

Spatial and Geochemical Techniques to Improve Exposure
Assessment of Manganese in Windsor, Ontario

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Abstract

This study was conducted to investigate the urban geochemistry of the city of Windsor (Ontario) and to provide added source apportionment information to work being carried out by the Canadian government. The goal of this study was to investigate the distribution, spatial variation and sources of manganese in urban Windsor soil. The literature indicates that human exposure to high levels of manganese, via inhalation, can cause respiratory and/or neurological effects. At the outset of the present study it was first hypothesized that vehicular traffic was the dominant source of anthropogenic manganese. An alternative hypothesis was that there were multiple anthropogenic sources of manganese in Windsor. The sample collection scheme was designed to determine (1) the current and background soil concentrations of manganese in Windsor, (2) the spatial distribution of manganese in order to reveal sources of manganese, and (3) the manganese content of moss-sequestered airborne particles, which can potentially deposit onto the soil surface, using low-technology biomonitoring. The first phase of the study consisted of a preliminary soil survey which identified elevated areas of soil manganese concentrations. During this survey, the field efficiency of a field portable X-ray fluorescence (FPXRF) instrument, as well as sample preparation methods were evaluated. Efficiency of the FPXRF was determined by comparison to ICP-MS, a traditional trace element analysis method. The preliminary soil survey identified several areas of elevated (ranging from 884 to 2390 ppm) soil manganese which were further investigated during the second, more complete, soil survey. The moss biomonitoring technique of using moss bags was used to collect airborne particles for semi-quantitative analysis. Analysis of soil samples included total manganese and other trace elements, pH, moisture and carbon content, and manganese speciation. Urban Windsor soil manganese distribution revealed both natural and anthropogenic sources of soil manganese and three distinct soil sample types, transect, baseline and natural. In general, manganese in Windsor had a west-to-east trend of decreasing levels in soil and moss-sequestered airborne particles. The latter showed a modern-day elemental signature while the former (collocated soil) a legacy elemental signature. It was concluded that both the FPXRF instrument and the moss biomonitoring technique can be useful screening tools in studies of urban environments.

Résumé

Cette étude a été menée pour étudier la géochimie urbaine de la ville de Windsor (Ontario) et pour fournir des informations supplémentaires à celles déjà obtenues par le gouvernement canadien sur la répartition des sources. L'objectif de cette étude était d'étudier la distribution, les variations spatiales et d'identifier les sources de manganèse dans le sol de la ville de Windsor. D'après la littérature, l'exposition humaine à des niveaux élevés de manganèse, par inhalation, peut provoquer des effets respiratoires ou neurologiques. Au tout début de cette étude, l'hypothèse était que la circulation routière serait la source anthropique dominante de manganèse. Une hypothèse alternative était qu'il y avait plusieurs sources anthropiques de manganèse à Windsor. Le régime de prélèvement d'échantillons a été conçu pour déterminer (1) les concentrations de manganèse actuelles et de fond dans le sol de Windsor, (2) la distribution spatiale de manganèse dans le but d'identifier les sources, et (3) la teneur en manganèse dans des particules en suspension – qui autrement se déposeraient à la surface du sol – piégées par de la mousse en utilisant la biosurveillance. La première étape de l'étude consistait en une enquête préliminaire du sol qui a servi à identifier les zones ayant une teneur élevée en manganèse. Au cours de cette enquête, l'efficacité d'un appareil portable fonctionnant par fluorescence aux rayons X (FPXRF), ainsi que les méthodes de préparation des échantillons ont été évalués. L'efficacité de l'instrument FPXRF a été déterminée par comparaison à l'ICP-MS, une méthode traditionnelle d'analyse d'éléments traces. L'enquête préliminaire du sol a permis l'identification de plusieurs zones à haute concentration (dans une gamme de 884 à 2390 ppm) de manganèse dans le sol. Ces zones ont été étudiées en détail au cours de la deuxième enquête du sol, plus rigoureuse. La technique de biosurveillance à base de mousse a mis à profit des sacs de mousse pour collectionner les particules en suspension pour en faire une analyse semi-quantitative. L'analyse des échantillons de sol comprenait la mesure du manganèse total et d'autres éléments en trace, du pH, de la teneur en eau et de carbone, et de la spéciation du manganèse. L'étude de la distribution de manganèse dans le sol de la ville de Windsor a dévoilé des sources naturelles et anthropiques de manganèse ainsi que trois types distincts d'échantillons de sol: transect, de base et naturel. De façon générale, le niveau de manganèse dans le sol et dans la mousse tendait à diminuer de l'ouest à l'est de Windsor. Le manganèse capturé par

la mousse présentait un signal élémentaire récent tandis que le manganèse dans le sol portait un signal élémentaire ancien. Il a été conclu que l'instrument de FPXRF et la technique de biosurveillance de la mousse peuvent être des outils de dépistage utiles dans les études des milieux urbains.

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Chapter 1 - Introduction

Purpose

The purpose of this work was to examine the concentration and spatial distribution of manganese in outdoor particles (surface soil and airborne particulate matter) collected in Windsor, Ontario. Geochemical investigations included field and analytical method development for the purpose of adding source apportionment information, as well as geochemical data, to work that is being carried out by the Canadian government. For example, an innovative technique was used to improve soil surveying methods. A field-portable X-ray fluorescence (FPXRF) instrument was used to determine elemental concentrations of manganese and other trace elements in an urban environment. Comparison of FPXRF results with corresponding ICP-MS results was done to determine the analyzer's field efficiency. Testing was done to find the optimal field sample preparation technique(s).

The study design for this thesis is discussed in Chapter 3. The following objectives were investigated and discussed in Chapters 5, 6, 7, and 8 of this work:

- 1) determine the levels of soil manganese in urban Windsor soil,
- 2) identify sources of manganese and the distribution of manganese in their surrounding area,
- 3) establish the natural background range of soil manganese for the Windsor area,
- 4) determine the spatial distribution of manganese in Windsor soil,
- 5) investigate specific characteristics (i.e., mineralogy) of Windsor soil,
- 6) identify significant soil elemental signatures of urban Windsor soil and distinguish between natural and anthropogenic signals,
- 7) evaluate the field efficiency of a field-portable X-ray fluorescence instrument for soil manganese determination in an urban setting, and
- 8) evaluate the manganese content of airborne particles in Windsor, Ontario using low-technology biomonitoring stations in order to identify present-day anthropogenic sources separate from re-suspended soil manganese (natural and anthropogenic).

Spatial analysis using ArcGIS[®] as well as statistical analyses were used to distinguish the anthropogenic contribution of manganese and the natural background soil manganese. Elemental associations were investigated in all environmental media collected with the goal of finding signatures that would distinguish sources of manganese.

Scope

This source identification work complements Health Canada's Windsor residential sample collection of 2005-2006 and human exposure modeling efforts. Health Canada sampled air and indoor settled dust, but did not include soil sampling (Wheeler et al., 2011). Therefore, direct sampling of manganese in air or the indoor environments was not performed in this evaluation of Windsor soil

Toxicological information regarding manganese is discussed in the literature review below, however as stated above, the present work is a source identification study, not a toxicology study. The literature review was to show both the important role manganese plays in the environment and to show the risk it can pose when found elevated in the human environment. This present study of urban soil in Windsor was not intended to address toxicological research questions.

While soil cores were taken at certain sampling sites, this study is an investigation of manganese in surface soil (0-5 cm). For the most part, the focus of this work is total manganese. However a select group of samples underwent speciation by solid sample analysis using synchrotron micro-analyses. The purpose of this speciation was to assist in source identification.

Background

Health Canada and Environment Canada are carrying out research in the Great Lakes Basin (Environment Canada, 2005b) in an effort to characterize air quality and human health issues associated with a wide range of pollutants. One of the initiatives of this research is the Windsor, Ontario Exposure Assessment Study (WOEAS) (formerly known as the Canada-US Border Air Quality Strategy (BAQS)). The goal of the WOEAS was to assess community and personal exposure from all air pollution (Environment Canada, 2005a).

Pollutants of interest of this study included manganese and other trace element constituents of airborne particulate matter. The Windsor-Detroit area is the busiest Canada-US border crossing because of the Ambassador Bridge and the Detroit Windsor tunnel. Due to the heavy traffic and industrial emissions and transboundary long-range transport of air pollutants, this area is known for high levels of fine particulate matter (PM_{2.5}) which contribute to local air pollution (Health Canada, 2006). To thoroughly evaluate the role of manganese with respect to human health, it is important to consider all components of the human environment this includes soil, not just air. Evaluating the geochemical distribution and sources of manganese in Windsor soil and air particulate matter would be beneficial to human health exposure studies like the WOEAS as well as add to the geochemical knowledge of the soil in this area. Geochemical and spatial distributions of soil manganese in urban Windsor, Ontario have never been determined.

Literature Review

1.0 Soil manganese

Physical chemistry of manganese

Manganese (atomic number (Z) = 25) is a transition metal and has similar geochemical behavior as its neighbour in the periodic table, iron (Z = 26) (Kabata-Pendias and Mukherjee, 2007). Several physical characteristics and chemical properties of manganese are listed in (Table 1). Manganese does not occur in nature in a pure metallic form. It is a base metal and reacts with oxygen. Manganese is the twelfth most abundant element in the Earth's crust (0.10 %). It is widely distributed in the various environmental compartments (Schafer, 2004) (Table 2).

Table 1 Physical characteristics and chemical properties of manganese.

Colour	Whitish-grey, steel-gray to silvery white, often tarnished
Malleability	Brittle
Mohs hardness	6.0
Specific gravity	7.21 g/cm ³
Atomic number	25
Atomic weight	54.94 g/mol
Atomic radius	140 picom
Covalent radius	139 picom
Oxidation states^a	2, 3, 4, 5, 6, and 7
Stable isotope	⁵⁵ Mn
Electronegativity	1.55 (Pauling scale)
Melting point	1244 ± 3 °C

^a Bold oxidation states indicate most environmentally stable.
(Sources: Adriano, 2001; Schafer, 2004)

Table 2 Abundance of manganese in various environmental compartments.

Environmental Compartment	Abundance
Soils ^a (see also Table 4)	270 to 525 mg/kg (dry weight)
Rocks ^a	350 to 2000 mg/kg
Earth's crust ^{a, c}	~ 950 mg/kg, 650 mg/kg ^d
Earth's core ^a	1.5 %
Air	
Rural non-polluted (USA) ^a	0.01 to 0.03 µg/m ³
Rural (worldwide) ^b	40 ng/m ³ (6.5 to 199 ng/m ³)
Urban (no significant source) (USA) ^a	0.03 to 0.07 µg/m ³
Urban (USA) ^b	93 ng/m ³ (5 to 390 ng/m ³)
(Canada) ^b	65 ng/m ³ (20 to 270 ng/m ³)
(Europe) ^b	166 ng/m ³ (23 to 850 ng/m ³)
Surface waters	1 to 500 µg/L ^a < 200 µg/L ^b
Open oceans ^a	0.01 to 0.16 µg/kg (dissolved Mn)
Vegetation ^a	17 to 334 mg/kg (dry matter in grass) 25 to 119 mg/kg (dry matter in clover)

^a (Schafer, 2004)^b (World Health Organization, 2004)^c (Enghag, 2004; Wedepohl, 1995)^d (Gilkes and McKenzie, 1988)

The most important, and most commonly found oxidation states in the environment are Mn²⁺, Mn³⁺, and Mn⁴⁺ (Schafer, 2004; Gilkes and McKenzie, 1988). Manganese (II) is thermodynamically unstable above a pH of 4 (Gilkes and McKenzie, 1988), therefore Mn³⁺ and Mn⁴⁺ will dominate in alkaline environments. However in reducing conditions ($pE < 6$ and $pH < 8$), Mn²⁺ will dominate whereas in oxidizing conditions Mn⁴⁺ will be dominant (Campbell and LaZerte, 1988; Norvell, 1988; Adriano, 2001) (Figure 1). Manganese (III) will readily disproportionate to either Mn²⁺ or Mn⁴⁺ depending on the redox conditions (Hughes and Williams, 1988). The abiotic oxidation of manganese from oxidation state + II to + III, or + IV is thermodynamically favored throughout the pH range of soils (Norvell, 1988). Above pH 8, the biotic oxidation of manganese becomes more important than the abiotic reaction (Norvell, 1988).

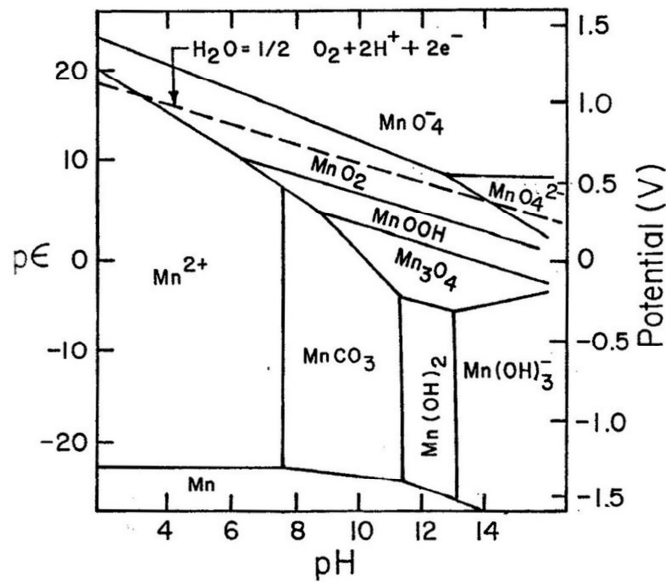


Figure 1 Manganese Eh-pH stability diagram. (Source: Stokes et al., 1988)

Microorganisms are ubiquitous in the soil environment. Soil manganese can be used as an energy source for certain bacteria and fungi (Ehrlich, 2008). These manganese-oxidizing and -reducing bacteria are found in diverse environments and include both gram-positive and -negative forms (Ehrlich, 2008). For example, bacteria oxidizers like *Arthrobacter* and *Bacillus*, or fungi such as *Cladosporium*, *Curvularia*, oxidize Mn^{2+} to Mn^{4+} (Adriano, 2001). The ubiquity of microorganisms in every component of the environment (water, air, soil) must infer that manganese-oxidizing and -reducing microorganisms play an important role in the geochemical cycling of manganese (Ehrlich, 2008). Their influence on the distribution of manganese in soil, though outside the scope of this work, must be acknowledged.

Manganese in soil

Soils can be defined as the overburden overlying bedrock or as the unconsolidated, thin, layer of material covering the earth's surface (Hollis, 1991; Singer and Munns, 1996). Soils are formed from the weathering of parent material. Other factors that can affect both soil formation and its composition are climate, vegetation, topography, and time. Soil is a

dynamic, heterogeneous environment. Reactions which influence its chemistry and composition (i.e., oxidation, reduction, dissolution, precipitation, exchange) are occurring simultaneously within, and between the different soil phases (solid, gaseous and liquid). The soil solid phase includes minerals (weathered and unweathered) and organic material (OM). Most often, the product of mineral weathering are clays and oxide minerals (Singer and Munns, 1996). These have highly charged surfaces which make them very reactive substances in the soil environment.

The gaseous and liquid soil phases are contained within the soil pores, spaces between the solid components. Most surface soils are in direct contact with the atmosphere. The composition of their gaseous phase is therefore quite similar to the atmosphere. The most important soil gas is oxygen. It plays a major role in soil reactions of oxidation and reduction (redox). The liquid soil phase, or soil solution, contains water dissolved substances, namely cations (including manganese), anions, organic, and inorganic compounds (Singer and Munns, 1996). In favorable conditions, i.e., increasing pH, manganese oxides can precipitate out of solution and become part of the solid soil phase. Manganese in soil exists incorporated into minerals (primary and secondary), sorbed onto surfaces (i.e., mineral or organic matter), in soil solution, and/or incorporated into organisms (Gilkes and McKenzie, 1988). Manganese dioxide (Mn(IV)) is the most stable manganese compound in oxidizing environments (Adriano, 2001; Schafer, 2004) and is found in several soil minerals.

Manganese minerals are widely distributed in the environment and occur in over 200 primary and secondary minerals (Adriano, 2001; Schafer, 2004). Due to its chemical properties and reactive nature, manganese tends to form oxides, hydroxides and carbonates in soil (Campbell and LaZerte, 1988; Adriano, 2001; Schafer, 2004). The common oxidation state of primary manganese minerals is usually Mn^{2+} since the environmental conditions at the time of their formation was reducing (Gilkes and McKenzie, 1988; Adriano, 2001; Schafer, 2004). Primary manganese minerals are described by Gilkes and McKenzie (1988) as being of “limited occurrence”. When exposed to air and water, these minerals oxidize to form secondary minerals of Mn^{3+} and Mn^{4+} . Therefore, Mn^{3+} and Mn^{4+} minerals are

dominant in oxidized environments and manganous (Mn^{2+}) oxides are dominant in reducing environments and soil solutions (Ehrlich, 2008; Adriano, 2001). Table 3 lists common manganese minerals of which the most commonly found is pyrolusite, a manganese dioxide mineral.

Table 3 Common manganese minerals

Mineral Name and Composition	Oxidation State
Pyrochrosite ($\text{MnO} \cdot \text{H}_2\text{O}$) Rhodocrosite (MnCO_3) Manganosite (MnO) Hauerite (MnS_2) Hausmannite (Mn_3O_4) Rhodonite (MnSiO_3)	Mn^{2+}
Manganite ($\text{Mn}_2\text{O}_3 \cdot \text{H}_2\text{O}$) Bixbyite (Mn_2O_3) Braunite ($3\text{Mn}_2\text{O}_3 \cdot \text{MnSiO}_3$)	Mn^{3+}
Pyrolusite (B- MnO_2) (15 crystalline forms exist) Most commonly found include: Birnessite ($(\text{Na}, \text{Ca})\text{Mn}_7\text{O}_{14} \cdot 2.8\text{H}_2\text{O}$) Vernadite (MnO_2) (Poorly crystalline) Psilomelane (Romanèchite) $(\text{Ba}, \text{K}, \text{Mn}, \text{Ca})_2\text{Mn}_5\text{O}_{10}$ Cryptomelane ($\text{K}_2\text{Mn}_8\text{O}_{16}$) ^a or $(\text{KMn}_8\text{O}_{16})$ ^b Jacobsite (Fe_2MnO_4) ^b Bementite ($\text{Mn}_3\text{Si}_2\text{O}_5(\text{OH})_4$)	Mn^{4+}

(Sources: Schafer, 2004; ^aGilkes and McKenzie, 1988; ^bWellbeloved et al., 2002)

Due to their similar ionic radii and chemical charge, Mg^{2+} , Ca^{2+} and Fe^{2+} can substitute for Mn^{2+} and vice versa (Hughes and Williams, 1988; Schafer, 2004). Aluminum, lithium (lithiophorite) and potassium (cryptomelane) are essential elements in manganese oxides whereas Co, Cu, Ni, Zn, Pb, Cr, and V are minor elements which accumulate in manganese oxides (Norvell, 1988). This accumulation can be explained by the high specific surface area of manganese oxides and their surface charge (Gilkes and McKenzie, 1988).

Manganese oxides often precipitate out of soil solution and occur as surface coatings. These coatings have a large surface area. This along with the fact that, at circumneutral pH values ($\text{pH} > 5$), manganese minerals have very high negative surface charges (Gilkes and McKenzie, 1988), means that they can therefore adsorb trace metal cations (Campbell and LaZerte, 1988). Adsorption of cations by manganese oxides increases with increasing pH (Balistrieri and Murray, 1982; McKenzie, 1981). Mn(IV) oxides are amphoteric, i.e., they react as either acid or base depending on their surface charge which in turn depends on the number of cations absorbed to its surface (Ehrlich, 2008; Adriano, 2001).

McKenzie (1981) and Norvell (1988) (and references therein) suggested the following affinity series for Birnessite and other related manganese oxides: $\text{Pb} > \text{Cu} > \text{Co} \geq \text{Mn} > \text{Zn} > \text{Ni} > \text{Ca} > \text{Mg}$. Campbell and LaZerte (1988) reported that the affinity of cobalt (II) for manganese oxides was unique. Over time, the strong association between cobalt and the manganese oxide becomes stronger and cobalt can sometimes possibly replace the manganese in the crystal structure (Murray and Dillard, 1979).

Not only are manganese oxides efficient adsorbers of trace elements in soil, but manganese itself can be adsorbed onto solid surfaces. Adsorption of manganese can occur on both organic matter (Campbell and LaZerte, 1988; Adriano, 2001) and clay minerals (i.e., kaolinite, illite and bentonite) (Reddy and Perkins, 1976) as well as other minerals (i.e., aluminosilicates, carbonates, various oxides of Al, Fe, Si and Mn) (Campbell and LaZerte, 1988). Therefore, manganese species in soil can be in soil solution, mineral form, and adsorbed to soil components.

Soil manganese speciation is difficult due to the specificity of extraction reagents. Sequential chemical extractions have been used extensively in the past, in fact manganese oxides are one of the fractions common in the extraction schemes. However, recently there has been debate over the use of these extractions because of their operationally-defined bias (Bacon and Davidson, 2008). Relevant to the present study is the fact that several analytical methods, such as ICP-MS, AAS, XRF, have been used to reliably determine the total soil manganese concentrations.

Adriano (2001) states that as a general rule, manganese concentrations are expected to be highest in surface soil. However, the 1981 WHO report states that accumulation of manganese in soil usually occurs in the subsoil (“sand fraction”). The distribution of manganese in soil is dependent on pH, redox conditions, the characteristics of ligands and other adsorbent surfaces, the activity of microorganisms, and plant uptake and decomposition (World Health Organization, 2004; Norvell, 1988). Soil manganese concentrations will therefore vary widely. Table 4 presents a summary of soil manganese levels found in Canada and around the world. This list is by no means exclusive. Based on these studies (Table 4), soil manganese in Ontario appears to have a mean of approximately 600 ppm. There are currently no Canadian guidelines for acceptable levels of soil manganese (Canadian Council of Ministers of the Environment, 1999).

Table 4 Selected domestic and international mean soil manganese levels.

	Location	Soil Description	Manganese Concentration (min-max range)	Reference
Domestic	Ontario	Agricultural clay soils	662 ± 469 ppm (140 to 3000)	Frank et al. (1976)
		Urban parkland Rural parkland	~600 µg/g (up to 1300) ~ 850 µg/g (up to 2200)	Ontario Ministry of the Environment (1993)
	British Columbia	Uncontaminated soil	284 to 1359 mg/kg	Reimer (1999 in WHO (2004))
	Canada	Uncultivated surface soils	520 ppm (100 to 1200)	McKeague and Wolynetz (1980)
International	United States (conterminous)	Surface soils	AM ¹ = 550 ppm (< 2 to 7000) GM ² = 330 ppm	Shacklette and Boerngen (1984)
	China	Soil	582 µg/g (GM ² = 432 µg/g)	Chen et al. (1991)
	New Zealand	Garden soil	325 ± 57 µg/g (235 to 458)	Fergusson et al. (1986)
	Central Russian region	Plow layer	740 ppm (472 to 1250)	Krupskiy et al. (1978 in Adriano (2001))
	World	Average soil content	(20 to 10 000 ppm)	Adriano (2001)
Urban	Aberdeen, Scotland	Public parks	286 ± 52 mg/kg	Paterson et al. (1996)
	Uppsala, Sweden	Playground soils	Median = 494 mg/kg (199 to 833)	Ljung et al. (2006)
	Palermo (Sicily), Italy	Topsoil of green spaces	519 ± 250 mg/kg (142 to 1241)	Manta et al. (2002)
	Alcala de Henares (Madrid), Spain	Municipal gardens University campus	94.4 ± 52.9 µg/g 192.5 ± 50.8 µg/g	Granero and Domingo (2002)
	Madrid, Spain	Urban soil samples	437 ± 118 µg/g (323 to 1150)	De Miguel et al. (1998)
	Bangkok, Thailand	Sampled along transect	340 ± 210 mg/kg (50 to 810)	Wilcke et al. (1998)

¹ Arithmetic Mean, ² Geometric Mean

Mining and industrial uses

Canadian deposits of manganese are ‘confined to the Maritime Provinces and to British Columbia. In other parts of Canada, there are only a few, small, non-commercial bog desposits’ (Hanson, 1932). Hanson (1932) states that manganese deposits are not likely to occur in the St.Lawrence region of Canada, where Windsor is located. The largest deposits of manganese are in South Africa, Gabon, Brazil, Ukraine, Australia, and China (Adriano, 2001).

Large reserves of manganese exist in the deep oceans (approximate depth 5000 m) (Enghag, 2005; International Manganese Institute, 2009). These reserves are in the form of polymetallic nodules, which formed by the precipitation of ferromanganese oxides (Schafer, 2004; International Manganese Institute, 2009; Considine and Kulik, 2008) which grow at a rate of a few mm per million years (Considine and Kulik, 2008). Deep ocean nodules can contain up to 55 % Mn, 35 % Fe and 2 % Ni, Co and Cu (Considine and Kulik, 2008). The chemical composition of these nodules can vary within the nodule itself and within the area. Schafer (2004) states that Falbe and Regitz (1999) estimated that manganese nodules in the three major oceans contain 1 to 3 trillion tons of ore. Recovery of these deep ocean nodules is however difficult and expensive and they therefore remain a future manganese resource, as surface exploitation of manganese ore remains the most viable reserve.

The amount of manganese needed worldwide depends on the needs of the steel industry (International Manganese Institute, 2009). According to the International Manganese Institute (2009) the average unit consumption for industrialized countries is a little over 7.5 kg Mn/ ton of steel produced. Steel is an iron-carbon alloy. In the 19th century, the use of manganese in steel manufacturing was first patented and since then manganese has become an essential element of steel and other alloys. Its ability to deoxidize and combine with sulfur is responsible for removing both oxygen and sulfur from steel, making it even harder and stronger (Schafer, 2004). Steel alloys commonly consist of manganese, nickel, chromium, molybdenum, silicon and boron.

The International Manganese Institute (2009) reported that world manganese reserves were estimated at several billion tons and in 2007, 38 million tons of manganese ore were being mined annually. Economically significant manganese ores contain from 35 to 50 % manganese (Hanson, 1932; Schafer, 2004; Enghag, 2004; International Manganese Institute, 2009). There are three types of manganese ore: metallurgical grade ore (38-55 % Mn) used in the iron and steel industry, battery grade ore (54 % Mn), and chemical grade ore (% varies depending on the end product) (Schafer, 2004). With the exception of China, the largest deposits are also the major producers of manganese in addition to Ghana and India (Adriano, 2001; Schafer, 2004; International Manganese Institute, 2009).

In 2009, the total world production of manganese alloys was 11.7 million metric tons (mt) (International Manganese Institute, 2009). Production was dominated by China (57 % or 6.6 million metric tons) (International Manganese Institute, 2009). China was also the largest producer of manganese ore (2.7 million mt), followed by South Africa (1.9 million mt), Australia (1.8 million mt), Gabon (956K mt), Kazakhstan (377K mt), India (845K mt) and Brazil (1 million mt) (Figure 2) (International Manganese Institute, 2009).

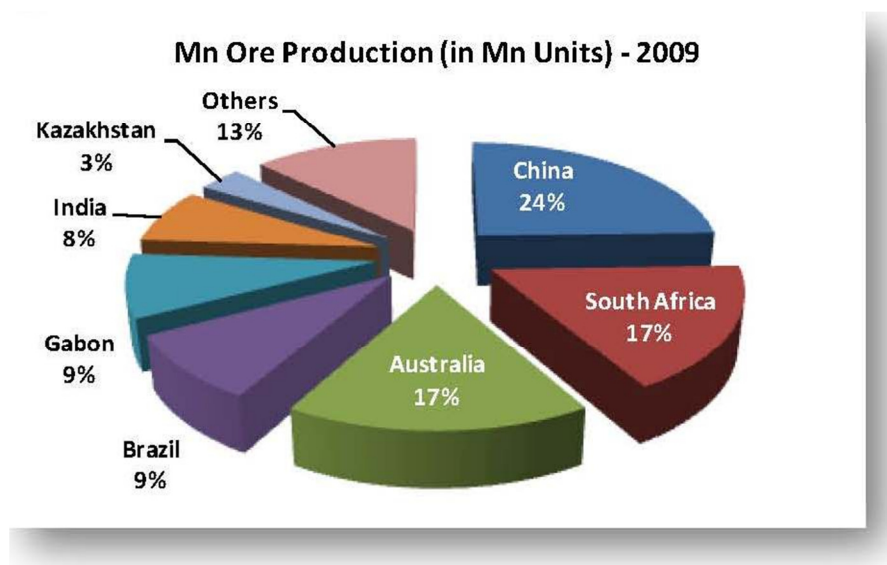


Figure 2 2009 manganese ore producers. (Source: IMnI, 2009)

There is evidence that manganese (Mn) has been used since the Stone Age (International Manganese Institute, 2009). It was recognized as an element in 1771 by the Swedish chemist Carl Wilhelm Scheele and isolated three years later by Johan Gottlieb Gahn (Appendix A). Since then, the use of manganese in the production of steel and alloys has grown as its importance and valuable properties were discovered.

According to Schafer (2004) and Enghag (2004), approximately 90% of manganese produced is used in the steel and metallurgical industries. Approximately 5% of the world production of manganese ore is consumed by other industries, including chemical, glass and battery industries as well as various others (Schafer, 2004).

Steel and alloys containing manganese are used in vehicles and building construction. Automotive industries use engineering steels which can contain from 0.6 to 1.5 % Mn (International Manganese Institute, 2009). High-manganese steel, like Hadfield steel, contains 13 % Mn which gives the steel “great toughness and wear resistance” (Enghag, 2004; International Manganese Institute, 2009). Silico-manganese (SiMn) is used in the production of steel long products also used in the construction industry. In 2007, production of SiMn was greater than the production of high-carbon ferromanganese and refined ferromanganese combined. Steel used for welding can have a manganese content of 1.0 to 1.8 % while stainless steels contain about 1.0 % (Enghag, 2004).

Manganese is also used in the production of other alloys. For example, aluminum-manganese alloys are used for producing aluminum beverage cans and sheets used in building construction (aluminum sheets for facing) (International Manganese Institute, 2009; Enghag, 2004). Some copper-manganese alloys can contain over 50 % manganese however most contain between 10 and 20 % Mn. One of these high-manganese copper alloys is used in temperature control devices in cars and other vehicles and contains 72 % Mn, 18 % Cu and 10 % Ni (International Manganese Institute, 2009).

As well as being used in the production of various alloys, manganese has many non-metallurgical, past and present, uses (Table 5) which include commercial, chemical and biological applications and products. According to the International Manganese Institute

(2009), the second most important market for manganese, after steel manufacturing, is MnO_2 in portable dry batteries. In summary, manganese is a very versatile element used in many household items. Everyday usage and wear-and-tear of these manganese-containing products yields the potential for release of manganese to the environment.

Table 5 Other uses of manganese (this list is not exclusive).

Manganese Species	Use(s)	Manganese Species	Use(s)
Maneb [®] (manganese-ethylene bisdithiocarbamate)	Pesticide	MMT [®] (Methylcyclopentadienyl manganese tricarbonyl)	Anti-knock agent (octane enhancer and combustion aid in heating oils)
MnO (78 % Mn), MnSO ₄ · 4 H ₂ O (24 %)	Fertilizers	Unspecified formula	- Vehicle components - Welding rods - Gyratory crushers, jaw-crushers, railway points, crossover components, teeth for earth- moving equipment - Retainer rings for turbo alternators and collars on oil rigs - Metallurgy - Constituent and activator of several enzymes and proteins - Deoxidizing agent
MnO, MnCl ₂	Animal feed additives		
MnCl, Mn(NO ₃) ₃ , and others	Glass, ceramic, brick and paint colorants		
MnO ₂	Dry-cell batteries and alkaline batteries		
KMnO ₄	- Dye bleach - Medicine (antiseptic, deodorant, disinfectant) - Water and air purification		

(Source: Schafer, 2004)

Environmental anthropogenic and natural sources

Sources of environmental manganese include vehicular (fuel combustion, tire and vehicle component wear) and industrial emissions, naturally occurring sources, local and long-range transport of airborne particulate matter. Atmospheric deposition of manganese is an important source of soil manganese and vice versa, soil manganese can be a source of atmospheric manganese (Stokes et al., 1988; World Health Organization, 2004). Lee et al. (2006) found that an estimated (modeled) 4 % of urban PM_{2.5} mass (2.69 ng Mn/m³) collected at a Supersite in Illinois was airborne soil. The majority of manganese particulates re-suspended from the ground or emitted to the atmosphere will settle within a few kilometers of the source (Hutchinson and Whitby, 1974; Adriano, 2001). Garrels et al. (1975) also indicated that manganese will settle out near its source because of its low volatility but also suggested that as a fine particulate material, it can also be distributed worldwide. The major anthropogenic sources of manganese to the environment include the manufacture of steel and alloys, iron products, production and use of fertilizers and fungicides, fuel additive use, wastewater and sewage sludge, mining and ore processing, and combustion of fossil fuels (Abbott, 1987; Schafer, 2004; World Health Organization, 2004). Other sources include municipal incinerators (Adriano, 2001) land disposal of manganese-containing wastes (World Health Organization, 2004) and agriculture.

Vehicular

Heavy traffic can be an important source of manganese to the environment due to the wear and tear of Mn-alloys vehicle components and past combustion of MMT-added fuel. In a preliminary study done in Montréal (QC), Forget (1992 in Loranger (1994)) found that manganese concentrations were higher in soils near high traffic streets compared to streets with low traffic density. Loranger et al. (1994) found a relationship between manganese in airborne particles and high traffic density in Montréal. The researchers however were unable to distinguish between Mn emitted from vehicles, Mn-enriched road dust and crustal material, as are most researchers today (Zayed, 2001). In Toronto, Bhuie et al. (2000) and Bhuie and Roy (2001) found a trend of decreasing manganese concentrations with distance from a highway. This decrease however was not statistically significant. In 2005, Bhuie et

al. reported that the amount of manganese depositing onto the soil surface near a high traffic density highway was negligible compared to the natural soil background. In Utah, Lytle et al. (1995) investigated manganese accumulation near roadways of varying traffic densities. They found elevated levels of manganese associated with high traffic density roads and a trend of decreasing manganese away from the road.

MMT is the anti-knock fuel additive which completely replaced tetra-ethyl lead (TEL) in gasoline in the 1990's. There has been a trend by gasoline refiners in Canada to voluntarily suspend the addition of MMT to fuel (Sierra Club of Canada, 2004; Blumberg and Walsh, 2004). Combustion products of MMT-fuel include manganese-phosphate, -sulfate, and -oxides, especially Mn_3O_4 , particles (Zayed et al., 1999a; Ressler et al., 2000; Molders et al., 2001; Zayed, 2001). The majority of these particles have a mass median aerodynamic diameter of $< 5 \mu\text{m}$ and are therefore respirable (Lynam et al., 1999; Thibault et al., 2002). It was speculated that use of MMT in gasoline could potentially lead to increased levels of manganese in the environment near high traffic density areas (Sierra et al., 1998; Adriano, 2001). Since these predictions, several studies have shown that roadside air, soils, plants and animals are contaminated by elevated Mn concentrations (Thibault et al., 2002; Zayed et al., 1999b). Contrary to these authors, Cooper (1984) and Lynam et al. (1999) predicted that small increases in airborne manganese due to MMT-gas combustion would not have any adverse impacts on health. Ambient monitoring data for manganese in Canadian cities, without industrial sources for the period of 1989-1992 did not reflect the peak usage of MMT: fine particulate matter ($\text{PM}_{2.5}$) air manganese levels remained constant at 11-13 ng/m^3 for small cities and 20-25 ng/m^3 for large cities (Health Canada, 1994; Egyed and Wood, 1996). Whether these elevated manganese levels are due to MMT-added fuel combustion or rather due to other sources is unknown. Bankovitch et al. (2003) noted that the contribution of MMT to the overall manganese levels in the environment is complex and difficult to establish, since it may be masked by more substantial variation associated with other activities including industrial, road dust and/or windblown dust.

Industrial

As previously mentioned, the major use of the world's manganese is in the production of steel and alloys. Production of manganese-containing alloys produces, among other compounds, considerable amounts of raw material and condensed manganese droplets (Schafer, 2004). Emissions from steel production were found to be the predominant source of manganese in urban particulate matter in Illinois by Sweet et al. (1993). Manganese can also be released to the atmosphere through use of manganese-containing products such as welding or fungicide application (World Health Organization, 2004).

Several studies have reported urban air manganese levels in Canada. For example, Stokes et al. (1988) reported an annual geometric mean concentration of air manganese from < 10 to 30 ng/m^3 in the Vancouver (B.C.) area in 1984. Over the period 1981-1992, Loranger and Zayed (1994) found average manganese concentrations in Montreal (QC) of 20 and 60 ng/m^3 in areas of low and high traffic density, respectively. More recently, Loranger and Zayed (1997) found the average concentration of total manganese in an urban site in Montreal to be 27 ng/m^3 . Manganese concentrations in air tend to be highest in proximity to industrial sources (Stokes et al., 1988). The WHO (1981) reported annual average content of ambient air manganese near manganese foundries of 0.2 to $0.3 \text{ } \mu\text{g/m}^3$ and over $0.5 \text{ } \mu\text{g/m}^3$ near ferro- and silico-manganese industries. Stokes et al. (1988) reported average air manganese concentrations in urban areas of approximately 65 to 166 ng/m^3 . Egyed and Wood (1996) reported that mean ambient concentrations of PM_{10} manganese increased with the size of the urban centre (i.e., small: St. John (NL) and large: Vancouver (B.C.)). They stated the highest concentrations (up to $0.2 \text{ } \mu\text{g/m}^3$) were found in urban centres like Hamilton and Sault Ste. Marie which have high concentration of ferro-manganese industries. Therefore, based on the literature, industrial and large urban areas appear to have higher air manganese concentrations than smaller urban areas.

Lynam et al. (1994) reported annual geometric mean air manganese concentrations from the annual Ontario Ministry of the Environment air quality reports for Windsor (ON) of 0.064 (1987), 0.057 (1988), 0.048 (1989) and 0.071 (1990) $\mu\text{g/m}^3$. Henderson (1995)

reported airborne PM manganese concentrations of 42 to 52 ng/m³ (depending on height of sampler) at a site located on the University of Windsor campus, and of 19 to 26 ng/m³ at two other sites in Windsor, Ontario. Unpublished Health Canada results (Rasmussen, 2010 pers. comm.) indicated that the mean and standard deviation manganese concentrations for outdoor (ambient) PM₁₀ were 13 ± 11 (n = 1002) ng/m³ in the city of Windsor in 2005-2006. Fewer than 1 % of the ambient PM₁₀ values exceeded the proposed 50 ng/m³ threshold. With respect to bulk concentrations of airborne particulate matter (µg/g), in 2007, Rasmussen et al. reported a median outdoor manganese concentration of 182 µg/g (n = 8) in a pilot study of Windsor air particulate matter (PM_{2.5}). Available air concentration (ng/m³) results for Windsor, Ontario would indicate that manganese is present at levels similar to other large Canadian urban centres. The level of manganese in airborne particles (µg/g) which can potentially deposit onto the soil surface in Windsor would require further investigation.

Natural

When evaluating the risk of pollutant sources to the environment, it is necessary to include an investigation of the contribution of the natural sources (World Health Organization, 2004). According to Stokes et al. (1988), two-thirds of manganese emissions to the atmosphere were from natural sources. Crustal sources are a major source of manganese found in the atmosphere as well as ocean spray, forest fires, vegetation and volcanic activity (Stokes et al., 1988; Adriano, 2001; World Health Organization, 2004). Manganese in atmospheric particulate matter collected in the Antarctic was likely associated with crustal material (Zoller et al., 1974). Snow cores (dated from 1967 to 1989) collected in central Greenland had manganese concentrations ranging from 0.016 to 0.236 µg/kg, a large portion of which was found to originate from road and soil dust (Veysseyre et al., 1998).

In summary, potential sources of manganese to urban soil, via the atmosphere, include vehicular emissions (wear-and-tear of vehicle components and past combustion of MMT-added fuel), industrial emissions (local and long-range), and finally natural sources of manganese.

Exposure and toxicity

Manganese is an essential micronutrient for plants and animals (World Health Organization, 1981, 2004; Abbott, 1987; Adriano, 2001; Schafer, 2004). Manganese is a cofactor for several enzymes (hydrolases, kinases, decarboxylases, transferases and metalloenzymes (i.e., arginase, pyruvate carboxylase, superoxide dismutase) (Adriano, 2001). According to Aschner and Aschner (2005 in Health Canada (2008)), manganese is also necessary for normal amino acid, lipid, protein and carbohydrate metabolism. Deficiencies of manganese in humans are uncommon if a normal diet is consumed (World Health Organization, 1981; Adriano, 2001). The majority of manganese necessary for good human health is obtained from food (World Health Organization, 1981; Adriano, 2001). The World Health Organization (1981) estimates the daily intake of an adult male to be between 2 and 9 mg. This value concurs with the recommendation by Adriano (2001) of a manganese intake of 8 mg per day. The intake of manganese via the atmosphere is very low, < 2 µg/day (area with no manganese emitting industries), and increases to 10 µg/day in areas of ferro- and silico-manganese industries (World Health Organization, 1981). The two major routes of exposure for humans are ingestion and inhalation. Adriano (2001) suggested the increased toxicity of manganese inhalation over ingestion may be due to the differences in the intake routes. Inhaled manganese, absorbed into the blood through the lungs, must first pass the brain, whereas ingested manganese is sent directly to the liver where it has a higher probability of being metabolized and eliminated (Frumkin and Solomon, 1997; Adriano, 2001; Health Canada, 2008). Absorption after ingestion is expected to be below 5 % for a healthy adult male while absorption following inhalation of manganese is unknown (World Health Organization, 1981). The average human body burden (male, 70 kg) is 10-20 mg (World Health Organization, 1981). Manganese is transported through the body in the plasma bound to albumin and/or transferrin (World Health Organization, 1981; Schafer, 2004). It can also cross the blood-brain barrier and the placenta. Manganese in blood will concentrate in mitochondria-rich areas like the liver, pancreas, kidney and intestines (World Health Organization, 1981; Schafer, 2004). The residence half-time of manganese in the human body is approximately 37 days. Its residence half-time in the brain is longer than the whole body (World Health Organization, 1981). Manganese is mainly excreted out of the body. Some of the inhaled manganese can be exhaled, deposited into the lung tissue or

absorbed into the blood (Abbott, 1987). Manganese toxicity in humans is usually the result of exposures to high levels of manganese via inhalation such as in occupational settings or in areas of manganese emitting industries (Adriano, 2001). It is known to be toxic to the human neurological, respiratory and reproductive systems (Adriano, 2001) depending on the compound. Its primary target organ is the central nervous system (Health Canada, 2008). Little is known about the toxicity of manganese to the human reproductive system, however studies on rats and mice have shown decreased genital size and fertility as well as an increase in maternal and fetal toxicity (Frumkin and Solomon, 1997). According to Frumkin and Solomon (1997), manganese is a pulmonary toxin which could aggravate existing airway diseases. Health Canada (2008) and Frumkin and Solomon (1997) reported that infants and children, older persons and persons with asymptomatic pre-parkinsonism, congenital liver disease as well as iron deficiencies were sensitive subpopulations.

Manganism is a neurological disease characterized by psychiatric and movement disorders (Adriano, 2001; Health Canada, 2008) which displays symptoms similar to Parkinson's Disease. The first documented occurrence of harmful manganese exposure to humans was in 1837 by Couper (Mergler et al., 1999). Frumkin and Solomon (1997) summarized the results of several occupational studies done using sensitive neurobehavioral tests on workers from manganese mines, refineries and manufacturing plants exposed to low levels of airborne manganese. In general, the various investigators found that the exposed workers had significantly decreased hand-eye coordination, hand tremors, decreased libidos, fatigue, moodiness, increased reaction time, loss of coordination, to name only a few of their symptoms. Mergler et al. (1999) conducted a community-based study in an area of Québec, the former location of a manganese alloy-production plant, in order to assess the nervous system functions of residents. Their findings showed "that higher levels of blood manganese were associated with poorer performance for coordinated upper limb movements. Recently, several studies have shown that children living in areas of elevated manganese had neurodevelopmental, intellectual and behavioural problems (Wright et al., 2006; Wasserman et al., 2006; Bouchard et al., 2007, Riojas-Rodriguez et al., 2010; Henn et al., 2010). "Manganese is a potential health hazard of both acute and chronic poisoning as a result of either environmental and/or occupational exposures" (Schafer, 2004). Consequently, the

greater toxicity potential of inhaled manganese means airborne particulate matter containing manganese is also of great importance and by extension, soil manganese.

2.0 Soils in the built environment

Urban soils, by definition, are different than non-urban soils. Craul (1985) best summarized the differences between urban and non-urban soils:

- 1) modified soil temperature regimes
- 2) presence of anthropogenic materials and other contaminants,
- 3) modified soil structure leading to compaction,
- 4) interrupted nutrient cycling and modified soil organism activity,
- 5) greater vertical and spatial variability,
- 6) modified soil reaction, usually elevated,
- 7) presence of a surface crust on bare soil, usually water-repellent, and
- 8) restricted aeration and water drainage.

The main difference in physical characteristics is the loss of soil structure and soil compaction of urban soil (Bullock and Gregory, 1991). The most commonly used definition is by Brockheim (1974) “a soil material having a non-agricultural, man-made surface layer more than 50 cm thick, that has been produced by mixing, filling, or by contamination of land surface in urban and suburban areas” (Craul, 1985). The natural soilscape has been modified by the construction of buildings, roads, utility networks and traffic (Craul, 1985; Kelly et al., 1996). The majority of soils in urban areas have been moved or disturbed at some point in time (Bullock and Gregory, 1991). Therefore, human activity and urbanization are the predominant factors acting on urban soils.

A broader range of materials make up the solid phase of urban soils. For example, in addition to minerals and organic matter, they can include construction debris, waste, industrial and traffic residue, and decomposition by-products of these materials (Bullock and Gregory, 1991; Kelly et al., 1996). These additional soil materials, which contain manganese, become mixed into the soil and affect its physical, chemical and biological properties (Kelly et al., 1996). This will consequently have an effect on soil solution and the

trace element content. The trace element concentration of urban soils depends on several factors including the original soil concentration, past and present site activities, and meteorological factors.

3.0 Field-portable X-ray fluorescence (FPXRF) analyzer

X-ray fluorescence spectrometry is one of the oldest and widely accepted methods of analysis, its beginnings going back to the early 1900's (Piorek, 1997; Schmehl et al., 1999; Kalnicky and Singhvi, 2001). The first-generation portable XRF analyzers were developed in the mid-seventies and by the nineties, they had evolved to fourth-generation (Piorek, 1997).

FPXRF analyzers are used as field screening tools whose main purpose is to guide on-site decision making and identify contaminated areas (Melquiades and Appoloni, 2004). Traditional sampling and analysis is time-consuming, expensive, labor-intensive (Schmehl et al., 1999), destructive and generates waste. Field-portable instruments, like the FPXRF, have a quick analysis time, require minimal operator training, are inexpensive (excluding the initial cost) and non-destructive, allow for a larger number of samples, are applied *in situ* for real-time analyses, and results are qualitative and quantitative, and are comparable to traditional analyses (i.e., ICP-MS) (Kuruvilla et al., 2004). Field-portable X-ray fluorescence analyzers are less sensitive (i.e., have higher detection limits) than laboratory methods, such as ICP or atomic absorption spectroscopy (AAS), and are subject to physical and chemical matrix effects (discussed below) (Kalnicky and Singhvi, 2001). Purchase and use of these field-portable instruments is subject to licensing in Canada. Piorek (1997) summarized FPXRF analyzers quite well: "There are not that many analytical techniques that can rival FPXRF in simplicity, speed of operation, and relaxed requirements of sample preparation".

Theory and principle of FPXRF analyzers

There are two categories of X-ray fluorescence spectrometers, wavelength-dispersive (WDXRF) and energy-dispersive (EDXRF) instrument. The latter provides the basis for the field-portable XRF analyzers. The WDXRF instruments use the wavelength of the

characteristic X-rays and crystal optics to identify analytes of the target sample whereas the EDXRF instruments use the energy of the X-rays emitted by the sample to make the identification (Piorek, 1997). Where WDXRF instruments provide better resolution, they however require stronger sources and specialized crystal optics (Palmer et al., 2009). The EDXRF instruments can use sealed sources and compact detectors making them ideal for use in field-portable technology.

An FPXRF analyzer has three essential components: source, detector and processor. FPXRF contain radioactive material, typically source material is Fe-55 (40 mCi), Cd-109 (20 mCi) and Am-241 (30 mCi) (Piorek, 1997; Kalnicky and Singhvi, 2001) as their source of X-rays. These sources, which contain a few grams of the radioisotope material, are sealed, rugged, compact, lightweight and drift-free (Piorek, 1997). There are three types of detectors used in FPXRF analyzers, gas-filled proportional, semi-conductors and scintillation detectors (Piorek, 1997; Kalnicky and Singhvi, 2001). These differ in their analyte sensitivity and resolution, which is the ability of the detector to separate X-rays of different energies. A detector with high resolution is important in order to minimize spectral intensity interferences and overlap (Kalnicky and Singhvi, 2001). Semiconductors have the best resolution and are usually used in FPXRF analyzers (Piorek, 1997; Kalnicky and Singhvi, 2001). An example of a semi-conductor FPXRF detector is the silicon positive intrinsic negative (Si-PIN) diode detector. The incoming X-rays interact with the atoms of the central silicon slab of the detector creating an electrical current which is then interpreted by the analyzer's processor (Thomsen and Schatzlein, 2002). Modern FPXRF analyzers are lightweight and small in size. They are battery powered and can be operated manually, via the instrument's trigger, or via a computer interface.

X-ray fluorescence spectrometry is an "emission spectroscopic technique" which uses the physical characteristics of the interaction between incident gamma rays (or X-rays) and the base electronic structure of atoms in a target analyte (Piorek, 1994; Palmer et al., 2009). Incident X-rays, generated by the radioisotope material sealed in the FPXRF analyzer, strike atoms in the surface of the sample thereby exciting the atoms. If the incident X-rays are of sufficient energy (i.e., high enough energy to remove an electron from the inner shell of an

atom), an electron from one of the atom's inner electron shells, usually K or L, is ejected. This creates a vacancy in the inner shell of the atom which needs to be filled. The atom relaxes to its ground state when this void is filled by an outer shell electron. This is accompanied by a release of energy. This energy is released in the form of an X-ray photon and is proportional to the difference in energy between the two atomic shells involved. The energy of the photon released is unique to the atom. This characteristic energy is detected by the FPXRF analyzer's detector and used to identify the element present in the sample. "The number of photons detected at a specific energy is proportional to the concentration of that element in the sample" (Palmer et al., 2009). The detector converts the characteristic energy into a voltage signal which is then interpreted by the processor as units of part per million (ppm) (Schmehl et al., 1999; Piorek, 1994, (1997); Kalnicky and Singhvi, 2001; Harper et al., 2004; Palmer et al., 2009).

Influential factors affecting FPXRF measurements

The following are factors which can potentially affect FPXRF analyzer results: sample moisture, count time, sample placement, sample thickness, film thickness and, physical and chemical matrix effect (Kalnicky and Singhvi, 2001). Sample moisture content refers to pore water rather than structural water molecules (Ge et al., 2005). Water will absorb X-rays more strongly than air in pores (Ge et al., 2005). Water can affect FPXRF analyzer results by either absorbing the characteristic X-rays emitted from atoms thereby decreasing the intensity of the X-rays (i.e., diluting the concentration) (Kalnicky and Singhvi, 2001; Ge et al., 2005) and/or can scatter incident X-rays. The amount of scattering increases with increasing water content (Ge et al., 2005). A high water content can lead to lower precision, poorer detection limits and lower accuracy and has a more significant influence on analytes with atomic numbers less than twenty-six (iron) (Kalnicky and Singhvi, 2001; Ge et al., 2005). If the moisture content of the sample is small (5 to 20 %), the overall error may be minor (Kalnicky and Singhvi, 2001). Samples have been dried in the field using microwave, air drying and using paper towels (Binstock et al., 2008; Markey et al., 2008). This sample preparation step can however have its drawbacks, for example the need for electricity and the loss of sample to wind or paper towels. Reames and Lance (2002) did not dry their soil samples before FPXRF analysis and found that FPXRF results

were strongly correlated to laboratory results. They concluded that drying of samples may not be necessary. It is quite possible that their samples had soil moisture contents below 20 % and therefore did not require drying. Kalnicky and Singhvi (2001) recommend drying the sample before analysis if the moisture content is greater than 20 %.

Count time refers to the length of time the sample is exposed to each radioactive source (Kalnicky and Singhvi, 2001) and is sometimes referred to as “Nominal seconds”. Count times can vary from 30 to 300 seconds depending on the quality of the data required. Longer count times allow the detector to collect more characteristic X-rays, including those from lower concentration elements. Longer count times also correspond to smaller detection limits (Kalnicky and Singhvi, 2001). *In situ* analyses typically use 30 to 60 second count times. Kilbride et al. (2006) investigated different count times and found smaller relative standard deviations and higher correlation coefficients (between FPXRF and traditional analysis) for copper, manganese and lead with increased count times. The authors recommended 120 seconds as an appropriate count time for these, and other elements presented in their study. A review of the literature (see below), which used FPXRF analyzers in the field, found that count times from 30 to 300 seconds had been used.

The position of the FPXRF analyzer is of importance to reliable results. The distance between the analyzer’s window and the sample should be minimize and remain constant during analysis. X-ray signal strength is inversely proportional to the distance from the radioactive source (Kalnicky and Singhvi, 2001). A good sample placement should maximize surface to surface contact with the analyzer window (Kalnicky and Singhvi, 2001) otherwise X-ray signal attenuation and consequently erroneous results could occur. X-ray penetration into a sample using a sealed source is approximately 2 mm in a soil matrix (Kalnicky and Singhvi, 2001). When doing FPXRF *in situ* analyses, sample thickness is not a concern. Kalnicky and Singhvi (2001) and NITON (2002) recommend a 5 mm sample thickness when using XRF-cups for FPXRF analysis. If XRF-cups or plastic sample bags are used for FPXRF analysis, the thickness and composition of the film between the sample and the analyzer window must be taken into consideration. The film can potentially affect the absorption of light element X-rays (i.e., potassium (3.3 KeV)) (Kalnicky and Singhvi,

2001; Weston, 1992). Reames and Lance (2002) evaluated FPXRF measurement of soil lead using a plastic sample baggie. They found that the baggie measurements were less accurate than the *in situ* and XRF-cup measurements and suggested that this was because of the baggie thickness. Mylar[®] film, which is commonly used in XRF-cup assembly, has negligible X-ray attenuation effects (Kalnicky and Singhvi, 2001; Weston, 1992).

The physical, as well as the chemical composition of the sample matrix can influence the FPXRF analyzer results. Physical matrix effect is due to variations in the physical character of the sample (i.e., particle size, uniformity, heterogeneity and surface condition) (Kalnicky and Singhvi, 2001). For example, analytes preferentially bound to smaller particles may not be represented accurately in the FPXRF result if the sample is mostly coarse-grained (i.e., the analyzer will “see” the coarse-grained particles). Grinding and sieving samples before FPXRF analysis should reduce the impact of this matrix effect thus presenting a homogeneous surface for analysis. Clark et al. (1999) concluded that soil samples should be sieved to less than 125 μm prior to FPXRF analysis. According to the U.S. Environmental Protection Agency (1998), sample heterogeneity has the largest impact on comparability with laboratory results. Vanhoof et al. (2004) also found that sample preparation prior to FPXRF analysis had a significant impact on the variance of both soil lead and zinc results. Shefsky (1997) also recommended mixing and homogenizing the soil before FPXRF analysis. However, Reames and Lance (2002) found no significant difference between soil samples which were ground and sieved and those which were only ground. It is possible that by grinding their soil samples, Reames and Lance effectively homogenized their soil samples effectively creating no significant difference between the two sample preparation techniques (grinding alone vs grinding and sieving).

The chemical matrix effect refers to the spectral interferences (or peak overlap) and, absorption and enhancement of characteristic X-rays. For example arsenic and lead peaks can overlap. If the detector’s resolution is low enough, this effect can be minimized. The second chemical matrix effect refers to the absorption and enhancement of characteristic X-rays by elements, and other characteristic X-rays, in the sample other than the target analyte. For example, iron can absorb copper X-rays, this effectively reduces the FPXRF copper

concentration of the sample. The intensity of lower energy characteristic X-rays (i.e., Cr) can be enhanced by the emission of higher energy characteristic X-rays (i.e., Fe) (U.S. Environmental Protection Agency, 1998). These matrix effects can be corrected mathematically using fundamental parameter (FP) coefficients (U.S. Environmental Protection Agency, 1998).

There are two main calibration methods for FPXRF analyzers, the empirical method and the fundamental parameters (FP) method. The former uses site-specific calibration standards and regression mathematics to generate a site-specific calibration (Kalnicky and Singhvi, 2001). Also, if the number of analytes increases, so does the number of site-specific calibration standards required for the empirical calibration method. The fundamental parameters calibration method however is not site-specific and uses X-ray theory to “mathematically pre-determine interelement matrix effects combined with pure element or known standard intensity responses to develop a quantitative algorithm for a specific sample type” (i.e., soil, water, dust) (Kalnicky and Singhvi, 2001). Therefore the FP calibration method is multi-site capable and all elements can be measured. FP calibrations are done by the manufacturer. Modern FPXRF analyzers usually feature the latter calibration method (Piorek, 1997). Factors which can affect the FPXRF calibration are detector resolution, matrix effect (depends on content of interfering elements and their impact on the measured X-ray intensity of the target element), and standards used (matrix must be similar to sample) (Kalnicky and Singhvi, 2001).

The factors which can potentially influence FPXRF analyzer results can be minimized. The influence of soil moisture on the XRF readings is difficult to minimize in the field. Some authors have suggested air drying the sample before FPXRF measurement. *In situ* sieving, or settling, of the samples can reduce the effect of particle size though Kalnicky and Singhvi (2001) have suggested that analyzing settled soil samples will introduce a bias for elements concentrated in those particles. Removal of debris and vegetation as well as creating a smooth, even surface should also minimize the influence of soil morphological and physical properties on the *in situ* FPXRF measurement. Pre-treatment of samples (sample preparation) prior to FPXRF analysis may be necessary in

some cases to improve data quality (Vanhoof et al., 2004), however the degree of sample preparation depends on the condition of the samples (moisture content, heterogeneity, etc.) and the amount of time and resources available to the investigator.

FPXRF analysis results have usually been confirmed by traditional analytical methods such as inductively coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectroscopy (AA). FPXRF analysis results have been found to be very well correlated to these types of laboratory analysis (Piorek, 1997; Shefsky, 1997; Reames and Lance, 2002; Vanhoof et al., 2004; Binstock et al., 2008; Markey et al., 2008; Hurkamp et al., 2009a, b). As well as a near-perfect correlation between the FPXRF and ICP-AES results for lead in soil, Binstock et al. (2008) also found no statistical differences between the method results. Bernick et al. (1995) also found no statistical difference between the *in situ* and laboratory method results, or between direct (*in situ*) and XRF-cup measurement of soil samples from hazardous waste sites. Markey et al. (2008) and Hurkamp et al. (2009b) reported that the *in situ* method was consistently lower than the laboratory method. Hurkamp et al. (2009b) attributed this difference to the presence of elevated soil moisture content in their samples (5 to 44 %). Potential differences between the *in situ* and laboratory methods include the difference between total digestion and the matrix struck by X-rays. Some acid digestions “do not constitute complete digestion”, for example silicates are not completely digested, whereas FPXRF measurements are derived from the entire matrix which therefore represents a total analysis (Kilbride et al., 2006). On the other hand, as previously discussed, *in situ* FPXRF analysis can be biased by the particles at the surface whereas the sample used in laboratory analysis is homogenized and represents usually 0 to 5 cm of the sample surface versus the 5 mm “seen” by the FPXRF.

In situ use

FPXRF analyzers have commonly been used in environmental and occupational exposure studies using several different types of media, for example, **soil** (Bernick et al., 1995a, b; Shefsky, 1997; Clark et al., 1999; Reames and Lance, 2002; Gasana and Chamorro, 2002; Vanhoof et al., 2004; Petrosyan et al., 2004; Clark et al., 2005; Puckett and Shaw, 2005; Dixon et al., 2006; Herman et al., 2006; Kilbride et al., 2006; Markey et al.,

2008; Binstock et al., 2008; Hurkamp et al., 2009a, b) and **sediment** (Bernick et al., 1995b; Stallard et al., 1995; Kirtay et al., 1998), **air filters** (Bernick and Campagna, 1995; Morley et al., 1999; Gasana and Chamorro, 2002; Drake et al., 2003; Harper et al., 2004, Harper et al., 2004, 2005, 2006; Harper and Pacolay, 2006; Kim et al., 2007), **paint** (Schmehl et al., 1999; Gasana and Chamorro, 2002; Choe et al., 2002) and **pigments** (Clark et al., 2005; Herman et al., 2006; Roldan et al., 2010), **dust wipes** (Dost, 1996; Sterling et al., 2000; Harper et al., 2002; Gasana and Chamorro, 2002; Kuruvilla et al., 2004; Petrosyan et al., 2004; Clark et al., 2005; Herman et al., 2006) as well as **steel** (or alloys), **water** (Gasana and Chamorro, 2002), and/or any **solid surface** (Dost, 1996; Williams-Thorpe et al., 1999; Kuruvilla et al., 2004) including food (Palmer et al., 2009). Melquiades and Appoloni (2004) provided a summary of additional studies which used FPXRF analyzers for analysis of various environmental samples.

The majority of studies using FPXRF analyzers to investigate elemental concentrations in soil have focused on lead in soil (Shefsky, 1997; Clark et al., 1999; Reames and Lance, 2002; Clark et al., 2005; Puckett and Shaw, 2005; Dixon et al., 2006; Herman et al., 2006; Binstock et al., 2008; Markey et al., 2008; Hurkamp et al., 2009a, b). Clark et al. (1999) also measure other elements such as copper, zinc and arsenic using an FPXRF whereas Vanhoof et al. (2004) measured lead and zinc only. Bernick et al. (1995b) measured lead and several other elements, excluding manganese. In a comparison study of FPXRF and ICP-OES analysis methods, Kilbride et al. (2006) found good correlation between the *in situ* and laboratory methods for lead and other elements including manganese. Petrosyan et al. (2004) analyzed lead and manganese using and FPXRF analyzer in Armenian soil however only lead was discussed. To date, no studies were found which focused solely on field-portable X-ray fluorescence measurement of soil manganese in non-mining area urban settings.

Overall, the majority of authors reported that use of FPXRF analyzers for *in situ* environmental analysis was acceptable (Bernick et al., 1995b; Shefsky, 1997; U.S. Environmental Protection Agency, 1998; Clark et al., 1999; Kalnicky and Singhvi, 2001; Vanhoof et al., 2004; Kilbride et al., 2006; Binstock et al., 2008; Markey et al., 2008;

Hurkamp et al., 2009b). Further support for use of FPXRF analyzers in the field comes from Petrosyan et al. (2004), Clark et al. (2005), Puckett and Shaw (2005), Herman et al. (2006), Dixon et al. (2006), and Hurkamp et al. (2009a) who used FPXRF as their primary analytical tool. Clark et al. (1999) recommended that the usefulness of FPXRF analysis of other elements (besides lead) should be explored. Currently, no studies have reported using FPXRF for analysis of soils in Canada.

4.0 Low-technology biomonitoring of atmospheric trace elements

Indigenous mosses have been used in Canada to evaluate atmospheric pollution by trace elements (Barclay-Estrup and Rinne, 1979; Rinne and Barclay-Estrup, 1980; Arafat and Glooschenko, 1982; Beckett et al., 1982; Boileau et al., 1982; Nieboer et al., 1982; Percy, 1983; Glooschenko and Arafat, 1988; Pott and Turpin, 1998; Plouffe et al., 2004). Use of the moss bag biomonitoring technique in Canada has been limited to evaluating trace element deposition near mining areas (Archibold, 1985; Goodarzi et al., 2003). Archibold (1985) investigated the trace element content of wind-blown dust near uranium mine tailings located north of Lake Athabasca in Northern Saskatchewan while Goodarzi et al. (2003) investigated the spatial distribution and accumulation of trace elements in soil in the Trail area of British Columbia. Of these two Canadian studies, Archibold (1985) was alone in analyzing manganese in the exposed moss. Therefore, the moss bag biomonitoring technique has never been used in Canada in order to do a semi-quantitative investigation of manganese in urban atmospheric particles.

Little and Martin (1974), Goodman and Roberts (1971), as well as other authors, have shown that plants can be used as indicators of atmospheric trace element deposition. The practice of using organic material (organisms or plants) to monitor trace element pollution, i.e., biomonitoring, has been widely used for over forty years. In order to be effective, biomonitors must be present in abundance in the study area and they should either respond to changes in the environment due to pollutant(s) or accumulate and retain the pollutant during the exposure period (Martin and Coughtrey, 1982; Szczepaniak and Biziuk, 2003). Several types of biomonitors have been used in the past, for example **grass** (Goodman and Roberts, 1971; Yule and Lloyd, 1984; Gailey and Lloyd, 1985), **lichen**

(Puckett et al., 1973; Gailey and Lloyd, 1983; Gailey et al., 1985; Bari et al., 2001; Zschau et al., 2003) and **moss** (Ruhling and Tyler, 1970, 1971; Little and Martin, 1974; Barclay-Estrup and Rinne, 1979; Percy, 1983; Thomas, 1986; Glooschenko and Arafat, 1988; Bargagli et al., 1995; Pott and Turpin, 1998; Fernandez and Carballeira, 2001; Adamo et al., 2003; Culicov et al., 2005; Giordano et al., 2005; Sun et al., 2009; and numerous others). However, mosses and lichens are the most frequently used biomonitors of atmospheric trace element pollution (Szczepaniak and Biziuk, 2003). When both are compared, mosses are typically the more effective biomonitors (Martin and Coughtrey, 1982; Adamo et al., 2006). Note from this point forward the discussion regarding biomonitoring refers to mosses only.

The moss biomonitoring technique has been applied from the small scale study (i.e., industrial area, town) (Swaine et al., 1983; Gailey and Lloyd, 1986d, 1993; Goodarzi et al., 2003; and several others (too many to enumerate here)) to country-wide surveys (Grodzinska, 1978; Steinnes et al., 1992; Herpin et al., 1996; Markert et al., 1996; de Caritat et al., 2001; Figueira et al., 2002; Lucaciu et al., 2004; Makhholm and Mladenoff, 2005). One way of using the moss monitoring technique is by using indigenous moss, where the plant is collected in the field and, digested and analyzed in the laboratory. The use of indigenous flora is dependent on several factors (i.e., availability, species, age, health, temperature, etc.) (Szczepaniak and Biziuk, 2003). The main disadvantage of using indigenous mosses is the uncertainty regarding their sampling period (Yule and Lloyd, 1984). In the event that the study area does not support any indigenous biomonitors and/or to avoid the above mentioned factors which can affect the accumulation of trace elements by indigenous biomonitors, transplants can be used. This alternative method of moss biomonitoring is done through the use of moss transplants. Moss is harvested from an unpolluted area and transplanted in the study area for a specific amount of time, as a carpet, sown into the study area, or in moss bags.

The moss bag method of biomonitoring atmospheric trace element pollution was pioneered by Roberts (1972 in Little and Martin (1974), and Little and Martin (1974) and has since been extensively used (Little and Martin, 1974; Muskett, 1976; Crump and Barlow, 1980; Davies and White, 1981; Archibold and Crisp, 1983; Swaine et al., 1983; Archibold,

1985; Gailey and Lloyd, 1986a, b, c, d, 1993; Harrison and Chirgawi, 1989; Ainsworth et al., 1990; Wegener et al., 1992; Viskari et al., 1997; Lodenius, 1998; Vasconcelos and Tavares, 1998; Ceburnis and Valiulis, 1999; Fernandez and Carballeira, 2000; Fernandez et al., 2000; Tan et al., 2000; Adamo et al., 2003; Goodarzi et al., 2003; Fernandez et al., 2004; Kupiainen and Tervahattu, 2004; Vingiani et al., 2004; Culicov et al., 2005; Giordano et al., 2005; Makholm and Mladenoff, 2005; Adamo et al., 2006; Tretiach et al., 2006; Naszradi et al., 2007; Szczepaniak et al., 2007; Cao et al., 2009; Sun et al., 2009).

Advantages and disadvantages

The moss biomonitoring technique is an inexpensive and straight-forward method to use. Unlike the more conventional method of collecting airborne particulate matter using high-volume air samplers, the moss bag method does not require a power supply, is low maintenance, the risk of vandalism is low, and is not labor intensive. Unlike the indigenous biomonitoring, it has a well-defined exposure period. Because of these advantages, the moss bag method can be used in abundance in a study site and/or in areas where the conventional methods cannot be used (Martin and Coughtrey, 1982; Yule and Lloyd, 1984; Szczepaniak and Biziuk, 2003).

The major disadvantage of using moss bags to collect airborne particles is that sources of airborne particles act at the same time and there is no way of separating them (Ceburnis and Valiulis, 1999; Szczepaniak and Biziuk, 2003). The retention of airborne trace element by moss is dependent on windspeed, particle size, rainfall and emission rates therefore moss bag results can only be compared to air concentrations if information for these factors is known (Martin and Coughtrey, 1982; Dmuchowski, 2005). (A discussion of the comparison of moss collected airborne particles to air concentrations will be discussed below.)

Despite these disadvantages, the moss biomonitoring technique is a useful, inexpensive and convenient tool and is efficient in identifying areas and trends of elevated airborne trace elements (Goodman et al., 1974; Little and Martin, 1974; Martin and Coughtrey, 1982). The moss bag biomonitoring technique can be used in addition to, or

instead of, conventional high-volume air samplers and can be considered as an artificially simulated soil surface (Bargagli, 1998; Goodarzi et al., 2003). This method “has become firmly established as a valuable and widely utilized pollution monitoring technique” (Onianwa, 2001).

The moss bag biomonitoring technique

The moss bag technique consists of first collecting moss from an unpolluted area. The moss is then cleaned of debris and pre-treated (i.e., nitric acid wash). This pre-treatment removes both trapped particles and ions from exchange sites, but kills the moss which becomes fragile (Makholm and Mladenoff, 2005). However, moss accumulation of atmospheric trace elements can occur even after death. No differences in trace element accumulation have been found between living and dead moss (Martin and Coughtrey, 1982; Tyler, 1990; Ceburnis and Valiulis, 1999; Adamo et al., 2006). The cleaned moss is inserted into mesh bags of various sizes and shapes (discussed below), and these bags are exposed in the desired area of study for a defined exposure period. At the end of the exposure period, the moss is removed from the mesh bags, digested and analyzed. Analyses of moss-sequestered airborne particles include a variety of conventional methods (i.e., AAS, FAAS, INAA, XRF, ICP).

Sphagnum moss

Mosses have a great capacity to accumulate trace elements (Martin and Coughtrey, 1982), especially *Sphagnum* moss species. They are the most sensitive biomonitors of airborne trace elements (Martin and Coughtrey, 1982) and are most frequently used in moss bag biomonitoring (Bargagli, 1998). Numerous studies have used various *Sphagnum* moss species in the moss bag biomonitoring technique (Goodman et al., 1974; Little and Martin, 1974; Muskett, 1976; Crump and Barlow, 1980; Davies and White, 1981; Archibold and Crisp, 1983; Swaine et al., 1983; Gailey and Lloyd, 1986a, b, c, d, 1993; Harrison and Chirgawi, 1989; Ainsworth et al., 1990; Wegener et al., 1992; Lodenius, 1998; Vasconcelos and Tavares, 1998; Adamo et al., 2003; Kupiainen and Tervahattu, 2004; Vingiani et al., 2004; Culicov et al., 2005; Giordano et al., 2005; Makholm and Mladenoff, 2005; Tretiach et al., 2006; Szczepaniak et al., 2007). Of these studies, Goodman et al. (1974), Archibold and

Crisp (1983), Archibold (1985), Gailey and Lloyd (1986a, b, c, d, 1993), Vasconcelos and Tavares (1998), Adamo et al. (2003), Goodarzi et al. (2003), Kupiainen and Tervahattu (2004), Culicov et al. (2005), and Makhholm and Mladenoff (2005) measured manganese in atmospheric particles collected by the moss bag biomonitoring technique.

Physical characteristics

The efficiency of mosses to accumulate atmospheric particles stems from their physical characteristics and chemical composition. Moss retention of atmospheric particles is both a physical retention and ion exchange process (Swaine et al., 1983; Makhholm and Mladenoff, 2005). Figure 3a shows the branched morphology structure of mosses. Approximately two-thirds of the dry weight of *Sphagnum* moss is leaves. These leaves are one cell layer thick and are positioned in a spiral around the stem (Bargagli, 1998). Their physical structure therefore provides them with a very large surface area (Little and Martin, 1974; Bargagli, 1998). As well as having a branched morphology which provides them with a very large surface area (Bargagli, 1998), the surface of their leaves is composed of small holes and folds (Goodarzi et al., 2003) approximately 10 μm in diameter (Corcoran et al. (year unknown) in Swaine et al. (1983)) which help capture and retain the airborne particles (Figure 3c).

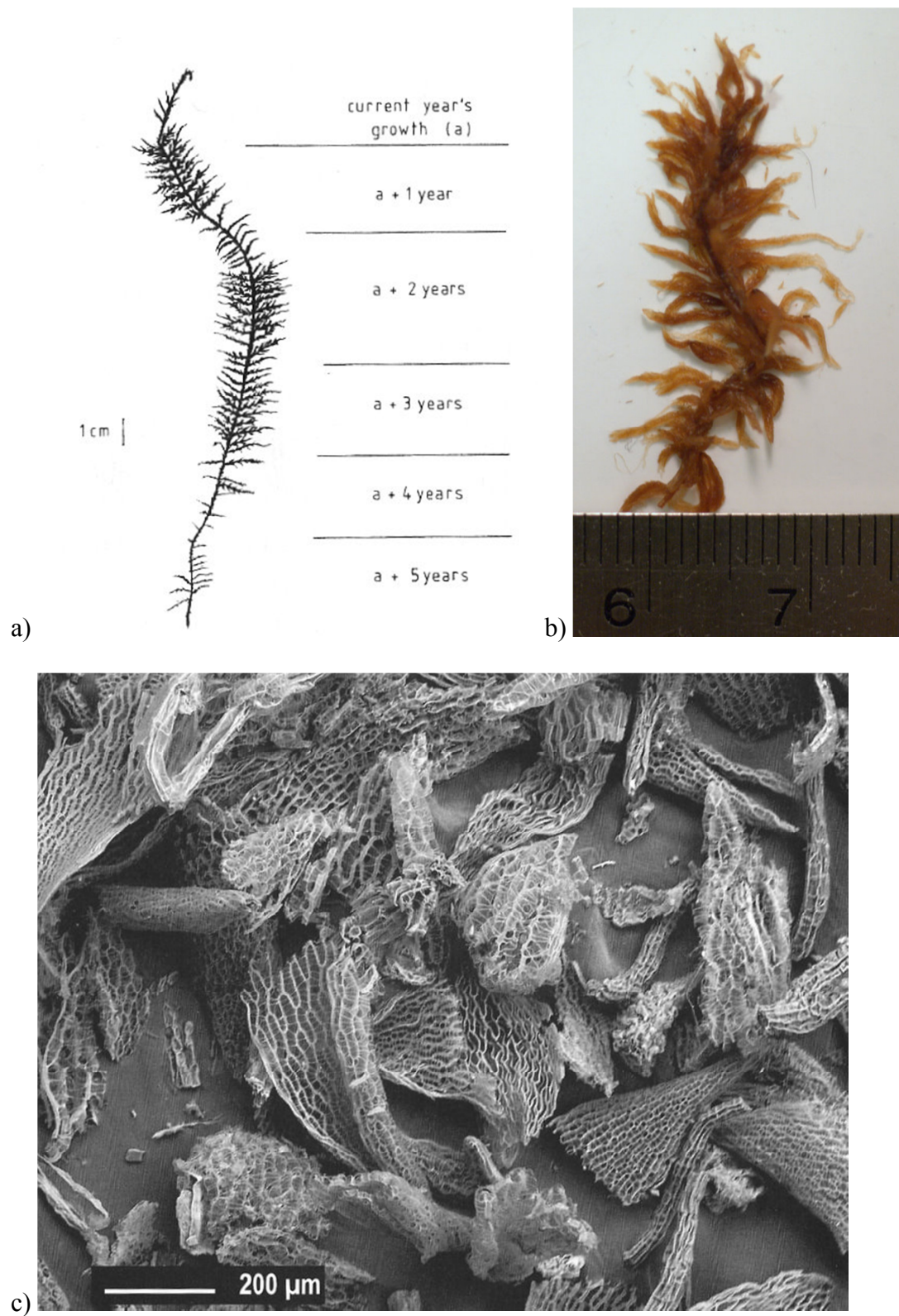


Figure 3 a) Schematic (Martin and Coughtrey, 1982), b) photo (by M.Nugent Ayres) and c) SEM (Goodarzi et al., 2003 (used with permission)) of *Sphagnum fuscum*.

Mosses have no root system nor do they have a cuticle or epidermis which allows trace elements to penetrate the cell wall (Szczepaniak and Biziuk, 2003). There is also a lack of vascular tissue therefore transport of nutrients between segments is limited (Szczepaniak and Biziuk, 2003). They depend on atmospheric deposition of nutrients and water for their survival (ectohydric nature) (Bargagli, 1998). The atmospheric elemental composition of gaseous, dissolved and/or particulate elements is reflected in their elemental composition (Bargagli, 1998). Moss can also retain large amounts of water. For example, *Sphagnum* moss can retain over 20 times its structural weight in water (Little and Martin, 1974; Martin and Coughtrey, 1982; Szczepaniak et al., 2007). Moisture content decreases as moss exposure increases, resulting in a more open moss structure and a more physically heterogeneous collecting surface (Gailey and Lloyd, 1986a). This water retention facilitates ion exchange between the soluble trace elements and the cell walls of the moss (Clymo, 1963). This physical structure aids in the capture and retention of atmospheric particles and water.

Chemical characteristics

The chemical composition of the moss cell walls also aids in the accumulation of atmospheric trace elements by enabling ion exchange and complex formation (Onianwa, 2001; Szczepaniak and Biziuk, 2003). The cell walls are composed of a variety of organic functional groups that are capable of chelate formation and ion exchange (Vasconcelos and Tavares, 1998; Onianwa, 2001). These ion exchange sites are protonated anionic functional groups in the form of uronic acids (Knight et al., 1961; Clymo, 1963; Vasconcelos and Tavares, 1998) which rapidly absorb cations in solution (Szczepaniak et al., 2007). These functional groups give moss a high cation exchange capacity. The trace metal ions are bound to the negative sites on the surface of the moss (Tyler, 1990; Bargagli, 1998). Tyler (1990) reported that trace elements are incorporated into the cell interior at a slow rate. According to Onianwa (2001), the location where the trace element ions are bound in the moss is dependent on the moss species, however the author also stated that there is no doubt that under field conditions, the strength of the trace element sorption to moss is strong enough to withstand desorption. *Sphagnum* moss has a greater proportion by weight of ion

exchange sites than any other type of plant (Clymo, 1963). Their large surface area, physical structure and high cation exchange capacity means that mosses, especially *Sphagnum* species, are highly efficient at accumulating airborne particles.

Retention

The sorption and retention of divalent (or polyvalent) ions on moss will be stronger than monovalent ions (Knight et al., 1961; Clymo, 1963). Ruhling and Tyler (1970) evaluated the sorption and retention of trace elements (including manganese) by indigenous mosses. They found the following decreasing order of trace element sorption: Cu, Pb > Ni > Co > Zn, Mn. This order was valid over a wide range of concentrations of pure and mixed ion solutions. Martin and Coughtrey (1982) stated that Ruhling and Tyler's (1970) sorption order has since been confirmed by other authors (references not stated). (See exposure period section for a discussion of trace element displacement). Vasconcelos and Tavares (1998) evaluated the uptake of trace elements by moss under field conditions and found the following order: Zn > Fe > Pb > Cu > Mn > Ni > Cr. At a second site, which had higher airborne trace element concentrations, Vasconcelos and Tavares (1998) found a slightly different order (Fe > Zn > Pb > Ni, Mn > Cu > Cr) however since this site did not have collocated air sampling results, as did the former site discussed here, they felt a comparative analysis could not be done. The authors suggested several possible factors which could be responsible for the differences between their trace element uptake order and Ruhling and Tyler's (1970) lab-based sorption order. These included 1) differences in the nature and concentrations of the trace elements already sorbed onto the moss (Both Ruhling and Tyler (1970) and, Vasconcelos and Tavares (1998) did not pre-clean their moss before exposure. Therefore the moss already contained a certain level of trace elements.) and 2) a combination of several other factors (i.e., competition of elements, atmospheric particle dimension). Further discussion of the factors affecting the trace element affinity of moss is outside the scope of this thesis. It is therefore possible that the moss sorption order may be different under field conditions when using acid-washed moss. At the present time, no such study could be found.

Influential factors affecting capture and retention of airborne particles

Adamo et al. (2006) stated that there was a lack of standardization (shape and size of bags, exposure time) and much is still poorly understood regarding the uptake and accumulation processes, and climatic and environmental effects. These factors (bag shape and size, exposure period and height) are important to consider since they will have an impact on the collection efficiency of the moss.

Shape

Moss bags can be any shape. The two most commonly used shapes are spherical and flat. Regardless of the shape, a moss bag is basically a mesh (~1 mm) with moss sown inside. The spherical moss bags are typically a square (i.e., 10 cm x 10 cm) mesh with the ends gathered and sown together. These provide a uniform exposure (particles can collect from every direction as opposed to flat bags) and have demonstrated higher and consistent trace element concentrations (Gailey and Lloyd, 1986a; Martin and Coughtrey, 1982). However Little and Martin (1974) found that spherical moss bags allow for gravitational sedimentation, impaction and filtration of the airborne particles to occur within the moss sphere. Flat moss bags are mesh envelopes (sometimes with pockets) with the moss secured inside (see Chapter 4 for a complete description of the flat moss bags used in this study). These moss bags allow the investigator to determine particle deposition rates. However they must also make a decision regarding the orientation of the bag during exposure which makes them strongly susceptible to directional environmental influences like wind and rainfall (Martin and Coughtrey, 1982; Swaine et al., 1983). Swaine et al., (1983) while assessing the accumulation of trace elements near a power station in New South Wales, Australia, investigated the use of vertical and horizontal moss bags. They found similar results between the two directions and suggested that this was because dry deposition (120 mm of rain) was the main contributor of trace elements during their study period. Gailey and Lloyd (1986c) also investigated vertically and horizontally positioned moss bags. They noted a slight difference in reproducibility between the vertical and horizontal moss bags and concluded it was probably due to the difficulty of maintaining the horizontal position of the frame. A great majority of studies have used spherical moss bags but only a handful have

used flat moss bags (Archibold and Crisp, 1983; Swaine et al., 1983; Goodarzi et al., 2003; Cao et al., 2009).

Size

As Adamo et al. (2006) stated there is no standard moss bag size. Gailey and Lloyd (1986a) investigated the effect of sampler size of low technology monitoring. They investigated moss weights between 0.1 to 2.5 grams used in spherical moss bags exposed in Armadale, Scotland. All sampler sizes collected measurable amounts of trace elements (Fe, Mn, Zn, Pb, Cu and Cr). In general they found an inversely proportional relationship up to 1 gram of moss, i.e., as the size increased, the trace element content decreased. Coefficients of variation increased with the size of the spherical moss bags. The authors concluded that a dry weight of 0.1 to 0.2 g of moss gave the “highest and most replicable concentrations for most metals” collected with a spherical moss bag. Ultimately the size of the moss bag depends on the study design (some studies retrieve moss samples from the bag at regular intervals during the exposure period) and on the material available.

Exposure time

The exposure period is determined by the investigator and depends on the purpose of the study as well as available resources. There are certain factors which need to be considered when choosing an exposure time for moss bag biomonitoring, ion displacement and moss saturation. As previously discussed mosses have a high exchange capacity, i.e., large amount of ion exchange sites. As discovered by Ruhling and Tyler (1970), and other authors, moss also has a trace element affinity order (see above discussion). If the exposure period is too long, the ion exchange sites become saturated which can cause preferential displacement or exchange of elements sorbed onto the moss which alters the final trace element composition of the moss (Bargagli, 1998; Onianwa, 2001; Szczepaniak and Biziuk, 2003; Makhholm and Mladenoff, 2005). If a trace element cation has a higher atmospheric concentration or if the moss has a greater affinity for it, this cation can replace previously bound cations on the exterior of the cell (Ruhling and Tyler, 1970; Little and Martin, 1974; Bargagli, 1998). For example, lead ions will replace zinc ions if there is saturation of ion exchange sites (Ruhling and Tyler, 1970; Little and Martin, 1974; Bargagli, 1998).

Similarly, if there is saturation of ion exchange sites, manganese and zinc ions can be replaced by copper or lead ions (Martin and Coughtrey, 1982).

Loss of trace elements can also occur through leaching when the amount of precipitation is excessive. Ceburnis and Valiulis (1999) found heavier precipitation reduced the trace element uptake efficiency, for example, manganese was leached from the moss with precipitation. However, the moss used was not treated before exposure (i.e., acid- or water-washed) therefore the ion exchange sites of the moss were partially occupied before being exposed. Martin and Coughtrey (1982) found that there was relatively little loss of water, i.e., leaching, from the moss bag even in heavy and/or prolonged rain. Due to its high capacity to retain water, the loss of trace elements from *Sphagnum* moss would be prevented, unless under extreme conditions (i.e., heaviest rainstorm) (Martin and Coughtrey, 1982). Therefore, ion displacement and moss saturation problems are not likely to be an issue for moss bag biomonitoring unless the soluble trace element content is excessively elevated, the exposure period too long or under extreme weather conditions (Martin and Coughtrey, 1982). Makholm and Mladenoff (2005) recommend using minimum required exposure periods to detect trends and/or by pre-treatment of the moss (i.e., nitric acid wash) to avoid ion displacement and moss saturation. If moss is pre-treated with acid, the fragile dead moss material can be lost if used for an extended exposure time (Makholm and Mladenoff, 2005).

The majority of surveys have used exposure times from a few weeks to several months. Goodman et al. (1974) investigated the use of moss bags as monitors of atmospheric deposition of trace elements and found moss bag retention of trace elements was directly proportional to exposure time, and linear, for up to 10 weeks. Makholm and Mladenoff (2005) used three sets of moss bags exposed for three different exposure times, 10, 20 and 23 weeks, respectively to monitor the efficiency of moss bags to detect trends on a regional scale. They found tissue and moss compaction after both of the longer exposure periods (20 and 23 weeks). They concluded that shorter exposure periods, 4 – 6 weeks, would be more appropriate to examine seasonal differences in airborne particles. Gailey and Lloyd (1986b) investigated the effect of exposure duration. They measured trace element (Fe, Mn, Zn, Pb, Cr, Ni, Cd, and Co) accumulation of low technology samplers (i.e.,

spherical moss bags) weekly for up to 10 weeks. Mean trace element values increased over time continuously for up to 5 weeks. After the initial 5 weeks, the increase was irregular (except for nickel). The rate of increase was not uniform. Most trace element contents decreased between weeks 9 and 10, except for manganese, lead and zinc. The coefficients of variation decreased as the exposure time increased. The authors concluded that an exposure of between 7 and 9 weeks would result in high and consistent concentrations for most of the trace elements (including manganese).

Exposure height

In studies of atmospheric deposition of trace elements, biomonitors (i.e., moss bags) should be clear of overhead obstructions such as trees, rooftops, lampposts and anything that could cause run-off or dripping. Ideally the moss bags should be installed at a height similar to the surface investigated, for example, low to the ground for soil or higher off the ground for human exposure. However, field conditions are never ideal. Martin and Coughtrey (1982) recommend using a standard reference height when comparing deposition to moss bags with deposition to the soil surface since wind velocity affects the efficiency of airborne particle capture by the moss bags, which in turn depends on the height above ground (velocity increases with height). Typically, biomonitors have been placed between 1.5 to 2.5 meters above the ground.

Particle size

Mosses collect particles similar in size to those that accumulate on vegetation (Martin and Coughtrey, 1982). Little is known of the particle size of moss-bound particles. Yule and Lloyd (1984) investigated the size and shape of atmospheric particles in Armadale, Scotland. Their study was not yet completed at the time the report was published, however they were able to determine that a wide variety of particle shapes (spherical, irregular and fibre-like) had been captured by the low-technology samplers. In the study of atmospheric deposition of trace elements near uranium mine tailings in Northern Saskatchewan, Archibold (1985) reported two particle sizes, in which one was 0.14 μm by 0.06 μm and the other had a diameter of 0.10 μm . The ability of moss bags to capture airborne particles depends on particle size and wind velocity (Clough, 1975; Martin and Coughtrey, 1982). The moisture

content of the moss may also be important to airborne particle capture. Martin and Coughtrey (1982) found that larger particles ($> 5\mu\text{m}$ in diameter) were retained more efficiently on wet moss bags while dry moss bags were more efficient collectors of sub-micron particles.

