

PREDICTING POTENTIAL ANTHROPOGENIC INFLUENCES AND EVALUATING
METAL CONCENTRATIONS WITHIN URBAN SOILS HALIFAX, NOVA SCOTIA

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Abstract

Canada lacks a uniform method for sampling metals in urban soils, posing challenges for comparing studies and hindering the recognition of trends. Although problematic, the absence of a standard methodology is not unfounded. The extensive variability of soil properties throughout time and space makes it difficult to evaluate a study area. Methods designed to be used ubiquitously not only allow studies to be comparable, but may add to the effectiveness of environmental and health risk assessments.

This study focuses on developing a protocol for predicting and potentially mitigating elevated metals in city soils within Halifax, N.S. One aspect of the study aims to predict where high metal concentrations may arise in a city, by identifying past land use activities that are strongly associated with a particular metal(s). Another aspect of the study involves developing a preliminary urban background for the city of Halifax. A total of 96 depth-based samples at 0-5 cm and 0-15 cm sample depths were collected and evaluated through X-ray fluorescence (XRF) analysis. Of these samples, those that had metal concentrations above Canadian Council of Ministers of the Environment (CCME) guidelines were sieved to particle sizes of < 2 mm and < 0.5 mm. Comparing metal concentrations with depth and particle size determined the following results. Metal concentrations are notably higher in 0-15cm depth based samples due to leaching that is occurring with developed soil. Lead, Barium and Zinc concentrations are elevated for samples proximal to older wooden buildings, suggesting buildings act as anthropogenic point sources. Metal concentrations are elevated in finer particle sizes, however the difference is not significant due to siltier soil composition. The intent of this study is to build a foundation for determining the 'best practice' for assessing elevated metal concentrations in city soils.

Keywords: soil, urban soil, soil geochemistry, metals, urban background, geoavailable, bioaccessible, bioavailable

Table of Contents

Abstract	iii
Table of Contents.....	iv
List of Figures	vi
List of Tables	ix
Acknowledgements	x
1.0 Introduction	1
1.1 General Statement.....	1
1.2 Purpose of Study	3
2.0 Background	5
2.1 Defining Soils	5
2.2 Urban Soils.....	7
2.3 Soil Variability and Assessment	7
2.4 Halifax Soil	8
2.5 Halifax Study Area	9
2.6 Halifax Soil Development	9
2.6.1 Halifax Bedrock.....	10
2.6.2 Glacial Till	13
2.6.3 Naturally Elevated Metals in Soils	14
2.6.4 Climate and Vegetation.....	15
2.6.5 Topography and Drainage.....	16
2.7 Factors to Consider for Metal Concentration, Mobility and Dispersivity.....	17
2.7.1 Chemical and Physical Properties of Metals.....	18
2.7.2 Geochemical Associations, Gradients and Barriers.....	19
2.7.3 Metal Mobility with Varying Environmental Conditions	22
2.7.4 Metal Dispersivity in Surficial Environment.....	26
2.7.4.1 General Assumptions for Metal Distribution: Grain Size	26
2.7.4.2 Air	26
2.7.4.3 Water	29
2.8 Halifax Anthropogenic Influences	30
2.8.1 Halifax Air.....	30
2.8.2 Halifax Water	30
2.8.3 Halifax Anthropogenic Dispersion: Halifax History and Development	34
2.8.4 Metal Toxicity: Human & Environmental Health	35
2.8.5 Federal and Provincial Guidelines	39
2.9 Previous work.....	40
2.9.1 Halifax Future Growth and Development.....	47
3.0 Materials and Methods.....	49
3.1 Halifax Study Area	50
3.2 Soil Assessment: Depth – Based Sampling.....	51
3.3 Soil Assessment: Particle Size Fractions.....	53
3.4 Accuracy and precision of Analysis.....	55
3.5 Soil Assessment: pH, Conductivity, TDS and Soil Texture.....	56

3.6 GIS Component: Potential locations for Halifax Metal Hotspots.....	57
4.0 Results	59
4.1 Soil Properties: pH, Conductivity, TDS and Texture.....	59
4.2 Soil Assessment: Depth Based Sampling.....	74
4.3 Soil Assessment: Particle Size	92
4.4 Soil Texture	97
4.5 Predicting metal abundance	100
5.0 Discussion	104
5.1 Soil Properties.....	104
5.2 Soil Assessment: Depth – Based Sampling.....	107
5.3 Urban background.....	109
5.4 Particle Size Sieving.....	109
5.5 Predicting Metal Abundance.....	111
6.0 Conclusion	113
7.0 Recommendations.....	114
References.....	116
8.0 Appendix Outline	122

List of Figures

FIGURE 1: HALIFAX MAP OF THE DOWNTOWN CORE, DEPICTING STUDY AREA WITH ORANGE BOX.	4
FIGURE 2: SOIL LAYERS CLASSIFIED DEPICT HORIZONS THAT DEVELOP IN TEMPERATE HUMID CLIMATE. FIGURE AT LEFT IS OBTAINED FROM THE USDA AND DESCRIPTION IS MODIFIED FROM SIEGEL, 2002.	6
FIGURE 3: STUDY AREA AT DALHOUSIE STUDLEY CAMPUS AND SAMPLE LOCATIONS DEPICTED IN DIFFERENT COLOURED CIRCLES.	9
FIGURE 4: SIMPLIFIED GEOLOGIC MAP DEPICTING MEGUMA TERRANE OF SOUTHERN NOVA SCOTIA. LOCATION OF HALIFAX SHOWN WITH BLACK BOX. CCSZ (COBEQUID-CHEDEBUCTO SHEAR ZONE) AND CPSZ (CHEBOGUE POINT SHEAR ZONE). (FIGURE ADAPTED FROM WHITE AND GOODWIN, 2011).	10
FIGURE 5: SIMPLIFIED GEOLOGIC MAP OF HALIFAX REGIONAL MUNICIPALITY. (MODIFIED FROM WHITE AND GOODWIN, 2011.).....	12
FIGURE 6: SURFICIAL GEOLOGICAL MAP OF HALIFAX MODIFIED FROM THE DEPARTMENT OF NATURAL RESOURCES DATABASE PAGE (UTTING, 2011).....	14
FIGURE 7: ADAPTED GRAPHICAL REPRESENTATION OF AVERAGE PRECIPITATION DATA FROM BETWEEN 1971-2000, (MODIFIED FROM STATISTICS CANADA, 2016).....	15
FIGURE 8: TOPOGRAPHIC AND ELEVATION MAP OF HALIFAX (TOPOGRAPHIC MAPS, 2017).....	16
FIGURE 9: MOBILITY OF ELEMENTS WITHIN THE SURFICIAL ENVIRONMENT IN RELATION TO IONIC POTENTIAL (ROSE ET AL., 1979).	19
FIGURE 10: EH AND PH CONDITIONS IN NEAR SURFACE ENVIRONMENTS. SHADED AREA ARE APPROXIMATE CONDITIONS FOR GEOLOGICALLY AND GEOCHEMICALLY DIVERSE MINE DRAINAGE WATERS (PLUMLEE ET AL., 1999 AND MODIFIED FROM SMITH AND HUYCK, 1999).....	21
FIGURE 11 (A-C): PERIODIC TABLE DEPICTING ELEMENT MOBILITY BASED ON DIFFERENT ENVIRONMENTAL CONDITIONS. RARE EARTH ELEMENTS OR ELEMENTS WITH LACK OF SHADING ARE NOT ASSIGNED A MOBILITY DUE TO LOW ABUNDANCE OR LACK OF DATA. (OBTAINED FROM SMITH AND HUYCK, 1999)	23
FIGURE 11 (D-E): CONTINUED FROM PREVIOUS FIGURE, DEPICTING MOBILITY CHARACTERISTICS FOR CERTAIN ELEMENTS UNDER GIVEN ENVIRONMENTAL CONDITIONS. (OBTAINED FROM SMITH AND HUYCK, 1999).....	24
FIGURE 12: CHARACTERISTICS OF ELEMENTS UNDER SURFICIAL CONDITIONS OR NEAR SURFACE AQUEOUS SYSTEMS (OBTAINED FROM SMITH AND HUYCK, 1999).....	25
FIGURE 13: MAP OF HALIFAX IN 1779 BY J.F. DESBONES OBTAINED FROM NOVA SCOTIA ARCHIVES.....	31
FIGURE 14: MAP OF HALIFAX IN 1784 BY CHARRES BLASKOWITZ, DEPICTING RIVERS AND TOPOGRAPHY OF PENINSULA.	32
FIGURE 15: MAP OF HALIFAX IN 1914 DISPLAY NEW DEVELOPMENT OBTAINED FROM NOVA SCOTIA ARCHIVES.	33
FIGURE 16: POCKWOCK LAKE WATERSHED AND HALIFAX WATER SUPPLY (OBTAINED FROM HALIFAX WATER, 2017).....	38
FIGURE 17: DEPICTING THE LOCATION OF THE HALIFAX COUNTY. (MODIFIED MAP FROM MACDOUGALL ET AL., 1963).....	41
FIGURE 18: OBTAINED MAP FROM GOODWIN 2002 STUDY, DEMONSTRATING LOCATION OF STUDY AREA AND SAMPLING POINTS.....	42
FIGURE 19: DATA FROM HEAVY METAL PILOT STUDY DEMONSTRATES LOCATIONS.....	44
OF SAMPLES COLLECTED (ARCHIBALD ET AL., 2014).	44
FIGURE 20: DEPICTION OF FOLEY, BELL, AND LIVERMAN'S SAMPLE SITE LOCATIONS IN ST. JOHN'S, NEWFOUNDLAND. MAP OBTAINED FROM FOLEY, BELL AND LIVERMAN'S STUDY (2011).	46
FIGURE 21: POPULATION DENSITY MAP OF HALIFAX NOVA SCOTIA, MODIFIED FROM ZACK TAYLOR METAPOLIS CONSULTING BASED ON 2011 CENSUS DATA.	48
FIGURE 22: ILLUSTRATES WORKFLOW FOR THE METHODS SECTION AND RELATION TO GENERAL OBJECTIVES.	49

FIGURE 22: (A) EXAMPLE OF SAMPLE BAGS WITH SOIL DRY	52	FIGURE 22: (B) OPEN BAG FOR SOIL TO AIR DRY	52
FIGURE 23: (A) SIEVING TOOL	55	FIGURE 23: (B) SIEVING INSTRUMENT	55
FIGURE 24: EXAMPLE OF A GEO-REFERENCED IMAGE OF A 1910 MAP ON ARC GIS 10.3 SOFTWARE	58		
FIGURE 25: DEPICTING CONDUCTIVITY, TDS AND PH DATA. (1) DEMONSTRATES A POSITIVE RELATIONSHIP BETWEEN CONDUCTIVITY AND TDS (2) RELATIONSHIP BETWEEN CONDUCTIVITY AND TDS COULD NOT BE IDENTIFIED	60		
FIGURE 26: GRAPHICAL REPRESENTATION OF AVERAGE MANGANESE (MN) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) AT 0-15 CM DEPTH. THERE ARE NO CCME OR NS GUIDELINES FOR MN.	63		
FIGURE 27: GRAPHICAL REPRESENTATION OF AVERAGE ARSENIC (AS) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. BLACK LINES DEPICT CCME (DASHED) AND NS (BOLD) GUIDELINES.	64		
FIGURE 28: GRAPHICAL REPRESENTATION OF AVERAGE IRON (FE) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. THERE ARE NO CCME GUIDELINES FOR FE.	65		
FIGURE 29: GRAPHICAL REPRESENTATION OF AVERAGE LEAD (PB) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. BLACK DASHED LINE DEPICTS THE CCME GUIDELINE.	66		
FIGURE 30: GRAPHICAL REPRESENTATION OF BARIUM (BA) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. BLACK DASHED LINE DEPICTS THE CCME GUIDELINE.	67		
FIGURE 31: GRAPHICAL REPRESENTATION OF AVERAGE STROTIUM (SR) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. THERE ARE NO CCME GUIDELINES FOR SR.	68		
FIGURE 32: GRAPHICAL REPRESENTATION OF AVERAGE COPPER (CU) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. BLACK DASHED LINE DEPICTS THE CCME GUIDELINE.	69		
FIGURE 33: GRAPHICAL REPRESENTATION OF AVERAGE NICKEL (NI) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. BLACK DASHED LINE DEPICTS THE CCME GUIDELINE.	70		
FIGURE 34: GRAPHICAL REPRESENTATION OF AVERAGE ZINC (ZN) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. BLACK DASHED LINE DEPICTS THE CCME GUIDELINE.	71		
FIGURE 35: GRAPHICAL REPRESENTATION OF AVERAGE VANADIUM (V) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. THERE ARE NO CCME GUIDELINES FOR V.	72		
FIGURE 36: GRAPHICAL REPRESENTATION OF AVERAGE CHROMIUM (CR) CONCENTRATION VERSUS PH LEVEL AT (1) 0-5 CM DEPTH AND AT (2) 0-15 CM DEPTH. BLACK DASHED LINE DEPICTS THE CCME GUIDELINE.	73		
FIGURE 37: GRAPHICAL REPRESENTATION OF (1) MN, (2) AS, (3) FE METAL CONCENTRATIONS AT 0-5 CM AND 0-15 CM DEPTH.	75		
FIGURE 38: GRAPHICAL REPRESENTATION OF (1) PB AND (2) BA CONCENTRATIONS VERSUS 0-5 CM AND 0-15 CM DEPTH. (1A) DEPICTS RELATIVELY LOW PB CONCENTRATIONS AND (1B) HAS RELATIVELY HIGH PB CONCENTRATIONS.	76		
FIGURE 39: CONTINUED FIGURE, GRAPHICAL REPRESENTATION OF (3) SR CONCENTRATIONS RELATIVE TO 0-5 CM AND 0-15 CM DEPTH.	77		
FIGURE 40: GRAPHICAL REPRESENTATION OF (1) CU AND (2) NI CONCENTRATIONS VERSUS 0-5 CM AND 0-15 CM DEPTH.	78		
FIGURE 41: CONTINUED FIGURE, GRAPHICAL REPRESENTATION OF (3A) ZN RELATIVELY LOW CONCENTRATIONS AND (3B) RELATIVELY HIGH CONCENTRATIONS AT 0-5 CM AND 0-15 CM DEPTH.	79		
FIGURE 42: GRAPHICAL REPRESENTATION OF (1) V AND (2) CR CONCENTRATIONS RELATIVE TO 0-5 CM AND 0-15 CM DEPTH.	80		

FIGURE 43: REPRESENTATION OF (1) MN CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) MN CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	82
FIGURE 44: REPRESENTATION OF (1) ARSENIC CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) ARSENIC CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	83
FIGURE 45: REPRESENTATION OF (1) FE CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) FE CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	84
FIGURE 46: REPRESENTATION OF (1) PB CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) PB CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	85
FIGURE 47: REPRESENTATION OF (1) BA CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) BA CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	86
FIGURE 48: REPRESENTATION OF (1) CU CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) CU CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	87
FIGURE 49: REPRESENTATION OF (1) NI CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) NI CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	88
FIGURE 50: REPRESENTATION OF (1) ZN CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) ZN CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	89
FIGURE 51: REPRESENTATION OF (1) V CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) V CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	90
FIGURE 52: REPRESENTATION OF (1) CR CONCENTRATIONS DISTAL TO OLD WOODEN BUILDINGS (> 2 M) AND (2) CR CONCENTRATIONS PROXIMAL TO OLD WOODEN BUILDINGS (< 2 M) AT 0-5 AND 0-15 CM DEPTH.....	91
FIGURE 53: (1, 2, 3) SHOW VARIATIONS OF METAL CONTENT WITH PARTICLE SIZE < 2 MM AND < 0.5 MM FOR MN, AS, AND FE.....	93
FIGURE 54: (1, 2, 3) SHOW VARIATIONS OF METAL CONTENT WITH PARTICLE SIZE < 2 MM AND < 0.5 MM FOR PB, SR, AND BA.....	94
FIGURE 55: (1,2,3) SHOW VARIATION OF METAL CONTENT WITH PARTICLE SIZE FOR CU, NI, AND ZN.....	95
FIGURE 56: (1,2,3) SHOW VARIATION OF METAL CONTENT WITH PARTICLE SIZE FOR V AND CR.....	96
FIGURE 57: RANGE OF SOIL TEXTURES BASED ON FIELD TEST DATA: QUALITATIVE RATHER THAN QUANTITATIVE DATA. BLUE SHAPES DEPICT TWO SOIL TEXTURAL GROUPS FOR SAMPLES IN 0-5 CM DEPTH: (1) SANDY-CLAY RICH AND (2) SILTY-CLAY RICH, BOTH GROUPS ARE QUITE LOAMY IN NATURE (OBTAINED FROM USDA, 2017).....	98
FIGURE 58: RANGE OF SOIL TEXTURES BASED ON FIELD TEST DATA: QUALITATIVE RATHER THAN QUANTITATIVE DATA. BLUE SHAPES DEPICT TWO SOIL TEXTURAL GROUPS FOR SAMPLES IN 0-15 CM DEPTH: (1) SANDY-CLAY RICH AND (2) SILTY-CLAY RICH, BOTH GROUPS ARE QUITE LOAMY IN NATURE (OBTAINED FROM USDA, 2017).....	99
FIGURE 59: 1700'S METAL ABUNDANCE MAP DEPICTING POI'S IDENTIFIED IN ORANGE AND OLDER RIVERS DEPICTED AS BLUE LINES.....	101
FIGURE 60: 1800'S METAL ABUNDANCE MAP DEPICTING POI'S FOR BOTH 1700'S AND 1800'S IN BLUE AND ORANGE. RIVERS AT STILL SURFACE DEPICTED AS BLUE LINES.....	102
FIGURE 61: 1900'S METAL ABUNDANCE MAP DEPICTING POI'S FOR 1700'S, 1800'S AND 1900'S WITH ORANGE, BLUE, GREEN AND PINK.....	103

List of Tables

TABLE 1: APPROXIMATIONS OF WORLDWIDE METAL EMISSIONS FROM NATURAL SOURCES INTO THE ATMOSPHERE (NRIAGU, 1989).....	27
TABLE 2: CLASSES THAT CATEGORIZE THE BEHAVIOUR OF ELEMENTS IN FLY ASH (KLEIN ET AL., 1975)..	28
TABLE 3: MODIFIED FROM SIEGEL 2002, LISTED ANTHROPOGENIC PRODUCTS, ACTIVITIES, AND INFLUENCES THAT CONTAIN OR EMIT METALS.....	36
TABLE 4: PROVINCIAL AND FEDERAL GUIDELINES FOR RESIDENTIAL SOILS ADAPTED FROM CCME AND NS CONTAMINATED SITES REPORTS AND TABLES (CAREY ET AL., 2014; CCME, 1999).....	40
TABLE 5: SAMPLES ABOVE CCME AND NS RESIDENTIAL ABOVE METAL GUIDELINES WERE SIEVED; THE TABLE PROVIDES AN OUTLINE FOR CHOOSING SAMPLES TO BE SIEVED.....	54
TABLE 6: TABLE DEMONSTRATING PH AVERAGES AND PH RANGES OF SOIL FOR EACH LOCATION AND FOR THE SAMPLES TAKEN AT THAT LOCATION.....	61
TABLE 7: P-VALUES CALCULATED FROM UNEQUAL VARIANCE T-TEST.....	81
TABLE 8: PRELIMINARY URBAN BACKGROUND FOR SAMPLES CLOSE TO AND FAR AWAY FROM OLDER WOODEN BUILDINGS.....	92

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1.0 Introduction

1.1 General Statement

The use of a holistic approach is required to adequately understand and assess the complexity of the earth system. Soils are a component of the earth system that interacts with the surficial environment and can be defined as composite of material that is produced from weathering and erosion processes (Drever, 1997). The health of ecosystems is reliant on the abundance, presence, and absence of heavy metals or metalloids within a soil (Siegel, 2002). Contamination of these ecosystems by potential toxic metals or metalloids is a global issue that is expected to increase in concern alongside rapid urbanization growth (Ljung et al., 2006). Cities are anthropogenic hubs that have become stations of industrial development and high population density (UN, 2014). Over half of the world's population currently resides in urban areas, an amount that is forecasted to increase to 66 % by 2050 (Ljung et al., 2006; UN, 2014). A soil's chemical composition is influenced by the composition of the parent material such as bedrock, providing the potential for naturally elevated metal concentrations or natural contamination (Drever, 1997). In addition, cities influence metal abundance of soils by the presence of certain anthropogenic influences, such as waste disposal sites, traffic emissions, industrial emissions, effluents, and other products containing potentially toxic metals or metalloids (Siegel, 2002).

There are two major concerns that address the significance for studying urban soils:

1. High metal concentrations in urban soils have the potential to impact the health of the urban inhabitants (especially children) and the immediate environment.
2. Canada lacks a unified standard methodology for evaluating metal concentration within urban soils.

Health impacts from the ingestion of heavy metals or metalloids from soils often occurs through inhalation, food and drinking water (Crouse et al., 1983). Exposing humans to metal toxicity can manifest in many different ways and over a long period of time. The number of inhabitants with the potential to be affected by metal toxicity will continue to rise as population density increases in urban areas (Yu and Li, 2011). Furthermore, as population increases, more people are in close proximity to sites of concern, increasing the likelihood of inhabitants becoming exposed to metal toxicity.

The aim of this study is to provide an all-encompassing holistic approach to broaden the capacity to which we can evaluate urban soils. The holistic approach used in this study is divided into two strategies, the geochemical assessment of urban soils and use of Geographic Information System (GIS) methods to evaluate the influences of city development of Halifax soils. A number of questions have been raised to guide the objectives of this study:

1. What are the conditions of Halifax soils and soil properties (pH, conductivity, TDS and texture)?
2. What does metal content and soil properties infer about the health of Halifax soils based on residential CCME and NS contaminated sites guidelines?
3. What can be inferred about metal mobility based on metal content and soil properties?
4. Does it make a difference whether a sampling method uses 0-5 cm depth-based samples opposed to 0-15 cm depth-based samples; what does that infer about sampling protocols and guidelines?
5. How do metal concentrations vary with location, proximal (< 2 m away from older wooden buildings) and distal (> 2 m away from older wooden buildings) older wooden buildings? Do these older wooden buildings act as anthropogenic point sources, and if so for which metals?
6. What does metal abundance relative to depth and particle size suggest about metal accumulation?
 - a. How does metal concentration vary with 0-5 and 0-15 cm depth based samples?

- b. How does metal concentration vary with < 2 mm and < 0.5 mm grain size?
7. Can an urban background for metal concentrations be provided from depth-based sampling data that is representative of Dalhousie Studley Campus soil and to an extent Halifax city soils?
8. What potential anthropogenic influences are acting on Halifax soils and how does this change through the process of city development?
9. What does the analysis of Halifax soils infer about how to approach the assessment of metal content within urban soils? What recommendations can be made?

By attempting to answer these questions we can gain a stronger understanding regarding the evaluation process for urban soils and the role of evaluating urban soils for the future.

1.2 Purpose of Study

Currently, Canada lacks a unified standard methodology for studying urban soils. Having a unified method would aid in the effectiveness of environmental and health risk assessments. It would further the identification of trends and anomalies by providing commonalities when comparing studies. The lack of a unified standard methodology for evaluating urban soils is due in part to the underlying issue of variability. When evaluating the metal content in urban soils one must consider both large and small-scale factors. Some of these factors may include: regional geology, climate, topography, soil composition, soil properties, anthropogenic influences, metal behaviour, and the variability of these factors over time (Siegel, 2002). In Nova Scotia, recent glaciation has stripped older soils in some areas and deposited till in others, further influencing the nature and composition of the soils. Furthermore, certain anthropogenic activities that contribute to elevated metal(s) concentrations in soils are relatively widespread, making the issue of elevated metal(s) a significant concern for all urban areas.

Although there is a lack of a unified methodology for studying urban soils, there are broad guidelines provided both federally and provincially on acceptable metal concentrations within soil, for both human (Health Canada) and environmental health (Environment Canada).

Both federal and provincial guidelines aim to contribute precautionary steps and procedures for sampling and assessing soils; however, procedures that are used for evaluating soils vary on both federal and provincial levels and depending on the type of assessment (environment versus human health, for example). This study aims to investigate how best to evaluate urban soils within the city of Halifax and gain an understanding of how to approach the creation of a standard methodology for city soil evaluation. This is addressed by assessing the variability of soils on Dalhousie Studley Campus, central and near to downtown Halifax, (Figure 1).



Figure 1: Halifax map of the downtown core, depicting study area with orange box.

The study predicts anomalous metal abundance locations, evaluates soil variability, metal concentration and metal mobility, creates a preliminary urban background based on sample depth, particle size, pH, conductivity and total dissolved solids (TDS), and soil texture. Sample depths are chosen based on Health Canada (0-5 cm depth) and Environment Canada (0-15 cm depth) sampling guidelines (CCME, 1999). Provincial and federal metal concentration guidelines are used as a foundation for evaluating the acceptable metal content in Halifax soil.

By assessing the uncertainties that exist and proposing key considerations that are critical to developing an for metals in soils in Halifax, this study will aid the larger overarching issue, which is to develop a unified method for evaluating urban soils.

2.0 Background

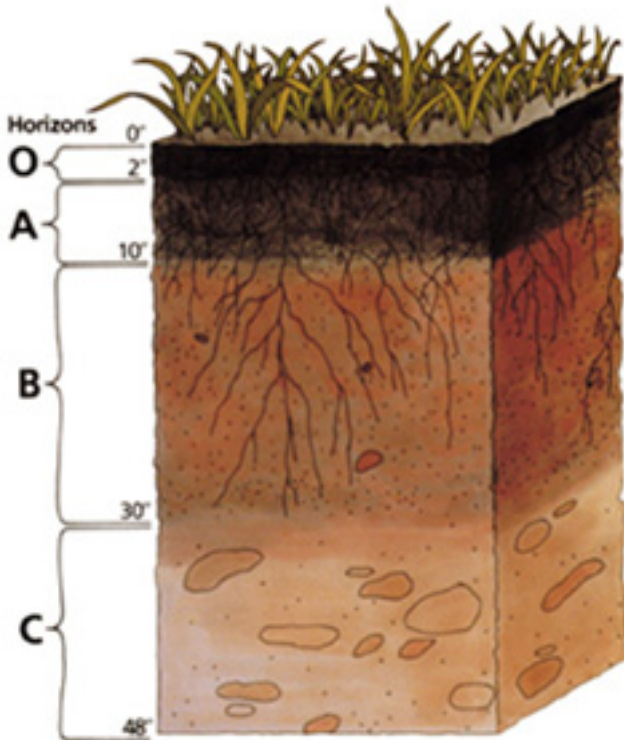
2.1 Defining Soils

Summarized by Siegel (p. 18-21) soils are a product of the weathering process, which involves the disintegration and decomposition of preexisting rock when exposed to air, water, and organisms at or near to the earth's surface (Drever, 1997). Under ambient conditions, stable new minerals and solid particles form from the weathering process resulting in the formation of soils. Soil development rates range from 100s to 1000s of years and depends primarily on temperature, precipitation, topography, drainage, vegetation, biological activity, parent rock, and time (Strakhov, 1960). All of these factors define a soil's chemical make up, chemical mobility and bioavailability.

The natural chemical composition of soils commonly reflects the composition of the rock from which it originated (Simpson and Beck, 1965). Since bedrock varies regionally, chemical composition of the soils will as well, resulting in varying baselines or natural background concentrations of metals in soils within different areas. For example, soils formed from basalts can be expected to have elevated metal concentrations of Cr, Ni, and Co, relative to soil formed from bedrock of granitic composition (Siegel, 2002). It is also important to consider other natural influences or geological processes that contribute to the chemical composition of soils. Glacial processes can have a strong influence on soil chemical composition (Selinus, 1995). When glaciers melt they deposit till as a blanket of unsorted sediment of variable thickness. Soils form from these sediments and if high metal values are found in till, these values will also be reflected in till-based soil.

Overtime, soils differentiate into distinct horizons, comprising a soil profile (Drever, 1997). Each horizon is composed of different proportions of earth materials, (Figure 2). There are four main horizons, O, A, B, and C, which can be further subdivided

(Drever, 1997). The O-horizon is the organic horizon composed mostly of organic matter and decomposing vegetation (humus). The next horizon below, A-horizon is composed of mineral and organic phases, which are subject to leaching as rainwater infiltrates downward (Drever, 1997).



O – Mostly composed of organic matter including decomposing leaves, twigs etc.

A – Comprised of mineral and organic matter. Zone of leaching occurs to the B horizon through the process of eluviation by rain, groundwater or other fluids that can move clay and dissolved elements. Lower part of the A horizon encompasses the E horizon.

B – This horizon is known as the horizon of accumulation (illuviation). Earth materials within this horizon are enriched in clay, Fe-oxides, CaCO_3 and other constituents leaching from the overlying A horizon.

C – Composed of partially weathered (disintegrated) parent rock.

Figure 2: Soil layers classified depict horizons that develop in temperate humid climate. Figure at left is obtained from the USDA and description is modified from Siegel, 2002.

Seeping waters move clay size particulates and mobilized chemical elements into the underlying B-horizon. The C-horizon is composed of partially altered parent rock from which the soil is continually forming. The underlying material is unaltered parent rock (Drever, 1997).

2.2 Urban Soils

Factors that are considered fundamental migration pathways for metal distribution and deposition within a soil may be affected to some degree by anthropogenic activities (Smith and Huyck, 1999). For example, the presence of metals in air particulate matter can be caused by coal power plant emissions. Urban soils are more likely disturbed due to anthropogenic activities and affected by physical transport and dispersion through city development and growth, thus hindering development of a defined soil profile, particularly in recently developed sections of a city (Smith and Huyck, 1999). The metal concentration and composition of particulate matter transported through rivers or streams can be affected by effluent from certain industries. City development can also influence the presence and redirect the flow pathway of rivers and streams, thus influencing where material may be deposited (Siegel, 2002). Anthropogenic activities, city development, infrastructure, and certain industries can shape the immediate environment of an urban area, affecting the conditions to which an urban soil may develop, and form its physical characteristics and chemical composition (Siegel, 2002). For the purpose of this study, urban soils will be defined as regosols that are strongly influenced by anthropogenic undertakings. In this case, regosols are defined as loose material above bedrock.

2.3 Soil Variability and Assessment

Soils act as the geologic medium for an open system, allowing for various processes to interact, interrelate, and contribute to the conditions of the soil over time. A given region will have different natural or geologic processes that influence the background metal concentrations within the soils (Drever, 1997). Local or small-scale factors, such as soil properties, pH, and conductivity will vary within a given area, influencing metal mobility, immobility and thus accumulation. In addition, metals will vary in horizontal and vertical extent (Siegel, 2002). Metal concentrations will vary with depth, in different soil horizons if developed, particle sizes and in the presence or absence of organic matter.

Understanding how the presence or absence of metals affects an ecological system is

vital in evaluating a given ecological systems health. Determining what metals are bioaccessible and bioavailable aids our understanding of what metals are potentially toxic to organisms within an ecological system (Dupuis, 2013). Bioaccessibility of a metal can be defined as the potential for a metal to enter an organism's system (Dupuis, 2013). Bioavailability refers to the metals that are available within the environment and able to enter an organisms system (Dupuis, 2013). However, before determining the availability of a metal and the impacts on an ecological system, one must determine which metals are present, and if present, in what quantities. This study aims to access the presence and amount of potentially toxic metals in urban soils for 0-5 cm and 0-15 cm soil fractions and for particle size < 2 mm and < 0.5 mm. Evaluating a soil's health is complex, understanding the relationship of developing toxicity to the health of the environment and organisms within it, even more so.

2.4 Halifax Soil

Most of Halifax soils may be considered as immature soils that have not had time to develop due to the amount of disturbance and human activity (regosols). The Halifax county soils overall are classified to range from stony loam to sandy/silty loam soil texture (MacDougall et al., 1963). However, the type of soil and how it develops within Halifax varies depending on the abundance of vegetation present, whether the soil classified is in an area of poor or good drainage, the amount of till veneer present and which bedrock formation it has developed from and the extent of anthropogenic influences (MacDougall et al., 1963).

2.5 Halifax Study Area

The study area for this project is mainly focused on the Dalhousie Studley Campus, (Figure 3). Some of Dalhousie campus buildings are older wooden buildings, that are approximately over > 60 years of age, but other locations on campus are much more recently disturbed due to landscaping or building development in recent years.



Figure 3: Study area at Dalhousie Studley Campus and sample locations depicted in different coloured circles.

2.6 Halifax Soil Development

Soils are formed from parent materials by the weathering process that is contingent on a region's climate, vegetation, topography, drainage and time (MacDougall et al., 1963). The natural effects of these factors for soil development within Halifax are described below. A significant step in understanding the composition of our soil, involves

understanding the parent material from which Halifax soil develops. There are two parent materials that are significant towards this study: Halifax's bedrock and glacial till.

2.6.1 Halifax Bedrock

The Meguma zone lies south of the Cobequid-Chedabucto Fault zone that runs through mainland Nova Scotia, (Figure 4). The southwestern portion of this zone consists of Cambrian – Ordovician sedimentary rocks and Devonian granitic rocks. Sequences of sedimentary and volcanic rocks of Carboniferous and Triassic age overlay these formations. This section will focus on the geologic record responsible for influencing metal concentrations reflected within Halifax soils.

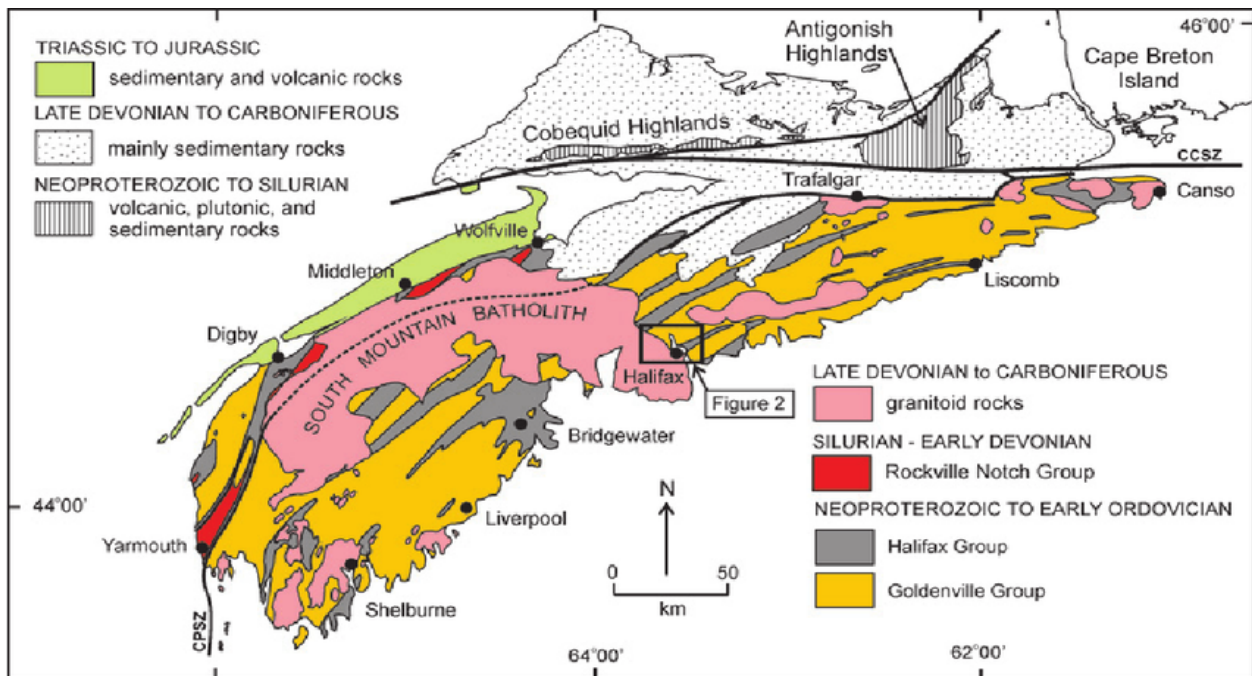


Figure 4: Simplified geologic map depicting Meguma terrane of southern Nova Scotia. Location of Halifax shown with black box. CCSZ (Cobequid-Chedabucto shear zone) and CPSZ (Chebogue Point Shear Zone). (Figure adapted from White and Goodwin, 2011).

Halifax is underlain by three main geological units, which can be broken down into subunits (Figure 4 and Figure 5). The Goldenville Group is the oldest unit within the Halifax Regional Municipality (HRM) and is divided into two formations: Taylors Head Formation and Beaverbank Formation (White and Goodwin, 2011). Taylors Head

Formation is composed of thickly bedded and weakly cleaved grey metasandstone interbedded with green to grey, cleaved metasilstone, and black to rusty coloured slate. Calc-silicate nodules and pyrite cubes are common. The Beaverbank Formation conformably overlies the Taylor's Head Formation and its contact can be identified by the decreasing thickness of metasandstone beds (White and Goodwin, 2011). The Beaverbank Formation consists of grey to black cleaved metasilstone interbedded with thin grey metasandstones and black graphitic slates. Brown to black manganese rich limestone beds and nodules are considered common. Close to the granitic contact of the South Mountain Batholith (SMB), manganese rich limestone beds and nodules were baked into garnet (spessartine) rich coticles (White and Goodwin, 2011).

The other significant geologic unit to consider, the Halifax Group, is subdivided into the Cunard and Bluestone formations, (Figure 5). Within Halifax, the Cunard Formation conformably overlies the Beaverbank Formation of the Goldenville Group. This formation is characterized by black, rusty weathered surfaces, graphitic slate and metasilstone interbedded with fine-grained, cross laminated, metasandstone (White and Goodwin, 2011). The Cunard Formation contains typically an abundance of pyrrhotite and pyrite, with lesser amounts of chalcopyrite, galena, sphalerite and arsenopyrite, where as the conformably overlying Bluestone Formation consists of grey-bedded metasilstone and slate, with a small presence of metasandstone and calcareous nodules (White and Goodwin, 2011). The Bluestone Formation, unlike the underlying Cunard Formation, generally lacks sulphide minerals (White and Goodwin, 2011).

The Goldenville and Halifax groups were regionally metamorphosed to greenschist facies and were deformed into northeast striking upright folds during the Neocadian Orogeny (406-388 Ma) (White and Goodwin, 2011). The SMB intruded into the Goldenville and Halifax groups from 380-373 Ma, creating a narrow, metamorphic contact aureole that baked regional greenschist facie mineral assemblages and textures (White and Goodwin, 2011). A major northwest striking shear zone is present in the contact aureole neighboring the northeastern margin of the SMB and was active during intrusion (White and Goodwin, 2011).

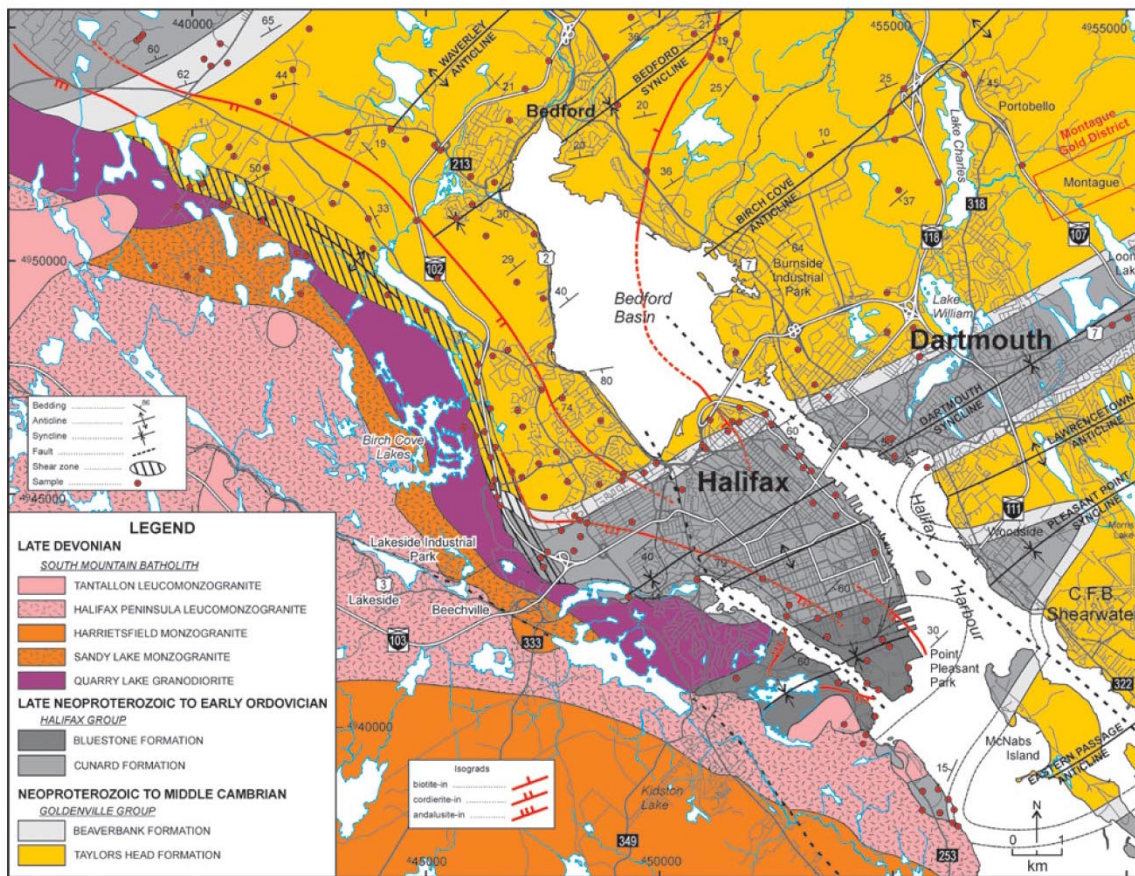


Figure 5: Simplified geologic map of Halifax Regional Municipality. (Modified from White and Goodwin, 2011.)

The SMB is composed of 5 distinct groups (Figure 5). The oldest of these groups is the Quarry Lake granodiorite, which resides along the contact of the country rocks. This unit contains an abundant amount of metasedimentary xenoliths (Macdonald and Horne 1987).

Towards the southwestern interior of the batholith, several units are defined: Sandy Lake and Harrietsfield monzogranites, and the Halifax Peninsula leucomonzogranite. These units range from fine to coarse grained to megacrystic monzogranite to leucomonzogranite (Macdonald and Horne 1987; MacDonald 2001). Subsequently the medium grained lucomonzogranite intruded these units (White and Goodwin, 2011) .

2.6.2 Glacial Till

In the last 70 000 years, surficial glacial deposits and associated landforms were shaped by the Wisconsinan glaciation. Nova Scotia has a relatively complex ice flow history based on the evidence provided by superimposed till sheets and multiple flow direction indicators (Goodwin, 2004). The oldest flow patterns represent movements that occurred towards the east and southeast, responsible for the deposits of the Hartlen Till. The Hartlen Till is composed of tightly compacted metasediments and granitic clasts associated with the Caledonia Phase that occurred from 75-40 thousand years ago (ka) (Goodwin, 2004). South and southwest ice flows followed, denoting the Escuminac Phase that occurred from 22-18 ka. These deposits make up what is known as the Lawrencetown Till, which derives from Carboniferous redbeds from northern Nova Scotia, Prince Edward Island, and erratics from Cobequid Highlands. From 18-15 ka, an ice flow diverged to create the Beaver River Till. The Beaver River Till is classified as a diamicton that is mostly derived from local bedrock sources and can be categorized into three distinct lithological units: granites, slates and metasandstone facies (Goodwin, 2004). The Chignecto Phase from 12-12.5 ka represents the decline of the Scotian Phase glacier and is characterized by small ice caps and shifting ice flow (Goodwin, 2004). Halifax is mainly covered with till veneer, which comprises of the Beaver River Till deposited by sub-glacial erosion and has a thickness that ranges approximately from 0.5-5 metres (m) (Figure 6). Depending on the given area, thickness and coverage of bedrock varies (Utting, 2011). Drumlins are landforms that are featured throughout Halifax large remnants of glacial deposits, (MacDougall et al., 1963).

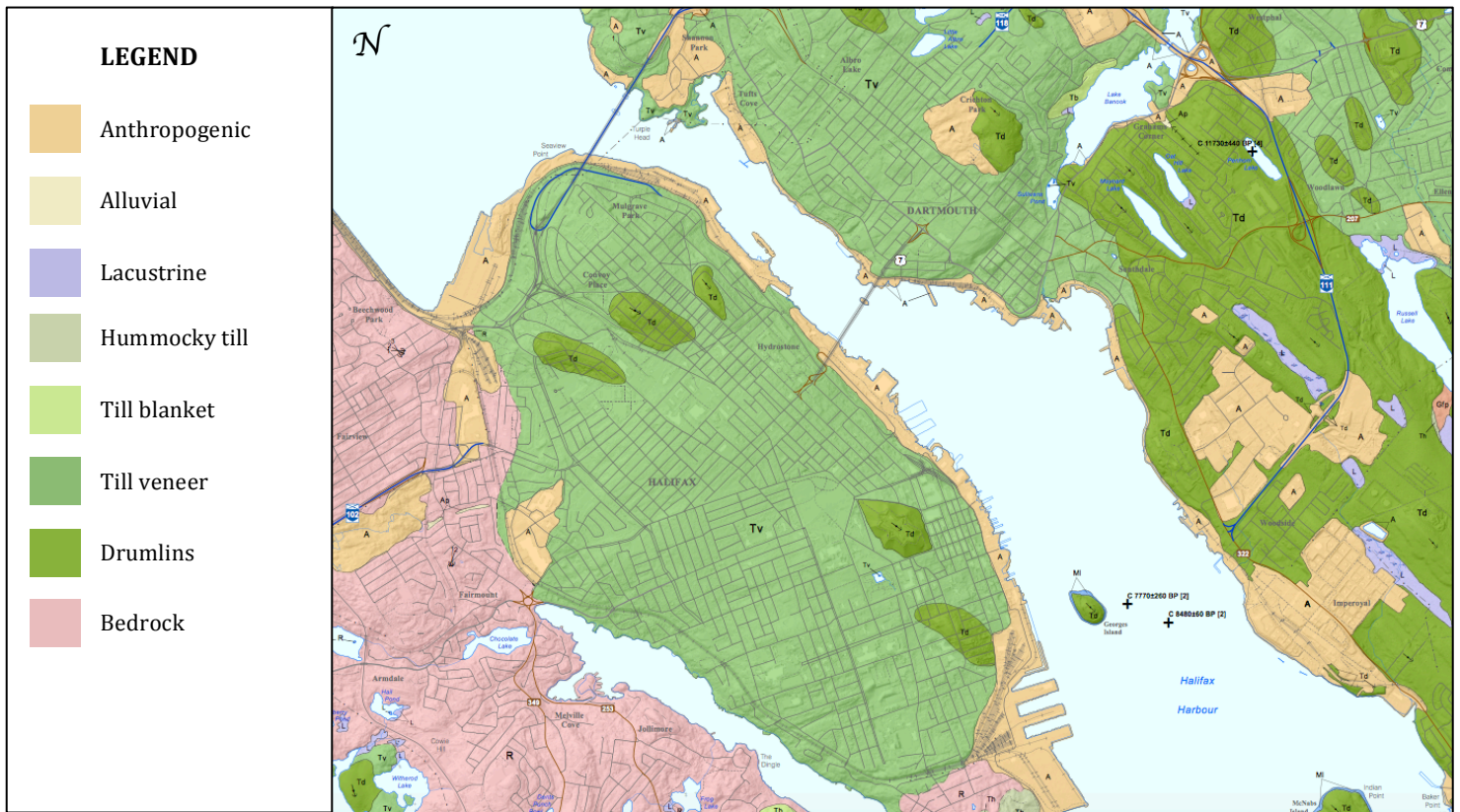


Figure 6: Surficial geological map of Halifax modified from the Department of Natural Resources database page (Utting, 2011).

2.6.3 Naturally Elevated Metals in Soils

The Taylors Head Formation is typically low in CaO and MnO, where as the metasilstone rich Beaverbank Formation is higher in CaO and MnO, with the metasilstone and slate having higher concentrations than the metasandstone (White and Goodwin, 2011). Coticule nodules and layers have higher MnO, CaO and Fe₂O₃. Within the overlying Cunard Formation there is low concentrations of CaO and MnO, however Fe₂O₃ is high in concentration (White and Goodwin, 2011). The Bluestone Formation is similar in concentrations of CaO, MnO and Fe₂O₃.

