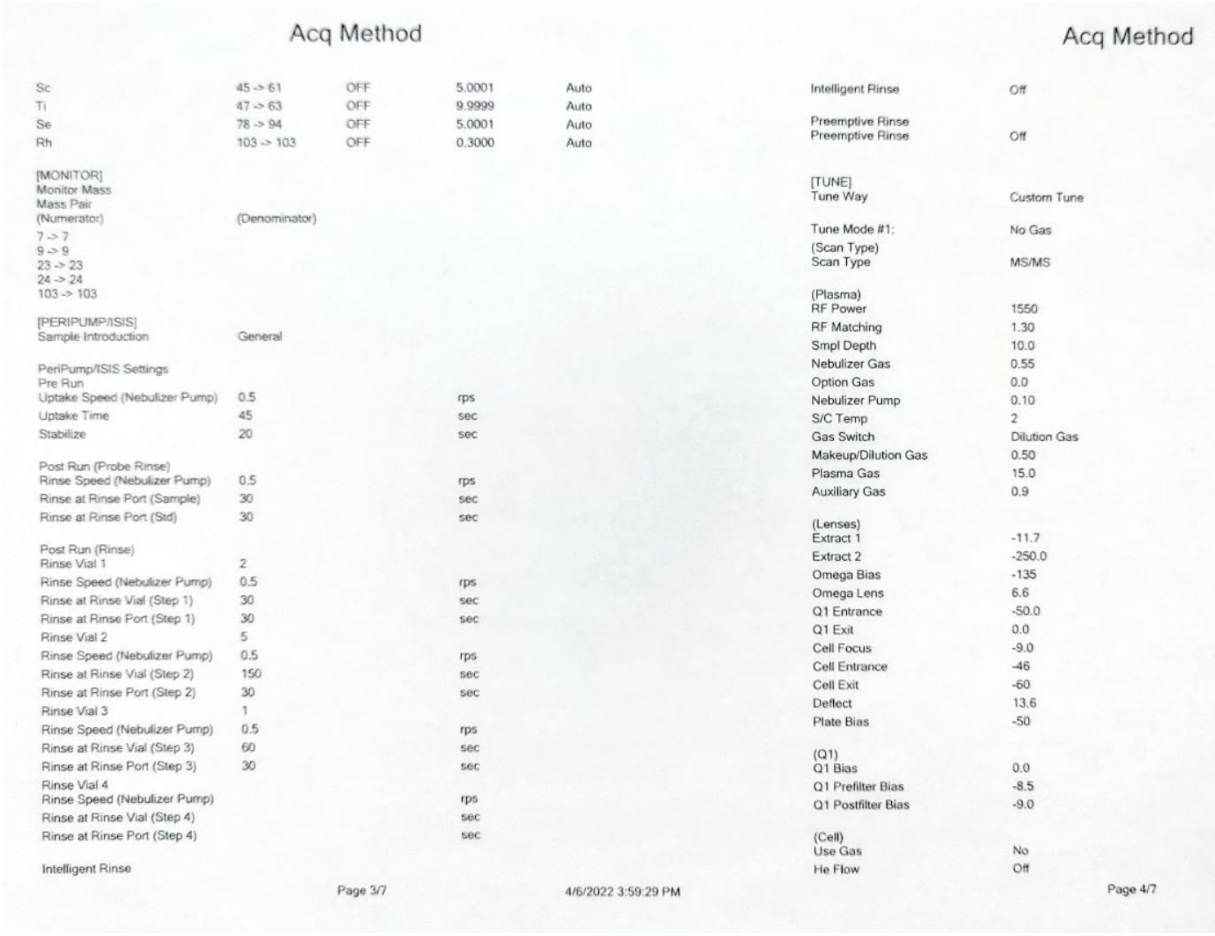
Acq Method

Mn	55 -> 55	OFF	2.0001
Fe	56 -> 56	OFF	2.0001
Co	59 -> 59	OFF	0.9999
Ni	60 -> 60	OFF	2.0001
Cu	63 -> 63	OFF	2.0001
Zn	66 -> 66	OFF	2.0001
As	75 -> 75	OFF	5.0001
Rb	85 -> 85	OFF	9.9999
Sr	88 -> 88	OFF	2.0001
Y	89 -> 89	OFF	2.0001
Zr	90 -> 90	OFF	0.9999
Mo	95 -> 95	OFF	0.9999
Rh	103 -> 103	OFF	0.3000
Ag	107 -> 107	OFF	0.9999
Cd	111 -> 111	OFF	2.0001
Sn	118 -> 118	OFF	5.0001
Sb	121 -> 121	OFF	5.0001
Cs	133 -> 133	OFF	5.0001
Ba	137 -> 137	OFF	2.0001
W	182 -> 182	OFF	0.9999
[Hg]	199 -> 199	OFF	9.0000
[Hg]	200 -> 200	OFF	9.0000
Hg	201 -> 201	OFF	9.0000
[Hg]	202 -> 202	OFF	9.0000
[Pb]	204 -> 204	OFF	2.0001
Tl	205 -> 205	OFF	0.9999
[Pb]	206 -> 206	OFF	2.0001
[Pb]	207 -> 207	OFF	2.0001
Pb	208 -> 208	OFF	2.0001
Bi	209 -> 209	OFF	2.0001
Th	232 -> 232	OFF	0.9999
U	238 -> 238	OFF	0.9999

Tune Mode #3:	O2
Quick Scan	OFF
Independent P/A Factors	ON
Stabilization Time	15 sec
Scan Type	MS/MS
Number of Masses	7

Element Name	Q1 -> Q2	+0.5 u	IntegTime/Ma [sec]
P	31 -> 47	OFF	5.0001
S	32 -> 48	OFF	5.0001
Ca	44 -> 60	OFF	5.0001

Table A29: ICP-MS Acquisition Method for Blueberries Analysis at the CNSC Lab (p. 1 of 4).



Acq Method

Sc	45 -> 61	OFF	5.0001	Auto
Ti	47 -> 63	OFF	9.9999	Auto
Se	78 -> 94	OFF	5.0001	Auto
Rh	103 -> 103	OFF	0.3000	Auto

[MONITOR]
Monitor Mass
Mass Pair
(Numerator) (Denominator)
7 -> 7
9 -> 9
23 -> 23
24 -> 24
103 -> 103

[PERIPUMP/ISIS]
Sample Introduction General

PeriPump/ISIS Settings
Pre Run
Uptake Speed (Nebulizer Pump) 0.5 rps
Uptake Time 45 sec
Stabilize 20 sec

Post Run (Probe Rinse)
Rinse Speed (Nebulizer Pump) 0.5 rps
Rinse at Rinse Port (Sample) 30 sec
Rinse at Rinse Port (Std) 30 sec

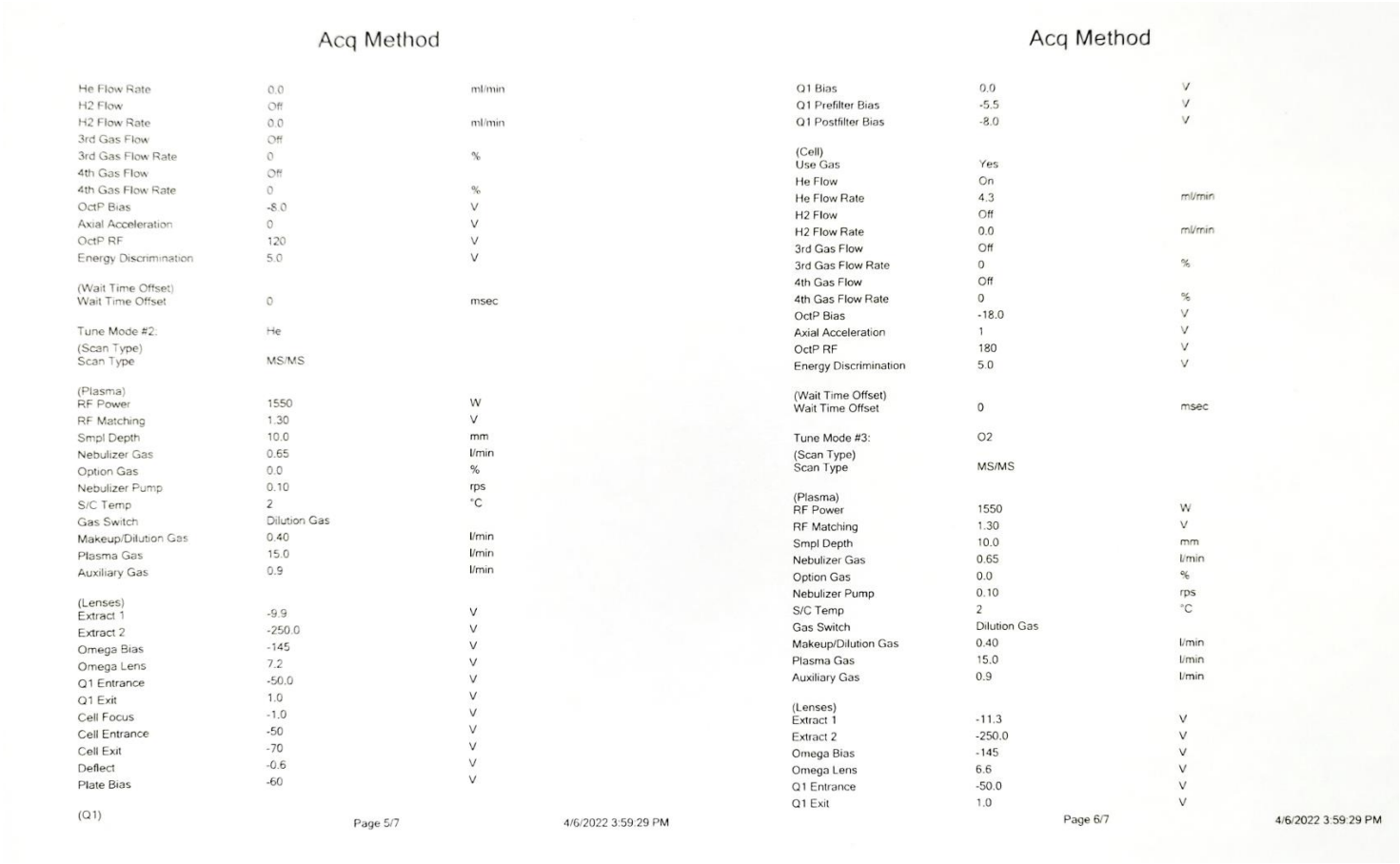
Post Run (Rinse)
Rinse Vial 1 2
Rinse Speed (Nebulizer Pump) 0.5 rps
Rinse at Rinse Vial (Step 1) 30 sec
Rinse at Rinse Port (Step 1) 30 sec
Rinse Vial 2 5
Rinse Speed (Nebulizer Pump) 0.5 rps
Rinse at Rinse Vial (Step 2) 150 sec
Rinse at Rinse Port (Step 2) 30 sec
Rinse Vial 3 1
Rinse Speed (Nebulizer Pump) 0.5 rps
Rinse at Rinse Vial (Step 3) 60 sec
Rinse at Rinse Port (Step 3) 30 sec
Rinse Vial 4
Rinse Speed (Nebulizer Pump) rps
Rinse at Rinse Vial (Step 4) sec
Rinse at Rinse Port (Step 4) sec