Reproducibility

Little and Martin (1974) evaluated the reproducibility of six moss bags located at a single site, they found a certain degree of variation for zinc, lead and cadmium which was considered to be within acceptable limits (not specified). Martin and Coughtrey (1982) found good agreement between replicate moss bags both in the field and in wind tunnel experiments. The reproducibility of trace element concentration of moss bags was investigated by Gailey and Lloyd (1986c). In general they determined moss bags had the highest degree of reproducibility compared to six other samplers, including indigenous and synthetic samplers. They also determined that an acceptable upper limit for the coefficient of variation for their study was between 30 and 35 % which has been used by other authors (i.e., Makholm and Mladenoff, 2005).

Comparison to high-volume air samplers

According to Little and Martin (1974), the moss bag biomonitoring technique was developed as an inexpensive alternative to the more sophisticated high-volume air samplers. Moss bag biomonitoring results cannot be used directly as a true measure of atmospheric particle deposition to the ground (Martin and Coughtrey, 1982; Archibold, 1985). These more sophisticated samplers measure quantitatively atmospheric deposition of trace elements but are costly, high-maintenance, require a power supply and are labor intensive. Comparison of the moss bag biomonitoring technique to these samplers has been done by several authors (below). No simple relationship between the airborne trace element concentration and deposition to moss bags exists (Goodman et al., 1974; Dmuchowski, 2005).

There are inherent differences between the two methods. Moss bags accumulate airborne particles that settle through wet (precipitation) and dry deposition whereas the high-

volume air samplers collect trace elements from the ambient air, including particles that settle as well as those that do not (Goodarzi et al., 2003). Airborne particles can be leached out of the atmosphere by precipitation, consequently reducing the ambient level of elements. The wet deposition of airborne particles can however be collected by the moss bags. Moss bags retain trace elements through physical and chemical processes while the air samplers retain them using a pump and filter system. Goodarzi et al. (2003) compared their moss bag biomonitoring results with the results of collocated high-volume air samplers. They found a good correlation between the two methods for lead and zinc. However, they also found evidence of a seasonal effect due to the nature of the methods' measurement (described above). Similar trace element profiles and significant correlations of trace element (including manganese) concentrations in moss bags and collocated air samplers were found by Vasconcelos and Tavares (1998)). Little and Martin (1974) also found strong correlations between the air samplers and the moss bag biomonitoring technique.

Approach and Hypotheses

Two types of sampling were used in this study's design: 1) transect sampling and 2) random sampling.

Soil transects were established in the immediate vicinity of the Ambassador Bridge to test the hypothesis that vehicular traffic was the dominant source of anthropogenic manganese to the soil in this area. Due to its long history of heavy traffic and numerous traffic delays at the customs gate located at its base, the Ambassador Bridge was selected to test this hypothesis because it represented the most extreme example of high traffic density in this area and it was therefore the most likely area where a traffic pollution halo would form. This approach to sampling is solidly based on many examples in the literature showing that emissions of metals from traffic causes a significant increase of metals in soil and road dust in the vicinity of roadways (e.g., Ward et al., 1977; Ho and Tai, 1988; Garcia and Millan, 1998; Legret and Pagotto, 2006; Preciado et al., 2007). These transects were made long enough to capture the potential radius of influence of the bridge traffic (~ 30 m from the road) and to extend beyond this to reach the background, or urban baseline soil manganese levels.

Random sampling of soil across Windsor was conducted to test the alternate hypothesis, that there are multiple anthropogenic sources of manganese to urban soil in the Windsor area. This soil sampling was used to determine the urban soil manganese baseline which included sites from 1) all of the National Pollutant Release Inventory's (NPRI) (Environment Canada, 2007) industrial manganese-emitting sources as well as 2) sites located in residential areas, including those studied by Wheeler et al. (2011). This random sampling served a number of purposes, one was to provide the context for assessing "elevated" vs "background" manganese concentrations found in the transect sampling. Another key purpose was to investigate spatial trends using GIS modelling and to determine whether other areas of elevated soil manganese existed. The areas where such hotspots were found were further investigated using follow-up soil sampling techniques.

Chapter 2 - Study Area

1.0 Geography

The city of Windsor (42°16.800' N, 83°57.600' W) (Figure 4) is located in Essex County in the southwestern most part of the province of Ontario. Windsor is located on the southern shore of Lake St. Clair and on the eastern shore of the Detroit River. The Windsor Census Metropolitan Area (CMA) includes the towns of Amherstburg, LaSalle, Lakeshore and Tecumseh. The city of Windsor lies 189.6 meters above sea level and covers approximately 147 km², while the Windsor CMA covers a total of 1022.84 km² (Statistics Canada, 2007 as reported by The City of Windsor (2009)). For the remainder of this thesis work, “city of Windsor” will refer to the 147 km² area and not the Windsor CMA area. The closest U.S. city is Detroit, Michigan.

Windsor lies within the Little River, Turkey Creek and Detroit River watersheds (The City of Windsor, 2009). Its location provides a Carolinian forest and prairie ecosystem that is unique in Canada (The City of Windsor, 2009). The majority of Essex County has little topographic relief (Richards et al., 1949; Morris, 1994) and the area lies within the St. Clair Clay Plain of the St. Lawrence Lowlands physiographic region which is “generally flat with a low gradient rising southward from Lake St. Clair” (Morris and Kelly, 1997).

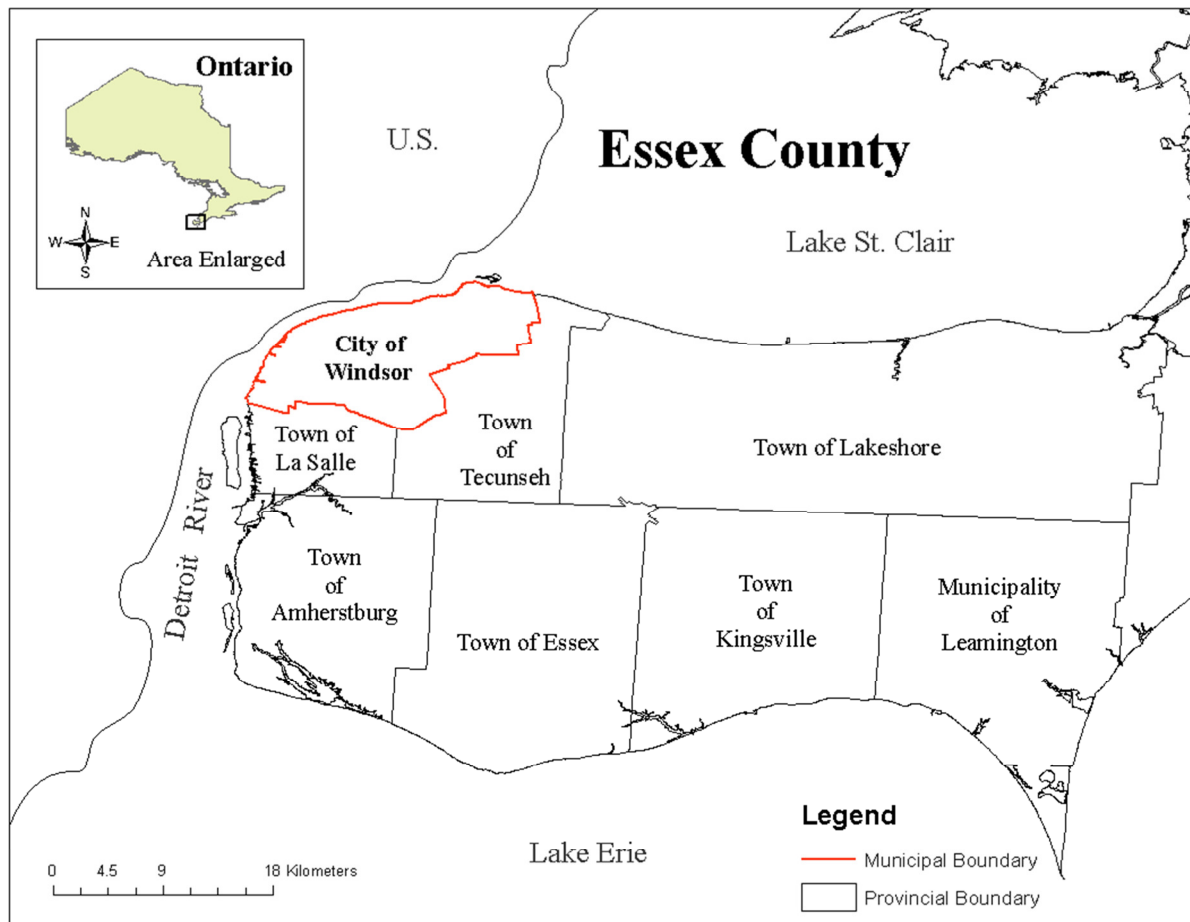


Figure 4 Map of Essex County and Windsor, Ontario.

2.0 History

The Windsor area was first settled in 1749 by French farmers. In 1854, it was established as a village (incorporated) and became a town in 1858. Windsor gained city status in 1892. The current municipal boundaries (Figure 4) of Windsor are the result of two amalgamations. The first took place in 1935 when the towns of Windsor, Sandwich, Walkerville, and Ford City were amalgamated. The second amalgamation in 1966 added the towns of Ojibway, Riverside, Sandwich West and parts of Sandwich East to the city.

Windsor's cityscape is as dynamic as any other Canadian metropolitan area. In the 1930's, the city's downtown was a very busy industrial area (Figure 5a). Railroads were operating on the waterfront and textile, automotive and other manufacturers were operating in what is present-day's downtown business core (Figure 5b) (personal communication with

Mr. B. McBride). Today, the waterfront is a recreational area with bike paths and sculpture parks and numerous businesses. Industrial and commercial parks are still located in proximity to the downtown area however they are currently being relocated to the south east of the city, in the Twin Oaks area (personal communication with Mr. B. McBride).



Figure 5 Aerial photo of downtown Windsor, Ontario a) circa 1931 and b) circa 2010. (Sources: a) National Air Photo Library; b) Google Earth™ mapping service, 2010)

3.0 Industry

Essex County is the most agriculturally productive area in Canada (County of Essex, 2009). Due to the mild climate and fertile soil, crops are numerous and include traditional grains, oilseeds, vegetables, fruits and grapes (County of Essex, 2009). Over sixty years ago, 87% of the surface of Essex County was farmed, but with urban development, that percentage has decreased. The main center of employment for the population of the Essex region is in the city of Windsor (The City of Windsor, 2009). Windsor's economy is primarily based on tourism and manufacturing. Twenty-eight percent of the labour force of Essex County is employed by manufacturers, the majority of which are located in Windsor (County of Essex, 2009).

The city boasts a beautiful waterfront and casino, and the surrounding area provides numerous wineries and natural hiking/walking trails. Windsor is known as the "Automotive Capital of Canada". In the early 1900's, Ford established a manufacturing plant and created "Ford City". The General Motors Corporation (GM) established plants in Windsor in the 1920's. As well as Ford and GM, Daimler Chrysler has also had plants operating in Windsor. Small tool and die, as well as smaller automotive parts manufacturers are also located in Windsor.

Other employers include, a Hiram Walker and Sons Limited distillery, H.J. Heinz Company, Windsor Salt mine, metal and plastic products, high-tech equipment, machinery and pharmaceuticals. The Windsor Port Authority (WPA), which operates in the northwestern corner of Windsor, has terminals that are used for cement, fuel, grain, general cargo, salt & fluorspar, and sand and stone shipments (Port of Windsor, 2009).

All industries located in Windsor, and throughout Canada, are required by law to report their pollutant releases to the environment to Environment Canada. Environment Canada in turn makes this information public through their National Pollutant Release Inventory (NPRI) which is available online. This database details industrial pollutant releases (to air, water and land), disposals and transfers of material for recycling in Canada. The NPRI is legislated under the *Canadian Environmental Protection Act, 1999*. When the

NPRI database was consulted (Environment Canada, 2007), the 2002 inventory was the latest data which had been reviewed. Table 6 lists the 2002 Windsor industries which reported releasing manganese and its compounds. The NPRI equivalent in the U.S. is the U.S. Environmental Protection Agency (USEPA)'s National Emissions Inventory (NEI). Figure 6 shows the location of all industries listed in Table 6 as well as the NEI industries from surrounding Michigan Counties, namely Monroe, Macomb, Wayne, Oakland and St. Clair.

Table 6 2002 Windsor industries that reported releasing manganese and its compounds.

Industry Name	Other Reported Elements	Years Mn was Reported
Aradco Management Ltd.	Cr and Hg	2001 - 2006
Aramco Management Ltd.	Cd, Cr, Pb, Hg, and Zn	2002 - 2006
Ford Motor Company – Windsor Casting Plant	As, Cd, Cr, Cu, Pb, and Zn	1994 - 2007
Ford Motor Company – Windsor Engine Plant	Cu, Pb and Ni	1995 - 2009
Ground Effects Ltd.	n/a	1997 - 2003
Nemak of Canada Corporation – Essex aluminum plant	As, Cd, Cr, Co, Cu, Pb, Ni, Ag, and Zn	1997 - 2009
Martinrea Fabco Metallic Inc. – Windsor Plant *	Cr and Pb	1994 - 2009
Titan Tool & Die Limited	Cr and Zn	2001 - 2009
Titan Tool & Die Limited – Devon Assembly Plant	Cr and Zn	2001 - 2009
Veltri Metal Products, Co. – Howard Ave Site	Zn	2002 -2009
Veltri Metal Products, Co. – North Talbot Division	Zn	2002
Zalev Brothers Co.	Cd, Cu, Pb, Ni, and Zn	1995 - 2009

* This industry was previously ThyssenKrupp PABCO Corp. – Windsor plant.
(Source: Environment Canada, 2007)

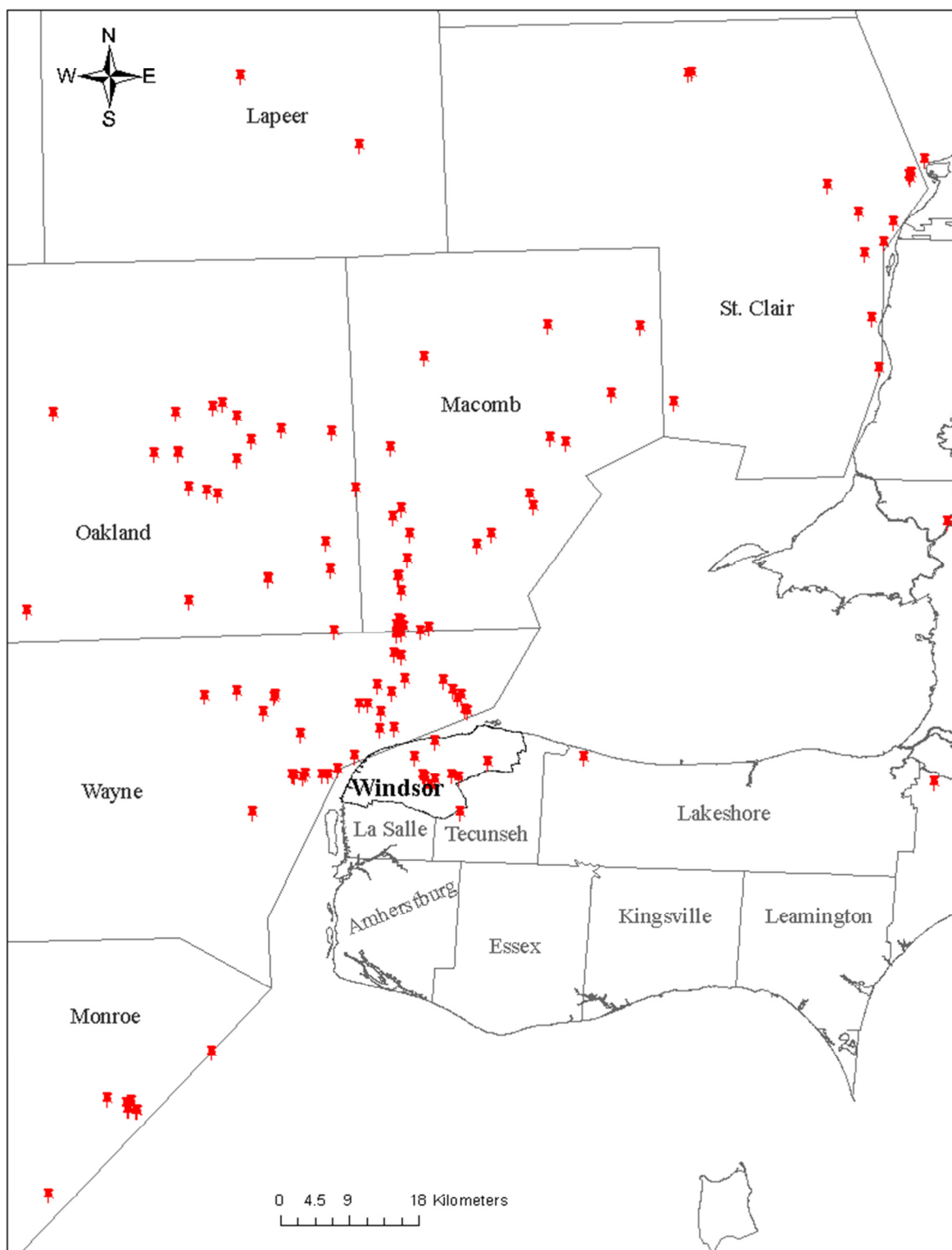


Figure 6 Location of National Pollutant Release Inventory (NPRI) and National Emissions Inventory (NEI) industries.

4.0 Climate

According to The Weather Network, Windsor is the “Smog capital of Canada” (The Weather Network, 2009). Climate Normals for Windsor summarized in Table 7, that show an average yearly temperature of 9.4°C and an average of 21.5°C for the summer months (June, July and August) (Environment Canada, 2003). The average yearly rainfall for the past 30 years was 805 mm. The most frequent wind direction, and the direction of the maximum gust (i.e., direction of the maximum reading during the day), according to the Climate Normals, was south with an average wind speed is 16 km/h.

Table 7 Selected meteorological parameters of Canadian Climate Normals from 1971 to 2000 for the city of Windsor. (Source: Environment Canada, 2003)

Meteorological Parameter:	May	June	July	August	September	Year
Daily average temperature (°C) (standard deviation)	14.9 (2.1)	20.1 (1.3)	22.7 (1.1)	21.6 (1.2)	17.4 (1.3)	9.4 (0.8)
Rainfall (mm)^a	80.7	89.8	81.8	79.7	96.2	805
Precipitation (mm)^b	80.8	89.8	81.8	79.7	96.2	918
Wind speed (km/h)^c	15.6	14.2	12.6	11.6	13	16
Most frequent wind direction^{d, h}	S	S	S	S	S	S
Maximum hourly speed	76	59	74	64	85	n/a
Maximum gustⁱ speed^{e, f, g}	107	124	145	109	113	n/a
Direction of maximum gust^{d, i}	SW	NW	S	SW	NW	S
Days with winds $\geq$ 52 km/h^e	1.1	0.9	0.7	0.3	0.4	14
Days with winds $\geq$ 63 km/h^e	0.5	0.3	0.4	0.2	0.1	4.7

^a amount of liquid precipitation such as rain, drizzle, freezing rain, and hail.

^b Precipitation is the water equivalent of all types of precipitation.

^c Observed at 10 m above ground.

^d The direction from which the wind (or gust) blows. (True or geographic, not magnetic)

^e (n = 29)

^f This value is only reported if the maximum gust speed exceeds 29 km/h.

^g The duration of a gust typically corresponds to an elapsed time of 3 to 5 seconds.

^h The direction with the highest average counts is assigned the most frequent wind direction for the month. Most frequent direction for the year is deduced as the direction with the highest average occurrence count for all months.

ⁱ The gust is the maximum reading during the day.

Note: The WMO considers thirty years long enough to eliminate year-to-year variations.

5.0 City profile - Census, Housing & Traffic

In 2006, the city of Windsor had a population of 216 473 (1.8% of the population in Ontario) and a population density of 1474 people per square km. The population density of the Windsor CMA was 316 people per square km (Statistics Canada, 2007 as reported by The City of Windsor (2009)). Forty-nine percent of its housing was built before 1960 (based on 2001 data) (The City of Windsor, 2009).

Major traffic corridors include major roads (listed in Appendix B), municipal highways, the E.C. Row Expressway, and the King's Highway 401 (a.k.a. Macdonald-Cartier Freeway), which begins in Windsor (Figure 6). The daily average traffic counts based on non-consecutive years between 1997 and 2008 (The City of Windsor Ontario, 2009) are shown in Figure 67. High traffic areas are located near major roads, highways and expressway. Windsor's link to Detroit is four-fold, and includes the Ambassador Bridge, the Detroit Windsor Tunnel, the Canadian Pacific Railway tunnel and the Detroit Windsor Truck Ferry, which operates out of the Port of Windsor. The Ambassador Bridge alone is the most important Canada-U.S. border crossing.

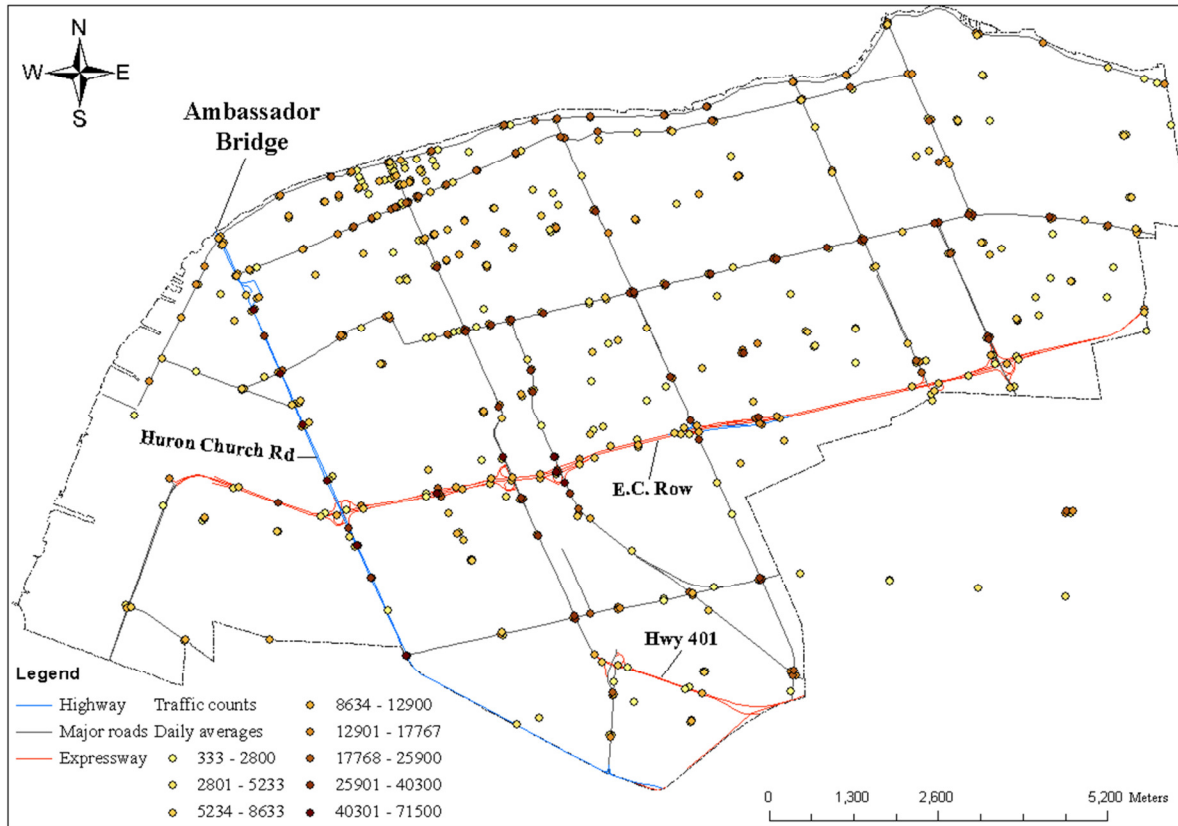


Figure 7 Map of Windsor showing the average daily traffic count of major roads, highways and expressway. (Data source: The City of Windsor Ontario, 2009)

6.0 Geology and Geochemistry

Note: The soils sampled during this study were urban soils. It is a safe assumption that they have been disturbed at least once in the past (see page 23). Therefore, they may not necessarily reflect the behaviour, speciation and concentrations of the soils and soil groups mentioned below which refer to undisturbed soils.

The majority of soils within the city of Windsor's municipal boundaries belong to the Brookston Clay unit (Figure 8). Several different units are dominant on the west side of the Ambassador Bridge and on the southern shore of Lake St. Clair opposite Peach Island (Table 8). These soil units are from two soil groups: the Grey-Brown Podsollic and the Dark Grey Gleisolic Great Soil Groups. Every effort was made to find areas where the clays could be sampled.

The Ontario Geological Survey Report (no. 5886) did not report any results for manganese in soil in Windsor or Essex County (Morris, 1994). While Weis and Barclay (1985) evaluated the distribution of trace elements in soils of Windsor and Essex County, only results for lead and cadmium were reported. Therefore, no other soil manganese data for the city of Windsor could be found in the literature.

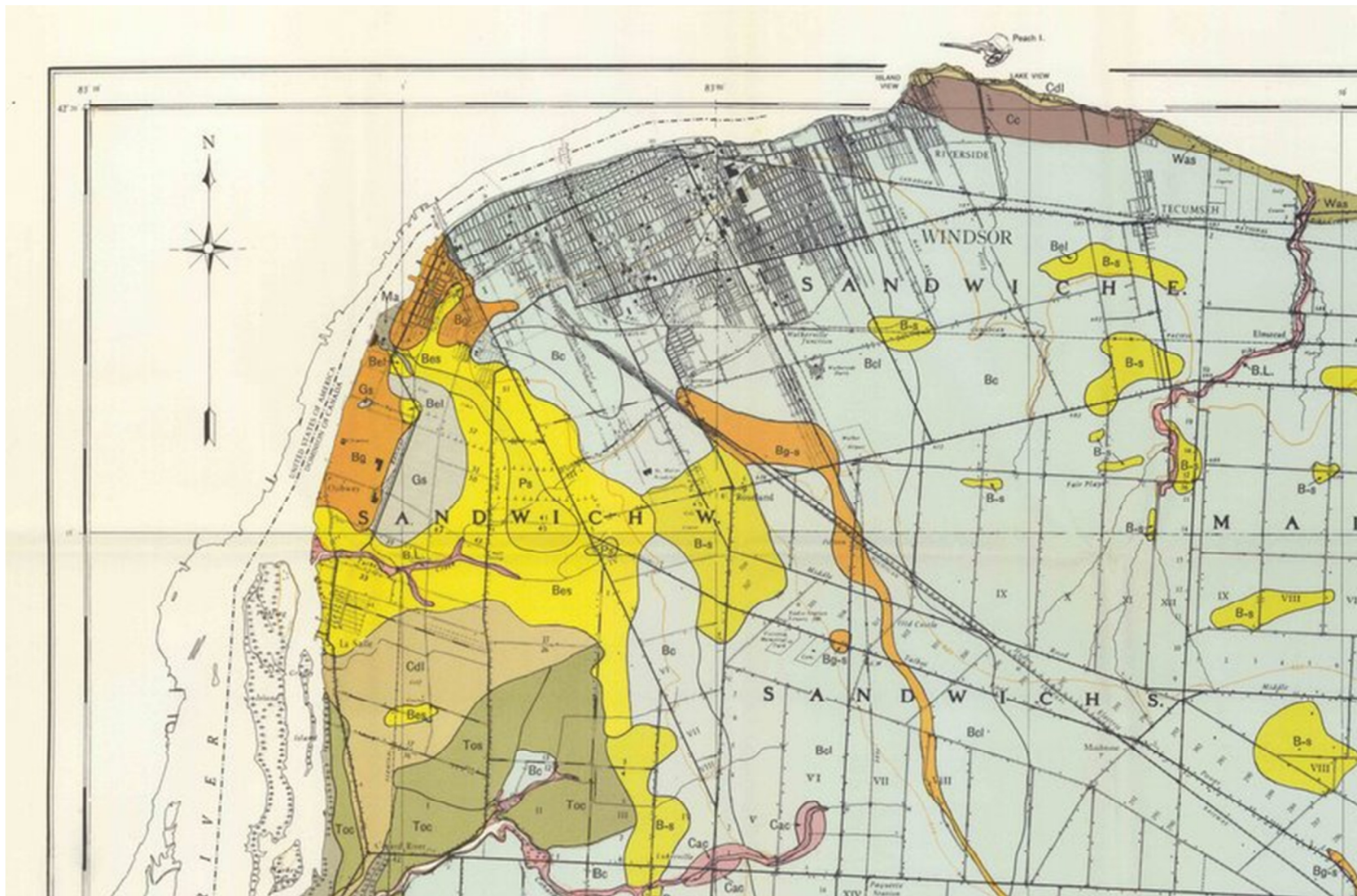


Figure 8 Portion of a surface and subsoil map which includes the city of Windsor and the surrounding area. (Source: Richards et al., 1949)

SYMBOL	CLAY SOILS						CLAY LOAMS			SILT LOAM	LOAMS								FINE SANDY LOAMS	
	Bc	Tec	Cc	Jc	Cac	Pc	Pcl	Cacl	Bcl	Tos	Bg	Bg-s	Hi	Pi	P-r	Tfs	Cdl			
NAME OF SOIL	BROOKSTON CLAY	TOLEDO CLAY	CLYDE CLAY	JEDDO CLAY	CAISTOR CLAY	PERTH CLAY	PERTH CLAY LOAM	CAISTOR CLAY LOAM	BROOKSTON CLAY LOAM	TOLEDO SILT LOAM	BURFORD LOAM	BURFORD LOAM SHALLOW PHASE	HARROW LOAM	FARMINGTON LOAM	PARKHILL LOAM	PARKHILL LOAM RED SAND SPOT PHASE	TUSCULA FINE SANDY LOAM	COLWOOD FINE SANDY LOAM		
ACREAGE	26,600	17,300	2,300	1,500	13,500	4,500	8,500	1,500	30,800	1,800	1,300	1,300	4,800	2,800	1,000	1,000	4,800	7,800		
DESCRIPTION OF SURFACE AND SUBSOIL	Dark clay over mottled clay then blue-grey compact gritty clay; few stones.	Black clay over mottled clay then heavy plastic stratified blue-grey clay; stoniness.	Deep black clay over mottled blue-grey clay; stoniness.	Dark grey clay over mottled clay then compact grey clay; few stones.	Grey-brown clay over grey clay then brown or mottled grey clay; then brownish gritty clay.	Dark grey-brown clay over grey clay then brown or mottled grey clay over stony clay loam.	Dark grey-brown clay loam over light brown clay then brown or mottled grey clay loam over compact grey clay; commonly gritty or stony.	Dark grey-brown clay loam over light brown clay then brown or mottled grey clay loam over compact grey clay; commonly gritty or stony.	Dark grey loam over mottled and blue-grey gritty clay and clay loam; few stones.	Black silt loam over mottled silt and clay, then heavy stratified silt and clay; stoniness.	Brown gravelly loam over reddish brown clay loam then grey stratified sand and gravel; many subhorizons.	Similar to Burford loam except gravel stony often mottled and shallow over clay or stony clay loam.	Brown loam and silt loam over dark brown loam to clay loam then brownish clay loam to more or less stony.	Shallow light brown stony loam over limestone bedrock.	Dark brown loam over mottled brown and grey loam, silt and clay loam; few to many stones.	Similar to Parkhill loam except for frequent reddish sandy loam and gravelly mottled silt and clay; mottled.	Dark grey to brownish sandy loam to heavy mottled yellowish stratified silt and clay; mottled.	Black and dark grey sandy loam over mottled and grey fine sand, silt and clay; few stones.		
TOPOGRAPHY AND DRAINAGE	Almost level with poor natural drainage.						Smooth to undulating in topography. Fair to poor natural drainage.				Almost level with poor natural drainage.		Undulating to rolling topography. Good natural drainage.		Smooth. Fair drainage.		Smooth to undulating topography. Drainage fair to poor.		Almost level. Poor drainage.	
REACTION	Slightly acid to slightly alkaline.			Moderately acid.			Slightly alkaline to slightly acid.		Moderately acid.		Slightly acid to slightly alkaline.		Slightly alkaline to slightly acid.		Moderately acid.		Alkaline.		Slightly alkaline to slightly acid.	
PRESENT LAND USE	General farming and dairying. Cash crops are corn, wheat, raising crops, (potatoes, corn, etc.) tobacco, sugar beets and apples. Woodlots are scarce and commonly pastured.						General farming and dairying. Wheat and corn main cash crops. Considerable area in pasture and woodlots.				General farming and dairying. A few orchards. Cash crops are corn, tobacco and raising crops.		General farming and dairying. Cash crops are corn, wheat, raising crops, (potatoes, corn, etc.) tobacco, sugar beets and apples. Woodlots are scarce and commonly pastured.		General farming and dairying. A few orchards. Cash crops are corn, tobacco, and raising crops.		Mostly in pasture and woods.		General farming and dairying. Truck crops are important in some areas; other cash crops are corn, tobacco and raising crops.	
MAIN FERTILITY NEEDS	PHOSPHATE			PHOSPHATE and LIME			ORGANIC MATTER, PHOSPHATE and LIME		ORGANIC MATTER, PHOSPHATE, LIME		PHOSPHATE		ORGANIC MATTER, PHOSPHATE and potash.		ORGANIC MATTER.		PHOSPHATE and potash.		PHOSPHATE and POTASH.	

NOTE:—These descriptions have reference to general soil conditions. On many farms the drainage has been artificially improved. Fertility needs may vary with individual farm management and the requirements of the crop to be grown.

SANDY LOAMS						SANDS				MISCELLANEOUS SOILS			
His	Fsl	Bel	C-s	B-s	Was	Gs	Bes	Ps	Es	B.L.	Ma	M	
HARROW SANDY LOAM	FOX SANDY LOAM	BERRIEN SANDY LOAM	CAISTOR SAND SPOT PHASE	BROOKSTON CLAY SAND SPOT PHASE	WAUSEON SANDY LOAM	GRANBY SAND	BERRIEN SAND	PLAINFIELD SAND	EASTPORT SAND	BOTTOM LAND	MARSH	MUCK	
3,500	5,300	16,000	1,500	18,000	3,000	1,000	8,000	1,700	2,500	7,300	7,000	1,700	
Light brown sandy loam and fine sandy loam over brown loam over greyish sandy loam and loam; locally very stony.	Light brown and yellow sandy loam (or sand) over reddish brown loam then stratified sand or gravel.	Brown sandy loam over yellow and then mottled sand with clay at about 3 to 6 feet; stone-free.	Mixed areas of shallow sand knolls over clay; inter-mixed with Caistor clay and clay loam.	Mixed areas of shallow sand knolls less than 3 feet over clay inter-mixed with Brookston clay and clay loam.	Dark grey sandy loam over grey or mottled sand with clay at depths of 3 feet or more.	Dark grey sandy loam over grey or mottled sand with clay at depths of 3 feet or more; stone-free.	Brown sand over yellow and then mottled sand with clay at about 3 to 6 feet; stone-free.	Light brown and yellow sand over grey sand; subject to drifting.	Loose greyish sand along the lake shore back of the beach; stone-free; very little humus.	Low lying land along stream courses; subject to occasional flooding; variable texture.	Low lying areas subject to flooding; covered with water most of the year.	Black, well decomposed herbaceous and woody material of varying depths over sand, clay or marl; stone-free.	
Undulating to rolling. Well drained.		Smooth to undulating. Fair to poor drainage.		Almost level. Poor natural drainage.			Undulating. Fair to poor.		Undulating to rolling. Good to excessive drainage.		Undulating. Drainage variable.	Very flat. Very poor natural drainage.	
Moderately acid.			Slightly acid to slightly alkaline.				Moderately acid where not eroded.			Variable.			
Early vegetables, melons, blue tobacco, peaches and other tree fruits.		General farming, dairying and canning crops. Locally used for tree and small fruits and tobacco.				Some general farm crops. Mostly woodlots and pasture.		Summer homes and recreation.		Chiefly wasteland, forest and pasture.		Truck crops and woodlots.	
ORGANIC MATTER, PHOSPHATE, POTASH and lime.					PHOSPHATE and potash.		ORGANIC MATTER, phosphate and potash.			Variable			Phosphate and potash.

Figure 8 (cont'd.) Legend for surface and subsoil map. (Source: Richards et al., 1949)

Table 8 Description of surface soil units within the city of Windsor and the study area. (Source: Richards et al., 1949)

Unit Name	Origin	Great Soil Group		A _c Horizon Description	Additional Note
		Grey-Brown Podsollic	Dark Grey Gleisolic		
Brookston clay (Bc) Brookston clay loam (Bcl) Brookston clay sand spot phase (B-s)	Soils formed from lacustro-moraine materials (depth varies from 0 to 2 - 3 ft)		X	6 - 8 inches of dark grey brown clay; almost stonefree; pH 6.8 - 7.0	Limestone parent material with some shale
Perth clay (PC) (Not shown on Figure 8)		X		6 inches of dark grey clay loam; some stones; pH 6.5	Limestone parent material with some shale; profile is of a cultivated soil
Clyde clay (CC)	Soils formed from lacustrine materials	Weisenboden Great Soil Group		10-12 inches of dark grey to black clay; stonefree; pH 7.0	Formed under grasses, reeds and sedges
Colwood fine sandy loam (Cdl)			X	6 inches dark grey, fine sandy loam; stonefree; pH 6.8	
Burford loam (Bg) Burford loam, shallow phase (Bg-s)	Soils formed from well sorted outwash materials (contain a large proportion of limestone materials with less amounts of dark brown shale)	X		6 inches of dark brown loam; medium organic matter content; pH 6.5; ("The Burford series is intensively cultivated.")	Gravelly materials; Profile is of a cultivated soil
Granby sand (Gs)			X	6 inches of very dark brown sandy loam; high in organic matter; pH 6.8	
Plainfield sand (Ps)		Arizona Group		3 - 4 inches of yellow grey sand; low in organic matter; stonefree; pH 6.0	Sandy materials
Harrow sandy loam (Hs) (Not shown on Figure 8)	Soils formed from poorly sorted outwash materials	X		3 - 6 inches of dark grey brown sandy loam; low in organic matter; occasional stones and large boulders; pH 6.2 to 6.5	
Berrien sandy loam (Bel) Berrien sand (Bes)	Soils formed from shallow sands over clay (sand bars 3 to 6 ft deep)	X		4 - 6 inches of grey brown sand or sandy loam; stonefree; pH 6.0 to 6.5	

Note: Mechanical analysis: sand → 1.0 - 0.05 mm in diameter; clay → < 0.002 mm in diameter.

Soil classes: clay soils → > 20 % clay [clay loam → 20-30 % clay + < 50 % silt; clay → > 30 % clay]; loam → < 20 % clay + < 50 % silt + < 50 % sand; sandy loam → < 20 % clay + 50-80 % sand; sand → > 80 % sand

The bedrock underlying the study area (city of Windsor) and the surrounding areas is composed of sedimentary and volcanic rocks from the Paleozoic and Devonian (416-359.2 million years B.P.) eras and consists of “sedimentary and volcanic rocks; shale, limestone, dolomite; conglomerate, sandstone; volcanic rocks; salt; oil and natural gas” (Natural Resources Canada, 1956).

A description of the quaternary geology of the study area can be found in the Ministry of Northern Development and Mines’ 1994 survey of Essex County (Morris, 1994). The development of the overburden can be summarized by the following events (Morris and Kelly, 1997):

- 1) Catfish Creek Till was deposited over the bedrock during the Nissouri Stadial (23 000 to 16 000 yr B.P.) as ice advanced South;
- 2) During the ice retreat (Erie Interstade) (estimated at 15 500 yr B.P. (Ehlers and Gibbard, 2004), fine-grained glaciolacustrine material was deposited over the Catfish Creek Till;
- 3) Tavistock Till was deposited over this fine-grained glaciolacustrine material as ice advanced south again during the Port Bruce Stadial (15 000 to 14 000 yr B.P.);
- 4) The area was covered by a fine-grained glaciolacustrine deposit;
- 5) These deposits were subsequently exposed to physical and chemical weathering.

As discussed in the proceeding chapter (Chapter 3), it was not possible to sample all of these lithologies for manganese.

The fine-grained glaciolacustrine deposits (event 4) were divided into 3 units: lower, upper and upper weathered glacio-lacustrine material (Table 9). This material formed much of the surface cover of Essex and Kent Counties’ (Morris and Kelly, 1997). The deposit is less than “1 meter thick in the east and thickens westward to over 6 meters” and is “composed of rhythmically laminated silt and clay” (Morris and Kelly, 1997).

According to Morris and Kelly (1997), there was some debate as to whether the surface material in Essex County was till or glaciolacustrine material. The official Ontario

Geological Survey (OGS) Open File Report (1994) states that the surface material had “distinctly different properties” from the till and that the structural properties of the surface material were more consistent with a glaciolacustrine deposit (Morris, 1994).

Table 9 Properties and geochemistry of the fine-grained glaciolacustrine materials. (Source: Morris and Kelly, 1997)

Properties		Fine-grained Glaciolacustrine Material		
		Upper-weathered (brown loam) (n = 48)	Upper (n = 28)	Lower (n = 8)
Grain size	% clay (< 0.002 mm)	37	37.2	35
	% silt (< 0.062 mm & > 0.002 mm)	37.3	40.9	52.6
	% sand (> 0.062 mm)	25.7	17.6	12.4
Carbonates ^a	% total	10.6	21	29.6
	ratio	0.8	0.9	1.5
Geochemistry ^b (ppm)	Co	13	10.9	11.2
	Cr	77	63.9	59.8
	Cu	30.8	28.3	26.5
	Ni	40.3	32.5	31.5
	Pb	19	12	11.8
	Zn	114	83.3	70.2
	Fe	2.5 ($\frac{1}{2}$ LOD)	2.5 ($\frac{1}{2}$ LOD)	2.5 ($\frac{1}{2}$ LOD)

^a Carbonate analysis was done on the 0.74 mm fraction using a Chittick apparatus.

^b Digestion using a total extraction (HNO_3 -HF) and analysis by atomic absorption analysis.

The pH of Essex County surface soils ranged from 6 to 7 (Richards et al., 1949). The drift over the county “contains a considerable amount of limestone as well as appreciable amounts of shale and some igneous rock material”. The county’s surface soil is described as “predominantly a smooth clay plain with scattered sandy and gravelly knolls and ridges” (Richards et al., 1949).

Chapter 3 - Study Design

1.0 Study Description

This study was carried out by two soil surveys. The first was a preliminary soil survey whose goal was to obtain preliminary data on the concentration and distribution of manganese in the city of Windsor. Real-time identification of elevated soil manganese areas was possible by using the *in situ* technique, FPXRF, which enabled further investigation of these areas during the preliminary survey. This survey also served as a reconnaissance survey to sample areas of high traffic and areas surrounding manganese-emitting industries.

The follow-up to the preliminary soil survey was the complete soil survey. The purpose of this comprehensive soil survey was to further investigate areas of elevated manganese identified during the preliminary survey, to gain a better idea of the sources of manganese particles in the surface soil and to ensure an even distribution of sampling sites in, and complete coverage of, the city of Windsor. Manganese levels of airborne particles collected during the complete soil survey using biomonitoring stations were determined in order to compare them to surface soil manganese levels and to aid in source apportionment. Natural (non-polluted) material was collected during this survey in order to determine background manganese levels.

Meteorological details of the sampling periods as well as a description of the different soil sample types are given below.

2.0 Sampling Periods

Soil sampling took place during the summers of 2007 and 2008. The preliminary soil samples were retrieved from the field between June 12th and 16th, 2007. Additional soil samples were retrieved between August 8th and 11th, 2007. Biomonitoring stations were installed and exposed in the city of Windsor and the surrounding area from June 23rd to August 27th, 2008, at which time collocated soil samples were collected.

Since soil particles can be transported, deposited and re-suspended via wind action, information about gust speed and direction are included in Table 10 and Table 11. Since both the field-portable X-ray fluorescence readings and the biomonitoring station technique can be affected by rain, other meteorological parameters for both summers are included in these tables. Other meteorological parameters for both summers are also presented.

Table 10 Daily averages for the city of Windsor during the summer of 2007 soil sampling from the Windsor A station.

Meteorological Parameter	June 2007						August 2007				
	12	13	14	15	16	Monthly average (n = 30)	8	9	10	11	Monthly average (n = 31)
Mean temperature (°C)	23.1	25.6	24.4	22.5	22.7	22.1	27.7	23.2	24.3	23.4	23.3
Total rain (mm)	0	0	0	0	0	65.2	3.0	10.0	trace	0	159
Direction of maximum gust^a	40 ^c	30 ^c	n/a	n/a	n/a	310 ^{c,d}	n/a	n/a	n/a	n/a	340 ^{c,d}
Speed of maximum gust (km/h)^b	33 ^c	37 ^c	<31	<31	<31	65 ^{c,d}	<31	<31	<31	<31	61 ^{c,d}

^a The direction from which the wind blows. (True or geographic, not magnetic). This value is only reported if the maximum gust speed exceeds 29 km/h.

^b This value is only reported if the maximum gust speed exceeds 29 km/h.

^c Estimated

^d Extreme

(Source: Environment Canada, 2003)

Table 11 Monthly averages for the city of Windsor during the biomonitoring station exposure period (summer of 2008) from the Windsor A station.

Meteorological Parameter	June 2008	July 2008	August 2008	Summer average
Mean temperature (°C)	22.0	29.2	27.8	26.3
Total rain (mm)	44.4	83.0	5.2	133
Direction of maximum gust^{a, g}	290 ^{c,d,e} (W)	350 ^{c,d} (N)	330 ^{c,d} (NW)	335 ^{c,d} (NW)
Speed of maximum gust (km/h)^b	78 ^{c,d}	61 ^{c,d}	52 ^{c,d}	64 ^f
Range for direction of maximum gust (degrees)	10 - 290	200 - 350	10 - 340	10 - 350

^a The direction from which the wind blows. (True or geographic, not magnetic). This value is only reported if the maximum gust speed exceeds 29 km/h.

^b This value is only reported if the maximum gust speed exceeds 29 km/h.

^c Estimated

^d Represents the extreme for the month or year.

^e An error was found in the extreme direction of maximum gust value for June 2008 of the Environment Canada statistics. The value reported in this table is correct and was verified by the daily data report for June 2008.

^f More than one occurrence and estimated.

^g The gust is the maximum reading during the day.

Note: Biomonitoring station MB-19 and associated samples were closer to the Environment Canada Harrow CDA weather station which had an average rainfall of 148 mm and average direction of maximum gust of 240 (SW).

(Source: Environment Canada, 2003)

3.0 Sampling Scheme

Additional information and descriptions of sampling schemes and sample locations can be found in Chapters 5 to 8.

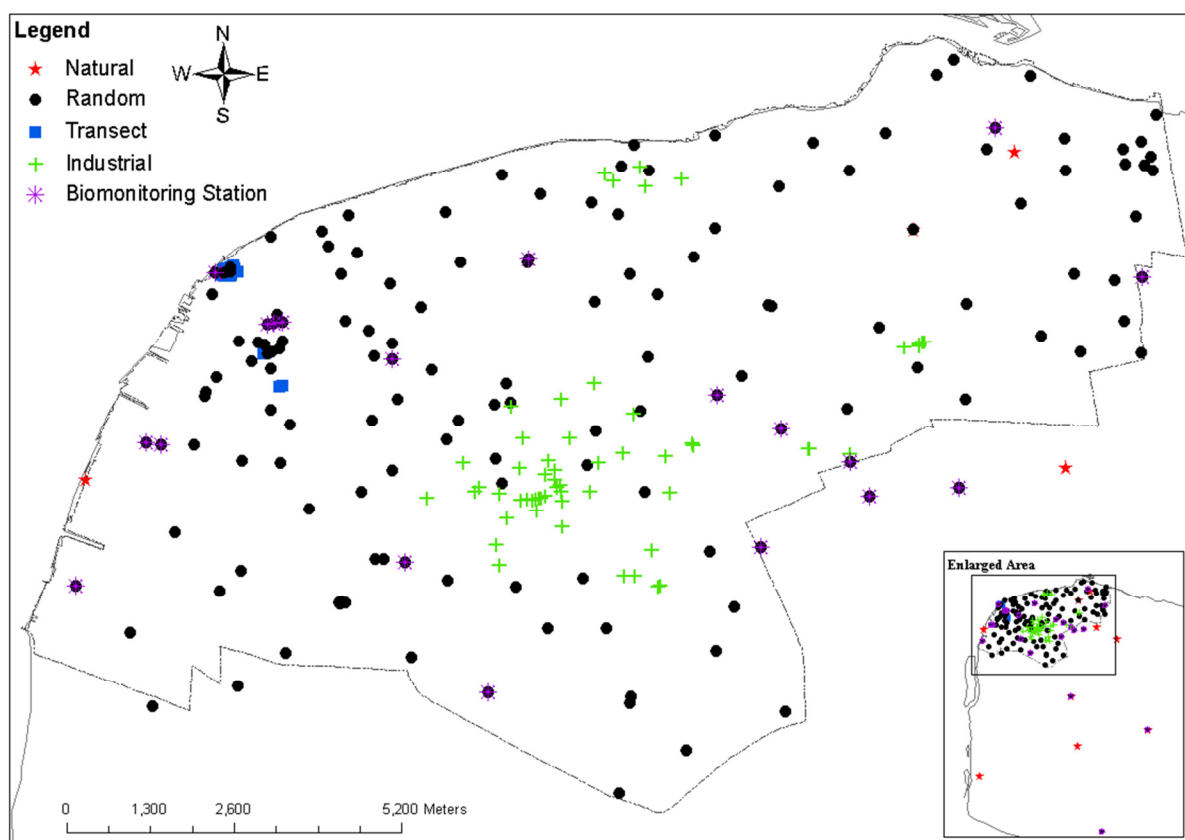


Figure 9 Location of transect, industrial, random, and natural soil samples, and biomonitoring stations within the city of Windsor.

3.1 Transects (2007)

Transect sampling was chosen as the best possible technique to use in order to ascertain if the surface soil in proximity to the Ambassador Bridge had been negatively impacted by the high volume of traffic and by the presence of the bridge itself. Ideally, these transects would be perpendicular to the bridge, and to Huron Church Road (road leading onto the bridge (Figure 7) and sufficiently spaced out along its length. Unfortunately, the

Ambassador Bridge is located in a residential area and Huron Church Road runs along a well developed corridor. Therefore locating sites suitable for long transects was difficult. Two different areas were found suitable for transect sampling. The first was near the Ambassador Bridge and the second was further south along Huron Church Road. Three transects were done at the first transect area (Figure 9, blue squares nearest the northern shore). These transects extended west to east from the bridge and were approximately 100 m long. The distance between the sampling sites for each transect varied between 3 and 10 m. The bridge itself was surrounded by a chain link fence, therefore transects started next to this fence.

The second transect area was much smaller than the Ambassador Bridge transects. Only two transects were done in this second transect area next to Huron Church Road (Figure 16). The length of these transects was up to 20 m long. The soil sampling sites of the individual transects were an average of 4 m apart.

3.2 Industrial Samples (2007)

An important source of manganese to investigate was industrial emissions. Using the list of industries in Table 6, the locations of manganese-emitting industries in Windsor were found. Surface soil samples were retrieved in the immediate and/or surrounding area of these industries (Figure 9, green cross). Wherever possible, soil samples were taken all around the industry. However, in the majority of the cases this was not possible due to the industries being located in highly developed areas of Windsor. Industrial soil samples were therefore retrieved wherever exposed soil (not covered by asphalt or other impermeable cover) was available near the industry.

3.3 Random Samples (2007)

One of the main goals of this study was to determine the soil manganese levels of surface soils in the city of Windsor. In order to achieve this goal, an adequate number of random soil samples (Figure 9, black circle) was needed to provide both statistical power and spatial significance. These soil samples were taken at randomly chosen locations, evenly spread within the city's boundaries. The random soil samples, as well as all other soil

samples, were taken from public land only; this includes parks, empty lots, sidewalk grass, nature areas, school yards, and fields.

3.4 Natural Background Samples (2007 and 2008)

In order to determine the natural background manganese concentration of surface soil in the study area, soil samples were retrieved wherever possible (Figure 9, thick red star). Ideally, these natural background soil samples (low to no exposure to contaminants) would be collected from road cuts or quarries; these would normally expose the older layers of soil, making them available for sampling the ‘natural’ soil. Due to the lack of road cuts (because of Windsor’s low topographic relief) and since the only quarry in the area was privately owned (and closed to the public), these locations were not available for sampling.

As an alternative to road cuts, glacial deposits (parent soil material) were collected either by coring or by sampling exposed parent material along riverbanks. Riverbanks impacted by limited urban activity (i.e., located in rural areas or nature areas) were sampled. The second approach for retrieving natural parent material was using a soil auger to penetrate deep into glacial parent material in various parts of the the glaciolacustrine clay basin. It is recognized that the geochemistry of clay basins is likely to vary spatially, and a number of samples were collected across Windsor wherever possible to define the full range of natural soil manganese concentrations. The selection of these natural soil sample sites depended on several factors including the ownership and accessibility to the land, the level of urban activity observed and the site had to be within the boundary of the geological unit of interest, namely Glaciolacustrine Silty Clay (Unit 3) (Morris, 1994; surface geology maps P. 3252 and 3253). These natural sites included a small forested area south of Windsor, the vicinity of a conservation area, a construction site which was exposing virgin soil, and two agricultural areas. These soil cores were taken at the maximum depth possible (i.e., length of the soil auger (~ 100 cm)).

3.5 Biomonitoring Station Samples (2008)

A biomonitoring station technique was used to investigate the geochemical signature of atmospheric particles which could potentially deposit onto the soil surface. Ideally, the biomonitoring stations would have been installed at locations in proximity to the areas of elevated manganese identified during the preliminary soil survey. However, one of the challenges in designing this study was finding suitable station locations, since site selection was limited to public property. The city of Windsor was contacted for permission to install the biomonitoring stations in public areas of the city during the exposure period. After discussions with Ms. Karina Richters, the city of Windsor Project Manager for Environmental Services and her colleagues, it was agreed that the stations would be installed in various secure, city-maintained locations (Figure 9, thin purple star). Other biomonitoring stations were also installed on campuses of the University of Windsor and St. Clair College, and the grounds of the Bloomin' Gardener, a commercial rural gardening center, the Essex County Conservation Authority offices, and Agriculture and Agri-Foods Canada in Harrow, ON.

Within these secure locations, the biomonitoring stations were installed in locations which minimized overhead obstructions (tall buildings, trees, etc.) and maximized exposure to wind.

Chapter 4 - Materials and Methods

1.0 Soil samples

Note: The following sample preparations and analyses were conducted by the PhD candidate except for 1) the pH determination which was done by an undergraduate student under the direction of the PhD candidate, and 2) synchrotron work in which the PhD candidate actively participated. Elemental analysis of soil and moss-bound airborne particles were performed by a private lab, Activation Laboratories Ltd, and Marc Chénier (Health Canada), respectively. Work done by the PhD candidate is marked with an asterisk (*).

Loose soil*

Soil samples were retrieved from various locations in the city of Windsor, ON (Chapter 3). Debris (rocks, grass, roots) was removed from a sampling area (approximately 10-15 cm²) by hand, using PTFE-lined tweezers and/or a pry-bar. If metal tools were used to remove debris, a plastic trowel was used to remove a thin layer of soil. Using the trowel, or a large plastic scoop, the top layer of soil (0-5 cm) was put into a plastic sample bag, sealed and labelled. Bags were stored in a cooler with frozen ice packs. When not in transit, soil samples were stored in a refrigerator.

Soil cores*

Soil cores were retrieved from natural background and biomonitoring station sites. Cores were taken at both shallow (0 – 30 cm) and deeper (30 – 90 cm) depths. (For a detailed look at the different depths consult Appendix G.) The majority of the soil surface cover (i.e., grass, rocks) was removed from the sampling area. A 4-foot long stainless steel auger was used to retrieve the cores at the chosen sites. When a sufficient depth was reached, the auger was pulled out of the hole and the soil core was gently deposited on top of a Ziploc[®] bag. The bag was then tightly wrapped and taped around the core to keep it intact. The top and bottom of the core were labelled. The wrapped core was then put inside another Ziploc[®] bag, tightly sealed and put in a cooler with ice packs for transport. The depth of the

hole was measured and documented. All tools used to extract soil cores were cleaned between each sample to avoid contamination.

1.1 Soil preparation

1.1.1 Soil core slicing*

Soil cores were removed from their Ziploc[®] storage bags and placed onto a plastic-covered lab bench. The soil core length was measured and documented along with color and any distinguishing features (i.e., rocks, grass, worms, cracks, core cohesiveness). Because of their contact with the stainless steel soil auger, a thin layer from the surface of the intact cores (Figure 10a) was removed with a plastic spoon. A plastic ruler was used to measure 5-cm sections. The soil cores were then sliced into the sections using the handle of a plastic spoon or the plastic ruler. The soil core sections were placed in large styrene weigh boats and spread evenly to dry. Rocks and similar debris were removed from the soil core, every effort was made to remove them cleanly from the sample. The plastic spoons and gloves were discarded between each sample while the bench and plastic ruler were wiped clean.

Some soil cores lost their cohesiveness (i.e., loose soil core became loose soil) (Figure 10b). All efforts were made to handle these uncohesive soil cores the least amount possible. These were removed from their Ziploc[®] storage bags by cutting the bag open. The thin layer of the outer soil core could not be removed from these uncohesive cores for obvious reasons.

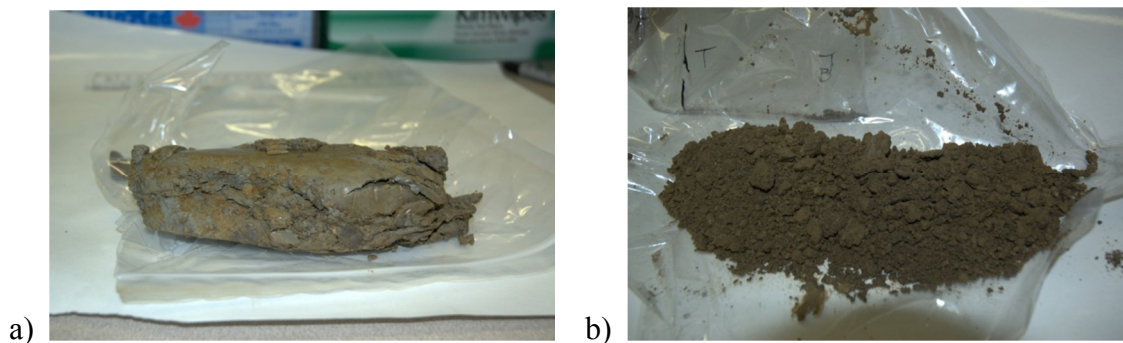


Figure 10 Examples of a) intact and b) uncohesive soil cores.

1.1.2 Drying*

All soil samples from this study were first air-dried in the Health Canada laboratory in Ottawa, Ontario, except for the preliminary soil survey samples. Soil samples were put into large styrene weigh boats and evenly distributed using a PTFE-coated spatula. Soil clumps were broken up into smaller pieces using the spatula. The weigh boats were left to air-dry on large shelving units in a locked room at Health Canada's Environmental Health Centre for 5 days. The soils were then transferred to large amber glass wide-mouth jars with PTFE-lined caps for further sample preparation and storage. The preliminary soil survey samples did not undergo this air-drying but were sent directly to a private laboratory, Activation Laboratories, Ltd (Actlabs) for sample preparation (drying and sieving), digestion and analysis. These soil samples were oven dried at 60 °C to a constant weight by Actlabs technicians.

1.1.3 Crushing*

After air-drying, all transect, industrial, random and natural soil samples, except the preliminary soil survey samples which were prepared by Actlabs, were crushed (see following section for sieve sizes). An agate mortar and pestle were used and the (ASTM) method D421 was consulted. The mortar and pestle were cleaned with Kimwipes® between each soil sample. Two biomonitoring station soil samples and all soil core samples were crushed by Activation Laboratories Ltd technicians before sieving. The practice at Actlabs is to crush the soil sample between two stainless steel plates.

Due to poor shipping practices (sample envelopes were not properly sealed for their return from the private laboratory), the sieved preliminary soil survey samples suffered an unknown amount of cross-contamination. Since the < 63 µm soil fraction of these samples was needed for further analysis (FPXRF XRF-cup analysis), the > 63 µm soil sample fractions, which had been returned in properly sealed bags, were crushed by the PhD candidate using the same procedure used to crush the samples after air drying.

1.1.4 Sieving*

All soil samples, excluding those of the preliminary soil survey, were first sieved to < 2 mm for pH analysis. The ASTM standard test methods for particle analysis of soils D422 and D421 were consulted. Stainless steel 2-mm and < 63 µm (standard size fraction for geochemical soil analysis) sieves from the Newark Wire Cloth Company (which met ASTM E-11 specifications) were used. The sieves were placed on top of a vortex mixer set at a speed of 8. Twigs, leaves, roots and rocks were removed from the sample using stainless steel tweezers. The soil samples were sieved for 3 minutes. When possible, the oversized fractions were crushed (section 1.1.3) then sieved a second time. The oversized fractions were stored in plastic sample bags while the sieved fractions were returned to their amber glass storage jars. The sieves were cleaned using compressed air and Kimwipes® between each sample. Though sieving was standard procedure in the private laboratory's analysis practices, the PhD candidate proceeded with the < 63 µm sieving of all soil samples in order to provide a more representative aliquot for analysis.

1.2 Analysis

1.2.1 Gravimetric moisture content*

Moisture is an important soil characteristic. If it is over 20 %, it can affect readings of the field-portable X-ray fluorescence analyzer (Kalnicky and Singhvi, 2001). The preliminary soil survey sites (n = 99) were used for the FPXRF study (Chapter 7) therefore soil moisture was determined for these samples only. A subset of these soil samples was chosen based on a visual assessment of the presence of condensation inside the sample bag upon their removal from the refrigerator. This subset consisted of a total of 27 samples. Approximately 1 g of soil was placed into aluminum drying dishes. These samples were dried in a VWR Laboratory drying oven at 100 °C until constant weight was obtained. Total drying time was approximately 65 hours. Total soil moisture content was then calculated using the following Equation (1):

$$\text{Soil moisture (\%)} = ((\text{wet soil} - \text{dry soil}) / \text{dry soil}) * 100 \quad [\text{Eqn 1}]$$

1.2.2 pH determination

Only the preliminary soil survey samples were used for this analysis. The American Society for Testing Materials' (ASTM) method D4972 "Standard Test Method for pH of Soils" (American Standard and Testing Materials, 2001) (method A) was used to determine the pH of the soils in Windsor. This method uses a soil:water slurry (1:1 by volume). An aliquot of approximately 10 g of the dried and sieved (2.0 mm) soil sample was introduced into a 50 mL Fisherbrand® Falcon tube (* this was done by the PhD candidate). The pH-meter used was a handheld VWR symphony meter with a VWR symphony Ag/AgCl pH electrode. Instrument calibration was done at the beginning of each day using pH buffers 4, 7 and 10. Calibration verification was done after every 10 samples to verify the calibration.

1.2.3 Elemental analysis

Soil sample digestion and elemental analysis were conducted by the private lab, Activation Laboratories Ltd. in Ancaster, Ontario. The soil samples used had a size fraction of < 63 µm. The majority of soil samples were digested using a four-acid (HF, HClO₄, HNO₃ and HCl) digestion and analyzed using an inductively-coupled plasma mass spectrometer (ICP-MS). Instrumental neutron activation analysis (INAA) was used to analyze a subset of soil samples. This analysis was performed to determine the concentration of elements which had lower detection limits (LOD), such as those from the platinum group. Unfortunately, Actlabs INAA suite of reported elements did not include any platinum group elements. Blind certified reference material (CRM), sample and digest duplicates were also submitted for digestion and elemental analysis in order to verify the precision and accuracy of the instruments. Detection limits of manganese and other elements are reported in Appendix J.

1.2.4 Carbon content*

Carbon content of the majority of the soil samples was determined. Total carbon (TC) and total inorganic carbon (TIC) analyses were done using an Elementar varioMAX CN® analyzer and SoliTIC® instrument, respectively. The total organic carbon content of the soils was determined by subtraction of the TIC from the TC. Steel crucibles were used for

the total carbon analysis and quartz glass boats for the total inorganic carbon analysis. The analyses were performed according to manufacturer's instructions. Approximately 100 mg of soil sample was used for each of the analyses. L-glutamic acid (40.78 % C) and calcium carbonate (12 % C) were used to calculate the daily factor for TC and TIC analyses, respectively. Four certified reference materials (CRM) were used to determine the recovery potential of the instruments, namely Eurovector Soils #1 (3.5 % C; 0.887 % TIC) and #4 (2.417 % C; 2.089 % TIC) and the Canadian Certified Reference Materials Project soils, TILL #1 (7.3 % C; 6.3 % TIC) and #3 (4.6 %C; 3.6 % TIC). One of these CRMs was analyzed after every 10 samples and sample duplicates were analyzed after each CRM. Ultra-high purity helium (99.99 %) was used as the carrier gas and ultra-high purity oxygen (99.9995 %) was used as the combustion gas. Diluted HCl (5 %; Baseline[®]) was used for the inorganic carbon determination. The combustion temperatures of the furnace and the CO₂ column were 900 °C and 250 °C, respectively. The calculated detection limits were 0.06 % for total carbon and 0.48 % for total inorganic carbon (Appendix C).

1.2.5 Micro X-ray diffraction and micro X-ray fluorescence

Only three soil samples were used for manganese speciation studies. The micro X-ray diffraction (μXRD) and micro X-ray fluorescence (μXRF) data gathering were performed by Dr. S. Walker, with the assistance of the PhD candidate and a Queen's University graduate student, Z. Walden, at the Brookhaven National Laboratory's National Synchrotron Light Source (NSLS) in Upton, New York in April 2009. The analyses were carried out using the NSLS's X26A beamline. The soil samples used for this analysis were air-dried, dried at 60 °C and sieved to < 63 μm. Aliquots of these samples were shipped in small amber glass vials to Queen's University in Kingston, ON for sample preparation. Sample preparation consisted of a strip of Kapton tape being placed and sealed over the opening of the vial. The vial was then overturned several times to allow enough of the soil sample to adhere to the tape. A layer of Ultralene[™] (polyethylene) was placed over the soil sample, sealing it between the Kapton tape and Ultralene[™]. The taped soil samples were then mounted onto a 35-mm cardboard frame.

2.0 Field-portable X-ray fluorescence (FPXRF) samples

2.1 FPXRF specifications

The field-portable X-ray fluorescence (FPXRF) analyzer (Figure 11) used in this study was a Thermo Scientific[®] (formerly NITON) model XLp 700 series analyzer. This analyzer used sealed cadmium¹⁰⁹ and americium²⁴¹ radioactive sources. These sources had half-lives of 463 days and 432 years, respectively. The radioactive sources are able to detect different groups of elements. There is very little overlap between their groups of elements. When both sources are used, elements with atomic masses from 22 (Ti) to 92 (U) can be detected by the analyzer. When the trigger is pressed, the soil is exposed to each source for 45 nominal seconds (each) for a total of 90 nominal seconds per soil sample. The penetration depth of the FPXRF analyzer is approximately 1 cm for soil samples (personal communication with R. Datar from Elemental Controls). The Cd¹⁰⁹ source of this analyzer was last replaced in 2006. Because of its long half-life, the americium source has not required replacement. The FPXRF uses a Si-PiN, Peltier cooled detector. A battery pack was used to power the FPXRF. The instrument was never used with less than 70 % battery power. The instrument was last calibrated after the cadmium source's replacement in 2006. An internal calibration was done at the beginning of each day. According to the manufacturer, this is all the calibration needed. Certified reference materials (CRM) were used to verify the analyzer's performance. These were provided by the manufacturer in the form of X-ray fluorescence (XRF) cups, and consisted of National Institute of Standards and Technology (NIST) soils, namely 2709, 2710 and 2711, and a SiO₂ blank. The calculated method detection limit for manganese in soil was 93.4 ppm (see Chapter 7 for calculation). The analyzer was allowed to warm up for 10 minutes after every period of inactivity longer than 30 minutes.



Figure 11 Field-portable X-ray fluorescence analyzer. a) Laboratory use; b) Field use.

2.2 Sample preparation

2.2.1 Direct soil*

As previously stated, the preliminary soil survey sites were used for FPXRF analysis. Debris (rocks, grass, roots) were removed from the sampling site. An area of approximately 10 to 15 cm² was prepared. For example, if the site was grass-covered, the grass was removed by hand or with the help of the curved end of a pry-bar. Roots were removed by hand and/or with PFTE-lined tweezers. If metal tools were used to remove debris (i.e., grass, roots), a plastic trowel was used to remove the thin layer of soil which came into contact with the metal tool. The trowel was also used to smooth the area where the muzzle of the FPXRF analyzer was placed. Soil disturbance was kept to a minimum.

2.2.2 XRF-cup assembly*

All preliminary soil survey samples were also used in XRF-cup assembly which followed the manufacturer's instructions as presented in the FPXRF manual (NITON LCC, 2002). The XRF-cup components were purchased from Premier Lab Supply, Inc. The cups were made of polypropylene plastic. Mylar[®] X-ray film (6μ) was used in the XRF-cup assembly and served as the cup's window. Approximately 3-5 grams of soil sample (size fraction < 63 μm) was used to fill the cups. The small end of a ceramic pestle was used to compress the soil into the cup. A Whatman[®] hardened ashless filter paper (42.5 mm in diameter), cut to fit the XRF-cup, was used to provide a barrier between the sample and the

stuffing, which keeps the contents of the XRF-cup from shifting. Polyester fibre fill was used as the stuffing. The finished XRF-cup provided a soil sample surface free of cracks and crease-less Mylar[®] film.

2.3 Analysis

2.3.1 Direct soil*

The FPXRF analyzer was used according to the manufacturer's recommendations. The analyzer was allowed to warm up for 10 minutes, after which an internal calibration was done. Certified reference materials were analyzed at the beginning of each day and randomly throughout the day. The FPXRF analyzer's Kapton window was placed directly onto the prepared soil surface. Firm pressure was applied to the top of the analyzer (opposite end of the Kapton window) in order to ensure that the entire window was in contact with the soil. Movement of the analyzer by the operator was kept to a minimum while the measurement was being done. Analysis start was initiated either using the computer-analyzer interface or the analyzer's trigger. When necessary, the Kapton window was cleaned with cotton Q-tips[®].

2.3.2 XRF-cup and sample baggie*

The FPXRF analyzer was used according to the manufacturer's recommendations. The analyzer was allowed to warm up for 10 minutes, after which an internal calibration was done. Certified reference materials were analyzed at the beginning of each day and randomly throughout the day. The bagged soil samples and the XRF-cups were analyzed in the laboratory using the FPXRF analyzer and its accessory stand (Figure 11). Both the baggies and cups were analyzed in triplicate in order to provide statistical power. Analysis followed the same procedure detailed in section 2.3.1 with the only difference being where the Kapton window was placed.

The bagged soil samples were removed from the refrigerator and left to acclimate to room temperature with minimal handling. The samples were then gently agitated by hand to settle the smaller particles on the bottom-side of the bag. The baggies were then turned

over in order to have the bottom-side of the bag, and consequently the layer of finer settled particles, facing upwards. Bagged soil sample analyses were carried out by placing the FPXRF analyzer's Kapton window directly on the baggie. The XRF-cups were placed in the FPXRF's stand drawer (Figure 11).

3.0 Biomonitoring station samples

3.1 Moss origin

The moss used in this study for biomonitoring station purposes was the species *Sphagnum fuscum*. It was harvested for the Geological Survey of Canada (GSC) in Calgary from a remote area of the Mackenzie River Delta, Northwest Territories, Canada in 1997. This site was chosen to minimize the influence of anthropogenic 'pollution' sources. The "moss harvest was confined to the upper parts of the beds to avoid contamination by soil materials" (Goodarzi et al., 2003).

A sub-sample of the Mackenzie Delta moss was cleaned of debris (i.e., twigs, leaves), air-dried, but not acid-washed. It was then digested and analyzed in order to determine its original elemental content (Appendix J). Digestion and elemental analysis procedures are described below.

3.2 Moss and moss bag cleaning*

Approximately 65 large handfuls of Mackenzie Delta moss were cleaned (~1 handful/moss bag). The moss was spread between large plastic sheets and kept covered to prevent its drying. Debris (twigs, leaves, dead stalks, small plants) was removed from the moss. This was done using gloved hands or stainless steel tweezers. Moss bags were first vacuumed clean of old moss particles. The moss and moss bags were cleaned using the same procedure but in separate cleaning batches. They were acid-washed with 0.5 M HNO₃ and rinsed with deionized water several times following the procedure by Goodarzi et al. (2003). This series of washes and rinses were done using new 10 L white HDPE buckets which were acid-washed with 0.5 M HNO₃ prior to their use. Several methods were used to remove the moss from the acid or water washes, including using large Ziploc[®] bags with perforations

(“Freshness vents”) or removing cupfuls of the wash and removing the moss within it. Ultimately, the most effective method was using a plastic colander. The gradual build-up of moss in the bottom of the colander acted as a filter for the wash (acid or water). The drained wash liquid was always clean and clear of moss particles (Figure 12) (Note: The plastic colander did have a metal screw in the handle. However, the amount of moss in the colander was never allowed to come into contact with the metal screw.) Once there was a sufficient amount of moss in the colander, the excess water was removed by squeezing it between gloved hands. The clean moss was then either transferred to the next waiting wash or to a new plastic Ziploc[®] bag for storage. The bags were dried on absorbent diapers on a lab bench overnight.

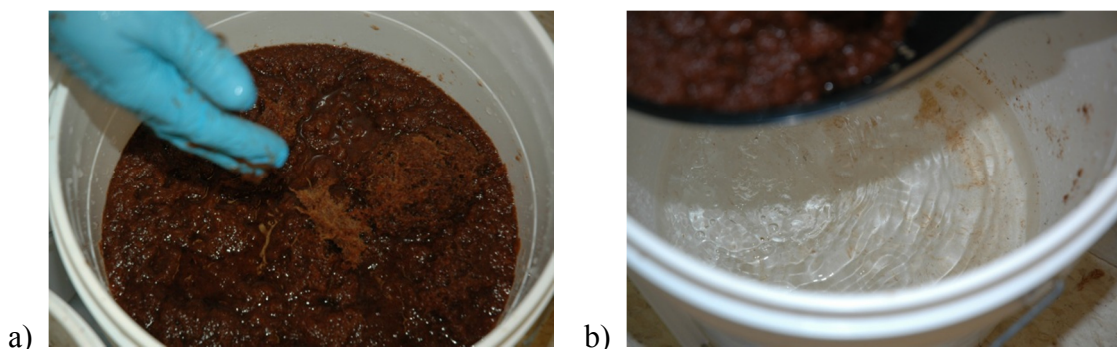


Figure 12 HDPE bucket containing a) moss in a wash (acid or water) and b) clear wash drained from moss.

3.3 Moss bag filling

The flat moss bags used in this study were made of fine mesh nylon. They were sewn into four quadrants (or pockets) (8 cm x 8 cm) with cotton thread (Figure 13a). The moss bags were reinforced with a second layer of nylon mesh on the bottom to prevent sample loss during exposure (Goodarzi et al., 2003). Each pocket was filled with acid-washed moss. New gloves, a clean plastic bench cover and a new natural bamboo skewer were used to insert the clean moss in to the pockets of the moss bags. Small amounts of moss were spread inside the pockets using the skewers. The precise amount of clean moss used could not be measured because the moisture in the moss would start to evaporate making measurements impossible. Dry moss would have been too brittle to spread in the pockets. The moss inside the finished pockets measured approximately 7 cm² and was 2-5

mm thick. The moss not yet inserted into the moss bags was kept moist with deionized water. Small zip-ties (19 cm long) were used to keep the individual pockets closed. Completed bags were stored in new Ziploc[®] bags, stored and transported flat to keep the moss from shifting. A moss bag laboratory blank (completed but not exposed) (“Lab Blank”) was kept in its Ziploc[®] bag in the laboratory for the duration of the exposure period. Once in the field, it was determined that more moss bags were needed. The same materials were used as those used to do the assembly in the laboratory. However no laboratory was available at the time, therefore they were assembled in the hotel room. One of these moss bags was also kept in its Ziploc[®] bag as a blank (“WINDSOR QS BLANK”).

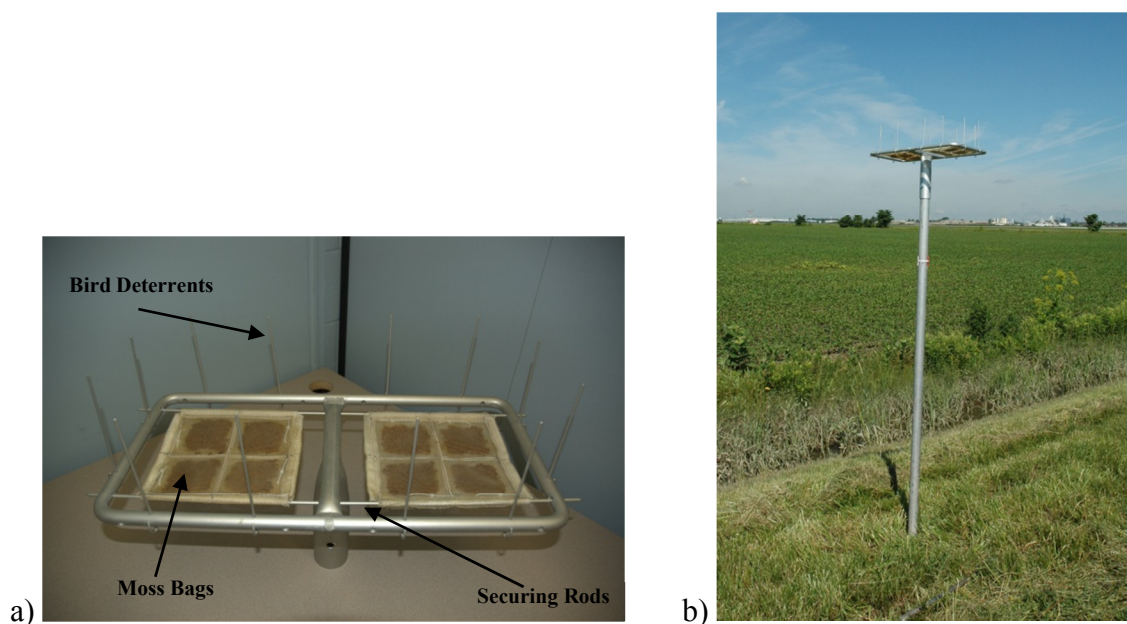


Figure 13 a) Support frame with moss bags of b) biomonitoring station.

3.4 Field installation of biomonitoring stations*

The biomonitoring stations (Figure 13b) belonged to Dr. F. Goodarzi of the Calgary GSC. Each anodized aluminum support frame (60 cm x 30 cm x 23 cm) held 2 moss bags which were secured with pegs (Figure 13a). When handling the moss bags, only the edges were touched with gloved hands. Small vertical pegs are installed around the support frame to deter birds (Goodarzi et al., 2003).

A soil auger was used to dig a hole for the aluminum pole. The depth of the holes was usually approximately 60 cm. At some sites, a “monkey hammer” was used to help drive the pole deeper into hard ground. In some cases however, the soil was too hard and the pole could only be slightly pushed into the ground (~ 20 cm). In other cases, the pole had to be secured to a pre-existing structure (i.e., cement pylon). The support frame was placed on top of the 250 cm-long galvanized aluminum pole. Except for the sites where the biomonitoring station was secured above ground (n = 2), the support frames and moss bags were at an approximate height of 2 m above the ground.

The direction of maximum gust (Table 7) was used as the preferred direction to position the support frame. Both moss bags were positioned to face this direction. The support frames were then secured with a large bolt or hose clamps and duct tape. Important characteristics of the immediate area (i.e., proximity to heavy traffic, industries, etc.) and of the biomonitoring station itself (i.e, geographic coordinates, height of moss bags above ground, etc.) were documented.

3.5 Field retrieval of biomonitoring stations*

The moss bags were exposed for a period of 2 months during the summer of 2008 (June to August). This length of exposure minimizes the chance of cation exchange site saturation and moss disintegration (Martin and Coughtrey, 1982; Gailey and Lloyd, 1986b). Before removing the moss bags from the respective support frame, the condition of the station, height of moss bags above ground, direction of the moss bags, and condition of the moss bags (i.e., bird droppings, dryness, holes, bugs, coloration) were documented. The moss bags were labelled “Left” (L) and “Right” (R), for example the left moss bag was on the left-hand side of the support frame if the wind was at your back.

Retrieval of the moss bags started with removing the support frame from the pole. The securing rods, and subsequently the moss bags, were removed (only the sides of the bags were handled with gloved hands) and stored in new Ziploc[®] bags. These were laid flat in a container for transport back to the laboratory. The moss bags were kept in the Ziploc[®] bags until it was time to remove the moss from the bags.

3.6 Preparation

“Clean Moss” blanks

To demonstrate the effectiveness of the acid-washing procedure and to monitor procedural contamination, samples of the unexposed acid-washed moss were used as control samples during the oven-drying, crushing, digestion and elemental analysis of the exposed moss. These control samples were called: “Clean Moss Blanks”. One clean moss blank was processed consistently with the same batch (sections 3.6.2, 3.6.6 and 3.7) of exposed moss samples.

3.6.1 Removal of exposed moss*

A large plastic sheet was spread over the bench area. A moss bag was removed from the Ziploc bag and placed on the plastic. The dimensions of the moss inside the pockets were measured. Any debris (i.e., bird droppings, insect parts) was removed with stainless steel tweezers from the surface of the moss bag and stored in a labelled jar. The zip-ties were cut and removed from all pockets of the moss bag. Long bamboo skewers were used to remove the moss from each pocket. First, a section of moss (approximately 6 cm²) was removed for future SEM analysis (not part of this thesis). The rest of the moss was carefully removed but its integrity was not essential. Once all of the moss was removed, larger pieces were broken down into smaller pieces using the bamboo skewers. The entire content of the moss bag was mixed and separated into two sub-samples and stored in individual polystyrene jars. One jar was used for digestion and chemical analysis (section 3.7) and the other was kept for future uses. Given the fact that the exposed moss was dry, its handling created fine particles that clung to clothing and surfaces. To prevent cross-contamination, all surfaces were washed between samples and lab coat, exposed skin and hair cap were all thoroughly vacuumed. New bamboo skewers and plastic bench covers were used for each sample.

3.6.2 Drying*

Though the exposed moss was quite dry when it was brought back from the field, it required further drying for processing. Both the exposed moss and the Clean Moss blanks¹ were dried in a VWR laboratory drying oven at 40 °C for 24 hours. (Note: The WINDSOR QS BLANK sample required 6 days to dry because it was still moist after the first 24 hours.) The moss samples were dried to constant weight measured with a 5-decimal place Mettler Toledo balance (model: AX204).

3.6.3 Crushing*

For a more homogeneous sample, the exposed moss samples were crushed. This added step in the sample preparation allowed for further mixing of the sample. An agate mortar and pestle were used to crush the exposed moss into smaller uniform particles. The size of the particles was not determined. Twigs and leaves remaining in the samples were removed with stainless steel tweezers. The crushed samples were stored in clean amber vials. The precautions used to prevent cross-contamination during the removal of the exposed moss from the bags were also used during moss crushing. The Clean Moss blanks were also crushed.

3.7 Moss and air particle digestion* and analysis

Based on the literature, microwave digestion is the most commonly used digestion method for moss samples. A brief trial experiment was conducted using certified reference materials (CRM) (NIST 1573a - Tomato Leaves and NIST 1575 - Pine Needles) and a microwave digestion protocol used by Health Canada on dust samples to determine its feasibility for use in digesting air particles trapped on the surface of the exposed moss. Excellent manganese recoveries were achieved using this protocol for both the NIST 1573a (87 %) and NIST 1575 (90%).

¹ The Clean Moss blanks were first air-dried. A thin layer of the moist moss was spread in styrene weigh boats and left to air-dry on shelves in a closed-door lab for 3 days. Once the clean moss was air-dried, it was stored in clean plastic jars.

A Milestone[®] Ethos Microwave Labstation was used to digest the exposed moss and its associated airborne particles. The reagents used were 8 mL of HNO₃ (65 %; Seastar[™]) and 2 mL of H₂O₂ (35 %; EMD[™]). A 150 g aliquot of the dried and crushed moss was used for the digestion. This model of laboratory microwave can accommodate 10 high-pressure vessels. Therefore, the digestion of the moss samples was done in 9 batches. Each batch consisted of one reagent blank (also used to monitor the temperature), one CRM, one Clean Moss blank and 7 exposed moss samples. The complete digestion took approximately 50 minutes. The cooled airborne particle and moss digests were introduced into clean 50 mL flasks and the volume was completed using deionized water. Very little residue was left after the digestions. Thirteen out of twenty-three biomonitoring station moss bags (i.e., both duplicates), and six single (i.e., only one of the duplicates) moss bags had residue. These residues were probably silicates. Filtration of the moss digest was deemed unnecessary. They were carefully decanted for analysis.

The airborne particle/moss digests were analyzed by Mr. M. Chénier (Health Canada) using a Perkin-Elmer ELAN inductively-coupled plasma mass spectrometer (ICP-MS). The detection limit for manganese in airborne particles was 0.3 ppm (Appendix I).

4.0 Data analysis*

4.1 Statistical analysis

Statistical analyses of the various results of this work were done using the statistical software SPSS base[®] (version 15.0). The tests used in the following chapters included: descriptive statistics (e.g., mean, standard deviation, percentiles, etc.), normal distribution, non-parametric tests comparing two different means (e.g., Mann-Whitney test, Wilcoxon signed-rank test, Kruskal-Wallis test and Friedman's ANOVA), correlation, and, simple and multiple regression analyses. Definitions of the statistical terms used can be found in Appendix E. Results below detection limits were replaced with ½ their respective detection limit values.

4.2 Spatial Analysis

Maps found in this work were created by the PhD candidate using ArcGIS software (version 9.2) by ESRI® Canada (2009). Interpolation was done using the ordinary kriging technique.

Chapter 5 - Manganese Distribution and Sources in Urban Soil of Windsor, Ontario

Purpose

Several field studies were undertaken to investigate manganese geochemistry in urban soils in the city of Windsor, Ontario. The specific goals were to determine the spatial distribution, with focus on identifying sources of elevated areas of manganese in the city. This included establishing the natural background range of manganese for the Windsor area, which was unknown at the time of sampling, in order to quantify the potential anthropogenic inputs of manganese to urban surface soil. Specific characteristics of the soil (pH, carbon content and mineralogy) were also investigated.

Design

A preliminary soil survey was conducted in June 2007 and consisted of retrieving 98 surface soil samples in order to provide initial estimates of the concentration of manganese in surface soils in Windsor, Ontario. Soil sampling sites were located to evaluate the hypotheses stated on page 46; that vehicular traffic was the dominant source of manganese and (alternate hypothesis) that there are multiple anthropogenic sources of manganese in Windsor.

- (a) Samples were taken along transects that were perpendicular to the busiest border crossing in Canada, the Ambassador Bridge, connecting Windsor, Ontario and Detroit, Michigan. These will be referred to as ‘Transect’ samples.
- (b) Soil samples were also retrieved near manganese-emitting industries within the boundary of the city of Windsor (‘Industrial’). The 2002 National Pollution Release Inventory (NPRI) database indicated that there were eleven manganese-emitting industries in Windsor, Ontario (Chapter 2).
- (c) Soil samples representative of the naturally occurring soil manganese concentrations were retrieved from locations across Windsor and the surrounding area. A total of 10 sites (14 samples) were found that could be used with

confidence as representatives of the naturally occurring soil manganese range. All except one of these sites were located within the same geological unit (Chapter 3).

- (d) In order to adequately investigate the spatial distribution of soil manganese (Objective 1) in Windsor, samples of a fourth sample type, “random” (fill-in), were retrieved from selected sites across the city. Wherever a large gap in the sampling site distribution existed (determined visually on a map of the city), one, or several random samples were retrieved thereby providing good coverage and an even distribution of samples across the city.

In August 2007 and June 2008, follow-up soil surveys of Windsor, Ontario were conducted to complete the coverage required to test the above hypotheses. The main goal of this survey was to increase the number of surface soil samples as required for GIS interpretation; i.e. an adequate amount of samples would ensure that all areas of Windsor were represented, and consequently, allow an accurate analysis of spatial distribution of manganese in the soil. The complete (2007-2008) soil survey was also conducted to further investigate elevated areas identified during the preliminary soil survey. Firstly, additional soil samples were retrieved, in triplicate, along the Ambassador Bridge transects and the length of most transects were extended. Triplicate samples were usually taken within a 40 cm² area. In addition to supplementing and extending the June 2007 transects, two additional samples were taken at the pre-existing transect sites (June 2007) to ensure that all transect samples were field triplicates. And secondly, an additional 507 surface soil samples (including some field duplicates) were taken at selected sites across the city of Windsor. These samples included soil samples destined to further investigate elevated soil manganese concentrations that were discovered in the preliminary survey.

Details of the following methods can be found in Chapter 4. Briefly, the surface soil samples were taken from the 0-5 cm depth, and samples were dried, sieved, digested and analyzed by ICP-MS for a suite of elements which included manganese. The ICP-MS detection limit for manganese was 1 ppm. All soil samples were above this detection limit.