Both the Goldenville and Halifax Group are rich in sulfides and it is generally known that there is a positive correlation between sulfides and metals of Cu, Pb, Zn, however only the Cunard Formation from the Halifax Group, reflects this trend (White and Goodwin, 2011). In the HRM most of the enrichment of metals containing Pb, Zn, Cu, and As appear in association within the contact aureole and metamorphic effects from the SMB according to the acid rock drainage study by White and Goodwin (2011). In summary, metals to

consider that may be naturally elevated in Halifax soils are Mn, Fe, and As. Near the contact it is important to note that Pb, Zn, and Cu may also be naturally elevated (White and Goodwin, 2011).

In terms of glacial deposits and the influence of surficial till on metal concentrations within soil it is important to recognize that much of Halifax is lightly covered by till veneer, which ranges in thickness from 0.5 to 5 m. Since the Beaver River Till is derived from local sources, the elements in which it would be enriched are similar to that of the bedrock discussed in detail above (Goodwin, 2004; Utting, 2011). However, depending on the depth of the till veneer influences of metal concentrations within the soil may only influence the soil profile that is near to surface, but this also depends upon how much leaching is prevalent within the soil as it develops.

2.6.4 Climate and Vegetation

The climate of Halifax is moderately humid with few extremes in temperature during the winter and summer months (MacDougall et al., 1963). From the 1970s to the 2000s average temperatures have not varied to a great extent. Winter temperature averages often range from -6°C to -2°C (Statistics Canada, 2016). Summer average temperatures range 14°C to 18°C based on the temperature data provided from 1970 to 2000's, (Figure 7).

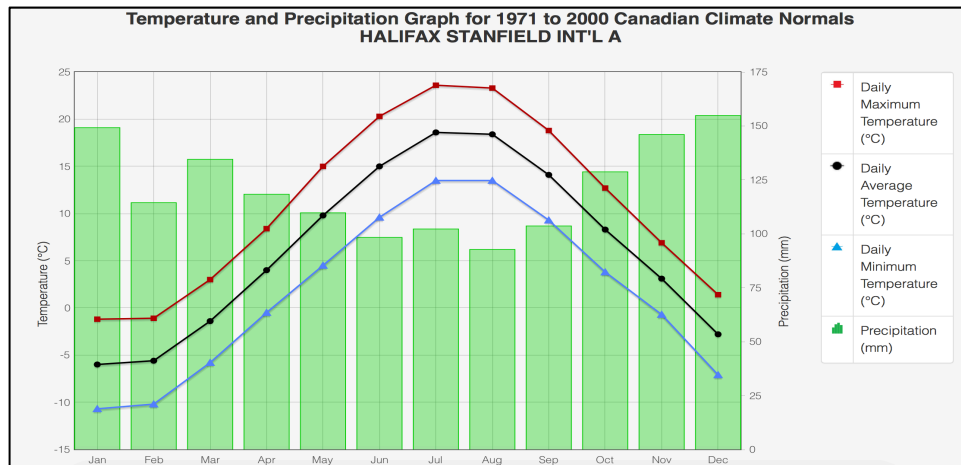


Figure 7: Adapted graphical representation of average precipitation data from between 1971-2000, (Modified from Statistics Canada, 2016).

Within an urban area, the native vegetation presence will vary, especially with the strong influence of anthropogenic activities on the type of vegetation present, the location of vegetation present and vegetation abundance. Vegetation is mainly present in parks, along boulevards and in residential districts of the city. Generally, however, poorly drained areas naturally support stunted stands of fir, black spruce, red maple, tamarack, hemlock and alder, whereas well drained areas may contain more forest growth such as soft wood species, like red spruce, balsam fir, black spruce, white spruce, hemlock and pine and hardwoods such as red maple, yellow birch, white birch and other such as white ash, sugar maple and beech (MacDougall et al., 1963).

2.6.5 Topography and Drainage

Underlying metasediments of Halifax have been steeply folded and faulted, resulting in bedrock that is susceptible to erosion and weathering, creating undulated topography, (Figure 8) (MacDougall et al., 1963). The slates are softer, which is more conducive to erosion than harder metasandstones. Smoother slopes and ridges characterize metasediments of the Halifax and Goldenville Groups (MacDougall et al., 1963).

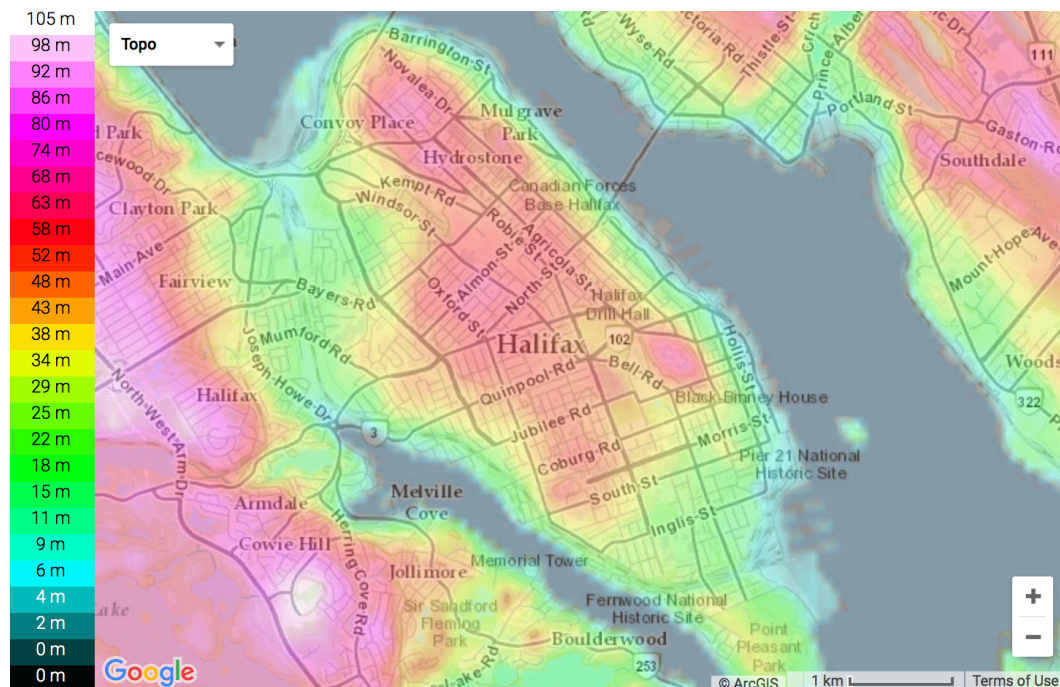


Figure 8: Topographic and elevation map of Halifax (topographic maps, 2017).

2.7 Factors to Consider for Metal Concentration, Mobility and Dispersivity

Metal contaminants can physically spread or become chemically mobile, depending upon the conditions of the soil and the conditions of the region (Smith and Huyck, 1999). The controlling parameters of metal mobility and immobility often involve factors such as pH, redox potential, and temperature (Siegel, 2002). These factors can be assisted by bacterial processes, which influence the solubility, mobilization, and precipitation or deposition of potentially toxic metals (Smith and Huyck, 1999). Other parameters that influence metal mobility and concentration include texture of the soil (grain size), composition (mineralogy and organic matter), and water (rivers, streams, precipitation) (Siegel, 2002). All of these factors vary from one location to another, especially with different influences, which contribute to a soil's chemical composition (bedrock, till, anthropogenic influences) (Smith and Huyck, 1999).

In urban environments, contributions to the metal soil budget also commonly come through physical spreading of metals. Physical spreading of contaminants or transport may occur through moving water (i.e. surface water such as rivers or streams), anthropogenic redistribution of soil (physically picking up soil and moving), airborne dust particles (short transport) and long-range atmospheric transport (Ljung et al., 2006). Even if certain substances carrying potentially toxic metals are now appropriately contained or banned, this will not prevent the accumulation of pre-existing metal abundance as a result of past usage. Even in cases where point source contaminants have been removed, metals associated with past point source contamination may still be found within the soils (Ljung et al., 2006).

It is important to recognize the conditions that exist and identify which metals based on these conditions may be more mobile than others. This section focuses on clarifying the associations and behaviour of metals that are used to predict metal mobility based on the chemical and physical properties of metals, geochemical associations, gradients, barriers, and environment conditions that affect mobility and dispersivity within the surficial environment.

2.7.1 Chemical and Physical Properties of Metals

The behaviour of an element or a particular metal in an environment is dictated by their innate chemical or physical properties. The chemical and physical properties of elements are reliant on how atoms exchange, interchange, and share valence electrons (Nordstrom, 1999). There are four main components that are vital towards an element or metal's behaviour: electronegativity, oxidation state, ionic radii, and ionic potential (Smith and Huyck, 1999). Electronegativity, which is the tendency for an atom to require a negative charge, is usually indicative of the type of compounds and chemical bonds an element will form (Huheey, 1993). For example metals commonly have low electronegativity, are easily ionized and tend to combine with non-metallic elements of high electronegativity. Oxidation states will influence an element's geometry, ionic radius (size), binding sites and chemical reactions, which are significant in accounting for an element's behaviour in different compound forms. Ionic radius or size of an ion is dependent on oxidation state. Ionic radius determines whether an element can take part in a given reaction and can also allow for substitution to occur based on similar ionic radii and charge (Cotton and Wilkinson, 1988). A significant example of this is Cd^{2+} substituting in for Ca^{2+} in geochemical and biological systems. Depending on concentrations, this can hold the potential for toxic affects (see section 2.8 on Metal Toxicity). Ionic potential of a given element is commonly correlated with an element's mobility (Rose et al, 1979). Elements with low ionic potential are generally more mobile in aquatic environment as cations (e.g. Na^+ , Ca^{2+}) and elements with high ionic potential tend to be mobile as oxyanions (e.g. SO_4^{2-} , MoO_4^{2-}). Elements with high ionic potential allows for the formation of covalent bonds rather than ionic bonds. Elements with intermediate ionic potential tend to strongly sorb or hydrolyze and exhibit low solubility resulting in immobility (Smith and Huyck, 1999). Identifying an element's ionic potential acts as a tool for understanding how elements with different chemical properties behave similarly in terms of their mobility within a given environment (Figure 9) (Rose et al., 1979).

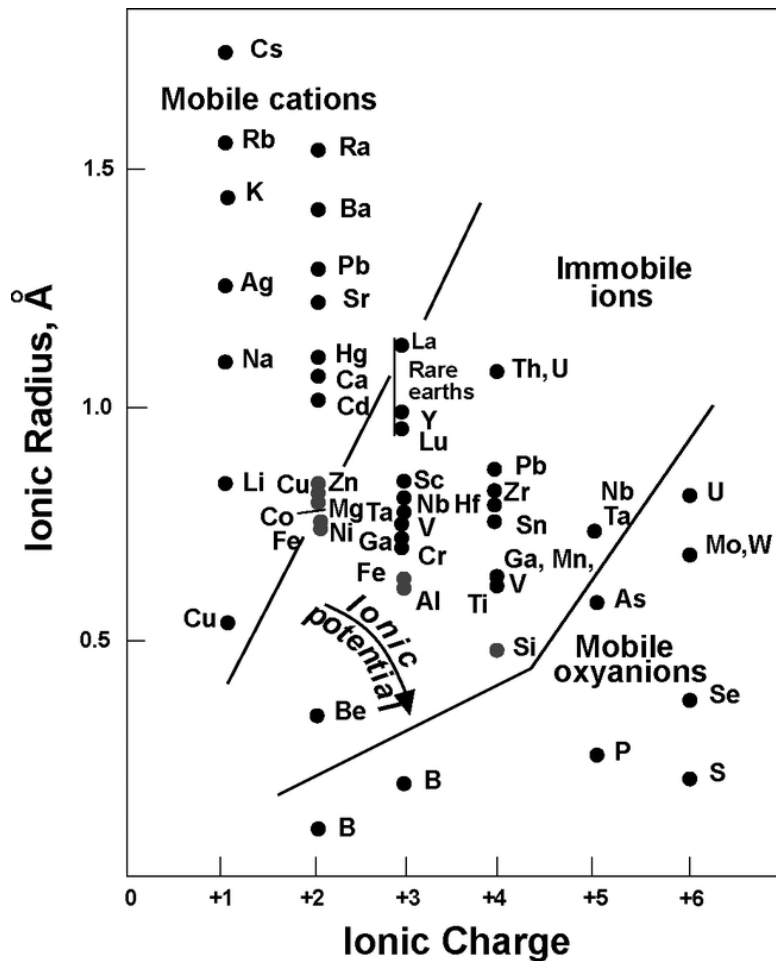


Figure 9: Mobility of elements within the surficial environment in relation to ionic potential (Rose et al., 1979).

2.7.2 Geochemical Associations, Gradients and Barriers

Understanding geochemical associations, gradients and barriers is useful for predicting element mobility and dispersivity in soils, sediments, water and air. Geochemical gradients reflect gradual changes of a landscape, such as vertical and horizontal distribution of certain elements from a mineral deposit or a given point source with idealized constant lithology (Perel'man, 1977). For a given element, anomalous concentrations eventually decline to a background concentration at some distance from a given deposit or point source. A prime example of a point source would be concentrations of a plume for some metals or elements downwind of a smelter (Perel'man, 1986). Geochemical barriers on the other hand denote abrupt changes in physical or chemical environment reflecting a disruption in the path of migration of elements resulting in

associated element accumulation, concentration, or precipitation of elements from a solution. (Perel'man, 1986; Nordstrom and Alpers, 1999).

Geochemical barriers involve mechanical, physiochemical, biochemical and anthropogenic instigators, all of which may fall into categories of physiochemical barriers, which include acid, alkaline, reducing, oxidizing, evaporation, adsorption, and thermodynamic barriers. Acidic barriers develop when pH drops resulting in conditions under which certain elements will form anions (e.g. molybdenum) and certain complexes become less mobile (Nordstrom and Alpers, 1999). For metals that form cations (e.g. copper) the drop in pH allows these metals to become more mobile. Solubility relationships are also significant within these conditions, for example aluminum is relatively soluble at low pH, but precipitates in more basic conditions between a pH of 5 and 9. However, silicon is relatively insoluble at low pH and becomes more soluble in more basic conditions. Alkaline barriers mostly retains elements that migrate easily under acidic conditions and precipitate as hydroxides or carbonates (e.g. Fe, Al, Cu, Ni, and Co). Reducing barriers develop with the absence of free oxygen or other electron acceptors and can be divided into barriers that contain hydrogen sulfide and those that do not: the latter are known as reducing gley environments (Nordstrom and Alpers, 1999). Reducing hydrogen sulfide barriers occur where oxidizing or reducing conditions come in contact with a reducing hydrogen sulfide environment, with sulfide minerals, or when deoxygenated sulfate rich water interacts with an accumulation of organic matter. Reducing gley barriers may form when water infiltrates soil or weathering bedrock and free oxygen is lost or consumed (Perel'man, 1986). Elements such as selenium, copper, uranium, molybdenum, rhenium, vanadium, chromium, silver and arsenic are known to accumulate at some reducing gley barrier conditions (Perel'man, 1986). Oxidizing barriers result when oxygen is introduced into anoxic conditions or when anoxic groundwater is discharged into the surficial environment. Precipitation of iron and manganese may occur at these barriers. Hydrous iron and manganese oxides are known as good sorbents for metals (e.g. Cu and Co), complex barriers may form by combining an oxidizing barrier with adsorption barrier (Nordstrom and Alpers, 1999). Oxidizing-reducing conditions (pH and Eh) can form naturally in a number of different environments. These characteristics of a

given environment is important for understanding the type of geochemical barriers that might be present in different conditions (Figure 10) (Nordstrom and Alpers, 1999).

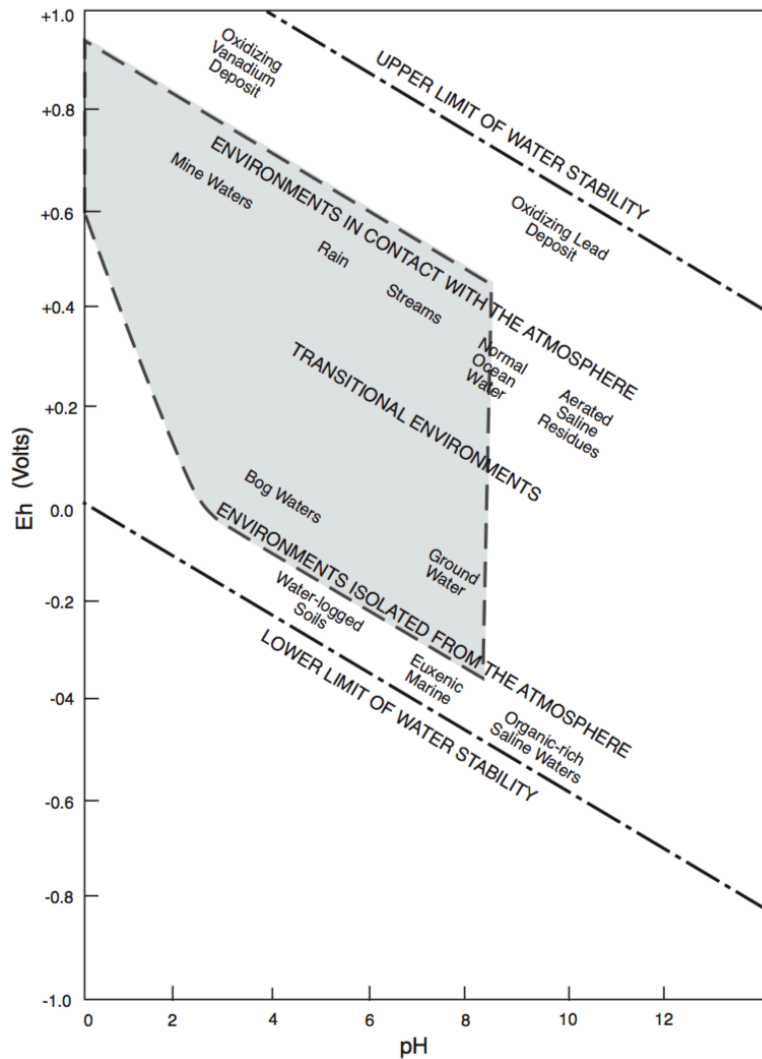


Figure 10: Eh and pH conditions in near surface environments. Shaded area are approximate conditions for geologically and geochemically diverse mine drainage waters (Plumlee et al., 1999 and Modified from Smith and Huyck, 1999).

Evaporation barriers indicate the presence of salt crusts or efflorescent salts. Sodium, magnesium, calcium, chlorine, sulfur and carbonate salts precipitate at these barriers. Evaporation barriers may temporarily relate to changing climatic conditions (e.g. dry versus wet season) (Nordstrom and Alpers, 1999). Adsorption barriers are typically considered complex barriers, common sorbents such as hydrous iron, aluminum,

manganese oxides, organic matter and clay minerals, hold different affinities for elements under specific geochemical conditions (Smith, 1999). Thermodynamic barriers commonly form in areas with temperature and pressure variations. For example, in the case of degassing of carbon dioxide rich ground water, as pressure drops, deposition of carbonate minerals occur. Elements such as lead and cadmium can precipitate as carbonate minerals or co-precipitate with CaCO_3 due to similarities in atomic properties of calcium with lead and/ or cadmium, such as ionic radius discussed in section 2.7.1 (p. 16-17). Barrier types are complex especially when two or more barrier types are superimposed (Nordstrom and Alpers 1999). These concepts are vital towards understanding and anticipating element transport, mobility, accumulation, and distribution in the surficial environment (Perel'man 1977,1986; Smith and Huyck, 1999).

2.7.3 Metal Mobility with Varying Environmental Conditions

In surficial environments it is difficult to predict and evaluate quantitatively metal mobility and behaviour. Mobility, rather, should be considered heuristically as the behaviour of elements under changing environmental conditions, Figure 11(a-e) (Smith and Huyck, 1999). Although the data from Figure 11(a-e) is derived from a wide range of information regarding mine-drainage systems we can use this information to provide a generalization of trends and relative mobility of elements under different surficial conditions (Smith and Huyck, 1999). It is important to note that some elements are more redox sensitive than others (Figure 12). For example, chromium (VI) is more toxic, and more mobile in soils than Chromium (III). By comparing data in two periodic tables provided in Figure 11 (a-e) it is possible to estimate the behaviour of a given element at acidic or alkaline geochemical barrier under oxidizing conditions.

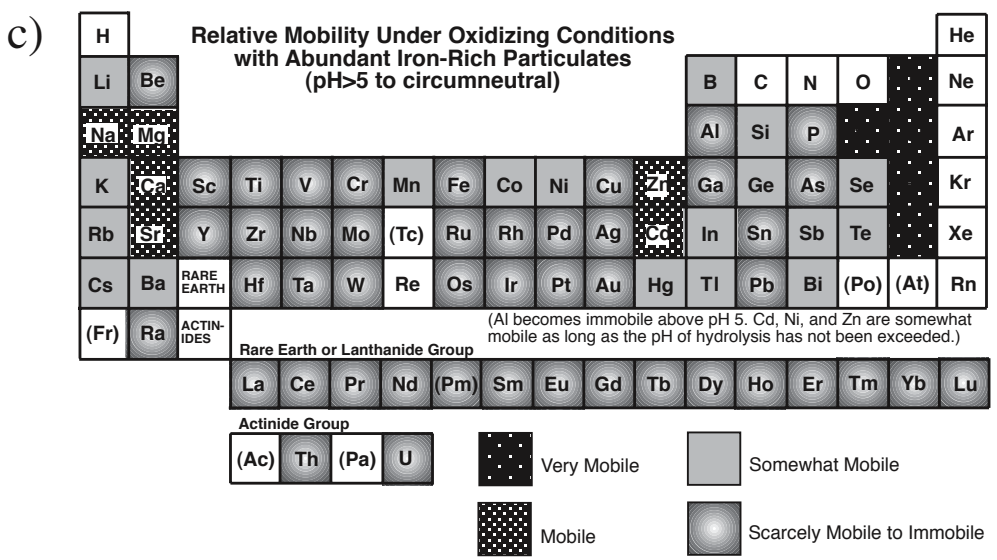
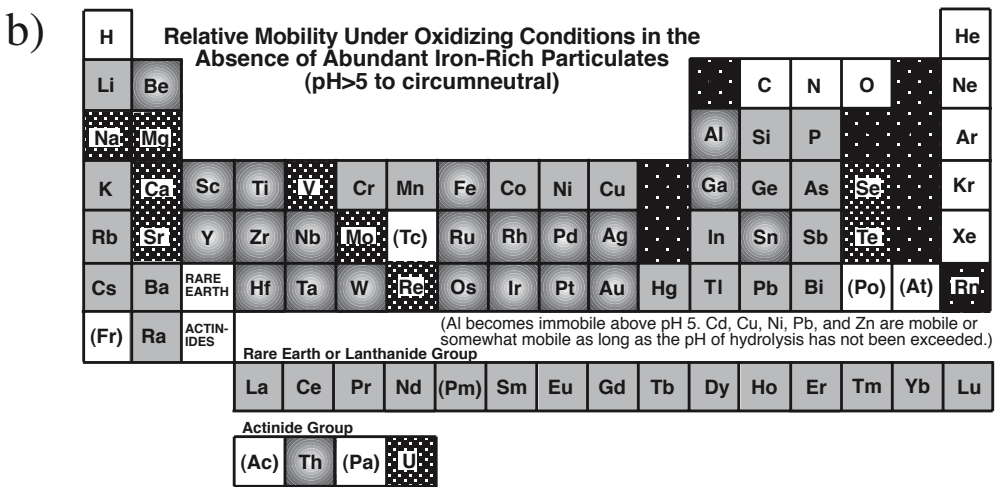
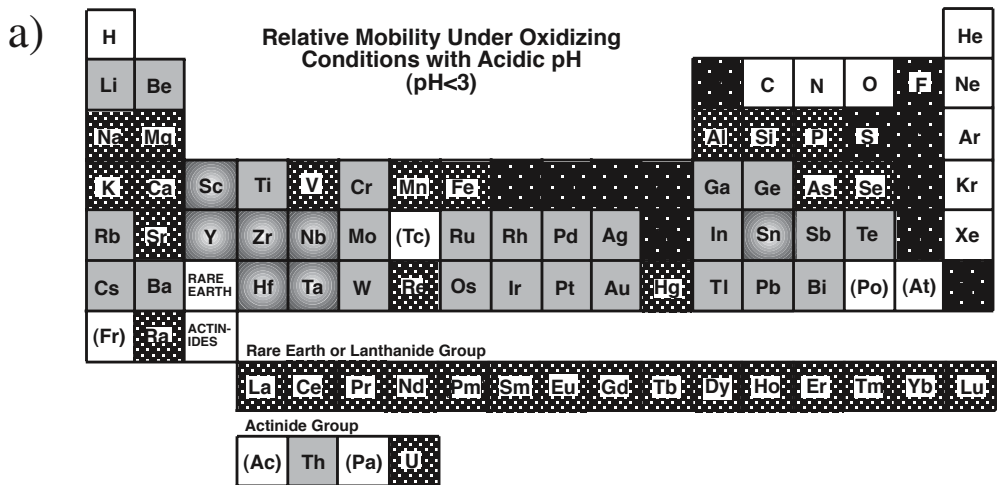


Figure 11 (a-c): Periodic table depicting element mobility based on different environmental conditions. Rare earth elements or elements with lack of shading are not assigned a mobility due to low abundance or lack of data. (Obtained from Smith and Huyck, 1999)

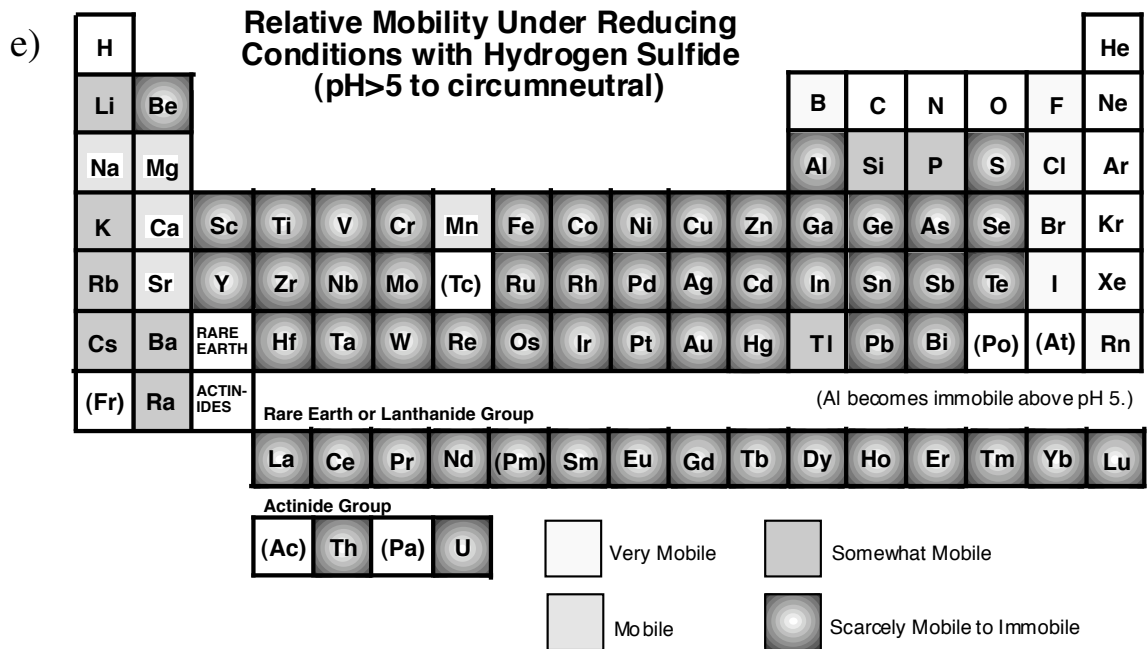
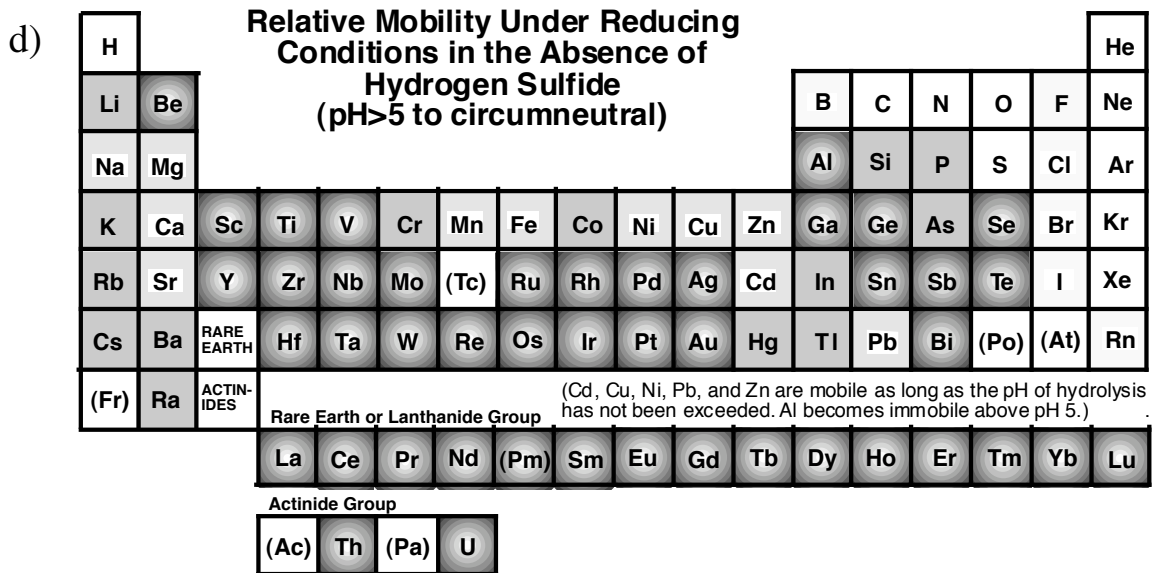


Figure 11 (d-e): Continued from previous figure, depicting mobility characteristics for certain elements under given environmental conditions. (Obtained from Smith and Huyck, 1999).

Element	Anionic ⁽³⁾	Cationic	Redox-sensitive ⁽⁴⁾
Aluminum (Al)		X	
Antimony (Sb)	X		X
Arsenic (As)	X		X
Barium (Ba)		X	
Beryllium (Be)		X	
Boron (B)	X		
Cadmium (Cd)		X	
Chromium (Cr)	X	X	X
Cobalt (Co)		X	
Copper (Cu)		X	X
Iron (Fe)		X	X
Lead (Pb)		X	(X ⁽⁶⁾)
Lithium (Li)		X	
Manganese (Mn)		X	X
Mercury (Hg)		X	X
Molybdenum (Mo)	X	X ⁽⁵⁾	X
Nickel (Ni)		X	
Selenium (Se)	X		X
Silver (Ag)		X	
Thorium (Th)		X	(X ⁽⁶⁾)
Uranium (U)	X	X	X
Vanadium (V)	X	X	X
Zinc (Zn)		X	

Figure 12: Characteristics of elements under surficial conditions or near surface aqueous systems (Obtained from Smith and Huyck, 1999).

Estimating metal behaviour in surficial environments based on these assumptions provided in Figure 11(a-e) and 12 are general stipulations for what may occur under given environmental conditions (Smith and Huyck, 1999). There are many additional factors that may impact metal mobility, such as the rates of geochemical and biological reactions (Langmuir and Mahoney, 1984). Many metal reactions are kinetically controlled and biologically mediated. This rate dependence raises a great deal difficulty when attempting to predict mobility of certain metals (Langmuir and Mahoney, 1984). Furthermore, the

success involved in estimating metal behaviour in certain environments usually involves the scale of the assessment under consideration (Smith and Huyck, 1999). At a regional scale generalizations often can be used to predict broad trends, as the scale becomes increasingly smaller, estimating metal behaviour becomes less accurate resulting in the difficulty of predicting metal behaviour. Factors such as acidic rainfall, complex behaviour of feedback mechanisms and compounding synergisms and antagonisms are difficult to identify, evaluate, and address (Smith and Huyck, 1999).

2.7.4 Metal Dispersivity in Surficial Environment

2.7.4.1 General Assumptions for Metal Distribution: Grain Size

Amongst grain size fractions, metals are not homogeneously distributed. It's common for finer grained, clay size fractions to sorb the highest metal concentrations due to surface area to volume ratio, and the presence of metal oxide and organic coatings on mineral surfaces (Filipek and Owen, 1979). In silt and sand size fractions, metal concentrations generally increase due to the greater abundance of quartz and lower oxide and organic matter content. The coarse fractions either increase in metal concentrations if coarser fractions include metal containing minerals, such as sulfide minerals, or decrease in metal concentrations (Filipek and Owen, 1979).

2.7.4.2 Air

Metals emitted into the atmosphere can be transported long distances and atmospheric deposition is a significant migration pathway for worldwide metal contamination of terrestrial and aquatic ecosystems (Pacyna, 1996). Metal distribution through atmospheric deposition may impact the chemistry of soils, rivers, lakes, estuaries and oceans (Smith and Huyck, 1999). Metals enter the atmosphere as gases, vapors, aerosols, and particles originate as both natural and anthropogenic sources (Table 1) (Nriagu, 1989).

Table 1: Approximations of worldwide metal emissions from natural sources into the atmosphere (Nriagu, 1989).

Source (median values)	As	Cd	Co	Cr	Cu	Hg	Mn
Wind-borne soil	2,600	210	4,100	27,000	8,000	50	221,000
Seasalt spray	1,700	60	70	70	3,600	20	860
Volcanoes	3,800	820	960	15,000	9,400	1,000	42,000
Forest fires	190	110	310	90	3,800	20	23,000
Biogenic							
Continental particulates	260	150	520	1,000	2,600	20	27,000
Continental volatiles	1,300	40	60	50	320	610	1,300
Marine	2,300	50	80	60	390	770	1,500
Total Natural Sources (Median value)	12,000	1,300	6,100	44,000	28,000	2,500	317,000

Source (median values)	Mo	Ni	Pb	Sb	Se	V	Zn
Wind-borne soil	1,300	11,000	3,900	780	180	16,000	19,000
Seasalt spray	220	1,300	1,400	560	550	3,100	440
Volcanoes	400	14,000	3,300	710	950	5,600	9,600
Forest fires	570	2,300	1,900	220	260	1,800	7,600
Biogenic							
Continental particulates	400	510	1,300	200	1,120	920	2,600
Continental volatiles	60	100	200	40	2,600	130	2,500
Marine	80	120	240	50	4,700	160	3,000
Total Natural Sources (Median value)	3,000	30,000	12,000	2,400	9,300	28,000	45,000

Residence time of metals in the atmosphere is fairly short, generally ranging from days to weeks (Salomons and Forstner, 1984), however, some particulate matter, such as volcanogenic particles, can remain in the upper atmosphere for much longer periods of time (Nriagu, 1989). Distance of airborne transport and deposition is dependent upon the source, size, shape, density of the particles, ground cover, changes in particulate matter characteristics during transport (reactions with different metals and atmospheric gases) and on meteorological conditions (Nriagu, 1989). Atmospheric particulate matter can undergo diffusion, coagulation, condensation, sedimentation, scavenging via precipitation and reaction of atmospheric gases (Nriagu, 1989).

On average, wind borne soil particulates emitted from natural sources account for half of chromium, cobalt, manganese and vanadium, and for one third to one half of the molybdenum, nickel, and zinc (Nriagu, 1989). Volcanoes emit more than half of cadmium and substantial amounts of arsenic, chromium, copper, lead, mercury and nickel (Nriagu, 1989). Biogenic sources are known to be leading producers of mercury, selenium and significant sources of arsenic. The largest amount of metals emitted into the atmosphere by

anthropogenic sources such as lead, arsenic cadmium, copper, and zinc were accounted for in 1983 by gasoline combustion (Nriagu and Pacyna, 1988). Metals when sourced from urban waste incinerators can transport as different forms when associated with fly ash. Behaviour of elements in fly ash correlates with the four classes suggested by Klein et al. 1975, (Table 2) (Fernandez et al. 1992).

Table 2: Classes that categorize the behaviour of elements in fly ash (Klein et al., 1975).

Class	Description
Class I	Elements that make up the matrix of fly ash and are only minimally deposited on fly ash surface: Al, Ba, Be, Ca, Fe, K, Mg, Mn, Si, Sr, and Ti
Class II	Elements that volatilize during combustion and condense on surface of fly ash particles, forming soluble compounds. Elements tend to be enriched in smaller particle size fly ash: As, Cd, Cu, Ga, Pb, Sb, Se, and Zn
Class III	Elements that volatilize but do not condense: Br, Cl, and Hg
Class IV	Element behaviour that is a combination of the above classes

2.7.4.3 Water

Another natural form of dispersion that acts as a migration pathway for sediments or particulate matter (which may contain a high concentration of elements such as heavy metals) occurs through hydrological and geomorphological processes. (Smith and Huyck, 1999). These processes include and are not limited to: erosion, surface water transport, runoff, ground water transport (vertical and horizontal transport), precipitation (percolation), sediment deposition and compaction (Smith and Huyck, 1999). For transport to occur via hydraulic processes the flow rate of water must exceed a certain critical velocity, depending on grain size and density. For deposition the flow must decrease below another critical value. In rivers and estuaries, sand and gravel size bedload fractions move along the bottom of the riverbed via rolling or 'leaping' (Smith and Huyck, 1999). Particles are not usually transported long distances before deposition, whereas finer grained sediments are carried in suspension over longer distances before deposition occurs (Horowitz, 1991). Within the water column metals are associated with suspended particulate matter of fine-grained sediments. Suspended load can transport significant metal concentrations due to adsorption that occurs (Horowitz et al., 1990). Furthermore the transport range will vary depending on the time of year and weather; for example during spring runoff and storm events, suspended load is highest (Horowitz et al., 1990). Physical transport of particulates that occur through migration pathways such as ground water encompasses many of the factors involving surface water. The flow paths are often quite complex depending on structural components, geology, topography, and on a smaller scale pore space (Ranville and Schmiermund 1999). Due to the scope of this study groundwater as a migration pathway is not further explored.

2.8 Halifax Anthropogenic Influences

2.8.1 Halifax Air

Measurements for aerosol particulate matter were obtained by a study two to three years ago by Crystal Weagle and Robyn Latimer in Halifax, Nova Scotia (Crystal Weagle, personal communication, March 2017). Although metal content measurements within the sampled particulate matter were not analyzed, measurements that have been taken globally show that the total metal oxides count for approximately 25 metal oxides, make up less than one percent of fine particulate matter (PM 2.5) (Crystal Weagle, personal communication, March 2017). In Halifax, PM 2.5 concentrations range from 3-7 ug/m³, allowing for us to assume that metal content within the particulate matter is quite small. Future analysis of metal concentrations within Halifax air particulates is likely to continue, however, a generalized assumption can be made that atmospheric particulate matter contributes a very small amount to metal deposition and concentration within Halifax soils (Crystal Weagle, personal communication, March 2017).

2.8.2 Halifax Water

Over an anthropogenic time frame (1700's -present) Halifax surface waters have evolved throughout the process of city development. Most of the streams and rivers that were present within the peninsula during the mid 1700's are no longer at surface and therefore are no longer acting as potential migration pathways (at surface) for metal contaminants to be deposited down stream. However, earlier in Halifax's history the peninsula was filled with a network of rivers. The first record of these waterways is illustrated in maps created by the early explorers during the time of Halifax's first colonization in the mid 1700's (Figure 13 and Figure 14). Both of figures illustrate rivers that and streams that are quite prominent within the 1700's and located in the downtown core. As Halifax developed industries such tanneries could have deposited effluents into some these rivers, which would have resulted in deposits of metals further down stream. Throughout time from the 1700's through till the 1900's we see Halifax's growth continue, while it's surficial waterways disappear and get buried by development (Figure 15).

REF. or DRAWING NO. V.61240 - c.1779
DETAILS Halifax based on Map by J.F. Desbones.



Figure 13: Map of Halifax in 1779 by J.F. Desbones obtained from Nova Scotia Archives.



HALIFAX 1784
CHARRES BLASKOWITZ
A PLAN OF THE PENINSULA
 upon which
 The TOWN OF HALIFAX is situated,
 showing
 The HARBOUR, the NAVAL-YARD
 and the several WORKS constructed for their Defence.
 Drawn by the Author in 1784, by Order of the Honble. the Admiralty
 under the Direction of J. G. S. Major, Chief Engineer in Chief
 of the Halifax Station.
 M.D.CCLXXXIV.

- REFERENCES.**
- A. A. - The Harbour and Fortifications shown by an Engraving taken for the Purpose of the
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REF. OF DRAWING No. V.1290-1784
 Halifax

REF. OF DRAWING No. V.1290-1784
 HALIFAX

Figure 14: Map of Halifax in 1784 by Charres Blaskowitz, depicting rivers and topography of peninsula.

REF. or DRAWING No. Vo [246] - [1914]

DETAILS METROPOLITAN HALIFAX

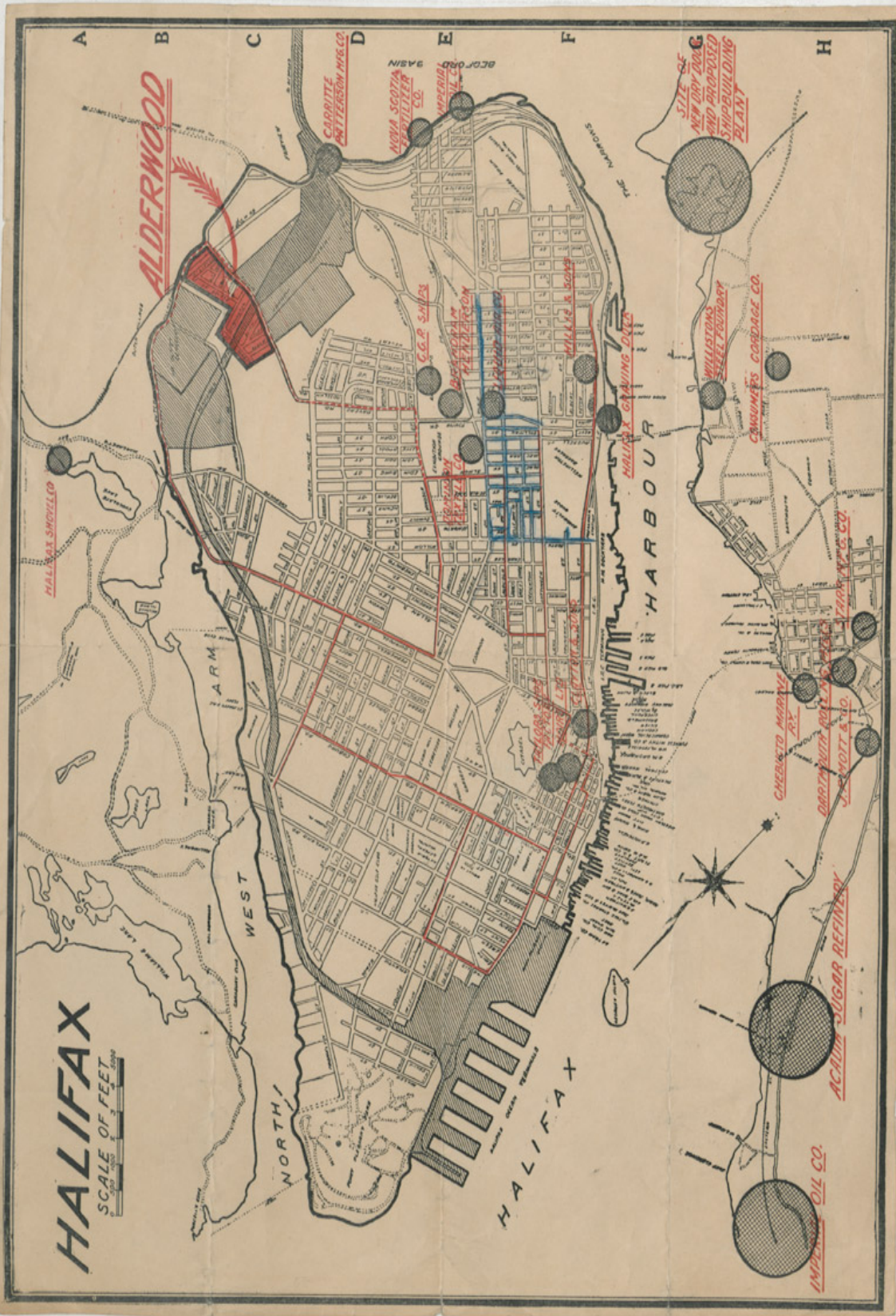


Figure 15: Map of Halifax in 1914 display new development obtained from Nova Scotia Archives.

2.8.3 Halifax Anthropogenic Dispersion: Halifax History and Development

The first permanent fortified settlement was established in 1749 on the Chebucto peninsula by Hon. Edward Cornwallis and 2500 colonists. The community christened as Halifax in Honour of Lord Halifax who was President of the British Board of Trade at the time (HRM, 2014). Later, in 1750, Dartmouth was founded. Halifax began to develop with a strong military presence as a port city. It had the first newspaper in Canada known as the Gazette, first printing presses and the first post office operation in 1755. In 1758, the dockyard was completed and a year later Halifax served as a base for British operations against the French (HRM, 2014). Periods of international unrest and war contributed towards the industrial development and prosperity of the HRM. The Seven Years' War was the first of the significant conflicts and was soon followed by the War of American Independence in the 1770's. It was not until the 1800's that Halifax experienced peaceful development (HRM, 2014).

There were many industries and anthropogenic activities that influenced Halifax's soil chemical composition and metal abundance throughout history. The city was a major center for shipping and manufacturing. The focus of industrial development mainly surrounded shipbuilding, electrical appliances and equipment, paints, varnishes, building materials, and fish products (MacDougall et al., 1963). A large naval base and presence allowed Halifax to be exposed to a larger market and aided considerable development during the 1900's. Dartmouth, across the harbor, rapidly grew alongside Halifax. In the 1960's Dartmouth was well developed in the sense it had an oil refinery, an aviation plant, shipyards, woodworking and building supply establishments (MacDougall et al., 1963). During World War I and World War II Halifax was a central hub for many naval operations (HRM, 2014).

In particular when thinking about industrial development and soil chemistry, the Halifax explosion is a significant event that must be taken in to account. The Halifax explosion occurred in 1917 due to a mis-communication between two ships causing a collision (HRM, 2014; Scanlon, 2000). One of the ships carried TNT explosives, which added to the devastating explosion that destroyed the north end of the city and killed approximately 2000 people (HRM, 2014; Scanlon, 2000). Overall Halifax has a heavy

history of industrial development that is necessary to consider as having had a large anthropogenic influence upon soil development and metal abundance.

2.8.4 Metal Toxicity: Human & Environmental Health

When considering the potential effects of elevated metal concentrations in soil there are a number concerns that need to be addressed. The first is that the soil maybe contaminated, therefore direct ingestion of the soil has the potential to cause toxicity. Second, is that leaching of metal contaminants from soil can cause potential contamination of groundwater systems, although the contamination of these systems is reliant on the abundance of metals concentrated within the soils and conditions of environment. Third is uptake of potentially toxic metals into plants, which can then be ingested by humans or animals; while beyond the scope of this thesis the toxicity potential for humans will be outlined briefly.

Ingestion of toxic metals or metalloids occurs via food, respiration, and water intake (Siegel, 2002). Health impacts from ingesting toxic metals manifest over a long periods of time and have long-term implications (Siegel, 2002). These health effects may include, for example, loss of motor control, organ dysfunction, cancer, chronic illness, degradation of mental acuity, incapacitation, and death, *Table 3*.

