BIOACCESSIBILITY OF METALS IN SOILS IN SELECTED PARKS IN MONTREAL

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Abstract

The main focus of this study was to determine the concentrations and bioaccessibility of metals in Montreal city parks. Surface soil samples were collected from nine parks located across Montreal city and analyzed for total metals, pH, carbon content and bioaccessibility. Metal concentrations were below the Canadian Council of Minister of the Environment soil quality guidelines for residential/parkland use except for Cu in one sample. The order of mean bioaccessibility was Cd (78.9%) > Ba (64.9%) > Pb (53.4%) > Cu (33.0%) > Zn (31.4%) > Co (26.1%) > As (23.9%) > Ni (13.9%) > Fe (7.7%) and Cr (6.7%). Significant relationships between bioaccessibility and soil physicochemical properties were observed for some of the metals. The overall risk associated with the ingestion of metals in soils samples was considered low based on the metal concentrations and bioaccessibility data obtained.

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Introduction

Background

The influences of industrialization and urbanization are having great impacts on the lives of city dwellers. Industrialization has led to geometric increase in anthropogenic activities, which result in high concentrations of metals in city soils (Luo et al., 2012). Increased industrial activities, vehicular exhaust and waste disposal management among others have contributed to deposition and build-up of metals in city soils (Appleton, Cave, Palumbo-Roe & Wragg, 2013; Guney, Zagury, Dogan, & Onay, 2010; Luo et al., 2012).

The major sources of metals in city soils could be attributed to anthropogenic sources. This could include point or diffuse sources. Among these sources, atmospheric deposition often represents a significant portion (Hu et al., 2012). Metals are non-biodegradable and persist in the environment leading to their accumulation in city soils. Metals such as arsenic (As), barium (Ba), lead (Pb), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), manganese (Mn), zinc (Zn), and nickel (Ni) that accumulate in the city soils can pose major environmental risks to ecosystem and human health, especially to children who frequent city parks (Luo et al., 2012). Metals such as As, Pb and Cd have no known useful biochemical function in organisms (Abrahams, 2002). In contrast, Co, Cr, Cu, Fe, Mn and Zn are essential micronutrients required to maintain wellness in humans. However, they can become harmful when intake through major exposure pathways such as ingestion and inhalation exceeds the required minimum level (Abrahams, 2002). Knowledge of hazards associated with increased metal contaminants in city soil is very important because it has health impact on city dwellers’ wellness at a period of dwindling budgetary allocation to health services. In the light of the potential toxicity of these metals (As, Ba, Cd, Cr, Co, Cu, Pb, Mn, Ni and Zn,), especially to children through inadvertent soil ingestion, it is pertinent to identify and quantify the concentration of contaminants in city park soils. The data could be used to determine the level of contaminant exposure to park users.

Several studies have been conducted in major cities around the globe to estimate the concentration of metals in the city soils and the bioavailable fraction that can pose threat to human health. The assessment of these increased metal contaminants may be based on soil impacted by anthropogenic activities, eg., Poznan, Poland (Diatta & Grzebisz, 2011); Istanbul, Turkey (Guney et al., 2010); Xiamen, China (Luo et al., 2012); Newcastle upon Tyne, England (Okorie, Entwistle & Dean, 2011) or natural geogenic sources relating to soil parent material and soil forming processes, e.g., England, (Appleton, 2013); Balya, (Karadaş & Kara, 2011); and Nova Scotia, (Meunier, Walker, Wragg, Parsons, Koch, Jamieson, & Reimer, 2010). Currently, there is an ongoing Canada wide study of metal bioaccessibility in city soils in Halifax, Regina, Toronto, Ottawa and other cities (Royal Roads University, 2010). This study is a subset of the ongoing Canada wide project. Results to date show occasional metal contaminant concentrations that are higher than tolerable daily intake, background level or regulatory soil quality guideline values for their areas of jurisdiction.

Marr, Fyles and Hendershot (1999) studied the uptake of Cd, Cu, Mn, Pb and Zn by *Taraxacum officinale* Weber (dandelion) grown on abandoned industrial sites, community gardens and parks in Montreal and evaluated their bioavailability. They evaluated total metal concentrations by comparing them to the Interim Canadian Council of Ministers of the Environment (CCME) soil quality guidelines (CCME, 1991). Their findings indicated that the total metal concentrations were above the CCME guidelines for industrial sites while tissue concentrations remained normal for all land use types. The use of total metal concentrations tends to overestimate the health risks associated with metal contaminants in ingested soil. This depends on the soluble fraction of the metals in the digestive tract that are available for absorption (Luo et al., 2012; Wragg et al, 2011). Hence, this study seeks to investigate the safety of Montreal parks for city dwellers based on the determination of the bioaccessible and bioavailable fraction.

Description of Study Area

Montreal is the largest city in Quebec and the second largest in Canada after Toronto, with a population of 1,649,519 million (Statistics Canada, 2011). Montreal has 19 large parks covering an area of nearly 2,000 hectares where Montrealers enjoy leisure hours of recreational, educational and cultural activities. The majority of these parks are located near highways or in the city center with close proximity to high vehicular exhaust, and other anthropogenic activities such as construction and industrial activities which are potential sources of metal contaminants into city soils (Guney et al., 2010; Karadaş & Kara, 2011; Luo, Yu, & Li, 2012).

Research Objectives, Questions and Approach

Objectives. The objectives of this study are:

- To evaluate As, Cd, Cr, Cu, Co, Ni, Pb, and Zn bioaccessibility in soil samples collected from picnic areas in parks around Montreal city.
- To investigate the influence of total metals, soil composition and soil properties including total organic carbon, and pH on bioaccessibility.
- To compare the study results with other Canadian major cities and examine the compliance level with the Canadian Council of Ministers of the Environment (CCME, 1999) guidelines for residential and parkland use.

Research questions. The research questions for this study are:

1. What are the concentrations of total metals and their bioaccessibility in selected city parks in Montreal?
2. What roles do soil composition and soil properties such as pH, soil particle size, speciation and total organic carbon (TOC) have on metal bioaccessibility?
3. Are the results comparable to similar studies across Canadian major cities?

Approach. To achieve the objectives of this study, nine parks were selected and randomly sampled out of 11 parks approved by the city of Montreal. Some of the selected parks were situated along major highways, bounded by rivers, differ in size and vegetation, and in different areas of the city. Determination of the total metals concentration of the soil samples was conducted with inductively plasma mass spectroscopy (ICPMS) after acid digestion. This was followed by an in vitro extraction procedure to estimate the bioaccessibility of As, Ba, Ca, Co, Cu, Pb, Ni and Zn using United States Environmental Protection Agency (US EPA) protocol (US EPA, 2012). The influence of soil pH and total organic carbon on metal bioaccessibility was evaluated.

Research significance. The significance of this study includes:

- To provide Montreal city planners with soil geochemical data that can be used in policy formulation.
- To improve the sustainable management of identified risks associated with the parks and safeguard the health of city dwellers who frequently use the parks.

Literature Review

Sources of Metals in the Environment

Numerous studies show that continuous influx of metal contaminants in the environment can be classified into two broad sources groupings, namely natural rock weathering or geogenic sources and anthropogenic sources (Appleton et al., 2013; Diatta & Grzebisz, 2011; Wragg et al., 2011). Metals occur in soil as mineral ore that exhibit chemical bonding with other minerals (Ruby, 2004). Metal mobility and availability in the soil is a function of the physicochemical properties of the soil including mineralogy, particle size and soil pH (Pelfrêne et al., 2012; Ruby, 2004). Metals availability and concentration are often affected by physical and chemical weathering, biological and geological processes, water hydration and anthropogenic activities (Pelfrêne et al., 2012; Ruby 2004). A study by Ruby et al. (1999) on Pb and As further reveal that the limiting factors on bioavailability include the metal form, solubility and site-specific soil chemistry. Anthropogenic and natural sources contribute between 11-35% and 22-29% of the total metal pollution respectively into the environment (Environment Canada, 2012). Furthermore, acidification processes of water and soil ecosystems resulting from sulphur dioxide (SO_2) and nitrogen oxide (NO_x) emissions and deposition also contribute to the liberation of heavy metals from rocks and soils with consequential increase in metals concentrations incorporated into top soils (Environment Canada, 2012).

Geogenic sources. Metals are naturally occurring components of soils derived from both physical and chemical rock weathering that are governed by the geochemistry and geological conditions of the local rocks, soils and biological processes (Garrett, 2000; Pelfrêne et al., 2012; Ruby 2004). These processes influence the translocation distances, dissolution and transportation of metals in the soil (Garrett, 2000).

Anthropogenic sources. Soil is the ultimate sink for contaminants that enter the environment through mining, mineral processing activities and smelting, large-scale agricultural application of fertilizers and chemicals, expanding industrial processes and products (Guney et al., 2010). Ever increasing fossil fuel combustion, waste disposal and cities' population growth account for increases in anthropogenic sources of contaminants such as metals in the cities' soils (Appleton et al., 2013; Diatta & Grzebisz, 2011; Wragg et al. 2011). Atmospheric particulates resulting from anthropogenic activities are important sources of air pollutants (Hu et al, 2012) that have long range dispersion and contribute to the deposition and build-up of metals in the urban environment.

Health Impacts of Metals on Humans

The impacts of metals on human health depend on the bioavailability of the metals. Metals are present in soils as complex mixtures of discrete mineral phases. Their availability depends on the relationship between the phases and the soils which govern their dissolution properties (Ruby et al., 1999). Studies have enumerated various potential metal contaminants exposure pathways into humans (Appleton et al., 2013; Diatta & Grzebisz, 2011; Guney et al., 2010). These pathways are broadly grouped as occupational and non-occupational exposure (Appleton et al., 2013; Diatta & Grzebisz, 2011; Yu & Landis, 1998). For the purpose of this study, non-occupational exposure pathways are the main focus. Several studies have explored non-occupational routes which include particulates inhalation, dermal contact and the most direct exposure pathway, oral ingestion of soil (Appleton et al.,2013; Diatta & Grzebisz, 2011; Guney et al., 2010; Hu et al., 2012; Martinez-Sanchez et al., 2013; Luo et al., 2012). Oral ingestion is common among children who frequent recreational parks and playgrounds through intentional or accidental mouthing of soils, dirty hands and toys (Guney et al., 2010; Hu et al., 2012; Martinez-Sanchez et al., 2013; Luo et al., 2012; Wragg & Cave, 2003).

Children are susceptible to adverse health impacts from exposure to metal contaminated soils. This is due to ingestion of large amounts of soil, high absorptive rate of metals from digestive tracts and higher haemoglobin-metal affinity in children than adults (Diatta &

Grzebisz, 2011; Wragg & Cave, 2003). Numerous studies have suggested different rates of soils ingestion among children: Guney et al. (2010) reported 137 mg/d with upper level of 1432 mg/d; while US EPA (2008) suggested mean value of 50 mg/d for soil, 100 mg/d as central tendency values for soil and dust and upper percentile 1g/d for children with pica behaviour.

Generally, assessment of health risk of potentially toxic metals involves the quantitative assessment of the possibility of the deleterious impacts occurring in a given set of conditions (Philip, 2001). Table 1 gives a snapshot of metal impacts on human health, risk manifestation and major biomarkers of importance.

Table 1: Human Health Impacts for Metals

Metal	Human Health Impacts	Most common Biomarkers of exposure	Mean concentration in soil and sediment (mg/kg)	Reference
Arsenic	Affects: skin, digestive, hepatic, nervous, respiratory system; major human carcinogen. Causes: skin discoloration, appearance of small corns or warts, nausea and vomiting, decreased production of red and white blood cells, abnormal heart rhythm, damage to blood vessels and lower IQ scores in children.	Urinary arsenic liver, lungs	<0.1–97 mg/kg, and 7.2 mg/kg	ATSDR (2007a), Arsenic
Barium	Affects: cardiovascular, digestive, reproductive systems. Causes: gastrointestinal disturbances followed by hypokalemia, hypertension, and heart rhythm abnormalities following acute oral exposure to high doses of barium.	Bone, blood, urine, and feces.	Mean values ranging between 265 and 835 mg/kg, depending on soil type	ATSDR (2007b) Barium.

Metal	Human Health Impacts	Most common Biomarkers of exposure	Mean concentration in soil and sediment (mg/kg)	Reference
Cadmium	Affects: cardiovascular, developmental (during periods when organs are developing), digestive system, nervous system, urinary system, reproductive, respiratory (From the nose to the lungs) major human carcinogen. Causes: Increased risk of osteoporosis, renal tubular damage, glomerular damage, decreased lung function	Blood, urine, feces, liver Kidney and bone	0.06 to 1.1 mg/kg without anthropogenic contribution	ATSDR (2012a)
Chromium	Affects: immune, urinary, respiratory and cardiovascular systems. Major human carcinogenic and genotoxic Causes**:** allergic dermatitis, low birth weight	Blood or urine	37.0 mg/kg	ATSDR (2012b), Chromium
Cobalt	Affects: cardiovascular, organs development, haematological, respiratory known human carcinogen Causes: nausea and vomiting dermatitis	Urine and blood		ATSDR (2004a), Cobalt
Copper	Affects: gastrointestinal, liver, respiratory tract, immune system, and developmental Causes: liver and kidney damage, immunotoxic, and death	Blood, urine, hair, and nails	5 to 70 mg/kg	ATSDR (2004b), Copper
Manganese	Affects: heart and blood vessels, liver, nervous system, respiratory system, neurodevelopmental Causes**:** memory loss, and impair learning ability in children	Blood and urine	330 mg/kg	ATSDR (2012c), Manganese
Nickel	Affects: skin, cardiovascular respiratory system, immune system, developmental. Known	Serum and urine nickel	4 to 80 mg/kg.	ATSDR (2005a), Nickel

Metal	Human Health Impacts	Most common Biomarkers of exposure	Mean concentration in soil and sediment (mg/kg)	Reference
	human respiratory carcinogen. Causes: dermatitis, allergic reaction, chronic bronchitis			
Lead	Affects: central nervous system, impair neurodevelopment in children, metabolic processes, renal, gastrointestinal, ocular and musculoskeletal. Causes: nausea ,anorexia, severe abdominal cramps, colic, weight loss, renal tubular dysfunction, abortion, muscle and joint pains and strong biochemical effect behavioural disorders, low intelligence, strokes	Blood, bone, and urine	<10 to 30 mg/kg	ATSDR (2007c), Lead
Zinc	Affects: digestive, haematological, and respiratory system Causes: anemia, pancreas damage, and decrease high-density lipoprotein (HDL) cholesterol.	Serum zinc level. High levels of zinc in feces or urine are indicative of recent exposure.	<5 to 2,900 mg/kg with a mean of 60 mg/kg.	ATSDR (2005b), Zinc

Ecological Impact of Metals

Soil ecological function, including nutrient recycling and primary production is influenced by increased levels of metal contaminants in the soil soil. Also affected is the health of wildlife and humans through bioaccumulation in the food chain (Hawkins et al., 2013) with the lasting impact of metal tolerance development among certain organisms. Arsenic, for example is toxic to a wide range of plants (e.g., beans, peas, and rice) and animals including marine species (Philp, 2001). Furthermore, harmful ecological impacts of metals may include info-disruption, that impact intra and interspecies interaction among freshwater organisms and microbes. Some metals have been implicated to modify the immune system thereby affecting pathogen-host relationship (Boyd, 2010). Hyper accumulation of naturally occurring metals by terrestrial plants was reported to provide defensive benefits for such plants (Boyd, 2010).