Manganese recovery of the ICP-MS method was quite satisfactory at $93.3 \pm 5.1 \%$ ($n = 8$) using Certified Reference Materials (NIST 2702, 2710, 2711; CCRMP TILL-1, -2, -4). The pH and carbon content of the soil samples was also determined. Mineralogical characterization of the urban soil was done using micro-X-ray diffraction (μ -XRD) and micro-X-ray fluorescence (μ -XRF) by synchrotron. The μ -XRD and μ -XRF data was gathered by M. Nugent Ayres and Z. Walden (Queen's University M.Sc. candidate) under the supervision of Dr. Stephen R. Walker (Queen's University). Data reduction and interpretation of the synchrotron-based solid-phase speciation of manganese was done by Dr. Walker. His report (Walker, 2010) summarized the results of the micro-X-ray diffraction and micro-X-ray fluorescence analyses. The focus of the characterization work was the identification of possible forms of manganese present in the soil samples. Due to time constraints, the synchrotron analysis was limited to three samples.

This chapter will briefly describe the results of the preliminary soil survey (section 1) followed by a detailed presentation of the complete soil survey manganese results (section 2). Spatial distribution and elevated areas of soil manganese are described in section 3. The chapter concludes with a description of the synchrotron-based solid-phase speciation of manganese in urban Windsor soil (section 4), followed by a discussion of the results from the complete soil survey.

Results

1.0 Preliminary Soil Survey

Manganese concentrations for the preliminary soil survey ($n = 98$) of urban Windsor, ON are summarized in Figure 14a. Three additional samples were retrieved to represent naturally occurring manganese sites (not included in Figure 14). Data distribution was evaluated using the Shapiro-Wilk test, which is considered more accurate than other normal distribution tests (Field, 2005). The preliminary soil survey manganese data was not normally distributed ($W(98) = 0.736, p < .05$), nor was it found to be log-normally distributed ($W(98) = 0.971, p < .05$). However, after log-transformation of the soil manganese results, the preliminary soil survey data deviated less from the normal

distribution (Appendix F) than the non-transformed data. The preliminary soil survey samples ($n = 98$) had a median soil manganese content of 527 ppm (Figure 14a) and a geometric mean of 525 ppm. The 5th and 95th percentiles were 278 and 1091 ppm, respectively.

Areas of elevated soil manganese (or extreme values) were identified by using the mean (571 ppm) and standard deviation (σ) (283 ppm) derived from the preliminary soil survey results. Any result exceeding the “mean + 2 σ ” value, defined as the mean plus two times the standard deviation (Figure 14a, red thick line), was selected for further investigation. The boxplot is a statistical tool which can also be used to identify extreme values (i.e., outliers) (Appendix E). Field (2005) recommends using the boxplot of the log-transformed results to identify extreme values if the results are not normally distributed. Three soil samples from the preliminary soil survey exceeded the “mean + 2 σ ” limit, namely ABW-T1-4 (1530 ppm), I-ZB-B (2390 ppm), and I-ZB-E (1200 ppm) (Figure 14a). Samples ABW-T1-4 (case #11) and I-ZB-B (case #92) also plotted above the upper boxplot whisker (Figure 14b). ABE-T1-1 (1090 ppm), ABE-T2-1 (881 ppm), ABW-T1-3 (1100 ppm), HS-Q (884 ppm), and ABW-BTW-T12 (876 ppm) had soil manganese concentrations less than the “mean + 2 σ ” value, but above the “mean + 1 σ ” value thus further investigation of these samples was also justified (Figure 14a, green thin line). The samples representative of naturally occurring manganese ($n = 3$) from the preliminary survey had an average soil manganese of 541 ± 13.6 ppm.

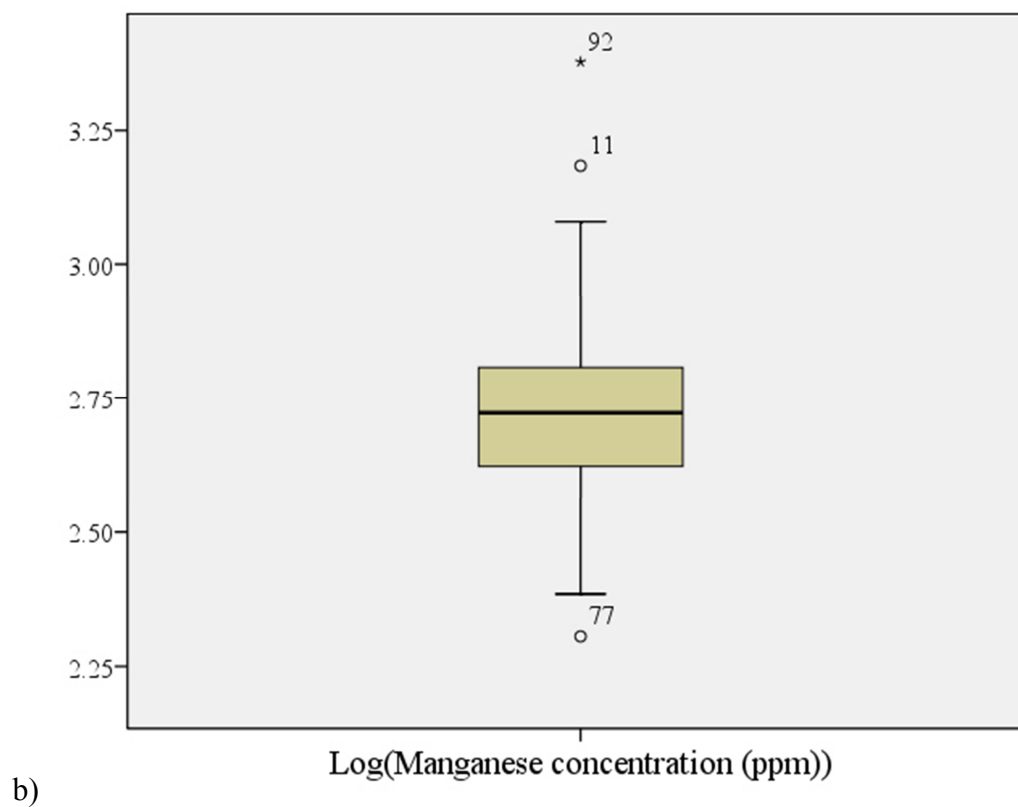
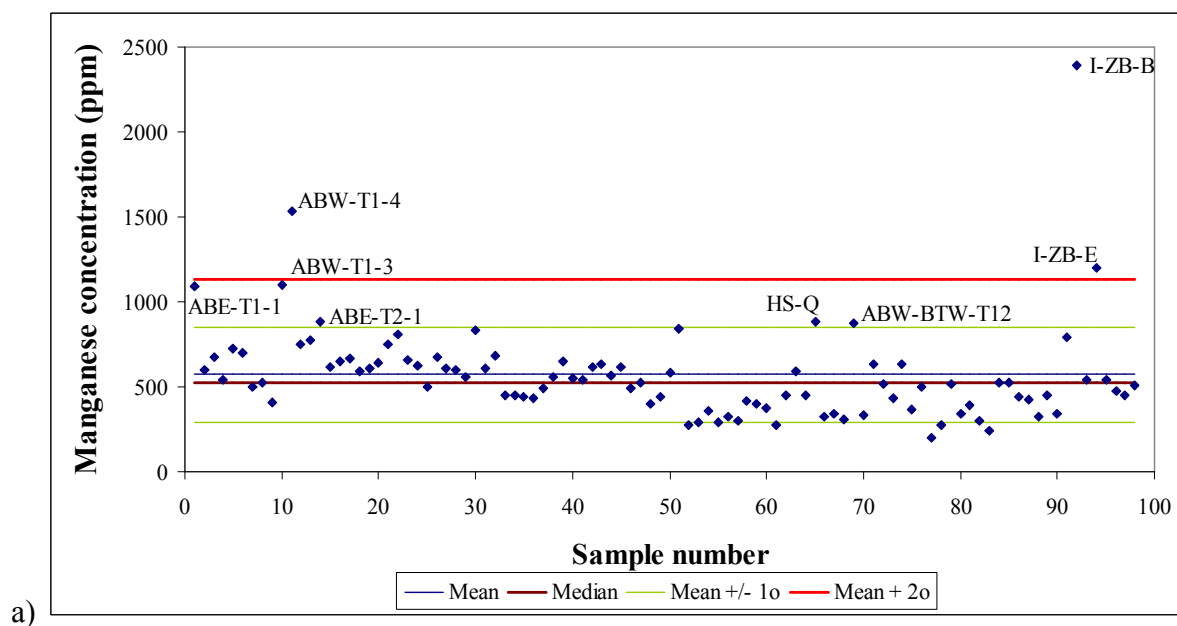


Figure 14 a) Preliminary soil survey manganese concentrations (extreme values are labelled) and b) boxplot of log-transformed soil manganese results.

Selection of sites for follow-up investigation

The purpose of the preliminary soil survey was to provide initial estimates of the surface soil manganese concentrations in the city of Windsor in order to identify potentially elevated areas of soil manganese for further investigation. The median manganese concentration for the soil samples of the preliminary soil survey was 527 ppm ($n = 98$). Three main areas in urban Windsor were selected for further investigation.

(a) Testing hypothesis of vehicular influence. The ABW-T1-4 soil sample exceeded the “mean+2 σ ” limit and plotted above the upper boxplot whisker. Several other Ambassador Bridge transect soil samples were above the “mean+1 σ ” limit. Therefore, the Ambassador Bridge transects were chosen for further soil manganese investigations.

According to the first hypothesis stating dominant vehicular sources, soil samples should have been elevated closer to the bridge, and decrease with increasing distance from the bridge. This was the reason for choosing the location of the transects, i.e. to thoroughly test that hypothesis. It was noted from the results of the preliminary survey that the transect samples did not display this trend.

(b) Industrial influence. Soil sample I-ZB-B was also identified as an extreme value as was I-ZB-E. These two soil samples were retrieved from the surrounding area of a recycling facility identified by the National Pollutant Release Inventory (Environment Canada, 2007), however due to its location within the vicinity of the old CN railway line, this site may be additionally influenced by various overlapping historical industrial sources. This industrial area will be referred to as the ‘Devon-CN area’.

(c) Natural background. The mean soil manganese level of the three natural soil samples retrieved during the preliminary soil survey was 541 ppm. Additional natural soil samples were needed to establish a reliable natural background soil manganese level which could be compared to the baseline soil manganese concentration found in the Windsor area. The preliminary investigation revealed a severe lack of road cuts and other areas conducive to natural soil sampling. By comparing older geological maps (Morris, 1994) with recent up-

to-date road maps of Windsor and the surrounding area, several locations were selected to represent the natural background manganese level. These locations were as far removed from manganese-emitting industries and other activities as possible and these samples were taken at depth wherever possible.

(d) Random site. A baseline-random sample, HS-Q, exceeded the “mean+1 σ ” limit. This surface soil sample was taken in a wooded area near a residential area. It was selected for follow-up due to its elevated soil manganese concentration.

2.0 Complete soil survey – Manganese in urban soil

2.1 Soil manganese concentrations

2.1.1 Transect, industrial, random and biomonitoring station soil sample types

In addition to the 98 sampling sites of the preliminary survey (Figure 15a), 220 sites were subsequently sampled in August 2007 and June 2008 (Figure 15b). These included (a) transects to test for vehicular sources, (b) sites near industrial sources, (c) sites to represent natural sources and (d) additional random sites. Soil samples were also collected to support the moss biomonitoring study (described in Chapter 8). These (e) biomonitoring station soil samples were located at each of the moss biomonitoring stations.

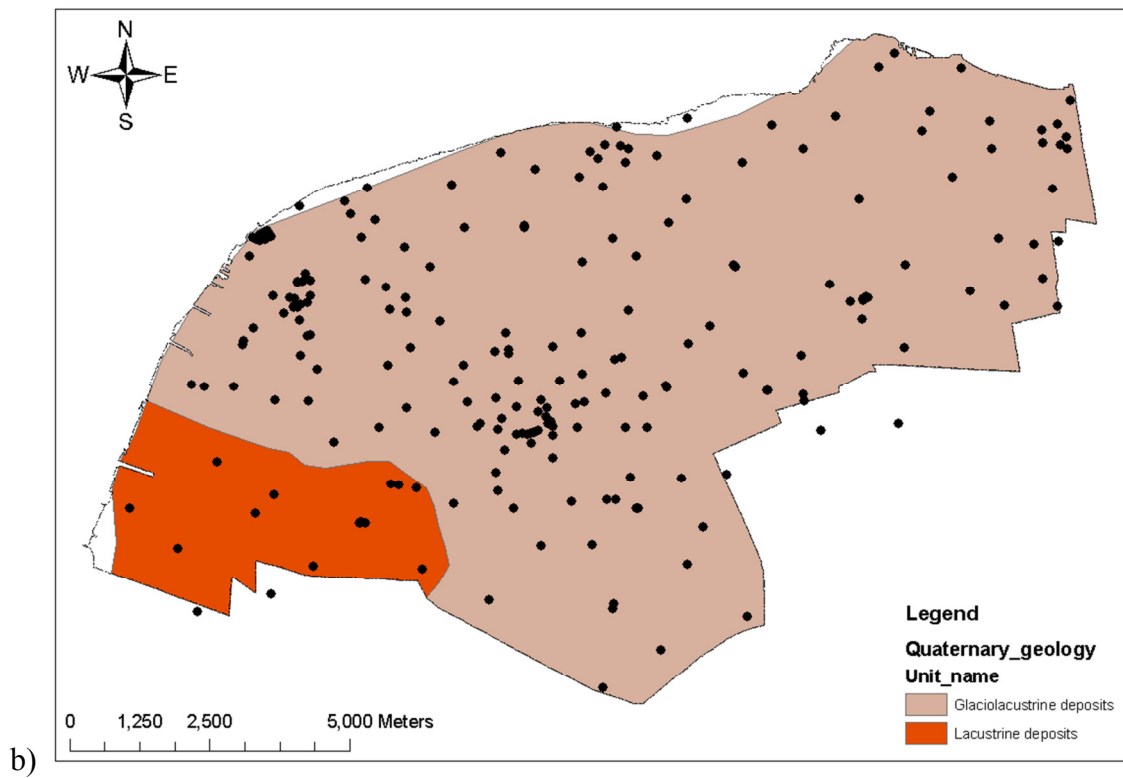
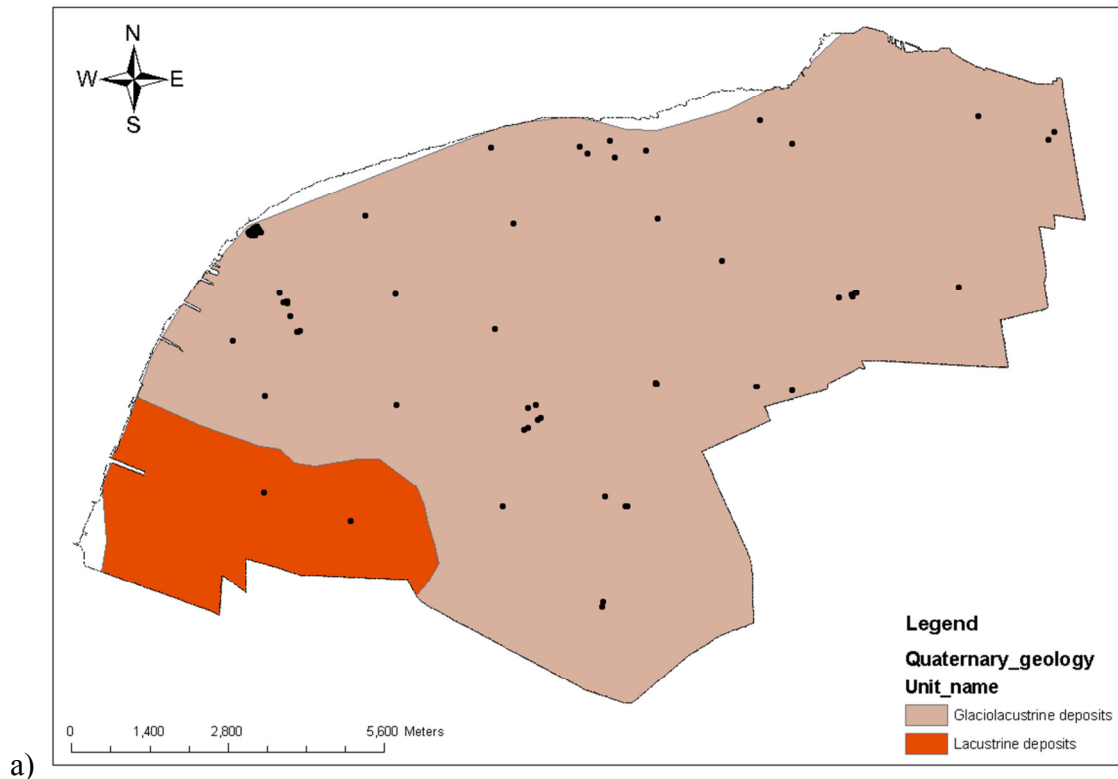


Figure 15 Sample locations for the a) preliminary (n = 98) and b) complete soil surveys ((a) transect (n = 99) and (b,d,e) baseline (n = 219)).

The data distribution of these sample types was evaluated. The result of the Shapiro-Wilk test for the individual soil sample types can be found in Table 12. (a) Transect, (b) industrial and (d) random soil samples were significant ($p < .05$) indicating distributions deviating from a normal distribution. The (c) natural background and (e) biomonitoring station soil samples did not have a significant test ($p > .05$) indicating the results were normally distributed. After log-transformation of their results, neither the (a) transect, (b) industrial or the (d) random soil sample types showed a significant log-normal distribution (Table 12). However, as was the case with the preliminary soil manganese data, after log-transformation, the distribution of the results of each of these soil sample types was closer to the expected normal distribution (Appendix F, Figure F-2).

Table 12 Data distribution for each complete soil survey sample type ($p = 0.05$).

Sample Type	Number of Sites	Normal		Log-normal	
		W	p -value	W	p -value
Transect	99	0.88	$1.9 \times e^{-7}$	0.96	0.007
Industrial	58	0.49	$7.3 \times e^{-11}$	0.85	$3.0 \times e^{-6}$
Natural	14	0.89	0.069	n/a	n/a
Random	138	0.84	$5.0 \times e^{-11}$	0.96	0.001
Biomonitoring station	23	0.93	0.130	n/a	n/a

Note. A p -value in **bold** indicates statistical significance.

The (c) natural soil sample type was considered a specific soil sample type because they were inherently different from the urban soil sample types (transect, industrial, random and biomonitoring station). The differences between statistical means of these urban soil sample types were investigated. Using the non-parametric Kruskal-Wallis test for comparison of means, a significant difference ($H(3) = 92.5, p < .05$) was found between (a) transect, (b) industrial, (d) random and (e) biomonitoring station soil sample types. To investigate if this difference existed between all, or just certain sample types of this test, a *post hoc* test was used (Appendix E). The *post hoc* Mann-Whitney test ($p = 0.008$) revealed

that significant differences, ($U = 1300, r = -.46$), ($U = 1887, r = -.62$) and ($U = 483, r = -.39$), existed between (a) transect soil samples and the other soil sample types ((b) industrial, (d) random and (e) biomonitoring station, respectively). There was no significant difference found between the means of the industrial, random and biomonitoring station soil sample types ($H(2) = 2.9, p > .05$). Therefore, from this point forward, the term ‘baseline soil’ will be used to refer to the results of (b) industrial, (d) random and (e) biomonitoring station soil sample types. Consequently, significant differences were found between: the baseline and (a) transect soil sample types ($U = 3669, p < .05, r = -.53$), between the baseline and (c) natural soil sample types ($U = 968, p < .05, r = -.15$) and, between the (a) transect and (c) natural soil sample types ($U = 446, p < .05, r = -.20$).

2.1.2 (a) Transect soil

Due to the heavy traffic volume of the Ambassador Bridge, the area most affected by vehicular manganese emissions was expected to be in the immediate vicinity of the bridge. Therefore, three soil transects were located perpendicular to, and extending east and west from the Ambassador Bridge, in order to investigate soil manganese anomalies related to vehicular traffic (AB sites) (Figure 16). Two soil transects were also located directly south of the bridge to evaluate the soil manganese concentration farther away from the bridge but along the same road, Huron Church Road, (HC sites) (Figure 16). No significant difference in soil manganese existed between the AB soil transects next to the bridge and the HC transects farther south ($U(99) = 0.47, p > .05, r = -.09$). Therefore, unless otherwise specified, ‘transect soil’ will refer to all transect sites, both AB and HC.

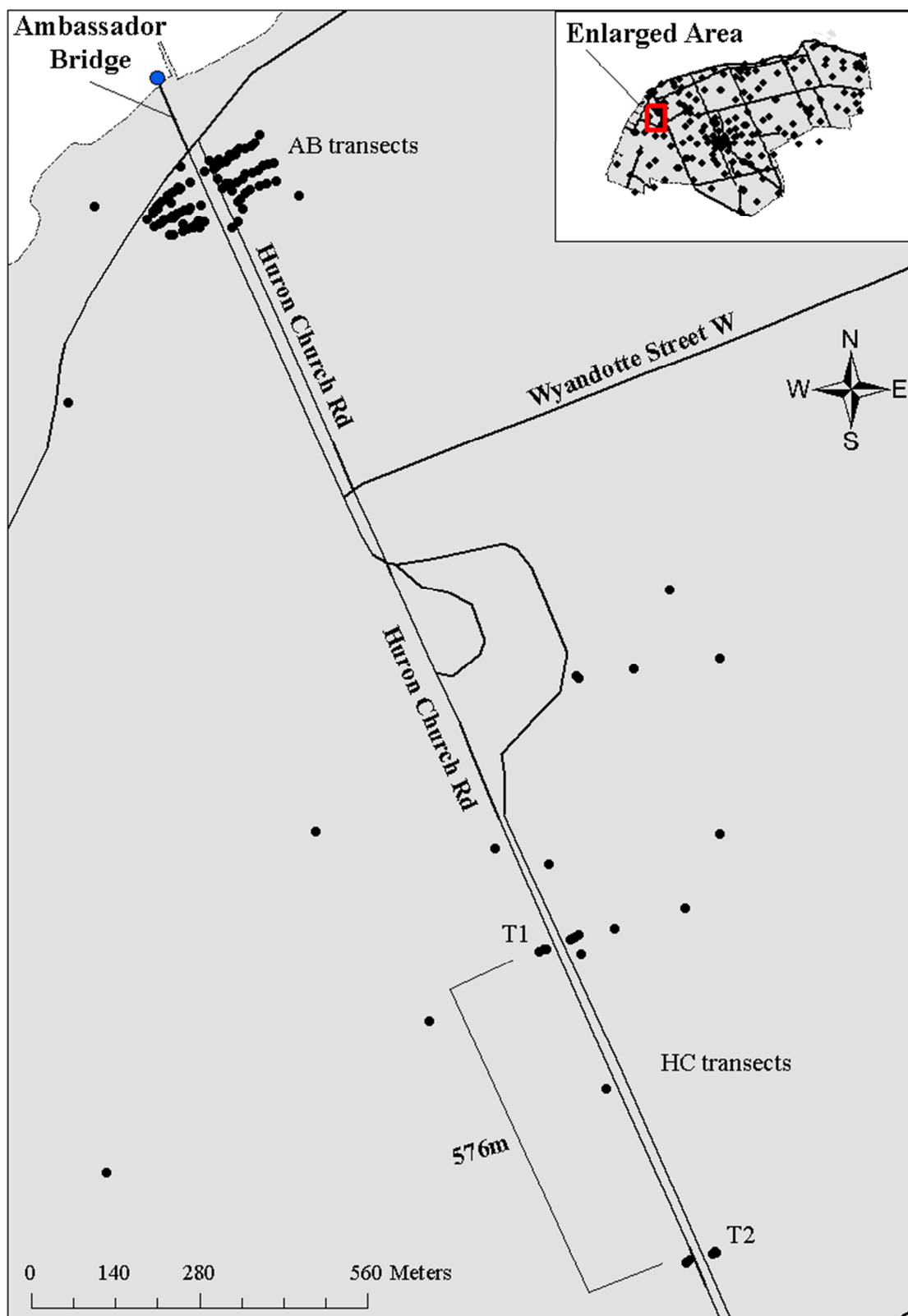


Figure 16 Location of Ambassador Bridge and Huron Church Road transects

The transect soil was not normally distributed ($W(99) = 0.88, p < .05$). Further investigation into the transect manganese data distribution revealed it was also not log-normally distributed ($W(99) = 0.96, p > .05$). As stated in section 2.1.1, the distribution of the log-transformed transect soil data was closer to the expected normal data distribution than the non-transformed data. Each transect site was the average of three field replicates (except the HC sites). The median transect soil manganese concentration was 553 ppm ($n = 99$; range = 361 to 1163 ppm). The corresponding geometric mean was 565 ppm. The 5th and 95th percentile values were 427 and 860 ppm, respectively. The log-transformed transect soil boxplot showed ABW-T1-4 (case #48), ABW-T1-13 (case #59) and ABW-T1-3 (case #46) samples plotted above its upper whisker (Figure 17).

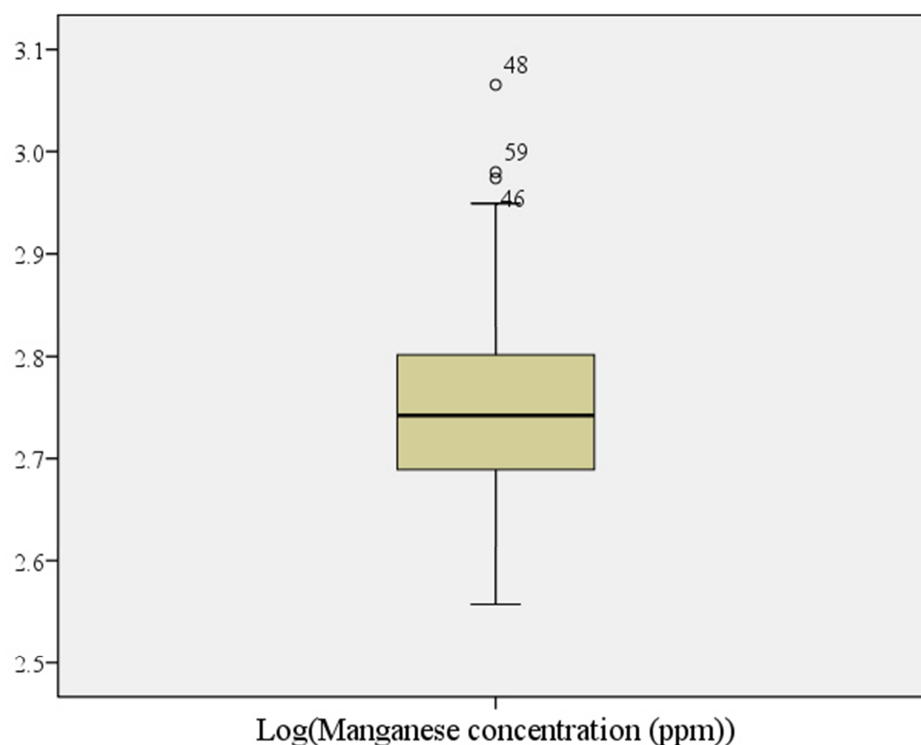


Figure 17 Boxplot of the log-transformed transect soil manganese data.

Transect site soil manganese variability

The Ambassador Bridge sites (n = 86) were sampled in triplicate. The variability of the transect soil manganese results can be measured by the relative standard deviation (RSD) (Equation 2). An acceptable amount of variability for field results is usually an RSD value less than 10 %. The average within-site RSD value, i.e., average variability between triplicate samples, was 8.5 % (n = 86). The relative standard deviation between the transect sites was 22.6 %. Only 3 of the transect sites had an RSD exceeding the between-site RSD value.

$$\text{RSD} = (\text{standard deviation} / \text{mean}) * 100 \quad [\text{Eqn 2}]$$

A closer look at the within-site variability of the transect sites revealed a total of 34 % of the transect Ambassador Bridge sites had RSD values exceeding the 10 % limit. Ninety percent of these samples were J/A soil samples². The remaining ten percent of samples above 10 % were non-J/A samples and were approximately equal to 10 %. If only the duplicate samples (August samples only) of all transect sites are considered, the number of samples with a relative percent difference (RPD) (Equation 3) above 10 % decreases to 22 %, of which only 47 % correspond to J/A samples. The figures of Appendix G show the difference between the overall trend in soil manganese concentration of the triplicate (June + August samples) and duplicate (August samples only) samples.

$$\text{RPD} = ((| \text{value1} - \text{value2} |) / ((\text{value1} + \text{value2}) / 2)) * 100 \quad [\text{Eqn 3}]$$

Huron Church Road transects

During the preliminary soil survey, two small transects south of the Ambassador Bridge were sampled. These transects, HCE/W-T1 and HCE/W-T2, were perpendicular to Huron Church Road, the major road leading to the Ambassador Bridge (Figure 16) and were approximately 1591 m and 2163 m away from the bridge, respectively (distance measured from the transect to the shore of the Detroit River (blue circle in Figure 16)). HCE-T1 was

² These samples differ from the rest of the triplicate soil samples because the first soil sample of the triplicate was taken in June 2007, during the preliminary soil survey, and the second and third were retrieved during the complete soil survey in August 2007. These June/August (J/A) samples are marked by an asterisk (*) in Figure 20. All other transect soil samples had their triplicate samples taken at the same time in August 2007.

20 m in length and HCE-T2 was 12 m and each consisted of 4 and 3 sites, respectively (n = 1 sample/site). HCW-T1 and HCW-T2 each included 3 sites (n = 1 sample/site) and were approximately 16 m and 13 m long, respectively. The mean soil manganese levels for these transects ranged from 446 to 605 ppm (Table 13). Both T2 transects were higher than the T1 transects (Figure 18). Likewise, the western transects were higher than their eastern counterparts. None of these transect samples was identified as an extreme value (Figure 17).

Table 13 Soil manganese mean and standard deviation values (ppm) for Windsor transects.

Transect	Western Transects				Eastern Transects			
	name	n ^a	mean Mn	stdev (RSD %)	name	n ^a	mean Mn	stdev (RSD%)
Huron Church Road (HC)	WT1	3	567	82.8	ET1	4	446	9.0
	WT2	3	605	36.3	ET2	3	572	41.5
Ambassador Bridge (AB)	WT1	17*	673	202 (30)	ET1	17*	552	117 (21)
	WT2	16*	523	95.8 (18)	ET2	14*	580	91.5 (16)
	WT3	11*	608	82.6 (14)	ET3	11*	550	77.7 (14)

^a n indicates the number of sampling sites per transect

* indicates triplicate soil samples per sampling site.

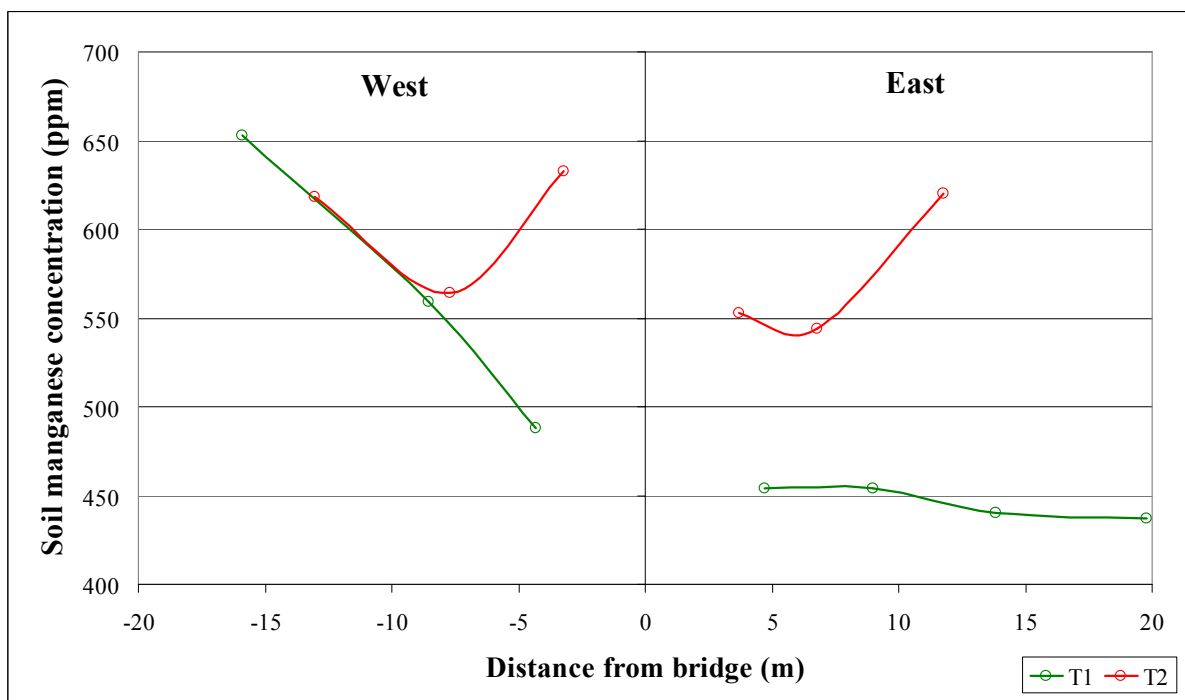


Figure 18 Huron Church Road transect soil manganese concentrations.

Ambassador Bridge transects

The Ambassador Bridge transects were nearer to the Detroit River shore than the Huron Church Road transects. The ABE-T1 and ABW-T1 were approximately 168 m away from the Detroit River shore (Figure 19, blue circle). Transects were between 26 and 50 m apart (Figure 19). The first two eastern soil transects (ET1 and ET2) extended 109 and 112 m, respectively, perpendicular to, and away from the Ambassador Bridge (Figure 19) and were located in Assumption Park. The third eastern transect (ET3) reached 130 m and was located on the south side of University Avenue, next to the Roman Catholic Church's yard. (Note: The majority of the sites from this transect were offset to the north of the original June 2007 preliminary soil survey ET3 sites by approximately 25 m due to the fence surrounding the church's yard.) The first western transect (WT1) was 90.5 m in length while the second (WT2) and third (WT3) western transects reached distances of 86 m and 65 m, respectively (Figure 19). The former two transects (WT1 and WT2) were located in an area which was a University of Windsor faculty and staff outdoor parking lot and unused field. The third western transect was on the grassy area between the sidewalk and University Avenue. WT1 had the highest average soil manganese concentration of the western transects, 673 ± 202

ppm, while the lowest concentration was found at the WT2, 523 ± 95.8 ppm (Table 13). Of the eastern transects, ET2 had the highest average manganese level, 580 ± 91.5 ppm. Both WT1 and WT3 had higher manganese concentrations than their eastern counterparts whereas ET2 was higher than WT2.

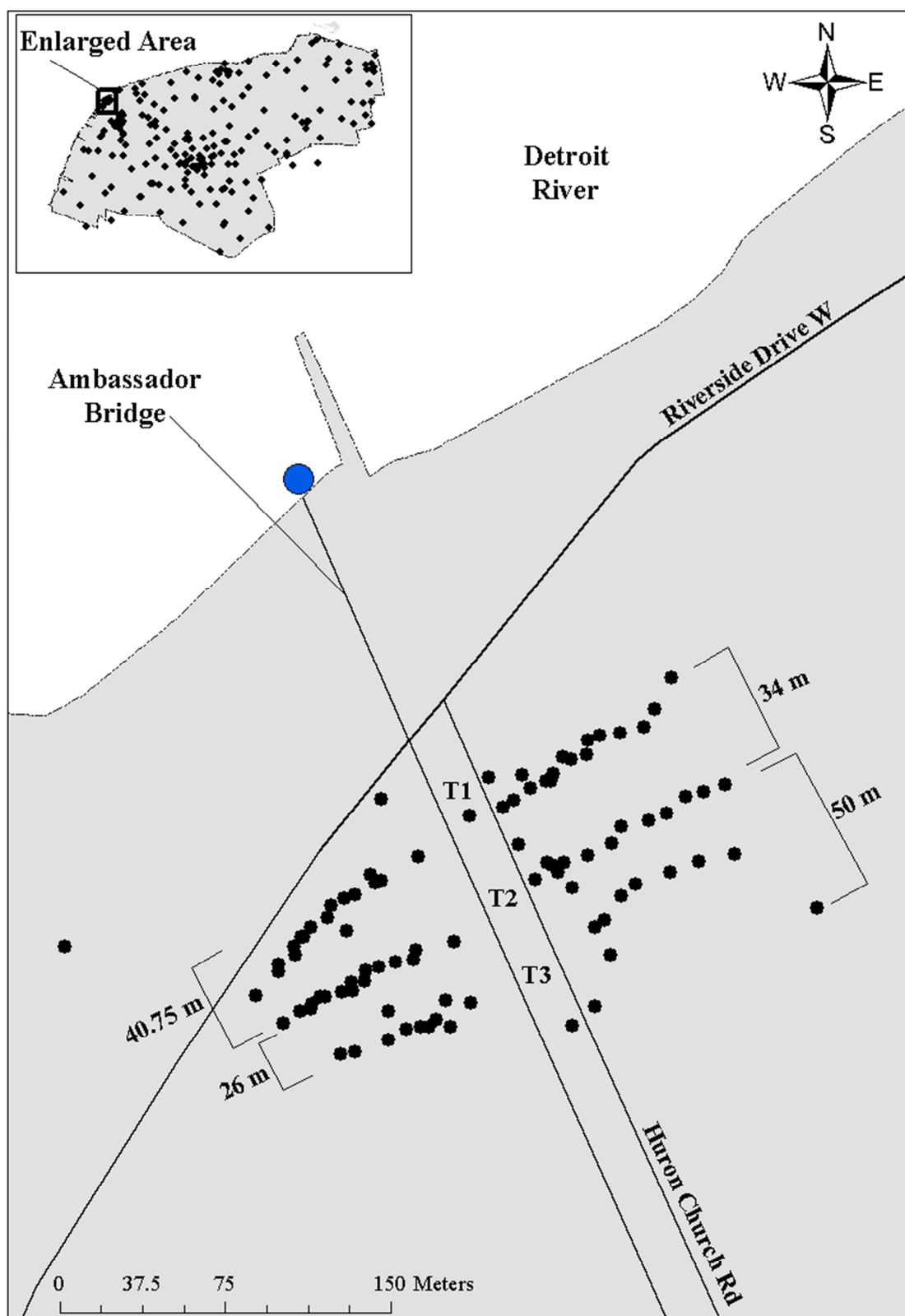


Figure 19 Location of Ambassador Bridge transects and transect sites.

Figure 20 shows the average soil manganese concentrations of the individual sites of the three transects as a function of distance from the bridge. The eastern side of the first (ET1) and second (ET2) transects had higher soil manganese concentrations directly next to the bridge (0 m) than their western counterparts (Figure 20). While the third transect (T3) had similar soil manganese levels on both sides of the bridge, the eastern T3 sample nearest to the Ambassador Bridge was lower than its ET1 and ET2 counterparts (Figure 20). The soil manganese of the majority of the transects (both eastern and western) fluctuated between 400 and 800 ppm except for WT2 which appeared to have a general trend of decreasing soil manganese levels away from the Ambassador bridge (Figure 20). The largest soil manganese peaks were found in the WT1 transect where the soil manganese concentrations fluctuated widely between 0 and 40 m from the bridge (Figure 20).

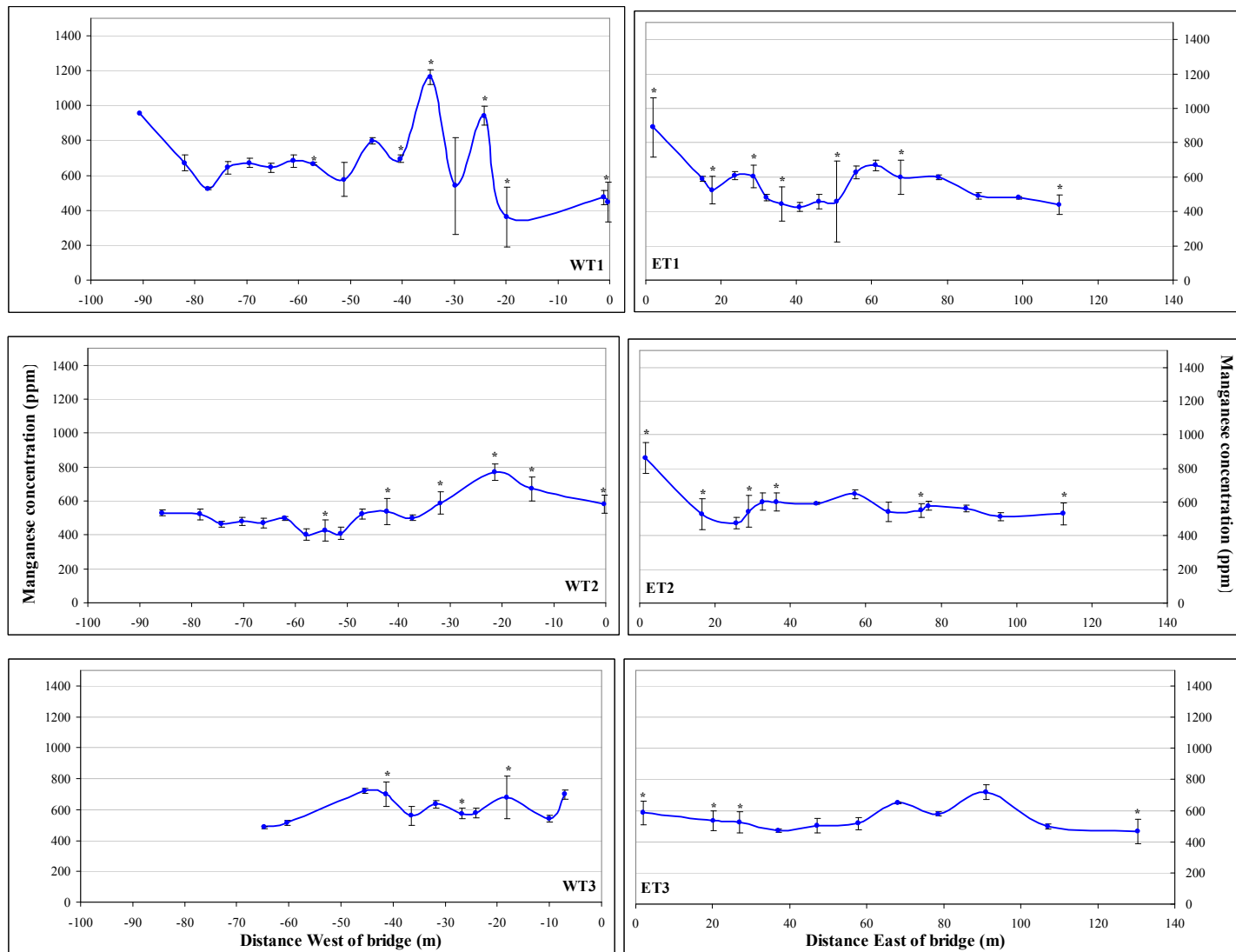


Figure 20 Soil manganese concentrations of the Ambassador Bridge transect sites. The bridge is located at distance 0m. (Error bars represent one standard deviation of the mean; For all sites, n = 3 except ABW-T1-4 and -5 where n = 4.) (* indicates a June/August triplicate sample².)

2.1.3 (b, d, e) Baseline soil

The baseline soil data was not normally distributed ($W(219) = 0.49, p < .05$). It was also not log-normally distributed ($W(219) = 0.90, p < .05$). Comparison of the histograms (Figure 21a and b) and quantile-quantile plots (Figure 21c and d) of the non-transformed and log-transformed baseline data showed that the log-distribution better approximated a normal distribution. The median baseline soil manganese concentration was 385 ppm ($n = 219$; range = 164 to 3430 ppm). This soil manganese ranged from 249 (5th percentile) to 806 (95th percentile) ppm and had a geometric mean of 407 ppm.

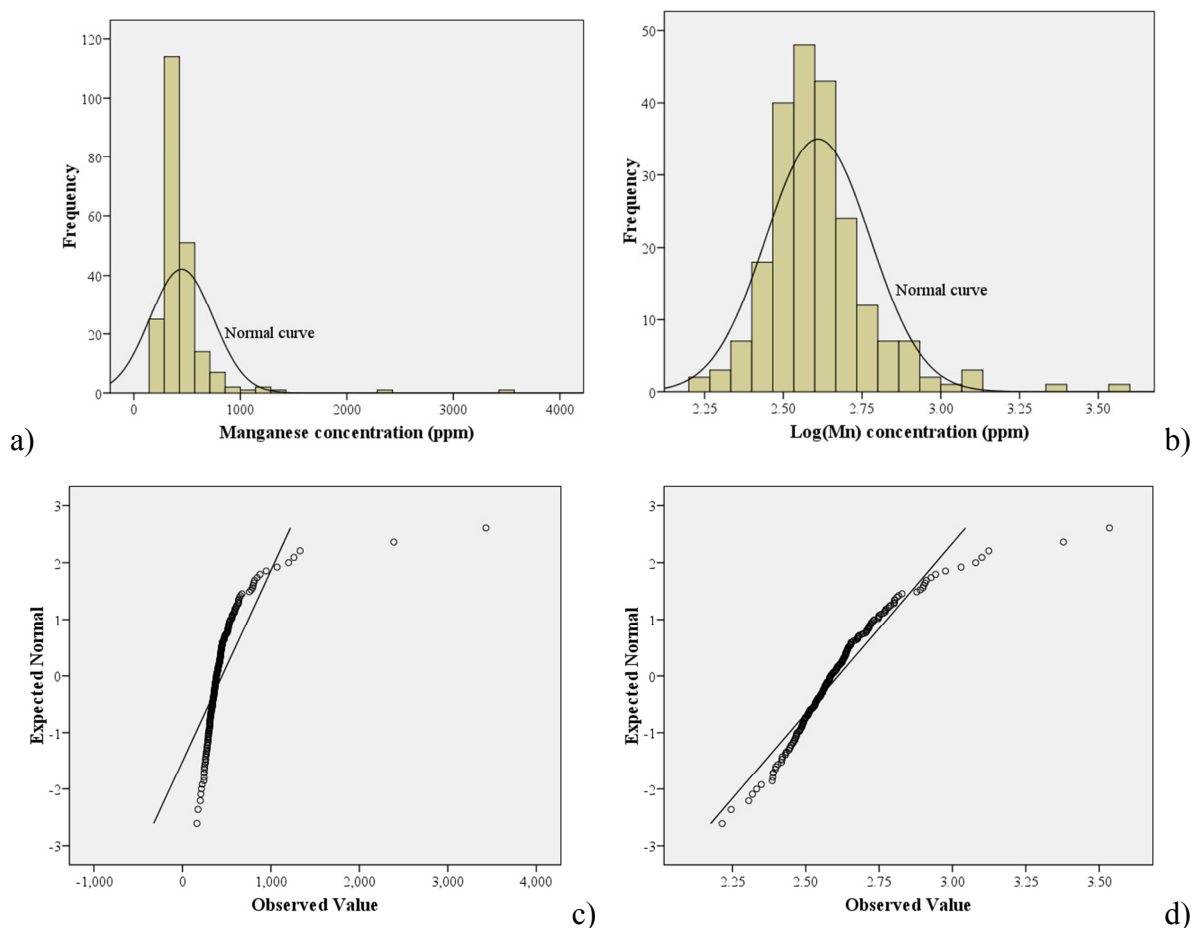


Figure 21 Histograms and normal QQ-plots for non-transformed (a and c) and log-transformed (b and d) baseline data.

Since the baseline soil manganese results were not normally distributed, the boxplot of the log-transformed data ($n = 219$) (Figure 22) was used to identify samples which should be considered extreme values. Based on Figure 22, cases 21, 91, 104, 196, 190, 191, 194 and 192 plotted above the upper boxplot whisker. These cases correspond to soil samples ABW-BTW-T12, HS-Q10, HS-R3, I-ZB-E, -40, -41, -B, and -42, respectively. I-ZB-12 (164 ppm) (case #170) and HS-E4 (176 ppm) (case #44) plotted below the lower boxplot whisker indicating they were lower extreme values.



Figure 22 Boxplot of log-transformed baseline soil manganese data.

2.1.4 (c) Natural background

This study area, i.e., the city of Windsor, is underlain by two main quaternary geological units (Chapter 2) (Figure 23). An effort was made to retrieve the natural samples from within the same geological unit as the city of Windsor. One of the natural samples, Brighton Beach (BB), was taken from a different geological unit (Figure 23) in order to represent the small number of baseline soil sampling sites (approximately 15) which were located on this unit. Ten sites and fourteen soil samples were selected to represent the naturally occurring soil manganese concentration of the Windsor area (Figure 23). These samples will be known as the ‘natural’ soil sample type. The lack of road cuts in the Windsor area meant that these samples had to be retrieved from non-impacted (i.e., away

from industrial and heavy traffic sources) natural riverbanks (LR-group of samples (namely - L, -R, -2 and -3) and PC samples), at depth in natural areas (MacGregor and Brighton Beach), in an excavation site (FSV and Amherstburg) and at depth near undeveloped urban areas (Town of Essex, PEN, MB-22 and MB-23). Several of these natural soil samples represent the average of a soil core taken at the soil surface or at a specified depth. Appendix H shows the manganese results of all soil cores taken during this study of urban Windsor soil.

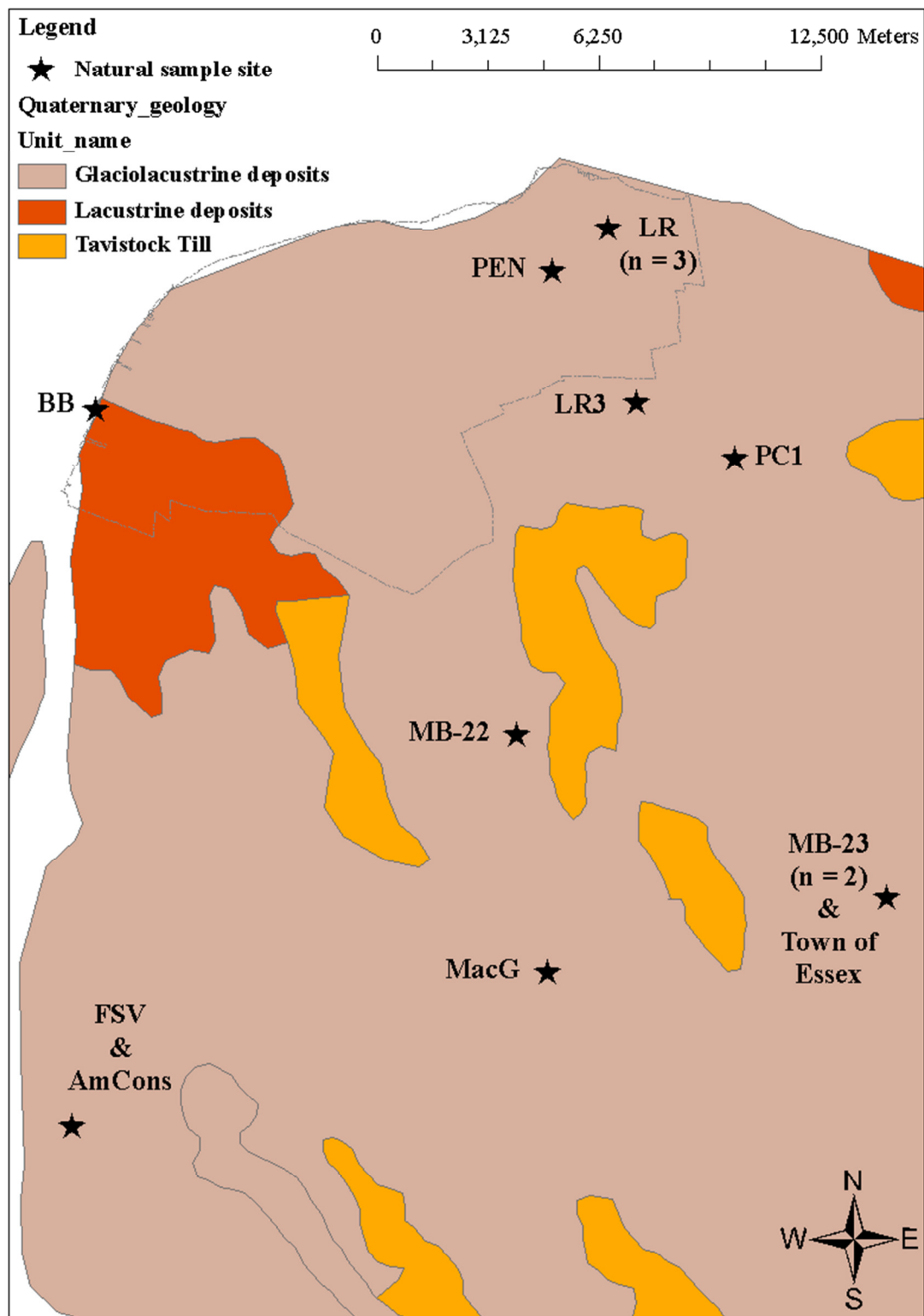


Figure 23 Location of natural soil samples and the quaternary geological units underlying Windsor and the surrounding area (n = # of different soil samples/site).

The manganese results for natural soil sample type were found to be normally distributed based on the Shapiro-Wilk test for normality ($W(14) = 0.89, p > .05$). The natural soil samples had a mean manganese concentration of 506 ± 173 ppm ($n = 14$), a median of 502 ppm and a geometric mean of 481 ppm. The natural soil manganese results ranged between 251 and 970 ppm (minimum and maximum values which also corresponded to the 5th and 95th percentile values). Figure 24 shows the soil manganese concentrations of the natural samples. The relative standard deviations (RSD) for the natural soil sample type ranged from 7 % for the FSV sample to 16 % for MB-23s. Natural soil site MB-22d had an RSD of 23 % while the TownEd site had 47 % variability. The three LR samples (-L, -R and -2), which were taken at the same location but could not be used as field replicates because they did not originate from the same hole or directly next to it, had very little variability in their individual soil manganese levels. Case #11, or the Town of Essex depth sample ($n = 4$), was located above the upper natural soil boxplot whisker (Figure 25) which would indicate it was an extreme value.

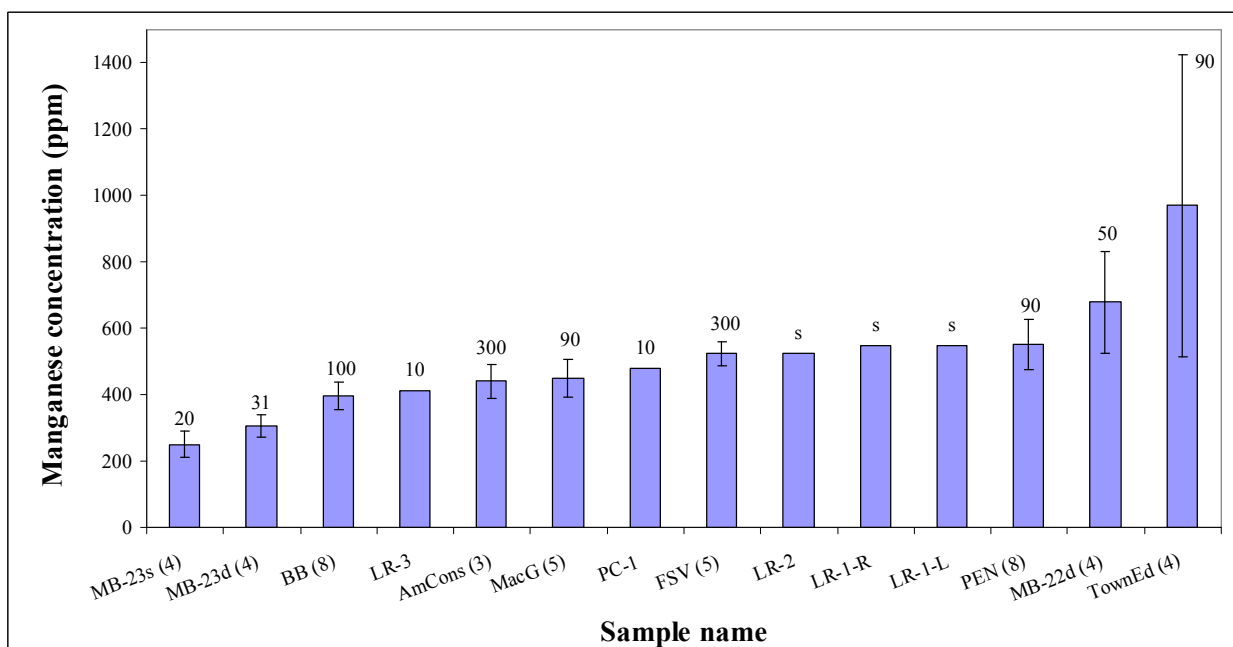


Figure 24 Average natural soil manganese concentrations. [The number above the error bar is the depth (cm) of the soil core (s = surface sample (0 - 5 cm)). Error bars represent one standard deviation. The number next to the sample name on the x-axis represents the number of samples used to calculate the average soil manganese concentration.]

The Town of Essex depth site result represented the average soil manganese of four soil core sections (970 ppm). This soil core was retrieved at a depth of 67 to 80 cm and was then sectioned (5 cm / section). The soil manganese of the different core sections increased with depth from 452 ppm to 1550 ppm. The natural soil site MB-23 was located very near the Town of Essex depth site, approximately 2 m away. The former site included two natural soil samples, MB-23 surface (s) (0 – 20 cm) and MB-23 depth (d) (20 – 31 cm) which were taken from the same hole. These two core soil samples (n = 4 each) had 251 ppm and 306 ppm soil manganese concentrations respectively.

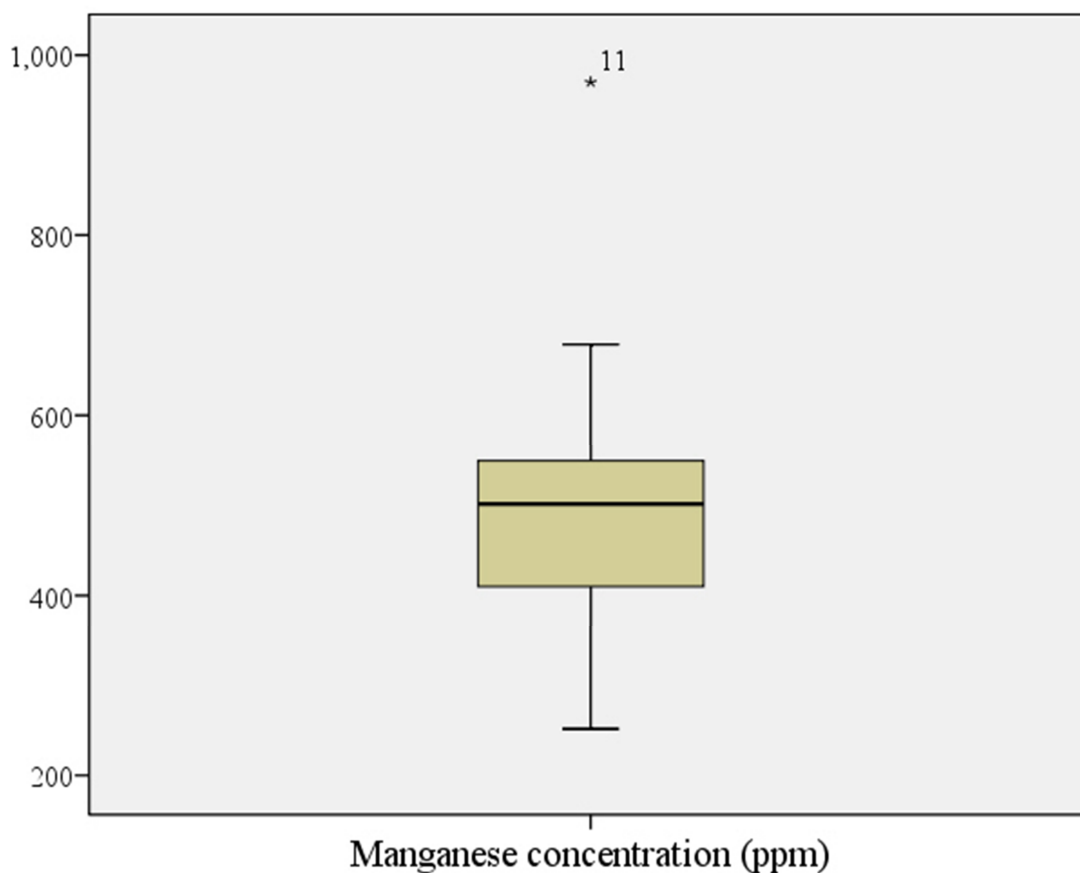


Figure 25 Boxplot of natural soil manganese concentrations (ppm).

2.2 Spatial distribution of soil manganese in urban Windsor, Ontario

The spatial distribution in Windsor was interpreted by visual observation of soil manganese concentrations (Figure 26) and by interpolation (kriging) of the levels (Figure 27). Three samples lie outside the city of Windsor boundary (Figure 27 inset). These three soil samples were associated with (e) biomonitoring stations (Chapter 8). The two samples closest to Windsor had soil manganese concentrations below 300 ppm whereas the one furthest away near the southern Ontario border, MB-19, had 571 ppm of manganese. There are large distances between these samples, and between these samples and the remainder of the data set. A consequence of these distances is that the interpolation of these large gaps would be very unreliable. In order to better view the bulk of the soil samples, these three samples were not included in the spatial distribution analysis (Figure 26) and subsequent data interpolation (Figure 27).

Above average soil manganese sites were found mostly in the western part of the city (Figure 26). A small industrial area in the center of the city (Devon-CN) and another area in the north-central part of the city are also well above the average manganese soil concentration (385 ppm). Several random sites located in the east are slightly above the average soil concentration. An interpolation of the soil manganese data (Figure 27a) also shows this trend of higher soil manganese in the west of the city. The soil in the south and east of the city of Windsor was closer to the average manganese concentration. Figure 27b shows the prediction standard error map. Areas of high error indicate areas where the prediction is less reliable (i.e., additional soil samples would be needed to improve the soil manganese interpolation in this area). The area of highest error was the southwestern part of the map.

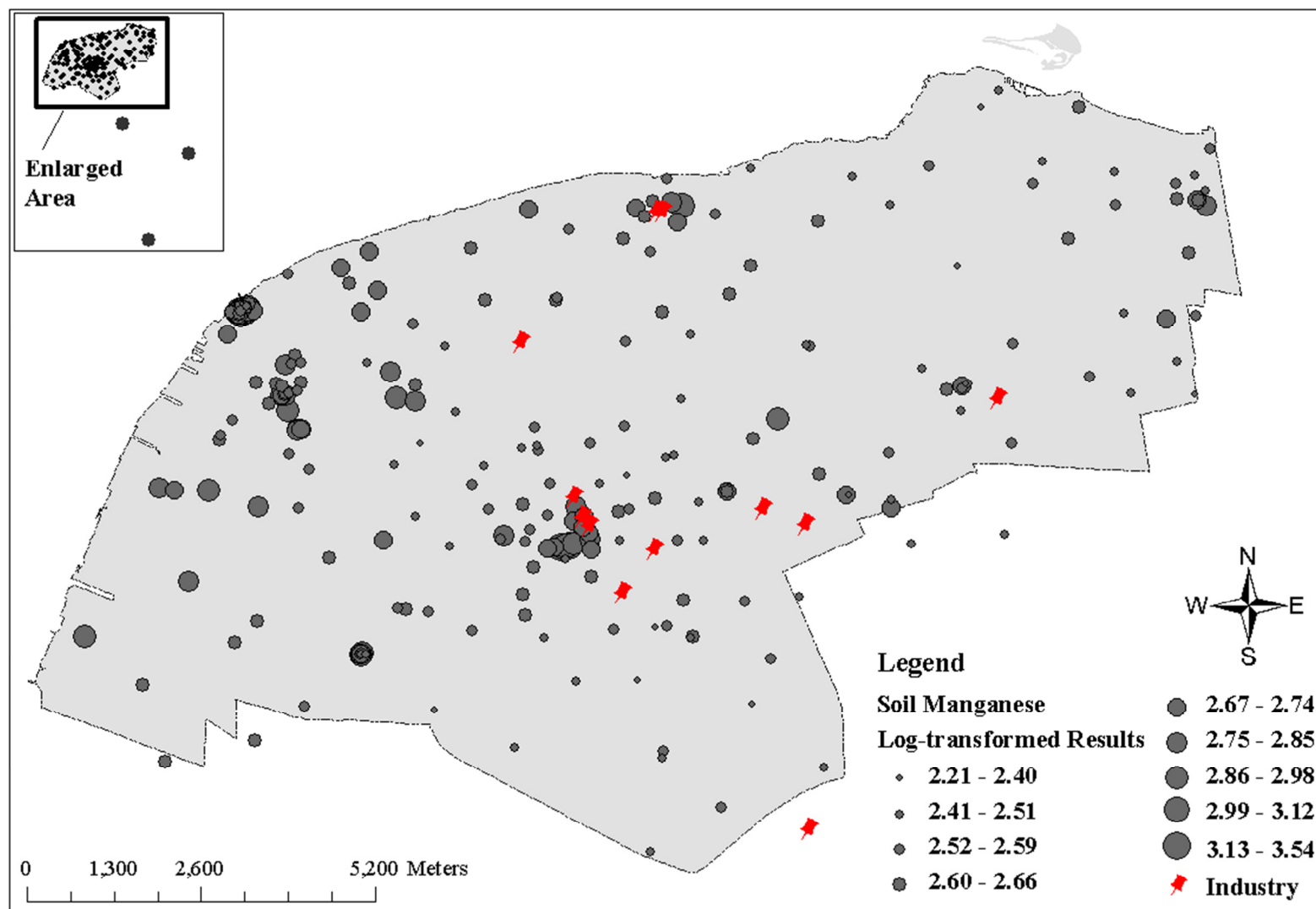


Figure 26 Spatial distribution of both (a) transect and (b,d,e) baseline log-transformed soil manganese concentrations.

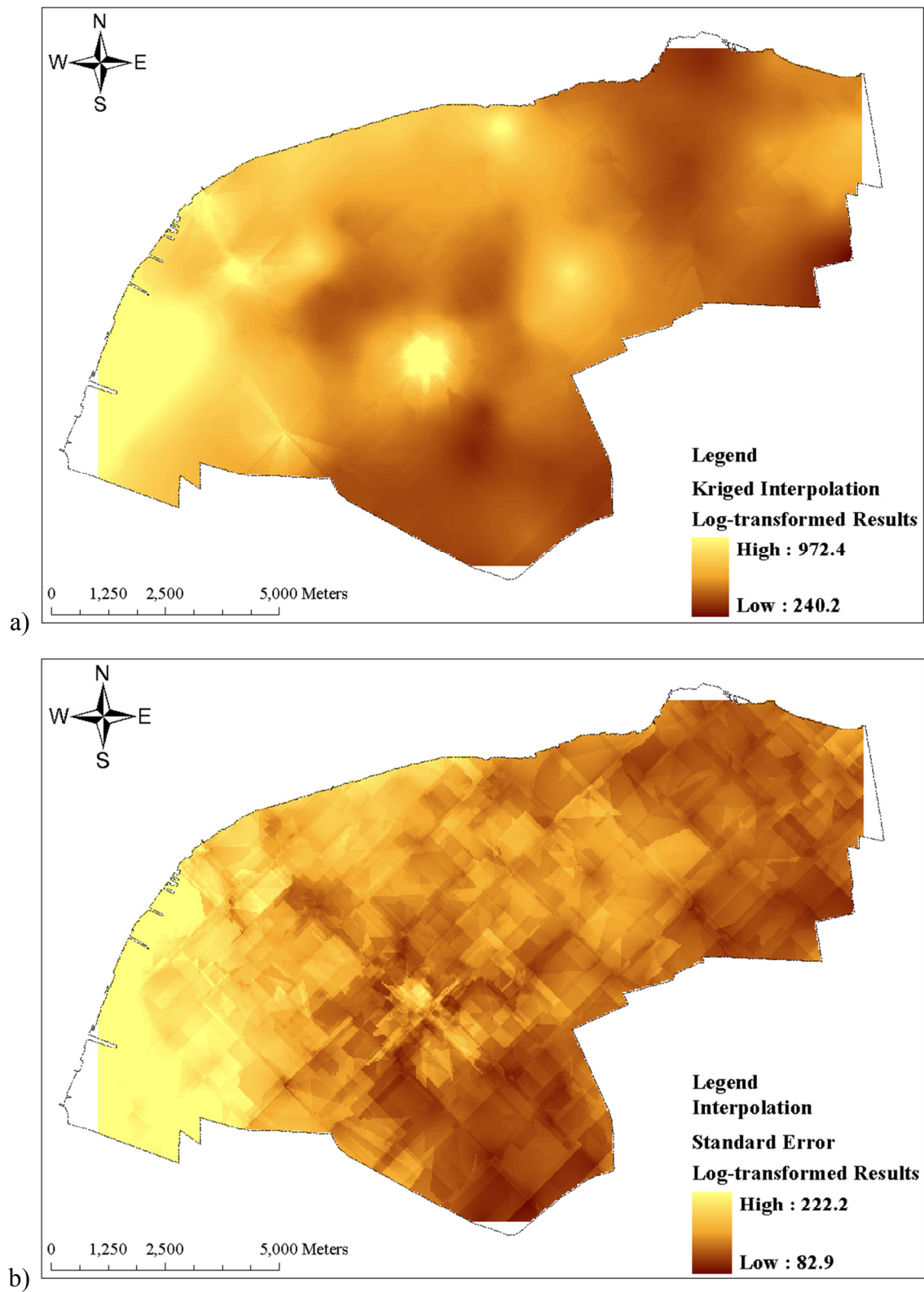


Figure 27 a) Interpolated (kriged) surface and b) prediction standard error maps of both (a) transect and (b,d,e) baseline log-transformed soil manganese concentrations.

2.3 Elevated soil manganese areas (extreme values)

2.3.1 (a) Transect

Ambassador Bridge area

Several transect samples were identified as extreme values in the preliminary soil survey, namely ABW-T1-4, ABW-T1-3, ABE-T1-1 and ABE-T2-1. To further investigate these extreme values, two additional samples (named e.g., ABW-T1-3B and -3C) were taken at each of these transect sites during the complete soil survey (August 2007). A duplicate sample was also taken of ABW-T1-4 (1163 ppm) (ABW-T1-4Dup). This duplicate had a soil manganese concentration of 924 ppm, while the two additional ABW-T1-4 samples, B and C, had manganese concentrations of 1220 and 979 ppm, respectively. The ABW-T1-4 site ($n = 4$) therefore had an average soil manganese of 1163 ± 276 ppm. A soil core was also retrieved from this elevated soil manganese site. This soil core represented a depth of 0 to 19 cm and was sliced into four sections. The average soil manganese concentration of this soil core was 1315 ± 25 ppm (Appendix H). The transect sites nearest to the elevated ABW-T1-4 site were ABW-T1-5, (approximately 6 m west) and ABW-T1-3.1 (approximately 5 m east). Their soil manganese concentrations were 695 ± 42.6 and 539 ± 55.5 ppm, respectively ($n = 3$).

The duplicate samples of ABW-T1-3 (1100 ppm) had soil manganese concentrations of 961 and 764 ppm, respectively which resulted in an average of 942 ± 169 ppm ($n = 3$) for this transect site. Two additional samples were also taken of the eastern transect extreme values, ABE-T1-1 and ABE-T2-1. However, due to their isolated location between the Ambassador Bridge fence and Huron Church Road, no additional sites could be sampled in close proximity to these sites to shed light on their elevated soil manganese levels. The B and C duplicates of ABE-T1-1 (1090 ppm) had similar soil manganese concentrations, 779 and 802, respectively. The average and standard deviation for this extreme value was 890 ± 173 ppm ($n = 3$). The duplicate soil samples of ABE-T2-1 (881 ppm) were found to contain 760 (B) and 940 (C) ppm of manganese resulting in an average manganese concentration of 860 ± 91.8 ppm for this transect site ($n = 3$).

The complete soil survey, as well as identifying the above mentioned ABW-T1-4 and -3 as elevated soil manganese sites, singled out the transect soil sample ABW-T1-13. This transect sample had a soil manganese concentration of 955 ppm and plotted above the upper transect soil boxplot whisker. The baseline soil sample ABW-BTW-T12 also had an elevated soil manganese concentration, 876 ppm. This soil sample was located between the Ambassador Bridge western transects T1 and T2, parallel to the ABW-T1-5.1 and ABW-T2-5 soil sampling sites. The former soil sample had a soil manganese concentration of 798 ppm, while the manganese levels of the latter were 538 ppm.

2.3.2 (b,d,e) Baseline

Devon-CN area

Two elevated soil manganese samples, IZB-B and I-ZB-E, of the Devon-CN area of Windsor were identified during the preliminary soil survey (section 1.0) (Figure 28). An additional 33 soil samples were taken from the area surrounding these samples (Figure 29). The IZB-group of samples extended up to a distance of approximately 2 km around the Devon-CN industrial zone (IZB). Three of the additional samples, I-ZB-40, I-ZB-41 and I-ZB-42, also showed elevated soil manganese concentrations (1260, 1330, and 3430 ppm, respectively). These samples were located in very close proximity to the original elevated samples (I-ZB-B and I-ZB-E) and consequently to the industrial zone.

Figure 29 shows the spatial distribution of all IZB-group samples. Samples located north and south of the IZB compound (I-ZB-7 and I-ZB-1) had relatively low soil manganese concentrations, 342 ppm and 310 ppm, respectively. Similarly I-ZB-32 and I-ZB-4, samples located immediately west (~300 m) of an industrial compound, had manganese levels of 475 and 515 ppm, respectively. I-ZB-A, a soil sample from the preliminary survey which was located near I-ZB-B had a high soil manganese concentration of 793 ppm. I-ZB-13 located approximately 0.9 km west of the IZB grounds had a soil manganese concentration higher than the baseline average, namely 640 ppm. IZB samples taken immediately east (~300 m) of the industrial compound had between 508 and 616 ppm of manganese while farther east (~1 km) those levels decreased to approximately 300 to 400 ppm.

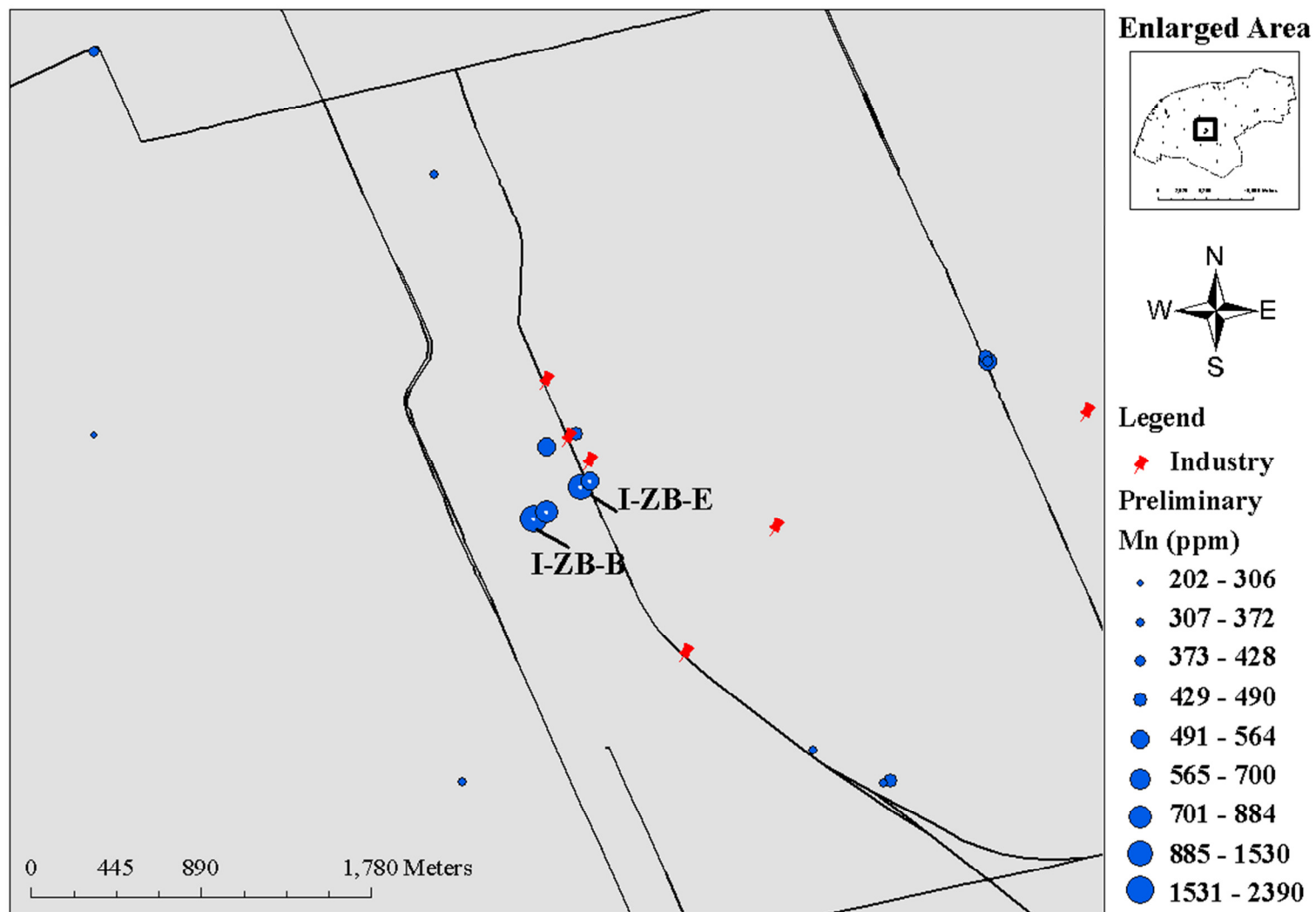


Figure 28 Spatial distribution map of the preliminary soil survey manganese concentrations in the Devon-CN area of Windsor. (IZB samples are represented by blue symbols with white centers.)

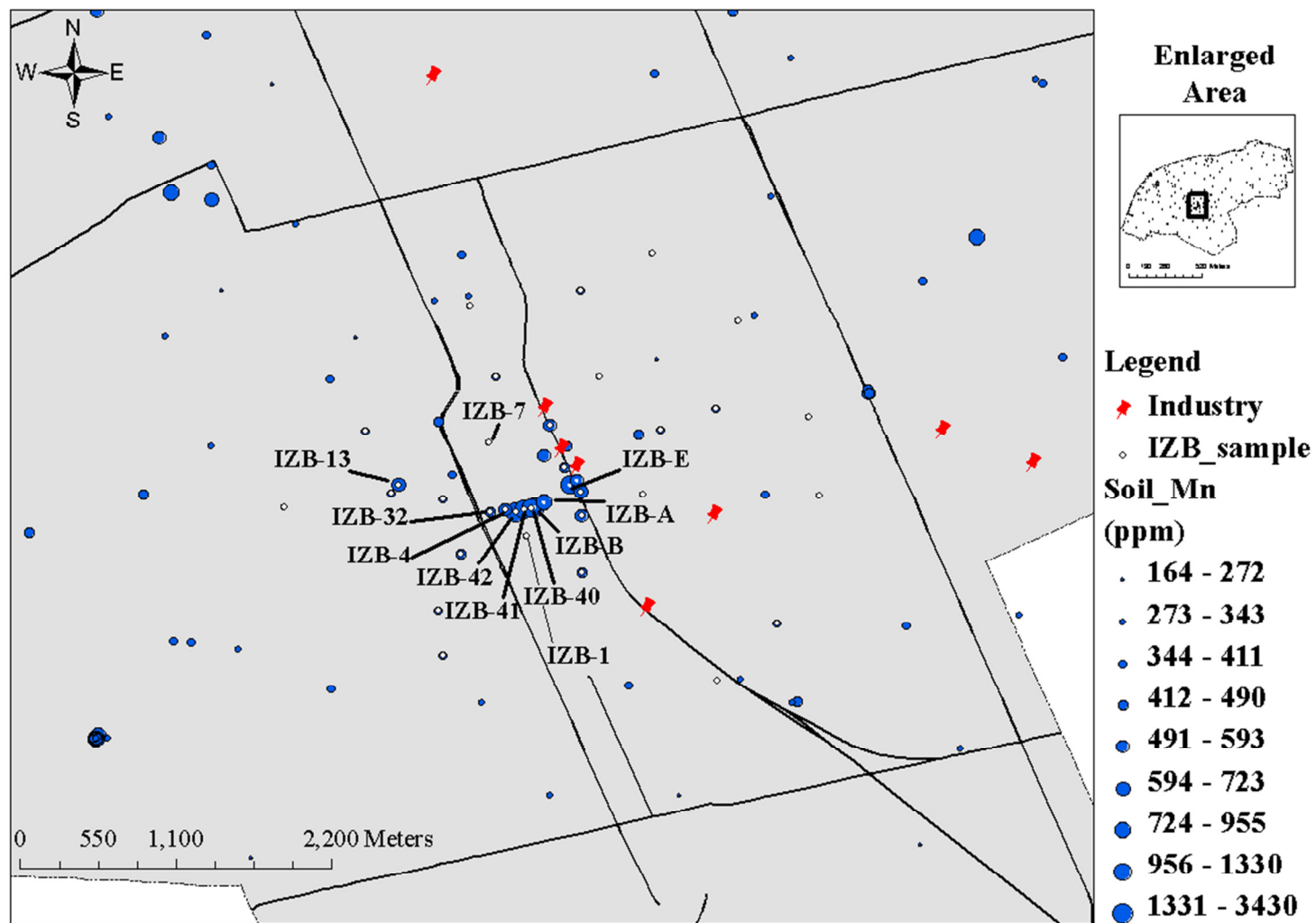


Figure 29 Spatial distribution map of the complete soil survey manganese concentrations in the Devon-CN area of Windsor. The IZB-group samples are represented by blue symbols with white centers. The purely blue symbols are other complete soil survey samples.

HS-Q

A baseline sample, which belonged to the 'random' soil sample type, HS-Q, was identified as an area of elevated soil manganese, 880 ppm (section 1.0). In August 2007, a duplicate sample was taken as well as 10 additional samples located in the immediate vicinity of the original sample in order to further investigate the source of high manganese in this area (Figure 30). The duplicate HS-Q soil sample had a manganese concentration of 746 ppm, therefore the average of this site was 815 ppm. HS-Q2, -Q3, -Q4, and -Q5 which surrounded the original HS-Q soil sample east, north, west and south, respectively, had soil manganese levels between 532 ppm and 656 ppm. Farther east, HS-Q8 was also within this range, 635 ppm. Samples farther west, HS-Q6 and -Q7, and northeast, -Q9, and -Q9Dup, had lower soil manganese concentrations, between 300 and 400 ppm. HS-Q10, which is located over 15 m northeast from the original HS-Q sample location, had a soil manganese concentration of 947 ppm.

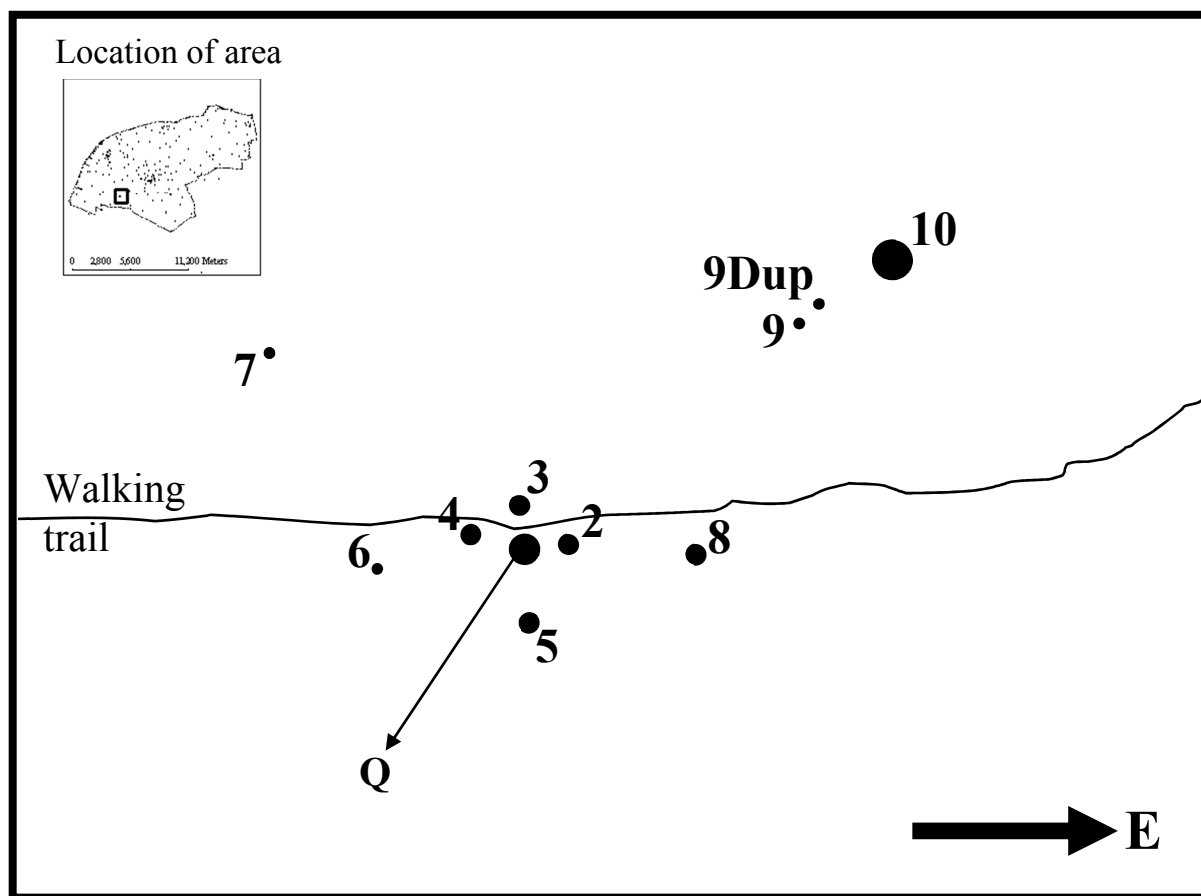


Figure 30 Schematic representation of the spatial distribution of the HS-Q-group of samples.

Miscellaneous samples

A random baseline soil sample, HS-R3, from the north-central area of Windsor, was identified by the complete soil survey baseline boxplot as an extreme value. It had a soil manganese concentration of 1070 ppm. Several other baseline soil samples were located near this extreme value. Baseline sample I-FD-D was east of this location and had a soil manganese concentration of 279 ppm. Two other soil samples, I-FD-C and HS-QQQ (unrelated to the HS-Q-group of samples), west of the extreme value sampling site, had 398 and 444 ppm soil manganese concentrations, respectively. Located approximately 255 m south of HS-R3 was the baseline soil sample I-FD-E which had a soil manganese concentration of 290 ppm.

Baseline soil samples I-ZB-12 and HS-E4 both plotted below the lower boxplot whisker. The I-ZB-12 soil sample had a soil manganese concentration of 164 ppm. The soil samples nearest to its location were DGLN (357 ppm) and HS-SS (208 ppm) to the west and I-FB-C (325 ppm) to the east. Located southeast were I-FB-A (449 ppm) and -B (339 ppm) samples. Still farther east was I-ZB-25 which had a soil manganese concentration of 398 ppm. The second baseline sample with a low soil manganese level was HS-E4 (176 ppm). The nearest samples to this baseline soil sampling site were HS-F4 to the north and HS-G4 to the west which had soil manganese concentrations of 316 ppm and 269 ppm, respectively.

The complete soil survey also identified a random baseline soil sample, ABW-BTW-T12, as an extreme value. Due to its location amongst the Ambassador Bridge transects, it was discussed in the transect section (2.3.1).

4.0 Characterization of urban Windsor surface soil

4.1 pH and carbon content

The pH of the soil in Windsor was determined by analysis of a subsample of soil samples from both the preliminary and complete soil surveys. These included soils from a variety of locations across Windsor, including a natural site. The average soil pH was found to be 7.4 for both transect ($n = 86$) and baseline ($n = 58$) soils. The pH analysis of the two natural soil samples averaged 8.2.

The soil carbon content (total, organic, and inorganic) was determined for all soil sample types. The average total carbon (TC) content for the transect, baseline and natural soils (Table 14) were significantly different ($H(2) = 46.21, p < .05$). Due to the small sample size and time restrictions, a subsample of 19 transect, 51 baseline and 6 natural soil samples were used for the total inorganic carbon (TIC) analysis. A little over half of the baseline, 7 of the transect and one of the natural soil samples were below the instrument's TIC measurement detection limit (0.48 %). The results below this limit were substituted with $\frac{1}{2}$ the LOD value (i.e., 0.24 %). The natural soil contained significantly ($H(2) = 6.11, p < .05$) more inorganic carbon than the transect and baseline soils (Table 14). The total organic

carbon (TOC) results of the transect, baseline and natural soil sample types were determined by subtraction and were significantly different ($H(2) = 17.25, p < .05$) from one another.

Table 14 (a) Transect, (b,d,e) baseline and (c) natural soil sample type carbon contents (total (TC), inorganic (TIC) and organic (TOC)).