Furthermore, inhabitants of urban areas that are most at risk to toxicity effects from contaminated city soils are children (Sénéchal, 2016; Ljung et al., 2006). Children are more susceptible to negative health effects of soil contaminants due to intentional or unintentional soil ingestion by common hand-to-mouth behavior and physiological factors which influence the amount a child can ingest before toxicity affects occur (which is much less than the average adult) (Bergstrom et al., 2011). Children up to 5 years of age are more likely to ingest soil either intentionally or unintentionally (Bergstrom et al., 2011). According to a recent study from Japan, unintentional ingestion represents what remains on children's hands after human subjects were asked to rinse soil particles adhered to their hands with ultrapure water, who used a laser scattering particle size distribution analyzer to measure particle sizes that ranged from 0.6 to 600 μm (Yamamoto et al., 2005). It's important to note that concentrations of chemical contaminants are generally higher in concentration for finer soil particles. Additionally, these finer soil particles adhere to human hands more efficiently, which suggests that the risk of ingestion of

contaminants via soil intake may be under-estimated (Yamamoto et al., 2005) .

The following table, Table 3 identifies specific metals that are found within certain anthropogenic products. Most metals are associated with many anthropogenic influences and a variety of products; however, it is important to keep in mind not only which metals are present or contributed by certain anthropogenic activities, but also to what extent and in what quantities.

Table 3: Modified from Siegel 2002, listed anthropogenic products, activities, and influences that contain or emit metals.

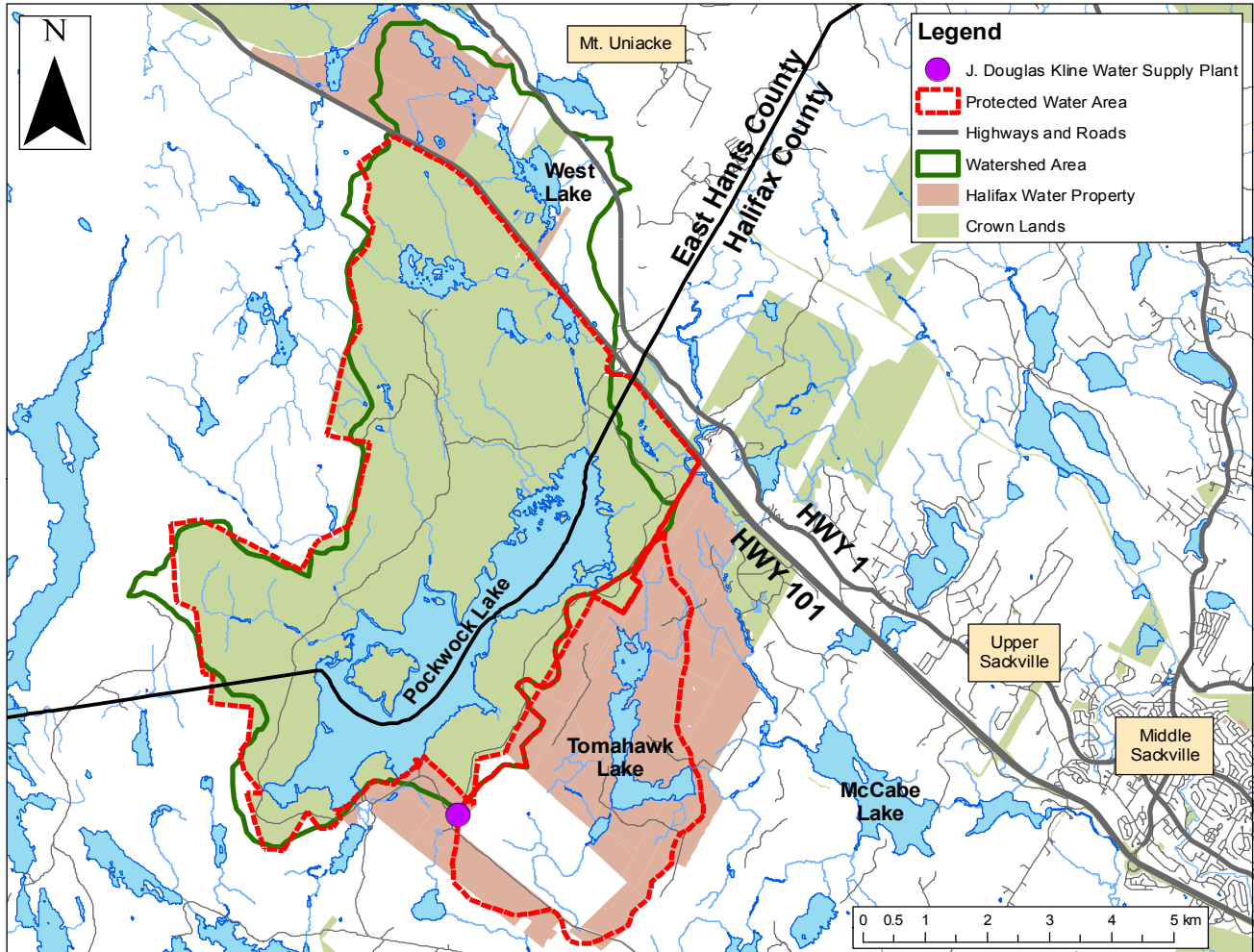
Element	Anthropogenic Influences/Products
Arsenic (As)	Animal feed, wood preservation (copper, chrome arsenate), special glasses, ceramic, pesticides, insecticides, herbicides, fungicides, rodenticides, algicides, electronic components, non ferrous smelters, metallurgy, coal fired and geothermal electrical generating facilities, textile and tanning, pigments and antifouling paints, light filter, fireworks, veterinary medicine.
Cadmium (Cd)	Ni/Cd batteries, pigments, anticorrosive coating of metals, plastic stabilizers, alloys, coal combustion, neutron absorber in nuclear reactors
Chromium (Cr)	Manufacturing of ferro alloys (special steels), plating operations, pigments, textiles and leather tanning, passivate the corrosion of cooling circuits, wood treatment, audio, video and data storage
Copper (Cu)	Conductor for heat and electricity, water pipes, roofing, kitchenware, chemicals and pharmaceutical equipment, pigment, alloys
Iron (Fe)	Cast iron, wrought iron, steel, alloys, construction, transportation, machine manufacturing
Mercury (Hg)	Extracting of metals by amalgamation, mobile cathode in the chloralkali cell for the production of NaOH and Cl ₂ from brine, electrical and measuring apparatus, fungicides, catalysts, pharmaceuticals, dental fillings, scientific instruments, rectifiers, oscillators, electrodes, mercury vapour lamps, X-Ray tubes, solders
Manganese (Mn)	Production of ferromanganese steels, electrolytic manganese dioxide for use in batteries, alloys,

	catalysts, fungicide, antiknock agent, pigments, dryers, wood preservatives, coating welding rocks
Molybdenum (Mo)	Alloying element in steels, cast irons and non ferrous metals, in chemicals such as catalysts and dyes, lubricants, corrosion inhibitors, flame retardants, smoke repressants, electroplating
Nickel (Ni)	As an alloy in the steel industry, electroplating, Ni/Cd batteries, arc welding rods, pigments for paints and ceramics, surgical and dental prostheses, molds for ceramic and glass containers, computer components, catalysts
Lead (Pb)	Antiknock agents, tetramethyllead, lead acid batteries, pigments, glassware and ceramics, plastics, in alloys, sheets, cable sheathings, solder, ordinance, pipes or tubing, leaded gasoline, paints
Antimony (Sb)	Type metal alloy (lead to prevent corrosion), in electrical applications, Britannia metal, pewter, Queen's metal, Sterline, in primers and tracer cells In munitions manufacture, semiconductor, flameproof pigments and glass, medicines for parasitic diseases, as a nauseant, as an expectorant, combustion of fossil fuels
Selenium (Se)	Glass industry, semiconductors, termoelements, photoelectric and photocells and xerographic materials, inorganic pigments, rubber production, stainless steel, lubricants
Tin (Sn)	Tin plated steel, brasses, bronzens pewter, dental amalgam, stabilizers, catalysts, pesticides
Vanadium (V)	Steel production, alloys, catalyst, combustion of fossil fuels, steel works and other industry
Zinc (Zn)	Zinc alloys (bronze, brass), anti corrosion coating, batteries, cans, PVC stabilizers, precipitating Au from cyanide solution, in medicines and chemicals, rubber industry, paints, soldering and welding fluxes

Halifax does not rely on groundwater as a water supply, primarily due to the naturally elevated arsenic levels that are considered well above Canadian safety guidelines for water containing arsenic, which is 50 ng As/ml. The arsenic is geogenic, sourced

primarily from the Meguma Terrane that covers most of southern mainland Nova Scotia. Arsenic-rich geological units are primarily the Halifax and Goldenville group, which contain sulphide-bearing metasediments and gold-bearing metasediments as previously discussed in section 2.6.1. Due to these factors affecting groundwater, Halifax relies on Pockwock Lake as its public water supply, (Figure 16).

Pockwock Lake and Tomahawk Lake Watershed Areas



* This map is for informational purposes only and should not be used for legal, engineering, or surveying purposes.

Figure 16: Pockwock Lake watershed and Halifax water supply (Obtained from Halifax Water, 2017).

The Pockwock Lake Watershed is primarily on Crown land, covering 5661 hectares, 86 % of which is protected by provincial designation and regulations. Since this lake is located

away from the city and not near urban soils, the potential for metal contamination via urban soil is not of concern.

There is not strong concern for vegetation uptake except within community gardens, and backyard recreational gardens. Metal uptake depends on the type of plant and on the type of soil. For the purpose of this study we do not consider issues pertaining to bioaccessibility and bioavailability of metals to plants. We will primarily focus on geo-availability and anthropogenic influences of metals within the soil, which can provide a basis for further studies on bioaccessibility and bioavailability, if required.

2.8.5 Federal and Provincial Guidelines

The Canadian Council of Ministers of the Environment (CCME) provide generic soil quality guidelines from consistent procedures that are developed based on available scientific data and used to apply generic assumptions (CCME, 1999). Guidelines are derived to approximate a no -to- low effect threshold level based on toxicological information and other scientific data. The attempt of CCME guidelines is to apply limit values to a broader range of sites with different exposure pathways and physical conditions, *Table 1 (CCME, 1999)*.

The Nova Scotia contaminated sites guidelines, is intended to provides a basis and rational for the development of environmental quality standards for contaminated sites in Nova Scotia (Carey et al., 2014). The focus is to provide professionals and others with technical background, with environmental quality standards and guidance on how to apply these standards in conjunction with the Contaminated Sites Regulation. The guidelines used for this study focus on the residential land use guidelines of CCME. Residential land use is defined as residential or recreational activity (Carey et al., 2014). It assumes parkland can be a buffer between areas of human residency, includes campgrounds, but does not include undeveloped land areas such as national or provincial parks (Carey et al., 2014). Recreational parks are also included within this category, but primarily it involves a generic residential property for a single-family home with a backyard that would typically allow children such as toddlers to play. Long term care institutional facilities also may be considered as residential (Carey et al., 2014). The following table dictates the limitations

and guidelines for Nova Scotia. Variation in data relative to CCME guidelines includes a general baseline for Nova Scotia metal concentrations, (Table 4).

Table 4: Provincial and Federal Guidelines for residential soils adapted from CCME and NS Contaminated Sites reports and tables (Carey et al., 2014; CCME, 1999).

Element	NS	CCME	Element	NS	CCME
Be	38	4	Zn	5600	200
Sr	9400		Mo	110	10
Ba	10000	500	Ag	77	20
V	39	130	Cd	14	10
Cr	220	64	Hg	6.6	6.6
Cr(VI)	160	0.4	U	23	23
Mn	--	--	Al	15400	
Fe	11000		Sn	9400	50
Co	22	50	Pb	140	140
Ni	330	45	B	4300	--
Cu	1100	63	As	31	12
Sb	7.5	20	Se	80	1

2.9 Previous work

There have been several studies completed within the Halifax region that have covered different aspects of urban soils. These include: the soil study of the Halifax County conducted by Macdougall et al. (1963), soil and till geochemistry of the Halifax Regional Municipality conducted by Goodwin (2002), the community garden heavy metal study conducted Monfared (2011), a pilot study providing an analysis of heavy metal concentrations in residential soils within the Halifax peninsula conducted by Archibald et al. (2014), and finally Lake et al. (2015) preliminary results on sampling of soils for background substances in Halifax. A brief overview of each study and results obtained

outline the work that has been done to date within the Halifax region soils. A study conducted in St. John's Newfoundland, Foley et al. (2011) is also compared to this study.

The study conducted by Macdougall (1963) is a report that describes factors affecting the development of soils within the Halifax county that comprises 2293 square miles, (Figure 17).

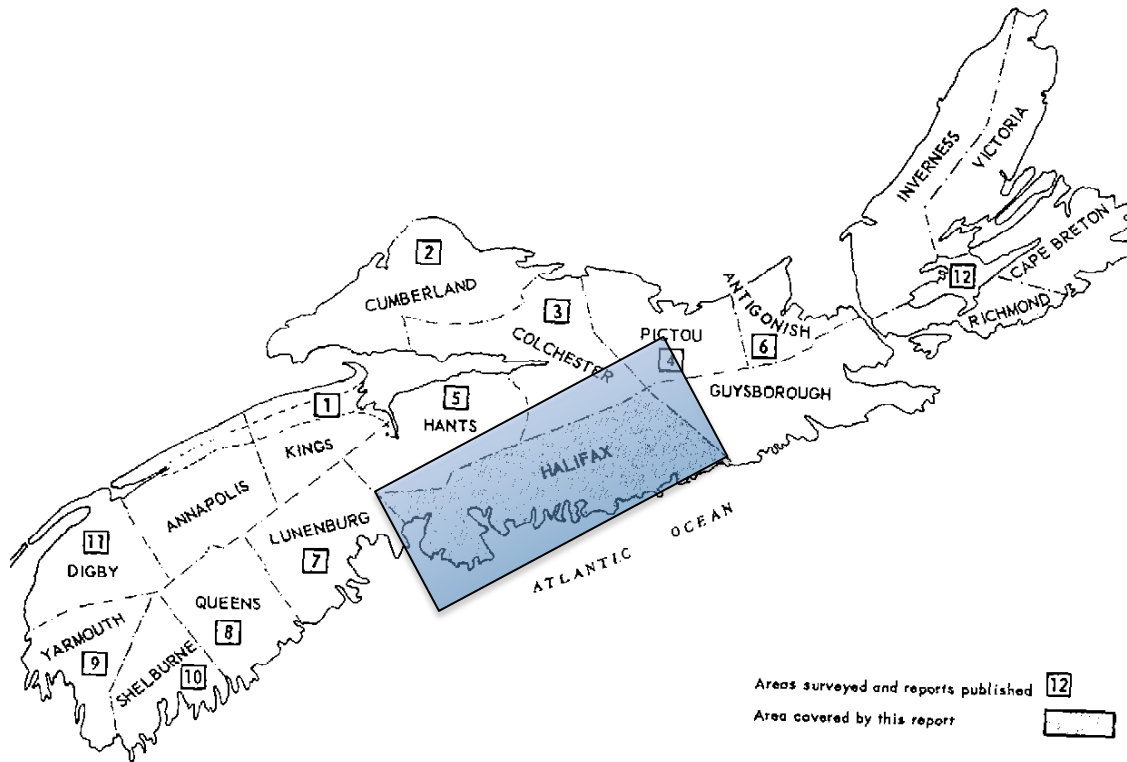


Figure 17: Depicting the location of the Halifax County. (Modified map from Macdougall et al., 1963).

The purpose for evaluating these soils was to aid in the understanding of the usefulness these soils had towards agriculture. The sampling survey was conducted from 1957 to 1958 using different sampling techniques than those used in this study. Sampling was done in fields, forested areas and near roadside exposures (Macdougall et al., 1963). Notably these areas were not near or exposed to substantial human activity. Soil horizons in these areas were relatively well developed, allowing for horizon based sampling. These soils were defined broadly either as well-drained Podzols or poorly drained Gleysols (Macdougall et al., 1963). No metal analysis was undertaken for this study.

The study conducted by T.A. Goodwin (2002) focused both on soil and till sampling geochemical analysis within the Halifax Regional Municipality (Figure 18.)

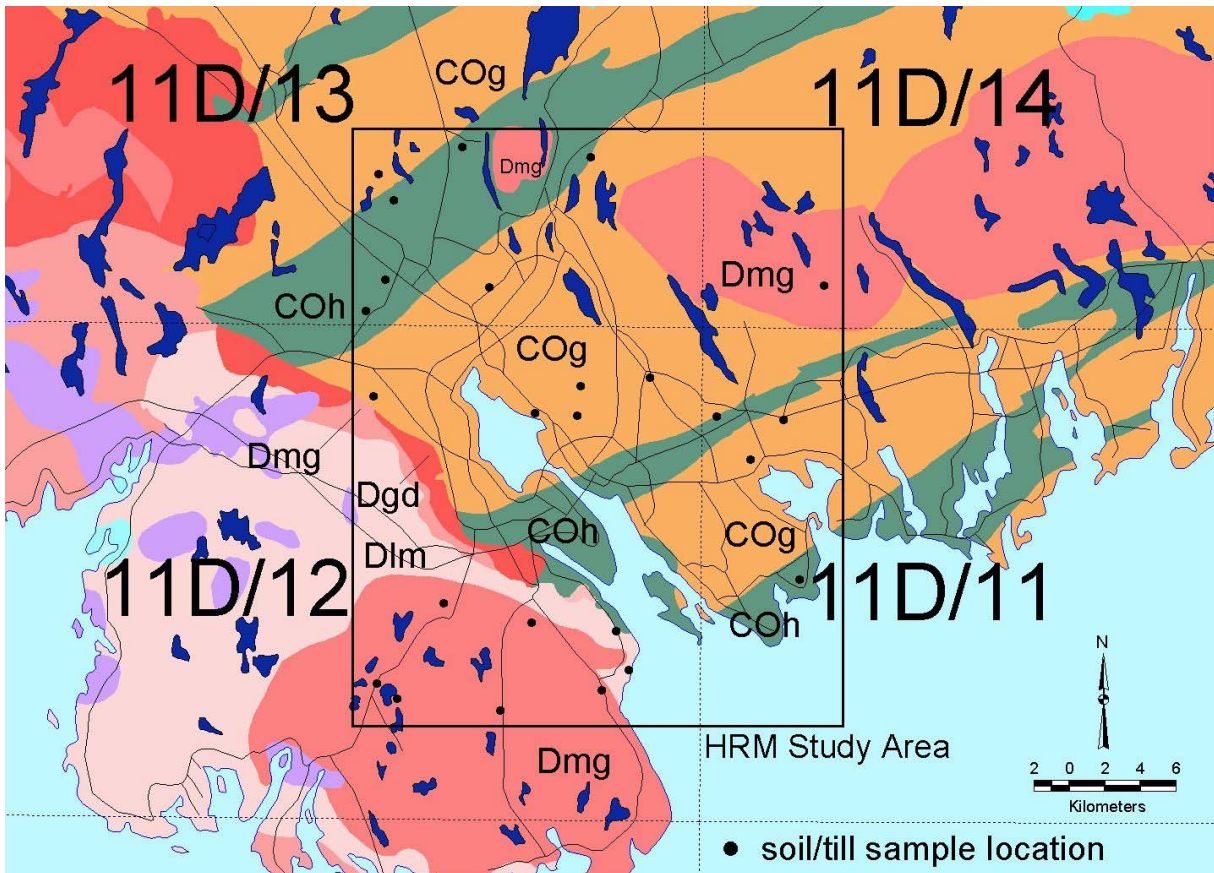


Figure 18: Obtained map from Goodwin 2002 study, demonstrating location of study area and sampling points.

The goal of Goodwin's study was to establish a historical geochemical baseline for the HRM, compliment a study by Lewis et al. (1998). At each sample site, B horizon soils were collected for geochemical analysis (Goodwin, 2002). Soils and till samples were dried to 35°C and sieved to <math><63 \mu\text{m}</math> at DalTech Minerals Engineering Centre in Halifax and shipped for Hg analysis by Cetac Cold Vapor Atomic Absorption. Samples were also sent to ALS CHEMEX for trace element geochemical analysis (Goodwin, 2002). However, in Goodwin's study no samples were taken within the peninsula of Halifax (Figure 18).

Monfared's (2011) community garden soil study focuses on study soil in community gardens. Monfared evaluates the presences of four heavy metals, Pb, As, Cu and Zn as potential contaminants within the soils of urban gardens in the HRM. The principal objective of his study was to develop preliminary recommendations for existing and future gardens for managing and mitigating heavy metal concentrations within urban garden soils (Monfared, 2011). Monfared collected 220 samples from 44 locations that were selected based on potential community garden areas and in active community gardens throughout the HRM. Depth -based samples were collected within this study at 0-10cm sample depths (Monfared, 2011). Soil samples were air dried, ground with mortar and pestle and sieved to 2 mm sieving size. Heavy metal concentrations were analyzed using ICP-IOS, soil pH measurements were collected and organic matter was (OM) analyzed by loss of ignition method. Monfared focused on bioavailability of potentially toxic metals and concluded that pH of soils were slightly acidic ranging from 4.07 to 6.88 pH level (Monfared, 2011). The OM of the soil ranged largely from a minum of 2% to a maximum of 32%. Relative to CCME soil quality guidelines for agricultural land use there were a number of samples above guidelines (Monfared, 2011). One third of the samples had lead concentrations above CCME guidelines, half of the samples had arsenic concentrations above CCME guidelines and there were a few copper and zinc concentrations that were above guidelines (Monfared, 2011).

The pilot study conducted by students Archibald, Broom, Desjardins under the supervision of Dr. Anne Marie Ryan focused on heavy metal concentrations within residential soils in Halifax (Archibald et al., 2014). The main objective of the study involved determining metal concentrations for 0-15 cm depth- based samples, identify metals above CCME guidelines, determine whether metal concentrations vary between drip line, roadside and ambient soils, and identify geographic distribution of elevated metals (Archibald et al., 2014). Students obtained 120 samples from the top 15 cm of soil at three different locations at each of the 32 residential sites throughout the Halifax Peninsula (Figure 19)(Archibald et al., 2014).

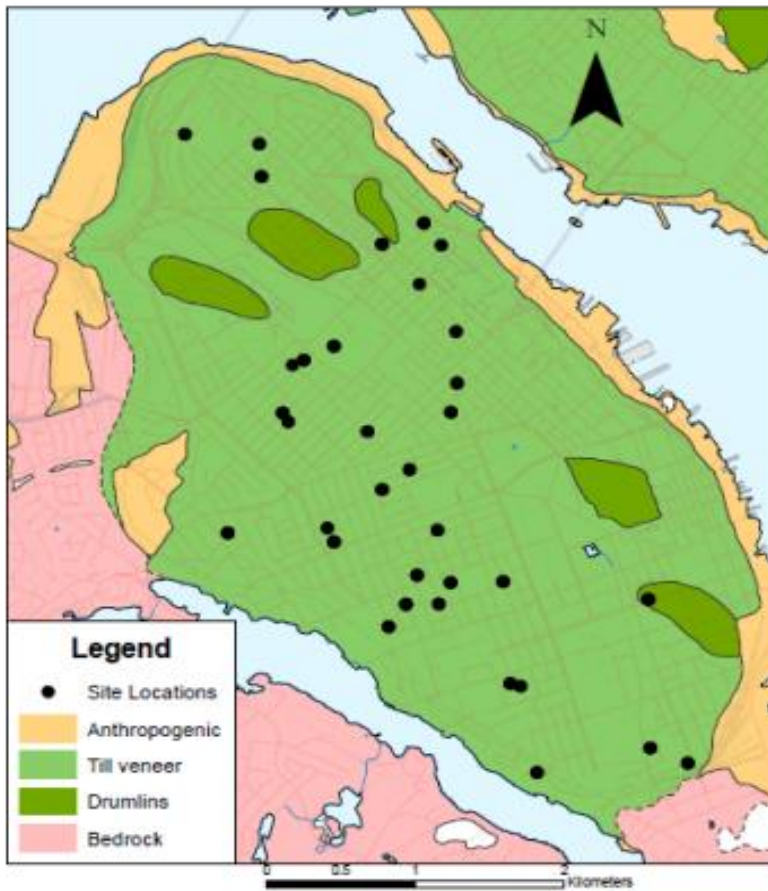


Figure 19: Data from heavy metal pilot study demonstrates locations of samples collected (Archibald et al., 2014).

At each location samples were taken by the drip-line, was an approximately 1 m from the house, roadside within 1 m from the road, and an ambient sample in an open yard, away from the house or road. Samples were air dried and sieved to < 1 mm and analyzed for heavy metal concentrations using Olympus X-5000™ portable XRF. Metals of focus within this pilot study were covered in the CCME guidelines, including Pb, As, Cr, Cu, Zn, Ba, V, Cd, Co, Se, Mo, and Sn (Archibald et al., 2014). The results of their study show that there were a significant number of samples, which had metal concentrations above CCME guidelines. Metals such as Pb, Zn, Cu, Cr, As, and Ba, were above CCME guidelines where as Cd, B, Co, Se, Mo, and Sn were below CCME guidelines (Archibald et al., 2014). Primarily

conclusions show metal concentrations were significantly higher than CCME guidelines at a number of locations within the peninsula. This pilot study provided evidence for elevated metal concentrations within downtown Halifax (Archibald et al., 2014).

The aim of Lake and King's 2015 study is to determine background level concentrations for inorganic metals and polycyclic aromatic hydrocarbons within soil in the HRM (2015). Nova Scotia of Environment enlisted the aid of Dalhousie University to provide sampling protocols and to complete sampling. Soils were sampled in areas without identifiable point source contamination and were taken at 0-30 cm sample depths (Lake et al., 2015). A total of 50 samples were collected at commercial and residential properties to provide a geographical distribution of locations around the HRM. AGAT laboratories in Dartmouth, Nova Scotia tested for metals using ICP-MS. Results are preliminary and in the process of being analyzed (Lake et al., 2015). A minimal number of their 50 samples exceed CCME guidelines. Lake and King sampled the 0-30cm depths and recommend continued use of this protocol; however, many soils in Halifax are thin and it is not always possible to sample to this depth. As well Health Canada recommends sampling to a depth of just 0-5 cm.

A Newfoundland and Labrador study was conducted in St. John's on geochemical hazards of urban soils by Foley et al. (2011). Ten metals including Ba, Cu, As, Pb, Zn, V, Cd, Ni, Cu, Cr were mapped on residential properties based on CCME guidelines, (Figure 20) (Foley, et al., 2011). Concentrations of all the metals were elevated above background levels. Within study areas near the down town core of St John's, high levels of metal contamination were found, primarily on residential properties predating the 1950s. Foley et al. (2011) acknowledge that it is possible that other cities share an urban history of weathered paint, vehicular emissions and coal burning, which they have identified as important sources for contaminated soil samples.

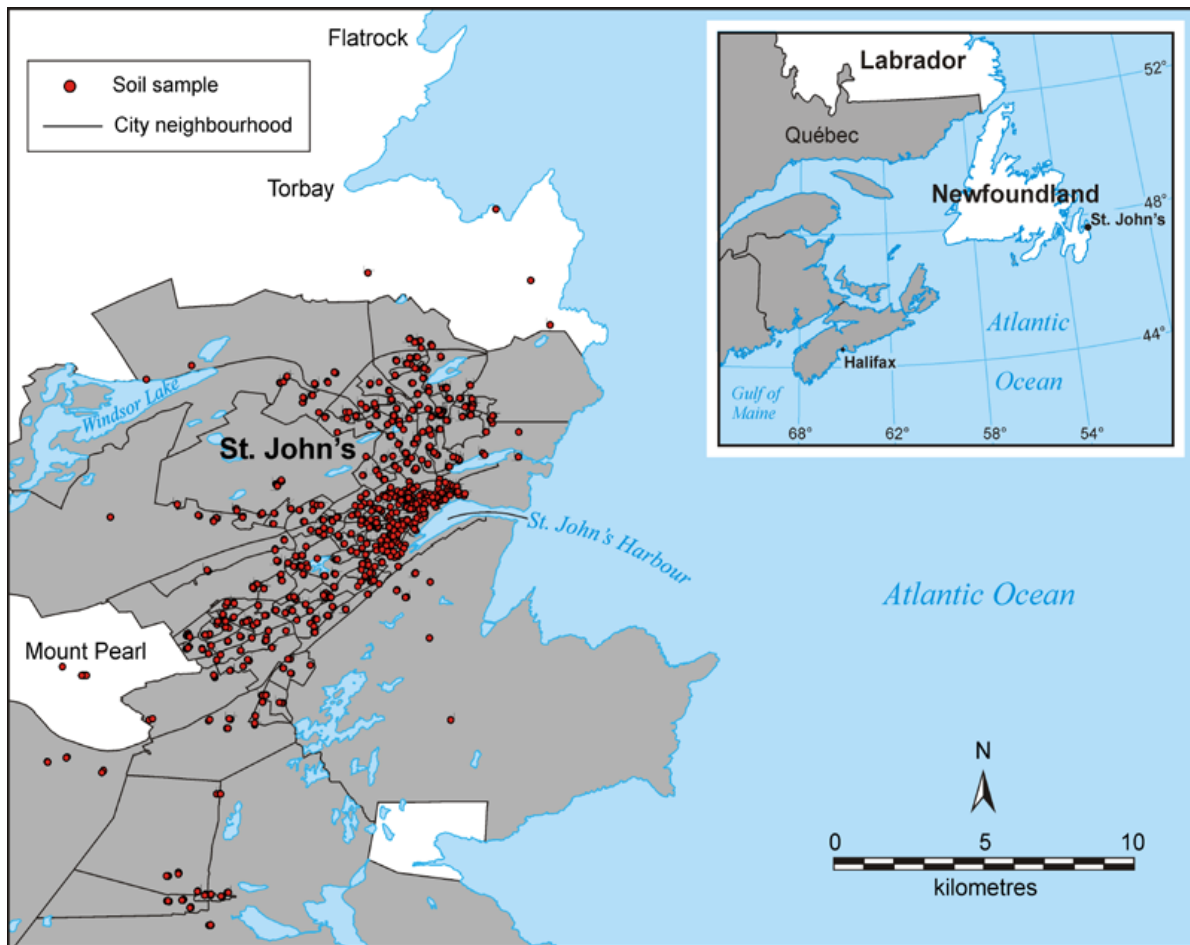


Figure 20: Depiction of Foley, Bell, and Liverman's sample site locations in St. John's, Newfoundland. Map obtained from Foley, Bell and Liverman's study (2011).

Their study emphasizes similarly the influence of an urban history on the condition and contribution to metal concentrations within urban soils. St John's was founded in 1497 and similar to Halifax, is one of the oldest cities in Canada, providing it with a rich history of urban development. Samples were collected within two stages (Foley, et al., 2011). The first was a pilot sampling program to gain an understanding of the range of metal concentrations in St John soils. A total of 260 samples were obtained from public parks, school properties, playgrounds, backyards and roadsides. The second stage involved 1231 samples collected from only residential properties (Foley, et al., 2011). Samples were taken 5 m from roadside, 1 m from the dripline, the foundation of the house and in an open area of the property away from buildings and roadside. Samples were taken at surface, 0-2 cm depth, and other samples were collected below the sod layer up to 10 cm depth. Sample

analysis was conducted at the Geochemical Laboratory of the Newfoundland and Labrador Geological Survey in St. John's using the ICP-ES digestion process (Foley, et al., 2011). Conclusions drawn from this study establish that residential soils in St. John's have elevated metal concentrations above background levels for ten metals. Foley et al. (2011), identified that the majority of contaminated soil samples were concentrated in the oldest parts of the city, within the downtown core, especially on properties that predate the 1930's (Foley, et al., 2011). Lead, Zn, and Cd are enriched at dripline sites, and in some ambient locations and roadside samples were also elevated (Foley, et al., 2011). This study provides us with a better understanding of how urban history contributes to elevated metal concentrations and the relationship of city development to metal abundances in certain areas. My study assesses the variability between different grain sizes at different sampling depths in an attempt to establish optimum sampling criteria for urban soils in Halifax.

2.9.1 Halifax Future Growth and Development

The most recent population estimate for the Halifax region is 417, 800 people (Statistics Canada, 2015). Approximately 60 000, of which are families with children and the average age of the population is 40 (Figure 21) (Statistics Canada, 2015). Population growth according to statistics Canada census data has fallen below the national growth rate over the last five years however has increased by 3.3 % since the last census in 2011 (Metronews, 2017). Although the population of the province is not expected to increase significantly in the next few decades, there is a notable migration from rural counterparts to urban districts (Nova Scotia Water for Life, 2010). Urban centers such as Halifax are increasing in density, while populations in rural communities are declining.

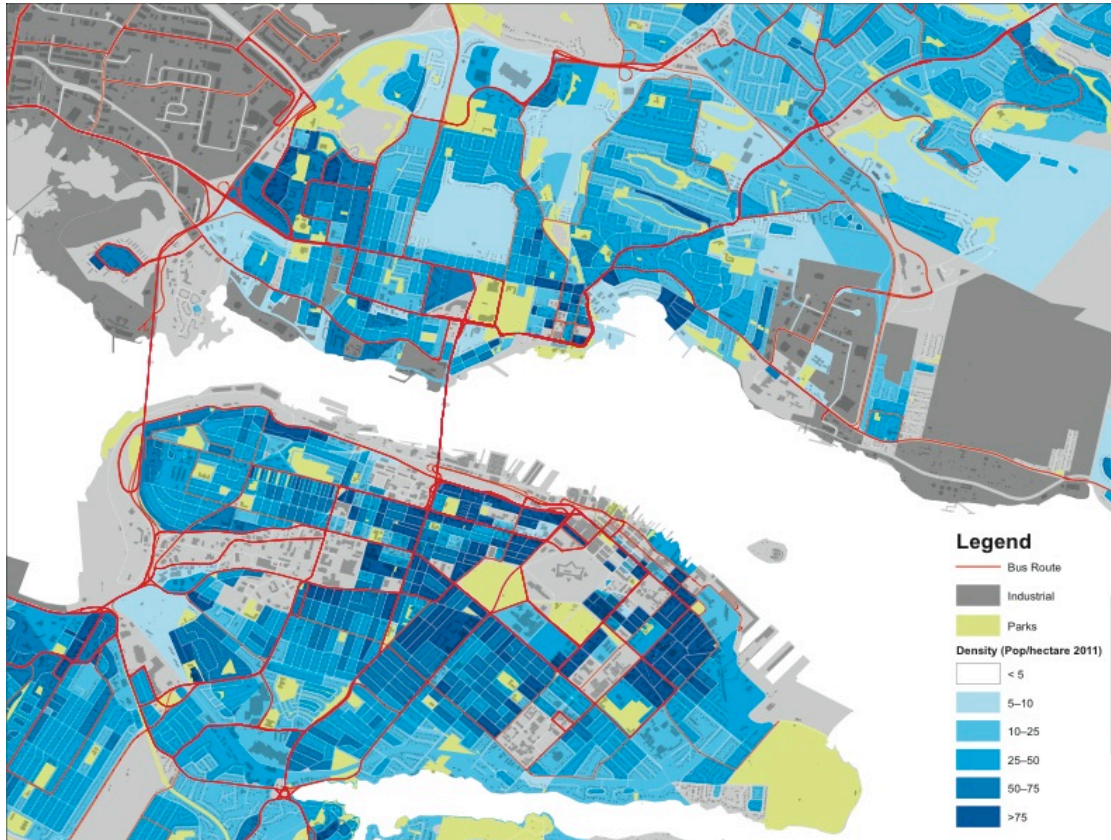


Figure 21: Population density map of Halifax Nova Scotia, modified from Zack Taylor Metapolis Consulting based on 2011 census data.

It is important to take a holistic approach when thinking about metal concentrations within urban soils and their relation to human health. As population density increases for Halifax, there is the potential for more inhabitants to be affected by potential metal toxicity. With greater influx of people into the city, there will also be more development, more housing and thus more physical dispersion of soil. It's important to note this will likely change our soils for the future.

3.0 Materials and Methods

A general approach for the method section and how it relates to the general objectives of this thesis is demonstrated in the workflow below (Figure 22). Methodologies of this section can fall under two categories: the first is the assessment of metals in Halifax soils using geochemical methods and the second, is a preliminary assessment of Halifax development over time, using GIS methods.

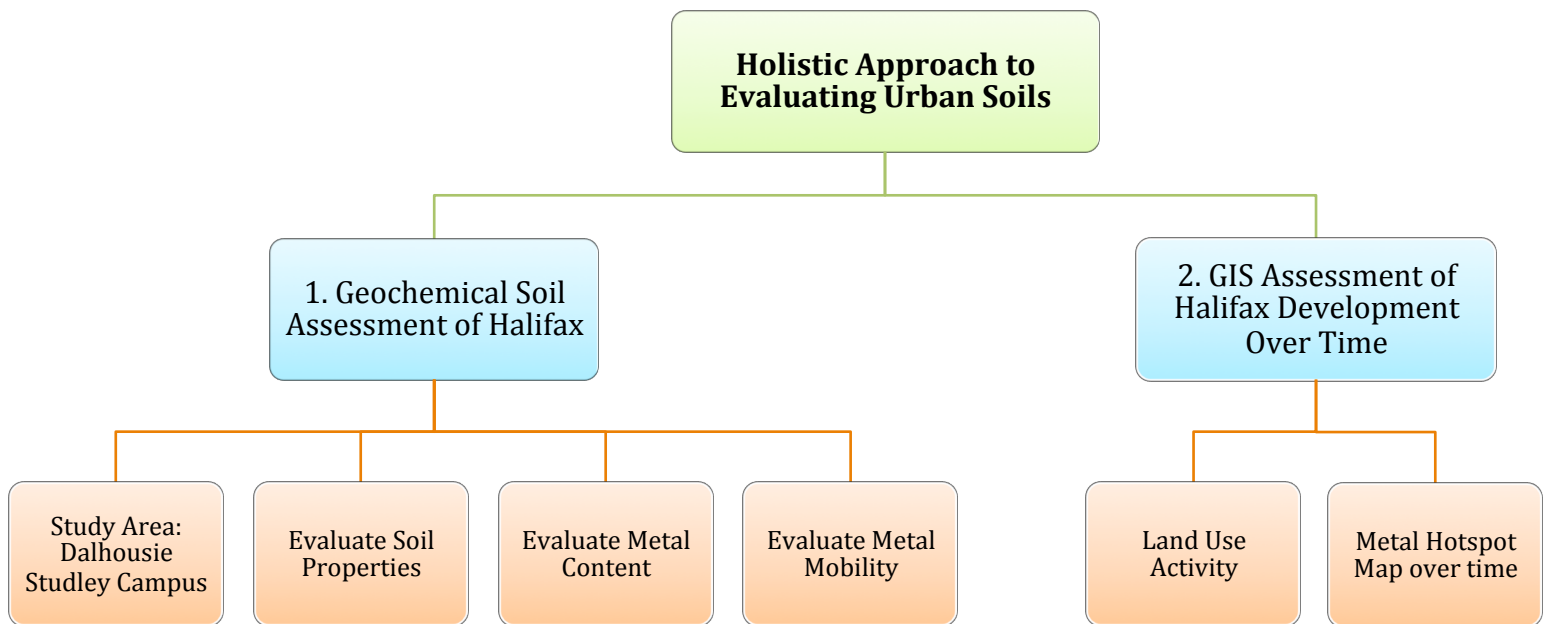


Figure 22: Illustrates workflow for the methods section and relation to general objectives.

Four approaches were taken to generate a soil assessment of Halifax soils and the conditions of the soils at Dalhousie Studley Campus:

1. To determine relationships between metal concentration and depth: Take depth-based samples from 0-5 cm and 0-15 cm depths.
2. To determine relationships between metal concentration and particle size: Chosen particle size fractions of < 2 mm and < 0.5 mm.
3. Evaluate soil properties by measuring pH, conductivity, total dissolved solids (TDS) and identify soil texture.

The following sections, 3.1 to 3.4 describe methods and rationale for depth based sampling, particle size fractions, analysis of depth and particle size using XRF, and measuring pH, conductivity, TDS, and evaluating soil texture. Section 3.5 delves into reasoning and methods for the preliminary assessments of Halifax development, and its potential impact on city soils.

3.1 Halifax Study Area

Halifax was founded in 1749, confirming it as one of the oldest cities in Canada. When studying urban soils, having city development occur over a longer time frame can prove to be advantageous. Having an older city as a region to study soils provides a good basis to understand how anthropogenic influences can affect the conditions of soils over a longer period of time (anthropogenic time frame). In addition to this, a longer time frame of development also provides a wider scope for the type of anthropogenic activities that could have influenced metal concentrations within soils. This is due to certain anthropogenic activities being more common practice and prevalent in certain centuries than others.

There were a few roadblocks preventing the study from sampling different areas throughout the Halifax peninsula. Declined permission from the municipality required another choice of sampling grounds. Dalhousie Studley Campus was initially chosen as the study area because of sampling permission, however, this site can still be considered representative of residential downtown area and a suitable location for sampling, (Figure 3). Downtown cores usually represent the original city and soils within their cores area are more likely to be exposed to various anthropogenic influences over time, such as industrial development. Dalhousie Studley University Campus is conveniently located near the downtown core and provides data that has the potential to be representative of Halifax soils in residential areas near the downtown area (Figure 3)

3.2 Soil Assessment: Depth – Based Sampling

Urban areas are unlikely to have well developed soil horizons due to the amount of redistribution and disturbance that is attributable to anthropogenic activities, and Halifax is no exception. Since soil horizons are not well developed, the depth-based sampling method (as suggested by Environment Canada and Health Canada) was the appropriate choice. The purpose of collecting depth-based samples was to compare the relationships of metal content with sample depth, metal content close to and far away from older wooden buildings, and to suggest a preliminary urban background as a baseline for metal concentrations within an urban area. For the purpose of this study an urban background will be defined as a background concentration for metals within soils residing in an urban area. An urban background provides a potential baseline for predicting what is considered “normal” for a given area.

A total of 96 soil samples were collected at different sites around Dalhousie University by the fourth year Environmental Geoscience class, (Figure 3). At each site samples of 0-5 cm and 0-15 cm depths were collected (the distance between these samples were typically a few centimeters from each other at each site). Depths were chosen based on Health Canada (0-5 cm depth) and Environmental Canada (0-15 cm depth) sampling method guidelines. Samples were collected < 2 m (proximal) and > 2 m (distal) to older wooden buildings approximately 60 or more years of age. The purpose of collecting near wooden buildings was to understand the effects of potential point source contamination. For example, older wooden buildings are likely to have leaded paint. Would elevated lead concentrations be reflected in the soil, if so in what quantities? Does this suggest that older wooden buildings do act as an anthropogenic point source for elevated lead concentrations with soils that are in close proximity? Additionally, by sampling near older wooden building potential trends and relationships of how metal concentrations affected by these potential point sources, accumulate over time and under longer-term exposure. There were 38 (29 samples at 0-5 cm depths) samples collected proximal to older wooden buildings and 58 (29 samples at 0-15 cm depths) samples collected distal to older wooden buildings.

Samples were collected using either plastic or non-metal material so as to not affect metal concentrations. Small plastic shovels and trowels were used to excavate the soil hole. Plastic rulers were used to measure the depth of each sample and latex gloves were worn to prevent cross contamination. Prior to sampling, the rich organic layer was removed by scraping it back with shovels. Between each collected sample, trowels and shovels were washed with water to avoid potential cross contamination. To ensure equal amount of sample was taken at each site and at a given depth sample were taken in a uniform shape (approximate cylindrical size) at both depths. Field notes were recorded and taken for all samples, describing soil horizons if present, clast sizes, abundance of anthropogenic materials, organisms found in sample and the conditions of each sample site Refer to the Appendices section blank for field note descriptions. At each site holes were filled with garden soil and covered with the organic layer that was removed prior to sampling. Weight of the 0-5 cm depth soil sample was approximately 0.5 kg and for the 0-15 cm depth soil sample was approximately 1 kg of soil (Figure 22 (a) and (b)).

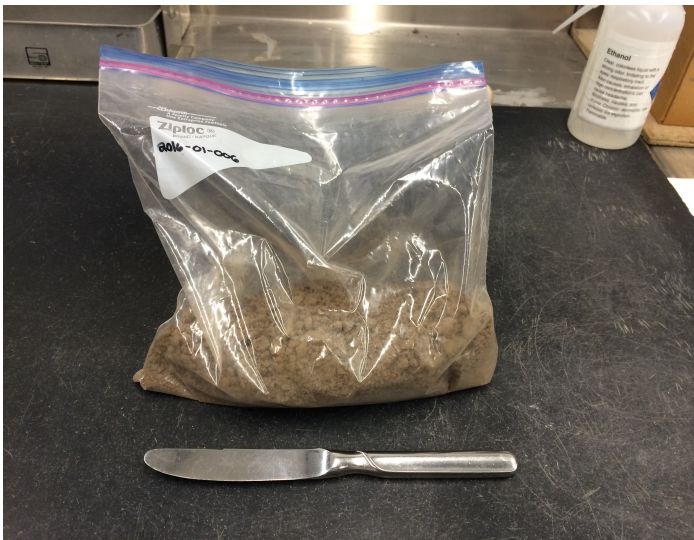


Figure 22: (a) Example of sample bags with soil



Figure 22: (b) Open bag for soil to air dry

Following collection, samples were left in open bags to air dry over a process of a few weeks. Within that time period roots, clasts, plastics, nails were removed from each

sample, to ensure that once analyzed the majority of metals within the sample would provide a wholesome representation of metal concentrations within the soil. Soils were also homogenized (rotated) to aid in air drying efficiency. Once the soils were dried, 100 grams of soil that had just been homogenized were placed into plastic bags for analysis. A portable X-Ray fluorescence (XRF) spectrometer was used at the Department of Natural Resources (DNR) to determine metal concentrations within the soil samples. A total of 96 un-sieved samples were analyzed using XRF analysis by students from the Environmental Science fourth year class, under the supervision of DNR geologist, Dr. Bob Ryan. Each sample was homogenized before XRF analysis and samples were duplicated if anomalies were identified within the data. The focus of this study was to analyze heavy metal concentrations within soil, therefore, heavy metals with CCME and NS guidelines were the elements used for the analysis (*Table 3.1*).

3.3 Soil Assessment: Particle Size Fractions

Out of the total 96 samples that were collected at Dalhousie University, samples that were identified as having elevated metals above CCME guidelines were sieved to two different sized fractions by the author. The purpose of analyzing the particle sizes for these soils was to determine whether metal content varied with grain size. For metals that do not have CCME residential guidelines Nova Scotia residential guidelines were used (*Table 5*).

There is a known correlation between finer sediment containing more heavy metal content than coarser size fractions. A common theory behind this correlation is that smaller particle sizes fractions have a larger surface to volume ratio (Smith and Huyck, 1999). Consequently, 52 of the 96 un-sieved samples were sieved to < 2mm, < 1mm and < 0.5 mm particle sizes (allowing for a total of 104 sieved samples). Locations of which samples were sieved can be found in the Appendix C. Only the < 2 mm and < 0.5 mm data are used for the analysis between metal content and particle size relationships, as preliminary assessment of the 1 mm size fraction showed little variation from the 2 mm size fraction. These particle sizes were chosen based on previous study conclusions, the largest size fractions, < 2 mm represent the larger end of soil particle size fractions, which can unintentionally adhere to children's hands, where as the smaller size fraction < 0.5 mm

represents the smaller range particle size fractions that can unintentionally adhere to human hands in general (Bergstrom et al., 2011). Although Bergstrom’s study incorporates smaller particle size fractions, this study does not, as the purpose of looking at particle size fractions is to understand how our metal content varies with particle size not how fine of a particle size can be retained on a human hand. As well, the aim was to assess representative soil samples and not “high-graded” samples.

Table 5: Samples above CCME and NS residential above metal guidelines were sieved; the table provides an outline for choosing samples to be sieved.

Element	NS Res	CCME Res	Notes
Ag	77	20	
As	31	12	*Use NS. Value due to naturally high occurrence As
Ba	10000	500	
Cd	14	10	
Cr	220	64	USE CCME normal guidelines Cr (III)
Co	22	50	LOD (Lower than detection limit)
Cu	1100	63	
Fe	11000	-	Use only the highest values - Outliers? >50000
Hg	6.6	6.6	
Mn	-	-	No Values Can't Use
Mo	110	10	
Ni	330	45	
Pb	140	140	
Sb	7.5	20	
Se	80	1	
Sn	9400	50	
Sr	9400	-	NA
Ti	-	-	No Values Can't Use
U	23	23	LOD (Lower than detection limit)
V	39	130	USE CCME guidelines - above - all NS
Zn	5600	200	

Before sieving took place, mud clasts and peds that were prominent in samples were rolled out. Samples were sieved using mechanical sieving for three-minute intervals: each sample had a total of six to nine minutes of sieving (Figures 23 (a) and (b)).