Intelligent Rinse

Acq Method

Intelligent Rinse	Off
Preemptive Rinse	
Preemptive Rinse	Off
[TUNE]	
Tune Way	Custom Tune
Tune Mode #1:	No Gas
(Scan Type)	
Scan Type	MS/MS
(Plasma)	
RF Power	1550
RF Matching	1.30
Smpl Depth	10.0
Nebulizer Gas	0.55
Option Gas	0.0
Nebulizer Pump	0.10
S/C Temp	2
Gas Switch	Dilution Gas
Makeup/Dilution Gas	0.50
Plasma Gas	15.0
Auxiliary Gas	0.9
(Lenses)	
Extract 1	-11.7
Extract 2	-250.0
Omega Bias	-135
Omega Lens	6.6
Q1 Entrance	-50.0
Q1 Exit	0.0
Cell Focus	-9.0
Cell Entrance	-46
Cell Exit	-60
Deflect	13.6
Plate Bias	-50
(Q1)	
Q1 Bias	0.0
Q1 Prefilter Bias	-8.5
Q1 Postfilter Bias	-9.0
(Cell)	
Use Gas	No
He Flow	Off

Table A30: ICP-MS Acquisition Method for Blueberries Analysis at the CNSC Lab (p. 2 of 4).



Acq Method

He Flow Rate	0.0	ml/min
H2 Flow	Off	
H2 Flow Rate	0.0	ml/min
3rd Gas Flow	Off	
3rd Gas Flow Rate	0	%
4th Gas Flow	Off	
4th Gas Flow Rate	0	%
OctP Bias	-8.0	V
Axial Acceleration	0	V
OctP RF	120	V
Energy Discrimination	5.0	V
(Wait Time Offset)		
Wait Time Offset	0	msec
Tune Mode #2:	He	
(Scan Type)		
Scan Type	MS/MS	
(Plasma)		
RF Power	1550	W
RF Matching	1.30	V
Smpl Depth	10.0	mm
Nebulizer Gas	0.65	l/min
Option Gas	0.0	%
Nebulizer Pump	0.10	rps
S/C Temp	2	°C
Gas Switch	Dilution Gas	
Makeup/Dilution Gas	0.40	l/min
Plasma Gas	15.0	l/min
Auxiliary Gas	0.9	l/min
(Lenses)		
Extract 1	-9.9	V
Extract 2	-250.0	V
Omega Bias	-145	V
Omega Lens	7.2	V
Q1 Entrance	-50.0	V
Q1 Exit	1.0	V
Cell Focus	-1.0	V
Cell Entrance	-50	V
Cell Exit	-70	V
Deflect	-0.6	V
Plate Bias	-60	V
(Q1)		

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Acq Method

Q1 Bias	0.0	V
Q1 Prefilter Bias	-5.5	V
Q1 Postfilter Bias	-8.0	V
(Cell)		
Use Gas	Yes	
He Flow	On	
He Flow Rate	4.3	ml/min
H2 Flow	Off	
H2 Flow Rate	0.0	ml/min
3rd Gas Flow	Off	
3rd Gas Flow Rate	0	%
4th Gas Flow	Off	
4th Gas Flow Rate	0	%
OctP Bias	-18.0	V
Axial Acceleration	1	V
OctP RF	180	V
Energy Discrimination	5.0	V
(Wait Time Offset)		
Wait Time Offset	0	msec
Tune Mode #3:	O2	
(Scan Type)		
Scan Type	MS/MS	
(Plasma)		
RF Power	1550	W
RF Matching	1.30	V
Smpl Depth	10.0	mm
Nebulizer Gas	0.65	l/min
Option Gas	0.0	%
Nebulizer Pump	0.10	rps
S/C Temp	2	°C
Gas Switch	Dilution Gas	
Makeup/Dilution Gas	0.40	l/min
Plasma Gas	15.0	l/min
Auxiliary Gas	0.9	l/min
(Lenses)		
Extract 1	-11.3	V
Extract 2	-250.0	V
Omega Bias	-145	V
Omega Lens	6.6	V
Q1 Entrance	-50.0	V
Q1 Exit	1.0	V

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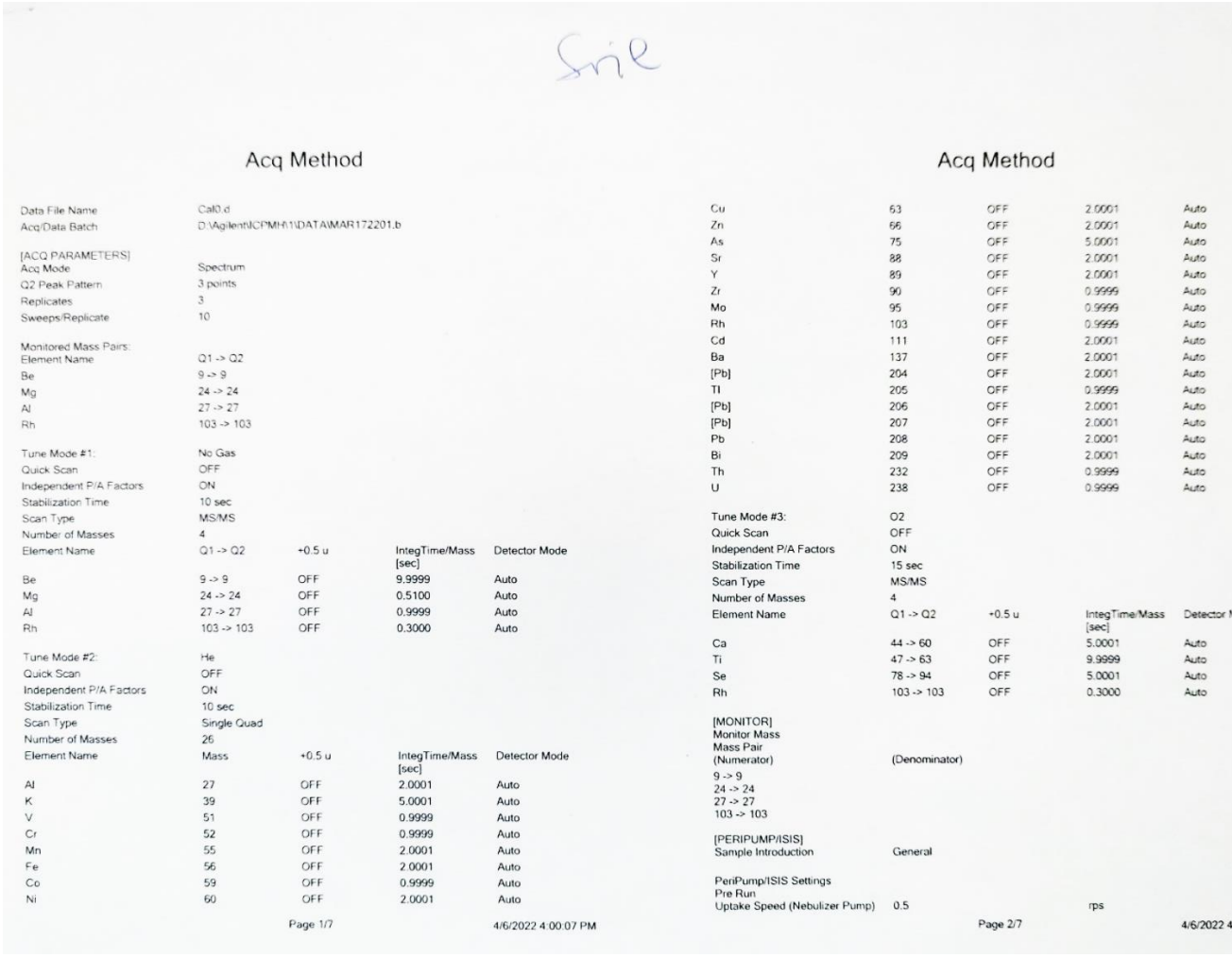
Table A31: ICP-MS Acquisition Method for Blueberries Analysis at the CNSC Lab (p. 3 of 4).

Acq Method

Cell Focus	3.0	V
Cell Entrance	-50	V
Cell Exit	-66	V
Deflect	2.6	V
Plate Bias	-60	V
(Q1)		
Q1 Bias	-1.0	V
Q1 Prefilter Bias	-5.5	V
Q1 Postfilter Bias	-9.0	V
(Cell)		
Use Gas	Yes	
He Flow	Off	
He Flow Rate	0.0	ml/min
H2 Flow	Off	
H2 Flow Rate	2.0	ml/min
3rd Gas Flow	Off	
3rd Gas Flow Rate	0	%
4th Gas Flow	On	
4th Gas Flow Rate	30	%
OctP Bias	-5.0	V
Axial Acceleration	-1.5	V
OctP RF	180	V
Energy Discrimination	-5.0	V
(Wait Time Offset)		
Wait Time Offset	0	msec

Table A32: ICP-MS Acquisition Method for Blueberries Analysis at the CNSC Lab (p. 4 of 4).