Sample Type	n	TC (%)	n	TC (%)	TIC (%)	TOC (%)
Transect	99	7.3 ± 1.6	19	7.7 ± 2.1	1.2 ± 0.9	6.5 ± 1.6
Baseline	219	6.5 ± 2.7	51	7.4 ± 3.5	1.2 ± 1.9	6.1 ± 3.0
Natural	13	2.8 ± 1.6	6	3.2 ± 1.3	2.3 ± 1.4	0.97 ± 0.39

4.2 Synchrotron-based solid-phase manganese speciation at the grain-scale

Three soil samples, one from each sample type ((a) transect, (b,d,e) baseline and (c) natural), namely ABW-T1-4, I-ZB-B and FSV45, were chosen for synchrotron-based μ -XRF and μ -XRD analysis using the National Synchrotron Light Source of the Brookhaven National Laboratory in Upton, New York (USA). Subsequent data reduction and interpretation was done by Dr. Stephen R. Walker at Queen's University in Kingston, Ontario. The soil samples used were dried and sieved to less than $< 63 \mu\text{m}$. ABW-T1-4 had one of the highest soil manganese concentrations of the transect soil samples, near the Ambassador Bridge. The June 2007 triplicate sample was used. Similarly, I-ZB-B was chosen because it was the highest soil manganese concentration of the baseline soil samples. It was therefore chosen as an anomalous sample, as defined by the baseline soil survey, and to characterise the elevated manganese particles caused by industrial sources of the Devon-CN area. The natural soil sample representative, FSV45, was chosen for manganese speciation because it was within one standard deviation of the average natural soil manganese concentration, and, due to both its location and depth, it was thought to be a relatively untouched natural soil sample.

Note: The following descriptions and terms are based on the report by Walker (2010).

4.2.1 General observations

A manganese XRF signal was detected in all of the three sample maps, always in combination with other elements. A strong and abundant iron XRF signal was also produced in all sample maps and manganese was consequently always found in combination with iron. All three Windsor soil samples contained Mn-rich hot spots in intensities from the thousands to the tens of thousands counts per second (cps) (Figure 31). Each sample also contained many particles of “lower apparent concentrations”, down to trace amounts (i.e., tens of cps) (Figure 31) (Walker, 2010).

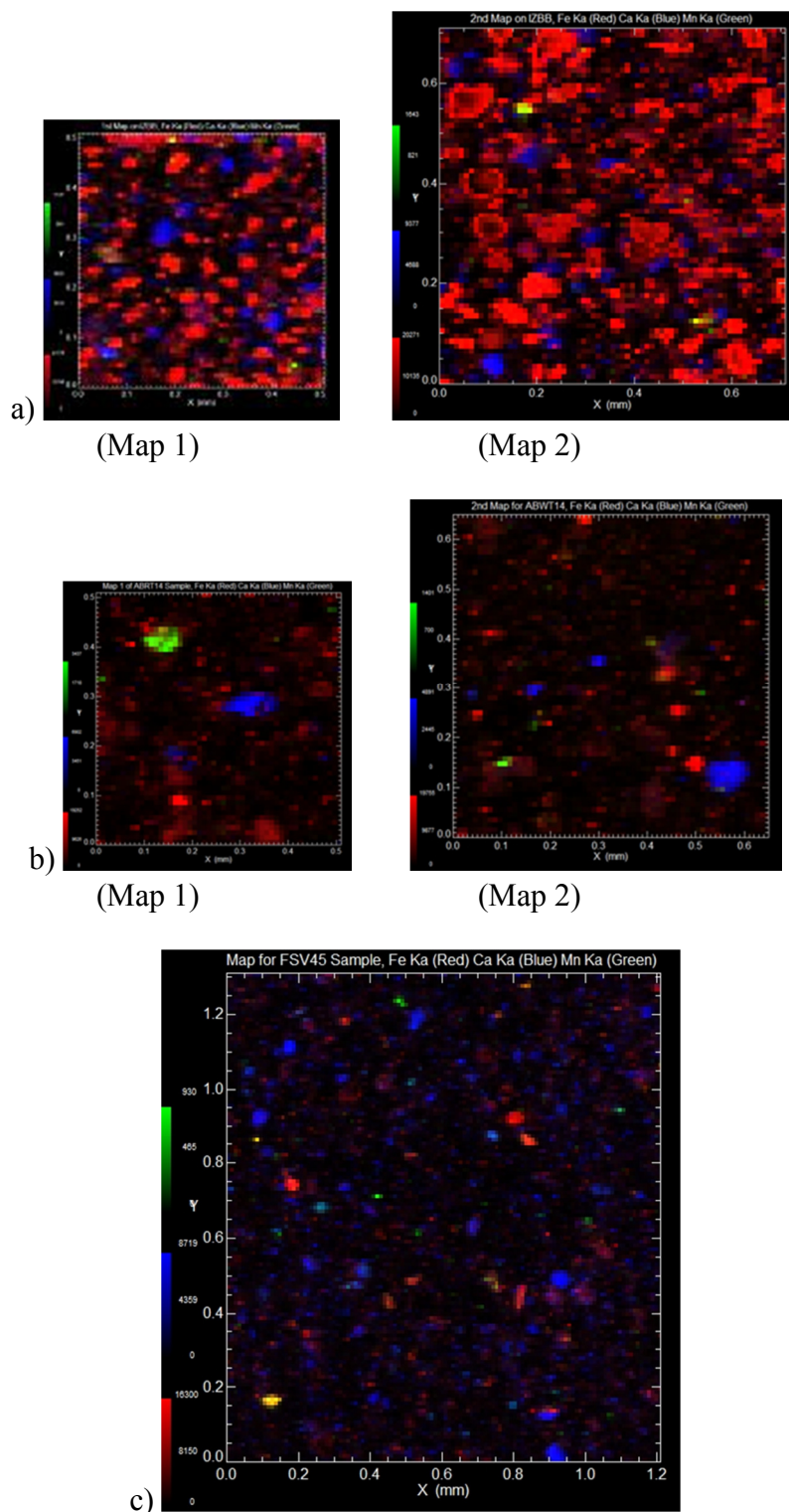


Figure 31 XRF mapping for a) I-ZB-B, b) ABW-T1-4, and c) FSV45 for Fe (red), Ca (blue) and Mn (green). Note: Due to scaling, high Mn regions may contain some Ca or Fe. All maps were plotted at equivalent X, Y, Z scale. Z = 80 % full scale to highlight weaker regions. (Figure by Dr. S. Walker (2010) (Used with permission).)

Based on the element distribution maps, all three soil samples had similar apparent grain size distributions. The maximum observed grain size was approximately 100 μm except for the FSV45 sample whose maximum observed grain size was less than 50 μm in diameter. The soil sample I-ZB-B appeared to have the highest content of coarse grains ranging from 40 to 80 μm in diameter.

4.2.2 Manganese speciation based on combined $\mu\text{-XRD}$ and $\mu\text{-XRF}$ analyses

4.2.2.1 (a) Transect - ABW-T1-4

Manganese-rich grains in this transect sample appeared to be aggregate grains whose composition consisted of: 1) finely crystalline 10Å phyllosilicates (spotty rings), 2) very fine to nano-crystalline clay minerals (smooth rings), and 3) very fine to nanocrystalline Fe-oxyhydroxides and Mn-oxyhydroxides (smooth rings) (Figure 32) (Walker, 2010). Since similar composite grains (phyllosilicate, clay minerals and Fe-oxyhydroxides) were also found that had a trace to low manganese content, the “associations of manganese with the phyllosilicates and clay minerals appeared to be a physical one rather than chemical or mineralogical” (Walker, 2010). The origin of the manganese was assumed not to be the primary phyllosilicates themselves due to the presence of these similar but lower content manganese grains. According to Walker (2010), “significant manganese substitution is generally rare in the mica group minerals that the $\mu\text{-XRD}$ patterns most closely reflect”.

The spotty-ringed phyllosilicate XRD patterns appeared to fit best a muscovite-type phyllosilicate. However, due to its spotty nature and the consistent association of these grains with iron, it could also be from the biotite group of micas. The poorly crystalline Fe-oxyhydroxide (nanocrystalline goethite) and Mn-oxyhydroxide (phylломanganate) had much weaker diffraction patterns than the phyllosilicate and clay mineral. The nearly amorphous nature of the oxyhydroxides or their low abundance and weak diffraction, may have been obscuring them in the background of the stronger diffraction. Only the high-manganese composite grains had XRD patterns which could clearly be identified as probable Mn-oxyhydroxide phases (e.g., phylломanganate). Walker’s (2010) interpretation of the difference in the manganese content of the similar composite grains (phyllosilicate, clay

minerals, and Fe-oxyhydroxide) was that the low manganese content grains were more likely not to contain distinct Mn-oxyhydroxide phases but that the manganese was incorporated into the Fe-oxyhydroxide phase of the composite grains. Less abundant than the I-ZB-B sample, distinct Fe-rich particles in the ABW-T1-4 sample also contained minor to trace manganese. The iron particles were identified as ferrihydrite (2-line variety) and mixtures of lepidocrocite and goethite. Walker (2010) also noted that the relationship between phyllosilicates and Mn-Fe oxyhydroxide minerals was suggestive of a precipitation process involving microbially mediated mechanisms.

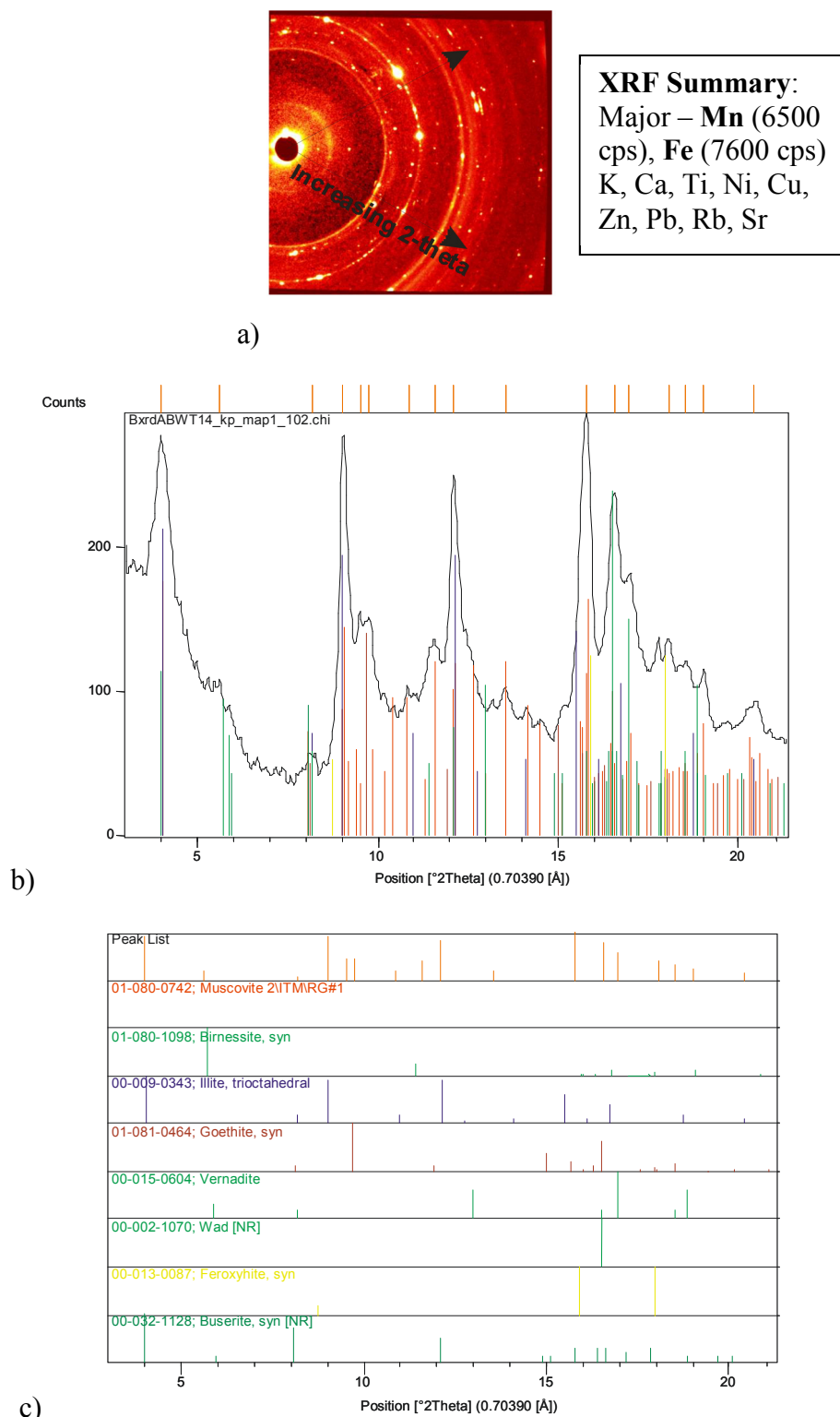


Figure 32 a) 2D-μXRD pattern of Mn- and Fe-rich grain in ABW-T1-4 (image was flipped from source for presentation purposes) and associated and background elements; b) Integrated XRD pattern (spots masked); c) Peak listing of selected phases from ICDD database. (Figure by Dr. S. Walker (2010) (Used with permission).)

4.2.2.2 (b,d,e) Baseline - I-ZB-B

Spectrum maps of this baseline soil sample were dominated by a large abundance of Fe-rich grains. These grains were apparently related to corrosion products of iron and steel (Walker, 2010). Remnants of these products remain in the soil. The two-dimensional micro-XRD pattern in Figure 33b indicates a grain of steel alloyed with minor amounts of chromium and manganese. Furthermore, Figure 33d shows the 2D- μ XRD pattern of a grain of mullite which is a rare mineral in nature (Schneider, 2005; Wenk and Bulakh, 2005) but relatively common aluminosilicate product in various high temperature melting and firing processes. (Berry and Mason, 1959; Wenk and Bulakh, 2005; Walker, 2010). All of the iron grains in this baseline soil sample were associated with manganese, whose content ranged from trace to minor. Due to their high abundance in this sample, these Fe-rich grains were an important source of manganese. Less abundant were Fe-Mn grains with high manganese content. These were related to mixtures of carbonates (e.g., dolomite) and Fe-oxyhydroxides. It is unknown which member of this mixture that manganese forms its association.

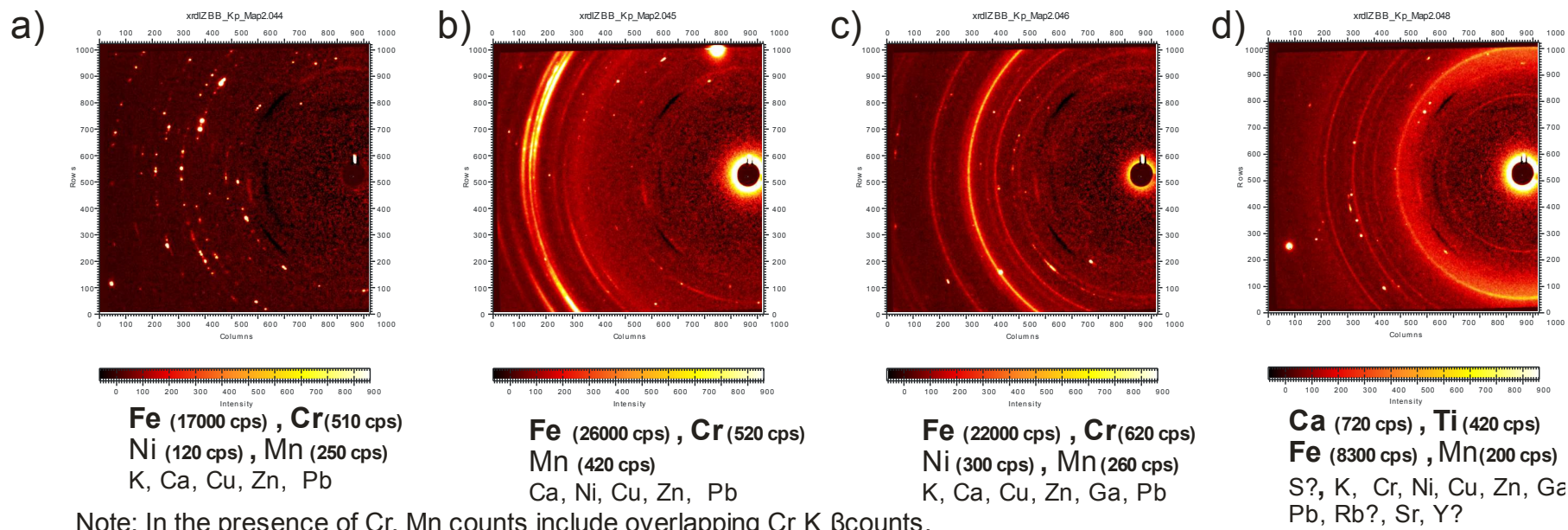


Figure 33 2D-μXRD patterns for Fe-rich grains of the I-ZB-B soil sample with associated and background elements. “a) Bright spotty rings of relatively coarse (micron to sub-micron) crystallites of hematite ($\alpha\text{Fe}_2\text{O}_3$) with associated Cr, Ni and Mn. b) Smooth arcs fit two types of Fe (alpha-iron and martensite) and cementite (Fe_3C) indicating a steel alloyed with minor amount of Cr and Mn. c) Smooth rings are nano-crystalline maghemite with associated Cr, Ni and Mn. d) Smooth rings are mullite (e.g. $\text{Al}_6\text{Si}_2\text{O}_{13}$ or $\text{Al}_{(4+2x)}\text{Si}_{(2-2x)}\text{O}_{(10-x)}$ where $x = 0.17$ to 0.59) typically a high performance ceramic and refractory” (Walker, 2010). (Figure by Dr. S. Walker (2010) (Used with permission).)

4.2.2.3 (c) Natural - FSV45

The natural sample had less distinct manganese associations in the XRF map than the other two Windsor soil samples. The association between manganese and the phyllosilicates appeared again, though their specific form was unclear. Iron was typically less abundant in this sample. However, minor amounts of manganese were again found associated with distinct Fe-rich grains. Nanocrystalline goethite was also observed in the sample. One large, non-diffracting, Fe-rich grain with minor manganese content was most likely a coarsely crystalline grain, possibly a primary silicate containing iron and manganese. A Ca-rich grain with minor amounts of manganese and iron, whose diffraction was not definitive, may have been a coarsely crystalline carbonate (e.g., carbonate). The only direct evidence of anthropogenic influence on this natural soil sample was observed by the presence of steel particles.

Discussion

Transect Soil

A large portion of the soil samples taken during the preliminary soil survey were from transects perpendicular to the Ambassador Bridge in order to test the hypothesis that vehicular sources were responsible for soil manganese levels in this area. These transects were extended (i.e., additional samples were retrieved) and statistical tests showed that the transect soil sample type of the complete soil survey was different from the baseline soil sample type. The median transect soil manganese was 553 ppm (range = 361 to 1163 ppm). This soil manganese level was very similar to mean Ontario soil manganese concentrations found by Frank et al. (1976), McKeague and Wolynetz (1980) and by the Ontario Ministry of the Environment (1993) (These studies are discussed in detail below in the Baseline soil section). The transect median was also quite similar to soil manganese results of Montréal- and Toronto-based studies.

Forget et al. (1994) found an average soil manganese concentration of 524 µg/g in a study of the Montréal Botanical Gardens. This result was an average of the soil levels of both their high (n = 12) and low (n = 6) exposure sites. While evaluating the potential of

using dandelions as potential bioindicators of manganese soil contamination, Normandin et al. (1999) found 734 (± 92) ppm and 768 (± 15) ppm of manganese in soil 10 and 50 m from an important highway in Montréal, respectively and 523 (± 28) ppm, 100 m from the highway. Boudissa et al. (2006) investigated soil manganese levels near a closed ferroalloy plant near Montréal, QC and found levels from 3000 to 266 000 ppm. Bhuie et al. (2000) and Bhuie and Roy (2001) reported soil manganese concentrations found near highways in the Toronto area. Bhuie et al. (2000) found an average of 667 ppm at one site and 688 ppm at another. In their 2001 article, Bhuie and Roy reported soil manganese concentrations between 541 and 583 ppm for three of their four sites and 261 ppm for their fourth. This similarity between the Windsor transect soil manganese results and the Montréal and Toronto studies may be due to the fact that these latter studies were also located near high-density traffic highways.

Site variability

The variability within the transect sites was less than the variability between the sites. It appears that the larger of the within-site variability of the transect samples was due to the different sampling times of the sample triplicates. This temporal effect of the J/A samples on the transect soil manganese concentration was not large enough to affect the overall pattern of transect soil concentrations. In fact, these J/A samples had high variability even when only the August duplicates were considered, suggesting that there was inherent soil manganese variability. In future studies, when a temporal component is used in sampling, it is recommended not to rely solely on GPS coordinates but to clearly identify sample locations in the field (e.g., a marker).

Elevated soil manganese areas

Elevated areas of transect soil manganese were found in both the western and eastern soil transects. There was no clear decrease in soil manganese levels with increasing distance away from the bridge as would be expected if vehicular emissions from the Ambassador Bridge traffic were the dominant source of soil manganese in this area. The elevated transect soil manganese concentrations of the Ambassador Bridge area, in general, were on the western side of the bridge. The second transects were the exception where the eastern had

higher soil manganese levels than the western. A possible explanation for this difference is the location of the western T2 transect. For a long period of time, the majority of the sites of this transect were covered beneath buildings which stood on this location up until 1992 (Figure 34). Contrary to WT2, the second eastern transect soil has been a park for many years and was undeveloped land before that. Therefore the surface soil of the second eastern transect had been accumulating manganese from various environmental sources long before the sites of the second western transect.

The most important western transect site was ABW-T1-4. Both the additional and duplicate soil samples of this transect soil sample had similarly elevated manganese concentrations (stdev = 276 ppm), confirming it was an elevated soil manganese site. Transect soil samples nearest to this elevated site (ABW-T1-3.1 and ABW-T1-5) were below the 95th transect percentile manganese concentration (860 ppm). However, the soil manganese concentration of ABW-T1-3, which was located 10.4 m east of ABW-T1-4, was identified as an elevated soil manganese sample of the complete soil survey and exceeded the 95th transect percentile value. The soil core retrieved from this site also confirmed its elevated soil manganese status and showed that these levels were not only superficial in nature but extended at least 20 cm in depth suggesting this soil manganese contamination was historical. The western side of the Ambassador Bridge had two other soil samples which exceeded the upper transect percentile value, ABW-T1-13 and ABW-BTW-T12. The former transect soil site was located 56 m away from ABW-T1-4, and 91 m away from the bridge, along the same transect. The latter soil sample, which was considered a “random” baseline soil sample but was located between the first and second western transects, was one of the baseline soil samples that was identified as an extreme value by the preliminary and/or complete soil survey baseline boxplot and it also exceeded the 95th baseline soil percentile (806 ppm).

These elevated transect soil manganese sites were located north of the western T2 transect and west of the bridge. Their somewhat discontinuous pattern of soil manganese contamination would suggest a source other than vehicular emissions which would deposit decreasing soil manganese amount with increasing distance from the bridge. There was

evidence that heavy machinery was being operated in the area of the field where ABW-T1-3 and -4 were located. However, the ABW-T1-3.1 site was less than the median transect soil manganese concentration and was located between these two sites, it is more likely that the source of these elevated manganese sites is historical. The uniformity of the elevated soil manganese depth profile found at the ABW-T1-4 site would support the conclusion that the source of manganese in this area occurred over a long period of time. Historical air photos of this area, for the period of 1931 to 1988, indicate that some kind of commercial business operated on this land. Figure 34 shows a close-up of one such air photo where a large building can be seen where the first western AB transect would later be located and several cars are visible. A later 1992 air photo shows an empty lot which probably indicates the time when the Ambassador Bridge Company purchased the land and before the University of Windsor parking lot was opened (Appendix I). The lower soil manganese levels of the western Ambassador Bridge T2 sites may be because these were covered by several buildings during the time period previously stated. In fact, the presence of these buildings was detected in air photos from 1931 to 1988 except for the large building (X on Figure 34) which appeared later on. Future investigations of other elements in transect soil may reveal additional evidence supporting the conclusion that the source of elevated soil manganese in this area was legacy.



Figure 34 Air photograph of western side of Ambassador Bridge, circa 1988 (inset: circa 2010). (Source: National Air Photo Library; inset: Google Earth[®])

ABE-T1-1 and ABE-T2-1 were also singled out as elevated areas of soil manganese in the preliminary soil survey because their soil manganese results exceeded the “mean + 1 σ ” limit. These transect soil sites did not meet the criteria for extreme values of the complete soil survey, i.e., they did not plot above the upper transect boxplot whisker. They did however exceed the 95th transect soil percentile value and so deserve a brief scrutiny. If these higher concentrations were due to erosion of the bridge falling on the soil directly next to it, debris would be expected to fall more-or-less equally on both sides of the bridge, therefore the first samples of both the western and eastern transects should have had similar elevated soil manganese levels. However the western soil sites directly next to the bridge, ABW-T1-1 and ABW-T2-1, had relatively low soil manganese concentrations. The eastern samples, T1-1 and T2-1, had higher soil manganese concentrations than the remainder of their respective transects indicating the presence of a source of elevated soil manganese. One possible source is the manganese-bearing particles produced by repair activities conducted underneath the bridge which may have been preferentially blown onto the eastern side of the bridge by westerly winds. Another possible source of manganese is vehicular emissions from traffic travelling along Huron Church Road and at the intersection with University Avenue (between 4500 to 10350 vehicles/day (The City of Windsor Ontario, 2009)). Then we would expect the second soil sites on the other side of the Huron Church Road to also have elevated soil manganese, which is not the case. Therefore the source of elevated soil manganese at these individual locations is unknown although their location directly next to the bridge would suggest the source is related to the bridge and/or its activities.

Baseline Soil

The baseline soil represented three sample types (industrial, random and biomonitoring station soils). The urban Windsor baseline soil manganese concentration found in the present study (median = 385 ppm; range = 164 to 3430 ppm) is lower than what other studies have found elsewhere. For instance, a survey of uncultivated surface soils across Canada revealed soil manganese concentrations ranging from 100 to 1200 ppm, with a mean of 520 ppm (McKeague and Wolynetz, 1980). The same study also looked at the soil manganese concentration of the different Canadian physiographic regions, including the St.

Lawrence Lowlands, which includes the county of Essex and consequently the city of Windsor. The same authors reported a mean soil manganese concentration of 660 ± 73.5 ppm ($n = 40$) for the area. In an older study, Frank et al. (1976) carried out an agricultural soil survey of 34 out of the 42 counties in Ontario and found that clay soils had an average soil manganese concentration of 662 ± 469 ppm ($n = 60$). The soil manganese concentration for all agricultural soils (organic, sandy, loam, and clay) was slightly lower than the clay soil value, 530 ± 531 ppm ($n = 296$). The range of soil manganese concentration was similar for clay and agricultural soil types, 140 to 3000 ppm (Frank et al., 1976). Finally, the Ontario Ministry of the Environment (OMOE) (1993) reported a typical range (OTR) of manganese in “old (> 40 years) urban parkland” Ontario soil up to 1300 $\mu\text{g/g}$ ($\text{CV} = 16\%$), with an approximate mean of 600 $\mu\text{g/g}$. The OTR for rural parkland was 2200 $\mu\text{g/g}$ with an approximate mean of 850 $\mu\text{g/g}$. The OMOE defined parkland as land which is not residential, commercial, industrial, agricultural nor is it for transportation; it includes parks, cemeteries, schools, forests, woodlots, and undeveloped areas (OMOE, 1993). All of these studies indicate that the soil in Windsor is expected to have manganese levels of approximately 600 ppm.

Some differences between the Ontario-based studies and the Windsor results were expected because of 1) sampled density; 2) the differences between land uses (i.e., urban, agricultural, uncultivated or parkland); and 3) the inherent differences between soils. For example, the sample density of the study in the city of Windsor is much higher than the other studies ($n = 219$ samples / 147 km^2). The soil manganese result of the Frank et al. (1976) study represented clay agricultural soils ($n = 60$) from across Ontario whereas the McKeague and Wolynetz (1980) study of the St. Lawrence Lowlands characterized 40 samples in a region spanning several $100\,000 \text{ km}^2$. The soil manganese concentration reported by the OMOE (1993), was calculated based on 60 samples from an area bounded by the following Ontario counties: Prescott-Russell (East), Essex (West), Muskoka and Haliburton (North), and the northern shores of Lakes Ontario and Erie (South). The variability of the mean reported by Frank et al. (1976) was quite high, as was the average variability around the OMOE’s value, which was among the higher variabilities of all elements reported by the OMOE report (1993).

The Windsor baseline soil manganese concentration was quite similar to soil manganese levels found near a Coniston smelter, east of Sudbury, Ontario. Hutchinson and Whitby (1974) found an average of 250 ppm ($n = 14$) of manganese along a transect extending away from the smelter. Hazlett et al. (1984) found similarly low soil manganese concentrations. McKeague and Wolynetz (1980) reported a mean soil manganese concentration for the Canadian Shield physiographic region, on which Sudbury Ontario lies, of 430 ppm ($n = 12$). Despite this similarity between Windsor and Coniston soil, the uncultivated soil of the St. Lawrence Lowlands was significantly different ($p = 0.05$) from the Canadian Shield soil (McKeague and Wolynetz, 1980). Therefore the results of the Sudbury area should be used with caution in comparison with the Windsor baseline soil manganese results. It would therefore be preferable to compare the levels of soil manganese found in Windsor to other urban centres of the same physiographic region, for example Montréal and/or Toronto. Mean soil manganese levels found in Montréal and Toronto by Forget et al. (1994), Normandin et al. (1999), Boudissa et al. (2006), Bhuie et al. (2000) and Bhuie and Roy (2001) (discussed above) were higher than the baseline soil manganese median. The difference between these urban city centres may be due to the focus of the studies. The Montréal and Toronto studies (with the exception of Boudissa et al. (2006)) were concentrated around heavy traffic areas, whereas the Windsor baseline soil samples were from a variety of locations from across the city. The majority of the Windsor soil manganese results were not even remotely near the levels found by Boudissa et al. (2006). The highest soil manganese concentration found in this Windsor study, 3430 ppm, was only slightly higher than the lowest soil manganese level found by Boudissa et al. (2006), 3079 ± 843 ppm. The Windsor urban baseline soil manganese median concentration was within the normal average soil manganese concentration range for this area according to past Ontario-based soil geochemistry surveys (Frank et al., 1976; McKeague and Wolynetz, 1980; Ontario Ministry of Environment, 1993).

The worldwide mean soil manganese levels are varied (Chapter 1). Shacklette and Boerngen (1984) conducted a study which lasted 14 years and found a geometric mean for soil manganese of the conterminous United States to be 330 ± 2.77 ppm ($n = 1317$) and an

arithmetic mean of 550 ppm (range < 2 to 7000 ppm). Chen et al. (1991) found an average soil manganese concentration of 582 µg/g (n = 3990), and a geometric mean of 432 µg/g, in a large-scale geochemical survey of China. Adriano (2001) reported a study of soils by Krupskiy et al. (1978) which found a mean soil manganese concentration of 740 ppm (range 472 to 1250 ppm) in central Russia, whereas McKeague and Wolynetz (1980) warn that “world means for some elements probably differ from Canadian means because our soils are only slightly weathered relative to soils developed in ancient materials”.

Elevated areas of soil manganese

The preliminary soil survey identified an elevated soil manganese sample near a manganese-emitting industry (recycling facility) in the Devon-CN area. This soil manganese concentration exceeded the 95th baseline soil percentile value. In a two kilometre radius around this industry, baseline soil sample manganese levels revealed low concentrations (less than the 95th baseline soil percentile value (806 ppm)) except for the samples immediately next to the industry. This manganese-emitting industry (IZB) is located directly North of an E.C. Row expressway on-ramp (average 10200/day; based on 1999 and 2004 data (The City of Windsor Ontario, 2009)) and east of active train tracks. A visual observation of this commercial and industrial area showed a red dust which no doubt emanated from this recycling industry and covered the sidewalks and streets of the surrounding area. The dust was ingrained into the concrete and asphalt, it was not mixed into the cement since traffic tire tracks were visible on the major street, much like tire tracks in the snow. There was a small dirt road between the expressway's and the industry's fences with lots of foliage and where large metallic debris (e.g., car frame, rusty metal) was found littering the side of the dirt road. The I-ZB-B soil sample was taken where this dirt road and Grand Marais Road East intersect. The other elevated sample, I-ZB-E, was retrieved from the southwest corner of the intersection between Grand Marais Road East and Howard Avenue. The three additional IZB samples, (complete soil survey) which were identified as elevated samples and were also well above the 95th baseline soil percentile value were retrieved along the dirt road between I-ZB-B and the train tracks (Figure 29). The manganese concentration was highest in the soil sample taken directly next to the train tracks. This sample was brick-red in colour. The elevated soil manganese contamination of this industrial zone appears to be localized to the

area along the dirt road and next to the train tracks. The source of these elevated soil manganese levels could be the industry located nearby, the activity of the train tracks or other legacy industrial sources but most likely is a result of a combination of all, or some of these sources. I-ZB-A was a preliminary soil survey sample taken just outside the fence of the IZB industry. Its soil manganese level was almost equal to the upper baseline soil percentile value. However, compared to the other elevated soil manganese IZB sites, this sample site was covered with grass. The slightly higher than baseline median soil manganese concentrations of the areas directly west and east of the industry may suggest that some transport of the emitted manganese from this industry to the surrounding areas is occurring. These soil manganese levels however did not exceed the 95th baseline soil percentile value (806 ppm). The soil manganese concentrations appeared to start decreasing 1 km away from the manganese-emitting industry. The expressway in close proximity to these elevated soil manganese locations, has a large volume of vehicles (over 30 000/day) (The City of Windsor Ontario, 2009) in both east and western directions, but is an unlikely source of the elevated soil manganese, as the opposite side of the E.C. Row expressway does not have corresponding elevated soil manganese concentrations. A baseline soil sample was taken directly south of the E.C. Row Expressway, opposite to the IZB industry, which had an ICP-MS manganese result of approximate 300 ppm. Also as previously mentioned, the remainder of the soil samples surrounding this area, which included the E.C. Row expressway, were low (< 450 ppm).

The second baseline soil elevated manganese area, HS-Q group of samples, was located in a wooded area next to a residential community, west of Huron Church Road in the southwest corner of Windsor. Samples were taken on either side of a walking trail as well as in the immediate vicinity of the original HS-Q sample. The area had tall grasses, shrubbery and mature trees. The HS-Q sample duplicate was very close to the original sample's soil manganese concentration confirming the preliminary soil survey levels. The general pattern of soil manganese found in the vicinity of the original HS-Q sample was of decreasing soil manganese concentrations with increasing distance away from this sample. Samples immediately surrounding the original HS-Q sampling site (i.e., HS-Q2 to 5 and HS-Q8), were generally above the baseline soil median but were always within the 5th to 95th

percentile range. The samples further away (HS-Q6, -Q7 and -Q9) were less than or equal to the baseline soil median. Of the additional soil samples retrieved in August 2007, only HS-Q10, which was over 15 m away from the original elevated soil manganese sample, was also identified as an elevated manganese soil sample and exceeded the 95th baseline soil percentile value. The elevated soil manganese contamination of this area therefore appeared to be discontinuous. Upon observation of residential communities under construction in Windsor, it was observed that construction debris and soil was bulldozed into the edge of these communities which would correspond to the location of HS-Q group of samples. Upon further investigation of the HS-Q area, such debris was found in its vicinity. It is therefore very probable that the elevated soil manganese in this area (HS-Q) is due to buried construction debris from the construction of the nearby residential area. No other potential anthropogenic sources of manganese were found in this area.

A random baseline soil sample from the complete soil survey was also identified as an elevated manganese sample which exceeded the 95th baseline soil percentile value. HS-R3 was retrieved next to active train tracks adjacent to the A.H. Weeks Water Treatment Plant, located near Central Avenue and Wyandotte Street East. This soil sample was located amongst the IFD-group of industrial samples. These were taken to investigate an NPRI (Environment Canada, 2007) manganese-emitting industry during the preliminary soil survey. Possible sources of manganese in this area were the activities on the train track, the activities of the water treatment plant and/or emissions of the IFD industry. There was no obvious evidence of activities being conducted outside the perimeter of the water treatment plant. The IFD soil samples near the HS-R3 sample, as well as another random sample (HS-QQQ), were either slightly above or below the baseline soil median manganese concentration. This evidence suggests that this localized elevated soil manganese contamination was probably due to the activity on the train tracks. The HS-QQQ soil sample site (unrelated to the HS-Q group of samples) was retrieved next to the train tracks approximately 440 m away from HS-R3 in a grass covered area. Further soil investigation of the immediate area of HS-R3, and along the train tracks, may shed more light on the source of elevated manganese in this specific area.

The two baseline soil samples identified as low extreme values were both located in relatively undisturbed areas. I-ZB-12 was retrieved in tall grass next to train tracks near Howard Avenue and Maguire Street, south of the IZB industry. On the west side of the tracks, where I-ZB-12 was located, are residential areas with very large back yards and to the east of the tracks lies the Devonshire Mall and a small industrial area. Windsor soil sites located near I-ZB-12 included I-FB-C, -B and -A (east), DGLN (west), HS-SS (southwest) and I-ZB-25 (northeast). Their soil manganese concentrations were between 208 and 449 ppm. Historic aerial photos showed that this location has indeed been relatively undisturbed at least since 1931 (Appendix I). Similarly, HS-E4 was taken in tall grass located at the southwest corner of the intersection of Banwell Road and E.C. Row Expressway. Near the Twin Oaks Business Park, in the southwest corner of Windsor, it was surrounded by agricultural fields to the South and residential areas East, North and West. Only two baseline soil samples were located near this low extreme value, HS-F4 and HS-G4 which had 316 ppm and 269 ppm, respectively. HS-E4's location has also been left relatively undisturbed in the past (Appendix I). Elevated soil manganese levels were not expected at these baseline soil sample sites. They are located far away from any sources of manganese and the low soil manganese concentration of their neighbouring soil sample sites further indicates that these baseline soil samples were simply evidence of the inherently low soil manganese of this particular area of the city of Windsor. Future studies of urban Windsor soil should use the average of the transect and baseline 95th percentile values, 830 ppm, as a threshold value for determining which soil manganese concentrations are to be considered elevated.

Natural background

All of the natural soil sample type representatives (n = 14) had a clayey texture (Appendix H) which corresponds to the major geological unit underlying the city of Windsor (Chapter 2). The natural soil manganese mean concentration in Windsor and the surrounding area was 506 ± 173 ppm. Overall, the variability of the natural soil samples was acceptable (RSD < 10 %). One elevated soil manganese site was identified (Town of Essex depth). As described in section 3.0, the soil manganese samples of the natural soil site MB-23 had low soil manganese concentrations. The baseline biomonitoring station soil sample, MB-23 (Chapter 8) which was also taken at this location, also had a low soil manganese

concentration, 245 ppm. It would therefore appear that the Town of Essex sample is higher than the other soil samples taken from this site. Furthermore, when the Town of Essex depth soil core was sectioned, the presence of small (~ 1.5 cm diameter) rocks was observed. These were of course removed before soil analysis; however their location coincided with the elevated soil manganese level of the depth profile. Both the existence of the lower soil manganese samples and the presence of these small rocks suggest that the Town of Essex depth sample was indeed an extreme value, or outlier, of natural soil manganese.

The variability of the Town of Essex depth site, 47 %, was the highest of all ($n = 47$) soil cores retrieved during this study. This large variability and elevated soil manganese value inevitably had an affect on the natural soil manganese median and concentration range (Figure 25). If this extreme value is treated as an outlier and excluded from the natural soil manganese mean calculation, the newly calculated natural soil manganese mean is 470 ± 113 ppm (median 480 ppm) and the 5th and 95th percentile values are 284 ppm and 603 ppm, respectively (Figure 35). The difference between the two natural soil mean values is relatively small, 36 ppm, but the difference in the 95th percentile value is significant, a difference of over 300 ppm. It is therefore concluded that the average natural soil sample type for Windsor and the surrounding area is approximately 500 ppm and that the initial percentile range of 251 ppm to 970 ppm was overestimated by the extreme value (Town of Essex depth). A more conservative range would be 284 to 603 ppm for natural soil manganese.

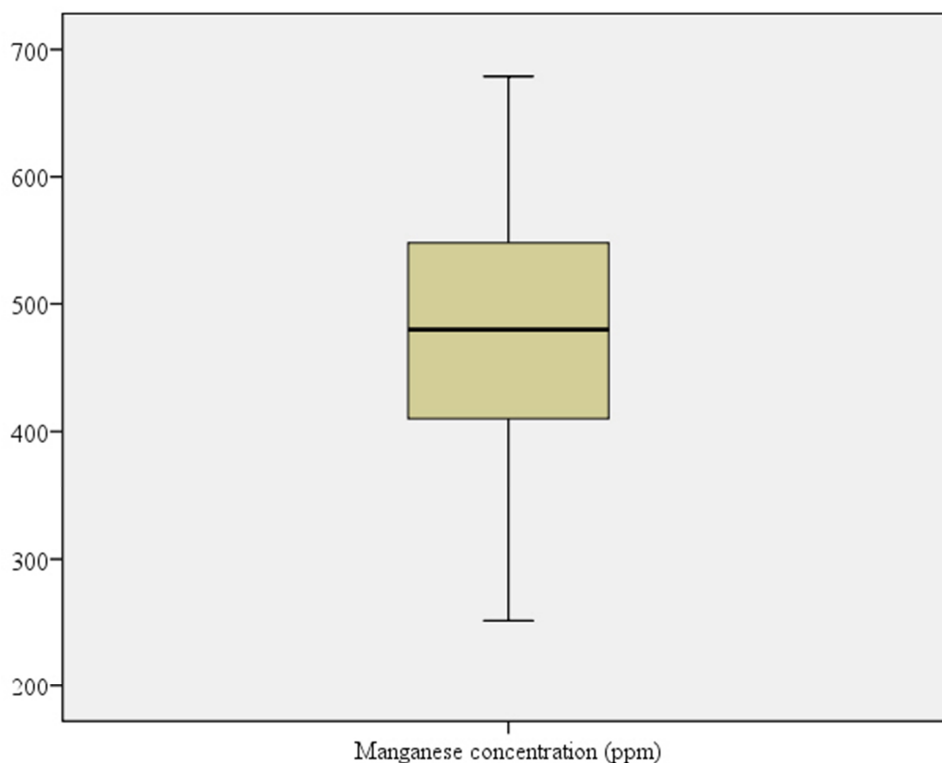


Figure 35 Boxplot of natural soil manganese concentration (ppm) without the Town of Essex depth sample.

Spatial distribution

The investigation of the spatial distribution of manganese in urban soil revealed that the majority of elevated soil manganese sites were found in the western part of the city of Windsor while the south and east generally had lower soil manganese levels. Most of these elevated areas have already been discussed, including Devon-CN, HS-Q and the Ambassador Bridge area. The spatial interpolation of baseline and transect soil manganese results revealed a large area in the southwestern corner of the city, a smaller area south of the Ambassador Bridge and two others, north-central and central Windsor, with elevated soil manganese. All of these elevated areas located on the interpolation map (Figure 27a), except the south western corner, were due to individual soil samples in the upper Windsor soil manganese concentration range (near 800 ppm). For example, the north-central area was the result of the elevated baseline soil manganese concentration of the HS-R3 sample (previously discussed). The largest area of elevated soil manganese interpolation was found

in the southwest corner of Windsor. The interpolation's standard error prediction map (Figure 27b) was also quite high in this area, suggesting that additional soil samples would be needed to improve the reliability of the spatial interpolation in this area. It is unknown whether the high soil manganese concentration in the southwest is due to high soil manganese or to a low of sample density. Additional soil samples may reveal an elevated soil manganese content in this area since it has mainly hosted past and present industrial activities (Appendix I). Additional soil samples will be required to improve the reliability of this assessment regarding the south western corner of Windsor.

pH and carbon content

All three soil sample types had neutral pH. The baseline and transect soil sample types had fairly similar total carbon content and both were higher than the natural soil sample type. Due to the time restrictions a subset of baseline, transect and natural soil samples were used for TIC and TOC determination. The total carbon content of the soil sample types (n = 219 (baseline), 99 (transect) and 13 (natural)) were similar to, though slightly lower than, the average total carbon content of the smaller subset. The natural soil samples averaged twice as much total inorganic carbon as the baseline and transect soil samples. Consequently, both of the latter sample types had much more total organic carbon than the natural soil, possibly because the majority of these samples were retrieved at the surface instead of at depth where organic matter tends to accumulate and decompose. The total organic carbon content of the different Windsor soil sample types was approximately 6 % TOC for transect and baseline, and 1 % for the natural soil. These values are in agreement with Singer and Munns (1996) who stated that most soils have less than 5 % organic matter and with Rasmussen (2004) who found 4 % (n = 48) in outdoor soils of Ottawa, Ontario. The differences in carbon contents between the different soil sample types further support the conclusion that there exists both a natural and anthropogenic soil in Windsor, Ontario. These differences were further demonstrated by the results of the synchrotron-based manganese speciation.

Manganese speciation

The transect soil representative chosen for synchrotron-based manganese speciation, ABW-T1-4, was chosen because of its high soil manganese concentration and its location on the western side of the Ambassador Bridge. Walker (2010) found aggregated manganese-rich grains composed of phyllosilicates (e.g., muscovite or biotite), clay minerals and, Fe- and Mn-oxyhydroxides (e.g., goethite and phyllomanganate (buserite)), all common secondary minerals (Sparks, 1995; Certini and Scalenghe, 2006). The association of manganese with the phyllosilicates and clay minerals appeared to be physical rather than mineralogical in nature. Only high manganese grains could be identified as a distinct manganese phase, Mn-oxyhydroxides. Similarly composed, low-manganese content grains were most likely Fe-oxyhydroxide phases with incorporated manganese. Less abundant Fe-rich grains with low manganese content were also found. The presence of similarly composed, low-manganese composite grains and the mainly physical association of manganese with the phyllosilicates and clay minerals support the conclusion that the source of manganese of this soil sample was probably anthropogenic in nature and that the manganese was, overtime, being incorporated into existing distinct mineral phases. Evidence of microbially mediated mechanisms were also found.

The second soil sample that underwent manganese speciation investigation was the baseline soil representative, I-ZB-B. This sample was also chosen because of its elevated manganese concentration which was possibly due to its proximity to a manganese-emitting industry (recycling activities) (Environment Canada, 2007). Walker (2010) found a large abundance of Fe-rich grains which were related to steel corrosion products and associated with trace, to minor amounts of manganese. This is consistent with the previous interpretation that the IZB manganese-emitting industry in the Devon-CN area is the source of the manganese contamination to the area in direct proximity to the recycling industry. Walker (2010) also noted the presence of Mn-Fe grains, though less abundant than the steel products, that had a high manganese content. These grains, which were related to carbonates or oxyhydroxides, common secondary minerals in soil (Sparks, 1995; Certini and Scalenghe, 2006), may be evidence of the inherent species of manganese present in the soil in this area of Windsor. Another possible explanation could be that manganese of an

anthropogenic origin was sorbed onto the carbonates and/or oxyhydroxides which have high cation exchange capacities (Sparks, 1995; Certini and Scalenghe, 2006). These manganese speciation findings support the conclusion that the source of manganese in baseline soil, and more specifically in the elevated manganese I-ZB soil samples, was a combination of anthropogenic, likely originating from the nearby recycling facility, and inherent natural manganese.

The manganese speciation of the FSV45 soil sample was more ambiguous than the other two Windsor soil representatives. The natural soil sample type representative, FSV45, was retrieved from a construction site southwest of the city of Windsor but within Windsor's geological unit (Figure 23). The site was directly next to a residential area which was next to an agricultural field. This natural soil sample had an average soil manganese concentration similar to the average natural soil manganese level. According to Walker (2010), the manganese in this sample appeared to be associated with phyllosilicates. The sample was retrieved from an excavation pit (3 m deep) using a shovel. Care was taken to remove an outer layer of the sample of clay to remove any contamination from the shovel before analysis. Walker (2010) also found evidence of steel particles. It is also possible that the assumption that this site and its soil samples was untouched by anthropogenic activities was erroneous however in all likelihood, the steel particle came from the shovel or activity of the construction equipment in the vicinity at the time of sampling.

In summary, manganese speciation showed both similarities and differences between the three Windsor soil samples. The principal mineral phases manganese was associated with in the I-ZB-B sample were carbonate or oxyhydroxides whereas the transect soil sample contained manganese-rich aggregate grains consisting of phyllosilicates, clay minerals and oxyhydroxides. The natural soil sample's manganese-grains were mostly associated with phyllosilicates. All of these mineral phases are common secondary minerals in soils. Direct evidence of anthropogenic particles was found in the I-ZB-B sample. The manganese speciation of the ABW-T1-4 sample suggested that the manganese was being incorporated into existing mineral phases from another source, natural or anthropogenic. The steel particle found in the natural sample was most likely due to contamination. Though a good

start, one sample is a poor representation of an entire sample type's manganese speciation, therefore, additional analyses are necessary. These future analyses may benefit from further sieving (i.e., $< 2 \mu\text{m}$) of the soil samples in order to more closely examine the less crystalline phases.

Summary

The purpose of this study was to determine the level of manganese in urban soils in the city of Windsor, Ontario. As well as discovering three soil sample types, three areas of elevated soil manganese were identified and further investigated. Sample size and distribution allowed for an adequate spatial distribution analysis of soil manganese. Synchrotron manganese speciation revealed supporting evidence of anthropogenic and natural sources of manganese to the urban Windsor soil.

Conclusions

The survey of urban Windsor soil revealed anthropogenic and natural sources of manganese. Both carbon content and manganese speciation analyses supported the conclusion of the presence of these two different soils in urban Windsor, anthropogenic ((a) transect and (b,d,e) baseline) and (c) natural. The manganese speciation also showed the differences between the baseline and transect, and the natural soil sample types. The median level of manganese in urban Windsor baseline soil was 385 ppm (range = 164 to 3430 ppm) while the transect soil sample type median was 553 ppm (range = 361 to 1163 ppm). The median soil manganese concentration of natural soil in Windsor and the surrounding area was 502 ppm (range = 251 to 970 ppm; see page 146 of discussion).

The suspected sources of elevated soil manganese appeared to be related to (a) land-use, (b,d,e) modern, and probably legacy, industrial, and (c) natural sources. No conclusive evidence was found from the study of transects to support the conclusion that vehicular emissions were the dominant source of soil manganese levels surrounding the Ambassador Bridge. Instead, historical evidence points to past land-use as the source of elevated soil manganese in this area. Past land-use (landfill) was also suspected to be the source of elevated soil manganese in another area in Windsor. The long-range transport and

subsequent deposition of manganese-bearing particles is also a possible source of soil manganese and will be discussed later (Chapter 8).

Areas of concern in the city of Windsor are the industrial zone of the Devon-CN area, the portion of land directly west of the Ambassador Bridge between University Avenue and Riverside Drive W, and finally, any areas where construction debris may have been buried instead of properly disposed or recycled. Elevated areas of soil manganese in Windsor should be defined as exceeding the upper limit of background manganese which is estimated at 830 ppm. This value represents the average of the 95th percentile values of the baseline and transect soil sample types. Future soil manganese investigations should focus on the south western area of Windsor and include more manganese speciation analyses of Windsor soils.

Chapter 6 - Manganese and Associated Elements in Urban Soil

Purpose

The purpose of this study was to identify significant relationships between manganese and other elements in the urban soil of Windsor, Ontario and to distinguish between natural and anthropogenic signals. Elemental results of the samples from the soil surveys (transect, baseline and natural) were compared.

Design

Surface soil samples were retrieved all across the city of Windsor in the summer of 2007 at a depth of 0-5 cm. Samples belonged to one of the three sample types: transect, baseline or natural (For a description of these sample types consult the 'Design' section of Chapter 5). The samples were sieved, digested and analyzed according to methods described in Chapter 4. The ICP-MS soil analysis consisted of a suite of 50 elements. Elements with less than 15 % of values below the detection limit are reported here. A total of 49 elements met this criterion, including manganese. The ICP-MS detection limit for soil manganese was 1 ppm. Detection limits for other elements can be found in Table J-1 of Appendix J. Element recoveries were between 88 % and 114 % except for Ca, Sb and Mo (336 %, 228 % and 66 %, respectively). The statistical software SPSS was used to determine the data distribution, significant correlation and regression coefficients. A multiple regression was done using the results of the transect and baseline soil analyses in order to investigate what proportion of the variability of soil manganese was accounted for by the significant predictor elements.

Section 1.0 will look at significant associations between manganese and other elements of the three soil sample types, transect, baseline and natural. Section 2.0 presents an elemental signature comparison of these three soils. This is followed by a brief discussion and conclusion.

Results

1.0 Significant relationships of manganese in urban soil

1.1 Transect soil

The transect sample type elements, with the exception of Cs, Rb, Zr, Ge and Nd, were not normally distributed ($n = 99$). Transect soil manganese (median = 553 ppm) was neither normally distributed ($W(99) = 0.879, p < .05$) or log-normally distributed ($W(99) = 0.963, p < .05$), however the log-transformation of the data approached the expected normal distribution curve. The non-parametric Spearman correlation coefficient, ρ , was therefore used to describe the elemental relationship between soil manganese and the other elements found in the soil. All elements (except As and Ca) shown in Table 15 had a significant relationship with transect soil manganese. Statistically significant correlations with large coefficients ($> .5$) (Field, 2005) are reported in **bold**. Reimann et al. (2008) suggest anything above $\pm .7$ is a strong relationship.

The elements of Table 15 had correlation coefficients above .3 with soil manganese, with the exception of Sb, Mg, Cs, and Sr whose correlation coefficients were .2. Not included in Table 15, selenium and barium also had significant, but not strong ($r_s = .2$), relationships with transect soil manganese (Table 28).

Manganese in transect soil was significantly correlated with Zn ($r_s = .58$), Mo ($r_s = .61$), Sn ($r_s = .51$), Cd ($r_s = .67$), Cu ($r_s = .60$), and Pb ($r_s = .64$) (All $p < .01$). Figure 36 to Figure 41 show the linear regressions of the log-transformed manganese results and correlated elements. Based on the simple linear regressions of Figures 36 and 40, copper accounted for 42.6 % (R^2) of the variability of soil manganese while lead accounted for 36.2 % (R^2).

Table 15 also presents elements which had significant relationships with manganese but with smaller correlation coefficients ($.4 < r_s < .5$), namely Fe, Ni, Ag and Co. The linear regressions of these elemental associations are shown in Figure 42.

A significant relationship existed between copper and lead ($r_s = .83, p < .01$) and between copper and zinc ($r_s = .80, p < .01$). Iron and nickel also had a large significant correlation ($r_s = .81, p < .01$), as did Fe and Co ($r_s = .85, p < .01$) (Table 15). The linear regressions of these associations can be found in Figure 43.

Table 15 Spearman correlation matrix for the transect soil sample type elemental concentrations (n = 99) ($p = 0.01$).

	Mg	K	Ca	Cd	Cr	Mn	Fe	Ni	Ag	Cs	Co	Zn	As	Sr	Mo	Sn	Sb	Cu	Pb
Mg	1																		
K	-.40	1																	
Ca	.91	-.56	1																
Cd	ns	-.41	ns	1															
Cr	ns	ns	ns	.61	1														
Mn	.22*	-.31	ns	.67	.39	1													
Fe	ns	.33	-.28	.44	.57	.46	1												
Ni	ns	.31	-.23*	.50	.63	.47	.81	1											
Ag	ns	-.23*	.20*	.69	.67	.47	.35	.51	1										
Cs	-.41	.91	-.58	-.27	ns	-.25*	.43	.49	ns	1									
Co	-.27	.46	-.34	.28	.43	.41	.85	.74	.24*	.50	1								
Zn	.30	-.52	.39	.69	.53	.58	.27	.21*	.52	-.50	ns	1							
As	-.30	ns	-.24*	.53	.45	ns	.43	.49	.53	ns	.24*	.23*	1						
Sr	.64	-.58	.71	ns	ns	.23*	ns	-.30	.22*	-.67	-.34	.54	ns	1					
Mo	.40	ns	.32	.40	.36	.61	ns	.36	ns	ns	.33	.41	ns	ns	1				
Sn	ns	ns	ns	.59	.61	.51	ns	.60	.60	ns	.50	.44	.59	ns	.31	1			
Sb	.39	-.32	.43	.35	.50	.20*	ns	.24*	.43	ns	ns	.43	.34	.48	ns	.43	1		
Cu	ns	-.38	.22*	.75	.69	.60	.50	.44	.64	-.31	.32	.80	.55	.46	.33	.71	.55	1	
Pb	ns	-.25*	ns	.77	.65	.64	.52	.57	.74	ns	.38	.68	.62	.27	.30	.77	.44	.83	1

* Correlation is significant at the 0.05 level.

“ns” Indicates result was not statistically significant.

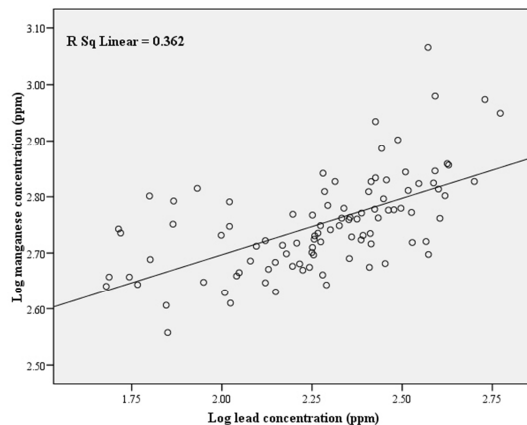


Figure 36 Scatterplot and linear regression trend line of log-transformed transect soil manganese and lead (n = 99).³

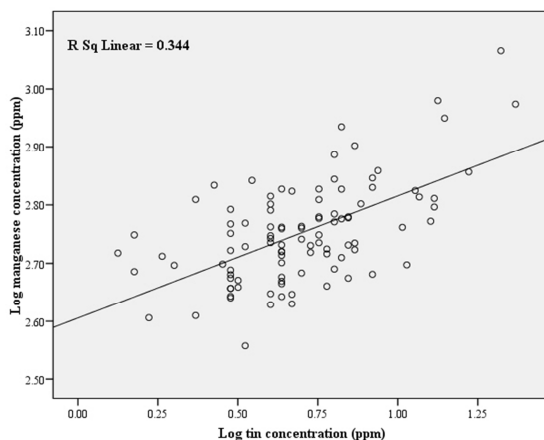


Figure 37 Scatterplot and linear regression trend line of log-transformed transect soil manganese and tin (n = 99).³

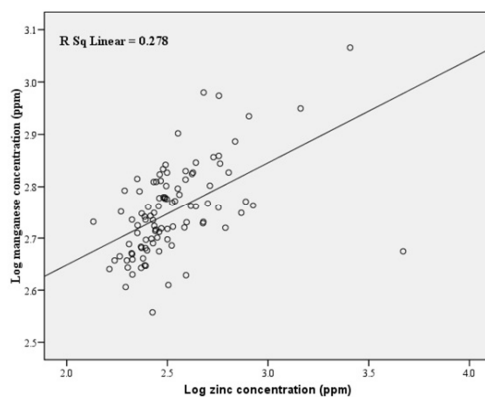


Figure 38 Scatterplot and linear regression trend line of log-transformed transect soil manganese and zinc (n = 99).³

³ Samples were from both the preliminary and complete soil surveys.

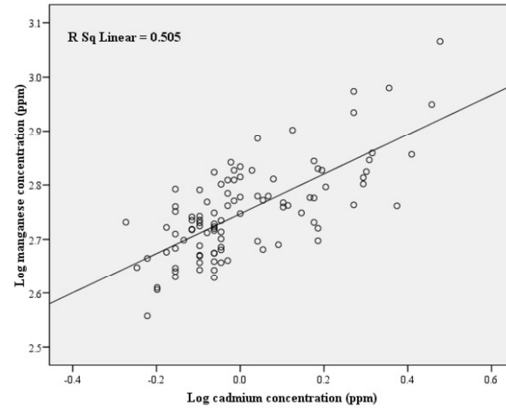


Figure 39 Scatterplot and linear regression trend line of log-transformed transect soil manganese and cadmium ($n = 99$).³

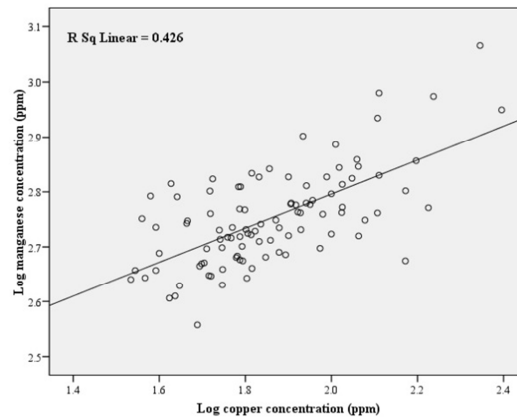


Figure 40 Scatterplot and linear regression trend line of log-transformed transect soil manganese and copper ($n = 99$).³

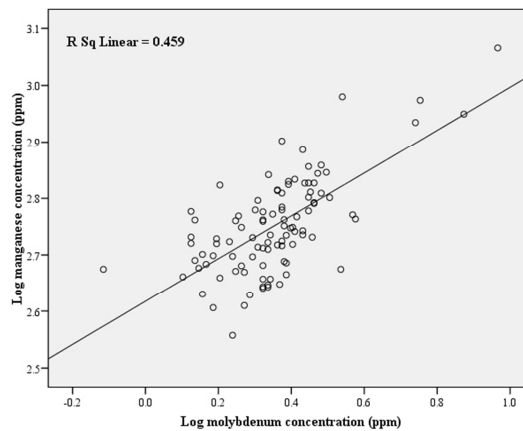


Figure 41 Scatterplot and linear regression trend line of log-transformed transect soil manganese and molybdenum ($n = 99$).³

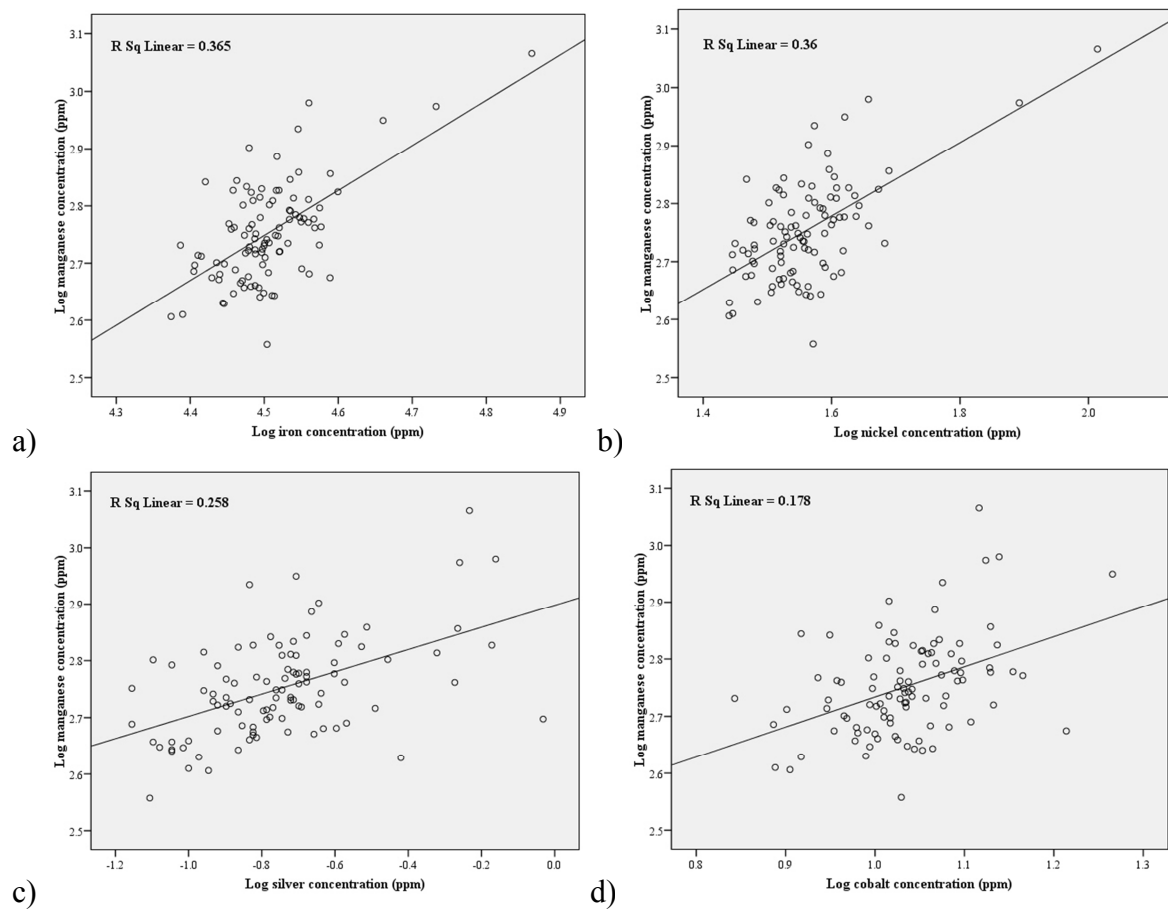


Figure 42 Scatterplots and linear regression trend lines of log-transformed transect soil manganese and a) iron, b) nickel, c) silver, and d) cobalt ($n = 99$). (Samples were from both the preliminary and complete soil surveys.)

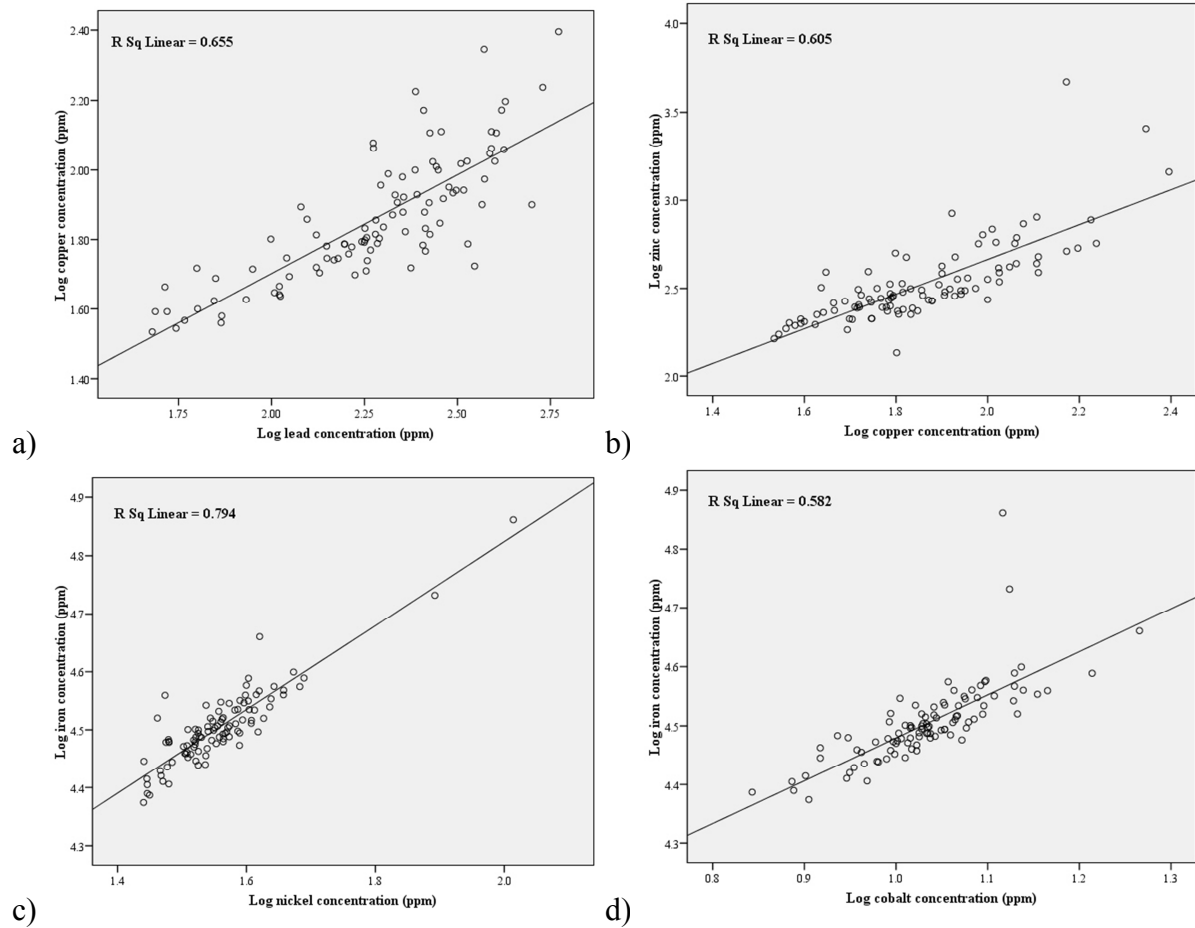


Figure 43 Scatterplots and linear regression trend lines of log-transformed transect soil a) copper and lead, b) zinc and copper, c) iron and nickel, and d) iron and cobalt (n = 99). (Samples were from both the preliminary and complete soil surveys.)

Multiple regression analysis

Regression is a statistical tool which allows the prediction of one variable from another (Field, 2005) (Appendix E). Multiple regression analysis serves the same purpose by using several predictor variables instead of just one. Besides its predictive value, multiple regression analysis can provide valuable information as to which predictors (i.e., elements) significantly contribute to the variability of soil manganese results as well as which cases (or samples) have undue influence over the model. The use of the multiple regression analysis tool in this study was not to predict an outcome (i.e., soil manganese), but to gain

information regarding the significant predictors and influential cases (potential extreme values).

When using a multiple regression tool, the parameters of the regression model first need to be evaluated in order to determine if the model generated is acceptable and consequently if the interpretation of its results is reliable. The following section discusses (1) the fit of a multiple regression model derived from the transect soil results in order to predict soil manganese, as well as (2) the model's significant predictors and (3) influential cases.

Model fit

The Windsor transect soil manganese results were used to generate a multiple regression model. All elements which had a significant correlation to transect soil manganese ($n = 18$) were included in this analysis (Mg ($r_s = .22$), K ($-.31$), Cd (.67), Cr (.39), Fe (.46), Ni (.47), Ag (.47), Cs ($-.25$), Co (.41), Se (.21), Zn (.58), Sr (.23), Mo (.61), Sn (.51), Sb (.20), Ba (.24), Cu (.60) and Pb (.64) (Table 15)). This first regression model of transect soil results used the 'Forced Entry' method where all variables (or elements) were used simultaneously in the regression model. This initial regression model resulted in an R -square of .82, in other words 82 % of the variance in transect soil manganese was accounted for by the model. The difference between the adjusted R^2 (.78), which measures *shrinkage*, or the loss of predictive power (Appendix E), and R^2 was 0.04. This difference suggests that if this model was derived from the population (instead of a subsample of the population), it would account for 4.1% less of the soil manganese variability; the smaller the difference, the better. The Durbin-Watson test (DW) indicates whether the assumption that residuals are uncorrelated was met. A Durbin-Watson statistic between 1 and 3 (or near 2) is desirable. The Durbin-Watson statistic was 1.506. To test the overall fit of the regression model, the statistical software does an analysis of the variance (ANOVA) which calculates an F-ratio. The overall fit of the transect soil multiple regression model was good (F-ratio > 1), $F = 20.458$, $p < 0.001$. In general, these parameters (R^2 , adjusted R^2 , Durbin-Watson, F-ratio) indicate that the model is a good fit for the Windsor transect soil manganese results.

Significant predictors

The regression coefficient (beta (b)), or standardized beta (β) (Appendix E), describe to what degree each predictor affects the outcome if the effects of all other predictors are held constant (Field, 2005). The p -value of the standardized beta determines whether a predictor has significant influence over the outcome (i.e., transect soil manganese results). Based on the initial forced entry multiple regression, the following predictors, Cd, Zn, Mo, Ni, K, Cr, Mg and Cs, had a significant effect ($p < 0.05$) on the outcome (Table 16); in other words a significant effect on the transect soil manganese results. If the p -value of a predictor exceeds the significance level, in this case 0.05, it does not have a significant influence over the outcome and can be removed from subsequent multiple regression analyses. These eight significant contributors were therefore used in a stepwise multiple regression to further investigate their influence on transect soil manganese. The stepwise multiple regression method is different from the forced entry method in that it includes contributor variables into the model one at a time (Appendix E) which gives information about the individual predictor not available from a forced entry multiple regression model. Based on the p -value of the stepwise multiple regression model (Table 16), none of the significant predictors needed to be removed from the stepwise model. The values of both the final R^2 and the difference between the R-squares (R^2 and adjusted R^2) of the stepwise regression model, 0.79 and 0.02, respectively, were lower than the values of the initial transect soil forced entry multiple regression model. This new stepwise regression model accounted for 2 % more of the variability of soil manganese than if the model had been derived from the population. The Durbin-Watson parameter was smaller (1.485) than the initial forced entry regression model and the F-ratio was significantly larger ($F = 41.741$, $p < 0.001$) indicating that this new stepwise model was even better at predicting soil manganese concentrations than the forced entry model.

Table 16 The standardized *beta* coefficients of the forced entry transect soil (n = 99) multiple regression model.

Predictors	Standardized Beta Coefficients (β)	t	p-value
Cadmium	.365	3.237	.002
Zinc	-.182	-2.011	.048
Molybdenum	.246	2.612	.011
Nickel	.686	4.214	.00007
Potassium	.510	2.521	.014
Chromium	-.246	-2.636	.010
Magnesium	.246	2.699	.008
Cesium	-.809	-3.697	.0004

Table 17 shows (1) the cumulative R^2 of the significant predictors and (2) their individual R^2 which describes how much of the transect soil manganese variance can be explained by the individual predictors. For the Windsor transect soil, cadmium accounted for half (51 %) of the variability of soil manganese concentration followed by molybdenum with 14 %. The other predictors each accounted for less than 5 % of this variability (Table 17), leaving 21 % of the transect soil manganese variability unaccounted for. The final stepwise regression model coefficients (b) were: Cs ($b_1 = -.921$), K ($b_2 = 1.046$), Ni ($b_3 = .714$), Cd ($b_4 = .248$), Mo ($b_5 = .171$), Cr ($b_6 = -.272$), Mg ($b_7 = .107$), Zn ($b_8 = -.057$). The generalized formula for this regression model is given in Equation 4.

$$\text{Soil (Mn}_{\text{Tr}}) = -2.164 + b_1 (\text{Cs}) + b_2 (\text{K}) + b_3 (\text{Ni}) + b_4 (\text{Cd}) + b_5 (\text{Mo}) + b_6 (\text{Cr}) + b_7 (\text{Mg}) + b_8 (\text{Zn}) + \varepsilon_i \quad [\text{Eqn 4}]$$

Table 17 Cumulative *R*-square values of the transect soil (n = 99) stepwise multiple regression.

Predictor	Cumulative R^2	Individual R^2
Cadmium	.505	.505
Molybdenum	.648	.143
Nickel	.662	.014
Cesium	.702	.040
Potassium	.738	.036
Chromium	.760	.022
Magnesium	.778	.018
Zinc	.788	.010
Total	.788	.788

Assessing the model parameters and multicollinearity

The confidence interval of the regression coefficient (*b*) is the range of values around the *b* that is believed to contain (with 95 % certainty) the true *b* value. A good model will have confidence intervals which do not include the zero (i.e., -4 to +4) and are “tight”, or small. The smaller the interval, the closer the calculated *b* is the true *b* value of the population (Field, 2005). All eight predictor variables of the transect soil stepwise multiple regression had significant confidence intervals (Table 18). These intervals were less than 0.1 for all predictors. The model’s estimates were therefore likely to be representative of the true population (Field, 2005).

Another way of assessing the presence of multicollinearity, besides high correlation coefficients (i.e., > .9), is by looking at the variance inflation factor, or VIF, of a multiple regression model. This indicates the presence of strong linear relationships between predictors (Field, 2005). Field (2005) states that according to Bowerman and O’Connell (1990), multicollinearity may be biasing the regression model if the average VIF value is above 1. In addition, Myers (1990 in Field (2005)) suggests that a VIF value above 10 may be cause for concern. The tolerance statistic, which is the reciprocal of the VIF value, also measures multicollinearity. A tolerance value < .1 indicates a “serious problem” that

collinearity does exist (Field, 2005). VIF and tolerance values were generated to characterize the multicollinearity of the transect soil stepwise multiple regression model. Both cesium and potassium had low ($< .1$) tolerance values (.085 and .089, respectively) and high (> 10) VIF values (Table 18). The average VIF value for the predictors of this stepwise regression model was 5. This is greater than 1 and according to Bowerman and O'Connell (1990 in Field (2005)), this indicates that multicollinearity may be biasing the regression model.

Table 18 The confidence intervals and collinearity statistics of the transect soil (n = 99) stepwise regression model.

Predictors	95% Confidence Interval for <i>b</i>		Collinearity Statistics	
	lower bound	upper bound	tolerance	VIF
Cadmium	.157	.338	.301	3.322
Molybdenum	.089	.254	.426	2.347
Nickel	.496	.932	.219	4.566
Cesium	-1.211	-.632	.085	11.771
Potassium	.632	1.459	.089	11.201
Chromium	-.448	-.096	.346	2.887
Magnesium	.034	.180	.506	1.977
Zinc	-.111	-.002	.437	2.288

In addition to the tolerance and VIF statistics, multicollinearity can also be assessed on the level of the individual predictors. According to Field (2005), a large condition index may indicate the existence of collinearity on the corresponding eigenvalue. Condition indices are an alternative way of expressing eigenvalues (Appendix E) (Field, 2005). Also, the variance of each predictor's regression coefficient can be broken down and attributed to the different eigenvalues. These are called variance proportions. Predictors which have their largest proportion of the same eigenvalue, or condition index, are suspected of collinearity and therefore, of biasing the regression model. The ninth condition index of Table 19 shows a significantly larger (6 times that of the previous) condition index. This would indicate that collinearity exists on this eigenvalue. Cesium and potassium had their largest variance

proportions associated with this eigenvalue (ninth), 76 % and 98 %, respectively. The Pearson correlation coefficient for cesium and potassium of the final stepwise regression was $r = .93$. However potassium was not normally distributed therefore the non-parametric Spearman correlation coefficient (Table 15), which best describes their relationship, was $r_s = .91$ ($p < 0.01$) (Figure 44).

Table 19 The colinearity diagnostics of the transect soil (n = 99) stepwise multiple regression model.

Dimension	Eigenvalue	Condition Index	Variance Proportions								
			Mn	Cd	Mo	Ni	Cs	K	Cr	Mg	Zn
1	7.834	1.000	.00	.00	.00	.00	.00	.00	.00	.00	.00
2	1.029	2.760	.00	.28	.00	.00	.00	.00	.00	.00	.00
3	.102	8.774	.00	.12	.55	.00	.00	.00	.00	.00	.00
4	.030	16.166	.00	.02	.04	.00	.08	.00	.00	.00	.01
5	.003	50.244	.00	.07	.05	.00	.01	.00	.00	.02	.90
6	.001	89.489	.00	.38	.00	.23	.11	.00	.09	.34	.01
7	.001	124.713	.01	.07	.04	.05	.03	.01	.71	.09	.00
8	.000	142.907	.01	.03	.31	.65	.00	.01	.20	.36	.02
9	1.10e⁻⁵	842.840	.99	.04	.00	.07	.76	.98	.00	.19	.05

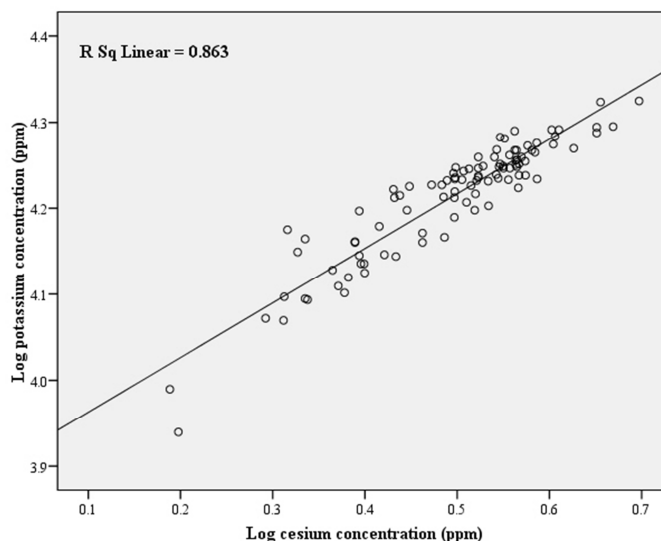


Figure 44 Scatterplot and linear regression trendline of log-transformed transect soil potassium and cesium (n = 99). (Samples were from both the preliminary and complete soil surveys.)

Residuals and influential cases

The difference between the model's predicted values of the outcome and the observed values is called a residual (Field, 2005). It can be standardized by dividing them by the estimate of their standard deviation. The standardized residuals can be compared to universal guidelines, based on properties of *z-scores*, of acceptable and unacceptable values (Field, 2005). For example, if over 5 % of the standardized residuals are above ± 2 , it indicates that the error in the model is unacceptable. The model's poor representation of the data can be further evidenced if more than 1 % of the standardized residuals are above ± 2.5 . As well as evaluating the level of error within the model, the residuals of a multiple regression (Table 20) can also be used to identify possible outliers (standard residuals > 3).

Four samples had standard residuals above ± 2 which is equivalent to 4 % of the total number of samples for the transect soil (Table 20). Of the 99 standardized residuals, 1 (1%) was above ± 2.5 (and ± 3), namely ABW-T1-6. This is within the acceptable limits set forth by Field (2005) for what is expected of an accurate model. ABW-T1-6 appears to be a case worthy of further investigation (i.e., outlier).

Some cases can exert an undue influence over the parameters of the regression model (Field, 2005). Several statistical tools exist which can be used to assess this influence. Four of these tools (a.k.a. statistics) were used to evaluate influential cases of the baseline soil regression model were the Mahalanobis and Cook's distances, Leverage and the standardized DFBeta values (Appendix E).

The distance between the observed values (a.k.a cases) and the mean(s) of the predictor variable(s) is called the Mahalanobis distance. The critical value above which cases are suspected to exert undue influence on the regression depends on the number of predictors and the number of observations (Field, 2005). Barnett and Lewis (1994) created a table of these critical values. For transect soil, a case with a Mahalanobis distance value above 20 would be exerting undue influence. The Cook's distance statistic measures a sample's overall influence on the model (Field, 2005). According to Cook and Weisberg (1982 in Field (2005)), values greater than 1 may be cause for concern. Leverage (Centered) values assess the influence of an observed value of soil manganese over the predicted values. There are two possible leverage values over which a sample is said to be exerting undue influence on the regression model. Hoaglin and Welsh (1978 in Field (2005)) recommend using 2x the average leverage value to identify samples with undue influences whereas Stevens (1992 in Field (2005)) suggests using 3x this average.

The DFFIT value is the difference between the adjusted predicted value (value predicted from a model which was generated with data not including this value) and the original predicted value of a specific sample (Appendix E) (Field, 2005). Similarly, if the parameter of a regression model is estimated using first all cases, then excluding one case, the difference between the two estimates is known as the DFBeta (Field, 2005). The standardized values of these two tools are used in order to be able to compare the model's statistics to the universal cut-off points (i.e., $> |1|$) (Field, 2005).

Casewise diagnostics of Table 20, which describe the above mentioned statistical tools, show that none of the cases exceeded the criteria for undue influence. Therefore, none of the transect soil samples ($n = 99$) had any undue influence on the stepwise regression model.

Table 20 The casewise diagnostics of the transect soil (n = 99) stepwise multiple regression model. (Includes cases with standardized residuals > 2 only.)

Case #	Sample Name	Standardized Residual	Mahalanobis Distance	Cook's Distance	Centered Leverage Value
17	ABE-T1-7	-2.195	1.07178	.01175	.01094
52	ABW-T1-6	3.712	2.36724	.05624	.02416
62	ABW-T2-3	2.313	8.18017	.06767	.08347
96	HCW-T1-3	2.307	10.39341	.08795	.10606
Undue influence criteria		n/a	> 20 ^a	> 1 ^b	> 1.636 (2xAvgL) ^c

^a (Barnett and Lewis, 1994)

^b (Cook and Weisberg, 1982 in Field (2005))

^c (Hoaglin and Welsch, 1978 in Field (2005))

Table 20 The casewise diagnostics of the transect soil (n = 99) stepwise multiple regression model. (Includes cases with standardized residuals > 2 only.) (**cont'd.**)

Case #	Sample Name	DFFIT	Standardized DFBETA								
			Mn	Cd	Zn	Mo	Ni	K	Cr	Mg	Cs
17	ABE-T1-7	-.33260	.10495	-.01112	.13640	-.08753	.01521	-.11663	-.04090	-.01683	.06522
52	ABW-T1-6	.77129	.22405	-.01056	.21787	-.14177	-.28676	-.16533	.04837	-.33198	.25628
62	ABW-T2-3	.80283	.12289	-.18474	.43225	-.34351	.33581	-.24601	-.27711	.36799	.17784
96	HCW-T1-3	.91592	.45187	-.00050	-.12763	.45520	-.25075	-.27254	-.12133	-.76300	.16698
Undue influence criteria		> 1 ^d	> 1 ^d	> 1 ^d	> 1 ^d	> 1 ^d	> 1 ^d	> 1 ^d	> 1 ^d	> 1 ^d	> 1 ^d

^d (Field, 2005)

Summary discussion

The vast majority of transect soil elemental results, including manganese, were not normally, or log-normally, distributed. Strong significant Spearman correlations were found between transect soil manganese and zinc, molybdenum, tin, cadmium, copper and lead. The stepwise regression model's fit parameters and the error within the model were both acceptable, and no cases exerted any undue influence over the model's parameters. This indicated that the generated model was satisfactory and that the elements which were significantly contributing to the variability of the transect soil manganese levels were Zn, Mo, Cd, Ni, K, Cr, Mg and Cs. The model also revealed that transect soil cadmium accounted for half of the variability of transect soil manganese. Both the correlation coefficients and the multiple regression parameters indicated that collinearity existed between the contributing predictors: cesium and potassium. Collinearity between nickel and magnesium was also indicated by the collinearity diagnostics however their correlation coefficient was not significant. Since the model did not reveal any collinearity between cadmium and any other predictor, it can be concluded that transect soil manganese is strongly and significantly correlated to zinc, molybdenum, tin, cadmium, copper and lead, and that cadmium accounts for half of the variability in transect soil manganese.

1.2 Baseline soil

All elements of the baseline sample type ($n = 219$) (except Rb and Th) were not normally distributed (including soil manganese (median 385 ppm; ($W(219) = 0.489, p < .05$)). Though its log-transformation did approach the expected normal distribution (Appendix E) more so than the untransformed data, soil manganese was not log-normally distributed ($W(219) = 0.957, p < .05$). Spearman correlations were used to describe the elemental relationships between soil manganese and the various elements. All elements shown in Table 21 had a significant relationship with baseline soil manganese and a correlation coefficient (*rho*) above .3. The Spearman coefficients shown in **bold** were statistically significant and represented strong correlations ($r_s > .5$) (Field, 2005). Ca, As, Sr, Mo, Mg, Cd, Cr, Ag, Sb, Cu, Pb, K, Ga, Rb, Sn, Al, Er, Dy, Tl, Y, Eu, La, Ce, and Sm also

had significant relationships with baseline soil manganese however their Spearman coefficients were small ($r_s = .1$) to small-medium ($r_s = .2$) (Field, 2005).

Baseline soil manganese had a significant positive correlation with Fe ($r_s = .54$), cobalt ($r_s = .54$) and calcium ($r_s = .51$) (All $p < .01$). Figure 45 to Figure 47 show the linear regressions of the log-transformed manganese, iron, cobalt and calcium baseline soil results. Magnesium, nickel, zinc, arsenic and strontium had smaller correlation coefficients ($.4 < r_s < .5$) which were statistically significant (Table 21). Linear regressions between the log-transformed manganese and these elements are shown in Figure 48.

Iron and cobalt were significantly correlated to each other ($r_s = .811$, $p < .01$). Their coefficient of determination was 0.665 for log-transformed results (Figure 49). Other large correlations between significant manganese-associated elements (Mg, Ni, Zn, As and Sr) included Fe and Ni ($r_s = .77$), Co and Ni ($r_s = .75$), Ca and Sr ($r_s = .70$), Mg and Sr ($r_s = .62$) and, Ni and Zn ($r_s = .52$), (All $p < .01$) (Table 21).

Table 21 Spearman correlation matrix for the baseline soil sample type elemental concentrations (n = 219) ($p = 0.01$).

	Mg	K	Ca	Cd	Cr	Mn	Fe	Ni	Ag	Cs	Co	Zn	As	Sr	Mo	Sn	Sb	Cu	Pb
Mg	1																		
K	ns	1																	
Ca	.91	-.33	1																
Cd	ns	-.43	.21	1															
Cr	.16*	ns	ns	.55	1														
Mn	.46	-.26	.51	.36	.34	1													
Fe	.26	.24	.18	.31	.62	.54	1												
Ni	.38	.18	.31	.46	.72	.43	.77	1											
Ag	ns	-.39	.18	.58	.45	.32	.29	.31	1										
Cs	ns	.88	-.32	-.36	ns	-.33	.33	.25	-.33	1									
Co	.26	.34	.18	.16*	.50	.54	.81	.75	ns	.36	1								
Zn	.23	-.40	.33	.85	.55	.43	.37	.52	.47	-.36	.19	1							
As	.20	ns	.21	.28	.34	.43	.43	.41	.34	ns	.47	.33	1						
Sr	.62	-.32	.70	.29	.14*	.42	ns	.23	.31	-.33	ns	.38	ns	1					
Mo	.37	-.39	.42	.43	.31	.45	.31	.41	.17*	-.31	.20	.53	.41	.30	1				
Sn	.18	-.37	.21	.53	.43	.28	.30	.34	.50	-.26	.15*	.58	.36	.23	.54	1			
Sb	.21	-.42	.28	.39	.30	.32	.25	.31	ns	-.33	.14*	.50	.31	.17*	.79	.68	1		
Cu	.25	-.35	.32	.77	.58	.36	.42	.58	.56	-.26	.28	.85	.39	.35	.49	.63	.45	1	
Pb	.21	-.46	.28	.80	.49	.33	.28	.41	.56	-.38	ns	.86	.41	.34	.49	.69	.51	.81	1

* Correlation is significant at the 0.05 level.