Figure 23: (a) Sieving tool



Figure 23: (b) Sieving Instrument

The weight of each sample varied between 60-100 grams. For a few smaller samples the weight was between 15 and 30 grams. All samples were analyzed through the use of a portable Innov-X 5000 XRF from the Department of Natural Resources (DNR). DNR geologist Dr. Bob Ryan and myself completed most of the analysis.

3.4 Accuracy and precision of Analysis

For both depth-based and sieved samples a number of steps were taken to ensure an appropriate representation of the sample. Before each XRF analysis, samples were homogenized. To obtain an appropriate representation of metal values, duplicates were obtained systematically. For depth-based samples, duplicates were obtained for samples that had exceptionally high values (well above CCME guidelines) or if they were well below (LOD). For sieved samples, duplicates were obtained for all samples analyzed (total of 104), additional XRF readings were run if duplicates had metal values that differed more than 10%. To account for accuracy of XRF instrument, internal standards for both analyses

were run periodically to monitor potential drift. The DNR consistently check data from this XRF instrument with alternate analytical methods to assure reasonable accuracy. Instrument precision was obtained from sieved samples XRF data, using precision calculation methods shown below from Thermo Scientific (2011).

$$\%RPD = \frac{(\text{sample result} - \text{duplicate result}) * 100}{(\text{sample result} + \text{duplicate result})/2}$$

Precision of XRF instrument was within 5% with a few that ranged between 10-12% and only two samples that had 20% precision (Appendix D)

3.5 Soil Assessment: pH, Conductivity, TDS and Soil Texture

For each soil analyzed, pH, conductivity, and TDS were measured using a hand held pH meter. This data was produced by two students undertaking an independent research project as part of their integrated science program. Methodology for evaluating the soil properties of the soil samples were based on guidelines Kalra 1995 study, which compared different methods for the evaluation of soil pH. This study chose to follow the first method due to its straight forward nature of evaluating soil pH. This method involved the use of a pH meter, which could record pH, conductivity, and TDS values, paper cups, and tap water. Measurements of distilled water pH were collected and it was found that, that due to dissolved gases in the pipes distilled water was more acidic (ranging from 5-6) than the tap water, which had a pH of approximately seven. Tap water was therefore used. A 2:1 ratio of water to soil was used, since the soils samples were rich in organic matter. Approximately 10 grams of soil were weighed into paper cups and 20 mL of water were added to each cup. Measurements were collected after a time period of 15 minutes, which allowed for suspended sediments to settle. Between each recorded measurement, pH meters were rinsed with tap water and temperature was collected for each measurement, usually resting at a room temperature of 21°C.

Soil texture was determined by using a standard field method, which involves combining a hand sample size of soil with water and kneading it into a bolus until soil no longer sticks to the palm and there is no apparent change in plasticity (soilquality.org.). This time frame ranged from one to two minutes. Once the bolus form was completed, it is sheared between a thumb and forefinger to create a ribbon structure approximately 2 mm thick and 1 cm wide. The length of the ribbon is recorded and compared to a table which suggests the soils likely field texture grade and classification.

3.6 GIS Component: Potential locations for Halifax Metal Hotspots

Predicting the potential locations of metal hotspots within an urban soil holds significant challenges. Metal hotspots are defined in this section as locations where elevated metal concentrations are found within soil. Urban soils are often disturbed and since Halifax is older city there are a variety of anthropogenic influences, which contribute to metal concentrations within the soils. Pinpointing anthropogenic activities and studying city development is important in identifying potential point sources and anthropogenic influences upon metal content within the soil. Building preliminary maps that pinpoint locations of potential metal hotspots can aid the holistic understanding of how city development can shape the conditions of its soils and can potentially aid future projects on choosing sampling locations.

Predicting the locations of potential metal hotspots within Halifax is primarily dependent upon the interpretation of land use data through time. Based on previous studies (refer to section 2.9.3) there is a significant correlation between certain land use activities and metal abundances within city soils. By pinpointing the locations of certain industries and land use activities known to contribute and influence certain metal concentrations within soils, potential locations for metal hotspots were identified, using maps available through N.S. Archives.

Maps of Halifax's development from 1746 till the late 1900's were obtained from the Nova Scotia Archives. Land use data were collected from these maps to determine potential hotspots, which were identified and geo-referenced through the use of the 10.3 Arc Geographic Information System (GIS) software, (Figure 24).

1910

RMS ERROR

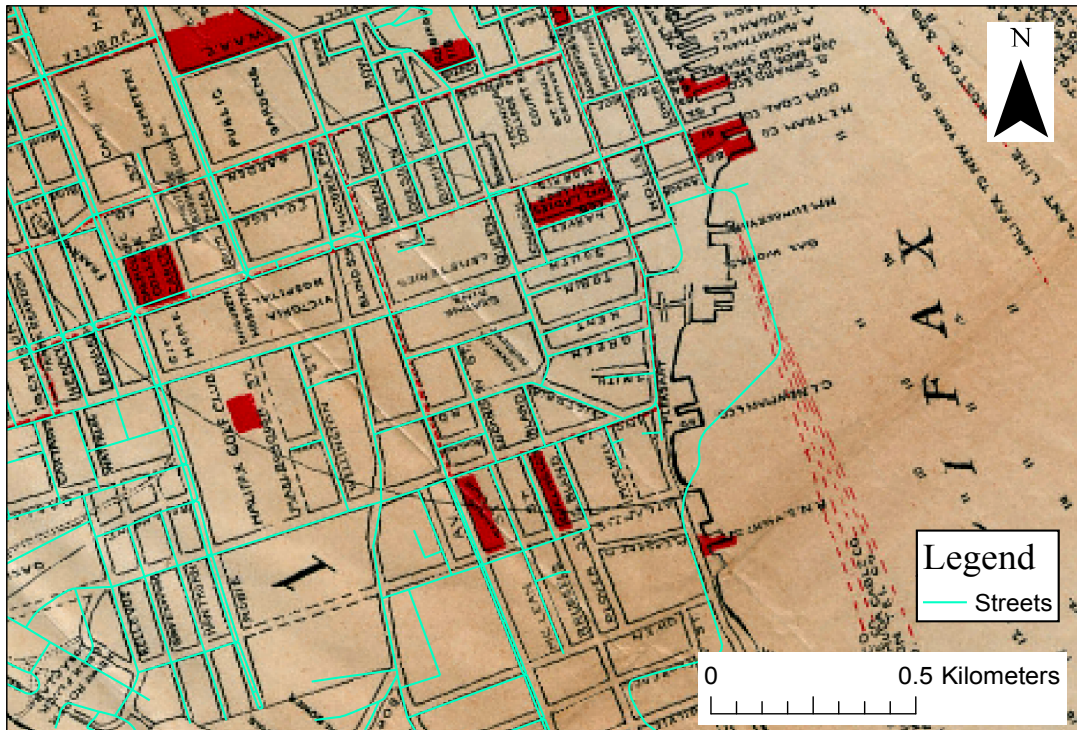


Figure 24: Example of a geo-referenced image of a 1910 map on Arc GIS 10.3 software

In addition to pinpointing land use activities that occurred, potential migration pathways, such as rivers and streams were also identified. Rivers and streams were denoted through the use of polylines, and potential hotspot locations are denoted through the use of polygons. Maps used to identify potential hotspots area available in Appendix A.

4.0 Results

The metals focused on within the results section are V, Cr, Mn, Fe, As, Ni, Cu, Zn, Sr, Ba, and Pb. Metals picked for graphing analysis are metals with CCME and NS contaminated sites, residential guidelines. Furthermore, other metals analyzed but omitted from graphing analysis are metals with the majority of sample concentrations lower than the detection limit (LOD). These metal concentrations are determined through the use of XRF analysis on soil samples both sieved and un-sieved. For all samples, metal concentrations represented graphically, are averages of the duplicated results. Additionally, it is important to note that outliers are included within the analysis, and therefore some outliers may drive or skew some of the results.

4.1 Soil Properties: pH, Conductivity, TDS and Texture

Metals behaviour is often influenced by different soil conditions or soil properties. For example, certain metals will be more mobile than others depending on the acidity or alkalinity of a soil. Conductivity and total dissolved solids (TDS) are strongly related to each other and as expected TDS values are proportional relative to conductivity values (Figure 25). There is no clear or consistent relationship, between conductivity (or TDS) and pH. Understanding of how metals may move within solutions is important for understanding the affects of migration pathways, however, that is slightly out of the scope of this thesis since the aim is to understand the mobility of metals within soil, not water. Soil texture aids our understanding of the dominant grain sizes and type of soil present, which also influences metal mobility and concentration. The focus of this section is pH and soil texture. Conductivity and total dissolved solids sample data is further provided in the Appendix B.

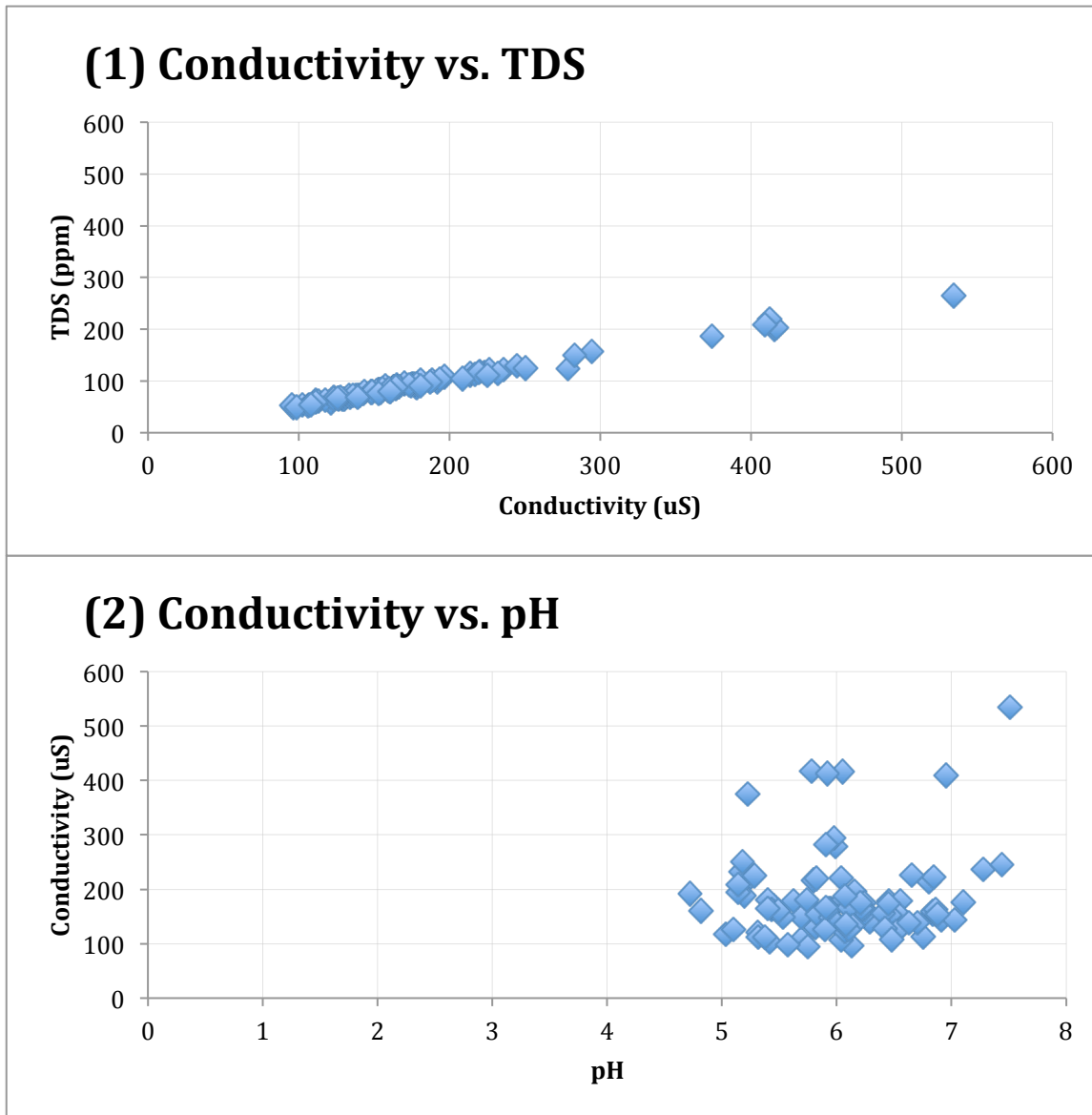


Figure 25: Depicting Conductivity, TDS and pH data. (1) demonstrates a positive relationship between conductivity and TDS (2) relationship between conductivity and TDS could not be identified.

There are ten locations that depict the general area where samples were taken across Dalhousie campus: Sheriff Hall, Colpitt House (1424-1444 Henry St.), Economics Buildings (6206, 6214, and 6220 University Ave.), Sir James Dunn Building, Life Sciences Centre (LSC), DeMille House (1411 Seymour Street), Killam Library, Dalplex (6260 South St.) and Novel Tech Ethics House (1379 Seymour) (Figure 3). Each of these sites exhibits some variability in terms of soil pH (Table 6).

Table 6: Table demonstrating pH averages and pH ranges of soil for each location and for the samples taken at that location.

Site	Soil pH (0-5 cm Depth)	Soil pH (0-15 cm Depth)
Sheriff Hall n= 12	Mean pH: 6.08 Range: 4.72-6.84 n= 12	Mean pH: 6.09 Range: 5.03-7.10 n= 12
Colpitt House	Mean pH: 6.5 Range: 5.82-7.02 n= 11	Mean pH: 6.4 Range: 5.90-6.88 n= 11
Economics Buildings	N/A	N/A
Sir James Dunn	Mean pH: 6.07 Range: 5.31-7.51 n=7	Mean pH: 6.08 Range: 5.49-7.28 n=7
Life Sciences Centre (LSC)	Mean pH: 6.12 Range: 5.69-6.55 n=7	Mean pH: 6.36 Range: 5.62-7.44 n=7
DeMille House	Mean pH: 6.28 Range: 5.23-6.53 n=7	Mean pH: 6.43 Range: 6.42-6.45 n=7
Killam Library	Mean pH: 5.70 Range: 5.19-6.65 n=6	Mean pH: 5.56 Range: 5.10-6.07 n=7
Dalplex	Mean pH: 5.70 Range: 5.44-6.24 n=7	Mean pH: 5.20 Range: 4.82-5.57 n=7
Novel Tech Ethics House	Mean pH: 6.37 Range: 6.04-6.80 n=3	Mean pH: 6.11 Range: 5.74-6.48 n=2

Note*: N/A: Some samples did not have enough soil required for the procedure of taking pH measurements. Details of sample numbers and given location provided in Appendix C.

The following graphical analysis compares a particular metal's concentration against pH level. Each metal has two sets of graphs, the first, is a graphical representation of metal concentration plotted against pH level at 0-5 cm depth and the second is metal concentration plotted against pH level at 0-15cm depth. Black lines within the figures represent averages of both pH level and metal concentration. All of the sample names are labeled with aliases for aesthetic purposes, a list of which alias is associated with which sample number is in Appendix C .

The goal is to identify whether a relationship exists between a particular metal concentration and pH level. The metals that are analyzed in the following graphs are also ordered and grouped in a specific manner. For the purposes of representation here, the first set of metals that are grouped together are Mn, As, and Fe. These metals are naturally elevated in concentration within Halifax soils. The second set of associated metals is Pb, Ba, and Sr. These metals are cations with similar ionic charge and radius. The third set of associated metals is Cu, Ni, and Zn. These metals are also cations with similar ionic radius and charge. The fourth set of associated metals is V and Cr, which can occur also as oxyanions, similar in ionic radius and charge. Most of the metals analyzed in the following graphs do not demonstrate a clear relationship between pH and metal content, however, some metals such as As, Fe, Ba, and V seem to possibly demonstrate an inverse relationship.

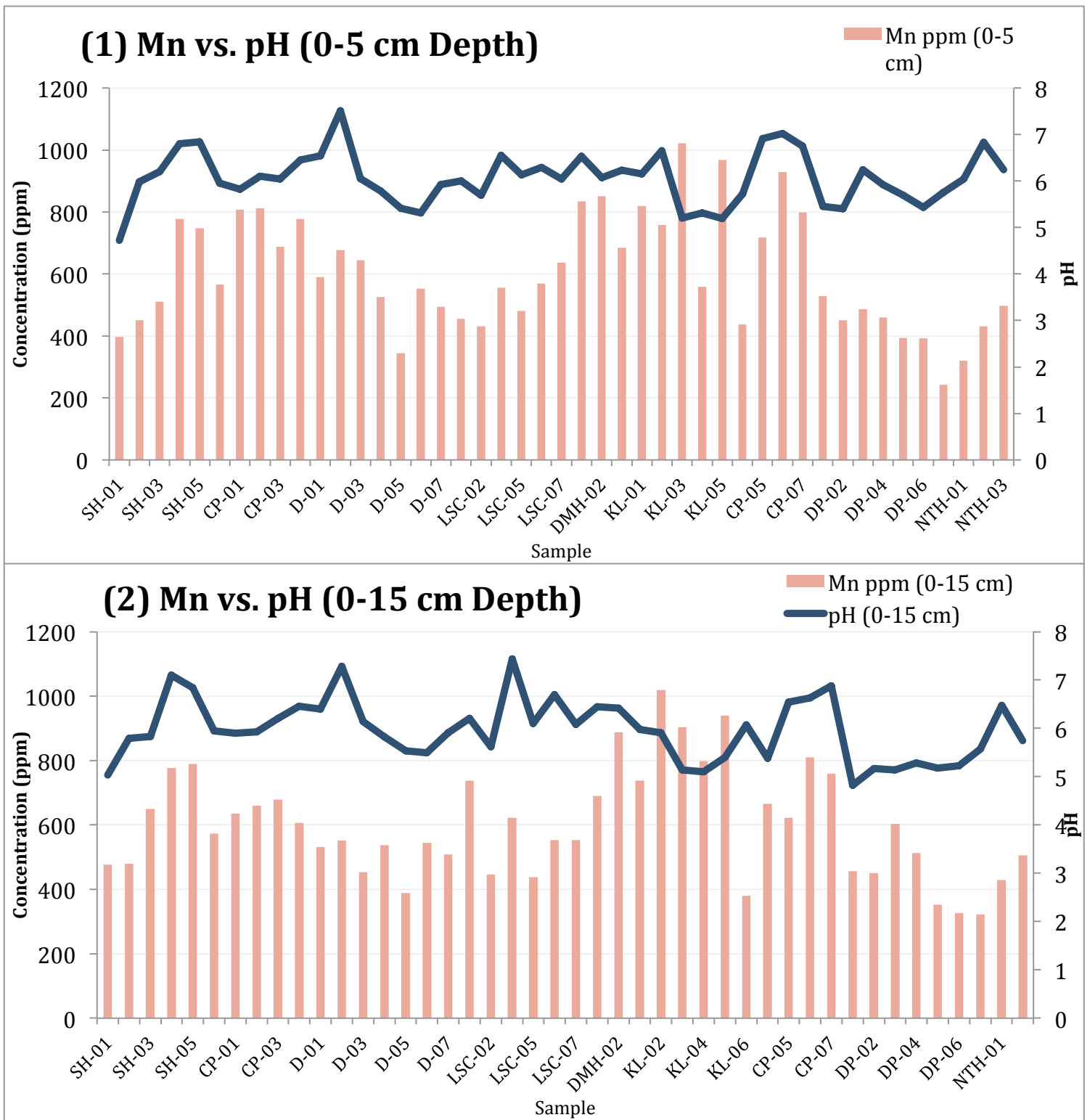


Figure 26: Graphical representation of average Manganese (Mn) concentration versus pH level at (1) 0-5 cm depth and at (2) at 0-15 cm depth. There are no CCME or NS guidelines for Mn.

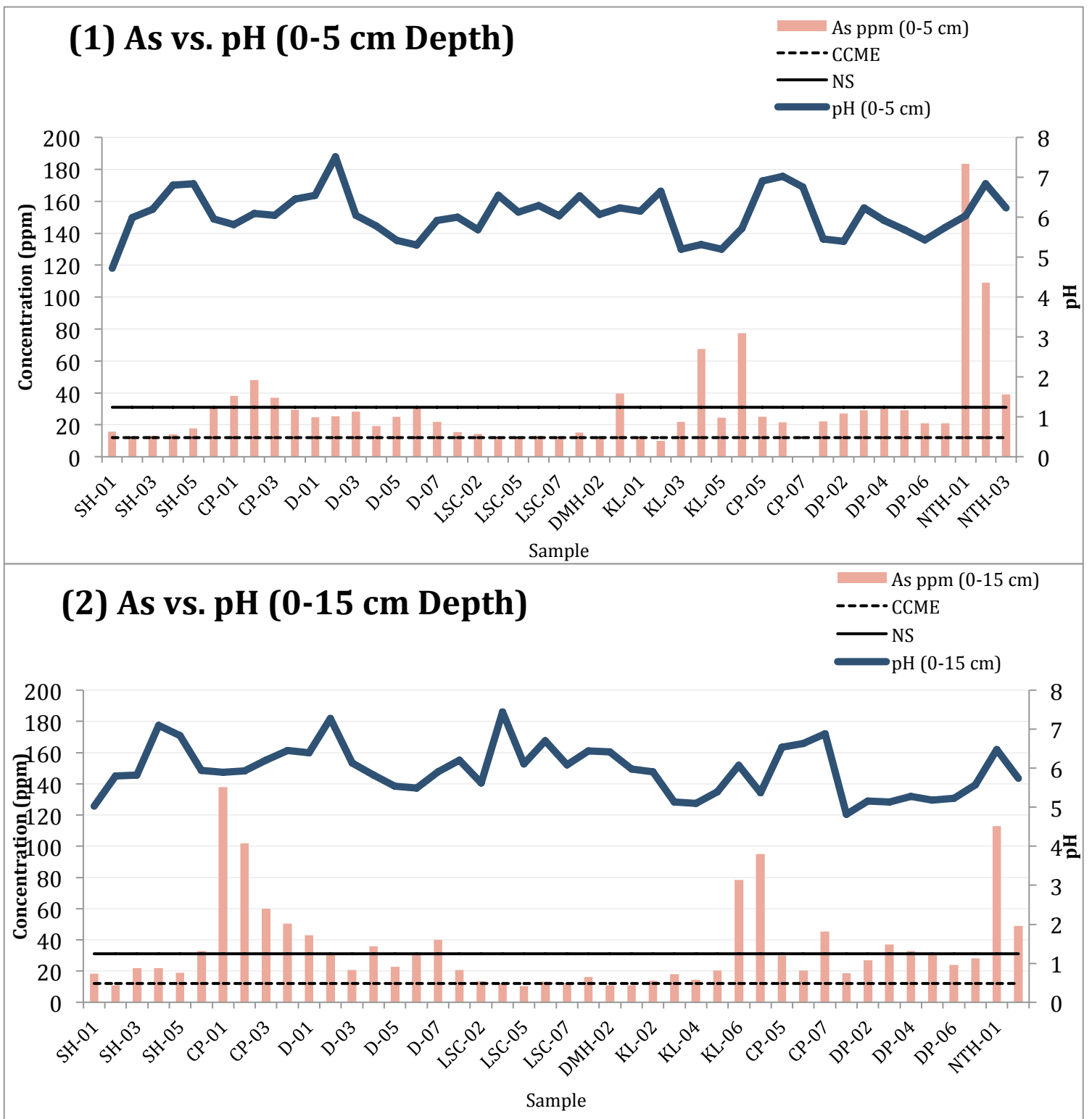


Figure 27: Graphical representation of average Arsenic (As) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. Black lines depict CCME (dashed) and NS (bold) guidelines.

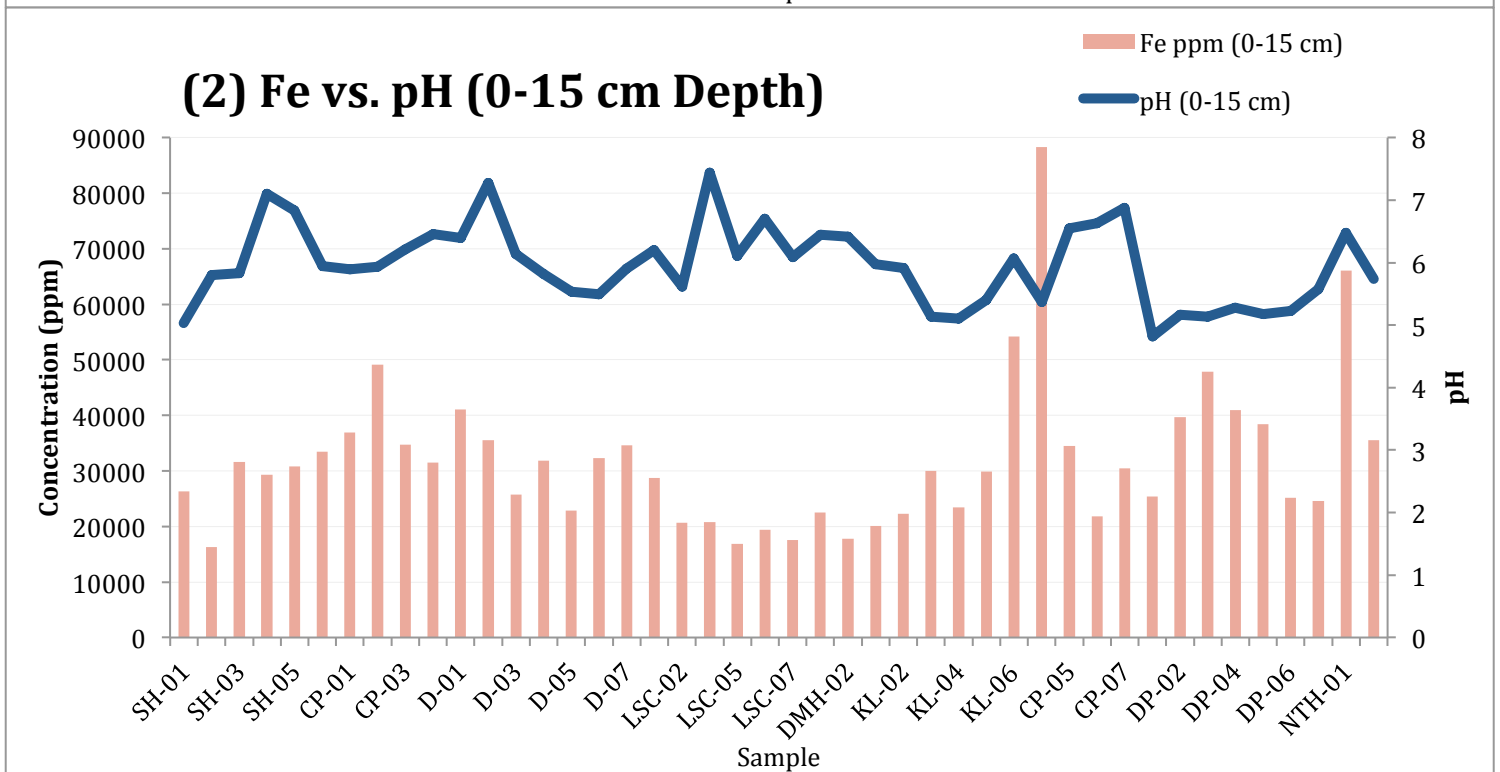
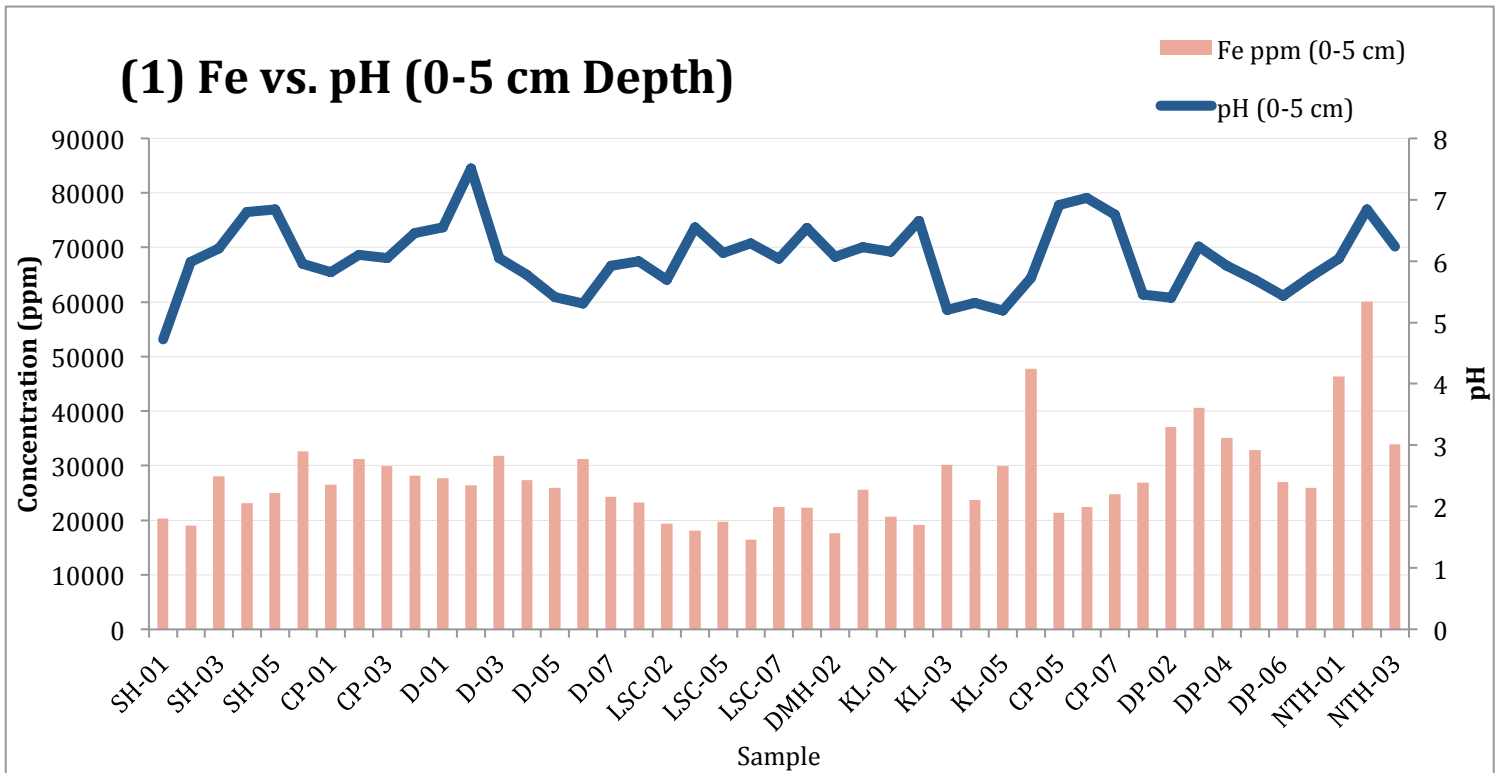


Figure 28: Graphical representation of average Iron (Fe) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. There are no CCME guidelines for Fe.

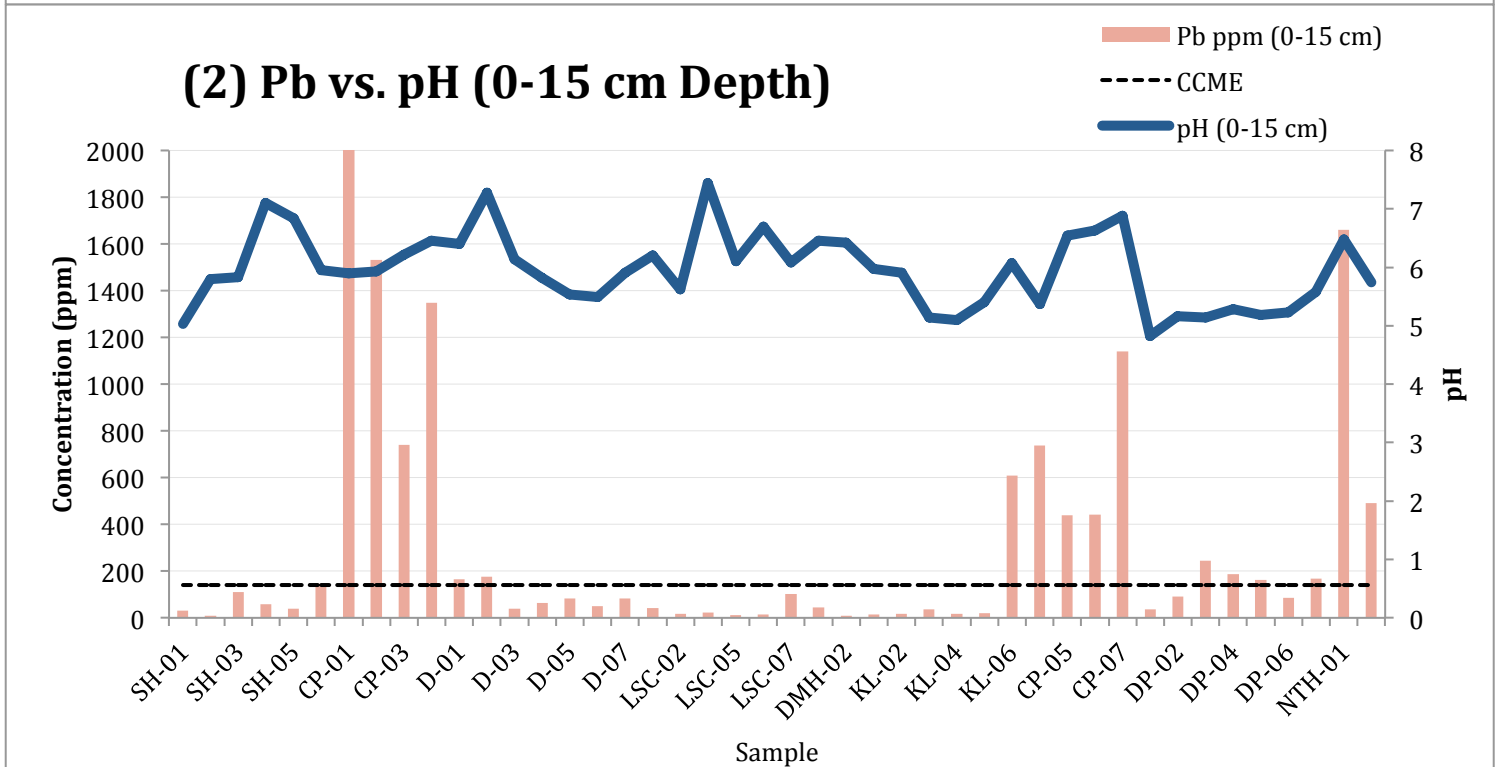
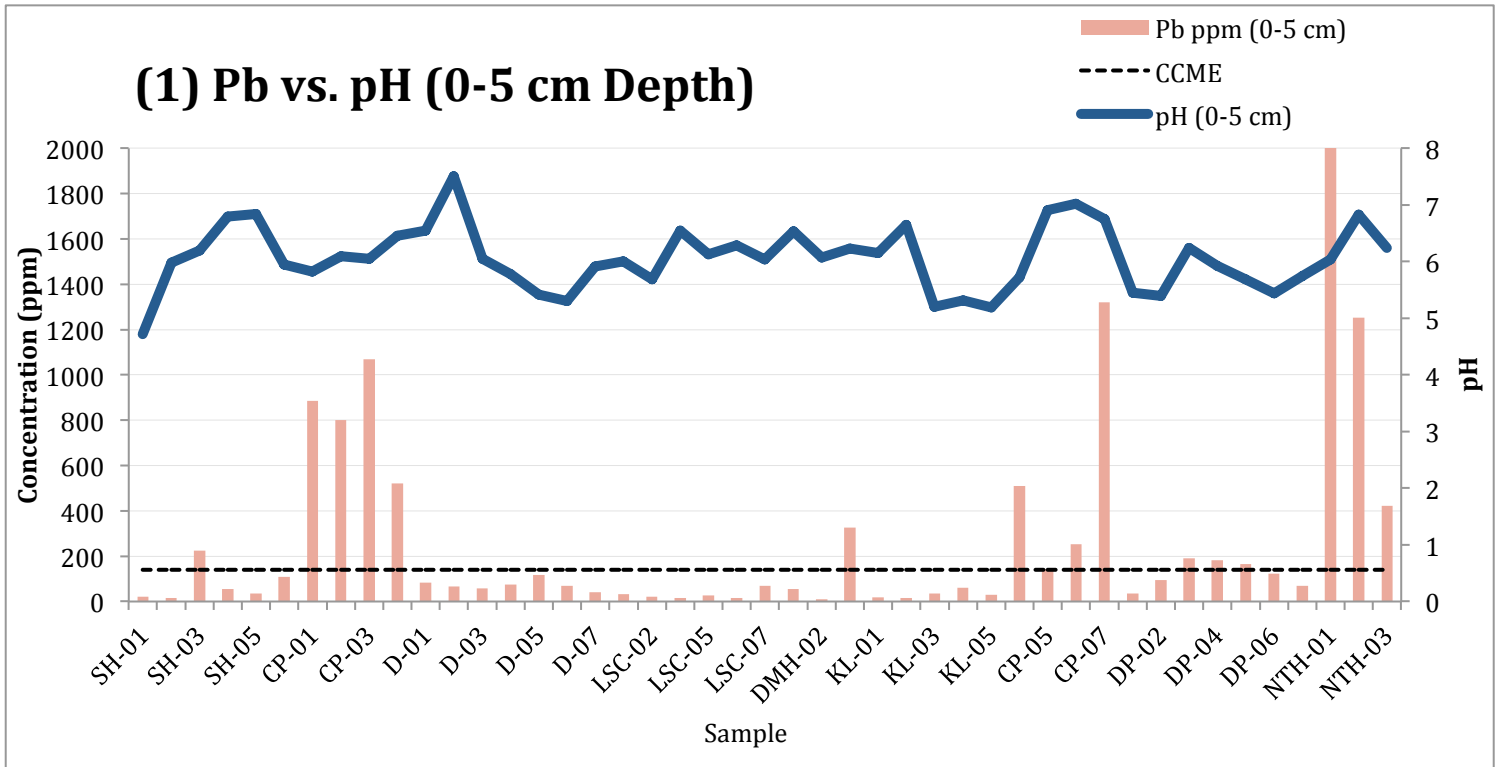


Figure 29: Graphical representation of average Lead (Pb) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. Black dashed line depicts the CCME guideline.

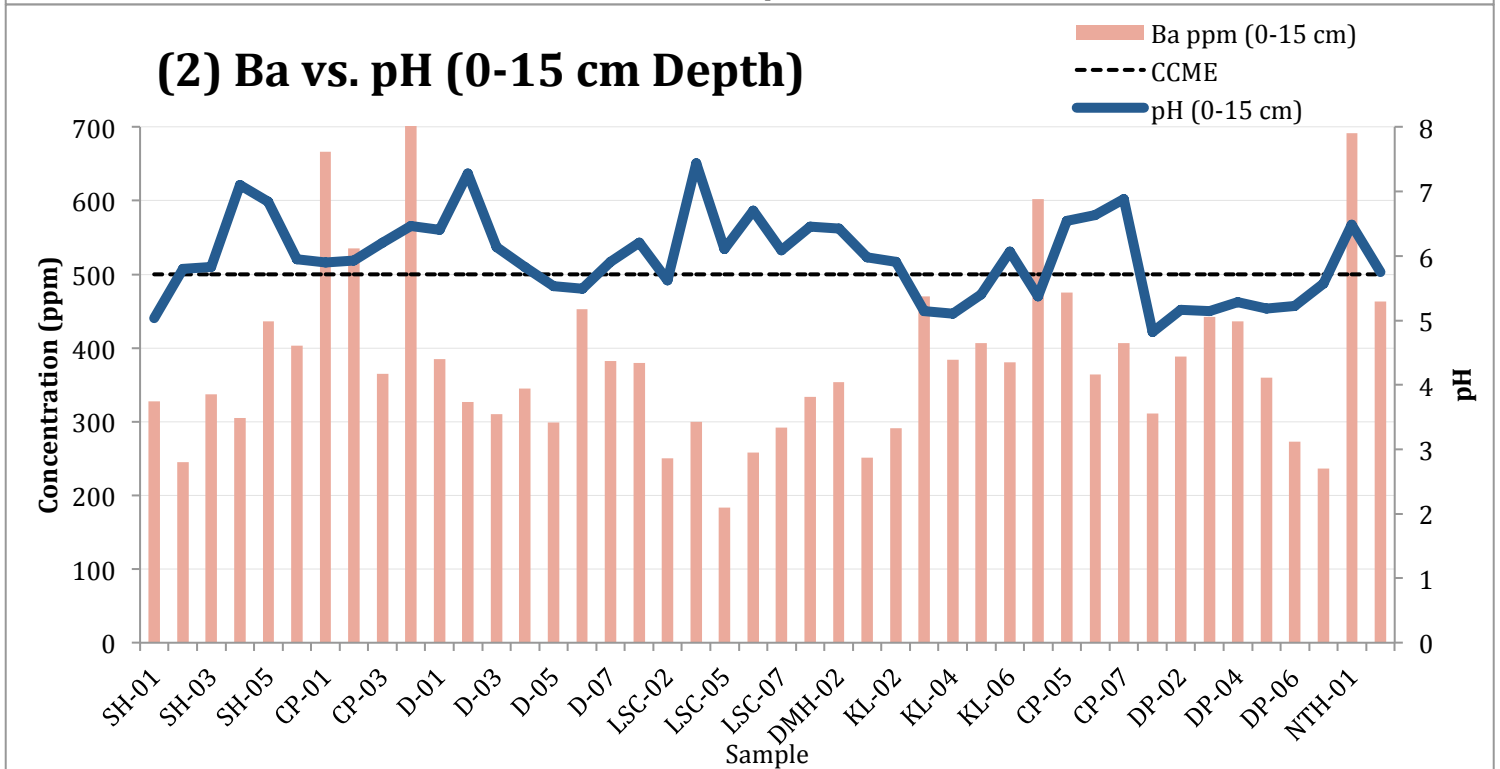
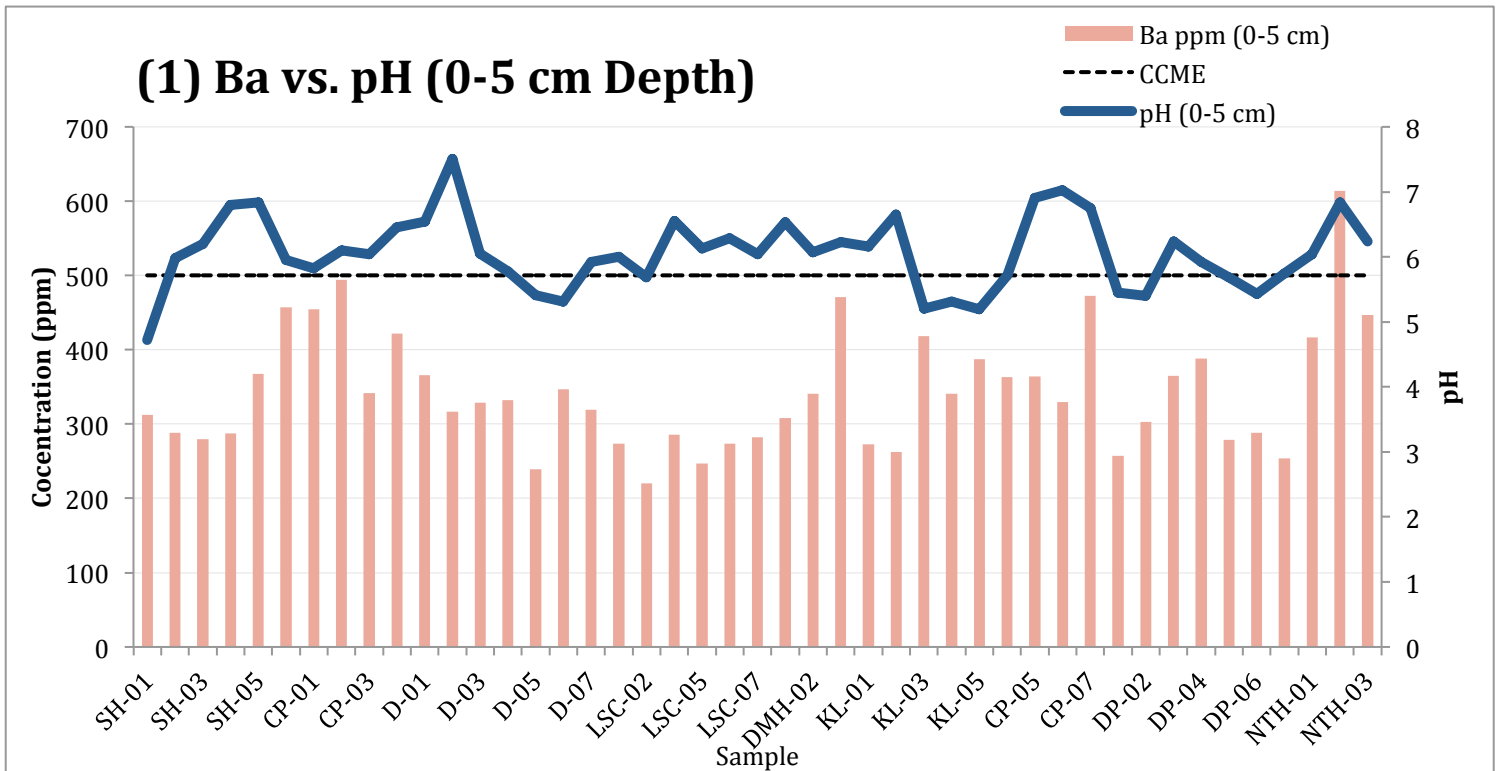


Figure 30: Graphical representation of Barium (Ba) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. Black dashed line depicts the CCME guideline.

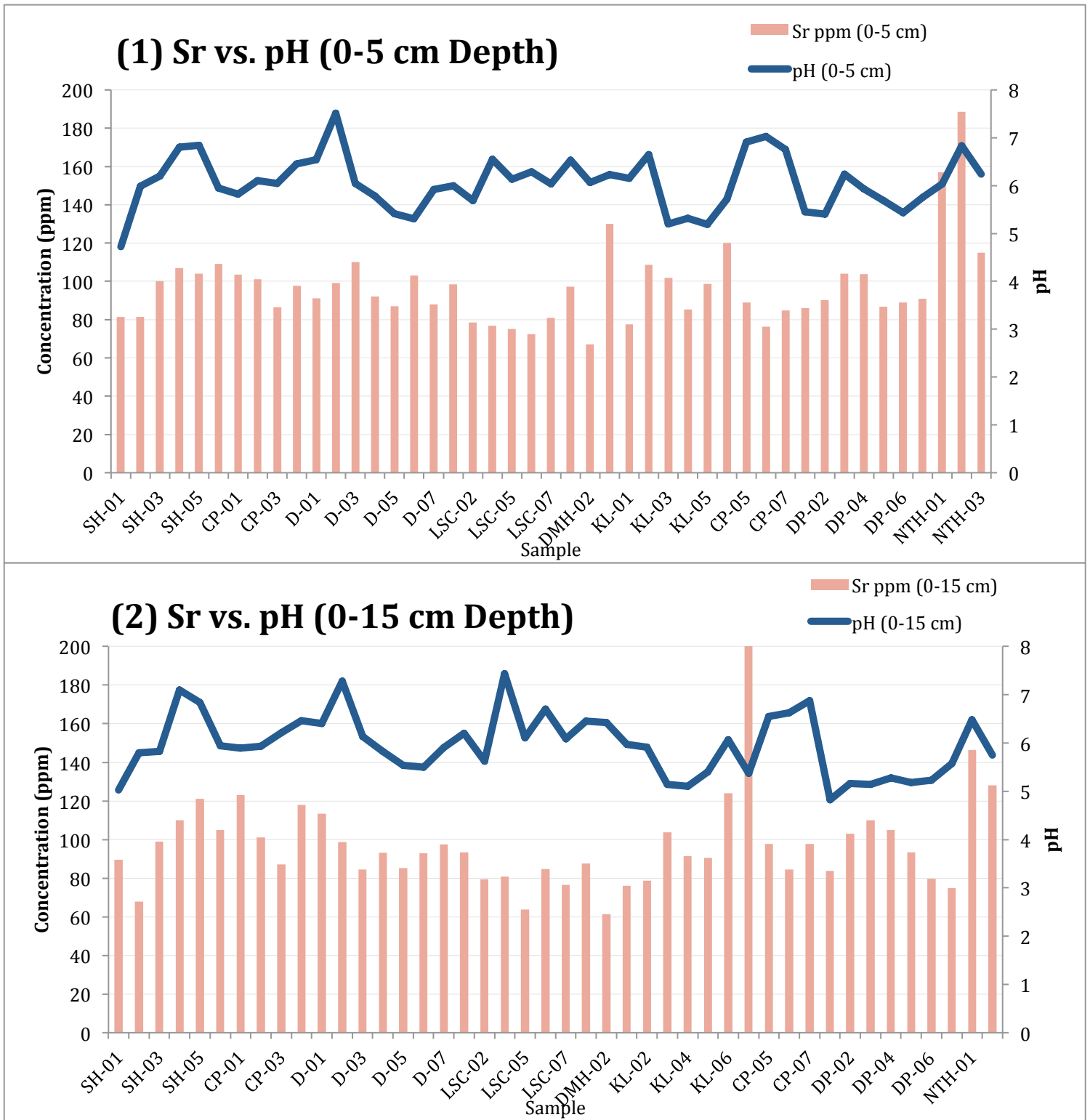


Figure 31: Graphical representation of average Strontium (Sr) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. There are no CCME guidelines for Sr.