Soil

Acq Method

Data File Name	Cal0.d
Acq/Data Batch	D:\Agilent\ICPMH1\DATA\MAR172201.b
[ACQ PARAMETERS]	
Acq Mode	Spectrum
Q2 Peak Pattern	3 points
Replicates	3
Sweeps/Replicate	10
Monitored Mass Pairs:	
Element Name	Q1 -> Q2
Be	9 -> 9
Mg	24 -> 24
Al	27 -> 27
Rh	103 -> 103
Tune Mode #1:	No Gas
Quick Scan	OFF
Independent P/A Factors	ON
Stabilization Time	10 sec
Scan Type	MS/MS
Number of Masses	4

Element Name	Q1 -> Q2	+0.5 u	IntegTime/Mass [sec]	Detector Mode
Be	9 -> 9	OFF	9.9999	Auto
Mg	24 -> 24	OFF	0.5100	Auto
Al	27 -> 27	OFF	0.9999	Auto
Rh	103 -> 103	OFF	0.3000	Auto

Tune Mode #2:	He
Quick Scan	OFF
Independent P/A Factors	ON
Stabilization Time	10 sec
Scan Type	Single Quad
Number of Masses	26

Element Name	Mass	+0.5 u	IntegTime/Mass [sec]	Detector Mode
Al	27	OFF	2.0001	Auto
K	39	OFF	5.0001	Auto
V	51	OFF	0.9999	Auto
Cr	52	OFF	0.9999	Auto
Mn	55	OFF	2.0001	Auto
Fe	56	OFF	2.0001	Auto
Co	59	OFF	0.9999	Auto
Ni	60	OFF	2.0001	Auto

Acq Method

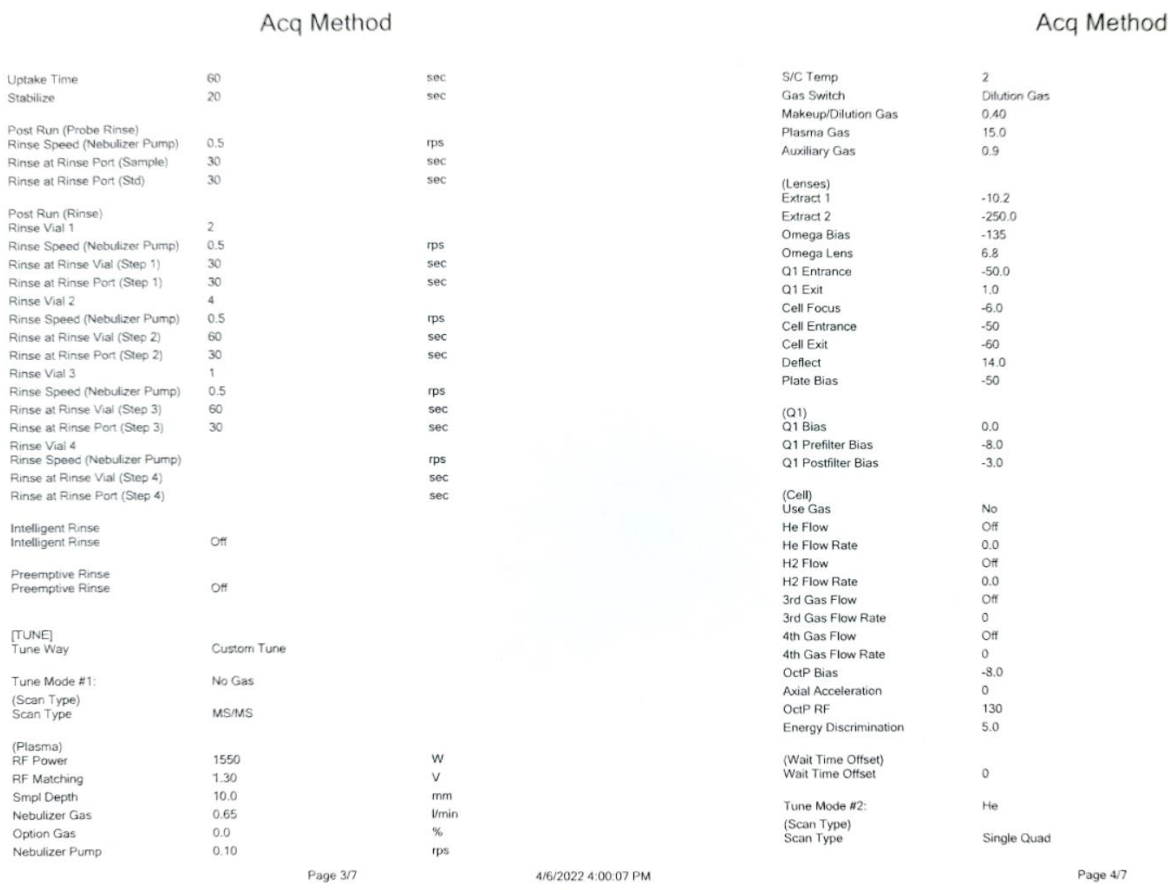
Cu	63	OFF	2.0001	Auto
Zn	66	OFF	2.0001	Auto
As	75	OFF	5.0001	Auto
Sr	88	OFF	2.0001	Auto
Y	89	OFF	2.0001	Auto
Zr	90	OFF	0.9999	Auto
Mo	95	OFF	0.9999	Auto
Rh	103	OFF	0.9999	Auto
Cd	111	OFF	2.0001	Auto
Ba	137	OFF	2.0001	Auto
[Pb]	204	OFF	2.0001	Auto
Tl	205	OFF	0.9999	Auto
[Pb]	206	OFF	2.0001	Auto
[Pb]	207	OFF	2.0001	Auto
Pb	208	OFF	2.0001	Auto
Bi	209	OFF	2.0001	Auto
Th	232	OFF	0.9999	Auto
U	238	OFF	0.9999	Auto

Tune Mode #3:	O2
Quick Scan	OFF
Independent P/A Factors	ON
Stabilization Time	15 sec
Scan Type	MS/MS
Number of Masses	4

Element Name	Q1 -> Q2	+0.5 u	IntegTime/Mass [sec]	Detector
Ca	44 -> 60	OFF	5.0001	Auto
Ti	47 -> 63	OFF	9.9999	Auto
Se	78 -> 94	OFF	5.0001	Auto
Rh	103 -> 103	OFF	0.3000	Auto

[MONITOR]		
Monitor Mass		
Mass Pair (Numerator)	(Denominator)	
9 -> 9		
24 -> 24		
27 -> 27		
103 -> 103		
[PERIPUMP/ISIS]		
Sample Introduction	General	
PeriPump/ISIS Settings		
Pre Run		
Uptake Speed (Nebulizer Pump)	0.5	rps

Table A33: ICP-MS Acquisition Method for Soil Analysis at the CNSC Lab (p. 1 of 4).



Acq Method

Uptake Time	60	sec
Stabilize	20	sec
Post Run (Probe Rinse)		
Rinse Speed (Nebulizer Pump)	0.5	rps
Rinse at Rinse Port (Sample)	30	sec
Rinse at Rinse Port (Std)	30	sec
Post Run (Rinse)		
Rinse Vial 1	2	
Rinse Speed (Nebulizer Pump)	0.5	rps
Rinse at Rinse Vial (Step 1)	30	sec
Rinse at Rinse Port (Step 1)	30	sec
Rinse Vial 2	4	
Rinse Speed (Nebulizer Pump)	0.5	rps
Rinse at Rinse Vial (Step 2)	60	sec
Rinse at Rinse Port (Step 2)	30	sec
Rinse Vial 3	1	
Rinse Speed (Nebulizer Pump)	0.5	rps
Rinse at Rinse Vial (Step 3)	60	sec
Rinse at Rinse Port (Step 3)	30	sec
Rinse Vial 4		
Rinse Speed (Nebulizer Pump)		rps
Rinse at Rinse Vial (Step 4)		sec
Rinse at Rinse Port (Step 4)		sec
Intelligent Rinse		
Intelligent Rinse	Off	
Preemptive Rinse		
Preemptive Rinse	Off	
[TUNE]		
Tune Way	Custom Tune	
Tune Mode #1:	No Gas	
(Scan Type)		
Scan Type	MS/MS	
(Plasma)		
RF Power	1550	W
RF Matching	1.30	V
Smpl Depth	10.0	mm
Nebulizer Gas	0.65	l/min
Option Gas	0.0	%
Nebulizer Pump	0.10	rps

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Acq Method

S/C Temp	2
Gas Switch	Dilution Gas
Makeup/Dilution Gas	0.40
Plasma Gas	15.0
Auxiliary Gas	0.9
(Lenses)	
Extract 1	-10.2
Extract 2	-250.0
Omega Bias	-135
Omega Lens	6.8
Q1 Entrance	-50.0
Q1 Exit	1.0
Cell Focus	-6.0
Cell Entrance	-50
Cell Exit	-60
Deflect	14.0
Plate Bias	-50
(Q1)	
Q1 Bias	0.0
Q1 Prefilter Bias	-8.0
Q1 Postfilter Bias	-3.0
(Cell)	
Use Gas	No
He Flow	Off
He Flow Rate	0.0
H2 Flow	Off
H2 Flow Rate	0.0
3rd Gas Flow	Off
3rd Gas Flow Rate	0
4th Gas Flow	Off
4th Gas Flow Rate	0
OctP Bias	-8.0
Axial Acceleration	0
OctP RF	130
Energy Discrimination	5.0
(Wait Time Offset)	
Wait Time Offset	0
Tune Mode #2:	He
(Scan Type)	
Scan Type	Single Quad

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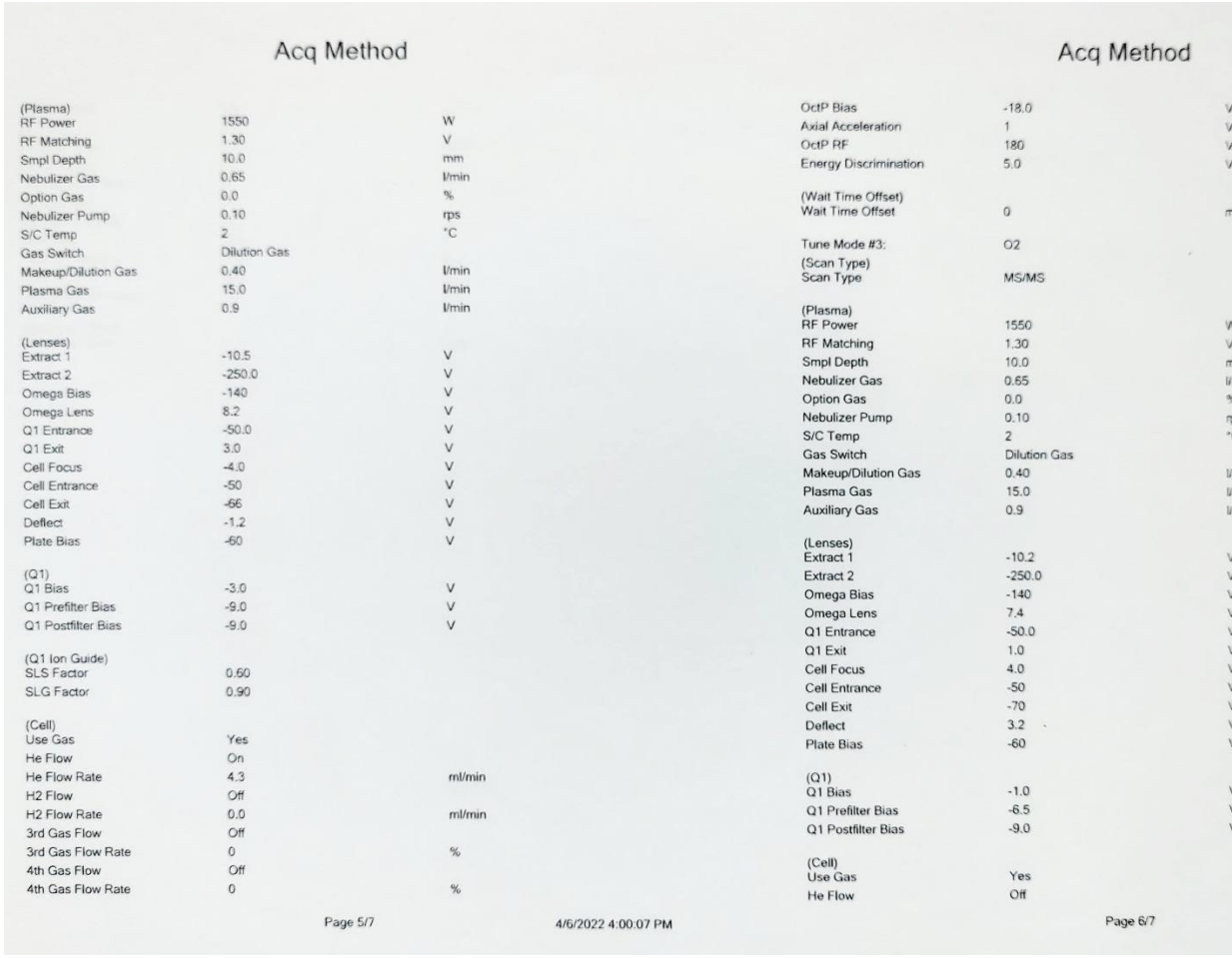
Table A34: ICP-MS Acquisition Method for Soil Analysis at the CNSC Lab (p. 2 of 4).