“ns” Indicates result was not statistically significant.

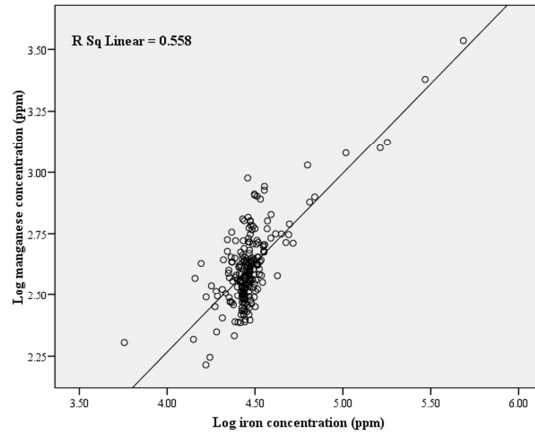


Figure 45 Scatterplot and linear regression trend line of log-transformed baseline soil manganese and iron results (n = 219).³

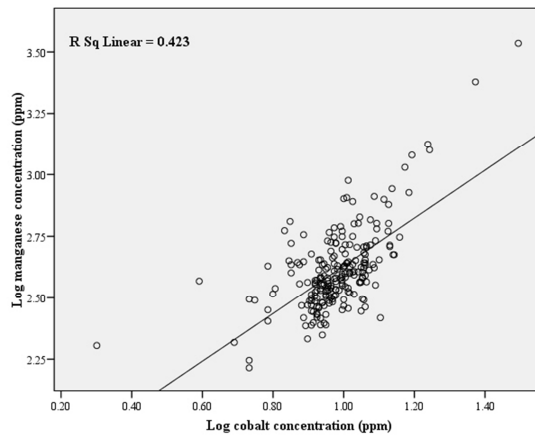


Figure 46 Scatterplot and linear regression trend line of log-transformed baseline soil manganese and cobalt results (n = 219).³

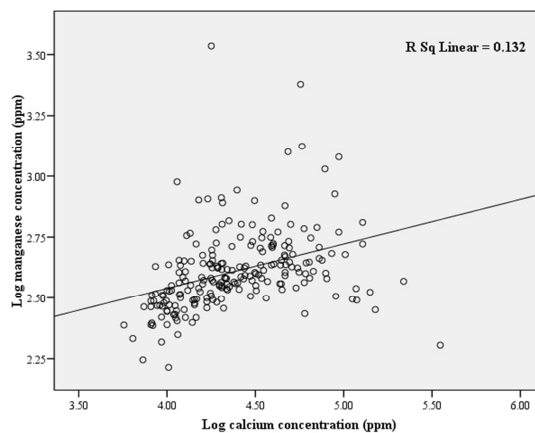


Figure 47 Scatterplot and linear regression trend line of log-transformed baseline soil manganese and calcium results (n = 219).³

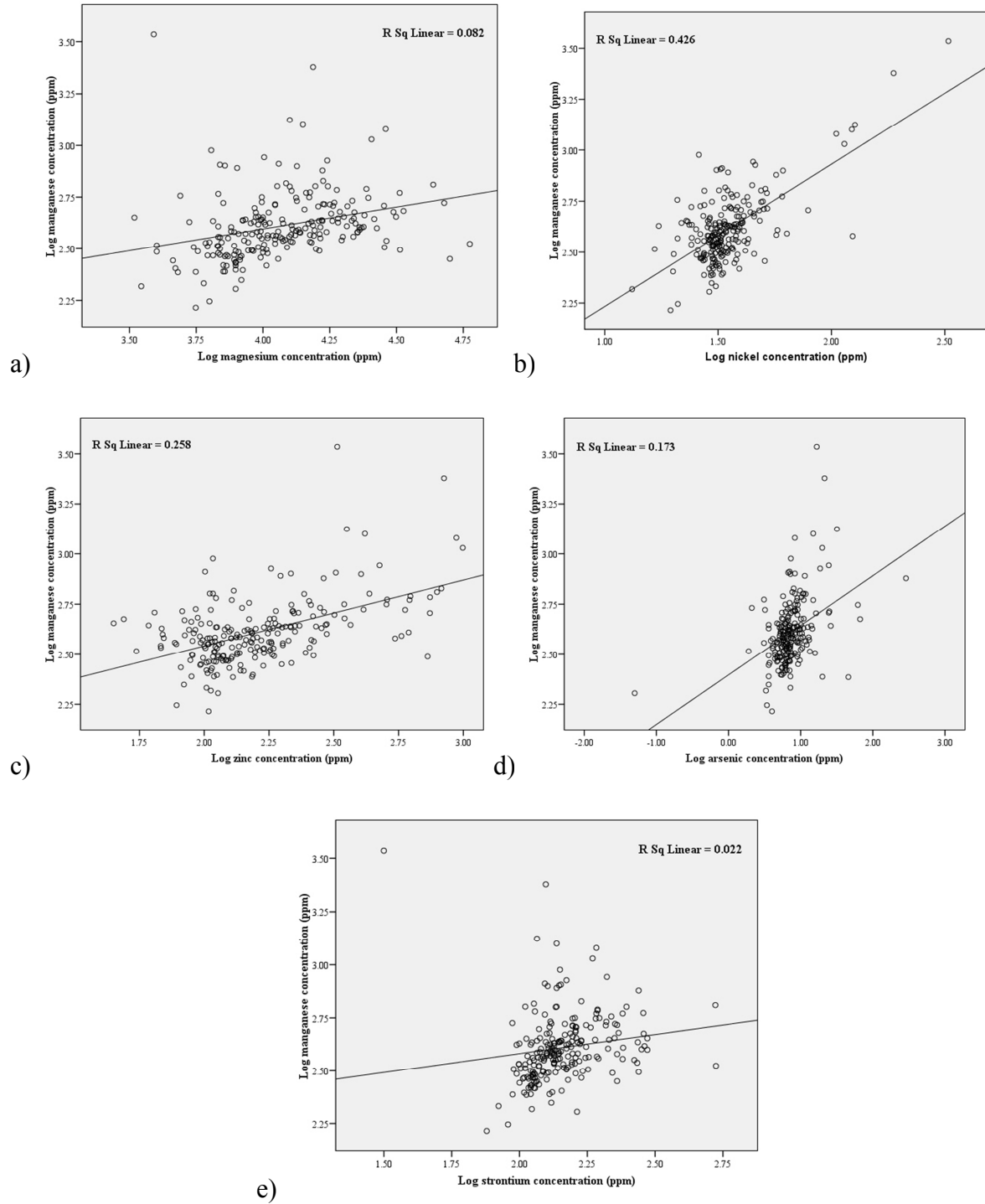


Figure 48 Scatterplots and linear regression trend lines of log-transformed baseline soil manganese and a) magnesium, b) nickel, c) zinc, d) arsenic, and f) strontium results (n = 219). (Samples were from both the preliminary and complete soil surveys.)

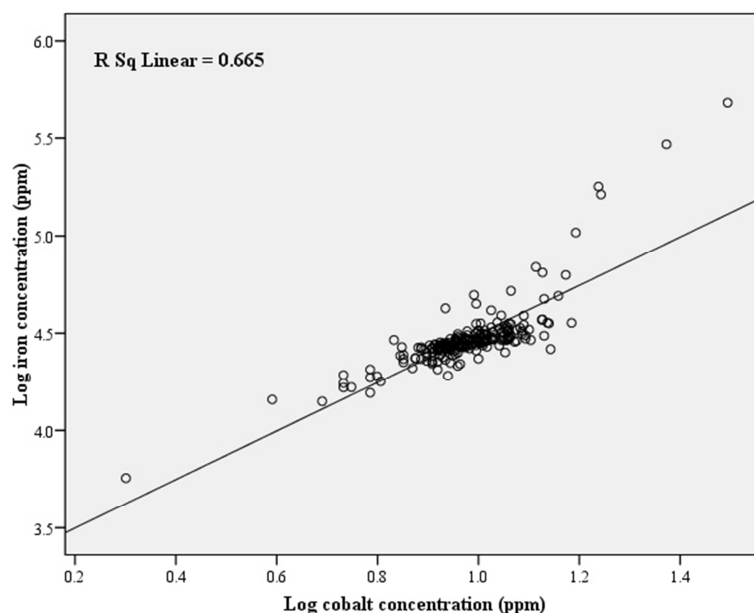


Figure 49 Scatterplot and linear regression trend line of log-transformed baseline soil iron and cobalt results ($n = 219$). (Samples were from both the preliminary and complete soil surveys.)

Multiple regression analysis

The following section discusses (1) the fit of a multiple regression model derived from the baseline soil results in order to predict soil manganese, as well as (2) the model's significant predictors and (3) influential cases.

Model fit

All elements ($n = 31$) which had a significant relationship ($.1 < r_s < .9$) with baseline soil manganese were included in a multiple regression analysis which used the 'Forced Entry' method (all predictors are included into the model simultaneously) and the log-transformed baseline soil results ($n = 219$). The R -square for this initial regression model was .86 and the adjusted R^2 was .84 resulting in a difference of 0.02. Therefore, the predictor variables included in the model accounted for 86 % of the variance in baseline soil manganese. The small difference between the R^2 and the adjusted R^2 indicates that if this model was derived from the population (instead of a subsample), it would account for 2 % less of the variance of the outcome, i.e., soil manganese. The Durbin-Watson value, which tests the assumption of independent error, for the baseline soil forced entry multiple

regression model was 1.739. The test for overall fit of the forced entry multiple regression model (analysis of variance (ANOVA)) calculated a significant ($p < 0.001$) F-ratio of 36.789. The above parameters indicate that this initial forced entry multiple regression model is a good fit for the baseline soil manganese results.

Significant predictors

The initial forced entry model's standardized beta coefficients, which describe the effect of predictors on the outcome, showed that the relationships between manganese and Ca, Fe, Co, Ni, Zn, Cs, Li, Rb and Yb were significant ($p < 0.05$) (Table 22). Subsequent stepwise multiple regression models were done with only these nine significant elements as predictors. The first baseline soil stepwise multiple regression model revealed that rubidium and ytterbium did not meet the criterion ($p < 0.05$) of significant predictors and were therefore excluded from further stepwise multiple regression analyses. The final significant predictors of the baseline soil stepwise regression model included only Fe, Ca, Cs, Co, Ni, Zn and Li. The R^2 of the final stepwise regression model was 0.82 and the difference between this new R^2 and its adjusted R^2 was 0.006 (or 0.6 %), an even smaller difference than the initial baseline soil forced entry model. The Durbin-Watson statistic of this final stepwise multiple regression model was smaller, (i.e., 1.548) than the initial forced entry model (DW = 1.739) however it was still within acceptable limits ($1 < DW < 3$). The F-ratio was significant and larger, 137.649 ($p < 0.001$), again indicating the good fit of the model.

Table 22 The standardized beta coefficients (β) of the Forced Entry baseline soil (n = 219) multiple regression model.

Predictors	Standardized Beta Coefficients (β)	t	p-value
Ca	.234	2.600	.010
Fe	.372	3.784	.0003
Co	.835	9.275	4.4e ⁻¹⁷
Ni	-.324	-3.544	.0005
Zn	.294	3.377	.001
Cs	-.486	-3.093	.002
Li	-.368	-3.055	.003
Rb	.341	1.980	.049
Yb	-.244	02.575	.011

The cumulative R^2 parameter of the significant predictors, as well as their individual R^2 , are shown in (Table 23). Iron accounted for 56 % of the variability seen in baseline soil manganese. All other significant predictors accounted for less than 10 % each, lithium less than 1 % (Table 23). This indicates that 18 % of the variability of baseline soil manganese was unaccounted for by the model's predictors. The final stepwise regression model coefficients were: Co ($b_1 = 1.138$), Ni ($b_2 = -.411$), Cs ($b_3 = -.253$), Fe ($b_4 = .269$), Zn ($b_5 = .151$), Ca ($b_6 = .108$), Li ($b_7 = -.211$) which resulted in the following regression model Equation 5:

$$\text{Soil (Mn}_{\text{Bsl}}) = 0.555 + b_1 (\text{Co}) + b_2 (\text{Ni}) + b_3 (\text{Cs}) + b_4 (\text{Fe}) + b_5 (\text{Zn}) + b_6 (\text{Ca}) + b_7 (\text{Li}) \quad [\text{Eqn 5}]$$

Table 23 Cumulative *R*-Square values of the baseline soil (n = 219) stepwise multiple regression.

Predictor	Cumulative R^2	Individual R^2
Iron	.558	.558
Calcium	.655	.097
Cesium	.694	.039
Cobalt	.779	.085
Nickel	.792	.013
Zinc	.817	.025
Lithium	.820	.004
Total	.820	.820

Assessing the model parameters and multicollinearity

As stated in the transect section, if the confidence interval of the regression coefficient (*b*) does not cross the zero (i.e., -4 to +4) and the interval is small, the model is good. The seven remaining predictors of the stepwise regression had significant (did not cross 0) and quite small (less than 0.1) confidence intervals (Table 24). This indicated that the regression coefficients of the current model were likely to be representative of the true population values.

The variance inflation factor (VIF) of the baseline stepwise multiple regression model, which is a measure of predictor multicollinearity, revealed only one element with a high (>10) VIF value, lithium (10.034). The average VIF value for the predictors of the stepwise multiple regression model was 5.8. None of the predictors had low (< .1) tolerance values. Table 24 shows that Fe, Cs, Co, Ni and Li had tolerance values above .1 but below .2. According to Menard (1995 in Field (2005)), a tolerance value < .2 may be “cause be for concern” that collinearity does exist. Both multicollinearity statistics indicate that collinearity could be biasing the baseline soil stepwise regression model.

Table 24 The confidence interval and collinearity statistics of the baseline soil (n = 219) stepwise multiple regression model predictors.

Predictors	95% Confidence Interval for <i>b</i>		Collinearity Statistics	
	lower bound	upper bound	tolerance	VIF
Iron	.117	.421	.137	7.323
Calcium	.072	.143	.661	1.514
Cesium	-.419	-.088	.107	9.314
Cobalt	.938	1.337	.185	5.393
Nickel	-.552	-.271	.191	5.226
Zinc	.099	.203	.515	1.942
Lithium	-.408	-.014	.100	10.034

In addition to the tolerance and VIF values, multicollinearity in the baseline soil stepwise multiple regression model was also assessed by investigating variance proportions and condition indices (Appendix E.). Table 25 shows the eigenvalues, condition indices and variance proportions of the model's significant predictors. According to Field (2005), correspondingly large condition indices (alternate expressions of eigenvalues) between significant predictors may indicate the existence of collinearity, in other words a bias in the regression model. Table 25 shows that 73 % and 84 % of the variance for the predictors cesium and lithium, was associated with the same eigenvalue, namely the seventh condition index. The multiple regression's Pearson correlation coefficient for their relationship was $r = .93$ ($p < 0.01$). Because cesium was normally distributed and lithium was log-normal, their relationship is best described using the Spearman correlation coefficient which was also significant and strong ($r_s = .86$) (Table 21). Figure 50 shows the linear regression between Cs and Li.

Table 25 The colinearity diagnostics of the baseline soil (n = 219) stepwise regression model.

Dimension	Eigenvalue	Condition Index	Variance Proportions							
			Mn	Fe	Ca	Cs	Co	Ni	Zn	Li
1	7.871	1.000	.00	.00	.00	.00	.00	.00	.00	.00
2	.105	8.672	.00	.00	.00	.08	.00	.00	.00	.00
3	.011	26.832	.00	.00	.09	.00	.10	.03	.01	.00
4	.008	32.392	.00	.00	.03	.03	.02	.00	.65	.00
5	.003	48.051	.01	.00	.49	.13	.01	.04	.03	.06
6	.002	67.432	.00	.00	.09	.02	.42	.63	.23	.00
7	.001	97.931	.04	.04	.12	.73	.01	.06	.07	.84
8	.000	263.075	.94	.95	.20	.00	.44	.25	.01	.09

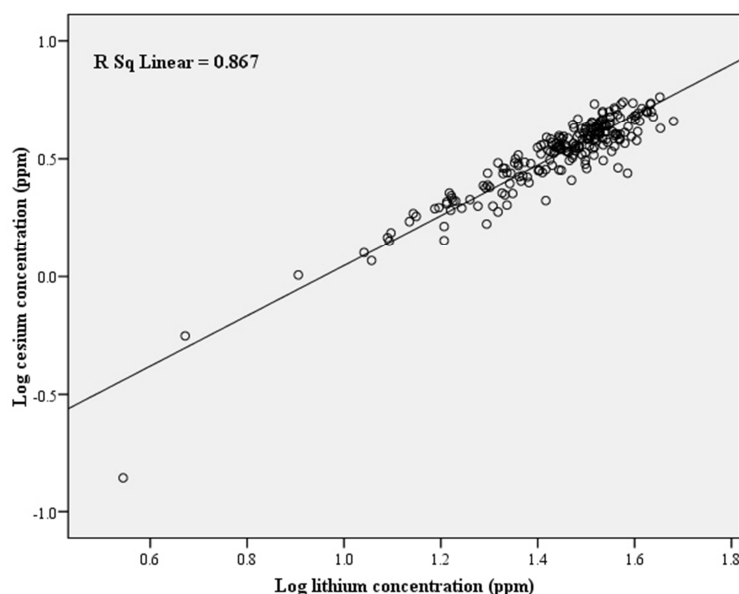


Figure 50 Scatterplot and linear regression trend line for baseline soil log-transformed cesium and lithium results (n = 219). (Samples were from both the preliminary and complete soil surveys.)

Residuals and influential cases

In the case of the standardized residuals of the baseline soil stepwise multiple regression model, fifteen cases had residuals above ± 2 (Table 26). This is equivalent to 6.8 % of the total number of samples for the baseline soil (n = 219) which exceeds the universal guidelines (discussed in the transect soil residuals section, i.e., 5%). Of the 219 soil samples,

2.3 % had standard residuals above 2.5 (> 1 % universal guideline) and three of these samples were above the standard residual value of 3, namely HS-O, HS-Q and HS-Q10. BCJP and HC-B were the other two samples above 2.5 standard residual. This high number of standard residuals (6.8 % and 2.3 %) would indicate that the model is a poor representation of the data. Possible outliers (standard residuals > 3) were HS-O, HS-Q and HS-Q10.

Contrary to the transect soil, the baseline soil multiple regression model revealed influential cases. The Mahalanobis distance of I-ZB-42 and I-NK-A baseline soil samples (Table 26) clearly exceeded all critical values listed in the table by Barnett and Lewis (1994). According to Cook and Weisberg (1982 in Field (2005)), the baseline soil case I-ZB-42 may be cause for concern because it exceeds their recommended limit of 1. Table 26 shows that the two soil samples, I-ZB-42 and I-NK-A, exceeded both the calculated Hoaglin and Welsch (1978 in Field (2005)), and Stevens (1992 in Field (2005)) recommended Centered Leverage limits, while HS-O only exceeded Hoaglin and Welsch's 2x the average leverage value limit. I-ZB-42 had a standardized DFFIT value over $|1|$ indicating this was an influential case. Standardized DFBETA values for this case showed it had undue influence over zinc and cesium (Table 26). I-NK-A also had a high standardized DFFIT, and DFBETA value above absolute 1 for nickel. The case HS-O had a DFFIT of 1.08636 (~ 1), but no DFBETA exceeding the undue influence criteria ($>|1|$).

Table 26 The casewise diagnostics of the baseline soil (n = 219) stepwise multiple regression model. (Includes cases with standardized residuals > 2 only.)

Case #	Sample Name	Standardized Residual	Mahalanobis Distance	Cook's Distance	Centered Leverage Value
6	BCJP	-2.572	6.96393	.03253	.03194
25	HC-B	2.502	11.57993	.05082	.05312
51	HS-G3	2.366	4.31603	.01791	.01980
69	HS-KK	2.443	5.93185	.02529	.02721
82	HS-O	3.470	16.11040	.13905	.07390
90	HS-Q	3.238	3.11367	.02566	.01428
91	HS-Q10	4.516	7.21269	.10364	.03309
95	HS-Q5	2.233	8.74947	.03053	.04014
98	HS-Q8	2.233	2.67219	.01075	.01226
101	HS-QQ	2.358	13.07748	.05128	.05999
138	HS-ZZ	-2.271	9.85694	.03556	.04522
155	I-NK-A	2.329	89.43955	.82139	.41027
186	I-ZB-30	-2.337	10.57048	.04041	.04849
192	I-ZB-42	-2.161	131.39036	2.29824	.60271
214	MB-18	2.071	6.63492	.02015	.03044
Undue influence criteria		n/a	> 23 ^a	> 1 ^b	> 0.07306 (2xAvgL) ^c > 0.10959 (3xAvgL) ^d

^a (Barnett and Lewis, 1994)

^b (Cook and Weisberg, 1982 in Field (2005))

^c (Hoaglin and Welsch, 1978 in Field (2005))

^d (Stevens, 1992 in Field (2005))

Table 26 The casewise diagnostics of the baseline soil (n = 219) stepwise multiple regression model. (Includes cases with standardized residuals > 2 only.) (cont'd.)

Case #	Sample Name	Standardized DFFIT	Standardized DFBETA							
			Mn	Ca	Fe	Co	Ni	Zn	Cs	Li
6	BCJP	-.51742	-.35112	.18869	.32524	-.32238	-.19643	.04940	-.19609	.24288
25	HC-B	.64638	-.21472	-.01911	.08513	-.15587	-.08438	.07218	-.52166	.55352
51	HS-G3	.38291	.13864	-.12933	-.03879	.18759	-.10690	.16369	.22241	-.29541
69	HS-KK	.45545	.15278	-.20485	-.03093	.21704	-.19301	.24187	.15557	-.26728
82	HS-O	1.08636	.13779	-.26308	-.17887	-.52790	.73934	.08354	-.04336	.07743
90	HS-Q	.46387	.13827	.00092	-.14501	.32869	-.08007	-.09130	-.01880	-.05191
91	HS-Q10	.95778	.38633	-.39156	-.08632	.50966	-.36058	.20974	.46669	-.66034
95	HS-Q5	.49923	.26086	-.12212	-.18489	.24711	.10013	.00506	.36036	-.37738
98	HS-Q8	.29612	.15085	-.03129	-.16002	.21533	.00391	-.06327	-.05422	-.01326
101	HS-QQ	.64820	.38474	-.33864	-.17231	.16659	-.04287	-.01644	.08942	-.28725
138	HS-ZZ	-.53907	-.08876	-.23212	.10302	.03684	-.07847	.03700	-.00356	.07821
155	I-NK-A	2.61543	.85338	.18550	-.88032	-.81628	1.63507	-.89245	-.28731	.02357
186	I-ZB-30	-.57511	-.28292	-.19011	.33519	-.23878	-.15765	.04345	-.03179	.15336
192	I-ZB-42	-4.40358	.02095	.96760	-.04460	-.50432	-.93597	1.54114	1.84201	-.59652
214	MB-18	.40482	.11134	-.14503	-.08665	.21560	-.17941	.27512	-.06154	-.03979
Undue influence criteria		> 1 ^e	> 1 ^e	> 1 ^e	> 1 ^e	> 1 ^e	> 1 ^e	> 1 ^e	> 1 ^e	> 1 ^e

^e (Field, 2005)

Summary discussion

In summary, baseline soil manganese, as well as most of baseline soil elements, was statistically neither normally, nor log-normally distributed. According to the Spearman correlation matrix, baseline soil manganese was significantly correlated to iron, cobalt and calcium. According to the multiple regression model fit parameters, the baseline soil multiple regression model used was a good fit to the soil manganese data.

Strictly speaking, the investigation of the standard residuals of the baseline soil stepwise multiple regression model revealed that it was a poor representation of the data because over 5 % of the residuals were above 2 and over 1 % were above 2.5. However, their exceedance of these guidelines was minimal to negligible. It can be concluded that due to these residuals, a bias exists in this model. These cases would need further investigation if this model were to be used to predict the baseline soil manganese concentrations. Three cases (or samples) exerted undue influence on the model parameters. These coincided with extreme values identified in Chapter 5 (see discussion below).

The following elements had a significant influence on soil manganese levels: Fe, Ca, Cs, Co, Ni, Zn and Li. Iron accounted for over half of the variability seen in the baseline soil manganese results and cobalt, 8.5 %. These baseline soil elements had a high correlation coefficient ($r_s > .8$) which could indicate collinearity. The tolerance statistics showed that baseline soil iron, cobalt, nickel, cesium and lithium predictors could pose a potential collinearity problem to the model. The variance proportions showed that collinearity may indeed exist between baseline soil iron and cobalt variables, though it appeared to be weak. The variance proportions also provided evidence of the collinearity which existed between the baseline soil cesium and lithium predictor variables. Therefore, it can be concluded that the association between baseline soil iron, cobalt and calcium with baseline soil manganese is significant. The amount of variability of baseline soil manganese accounted for by these elements cannot be reliably reported without further tests, however it can be stated that they account for a large proportion.

The influential cases of the multiple regression analysis (standardized residuals > 3) were also identified, and discussed, in Chapter 5. They were extreme value samples from areas of elevated soil manganese. The two cases which exerted undue influence over the parameters of the baseline soil multiple regression model were I-ZB-42 and I-NK-A. The former baseline soil sample had the highest soil manganese concentration (3430 ppm) and was located in one of the elevated areas identified in Chapter 5, the Devon-CN area. This sample was retrieved near the IZB industry next to the train tracks; the soil was brick-red. The latter influential baseline soil sample was located near one of Windsor's manganese-emitting industries; however this sample had one of the lowest soil manganese levels (202 ppm). This soil sample was taken next to the industry's perimeter fence where the soil was gravel (i.e., soil was grey, the same colour of the gravel stones).

1.3 Natural soil

The natural soil manganese had a mean of 506 ± 173 ppm. The majority of the elements in natural soil were normally distributed, including manganese ($W(14) = 0.885, p > .05$). Pearson's correlation coefficient (r) was used to describe their elemental associations. Of the elements reported in Table 27, calcium, antimony and lead were log-normally distributed and the non-parametric Spearman correlation coefficient (ρ) was used instead of Pearson's to describe their relationships with other elements. Natural soil strontium results were neither normally nor log-normally distributed. Therefore, the Spearman coefficient ρ was also used to describe its relationships. In order to have consistency between the tables of the different sample types, the same suite of elements is reported in Table 27, Table 21 and Table 15. The ρ s shown in **bold** were statistically strong ($r_s > .5$) and significant (Field, 2005).

Of the 49 elements, only two, iron ($r = .59, p < .05$) and cobalt ($r = .68, p < .01$), were positively significantly correlated to natural soil manganese. From the simple linear regression between manganese and iron, the calculated amount of variability in soil manganese that could be explained by iron (R^2) was 34 % (Figure 51). Figure 52 shows the linear regression ($R^2 = 0.46$) between manganese and cobalt. It is important to note that a strong significant correlation between iron and cobalt ($r = .95, p < .01$) in natural soil existed.

Their simple linear regression is shown in Figure 53. No other statistically significant association existed between manganese and any other element in natural soil.

Table 27 Pearson's correlation matrix for the natural soil sample type elemental concentrations (n = 14) ($p = 0.01$).

	Mg	K	Ca ^a	Cd	Cr	Mn	Fe	Ni	Ag	Cs	Co	Zn	As	Sr ^a	Mo	Sn	Sb ^a	Cu	Pb ^a
Mg	1																		
K	-.54*	1																	
Ca^a	.90	-.59*	1																
Cd	ns	ns	ns	1															
Cr	-.68	ns	-.82	.57*	1														
Mn	ns	ns	ns	ns	ns	1													
Fe	-.62*	.89	-.74	ns	.67	.59*	1												
Ni	-.63*	ns	-.70	ns	.76	ns	.96	1											
Ag	-.64*	ns	-.79	ns	.56*	ns	ns	ns	1										
Cs	-.62*	.92	-.75	ns	.58*	ns	.89	.87	ns	1									
Co	-.58*	.86	-.58*	ns	.65*	.68	.95	.95	ns	.81	1								
Zn	-.84	.59*	-.84	.74	.72	ns	.62*	.67	ns	.64*	.59*	1							
As	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	1						
Sr^a	.73	-.57*	.88	ns	-.71	ns	-.76	-.68	-.73	-.65*	-.60*	-.71	ns	1					
Mo	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	.57*	ns	1				
Sn	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	.66	ns	.70	1			
Sb^a	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	.74	ns	.89	.90	1		
Cu	ns	ns	ns	ns	ns	ns	ns	.57*	ns	ns	ns	ns	ns	ns	ns	ns	ns	1	
Pb^a	-.82	ns	-.81	.64*	.72	ns	ns	ns	.65*	.56*	ns	.93	ns	-.66*	ns	ns	ns	ns	1

^a Indicates a Spearman correlation coefficient was used because one or both of the elements were not normally distributed.

* Correlation is significant at the 0.05 level.

“ns” Indicates result was not statistically significant.

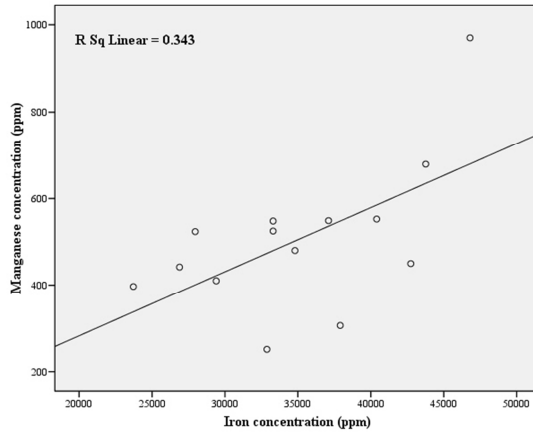


Figure 51 Scatterplot and linear regression trend line of natural soil manganese and iron results ($n = 14$).³

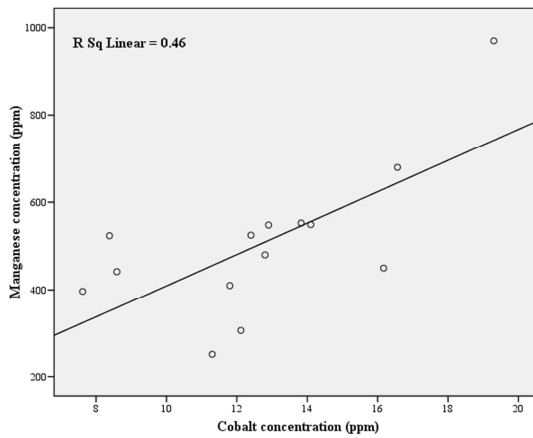


Figure 52 Scatterplot and linear regression trend line of natural soil manganese and cobalt results ($n = 14$).³

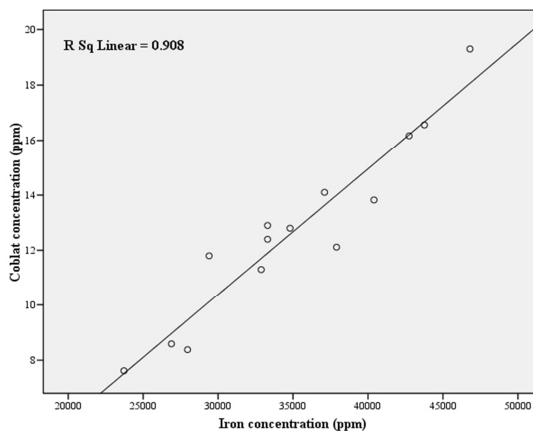


Figure 53 Scatterplot and linear regression trend line of natural soil iron and cobalt results ($n = 14$).³

Summary discussion

The natural Windsor soil manganese results were normally distributed. Only two elements were significantly associated with manganese: iron and cobalt. These elements were also very strongly correlated with each other. Collinearity is defined as “a strong correlation between two or more predictors in a regression model” (Field, 2005). If collinearity (or multicollinearity) exists between the variables of a model, this poses a problem to the model because high levels of collinearity affect the standard errors of the *beta*-coefficients which in turn affect their significance (Field, 2005). The importance of the predictors is then difficult to assess. There is evidence that collinearity exists between the iron and cobalt results of the natural soil, i.e., their correlation coefficient is well above .9. Evidence of collinearity between iron and cobalt in natural soil was also found in the multiple regression analysis of this soil sample type. Results of the multiple regression analysis are not presented here because the model fit parameters were not within acceptable limits therefore indicated that the model was not a good fit for the natural soil manganese results. Other predictors, besides the iron and cobalt results, would be needed in order to develop a better model for natural soil manganese. It can therefore be concluded that a significantly strong relationship exists between natural soil manganese and iron, and cobalt. Their individual importance (i.e., the variability of soil manganese accounted for by these predictors) cannot reliably be determined at this time. Iron and manganese oxyhydroxides (oxides and hydroxides) often occur together in soils and sediments (Gilkes and McKenzie, 1988; Tessier et al., 1996). Therefore the strong relationship observed between natural soil manganese and iron is not unexpected. Similarly, there is a known affinity between cobalt and manganese oxides in soils (Taylor and McKenzie, 1966; McKenzie, 1967, 1970). As mentioned in Chapter 1, over time sorbed cobalt can replace manganese in the manganese oxide structure (McKenzie, 1970).

2.0 Comparison of transect, baseline and natural soils

As previously discussed in Chapter 5, the baseline and transect soil manganese results were both not-normally distributed, non-parametric Mann-Whitney mean comparison tests were therefore used to compare all three sample types. The baseline (median = 385 ppm, n =

219) and transect (median = 553 ppm, n = 99) soil sample types were significantly different ($U = 3668.5, p < .05, r = -.53$) with respect to soil manganese concentrations. Manganese in the baseline soil was also significantly different ($U = 968, p < .05, r = -.15$) from the natural soil manganese (median = 502 ppm, n = 14). The transect and natural soil manganese were also significantly different ($U = 445.5, p < .05, r = -.20$). Table 28 shows the significant elemental associations ($|0| < r_s < |1|$) of soil manganese for the different sample types (natural, baseline and transect). Spearman correlation coefficients above .5 are considered to represent a strong relationship (Field, 2005) and are shown in **bold** in Table 28. Manganese in the natural soil was found to be significantly associated with only iron and cobalt ($r_s > .5$) (section 1.1). These relationships were also found in the baseline soil, though they had a slightly lower correlation coefficients, but still above .5. Calcium in baseline soil was also found to have a strong association with manganese ($r_s > .5$) (section 1.2), however this association was not significant for the other two sample types (Table 28). The relationship between transect soil manganese and iron, and cobalt was weaker still than baseline soil (Table 28). The transect soil manganese had significant correlations ($r_s > .5$) with zinc, molybdenum, tin, cadmium, copper and lead (section 1.3) which were weaker in baseline soil ($r_s < .5$) and not significant in natural soil.

Table 28 Comparison of transect (n = 99), baseline (n = 219) and natural (n = 14) sample type manganese elemental signatures.

Element	Transect	Baseline	Natural	Element	Transect	Baseline	Natural
Li	ns	-0.21	ns	Nb	ns	ns	ns
Na	ns	ns	ns	Mo	0.61	0.45	ns
Mg	0.22	0.46	ns	Sn	0.51	0.28	ns
Al	ns	-0.17	ns	Sb	0.20	0.32	ns
K	-0.31	-0.26	ns	Ba	0.24	ns	ns
Ca	ns	0.51	ns	Pr	ns	ns	ns
Cd	0.67	0.36	ns	Gd	ns	ns	ns
Cr	0.39	0.34	ns	Dy	ns	-0.16	ns
Fe	0.46	0.54	0.59	Cu	0.60	0.36	ns
Ni	0.47	0.43	ns	Ge	ns	ns	ns
Er	ns	-0.14	ns	Tm	ns	ns	ns
Be	ns	ns	ns	Re	ns	ns	ns
Ho	ns	ns	ns	Tl	ns	-0.15	ns
Ag	0.47	0.32	ns	Pb	0.64	0.33	ns
Cs	-0.25	-0.33	ns	Th	ns	ns	ns
Co	0.41	0.54	0.68	U	ns	-0.19	ns
Se	0.21	ns	ns	Hf	ns	ns	ns
Zn	0.58	0.43	ns	Eu	ns	-0.14	ns
Ga	ns	-0.21	ns	La	ns	-0.15	ns
As	ns	0.43	ns	Ce	ns	-0.14	ns
Rb	ns	-0.22	ns	Nd	ns	ns	ns
Y	ns	ns	ns	Sm	ns	-0.17	ns
Sr	0.23	0.42	ns	Tb	ns	ns	ns
Zr	ns	ns	ns	Yb	ns	-0.17	ns

“ns” indicates the relationship was not statistically significant.

Note: See specific soil sample type sections for information regarding type of correlation used (i.e., Spearman vs Pearson).

Discussion

It was concluded in Chapter 5 that the manganese results of soil samples retrieved in Windsor, Ontario belonged to three significantly different soil sample types, (a) transect, (b,d,e) baseline, and (c) natural. Further investigation into the relationships between manganese and the other soil elements has revealed more evidence of the differences existing between these sample types. The transect soil sample type had six significant correlations. These associations were not found significant in the natural soil, however they were found significant in the baseline soil but their correlation strengths were much weaker ($< .4$) than in the transect soil. Only three significant relationships (Fe, Co and Ca) were found for baseline soil manganese. Two of these relationships (Fe and Co) were also found in natural soil. This would indicate that baseline soil may have a component of natural soil. Walker (2010) found evidence that the baseline soil sample I-ZB-B consisted of anthropogenic particles and common naturally occurring secondary minerals (Chapter 5).

Conclusion

Several significant relationships were found between manganese and the other elements in urban Windsor soil. These associations varied between the different soil sample types. As well as distinguishing between the natural and anthropogenic elemental signals of the Windsor soil, two distinct anthropogenic signals, both of which different from the natural signal, were also found.

Chapter 7 - A Field-Portable X-Ray Fluorescence Analyzer for Determination of Manganese and Related Elements in Soil

Purpose

The purpose of this study was to evaluate a field-portable X-ray fluorescence analyzer for field determination of manganese and related elements in environmental soil samples. The FPXRF analyzer was used in the field, not as a substitute for more traditional methods such as inductively-coupled plasma mass spectrometry analysis (ICP-MS), but as a screening tool for preliminary detection of elevated areas of manganese. Such a tool would save time and money. In order to be a reliable investigative tool, the FPXRF must produce results which are at least capable of capturing the elevated metal contents, or distinguishing between elevated and background metal contents.

Three FPXRF measurement methods were evaluated. The first was a direct measurement (“direct”); second, measurement of the sample through the sample bag (“baggie”); and third was a measurement which used “XRF-cups”. The amount of sample preparation increased from one method to the next. The baggie measurement was size-fractionated through settling while the XRF-cup sample was dried, sieved and incorporated into an XRF-cup.

Design

In June 2007, during the preliminary soil survey, a field-portable X-ray fluorescence (FPXRF) analyzer was used to take measurements of the same soil sample after different degrees of sample preparation (i.e., using different methods). The efficiency of these methods was evaluated by comparison to the “Gold standard” of trace element environmental analysis, inductively-coupled plasma mass spectrometry (ICP-MS). For a detailed description of the field and analytical methods, consult Chapter 4. One hundred and one urban sites in Windsor, Ontario were measured using the FPXRF analyzer. Once the direct measurement was taken, soil samples were retrieved from the exact location of the direct measurement. The soil was placed in a clear plastic bag. Through handling of the sample bag, the soil settled. A second FPXRF measurement was taken of the settled soil,

through the plastic sample baggies. The soil samples were then dried and sieved and a sub-sample was used in the assembly of XRF-cups, the third and final of the FPXRF field methods. These last two FPXRF methods were done in the laboratory in triplicate but could easily have been done in the field. The remaining soil samples were sent to a private laboratory (Activation Laboratories Ltd.) for digestion and ICP-MS analysis. Gravimetric moisture content analysis was done on a small group of soil samples ($n = 27$) to ascertain the degree to which soil moisture influenced the FPXRF measurements. FPXRF measurement protocols and source information are described in detail in Chapter 4.

Results

1.0 Evaluation of quality assurance parameters

1.1 Method detection limit (MDL) determination

In this chapter, the method detection limit (MDL) was used to define the detection limit for the FPXRF results, and the limit of detection (LOD) was used to define the detection limit for ICP-MS analysis. In general, the detection limit is the lowest concentration of an analyte that can be reliably distinguished. Several ($n = 18$) XRF-cups were assembled (Chapter 4) using certified reference materials (CRM) which have a similar matrix to the soil samples examined in the present study (i.e., soil and sediment CRMs). To determine which CRM was suitable to use for each of the 8 reported elements, each CRM-filled XRF-cup was measured 11 times following the protocol outlined in Chapter 4. The CRM selected to calculate the individual MDL had to meet the following criteria:

- a. FPXRF analysis of the CRM-filled XRF-cup resulted in the lowest concentration for that particular element;
- b. A valid certificate of analysis existed for the CRM and results for the element in question were certified (certified or reference value); and
- c. At least seven of the 11 FPXRF measurements had to be valid (i.e., above the instrument's detection limit).

Method detection limits (MDL) were calculated using Equation 6 (Kalnický and Singhvi, 2001). Limits of quantification were calculated using Equation 7 (Stallard et al.,

1995). LOQ as defined by Stallard et al. (1995) is the level above which quantitative results may be obtained with a specified degree of confidence. Results located between the MDL and the LOQ are in a region of ‘less certain quantification’ (Stallard et al., 1995). Table 29 shows the FPXRF MDLs and LOQs for each reported element. The ICP-MS limits of detection (LOD) are also shown in Table 29. Results below the FPXRF MDL and the ICP-MS LOD were substituted with ½ the MDL, or LOD, value (Table 29) for the purpose of data analysis.

$$\text{MDL} = (\text{Standard deviation of CRM-filled XRF-cup}) \times 3 \quad [\text{Eqn 6}]$$

$$\text{LOQ} = (\text{Standard deviation of CRM-filled XRF-cup}) \times 10 \quad [\text{Eqn 7}]$$

Table 29. FPXRF method detection limit (MDL) and limit of quantification (LOQ), and ICP-MS limit of detection (LOD) for the 8 reported elements.

		Mn	Fe	Pb	Zn	Rb	Sr	Ba	Zr
Calculated MDL ¹ (ppm)		93.4	843	19.6	45.5	6.7	14.3	132	6.2
% of FPXRF results > MDL	Direct Baggie XRF-cup	84	100	91	86	99	100	98	99
		95	100	95	89	100	100	99	99
		98	100	95	98	100	100	99	99
LOQ		311	2810	65.3	152	22.3	47.7	440	20.7
% of FPXRF results > LOQ	Direct Baggie XRF-cup	70	100	52	53	97	100	18	97
		63	100	49	38	98	100	20	98
		81	100	65	68	99	100	33	99
n		10	13	8	7	8	8	8	8
Manufacturer's LOD ² (ppm)		230	230	15	60	7	15	80	18
ICP-MS LOD ³ (ppm)		1	100	0.5	0.2	0.2	0.2	1	1

¹ Based on a 90 Nominal second measurement time.

² Calculated using NIST CRMs and based on a 60 Nominal second measurement time.

³ LOD reported by private lab (Activation Laboratories, Ltd).

Detection limits

The calculated MDL values for manganese, zinc, rubidium, strontium and zirconium were lower than the manufacturer's LOD (Table 29). The opposite is true for lead, barium and iron; the latter element had an MDL over three times larger than the manufacturer's LOD. The ICP-MS analysis had the lowest detection limits (Table 29).

All of the ICP-MS results were above the LOD values. All of the reported elements had between 80 and 100% of their results above the FPXRF method detection limits. The majority of manganese FPXRF direct, baggie and XRF-cup results were above the limit of quantification, namely 70 %, 63 % and 81 %, respectively. The remaining results were between the MDL and LOQ values. The iron, rubidium, strontium and zirconium results were all well above their limit of quantification (LOQ). A little over half of the FPXRF lead and zinc results were also above this limit. The other half was between their MDL and LOQ values. FPXRF barium results were mostly in the region of less certain quantification (between MDL and LOQ).

Reported elements

Elements which had less than 20% of their measurements below the calculated MDL (section 1.1) or LOD were reported (Table 29). Eight out of 24 elements (i.e., Sr, Rb, Pb, Zn, Mn, Fe, Zn and Ba) met this criterion and are included in this report. Three of the 101 sampling sites were excluded from the method comparison because either a direct, baggie or XRF-cup result was missing.

Error rates

Only a small number of FPXRF results were false-negatives (i.e., a below detection limit FPXRF result was actually detected by the ICP-MS analysis). In the majority of the cases, 1 or 2 results were false-negative. Iron and strontium had no false-negative results. The FPXRF direct method had the larger number of false-negative results for lead, zinc and manganese, 9, 14 and 16, respectively. For both zinc and manganese, the FPXRF XRF-cup method had only 2 false-negative results.

1.2 Element recovery

The element recoveries were calculated using Equation 8 and the results of FPXRF measurements of CRM-filled XRF-cups which were interspersed between soil sample analyses. Element recoveries of the ICP-MS analysis were calculated using the results of blind CRM samples submitted to the private laboratory along with the soil samples for ICP-MS analysis. Table 30 shows the element recoveries for both FPXRF and ICP-MS methods for the reported elements.

$$\text{Element Recovery} = (\text{Average observed CRM value}) / \text{Certified value}) \times 100 \quad [\text{Eqn 8}]$$

Table 30. FPXRF and ICP-MS element recoveries (%) for the 8 reported elements.

	Mn	Fe	Pb	Zn	Rb	Sr	Ba	Zr
FPXRF	98	84	112	93	92	81	98	39
(n)	(15)	(15)	(15)	(15)	(9)	(14)	(15)	(8)
ICP-MS	104	95	97	92	53	88	80	40
(n)	(3)	(3)	(3)	(3)	(3)	(3)	(3)	(2)

1.3 Gravimetric Moisture Content

Soil moisture contents above 20 % can affect the accuracy of FPXRF measurements (U.S. Environmental Protection Agency, 1998). Twenty-seven of the 101 soil samples were selected for gravimetric soil moisture analysis. The samples chosen for this analysis were the wettest samples (i.e., the samples most likely to be influenced by soil moisture). Wetness was based on a visual observation of condensation inside the baggie after refrigeration. (Chapter 4 details the gravimetric moisture content analysis and calculation). This group of FPXRF soil samples had soil moisture contents ranging between 3.1 % and 34.1 %. The average was 16.4 ± 7.5 %. Seven samples (26 %) of this subgroup were above 20 % soil moisture.

1.4 Discussion

In general, the calculated method detection limits for the FPXRF analyzer were acceptable. The differences between the calculated MDL and the manufacturers' LOD can be attributed to the FPXRF source, measurement time and sample matrix (NITON LCC, 2002). In this case, differences are most likely attributed to the source strength and different measurement times. Stallard et al. (1995) reported a detection limit of 35 ppm for zinc and 14 ppm for lead for the measurement of soils by an FPXRF analyzer. Bernick et al. (1995b) reported minimum detection limits (mg/kg) for various elements from various waste types. In summary, the lead minimum detection limits ranged from 73 to 606 (mg/kg) and zinc from 90-111 mg/kg for one FPXRF analyzer (XMET 880) and for another analyzer (Spectrace 9000), the limit for lead was from 30-123 (mg/kg), zinc from 56-206 mg/kg and barium from 39-78 mg/kg for another analyzer (Spectrace 9000). These were for prepared samples varying in measurement times.

As previously mentioned, only a small number of FPXRF results were below the method detection limits and all of the ICP-MS results were above the LOD values. Reames and Lance (2002) used false-negative error rates (number of false-negative measurements / positive) to evaluate which FPXRF methods could correctly identify soil lead concentrations. They used the California regulatory level for soil lead in areas accessible to children, 400 ppm, as the cut-off level and a criterion of five percent or less as an acceptable false-negative error rate. Instead of using a regulatory level, the method detection limit was used to evaluate the FPXRF methods of this present study. Most of the FPXRF methods met the ≤ 5 % criterion. However this criterion was exceeded by the lead (10 %), zinc (16 %) and manganese (19 %) results of the FPXRF direct method. The FPXRF baggie method had zinc results which also had a high error rate, 12.5 %. The danger in high false-negative rates is underestimating elemental results in the field. Therefore caution should be exercised when using the above mentioned 'high false-negative rate' methods (i.e., Pb (direct), Zn (direct and baggie), and Mn (direct)) in an urban area where soil elemental concentrations are not expected to be high.

Typically, element recoveries within 20 % of certified values are deemed acceptable (Kalnicky and Singhvi, 2001). Most reported elements had element recoveries over 80 %. The FPXRF ICP-MS rubidium and both zirconium element recoveries were the exception. Manganese element recoveries were within 5 % of the certified values. Kalnicky and Singhvi (2001) reported manganese recoveries of 127 % and 94 % using an FPXRF analyzer and two different calibration models. They also found iron, zinc and lead recoveries between 87 and 96 % with the first calibration method and 94 to 103 % for the other. Barium recoveries were 60 and 103 %, respectively.

The average soil moisture of the wettest soil samples ($n = 27$ subsamples) was below the recommended 20 %. Also, only 26 % of the subsamples had soil moisture contents above this value. Therefore, on average, soil moisture did not have a negative influence on the accuracy of the FPXRF measurements. When taking direct measurements with an FPXRF instrument, it is necessary to evaluate the wetness of the samples to ensure that soil moisture does not exceed 20 %. Kalnicky and Singhvi (2001) suggested that soil samples should be dried when soil moisture exceeds 20 %. Ge et al. (2005) proposed an equation which corrects for the influence of water content on FPXRF measurements. Their tests showed the equation was effective for samples with up to 20% of water content (range of acceptable soil moisture). Reames and Lance (2002) did not dry their soil samples before FPXRF determination of lead and they stated that drying samples before FPXRF measurement may not be necessary to achieve accurate results. However they also stated that their soil samples had low moisture content which would not be expected to adversely affect the accuracy of the FPXRF results.

2.0 Comparison and efficiency of field FPXRF methods on urban soil samples.

The Shapiro-Wilk normality test (W) was used to evaluate the distribution of the FPXRF results and the corresponding ICP-MS results. The results of all three FPXRF methods were not normally distributed except for the direct and baggie rubidium, ($W(99) = .988, p > .05$) and ($W(99) = .993, p > .05$), respectively. Lead results for the FPXRF baggie method were log-normally distributed ($W(99) = .974, p > .05$). All other FPXRF method results were not log-normally distributed (All $p < .05$). All ICP-MS results associated to

FPXRF measurements were not normally distributed, except for lead ($W(99) = .980, p > .05$), nor were they log-normally distributed.

The eight reported elements are evaluated individually in the following sections. Basic descriptive statistics are given along with the results of various mean comparison tests. The “method accuracy” in each Table detailing the FPXRF results was calculated using Equation 9, and expressed as a percentage.

$$\text{Method Accuracy} = (\text{FPXRF method mean} / \text{ICP-MS mean}) * 100 \quad [\text{Eqn 9}]$$

The means of the three FPXRF methods were compared using the non-parametric Friedman analysis of variance (ANOVA). This test was used because elements were not normally distributed and the different methods were related (i.e., 3 results / sample). (Note: though FPXRF direct and baggie rubidium results were normally distributed, the non-parametric test must be used because they are being compared to data which is not normally distributed (i.e., FPXRF XRF-cup method results).) ANOVA tests the hypothesis that all group means are equal (Field, 2005). To compare the group means on a pairwise basis, *post hoc* tests were conducted. The Wilcoxon signed-rank test was used as the non-parametric *post hoc* test for comparing two related group means. This test uses the ranked differences between scores. The level of significance for these pairwise comparisons was corrected to control the familywise error (Appendix E) by dividing α (.05) by the number of tests conducted, in this case 3 ($p = .008$). The Wilcoxon signed-rank test was also used to compare the group means of each field FPXRF method with the ICP-MS elemental mean. Because the test was not used as a *post hoc* test, the level of significance was unchanged (i.e., $p = .05$). In most cases, the Spearman correlation was used to describe the relationship between methods. However, a Pearson coefficient (r) was used instead of Spearman's r_s for the rubidium FPXRF direct and baggie comparison since their results were normally distributed. Scatterplots were generated to visually illustrate the relationships between the results of the field FPXRF methods and the ICP-MS analysis.

2.1 Manganese

Descriptives

FPXRF direct, baggie and XRF-cup, as well as ICP-MS manganese results ($n = 99$), were not normally distributed (All $p < .05$) (Table 31). These results were also not log-normally distributed ($p < .05$). Median values for soil manganese ranged from 352 ppm to 458 ppm for the various FPXRF measurements (Table 31). The ICP-MS manganese median was 520 ppm. Both the FPXRF direct and baggie methods had a 5th percentile of 46.7 ppm, which is $\frac{1}{2}$ the manganese LOD value. The 5th percentile value of the FPXRF XRF-cup was 146 ppm. The 95th percentile value for direct, baggie and XRF-cup was 905, 623 and 913 ppm, respectively. The ICP-MS 95th percentile value was 890 ppm. The FPXRF XRF-cup method had the highest manganese result accuracy of the field methods (Table 31).

Table 31. Results of the Shapiro-Wilk normality test and descriptive statistics of manganese FPXRF method results and corresponding ICP-MS results.

Statistic (ppm)	Method			
	FPXRF			ICP-MS
	Direct	Baggie	XRF-cup	
Shapiro-Wilk statistic (W)	.471	.383	.334	.681
Shapiro-Wilk statistic (W) (Log(Mn))	.816	.880	.865	.955
Geometric mean	317	306	438	500
Median	382	352	458	520
5 th percentile	46.7	46.7	146	279
95 th percentile	905	623	913	890
Mean	455	385	543	539
Standard deviation	509	420	647	259
Method accuracy (%)	84	71	101	n/a

Method Comparison

The soil manganese means of the different field FPXRF methods were compared using the non-parametric Friedman ANOVA. There was a significant difference between all FPXRF method means for soil manganese ($\chi^2(2) = 40.3$, $p < .05$). This significant difference ($p < 0.008$) existed between each pair of FPXRF methods (Table 32). Though the means

were different, all FPXRF method results were significantly correlated (Table 32). Linear regressions were also significant between the three FPXRF methods (Table 32).

Table 32. Soil manganese FPXRF *post hoc* test, correlation and regression results.

Pairwise Comparison	<i>Post hoc</i> Wilcoxon signed-rank test ($p < 0.008$)	Spearman <i>rho</i>	R^2
Direct vs Baggie	$T = 1347, r = -.36$	.71	.46
Direct vs XRF-cup	$T = 1506, r = -0.31$	.51	.32
Baggie vs XRF-cup	$T = 365, r = -.073$	.74	.54

Using the non-parametric Wilcoxon signed-rank test, a significant difference was found between the direct, baggie and XRF-cup FPXRF and the ICP-MS soil manganese means, ($T = 1191, p < .05, r = -.45$), ($T = 208, p < .05, r = -.80$), and ($T = 1131, p < .05, r = -.47$), respectively. Figure 54 provides a visual comparison of the differences and similarities between the FPXRF method results and the corresponding ICP-MS results. In general, this visual assessment shows the FPXRF methods found elevated manganese levels which corresponded to elevated ICP-MS manganese results. Result statistics support this finding. For illustrative purposes, Figure 55 shows the scatterplots of the log-transformed soil manganese FPXRF methods' results individually plotted against the corresponding ICP-MS results and their linear regression trendlines. The Spearman ranking, which best describes non-parametric data correlations, showed that the ICP-MS soil manganese results were significantly correlated to direct ($r_s = .52, p < .05$), baggie ($r_s = .76, p < .05$) and XRF-cup ($r_s = .88, p < .05$) FPXRF results.

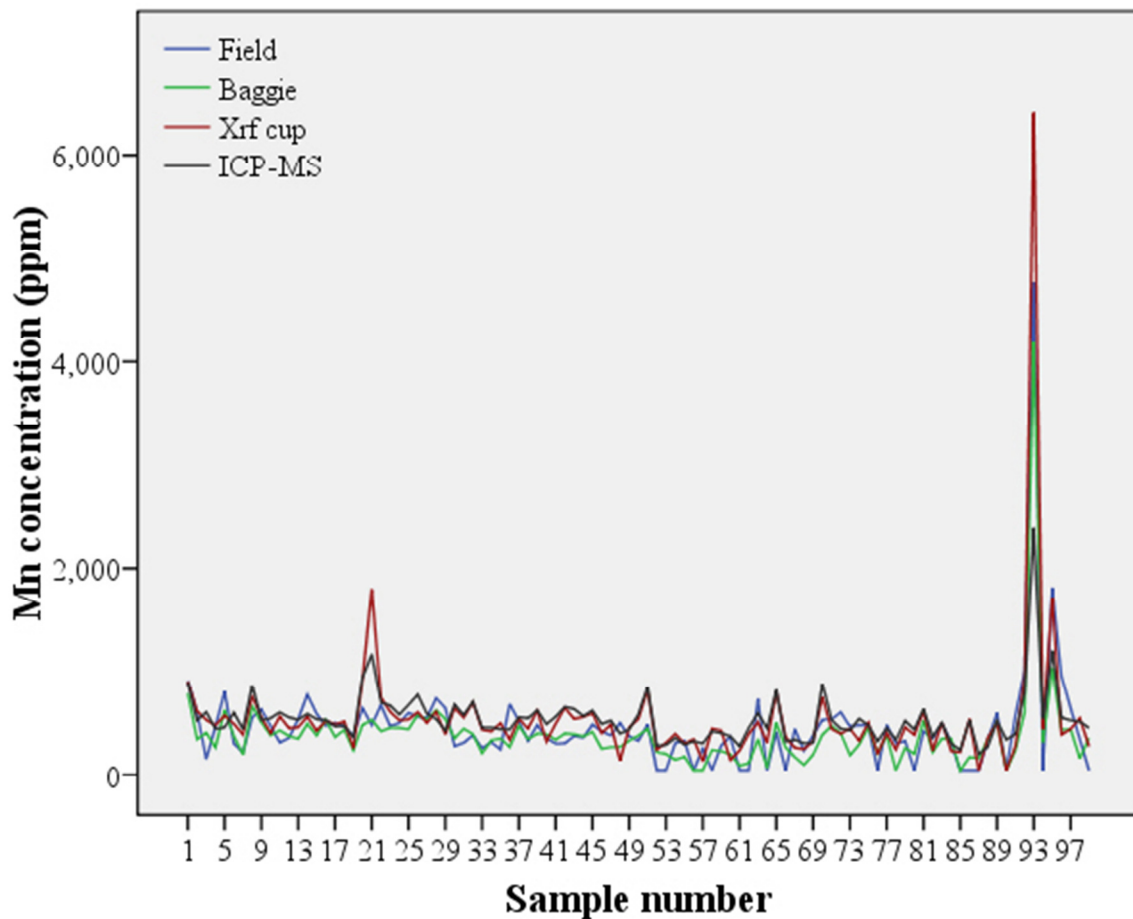


Figure 54 Visual comparison of soil manganese results from FPXRF methods and ICP-MS analysis (n = 99). (Samples were from the preliminary soil survey.)

Summary

FPXRF soil manganese results were not normally or log-normally distributed. All FPXRF soil manganese medians were lower than the ICP-MS median (520 ppm). The FPXRF XRF-cup method median (458 ppm) was closest to the latter. The highest accuracy corresponded to the XRF-cup method. The three FPXRF methods had different means suggesting the results were from different populations. However, their positive correlations showed that all FPXRF methods could correctly detect sites of elevated soil manganese. Figure 54 also displays this agreement in the results. The FPXRF means were also different from the “Gold standard” ICP-MS analysis of soil manganese mean. Positive correlations also existed between the results of the FPXRF methods and the ICP-MS analysis.

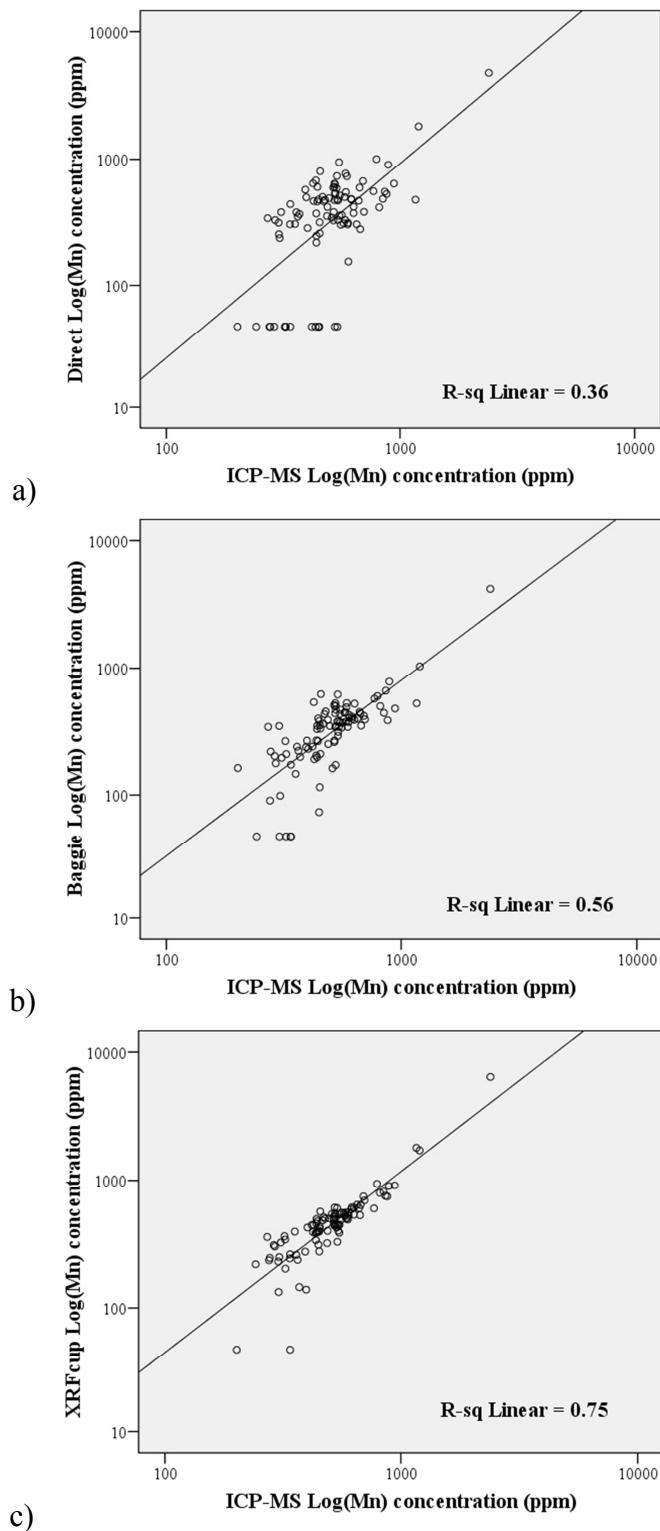


Figure 55

Scatterplots and linear regression trendlines of log-transformed soil manganese a) direct, b) baggie and c) XRF-cup FPXRF and ICP-MS results ($n = 99$). (Samples were from the preliminary soil survey.)

2.2 Iron

Descriptives

Iron FPXRF results (direct, baggie, and XRF-cup) ($n = 99$) were not normally distributed ($p < .05$) (Table 33). Their log-normal distribution was also not significant ($p < .05$) (Table 33). Neither were the ICP-MS results ($(W(99) = .256, p < .05)$ and $(W(99) = .577, p < .05)$, respectively). The FPXRF and ICP-MS method medians for soil iron as well as the 5th and 95th percentiles are shown in Table 33. The baggie method had the lowest median, 17 426 ppm, while the XRF-cup was the highest of the FPXRF methods, 25062 ppm. The ICP-MS median for iron was higher than these methods (Table 33). FPXRF direct and baggie methods had a similar range between the 5th and 95th percentiles, approximately 17 000 ppm and 14 000 ppm while the FPXRF XRF-cup and ICP-MS were closer, approximately 32 000 ppm and 29 000 ppm (Table 33). The FPXRF XRF-cup had a result accuracy of 95 %. Both the FPXRF direct and baggie methods had low result accuracies (Table 33).

Table 33. Results of the Shapiro-Wilk normality test and descriptive statistics of iron FPXRF method results and corresponding ICP-MS results.

Statistic (ppm)	Methods			
	FPXRF			ICP-MS
	Direct	Baggie	XRF-cup	
Shapiro-Wilk (W)	.221	.186	.155	.256
Shapiro-Wilk (W) (Log(Fe))	.696	.666	.527	.577
Geometric mean	19 239	17 647	26 276	31 772
Median	18 836	17 426	25 062	30 367
5 th percentile	12 539	11 779	19 933	25 100
95 th percentile	29 517	25 907	52 232	53 967
Mean	23 091	20 930	33 123	34 890
Standard deviation	31 666	29 750	61 800	28 319
Method accuracy (%)	66	60	95	n/a

Method Comparison

The soil iron means of the FPXRF methods were significantly different ($\chi^2 (2) = 161.5, p < .05$). *Post hoc* tests showed that a significant difference existed between the soil iron means of all three methods ($p < 0.008$) (Table 34). Despite these differences, significant soil iron relationships were found between all FPXRF methods ($p < 0.05$). A very strong correlation was found between the direct and baggie methods ($r_s = .91$). Figure 56 shows the strong relationship between the direct and baggie method results.

Table 34. Soil iron FPXRF *post hoc* test, correlation and regression results.

Pairwise Comparison	<i>Post hoc</i> Wilcoxon signed-rank test ($p < 0.008$)	Spearman <i>rho</i>	R^2
Direct vs Baggie	$T = 500, r = -.69$	.91	.94
Direct vs XRF-cup	$T = 94, r = -.84$	.59	.74
Baggie vs XRF-cup	$T = 1, r = -.87$	.62	.79

Mean comparisons of soil iron showed a significant difference between all FPXRF methods (direct, baggie and XRF-cup) and ICP-MS analysis ($T = 151, p < .05, r = -.82$), ($T = 39, p < .05, r = -.85$) and ($T = 277, p < .05, r = -.77$), respectively. The differences and similarities between these results can be seen in Figure 56. Soil iron measured using the FPXRF methods was significantly correlated to ICP-MS soil iron ($p < 0.05$). For illustrative purposes the linear regression trendlines are shown on the scatterplots of the log-transformed soil iron results (Figure 57). The Spearman correlation coefficients increased from direct to baggie and the association between XRF-cup and ICP-MS had a very large coefficient, $r_s = .57, .61$ and $.95$, respectively.

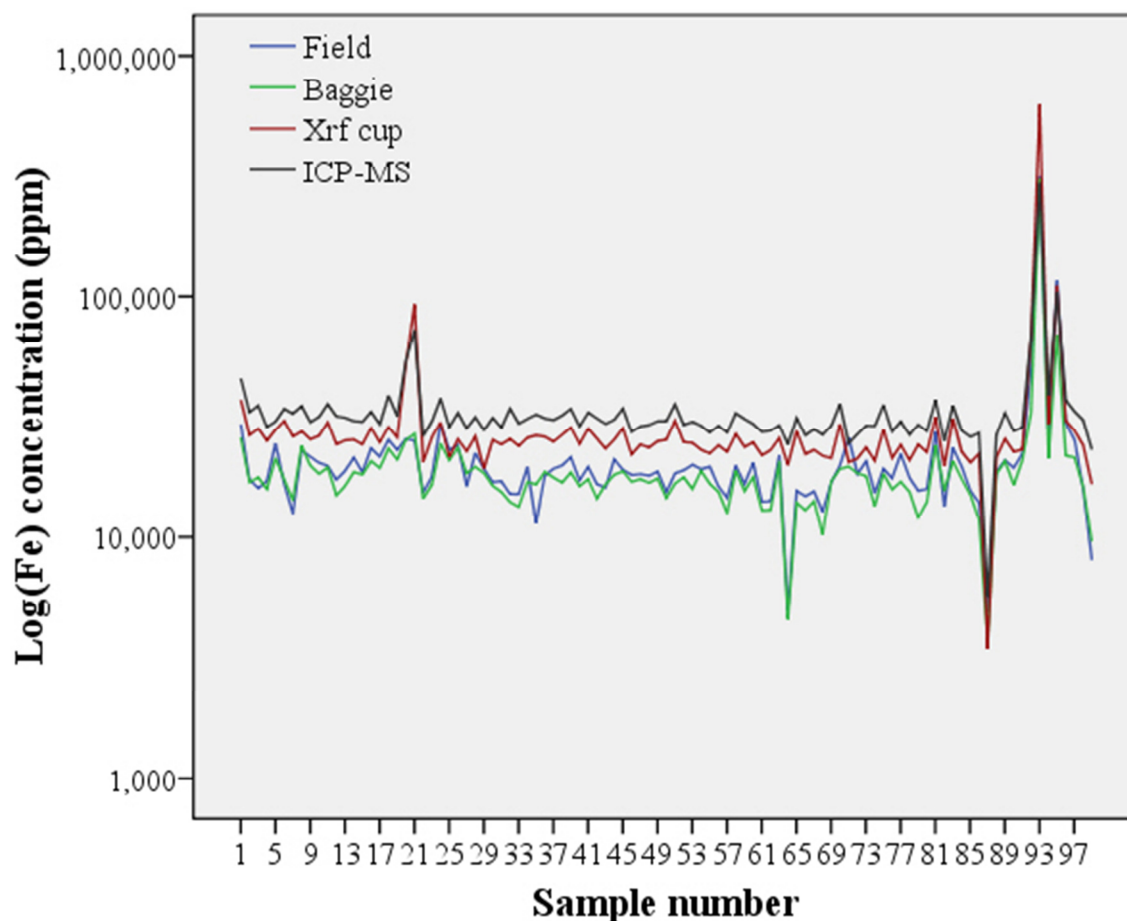


Figure 56 Visual comparison of logarithmic-scale soil iron results of FPXRF methods and ICP-MS analysis (n = 99). (Samples were from the preliminary soil survey.)

Summary

None of the field FPXRF methods, or the ICP-MS method, soil iron results were normally distributed. The XRF-cup method median (25 062 ppm) was lower than the ICP-MS median (30 367 ppm) but it was the closest. FPXRF XRF-cup method results had the highest results accuracy. All FPXRF method means for soil iron were significantly different but results were positively correlated. This included a very strong relationship between FPXRF direct and baggie methods. Each FPXRF method iron mean was significantly different from the ICP-MS mean. Results however showed excellent agreement between elevated soil iron peaks of the various methods and a near-perfect correlation between FPXRF XRF-cup and ICP-MS results.

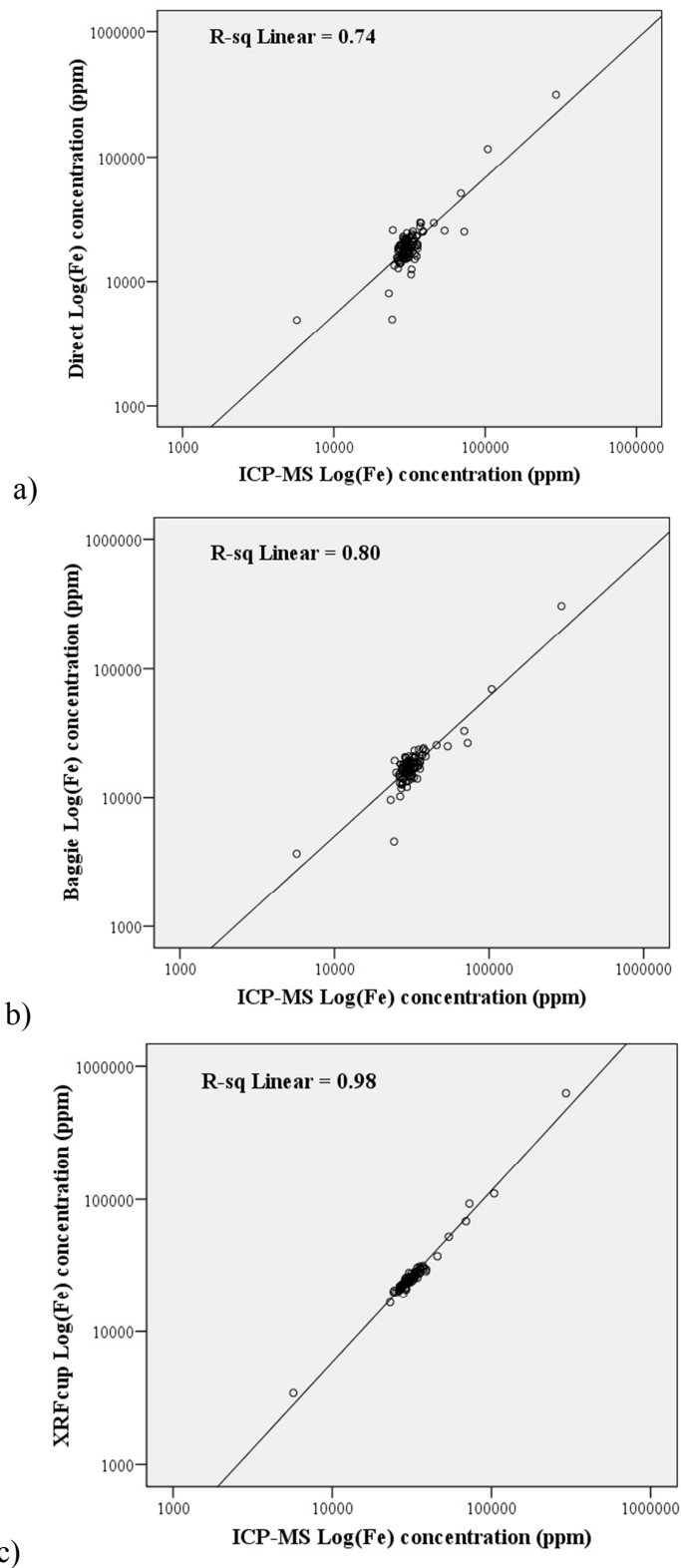


Figure 57 Scatterplots and linear regression trendlines of log-transformed soil iron a) direct, b) baggie and c) XRF-cup FPXRF and ICP-MS results (n = 99). (Samples were from the preliminary soil survey.)

2.3 Lead

Descriptives

FPXRF direct and XRF-cup soil lead results ($n = 99$) were neither normally distributed or log-normally distributed ($p < .05$) (Table 35). FPXRF baggie and ICP-MS lead results however were log-normally distributed, ($W(99) = .974, p > .05$) and ($W(99) = .980, p > .05$), respectively. FPXRF direct soil lead had a median of 70.6 ppm (Table 35). The baggie and XRF-cup method medians for soil lead were 63.1 and 88.9 ppm, respectively. ICP-MS analysis of soil lead resulted in a median of 92 ppm. The 5th percentile value of the three FPXRF methods was equal to $\frac{1}{2}$ the MDL value. The direct and baggie 95th percentiles were similar, 298 ppm and 271 ppm, respectively. The 95th percentile of the FPXRF XRF-cup method (476 ppm) and ICP-MS (460 ppm) were close. The FPXRF direct and baggie methods had similar results accuracies while the XRF-cup method was 104 % (Table 35).

Table 35. Results of the Shapiro-Wilk normality test and descriptive statistics of lead FPXRF method results and corresponding ICP-MS results.

Statistic (ppm)	Method			
	FRXPF			ICP-MS
	Direct	Baggie	XRF-cup	
Shapiro-Wilk (W)	.830	.853	.839	.974
Shapiro-Wilk (W) (Log(Pb))	.966	.826	.971	.980
Geometric mean	67.5	65.5	96.9	94.3
Median	70.6	63.1	88.9	92.0
5 th percentile	9.8	9.8	9.8	18.1
95 th percentile	298	271	476	460
Mean	102	96.1	150	144
Standard deviation	92.0	83.1	138	135
Method accuracy (%)	71	67	104	n/a

Method Comparison

The FPXRF method soil lead means were significantly different ($\chi^2 (2) = 104.6, p < .05$). *Post hoc* tests showed that significant differences did in fact exist between direct and XRF-cup and, baggie and XRF-cup but that no significant difference existed between the direct and baggie FPXRF soil lead means (Table 36). There is good agreement between the various FPXRF methods based on the visual assessment of Figure 58. All three FPXRF methods had strong, positive significant associations to each other ($p < 0.05$) (Table 36).

Table 36. Soil lead FPXRF *post hoc* test, correlation and regression results.

Pairwise Comparison	<i>Post hoc</i> Wilcoxon signed-rank test ($p < 0.008$)	Spearman <i>rho</i>	R^2
Direct vs Baggie	not significant	.96	.89
Direct vs XRF-cup	$T = 297, r = -.75$	.93	.82
Baggie vs XRF-cup	$T = 59, r = -.83$	.97	.91

Individual mean comparisons between ICP-MS analysis of soil lead and direct ($T = 316, r = -.76$), baggie ($T = 119, r = -.83$) and XRF-cup ($T = 1517, r = -.34$) FPXRF results showed significant differences ($p < 0.05$). However, Figure 58 shows that there was good agreement between the elevated areas of the FPXRF methods, soil lead results and the ICP-MS “Gold Standard” results. Figure 59 presents the individual scatterplots of the log-transformed soil lead results of the three different FPXRF methods and the ICP-MS analysis. The Spearman ranking between the FPXRF methods and the ICP-MS analysis was significant ($p < 0.05$) and positive. Correlation coefficients describing these relationships for soil lead were all above .9 ($r_s = .94$ (direct), .96 (baggie) and .98 (XRF-cup)).

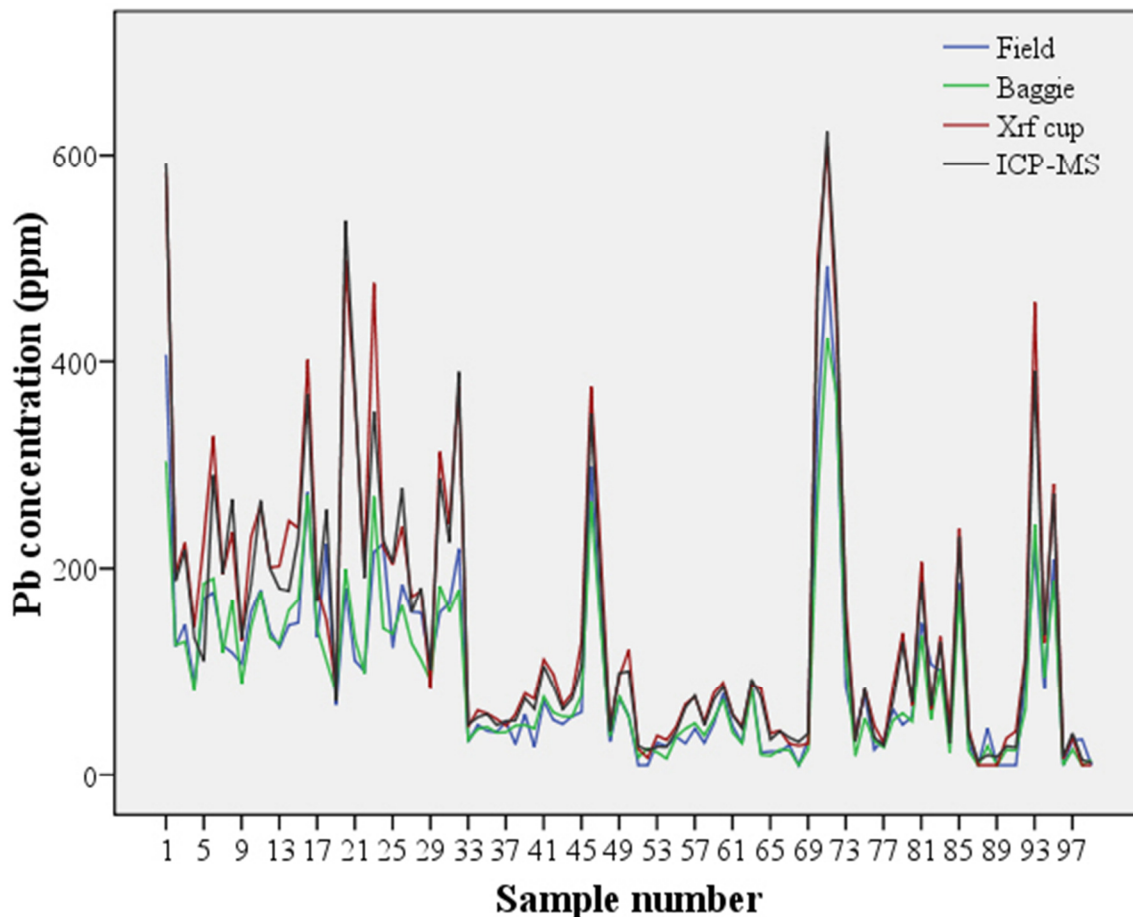


Figure 58 Visual comparison of linear soil lead results for samples of FPXRF methods and ICP-MS analysis (n = 99). (Samples were from the preliminary soil survey.)

Summary

Only FPXRF baggie and ICP-MS soil lead results were log-normally distributed. Median soil lead values were all below 100 ppm. The FPXRF XRF-cup median was lower than, but the closest to the ICP-MS median value. This method also had the highest accuracy. The relationships between the FPXRF methods were very strong. *Post hoc* tests revealed that direct and baggie FPXRF method means were from the same population. Though significant differences existed between the FPXRF methods soil lead and the ICP-MS analysis means, their correlations were very strong and nearly perfect for the XRF-cup and ICP-MS relationship.

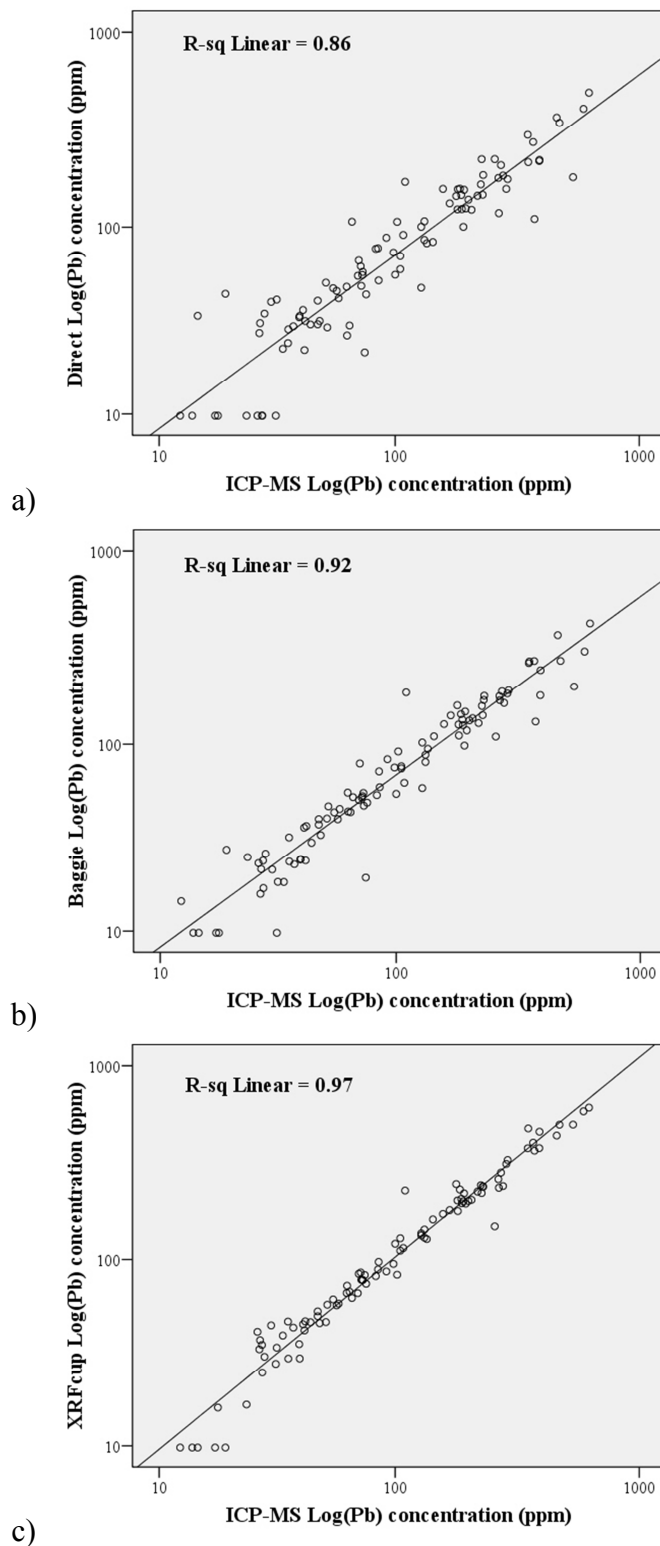


Figure 59

Scatterplots and linear regression trendlines of log-transformed soil lead for a) direct, b) baggie and c) XRF-cup FPXRF and ICP-MS analysis results (n = 99). (Samples were from the preliminary soil survey.)

2.4 Zinc

Descriptives

The soil zinc results of the three types of FPXRF methods, direct, baggie and XRF-cup, as well as the ICP-MS results ($n = 99$) were all not normally distributed ($p < .05$). Log-normal distribution of the results for this element by FPXRF and ICP-MS methods was also not significant ($p < .05$). The soil zinc direct FPXRF median was 156 ppm (Table 37). The baggie median was the lowest of all methods, 115 ppm. FPXRF XRF-cup and soil zinc ICP-MS medians were close, the latter being 10 ppm higher, at 220 ppm (Table 37). The spread of soil zinc results between the 5th and 95th percentiles was large for all methods and ranged between approximately 581 ppm for the baggie FPXRF method to 785 ppm for the XRF-cup (Table 37). The 5th percentile for FPXRF direct and baggie was 22.7 ppm, which was the $\frac{1}{2}$ LOD value. While both the direct and baggie FPXRF 95th percentile values were between 604 and 662 ppm, the FPXRF XRF-cup and ICP-MS were within 11 ppm of each other and were higher than the direct and baggie methods, between 834 and 843 ppm (Table 37). The FPXRF direct and baggie methods had similar results accuracies, 67 and 57 %, respectively. The FPXRF XRF-cup was 104 % accurate.

Table 37. Results of the Shapiro-Wilk normality test and descriptive statistics of zinc FPXRF method results and corresponding ICP-MS results.

Statistic (ppm)	Method			
	FRXPF			ICP-MS
	Direct	Baggie	XRF-cup	
Shapiro-Wilk (W)	.579	.482	.241	.408
Shapiro-Wilk (W) (Log(Zn))	.939	.973	.963	.954
Geometric mean	147	117	207	239
Median	156	115	210	220
5 th percentile	22.7	22.7	49.3	82.2
95 th percentile	662	604	834	843
Mean	236	200	366	351
Standard deviation	300	313	921	543
Method accuracy (%)	67	57	104	n/a

Method Comparison

Direct, baggie and XRF-cup method means were significantly different ($\chi^2 (2) = 112.7, p < .05$). *Post hoc* tests showed that significant differences existed between each of the means in the pairwise comparisons (Table 38). Further investigation into the soil zinc relationship between the three FPXRF methods revealed there was a significant positive correlation ($p < 0.05$) (Table 38).

Table 38. Soil zinc FPXRF *post hoc* test, correlation and regression results.

Pairwise Comparison	<i>Post hoc</i> Wilcoxon signed-rank test ($p < 0.008$)	Spearman <i>rho</i>	R^2
Direct vs Baggie	$T = 457, r = -.67$	.92	.69
Direct vs XRF-cup	$T = 839, r = -.56$	.88	.56
Baggie vs XRF-cup	$T = 27, r = -.85$	.93	.83

Wilcoxon signed-rank non-parametric mean comparison tests showed that the ICP-MS soil zinc mean was significantly different from FPXRF direct ($T=349, r = -.75$), baggie ($T = 4, r = -.87$) and also, XRF-cup ($T = 810, r = -.58$) (All $p < 0.05$). Though their means were different, elevated zinc results from FPXRF methods corresponded very well with high ICP-MS soil zinc levels (Figure 60). The scatterplots of Figure 61 show the linear relationships between these methods. The association between the FPXRF methods (direct, baggie and XRF-cup) and the ICP-MS analysis were indeed significantly correlated ($r_s = .88, .92$ and $.98$, respectively) (All $p < 0.05$).