Bioavailability and Bioaccessibility

Metal toxicity depends on the duration and intensity of exposure and bioavailability (Martinez-Sánchez, Martínez-López, Martinez-Martínez, & Pérez-Sirvent, 2013). The absorption rate of solubilized metal from the intestinal tracts is controlled by metal oxidation state and physical forms (US EPA, 2007). Determination of soil pollution based on total metal concentrations often results in overestimation of the inherent health risk (Luo et al., 2012; Wragg & Cave, 2003; US EPA, 2007). Furthermore, Heuscher, Brandt, & Jardine, (2004) reported in their study that soil-metal sequestering properties significantly reduced the bioaccessibility of arsenic and chromium upon ingestion. Therefore, the total metal concentration in soil is not available for complete absorption through the gastrointestinal system (Luo et al., 2012; Ruby, Davis, Schoof, Eberle, & Sellstone, 1996; U.S. EPA, 2007b).

Studies have shown that adsorption, precipitation reactions and presence of less soluble species of metals are important factors that contribute to reduced dissolution and absorption of metals from soil during the transition through the alimentary canal (Ruby et al., 1999; US EPA, 2007). In order to derive a more accurate exposure estimate for metal contaminants in soils, Ruby et al. (1999) and US EPA (2007) determined the bioavailability of metals in soil relative to the bioavailability of the solubilized species in water. Bioavailability of a metal contaminant can be defined in terms of its absolute or relative bioavailability.

For the purpose of this study oral or absolute bioavailability is the fraction of the ingested metal contaminant present in the soils that solubilise/dissolve in the gastrointestinal tract fluids and become absorbed into the systemic circulation from where adverse health impacts could manifest (Cave et al., 2011; Ruby et al., 1996; Luo et al., 2012; USEPA, 2007). Oral bioavailability is the fraction of the ingested dose that is of toxicological significance due to its hazardous impacts on health as governed by internal dose of the contaminants (Cave et al, 2011). Cave et al. (2011) further highlighted the influence of soil properties on metal contaminants availability through a stepwise mechanism that involves accessibility (release of contaminant from soil into solution), absorption and metabolism of the contaminants. Relative oral bioavailability denotes comparative bioavailabilities of metal contaminants from soil to water. The difference in bioavailabilities between the two media necessitate the introduction of a correction factor; relative bioavailability factor (RBA), which may be greater or less than 1.0 while absolute bioavailability never exceeds 1.0 (100%) (US EPA, 2007). The US EPA defined relative bioavailability as “the ratio of the bioavailability of a metal in one exposure context (i.e., physical chemical matrix or physical chemical form of the metal) to that in another exposure context (US EPA, 2007, p. 3). For this study, RBA is defined as “the ratio of bioavailability of metal in soil to metal in water” (US EPA, 2013).

Bioaccessibility can be defined as the fraction of the soil-borne contaminant released into solution in the gastrointestinal tract and is available for absorption (Cave et al., 2011; Ruby et al., 1996). It is a measure of the physiologically soluble metal at the portal of entry into the body (National Research Council (NRC), 2003). Bioaccessibility is not a direct measurement of bioavailability, but a reasonable surrogate since solubilisation in the gastrointestinal tract is a major requirement for systemic absorption process (US EPA, 2007). The bioaccessible fraction is usually higher than the bioavailable fraction and as such it provides only a conservative measure of bioavailability (Wragg & Cave, 2003).

Studies of metals bioavailability are mostly conducted via two models; in vivo and in vitro models. In vivo models are based on animal dosing to determine contaminant levels in the blood and tissue through assay of internal organs (Ruby et al., 1999; US EPA, 2007). In vivo models are time consuming, expensive and may be ethically challenging in nature. In vitro extraction tests estimate ingested metal bioaccessibility imitating the gastrointestinal tract of humans (Ruby et al., 1999; US EPA, 2007). In vitro extraction tests provide rapid and inexpensive methods, and overcome many hindrances associated with in vivo bioavailability models (Wragg & Cave, 2003).

Several in vitro tests have been reported in the literature for determining bioaccessibility in humans; example includes the physiologically based extraction test (PBET) (Ruby, 2004; Ruby et al., 1999; US EPA, 2013). Generally, PBET mimic the physiological conditions in the gastrointestinal tracts by simulating the dissolution/release of metal contaminants from soils, under the influence of enzymes and organic acids actions, while the temperature, pH, agitation, enzyme and chemical conditions are maintained to mimic human body (Karadaş & Kara, 2011; US EPA 2007). The total fraction of a particular metal extracted during transition through the stomach and the small intestine incubation periods denotes the fraction that is bioaccessible. This is the fraction that is soluble and available for absorption. This study was conducted by following the US EPA standard operating procedures (SOPs), for determining metal bioaccessibility by extraction with glycine-hydrochloric acid (US EPA, 2007; US EPA, 2013). Assessments of human health risks using data derived from in vitro bioaccessibility testing provide a more reliable alternative to risks calculated from soil total concentration for a specific site. This often results in a decrease in clean-up cost for a contaminated area. Furthermore, validated in vitro bioaccessibility has been widely used as a conservative predictor of bioavailability when comparable units of measurement are employed (Gunney et al., 2010; Wragg et al., 2011).

Soil Properties Affecting Bioaccessibility

Metals occur in soils as mineral ore that exhibit chemical bonding with other minerals (Ruby, 2004). Their mobility and availability in the soil is a function of the physiochemical properties of the soil such as mineralogy, particle size and soil pH (Pelfrêne et al., 2012; Ruby, 2004). The most significant soil properties governing metal bioaccessibility include pH, soil organic matter, clay content and particle size (Pelfrêne et al., 2012; Ruby, 2004; Wragg et al., 2011). Besides, metal bioavailability for all soils often cannot be predicted based on soil properties alone, due to the strong effects of contaminant source and speciation on soils property itself (Hawkins et al., 2013).

Soil pH. Different studies have reported the importance of pH in the evaluation of soil contaminants, enumerating its influence on the bioaccessibility data (Karadaş & Kara, 2011; Wragg & Cave, 2011). Cave et al. (2011) reported high solubility for most divalent metal cations in acidic soils compared to alkaline and neutral soils due to weak adsorption, which made them more bioaccessible. Furthermore, pH affects the soil organic carbon solubility and sorptive capacity of iron oxides, aluminum oxides and clay. Most metals have higher solubility at low pH in the stomach resulting in increased bioaccessibility (Martinez-Sanchez et al., 2013; Peijnenburg & Jager, 2003; Wragg & Cave, 2003).

Soil Organic Matter. Soil organic carbon (SOM) influences the sorption of metal cations to the negatively charged sites of the organic carbon thereby affecting metal ion species desorption, complex formation and mobility (Ruby et al., 1999). Meunier, Koch, & Reimer (2011) reported increase arsenic bioaccessibility with increase in soil organic carbon content, while aging of samples and presence of higher iron oxide content has been shown to decrease bioaccessibility. Besides, Hawkins et al. (2013) reported a limited role by soil organic matter in the sequestration of inorganic arsenic. They suggested the role was limited by the weak adsorption between arsenic oxyanions and negatively charged SOM.

Particle Size Distribution. Several studies on bioaccessibility of metal contaminants have reported fraction size of <250µm for particle size because this fraction is believed to adhere more to the children’s hands and are accidentally ingested (Guney et al., 2010; Pelfrêne et al., 2012). Ruby et al. (1999) reported that metal bioavailability is greater in small particle sizes due to large surface area to volume, which lead to faster dissolution. Richardson, Bright and Dodd (2006) suggested that finer fractions of < 10µm particle size are also common in dermal and ingestion exposures to contaminated soils. However, the Meunier et al. (2011) study on particle size effect showed there were no significant differences in percentage bioaccessibility between particle size fractions. They asserted that sieving to < 45µm often excludes relevant particles with more bioaccessible metals, leading to conservative estimates with undue influence on bioaccessibility measurements (Meunier, Koch, & Reimer, 2011)

Methodology

Sampling Site Description

For the purpose of this study the city of Montreal approved 11 parks for research. Out of these approved parks soil samples were collected from nine different parks within the city. The remaining parks were under the jurisdiction of the municipal government. A map of sampled parks is shown in Figure 1 and the comprehensive description of sampling sites and the GPS coordinates are provided in Appendix A. The parks were selected based on geographical location across the city, elevation and topography.

Sample Collection

Topsoil samples were collected between September 22th and 24th, 2013 at two locations in each of the parks that were easily accessible to park users such as picnic areas. Surface soil samples were taken from the 0 -5 cm depths from each sampling location. Surface soil was preferred because it represented the portion with the potential for exposure to park users, especially children (Wragg et al., 2011). All samples were collected with a plastic trowel. The trowel was washed with laboratory grade detergent and distilled water after each use at the collection site. Approximately 1 kg of the soil sample was collected at each site and placed into two zip-lock plastic bags and labelled as MONT-1 to MONT-18 in the order they were collected. All the samples were transported to the School of Environment and Sustainability Laboratory at Royal Roads University (RRU).

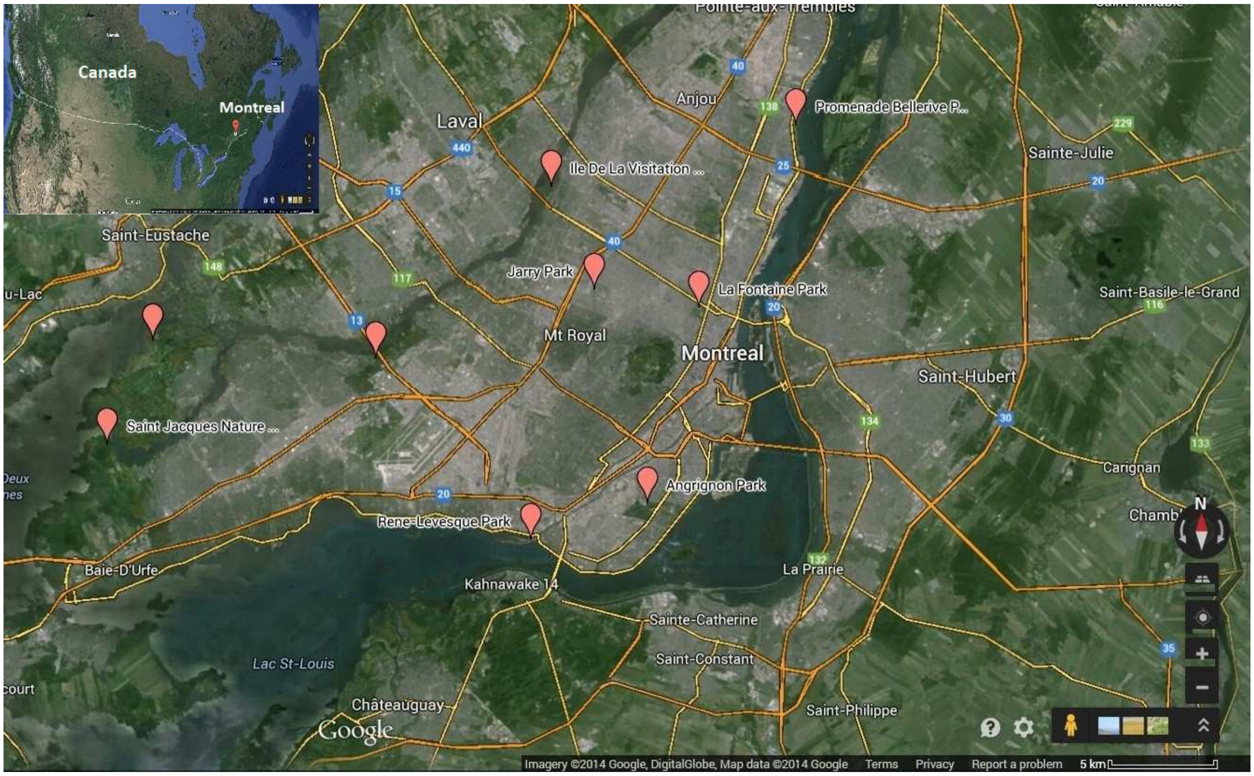

Figure 1: Map of Sampled Montreal City Parks

Sample Preparation

The samples were air dried in stainless steel bowls at ambient conditions in a fume hood. Each dried sample was gently disaggregated and sieved through a 250 µm USA Standard Testing Sieve ASTM E11 series using a Meinzer II Sieve Shaker. The 250 µm particle size was favoured since this is the optimum particle size that readily adhere to children's hands and available for incidental ingestion (Appleton, Cave, Palumbo-Roe & Wragg, 2013; US EPA, 2013). The sieved samples were stored in two separate glass jars before analysis. One set of samples was sent to Acme Laboratories for total metal analysis while the other set was retained at the School of Environment and Sustainability Laboratory at RRU. Detailed laboratory sample preparation data is given in Appendix B. Samples from two locations (MON-11 and MON-18) were prepared in duplicates and labelled Dup of MON-11 and MON-18, respectively.

Soil pH

The soil pH was measured using a soil to deionized water ratio of 1:2 (w/v). Approximately 10 g of dried soil sample was measured into a 50 mL beaker and 20 mL of water was added. Twenty millilitres of water was necessary as the samples were hydroscopic. The suspensions (water and sample particles) were allowed to settle for 1 hour. At the end of the hour, the pH of the supernatant was measured using a standard pH meter (Denver Instrument UB-10) and probe (pH/ATC electrode #300728). Detailed pH results are given in Appendix C.