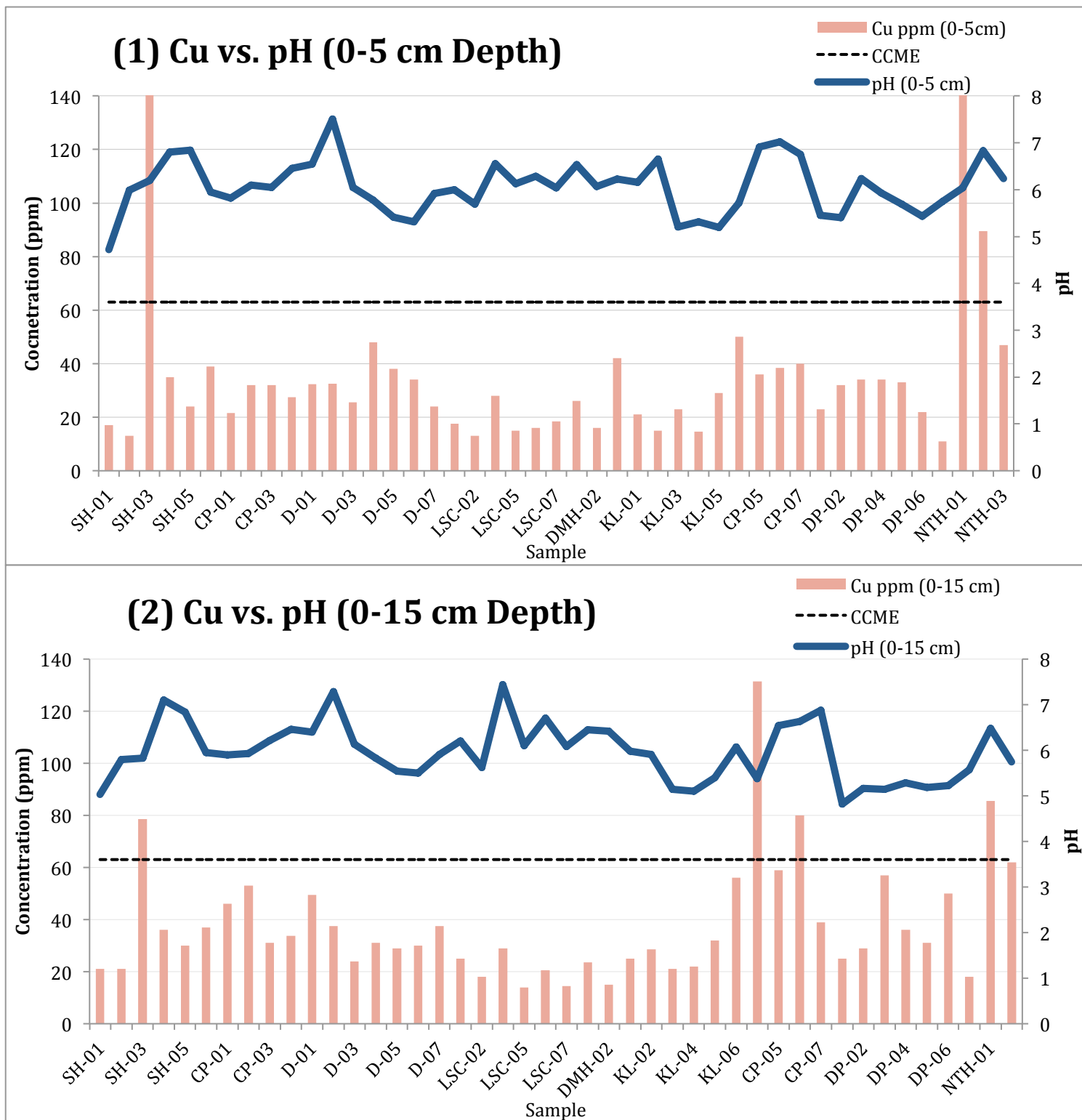


Figure 32: Graphical representation of average Copper (Cu) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. Black dashed line depicts the CCME guideline.

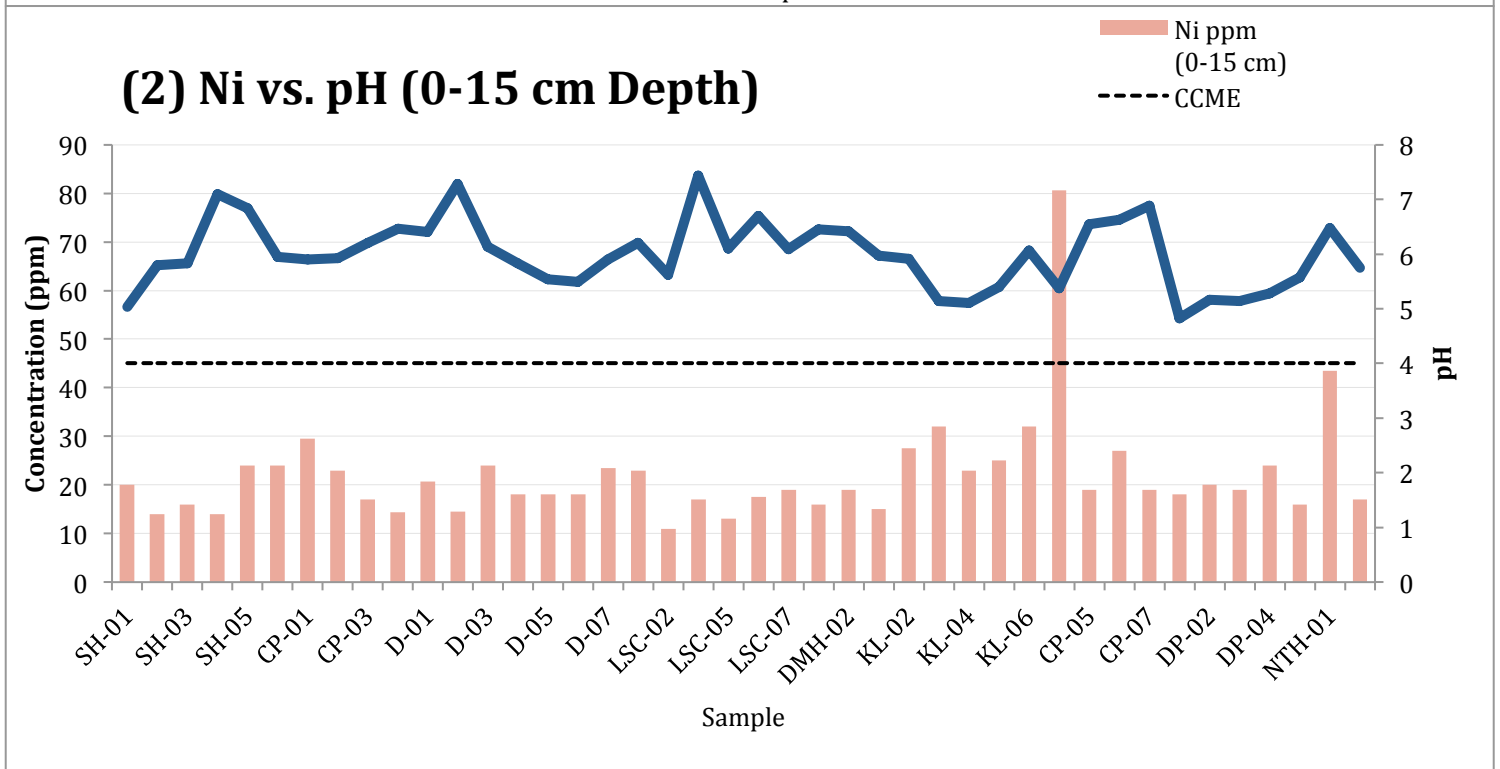
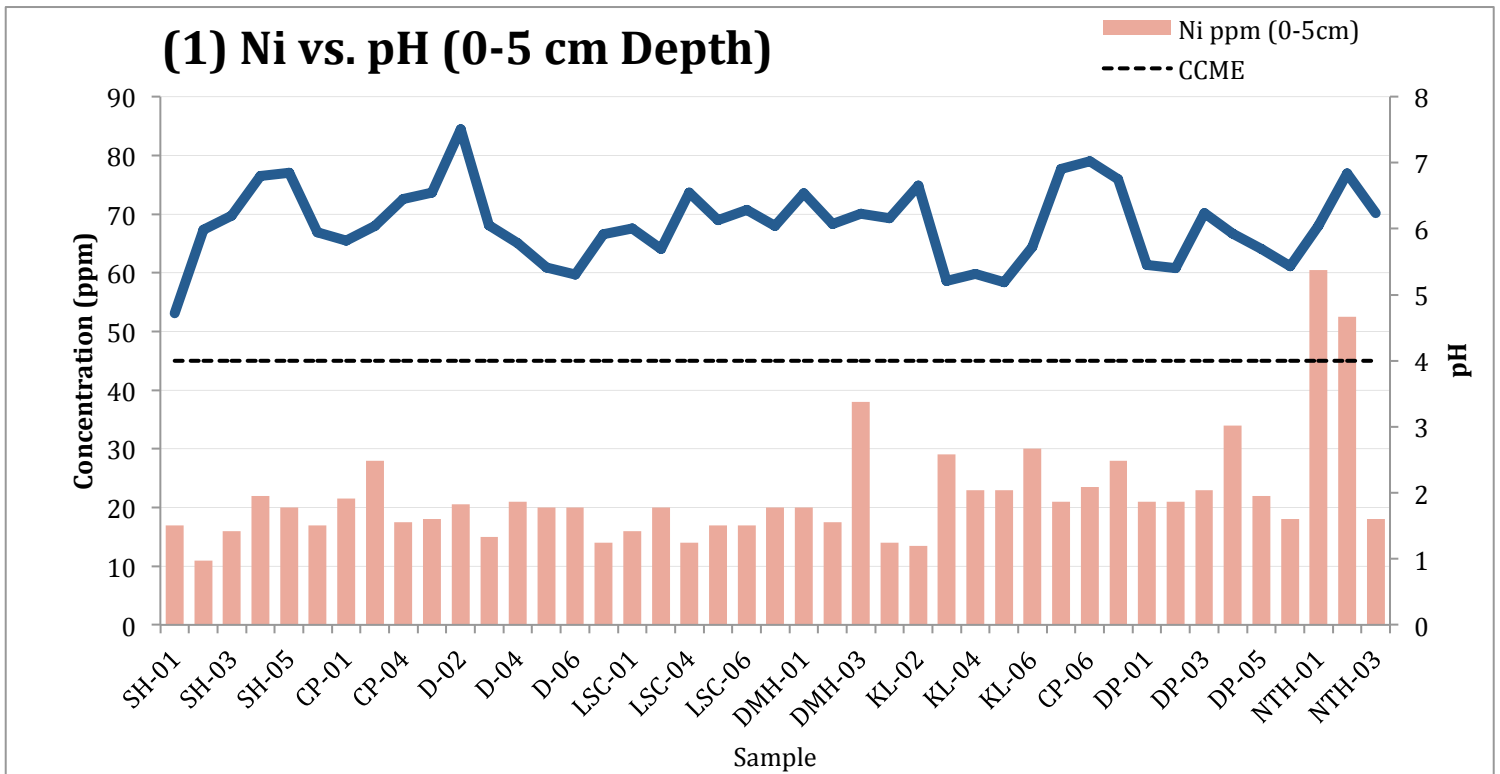


Figure 33: Graphical representation of average Nickel (Ni) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. Black dashed line depicts the CCME guideline.

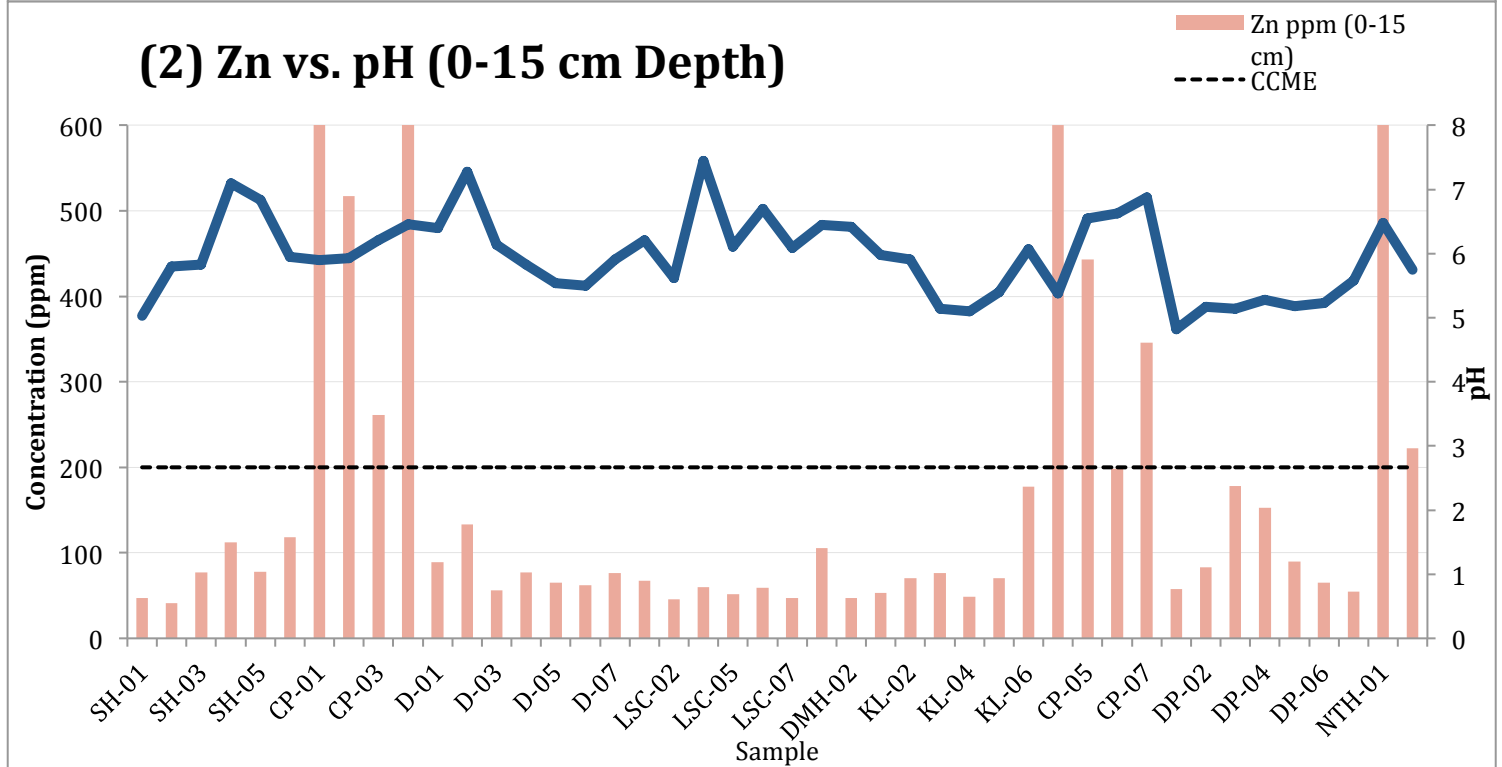
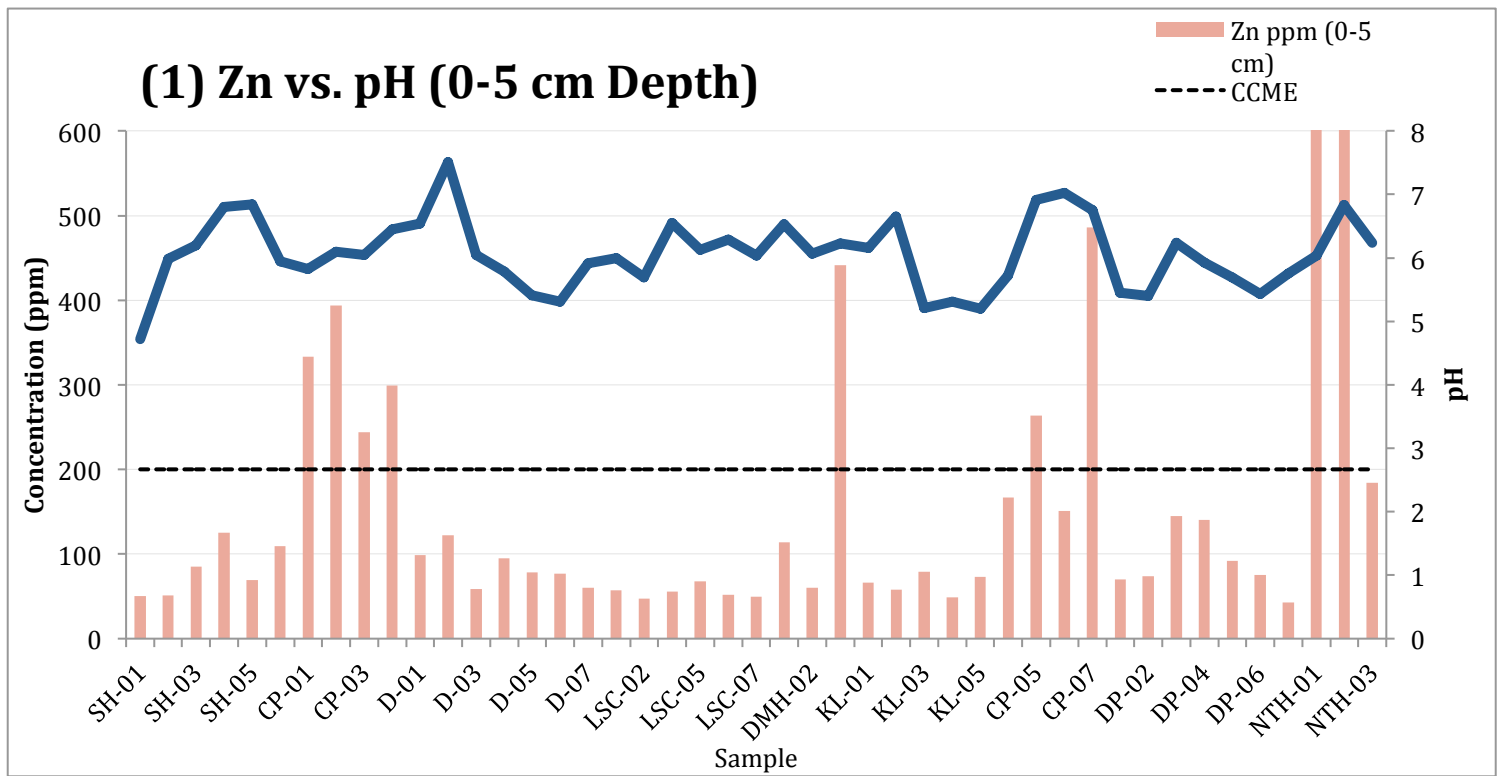


Figure 34: Graphical representation of average Zinc (Zn) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. Black dashed line depicts the CCME guideline.

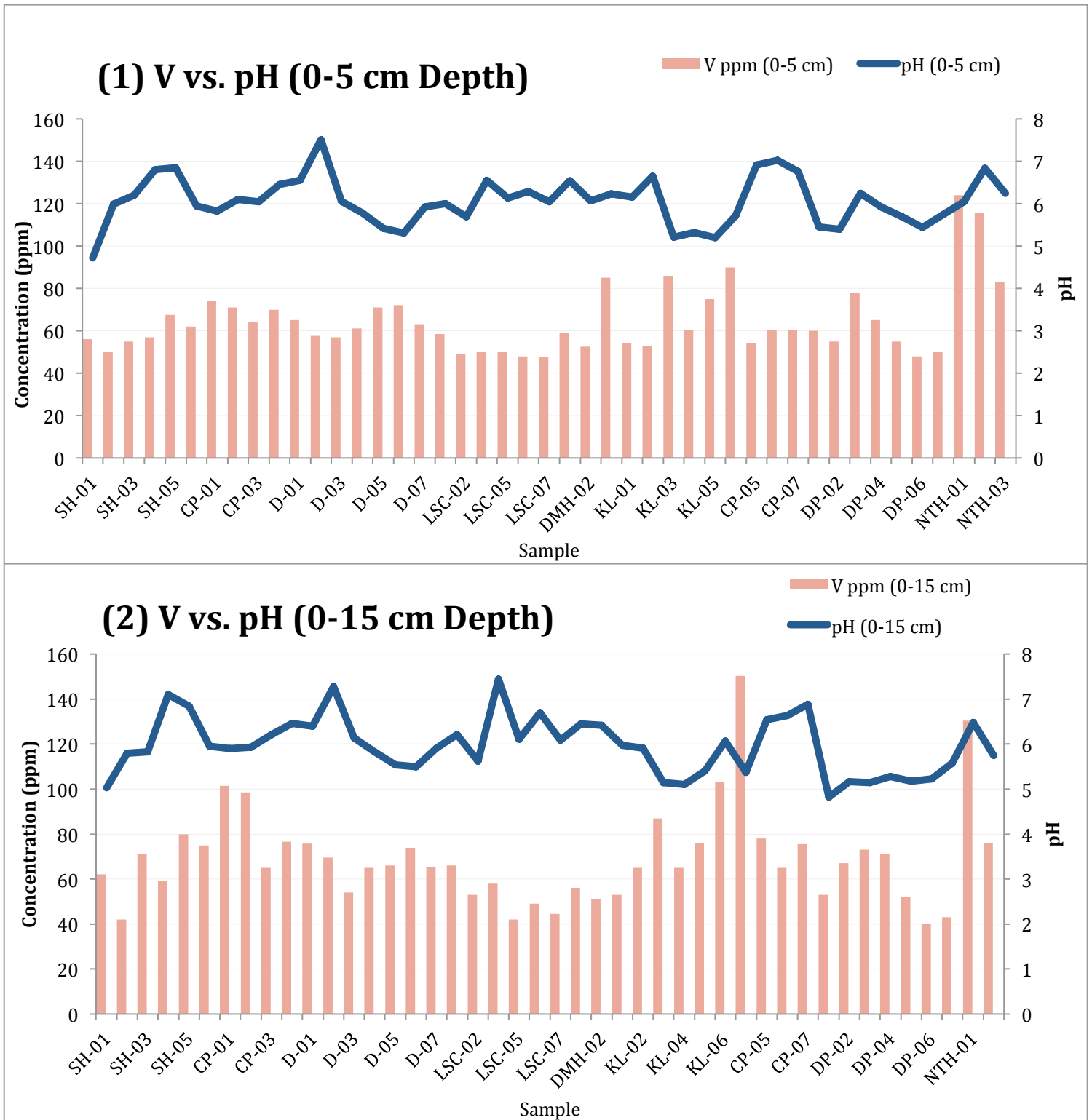


Figure 35: Graphical representation of average Vanadium (V) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. There are no CCME guidelines for V.

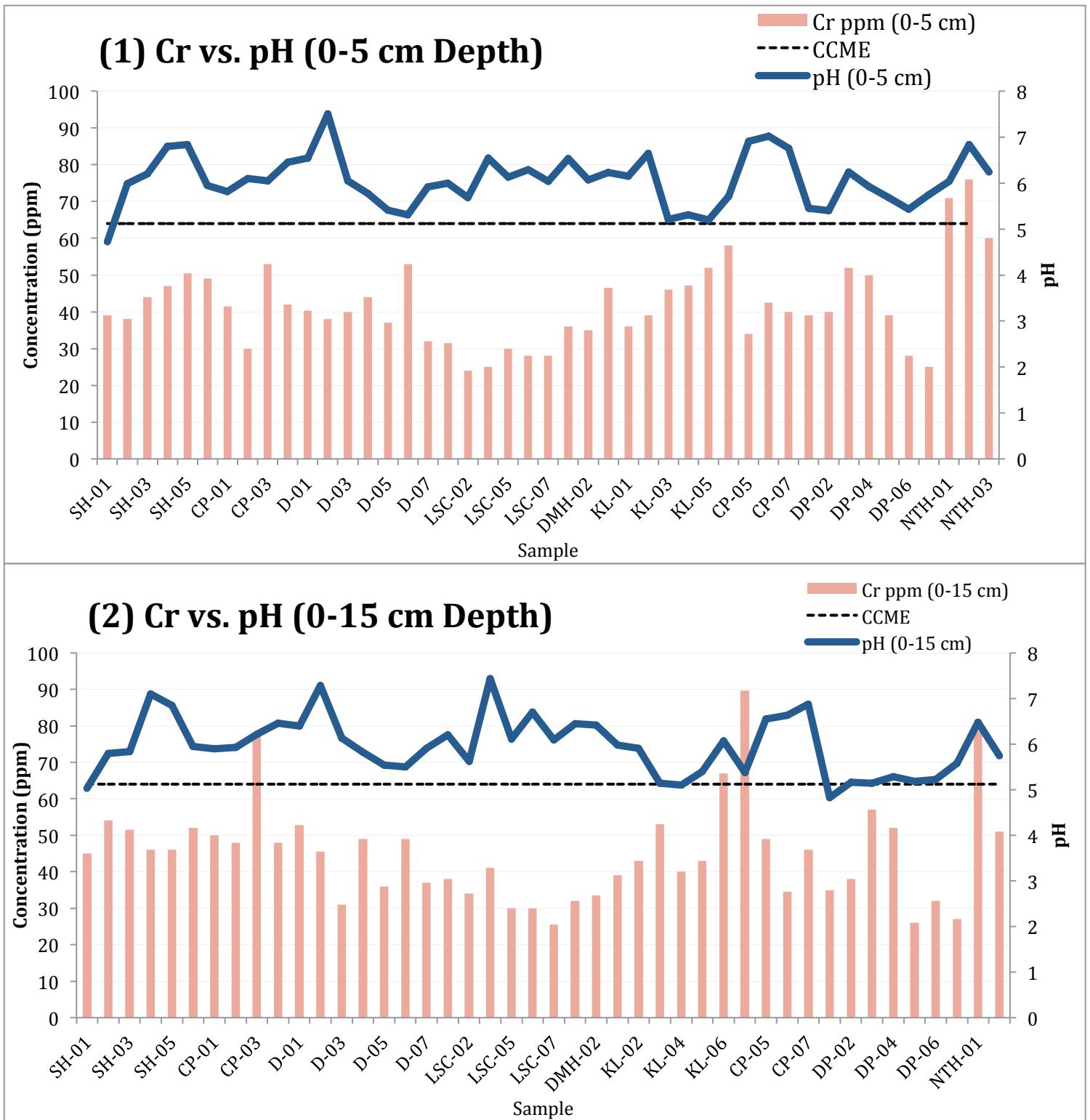


Figure 36: Graphical representation of average Chromium (Cr) concentration versus pH level at (1) 0-5 cm depth and at (2) 0-15 cm depth. Black dashed line depicts the CCME guideline.

4.2 Soil Assessment: Depth Based Sampling

Metal concentrations of depth based soil samples obtained by XRF analysis are demonstrated through graphical representations. The following graphing analysis attempt to answer three main questions associated with depth based sampling analysis:

1. How does metal concentration vary with 0-5 and 0-15 cm depth based samples?
2. How does metal concentration vary with location, proximal (< 2 m away from older wooden buildings) and distal to (> 2 m away from older wooden buildings) older wooden buildings? Do these older wooden buildings act as anthropogenic point sources?
3. Can an urban background for metal concentrations be provided from depth based sampling data that is representative of Dalhousie Studley Campus soil and to an extent Halifax soil?

The following graphs and T-test calculations are used to determine relationship of metal concentration with depth. Each graph depicts a specific metal and its concentration in 0-5 and 0-15 cm depth. The following graphs are ordered the same as section 4.1 in metal groups associated either with naturally occurring abundance or associated with like metal properties. The following graphical data and T-tests show that 0-15 cm depth have higher metal concentrations than 0-5 cm depth samples. T- test calculations are provided in Appendix C.

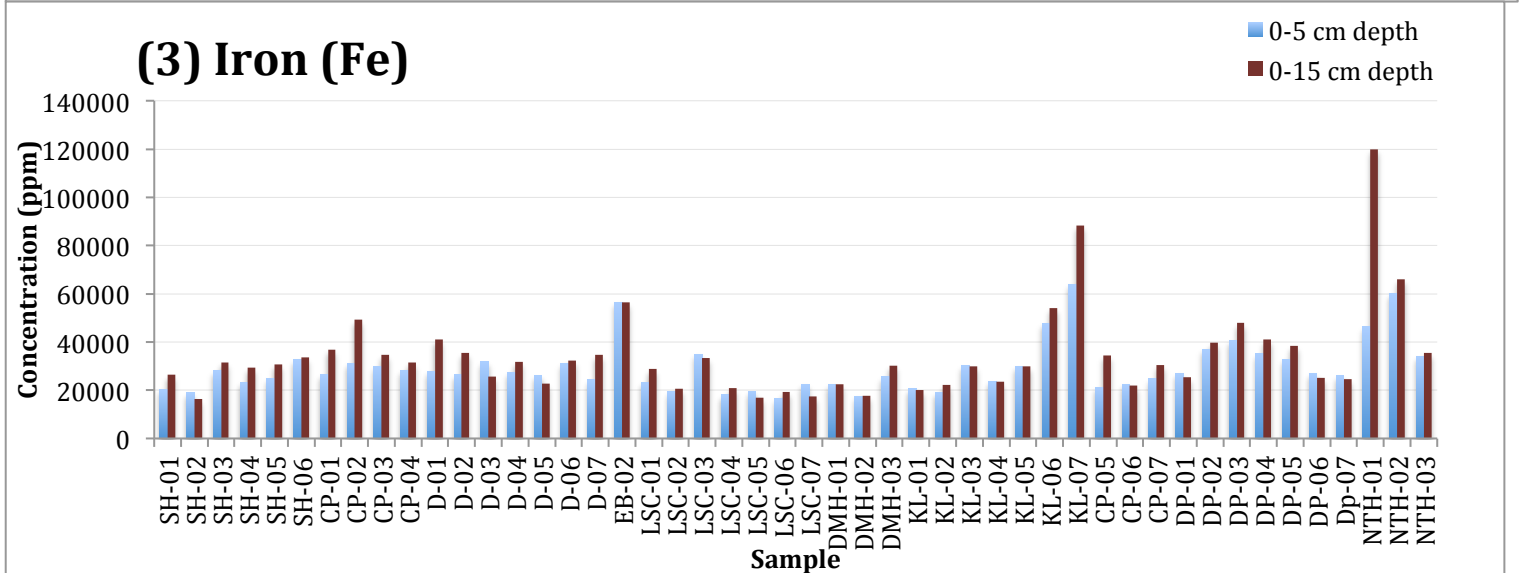
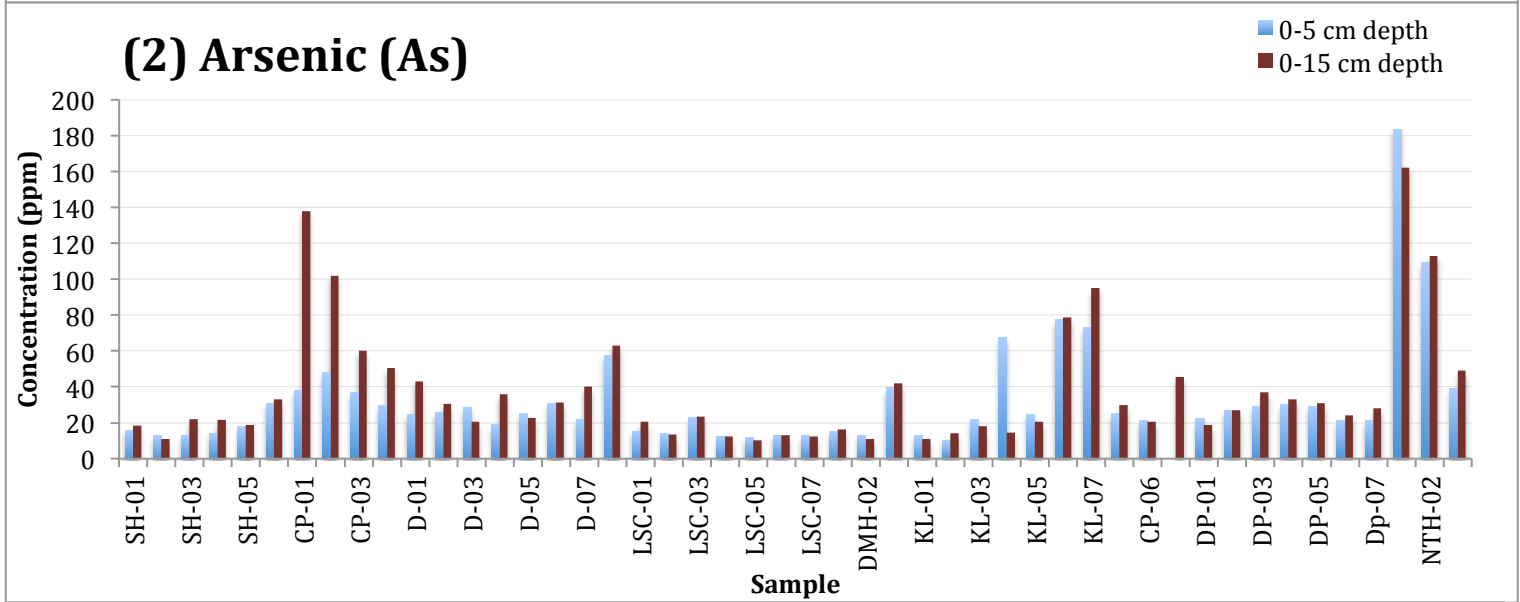
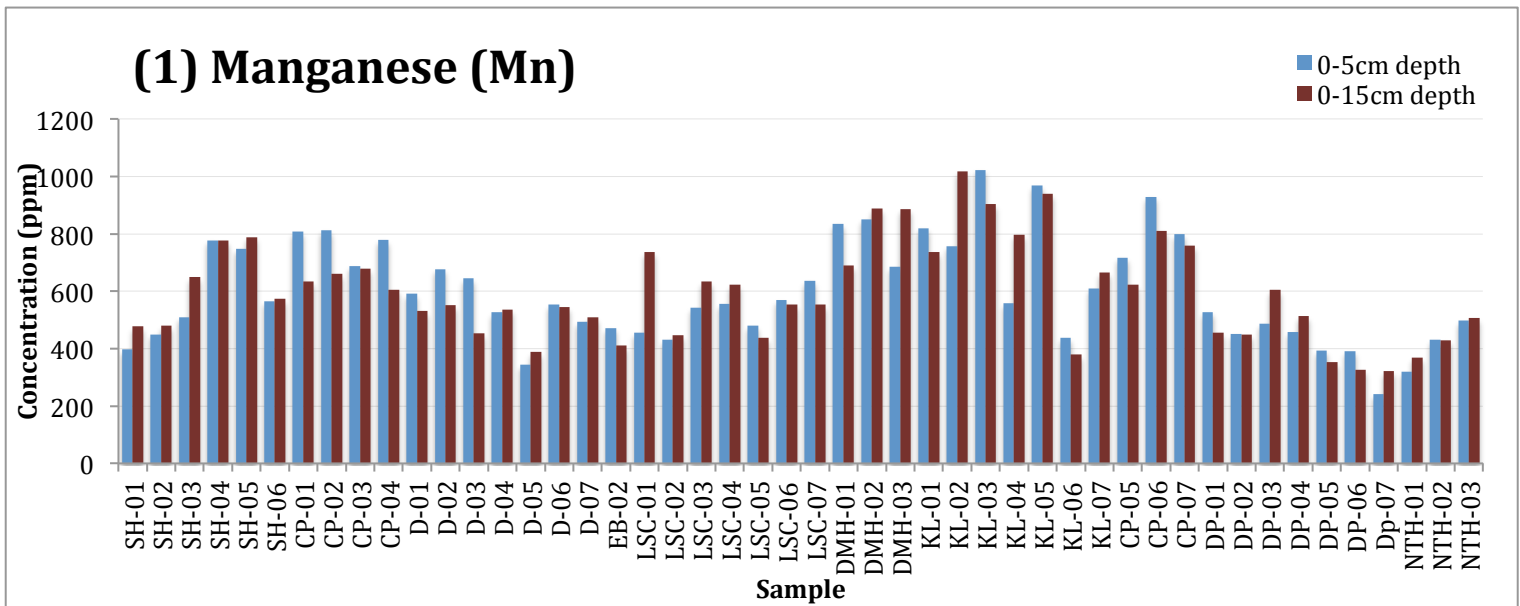


Figure 37: Graphical representation of (1) Mn, (2) As, (3) Fe metal concentrations at 0-5 cm and 0-15 cm depth.

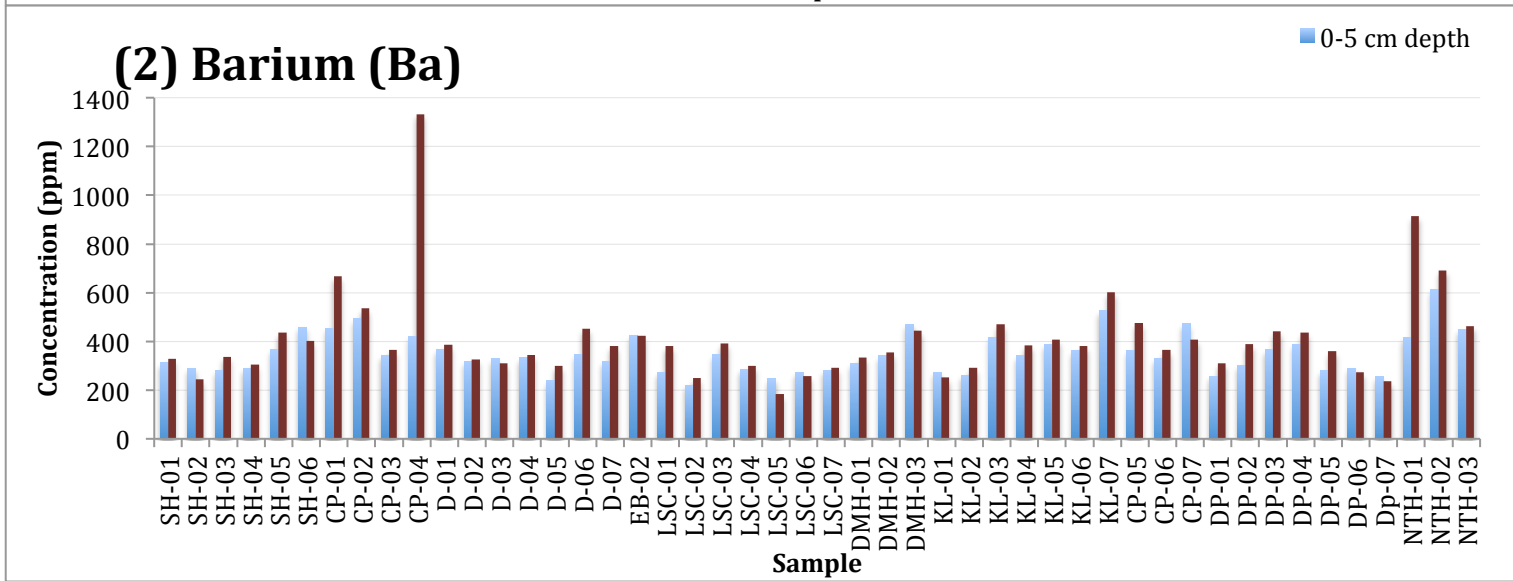
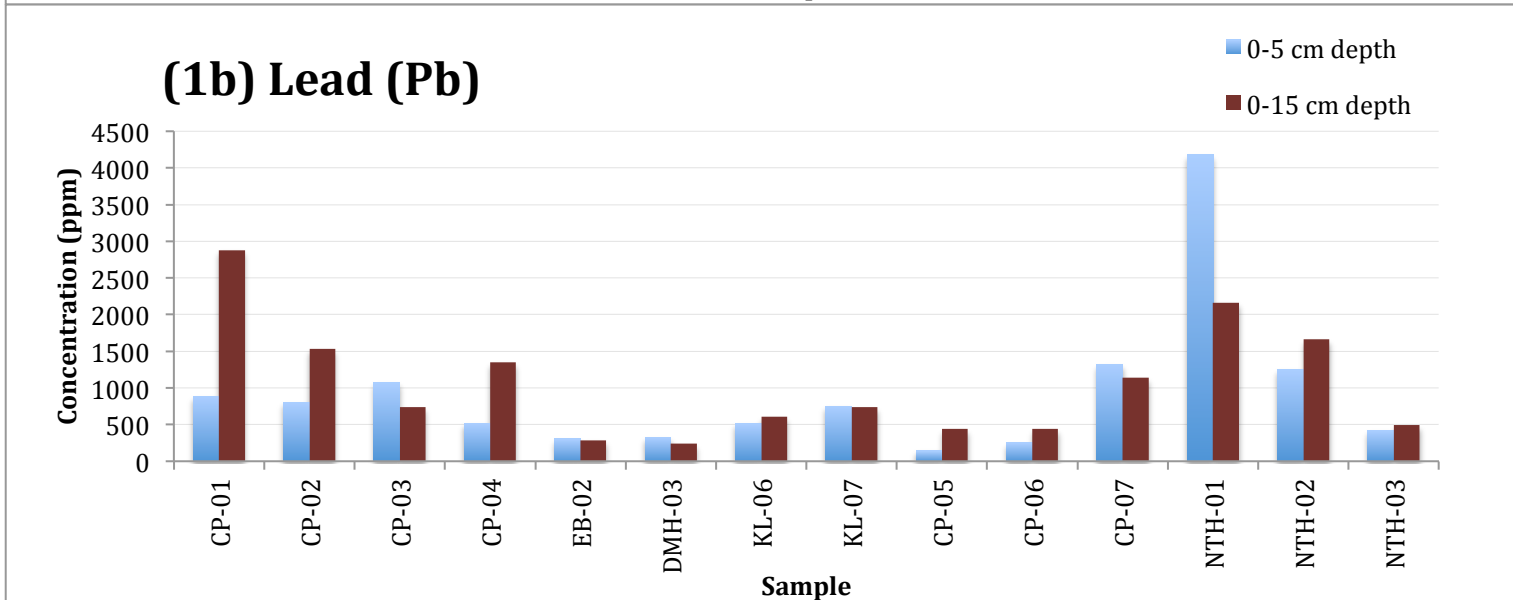
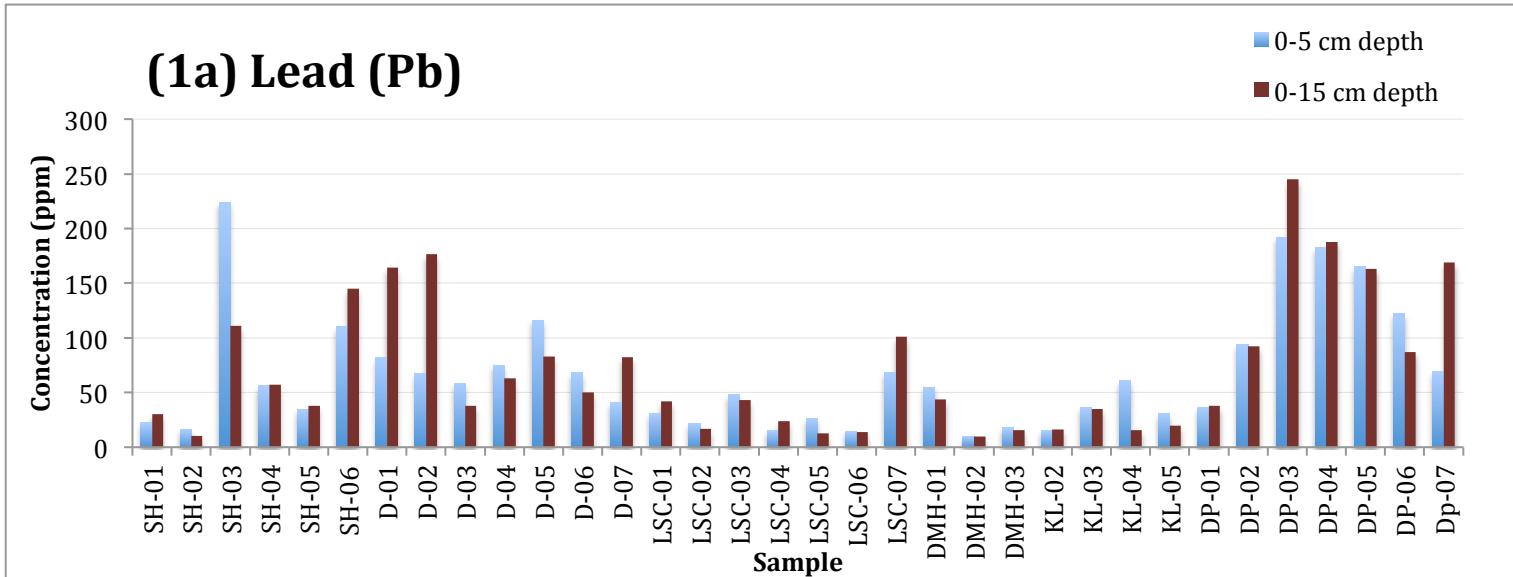


Figure 38: Graphical representation of (1) Pb and (2) Ba concentrations versus 0-5 cm and 0-15 cm

depth. (1a) depicts relatively low Pb concentrations and (1b) has relatively high Pb concentrations.