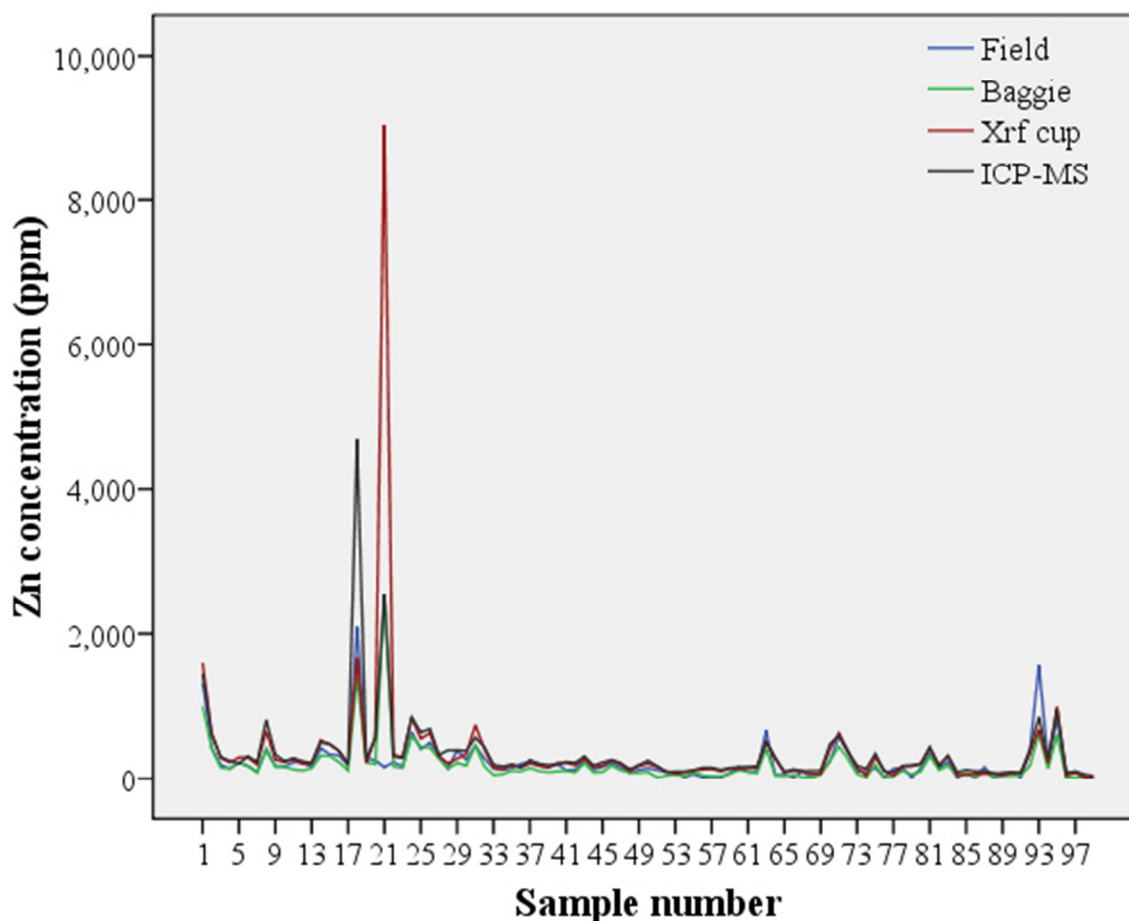


Figure 60 Visual comparison of soil zinc results of FPXRF methods and ICP-MS analysis (n = 99). (Samples were from the preliminary soil survey.)

Summary

FPXRF and ICP-MS soil zinc results were not normally distributed. The ICP-MS median (220 ppm) was higher than the FPXRF method means. The FPXRF XRF-cup median was the closest to the “Gold standard” median. The FPXRF XRF-cup method was also the most accurate of the FPXRF methods. All three field methods were significantly different, yet positively correlated. Non-parametric mean comparison tests showed the FPXRF method means were significantly different from the soil zinc mean of the ICP-MS analysis. As can be seen from Figure 60, elevated FPXRF levels of soil zinc correspond very well to elevated ICP-MS results. The FPXRF XRF-cup method results were nearly perfectly correlated to the ICP-MS zinc results.

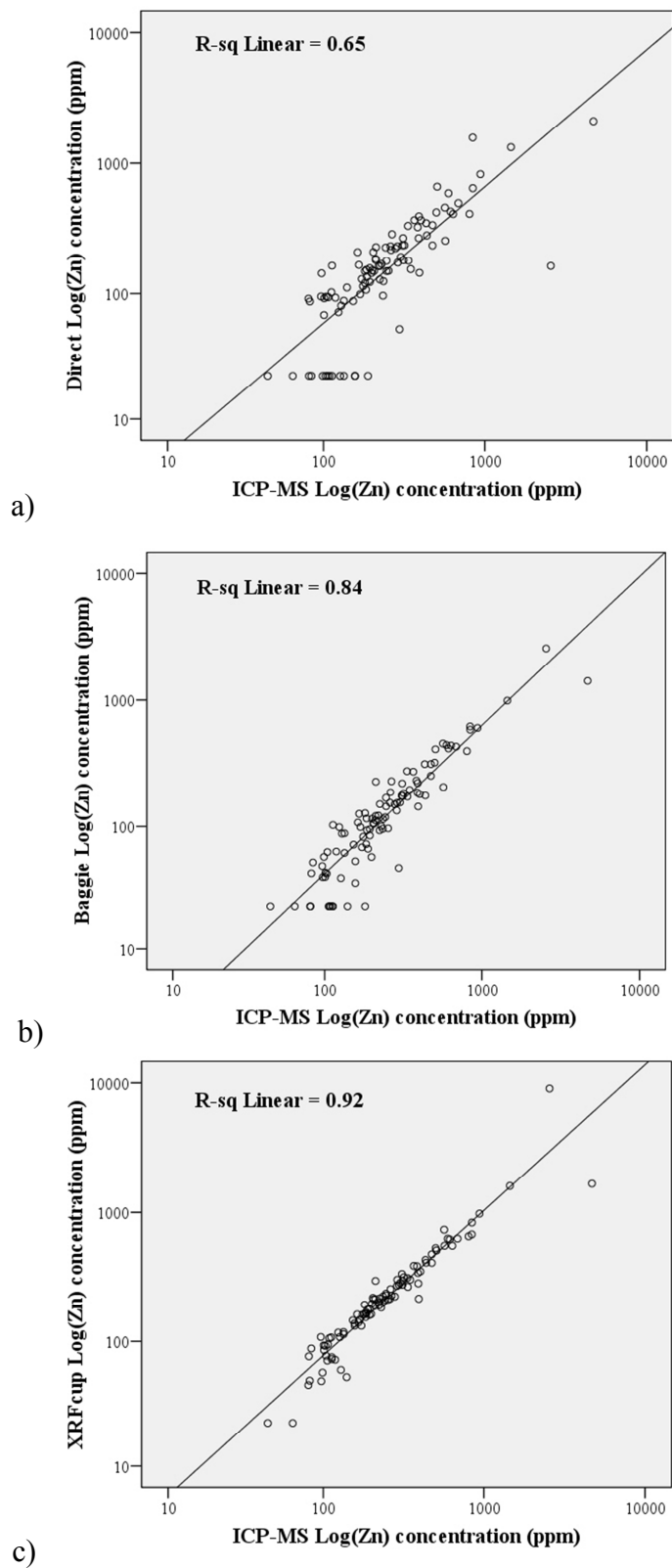


Figure 61

Scatterplots and linear regression trendlines for log-transformed soil zinc a) direct, b) baggie and c) XRF-cup FPXRF and ICP-MS analysis results (n = 99). (Samples were from the preliminary soil survey.)

2.5 Rubidium

Descriptives

Direct and baggie FPXRF soil rubidium results ($n = 99$) were normally distributed, ($p > .05$). XRF-cup FPXRF and ICP-MS results were neither normally nor log-normally distributed (Table 39). Median values of soil rubidium for the various methods were between 51 ppm and 91 ppm. The lowest was the FPXRF baggie and the highest the ICP-MS (Table 39). The spread of soil rubidium results between the 5th and 95th percentiles was similar to that for FPXRF direct and baggie methods, but smaller than that for XRF-cup and ICP-MS methods (Table 39). The percentiles of the FPXRF XRF-cup method were from approximately 40 ppm to 94 ppm. This was slightly higher and larger for the ICP-MS results span which was from 50 to 121 ppm. The accuracy of the rubidium results for the FPXRF direct, baggie and XRF-cup method was 60, 58 and 81 %, respectively.

Table 39. Results of the Shapiro-Wilk normality test and descriptive statistics for rubidium FPXRF method results and corresponding ICP-MS results.

Statistic (ppm)	Method			
	FPXRF			ICP-MS
	Direct	Baggie	XRF-cup	
Shapiro-Wilk (W)	.988	.993	.958	.970
Shapiro-Wilk (W) (Log(Rb))	n/a	n/a	.719	.799
Geometric mean	50.1	50.0	69.4	85.7
Median	54.0	50.9	75.3	90.8
5 th percentile	28.3	27.6	39.5	49.6
95 th percentile	79.9	76.0	94.4	121
Mean	53.4	52.2	72.5	89.3
Standard deviation	16.0	14.4	17.4	22.0
Method accuracy (%)	60	58	81	n/a

Method Comparison

The Friedman ANOVA mean comparison test indicated that a significant difference existed between the FPXRF methods ($\chi^2 (2) = 142.1, p < .05$) (Figure 62). *Post hoc* tests showed that a significant difference between direct and XRF-cup and, baggie and XRF-cup was found. However there was no significant difference between direct and baggie means

(Table 40). Though these differences existed between the soil rubidium means, all three FPXRF methods were strongly correlated to each other (Table 40).

Table 40. Soil rubidium FPXRF *post hoc* test, correlation and regression results.

Pairwise Comparison	<i>Post hoc</i> Wilcoxon signed-rank test ($p < 0.008$)	Spearman <i>rho</i>	R^2
Direct vs Baggie	not significant	.92	.85
Direct vs XRF-cup	$T = 6, r = -.87$	.85	.79
Baggie vs XRF-cup	$T = 4, r = -.87$	.89	.79

Non-parametric comparisons between FPXRF methods and ICP-MS means of soil rubidium revealed significant differences existed between direct ($T = 2, p < .05, r = -.86$), baggie ($T = 0, p < .05, r = -.87$), XRF-cup ($T = 312, p < .05, r = -.76$) and the ICP-MS analysis. The FPXRF methods' soil rubidium results were positively correlated to the ICP-MS results. Although Figure 62 does not show the same excellent agreement seen in the soil iron and zinc results, in general, elevated levels of rubidium detected by FPXRF methods correspond to high levels of ICP-MS rubidium results. The Spearman correlation results showed increasing correlation strength with increasing sample preparation. The direct-ICP association had a Spearman coefficient of .72 ($p < 0.05$) while the relationship between baggie and ICP-MS and, XRF-cup and ICP-MS had significant coefficients of $r_s = .78$ and $r_s = .70$ ($p < 0.05$), respectively. Linear regressions are shown in the scatterplots of Figure 63.

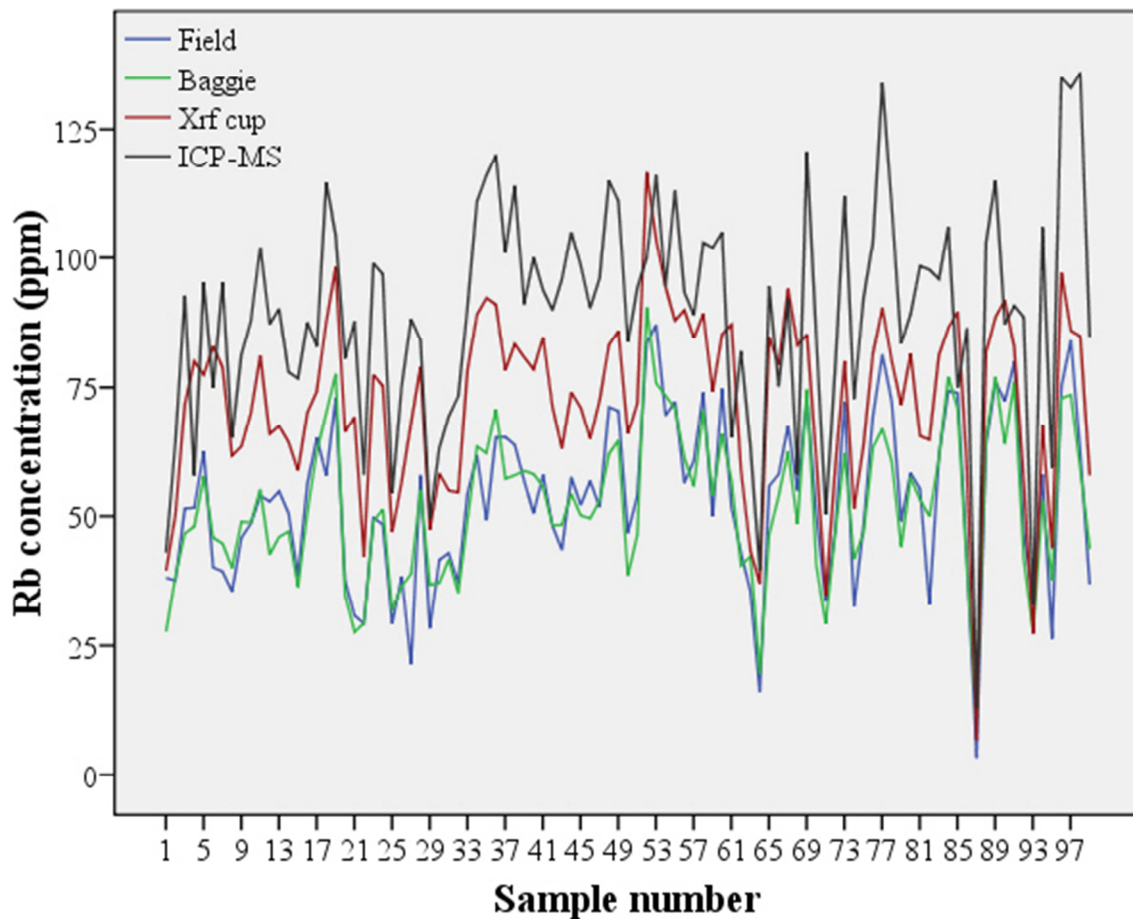


Figure 62 Visual comparison of soil rubidium results of FPXRF methods and ICP-MS analysis (n = 99). (Samples were from the preliminary soil survey.)

Summary

Soil rubidium direct and baggie FPXRF results were the only normally distributed results. FPXRF XRF-cup had a median of 75.3 ppm which was the highest of all FPXRF methods, but much lower than the ICP-MS rubidium median. The FPXRF XRF-cup method had the highest accuracy. Tests showed a significant difference between the means of all three FPXRF methods however *post hoc* tests showed that direct and baggie FPXRF soil rubidium means were similar. Strong correlations existed between all FPXRF method results. The FPXRF means were also significantly different from the ICP-MS rubidium mean. Their relationships were good and, in general, elevated soil rubidium results of the FPXRF methods and the ICP-MS analysis corresponded.

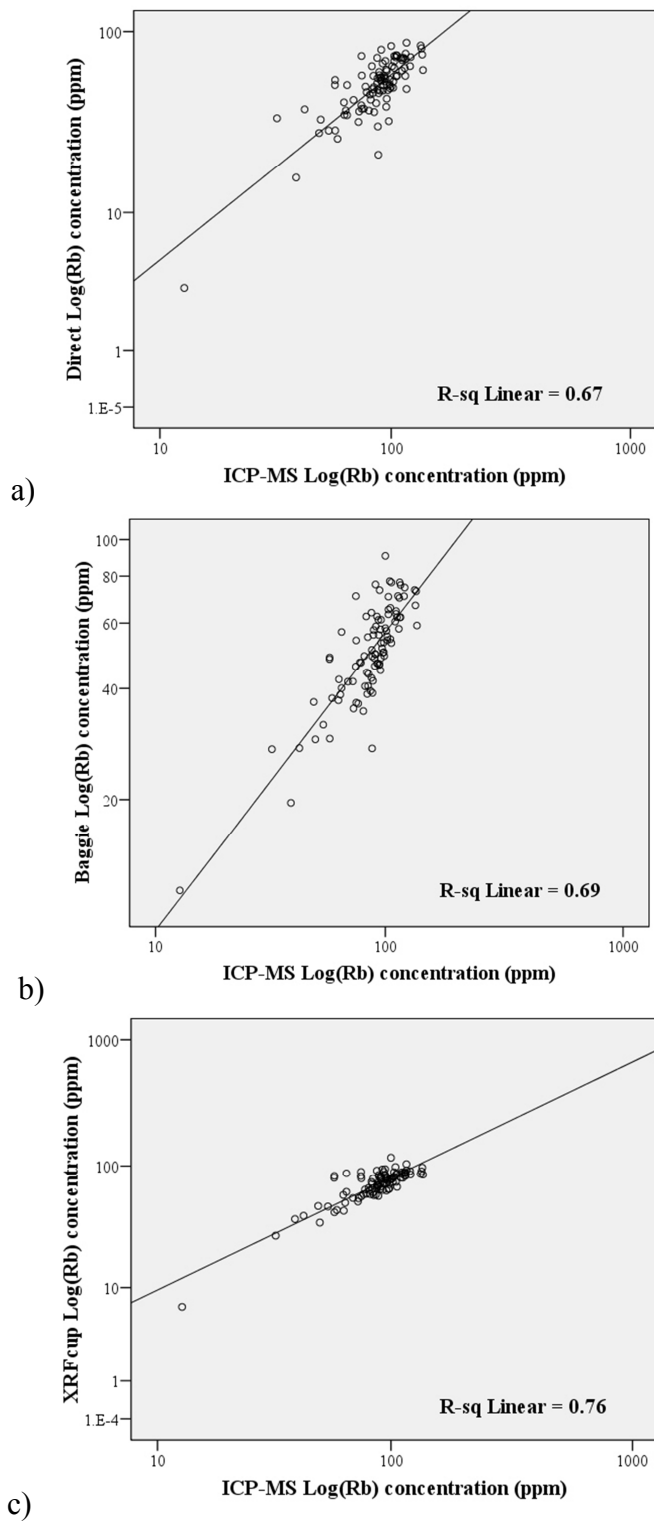


Figure 63

Scatterplots and linear regression trendlines of log-transformed soil rubidium a) direct, b) baggie and c) XRF-cup FPXRF and ICP-MS analysis results ($n = 99$). (Samples were from the preliminary soil survey.)

2.6 Strontium

Descriptives

Strontium results for direct, baggie and XRF-cup FPXRF methods, as well as the ICP-MS results were not normally distributed ($p < .05$) (Table 41). A log-normal distribution for soil strontium for the FPXRF and ICP-MS methods was also not found to be significant ($p < .05$) (Table 41). Median values ranged from 108 ppm for the baggie method to 140 ppm for the ICP-MS analysis (Table 41). The FPXRF direct and baggie 5th percentile values were quite close, 72.4 and 70.4 ppm, respectively, while the values for the XRF-cup was 88.6 ppm and the ICP-MS's was 100 ppm. FPXRF direct method had the lowest and the XRF-cup the larger 95th percentile (Table 41). The 95th percentile for all methods was between 219 and 286 ppm (Table 41). FPXRF baggie and ICP-MS both had 95th percentile values of 286 ppm. The result accuracy of the FPXRF methods were similar (Table 41).

Table 41. Results of the Shapiro-Wilk normality test and descriptive statistics of strontium FPXRF method results and corresponding ICP-MS results.

Statistic (ppm)	Method			
	FPXRF			ICP-MS
	Direct	Baggie	XRF-cup	
Shapiro-Wilk (W)	.764	.774	.653	.768
Shapiro-Wilk (W) (Log(Sr))	.961	.967	.901	.930
Geometric mean	113	109	129	153
Median	111	108	123	140
5 th percentile	72.4	70.4	88.6	100
95 th percentile	219	286	237	286
Mean	123	116	137	163
Standard deviation	56.3	47.8	59.3	66.0
Method accuracy (%)	75	71	84	n/a

Method Comparison

Comparison of the FPXRF method means using the Friedman ANOVA comparison test resulted in a significant Chi-square value of 98.3 ($p < 0.05$). Table 42 shows the results of the *post hoc* tests which show a significant difference between all FPXRF method means. Despite these differences, the methods had significant positive relationships. The Spearman

correlation coefficient was almost perfect for the direct and baggie comparison ($r_s = .98$, $p < 0.05$). Baggie and XRF-cup and, direct and XRF-cup were very similar, $r_s = .89$ and $r_s = .88$ ($p < 0.05$), respectively.

Table 42. Soil strontium FPXRF *post hoc* test, correlation and regression results.

Pairwise Comparison	<i>Post hoc</i> Wilcoxon signed-rank test ($p < 0.008$)	Spearman <i>rho</i>	R^2
Direct vs Baggie	$T = 840$, $r = -.57$	.98	.96
Direct vs XRF-cup	$T = 676$, $r = -.63$	.88	.78
Baggie vs XRF-cup	$T = 153$, $r = -.81$	.89	.80

In non-parametric mean comparison tests, direct (mean = 123 ppm), baggie (mean = 116.3 ppm) and XRF-cup (mean = 137 ppm) means all showed significant differences from the ICP-MS mean (162.7 ppm), ($T = 80$, $r = -.84$), ($T = 18$, $r = -.86$) and ($T = 0$, $r = -.87$) (All $p < 0.05$), respectively. Though the means were significantly different, the agreement between the results of the FPXRF methods and the ICP-MS analysis was excellent as shown in Figure 64. Figure 65 shows the individual scatterplots of the FPXRF and the ICP-MS method results. Again, for illustrative purposes, the linear regression trendlines are also shown. Spearman correlations were significant for the three FPXRF methods and the ICP-MS results. The positive correlation coefficient for the direct-ICP relationship was $r_s = .85$. The coefficient value for the baggie-ICP association was similar, $r_s = .86$. The XRF-cup and ICP correlation coefficient was very high, .96.

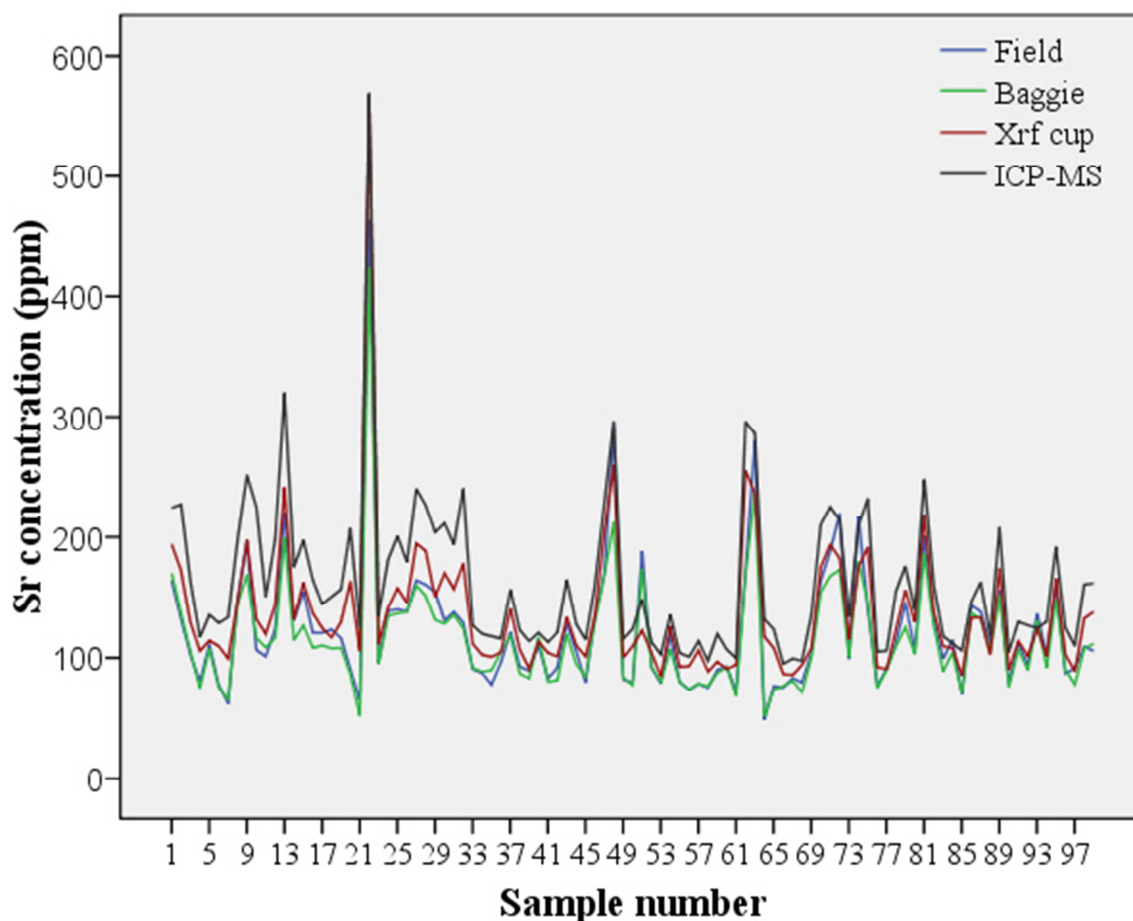
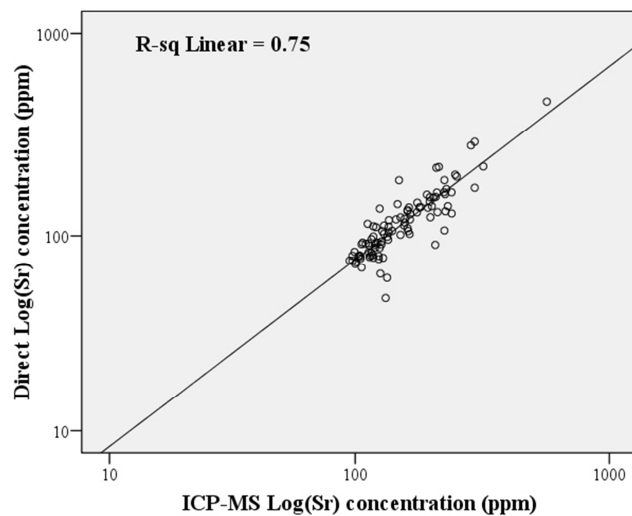


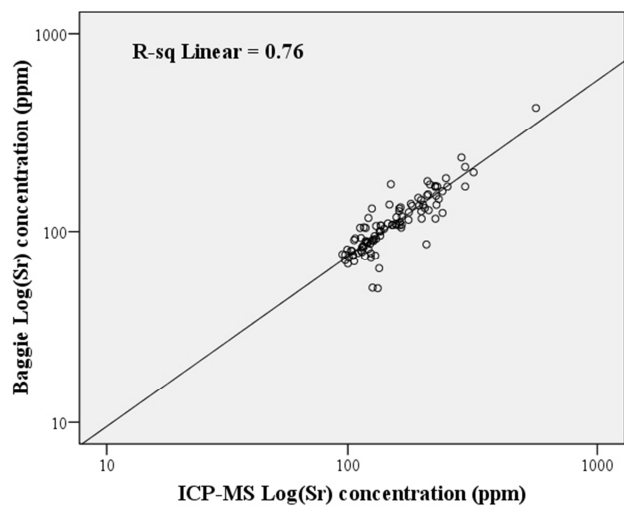
Figure 64 Visual comparison of soil strontium results FPXRF methods and ICP-MS analysis (n = 99). (Samples were from the preliminary soil survey.)

Summary

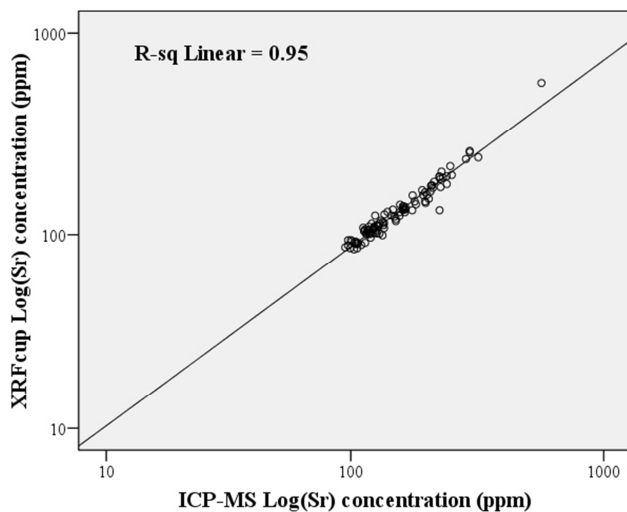
All FPXRF method results, as well as ICP-MS results, were not normally distributed. The FPXRF XRF-cup strontium median was highest of the FPXRF methods and closest to the ICP-MS median. Though the FPXRF methods had similar accuracies, the FPXRF XRF-cup had the highest. Significant differences did exist between soil strontium means of the FPXRF methods but their results were strongly and positively significant correlated. Though means were different, the FPXRF methods' and ICP-MS analysis' elevated levels corresponded well. The FPXRF XRF-cup and ICP-MS relationship was nearly perfect.



a)



b)



c)

Figure 65

Scatterplots and linear regression trendlines of log-transformed soil strontium a) direct, b) baggie and c) XRF-cup FPXRF and ICP-MS analysis results (n = 99). (Samples were from the preliminary soil survey.)

2.7 Barium

Descriptives

Normal and log-normal distribution of FPXRF soil barium results ($n = 99$) were not found to be significant ($p < 0.05$) (Table 43). In addition, the ICP-MS soil barium results ($n = 99$) did not indicate a normal or log-normal distribution either (Table 43). The FPXRF direct median concentration for soil barium was 377 ppm and was 394 ppm for the FPXRF baggie method. The FPXRF XRF-cup and ICP-MS median values were very close, 426 and 428 ppm, respectively. The ICP-MS soil barium results had the smallest percentile spread (5th to 95th), 152 ppm. Both FPXRF baggie and XRF-cup methods had approximately 240 and 246 ppm of a spread between percentiles and the FPXRF direct method had the largest at 310 ppm. The FPXRF XRF-cup method had an accuracy of 97 % while the direct and baggie methods had accuracies of 88 and 91 %, respectively.

Table 43. Results of the Shapiro-Wilk normality test and descriptive statistics for barium FPXRF method results and corresponding ICP-MS results.

Statistic (ppm)	Method			
	FPXRF			ICP-MS
	Direct	Baggie	XRF-cup	
Shapiro-Wilk (W)	.947	.933	.912	.799
Shapiro-Wilk (W) (Log(Ba))	.723	.711	.671	.445
Geometric mean	361	377	405	419
Median	377	394	426	428
5 th percentile	204	264	282	347
95 th percentile	514	504	529	499
Mean	376	386	415	427
Standard deviation	87.9	72.3	76.0	60.1
Method accuracy (%)	88	90	97	n/a

Method Comparison

FPXRF method means were significantly different from each other ($\chi^2 (2) = 33.9, p < .05$). Further investigation using *post hoc* tests revealed that baggie and XRF-cup and, direct and XRF-cup were significantly different (Table 44), whereas the direct and baggie FPXRF means were not ($T=1719, r = -.25$). Similar to other elements, though the means were

different, close relationships existed between the three FPXRF methods. The Spearman correlation coefficient for direct and baggie showed that a strong significant relationship existed between the soil barium results of these two FPXRF methods ($r_s = .82, p < 0.05$). Direct and baggie methods were also significantly correlated to the XRF-cup method (Table 44).

Table 44. Soil barium FPXRF *post hoc* test, correlation and regression results.

Pairwise Comparison	<i>Post hoc</i> Wilcoxon signed-rank test ($p < 0.008$)	Spearman <i>rho</i>	R^2
Direct vs Baggie	not significant	.82	.70
Direct vs XRF-cup	$T = 959, r = -.52$	.52	.48
Baggie vs XRF-cup	$T = 1157, r = -.45$	.56	.69

The difference between FPXRF direct and ICP-MS soil barium means was significant ($T = 720, r = -.62$) as was the difference between ICP-MS and FPXRF baggie and XRF-cup means, ($T = 631, r = -.65$) ($p < .05$) and ($T = 1720, p < .05, r = -.26$), respectively. Despite the differences found between the soil barium means, the agreement between the results of the various methods was good; peaks detected by FPXRF methods did generally correspond to elevated levels of ICP-MS barium. Figure 67 shows the scatterplots of the log-transformed FPXRF method results versus the ICP-MS analysis log-transformed results. FPXRF direct soil barium had a significant Spearman correlation ($r_s = .42, p < 0.05$) with ICP-MS barium. Positive significant relationships were also found between baggie ($r_s = .53$) and XRF-cup ($r_s = .71$) and the ICP-MS results (Both $p < 0.05$).

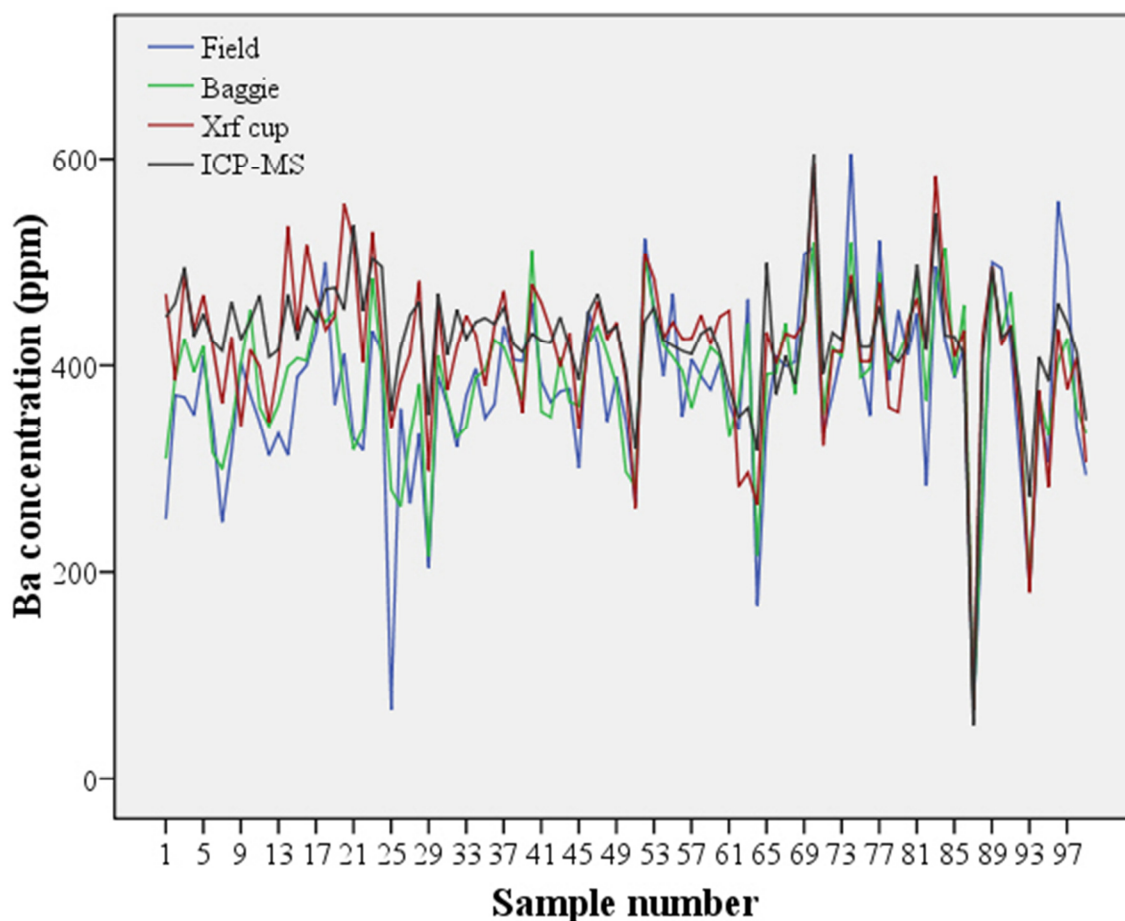


Figure 66 Visual comparison of soil barium results of FPXRF methods and ICP-MS analysis (n = 99). (Samples were from the preliminary soil survey.)

Summary

All of the various methods' soil barium results were not normally distributed. The FPXRF XRF-cup median (426 ppm) was closest to the ICP-MS median (428 ppm). The FPXRF barium result accuracies were all very high but the XRF-cup method was highest. While the Friedman ANOVA showed that significant differences existed between all FPXRF method soil barium means, *post hoc* tests showed that there was no difference between direct and baggie method means. A strong correlation was found between all FPXRF method results. Significant differences also existed between the ICP-MS and FPXRF method means. Though not as strong as some of the other elements (i.e., Fe, Mn or Zn), the FPXRF method results were correlated to the ICP-MS results.

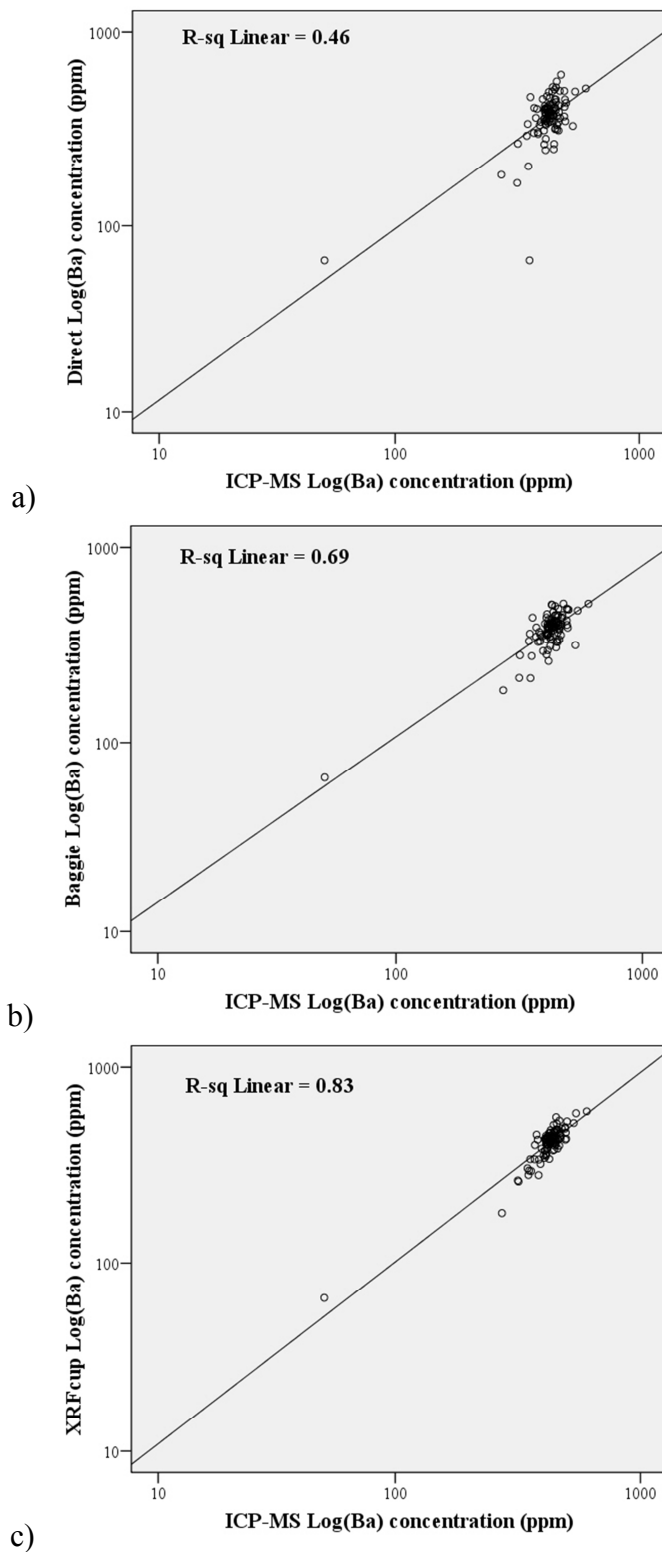


Figure 67 Scatterplots and linear regression trendlines of log-transformed soil barium a) direct, b) baggie and c) XRF-cup FPXRF and ICP-MS analysis results (n =99). (Samples were from the preliminary soil survey.)

2.8 Zirconium

Descriptives

Direct, baggie and XRF-cup FPXRF as well as the ICP-MS results for soil zirconium were not normally distributed ($p < .05$) (Table 45). These results were also not log-normally distributed ($p < .05$) (Table 45). Direct and baggie FPXRF soil zirconium medians were very similar, i.e., 60.9 and 58.6 ppm, respectively. FPXRF XRF-cup had a median of 119 ppm and ICP-MS zirconium had the highest, 131 ppm. The 5th percentile was also similar for direct and baggie FPXRF methods (Table 45). ICP-MS had a 5th percentile value of approximately 70 ppm while FPXRF XRF-cup had the highest 5th and 95th percentile (Table 45). These latter two methods had a large (> 100 ppm) span between percentiles. Direct and baggie had a similar, smaller span, 65.6 and 54.2, respectively. The zirconium result FPXRF XRF-cup accuracy was very high, 97 %, whereas the direct and baggie methods were below 50 %.

Table 45. Results of the Shapiro-Wilk normality test and descriptive statistics of zirconium FPXRF method results and corresponding ICP-MS results.

Statistic (ppm)	Method			
	FPXRF			ICP-MS
	Direct	Baggie	XRF-cup	
Shapiro-Wilk (W)	.971	.966	.869	.959
Shapiro-Wilk (W) (Log(Zr))	.769	.665	.549	.767
Geometric mean	56.8	54.6	117	122
Median	60.9	58.6	119	131
5 th percentile	29.6	26.2	80.9	69.7
95 th percentile	95.2	80.4	189	172
Mean	61.4	57.5	123	127
Standard deviation	20.6	14.8	35.0	32.1
Method accuracy (%)	48	45	97	n/a

Method Comparison

FPXRF methods had significantly different soil zirconium means ($\chi^2 (2) = 151.0, p < .05$) (Figure 68). *Post hoc* Wilcoxon signed-rank tests showed that significant differences existed between each of these methods (Table 46). Despite these significant differences, the FPXRF methods were significantly correlated to one another (Table 46).

Table 46. Soil zirconium FPXRF *post hoc* test, correlation and regression results.

Pairwise Comparison	<i>Post hoc</i> Wilcoxon signed-rank test ($p < 0.008$)	Spearman <i>rho</i>	R^2
Direct vs Baggie	$T = 1293, r = -.41$	.79	.75
Direct vs XRF-cup	$T = 3, r = -.87$	.48	.44
Baggie vs XRF-cup	$T = 0, r = -.86$	.57	.65

Non-parametric mean comparisons between direct and ICP results, and between baggie and ICP results revealed that strong significant differences existed, ($T = 3, p < .05, r = -.87$) and ($T = 0, p < .05, r = -.87$), respectively. This test also showed a significant difference ($T = 1856, p < .05, r = -.22$) between the FPXRF XRF-cup and ICP-MS results. Of all the elements discussed, zirconium had the least agreement between FPXRF methods' results and the corresponding ICP-MS results (Figure 68). In Figure 69, FPXRF log-transformed results of soil zirconium are presented in scatterplots against the log-transformed ICP-MS zirconium results for illustrative purposes. The XRF-cup-ICP relationship of soil zirconium was significantly correlated ($r_s = .47, p < 0.05$). A similar significant Spearman association was found between direct and ICP ($r_s = .57$) and, baggie and ICP ($r_s = .57$) ($p < 0.05$).

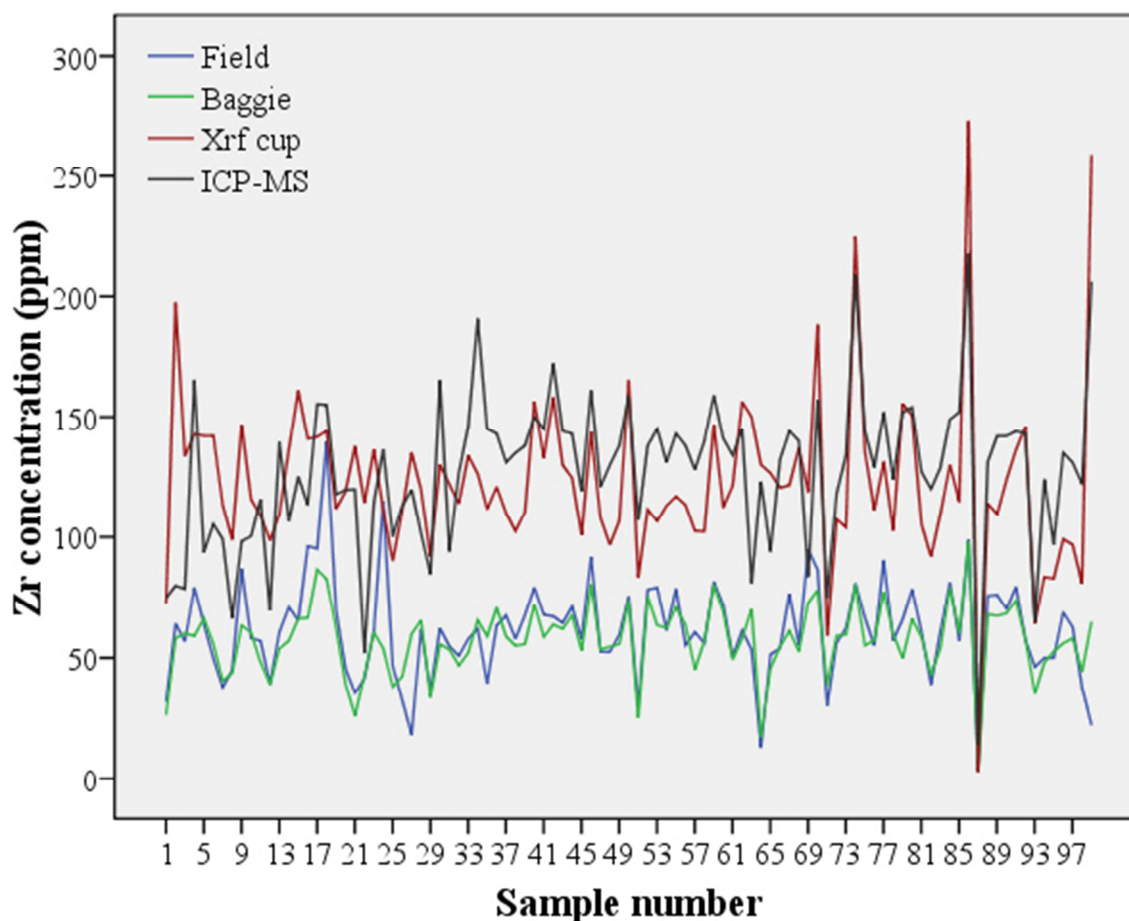
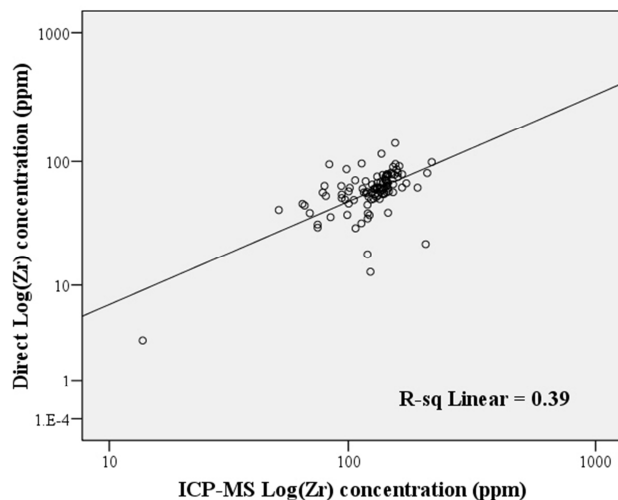


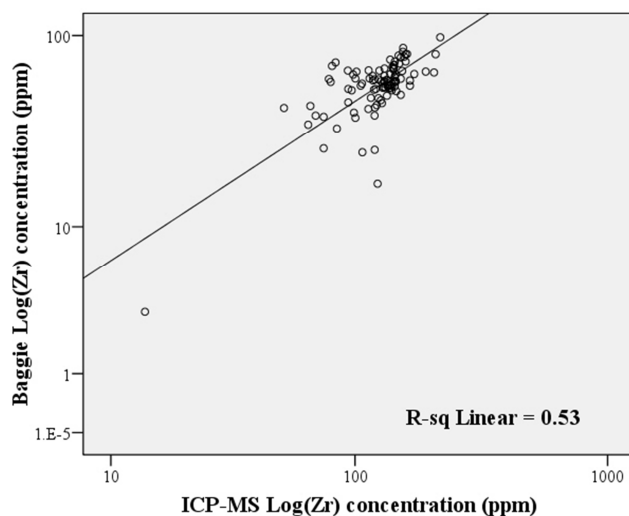
Figure 68 Visual comparison of soil zirconium results of FPXRF methods and ICP-MS analysis (n = 99). (Samples were from the preliminary soil survey.)

Summary

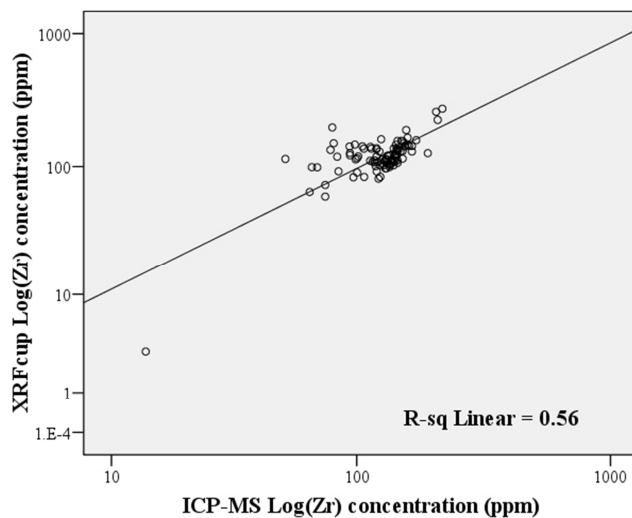
Soil zirconium results were not normally distributed. The FPXRF XRF-cup method had the highest zirconium median of the FPXRF methods and was also the closest to the ICP-MS median. The FPXRF XRF-cup method had the highest accuracy of the zirconium result. The three FPXRF methods had significantly different means but positively correlated results. The individual means for these FPXRF methods were significantly different from the ICP-MS soil zirconium mean. Relationships between the results of the three methods and the “Gold standard” ICP-MS analysis results were significant though smaller than those reported for the other elements of this study. Therefore, the elevated levels of zirconium detected by the FPXRF methods did not always correspond to high levels of zirconium detected by ICP-MS.



a)



b)



c)

Figure 69

Scatterplots and linear regression trendlines of log-transformed soil zirconium a) direct, b) baggie and c) XRF-cup FPXRF and ICP-MS analysis results ($n = 99$). (Samples were from the preliminary soil survey.)

Discussion

The purpose of this study was to evaluate the reliability of a field-portable X-ray fluorescence analyzer as a screening tool for the field determination of soil manganese and related elements. Three FPXRF methods with different sample preparations were evaluated.

The different field FPXRF methods (direct, baggie and XRF-cup) used in this study (see Chapter 4 for description) varied in their degree of sample preparation, time and expense required per sample. No sample preparation, except to remove debris and flatten the area, was needed for the direct method. It requires very little time and there are no additional costs. Because there is no sample preparation, soil moisture may influence the FPXRF analyzer's measurement. This must be taken into account when making sampling scheme decisions and result interpretation. The FPXRF baggie method requires slightly more time before FPXRF measurement due to sample preparation. The soil sample must be taken and put in a sample bag. The soil-filled sample bag is then hand-shaken to allow the sample to settle (smaller particles settle on the bottom). This FPXRF method is not as quick as the direct method and has the added cost of sample bags and tools. Soil moisture can also influence this FPXRF measurement. The third and final FPXRF method, XRF-cup, requires more time than the other two methods and is more costly. A soil sample must be retrieved, as in the baggie method, then it must be dried, ground and sieved. An XRF-cup is then filled with the prepared soil sample. Drying can take several hours to several days. Contrary to the other FPXRF methods, if soil drying is adequate, soil moisture should not influence the FPXRF measurements. Unfortunately expenses for this method are higher than the direct and baggie methods. Along with the purchase of sample bags and tools, sieves, drying vessels and rack, the XRF-cup and assemblage paraphernalia (filter and stuffing) must be purchased. In increasing order of sample preparation, time and costs, the field FPXRF methods are direct, baggie and XRF-cup.

The reported element (Mn, Fe, Pb, Zn, Rb, Sr, Ba, and Zr) medians of the standard laboratory ICP-MS analysis were always higher than the three FPXRF method means. Similarly, several other authors (Reames and Lance, 2002; Clark et al., 1999, Kirtay et al., 1998, Markey et al., 2008; Binstock et al., 2008) also found this underestimation of soil and

sediment elemental results by FPXRF analyzers. Stallard et al. (1995) however found that in general the ICP results of the major elements (including manganese) were lower than the FPXRF. They attributed this to incomplete digestion of the sediment. The private lab (Actlabs) contracted to do the digestion and analysis of the soil samples used an aggressive four-acid digestion (Chapter 4). Stallard et al. (1995) also used a commercial laboratory for digestion and analysis of their samples however they neglected to report the digestion method. Based on the results of the present study, the field-portable XRF analyzer is expected to underestimate soil manganese when it is used directly.

For most of the reported elements, the means of the three FPXRF methods were statistically different but strongly correlated. In the case of lead, rubidium and barium, the FPXRF direct and baggie method results were not different and also strongly correlated. This would indicate that if an investigator had to choose between the direct and baggie methods for determining soil lead, iron or barium, they could use the quicker and inexpensive direct method as there should be little difference between the results of the two methods. Bernick et al. (1995b) found no significant difference between the results of direct and prepared (XRF-cup) FPXRF results of two different FPXRF analyzers. Of the three FPXRF methods, the baggie method had the lowest median across all reported elements, except soil barium. Reames and Lance (2002), who also compared the use of direct, baggie and XRF-cup, found that the baggie method had a lower accuracy than the other FPXRF methods and speculated that this was probably due to the thickness of the sample bags. Kalnicky and Singhvi (2001) stated that the maximum depth of X-ray penetration for an FPXRF is 2 mm in a soil matrix. When using a sample bag, they recommend using the same thickness of plastic for calibrating the analyzer to minimise the effect of composition and thickness. This calibration was not used since the present study required that two other FPXRF measurements, which did not use plastic bags, be taken using the FPXRF analyzer. A brief analysis of the sample bags used in this study found that all reported elements were below the FPXRF detection limits ($n = 1$). Sackett et al. (1998) suggested taking a direct FPXRF measurement of the soil sample in the sample bag, however no other information was found regarding this method. The FPXRF XRF-cup method had the highest median for all reported elements which means it was closest to the ICP-MS median. The accuracy of the

FPXRF XRF-cup method for 6 out of the 8 elements described here, including manganese, was acceptable (within $\pm 5\%$ of the laboratory means (Reames and Lance, 2002)). Rubidium and strontium FPXRF XRF-cup methods however exceeded this criterion by 14 and 11 %, respectively. The other FPXRF methods (direct and baggie) did not meet the accuracy criterion. Therefore, the FPXRF XRF-cup method would return the most accurate manganese and related element results of the FPXRF methods.

The results of the three FPXRF methods were significantly different from those of the ICP-MS analysis. These differences are contrary to what has been found in past studies. Bernick et al. (1995b) found no significant differences between the soil lead results of their atomic absorption (AA) analysis and the FPXRF direct and prepared (XRF-cup) results of two FPXRF analyzers. This lack of difference between the AA and the FPXRF results may be due to the fact that prior to field FPXRF measurement, the soil was mixed to reduce heterogeneity of the soil sample. Also, the material used for AA analysis was an aliquot of the soil used in the prepared XRF-cups. Binstock et al. (2008) also found no differences between FPXRF soil lead results and the ICP-AES soil analysis. Here again, the authors used the soil from the XRF-cups for the ICP-AES analysis. It is assumed that having the same aliquot of soil sample used for the direct, baggie, XRF-cup and finally ICP-MS in that study, would not lead to significant differences, as it was the case in these past studies. The soil samples taken by Clark et al. (1999) for confirmatory testing also deviated somewhat from the exact location of their field FPXRF measurement. Here the authors stated that “the fact that the sample collected for later testing did not coincide exactly with the precise volume of soil measured *in situ* (direct) may account for part of the differences between the results using the different procedures.” The purpose of this study was not to prove that the analysis of an aliquot of the same soil sample, after different sample preparations, would return the same results, but to provide future soil investigations with knowledge that will aid in sampling design decision making (i.e., identifying the differences between these three FPXRF direct measurement methods if they were used in real field situations).

The results of all three FPXRF methods had a strong positive significant correlated with the ICP-MS results. The FPXRF XRF-cup method had a stronger relationship with the ICP-MS results than the baggie method which, in turn had a better correlation than the direct method. Near-perfect correlations (i.e., $r_s > .95$) with the ICP-MS results existed for iron, zinc, strontium and lead FPXRF XRF-cup method results. The lead FPXRF baggie method results also had a near-perfect correlation. Strong correlations between FPXRF results and standard laboratory analysis (ICP, AA, and FAAS) have also been found by other authors, though results are usually regarding soil lead. Reames and Lance (2002) found strong soil lead correlations ($.90 < r < .96$) for direct, baggie and XRF-cup with flame atomic absorption spectroscopy (FAAS) analysis results. The result from an industrial region of Poland by Clark et al. (1999) showed excellent correlations between an FPXRF analyzer and laboratory AA analysis of lead ($R^2 = .9966$) and zinc ($R^2 = .9757$) in soil. In a later study of an industrial area in India, Clark et al. (2005) observed again an excellent correlation between the results for FPXRF XRF-cup analysis and AA results. In a 1998 study of marine sediments, Kirtay et al. reported strong correlations between FPXRF results and laboratory (AA, ICP, or XRF) results for zinc ($R^2 = .87$) and lead ($R^2 = .70$ (without extreme values)). Similarly, Stallard et al. (1995) found good agreement between FPXRF XRF-cup and ICP measurements of marine sediments for zinc, lead and iron. These authors also measured manganese by FPXRF XRF-cup but did not report on its relationship to ICP analysis. However, based on the scatterplot of ICP manganese versus XRF-cup manganese they reported, there appears to be a good agreement for manganese between these two methods. FPXRF XRF-cup results from a residential soil lead-contamination study by Markey et al. (2008) showed near-perfect correlation with FAAS analysis. Near-perfect correlation between FPXRF XRF-cup and standard laboratory analysis was also found by Puckett and Shaw (2005) and Binstock et al. (2008).

The FPXRF method comparison results for soil manganese were very similar to those of the other elements measured by the field-portable X-ray fluorescence analyzer. All three FPXRF method medians were lower than the ICP-MS median. As it was the case for the other elements, the FPXRF method soil manganese means were different from each other and from the ICP-MS mean. The FPXRF XRF-cup method manganese results met the

accuracy criteria. Its relationship to ICP-MS were significant (direct $r_s = .515$) and strong (baggie $r_s = .755$ and XRF-cup $r_s = .884$). Kilbride et al. (2006), studying industrial soil in the UK, compared the use of two FPXRF analyzers (XRF-cup) to ICP-OES analysis. The manganese ‘proportion of variation’, or coefficient of determination (R^2), for the dual source FPXRF was .88 ($n = 19$) while the X-ray tube FPXRF had an $R^2 = .71$ ($n = 79$). Stallard et al. (1995) also measured manganese by FPXRF XRF-cup and ICP but in marine sediments. The authors, however, failed to report any useful results for comparison with the results of this present study besides a scatterplot of ICP and FPXRF manganese (as previously mentioned). There appeared to be a good agreement of their manganese results although the presence of three extreme values may be distorting this visual assessment.

In general, all three FPXRF methods underestimated the ICP-MS results. In the following discussion, references to the LOQ exclude lead, zinc and barium results. Regardless of the method used (direct, baggie, or XRF-cup), result generation is faster than analysis by ICP-MS. The FPXRF XRF-cup method was the only FPXRF method to have accurate results. It also had strong significant correlations to the ICP-MS manganese and related element results indicating it could correctly identify areas of elevated concentrations. The FPXRF XRF-cup method had the lowest number of false-negative results and the largest number of results above the LOQ. This method is however time-consuming and the most expensive of the methods. The FPXRF baggie method did not meet the criterion for result accuracy. The sample bag thickness may be attenuating the XRF signal. However, strong significant associations existed with the ICP-MS results. Therefore, the FPXRF baggie method could correctly identify areas of elevated levels of manganese and related elements, though they would be underestimated. The FPXRF baggie method had the lowest amount of results above the limit of quantification but an acceptable false-negative error rate (except for zinc). This method is not very costly and requires a minimal amount of time. In addition, the FPXRF direct method did not meet the result accuracy criterion, however its accuracy was usually better than the baggie method. Manganese and related element results had significant relationships with the ICP-MS results indicating that the FPXRF direct method can correctly identify elevated concentrations in the field. Though it had the highest false-negative error rate for lead, zinc and manganese, the majority of the FPXRF direct method

results were above the LOQ. This FPXRF method is the least expensive and has the shortest sample preparation time requirement.

Before selecting a field FPXRF method, several factors must be considered, such as available time, cost, field conditions and soil moisture. Both time and cost factors required by each FPXRF method described here have previously been discussed. The field conditions of the study area must be taken into account, for example 1) sufficient area for laying samples out to dry; 2) availability of electrical power for use of microwave drying (see below); and 3) shelter from the elements and contamination. Finally, if soil moisture is suspected of being an issue, it is recommended that the XRF-cup method be used for FPXRF measurement of manganese and related elements. If for some reason, the XRF-cup is not an option, the soil samples can be dried in the field for use in the FPXRF direct or baggie method. Soil samples can be air dried, exposed to sunlight or dried using a field stove or oven (Shefsky, 1997). Markey et al. (2008) dried their soil samples using paper towels before inserting them into XRF-cups. Binstock et al. (2008) dried soil samples in the field using a microwave connected to a car battery. After drying, Bernick et al. (1995b) suggested shaping the soil sample into a “2.5-cm thick cake” for direct FPXRF measurement. Alternatively, after drying, the soil sample can be put into a sample bag. This field drying of samples is of course, dependent upon the above mentioned factors, namely time, cost and field conditions.

If the purpose of a future study is to generate *in situ* urban soil results which are comparable to standard laboratory results, the FPXRF XRF-cup method is recommended for the determination of manganese and related elements. However, if the purpose of the study is to use an FPXRF analyzer as a screening tool, any of the three FPXRF methods evaluated here can be used to identify areas of elevated manganese and related element concentrations.

Conclusions

The FPXRF analyzer (XRF-cup method) can be used for field determination of urban soil manganese. As a precaution, when using the FPXRF direct and baggie methods for manganese and related element determination, samples should undergo standard laboratory analysis. The USEPA (1998) recommends confirming at least 5 % of FPXRF results by standard laboratory analysis. As a field screening tool, the FPXRF analyzer, and consequently the three FPXRF methods, is reliable for determining manganese and related elements in urban soil. Underestimation of standard laboratory analysis results by FPXRF analysis is to be expected. Selection of a field FPXRF method for future environmental soil investigations is dependent upon time and cost availability, and field conditions. If these factors are optimal, the FPXRF XRF-cup is recommended for manganese and related element soil determination.

Chapter 8 - Moss-sequestered airborne particle manganese concentrations from a biomonitoring survey of Windsor, Ontario

Purpose

This study evaluated the manganese content of airborne particles in Windsor, Ontario. Since this study was done in order to provide supporting information to Health Canada's air quality study in Windsor (WOEAS), a look at the air-surface interface was deemed essential. To that end, biomonitoring stations were used to collect airborne particles that could potentially deposit onto the urban soil surface and particles re-suspended from the soil to the air in Windsor, Ontario. Use of low-cost biomonitoring stations for the determination of urban airborne particle manganese concentrations have not been used in Canada. The airborne particle manganese elemental associations and spatial distribution were compared to those of soil samples collected near the biomonitoring stations (collocated).

Design

In order to evaluate the levels of manganese in airborne particles, these particles were collected using a moss-biomonitoring technique which uses stations specially designed by Goodarzi et al. (2003). The biomonitoring stations consisted of two mesh bags filled with clean *sphagnum* moss suspended inside an aluminum frame at the top of a pole. For a detailed description of the biomonitoring stations consult Chapter 4. *Sphagnum* moss from a remote area of the Mackenzie River Delta (harvested for the Geological Survey of Canada in Calgary), was cleaned using an acid-wash and water-rinse technique (Chapter 4) and inserted into the mesh bags.

The moss-filled mesh bags were then exposed in the field from June to August 2008. Twenty sites (MB-1 to MB-18, MB-20 and MB-21) were selected across the city of Windsor, Ontario, to represent the urban manganese concentration of airborne particles depositing onto the soil surface. For the safety and security of the equipment, these sites were city-controlled locations, school campuses and Windsor Airport grounds. One site was privately owned land. In all cases, permission was obtained before biomonitoring stations

were installed. Three additional sites were selected in rural areas to provide non-urban airborne particle samples (MB-19, MB-22 and MB-23). The main criterion for site selection within these secure locations was to minimize overhead obstructions (tall buildings, trees, etc.) thereby maximising exposure of moss to air. After retrieving the moss-filled bags from the field, the exposed moss was removed from the mesh bags, dried to a constant weight and crushed. The airborne particle matter trapped on the moss-substrate (moss-PM) was digested and analyzed following the procedures outlined in Chapter 4. The collocated soil samples were taken near the base of the biomonitoring stations. Biomonitoring station soil sampling corresponded with retrieval of exposed moss.

Analysis of the moss-PM consisted of a suite of 24 elements, including manganese. Soil analysis resulted in a similar suite of elements. All fractions of moss-PM were included in the elemental analysis whereas only the less-than-63-micron fraction was used in the analysis of collocated biomonitoring station soil. Results below the analytical limit of detection (LOD) were replaced by half the LOD value, unless over 20 % of an element's results were below the LOD. In this case, the element was not reported (i.e., Ni, As, Be, B, Al, Se, Ag and U). The limit of detection for moss-PM manganese was 0.3 ppm whereas it was 1 ppm for collocated soil manganese. All of the manganese results were above their respective LODs.

The results of the individual biomonitoring stations represent an average of the two mesh bag field duplicates. Biomonitoring stations MB-10 and MB-11 were also field duplicates. They were placed approximately 6.7 meters apart. Two certified reference materials (CRM) were used to evaluate the recovery of manganese in moss-PM during microwave digestion, including the National Institute of Standards and Technology (NIST) 1573a (pine needles) and NIST 1575 (tomato leaves). Both CRMs were organic materials which had 90.5 % and 87.1 % recoveries for manganese, respectively. The collocated soil recovery of manganese was 93.3 ± 5.1 % ($n = 8$) (Chapter 5).

The results of the moss blanks will first be discussed followed by an evaluation of manganese concentrations in moss-PM and in the collocated soil of biomonitoring stations. Finally, the manganese elemental associations and spatial distributions (i.e., proximity to sources) of moss-PM will be compared to the collocated soil levels.

Results

1.0 Moss blanks

Duplicate samples of unwashed Mackenzie River Delta moss were dried, crushed, digested and analyzed following the same procedure as the exposed moss samples (Chapter 4). The average manganese concentration for these samples was 299 ppm. Its relative percent difference (RPD) (Equation 10) was 1.6 %.

$$\text{Relative percent difference} = \left(\frac{(|\text{value 1} - \text{value 2}|)}{((\text{value 1} + \text{value 2})/2)} \right) * 100 \quad [\text{Eqn 10}]$$

For the purposes of *in situ* monitoring, this background level of manganese was unacceptably high. Therefore, the Mackenzie Delta River moss was washed (Chapter 4) and the subsequently clean moss was used for all samples and quality assurance blanks. Washing the Mackenzie River Delta moss with the acid/water method proved to be very effective, removing almost 100% of the manganese from the natural moss. Several aliquots of clean washed *sphagnum* moss (n = 7) were dried, crushed, digested and analyzed along with the exposed moss samples. These samples, named “Clean Moss blanks”, were never in contact with the mesh bags. The mean of the Clean Moss blanks was used as a correction factor to correct the airborne particle results for the negligible amount of manganese contained in the moss before exposure. This correction factor (average of the Clean Moss blanks) was 0.9 ± 0.1 ppm (n = 9) (Table 47).

Duplicate samples of a lab moss blank (#1) were analyzed. This blank consisted of a mesh bag which was filled with clean *sphagnum* moss, placed in a Ziploc[®] bag and left in the lab. While in the field, several mesh bags had to be assembled for use in the biomonitoring stations. Therefore, a second lab blank (#2) was created in the field and kept sealed in a

Ziploc[®] bag. These moss blanks were removed from their mesh bags after the two-month exposure period and underwent the same sample preparation and analysis as the other moss samples. The first lab blank had a manganese concentration of 3.0 ppm whereas the second had 1.8 ppm of manganese.

Table 47 Mean and relative percent difference of manganese concentrations in Mackenzie River Delta moss (unwashed vs washed) and the laboratory moss blanks.

	Mackenzie R. Delta Moss (unwashed)	Clean Moss Blank (washed)	Lab Blank #1	Lab Blank #2
Mean (ppm)	299	0.9	3.0	1.8
Relative percent difference (%) or standard deviation (ppm)	1.6 %	0.1 ppm	14.6 %	10.4 %
n	2	9	2	2

Within-, and between-station variability

Each biomonitoring station consisted of 2 field duplicate mesh bags filled with washed-moss. The moss-PM manganese results for these duplicates were averaged for a final manganese concentration for each biomonitoring station. The variability of moss-PM manganese between the field duplicates of each station was described by the relative percent different (RPD) between the two field duplicate moss-filled mesh bags. Since only two moss-filled mesh bag replicates were used at each station, calculating the relative standard deviation was impossible (standard deviation requires $n \geq 3$). Using the relative percent difference is an alternative to the RSD when $n = 2$. The biomonitoring station mesh bag RPD varied between 0.3 % and 44.0 %, and had an average of 13.5 %.

Two of the biomonitoring stations were field duplicates, MB-10 and MB-11. These stations were 6.7 m apart with no obstructions between them. The average moss-PM manganese concentration at these two biomonitoring stations was 55.2 ppm and the RPD

between these field duplicates was 3.7 %. Though the distance between biomonitoring stations MB-6 and MB-7 was larger than MB-10 and MB-11, they were installed on the same grounds and in close proximity to one another. Their average moss-PM manganese level was 56.5 ppm (RPD = 0.8 %). The variability of the manganese levels in moss-PM between all biomonitoring stations, as described by the relative standard deviation (RSD; Equation 11), was 63.7 %.

$$\text{Relative standard deviation} = (\text{standard deviation} / \text{mean}) * 100 \quad [\text{Eqn 11}]$$

2.0 Biomonitoring station moss-PM manganese

Moss-PM manganese results were log-normally distributed ($W(23) = .926$, $p < .05$). The moss-PM geometric mean manganese content for all biomonitoring stations was 27.4 ppm. The 5th percentile was 8.4 ppm and the 95th was 88.8 ppm. Figure 70 shows the manganese concentration of moss-PM at each biomonitoring station. Error bars represent the average relative percent difference, 13.5 %, of each pair of mesh-bag. It is important to note that the moss-PM manganese concentrations in Figure 70 are diluted by the moss substrate. Equation 12 describes the final moss-PM manganese concentration calculation. The term “mass” of Equation 12 (below) represented the combined weights of the moss-sequestered airborne particles and the moss substrate, which greatly outweighed the former. The factor by which it outweighs the moss-PM is unknown at this time. Therefore interpretation of the moss-PM manganese content will be limited to spatial variations and elemental associations. Here the term ‘spatial variation’ indicates proximity to sources (not to be confused with spatial distributions which are described below).

$$\text{Moss-PM (Mn}_{\text{final}}) = \frac{(\text{digest (Mn) (ng/mL)} * \text{digest volume (mL)} * \text{dilution factor})}{(\text{mass (g)} * 1000)} \quad [\text{Eqn 12}]$$

where, “digest (Mn)” represents the manganese concentration of the digest solution; “digest volume” is the volume to which the digest solution was diluted (50 mL); “dilution factor” is the factor by which the digest solution was diluted for analysis (in this case = 1); and “mass (g)” is the combined weights of the airborne particles and the moss substrate of each sample.

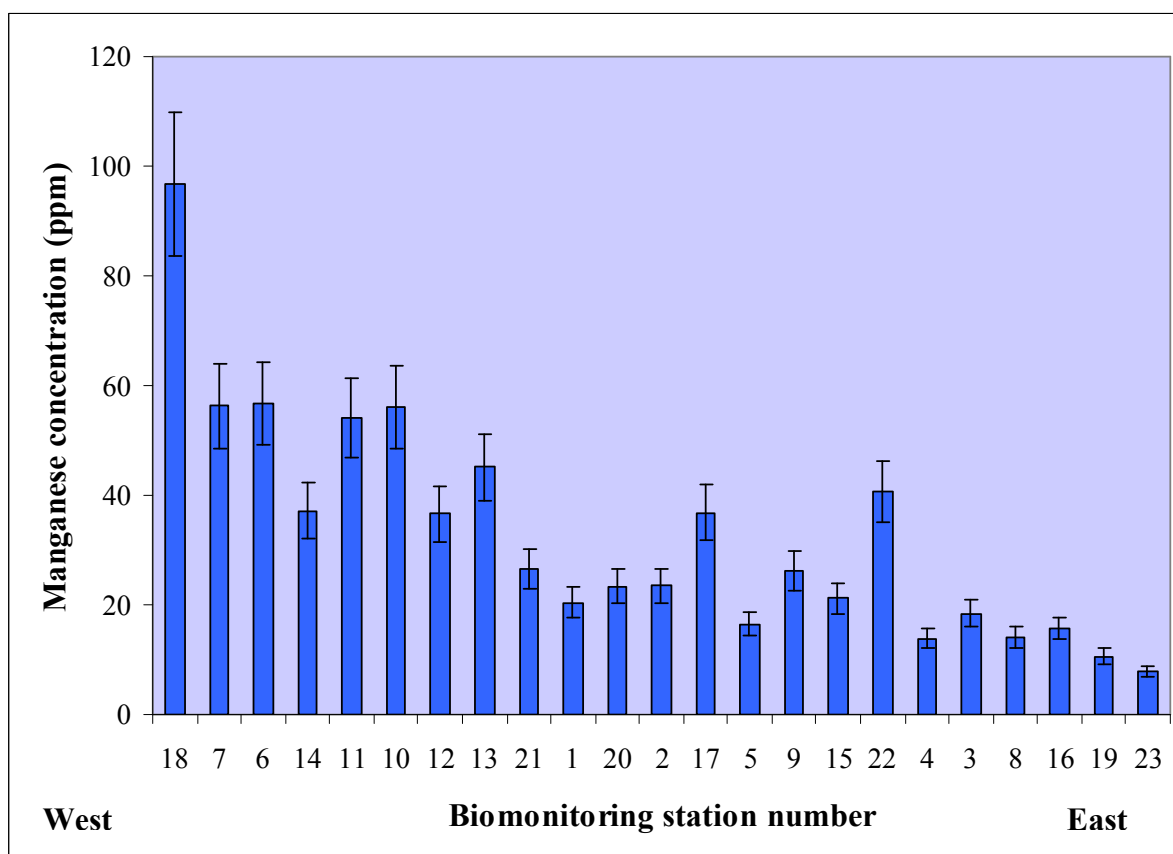


Figure 70 Biomonitoring station moss-PM manganese concentrations (including correction factor) (n = 2 / station).

Figure 71 shows the spatial distribution of manganese concentrations in moss-PM collected at the biomonitoring station. The higher concentrations of manganese were located in the western part of the city. The highest manganese levels were found at station MB-18 in the southwestern corner of the city of Windsor, followed by MB-6 and -7, and field duplicates MB-10 and -11. Two of the non-urban stations had the lowest manganese content (MB-19 and MB-23) (Figure 71). Table 48 describes the location of each biomonitoring station.

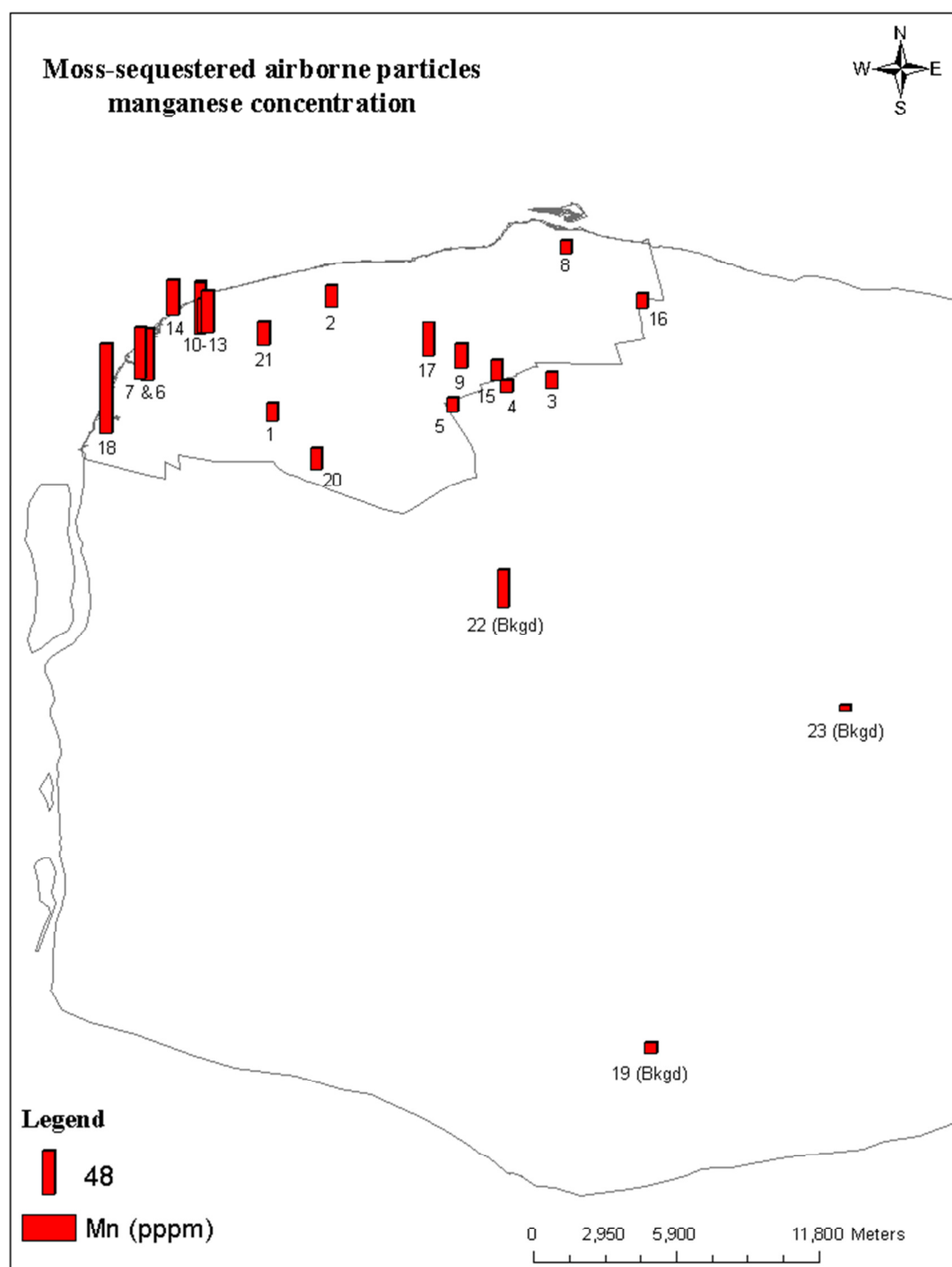


Figure 71 Spatial distribution of biomonitoring station moss-PM manganese levels (n = 23). (Station numbers are indicated underneath bars.)

Table 48 Description of biomonitoring station locations.

Station	Description	Station	Description
MB-1	Privately owned land	MB-12	University of Windsor campus
MB-2	City of Windsor nursery (Central)	MB-13	University of Windsor campus
MB-3	Windsor Airport grounds	MB-14	University of Windsor campus
MB-4	Windsor Airport grounds	MB-15	City of Windsor Pillette pumping station (south)
MB-5	Windsor Airport grounds	MB-16	City of Windsor Banwell pumping station (east)
MB-6	City of Windsor Lou Romano water reclamation plant (northwest)	MB-17	City of Windsor Grand Marais pumping station (central)
MB-7	City of Windsor Lou Romano water treatment plant (northwest)	MB-18	City of Windsor Maplewood pumping station (west)
MB-8	City of Windsor Little River Pollution Control Plant (north-East)	MB-19*	Agriculture and Agri-Food Canada Greenhouse and Processing Crops Research Centre, Harrow, Ontario
MB-9	City of Windsor, Environmental Services Centre (southeast)	MB-20	St. Clair College campus
MB-10	University of Windsor campus	MB-21	City of Windsor, Public Works compound (south-central)
MB-11	University of Windsor campus	MB-22*	Commercial gardening centre
MB-23*	Grounds of Essex Region Conservation Authority offices		

* Non-urban stations.

The majority of the elements in moss-PM were log-normally distributed, (except Ti, Cu and Y, which were normally distributed), therefore the non-parametric Spearman correlations were used to describe the relationships between manganese and the different elements in biomonitoring station moss-PM. Manganese in airborne particles trapped on the moss substrate was significantly correlated to fifteen elements (i.e., V, Cr, Fe, Ti, Co, Cu, Zn, Sr, Y, Mo, Cd, Sn, Sb, Ba and Pb) (Table 49). All of these significant associations were above $r_s = .5$. Very strong relationships existed between manganese and vanadium, chromium and iron, $r_s = .91$, $.93$ and $.96$, respectively. Figure 72 to Figure 86 show the scatterplots and R -square values for all of the significant relationships with log-transformed moss-PM manganese. Respectively, vanadium, chromium and iron accounted for 87 %, 88 % and 93 %, respectively, of the variability in moss-PM manganese. Strong ($r_s > .9$) significant positive intercorrelations were also observed in moss-PM between Y and Ti ($r_s = .96$); V and Fe ($r_s = .95$); Cr and Fe ($r_s = .93$); V and Ti ($r_s = .90$); Fe and Ti ($r_s = .90$); Mo and Ti ($r_s = .92$); and Cu and Zn ($r_s = .93$) (scatterplots can be found in Appendix L). Of these strong relationships, Ti and Y (both were normally distributed) and Log(V and Fe) (the regression was done with the log-transformed results) had R^2 values above 90 %.

Table 49 Spearman correlation matrix for the moss-PM elemental concentrations (n = 23) ($p = 0.01$).

	V	Cr	Fe	Ti	Mn	Co	Cu	Zn	Sr	Y	Mo	Cd	Sn	Sb	Ba	Pb
V	1															
Cr	.82	1														
Fe	.95	.93	1													
Ti	.90	.78	.90	1												
Mn	.91	.93	.96	.81	1											
Co	.77	.61	.77	.84	.64	1										
Cu	.73	.50*	.65	.56 ^a	.63	.56	1									
Zn	.77	.62	.76	.72	.73	.63	.93	1								
Sr	.68	.43*	.63	.71	.53	.57	.61	.64	1							
Y	.88	.75	.88	.96 ^a	.79	.86	.52 ^{a*}	.61	.64	1						
Mo	.88	.77	.86	.92	.80	.76	.77	.79	.64	.85	1					
Cd	.57	ns	.56	.43*	.54	.56	.79	.82	ns	ns	.52*	1				
Sn	.67	.78	.78	.61	.72	.53	.43*	.61	.61	.62	.51*	ns	1			
Sb	.65	.57	.67	.45*	.67	ns	.68	.77	.46*	.44*	.45*	.80	.70	1		
Ba	.86	.64	.81	.80	.74	.76	.77	.79	.82	.79	.78	.56	.72	.61	1	
Pb	.73	.73	.80	.60	.74	.59	.65	.75	.56	.63	.58	.64	.86	.82	.75	1

^a Indicates a Pearson coefficient was used because both elements were normally distributed.

* Correlation is significant at the 0.05 level.

“ns” Indicates result was not statistically significant.

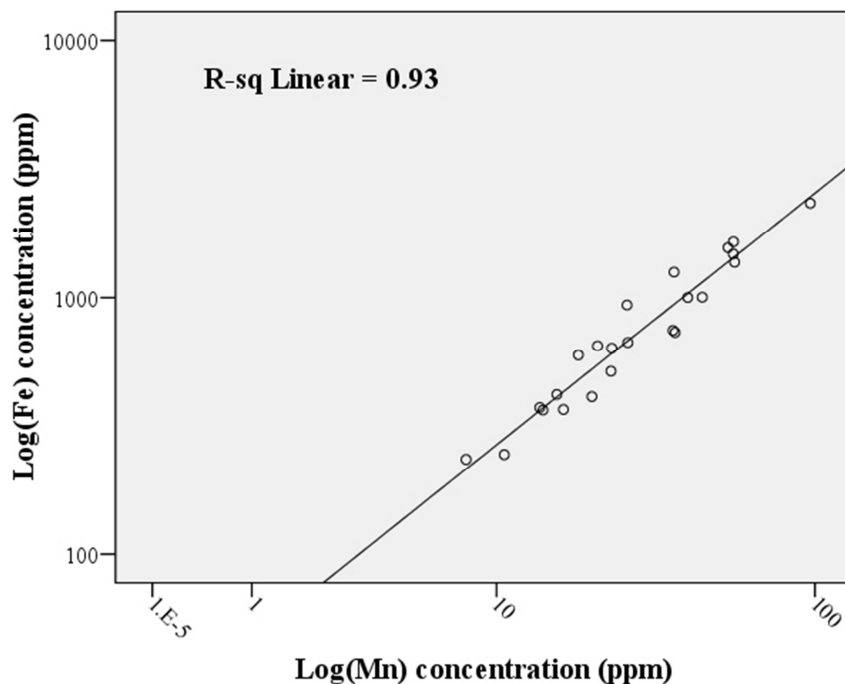


Figure 72 Scatterplot and linear regression trendline for log-transformed moss-PM iron and manganese (n = 23).

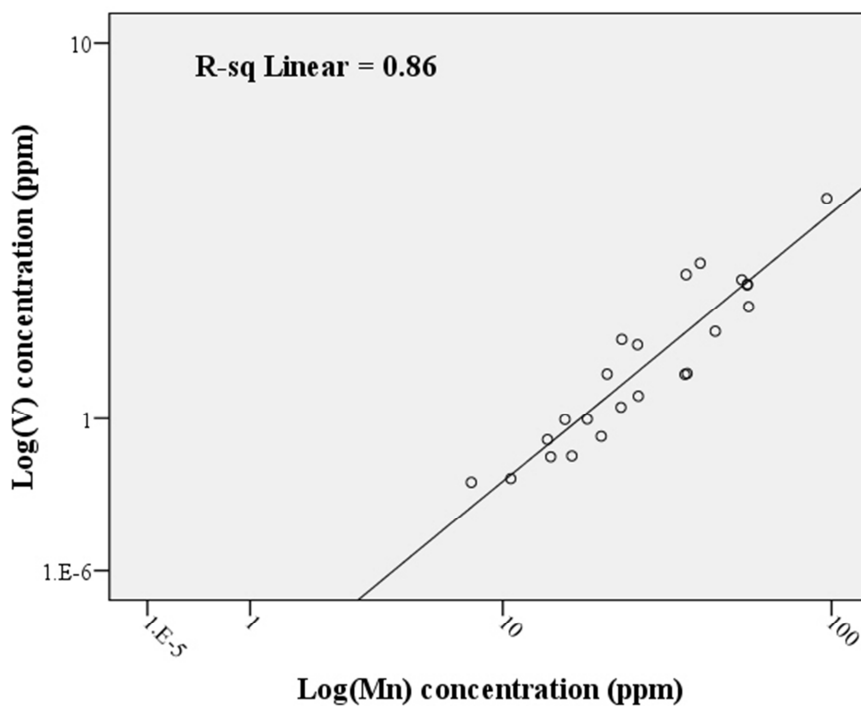


Figure 73 Scatterplot and linear regression trendline for log-transformed moss-PM vanadium and manganese (n = 23).

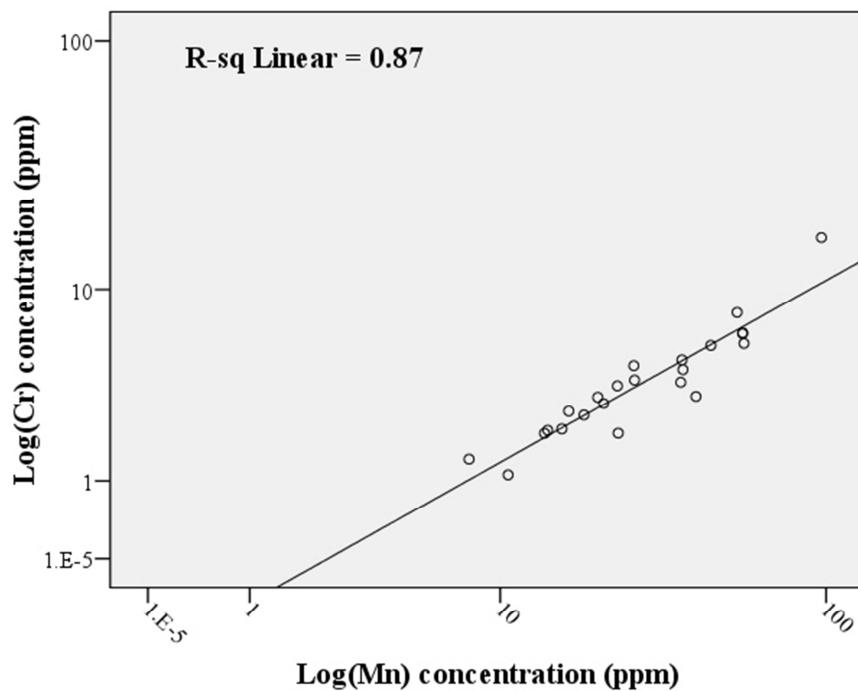


Figure 74 Scatterplot and linear regression trendline for log-transformed moss-PM chromium and manganese (n = 23).