Total Carbon

Total Carbon for this study was determined as described by Heiri, Lotter and Lemcke (2001) using the loss-on-ignition (LOI) method in two sequential phases to estimate the organic carbon (LOI 550) and carbonate content (LOI 950) of the soils. Samples were analyzed in triplicate for this procedure. Crucibles were clean and dried in a desiccator prior to use. Approximately 1 g of the sample was weighed directly into the crucible and placed in a pre-heated oven at 105°C overnight. The samples were removed and cooled to room temperature in a desiccator before being weighed. The samples were then placed back into the oven, pre-heated to 550°C, for four hours. At the end of the four hours, the samples were removed from the oven and cooled to room temperature (overnight) in a desiccator and weighed. The samples were placed back into the oven, pre-heated to 950°C, for two hours. At the end of the two hours, the samples were removed from the oven and cooled to room temperature in a desiccator before final weights were measured. The LOI data is given in Appendix D.

Total Soil Metal Contents

The sieved soil samples were analysed for total metals at Acme Analytical Laboratories, Vancouver, BC by inductively coupled plasma-mass spectrometry (ICP-MS) after aqua regia digestion. The entire dataset for total metals are provided in Appendix E.

Extraction

The extraction protocol was based on the Standard Operating Procedure for an In Vitro Bioaccessibility Assay for Lead in Soil, described by EPA Method 1340 (US EPA, 2013). The extraction fluid was prepared by dissolving 60.06 g of glycine (free base) in 1.9 L of deionized water (Millipore, Milli-Q Plus) in a volumetric flask. The solution was transferred to an Erlenmeyer flask, covered with a watch glass and placed in a water bath and heated until the temperature reached 37°C. At 37°C, trace metal-grade concentrated hydrochloric acid (HCl) (E M Science, Omni Trace) was added to the solution until the pH reached 1.5 ± 0.05. The pH was measured using a standard pH meter (Denver Instrument UB-10) and probe (pH/ATC electrode #300728). Approximately 60 ml of HCl was used. Following the addition of the HCl, the solution was transferred back into the water bath and maintained at 37°C. The solution was brought up to the final volume of 2 L (0.4 M glycine) after the pH was adjusted.

Approximately 1.00 ± 0.05 g of air dried sieved soil sample (<250 µm) was weighed by difference into a labelled 125 mL wide-mouth high-density polyethylene (HDPE) bottle. About 100 mL of the extractant solution was added to the soil sample in the bottle using a graduated cylinder. The initial pH of the mixture was measured. The sealed bottles were placed in the extractor jacket and the extractor was operated at 30 rpm end over end rotation in a water bath for one hour while the temperature remained constant at 37 ± 2 °C. When extraction rotation was completed, the bottles were removed. The water bath temperature at completion was also recorded. A 20 ml aliquot of the extract was drawn with a disposable plastic syringes with a Luer-Lock tip (National Scientific). A 0.45 µm cellulose acetate filter (25 mm diameter) was attached to the syringe and the sample was filtered into a clean 20 mL HDPE scintillation vial initially rinsed with the first few drops of the filtrate. The samples were stored in the refrigerator at 4°C until analysis. The pH of the solution remaining in the 125 ml extraction vessel was measured and recorded. The extraction was deemed complete by maintaining the difference between initial and final pH of extraction within ±0.5 pH units. Batch summaries that include the mass of soil used for the extraction, initial and final pH of the extracts, and temperatures of the extractor are included in Appendix F. The extracts were placed in a cooler and shipped to Maxxam Analytical Laboratory, Burnaby, BC for metal analysis by ICP MS. The summary of the metal concentrations in the extracts are shown in Appendix G.

Quality Assurance/Quality Control (QA/QC)

The QA/QC program consisted of the analyses of procedure blanks, reagent blanks, standard reference materials (SRM) and analytical duplicates. The procedure blanks was performed by running an aliquot of the extraction fluid, without test soil, through the complete extraction procedure once per batch. The procedure blank was deemed within control when it is lower than the limit of quantitation. The reagent blank involved the analysis of the unprocessed extraction fluid. A National Institute of Standards and Technology (NIST) SRM 2711 was used as the reference material. One analytical duplicate sample was collected from a park selected at random in Montreal. Overall daily batch extractions of soil samples from the study subset, one duplicate soil sample, one quality control soil and one blank were extracted. These steps were to ensure the accuracy and precision of the analytical procedures for the determination of total metals.

Bioaccessibility Calculation and Statistical Analysis

Metal bioaccessibility was calculated for As, Ba, Cd, Co, Cu, Pb, Ni, and Zn using the formula below:

$$\text{Bioaccessibility, \%} = \frac{(\text{concentration in extract, mg/L}) \times (\text{Vol of extract, L})}{(\text{concentration in soil, mg/kg}) \times (\text{mass of soil used, kg})} \times 100$$

Microsoft Office Excel 2010 and Minitab 17 statistical software were used to perform descriptive qualitative and quantitative statistical analysis.

The relationship between bioaccessibility and soil properties including pH and LOI was determined using linear regression analysis. The arithmetic mean and the relative percent difference (RPD) of the metal bioaccessibility values of the duplicate samples from the city were calculated to determine the reproducibility.

Results and Discussion

Total Metal in Soils

Total metal concentrations (As, Ba, Cd, Co, Cr, Ni, Pb and Zn) in the 18 soil samples collected (fraction <250µm) are presented in Table 2; the entire dataset is shown in Appendix E. The CCME (1999) soil quality guideline (SQG) for residential/parkland use for each parameter is included in Table 2 for comparison.

Table 2

Concentrations of Total Metals in Montreal Parks Soil Samples

	Total Metal Concentrations (mg/kg)										
Analyte	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
*CCME SQG**	*12*	*500*	*10*	*50*	*64*	*63*	-	-	*50*	*140*	*200*
MON-01	2.8	72.8	0.25	5.9	22.9	28.87	1.37	274	17.8	21.66	70.4
MON-02	10.2	76.7	0.34	6.6	20.8	37.98	1.55	395	20	72.2	90.7
MON-03	2.7	113.4	0.47	5.5	16.2	23.11	1.28	253	17.3	50.42	83.1
MON-04	5.4	98.6	0.6	8.9	20.1	37.35	2.13	352	25.3	70.51	126.6
MON-05	2.7	23.6	0.09	2.1	11.9	11.21	0.58	66	5.8	9.07	62.9
MON-06	3.1	80.2	0.07	3.7	9.5	14.17	0.93	397	9.2	15.1	44
MON-07	3.1	86.9	0.24	8	27.1	44.29	1.64	290	22.4	22.9	106.9
MON-08	2.9	54.2	0.2	5.4	12.6	**68.25**	1.13	270	13.7	15.72	64.7
MON-09	5.7	72.4	0.39	8.4	17.7	24.55	1.88	446	21.8	44.76	77.1
MON-10	6.2	120.9	0.53	11.9	24	37.95	2.16	1433	21.5	32.41	88.3
MON-11	7.3	157.2	0.28	14.2	47.8	22.52	2.78	594	33.1	24.16	93
MON-12	3.3	167.1	0.4	9.4	36.5	33.61	1.96	371	29.3	17.28	86.7
MON-13	7	104.9	0.63	10.2	28.3	43.15	2.15	502	28.5	78.28	143.2
MON-14	10.8	92.7	0.34	11.5	33.8	35.07	2.47	430	29.8	38.68	93.4
MON-15	2.8	173.8	0.1	9.3	16.5	56.77	1.53	407	16.2	10.9	58.2
MON-16	7.8	167.9	0.46	16.6	48	58.76	3.03	1028	49.3	39.28	93.9
MON-17	3.1	81.8	0.54	7.5	25.2	36.72	1.67	321	20.6	54.9	161.7
MON-18	4.0	57.2	0.04	11.7	18.7	21.93	1.59	798	22.9	12.14	39.9

* CCME SQG = CCME (1999) soil quality guideline for residential/parkland use; values in bold exceed the guideline

Overall, the total metal concentrations in most of the soil samples were lower than the CCME (1999) soil quality guidelines for residential/parkland use except for Cu in MON-08;

MON-08 contained 68.25mg/kg Cu which exceeded the CCME guideline of 63 mg/kg. This site was previously used as an excavation dumpsite during the construction of the Lious-Hippolyte-Lafontaine Tunnel, and also as a road salt depot and snow dump. Cadmium concentrations were generally low in all the soil samples collected and ranged between 0.04 mg/kg to 0.63 mg/kg. The two highest concentrations for Pb were 78.28 mg/kg and 70.51 mg/kg for MON-13 and MON-04, respectively; these were still lower than the CCME SQG value (140 mg/kg).

The mean total concentrations of As, Cd and Cu in the study area were comparable to the values reported by Barsby et al. (2012) in their investigation of the bioaccessibility of trace elements in soils in northern Ireland, UK (see Table 3). Likewise, Marr, Fyles, & Hendershot, (1999) reported a comparable value for Copper (37.4 mg/kg) but a lower value for Arsenic (0.15 mg/kg) in Montreal urban soils and leaves of *Taraxacum officinale*. However, soil As, Cd, Cr, Cu, Pb and Zn concentration reported by Okorie et al. (2010) for Newcastle Upon Tyne, UK were higher than those detected in the present study. Similarly, Luo et al. (2012) in their study on metals in urban soils in Xiamen, China reported higher mean concentrations for Cd (92 mg/kg), Co (27 mg/kg), Cu (57 mg/kg), Pb (49mg/kg) but a lower Zn concentration (39 mg/kg).

Table 3

Comparison of Mean Total Metal Concentrations between Montreal City Parks and Other Cities from Previous Studies

	Mean Metal Concentration (mg/kg)										
City	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Montreal	5.11	100.8	0.31	9.135	25.21	34.04	1.81	501	23.03	33.3	85.8
Northern Ireland, UK[a]	6.61	N/A	0.36	15.08	NA	34.68	N/A	N/A	45.10	23.2	69.1
Istanbul, Turkey[b]	6.3	N/A	NA	NA	50.6	93.4	N/A	N/A	33.1	11.1	72.6

	Mean Metal Concentration (mg/kg)										
City	As	Ba	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Xiamen, China[c]	NA	N/A	92	27	10	54	2.9	45	26	49	39.0
Newcastle Upon Tyne, UK[d]	820	N/A	11.0	N/A	163	240	N/A	N/A	7.8	11134	2816
Noonmati Kamrup , India[e]	N/A	N/A	N/A	N/A	N/A	N/A	9.571	172.2	N/A	43.03	4.237
Montreal, Canada[f]	N/A	N/A	0.15	N/A	N/A	37.4	N/A	49.7	N/A	117	265

[a] Barsby et al., 2012; [b] Guney et al., 2010; [e] Jayashree et al., 2012; [c] Luo et al., 2012; [d] Okorie et al., 2011; [f] Marr, Fyles, & Hendershot, (1999)
N/A = Not Analysed

Metal Bioaccessibility

The bioaccessibility for As, Ba, Cd, Co, Cu, Pb, Ni, and Zn as determined by the physiologically based extraction test (PBET) is summarized in Table 4. A few of the PBET extracts and soil samples had concentrations below detection limit and thus their bioaccessibility values were not calculated. Bioaccessibility varied among the soil samples and different metals; these may be due to soil sample texture, metal speciation and pH effects. The order of mean bioaccessibility was Cd (78.9%) > Ba (64.9%) > Pb (53.4%) > Cu (33.0%) > Zn (31.4%) > Co (26.1%) > As (23.9%) > Ni (13.9%) > Fe (7.7%) and Cr (6.7%). The relatively high bioaccessibility measures for Cd, Ba and Pb were of minimum concern since the total metal concentrations were all below the CCME SQG. Copper bioaccessibility was however high for MON-8 (72.5%) compared to other sites; this sample had a high concentration in soil (68.25 mg/kg) which exceeded the CCME SQG.

Table 4

Metal Bioaccessibility and Descriptive Statistics for Selected Metals in Montreal Parks Soil Samples

	Bioaccessibility (%)									
Sample ID	As	Ba	Cd	Cr	Co	Cu	Fe	Pb	Ni	Zn
MON-1	26.1	56.3	89.6	4.9	21.1	16.1	4.2	49.5	12.9	26.2
MON-2	26.2	71.7	94.0	2.9	26.1	35.2	2.5	69.2	16.8	32.8
MON-3	42.0	75.6	81.0	5.2	23.8	37.2	8.5	40.0	14.0	28.8
MON-4	21.4	73.2	71.4	3.4	29.1	24.3	4.3	50.1	14.4	23.9
MON-5	25.4	61.9	75.2	13.2	9.7	23.3	6.2	57.0	8.2	56.9
MON-6	17.0	28.8	96.3	23.5	23.8	14.6	36.1	56.6	17.2	46.0
MON-7	29.2	72.9	NC	6.9	21.0	45.5	5.4	66.4	14.6	37.5
MON-8	21.8	71.1	77.1	12.7	41.0	72.5	17.2	64.6	22.0	60.9
MON-9	19.5	73.0	77.1	NC	30.4	18.0	2.1	64.5	13.0	20.5
MON-10	10.6	66.9	80.3	NC	33.5	38.1	1.7	37.3	20.2	23.4
MON-11	11.8	68.1	68.4	2.6	13.0	19.7	1.9	40.6	6.2	14.9
MON-12	35.6	77.3	80.7	3.4	27.2	40.8	8.4	58.2	13.1	20.4
MON-13	20.3	66.9	83.0	4.9	27.9	38.5	3.3	63.8	15.0	41.2
MON-14	22.1	71.2	83.5	4.2	23.7	23.8	2.2	47.3	9.1	18.4
MON-15	26.0	30.2	57.1	6.3	24.4	40.4	4.8	39.3	10.2	29.6
MON-16	17.7	70.5	65.7	2.8	22.5	21.5	1.6	45.0	10.1	19.7
MON-17	29.9	85.4	81.5	5.4	28.1	49.7	5.7	72.7	16.1	37.2
MON-18	27.0	47.0	NC	5.0	43.8	34.4	22.9	39.8	17.5	26.9
Count	*18*	*18*	*16*	*16*	*18*	*18*	*18*	*18*	*18*	*18*
Mean	*23.9*	*64.9*	*78.9*	*6.7*	*26.1*	*33.0*	*7.7*	*53.4*	*13.9*	*31.4*
Std Dev	*7.7*	*15.3*	*10.1*	*5.5*	*8.2*	*14.6*	*9.0*	*11.7*	*4.1*	*13.1*
Median	*23.7*	*70.8*	*80.5*	*5.0*	*25.2*	*34.8*	*4.6*	*53.3*	*14.2*	*27.9*
Minimum	*10.6*	*28.8*	*57.1*	*2.6*	*9.7*	*14.6*	*1.6*	*37.3*	*6.2*	*14.9*
Maximum	*42.0*	*85.4*	*96.3*	*23.5*	*43.8*	*72.5*	*36.1*	*72.7*	*22.0*	*60.9*
95 Percentile	*36.5*	*78.6*	*94.6*	*15.8*	*41.4*	*53.1*	*24.9*	*69.7*	*20.5*	*57.5*

NC: not calculated since concentration in either extract or soil was below detection.