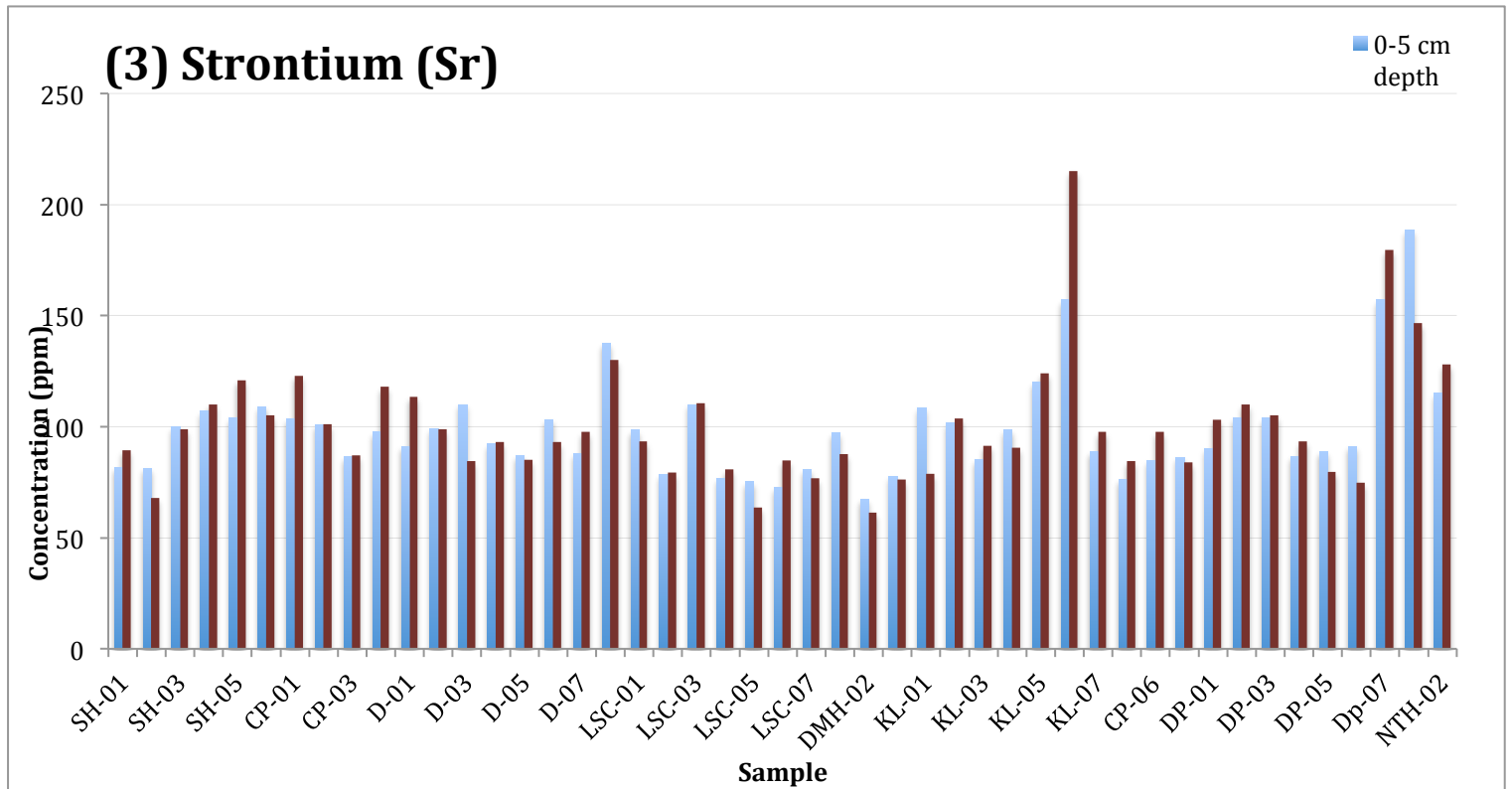


Figure 39: Continued figure, Graphical representation of (3) Sr concentrations relative to 0-5 cm and 0-15 cm depth.

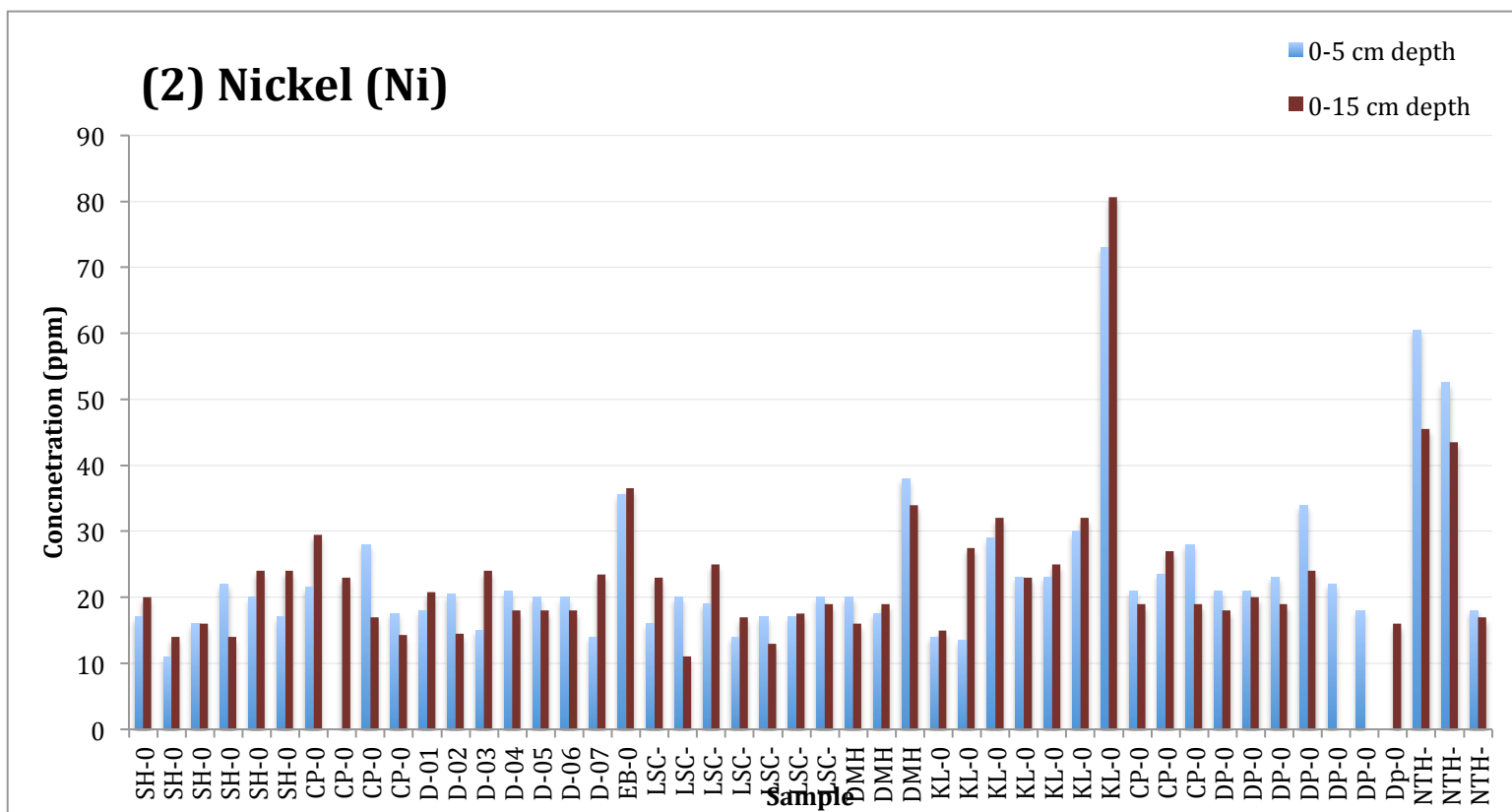
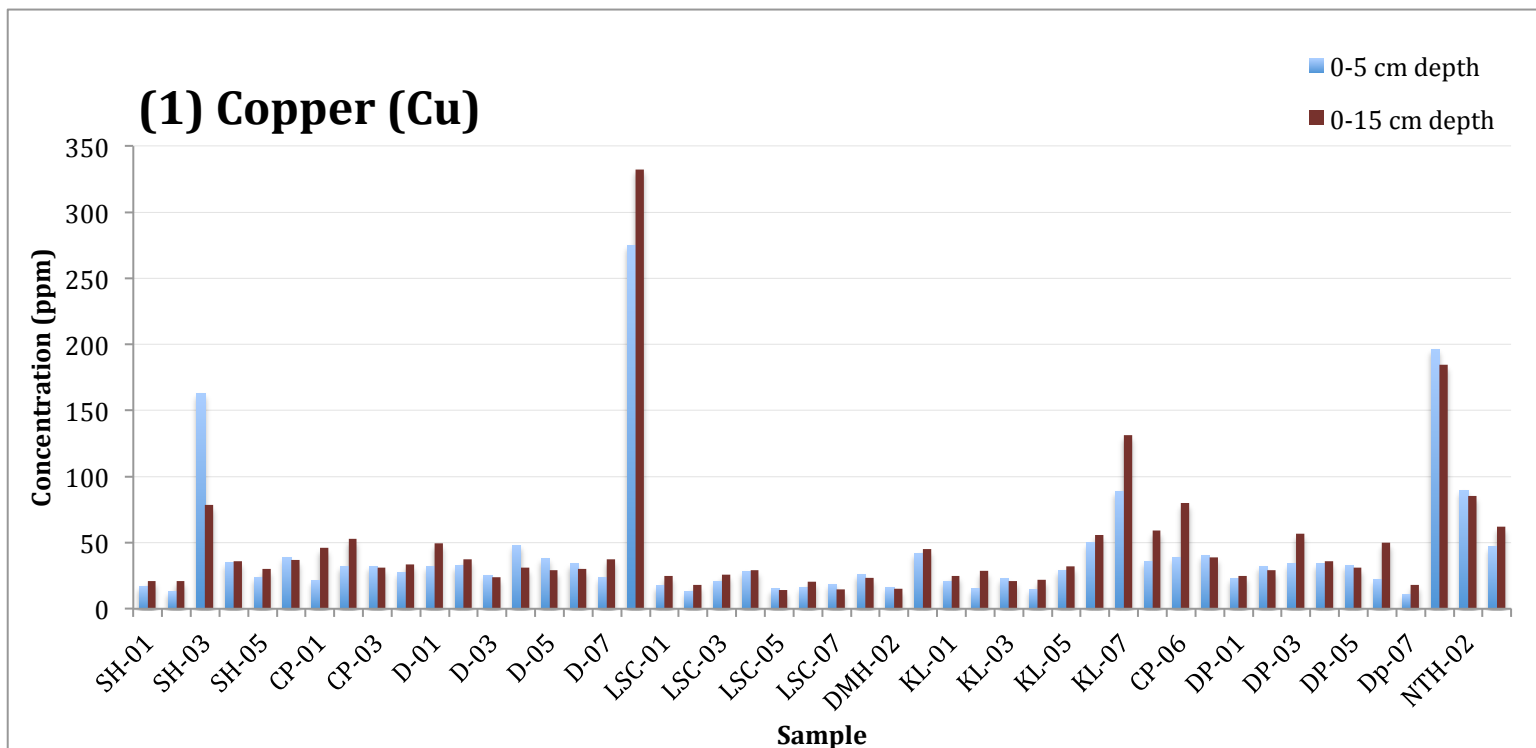


Figure 40: Graphical representation of (1) Cu and (2) Ni concentrations versus 0-5 cm and 0-15 cm depth.

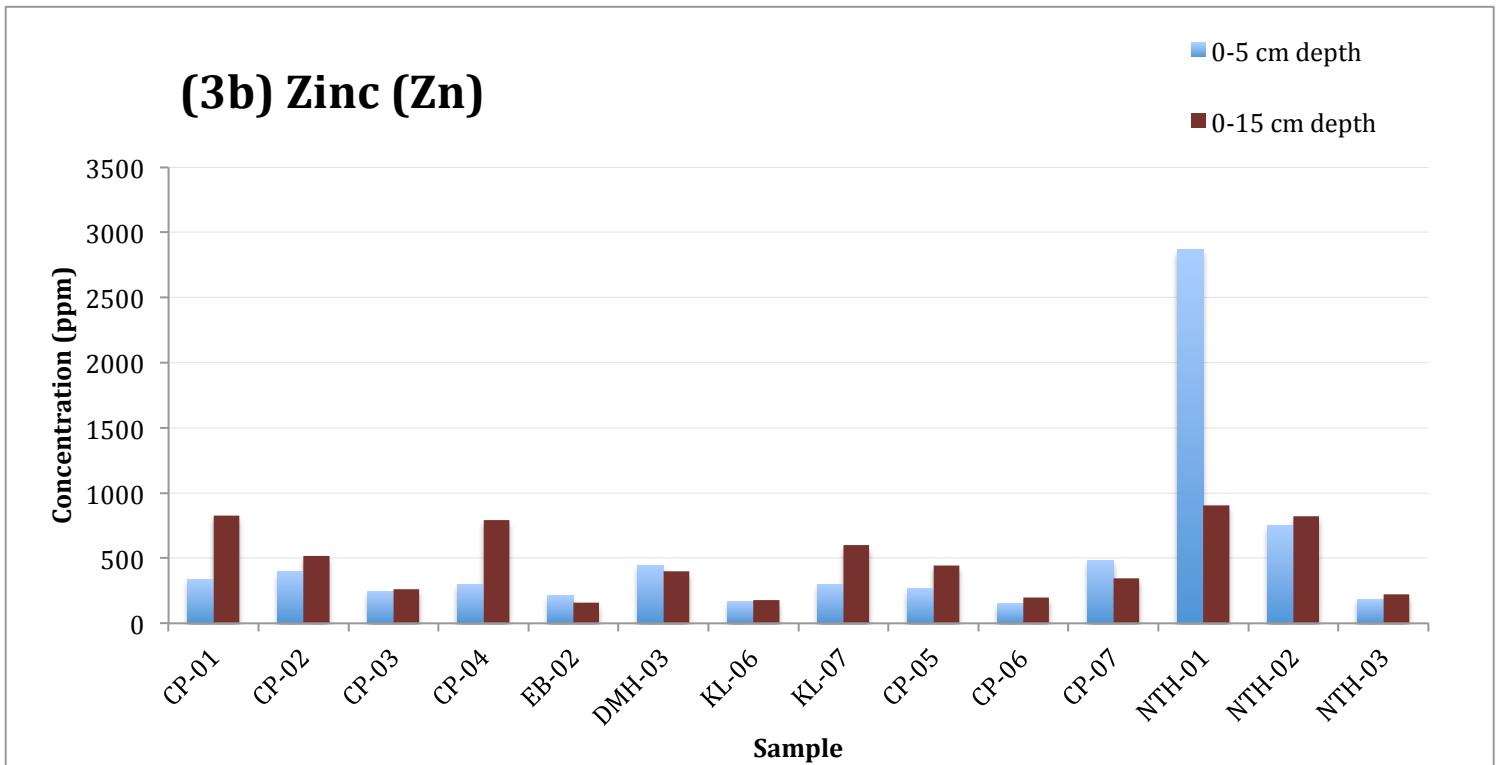
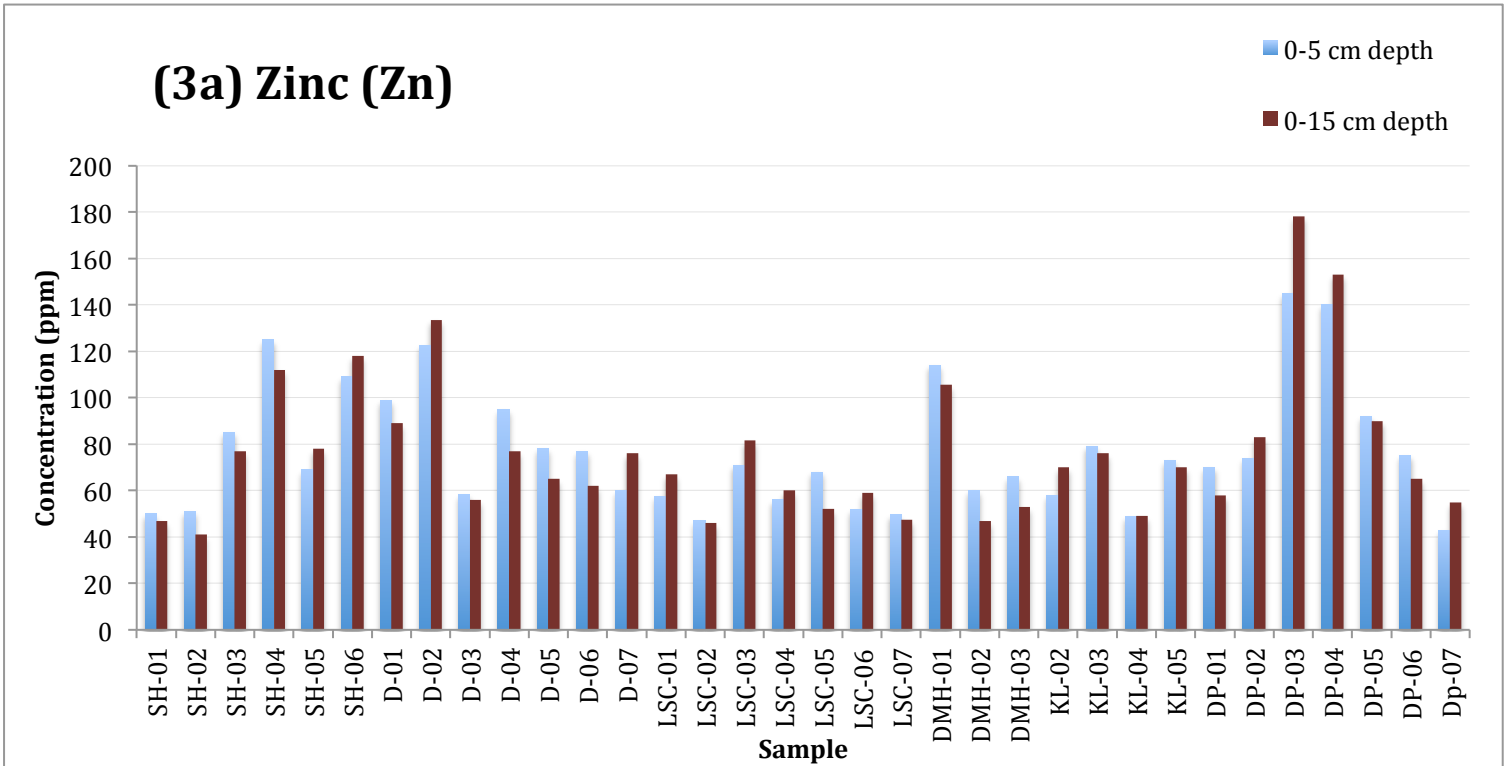


Figure 41: Continued figure, graphical representation of (3a) Zn relatively low concentrations and (3b) relatively high concentrations at 0-5 cm and 0-15 cm depth.

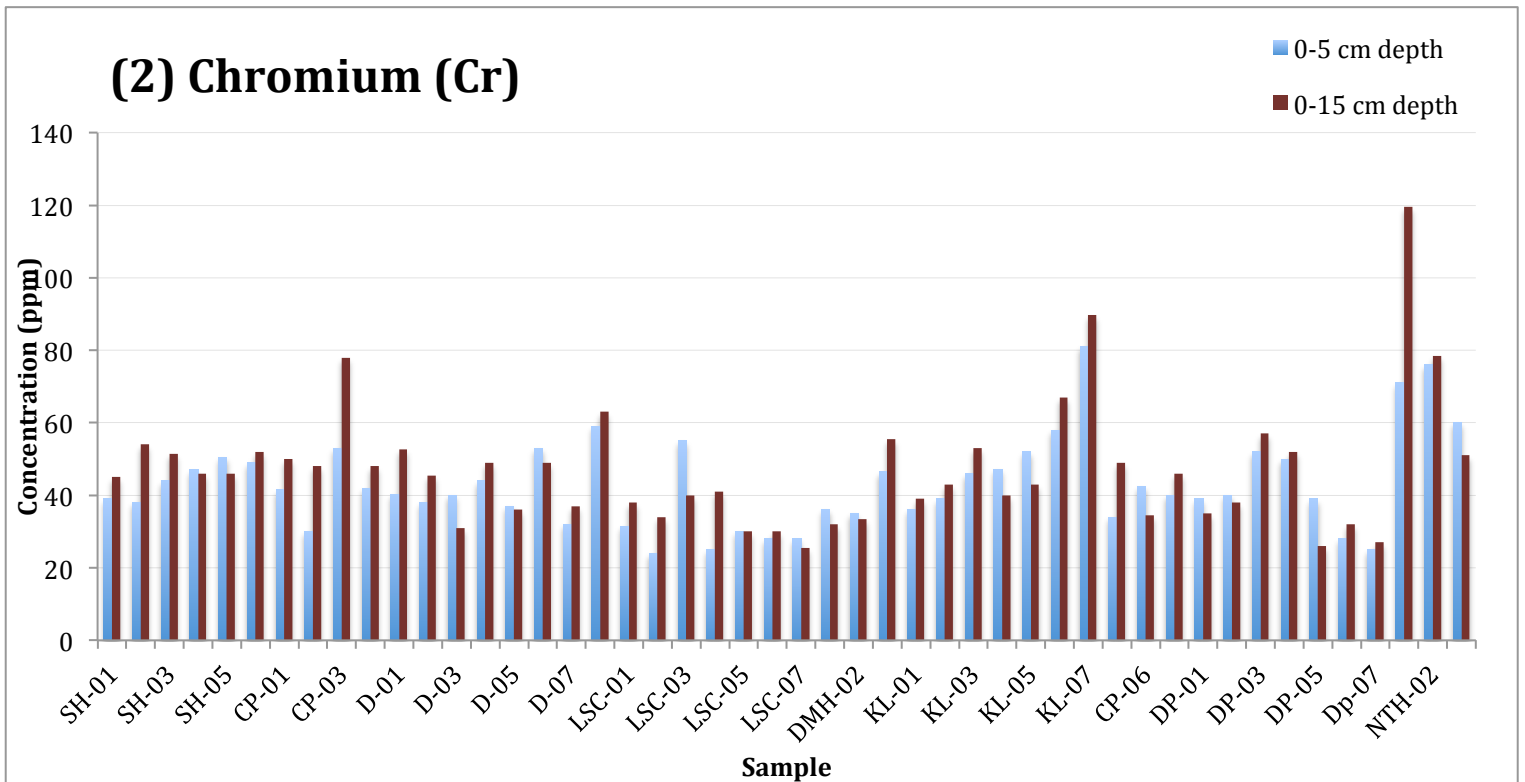
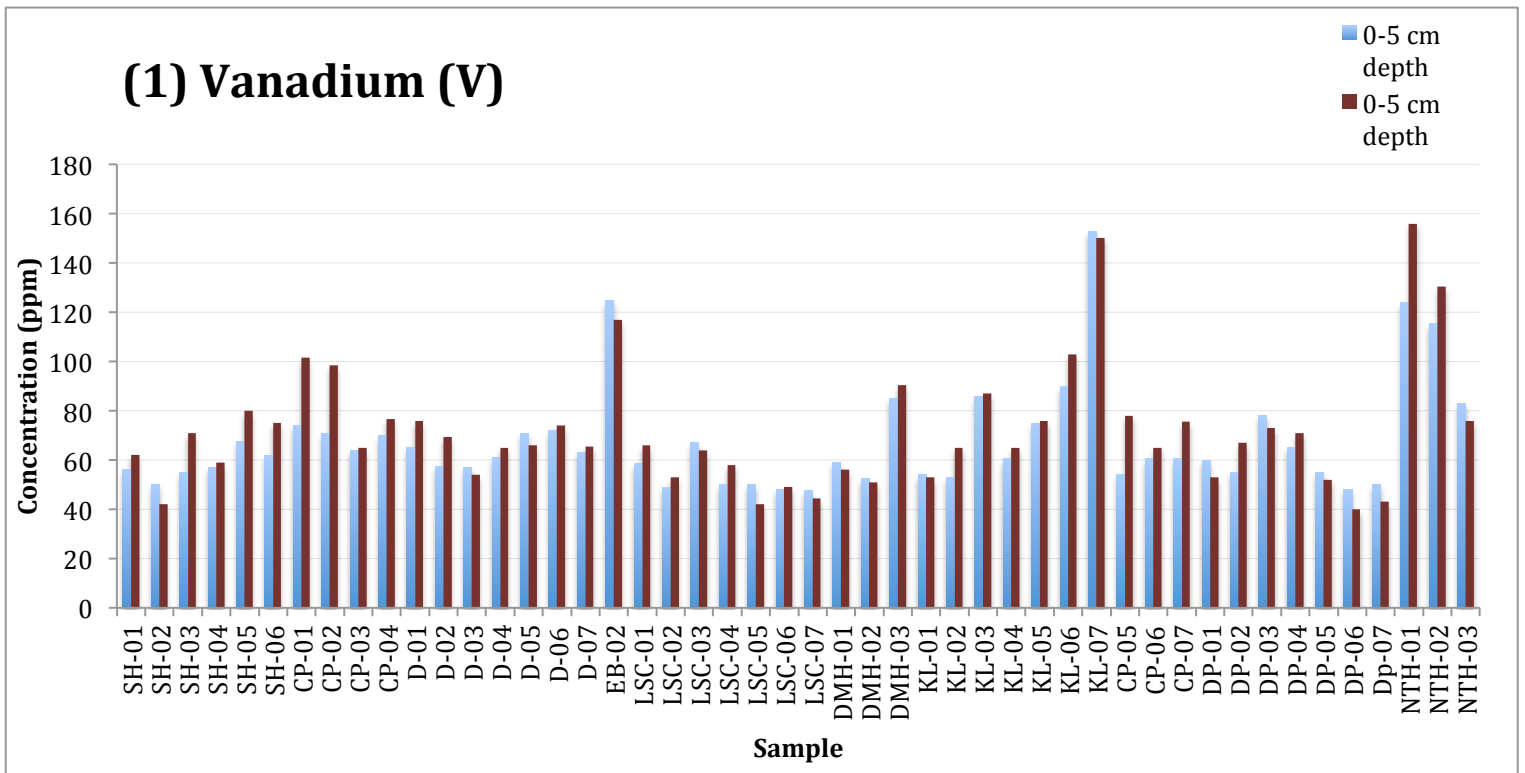


Figure 42: Graphical representation of (1) V and (2) Cr concentrations relative to 0-5 cm and 0-15 cm depth.

The unequal variances t-test was used to identify if there is any significant difference between the means, the test suggests otherwise. There is a lack of significant differences between 0-15 and 0-5 cm depth based sample metal concentrations based on the T-test, (Table 7). This may be due to the extremes in variability of metal concentrations, which is reflected in the extremes of their standard deviations.

Table 7: P-Values calculated from unequal variance T-test.

Element	P-Value	Standard Deviation
Mn	0.99	+/- 174
As	0.34	+/- 31
Fe	0.10	+/- 15068
Pb	0.73	+/- 640
Ba	0.05	+/- 146
Sr	0.81	+/- 25
Cu	0.60	+/- 49
Ni	0.90	+/- 11
Zn	0.90	+/- 334
V	0.33	+/- 23
Cr	0.20	+/- 15

The second notable relationship is that there are higher metal concentrations in samples that are close to (< 2 m) from older wooden buildings greater than 60 years of age on the Dalhousie campus. Where as samples farther away or not near (>2m) older wooden buildings have lower metal concentrations. The unequal variance test re-enforces the relationship that is seen visually amongst the graphs by rejecting the hypothesis that there is no difference between the means.

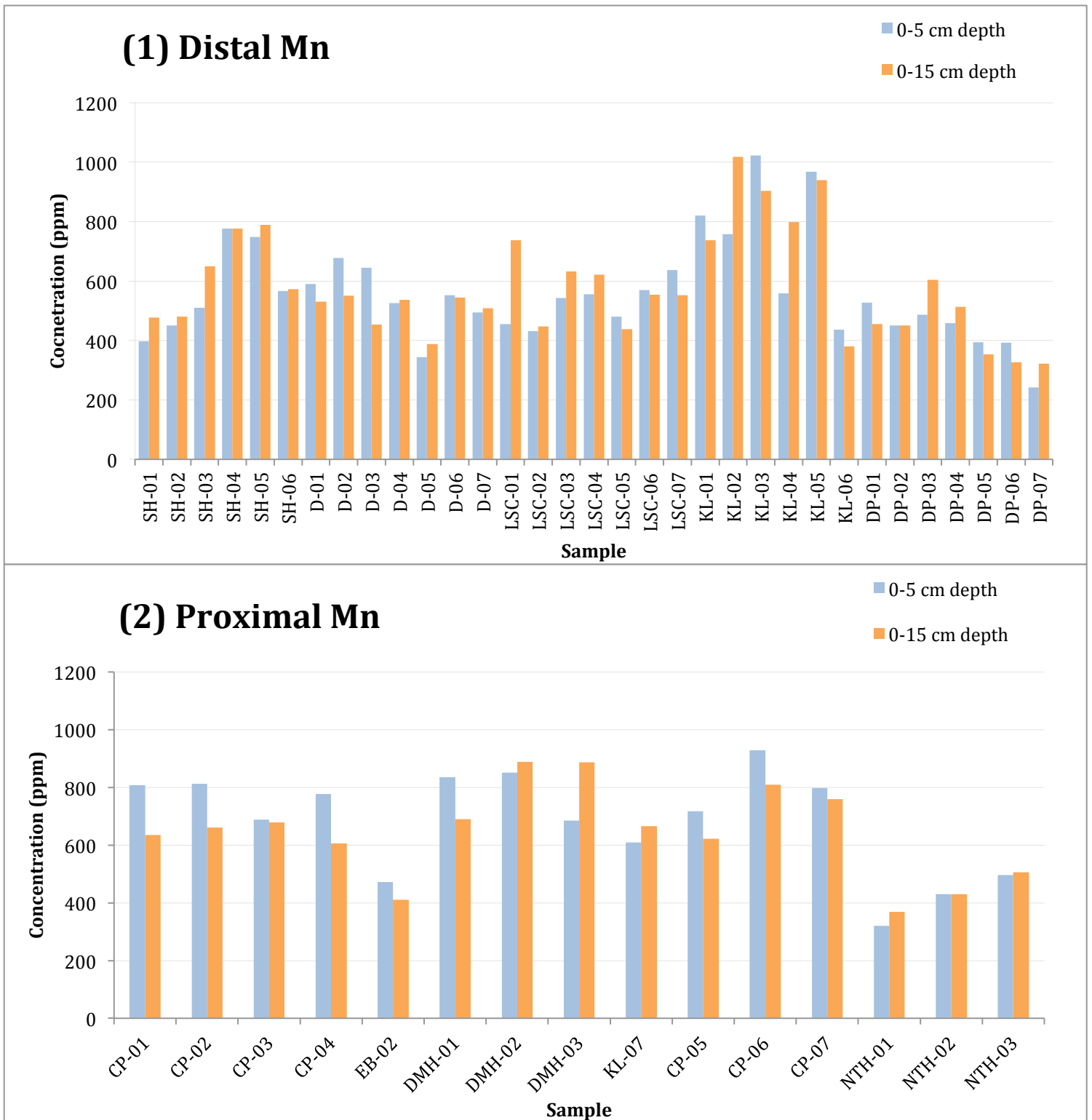


Figure 43: Representation of (1) Mn concentrations distal to old wooden buildings (> 2 m) and (2) Mn concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth.

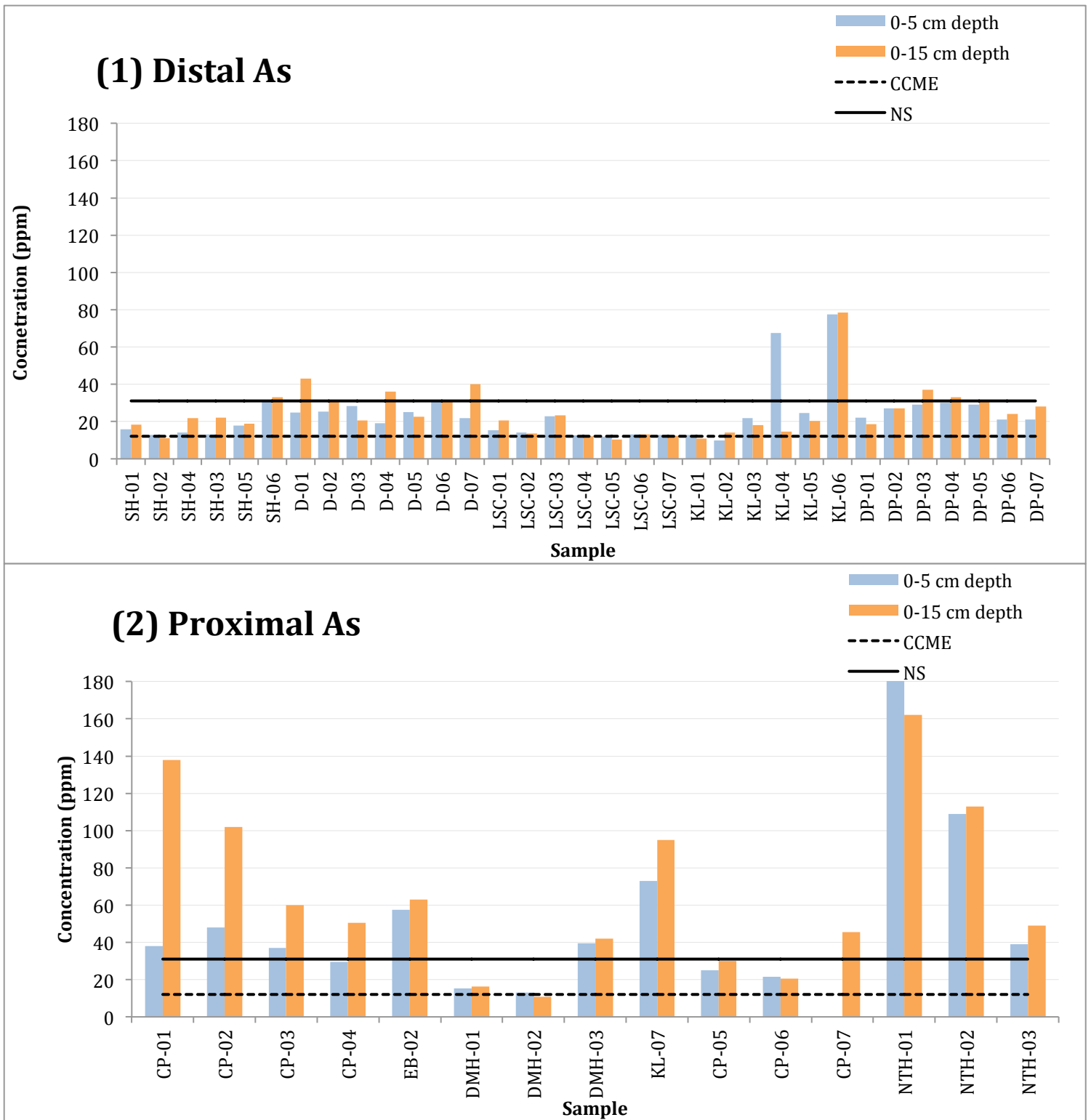


Figure 44: Representation of (1) Arsenic concentrations distal to old wooden buildings (> 2 m) and (2) Arsenic concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth.

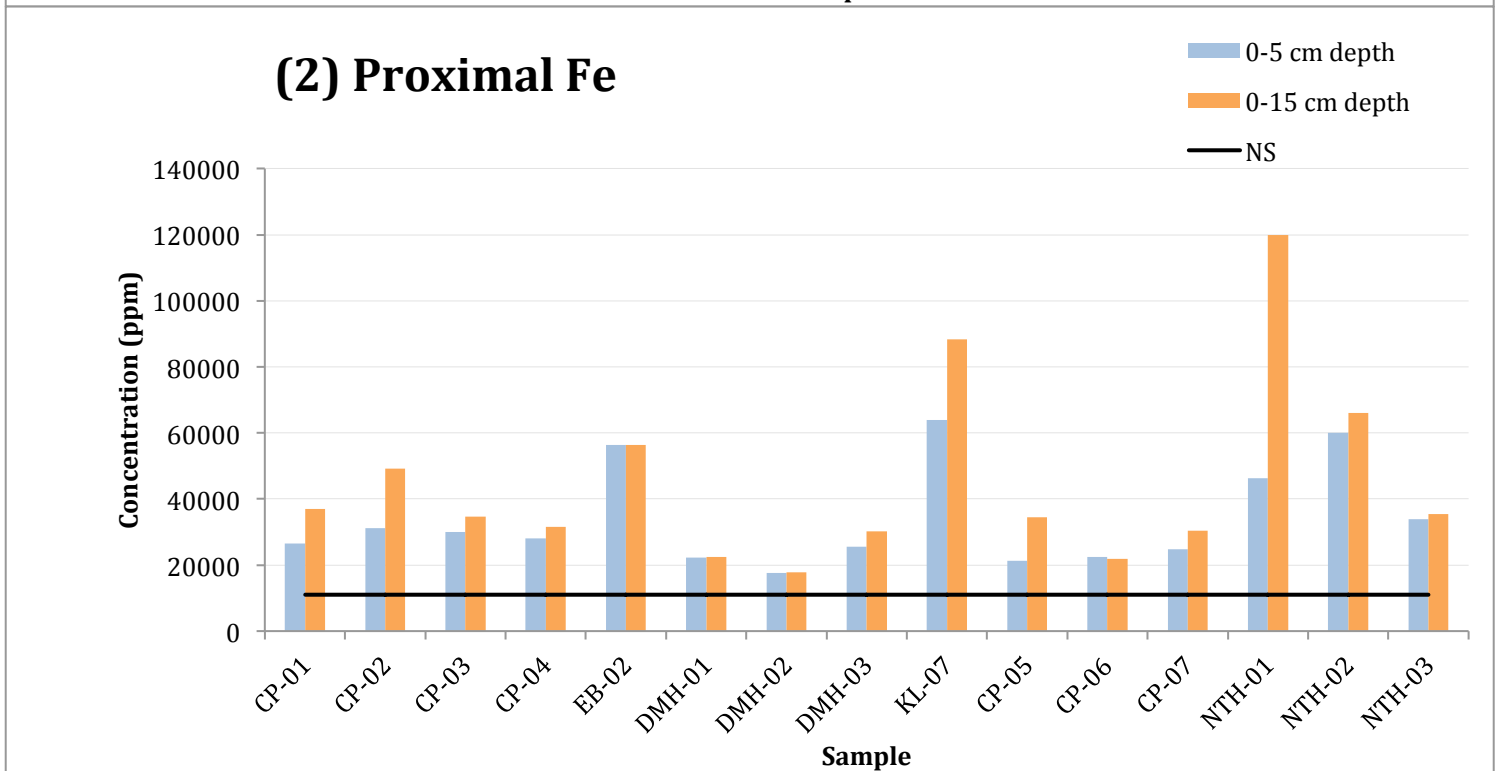
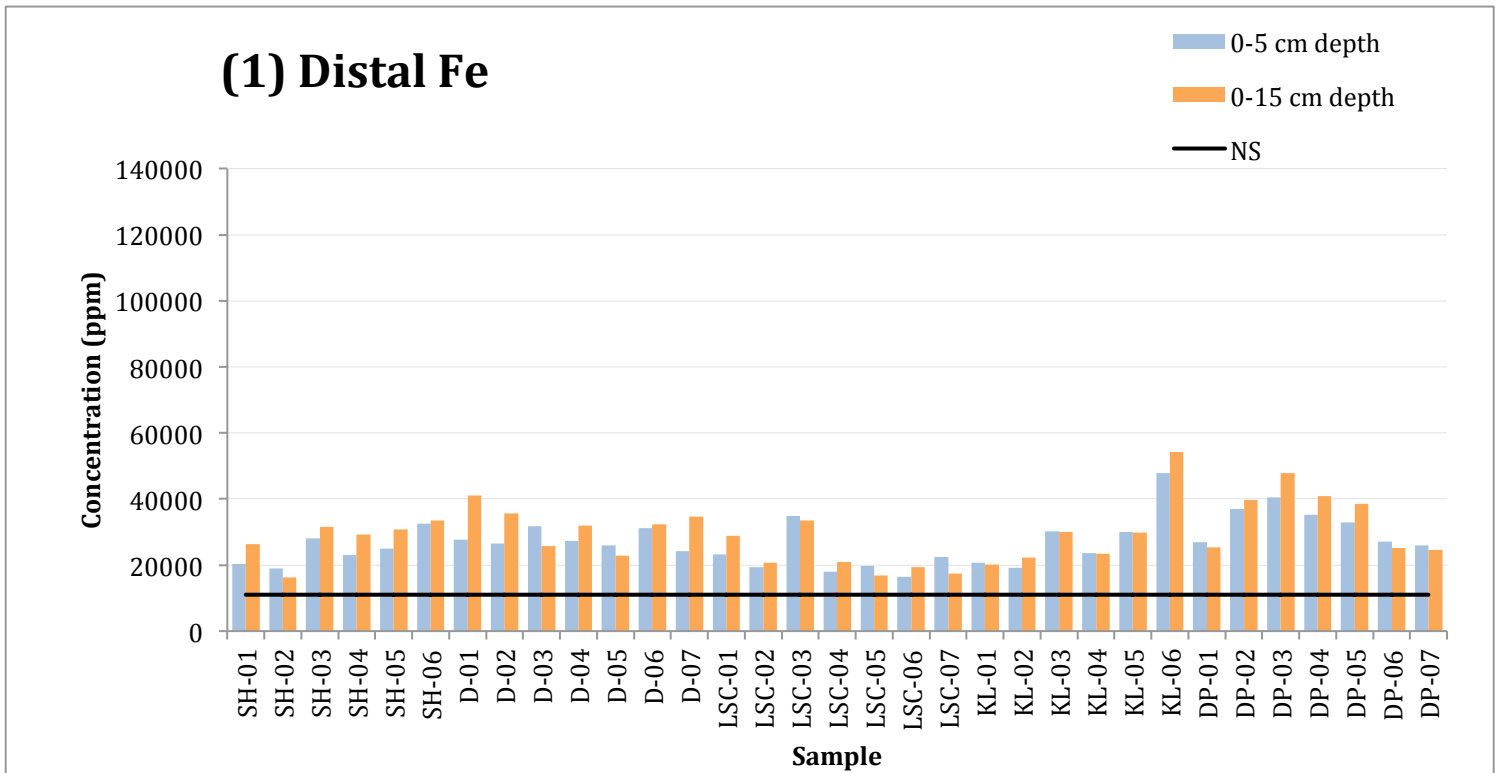


Figure 45: Representation of (1) Fe concentrations distal to old wooden buildings (> 2 m) and (2) Fe concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth.

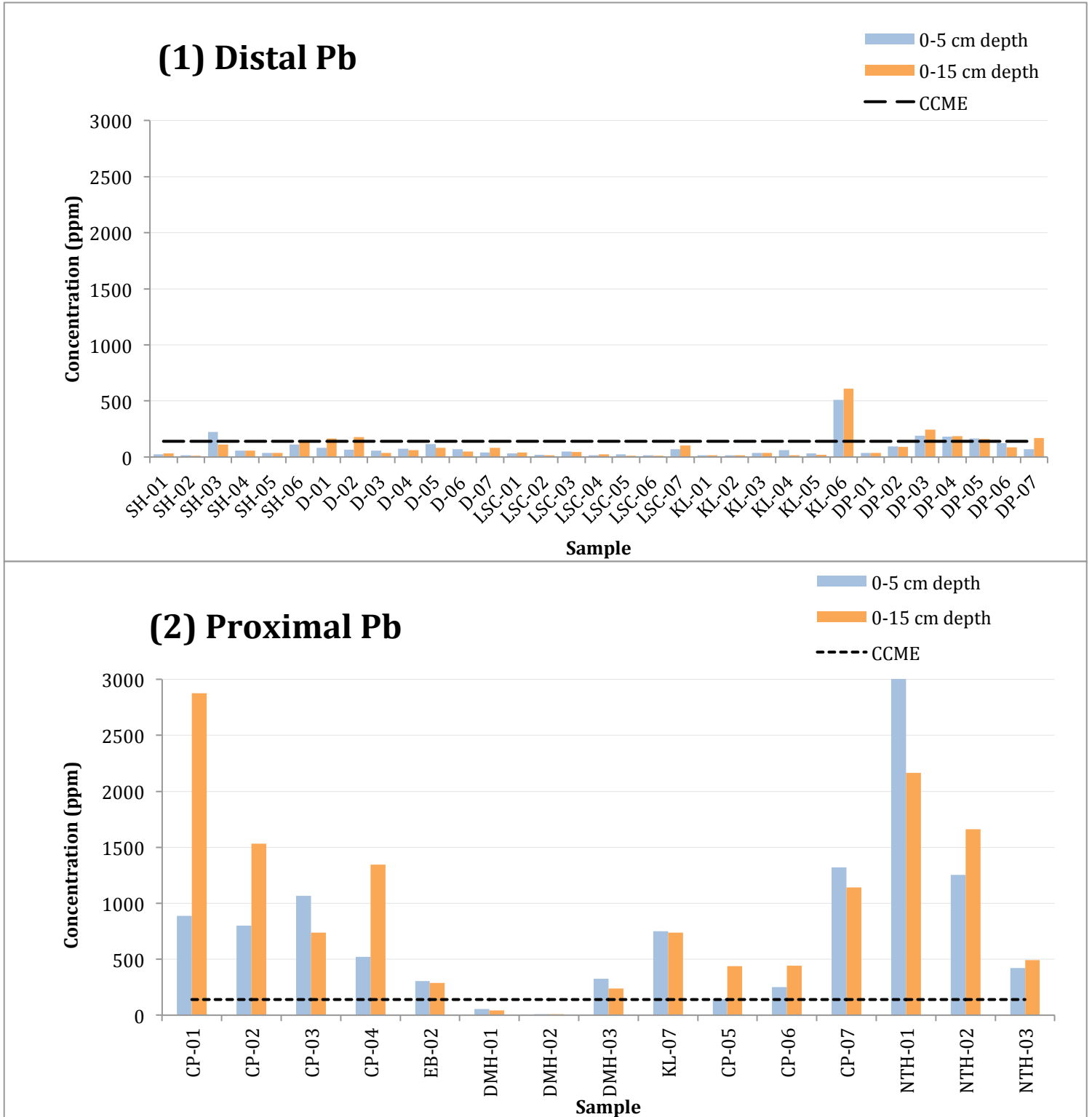


Figure 46: Representation of (1) Pb concentrations distal to old wooden buildings (> 2 m) and (2) Pb concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth.

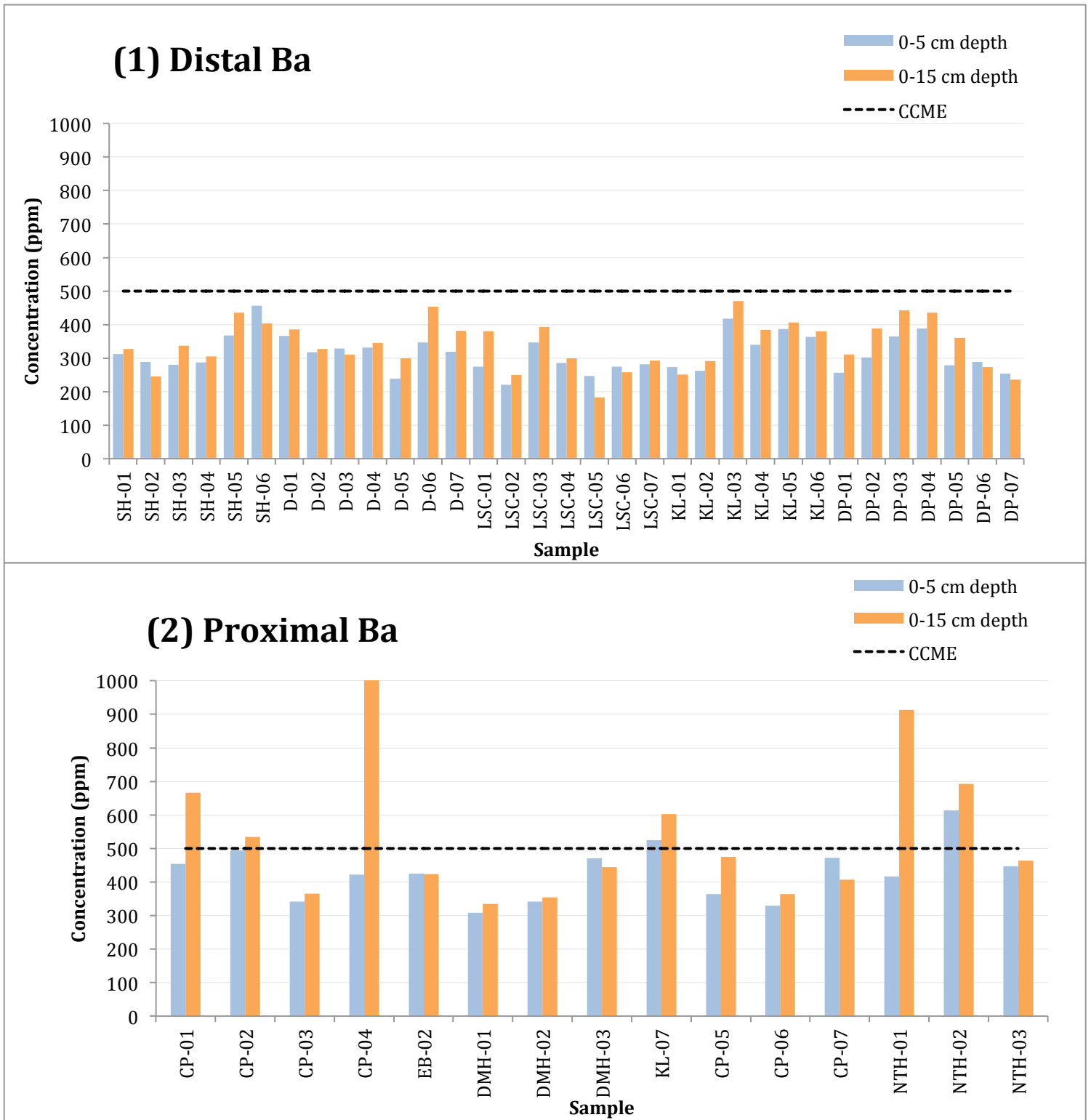


Figure 47: Representation of (1) Ba concentrations distal to old wooden buildings (> 2 m) and (2) Ba concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth.