Acq Method

(Plasma)		
RF Power	1550	W
RF Matching	1.30	V
Smpl Depth	10.0	mm
Nebulizer Gas	0.65	l/min
Option Gas	0.0	%
Nebulizer Pump	0.10	rps
S/C Temp	2	°C
Gas Switch	Dilution Gas	
Makeup/Dilution Gas	0.40	l/min
Plasma Gas	15.0	l/min
Auxiliary Gas	0.9	l/min
(Lenses)		
Extract 1	-10.5	V
Extract 2	-250.0	V
Omega Bias	-140	V
Omega Lens	8.2	V
Q1 Entrance	-50.0	V
Q1 Exit	3.0	V
Cell Focus	-4.0	V
Cell Entrance	-50	V
Cell Exit	-66	V
Deflect	-1.2	V
Plate Bias	-60	V
(Q1)		
Q1 Bias	-3.0	V
Q1 Prefilter Bias	-9.0	V
Q1 Postfilter Bias	-9.0	V
(Q1 Ion Guide)		
SLS Factor	0.60	
SLG Factor	0.90	
(Cell)		
Use Gas	Yes	
He Flow	On	
He Flow Rate	4.3	ml/min
H2 Flow	Off	
H2 Flow Rate	0.0	ml/min
3rd Gas Flow	Off	
3rd Gas Flow Rate	0	%
4th Gas Flow	Off	
4th Gas Flow Rate	0	%

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Acq Method

OctP Bias	-18.0
Axial Acceleration	1
OctP RF	180
Energy Discrimination	5.0
(Wait Time Offset)	
Wait Time Offset	0
Tune Mode #3:	O2
(Scan Type)	
Scan Type	MS/MS
(Plasma)	
RF Power	1550
RF Matching	1.30
Smpl Depth	10.0
Nebulizer Gas	0.65
Option Gas	0.0
Nebulizer Pump	0.10
S/C Temp	2
Gas Switch	Dilution Gas
Makeup/Dilution Gas	0.40
Plasma Gas	15.0
Auxiliary Gas	0.9
(Lenses)	
Extract 1	-10.2
Extract 2	-250.0
Omega Bias	-140
Omega Lens	7.4
Q1 Entrance	-50.0
Q1 Exit	1.0
Cell Focus	4.0
Cell Entrance	-50
Cell Exit	-70
Deflect	3.2
Plate Bias	-60
(Q1)	
Q1 Bias	-1.0
Q1 Prefilter Bias	-6.5
Q1 Postfilter Bias	-9.0
(Cell)	
Use Gas	Yes
He Flow	Off

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Table A35: ICP-MS Acquisition Method for Soil Analysis at the CNSC Lab (p. 3 of 4).

Acq Method

He Flow Rate	0.0	ml/min
H2 Flow	Off	
H2 Flow Rate	2.0	ml/min
3rd Gas Flow	Off	
3rd Gas Flow Rate	0	%
4th Gas Flow	On	
4th Gas Flow Rate	30	%
OctP Bias	-5.0	V
Axial Acceleration	-1.5	V
OctP RF	180	V
Energy Discrimination	-5.0	V
(Wait Time Offset)		
Wait Time Offset	0	msec

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Table A36: ICP-MS Acquisition Method for Soil Analysis at the CNSC Lab (p. 4 of 4).

SRC Analytical Laboratories
Standard Operating Procedure Summary

Lead-210 in Various Matrices by Beta Counting of the Bismuth-210 Successor Product

SOP Number: **Rad-101**

Summary:

Lead-210 is determined indirectly by the precipitation and counting of its high energy beta emitting progeny, bismuth-210. Bismuth is isolated by solvent extraction and subsequently precipitated as bismuth oxychloride. The precipitate is collected on a filter paper/disk assembly and beta counted in a low background counting system using a gas-flow proportional detector. This method may be used on a variety of sample types in conjunction with proper initial preparation procedures.

Scope and Detection Limit:

The reportable detection limit for a 1 litre water sample is 0.02 Bq/L, for a 0.5 gram soil/sediment sample it is 0.04 Bq/g, for a 10 gram vegetation sample it is 0.002 Bq/g and for a 20 gram tissue sample it is 0.001 Bq/g. The detection limit is based on the background count rate of the instrument.

Sample Requirements

Sample containers can be either plastic or glass. If Polonium-210 is required, plastic is preferred. Water samples must be preserved in the field with nitric acid to a pH of < 2. Soils, sediments, vegetation and biological samples must be kept frozen until initial preparation (drying, ashing) is performed. Hold time is 6 months at room temperature for water samples. Hold time for dried and/or ashed, soil, sediments, vegetation, and biological samples are indefinitely. Hold time is indefinite at room temperature for filter papers and dust fall jars.

Quality Control:

For each batch of samples a blank, a control sample and a calibration check standard are analyzed. One of every ten samples is analyzed in duplicate, if sufficient sample is available. Spiked samples are analyzed monthly. Lead-Bismuth tracer recovery is suspect if it is less than 25 % or greater than 100 %. Contamination monitoring is performed on microwave vessels, filter papers and grinders. All quality control results must be within specified limits otherwise corrective action is required.

SRC Analytical

Figure A1: SRC Analytical Laboratories Standard Operating Procedure Summary for Lead-210 (p. 1 of 2).

References:

This procedure follows ASTM Method D7535-09, Standard Test Method for Lead-210 in Water for the water preparation steps, with the following modifications:

- NaOH is used in place of NH4OH to precipitate iron hydroxides.
- A phenolphthalein solution is used to indicate pH endpoint of 8-9.
- Concentrated hydrochloric acid is used in place of 2 M hydrochloric acid.
- 1 L of sample is used instead of 500 mL.

This procedure follows The Determination of Lead-210, CANMET Report 78-22 for the analysis procedure with the following modifications:

- Ashed biological samples are digested with nitric and perchloric acids. Insoluble material is filtered off.
- Solid samples are prepared by microwave digestion.
- Water samples are held for 30 days to guarantee equilibrium between Pb-210 and Bi-210 only on client request.
- Citric acid and hydroxylamine hydrochloride are used in place of ascorbic acid for solid samples.
- Bi recovery is measured by ICP-AES.

Figure A2: SRC Analytical Laboratories Standard Operating Procedure Summary for Lead-210 (p. 2 of 2).

SRC Analytical Laboratories
Standard Operating Procedure Summary

Polonium-210 in Water, Solids and Biological Tissue by Alpha Spectroscopy

SOP Number: **Rad-103**

Summary:

Polonium-210 is plated onto a nickel disk and subsequently counted by alpha spectroscopy. The analysis incorporates use of Polonium 209, another alpha emitting isotope, as a tracer so that recovery can be calculated. This method may be used on a variety of sample types in conjunction with proper initial preparation procedures.

Scope and Detection Limit:

The reportable detection limit for a 1 litre water sample is 0.005 Bq/L, for a 0.5 gram soil/sediment sample it is 0.01 Bq/g, for a 10 gram vegetation sample it is 0.0005 Bq/g and for a 20 gram tissue sample it is 0.0002Bq/g. The detection limit is based on the background count rate of the instrument.

Sample Requirements

Sample containers can be either plastic or glass, but plastic is preferred. For water samples, a sample size of 1 litre is normally required. Water samples must be preserved in the field with nitric acid to a pH of < 2. Samples for dissolved Polonium-210 must be filtered before acidification. For soil or sediment samples a sample size of 0.5 gram is normally required. Soils, sediments, vegetation and biological samples must be kept frozen until initial preparation is performed. Hold time for urine samples is one month. Hold time for all other sample types is 3 months to ensure there is no significant decay of Polonium-210.

Quality Control:

For each batch of samples a blank, a control sample, and a calibration check standard are analyzed. Soil and Vegetation control samples are analyzed once every 6 months. One of every ten samples is analyzed in duplicate if sufficient sample is available. Spiked samples are analyzed monthly. Polonium-209 tracer recovery is suspect if it is less than 25 % or greater than 100 %. Contamination monitoring is performed on microwave vessels, filter papers and grinders. All quality control results must be within specified limits otherwise corrective action is required.

References:

This procedure follows ASTM Method D7535-09, Standard Test Method for Lead-210 in Water for the water preparation steps, with the following modifications:

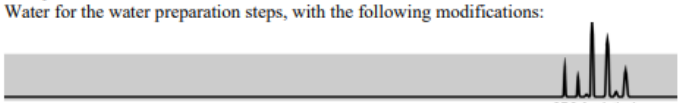


Figure A3: SRC Analytical Laboratories Standard Operating Procedure Summary for Polonium-210 (p. 1 of 2).

- NaOH is used instead of NH4OH to precipitate Iron hydroxides.
- A phenolphthalein solution is used to indicate pH endpoint of 8-9.
- Concentrated hydrochloric acid is used instead of 2M hydrochloric acid.
- 1 L sample size is used instead of 500 mL.

This procedure follows The Determination of Polonium-210, CANMET Report 78-22 with the following modifications:

- Po-209 is used as the tracer.
- Nickel discs are used in place of silver.
- Hydroxylamine Hydrochloride and Citric Acid are used in place of ascorbic acid for solid samples.
- Solid samples are digested by microwave digestion.
- Samples are plated at room temperature.

Figure A4: SRC Analytical Laboratories Standard Operating Procedure Summary for Polonium-210 (p. 2 of 2).