Comparison of Montreal city park data with data from previous studies in other cities showed that the order of bioaccessibility observed in this study were comparable, however the values were lower for all the metals as reported by Okorie et al., (2011) for Newcastle Upon Tyne, UK and Luo et al., (2012) for Xiamen, China (Table 5). The order observed for different cities as depicted in Table 5 demonstrated that soil metal bioaccessibility differ and vary significantly and thus the need for city-specific bioaccessibility determination.

Table 5

Comparison of Mean Metals Bioaccessibility for Montreal and Selected Cities

	Bioaccessibility (%)									
City	As	Ba	Cd	Co	Cr	Cu	Fe	Ni	Pb	Zn
Montreal, Canada	23.9	64.9	78.9	6.7	26.1	33.0	7.7	57.4	13.9	31.4
Fredericton, Canada[a]	11.1	45.4	61.3	15.1	4.1	46.5	36.9	6.6	37.7	24.1
Saint John, Canada[a]	13.0	52.1	52.6	12.7	5.9	43.7	27.3	8.7	46.7	26.5
Toronto, Canada[b]	41.1	N/A	75.5	N/A	N/A	65.4	N/A	18.9	75.5	43
Newcastle Upon Tyne, UK[c]	63.9	N/A	95.5	N/A	74.3	77.5	N/A	70.7	58.4	61.9
Xiamen, China[d]	N/A	N/A	92	27	10	54	N/A	26	49	39

[a]Dakane, 2012; [b]Dupuis, 2013; [c]Okorie, et al., 2011; [d]Luo et al., 2012; N/A = Not Analysed

Quality Assurance/Quality Control (QA/QC)

The quality assurance (QA) and quality control (QC) program followed in the extraction procedure for this study include analyses of procedure blanks, reagent blanks, standard reference materials (NIST 2711) and two sample duplicates. Both Maxxam Analytics (metals in extract analysis) and ACME Labs (total metals in sol analysis) followed strict Good Laboratory Principle and internal QA and QC protocols for all samples and extracts checked-in, verified, and maintained under standard chain-of-custody (U.S. EPA, 2012c).

Procedural blanks and standard reference material. The results of the procedural blanks and standard reference material are shown in Appendix H. The concentrations of As in the blanks (BL13-14A and BL13-14B) were <1.6 µg/l and within the control limit of <1.0 µg/L. Lead concentrations in the blanks (BL13-14A and BL13-14B) were 1.55 and 1.9 µg/L, respectively and also within control limit of <50 µg/L. The data indicate low interference from reagents and equipment.

Arsenic and Lead concentrations in the standard reference material were also within the acceptable control limits as indicated in Appendix H. There are no established control limits for the remaining elements.

Sample duplicates. The two sample duplicates for this study are summarized in Appendix I with their arithmetic means and relative percentage difference (RPD). The RPD show good reproducibility for all the metals because all the values were below 20%.

Relationship between Bioaccessibility and Soil Properties

The interaction of metals with soil constituent (including pH, LOI, total Fe, total Mn) influences its bioavailability and subsequent adverse effect. The relationships between metal bioaccessibility and these soil properties were therefore investigated using correlation analysis and linear regression analysis.

Soil pH. Soil pH was generally within the CCME (1999) soil quality guideline of 6 – 8 for the protection of environmental and human health for residential/parkland use except for MON-8 (pH = 8.10) and MON-18 (pH = 8.53). The pH data is given in Appendix C). The relationships between metal bioaccessibility and soil pH are summarized in scatter plots in Figure 2. Detailed data for the correlation analysis including Pearson correlation coefficients and *p* values are provided in Appendix J. There were no significance correlations between metal bioaccessibility and the sample pH except for Co which showed a weak positive correlation (r = 0.701, *p* = .001).

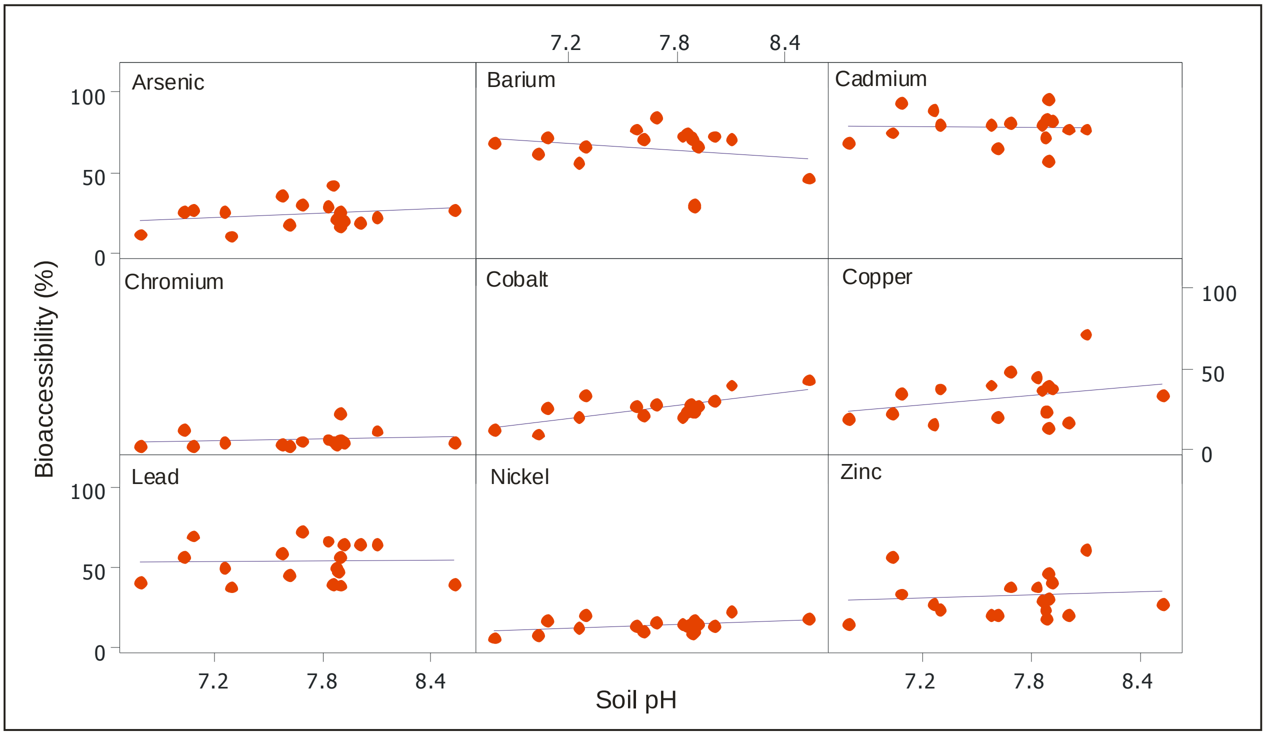

Figure 2: Scatter plots showing the relation between metal bioaccessibility and soil pH. There are no significance correlations between metal bioaccessibility and the sample pH except for Co which shows a weak positive correlation.

Loss on ignition. For LOI 550 (soil organic carbon) the regression analyses showed increasing trend line for only barium (i.e., bioaccessibility increased with organic carbon content (r = 0.448, *p* = .004)). This observation is evident in the scatter plots shown in Figure 3 which generally indicated the lack of significant relationships.

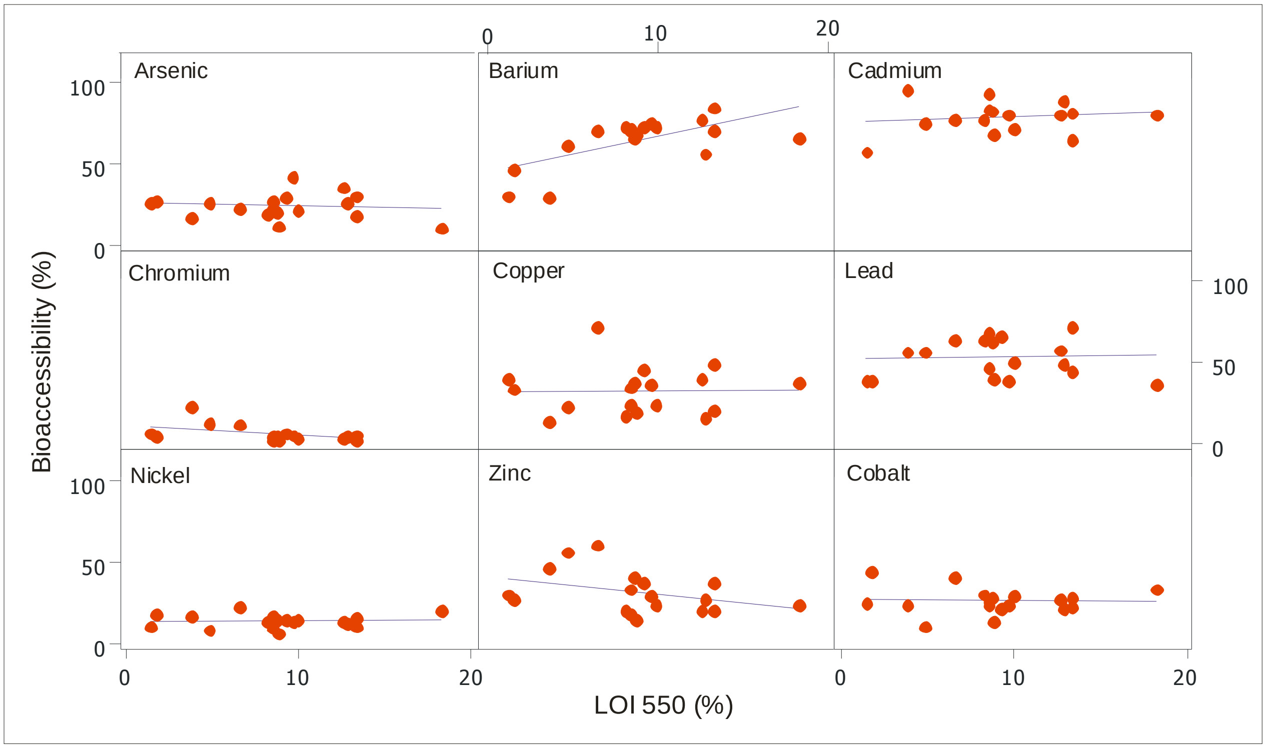

Figure 3: Scatter plots showing the relation between metal bioaccessibility and LOI 550 (soil organic carbon). The regression analyses show an increasing trend line for only barium.

The scatter plots for metal bioaccessibility against LOI 950 (inorganic carbon) as summarized in Figure 4 and the detailed correlation matrix (Appendix J) showed negative correlation for barium (r = -0.401, *p* = .004) and positive correlation for zinc (r = 0.577, *p* = .021), chromium (r = 0.681, *p* = .004), and cobalt (r = 0.546, *p* = . 019). The scatter plots however show the data was highly skewed and as such these trends were not deemed statistically significant.

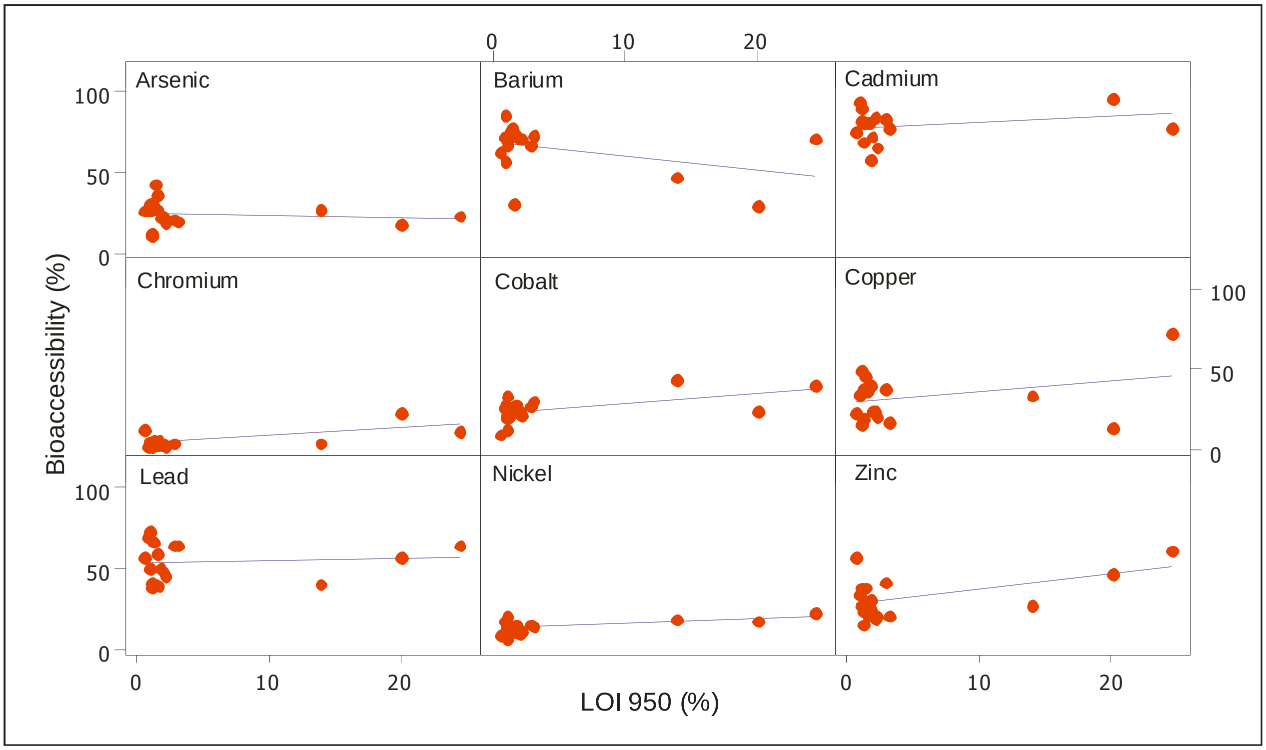

Figure 4: Scatter plots showing the relation between metal bioaccessibility and LOI 950 (soil inorganic carbon). Barium has a negative correlation while zinc, chromium, and cobalt all have positive correlations.