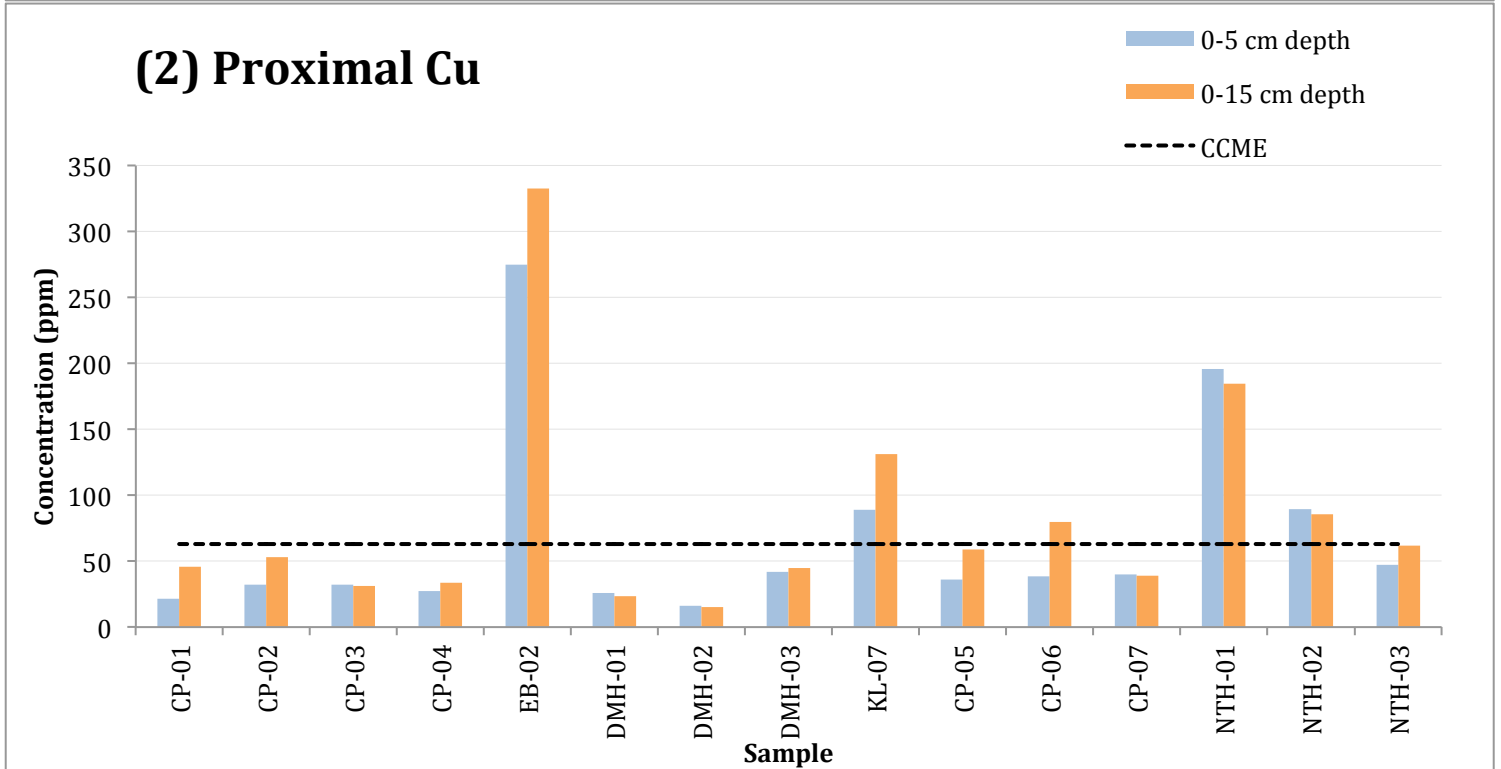
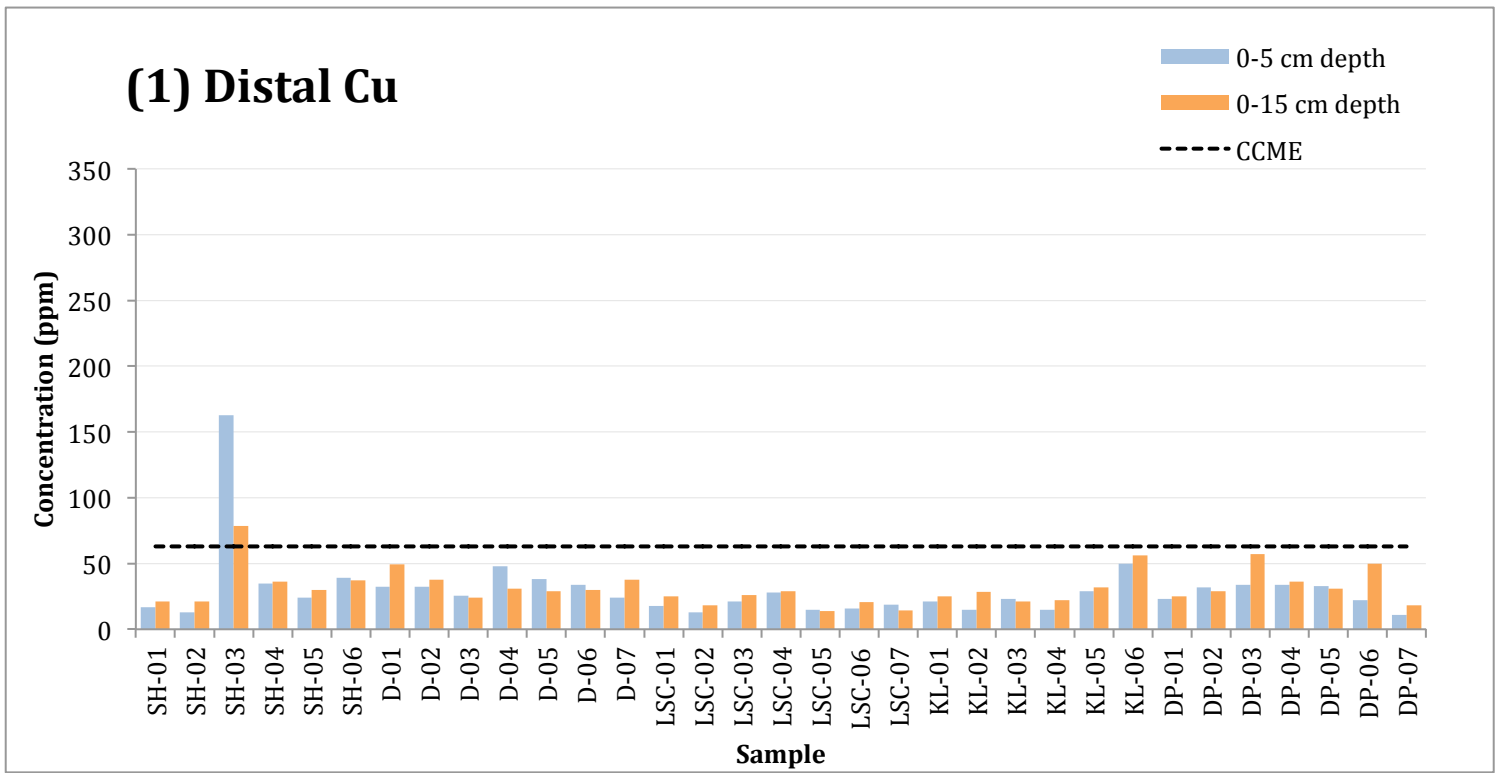


Figure 48: Representation of (1) Cu concentrations distal to old wooden buildings (> 2 m) and (2) Cu concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth

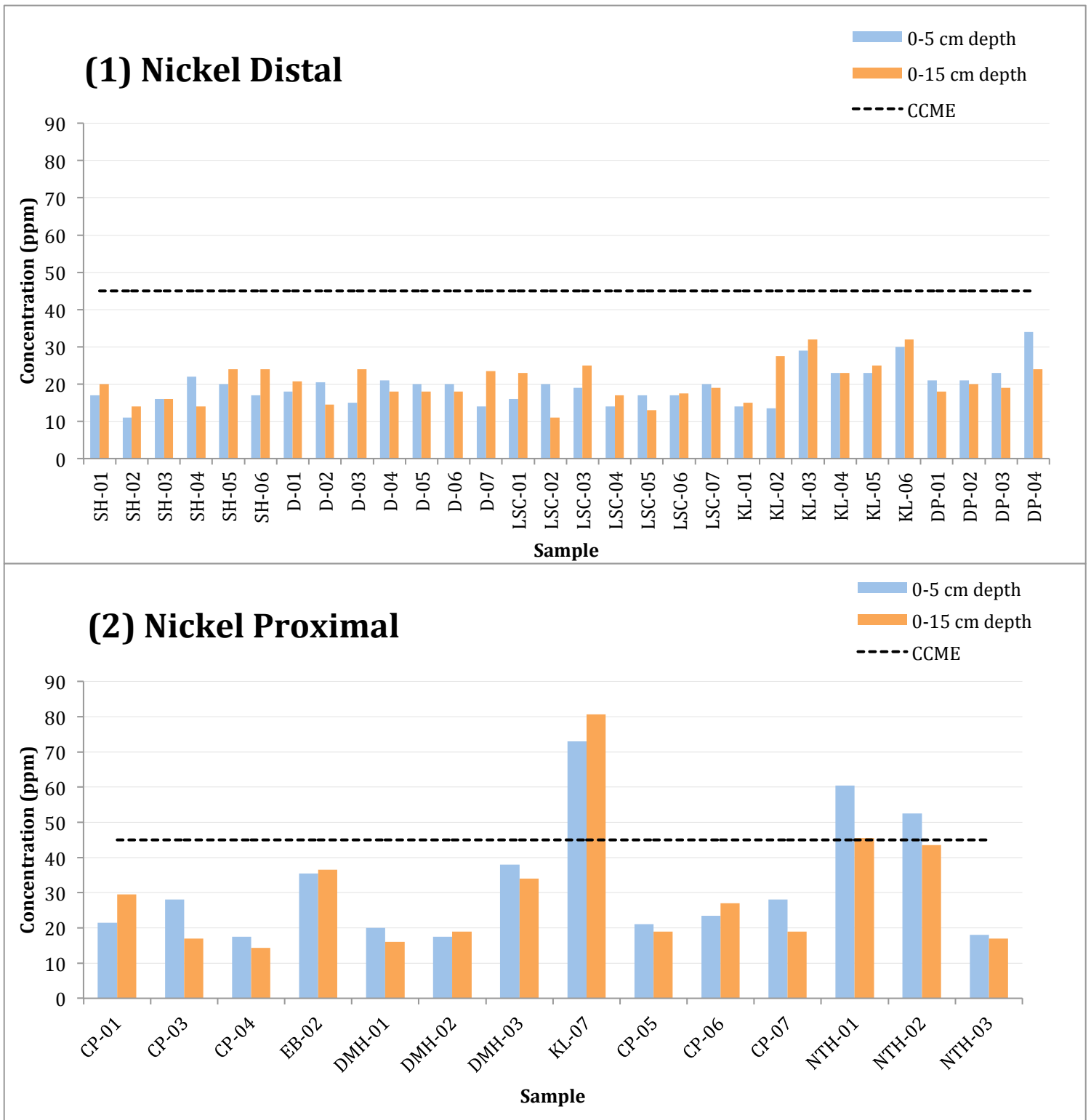


Figure 49: Representation of (1) Ni concentrations distal to old wooden buildings (> 2 m) and (2) Ni concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth

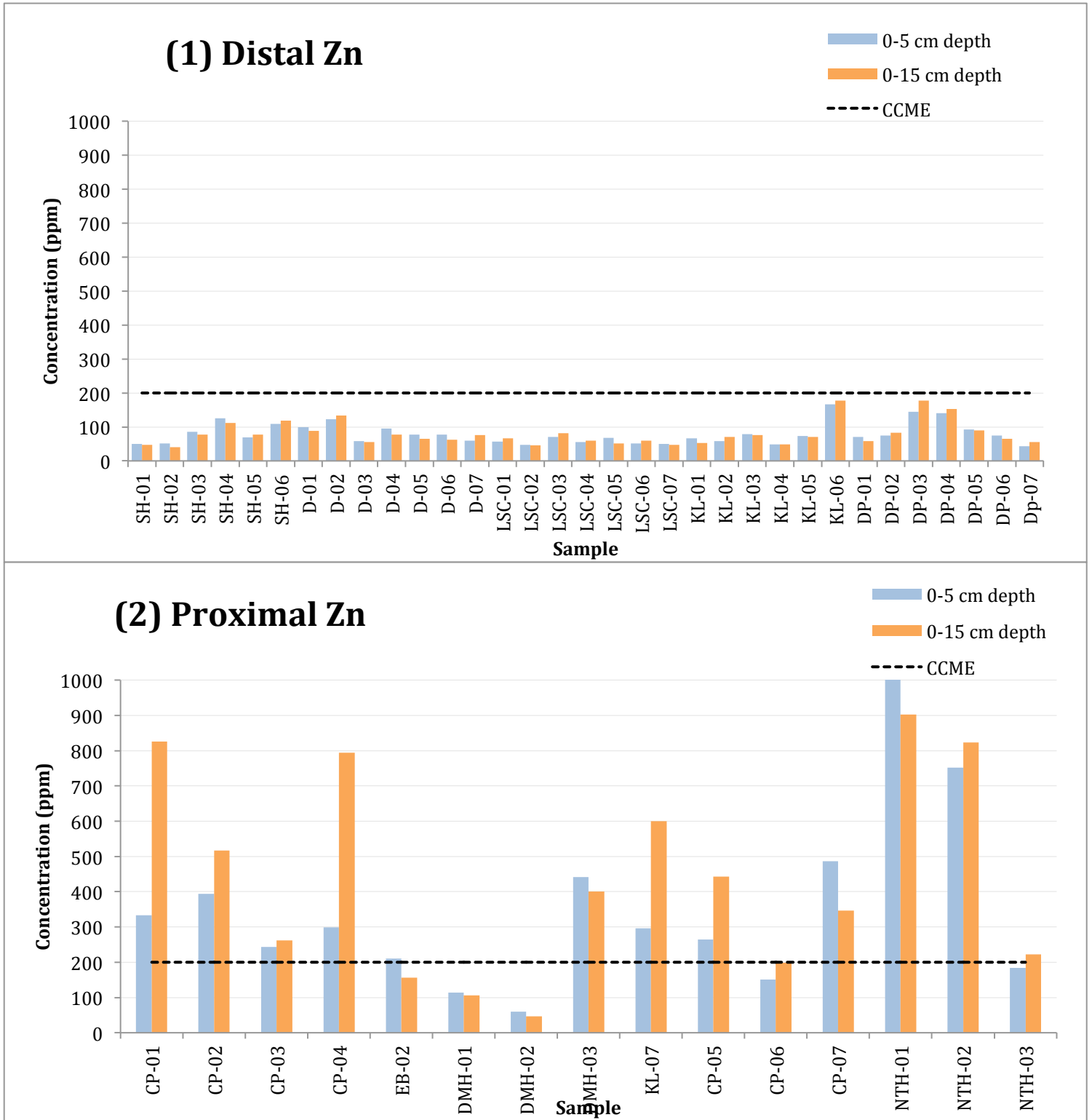


Figure 50: Representation of (1) Zn concentrations distal to old wooden buildings (> 2 m) and (2) Zn concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth

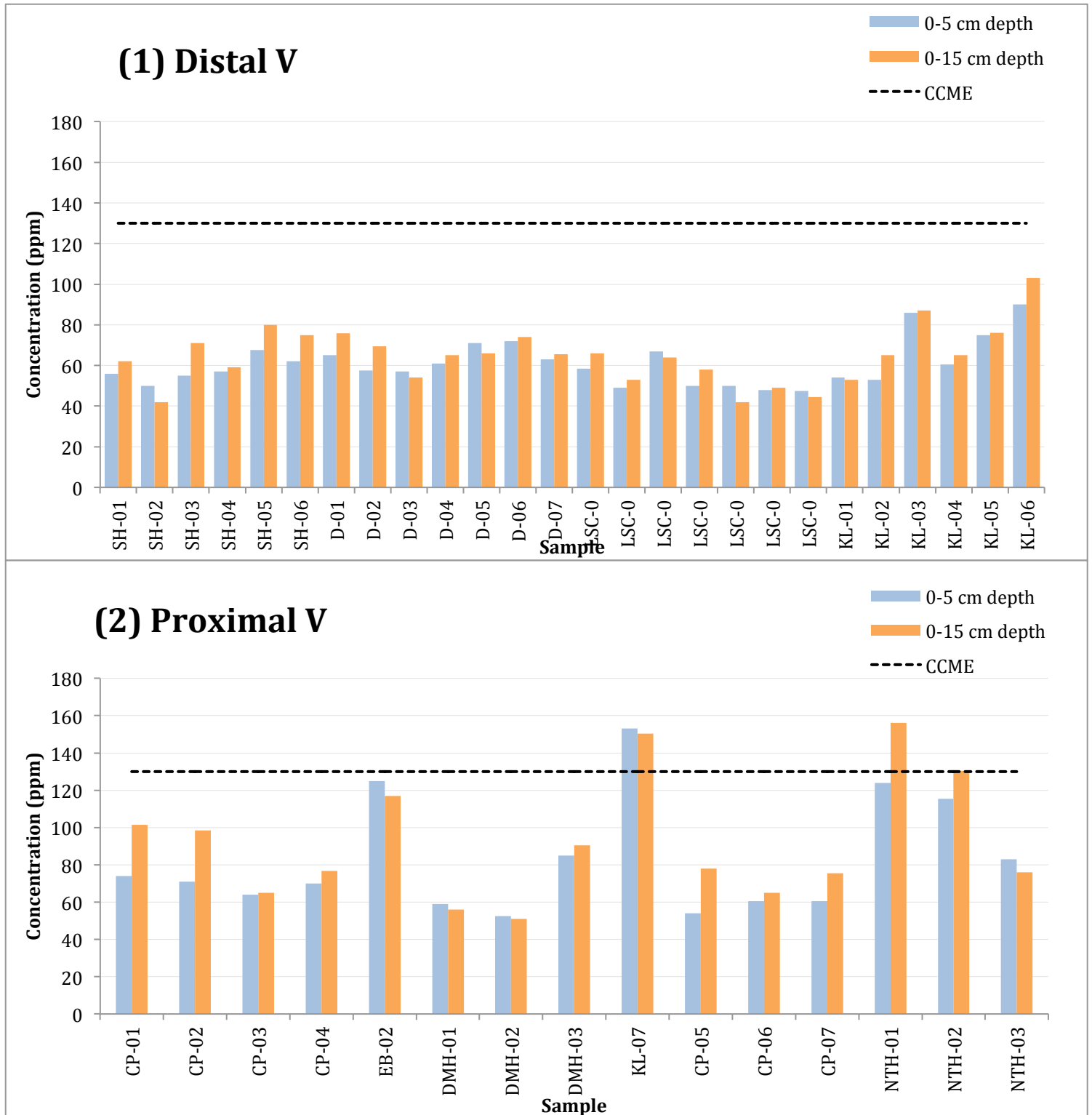


Figure 51: Representation of (1) V concentrations distal to old wooden buildings (> 2 m) and (2) V concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth.

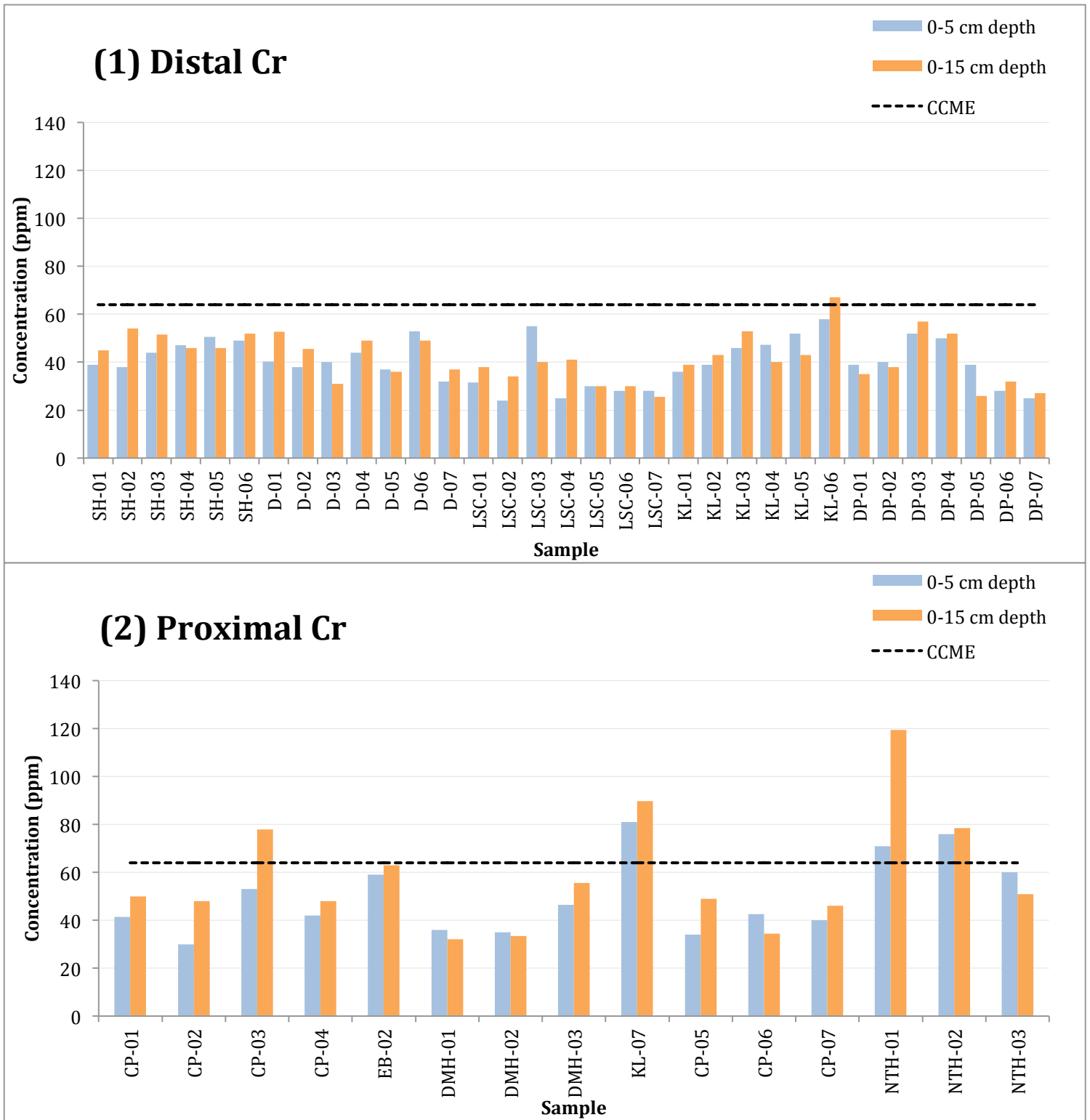


Figure 52: Representation of (1) Cr concentrations distal to old wooden buildings (> 2 m) and (2) Cr concentrations proximal to old wooden buildings (< 2 m) at 0-5 and 0-15 cm depth.

An urban background was for both soils close to and far away from potential anthropogenic point sources. These point sources specifically were in reference to older wooden buildings. Urban backgrounds were determined by averaging concentrations in both the 0-5 and 0-15 cm depth samples for each metal of concern, (Table 8).

Table 8: Preliminary urban background for samples close to and far away from older wooden buildings.

Metal	Distal	Standard Dev.	Proximal	Standard Dev.	CCME Guidelines	NS Guidelines
Lead	90	112	708	864	140	140
Copper	40	55	52	40	63	1100
Zinc	79	38	378	448	200	5600
Nickel	20	5	29	16	45	330
Barium	328	65	457	168	500	10000
Chromium	40	10	48	15	64	220
Vanadium	64	16	80	29	130	39
Arsenic	25	16	49	42	12	31
Manganese	560	155	654	186	-	-
Iron	28713	9563	36456	18282	-	11000

4.3 Soil Assessment: Particle Size

Assessment of particle size was conducted for elevated soil samples. Soils were sieved to < 2mm and < 0.5 mm particle sizes. There is a notable difference between individual samples but similar to depth based samples when using t-tests there is not a significant difference between the particle sizes as an overall distribution. The following graphs demonstrate metals analyzed for samples that were sieved.

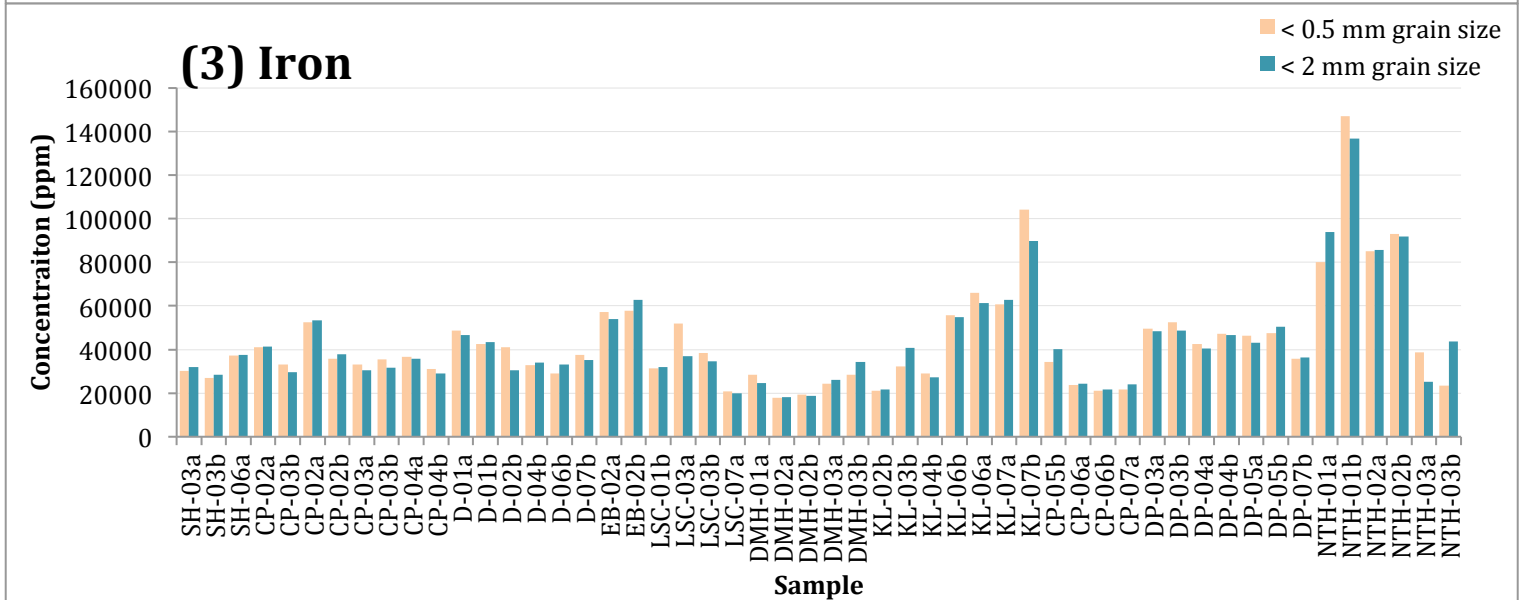
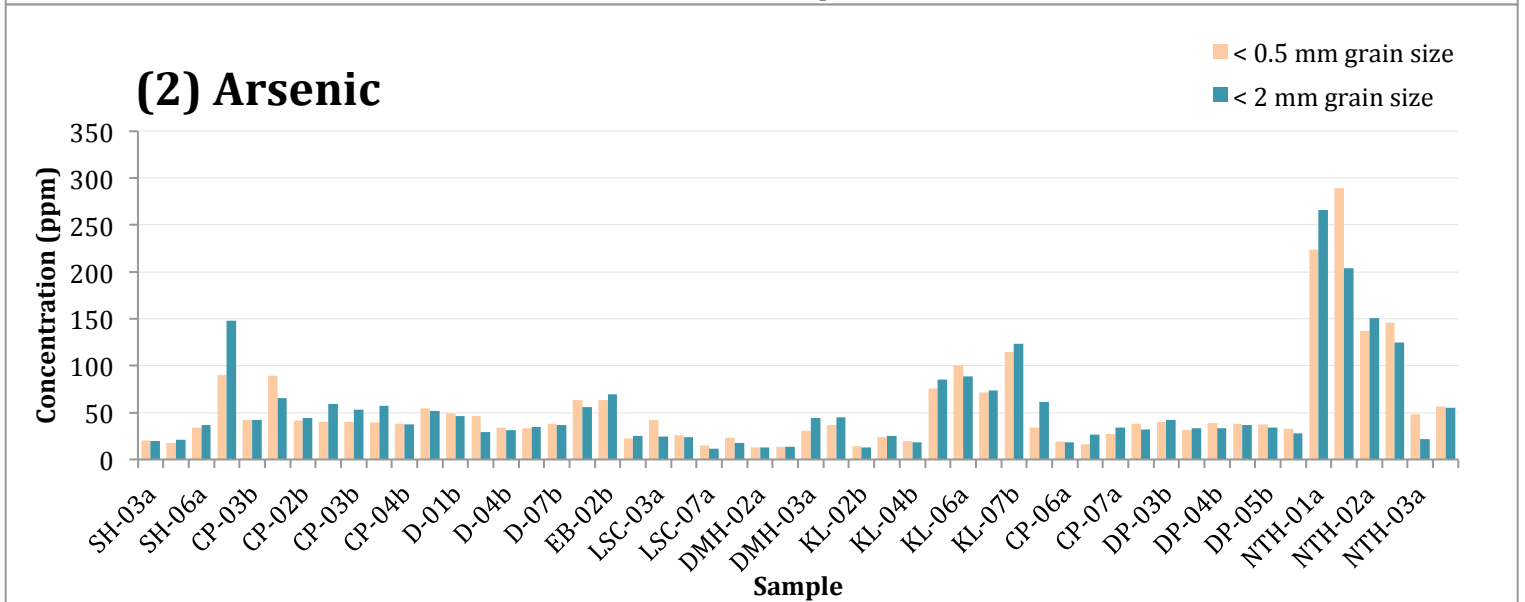
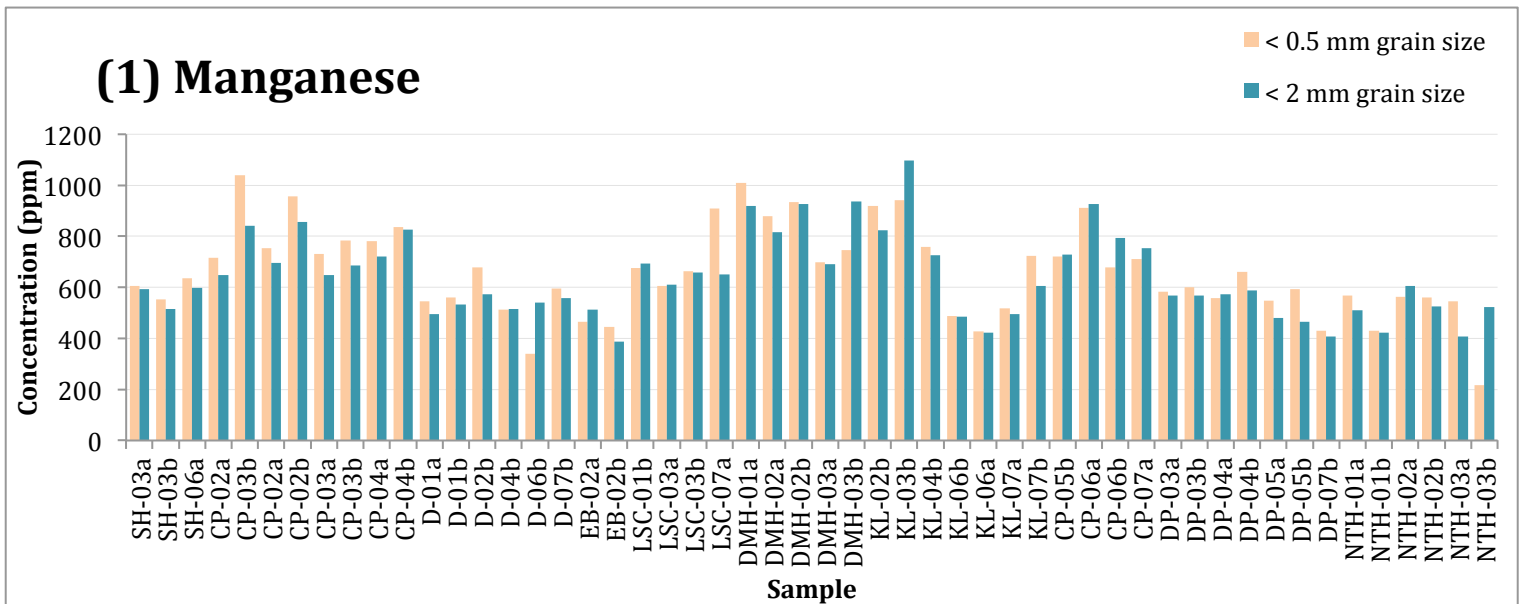
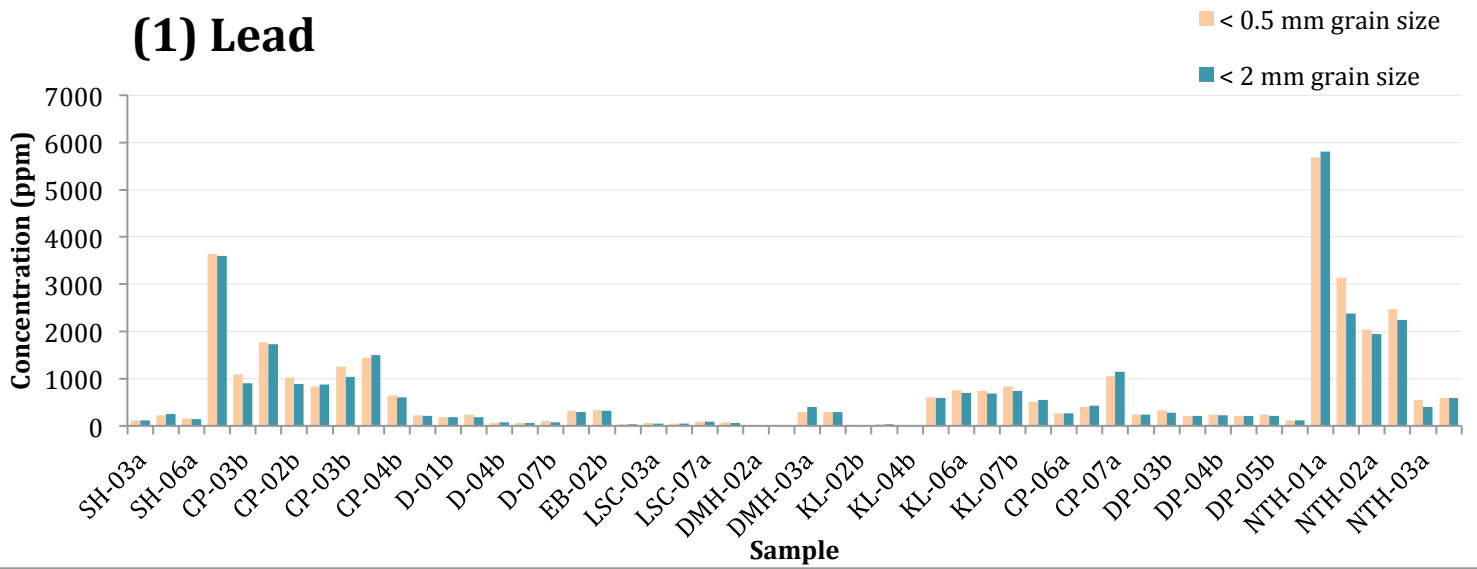
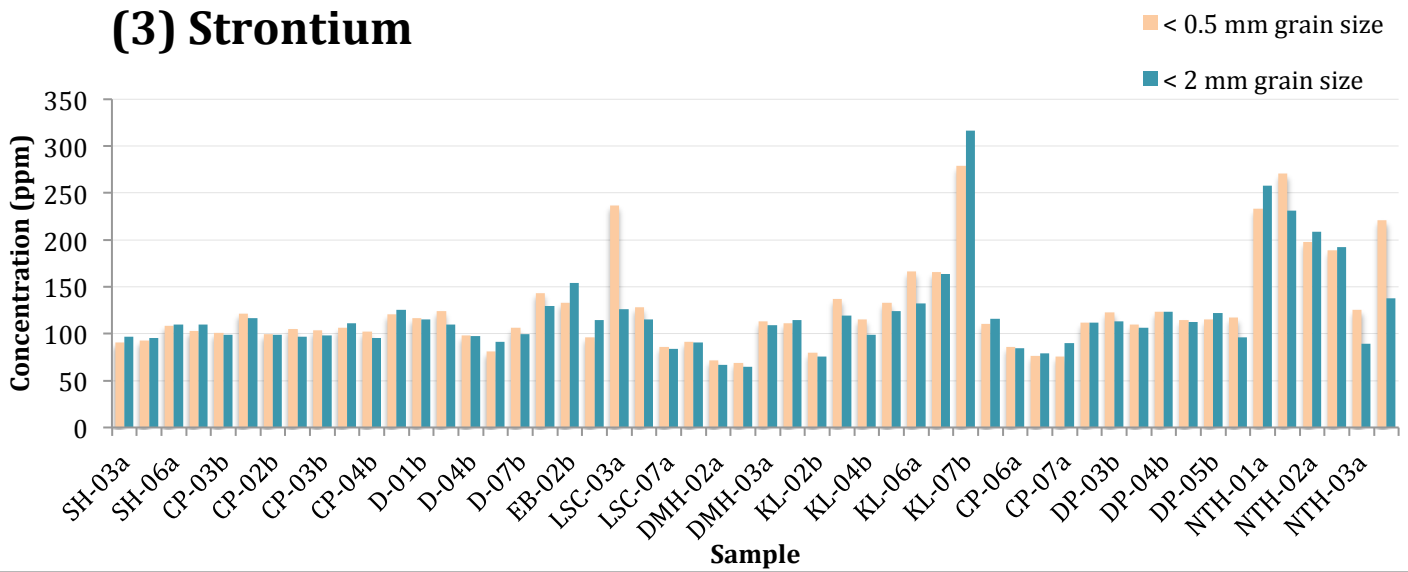


Figure 53: (1, 2, 3) show variations of metal content with particle size < 2 mm and < 0.5 mm for Mn, AS, and Fe

(1) Lead



(3) Strontium



(2) Barium

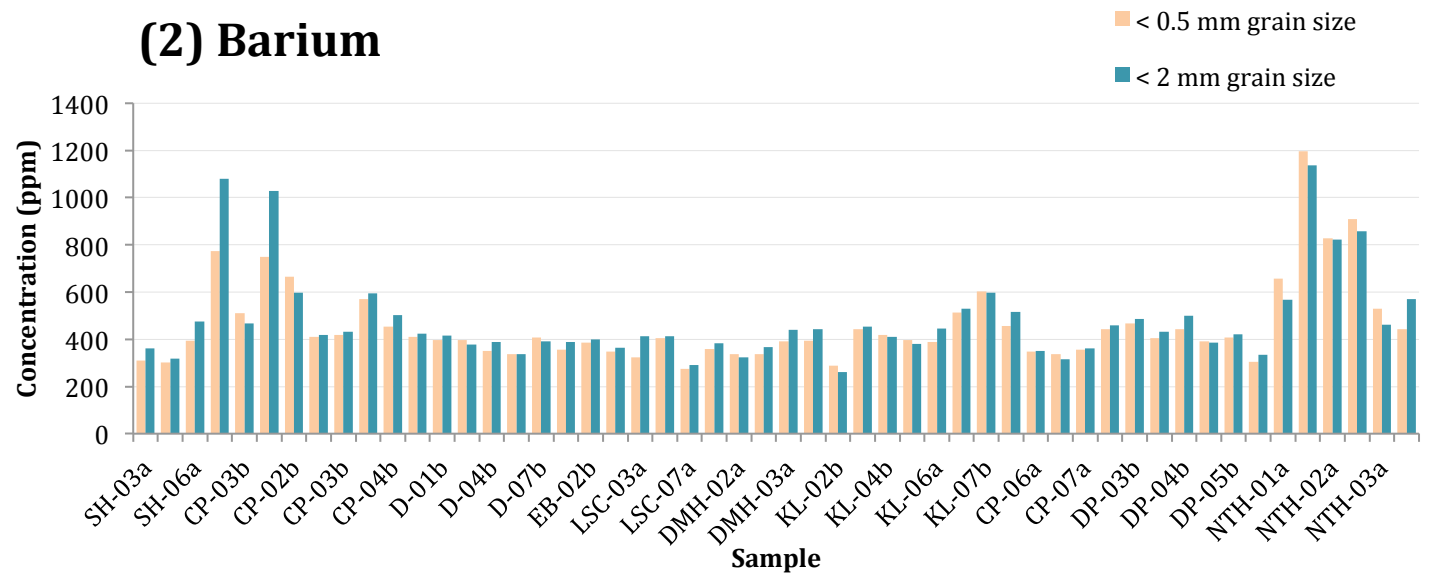


Figure 54: (1, 2, 3) show variations of metal content with particle size < 2 mm and < 0.5 mm for Pb, Sr, and Ba

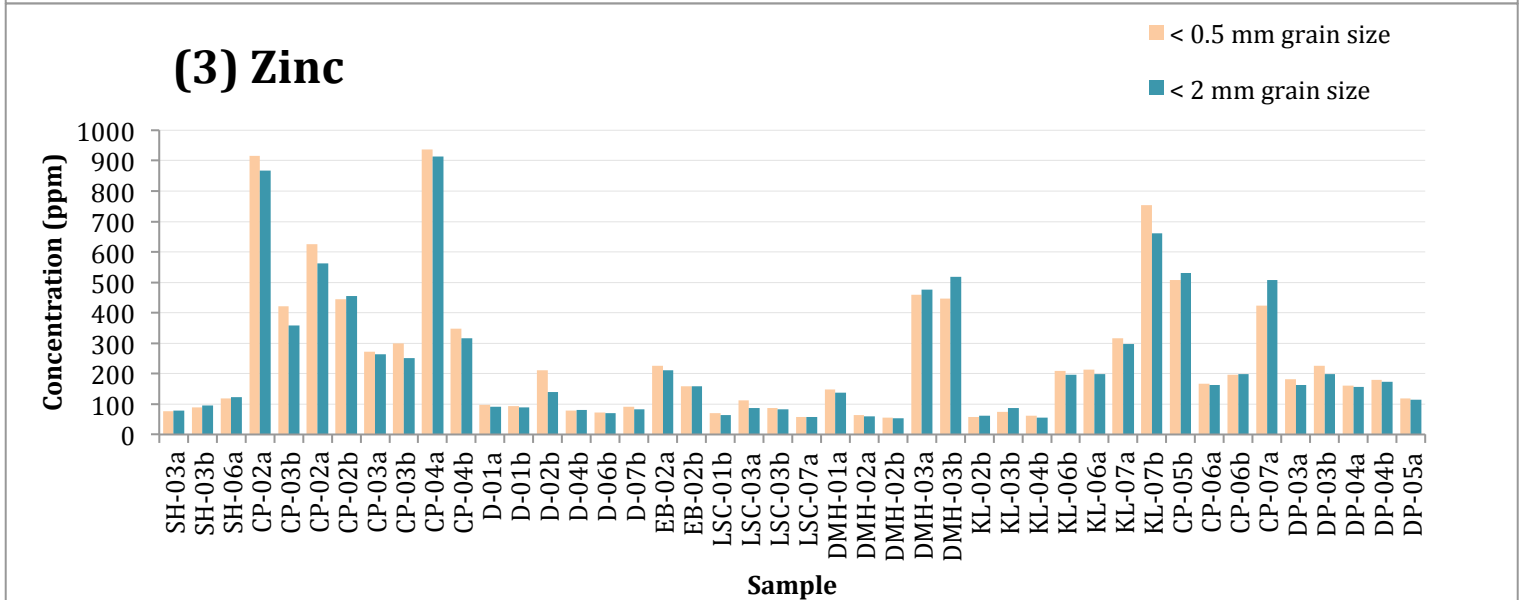
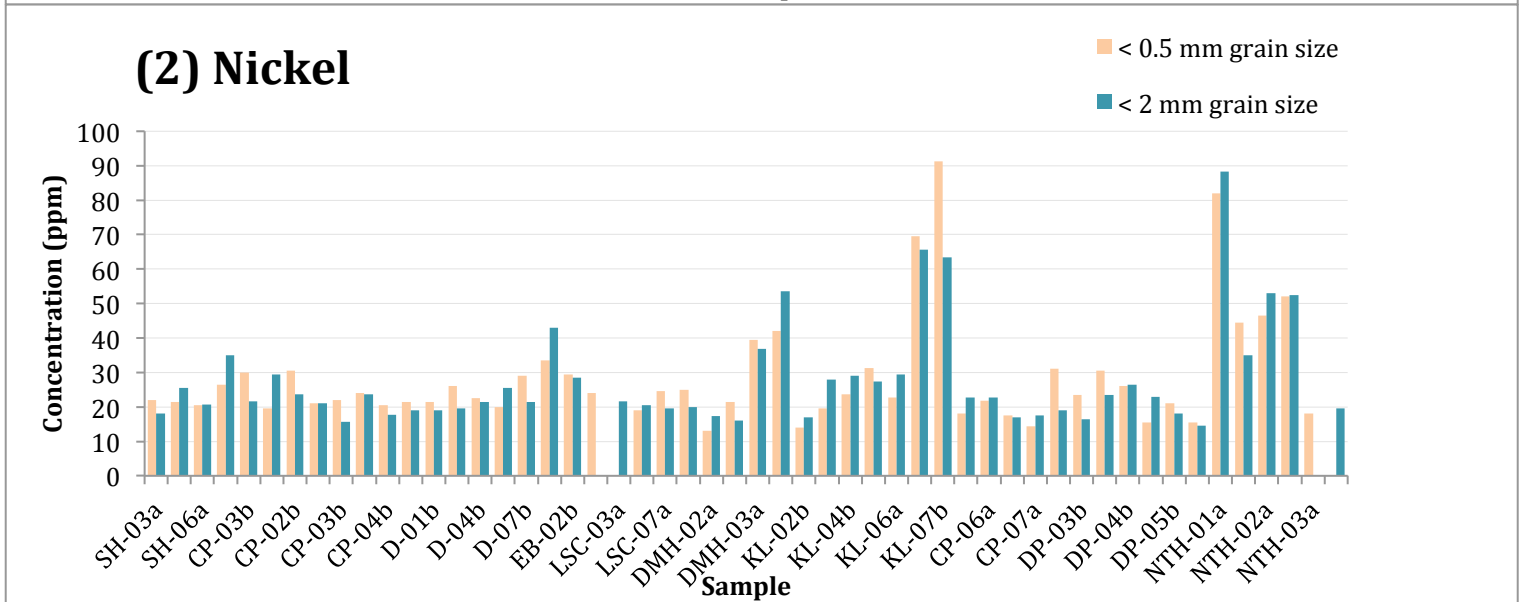
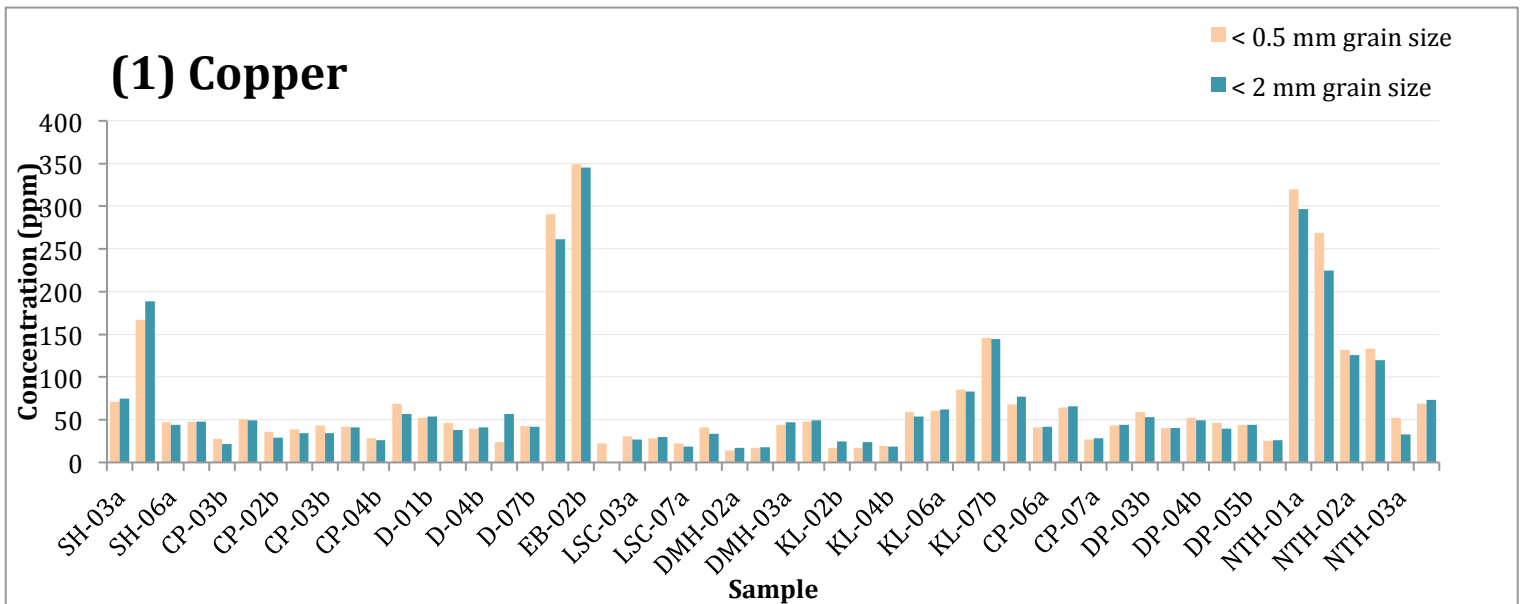


Figure 55: (1,2,3) show variation of metal content with particle size for Cu, Ni, and Zn.