SRC Analytical Laboratories
Standard Operating Procedure Summary

Radium-226 by Alpha Spectroscopy

SOP Number: **Rad-105**

Summary:

All radium isotopes and other actinide and lanthanide elements in the sample solution are separated by coprecipitation with lead sulfate. The precipitate is redissolved and the radium isotopes are separated from the other elements by coprecipitation with barium sulfate. The precipitate is filtered through a 0.45 µm membrane, which is mounted on a plastic disk. The disk is then counted on an alpha spectrometer. This method is used for water samples and a variety of different types of solid samples after suitable preparation.

Scope and Detection Limit:

The reportable detection limit for a 1 L water sample is 0.005 B/L, for a 0.5 gram soil/sediment sample it is 0.01 Bq/g, for a 0.5 gram vegetation ash sample it is 0.01 Bq/g and for a 1 gram tissue ash sample it is 0.005 Bq/g. The detection limit is based on the background count rate of the instrument.

Sample Requirements

Sample containers can be either plastic or glass. For water samples, a sample size of 1 litre is normally required. Water samples must be preserved in the field with nitric acid to a pH of < 2. Water samples that require dissolved radium must be filtered through a 0.45 µm membrane filter before acidification. For soil or sediment samples, a minimum sample size of 0.5 gram is normally required. Soils, sediments, vegetation and biological samples should be kept frozen until initial preparation (e.g., drying, ashing) is performed. Hold time is 6 months at room temperature for water samples. Hold time for dried and/or ashed soil, sediment, vegetation and biological samples is indefinite.

Quality Control:

For each batch of samples a method blank, a control sample, and a calibration check standard are analyzed. One of every ten samples is analyzed in duplicate if sufficient sample is available. At least one spiked sample is analyzed monthly. Barium-133 tracer recovery is suspect if it is less than 25 % or greater than 100 %. Contamination monitoring is performed on crucibles, microwave vessels, filter papers and grinders. All quality control results must be within specified limits, otherwise corrective action is required.

Figure A5: SRC Analytical Laboratories Standard Operating Procedure Summary for Radium-226 (p. 1 of 2).

References:

This procedure follows the National Uranium Tailings Program Radioanalytical Methods Manual with the following modifications:

- Seeding Suspension is not used.
- Some reagents vary in preparation to optimize the procedure.
- Amounts of Barium-133 tracer, sulfuric acid and potassium sulfate added to samples differ to optimize the procedure.
- Some steps after appropriate preparation of samples differ to optimize the procedure.

Figure A6: SRC Analytical Laboratories Standard Operating Procedure Summary for Radium-226 (p. 2 of 2).

SRC Analytical Laboratories
Standard Operating Procedure Summary

Gamma Spectroscopy

SOP Number: **Rad-300**

Summary:

Samples are counted on a HPGe Solid-state Photon Detector with digital spectrometer. The data may be used to calculate the concentrations of gamma emitting nuclides. The HPGe Solid-state Photon detectors and digital spectrometers used for analysis permit the analysis of the gamma spectra to determine the energy of emitted photons. Since each gamma-emitting radioisotope will emit a photon of characteristic energy, the analysis of the gamma spectra permits identification of radioisotopes in unknown samples. Calibration of the detector to determine the detection efficiency at distinct energy levels throughout the gamma spectrum permits quantification of isotopes identified in the sample. This method is applicable to the analysis of water, soil, sediment, biological tissue, vegetation and other materials. The method is applicable to such a wide range of matrices because there is no sample preparation required. However, higher density materials lead to greater absorption of gamma energies and hence the efficiency of the detection system is different for different materials. The efficiency calibration of the detector must be based on a material with similar density as the samples

Scope and Detection Limit:

Since each sample has a unique background and the background is different for each isotope in a particular gamma spectrum, the Minimum Detectable Activity (MDA) will be different for every sample and for every isotope within that sample. The software provided with the Ortec Gamma Spectroscopy instrumentation provides several formulae that can be selected and used to calculate the MDA for a particular sample. The available formulae are derived from formulae given in the MARLAP manual, ISO 11929 and other similar sources.

Sample Requirements

Sample containers can be either plastic or glass. Water samples must be preserved in the field with nitric acid to a pH of < 2. Water samples that require dissolved gamma spec analysis must be filtered through a 0.45 um membrane filter before acidification. Soil and sediment samples are dried and ground before analysis or analyzed 'as received' if the particle size is uniform or the sample cannot be dried (e.g., oily samples). Biological samples must be kept frozen until initial preparation is performed. Hold time is 6 months at room temperature for water samples. Hold time for solid samples is indefinite at room temperature. Hold time for biological samples is indefinite when frozen.

SRC Analytical

Figure A7: SRC Analytical Laboratories Standard Operating Procedure Summary for Gamma Spectroscopy (p. 1 of 2).

Quality Control:

Reference materials traceable to recognized standard agencies, such as NIST or NRC, are used to calibrate the detection equipment for energy and efficiency. Accuracy of the measuring equipment is ensured by regular participation in proficiency testing programs provided by the IAEA, ERA and other agencies. Quality assurance measurements (e.g., background count and QA sample count) are made to demonstrate that the equipment is operating properly. These measurements are made using the Automated Laboratory Quality Assurance Program included with the ORTEC GammaVision® -32 Software. One of every ten samples is analyzed in duplicate, if sufficient sample is available. All quality control results must be within specified limits, otherwise corrective action is required.

References:

This method follows Standard Methods for the Examination of Water and Wastewater, Part 7120, APHA-AWWA-WEF, without modification.

Compiled August 2020; DMH

SRC Analytical

Figure A8: SRC Analytical Laboratories Standard Operating Procedure Summary for Gamma Spectroscopy (p. 2 of 2).

National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1570a

Trace Elements in Spinach Leaves

This Standard Reference Material (SRM) is intended primarily for use in evaluating the reliability of analytical methods for the determination of major, minor, and trace elements in botanical materials, agricultural food products, and materials of similar matrix. A unit of SRM 1570a consists of 60 g of finely powdered dried spinach leaves.

Certified Mass Fraction Values: Certified mass fraction values for selected constituent elements, reported on a dry-mass basis, are provided in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or taken into account [1].

Reference Mass Fraction Values: Reference mass fraction values of constituent elements, reported on a dry-mass basis, are provided in Table 2. Reference values are noncertified values that are the best estimates of the true values based on available data; however, the values do not meet NIST criteria for certification [1] and are provided with associated uncertainties that may reflect only measurement reproducibility, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods.

Information Mass Fraction Values: Information mass fraction values for additional constituent elements are provided in Table 3. A NIST information value is a value that may be of interest to the SRM user, but insufficient information is available to asses the uncertainty associated with the value, therefore no uncertainty is provided [1]. Values are reported on a dry-mass basis.

Expiration of Certification: The certification of **SRM 1570a** is valid, within the measurement uncertainty specified, until **31 August 2023**, provided the SRM is handled and stored in accordance with the instructions given in this certificate (see "Instructions for Storage and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certified values before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet) will facilitate notification.

Coordination of analytical measurements for the characterization of this SRM was performed by D.A. Becker of the NIST Chemical Sciences Division. Revision of this certificate was coordinated by K.E. Murphy, D.J. O'Kelly, and L.J. Wood of the NIST Chemical Sciences Division.

Analytical measurements at NIST were performed by current and former staff at NIST, E.S. Beary, D.A. Becker, C.M. Beck II, M.S. Epstein, J.D. Fassett, K.M. Garrity, R.R. Greenberg, R.M. Lindstrom, E.A. Mackey, P. Morales, K.E. Murphy, P.J. Paulsen, B.J. Porter, T.A. Rush, R. Saraswati, J.M. Smeller, G.C. Turk, R.D. Vocke, Jr., R.L. Watters, Jr., and L.J. Wood.

Additional elemental analyses were performed by D.L. Anderson (Center for Food Safety and Applied Nutrition, U.S. Food and Drug Administration, College Park, MD), A.R. Byrne (Nuclear Chemistry Department, Jozef Stefan Institute, Ljubljana, Slovenia), and J. Kucera (Nuclear Physics Institute, Academy of Sciences of the Czech Republic, Rez, Czech Republic). Several elements were also measured in an International Atomic Energy Agency (IAEA, Vienna, Austria) interlaboratory comparison exercise.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 25 February 2014
Certificate Revision History on Page 5

Robert L. Watters, Jr., Director
Office of Reference Materials

Figure A9: Certificate of Analysis for Standard Reference Material NIST 1570a Trace Elements in Spinach Leaves (p. 1 of 6).

Statistical analysis of the experimental data was performed by W.F. Guthrie, S.B. Schiller, and L.M. Gill of the NIST Statistical Engineering Division.

Support aspects involved in the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

INSTRUCTIONS FOR STORAGE AND USE

Storage: The material should be kept in its tightly closed original bottle and stored in the dark at a temperature between 10 °C and 30 °C. It should not be exposed to intense sources of radiation. Ideally, the bottle should be kept in a desiccator under the conditions indicated above. Spinach leaves have a tendency to rapidly bleach and to turn a tan or light brown color in the presence of visible light. By monitoring SRM 1570, the original SRM, it was determined that there is no evidence of any change in elemental mass fractions as a result of the color change.

Instructions for Use: The contents of a bottle should be thoroughly mixed by rotating and/or rolling before each use. Allow the contents to settle for 1 minute prior to opening to minimize the loss of fine dust particles. A minimum sample mass of 150 mg of the material, dried as described in the section (see "Instructions for Drying"), should be used to relate analytical determinations to the certified values on this certificate. In some cases, especially for volatile elements such as mercury, it is preferable to analyze samples from the bottle without drying, determine the moisture content on a separate sample from the same bottle taken at the same time, and convert the analytical results to a dry-mass basis.

Digestion procedures should be designed to avoid loss of volatile elements, such as arsenic and mercury. Digestion of the SRM in nitric and perchloric acids was found to be incomplete, with a small residue of siliceous material remaining. This residue must be considered an integral part of this SRM and should be dissolved with a small amount of hydrofluoric acid to obtain total dissolution. All certified values are based on the total dissolution.

Instructions for Drying: Samples of this SRM must be dried by one of the following two procedures in order for certified values to be valid:

1. Drying in a desiccator at room temperature (approximately 22 °C) for 120 h over fresh anhydrous magnesium perchlorate. The sample depth should not exceed 1 cm.

2. Freeze-drying for 24 h at a pressure of 13.3 Pa or lower and a shelf temperature of –5 °C or lower after having frozen the sample (not to exceed 1 cm in depth) at –40 °C or lower for at least 1 h. At the end of the 24 h period, samples should be placed immediately in a desiccator with fresh anhydrous magnesium perchlorate. Samples should be weighed after allowing a minimum of 4 h to establish temperature equilibrium.

Note: An approximate mass loss on drying of 3.5 % was observed for the measurements reported here. Vacuum drying at room temperature and oven drying at elevated temperatures have resulted in excessive mass losses and therefore are **NOT** recommended.