Total Iron and Manganese. Bradham et al. (2011) reported inverse correlations between concentrations of iron, aluminium and manganese in soil and soil arsenic relative to bioavailability and bioaccessibility. The effect of iron and manganese concentration on the solubility and bioavailability of other metals in the soil is aided by the adsorption of these metals to the oxyhydroxide and oxides of Fe and M. This results in significant reduction in bioaccessibility of selected metals including As, Ba, Cd, Cr, Co, Cu, Pb, Ni and Zn (Appleton et al., 2013; Bradham et al., 2011). Pearson correlation analysis was conducted for this study to determine the relationship between bioaccessibility of other metals and total iron and manganese concentrations. Scatter graphs corresponding to these data are provided in Figures 5 and 6 and detailed correlation matrices are provided in Appendix J. The regression analyses showed a decrease in bioaccessibility with increasing iron concentration for arsenic (r = -0.417, p = .085), chromium (r = -0.671, *p* = .004), lead (r = -0.293, *p* = .237), copper (r = 0.213, *p* = .397) and zinc (r = -0.751, *p* <.001); however, barium showed an increasing relationship (r = 0.354, *p* = .150).

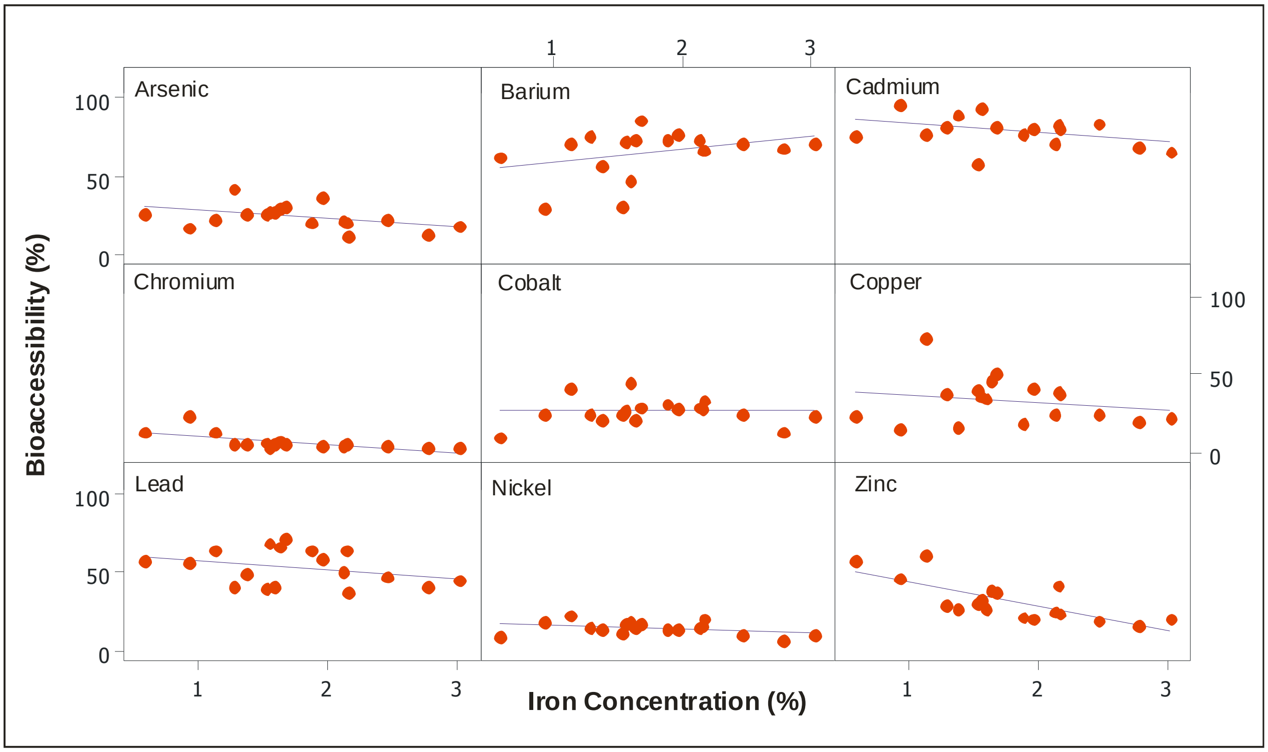

Figure 5: Scatter plots showing the relation between metal bioaccessibility and iron concentrations. The regression analyses shows decreasing relationship for arsenic, chromium, lead, copper and zinc, while barium has an increasing relationship.

Arsenic (r = -0.565, *p* = .014), lead (r = -0.500, *p* = .035), and zinc (r = -0.454, *p* = .058) bioaccessibility decreased with manganese concentration (Figure 5). Derka and Sarma (2013) reported in their study the efficiency of increased hydroxides of iron and manganese in lowering the concentration of cadmium or lead dissolved in contaminated soil and subsequently their bioaccessibility.

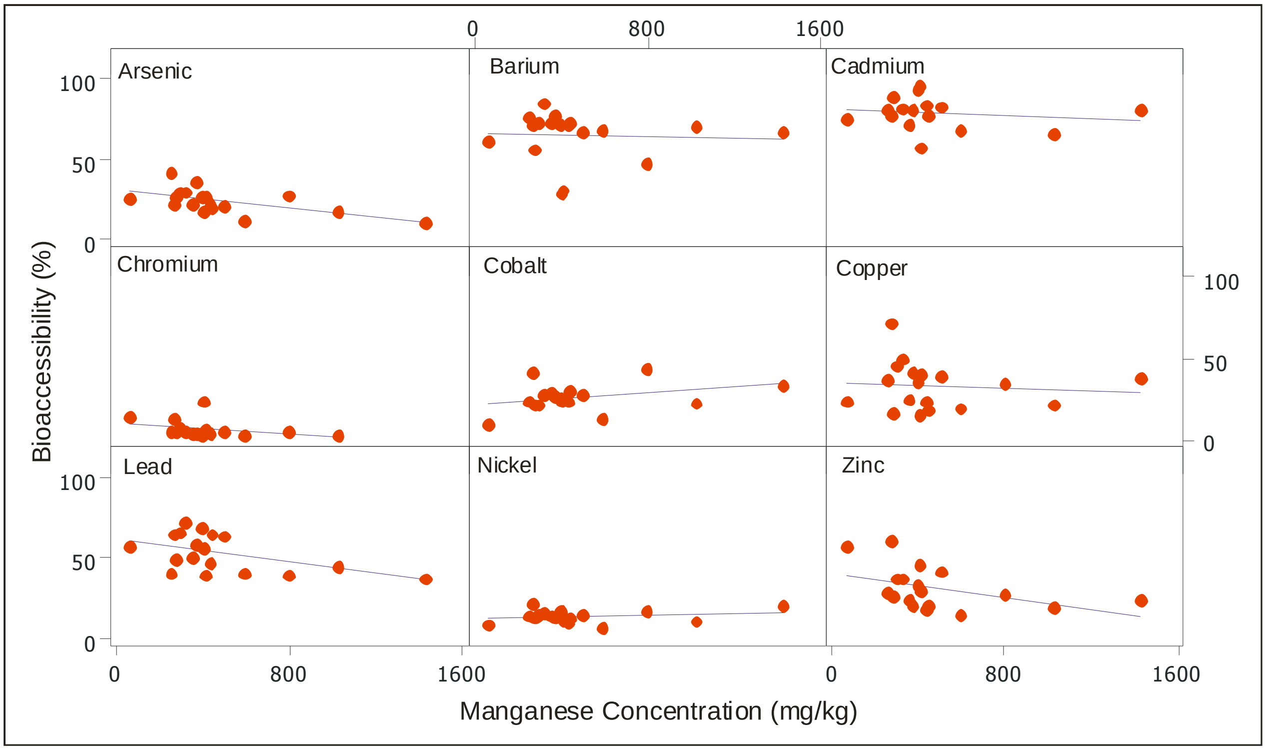

Figure 6: Scatter plots showing the relation between metal bioaccessibility and manganese concentrations. Arsenic, lead, and zinc show decreasing bioaccessibility with manganese concentration.

Conclusions

Data from this study show that the risk associated with the ingestion of metals in soils from the parks in Montreal are relatively low for children and other park users based on bioaccessibility and total metal concentration data, except for the sample (MON-08). This sample contained elevated copper concentration of 68.25 mg/kg which is above the CCME SQG for residential/parkland use of 63 mg/kg. The sample with elevated copper concentration has a bioaccessibility value of 72% and therefore poses a potential health risk to children through inadvertent oral ingestion of the contaminated soil.

Recommendations

Despite the overall low risks observed for the exposure to metals in the park soils collected in this study, it is appropriate to recommend further sampling and analysis for the park with elevated copper exceeding the CCME SQG for residential/parkland use to demarcate the contaminated area and identify the source(s) of contamination. If significant risks are uncovered from this additional investigation, remediation may be necessary.

Remediation methods discussed for managing metal contaminated parks and mitigating the associated risks includes phytoremediation which involves the use of plants to remove metal contaminants in the soil (Akhtar, Chali & Azam, 2013). This method is considered to be affordable, effective and environmentally sustainable, though it takes a number of years for effective result to manifest (Akhtar, Chali & Azam, 2013).

Furthermore, Harmsen and Naidu (2013) suggested a risk based remediation which relies on the bioavailability of contaminants to be more sustainable and cost effective. Knowledge of bioavailability could be used to design an effective plan aimed at reducing contaminant associated risks to all park users. For risk based remediation to achieve its purpose, a balanced approach to management which incorporates environmental, sociocultural and economic aspects (Harmsen & Naidu, 2013) is required.

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Appendix A: Sampling Site Locations and Description

Appendix A.1: Sampling Site Locations

Park Name	Park ID	GPS Coordinates	Longitude	Latitude	Sampling Time	Sampling Date
La Fontaine Park	MON-01	45: 31:632N 73:34: 309W	45.5263638	73.5693448	Sept-23-2013	11:59
La Fontaine Park	MON-02	45: 31: 561N 73: 34: 137W			Sept-23-2013	12:09
Angrignon Park	MON-03	45: 26: 718N 73: 35: 809W	45.4445195	73.601732	Sept-23-2013	14:57
Angrignon Park	MON-04	45: 26: 444N 73: 35: 889W			Sept-23-2013	15:18
Rene-Levesque Park	MON-05	45: 25: 678N 73: 40: 540W	45.4285358	73.6814883	Sept-23-2013	14:02
Rene-Levesque Park	MON-06	45: 25: 879N 73: 40: 529W			Sept-23-2013	16:22
Promenade Bellerive Park	MON-07	45: 36: 016N 73: 30: 572W			Sept-23-2013	
Promenade Bellerive Park	MON-08	45: 30: 360N 73: 45: 776W			Sept-23-2013	
Bois De Liesse Nature Park	MON-09	45: 30: 358N 73: 45: 773W	45.517286	73.739934	Sept-23-2013	18:00
Bois De Liesse Nature Park	MON-10	45: 29: 742N 73: 46: 735W			Sept-23-2013	18:33
Saint Jacques Nature Park	MON-11	45: 28: 162N 73: 55: 409W	45.4610448	73.9205009	Sept-24-2013	10:35
Saint Jacques Nature Park	MON-12	45: 28: 421N 73: 55: 726W			Sept-24-2013	10:47
Ile De La Visitation Park	MON-13	45: 34: 710N 73: 39: 483W	45.575558	73.663381	Sept-24-2013	13:17
Ile De La Visitation Park	MON-14	45: 35: 016N 73: 39: 254W			Sept-24-2013	14:59
Bois-De-L'ile-Bizard Park	MON-15	45: 30: 886N 73: 53: 857W	45.51006	73.8786577	Sept-24-2013	11:28
Bois-De-L'ile-Bizard Park	MON-16	45: 30: 982N 73: 53: 972W			Sept-24-2013	11:39
Jarry Park	MON-17	45: 32: 088N 73: 37: 853W	45.5352959	73.6284695	Sept-23-2013	9:55
Jarry Park	MON-18	45: 32: 123N 73: 37: 600W			Sept-24-2013	10:30

Appendix A.2: Sampling Sites Descriptions

Park Name	**Park ID**	**Park Descriptions**
La Fontaine Park	MON-01	Located in the heart of the city, have two linked ponds, picnic area bike and play tennis. There is an outdoor theater in the summer and the pond becomes a skating rink in winter. Soil samples were collected near the picnic benches area under the tree cover. Generally, soil in the park are loamy soil.
La Fontaine Park	MON-02	
Angrignon Park 7503, boulevard. de la Vérendrye, Montreal QC	MON-03	A stretch of green space with 1.1km pond in the middle. There are picnic tables, walking trails, bicycle path, and 10km cross country skiing trail. The park is bordered by metro station and number of bus routes. Soil samples were taken near picnic benches under tree canopy. Soil texture is loamy
Angrignon Park	MON-04	
Rene-Levesque Park 1 Chemin du Musee, Lachine, Montreal QC H8S 4H3	MON-05	Located on a peninsula and extend to west end Lachine canal. There is a marina with many private boats nearby. There are also 4 km walking trail and cycling in summer; for skiing and snowshoeing in winter. Soil samples were taken from the parking area which is mixture of gravel and silt, and near picnic area which is silt loam
Rene-Levesque Park	MON-06	
Promenade Bellerive Park Rue Notre-Dame East, Montreal QC H2K 4K3	MON-07	It is a 22 hectares east end waterfront park. Bordered by Port of Montreal and faces the Grandes battures Tailhandier and the iles de Bouchervilles across St. Lawrence. Site has been used for excavation dump during the construction of Lious-Hippolyte-Lafontaine tunnel, road salt depot and snow dump into the river. In summer Croisieres Navark runs ferry services from park over to the Iles de Boucherville provincial park. Soil samples were collected from picnic area fine gravel and sand
Promenade Bellerive Park	MON-08	
Bois De Liesse Nature Park 9432 Boulevard Gouin West, Pierrefonds,	MON-09	Located in Montreal's north end Bordered on the eastern by Prairie river, western by thickly wooded part of Ville Saint Laurent linked to the main park by a trail going under highway 13. The park is used for walking and cycling in the summer