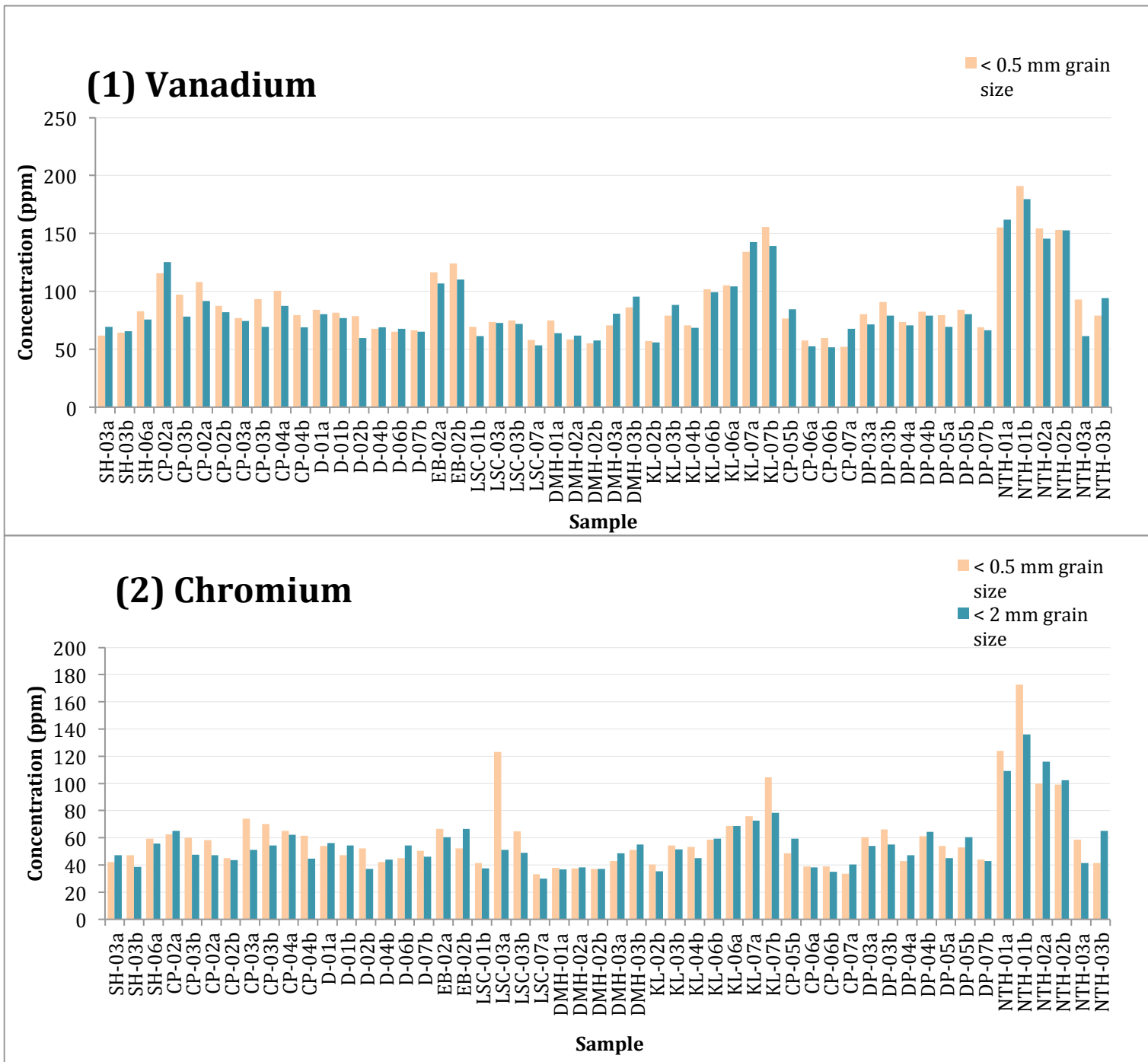


Figure 56: (1,2,3) show variation of metal content with particle size for V and Cr .

4.4 Soil Texture

Using field methods described in the methods Section 3.4, soil texture and type was determined. The following figures below (Figure 57 and 58) provide a visual representation of soil texture for 86 samples (from the 98 depth based samples collected and analyzed). Soil texture analysis was conducted qualitatively rather than quantitatively. The results show two different textures within the samples analyzed. One texture prominently shows soils that are sandy –clay loams and another texture is dominated by silty clays. Figures 57 and 58 below, demonstrate a general depiction of where these soils would generally reside on a soil texture diagram (locations identified by blue shapes on diagram). Figure 57 shows texture for soils in 0-5 cm depth and Figure 58 shows texture for soils in 0-15 cm depth. Overall these soils were found to be dominantly siltier and clay rich in nature and less so on the coarser sandy side.

Soil Textural Triangle

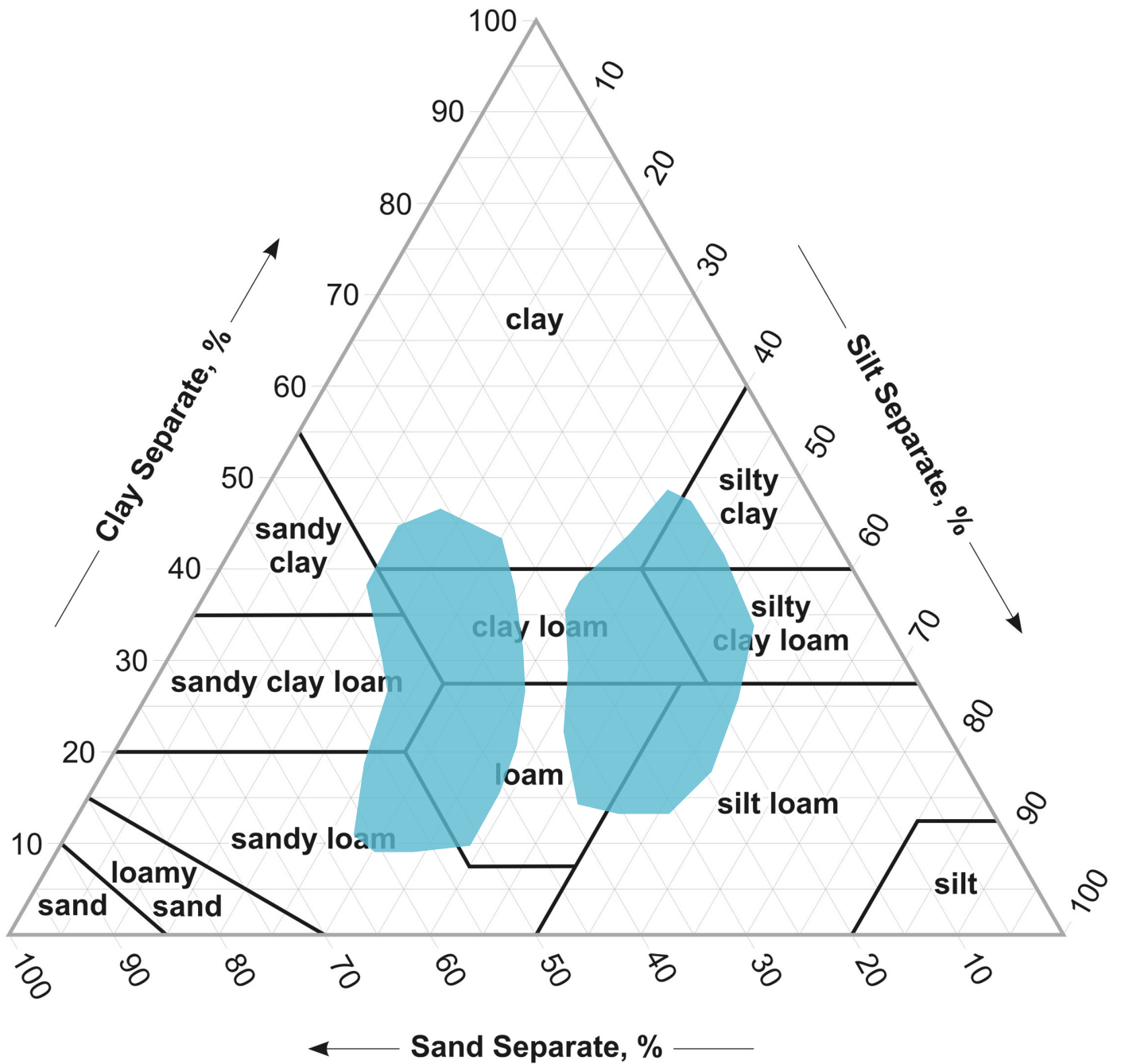


Figure 57: Range of soil textures based on field test data: qualitative rather than quantitative data. Blue shapes depict two soil textural groups for samples in 0-5 cm depth: (1) sandy-clay rich and (2) silty-clay rich, both groups are quite loamy in nature (Obtained from USDA, 2017).

Soil Textural Triangle

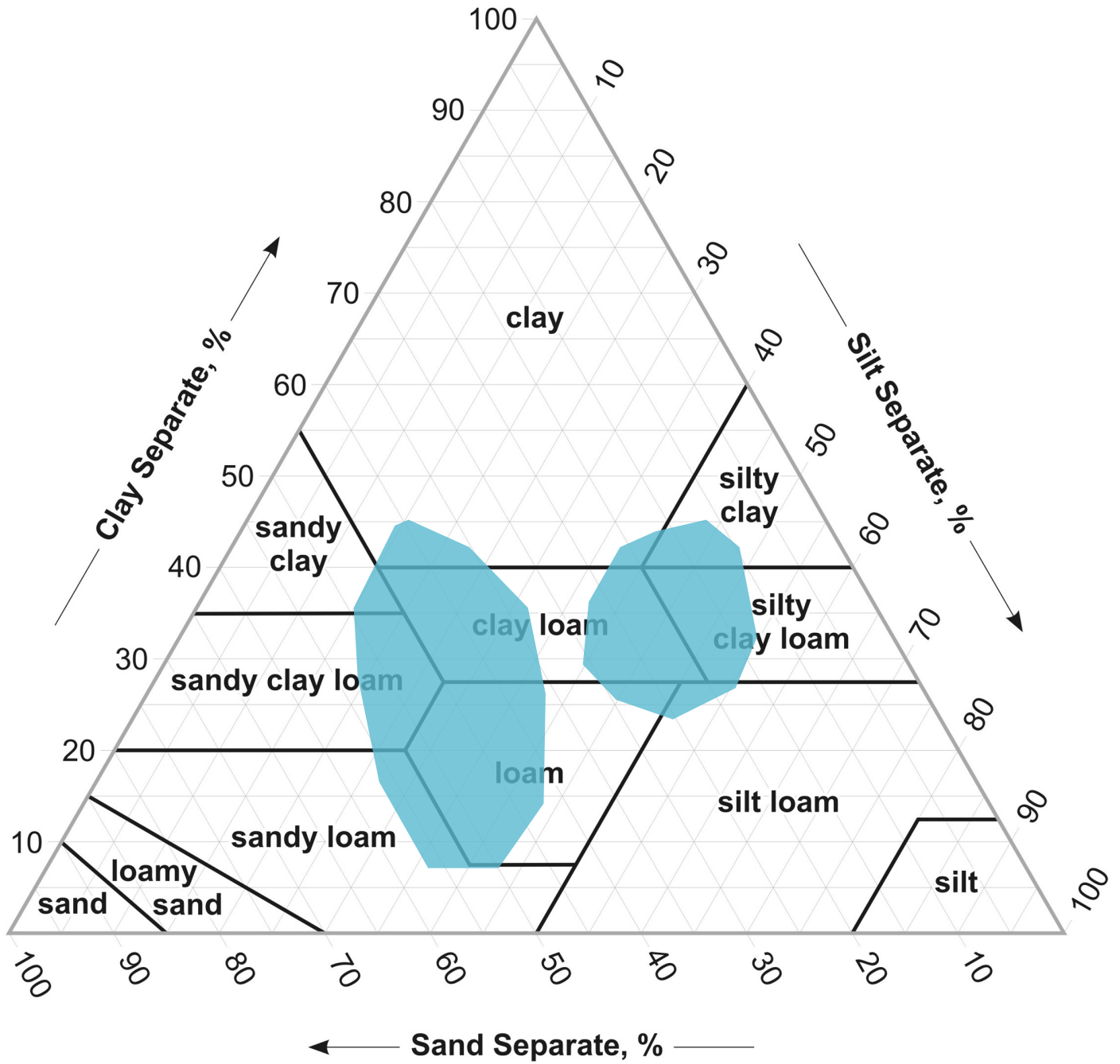


Figure 58: Range of soil textures based on field test data: qualitative rather than quantitative data. Blue shapes depict two soil textural groups for samples in 0-15 cm depth: (1) sandy-clay rich and (2) silty-clay rich, both groups are quite loamy in nature (Obtained from USDA, 2017).

4.5 Predicting metal abundance

Predictions of the potential locations for metal abundances within Halifax, Nova Scotia were designated as 'points of Interest' (POI's). The following maps were created for the 1700's, 1800's and 1900's depicting POI's as polygons and rivers as points Figure 59, 60, and 61. Rivers were identified to represent possible migration pathways and aid towards determining potential metal hotspots, depending on the location of certain industries and if industries were near water.

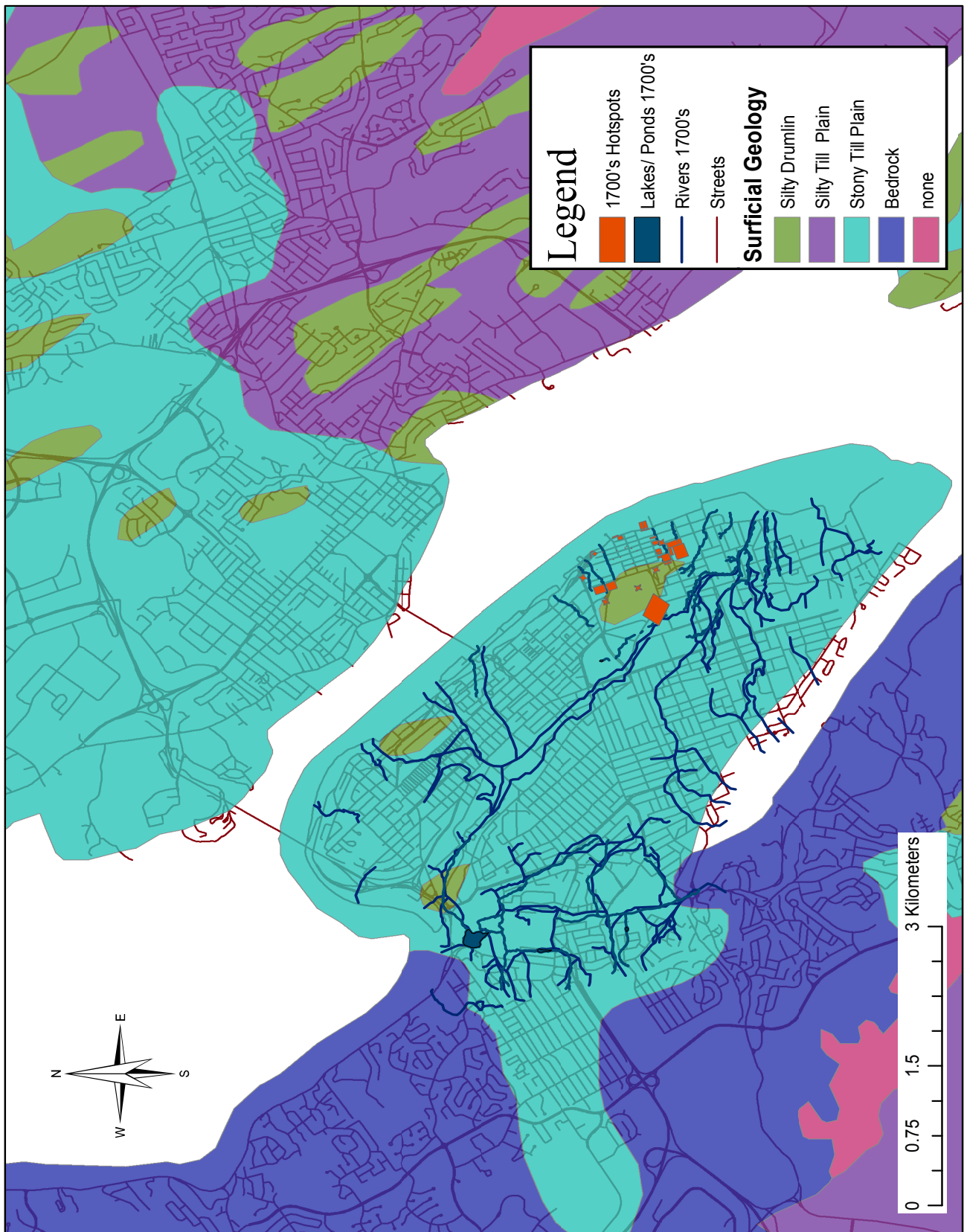


Figure 59: 1700's metal abundance map depicting POI's identified in orange and older rivers depicted as blue lines.

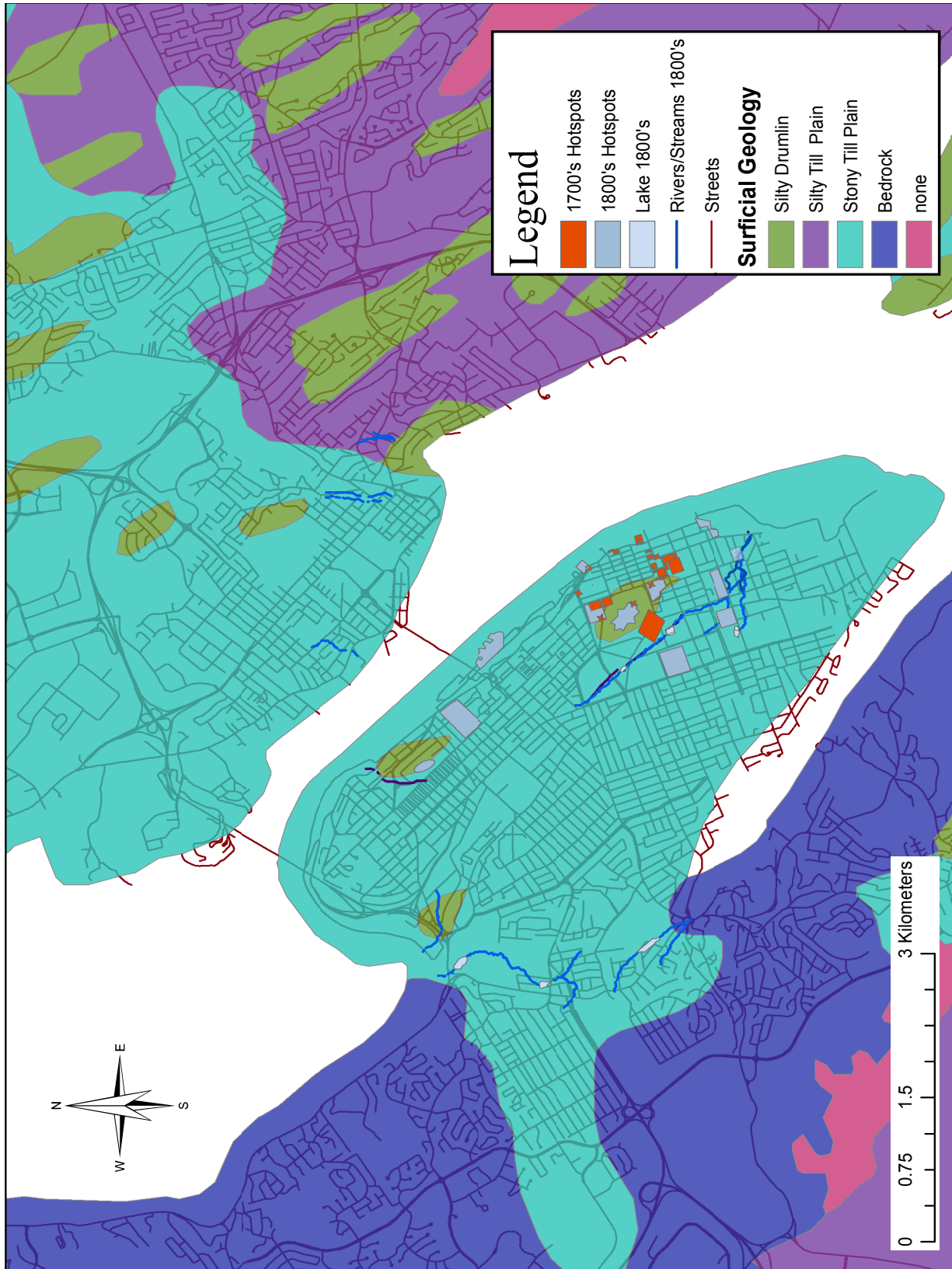


Figure 60: 1800's metal abundance map depicting POI's for both 1700's and 1800's in blue and orange. Rivers at still surface depicted as blue lines.

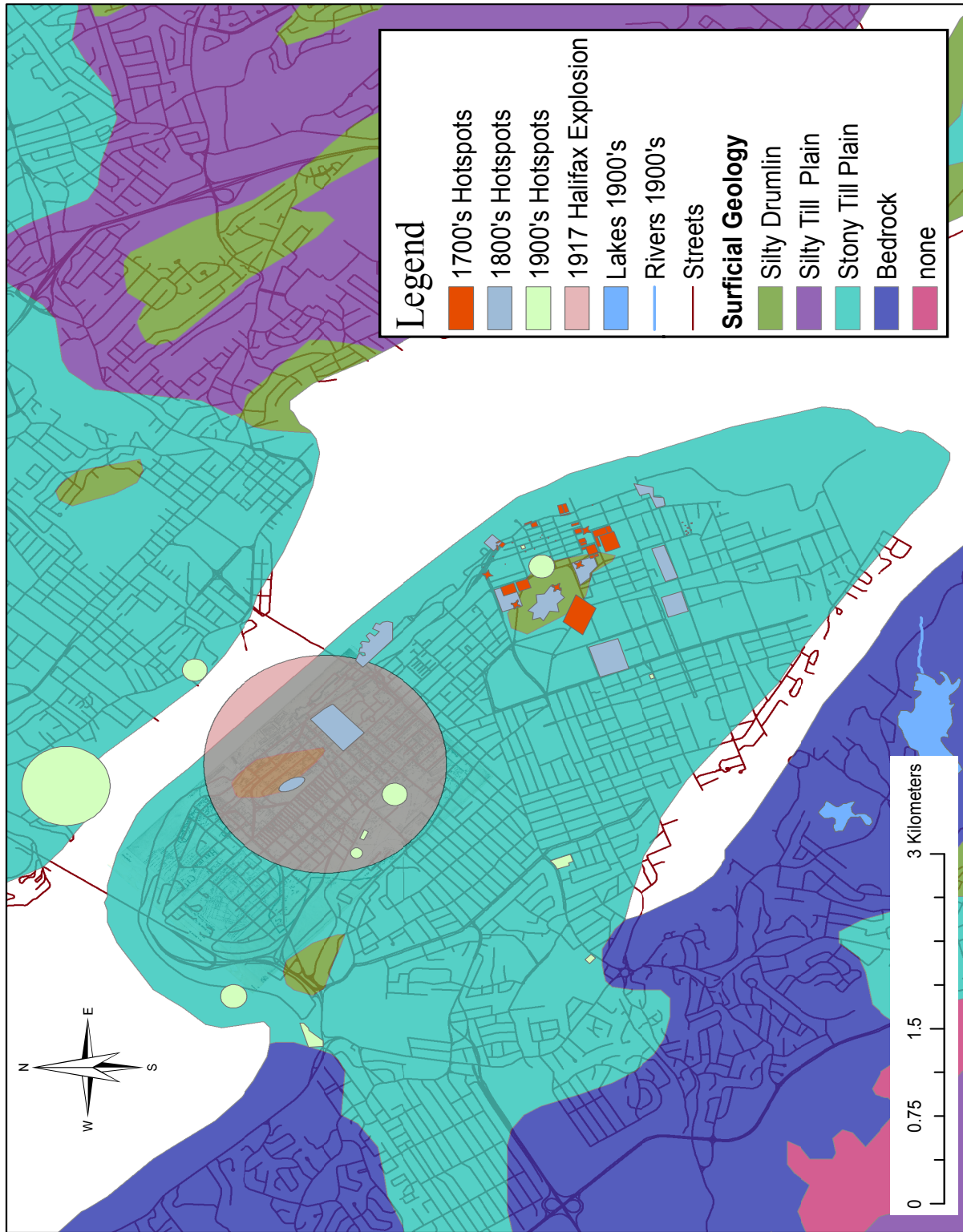


Figure 61: 1900's metal abundance map depicting POI's for 1700's, 1800's and 1900's with orange, blue, green and pink.

5.0 Discussion

Halifax soils, like many other soils within urban areas, have been exposed to intensive industrial development and anthropogenic activity. Although the state of a soil is due to the amalgamation of a number of different factors, anthropogenic influences are arguably the leading force that drives the condition of urban soils. As mentioned previously, the purpose of this study is to evaluate heavy metal concentrations within Halifax soils by using a holistic strategy. This involves assessing soils via a geochemistry approach and using GIS as a method of providing a preliminary assessment of potential anthropogenic influences acting on Halifax soils through the process of city development. The aim of applying a holistic approach is to broaden our understanding of how to evaluate urban soils and to answer a number of questions that have been raised within this thesis. As a review, the main questions regarding the geochemical assessment of Halifax soils and Halifax city development are given in Section 1.1. Section 5.1 will address questions 1-3 the nature of the soil itself, Section 5.2 will address questions 2, 4, 5, 6 and 7 variability of metal content within the soils studied, Section 5.3 attempts to answer question 8 regarding anthropogenic influences acting upon city soils and Section 5.4 answers question 9 which defines the broader question of how this analysis contributes to urban soil assessment and can provide recommendations for the evaluation of urban soils.

5.1 Soil Properties

Soil properties and environmental conditions (e.g. pH, reducing or oxidizing environments), are known to hinder or facilitate metal mobility, depending on the metal species, solubility and other geochemical characteristics (Smith and Huyck, 1999). Section 4.1 shows the results of a graphic analysis applied to geochemical data obtained from samples collected at Dalhousie campus. Metal concentrations for Mn, As, Fe, Pb, Ba, Sr, Cu, Ni, Zn, V and Cr were compared against pH level for a total of 89 samples (out of the 98 samples collected) (accounting for both 0-5 cm and 0-15 cm sample depths). There are two general trends that are identifiable, the first is a positive relationship, depicting a trend increasing of metal concentration with increasing pH level, and the second is an inverse relationship, a trend of decreasing metal concentration with increasing pH level. A positive

relationship is generally seen with the metals Mn and Sr, (Figure 26 and 31). Both sample depths (0-5 and 0-15 cm) demonstrate a correlation between increasing metal concentration with increasing pH values. Inverse relationships are obvious with metals Fe, As, Ba, V and Cr at both sample depths (Figure 27, 28, 30, 35 and 36). The inverse trend can also be seen with Cu, Ni and Zn, but it only appears prominent in 0-15 cm sample depths (Figure 32, 33, and 34). There are a few metals where trends do not appear to be present or the relationship is not clearly identifiable. A correlation is not clear with Pb graphical analysis for either 0-5 or 0-15 cm sample depths, and correlations between metal and pH for Cu, Ni, and Zn trends are not apparent at 0-5 cm depths.

Positive and inverse trends can to an extent suggest the mobility of a particular metal under given conditions within the soil system. Increasing concentrations with increasing alkalinity (increasing pH level) suggests that metals such as Mn and Sr are likely to accumulate under basic conditions (Figure 26 and 31). Inverse relationships suggests metals such as Fe, As, Ba, V, and Cr, accumulate under acidic conditions (Figure 27, 28, 30, 35 and 36). From graphical analysis we are able to draw upon understanding of how these metals may accumulate, however it's important to recognize that the mobility of metals are really an culmination of factors defined by the conditions of the environment. In this study these general relationships are drawn from just comparisons between metal concentration and pH. To further confirm these relationships, more work needs to be done, by collecting more data or by further defining the environmental conditions of these areas, such as oxidation conditions, which is another vital factor that impact's a metals mobility (refer to Figure 11 in Section 2). Some relationships and behaviors of metals are already generally known. For example, when pH drops (acidic conditions), elements that form anions such as molybdenum are generally known to become less mobile, whereas metals that form cations such as copper are generally known to become more mobile (Smith and Huyck, 1999). These general trends however can change depending on environmental conditions (oxidizing or reducing conditions). For example, lead under oxidizing conditions with acidic $\text{pH} < 3$ is somewhat mobile, where as under oxidizing conditions, with abundant iron rich particulates, and with $\text{pH} > 5$ lead is scarcely mobile to immobile (Smith and Huyck, 1999). When lead is under reducing conditions, without the presence of hydrogen sulfide,

and with a pH > 5, is mobile (Smith and Huyck, 1999). These brief examples of conditions that can exist within a surficial environment show that there are many factors that could impact the mobility regardless of whether it follows the general trend when just considering pH.

The relationship between conductivity, total dissolved solids (TDS), and pH was also considered. Within Section 4.1 it is clear that the results show a strong positive correlation and linear relationship between conductivity and TDS. Conductivity is a measure electric conductivity by estimating the total concentration of ionic solutes within an aqueous solution (Hem, 1985). TDS is the amount of dissolved solids within a solution. These two parameters are likely to be in close agreement since the TDS contributes to the amount of dissolved ions; the more dissolved solids, the higher the electric conductivity (Hem, 1985). Although measuring conductivity and TDS paints a picture of the quantity of ions from Halifax soils that could be dissolved within a solution, it does not add to our knowledge of how metals move within these soils. Graphical analysis of pH and conductivity show no obvious trend or relationship (Figure 25).

Based on the texture analysis provided in Section 4.1 the majority of the soil samples range from silty-to-clay rich loam. Soil textures influence metal accumulation in that metals tending to adsorb onto finer particle sizes and concentrate within the clays, as described, Section 2.7.4.1 (Smith and Huyck, 1999). Since these finer particle sizes are abundant within the soils studied, it should be expected that higher metal concentrations will accumulate in finer grain sizes, such as clay or silt layers.

The pH measurements collected show that our soil samples range from relatively acidic condition, lower than a pH 4 to 7. There are many factors, which influence the accumulation and distribution of metals within a soil, and pH is just one of these parameters. Climate, temperature, rainfall, topography, areas susceptible to drainage, physical disturbance by human activity, these are all examples of factors that can change the conditions present within a soil, and consequently change the pH over time. A soil's pH can change based on these conditions and therefore should not be considered static over time. The pH values measured for the soils collected at Dalhousie suggest relationships between some metals and pH, but do not predict how these metals will behave over time.

Since soil is an open system, it can be difficult to understand and predict metal mobility within the surficial environment over time. It is a combination of influences that affect a metal's mobility and understanding metal behaviour under varying conditions is no easy task (Smith and Huyck, 1999).

5.2 Soil Assessment: Depth – Based Sampling

The data collected for metal concentrations and their variability with depth, is representative of the area in which they were collected. Although the unequal variance t-test indicates that there is not a significant difference between metal concentrations of 0-5 cm and 0-15 cm sample depths, the difference is still notable within some metals Pb, Ba, As, Fe, Ni, and Zn (hence the variability). The excessive variability and deviations from the mean, contribute to the t-test results. The graphical data are averages of metal concentrations for 0-5 cm and 0-15 cm depths and the t-test involves an average of these averages and analyzes the variances present within the data. As previously mentioned, sampling at depths of 0-5 cm is consistent with Health Canada guidelines for analyzing soils for their affect on human health. This depth is representative of surface soil that will contribute to incidental exposure. Depths of 0-15 cm (as well as 0-30 cm) indicate the extent of the root depth (depth of roots from vegetation common within the soil profile) within a soil and these are the depths used to analyze nutrient abundance within a soil, to aid an environmental assessment of a soil's health based on Environment Canada protocols (Environment Canada, 2010). The different depths are used for different purposes, and thus you would expect that depths, based on sampling contribute to differences in results. With samples that have a higher metal concentration in 0-15 cm depth relative to the 0-5 cm depth, this could suggest that leaching is occurring during soil development. Although individual samples may show that some difference between 0-15 cm depths and 0-5 cm depths, t-test results demonstrate that for the overall distribution, there is not a significant difference.

Figures 43-52 suggest a strong correlation between certain metals and proximal to older wooden buildings (<2 m in proximity). Increasing proximity to older wooden buildings indicate statistically significant elevated metal abundance in Fe, As, Pb, Ba, and

Zn. Statistical analysis further confirms a significant difference between these metal populations and proximity to older wooden buildings based on t-test values divulged in section 4.2. T-test values indicate that V, Cr, Mn, Fe, Zn, As, Ba and Pb have a significant difference between proximal and distal statistical means and variances. This suggests that these older wooden buildings are acting as anthropogenic point sources for Fe, As, Pb, Ba, and Zn. Older wooden buildings likely used products containing these metals such as lead or barium in paint. These products are used on the older houses and metals leaching from these products are breaking down and becoming apart of the soil (such as paint) is likely what contributes to the elevated metal concentrations. It is less clear that however V, Cr, Mn and Cu are influenced by older wooden buildings, due to the low contrast between metal concentrations that are proximal and distal to older wooden buildings. The t-test further confirms that Mn and Cu do not have a significant difference between proximal and distal metal concentration means. Metals such as, V, Cr, Mn and Cu, which were not significantly elevated proximal to older buildings suggest that older buildings are not an anthropogenic point source for V, Cr, Mn and Cu.

Samples were purposely taken in areas near older wooden buildings, but avoiding drip-line. As identified within the background section 2.8.1, metal concentrations are not likely to be substantially the result of emission sources. Knowing that emission sources likely have little influence upon metal concentration within soils, this can further conclude that these older buildings are likely point sources to elevated metal concentrations closer to older wooden buildings.

The study area has a number of factors, which suggest the data collected can be extended towards representing Halifax values. Dalhousie University is relatively central to Halifax's downtown core. It has older wooden buildings (> 60 years of age) that can be representative of residential areas present near Halifax's downtown. Knowing that older wooden buildings likely act as point sources for elevated metal concentrations and can aid our understanding of what is considered the norm for soils closer to, and farther away from, these anthropogenic point sources.

5.3 Urban background

Cities are essentially metal hotspots, which poses difficulty in developing a background value within a city since all of soil in some way has been affected by anthropogenic activities and urban development. For this reason, it may be considered more appropriate to establish two urban backgrounds provided for metals within soils those proximal and distal from anthropogenic point sources. The reasoning behind developing a preliminary urban background provided in section 4.3 is to strengthen the understanding of what could be considered the norm for urban soils. Metal concentrations within cities should be expected to be elevated based on the various anthropogenic influences that have been identified, refer to (Section 4.5).

The results obtained from Dalhousie Studley Campus can, with caution, be applied for further studies on soils in the surrounding Halifax area. One aspect that is not considered within the urban background values provided in this study, and should be considered for the future studies, is how urban background will vary temporally and regionally. Time is a significant factor towards how soil develops, how metals move, and how they concentrate within the soil. By defining a time constraint on our urban background perhaps we can determine a better relationship between how metals concentrate within Halifax soils and what an urban soil background is like with soils that have been recently disturbed versus soils that haven't been disturbed in a city for a fair amount of time (arbitrarily, for example, 20 years). Time constraints can further suggest how leaching may occur with soil development, and enable us to understand more about what our urban background is representing. Urban background will vary depending on location, for factors mentioned previously in section 2.0 (natural vs. anthropogenic), obtaining more data to define an urban background throughout Halifax can contribute to understanding how geological processes and certain anthropogenic factors influence metal concentration within urban soils.

5.4 Particle Size Sieving

A main component of the particle size analysis involved looking at soil samples with metal concentrations that were above CCME and NS contaminated sites guidelines. Table

3.1 articulates the methods used in determining which guidelines to use for which metal. The majority of the metals above guidelines used the CCME analysis. Metals that were above guidelines were primarily V, Fe, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, Ba, Pb, and Th. Metals such as Ag, Mo, Sn, Sb, and Th mainly had samples lower than detection limits and thus were not chosen for graphical sieving analysis. Metals that were focused on for graphical analysis of sieving data included V, Fe, Ni, Cu, Zn, As, Ba, and Pb. Metals abundant that are a primary health concern are metals such as V, Ni, Cu, Zn, As, Ba and Pb. Iron above CCME is not of vital concern as it is more of an aesthetic issue.

One of the main findings is that the soils collected at Dalhousie were siltier and more clay rich in composition than anticipated. The particle sizes used for sieving (< 2 mm and < 0.5 mm) were compared for metal concentrations and how they vary with grain size. It was expected, as metals adsorb to clays and concentrate on finer particles, there would be a difference in metal concentration between particle sizes; however, although the difference can be seen in some samples analyzed, the t-tests confirm the difference between the two statistical means is not substantial or statistically significant. This is primarily due to finer particle sizes representing the majority of the soil analyzed. Within the < 2mm sample, it is estimated that finer grain sizes make up approximately 70 – 80 % of the grains. It is possible that a stronger relationship would be identified if a larger range in grain size comparison (finer particle size or larger particle size) were analyzed to capture the difference that is attributable to elevated metals concentrations with finer particle sizes. Furthermore, if the Halifax soil is siltier and contains a finer particle size fraction, then it could be interpreted that finer particle sizes are more likely to adhere to human hands, not for just the affinity but for the quantity of smaller particle sizes that exist within the Halifax soil. This may raise a concern in terms of metal toxicity for humans and children, since higher metal concentrations reside in smaller particle size fractions.

Reconfirming the findings showing distributions of sample proximal and distal to older wooden buildings confirm that samples closer to buildings had elevated metal concentrations for the same samples (Fe, As, Pb, Ba, and Zn) than those samples farther away from older wooden buildings. Since values were within similar ranges as they were for the depth based sample analysis, this can further suggest that values obtained for depth

based samples were real values. Sieved samples are less likely to contain large paint chips, which could skew metal concentration results compared to samples that are un-sieved; therefore, these values are more likely to be representative of the metal concentrations within the soil. Furthermore metals such as V and Cu that are not elevated in samples proximal to older wooden buildings could suggest that there are other point source influences that may be contributing to their abundance. Due to the scope of this study and the limitations in study area sampling the sources for the elevated metal concentrations of V and Cu remains unknown.

5.5 Predicting Metal Abundance

Throughout this report it has been established that there is strong connection between certain anthropogenic activities, such as industry effluents, emission, and products containing certain metals. More information about city development to determine POIs, with associated metals at these locations, are necessary to identify metal hotspots within the city of Halifax. Additionally, there are a multiple of other considerations in terms of metal hotspots distribution that are not immediately evident from archival maps. For example, one aspect to consider is the effect of the Halifax explosion on Halifax soil. We have to consider how debris of the Halifax explosion was disposed of and how that may effect metal concentrations in the soil in different parts of the city. On a larger scale, it is also important to consider how soil has been redistributed across the city as a whole, and perhaps how often major redevelopment takes place, causing further physical disturbance of soil and distribution of metal concentrations within soil. This will further implicate the determination and prediction of metal hotspots, type of metals present at hotspot locations throughout the city.

Another factor to consider for determining metal hotspots within the city of Halifax are migration pathways of metal contaminants. Key migration pathways are often rivers or streams, which effect where industry effluents may be disposed of and where the deposits of these effluents might be found (likely down stream). Overtime, Halifax waterways have changed and most downtown have gone underground due to city development. For example the Tannery near Queen Street probably disposed most of its effluent into the old

Fresh Water Brook, which now flows underground. The deposits from these effluents may reside downstream or in the Halifax Harbor. Rivers and streams such as, the Fresh Water Brook, has mostly been rerouted through storm water pipes, an important consideration for other migration pathways and rivers that aid in determining where these metal hotspots be predicted through time.

Overall, an urban area in its entirety is a hotspot. It should be expected and considered normal for metal concentrations to be elevated in urban areas. However, that means we should aim to identify sites that may hold more concern than others due to the type of metals that may be present, based on certain anthropogenic activities.

Furthermore, by identifying possible hotspots these sites can act as ways for predicting sampling locations that may contain a higher concentration of metals.

5.6 Limitations & Considerations

One of the main limitations for this study was not being able to sample other locations throughout the city, which hindered the ability for this study to provide an appropriate representation of the condition of Halifax soils. Having permission to have a larger sampling scope would have aided the understanding of metal variability throughout city soils and how anthropogenic influences may affect soil condition.

Although XRF analysis is cost effective and efficient, it has limits on precision, accuracy, and capability of detection limit for some elements. There are other instruments that could have been used that have higher precision and accuracy, such as Inductively coupled plasma mass spectrometry (ICP-MS) (Daniel Senechal, personal communication, February 2017). However, this study was conducted in part to identify metal hotspots, and there isn't a significant enough need for this study to have more exact data to really impact the results. Another aspect to consider for this study, are the outliers that exist as apart of the graphical analysis. Some of these outliers are likely caused by potential paint chips and are not a full representations of the soil samples metal concentrations, however further work needs to be done to pinpoint potential reasons behind outlier concentrations, before these concentrations can be omitted from graphical analysis data. Since outliers are included, it is important to note that some outliers may skew some of the results.

6.0 Conclusion

Anthropogenic activities and city development is a forceful influencer in shaping the condition and health of city soil. The condition of a soil is based on a multitude of factors that must be evaluated holistically in hope of understanding how these factors may influence metal concentrations within soils. There are several conclusions that can be drawn from the evaluation of the Halifax study area at Dalhousie Studley campus:

1. Metal concentrations are above guidelines and the metals that have been analyzed above guidelines are V, Fe, Ni, Cu, Zn, As, Ba, and Pb.
2. There is a strong relationship between metal abundance and the proximity of samples to older wooden buildings (< 2 m in proximity), which have been analyzed by comparing both unsieved (0-5 and 0-15 cm depth samples) and sieved samples (< 2 mm and < 0.5 mm samples).
3. Significantly higher metal concentrations closer to older wooden buildings suggests that older wooden buildings act as anthropogenic point sources for metals of Fe, As, Pb, Ba, and Zn.
4. Metals such as V and Cu that are above guidelines and do not vary substantially in concentration with proximity to older wooden buildings, suggesting that some other point sources or non point sources may be contributing to their abundances.
5. A preliminary urban background for soils proximal to and distal to older wooden buildings has been determined and may aid the use of further analysis and study of Halifax soils.
6. Soil texture analysis concludes that soils are siltier and clay rich, allowing for a smaller particle size fraction to absorb metal concentrations. Overall metals do not vary substantially with 0-5 and 0-15 cm depths and they do not vary substantially with particle sizes chosen < 2 mm and < 0.5 mm.

These results to an extent, may aid in understanding the conditions and metal content of Halifax soils.

7.0 Recommendations

Urban areas are hubs of anthropogenic activity and development, contributing to metal content within our soils. Due to the relationships between metal content and anthropogenic influences it can be expected that urban areas are essentially a metal hotspot. The nature of Halifax development in the urban core is expected to evolve with the forecasted increase in population density. As population density increases, elevated metal content within urban soils will become a rising concern in relation to urban inhabitant health. As discussed in the background Section 2.9.3, urban centers within Nova Scotia are expected to expand. Rural inhabitants are increasingly migrating towards living in city centers. It is important to think about how this process of development will evolve for the future and what impact that may have on the conditions of our soils. It is likely that there will be more people living vertically, in high rises or apartment buildings.

When evaluating urban soils it is important to avoid the alarmist view; high metal concentrations should be expected within soils that make up an urban environment. That, however, does not suggest the precautionary principle should not be taken into effect. The underlying question, which is what the best approach for evaluating urban soil and what recommendations can be made based on the conclusions derived from this study. These recommendations include but are not limited to:

1. Evaluating urban soils holistically
2. Determining natural and anthropogenic influences that may impact and source metal concentrations of urban soils. This may involve the evaluation of a cities development over time and studying a cities anthropogenic history.
3. Provide a geochemical analysis of soils by evaluating soil condition and metal content within soils.
4. Provide an urban background to aid in determining baseline metal concentrations you would expect to find far or near possible anthropogenic point sources

5. As development continues, evaluate the conditions of the soil on a land use basis. For example, if you intend to build a playground, a soil assessment should be conducted to determine the metal content within the soil and its condition to determine if remediation is necessary.

My study aims to assess the variability between 0-5cm and 0-15 cm depths, as well as between < 2 mm and < 0.5 mm particle size fractions. It is typical, that the longer time is allowed for soil development, the more downward leaching occurs, justifying why some soil sampling protocols must be context specific. Data in this study indicates significant variability depending on where the samples are taken. The variability between sites is considerably greater than the variability between sample depths. My study indicates that there is not typically extreme variability between the 0-5cm and 0-15 cm depths. The lack of a difference between metal concentrations at different depths can be attributed to the soil being disturbed by anthropogenic activity. Urban soils are likely to be disturbed due to development and other anthropogenic activity, which suggests that there is not significant difference between sampling soils at a shallower depth versus at a deeper depth within urban areas. Perhaps urban soils or soils that are relatively immature do not need more than one sampling depth to assess the soils condition and metal concentrations. As we continue to collect more data we may be able to better constrain optimal depth sampling protocols for urban soils.

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8.0 Appendix Outline

Appendix A	Maps 1700s -1800s
Appendix B	Soil Properties
Appendix C	Depth-Based Sample Analysis
Appendix D	Particle Size Sample Analysis