SOURCE, PREPARATION, AND ANALYSIS[1]

Source and Preparation of Material: The material (approximately 2270 kg) for this SRM was obtained from commercial supplier Oregon Freeze-Drying Corp. (Albany, OR). It consists of U.S. Grade A chopped frozen spinach. The material was thawed, placed in a ribbon mixer, thoroughly mixed, and blended. After mixing, the spinach was freeze-dried. The freeze-dried material was then ground in a stainless steel grinder and shipped to NIST. At NIST, the freeze-dried material was sieved through a polypropylene sieve having openings of 0.25 mm (equivalent to a U.S. Series 60 standard sieve). The sieved material was then jet milled and air classified to a particle size of approximately 75 µm (200 mesh). After mixing in a large blender, the spinach was irradiated with cobalt-60 radiation to a minimum absorbed dose of approximately 27.8 kGy for microbiological control and was bottled.

[1] Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Figure A10: Certificate of Analysis for Standard Reference Material NIST 1570a Trace Elements in Spinach Leaves (p. 2 of 6).

Elemental Analysis: Value assignment of the mass fractions of the elements in SRM 1570a was based on the combination of measurements from two or more different analytical methods at NIST and collaborating laboratories. NIST and collaborating laboratories provided measurements by using colorimetry (COLOR), cold-vapor atomic absorption spectrometry (CVAAS), flow injection hydride generation atomic absorption spectrometry (FI-HGAAS), inductively coupled plasma optical emission spectrometry (ICP), isotope dilution inductively coupled plasma mass spectrometry (IDICPMS), isotope dilution thermal ionization mass spectrometry (IDTIMS), instrumental neutron activation analysis (INAA), laser-excited atomic fluorescence spectrometry (LEAFS), prompt gamma activation analysis (PGAA), and radiochemical neutron activation analysis (RNAA). Data from an IAEA interlaboratory comparison exercise were also used where available. A list of analytical methods used for measurement of each element is provided in Appendix A.

Homogeneity Assessment: Samples from randomly selected bottles of SRM 1570a were tested for homogeneity. No evidence of statistically significant inhomogeneity was observed.

Certified Mass Fraction Values: Certified mass fraction values are weighted means of results from two or more different analytical methods combined using the DerSimonian-Laird procedure [2]. The uncertainty in the certified mass fraction values was calculated according to the methods in Supplement 1 to the ISO/JCGM Guide [3] and the results are consistent with the methods given in the ISO/JCGM Guide [4]. The uncertainty of each certified value is expressed as $U = ku_c$. The quantity u_c is the combined standard uncertainty, which accounts for the combined effect of within-method uncertainty from all potential sources and any bias between methods at the level of one standard deviation. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and a 95 % level of confidence for each analyte.

The certified values are reported on a dry-mass basis. For certified values to be valid, the material must be dried according to the instructions provided above. The measurand is the mass fraction of the element. The certified values are metrologically traceable to the SI unit of milligram per kilogram, expressed as percent.

Table 1. Certified Mass Fraction Values (Dry-Mass Basis) of Constituent Elements

Element	Mass Fraction (%)	Coverage Factor (k)
Calcium	1.526 ± 0.066	2.0299
Phosphorus	0.5187 ± 0.0067	1.9772
Potassium	2.900 ± 0.026	2.3226
Sodium	1.821 ± 0.023	1.9943

Element	Mass Fraction (mg/kg)	Coverage Factor (k)	Element	Mass Fraction (mg/kg)	Coverage Factor (k)
Aluminum	310 ± 15	2.0102	Mercury	0.0297 ± 0.0021	2.0492
Arsenic	0.068 ± 0.012	2.0561	Nickel	2.142 ± 0.058	1.9709
Boron	37.7 ± 1.2	2.0127	Selenium	0.1152 ± 0.0043	2.0371
Cadmium	2.876 ± 0.058	2.0464	Strontium	55.54 ± 0.50	2.5029
Cobalt	0.393 ± 0.030	2.0320	Thorium	0.0480 ± 0.0017	2.0053
Copper	12.22 ± 0.86	2.0488	Vanadium	0.568 ± 0.017	2.4938
Manganese	76.0 ± 1.2	1.9855	Zinc	82.3 ± 3.9	2.0136

Figure A11: Certificate of Analysis for Standard Reference Material NIST 1570a Trace Elements in Spinach Leaves (p. 3 of 6).

Reference Mass Fraction Values: Each reference value, expressed as a mass fraction on a dry-mass basis, is an equally weighted mean of results provided by NIST and/or collaborating laboratories. The uncertainty in the reference mass fraction values is calculated as $U = ku_c$. The quantity u_c is the combined standard uncertainty calculated according to the ISO/JCGM Guide [3,4], which accounts for the combined effect of within-method uncertainty and for any bias between methods at the level of one standard deviation. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and a 95 % level of confidence for each analyte.

These reference values are reported on a dry-mass basis. In order for these reference values to be valid, the material must be dried according to the instructions provided above. The measurand is the mass fraction of the element as determined by the method indicated. The reference values are metrologically traceable to the SI unit of milligram per kilogram, expressed as percent.

Table 2. Reference Mass Fraction Values (Dry-Mass Basis) of Constituent Elements

Element	Mass Fraction (%)
Nitrogen (Total)	6.06 ± 0.20

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Europium	0.0055 ± 0.0010	Rubidium	12.7 ± 1.6
Scandium	0.0055 ± 0.0006	Uranium	0.155 ± 0.023

Information Mass Fraction Values: Each information value, expressed as a mass fraction on a dry-mass basis, is an equally weighted mean of results provided by NIST and/or collaborating laboratories. Insufficient information is available to asses the uncertainty associated with the value, therefore no uncertainty is provided.

Table 3. Information Mass Fraction Values (Dry-Mass Basis) of Constituent Elements

Element	Mass Fraction (%)
Magnesium	0.9
Sulfur	0.5

Element	Mass Fraction (mg/kg)
Lead	0.2

Figure A12: Certificate of Analysis for Standard Reference Material NIST 1570a Trace Elements in Spinach Leaves (p. 4 of 6).

REFERENCE

[1] May, W.; Parris, R.; Beck, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definitions of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260–136, U.S. Government Printing Office: Washington, DC (2000); available at http://www.nist.gov/srm/upload/SP260-136.PDF (accessed Feb 2014).

[2] DerSimonian, R; Laird, N.; *Meta-Analysis in Clinical Trials*; Controlled Clin. Trials, Vol. 7, pp. 177–188 (1986).

[3] JCGM 101:2008; *Evaluation of Measurement Data – Supplement 1 to the "Guide to the Expression of Uncertainty in Measurement" - Propagation of Distributions using a Monte Carlo Method*; JCGM (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_101_2008_E.pdf (accessed Feb 2014).

[4] JCGM 100:2008; *Evaluation of Measurement Data - Guide to the Expression of Uncertainty in Measurement;* (GUM 1995 with Minor Corrections), Joint Committee for Guides in Metrology (2008); available at http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Feb 2014); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at http://www.nist.gov/pml/pubs/index.cfm (accessed Feb 2014).

Certificate Revision History: 25 February 2014 (Extension of certification period; updated certified values and uncertainties; removed reference and information values for proximates, calories, total dietary fiber, fatty acids, and nitrogen (organic and protein) due to instability of organic constituents; editorial changes); **08 October 2008** (Update of expiration date; editorial changes); **31 August 2001** (This technical revision reports the addition of reference and information values for proximates, calories, total dietary fiber, and fatty acids and a change from non-certified to reference and information values for several inorganic constituents); **15 July 1996** (Editorial changes); **20 October 1994** (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at http://www.nist.gov/srm.

Figure A13: Certificate of Analysis for Standard Reference Material NIST 1570a Trace Elements in Spinach Leaves (p. 5 of 6).

APPENDIX A

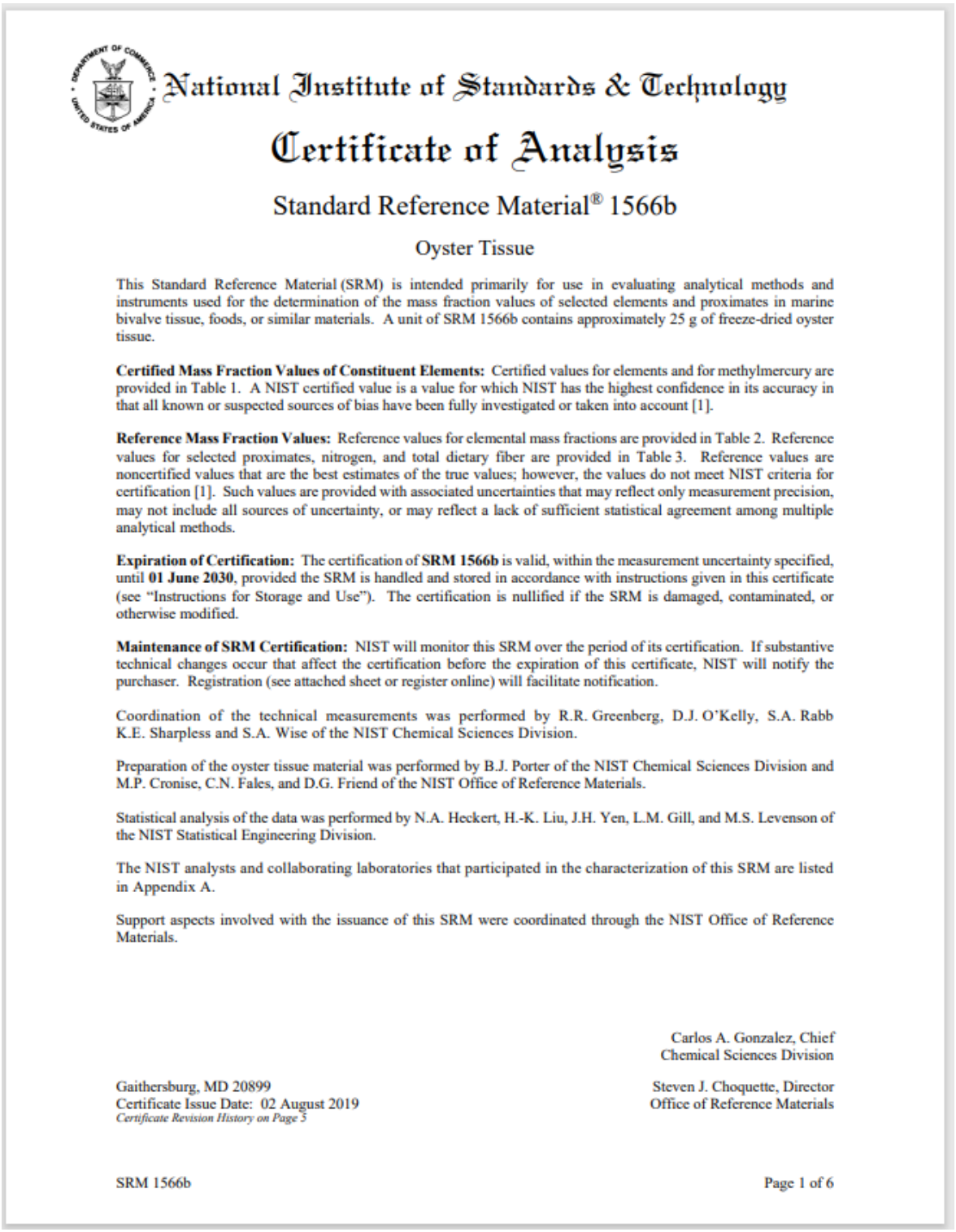
Methods Used in Elemental Determinations