Quebec H8Y 1T4		and skiing and snowshoeing in the winter. Soil textures at the two locations sampled are loamy; loamy and gravel
Bois De Liesse Nature Park	MON-10	
Saint Jacques Nature Park 20099 Boulevard Gouin West, Montreal QC, H9K 1C6	MON-11	Located on 302 hectares of land on thumb shaped peninsula on the western end of Montreal Island. Prairie river bisect the park. It is the largest park in Montreal. Soil texture at the two sampled locations are loamy and clayey loamy respectively.
Saint Jacques Nature Park	MON-12	
Ile De La Visitation Park 2425 Gouin Boulevard E., Montreal QC	MON-13	Park is located on 34 hectares of land which consist of an Island and waterfront facing Prairie river both linked by footbridges. Walking and cycling trails meander throughout the park. In winter park has cross- country ski trail and snowshoeing. Downriver of the park hosted Riviere des Prairies generating station. Soil samples were taken near the river was silt and gravel while the second location near picnic benches was loamy soil.
Ile De La Visitation Park	MON-14	
Bois-De-L'ile-Bizard Park 2115 Chemin du Bord du Lac, Lile-Bizard, QC H9C 1P3	MON-15	Located on an island north west of Montreal. The park includes beach, wetlands, and maple and cedar trees. Highway 19 overpass runs through part of the park. Bizard park is bordered to the north by Des Mille Iles River and to the south by Prairie River. Soil samples collected from the picnic benches area at the two sampled locations are different in texture silt gravel and loam respectively.
Bois-De-L'ile-Bizard Park	MON-16	
Jarry Park 285 Rue Gary-Carter, Montreal QC, H2R 2W1	MON-17	Jarry park is a 36 hectares park located in the heart of Montreal in the borough of Villeray, Saint-Michel and Park extension bordered by Rue Jarry, Rue Gary Carter and St Laurent Blvd. Soil samples were taken from picnic benches area and spectator stand are sand-silt and sand-gravel
Jarry Park	MON-18	

Appendix B: Sample Preparation

Sample ID	Wet Soil Used (g)	Dry Soil (g)	Moisture (%)	Soil Used for Sieving	<250 µm Soil (g)	< 250 µm Content (%)
MON-01	884.2	674.3	23.7	351.6	148.0	42.1
MON-02	943.7	731.4	22.5	340.2	109.7	32.2
MON-03	1048.2	809.3	22.8	370.8	140.7	37.9
MON-04	743.4	576.4	22.5	278.3	112.5	40.4
MON-05	932.4	823.0	11.7	469.0	389.7	83.1
MON-06	1141.3	1068.7	6.4	619.0	285.4	46.1
MON-07	1296.8	1114.7	14.0	644.9	191.2	29.6
MON-08	1444.2	1290.4	10.6	654.5	138.3	21.1
MON-09	808.0	634.5	21.5	373.7	101.8	27.2
MON-10	657.0	420.7	36.0	368.0	52.6	14.3
MON-11	664.5	530.3	20.2	363.9	63.6	17.5
MON-12	801.2	596.8	25.5	386.1	125.1	32.4
MON-13	930.0	852.3	8.4	461.0	145.6	31.6
MON-14	593.4	513.4	13.5	383.3	92.1	24.0
MON-15	931.5	930.6	0.1	601.0	262.6	43.7
MON-16	777.9	589.9	24.2	395.0	102.0	25.8
MON-17	833.2	667.3	19.9	382.9	129.9	33.9
MON-18	1243.9	1177.9	5.3	725.0	183.2	25.3

Appendix C: Soil pH Data

Sample ID	**Weight used**	**pH**
MON-01	10.20	7.26
MON-02	10.01	7.08
MON-03	10.02	7.86
MON-04	10.08	7.88
MON-05	10.04	7.03
MON-06	10.07	7.90
MON-07	10.05	7.83
MON-08	10.01	8.10
MON-09	10.01	8.00
MON-10	10.03	7.30
MON-11	10.00	6.79
MON-12	10.00	7.58
MON-13	10.01	7.92
MON-14	10.02	7.89
MON-15	10.02	7.90
MON-16	10.01	7.62
MON-17	10.01	7.68
MON-18	10.01	8.53

Appendix D: Loss on Ignition Data

Sample ID	LOI 105^{o}C (%) Mean	LOI 105^{o}C (%) Std. Dev.	LOI 550^{o}C (%) Mean	LOI 550^{o}C (%) Std. Dev.	LOI 950^{o}C (%) Mean	LOI 950^{o}C (%) Std. Dev.
MON-01	2.47	0.11	12.81	0.50	0.92	0.02
MON-02	1.81	0.02	8.46	0.05	0.80	0.05
MON-03	3.71	0.00	9.61	0.11	1.31	0.11
MON-04	2.38	0.05	9.99	0.14	1.73	0.08
MON-05	1.02	0.03	4.81	0.18	0.50	0.02
MON-06	0.31	0.03	3.81	0.04	20.11	0.35
MON-07	1.76	0.03	9.27	0.29	1.22	0.10
MON-08	0.88	0.04	6.54	0.11	24.52	0.08
MON-09	1.88	0.05	8.19	0.11	3.05	0.09
MON-10	4.26	0.07	18.23	0.04	1.12	0.06
MON-11	3.02	0.08	8.78	0.08	1.07	0.04
MON-12	3.14	0.07	12.64	0.16	1.41	0.07
MON-13	2.54	0.11	8.76	0.13	2.84	0.10
MON-14	2.53	0.02	8.46	0.40	1.95	0.37
MON-15	0.39	0.02	1.45	0.07	1.63	0.02
MON-16	4.70	0.04	13.31	0.22	2.14	0.16
MON-17	3.01	0.03	13.37	0.06	0.94	0.04
MON-18	0.42	0.01	1.76	0.02	13.88	0.02

Appendix E: ACME Laboratory Report for Total Metals in Soils

Analyte	**Ag**	**Al**	**As**	**Au**	**B**	**Ba**	**Bi**	**Ca**
Unit	PPB	%	PPM	PPB	PPM	PPM	PPM	%
Sample								
MON-01	86	1.03	2.8	4	<20	72.8	0.15	1.14
MON-02	113	0.99	10.2	4.1	<20	76.7	0.19	0.57
MON-03	60	0.82	2.7	0.8	<20	113.4	0.1	1.12
MON-04	80	1	5.4	2.2	<20	98.6	0.15	1.66
MON-05	17	0.59	2.7	0.7	<20	23.6	0.07	0.35
MON-06	28	0.24	3.1	0.7	<20	80.2	0.05	14.98
MON-07	91	1.13	3.1	2.2	<20	86.9	0.12	1.16
MON-08	92	0.63	2.9	4.9	<20	54.2	0.1	21.97
MON-09	92	0.98	5.7	1.3	<20	72.4	0.12	2.82
MON-10	97	1.1	6.2	2.3	<20	120.9	0.17	1.06
MON-11	74	2.11	7.3	1.6	<20	157.2	0.13	0.61
MON-12	143	1.31	3.3	2.1	<20	167.1	0.08	1.28
MON-13	210	1.2	7	7	<20	104.9	0.17	2.38
MON-14	110	1.6	10.8	3.4	<20	92.7	0.15	1.23
MON-15	50	0.58	2.8	<0.2	<20	173.8	0.14	1.18
MON-16	87	1.45	7.8	6.6	<20	167.9	0.2	1.76
MON-17	100	1.12	3.1	4	<20	81.8	0.16	0.91
MON-18	56	0.81	4	1.2	<20	57.2	0.09	12.27
MON-11	74	2.11	7.3	1.6	<20	157.2	0.13	0.61
MON-18	56	0.81	4	1.2	<20	57.2	0.09	12.27
Lab Duplicates								
MON-07	91	1.13	3.1	2.2	<20	86.9	0.12	1.16
MON-07	90	1.1	3.2	2.2	<20	92.7	0.12	1.14
Reference Materials								
STD DS10	1722	0.98	44.1	61.2	<20	369.3	12.62	1.04
STD OREAS45EA	256	2.85	8.3	49	<20	143.8	0.26	0.04
BLK	4	<0.01	0.3	<0.2	<20	<0.5	<0.02	<0.01

Appendix E: ACME Laboratory Report for Total Metals in Soils (Continued)

Analyte	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**Ga**	**Hg**	**K**
Unit	PPM	PPM	PPM	PPM	%	PPM	PPB	%
Sample								
MON-01	0.25	5.9	22.9	28.87	1.37	3.5	57	0.14
MON-02	0.34	6.6	20.8	37.98	1.55	3.2	95	0.14
MON-03	0.47	5.5	16.2	23.11	1.28	2.9	39	0.11
MON-04	0.6	8.9	20.1	37.35	2.13	3.8	41	0.14
MON-05	0.09	2.1	11.9	11.21	0.58	2	24	0.05
MON-06	0.07	3.7	9.5	14.17	0.93	0.9	9	0.07
MON-07	0.24	8	27.1	44.29	1.64	4	41	0.15
MON-08	0.2	5.4	12.6	68.25	1.13	1.7	21	0.13
MON-09	0.39	8.4	17.7	24.55	1.88	3	38	0.17
MON-10	0.53	11.9	24	37.95	2.16	3.6	78	0.18
MON-11	0.28	14.2	47.8	22.52	2.78	6.6	43	0.17
MON-12	0.4	9.4	36.5	33.61	1.96	4.3	41	0.16
MON-13	0.63	10.2	28.3	43.15	2.15	3.8	124	0.26
MON-14	0.34	11.5	33.8	35.07	2.47	5	43	0.26
MON-15	0.1	9.3	16.5	56.77	1.53	2.9	<5	0.16
MON-16	0.46	16.6	48	58.76	3.03	4.5	48	0.22
MON-17	0.54	7.5	25.2	36.72	1.67	4.1	72	0.17
MON-18	0.04	11.7	18.7	21.93	1.59	2.4	<5	0.27
MON-11	0.28	14.2	47.8	22.52	2.78	6.6	43	0.17
MON-18	0.04	11.7	18.7	21.93	1.59	2.4	<5	0.27
Lab Duplicates								
MON-07	0.24	8	27.1	44.29	1.64	4	41	0.15
MON-07	0.26	7.6	26.2	42.18	1.6	3.9	36	0.15
Reference Materials								
STD DS10	2.52	13	51.9	156.41	2.69	4	267	0.33
STD OREAS45EA	0.03	49.8	734.1	648.97	22.92	11.4	12	0.05
BLK	<0.01	<0.1	<0.5	<0.01	<0.01	<0.1	<5	<0.01

Appendix E: ACME Laboratory Report for Total Metals in Soils (Continued)

Analyte	**La**	**Mg**	**Mn**	**Mo**	**Na**	**Ni**	**P**	**Pb**
Unit	PPM	%	PPM	PPM	%	PPM	%	PPM
Sample								
MON-01	16.5	0.4	274	0.44	0.012	17.8	0.127	21.66
MON-02	16.1	0.34	395	0.59	0.009	20	0.098	72.2
MON-03	12.6	0.35	253	0.5	0.01	17.3	0.097	50.42
MON-04	17.6	0.52	352	0.93	0.012	25.3	0.114	70.51
MON-05	14.8	0.18	66	0.13	0.005	5.8	0.083	9.07
MON-06	10.9	2.2	397	0.87	0.085	9.2	0.082	15.1
MON-07	21.3	0.52	290	0.5	0.015	22.4	0.103	22.9
MON-08	7.7	0.89	270	0.39	0.024	13.7	0.1	15.72
MON-09	18.8	0.41	446	0.79	0.009	21.8	0.151	44.76
MON-10	16.1	0.31	1433	0.86	0.006	21.5	0.11	32.41
MON-11	36.9	0.68	594	1.35	0.017	33.1	0.078	24.16
MON-12	31.6	0.82	371	0.89	0.019	29.3	0.109	17.28
MON-13	23.1	0.56	502	0.89	0.014	28.5	0.151	78.28
MON-14	20.5	0.6	430	0.73	0.01	29.8	0.1	38.68
MON-15	23.4	0.73	407	0.6	0.021	16.2	0.1	10.9
MON-16	49.1	0.69	1028	0.96	0.01	49.3	0.181	39.28
MON-17	18.4	0.44	321	0.54	0.01	20.6	0.113	54.9
MON-18	22.5	0.9	798	0.29	0.018	22.9	0.29	12.14
MON-11	36.9	0.68	594	1.35	0.017	33.1	0.078	24.16
MON-18	22.5	0.9	798	0.29	0.018	22.9	0.29	12.14
Lab Duplicates								
MON-07	21.3	0.52	290	0.5	0.015	22.4	0.103	22.9
MON-07	22.4	0.51	281	0.55	0.015	21.1	0.097	22.48
Reference Materials								
STD DS10	15.5	0.76	880	14.18	0.064	75.6	0.072	154.43
STD OREAS45EA	6.7	0.1	407	1.39	0.021	357	0.026	14.37
BLK	<0.5	<0.01	<1	<0.01	<0.001	<0.1	<0.001	<0.01

Appendix E: ACME Laboratory Report for Total Metals in Soils (Continued)

Analyte	**S**	**Sb**	**Sc**	**Se**	**Sr**	**Te**	**Th**
Unit	%	PPM	PPM	PPM	PPM	PPM	PPM
Sample							
MON-01	0.07	0.29	2.1	0.3	39.4	0.02	1
MON-02	0.05	0.51	2.1	0.6	29.2	<0.02	1
MON-03	0.06	0.38	1.5	<0.1	45.6	<0.02	1.1
MON-04	0.07	0.65	3	0.4	75.2	0.05	1.8
MON-05	0.02	0.09	1.1	<0.1	14.5	<0.02	1
MON-06	0.24	0.45	1.8	<0.1	559	0.04	2.2
MON-07	0.07	0.48	2.9	0.3	52	0.04	1.7
MON-08	0.19	0.19	2.1	0.4	663.4	0.06	2.6
MON-09	0.05	0.21	3.1	0.3	95.5	0.05	1.9
MON-10	0.07	0.22	2.9	0.5	46.7	0.03	1.8
MON-11	0.04	0.17	5.6	0.3	28.3	<0.02	3.3
MON-12	0.07	0.18	3.9	0.4	53.5	<0.02	2.3
MON-13	0.07	0.47	3.4	0.3	86.8	0.03	2.1
MON-14	0.05	0.27	3.9	0.1	59.5	0.03	2.6
MON-15	0.03	0.07	2	<0.1	65.5	0.03	3
MON-16	0.08	0.17	5.1	0.3	67.1	<0.02	2.4
MON-17	0.07	0.5	2.5	0.4	38.8	0.05	1.3
MON-18	0.3	0.13	4.1	<0.1	253.4	<0.02	5.7
MON-11	0.04	0.17	5.6	0.3	28.3	<0.02	3.3
MON-18	0.3	0.13	4.1	<0.1	253.4	<0.02	5.7
Lab Duplicates							
MON-07	0.07	0.48	2.9	0.3	52	0.04	1.7
MON-07	0.06	0.48	2.7	0.3	52.2	<0.02	1.9
Reference Materials							
STD DS10	0.28	8.6	2.5	2.1	64.4	4.64	7.4
STD OREAS45EA	0.04	0.24	72.6	0.7	3.7	0.04	10.4
BLK	<0.02	<0.02	<0.1	<0.1	<0.5	<0.02	<0.1