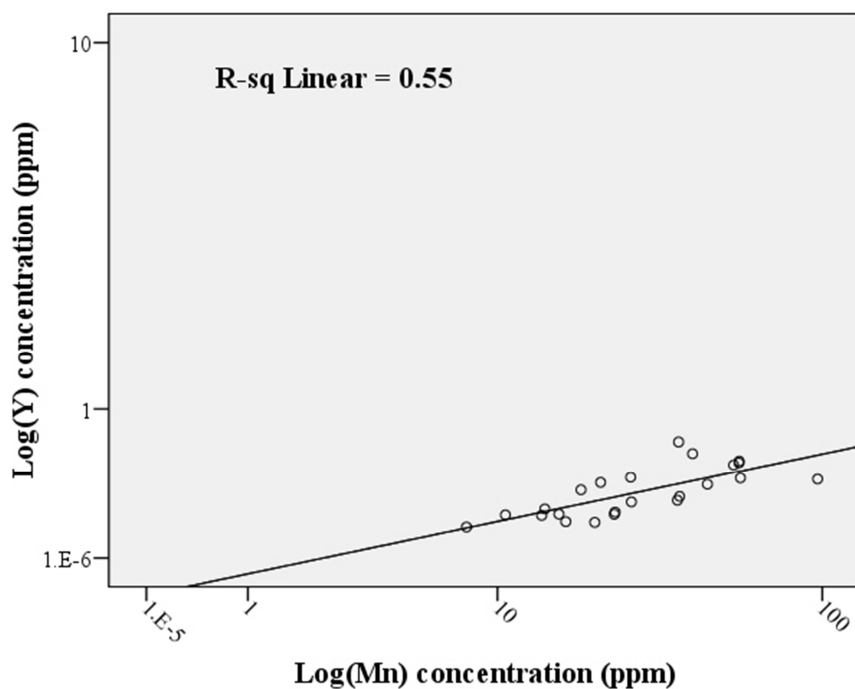


Figure 75 Scatterplot and linear regression trendline for log-transformed moss-PM yttrium and manganese (n = 23).

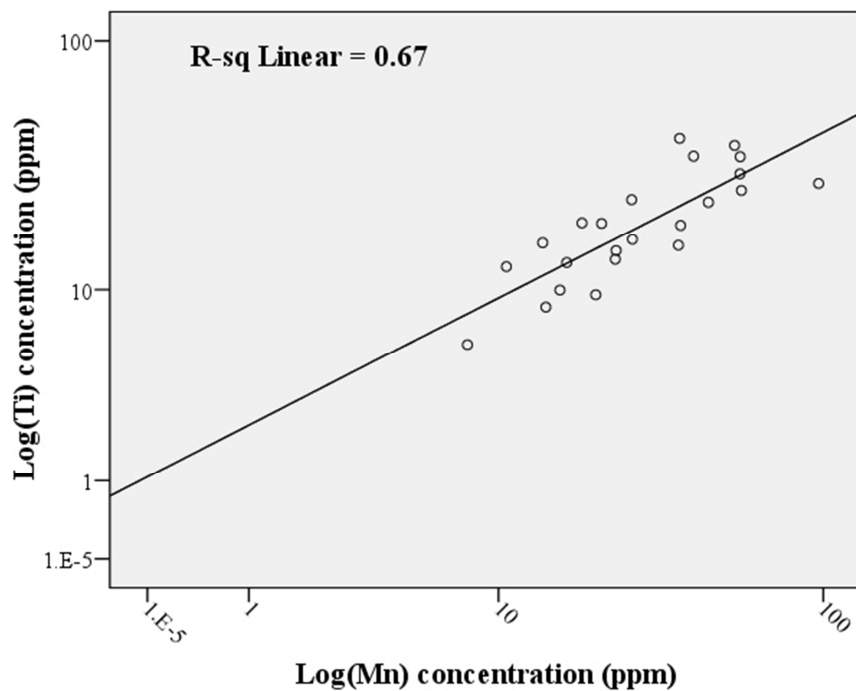


Figure 76 Scatterplot and linear regression trendline for log-transformed moss-PM titanium and manganese (n = 23).

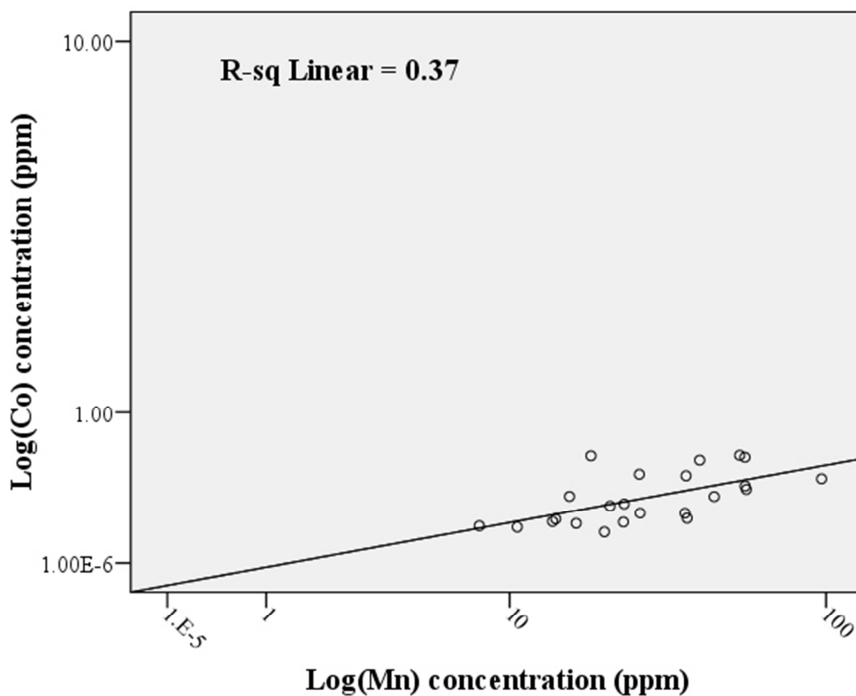


Figure 77 Scatterplot and linear regression trendline for log-transformed moss-PM cobalt and manganese (n = 23).

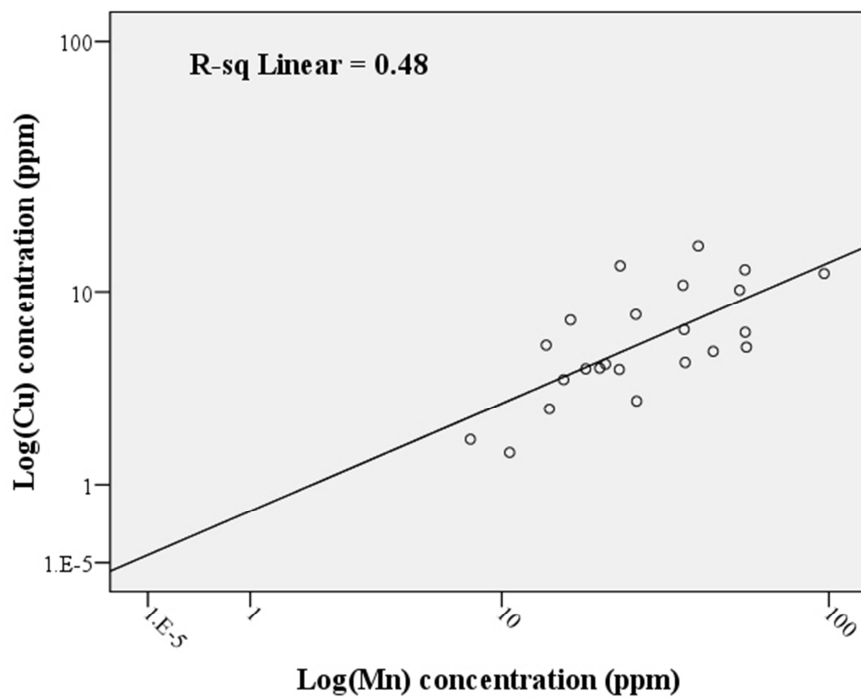


Figure 78 Scatterplot and linear regression trendline for log-transformed moss-PM copper and manganese (n = 23).

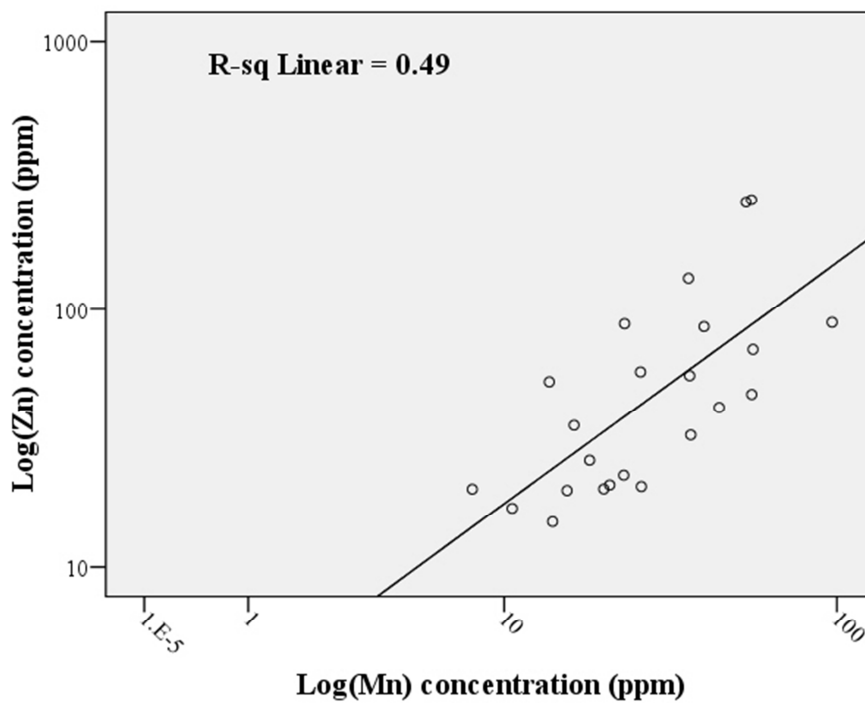


Figure 79 Scatterplot and linear regression trendline for log-transformed moss-PM zinc and manganese (n = 23).

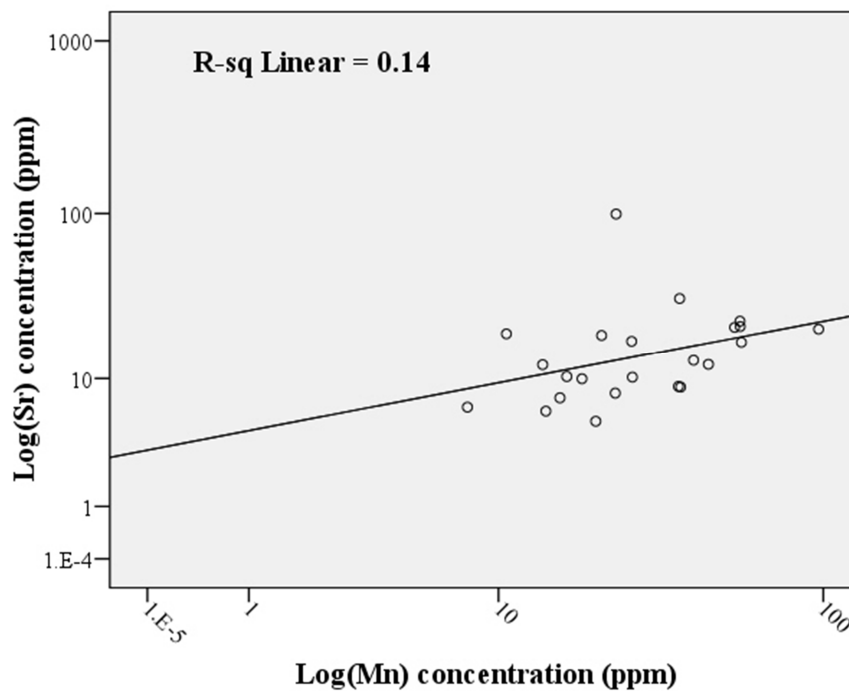


Figure 80 Scatterplot and linear regression trendline for log-transformed moss-PM strontium and manganese (n = 23).

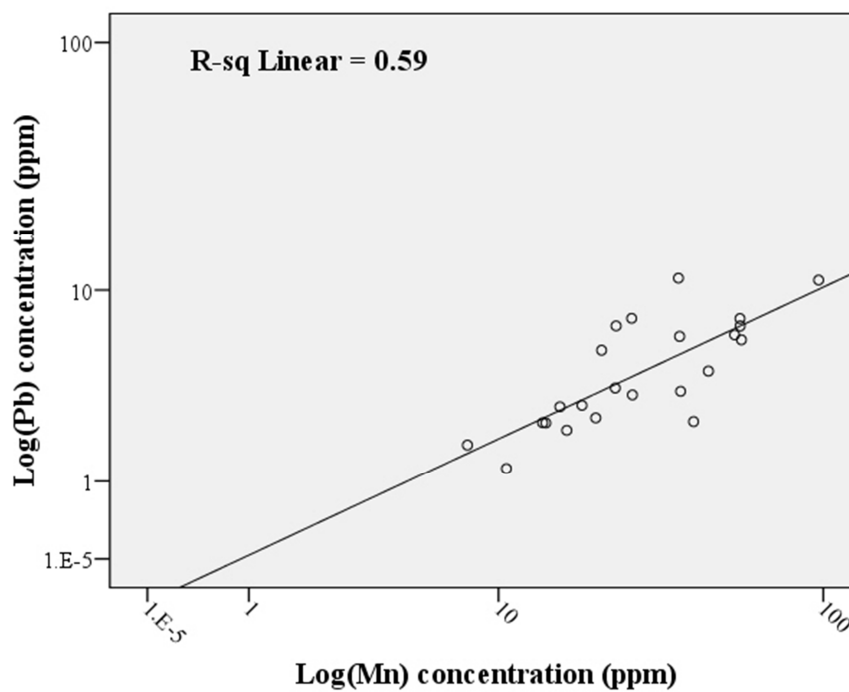


Figure 81 Scatterplot and linear regression trendline for log-transformed moss-PM lead and manganese (n = 23).

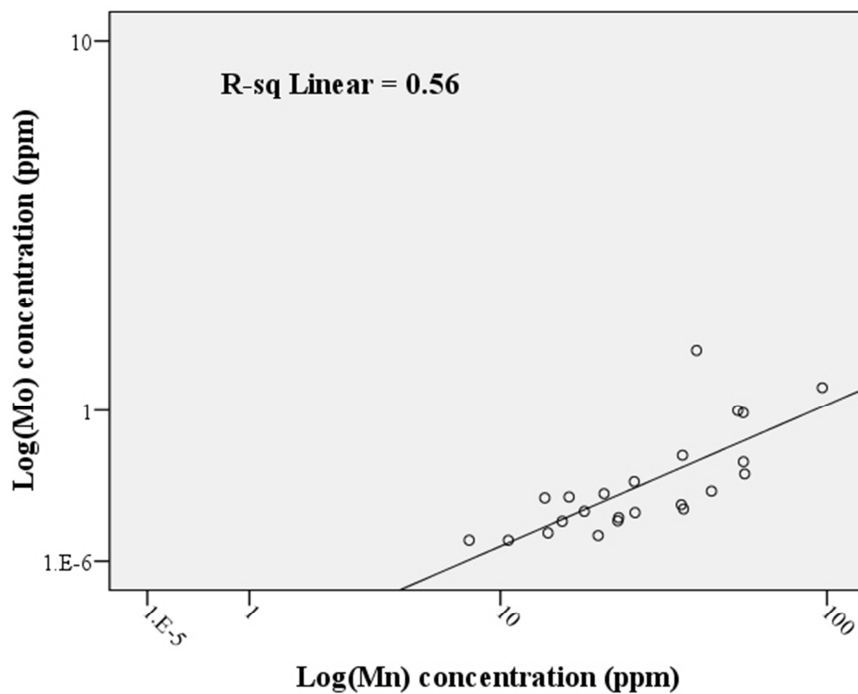


Figure 82 Scatterplot and linear regression trendline for log-transformed moss-PM molybdenum and manganese (n = 23).

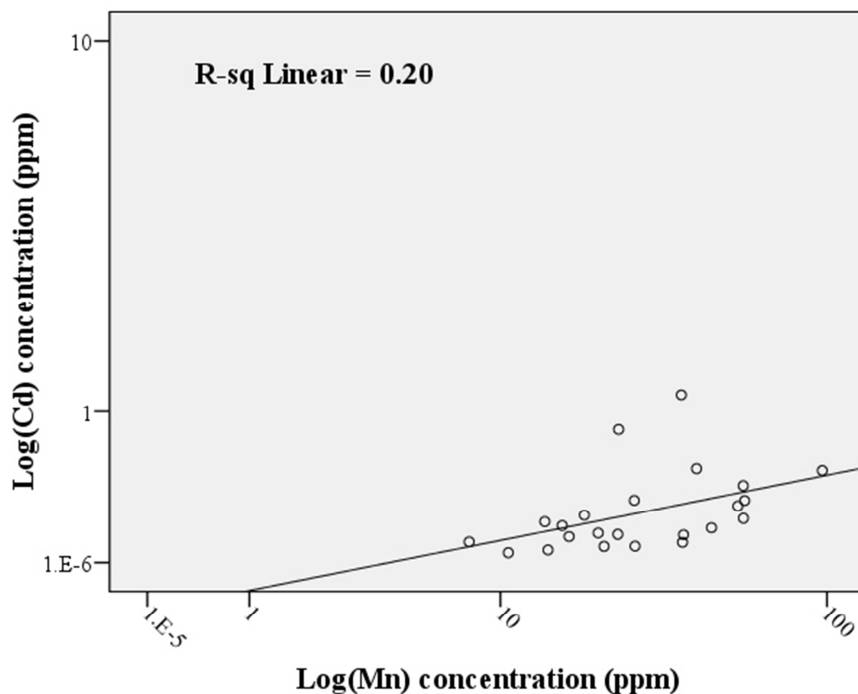


Figure 83 Scatterplot and linear regression trendline for log-transformed moss-PM cadmium and manganese (n = 23).

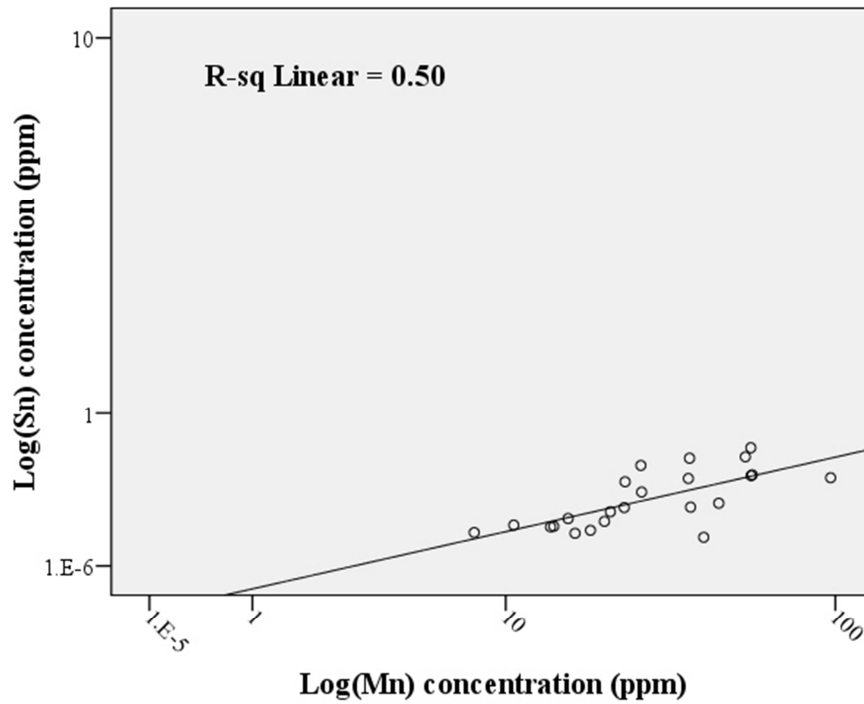


Figure 84 Scatterplot and linear regression trendline for log-transformed moss-PM tin and manganese (n = 23).

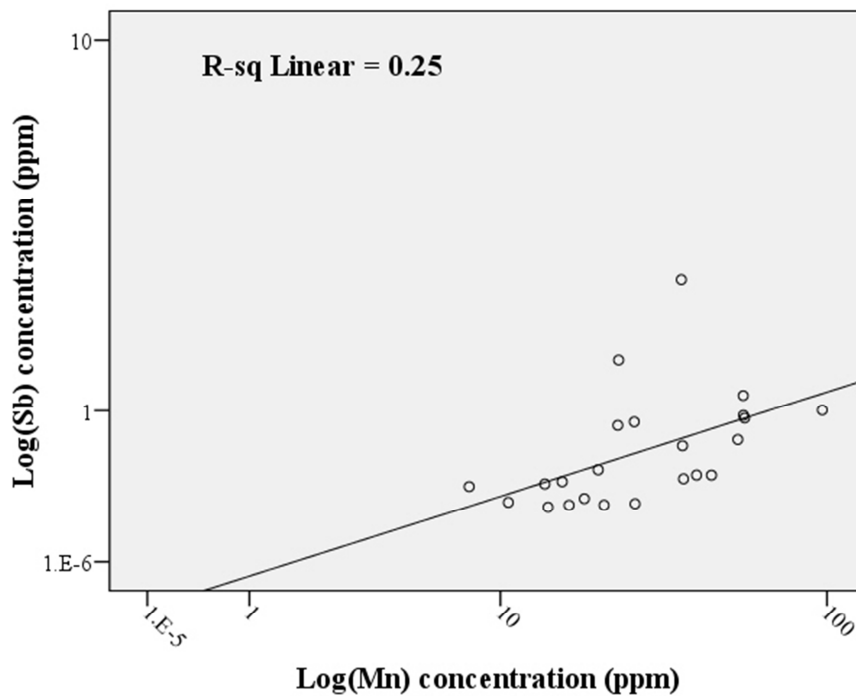


Figure 85 Scatterplot and linear regression trendline for log-transformed moss-PM antimony and manganese (n = 23).

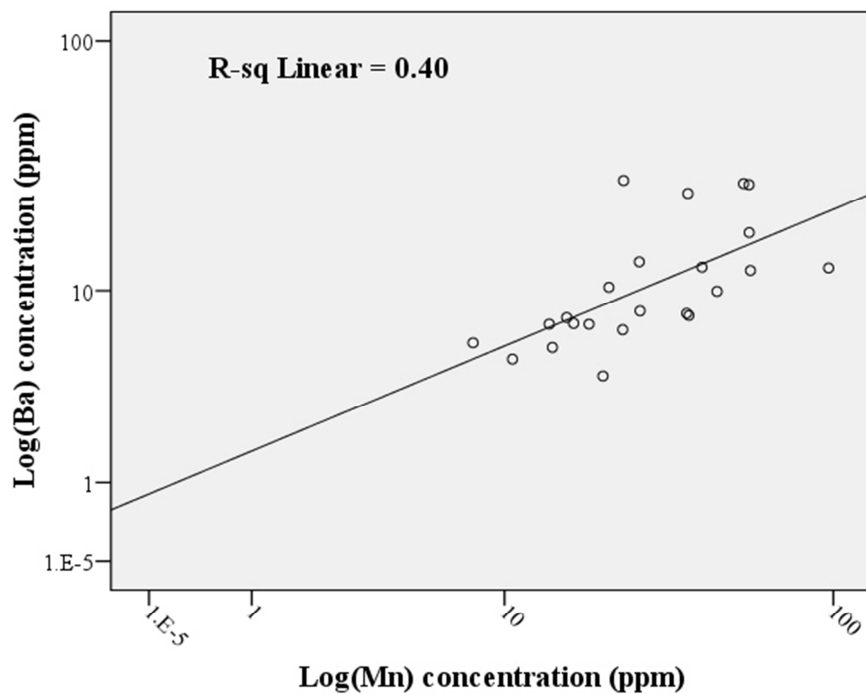


Figure 86 Scatterplot and linear regression trendline for log-transformed moss-PM barium and manganese (n = 23).

In summary, biomonitoring station moss-PM manganese concentrations were log-normally distributed. The urban airborne particles trapped on moss substrate had a geometric mean manganese concentration of 27.4 ppm. The moss-PM manganese concentrations were diluted by the moss substrate. The highest moss-PM manganese concentrations were in the southwest of the city. These manganese results were significantly correlated to fifteen elements including iron, chromium and vanadium. These three relationships were very strong. A high level of intercorrelation between the elements in moss-PM was also observed.

3.0 Collocated biomonitoring station soil manganese

The collocated biomonitoring station soil manganese was normally distributed ($W(23) = .130, p < .05$). Its mean and median were 427 ± 148 ppm and 390 ppm, respectively, and its geometric mean was 405 ppm. The 5th and 95th percentiles were 221 ppm and 774 ppm, respectively. Figure 87 illustrates the spatial distribution of collocated biomonitoring station soil manganese in Windsor and the surrounding area. High levels of manganese in biomonitoring station soil were found in the western part of the city. The lower manganese concentrations were found at two non-urban stations (MB-22 and MB-23), a station on the southern city boundary (MB-20), and another in the northeast (MB-8).

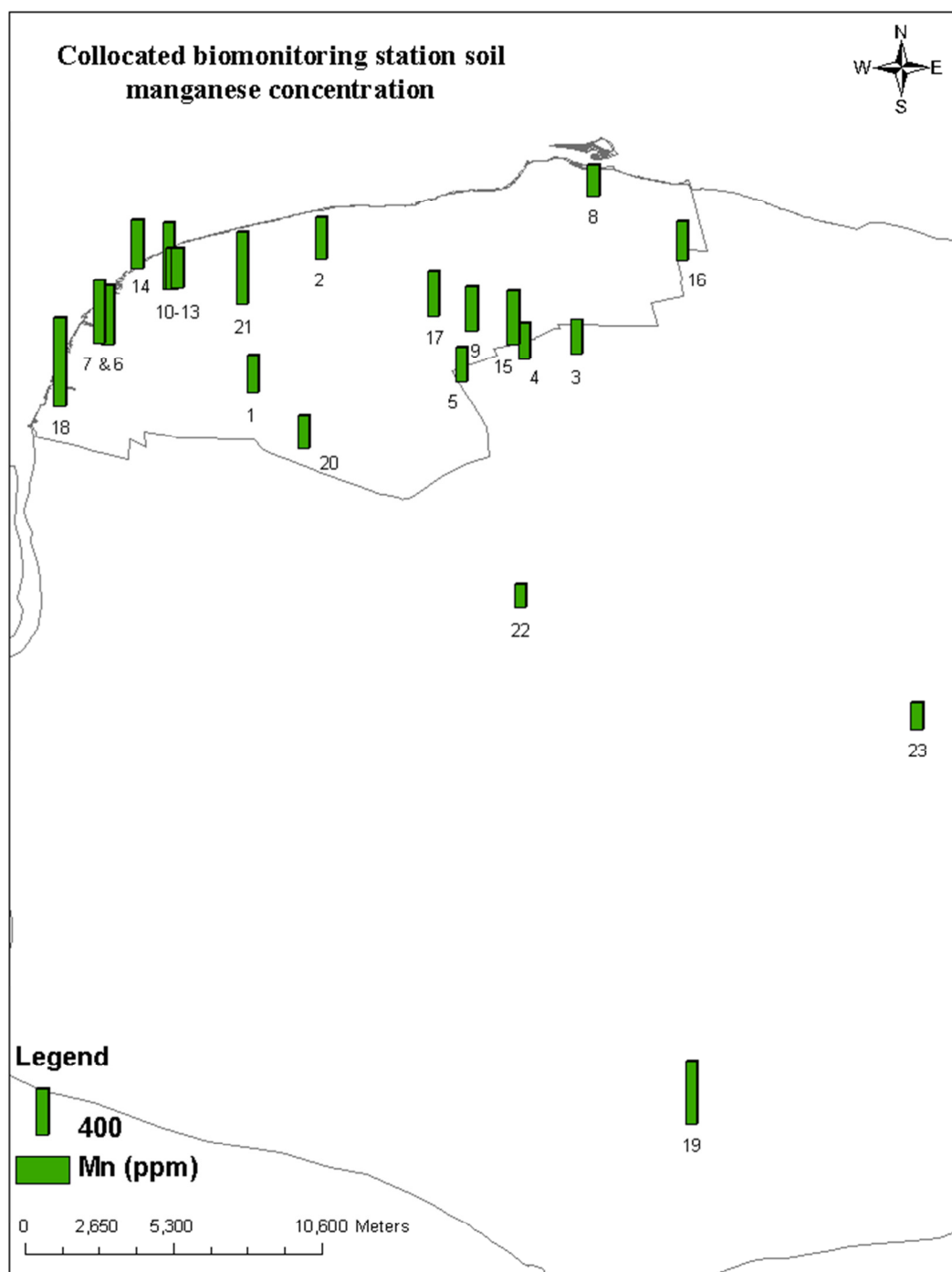


Figure 87 Spatial distribution of collocated biomonitoring station soil manganese levels (n = 23). (Station numbers are shown underneath bars.)

The collocated biomonitoring station soil manganese was significantly correlated to zinc, cadmium, lead, copper and strontium. Only the zinc and cadmium relationships were large ($r_s > .5$) (Table 49). The lead, strontium and copper associations were medium-large ($.4 < r_s < .5$) (Table 49). Figure 88 to Figure 92 show the scatterplots and linear regression trendlines for the various significant elemental relationships with collocated biomonitoring station soil manganese. Zinc accounted for 45 % of the collocated biomonitoring station soil manganese variability and cadmium 21 %. The other significant elements (i.e., Pb, Sr and Cu) could account for less than 20 % each. The elements correlated with collocated biomonitoring station soil manganese (i.e., Zn, Cd, Pb, Sr and Cu) were significantly and strongly intercorrelated. Zinc, copper and lead had strong ($r_s > .5$) Spearman correlation coefficients with strontium (Table 50). Correlations between zinc, copper, cadmium and lead were all between .8 and .9 except for the relationship between zinc and cadmium. This association was the strongest at $r_s = .92$ and it had an *R*-square of .79. See Appendix L for scatterplots and linear regressions of these relationships.

Table 50 Spearman correlation matrix for the collocated biomonitoring station soil elemental concentrations (n = 23) ($p = 0.01$).

	Cr	Fe	Mn	Co	Cu	Zn	Sr	Y	Mo	Cd	Sn	Sb	Ba	Pb
Cr	1													
Fe	.60^a	1												
Mn	ns ^a	ns ^a	1											
Co	ns ^a	.73^a	ns ^a	1										
Cu	.85	.55	.46*	ns	1									
Zn	.74	.50*	.72	ns	.86	1								
Sr	.45*	ns	.46*	ns	.63	.67	1							
Y	ns ^a	ns ^a	ns ^a	.75^a	ns	-.41*	ns	1						
Mo	.45 ^{a*}	ns ^a	ns ^a	ns ^a	.67	.66	.50*	-.56^a	1					
Cd	.81	.53	.51*	ns	.88	.92	.64	ns	.59	1				
Sn	ns	ns	ns	ns	.47*	.53	ns	ns	.46*	.52*	1			
Sb	ns	ns	ns	ns	.58	.58	.48*	-.80	.76	.55	.65	1		
Ba	ns ^a	.43 ^{a*}	ns ^a	.47 ^{a*}	ns	ns	ns	.51^{a*}	ns ^a	ns	ns	ns	1	
Pb	.70	.42*	.47*	ns	.84	.84	.70	ns	.65	.87	.49*	.43*	.48*	1

^a Indicates a Pearson coefficient was used because both elements were normally distributed.

* Correlation is significant at the 0.05 level.

“ns” Indicates result was not statistically significant.

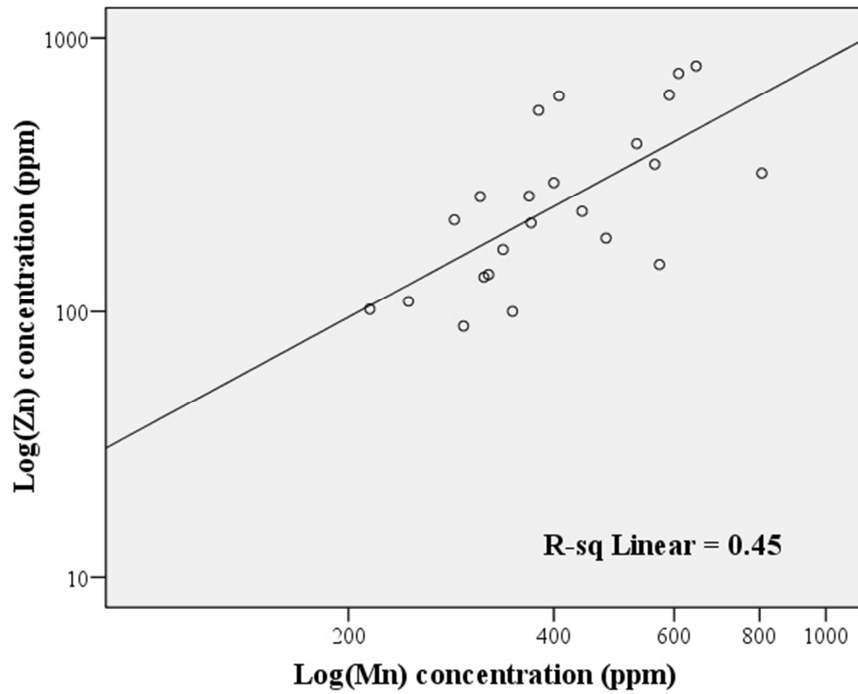


Figure 88 Scatterplot and linear regression trendline for log-transformed collocated biomonitoring station soil zinc and manganese (n = 23).

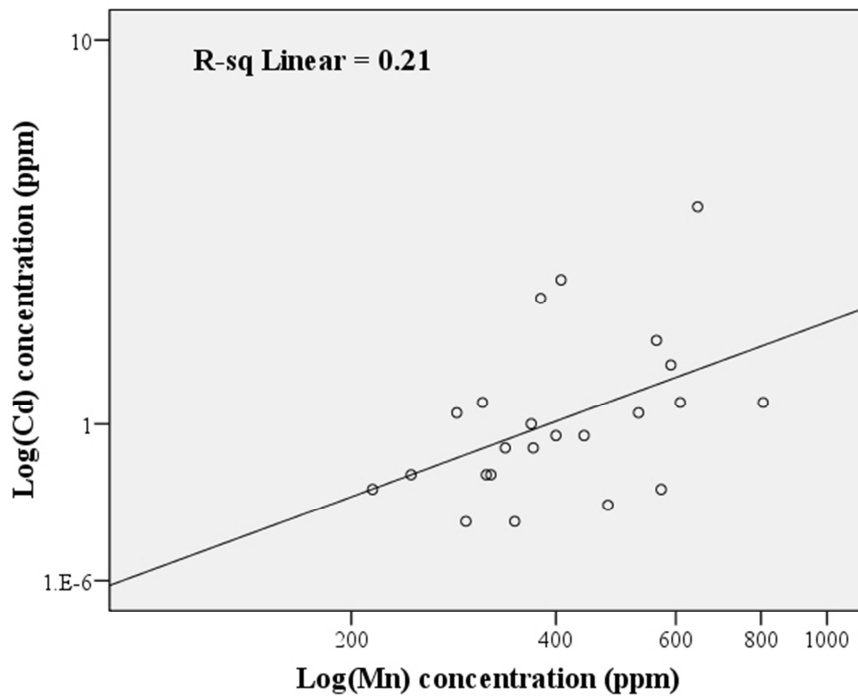


Figure 89 Scatterplot and linear regression trendline for log-transformed collocated biomonitoring station soil cadmium and manganese (n = 23).

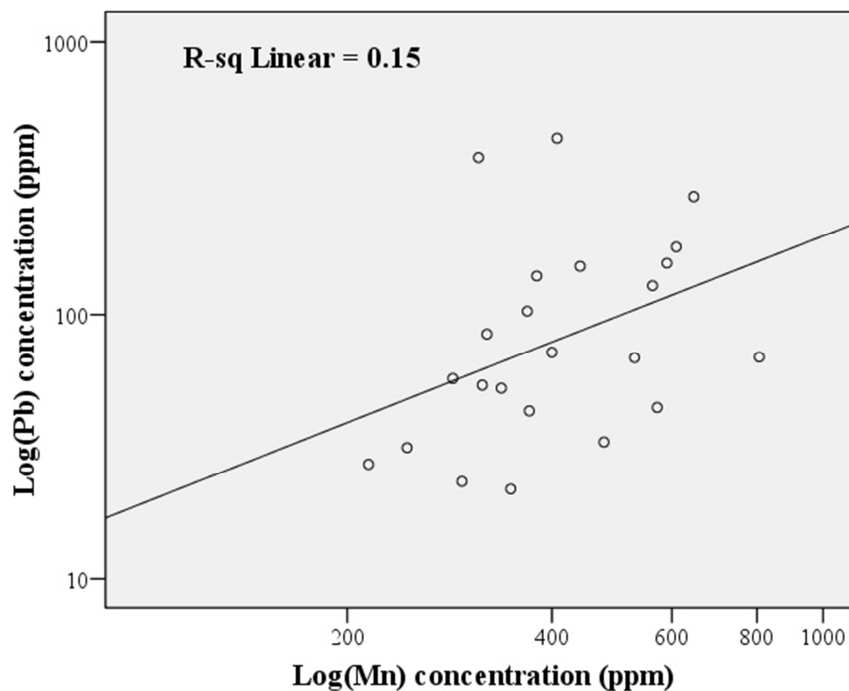


Figure 90 Scatterplot and linear regression trendline for log-transformed collocated biomonitoring station soil lead and manganese (n = 23).

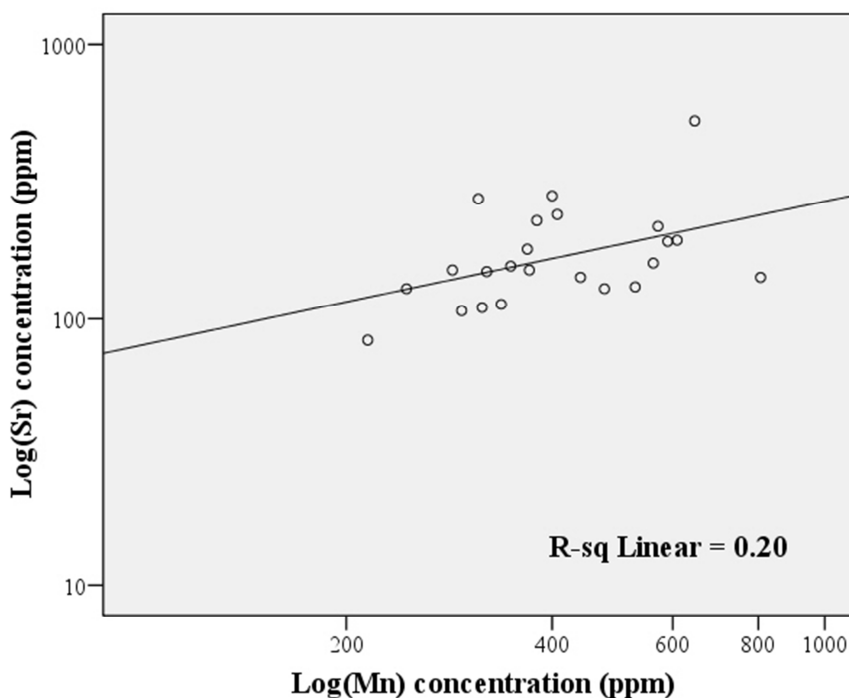


Figure 91 Scatterplot and linear regression trendline for log-transformed collocated biomonitoring station soil strontium and manganese (n = 23).

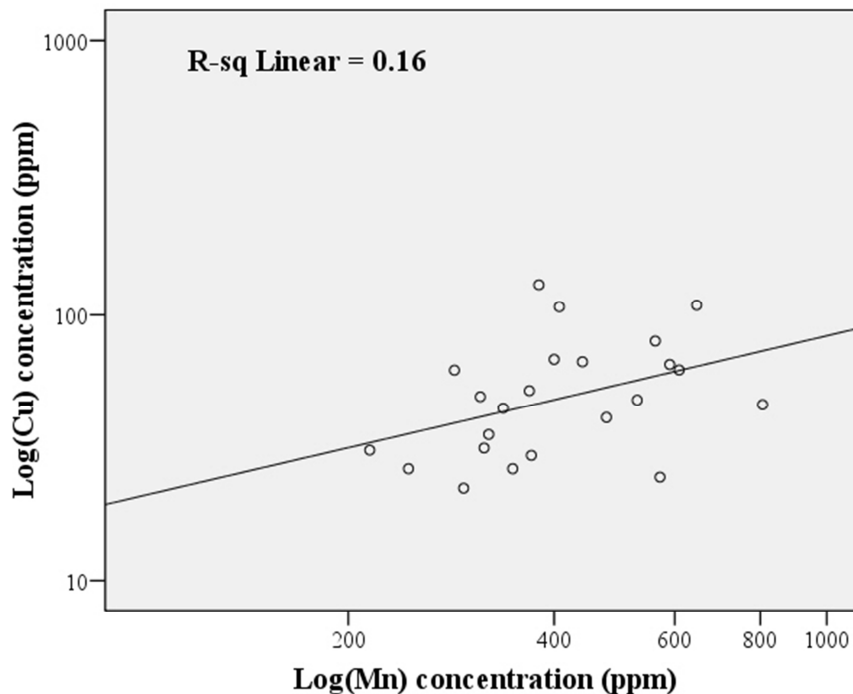


Figure 92 Scatterplot and linear regression trendline for log-transformed collocated biomonitoring station soil copper and manganese (n = 23).

The collocated biomonitoring station soil was normally distributed and had a mean manganese concentration of 427 ppm. Higher levels of soil manganese were found in the western part of the city. Zinc and cadmium were strongly correlated to the collocated biomonitoring station soil manganese levels. Intercorrelation existed between the elements correlated with collocated biomonitoring station soil manganese.

4.0 Comparison of biomonitoring station moss-PM and collocated soil

It is clear from Figure 93 that, overall, the collocated biomonitoring station soil manganese was an average of 17 times higher than the moss-PM manganese concentrations. As previously mentioned in section 2.0, it is important to remember that the moss-PM manganese concentrations were lower due to the dilution effect of the moss substrate. Figure 94 shows the Soil:Moss-PM manganese ratio (collocated biomonitoring station soil/manganese concentration in the moss-sequestered airborne particles). This ratio increased from west to east; except for stations MB-21 and MB-22. The former had a higher Soil:Moss-PM ratio than the other biomonitoring stations in its vicinity. Biomonitoring

station MB-22 was a rural background site with a much smaller ratio than the other eastern biomonitoring stations, in fact, it was the smallest of all the biomonitoring stations. The other two rural background sites, MB-19 and MB-23 had the highest soil to moss-PM ratios (Figure 94). The eastward increase of the Soil:Moss-PM ratios would indicate that the difference between the two manganese contents was increasing. The spatial distribution of biomonitoring station moss-PM and collocated soil manganese were similar. Higher levels of manganese were found in the western part of the city (Figure 95).

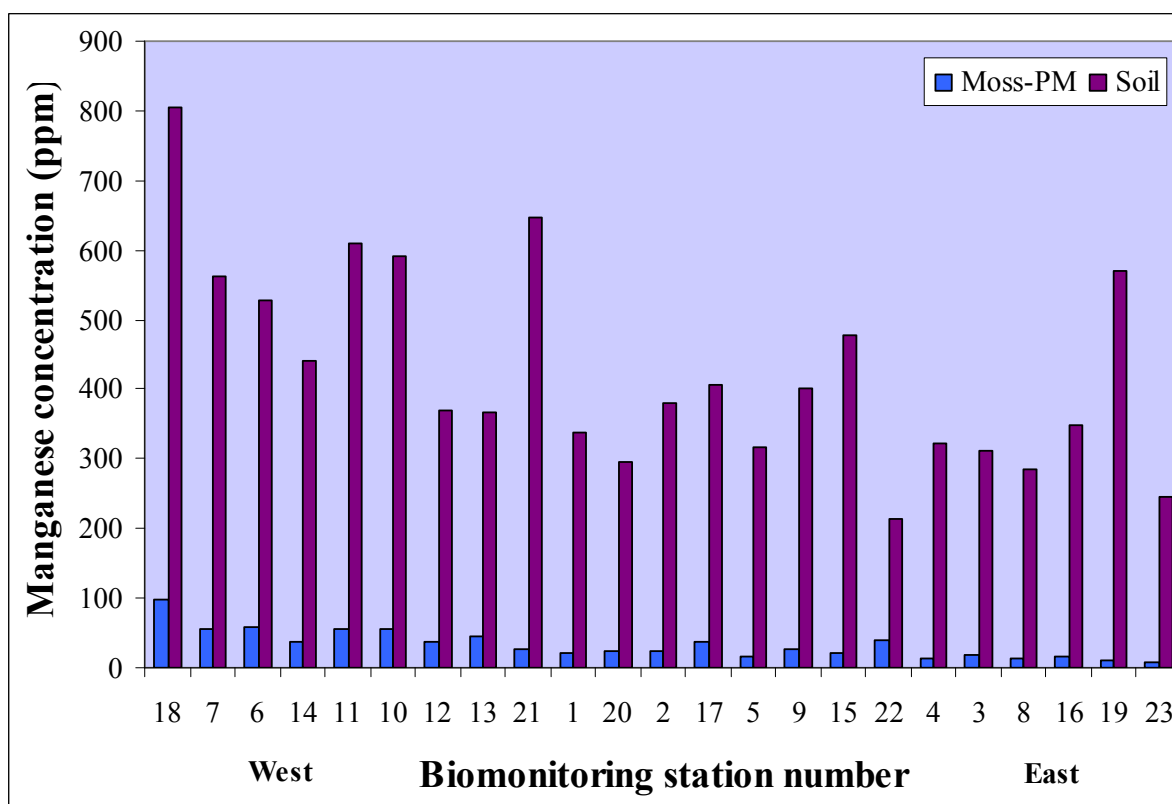


Figure 93 Moss-PM and collocated soil manganese concentrations of biomonitoring stations in a west-to-east order (n = 23).

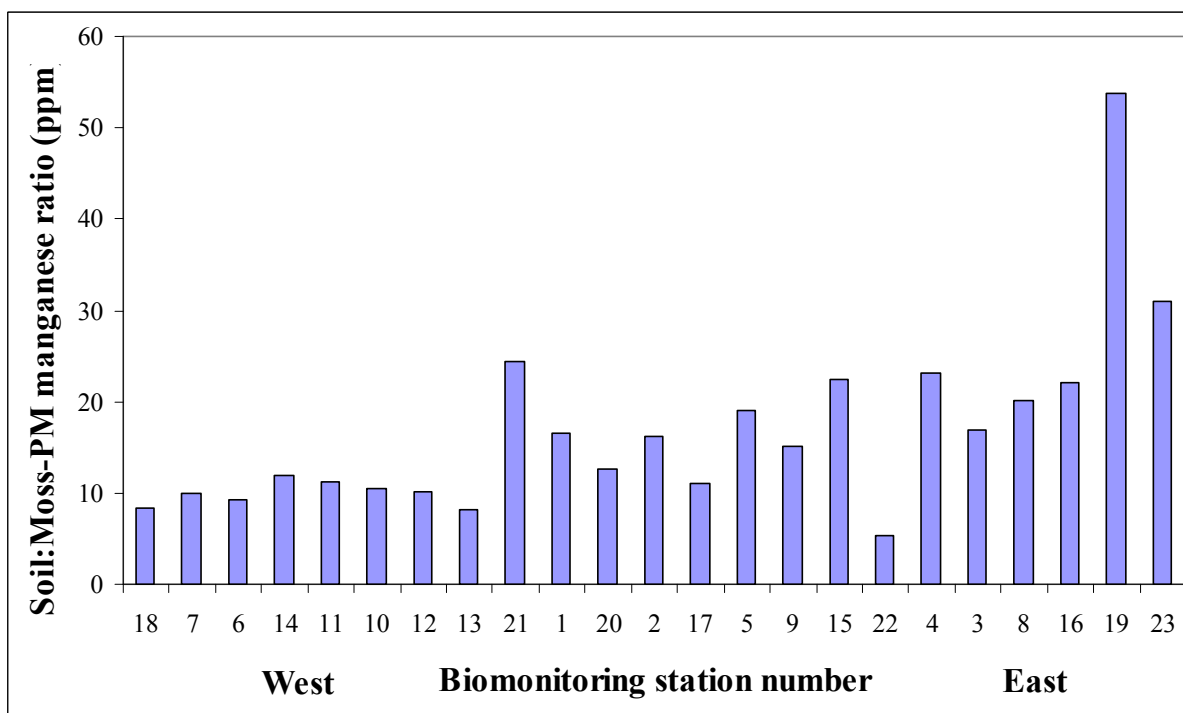


Figure 94 West-East collocated Soil:Moss-PM manganese ratio of Windsor biomonitoring stations.

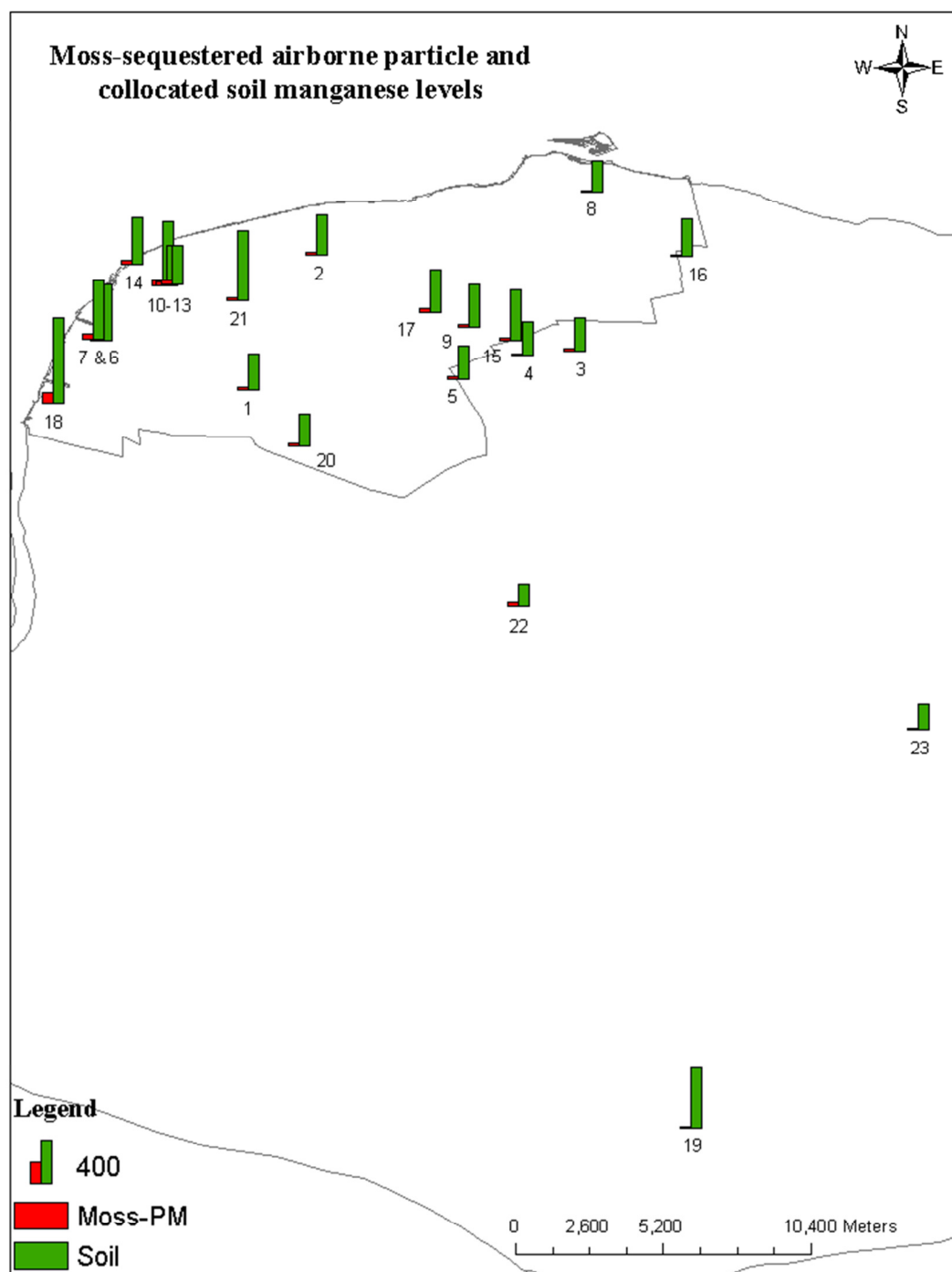


Figure 95 Spatial distribution of biomonitoring station moss-PM and collocated soil manganese levels (n = 23). (Station numbers are shown underneath bars.)

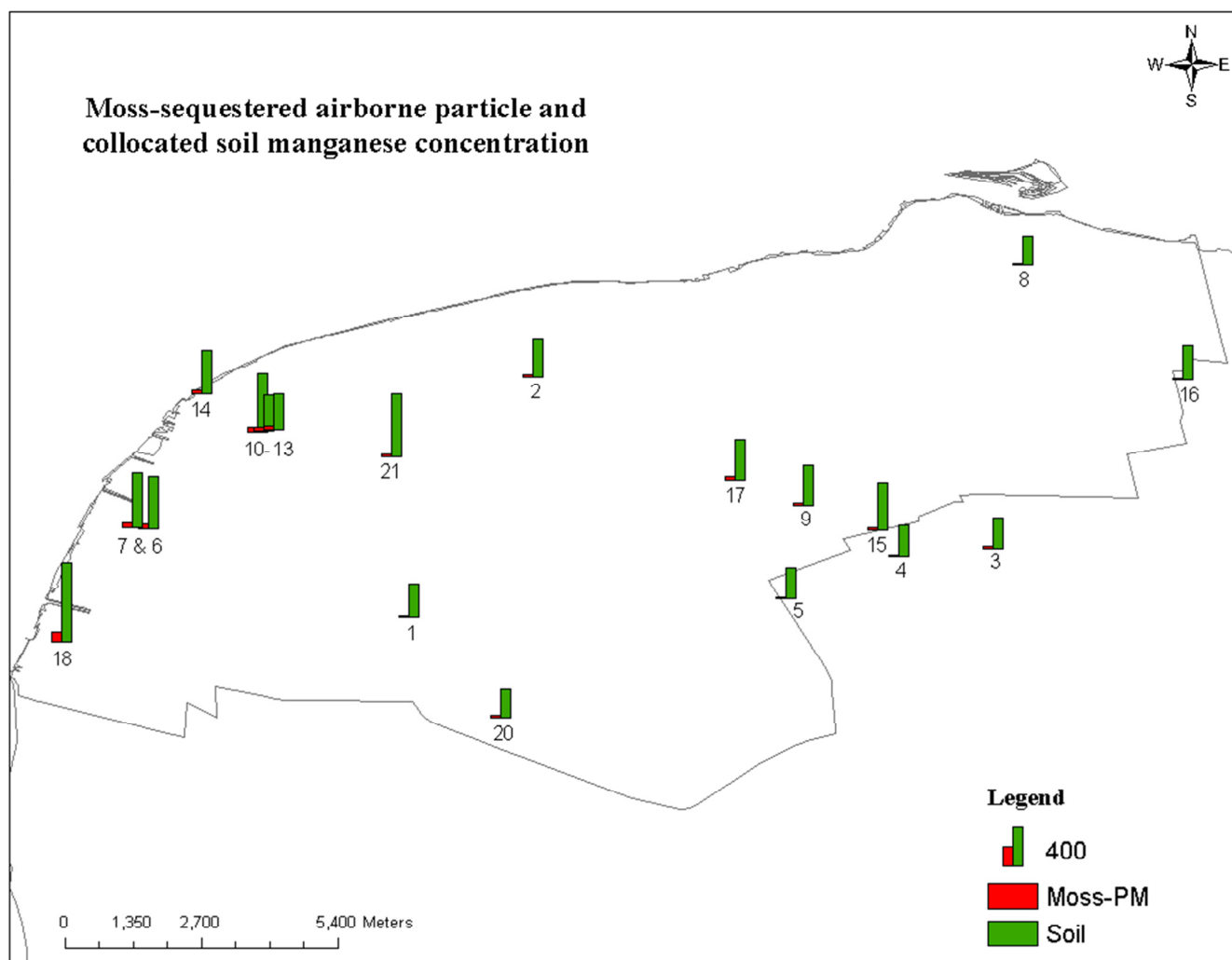


Figure 95 Spatial distribution of biomonitoring station moss-PM and collocated soil manganese levels ($n = 23$). (Station numbers are shown underneath bars.) (cont'd.)

The non-parametric Mann-Whitney mean comparison test was used to compare the manganese concentrations in the biomonitoring station moss-PM and collocated soil since the moss-PM results were log-normally distributed (except yttrium). An independent t-test was used for yttrium instead of the non-parametric test because both the moss-PM and collocated soil concentrations of yttrium were normally distributed. The Mann-Whitney tests found that the moss-PM means, for the elements reported here (except antimony), were significantly different from the collocated biomonitoring station soil means. The results of these mean comparison tests are shown in Table 51.

Table 51 Biomonitoring station moss-PM and collocated soil mean comparison Mann-Whitney and Independent t-test results (n = 23).

Element	Test Statistic ($p = .001$)	Element	Test Statistic ($p = .001$)
Chromium	$U = 0, r = -0.86$	Yttrium*	$T(22) = -19.083, r = 0.94$
Iron	$U = 0, r = -0.86$	Molybdenum	$U = 75, r = -0.61$
Manganese	$U = 0, r = -0.86$	Cadmium	$U = 42, r = -0.72$
Cobalt	$U = 0, r = -0.86$	Tin	$U = 18, r = -0.80$
Copper	$U = 0, r = -0.86$	Antimony	n/s
Zinc	$U = 29, r = -0.76$	Barium	$U = 0, r = -0.86$
Strontium	$U = 1, r = -0.85$	Lead	$U = 0, r = -0.86$

“n/s” not significant

* Independent t-test result; moss-PM and collocated soil element results were normally distributed ($p < .05$).

Elemental Associations

The five significant elemental associations found in collocated biomonitoring station soil, namely copper, zinc, strontium, cadmium and lead, were also found to be significant in the moss-PM (Table 52). The moss-PM manganese was also significantly correlated with all other elements reported in Table 49 whereas manganese in collocated biomonitoring station soil had no other significant associations (Table 50). The strongest moss-PM manganese association was with chromium and iron (near-perfect correlations) (Table 52). The

collocated biomonitoring station soil manganese relationships with iron and chromium were not found significant. The strongest manganese relationships in collocated biomonitoring station soil were with zinc and cadmium ($r_s > .5$) (Table 52). The amount of variability (R^2) between manganese and zinc was similar in both moss-PM (49 %) (Figure 79) and collocated soil (45 %) (Figure 88). The variability between moss-PM manganese and cadmium (31 %) (Figure 83) was slightly higher than the variability between collocated soil manganese and cadmium (21 %) (Figure 89). The opposite was found for strontium, variability between moss-PM manganese and strontium was lower than in collocated soil, 14 % (Figure 80) and 20 % (Figure 91), respectively. Moss-PM copper and lead had much higher R^2 values than their collocated biomonitoring station soil counterparts, 33 % (Figure 78 and Figure 81) and 46 % (Figure 90 and Figure 92) higher, respectively. As observed in sections 2.0 and 3.0 of this chapter, the level of intercorrelation between the elements associated with manganese was higher in moss-PM than in collocated biomonitoring station soil.

Table 52 Comparison of significant elemental associations of manganese in moss-PM and collocated soil (n = 23) ($p = 0.01$)

	Cr	Fe	Co	Cu	Zn	Sr	Y
Moss-PM	.93	.96	.64	.63	.73	.53	.79
Collocated Soil	ns	ns	ns	.46*	.72	.46*	ns
	Mo	Cd	Sn	Sb	Ba	Pb	
Moss-PM	.80	.54	.72	.67	.74	.74	
Collocated Soil	ns	.51*	ns	ns	ns	.47*	

* Correlation is significant at the 0.05 level.

“ns” Indicates result was not statistically significant.

Note: The significant relationship between moss-PM manganese and vanadium, and titanium, were excluded from this table since these elements were not measured in collocated soil. Therefore comparisons are impossible at this time.

An investigation of the elemental associations between moss-PM and collocated biomonitoring station soil revealed that five elements were significantly correlated to each other. Manganese in moss-sequestered airborne particles and collocated biomonitoring

station soil were significantly correlated, $r_s = .57$ ($n = 23$). Zinc had a similarly important association, $r_s = .50$ ($n = 23$). Iron, chromium and strontium also had significant relationships between the moss-PM and the collocated soil but were medium-large ($.4 < r_s < .5$) (Table 53). The moss-PM and collocated soil manganese scatterplot (Figure 96) shows an R^2 of .32, therefore 32 % of the variability of one variable can be explained by the other. Twenty-seven percent of the variability between moss-PM and collocated soil zinc was explained (Figure 97). This percentage was 15% for chromium (Figure 98). R -square values for iron (Figure 99) and strontium (Figure 100) were both approximately 10 %.

Table 53 Spearman correlation matrix for the biomonitoring station moss-PM and collocated soil elemental concentrations ($n = 23$) ($p = 0.01$).

Moss-PM Soil \	Cr	Fe	Mn	Co	Cu	Zn	Sr
Cr	.49*	.49*	.47*	ns	ns	ns	.48*
Fe	ns	.43*	.51*	ns	ns	ns	ns
Mn	.60	.61	.57	ns	ns	ns	.62
Co	.44*	ns	.42*	ns	ns	ns	ns
Cu	.46*	.50*	.47*	.47*	ns	ns	.48*
Zn	.63	.67	.63	.56	ns	.50*	.62
Sr	ns	ns	ns	.43*	ns	ns	.42*

* Correlation is significant at the 0.05 level.

“ns” Indicates result was not statistically significant.

Table 53 Spearman correlation matrix for the biomonitoring station moss-PM and collocated soil elemental concentrations (n = 23) (p = 0.01). (**cont'd.**)

Moss-PM \ Soil	Y	Mo	Cd	Sn	Sb	Ba	Pb
Y	ns ^a	ns	-.42*	ns	ns	-.50*	-.52*
Mo	.52*	ns	ns	ns	ns	.53	ns
Cd	.47*	ns	ns	.60	ns	.56	.49*
Sn	ns	ns	.41*	ns	ns	ns	ns
Sb	.44*	ns	ns	ns	ns	.46*	.42*
Ba	ns	ns	ns	ns	ns	ns	ns
Pb	.43*	ns	ns	.50*	ns	.47*	ns

^a Indicates a Pearson coefficient was used because both elements were normally distributed.

* Correlation is significant at the 0.05 level.

“ns” Indicates result was not statistically significant.

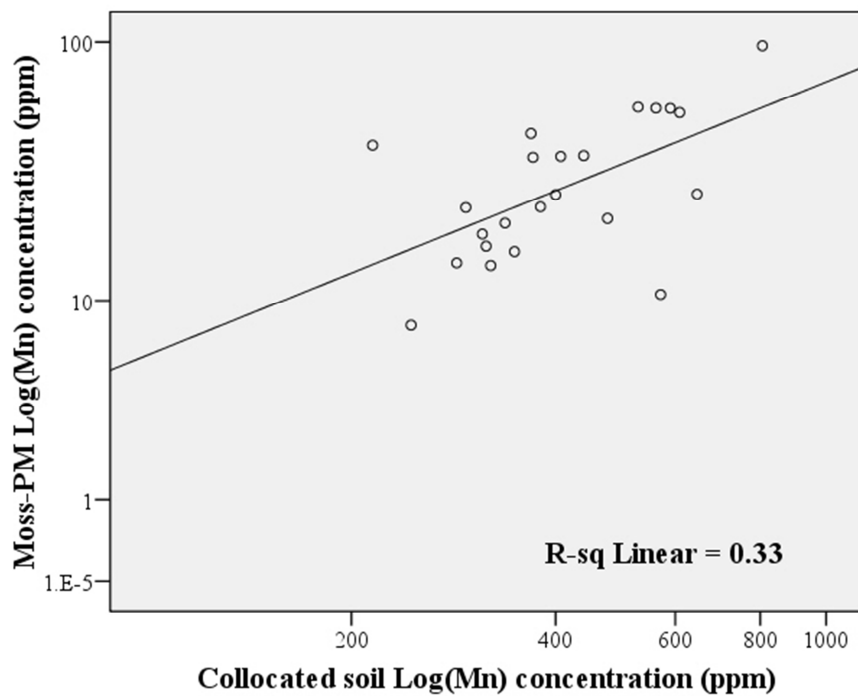


Figure 96 Scatterplot and linear regression trendline for log-transformed biomonitoring station moss-PM and collocated soil manganese (n = 23).

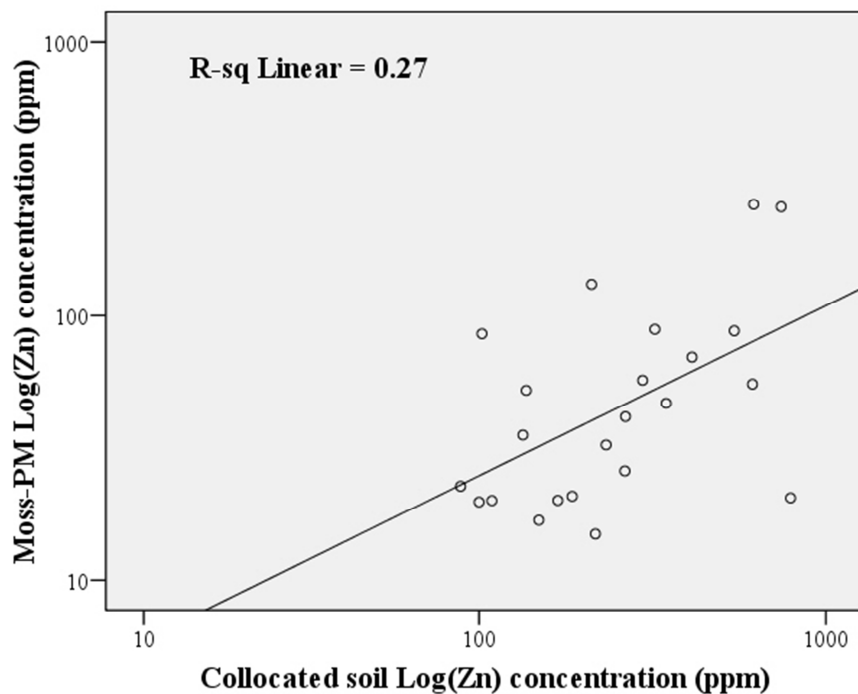


Figure 97 Scatterplot and linear regression trendline for log-transformed biomonitoring station moss-PM and collocated soil zinc (n = 23).

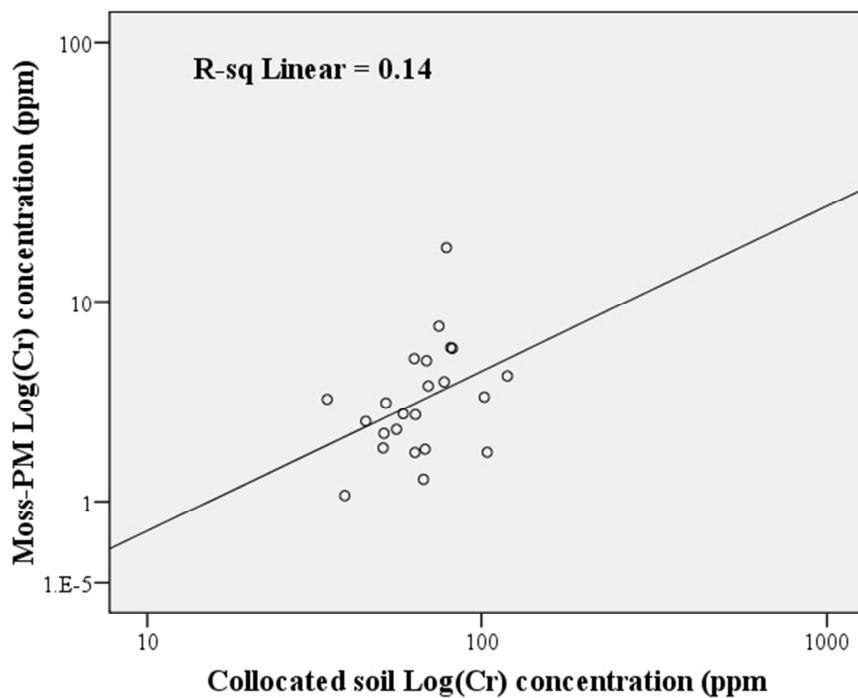


Figure 98 Scatterplot and linear regression trendline for log-transformed biomonitoring station moss-PM and collocated soil chromium (n = 23).

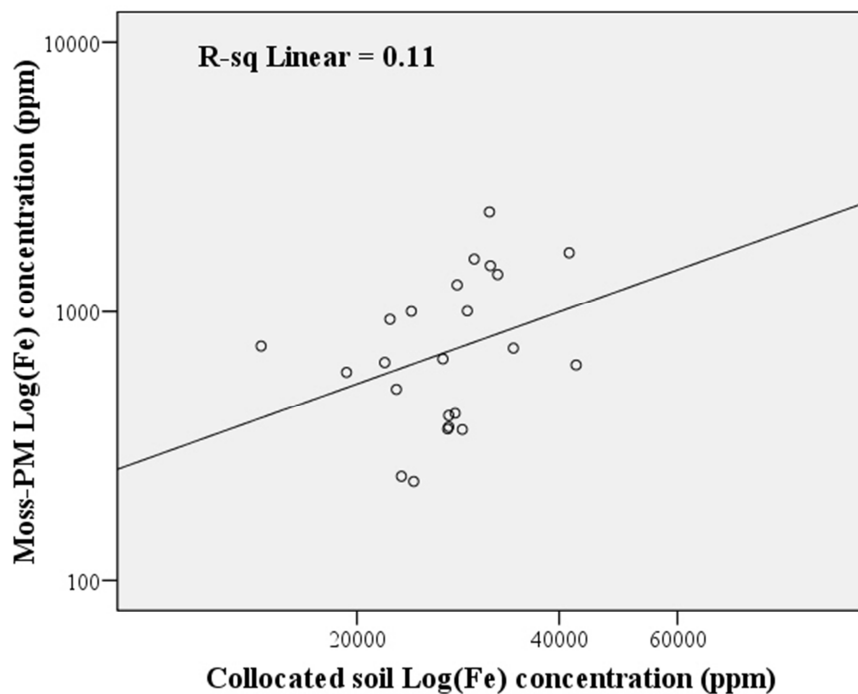


Figure 99 Scatterplot and linear regression trendline for log-transformed biomonitoring station moss-PM and collocated soil iron (n = 23).

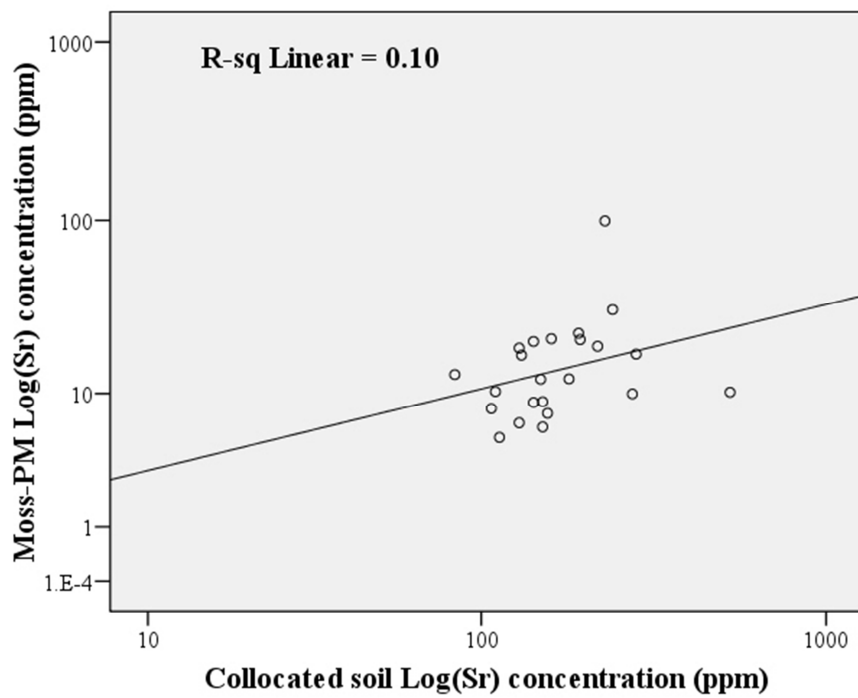


Figure 100 Scatterplot and linear regression trendline for log-transformed biomonitoring station moss-PM and collocated soil strontium (n = 23).

Discussion

This study evaluated the use of low-cost biomonitoring stations in order to collect airborne particles that could potentially be deposited onto, and re-suspended from the urban soil surface in Windsor, Ontario. The manganese elemental associations and spatial variations of both the urban moss-sequestered airborne particles and collocated biomonitoring station soil were successfully measured and compared.

The inexpensive moss bag technique was effective in capturing airborne particles in this urban environment. The acid/water method of cleaning the Mackenzie River Delta moss was very effective, removing almost 100% of the manganese from the rural moss. Therefore, the manganese found after the moss was exposed to the urban environment was not an artefact of the moss. Manganese recovery of the microwave method, used to digest the airborne particles trapped on the moss substrated, was very good, 91 % and 87 % for the two certified reference materials. Adamo et al. (2003) had higher manganese recoveries of 131 % (CTA-VTL-2) and 133 % (CRM-482) using a similar microwave digestion method. The Clean Moss blank found in this present study was 0.9 ± 0.1 ppm. Vasconcelos and Tavares (1998) had a moss blank of 0.22 ppm for manganese.

Every precaution was made to limit the amount of manganese contamination while filling the mesh bags with clean moss. However, manganese contamination, potentially due to the mesh bag filling process, and/or to the mesh bags themselves, was indicated by the slight increase in manganese levels of the two laboratory moss blanks (Table 47). Though only the mesh bags in the best condition possible were chosen for use in this study, after the two-month exposure period, several of the mesh bags were very dry and brittle, some even coming unravelled. Every attempt was made to remove the brittle mesh bag pieces from the moss samples before sample preparation and analysis. Roberts (1972 in Martin and Coughtrey (1982)) found that the nylon of the mesh bag itself retained concentrations of metals between 7 to 26 % of the values for the moss contained in the bags.

Each biomonitoring station had two moss-filled mesh bags, i.e. field duplicates. The relative percent difference (RPD), a measure of the variability between the mesh bags at each site, revealed that the average RPD was 13.5 %. In their Armadale, Scotland study of atmospheric heavy metal pollution, Gailey and Lloyd (1986c) used 30 to 35 % as an acceptable upper limit of the variance (calculated as coefficients of variance (CV; or RSD) in their moss bag results). Culicov et al. (2005) reported total reproducibility, which they defined as “a combination of analytical and field sampling variability” for manganese and other metals in the order of 10-20 % and deemed this variance satisfactory. The variation calculated between the moss-filled mesh bags at each biomonitoring station were well below these limits. Only one station exceeded the upper limit of 35 % recommended by Gailey and Lloyd (1986c), MB-22. Biomonitoring station MB-20 had an RPD approximately equal to this limit, 34.8 %. Both of these stations were in unsecured wide open locations (i.e., large empty field). The latter biomonitoring station was installed on the grounds of a commercial greenhouse while the former was on a college campus. One of the possible reasons for this large variation could be the orientation of the station head to the wind direction. If the wind direction shifted considerably, it could have resulted in one of the moss-filled mesh bags, the one more prominent to the wind, receiving a larger portion of the airborne and re-suspended particles. Makholm and Mladenoff (2005) used a similar biomonitoring station design as those used in Windsor with smaller, more cigar-shaped mesh bags. They found that some of the outer bags had higher element concentrations and that this within-site variability may have been related to the design of the stands. According to Martin and Coughtrey (1982), flat moss-filled mesh bags are “strongly directional with respect to wind and rainfall” since they require a “decision on the orientation (i.e., face-on, edge-on, horizontal, vertical)” during exposure. These decisions may therefore affect the results.

The between-site variability of the biomonitoring stations in Windsor was much higher than the average within-site variability. According to Gailey and Lloyd (1986d), factors such as meteorological factors, changes in the metal output of the sources and inherent properties of the moss bags (i.e., uptake competition, moisture content) could cause some of the variability in the metal deposition patterns. Overall, within-site variability is insignificant compared to the between-site variability. In their evaluation of manganese

concentrations in moss used in moss bags, Gailey and Lloyd (1986c) found a mean coefficient of variance of 7.5% ($n = 5$). Makhholm and Mladenoff (2005), who used Gailey and Lloyd's 30-35 % limit, found an average CV for elements (including manganese) ranging between 6 and 16 %. The biomonitoring station field duplicates also had an acceptable amount of variability, further indicating the good reproducibility of the moss bag technique in an urban environment.

The geometric mean manganese concentration of moss-PM collected in Windsor, Ontario during this study was 27.4 ppm. These moss-PM manganese concentrations were diluted by the presence of the moss substrate. The highest manganese level of moss-PM in Windsor was found at biomonitoring station MB-18. This site is a city pumping station. The biomonitoring station was installed behind the small structure which is located in the middle of a fenced-in area. A very strong odour emanated from the man-hole cover at the front of the small structure. These odours however were not detected behind the structure. Obstacles to using this location included overhead tree branches and a diesel exhaust pipe which was located behind the structure and, according to a city of Windsor employee, it was turned on only once a month. The biomonitoring station was installed as far away from the exhaust pipe as possible, avoiding the tree branches. This city pumping station was located opposite to a manufacturer of food oils (i.e., canola, vegetable, etc) which was located on the shore of the Detroit River. Since winds in this area commonly come from the northwest (Chapter 3), emissions from across the river in Detroit and from the oil manufacturing industry as well as emissions from the pumping station itself, were no doubt having an impact on the biomonitoring station.

Biomonitoring stations MB-6 and MB-7 also had high moss-PM manganese levels. These two stations were located on the grounds of the city of Windsor's Lou Romano water reclamation plant. MB-7 was located on the front lawn of the office building approximately 20 m away from the Ojibway Parkway, again in the western industrial part of the city. This road, which was dry and dusty, accommodated an average of between 14000 (based on data obtained from 1997, 2002 and 2006) and 15500 (2001 and 2005 data) vehicles per day (The City of Windsor Ontario, 2009). Similar to MB-18, the Lou Romano treatment plant is near

the shores of the Detroit River where emissions from industrial areas on both the eastern (Windsor) and western (Detroit) shores may be the source of airborne particles depositing onto the moss substrate of the biomonitoring stations. The MB-6 station was located behind the Lou Romano office building next to an unused train track, parallel to MB-7. MB-6 was approximately 230 m away from station MB-7 and the traffic and dust of the Ojibway Parkway but its moss-PM manganese levels were very similar to the biomonitoring station MB-7. Therefore, the traffic emissions and street dust re-suspension did not appear to be a major source of moss-PM manganese in this area. More likely, the emissions from the surrounding industries are the source of the moss-sequestered airborne particles which deposited onto the moss-filled mesh bags.

The field duplicate biomonitoring stations MB-10 and MB-11, located on the campus of the University of Windsor, within the university's fenced-in maintenance compound on Union Street, also had moderately high moss-PM manganese concentrations. The compound was directly southeast of the Ambassador Bridge customs building separated only by Patricia Road. All vehicles headed towards Detroit from Windsor via the Ambassador Bridge must use Patricia Road and drive by the university's maintenance compound. The two stations were installed next to the sidewalk inside the compound's fence. The elevated levels of moss-PM manganese of these biomonitoring stations could be the result of the heavy traffic of the area, re-suspension of soil particles and/or long-range northwest transport of industrial emissions. There were no industries in the immediate vicinity of these two biomonitoring stations; Windsor's western industrial area was southwest of the stations' location.

Two other biomonitoring sites which had moderately elevated moss-PM manganese levels were MB-13 and MB-17. The former was located in the University of Windsor's tree nursery which was opposite of a fire station (with training facilities) and next to functioning train tracks. Emissions from the fire station and particles from the trains and train tracks were a possible source contributing to the moss-PM manganese content of the moss bags. The latter station, MB-17, was located in a fenced-in pumping station on Grand Marais Street. The Grand Marais pumping station is in an industrial area and several automotive plants are located northwest of the station. An industrial area, including a metal recycling

facility, in south-central Windsor was located west-southwest of this station. It is possible that particles from the surrounding industrial emissions are a source of moss-sequestered airborne particles of this biomonitoring station. Soil particle re-suspension is also a possible manganese source of moss-PM.

The moss-PM manganese concentration of biomonitoring station MB-14 was not as high as those of the other western biomonitoring stations. This is possibly due to the station's location in the small courtyard of the University of Windsor's Great Lakes Institute for Environmental Research (GLIER) building on the northeastern shore of the Detroit River, directly west of the Ambassador Bridge. The GLIER building is three stories high with a small courtyard in the middle with trees as tall as the building. At the time of the station's installation, there was brick soldering and drilling activities taking place in close proximity to the station's location in the courtyard. The courtyard was accessible to occupants of the centre, therefore diverse activities of unknown particle emissions could have occurred during the 2008 summer, including a small BBQ in the courtyard's meeting place.

The biomonitoring stations with the lowest moss-PM manganese levels were MB-23 and MB-19, which were two of the rural background stations south of Windsor, and stations MB-4, MB-5 and MB-8, which were located in east Windsor. MB-4 and MB-5 were located on the Windsor airport grounds whereas MB-8 was located on the grounds of the city of Windsor's Little River Pollution Control Plant in the upper northeast corner of Windsor. This biomonitoring station was installed west of the facility's buildings. The area was mainly residential. The biomonitoring station MB-22 was also a rural background site, however its moss-PM manganese levels were higher than the other two background sites, i.e., MB-19 and MB-23. Personal communication with the proprietor revealed that odours from Zug Island (Detroit), a heavily industrialized island with reportedly poor air quality located west of Windsor (northwest of this site) where the River Rouge meets the Detroit River, were quite often detected at that location.

In general, the moss-PM manganese levels found in the city of Windsor are similar to manganese levels which have been found by other studies worldwide using the moss bag

technique. Gailey and Lloyd (Gailey and Lloyd, 1986a, b, c, d) did an extensive study of the use of moss bags in Armadale, an industrial town in Scotland. In one of their studies (1986b), they found a mean moss bag manganese concentration of approximately 60 $\mu\text{g/g}$ dry weight (range = 30.1-79.9 $\mu\text{g/g}$ dry weight; $n = 10$) after a 10-week exposure period. In a study of sampler sizes (1986a), they found mean manganese concentrations from approximately 10 (size 0.1g of moss) to 110 $\mu\text{g/g}$ dry weight (size 1 or 2g) ($n = 8$). In their study investigating the reproducibility of low technology samplers (including moss bags), Gailey and Lloyd (1986c) found manganese means of 104, 13.1, 18.1, 53.2 and 61.8 $\mu\text{g/g}$ at 5 different sites in Armadale Scotland. In another of their studies, they reported that the mean manganese concentration of exposed moss from different exposure batches varied between 15.2 and 115.5 $\mu\text{g/g}$ ($n = 37$ to 46). Culicov et al. (2005) measured industrial heavy metal pollution in Romania using moss bags which used two different mosses (Russian and Bulgarian). Results were reported based on moss type. During a 4-month exposure period, moss bags had an average manganese of 33 mg/kg (Russian moss) and 87 mg/kg (Bulgarian moss), respectively. Vasconcelos and Tavares (1998) evaluated moss as a monitoring medium for metals in the urban atmosphere in Oporto city, Portugal. Their results included metals (including manganese) which were combined with moss (i.e., exposed moss was washed before analysis). They measured manganese at two different sites during an 80-day exposure and found mean manganese concentrations of 0.2 ± 0.1 $\mu\text{g/g}$ per day (median = 0.08 $\mu\text{g/g/day}$) in moss at one site and 2 ± 1 $\mu\text{g/g/day}$ (median = 2 $\mu\text{g/g/day}$) at the second site. For an 80-day exposure period, site one had a mean of 16 $\mu\text{g/g}$ and a median of 6.4 $\mu\text{g/g}$ while the second site had 160 $\mu\text{g/g}$. These results are similar, and in some cases slightly higher, to the moss-PM manganese concentrations found in Windsor. The Windsor moss-sequestered airborne particle manganese did not exceed concentrations of 100 ppm, unlike some levels in Armadale (Scotland) and Oporto city (Portugal). None of these studies, nor the studies reported in the remainder of this discussion, have reported the manganese concentration dilution effect caused by the moss substrate found in this study.

Makholm and Mladenoff (2005) who investigated the state-wide efficiency of moss bags at nine sites in Wisconsin found much higher levels of manganese in moss bags, 233 ppm (range = 178 – 283) ($n = 9$) for a 10-week exposure. Adamo et al. (2003) investigated

the accumulation of trace elements (including manganese) of moss and lichens in Naples, Italy using the moss bag technique. After a 10-week exposure, they found a loss of manganese from the moss bags. They speculated that this loss “might be related to metabolic distress” i.e., the damage to the cell caused by the death of the moss may facilitate the loss of manganese from the cells during the wet periods. Since the moss used in this present study of manganese in urban airborne particles in Windsor was rigorously acid-washed before exposure, such a loss of manganese would not have registered since all absorption sites should have been available. The total amount of rain for the city of Windsor during the exposure period (June 23rd, 2008 to August 26th, 2008) was 133 mm (Chapter 3). Biomonitoring station MB-19 was located south of Windsor in Harrow County which received 148 mm of rain during this same period. According to Martin and Coughtrey (1982), *Sphagnum* moss has a high capacity to absorb and retain water, which means that relatively little drip from the moss bags, is likely to occur. Considering the small amount of rain during the exposure period, 13 to 15 cm, it is unlikely that loss of manganese from the moss bags occurred during this study of airborne particles in Windsor, Ontario.

The collocated soil samples taken at each biomonitoring station site had a median manganese concentration of 380 ppm. The collocated soil manganese mean was not significantly different from the random and industrial soil means (Chapter 5), therefore the results were included in the baseline soil mean calculation (Chapter 5). As a result, the collocated biomonitoring station soil median is similar to the baseline soil median (385 ppm) previously reported in Chapter 5, which was lower than the transect soil, as well as the natural soil medians (553 and 502 ppm, respectively). The highest collocated biomonitoring station soil manganese concentrations were west of the city’s center, stations MB-18, MB-6 and 7. Biomonitoring station MB-21 also had high collocated soil manganese levels but was located in the city’s public works yard in south-central Windsor, more specifically in one of the parking lots next to the main building. There were relatively little industrial emission sources in the immediate vicinity except for train tracks nearby and the activities and maintenance of vehicles in the yard. The rural background biomonitoring station MB-19 had an elevated collocated soil manganese concentration. This station was installed in a secure location on the grounds of Agriculture and Agri-Food Canada Greenhouse and Procession

Crops Research Centre in Harrow County, south of Windsor near the northern shore of Lake Erie. The fenced-in area was located away from any heavy traffic and industrial sources and 9 m away from a dirt road which was directly next to the fenced area and used by employees only. The soil at this location was different from the remaining soil samples, reddish sand, instead of dark clay. The elevated soil manganese at this site, compared to the soil from the other biomonitoring stations, was perhaps due to its inherent differences from the rest of the biomonitoring soils and not due to anthropogenic sources. It is also possible that the elevated manganese in the soil is due, in part, to past and present agricultural activities of the area or emissions from the southwest.

The lowest collocated soil manganese concentrations were found at the other two rural background biomonitoring stations, MB-22 and MB-23, and MB-8. Their locations were described above with regards to low moss-PM manganese concentration biomonitoring stations. MB-20 also had low collocated soil manganese levels. This site was a large field in the middle of the St. Clair College campus which was not being heavily used and was in a relatively residential area.

The spatial distributions and Soil:Moss-PM ratios indicated higher levels of manganese in moss-sequestered airborne particles and collocated soil in the western part of the city of Windsor, with lower levels in the east and south. The western edge of the city is mainly an industrial area which is opposite to Detroit's industrial area across the Detroit River. Zug Island, as previously mentioned, is a heavily industrialized island directly west of Windsor across the river. This west-to-east trend, found in moss-PM and collocated soil manganese concentrations, was also found in baseline soil manganese levels (Chapter 5).

The manganese content of the collocated biomonitoring station soil was found to be higher than moss-PM manganese concentrations. However, as indicated, this large difference may be due in part to the dilution by the moss substrate. Rasmussen et al. (2007) reported an average atmospheric fine particulate matter (PM_{2.5}) manganese concentration in Windsor, Ontario of 182 ppm (n = 8). They used volumetric air samplers (R&P ChemPass™ personal environmental monitors (PEM)) to collect the PM_{2.5}. Canepari et al. (2008)

investigated the size distribution of total airborne particulate mass collected in urban Rome. They found that 50 % of the mass was between 4.4 and 6.8 μm in size. In soil-resuspension experiments, Young et al. (2002) found that the majority of soil particles in the PM_{10} range were in the 45 to 75 μm size range ($< 63 \mu\text{m}$ was used in this study). Gailey and Lloyd (1986c) also found lower moss-PM manganese concentrations compared to their collocated soil manganese levels. As previously indicated, a discussion of the moss substrate dilution effect could not be found in the literature. This effect limited the direct comparison of moss-PM manganese concentrations with either collocated soil, or air particulate matter concentrations. Therefore, elemental associations and spatial distributions were compared.

The differences in elemental signatures between moss-sequestered airborne particles and collocated soil indicate a unique modern-day signal with some overlap (see Table 52). The high level of intercorrelation between the elements of the moss-PM may be evidence that these elements are associated with the same particles. Gailey and Lloyd (1986c), Adamo et al. (2003) and Makholm and Mladenoff (2005) all found a high level of intercorrelation between the elements (including manganese) of airborne particles in exposed moss and concluded that these elements were probably associated with the same particles. Furthermore, the significant correlations between certain elemental concentrations (Cr, Fe, Mn, Zn and Sr) in moss-PM and collocated soil provide evidence of a common source. An important one being air-surface exchange, for example soil re-suspension. Therefore, it can be concluded that there are two distinct elemental signatures of airborne particles in Windsor, Ontario, a modern-day anthropogenic signal (moss-PM) and an archived anthropogenic signal (collocated biomonitoring station soil).