Element	Method Code	Element	Method Code
Aluminum (Al)	ICP INAA	Nitrogen (N)	PGAA
Arsenic (As)	FI-HGAAS RNAA	Phosphorus (P)	COLOR ICP
Boron (B)	IDICPMS PGAA	Potassium (K)	IDTIMS INAA
Cadmium (Cd)	IDICPMS PGAA RNAA	Rubidium (Rb)	IAEA INAA
Calcium (Ca)	IDTIMS INAA	Scandium (Sc)	IAEA INAA
Cobalt (Co)	INAA RNAA	Selenium (Se)	FI-HGAAS INAA RNAA
Copper (Cu)	ICP RNAA	Sodium (Na)	PGAA INAA
Europium (Eu)	IAEA INAA	Strontium (Sr)	IDTIMS INAA
Lead (Pb)	IAEA IDICPMS	Sulfur (S)	PGAA IAEA
Magnesium (Mg)	IDICPMS	Thorium (Th)	INAA RNAA
Manganese (Mn)	INAA LEAFS	Uranium (U)	RNAA
Mercury (Hg)	CVAAS RNAA	Vanadium (V)	IDTIMS INAA
Nickel (Ni)	IDICPMS RNAA	Zinc (Zn)	ICP INAA

Key:

COLOR:	Colorimetry
CVAAS:	Cold-vapor atomic absorption spectrometry
FI-HGAAS:	Flow injection hydride generation atomic absorption spectrometry
IAEA:	Various methods from an IAEA interlaboratory comparison exercise.
ICP:	Inductively coupled plasma optical emission spectrometry
IDICPMS:	Isotope dilution inductively coupled plasma mass spectrometry
IDTIMS:	Isotope dilution thermal ionization mass spectrometry
INAA:	Instrumental neutron activation analysis
LEAFS:	Laser-excited atomic fluorescence spectrometry
PGAA:	Prompt gamma activation analysis
RNAA:	Radiochemical neutron activation analysis

Figure A14: Certificate of Analysis for Standard Reference Material NIST 1570a Trace Elements in Spinach Leaves (p. 6 of 6).



National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 1566b

Oyster Tissue

This Standard Reference Material (SRM) is intended primarily for use in evaluating analytical methods and instruments used for the determination of the mass fraction values of selected elements and proximates in marine bivalve tissue, foods, or similar materials. A unit of SRM 1566b contains approximately 25 g of freeze-dried oyster tissue.

Certified Mass Fraction Values of Constituent Elements: Certified values for elements and for methylmercury are provided in Table 1. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been fully investigated or taken into account [1].

Reference Mass Fraction Values: Reference values for elemental mass fractions are provided in Table 2. Reference values for selected proximates, nitrogen, and total dietary fiber are provided in Table 3. Reference values are noncertified values that are the best estimates of the true values; however, the values do not meet NIST criteria for certification [1]. Such values are provided with associated uncertainties that may reflect only measurement precision, may not include all sources of uncertainty, or may reflect a lack of sufficient statistical agreement among multiple analytical methods.

Expiration of Certification: The certification of **SRM 1566b** is valid, within the measurement uncertainty specified, until **01 June 2030**, provided the SRM is handled and stored in accordance with instructions given in this certificate (see "Instructions for Storage and Use"). The certification is nullified if the SRM is damaged, contaminated, or otherwise modified.

Maintenance of SRM Certification: NIST will monitor this SRM over the period of its certification. If substantive technical changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Registration (see attached sheet or register online) will facilitate notification.

Coordination of the technical measurements was performed by R.R. Greenberg, D.J. O'Kelly, S.A. Rabb K.E. Sharpless and S.A. Wise of the NIST Chemical Sciences Division.

Preparation of the oyster tissue material was performed by B.J. Porter of the NIST Chemical Sciences Division and M.P. Cronise, C.N. Fales, and D.G. Friend of the NIST Office of Reference Materials.

Statistical analysis of the data was performed by N.A. Heckert, H.-K. Liu, J.H. Yen, L.M. Gill, and M.S. Levenson of the NIST Statistical Engineering Division.

The NIST analysts and collaborating laboratories that participated in the characterization of this SRM are listed in Appendix A.

Support aspects involved with the issuance of this SRM were coordinated through the NIST Office of Reference Materials.

Carlos A. Gonzalez, Chief
Chemical Sciences Division

Gaithersburg, MD 20899
Certificate Issue Date: 02 August 2019
Certificate Revision History on Page 5

Steven J. Choquette, Director
Office of Reference Materials

Figure A15: Certificate of Analysis for Standard Reference Material NIST 1566b Oyster Tissue (p. 1 of 6).

NOTICE AND WARNINGS TO USERS

SRM 1566B IS INTENDED FOR RESEARCH USE; NOT FOR HUMAN CONSUMPTION.

INSTRUCTIONS FOR STORAGE AND USE

Storage: The material should be kept in its original bottle, tightly closed, and stored in a desiccator over magnesium perchlorate, $Mg(ClO_4)_2$, at temperatures between 10 °C to 30 °C. It should **NOT** be exposed to intense sources of radiation, including ultraviolet light or sunlight.

Use: A minimum sample mass of 250 mg of material is necessary for values in this certificate to be valid within stated uncertainties. This amount of material should be on a dry-mass basis (see "Instructions for Drying"). The contents of the bottle should be shaken well before each use, and the bottle should be closed tightly **immediately** after use and stored as described above.

Instructions for Drying: Prior to removal of test portions for elemental analysis, the contents of the bottle should be thoroughly mixed. Before the mass determination, samples of SRM 1566b must be dried to constant mass by one of the following procedures:

1. Drying at room temperature for *at least* 5 d over $Mg(ClO_4)_2$ in a desiccator.
2. Vacuum drying at room temperature for *at least* 24 h at a pressure of approximately 30 Pa (0.2 mm Hg) using a cold trap.
3. Freeze drying for *at least* 5 d at a pressure of approximately 30 Pa (0.2 mm Hg).

The analyst should ascertain that the material has indeed reached constant mass. Although the above procedures have been generally sufficient, in a few instances the time needed to reach constant mass was longer than listed above. If the constituents of interest are volatile, a separate test portion of the oyster tissue should be removed from the bottle at the time of analysis and dried to determine the mass fraction values on a dry-mass basis.

SOURCE, PREPARATION, AND ANALYSIS[1]

Source and Preparation of Material: The oysters (*Crassostrea virginica*, an American Eastern oyster) used for the preparation of SRM 1566b were purchased from Bon Secour Fisheries, Inc. (Bon Secour, AL). The oysters were collected from the Gulf of Mexico, shucked, rinsed twice to remove sediment and shells, packed and sealed in polyethylene bags, and frozen. The frozen oysters and fluids were shipped in coolers containing dry ice to NIST. At NIST, the oysters and fluids were ground in a Robot-Coupe Vertical Cutter Mixer that was equipped with a stainless steel bowl and titanium blades. The oyster tissue was blended for 100 s into a slurry; approximately 5 kg of slurry was poured into each of 40 specially cleaned aluminum trays outfitted with temperature probes, and frozen at –20 °C. The trays were taken to a large freeze-drying facility at the Frederick Cancer Research and Development Center, Natural Products Group in Frederick, MD. The freeze-dryer's initial temperature was –45 °C and gradually increased to a temperature of 10 °C over a period of five days. The freeze-dried material was stored at –20 °C, then broken into smaller pieces, blended in the Robot-Coupe Mixer, jet milled, and homogenized in a V-blender for 30 min to 40 min. The material was radiation sterilized (^{60}Co) at Neutron Products, Inc. (Dickerson, MD), for approximately 5 h to an absorbed dose of 30 kGy and then aliquoted into amber bottles.

Description of Calculations Used in Certified Value Assignment

Sulfur: The certified mass fraction value of sulfur is the result of a single NIST method, thermal ionization mass spectrometry (TIMS), with confirmation by a second NIST method, prompt gamma activation analysis (PGAA). Its uncertainty is expressed as an expanded uncertainty, U, and is calculated as $U = ku_c$. The quantity u_c is the combined standard uncertainty, calculated according to the JCGM Guide [2], that accounts for the combined components of uncertainty for the method at one standard deviation. The coverage factor, k, is determined from the Student's t-distribution corresponding to five degrees of freedom and a 95 % confidence. Because of heterogeneity, the uncertainty associated with sulfur takes the form of a prediction interval.

Methylmercury: The results for methylmercury are expressed as milligrams per kilogram as mercury. The certified value is the mean of results from four different laboratory analyses of SRM 1566b using four different analytical methods. The expanded uncertainty in the certified value is equal to $U = ku_c$ where u_c is the combined standard uncertainty calculated according to the JCGM Guide [2] and k is the coverage factor. The value u_c is intended to represent, at the level of one standard deviation, the combined effect of all the uncertainties in the certified value.

[1]Certain commercial equipment, instruments or materials are identified in this certificate to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Figure A16: Certificate of Analysis for Standard Reference Material NIST 1566b Oyster Tissue (p. 2 of 6).

Here, u_c is given by the standard error of the mean of the four analyses. The coverage factor, k, is determined from the Student's t-distribution corresponding to three degrees of freedom and 95 % confidence.

All Other Elements: All other certified mass fraction values are weighted means of results from two or more analytical methods. For these certified values, the uncertainty is calculated as $U = ku_c + B$. The quantity u_c is the combined standard uncertainty calculated according to the JCGM Guide [2], which accounts for the combined effect of the within variance for all methods at one standard deviation. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each element. The term B is a bias adjustment for the difference between methods, which is the maximum difference between the certified value and the method means [3]. Because of heterogeneity, the uncertainty associated with calcium and thorium takes the form of a prediction interval.