Appendix E: ACME Laboratory Report for Total Metals in Soils (Continued)

Analyte	**Ti**	**Tl**	**U**	**V**	**W**	**Zn**
Unit	%	PPM	PPM	PPM	PPM	PPM
Sample						
MON-01	0.043	0.09	0.78	26	0.12	70.4
MON-02	0.029	0.08	0.65	30	0.09	90.7
MON-03	0.025	0.07	0.8	22	0.11	83.1
MON-04	0.029	0.12	0.7	34	0.11	126.6
MON-05	0.037	0.03	0.43	14	<0.05	62.9
MON-06	0.01	0.05	0.56	12	0.23	44
MON-07	0.051	0.09	1.06	29	0.13	106.9
MON-08	0.004	0.03	0.45	10	0.06	64.7
MON-09	0.012	0.08	0.52	26	0.05	77.1
MON-10	0.006	0.11	0.95	24	0.13	88.3
MON-11	0.097	0.15	1.11	50	0.12	93
MON-12	0.087	0.13	1.1	39	0.1	86.7
MON-13	0.035	0.13	0.73	31	0.1	143.2
MON-14	0.035	0.12	0.74	36	0.1	93.4
MON-15	0.071	0.06	0.49	32	0.11	58.2
MON-16	0.029	0.14	1.1	43	0.07	93.9
MON-17	0.033	0.08	0.62	30	0.11	161.7
MON-18	0.008	0.06	0.72	12	<0.05	39.9
MON-11	0.097	0.15	1.11	50	0.12	93
MON-18	0.008	0.06	0.72	12	<0.05	39.9
Lab Duplicates						
MON-07	0.051	0.09	1.06	29	0.13	106.9
MON-07	0.049	0.09	1.01	29	0.12	103.6
Reference Materials						
STD DS10	0.07	5	2.58	42	2.68	363.4
STD OREAS45EA	0.089	<0.02	1.81	286	<0.05	30.1
BLK	<0.001	<0.02	<0.05	<2	<0.05	<0.1

Appendix F: Laboratory Batch Summaries

Extraction Batch #1

Date of extraction: October 23, 2013

Start Time: 12:35PM

Stop Time: 01:35PM

Initial Temperature of water bath (^oC): 37.0

Final Temperature of water bath (^oC):37.2

Sample ID	**EXT-ID**	**Weight (g)**	**Initial pH**	**Final pH**
MON-1	EX14-8	1.0265	1.53	1.60
MON-2	EX14-9	1.0109	1.48	1.56
MON-3	EX14-10	1.0224	1.52	1.57
MON-4	EX14-11	1.0128	1.53	1.57
MON-5	EX14-12	1.0344	1.48	1.55
MON-6	EX14-13	1.0233	1.51	1.66
BL13-14A[*]	BL13-14A	0.0000	1.53	1.61
SR13-14A[**]	SR13-14A	0.5117	1.53	1.59

* Procedural blank
**NIST 2711Standard reference material

Extraction Batch #2

Date of Extraction: October 24, 2013

Start Time: 09:38AM

Stop Time: 10:38AM

Initial Temperature of water bath (^{o}C): 37.0

Final Temperature of water bath (^{o}C):36.5

Sample ID	**EXT-ID**	**Weight (g)**	**Initial pH**	**Final pH**
MON-7	EX14-14	1.0065	1.51	1.59
MON-8	EX14-15	1.0435	1.51	1.51
MON-9	EX14-16	1.0078	1.59	1.60
MON-10	EX14-17	1.0180	1.54	1.57
MON-11	EX14-18	1.0175	1.53	1.54
DD13-14B***	DD13-14B	1.0150	1.53	1.54
BL13-14B*	BL13-14B	0.0000	1.52	1.56
SR13-14B**	SR13-14B	0.5051	1.56	1.62

* Procedural blank
**NIST 2711
***Duplicate MON-11

Extraction Batch #3

Date of Extraction: October 24, 2013

Start Time: 12:35PM

Stop Time: 01:35PM

Initial Temperature of water bath (^{o}C): 37.0

Final Temperature of water bath (^{o}C):36.5

Sample ID	**EXT-ID**	**Weight (g)**	**Initial pH**	**Final pH**
MON-12	EXT14-19	1.0136	1.56	1.63
MON-13	EXT14-20	1.0056	1.55	1.57
MON-14	EXT14-21	1.0283	1.54	1.59
MON-15	EXT14-22	1.0862	1.52	1.53
MON-16*	EXT14-23	1.0132	1.54	1.58
MON-17**	EXT14-24	1.0020	1.54	1.56
MON-18	EXT14-25	1.0075	1.54	1.57
DD13-14C***	DD13-14C	1.0095	1.48	1.55

* Procedural blank
**NIST 2711
***Duplicate MON-18

Appendix G: Total Metals in Extract by ICP MS

Metals by ICPMS	UNITS	BL13-14A	BL13-14B	EX14-8	RDL	EX14-9	EX14-10	EX14-11	RDL
Aluminum (Al)	ug/L	<40	<40	19600	40	16800	11300	11000	10
Antimony (Sb)	ug/L	<2.0	<2.0	<2.0	2.0	<0.50	0.54	<0.50	0.50
Arsenic (As)	ug/L	<1.6	<1.6	7.5	1.6	27.0	11.6	11.7	0.40
Barium (Ba)	ug/L	<4.0	<4.0	421	4.0	556	877	731	1.0
Beryllium (Be)	ug/L	<0.80	<0.80	1.01	0.80	1.91	1.42	1.84	0.20
Bismuth (Bi)	ug/L	<4.0	<4.0	<4.0	4.0	<1.0	<1.0	<1.0	1.0
Boron (B)	ug/L	<400	<400	<400	400	<100	<100	<100	100
Cadmium (Cd)	ug/L	<0.40	<0.40	2.30	0.40	3.23	3.89	4.34	0.10
Chromium (Cr)	ug/L	<8.0	<8.0	11.5	8.0	6.0	8.6	7.0	2.0
Cobalt (Co)	ug/L	<2.0	<2.0	12.8	2.0	17.4	13.4	26.2	0.50
Copper (Cu)	ug/L	57.5	46.5	99.7	4.0	187	140	144	1.0
Iron (Fe)	ug/L	<80	<80	5880	80	3850	11100	9260	20
Lead (Pb)	ug/L	1.55	1.90	110	0.80	505	206	358	0.20
Lithium (Li)	ug/L	<40	<40	<40	40	<10	<10	<10	10
Manganese (Mn)	ug/L	<4.0	<4.0	1250	4.0	2000	1570	2130	1.0
Mercury (Hg)	ug/L	<0.80	<0.80	<0.80	0.80	<0.20	<0.20	<0.20	0.20
Molybdenum (Mo)	ug/L	<4.0	<4.0	<4.0	4.0	<1.0	<1.0	<1.0	1.0
Nickel (Ni)	ug/L	<4.0	<4.0	23.5	4.0	33.9	24.7	36.9	1.0
Selenium (Se)	ug/L	<3.2	<3.2	<3.2	3.2	<0.80	<0.80	<0.80	0.80
Silicon (Si)	ug/L	<8000	<8000	<8000	8000	3780	3950	3720	2000
Silver (Ag)	ug/L	<0.40	<0.40	0.49	0.40	0.86	0.48	0.50	0.10
Strontium (Sr)	ug/L	<4.0	<4.0	284	4.0	235	420	657	1.0
Thallium (Tl)	ug/L	<0.20	<0.20	<0.20	0.20	0.129	0.084	0.090	0.050
Tin (Sn)	ug/L	<20	<20	<20	20	<5.0	<5.0	<5.0	5.0
Titanium (Ti)	ug/L	<40	<40	73	40	19	46	25	10
Uranium (U)	ug/L	<0.40	<0.40	1.24	0.40	1.37	2.54	1.76	0.10
Vanadium (V)	ug/L	<20	<20	39	20	48.5	47.3	49.4	5.0
Zinc (Zn)	ug/L	<40	<40	189	40	301	245	307	10
Zirconium (Zr)	ug/L	<8.0	<8.0	<8.0	8.0	<2.0	<2.0	<2.0	2.0
Calcium (Ca)	mg/L	<4.0	<4.0	95.6	4.0	58.6	110	157	1.0
Magnesium (Mg)	mg/L	<4.0	<4.0	7.5	4.0	2.9	6.9	13.0	1.0
Potassium (K)	mg/L	<4.0	<4.0	4.5	4.0	4.9	5.1	4.4	1.0
Sodium (Na)	mg/L	<4.0	<4.0	<4.0	4.0	1.1	1.3	1.2	1.0
Sulphur (S)	mg/L	<240	<240	<240	240	<60	<60	<60	60

RDL = Reportable Detection Limit

EDL = Estimated Detection Limit

Appendix G: Total Metals in Extract by ICP MS (Continued)

Metals by ICPMS	Units	EX14-12	EX14-13	EX14-14	EX14-15	EX14-16	EX14-17	EX14-18
Aluminum (Al)	ug/L	18500	3380	16500	6130	11900	22000	20400
Antimony (Sb)	ug/L	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Arsenic (As)	ug/L	7.1	5.4	9.1	6.6	11.2	6.7	8.8
Barium (Ba)	ug/L	151	236	638	402	533	823	1090
Beryllium (Be)	ug/L	0.87	1.69	1.70	2.25	2.76	5.74	3.93
Bismuth (Bi)	ug/L	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
Boron (B)	ug/L	<400	<400	<400	<400	<400	<400	<400
Cadmium (Cd)	ug/L	0.70	0.69	2.90	1.61	3.03	4.33	1.95
Chromium (Cr)	ug/L	16.3	22.8	18.7	16.7	<8.0	<8.0	12.6
Cobalt (Co)	ug/L	2.1	9.0	16.9	23.1	25.7	40.6	18.8
Copper (Cu)	ug/L	79.0	73.2	255	568	96.5	199	97.1
Iron (Fe)	ug/L	3690	34400	8990	20300	4010	3820	5350
Lead (Pb)	ug/L	53.5	87.4	153	106	291	123	99.8
Lithium (Li)	ug/L	<40	<40	<40	<40	<40	<40	<40
Manganese (Mn)	ug/L	216	3670	1420	2400	2800	8740	1360
Mercury (Hg)	ug/L	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80
Molybdenum (Mo)	ug/L	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
Nickel (Ni)	ug/L	4.9	16.2	33.0	31.5	28.5	44.2	21.0
Selenium (Se)	ug/L	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2
Silicon (Si)	ug/L	<8000	<8000	<8000	<8000	<8000	<8000	<8000
Silver (Ag)	ug/L	<0.40	<0.40	0.69	0.53	0.61	0.58	0.64
Strontium (Sr)	ug/L	115	7000	485	6840	909	378	162
Thallium (Tl)	ug/L	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Tin (Sn)	ug/L	<20	<20	<20	<20	<20	<20	<20
Titanium (Ti)	ug/L	59	<40	45	<40	<40	<40	60
Uranium (U)	ug/L	1.85	3.71	3.38	3.00	1.15	1.54	2.50
Vanadium (V)	ug/L	21	31	55	24	30	20	36
Zinc (Zn)	ug/L	370	207	403	411	159	210	141
Zirconium (Zr)	ug/L	<8.0	<8.0	<8.0	<8.0	<8.0	<8.0	<8.0
Calcium (Ca)	mg/L	36.3	1880	136	2670	314	120	57.8
Magnesium (Mg)	mg/L	4.7	230	13.9	74.2	10.9	5.3	8.0
Potassium (K)	mg/L	<4.0	<4.0	5.1	4.9	5.2	6.4	<4.0
Sodium (Na)	mg/L	<4.0	8.5	<4.0	<4.0	<4.0	<4.0	<4.0
Sulphur (S)	mg/L	<240	<240	<240	<240	<240	<240	<240

RDL = Reportable Detection Limit
EDL = Estimated Detection Limit

Appendix G: Total Metals in Extract by ICP MS (Continued)

Metals by ICPMS	Units	EX14-19	EX14-20	EX14-21	EX14-22	EX14-23	EX14-24	EX14-25
Aluminum (Al)	ug/L	15900	15600	17900	7170	18600	19900	3810
Antimony (Sb)	ug/L	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0
Arsenic (As)	ug/L	11.9	14.3	24.5	7.9	14.0	9.3	10.9
Barium (Ba)	ug/L	1310	706	679	571	1200	700	271
Beryllium (Be)	ug/L	2.81	2.40	3.77	1.96	5.03	2.41	1.97
Bismuth (Bi)	ug/L	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
Boron (B)	ug/L	<400	<400	<400	<400	<400	<400	<400
Cadmium (Cd)	ug/L	3.27	5.26	2.92	0.62	3.06	4.41	<0.40
Chromium (Cr)	ug/L	12.7	13.9	14.6	11.3	13.4	13.6	9.5
Cobalt (Co)	ug/L	25.9	28.6	28.0	24.6	37.9	21.1	51.6
Copper (Cu)	ug/L	191	219	138	301	180	235	128
Iron (Fe)	ug/L	16700	7200	5670	8060	5040	9530	36700
Lead (Pb)	ug/L	102	502	188	46.5	179	400	48.7
Lithium (Li)	ug/L	<40	<40	<40	<40	<40	<40	<40
Manganese (Mn)	ug/L	2110	2880	1730	2300	5300	2000	8040
Mercury (Hg)	ug/L	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80
Molybdenum (Mo)	ug/L	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
Nickel (Ni)	ug/L	39.0	43.0	27.8	18.0	50.6	33.2	40.3
Selenium (Se)	ug/L	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2
Silicon (Si)	ug/L	<8000	<8000	<8000	<8000	<8000	<8000	<8000
Silver (Ag)	ug/L	0.95	1.43	1.03	<0.40	0.69	0.85	<0.40
Strontium (Sr)	ug/L	418	755	518	287	428	347	2500
Thallium (Tl)	ug/L	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Tin (Sn)	ug/L	<20	<20	<20	<20	<20	<20	<20
Titanium (Ti)	ug/L	84	<40	<40	49	<40	46	<40
Uranium (U)	ug/L	3.83	1.72	1.59	1.65	1.89	1.65	5.50
Vanadium (V)	ug/L	97	44	42	<20	48	68	<20
Zinc (Zn)	ug/L	179	594	177	187	187	602	108
Zirconium (Zr)	ug/L	<8.0	<8.0	<8.0	<8.0	<8.0	<8.0	<8.0
Calcium (Ca)	mg/L	128	261	137	88.4	188	106	1370
Magnesium (Mg)	mg/L	20.6	20.4	10.7	33.3	25.1	9.0	68.4
Potassium (K)	mg/L	4.6	11.2	8.8	<4.0	6.3	7.1	4.9
Sodium (Na)	mg/L	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0
Sulphur (S)	mg/L	<240	<240	<240	<240	<240	<240	<240