Conclusion

The results presented here would indicate that the moss biomonitoring station method was successful in capturing airborne particles which could potentially deposit onto the soil surface as well as capturing re-suspended soil particles. Possible sources of these airborne particles have been discussed, and include heavy local traffic emissions, local and long-range industrial emissions. Higher levels of moss-PM manganese were found in the western part of the city of Windsor. This was also the case for the collocated soil. This west-to-east pattern of decreasing manganese levels was also seen in baseline soil (Chapter 5). The moss-PM showed a modern-day anthropogenic elemental signature whereas the collocated biomonitoring station soil displayed an archived anthropogenic signal. The existence of a relationship between some elements in moss-PM and collocated soil demonstrated the importance of soil re-suspension to atmospheric elemental levels, and thus showed the importance of including soil elemental concentrations in atmospheric modeling.

The major advantage of using the moss biomonitoring stations is the larger number of stations which can be installed in the field compared to the limited number of more expensive air samplers which often require a source of electricity and daily attention. The major limitation was the dilution effect of the moss substrate. Also, the limited use of the biomonitoring stations (secure areas only) was also a disadvantage, however it greatly reduced the likelihood of vandalism and loss of samples. Other disadvantages for using these biomonitoring stations were the dry and brittle mesh bags and the ineffective bird deterrents (Chapter 4).

The moss biomonitoring stations can provide valuable information for identifying areas of elevated airborne particle manganese concentrations. It is recommended that these stations be used as a prelude to more sophisticated air sampling (i.e., accurate quantitative results). It is also recommended that new or gently used mesh bags be used.

Summary of Conclusions

It was concluded in Chapter 5 that urban Windsor soil consists of both natural and anthropogenic sources of manganese. This conclusion was supported by elemental signatures (Chapter 6), soil carbon content and manganese speciation. Three soil sample types were collected, transect (median = 553 ppm), baseline (median = 385 ppm) and natural (median = 502 ppm), and were significantly different. The variability between transect sites (22.6 %), which were sampled in triplicate, was greater than the variability within these sites (8.5 %). The range of natural background soil manganese for the Windsor area was determined to be up to 600 ppm (mean ~500 ppm). Strong significant correlations between soil manganese and other trace elements, including iron, cobalt, calcium, cadmium, zinc, copper, lead, molybdenum and tin, were found. The iron and cobalt relationships with manganese were specific to natural and baseline soils. Future studies of Windsor urban soil should consider sites with soil manganese levels above 830 ppm to be elevated and investigate further.

Areas of elevated soil manganese were generally found in the western part of the city of Windsor (Chapter 5). Further investigation of the soil manganese in this area is recommended. Manganese speciation found evidence of steel products in the industrial soil sample. Areas of concern, with regard to elevated urban soil manganese, in Windsor, Ontario are in the immediate vicinity of industrial zones (i.e., Devon-CN), buried landfill or debris, and areas of past industrial or commercial activity. These areas reached soil manganese levels from 1163 ppm (ABW-T1-4) to 3430 ppm (I-ZB-42). Findings suggest vehicular emissions did not play a major role in soil manganese concentrations near the Ambassador Bridge as was first suspected. Proper disposal of construction debris is recommended to reduce soil manganese levels.

The field-portable X-ray fluorescence analyzer was a good pre-screening tool and found to be efficient for field determination of manganese and other trace elements in urban soil (Chapter 7). FPXRF recovery of manganese was 98 %. The three FPXRF sample preparation methods (direct, baggie and XRF-cup) showed soil manganese medians from

352 to 458 ppm ($n = 99$), which were lower than the corresponding ICP-MS median (520 ppm). Despite the significant difference between their means, the three FPXRF methods had positive significant correlations ($r_s = .51$ to $.74$). Ideally, the XRF-cup method of sample preparation should be used in the field provided the sample moisture is within acceptable limits. It had the best correlation to the traditional analysis method, ICP-MS ($r_s = .88$). If the goal of the investigator is to pre-screen a site, both the direct and baggie sample preparation methods would also be acceptable. Investigators should select their sample preparation method based on available time and resources, and the level of reliability (i.e., correlation with ICP-MS results).

Similar to soil manganese, moss-sequestered airborne particles with elevated manganese concentrations were found in the western part of the city (Chapter 8). The geometric mean for moss-sequestered moss was 27.4 ppm. It was determined that this result was diluted by the moss substrate. The elemental associations found in the moss-PM and the collocated soil revealed the influence of soil re-suspension on the level of manganese in the airborne particles. The biomonitoring study also revealed the legacy signature of collocated soils and the modern-day signature of the moss-sequestered airborne particles. A strong significant correlation was found between manganese in moss-PM airborne particles and collocated soil ($r_s = .57$). Other significant relationships between these two sample media were also found for chromium, iron, zinc and strontium. The biomonitoring study demonstrated the importance of considering soil manganese, and other trace elements, in human health air monitoring studies. The moss biomonitoring technique of using moss bags is therefore recommended for use as a preliminary tool to more sophisticated and quantitative high-volume air sampling.

Discussion and Interpretation

This study investigated manganese in soil in the city of Windsor, Ontario and was funded, in part, by Health Canada. It was undertaken in order to provide supporting information for Health Canada and Environment Canada's Windsor, Ontario Exposure Assessment Study (WOEAS), formerly known as the Border Air Quality Strategy (BAQS), which evaluated the exposure of adults and children in Windsor, Ontario to multiple air pollutants, including metals. According to Wheeler et al. (2011), outdoor sources of air pollutants include heavy traffic, car manufacturing industries and long-range transport from Detroit. Wheeler et al. (2011) provided an overview of the methodology and source apportionment modelling for the WOEAS study which did not include the contribution of soil emission or re-suspension to air quality.

The overall purpose of the present research was to develop an understanding of the levels and spatial distribution of manganese in Windsor, Ontario. A particularly important contribution was the discovery that significant geochemical signatures found in Windsor soil and airborne particles could be used to identify anthropogenic and natural sources of manganese. A field-portable X-ray fluorescence analyzer was used to pre-screen soil sampling sites, and its reliability for determination of manganese and other elements in urban soil was evaluated as part of this research. Both transect and random types of sampling were used in the study design (*Chapter 3, page 65*).

The hypothesis that vehicular traffic was the dominant source of anthropogenic manganese to the soil was tested using transect sampling near the Ambassador Bridge. The bridge was selected to represent the most extreme example of heavy traffic in the area and therefore, the most appropriate place to test soil concentrations for a traffic pollution halo (according to accepted methodologies cited on page 46). The length of the transects were sufficient to capture the traffic's potential radius of influence as well as the soil manganese urban background levels at the edge of a halo. The results of the transect sampling investigation showed that there was no traffic-related halo around the Ambassador Bridge. There was a large manganese peak of 1163 ppm, and two smaller peaks (800-900 ppm),

which exceeded the urban baseline median (385 ppm) by a factor of 2-3. These peaks were not spatially related to the bridge. There may be vehicular sources of manganese in this area, and in fact the moss biomonitoring did suggest the presence of vehicular sources in one location (*Figure 70, page 248*). However the influence of the vehicular traffic of the Ambassador Bridge was insignificant compared to the isolated areas of manganese enrichment away from the bridge (manganese peaks discussed above). These findings point to the importance of historical activity, and especially that of buried (subsurface) sources which strongly influenced the surface chemistry of the soil in this area.

The random sampling of soil across Windsor confirmed the alternate hypothesis, that there are multiple anthropogenic sources of manganese to urban soil in the Windsor area. This soil sampling was used to determine the urban soil manganese baseline, which included both industrial and residential sites, and to investigate spatial trends of soil manganese in Windsor in order to identify areas of elevated soil manganese. Further investigation of these elevated areas revealed an industrial hotspot related to one of the industries which reported manganese emissions to Environment Canada (manganese content up to 3430 ppm). Importantly, the soil survey revealed several elevated manganese areas which were not associated with known industrial emission sources, and therefore have never been included in source apportionment models. In these unreported hotspot locations, buried material reflecting past industrial activities appear to be the source of the elevated soil manganese. Since urban soils have a natural component, natural soil samples were also collected to determine natural geological background (median = 502 ppm) for this area.

Further investigation of the transect peaks and other “hotspots” encountered during random sampling across the city showed that buried sources are significant. These elevated soil manganese areas were due to various sources: past shipyards, past use of coal, past industrial activity with steel and car manufacturing, and landfill practices to name a few. It became clear that buried sources must be considered along with atmospheric deposition and geological background. This discovery pointed to the alternate hypothesis that soil manganese levels are influenced by multiple anthropogenic sources.

The Ambassador Bridge is the largest Canada-US border crossing. Three transects perpendicular to the bridge were established (*Figure 16, page 100*). As previously stated, the literature showed that metals tend to accumulate near roadways (*page 46*) creating a halo of high values. Instead of the expected halo, sporadic peaks of manganese along the transects were found (*Figure 20, page 108*). One site in particular (ABW-T1-4), located on the western side of the bridge, had one of the highest soil manganese values of the preliminary soil survey (1163 ppm). After further investigation of this area, it was determined that the elevated soil manganese could be due to buried landfill, mainly related to the car industry, and past activities.

The soils near industries, as well as in the residential areas of Windsor, were investigated in an effort to evaluate the alternate hypothesis (*page 46*). For this purpose, Environment Canada's National Pollutant Release Inventory (NPRI) database was used to locate manganese-emitting industries in Windsor, Ontario. In this database, industries report their yearly pollutant releases to the environment, including manganese. Eleven manganese-emitting industries, for example car manufacturers and recycling facilities, were found in the 2002 NPRI database (*Table 6, page 53*). Soil samples were collected from the industries' immediate areas and also from random locations across Windsor wherever possible. Some of these random sample sites were located near the Health Canada study (WOEAS) homes and the majority of the rest were selected as fill-in samples, i.e., they provided good coverage of the city for GIS interpolation purposes. In terms of elevated soil manganese areas, one industrial area was found which showed elevated soil levels (up to 3430 ppm). This was a metal recycling facility near a railroad (Devon-CN area). The impact of the industry however did not appear to extend much farther away from its immediate area (*Figure 29, page 122*). One random site (HS-Q) was also found to have elevated soil manganese (approximately 900 ppm). Upon further investigation of this site, it was determined that the elevated levels were the result of buried landfill. Synchrotron-based manganese speciation (*Chapter 5, section 4.2, page 126*) supported the conclusion that both the elevated transect and the metal recycling area sample sites were affected by anthropogenic input.

One of the goals of this study was to determine the level of manganese in urban Windsor soil. During this investigation, three soil sample types were found, namely transect, baseline and natural (*Chapter 5, section 2.1.1, page 96*). The transect sample type had a soil manganese median of 553 ppm (*Chapter 5, section 2.1.2, page 99*) while the baseline had a median of 385 ppm (*Chapter 5, section 2.1.3, page 109*). The natural soil sample type median was 502 ppm (*Chapter 5, section 2.1.4, page 110*). A subset of soil samples showed that the urban soil pH was neutral (*Chapter 5, section 4.1, page 125*). Total carbon contents of the three soil sample types ranged from 2.8 % to 7.3 %. The transect and baseline sample types had higher organic carbon contents while the natural type was higher in inorganic carbon (*Table 14, page 126*).

Interpolation of the results allowed for a spatial interpretation of soil manganese in Windsor. The interpolation used was a kriged surface of the log-transformed soil manganese results of all soil samples (*Figure 27a, page 118*). The majority of the elevated soil manganese sites, i.e., the transect area, the recycling industry and the random area of buried landfill, were located in the western part of the city. A large area of higher soil manganese existed on the interpolated surface in the southwestern part of the city (*Figure 27a, page 118*). Further confirmation of the high soil manganese levels in this area is recommended as the interpolation was based on an area of low sample density (5-6 sites). However, elevated levels of manganese were found in the moss-sequestered airborne particles of this area (*Figure 70, page 248*), which supports the finding of a broad region of elevated soil manganese. The possible sources of elevated soil manganese at these sites were a reclaimed landfill and emissions from industries in the Detroit/Windsor area. Also of importance in this area is the difference of the underlying geology compared to the rest of Windsor. Due to the low sample density and high error of the prediction in this area of the interpolation (*Figure 27b, page 118*), it is recommended that additional samples are needed in order to provide a more detailed spatial distribution in this specific area.

Field-portable X-ray fluorescence (FPXRF) analyzers have been shown to be useful tools for evaluating contaminated sites but they have been rarely applied to the urban environment. During the evaluation of the efficiency of one of these instruments in the

urban environment of Windsor, Ontario, three different field methods of obtaining elemental analyses using a field-portable XRF were used and their results compared with the “Gold Standard” of traditional methods, digestion and ICP-MS analysis. The three methods used were direct *in situ* measurement of the soil (*Chapter 4, section 2.2.1, page 80*), measurement of the soil through the sample bag (*Chapter 4, section 2.3.1, page 81*), and thirdly, use of an XRF-cup (*Chapter 4, section 2.2.2, page 80*). Eight of the twenty-four elements, including manganese, had sufficient results above the limit of detection (LOD) to be reported. These included Mn, Fe, Pb, Zn, Rb, Sr, Ba, and Zr. In the majority of the cases, the Spearman correlation coefficients, which described the relationships between the different field-portable XRF methods and the ICP-MS analysis results, improved as the sample preparation increased (*Chapter 7, page 195, see individual sections*). In fact, for all eight elements reported, the XRF-cup method had the highest method accuracy (81-104 %). Therefore, the field-portable XRF analyzer is a useful pre-screening tool for air quality and other urban environmental studies. However, it is important to note that the results of the field-portable XRF methods were consistently lower than those of the ICP-MS analysis.

Finally, a moss biomonitoring study was used to evaluate the manganese relationships at the air-surface interface. This biomonitoring consisted of 20 sampling stations located within the city limits and three located south of the city. The highest manganese level (97 ppm) was found at a city of Windsor pumping station (MB-18). Located in the western part of the city on the grounds of a large water treatment plant, moss-sequestered airborne particles of biomonitoring stations MB-6 and MB-7 also had high manganese levels (57 ppm). Stations MB-10 and MB-11 were field duplicates placed near the entrance to the Ambassador Bridge. High volumes of traffic are the suspected source of elevated manganese (55 ppm) at the latter sites. Quantitative manganese levels of airborne particles collected in Windsor are consistently higher than those reported using the moss technique due to the discovery of a methodological artefact best described as a moss dilution effect (*Chapter 8, page 247*). From these results (*Figure 70, page 248*), it was apparent that the levels of manganese in the moss-sequestered airborne particles decreased from west to east. One station (MB-22) in the eastern portion however was more elevated in manganese than the other eastern stations. It was located south of Windsor in a rural area on the grounds

of a commercial garden centre. The source of manganese at this location is unknown at this time.

Several different and significant geochemical signatures were found to represent the various sample types (summarized below in Table 54). Since airborne particles are collected on moss for a specific interval of time, their manganese content represents the “real-time” deposition whereas manganese accumulated on soil represents past deposition. Therefore, investigations into the associations between manganese and other elements in these airborne particles revealed a modern-day anthropogenic signature which was different from the collocated soil which showed an archived anthropogenic signal (*Chapter 8, page 243* and Table 54). When the relationship between the elements in the moss-sequestered airborne particles and those of the collocated soil was investigated, five elements (including manganese) were found to be significantly correlated to one another (*Table 53, page 274*). This would indicate the existence of a common source, and is interpreted as air-surface exchange of manganese through processes such as deposition and soil re-suspension.

Table 54 Significant geochemical signatures of various sample types.

Sample Type	Geochemical Signatures
Moss-sequestered airborne particles ($r_s > .9$)	Fe-Mn, Cr-Mn, V-Mn
($r_s > .5$)	Zn, Cd, Cu, Sn, Mo, Pb, Co, Sr, Ti, Y, Sb, Ba (all associated with manganese)
Collocated soil	Zn-Mn, Cd-Mn
Transect	Zn-Mn, Mo-Mn, Cu-Mn, Sn-Mn, Cd-Mn, Pb-Mn
Baseline	Fe-Mn, Co-Mn, Ca-Mn
Natural	Fe-Mn, Co-Mn

Several significant relationships were found between manganese and other elements in the urban Windsor soil sample types. The associations found in the transect (*Table 15, page 156*) and baseline (*Table 21, page 174*) soil sample types were quite different. Only iron and cobalt were significantly correlated with manganese in the natural soil (*Table 27, page 189*). These two significant associations were also found in the baseline sample type which would indicate that the baseline soil has a natural component. This conclusion was

supported by the synchrotron-based manganese speciation (*Chapter 5, section 4.2, page 126*).

With regards to manganese in urban Windsor soil, both a natural and anthropogenic (transect and baseline) component were found, and it was determined that the major traffic source in Windsor, the Ambassador Bridge, was not as important as buried landfill. In fact, other areas of buried landfill were also found to have elevated soil manganese making this an important source to consider as well as past site activities. Of the eleven manganese-emitting industries reported in the 2002 NPRI database, only one industrial location was found to be of significance to soil manganese. These discoveries indicated that there are several different sources of manganese in Windsor. These sources contribute to the west-to-east trend of decreasing soil manganese which was found not only in soil but also in the present-day airborne particles. The significant geochemical signatures for each of the different sample types (natural, transect and baseline soil, moss-sequestered airborne particles, and collocated soil) found will help Government of Canada air modellers with their source apportionment work.

Future urban environmental studies of soil manganese in Windsor, Ontario, and other urban environmental studies should consider the observations and conclusions of this research. First and foremost, soil sources and soil geochemistry should be considered in air quality and human health studies. Both the field-portable XRF analyzer and the use of moss biomonitoring stations are good pre-screening methods for urban environmental studies. Subsequent research of soil manganese in Windsor should include additional sampling sites located in the western part of the city. Similarly, additional manganese speciation analyses (synchrotron-based, scanning electron microscopy (SEM) or other speciation techniques) of both the soil and the moss-sequestered airborne particles would provide valuable information (particle size and composition) which could be used to further the understanding of manganese in Windsor, Ontario.

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Appendices

Appendix – A Notable manganese discoveries

Table A-55 Timeline of manganese discoveries

Time	Event	Time	Event
Stone Age	Evidence of first use of Manganese	1837	James Couper makes link between occupational exposure of Mn to “a form of Parkinson’s Disease (later called Manganism)”
17 000 years ago	Mn used as pigment in cave paintings	1840	Metallic manganese is produced by J.M. Heath
Ancient Greece	Spartans used Mn in iron ore	1841	Pourcel begins industrial-scale production of Speigelsen (pig-iron with high % of Mn)
1100 BC to 600 AD (estimated range)	Egyptians and Romans used Mn in glass making	1860	Sir Henry Bessemer develops the ‘Bessemer Process’ (adding Mn and carbon to steel)
1771	The Swedish chemist Carl Wilhelm Scheele recognizes Manganese as an element	1866	The use of ferromanganese in steelmaking is patented by Sir William Siemens
1774	Mn is isolated by Johan Gottlieb Gahn	1868	Leclanché develops the dry cell battery
1799 & 1808	Patents are awarded to British and French scientists for use of Mn in steelmaking	1875	Pourcel begins commercial production of ferromanganese (65 % content)
1816	German researchers observe “that manganese increased the hardness of iron, without reducing its malleability or toughness” ^a	1888	Hadfield steel is developed (13 % Mn content)
1826	Prieger produces ferromanganese containing 80 % Mn	20 th century & beyond	“a stream of new processes and metallurgical / chemical applications developed” ^b

(Sources: Mergler et al., 1999; Schafer, 2004; ^a International Manganese Institute, 2009; ^b Considine and Kulik, 2008)

Appendix – B List of major roads in Windsor

Huron Church Road
Talbot Road
Howard Avenue
Cabana Road W and E
Dougall Avenue
Tecumseh Road W and E
Sprucewood Avenue
Provincial Road
Walker Road
22 Regional Road
Lauzon Parkway
Todd Lane
Division Road
Ojibway Parkway
Sandwish Street
Prince Road
Riverside Drive W and E
Wyandotte Street W and E
Ouellette Avenue
Lauzon Road
Jefferson Boulevard
Crawford Avenue

Appendix – C Total carbon and total inorganic carbon limit of detection (LOD) calculation

Total carbon (TC) limit of detection.

Soil total carbon was analyzed using an Elementar varioMAX CN instrument (Chapter 4). The manufacturer's concentration range for this instrument is 0.02 to 400 mg sample. Therefore, the instrument should be able to detect 0.02 % C in a 100 mg soil sample. A more conservative detection limit would be $0.02 \% \times 5 = 0.1 \%$. The only reference material with a TC value that low was an in-house (Health Canada) reference material called RV HUNTER-1B which has a TC of 0.4 % C. Ten replicates of this sample were analyzed using the Elementar varioMAX CN in total carbon mode. The limit of detection was calculated by multiplying the standard deviation of the 10 replicates by three. The average TC ($n = 10$) of RV-HUNTER-1B was $0.434 \pm 0.203 \% \text{ C}$. Therefore, the LOD of the Elementar varioMAX CN instrument was $0.203 \% \text{ C} \times 3 = 0.609 \% \text{ C}$.

Total inorganic carbon (TIC) limit of detection.

The lower limit of the manufacturer's range for the Elementar SoliTIC instrument is 0.5 μg . To determine the TIC LOD, the level where the instrument's detector could not detect any TIC (i.e., the software shows a 'TICu' message when the TIC level is undetectable) needed to be found. From previous SoliTIC instrument results, it was determined that the lowest detectable total inorganic carbon level was between 0.353 % (undetectable) (Faraday dust 2K $\rightarrow$ 300) and 0.528 % (OP2-DUST-CBR3) (detected). Therefore the TIC limit of detection was probably approximately 0.4 %.

In order to calculate the actual TIC LOD, an appropriate sample needed to be created which would have an expected TIC content of $\sim 0.4 \%$. This was achieved by diluting a high TIC in-house reference material, Sample 9789.14, (TIC 0.80 %) with a certified reference material (CCRMP TILL-1) (not certified for TIC) which had consistently undetectable TIC results. After much experimenting, a soil mixture ratio of 25:75 (low material:high material) which had a TIC value of 0.39 % was used. The CCRMP was sieved, well-mixed and homogenized referenced material whereas the 9789.14 material was sieved. A 1.1 mg stock

25:75 soil mixture was made with 0.2572 mg of TILL-1 and 0.8252 mg of Sample 9789.14. The vial containing the 25:75 soil mixture was manually shaken for approximately 5 minutes and left to settle for 1 minute prior to analysis. Ten replicate samples of the 25:75 soil mixture was analyzed using the SoliTIC instrument. The limit of detection was calculated by multiplying the standard deviation of the 10 replicates by three. The average TIC value ($n = 10$) of the 25:75 soil mixture was 0.457 ± 0.161 %. Therefore, the LOD of the Elementar SoliTIC instrument was $0.161 \% \text{ TIC} \times 3 = 0.483 \% \text{ TIC}$.

Appendix – D XRF-cup assembly

Material: Mylar[®] 6μ, 32-mm double open ended XRF sample cells (cups) with caps and rings (from Premier Lab Supply) and a ceramic pestle

- Step 1: The XRF-cup (Mylar, body and ring) was first assembled. The Mylar must be smooth with no creases. The plastic XRF-cup body, ring and Mylar[®] film were first assembled.
- Step 2: The empty cup was placed on a work bench with the Mylar window facing down on a Kimwipe[®].
- Step 3: Approximately 3-5 g of soil sample (size fraction < 63 μm) was weighed and gently introduced into the cup
- Step 4: Using the handle-end of a ceramic pestle, the soil was flattened (compressed) to eliminate air.
- Step 5: A small filter was then placed inside the cup to provide a barrier between the sample and the stuffing. This filter should fit tightly in order to prevent shifting of the sample which could create cracks.
- Step 6: Polyester fiber stuffing was then added to the cup to prevent the sample and filter from moving.
- Step 7: The lid of the XRF-cup was placed over the back opening of the cup and snapped into place. Care had to be taken to prevent the stuffing from springing back out.
- Step 8: The finished XRF-cup Mylar window was inspected the cup window for creases and the soil for cracks or any shifting.
- Step 9: The finished XRF-cups were stored with their windows facing down on a clean kimwipe in a sealed container.

Appendix – E Glossary of statistical terms

Notice

**** The following definitions of statistical terms that were used in this work are a direct excerpt from the book *Discovering Statistics Using SPSS* by A. Field © 2005. ****

**Adjusted
predicted
value:**

A measure of the influence of a particular case of data. It is the predicted value of a case from a model estimated without that case included in the data. The value is calculated by re-estimating the model without the case in question, then using this new model to predict the value of the excluded case. If a case does not exert a large influence over the model then its predicted value should be similar regardless of whether the model was estimated including or excluding that case. The difference between the predicted value of a case from the model when that case was included and the predicted value from the model when it was excluded is the DFFit.

Adjusted R^2 :

A measure of the loss of predictive power or *shrinkage* in regression. The adjusted R^2 tells us how much variance in the outcome would be accounted for if the model had been derived from the population from which the sample was taken.

**Analysis of
variance:**

A statistical procedure that uses the F -ratio to test the overall fit of a linear model. In experimental research this linear model tends to be defined in terms of group means and the resulting ANOVA is therefore an overall test of whether group means differ.

***beta* (b_i):**

Unstandardized regression coefficient. Indicates the strength of relationship between a given predictor, i , and an outcome in the units of measurement of the predictor. It is the change in the outcome associated with a unit change in the predictor.

***Beta* (β_i):**

Standardized regression coefficient. Indicates the strength of relationship between a given predictor, i , and an outcome in a *standardized* form. It is the change in the outcome (in standard deviations) associated with a one standard deviation change in the predictor.

Appendix – E Glossary of statistical terms (cont'd.)

- Boxplot:** (Also known as box-whisker diagram)
A graphical representation of some important characteristics of a set of observations. At the centre of the plot is the *median*, which is surrounded by a box, the top and bottom of which are the limits within which the middle 50 % of observations fall (the *interquartile range*). Sticking out of the top and bottom of the box are two whiskers which extend to the most and least extreme scores respectively.
- Chi-square test:** Although this term can apply to any *test statistic* having a *chi-square distribution*, it generally refers to Pearson's chi-square test of the independence of two categorical variables. Essentially it tests whether two categorical variables forming a *contingency table* are associated.
- Coefficient of determination (R^2):** The proportion of variance in one variable explained by a second variable. It is the *Pearson correlation coefficient* squared.
- Condition Index(ces):** Are another way of expressing eigenvalues and represent the square root of the ratio of the largest eigenvalue to the eigenvalue of interest. (There) are no hard and fast rules about how much larger a condition index needs to be to indicate collinearity problems.
- Confidence interval:** For a given statistic calculated for a sample for observations (e.g., the mean), the confidence interval is a range of values around that statistic that are believed to contain, with a certain probability (e.g. 95 %), the true value of that statistic (i.e. the population value).
- Cook's distance:** A measure of the overall influence of a case on the model. Cook & Weisberg (1982) have suggested that values greater than 1 may be cause for concern.
- Covariance ratio (CVR):** A measure of whether a case influences the variance of the parameters in a *regression model*. When this ratio is close to 1 the case has very little influence on the variances of the model parameters. Belsey et al. (1980) recommend the following: if the CVR of a case is greater than $1 + [3(k + 1)/n]$ then deleting that case will damage the precision of some of the model's parameters, but if it is less than $1 - [3(k + 1)/n]$ then deleting the case will improve the precision of some of the model's parameters (k is the number of predictors and n is the sample size).

Appendix – E Glossary of statistical terms (cont'd.)

DFBeta: A measure of the influence of a case on the values of b_i in a *regression model*. If we estimated a regression parameter b_i and then deleted a particular case and re-estimated the same regression parameter b_i then the difference between these two estimates would be the DFBeta for the case that was deleted. By looking at the values of the DFBetas, it is possible to identify cases that have a large influence on the parameters of the regression model; however, the size of DFBeta will depend on the units of measurement of the regression parameter.

**Standardized
DFBeta:**

A standardized version of DFBeta. These standardized values are easier to use than *DFBeta* because universal cut-off points can be applied. Stevens (1992) suggests looking at cases with absolute values greater than 2.

DFFIT: A measure of the influence of a case. It is the difference between the *adjusted predicted value* and the original predicted value of a particular case. If a case is not influential then its DFFit should be zero – hence, we expect non-influential cases to have small DFFit values. However, we have the problem that this statistic depends on the units of measurement of the outcome and so a DFFit of 0.5 will be very small if the outcome ranges from 1 to 100, but very large if the outcome varies from 0 to 1.

**Standardized
DFFIT:**

A standardized version of *DFFit*.

**Durbin-Watson
test:**

Tests for serial correlations between errors in *regression models*. Specifically, it tests whether adjacent residuals are correlated, which is useful in assessing the assumption of *independent errors*. The test statistic can vary between 0 and 4 with a value of 2 meaning that the residuals are uncorrelated. A value greater than 2 indicates a negative correlation between adjacent residuals, whereas a value below 2 indicates a positive correlation. The size of the Durbin-Watson statistic depends upon the number of predictors in the model and the number of observations. For accuracy, you should look up the exact acceptable values in Durbin & Watson's (1951) original paper. As a very conservative rule of thumb, values less than 1 or greater than 3 are definitely cause for concern; however, values closer to 2 may still be problematic depending on your sample and model.

Appendix – E Glossary of statistical terms (cont'd.)

Effect size:	An objective and standardized measure of magnitude of an observed effect. Measures include Cohen's <i>d</i> , Glass' <i>g</i> and Pearson's correlations coefficients <i>r</i> .
Eigenvalues:	A comprehensive definition of 'eigenvalue' would be too lengthy to be included in this appendix. Refer to Field (2005) or other statistical reference for a detailed description.
F-ratio:	A test statistic with a known <i>probability distribution</i> (the <i>F</i> -distribution). It is the ratio of the average variability in the data that a given model can explain to the average variability unexplained by that same model. It is used to test the overall fit of the model in <i>simple regression</i> and <i>multiple regression</i> , and to test for overall differences between group means in experiments.
Familywise error rate:	The probability of making a <i>Type I error</i> in any family of tests when the null hypothesis is true in each case. The 'family of tests' can be loosely defined as a set of tests conducted on the same data set and addressing the same empirical question.
Frequency distribution:	A graph plotting values of observations on the horizontal axis, and the frequency with which each value occurs in the data set on the vertical axis (a.k.a. <i>histogram</i>).
Friedman's ANOVA:	A non-parametric test of whether more than two related groups differ. It is the non-parametric version of one-way <i>repeated-measures ANOVA</i> .
Geometric Mean⁴:	For a set of positive observations $x_1, x_2, \dots, x_n$, the geometric mean, <i>g</i> , is given by $g = (x_1 \times x_2 \times \dots \times x_n)^{1/n}$.
Kruskal-Wallis test:	Non-parametric test of whether more than two independent groups differ. It is the non-parametric version of one-way <i>independent ANOVA</i> .

⁴ This definition was taken from Upton and Cook (2011).

Appendix – E Glossary of statistical terms (cont'd.)

- Leverage:** Leverage statistics (or hat values) gauge the influence of the observed value of the outcome variable over the predicted values. The average leverage value is $(k + 1)/n$ in which k is the number of predictors in the model and n is the number of participants. Leverage values can lie between 0 (the case has no influence whatsoever) and 1 (the case has complete influence over prediction). If no cases exert undue influence over the model then we would expect all of the leverage values to be close to the average value. Hoaglin & Welsch (1978) recommend investigating cases with values greater than twice the average $(2(k + 1)/n)$ and Stevens (1992) recommends using three times the average $(3(k + 1)/n)$ as a cut-off point for identifying cases having undue influence.
- Mahalanobis distances:** Measures the influence of a case by examining the distance of cases from the mean(s) of the predictor variable(s). You need to look for the cases with the highest values. It is not easy to establish a cut-off point at which to worry, although Barnett & Lewis (1978) have produced a table of critical values dependent on the number of predictors and the sample size. From their work it is clear that even with large samples ($N = 500$) and five predictors, values above 25 are cause for concern. In smaller samples ($N = 100$) and with fewer predictors (namely, three) values greater than 15 are problematic, and in very small samples ($N = 30$) with only two predictors values greater than 11 should be examined. However, for more specific advice, refer to Barnett & Lewis's (1978) table.
- Mann-Whitney test:** A *non-parametric test* that looks for differences between two independent samples. That is, it tests whether the populations from which two samples are drawn have the same location. It is functionally the same as *Wilcoxon's rank-sum test*, and both tests are non-parametric equivalents of the *independent t-test*.
- Mean:** A simple statistical model of the centre of a distribution of scores. A hypothetical estimate of the 'typical' score.
- Median:** The middle score of a set of ordered observations. When there is an even number of observations the median is the average of the two scores that fall either side of what would be the middle value.

Appendix – E Glossary of statistical terms (cont'd.)

Multi-collinearity:	A situation in which two or more variables are very closely linearly related.
Multiple regression:	An extension of <i>simple regression</i> in which an outcome is predicted by a linear combination of two or more predictor variables. The form of the model is in which an outcome is predicted by a linear combination of two or more predictor variables. The form of the model is $Y_i = (b_0 + b_1X_1 + b_2X_2 + \dots + b_nX_n) + \varepsilon_i$ in which the outcome is denoted as Y , and each predictor is denoted as X . Each predictor has a regression coefficients b_i associated with it, and b_0 is the value of the outcome when all predictors are zero.
Non-parametric tests:	A family of statistical procedures that do not rely on the restrictive assumptions of parametric tests. In particular they do not assume that data come from a normal distribution.
Normal distribution:	A <i>probability distribution</i> of a random variable that is known to have certain properties. Is perfectly symmetrical (has a <i>skew</i> of 0), and has a <i>kurtosis</i> of 0.
Outlier:	An observation very different from most others. Outliers can bias statistics such as the mean.
Pairwise comparisons:	Comparisons of pairs of means.
Pearson's correlation coefficient (r):	(Also know as Pearson's product-moment correlation coefficient) A <i>standardized</i> measure of the strength of relationship between two variables. It can take any value from -1 (as one variable changes, the other changes in the opposite direction by the same amount), through 0 (as one variable changes the other doesn't change at all), to +1 (as one variable changes, the other changes in the same direction by the same amount).
Population:	In statistical terms this usually refers to the collection of units (be they people, plankton, plants, cities, suicidal authors, etc.) to which we want to generalize a set of findings of a statistical model.

Appendix – E Glossary of statistical terms (cont'd.)

<i>Post hoc</i> tests:	A set of comparisons between group means that were not thought of before data were collected. Typically these tests involve comparing the means of all combinations of pairs of experimental conditions. To compensate for the number of tests conducted, each test uses a strict criterion for significance. As such, they tend to have less power than <i>planned contrasts</i> . They are usually used for exploratory work for which no firm hypotheses were available on which to base planned contrasts.
Predictor variable:	A variable that is used to try to predict values of another variable known as an <i>outcome variable</i> .
Residual:	The difference between the value a model predicts and the value observed in the data on which the model is based. When the residual is calculated for each observation in a data set the resulting collection is referred to as the <i>residuals</i> .
Standardized residuals:	The <i>residuals</i> of a model expressed in standard deviation units. Standardized residuals with an absolute value greater than 3.29 (actually we usually just use 3) are cause for concern because in an average sample a value this high is unlikely to happen by chance; if more than 1 % of our observations have standardized residuals with an absolute value greater than 2.58 (we usually just say 2.5) there is evidence that the level of error within our model is unacceptable (the model is a fairly poor fit of the sample data); and if more than 5 % of observations have standardized residuals with an absolute value greater than 1.96 (or 2 for convenience) then there is also evidence that the model is a poor representation of the actual data.
Sample:	A smaller (but hopefully representative) collection of units from a <i>population</i> used to determine truths about that population (e.g. how a given population behaves in certain conditions).
Scatterplot:	A graph that plots values of one variable against the corresponding value of another variable (and the corresponding value of a third variable can also be included on a three-dimensional scatterplot).

Appendix – E Glossary of statistical terms (cont'd.)

Shapiro –Wilk test:

A test of whether a distribution of scores is significantly different from a *normal distribution*. A significant value indicates a deviation from normality, but this test is notoriously affected by large samples in which small deviations from normality yield significant results.

Shrinkage:

The loss of predictive power of a regression model if the model had been derived from the population from which the sample was taken, rather than the sample itself.

Simple regression:

A *linear model* in which one variable or outcome is predicted from a single predict variable. The model takes the form $Y_i = (b_0 + b_1X_i) + \varepsilon_i$, in which Y is the outcome variable, X is the predictor, b_1 is the regression coefficient associated with the predictor and b_0 is the value of the outcome when the predictor is zero.

Spearman's correlation coefficient (r_s):

A standardized measure of the strength of relationship between two variables that does not rely on the assumptions of a *parametric test*. It is *Pearson's correlation coefficient* performed on data that have been converted into ranked scores.

Standard deviation:

An estimate of the average variability (spread) of a set of data measured in the same units of measurement as the original data. It is the square root of the variance.

Standardization: The process of converting a variable into a standard unit of measurement. The unit of measurement typically used is *standard deviation* units (see also *z-scores*). Standardization allows us to compare data when different units of measurement have been used (we could compare weight measured in kilograms with height measured in inches).

Stepwise regression:

A method of multiple regression in which variables are entered into the model based on a statistical criterion (the semi-partial correlation with the outcome variable). Once a new variable is entered into the model, all variables in the model are assessed to see whether they should be removed.

Appendix – E Glossary of statistical terms (cont'd.)

- T-statistic:** Student's *t* is a *test statistic* with a known *probability distribution* (the *t*-distribution). In the context of regression it is used to test whether a regression coefficient *b* is significantly different from zero; in the context of experimental work it is used to test whether the differences between two means are significantly different from zero (see also *independent t-test* and *dependent t-test*).
- Test statistic:** A statistic for which we know how frequently different values occur. The observed value of such a statistic is typically used to test *hypotheses*.
- Transformation:** The process of applying a mathematical function to all observations in a data set, usually to correct some distributional abnormality such as *skew* or *kurtosis*.
- Two-tailed test:** A test of a non-directional hypothesis. For example, the hypothesis 'writing this glossary has some effect on what I want to do with my editor's genitals' requires a two-tailed test because it doesn't suggest the direction of the relationship (see also *one-tailed test*).
- Type I error:** Occurs when we believe that there is a genuine effect in our population, when in fact there isn't.
- Type II error:** Occurs when we believe that there is no effect in the population when, in reality, there is.
- Univariate:** This means 'one variable' and is usually used to refer to situations in which only one *outcome variable* has been measured (ie., *ANOVA*, *t-tests*, *Mann-Whitney tests*, etc.).
- Variance:** An estimate of average variability (spread) of a set of data. It is the sum of squares divided by the number of values on which the sum of squares is based minus 1.
- Variance proportion:** The variance of each regression coefficient can be broken down across eigenvalues and tells us the proportion of the variance of each predictor's regression coefficient that is attributed to each eigenvalue. These proportions can be converted to percentages. In terms of collinearity, we are looking for predictors that have high proportions on the same *small* eigenvalue, because this would indicate that the variances of their regression coefficients are dependent.

Appendix – E Glossary of statistical terms (cont'd.)

**Variance
inflation factor
(VIF):**

A measure of *multicollinearity*. The VIF indicates whether a predictor has a strong linear relationship with the other predictor(s). Myers (1990) suggests that a value of 10 is a good value at which to worry. Bowerman and O'Connell (1990) suggest that if the average VIF is greater than 1, then multicollinearity may be biasing the regression model.

**Wilcoxon
signed-rank
test:**

A *non-parametric test* that looks for differences between two related samples. It is the non-parametric equivalent of the *related t-test*.

**Wilcoxon's
rank-sum test:**

A *non-parametric test* that looks for differences between two independent samples. That is, it tests whether the populations from which two samples are drawn have the same location. It is functionally the same as the *Mann-Whitney test*, and both tests are non-parametric equivalents of the *independent t-test*.

z-scores:

The value of an observation expressed in standard deviation units. It is calculated by taking the observation, subtracting from it the mean of all observations, and dividing the result by the standard deviation of all observations. By converting a distribution of observations into z-scores you create a new distribution that has a mean of 0 and a standard deviation of 1.

Appendix – F Histograms and normal Q-Q plots

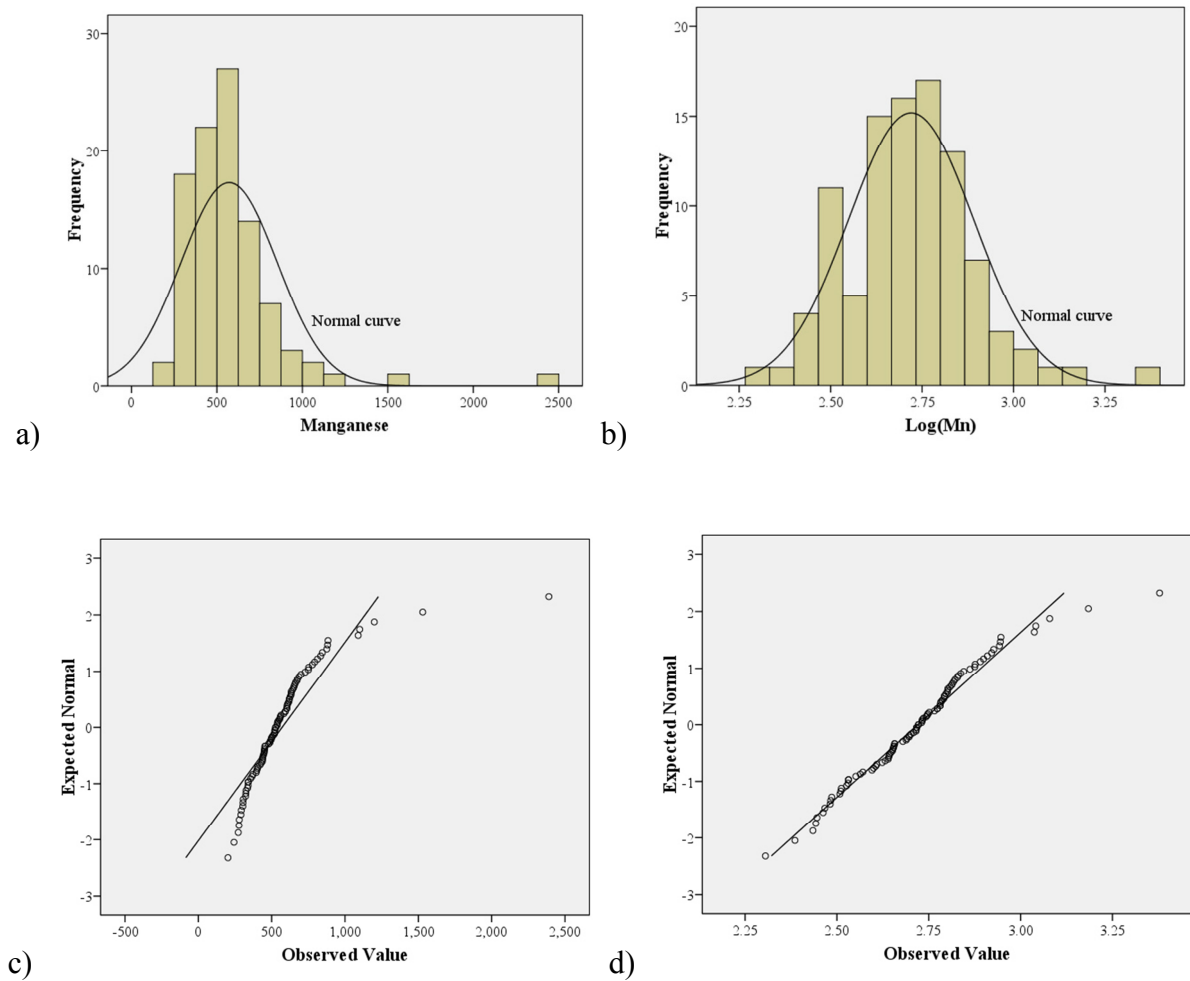


Figure F-101 Preliminary soil survey soil manganese a) histogram and c) normal Q-Q plot and log-transformed soil manganese b) histogram and d) normal Q-Q plot.

Appendix – F Histograms and normal Q-Q plots (cont'd.)

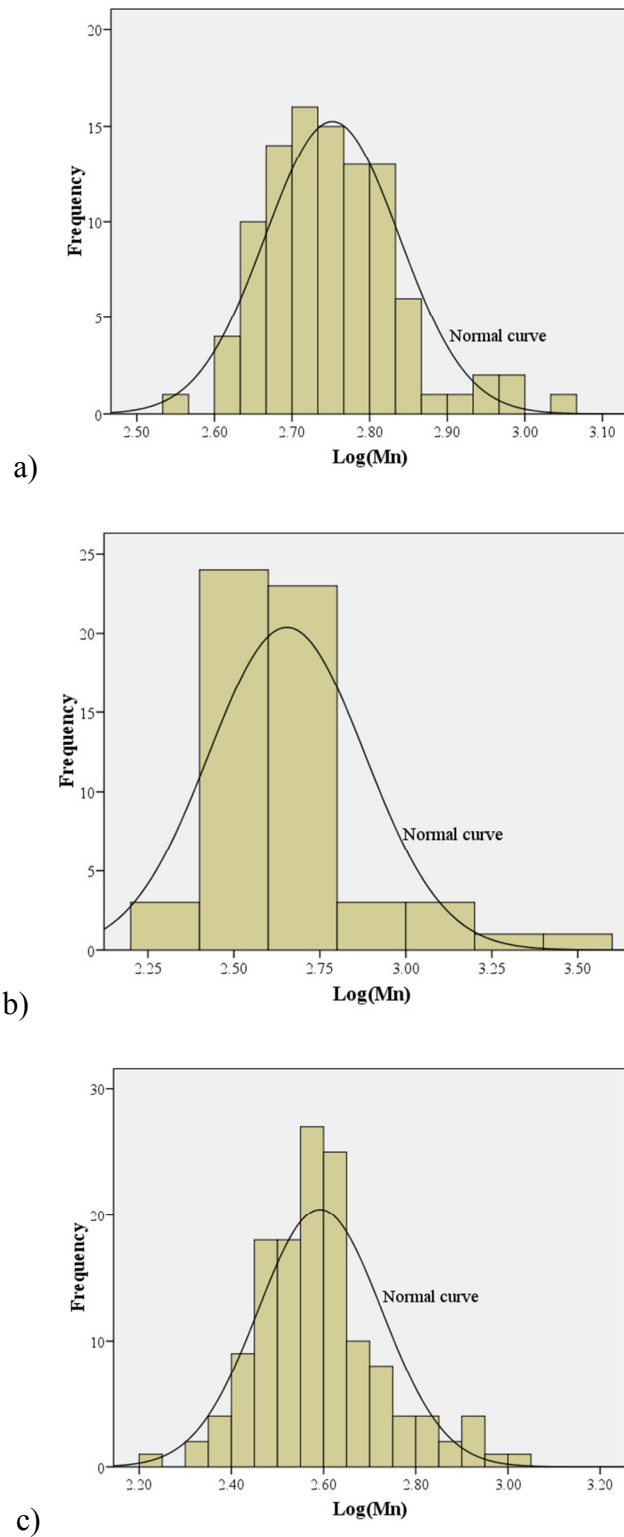


Figure F-102 Histograms of the complete soil survey log-transformed soil manganese a) transect, b) industrial, and c) random samples.

Appendix – G Comparison of triplicate and duplicate Ambassador Bridge samples

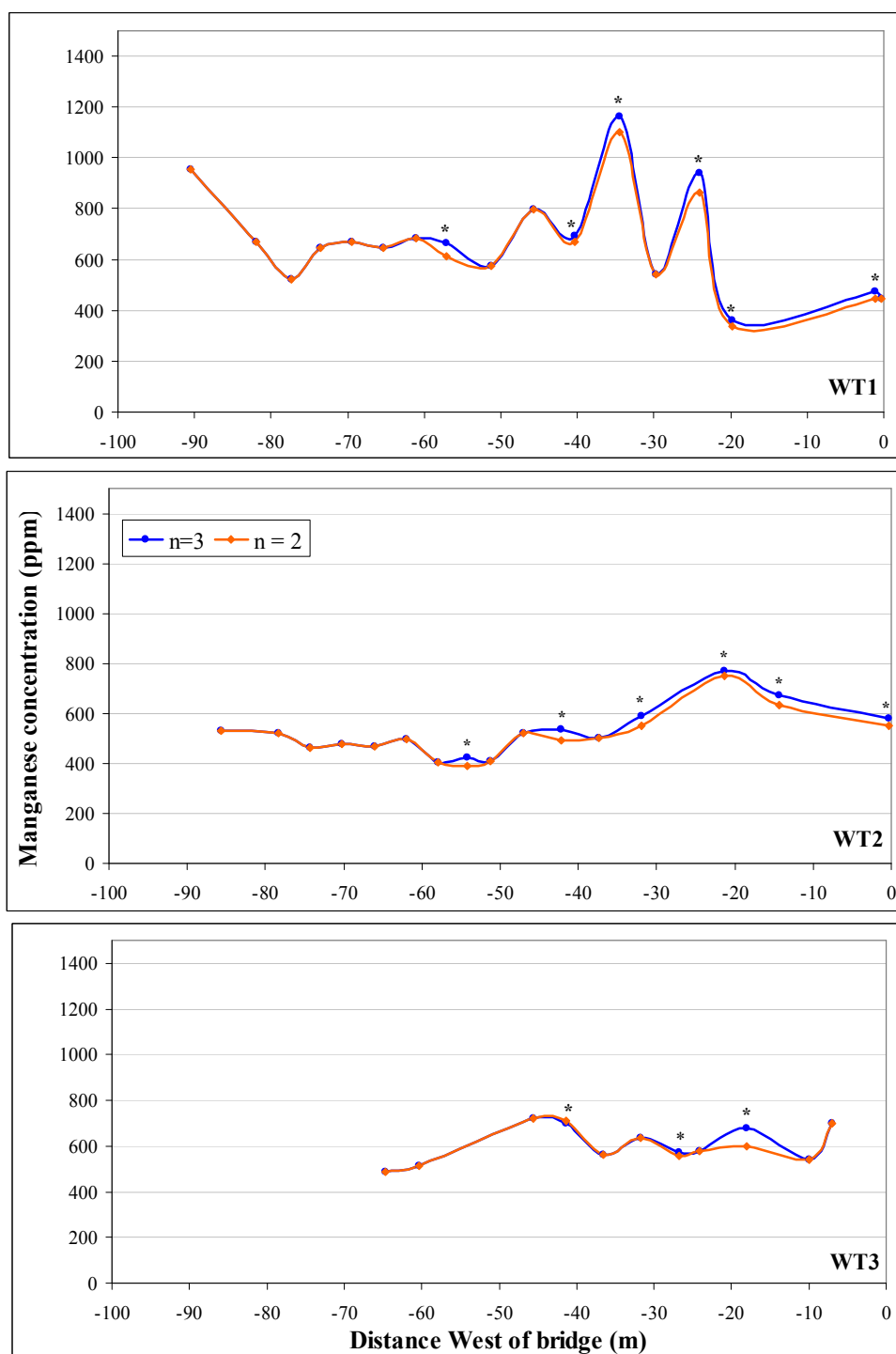


Figure G-103 Soil manganese concentrations of triplicate (n = 3) and duplicate (n = 2) samples from the western Ambassador Bridge (located at 0 m) transects. (*) indicates the location of June/August triplicate samples (see Chapter 5 text)).

Appendix – G Comparison of triplicate and duplicate Ambassador Bridge samples (cont'd)

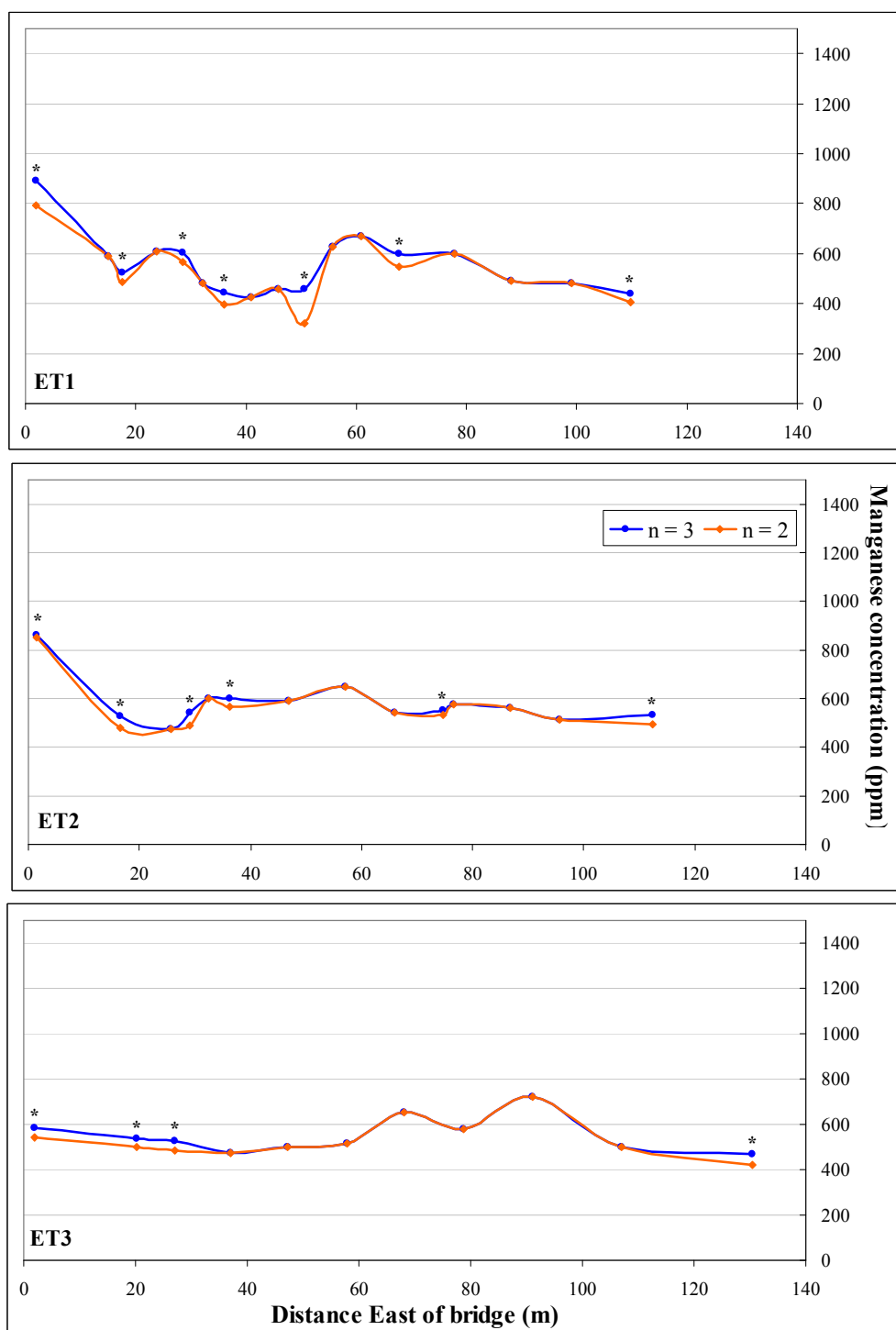


Figure G-104 Soil manganese concentrations of triplicate (n = 3) and duplicate (n =2) samples from the eastern Ambassador Bridge (located at 0 m) transects. (* indicates the location of June/August triplicate samples (see Chapter 5 text)).

Appendix – H Windsor soil core information

Table H-56 Summary information of Windsor soil core manganese results.

Core Type	Approximate Depth Range (cm)	Sample Name	Mean Core Manganese Concentration (ppm)	Core Standard Deviation (ppm)	Core Relative Standard Deviation (%)	n
Natural	18 - 33	LR-3	455	58.2	12.8	4
	70 - 90	Macgregor	450	60.0	13.3	5
	34 - 49	MB-22 depth	679	154	22.6	4
	0 - 20	MB-23 surface	251	40.6	16.2	4
	22 - 31	depth	306	33.4	10.9	4
	61 - 97	PEN	553	75.3	13.6	8
	0 - 20	PC-1	439	17.6	4.0	4
	67 - 80	TownEd	970	456	47.0	4
	0 - 20	ABW-T1-4	1315	25.2	1.9	4
	67 - 100	BB	397	43.4	10.9	8
Biomonitoring station	0 - 20	MB-1 surface	367	19.9	5.4	4
	22 - 35	depth	246	28.6	11.7	4
	0 - 20	MB-2 surface	445	18.1	4.1	4
	52 - 67	depth	379	43.5	11.5	4
	0 - 15	MB-3 surface	318	14.0	4.4	3
	37 - 51	depth	368	57.8	15.7	5
	0 - 20	MB-4 surface	310	31.8	10.3	4
	31 - 46	depth	237	11.7	4.9	4
	0 - 20	MB-5 surface	365	29.7	8.1	4
	21 - 34	depth 1	279	31.9	11.4	4
	39 - 54	depth 2	271	11.5	4.2	4
	0 - 20	MB-6 surface	649	46.5	7.2	4
	42 - 57	depth	503	37.3	7.4	4

Appendix – H Windsor soil core information (cont'd.)

Table H-56 Summary information of Windsor soil core manganese results. (cont'd.)

Core Type	Approximate Depth Range (cm)	Sample Name	Mean Core Manganese Concentration (ppm)	Core Standard Deviation (ppm)	Core Relative Standard Deviation (%)	n
Biomonitoring station (cont'd.)	0 - 20	MB-7 surface	599	38.6	6.4	4
	39 - 54	depth	331	15.1	4.6	4
	0 - 20	MB-8 surface	310	16.3	5.2	4
	0 - 20	MB-9 surface	460	32.2	7.0	4
	0 - 20	MB-10 surface	631	19.4	3.1	4
	0 - 20	MB-11 surface	764	24.5	3.2	4
	42 - 57	depth	452	5.8	1.3	4
	0 - 20	MB-13 surface	382	35.1	9.2	4
	35 - 50	depth	316	15.2	4.8	4
	0 - 20	MB-14 surface	440	34.7	7.9	4
	44 - 59	depth	504	33.9	6.7	4
	45 - 60	MB-17 depth	474	61.5	13.0	4
	0 - 18	MB-18 surface	884	38.1	4.3	4
	33 - 45	depth	828	30.3	3.7	4
	0 - 20	MB-19 surface	666	24.4	3.7	4
	45 - 60	depth	573	114	20.0	4
	0 - 20	MB-20 surface	252	10.6	4.2	4
	44 - 59	depth	434	21.5	5.0	4
	0 - 20	MB-21 surface	566	166	29.4	4
	0 - 20	MB-22 surface	241	19.2	8.0	4

Appendix – H Windsor soil core information (cont'd.)

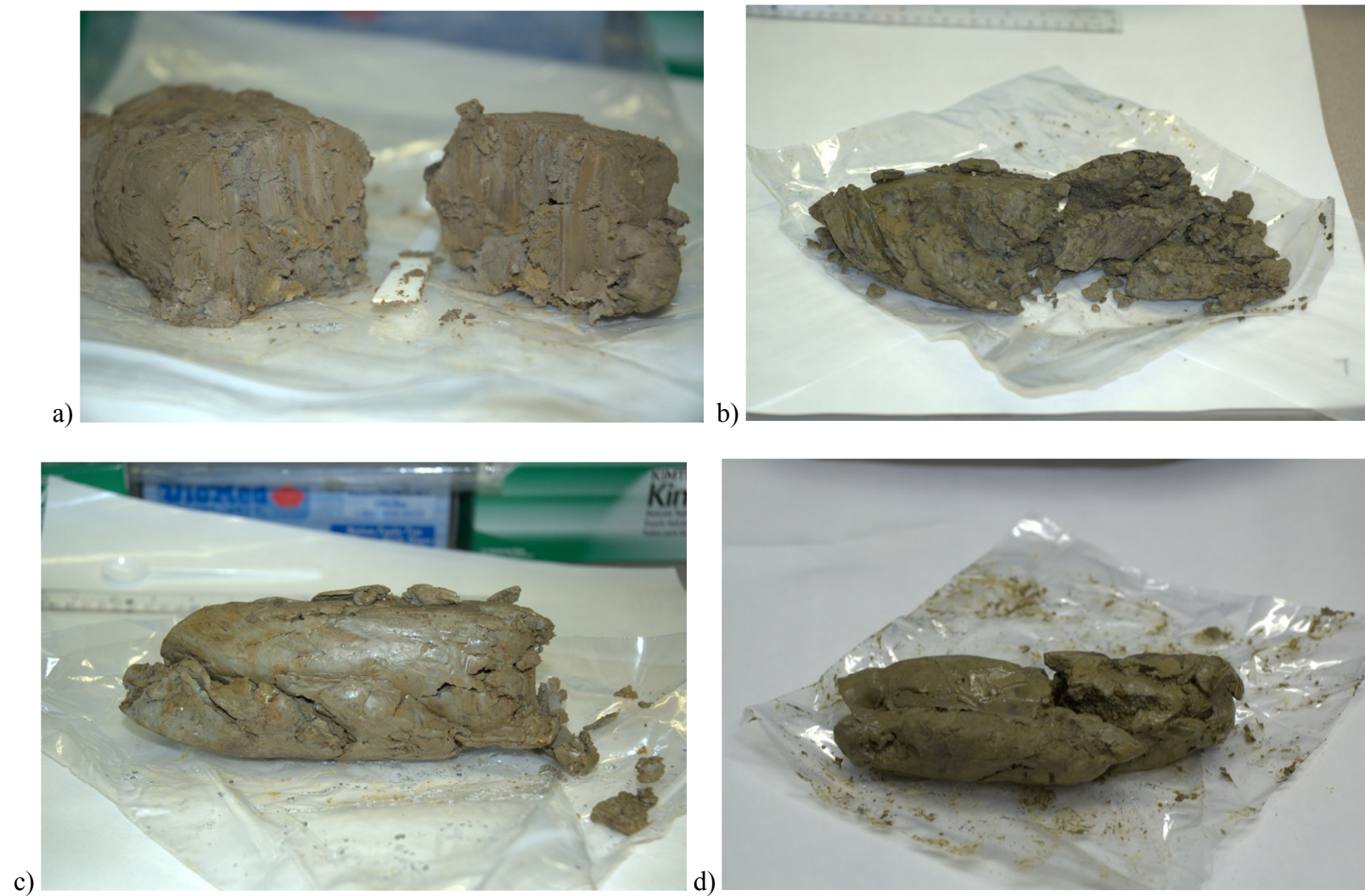


Figure H-105 Photos of natural soil cores: a) BB, b) MacGregor, c) Town of Essex depth (TownEd), and d) PEN.

Appendix – I List of air photos

Table I-57 List of National Air Photo Library (NAPL) air photos consulted.

Roll Number	Photo Number	Year	Roll Number	Photo Number	Year
A3271	15–31	1931	A27258	94-5	1988
A1164	67–70, 73–81, 204, 208–215, 219-220	1947	A27267	125-6, 129	1988
A1163	115-6, 119-20	1947	A27535	58	1989
A12563	103-4	1950	A27801	19, 21, 47-8, 51-4	1992
A13586	147-8	1952	A17632	63-4	1962
A13592	30, 57	1953	A12503	10, 42-3, 46	1950
A13595	10, 69, 73	1953	A17017	18, 20-1	1960
A17635	35, 47-8, 51, 58	1962	A17642	83	1962
A21617	13, 144-5	1970	A25380	1, 9	1977
A22030	26, 54, 58-9, 74	1970	A26858	3	1986
A23288	54, 56	1973	A27391	6	1988
A23252	109-10	1974	A31567	139, 163	1990
A24285	89, 91-2	1975	A25101	16	1977
A24318	129, 134-6	1976	A25926	7	1981
A25145	58–60, 69–70, 73-4	1979	A26422	90	1983
A23289	54, 155	n/a	A26858	31	1985
A25521	68	1980	A27552	11	1990
A25950	72, 78, 88	1982	A17466	45	1969
A31385	19	1984	A17016	89	1960
A26887	4-5, 7, 10	1988	A12504	104, 108-9, 127	1950

Appendix – J Limits of detection (LOD) and element recoveries

Table J-58 ICP-MS limit of detection (LOD) and recovery for reportable elements detected by Activation Laboratories Ltd. (soil analysis) (n = 8).

Element	LOD (ppm)	Recovery (%)	Element	LOD (ppm)	Recovery (%)
Lithium	0.5		Zirconium	1	
Sodium	0.001 %		Niobium	0.1	
Magnesium	0.01 %	114	Molybdenum	0.1	66
Aluminum	0.01 %		Tin	1	92 ^a
Potassium	0.01 %		Antimony	0.1	228
Calcium	0.01 %	336	Barium	1	
Cadmium	0.1	96	Praseodymium	0.1	
Vanadium	1		Gadolinium	0.1	
Chromium	0.5	88	Dysprosium	0.1	
Manganese	1	93	Copper	0.2	104
Iron	0.01 %	96	Germanium	0.1	
Nickel	0.5	108	Thulium	0.1	
Erbium	0.1		Rhenium	0.001	
Beryllium	0.1		Thorium	0.05	
Holmium	0.1		Lead	0.5	97
Sliver	0.05		Thorium	0.1	
Cesium	0.05		Uranium	0.1	
Cobalt	0.1	92	Hafnium	0.1	
Selenium	0.1		Europium	0.05	
Zinc	0.2	88	Lanthanum	0.1	
Gallium	0.1		Cerium	0.1	
Arsenic	0.1	88	Neodymium	0.1	
Rubidium	0.2		Samarium	0.1	
Yttrium	0.1		Terbium	0.1	
Strontium	0.2	94	Ytterbium	0.1	

^a n = 1

Appendix – J Limits of detection (LOD) and element recoveries (cont'd.)

Table J-59 ICP-MS limit of detection (LOD) and recovery for reportable elements detected by Health Canada (moss-sequestered airborne particle analysis).

Element	LOD (ppm)	Recovery (%)	
		NIST 1573a (n = 8)	NIST 1575 (n = 7)
Vanadium	0.1	120	n/a
Chromium	1.0	148	201
Iron	36	129	9.3
Titanium	0.7	n/a	n/a
Manganese	0.3	90.5	87.1
Cobalt	0.1	103	112
Copper	0.7	91.9	81.2
Zinc	2	93.6	n/a
Strontium	0.09	93.8	83.7
Yttrium	0.04	n/a	n/a
Molybdenum	0.03	89.7	n/a
Cadmium	0.04	88.3	68.2
Tin	0.07	n/a	n/a
Antimony	0.05	88.9	81.6
Barium	0.08	86.5	n/a
Lead	0.05	n/a	89.2

Appendix – K Complete elemental analysis of Mackenzie River Delta moss

Table K-60 ICP-MS element analysis result of Mackenzie River Delta moss (n = 2).

Element	Mean manganese concentration (ppm)
Vanadium	0.835
Chromium	0.715
Iron	161
Titanium	4.8
Manganese	299
Cobalt	0.103
Copper	1.7
Zinc	16.7
Strontium	6.2
Yttrium	0.065
Molybdenum	0.053
Cadmium	0.065
Tin	0.017
Antimony	0.016
Barium	31.5
Lead	0.371

Appendix – L Supplement linear regression graphs

Moss-sequestered airborne particle

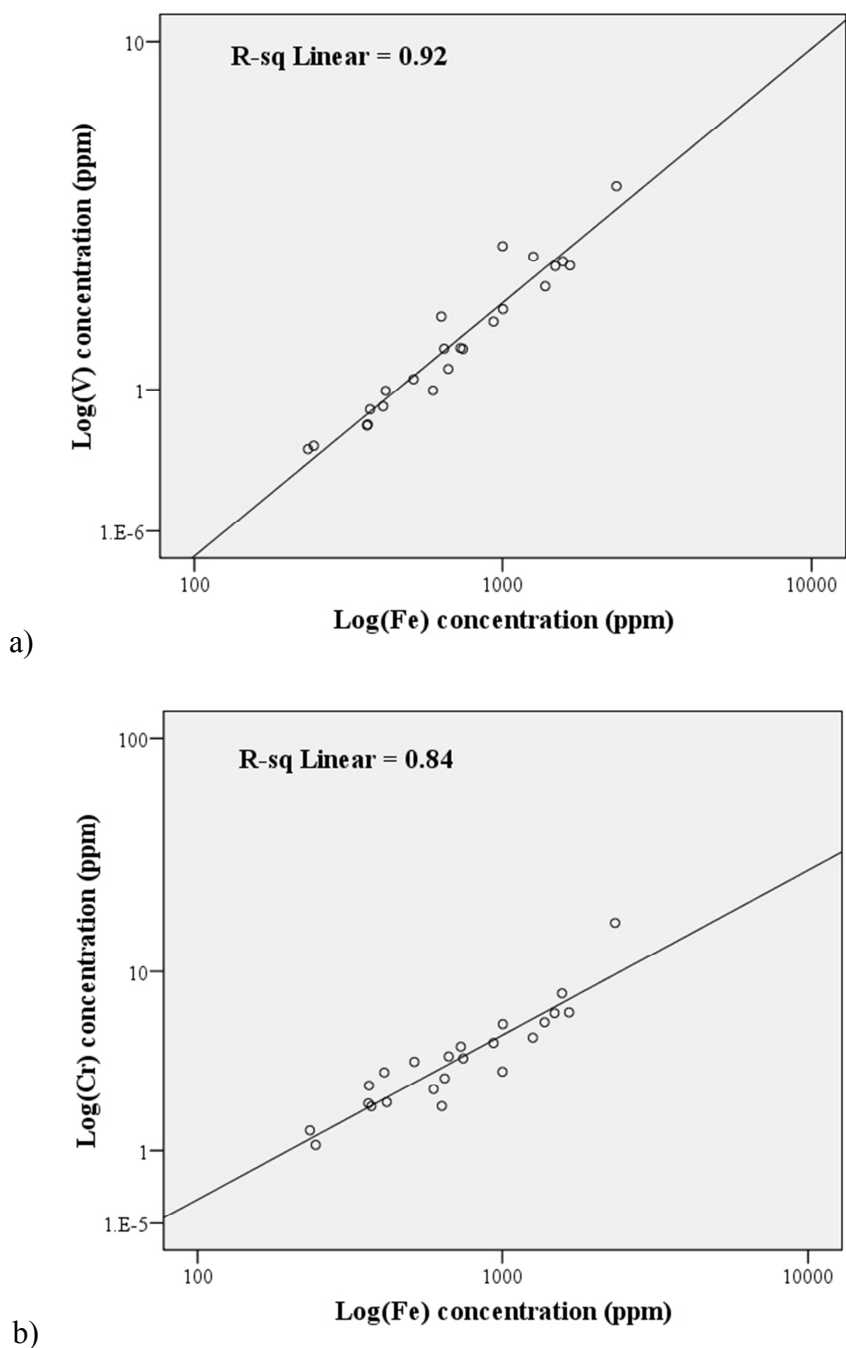
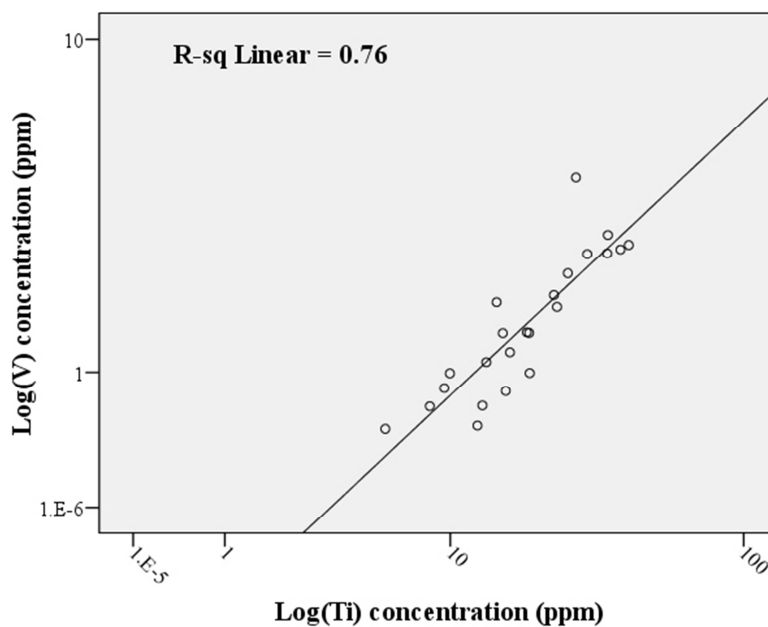
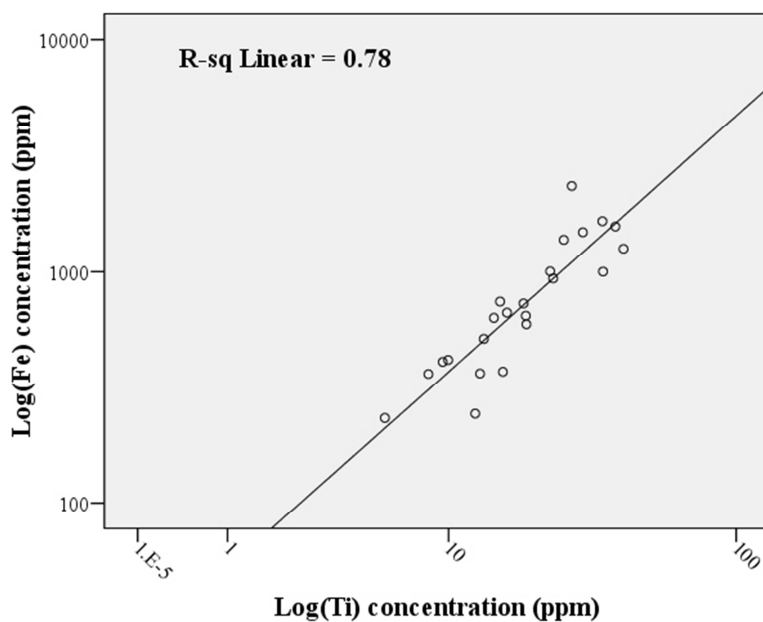


Figure L-106 Scatterplot and linear regression trendlines for log-transformed moss-sequestered airborne particle a) vanadium and iron, and b) chromium and iron (n = 23).

Appendix – L Supplement linear regression graphs (cont'd.)



a)



b)

Figure L-107 Scatterplot and linear regression trendlines for log-transformed moss-sequestered airborne particle a) vanadium and titanium, and b) iron and titanium (n = 23).

Appendix – L Supplement linear regression graphs (cont'd.)

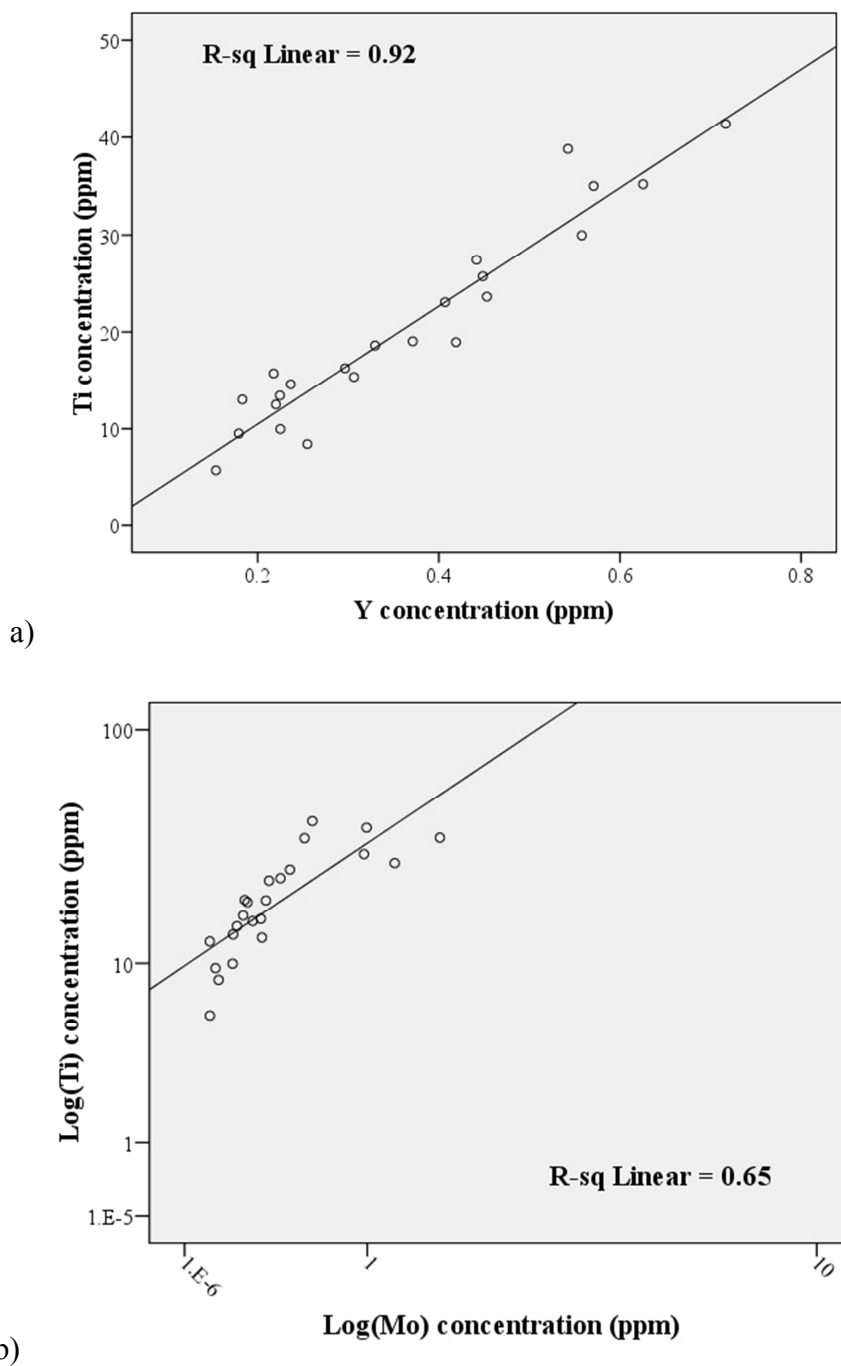


Figure L-108 Scatterplot and linear regression trendlines for moss-sequestered airborne particles a) titanium and yttrium, and for log-transformed b) titanium and molybdenum (n = 23).

Appendix – L Supplement linear regression graphs (cont'd.)

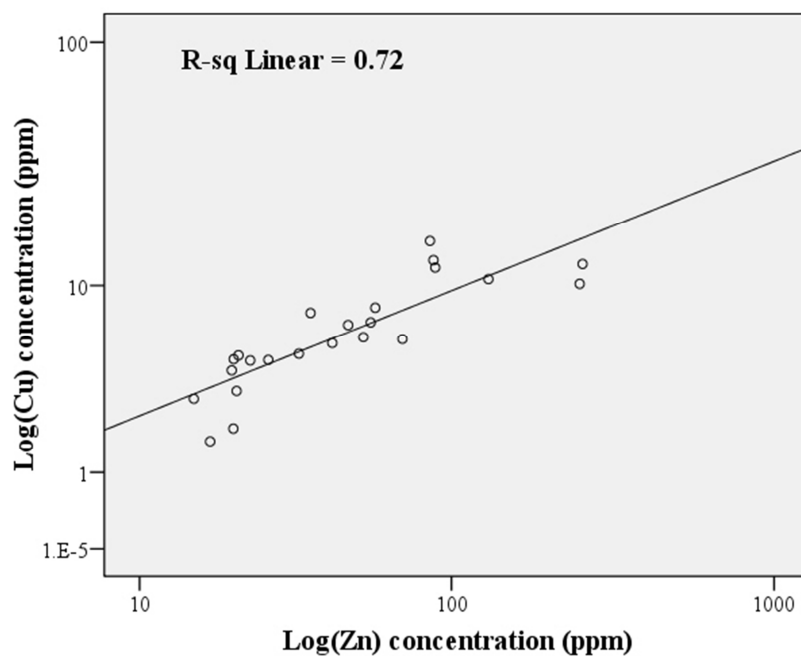
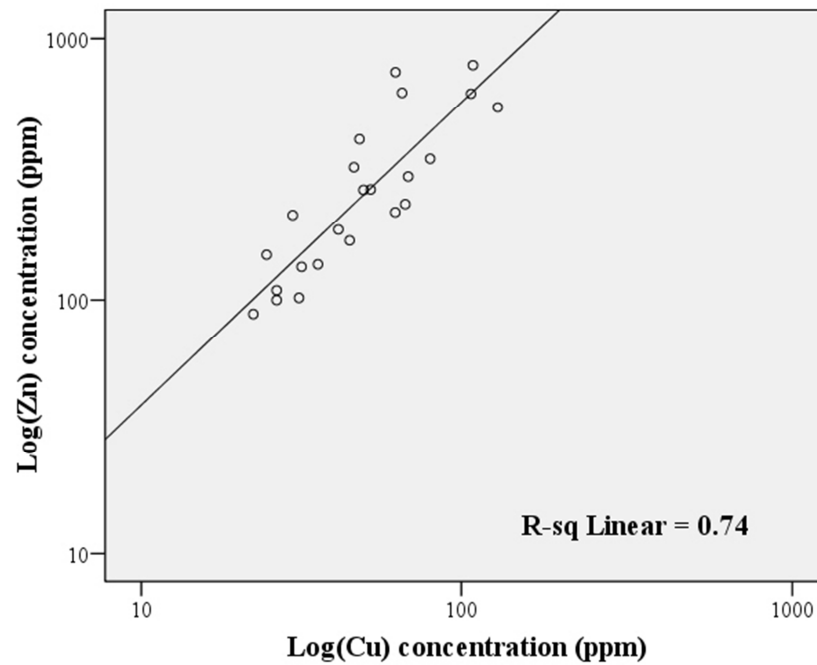


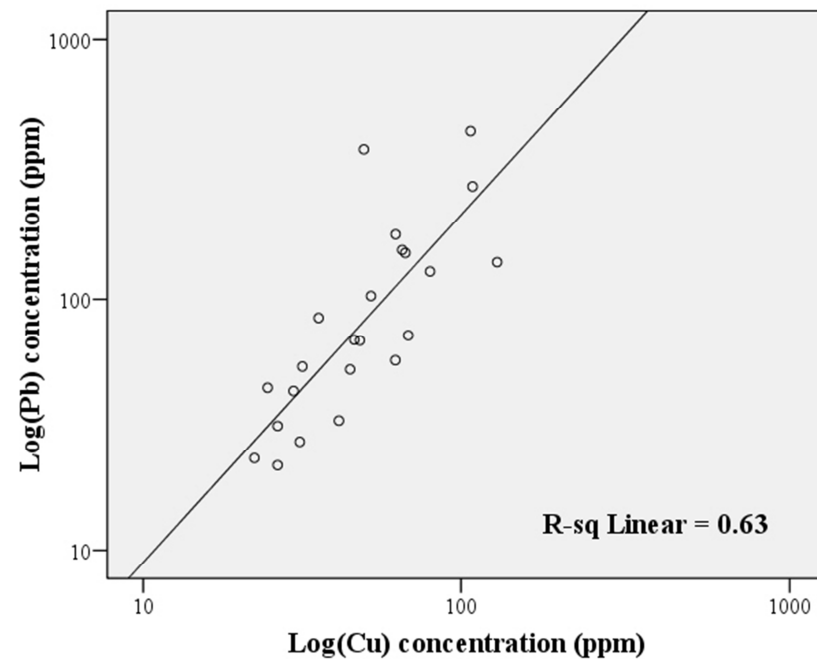
Figure L-109 Scatterplot and linear regression trendline for log-transformed moss-sequestered airborne particle copper and zinc (n = 23).

Appendix – L Supplement linear regression graphs (cont'd.)

Collocated biomonitoring station soil



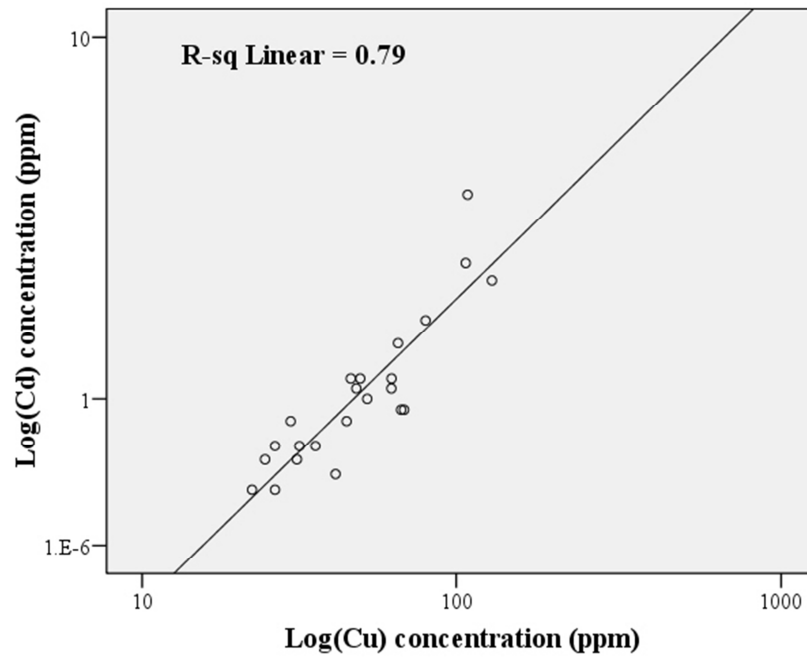
a)



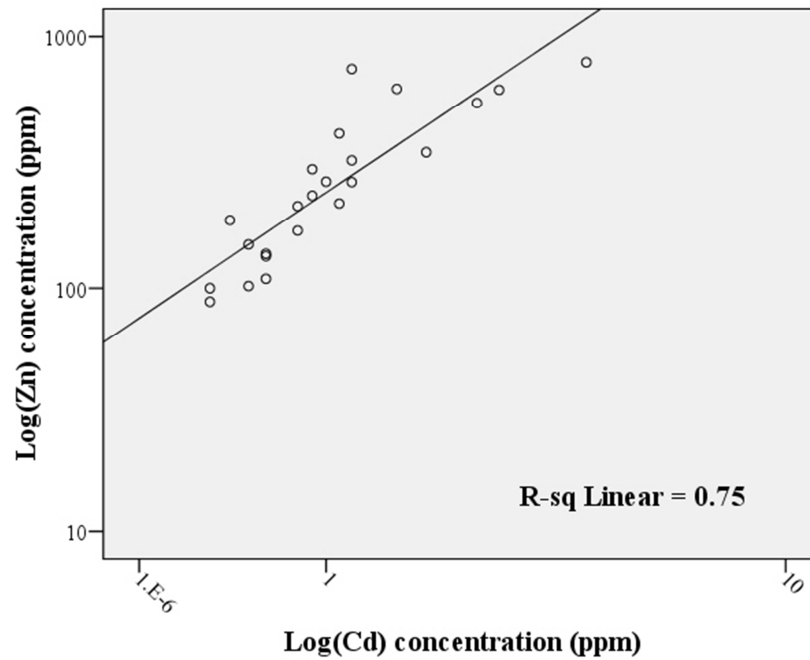
b)

Figure L-110 Scatterplot and linear regression trendlines for log-transformed collocated biomonitoring station soil a) zinc and copper, and b) lead and copper (n = 23).

Appendix – L Supplement linear regression graphs (cont'd.)



a)



b)

Figure L-111 Scatterplot and linear regression trendlines for log-transformed collocated biomonitoring station soil a) cadmium and copper, and b) zinc and cadmium (n = 23).

Appendix – L Supplement linear regression graphs (cont'd.)

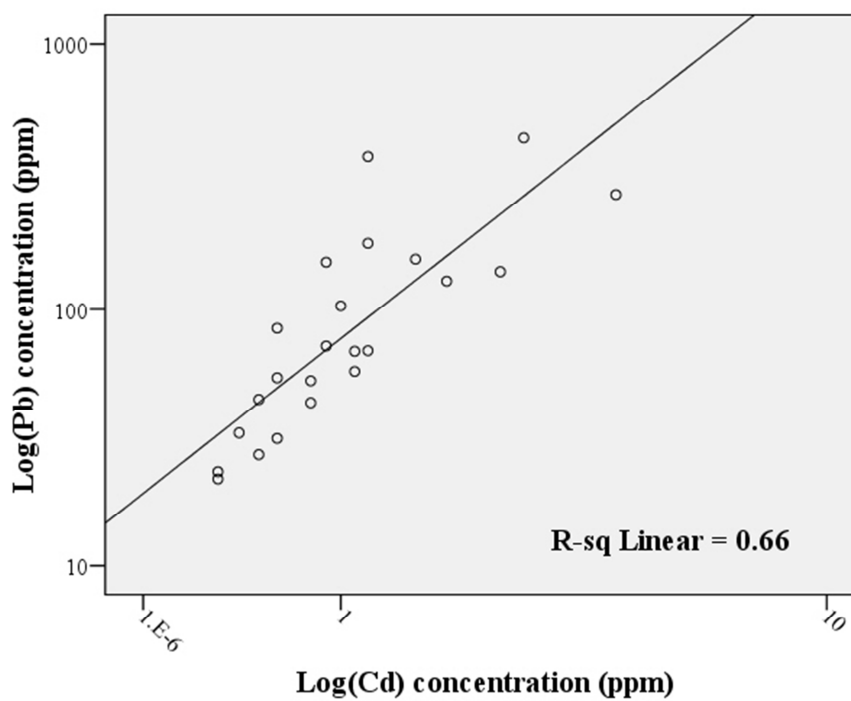


Figure L-112 Scatterplot and linear regression trendline for log-transformed collocated biomonitoring station soil lead and cadmium (n = 23).