Table 1. Certified Mass Fraction Values for Elements and Methylmercury[a]

Element	Mass Fraction (%)			Element	Mass Fraction (%)		
Calcium (Ca)[b,c]	0.0838	±	0.0020	Potassium (K)[c,d,e]	0.652	±	0.009
Chlorine (Cl)[c,d]	0.514	±	0.010	Sodium (Na)[c,f]	0.3297	±	0.0053
Magnesium (Mg)[b,c]	0.1085	±	0.0023	Sulfur (S)[d,g]	0.689	±	0.014

Element	Mass Fraction (mg/kg)			Element	Mass Fraction (mg/kg)		
Aluminum (Al)[c,h]	197.2	±	6.0	Mercury (total) (Hg)[i,j]	0.0371	±	0.0013
Arsenic (As)[c,k]	7.65	±	0.65	Methylmercury (as mercury)[l,m,n,o]	0.0132	±	0.0007
Cadmium (Cd)[p,q]	2.48	±	0.08	Nickel (Ni)[c,k,p]	1.04	±	0.09
Cobalt (Co)[c,p]	0.371	±	0.009	Rubidium (Rb)[c,p]	3.26	±	0.14
Copper (Cu)[c,p,q]	71.6	±	1.6	Selenium (Se)[c,k]	2.06	±	0.15
Iron (Fe)[c,e,r]	205.8	±	6.8	Silver (Ag)[c,p]	0.666	±	0.009
Lead (Pb)[h,p]	0.308	±	0.009	Thorium (Th)[h,c]	0.0367	±	0.0043
Manganese (Mn)[c,p]	18.5	±	0.2	Vanadium (V)[c,p]	0.577	±	0.023
				Zinc (Zn)[c,e]	1 424	±	46

[a] The measurands are the mass fractions of the elements listed in Table 1. Metrological traceability is to the SI derived unit for mass fraction (expressed on a dry-mass basis as a percent or milligram per kilogram).

Analytical Methods:

[b] Isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS) at NIST
[c] Neutron activation analysis (instrumental) (INAA) at NIST
[d] PGAA at NIST; confirmation method for S measurement only.
[e] ID-ICP-MS at National Research Council Canada (NRCC)
[f] Flame atomic emission spectrometry at NIST
[g] ID-TIMS at NIST
[h] ICP-MS at NRCC
[i] Cold vapor atomic absorption spectrometry (CVAA) at NIST
[j] Neutron activation analysis (radiochemical) (RNAA) at Jožef Stefan Institute (Ljubljana, Slovenia)
[k] Electrothermal atomic absorption spectrometry (AAS) at NRCC
[l] Gas chromatography with atomic emission detection (GC-AED) at NIST
[m] Gas chromatography with atomic fluorescence (GC-AFS) detection at Jožef Stefan Institute
[n] CVAA at Jožef Stefan Institute
[o] CVAA at Research Centre Jülich, (Jülich, Germany)
[p] ICP-MS at NIST
[q] RNAA at NIST
[r] Inductively coupled plasma optical emission spectrometry (ICP-OES) at NRCC

Figure A17: Certificate of Analysis for Standard Reference Material NIST 1566b Oyster Tissue (p. 3 of 6).

Table 2. Reference Mass Fraction Values for Elements[a]

Element	Mass Fraction (%)
Nitrogen (N)[b]	7.6 ± 0.4

Element	Mass Fraction (mg/kg)	Element	Mass Fraction (mg/kg)
Antimony (Sb)[c]	0.011 ± 0.002	Strontium (Sr)[f]	6.8 ± 0.2
Barium (Ba)[d]	8.6 ± 0.3	Tin (Sn)[d]	0.031 ± 0.008
Boron (B)[b]	4.5 ± 1.9	Titanium (Ti)[g]	12.24 ± 0.39
Gold (Au)[c,f]	0.0106 ± 0.0028	Uranium (U)[d]	0.2550 ± 0.0014
Hydrogen (H)[b]	7.2 ± 0.4		

[a] The measurands are the mass fractions of the elements listed in Table 2 as determined by the indicated method or methods. Metrological traceability is to the SI derived unit for mass fraction (expressed on a dry-mass basis as a percent or milligram per kilogram), as realized by the method used.

Analytical Methods:
[b] PGAA at NIST
[c] RNAA at NIST
[d] ID-ICP-MS at NRCC
[e] INAA at NIST
[f] ICP-MS at NIST
[g] ICP-OES at NIST

Reference Mass Fraction Values of Selected Proximates, Nitrogen, and Total Dietary Fiber: Each reference value, expressed as a mass fraction of the material on an as-received or dry-mass basis, for a stated measurand is an equally weighted mean of results from the collaborating laboratories listed in Appendix A. Each of four laboratories analyzed one portion from each of three bottles of SRM 1566b using their routine methods. Determinations were performed on the material "as-received," with conversion of results to a dry-mass basis using moisture values determined by the four laboratories on separate subsamples taken from each of the three bottles. The uncertainty in the reference values is expressed as an expanded uncertainty, U, at the 95 % level of confidence, and is calculated according to the method described in the JCGM Guide [2]. The expanded uncertainty is calculated as $U = ku_c$, where u_c is intended to represent, at the level of one standard deviation, the combined effect of between-laboratory and within-laboratory components of uncertainty. The coverage factor, k, is determined from the Student's t-distribution corresponding to the appropriate associated degrees of freedom and 95 % confidence for each analyte. Analytical methodology information is provided in Table 4. The measurands are the constituents listed in Table 3 as determined by the methods used by the laboratories. Metrological traceability is to the SI derived unit for mass fraction (expressed as-received and dry-mass basis as percent), as realized by the method used.

Table 3. Reference Mass Fraction Values of Selected Proximates, Nitrogen, and Total Dietary Fiber

Constituent	Mass Fraction as-received[a] (%)	Mass Fraction dry-mass basis[a] (%)
Moisture	4.6 ± 3.6	0 (by definition)
Solids	95.4 ± 3.6	100 (by definition)
Ash	3.87 ± 0.09	4.05 ± 0.15
Protein[b]	42.6 ± 1.3	44.7 ± 2.6
Protein Nitrogen[b]	6.82 ± 0.20	7.16 ± 0.42
Total Dietary Fiber	6.5 ± 1.6	6.8 ± 1.4

[a] Note that SRM 1566b was originally certified in 2001 and, at that time, reference and information values were provided for fatty acids. Those reference and information values are no longer valid as these compounds are not stable in this matrix for more than 10 y under these storage conditions.
[b] The protein mass fraction value was calculated from the nitrogen values reported by the laboratories using a conversion factor of 6.25. The value for protein is the mean of the individual protein calculations. If the mean nitrogen values above are used for calculation, the mean protein mass fraction values are 42.6 % and 44.7 % on as-received and dry-mass basis, respectively.

Figure A18: Certificate of Analysis for Standard Reference Material NIST 1566b Oyster Tissue (p. 4 of 6).

Table 4. Analytical Methods Used by Collaborating Laboratories for the Determination of Proximates, Nitrogen, and Total Dietary Fiber in SRM 1566b

Ash	mass after ignition in a muffle furnace
Moisture	mass loss after drying in a vacuum oven (3 laboratories) or forced-air oven (1 laboratory)
Protein nitrogen	Dumas (1 laboratory); modified Dumas (1 laboratory); Kjeldahl (2 laboratories)
Protein	calculated from nitrogen using a factor of 6.25
Solids	calculated; (sample mass – moisture)
Total dietary fiber	enzymatic gravimetry

REFERENCES

[1] May, W.; Parris, R.; Beck II, C.; Fassett, J.; Greenberg, R.; Guenther, F.; Kramer, G.; Wise, S.; Gills, T.; Colbert, J.; Gettings, R.; MacDonald, B.; *Definition of Terms and Modes Used at NIST for Value-Assignment of Reference Materials for Chemical Measurements*; NIST Special Publication 260-136 (2000); available at https://www.nist.gov/sites/default/files/documents/srm/SP260-136.PDF (accessed Jul 2019).

[2] JCGM 100:2008; *Evaluation of Measurement Data — Guide to the Expression of Uncertainty in Measurement* (GUM 1995 with Minor Corrections); Joint Committee for Guides in Metrology (2008); available at https://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (accessed Jul 2019); see also Taylor, B.N.; Kuyatt, C.E.; *Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results*; NIST Technical Note 1297; U.S. Government Printing Office: Washington, DC (1994); available at https://www.nist.gov/pml/nist-technical-note-1297 (accessed Jul 2019).

[3] Schiller, S.; Eberhardt, K.; *Combining Data from Independent Chemical Analysis Methods*; Spectrochimica Acta, Vol. 46B, No. 12, pp. 1607–1613 (1991).

Certificate Revision History: 02 August 2019 (Change of expiration date; editorial changes); 26 June 2017 (Corrected units for gold; editorial changes); 18 November 2015 (Added reference values for gold and titanium in Table 2; editorial changes); 07 February 2011 (Corrected the definition of ash in Table 4); 09 July 2010 (Removed reference and information concentration values of fatty acids and removed reference concentration values of caloric content, carbohydrates, and fat along with the corresponding analytical methods; changed the expiration date; editorial changes); 17 January 2001 (Original certificate date).

Users of this SRM should ensure that the Certificate of Analysis in their possession is current. This can be accomplished by contacting the SRM Program: telephone (301) 975-2200; fax (301) 948-3730; e-mail srminfo@nist.gov; or via the Internet at https://www.nist.gov/srm.

Figure A19: Certificate of Analysis for Standard Reference Material NIST 1566b Oyster Tissue (p. 5 of 6).

Appendix A

NIST Analysts, Chemical Sciences Division

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S.E. Long	R.P. Watson
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Collaborating Laboratories and Analysts for Elemental Determinations

Analytical Chemistry Division, National Research Council Canada (Ottawa, Canada): V. Boyko, J. Lam, S. Willie, and L. Yang
Jožef Stefan Institute, (Ljubljana, Slovenia): H. Akagi, V. Fajon, M. Horvat, K. Jereb, and M. Logar
Research Centre Jülich (Jülich, Germany): H. Emons and K. May

Collaborating Laboratories for Selected Proximates, Nitrogen, and Total Dietary Fiber Determinations

Covance Laboratories (Madison, WI)
Lancaster Laboratories (Lancaster, PA)
Medallion Laboratories (Minneapolis, MN)
Southern Testing and Research Laboratories (Wilson, NC)

Figure A20: Certificate of Analysis for Standard Reference Material NIST 1566b Oyster Tissue (p. 6 of 6).

Sample	^{210}Pb Bq/g dw, Decay Corrected Activity	^{210}Po Bq/g dw, Decay Corrected Activity	^{226}Ra Bq/g dw, Decay Corrected Activity
East Athabasca Blueberry 01 Washed	0.00300	0.00300	0.00400
Effective Dose Coefficients (mSv/Bq	0.00069	0.00120	0.00028
Annual Effective Dose (mSv)	0.01609	0.02799	0.00871
Combined Annual Effective Dose, Fresh Weight (mSv) =	0.00792		

Table A37: Ingestion Dose Calculation.