RDL = Reportable Detection Limit

EDL = Estimated Detection Limit

Appendix G: Total Metals in Extract by ICP MS (Continued)

Metals by ICPMS	Units	SR13-14A	SR13-14B	DD13-14A	DD13-14B	DD13-14C	RDL
Aluminum (Al)	ug/L	17000	16800	26700	20800	4150	40
Antimony (Sb)	ug/L	18.0	19.2	<2.0	<2.0	<2.0	2.0
Arsenic (As)	ug/L	561	581	526	9.7	13.0	1.6
Barium (Ba)	ug/L	1370	1420	319	1110	291	4.0
Beryllium (Be)	ug/L	4.37	3.81	1.29	3.60	1.84	0.80
Bismuth (Bi)	ug/L	10.1	10.1	10.4	<4.0	<4.0	4.0
Boron (B)	ug/L	<400	<400	<400	<400	<400	400
Cadmium (Cd)	ug/L	389	399	1.10	2.18	0.40	0.40
Chromium (Cr)	ug/L	12.9	10.4	<8.0	13.1	11.1	8.0
Cobalt (Co)	ug/L	36.9	37.9	358	19.3	55.7	2.0
Copper (Cu)	ug/L	536	551	1440	103	137	4.0
Iron (Fe)	ug/L	8820	8880	33100	5330	38700	80
Lead (Pb)	ug/L	10500	10400	226	118	57.0	0.80
Lithium (Li)	ug/L	<40	<40	<40	<40	<40	40
Manganese (Mn)	ug/L	3810	3720	1040	1350	8040	4.0
Mercury (Hg)	ug/L	<0.80	<0.80	<0.80	<0.80	<0.80	0.80
Molybdenum (Mo)	ug/L	<4.0	<4.0	<4.0	<4.0	<4.0	4.0
Nickel (Ni)	ug/L	39.5	41.2	33.9	21.0	40.8	4.0
Selenium (Se)	ug/L	3.7	<3.2	<3.2	<3.2	<3.2	3.2
Silicon (Si)	ug/L	9580	9000	<8000	<8000	<8000	8000
Silver (Ag)	ug/L	26.1	28.1	3.26	1.36	0.78	0.40
Strontium (Sr)	ug/L	339	337	157	161	2500	4.0
Thallium (Tl)	ug/L	4.17	4.12	0.24	<0.20	<0.20	0.20
Tin (Sn)	ug/L	<20	<20	<20	<20	<20	20
Titanium (Ti)	ug/L	<40	<40	52	61	<40	40
Uranium (U)	ug/L	2.19	2.19	41.7	2.51	5.71	0.40
Vanadium (V)	ug/L	48	48	<20	37	<20	20
Zinc (Zn)	ug/L	1130	1120	48	137	119	40
Zirconium (Zr)	ug/L	<8.0	<8.0	<8.0	<8.0	<8.0	8.0
Calcium (Ca)	mg/L	234	234	22.3	56.8	1420	4.0
Magnesium (Mg)	mg/L	18.5	17.6	<4.0	7.9	67.8	4.0
Potassium (K)	mg/L	13.3	13.1	<4.0	<4.0	5.1	4.0
Sodium (Na)	mg/L	<4.0	<4.0	<4.0	<4.0	<4.0	4.0
Sulphur (S)	mg/L	<240	<240	<240	<240	<240	240
RDL = Reportable Detection Limit							
EDL = Estimated Detection Limit							

Appendix H: Metal Concentrations and Control Limits for Procedure Blanks and NIST 2711 Control Samples

	Concentration in Blanks (mg/kg)			**Concentration in NIST 2711 (mg/kg)**		
Elements	**BL13-14A**	**BL13-14B**	**Control Limit**	**SR13-14A**	**SR13-14B**	**Control Limit**
Aluminum (Al)	<40	<40		17000	16800	
Antimony (Sb)	<2.0	<2.0		18	19.2	
Arsenic (As)	<1.6	<1.6	<1.0	561	581	590 ±90
Barium (Ba)	<4.0	<4.0		1370	1420	
Beryllium (Be)	<0.80	<0.80		4.37	3.81	
Bismuth (Bi)	<4.0	<4.0		10.1	10.1	
Boron (B)	<400	<400		<400	<400	
Cadmium (Cd)	<0.40	<0.40		389	399	
Chromium (Cr)	<8.0	<8.0		12.9	10.4	
Cobalt (Co)	<2.0	<2.0		36.9	37.9	
Copper (Cu)	57.5	46.5		536	551	
Iron (Fe)	<80	<80		8820	8880	
Lead (Pb)	1.55	1.9	<50	10500	10400	9220 ±1490
Lithium (Li)	<40	<40		<40	<40	
Manganese (Mn)	<4.0	<4.0		3810	3720	
Mercury (Hg)	<0.80	<0.80		<0.80	<0.80	
Molybdenum (Mo)	<4.0	<4.0		<4.0	<4.0	
Nickel (Ni)	<4.0	<4.0		39.5	41.2	
Selenium (Se)	<3.2	<3.2		3.7	<3.2	
Silver (Ag)	<0.40	<0.40		26.1	28.1	
Strontium (Sr)	<4.0	<4.0		339	337	
Thallium (Tl)	<0.20	<0.20		4.17	4.12	
Tin (Sn)	<20	<20		<20	<20	
Titanium (Ti)	<40	<40		<40	<40	
Uranium (U)	<0.40	<0.40		2.19	2.19	
Vanadium (V)	<20	<20		48	48	
Zinc (Zn)	<40	<40		1130	1120	

Appendix I: Mean and Relative Percent Difference for Metals Bioaccessibility in Duplicate Samples

Element	**Bioaccessibility (%)**			**Relative Percent Difference (%)**
	MON-11	**MON-11 Dup**	**Mean**	
Arsenic	11.8	13.1	12.5	10.0
Barium	68.1	69.6	68.9	2.1
Cadmium	68.4	76.7	72.6	11.4
Chromium	2.6	2.7	2.6	4.1
Cobalt	13.0	13.4	13.2	2.9
Copper	19.7	22.3	21.0	12.5
Iron	1.9	1.9	1.9	0.5
Lead	40.6	48.1	44.4	17.0
Nickel	6.2	6.3	6.2	0.2
Zinc	14.9	14.5	14.7	2.6

Element	**Bioaccessibility (%)**			**Relative Percent Difference (%)**
	MON-18	**MON-18 Dup**	**Mean**	
Arsenic	27.0	32.2	29.6	17.4
Barium	47.0	50.4	48.7	6.9
Cadmium	NC	99.1	NC	NC
Chromium	5.0	5.9	5.5	15.3
Cobalt	43.8	47.2	45.5	7.4
Copper	34.4	38.4	36.4	11.0
Iron	22.9	24.1	23.5	5.1
Lead	39.8	46.5	43.2	15.5
Nickel	17.5	17.6	17.5	0.8
Zinc	26.9	29.5	28.2	9.3

Appendix J: Correlation Analysis Metal Bioaccessibility and Soil Properties

J1. Correlations - Arsenic bioaccessibility, ph, LOI550, LOI950, Fe, Mn, and As

```
         Asbio      ph  LOI550  LOI950      Fe      Mn
ph       0.235
         0.349

LOI550  -0.105  -0.397
         0.678   0.103

LOI950  -0.167   0.515  -0.461
         0.508   0.029   0.054

Fe      -0.417  -0.106   0.463  -0.386
         0.085   0.675   0.053   0.113

Mn      -0.565  -0.018   0.426  -0.045   0.583
         0.014   0.944   0.078   0.859   0.011

As      -0.439  -0.232   0.206  -0.279   0.664   0.374
         0.068   0.355   0.412   0.262   0.003   0.126

Cell Contents: Pearson correlation
               P-Value
```

J2. Correlations – Barium bioaccessibility, ph, LOI550, LOI950, Fe, Mn, Ba

```
         Babio      ph  LOI550  LOI950      Fe      Mn
ph      -0.201
         0.423

LOI550   0.648  -0.397
         0.004   0.103

LOI950  -0.401   0.515  -0.461
         0.099   0.029   0.054

Fe       0.354  -0.106   0.463  -0.386
         0.150   0.675   0.053   0.113

Mn      -0.046  -0.018   0.426  -0.045   0.583
         0.855   0.944   0.078   0.859   0.011

Ba      -0.020  -0.150   0.276  -0.357   0.651   0.393
         0.936   0.554   0.267   0.146   0.003   0.107


Cell Contents: Pearson correlation
               P-Value
```

J3. Correlations – Cadmium bioaccessibility, ph, LOI550, LOI950, Fe, Mn, Cd

```
         Cdbio       ph  LOI550  LOI950       Fe       Mn
ph      -0.053
         0.844

LOI550   0.151  -0.397
         0.577   0.103

LOI950   0.243   0.515  -0.461
         0.365   0.029   0.054

Fe      -0.369  -0.106   0.463  -0.386
         0.160   0.675   0.053   0.113

Mn      -0.176  -0.018   0.426  -0.045   0.583
         0.515   0.944   0.078   0.859   0.011

Cd       0.004  -0.082   0.736  -0.476   0.543   0.255
         0.987   0.747   0.000   0.046   0.020   0.307


Cell Contents: Pearson correlation
               P-Value
```

J4. Correlations –Chromium bioaccessibility, ph, LOI550, LOI950, Fe, Mn, Cr

```
         Crbio       ph  LOI550  LOI950       Fe       Mn
ph       0.161
         0.552

LOI550  -0.491  -0.397
         0.054   0.103

LOI950   0.681   0.515  -0.461
         0.004   0.029   0.054

Fe      -0.671  -0.106   0.463  -0.386
         0.004   0.675   0.053   0.113

Mn      -0.341  -0.018   0.426  -0.045   0.583
         0.196   0.944   0.078   0.859   0.011

Cr      -0.628  -0.344   0.475  -0.439   0.876   0.391
         0.009   0.162   0.046   0.069   0.000   0.109


Cell Contents: Pearson correlation
               P-Value
```

J5. Correlations – Cobalt bioaccessibility, ph, LOI550, LOI950, Fe, Mn, Co

```
         Cobio      ph  LOI550  LOI950      Fe      Mn
ph       0.706
         0.001

LOI550  -0.041  -0.397
         0.873   0.103

LOI950   0.546   0.515  -0.461
         0.019   0.029   0.054

Fe      -0.016  -0.106   0.463  -0.386
         0.950   0.675   0.053   0.113

Mn       0.333  -0.018   0.426  -0.045   0.583
         0.177   0.944   0.078   0.859   0.011

Co       0.126   0.018   0.308  -0.263   0.933   0.722
         0.618   0.944   0.214   0.292   0.000   0.001


Cell Contents: Pearson correlation
               P-Value
```

J.6 Correlations – Copper bioaccessibility, ph, LOI550, LOI950, Fe, Mn, Cu

```
         Cubio      ph  LOI550  LOI950      Fe      Mn
ph       0.305
         0.219

LOI550   0.021  -0.397
         0.934   0.103

LOI950   0.318   0.515  -0.461
         0.199   0.029   0.054

Fe      -0.213  -0.106   0.463  -0.386
         0.397   0.675   0.053   0.113

Mn      -0.090  -0.018   0.426  -0.045   0.583
         0.722   0.944   0.078   0.859   0.011

Cu       0.625   0.235   0.154   0.129   0.302   0.185
         0.006   0.348   0.542   0.611   0.223   0.463


Cell Contents: Pearson correlation
               P-Value
```

J.7 Correlations – Lead bioaccessibility, ph, LOI550, LOI950, Fe, Mn, Pb

```
         Pbbio      ph  LOI550  LOI950      Fe      Mn
ph       0.020
         0.936

LOI550   0.031  -0.397
         0.904   0.103

LOI950   0.108   0.515  -0.461
         0.668   0.029   0.054

Fe      -0.293  -0.106   0.463  -0.386
         0.237   0.675   0.053   0.113

Mn      -0.500  -0.018   0.426  -0.045   0.583
         0.035   0.944   0.078   0.859   0.011

Pb       0.318  -0.016   0.351  -0.369   0.342   0.021
         0.199   0.951   0.153   0.132   0.164   0.933


Cell Contents: Pearson correlation
               P-Value
```

J.8. Correlations – Nickel bioaccessibility, ph, LOI550, LOI950, Fe, Mn, Ni

```
         Nibio      ph  LOI550  LOI950      Fe      Mn
ph       0.417
         0.085

LOI550   0.124  -0.397
         0.624   0.103

LOI950   0.577   0.515  -0.461
         0.012   0.029   0.054

Fe      -0.333  -0.106   0.463  -0.386
         0.176   0.675   0.053   0.113

Mn       0.205  -0.018   0.426  -0.045   0.583
         0.414   0.944   0.078   0.859   0.011

Ni      -0.328  -0.032   0.428  -0.336   0.937   0.505
         0.183   0.898   0.076   0.173   0.000   0.032


Cell Contents: Pearson correlation
               P-Value
```

J9. Correlations – Zinc bioaccessibility, ph, LOI550, LOI950, Fe, Mn, Zn

```
         Znbio      ph  LOI550  LOI950      Fe      Mn
ph       0.112
         0.659

LOI550  -0.377  -0.397
         0.123   0.103

LOI950   0.540   0.515  -0.461
         0.021   0.029   0.054

Fe      -0.751  -0.106   0.463  -0.386
         0.000   0.675   0.053   0.113

Mn      -0.454  -0.018   0.426  -0.045   0.583
         0.058   0.944   0.078   0.859   0.011

Zn      -0.126  -0.124   0.549  -0.490   0.432  -0.025
         0.619   0.625   0.018   0.039   0.073   0.921


Cell Contents: Pearson correlation
               P-Value
```