Dynamics of trace metals and de-icing salt in compost-amended urban soils

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Abstract

The accumulation of potentially toxic metals from vehicular emissions and the splashing of de-icing salt onto the soil in sidewalk tree pits can prove toxic to street trees and thereby shorten their life span. These same contaminants can also degrade groundwater quality. A collaborative study between McGill University and the City of Montreal sought to design an improved soil mixture in order to promote street tree health and improve urban runoff water quality. Before this is possible, it is necessary to understand how the presence of soil contaminants is related to different factors in the urban environment, and how theses factors can affect nutrient availability in urban soils.

Understanding the relationships among contaminant abundance, nutrient availability in urban soils, and urban environmental factors can inform soil quality standards for the presence of potentially toxic metals and provide a baseline for nutrient management in tree pit soils. Following these standards and baselines can decrease the stresses affecting street trees. A preliminary chemical analysis was therefore done on 73 tree pit soil samples selected based on land use category, soil age, and soil organic matter. Significantly higher concentrations of Cu, Zn, Cd, and Pb were observed in soils from commercial (*vs*. residential) streets, possibly as a result of the heavier traffic on commercial streets. A coefficient of variation exceeding one for Na levels in tree pit soils of commercial zones is likely linked to the application of de-icing salt on the street. An analysis of plant nutrients (Ca, Mg, K, P, and total mineral N, including NH_4^+ and NO_3^-) in tree pit soils showed no deficiencies as compared to the recommended concentration of available nutrients in horticultural soils. The use of wood chips as tree pit cover material and soil age had significant effects on K, P, and N availability. Street width and soil pH were positively correlated with Na availability in tree pit soil, possibly due to the heavier traffic on wider streets splashing more de-icing salt into the tree pits, and the consequent displacement of H^+ by Na^+ in the tree pit soil.

The addition of organic amendments, such as compost and biochar, to the soil can enhance soil physicochemical conditions for the sorption and retention of the potentially toxic metals present in urban runoff water. These soil amendments can also provide nutrients for trees and thereby improve their growth. Accordingly, an investigation was conducted into the efficiency of biochar and compost in immobilizing potentially toxic metals in tree pit soils in the

presence of de-icing salt. Using a central composite rotatable design, the soil used by the City of Montreal when transplanting nursery trees to sidewalk tree pits was amended with nine different combinations of compost (0-15% w/w) and biochar (0-10% w/w). The sorption and desorption of Na, Cu, Zn, Cd, and Pb were then evaluated for the different soil mixtures. The two amendments showed different abilities to immobilize potentially toxic metals in the tree pit soil impacted by de-icing salt. The soil amended with 7.5% compost indicated the best sorption and retention of Zn and Pb. The positive effect of compost on metal sorption and retention may be attributed to its high cation exchange capacity and its positive effect on soil pH. For Na, Cu, and Cd, soil alone appeared to be the best adsorbent. The biochar used in this study did not improve the ability of the soils to retain contaminants. However, the properties of biochar vary widely, depending on the feedstock from which it is produced and the pyrolysis conditions, so these results could be quite specific to this study.

Following the sorption and desorption tests, a phytotoxicity trial was conducted to evaluate metal bioavailability in the soil mixtures including 0, 5, or 10% (w/w) of compost. Soil mixtures, spiked with known concentrations (control, medium and high levels) of Na, Cu, Zn, Cd and Pb, were used in a 14-day growth trial of barley (*Hordeum vulgare* L.). Based on emergence, growth, and the measured concentrations of potentially toxic metals in the roots and shoots of the barley plants, compost-amended soils showed less Cu, Zn, Cd, and Pb absorption by barley plants than non-amended soil. This was probably attributable to the specific complexation of the metals and the provision of macronutrients such as Ca^{2+} and Mg^{2+} by the compost. These macronutrients possibly compete with trace metals for absorption by plants. Amendment with compost also decreased Na and Cd absorption by barley plants, likely through an indirect process involving its effects on CEC and pH. The contamination of soil with Na together with trace metals also affected metal bioavailability, possibly because of competition amongst potentially toxic metal cations for complexing sites. The amendment of soil with compost also increased Ca, Mg, K, and P availability. However, compost did not have a significant effect on NH_4^+ and NO_3^- availability for the barley plants.

We concluded that, in the short term, the addition of compost significantly reduced metal bioavailability and improved nutrient availability. However, more studies are required to investigate the long-term effects of compost on the retention and bioavailability of contaminants before recommending compost as a buffer to the impacts of urban contaminants in tree pit soils.

Although biochar appeared to be ineffective in this study, its properties vary widely depending on its feedstock and the conditions of its production. It must therefore be noted that our results are specific to the soil mixtures used in this study. Other types of soil, compost, and biochar could have very different abilities for metal sorption and retention.

Résumé

Dans le milieu urbain, les arbres peuvent être affectés par les émissions polluantes émises par les véhicules routiers et les giclures de sels de déglaçage sur leur fosse de plantation réduisant de ce fait leur durée de vie. Les contaminants peuvent aussi affecter la qualité de l'eau souterraine. Un projet de recherche en collaboration avec l'Université McGill et la Ville de Montréal été mis sur pied pour élaborer un mélange de sol qui favorise une meilleure santé des arbres de rues et pour améliorer la qualité de l'eau de surface. Avant de procéder il est nécessaire de comprendre l'interaction de différents facteurs dans l'environnement urbain et les contaminants du sol et de mesurer comment ces facteurs influencent la disponibilité des nutriments du sol.

L'étude des relations entre l'abondance de contaminants, la disponibilité des nutriments dans les sols urbains et les facteurs environnementaux permettra de développer des normes de qualité du sol pour la présence de métaux à des niveaux potentiellement toxiques et ainsi établir des critères de base pour une gestion des sols de fosse de plantation. En établissant ces limites il sera possible de diminuer les stress affectant les arbres urbains. Une analyse chimique préliminaire sur 73 échantillons de sol prélevés dans ces fosses sélectionnées selon leur catégorie de zonage, leur âge et leur taux de matière organique a été effectuée. Des concentrations significativement plus élevées de Cu, Zn, Cd et Pb ont été mesurées dans les fosses provenant des rues commerciales (vs résidentielles) en raison possible du trafic routier plus intense dans ces zones. Un coefficient de variation supérieur à 1 pour les niveaux de Na dans les sols de rues commerciales pourrait être relié à l'application de sels de déglaçage. Une analyse des éléments nutritifs (Ca, Mg, K, P et azote minéral, NH_4^+ et NO_3^-) dans les sols de fosses d'arbres de rues ne montre aucune carence pour les plantes en comparaison avec les concentrations recommandées en sol horticole. L'utilisation de copeaux de bois comme paillis et l'âge des sols ont un effet significatif sur la disponibilité de P, N et K. La largeur de rues et le pH des sols sont corrélés positivement avec le Na disponible dans les sols de fosses, possiblement dû au trafic routier plus intense sur les rues plus larges et, par conséquent, un giclement plus important de sels de déglaçage causant le déplacement chimique des ions H^+ par le Na^+ dans les sols.

L'ajout d'amendements organiques, tels du compost ou du biochar, peut améliorer les conditions physicochimiques du sol en favorisant la rétention et l'adsorption des métaux potentiellement toxiques qui, de ce fait, ne se retrouveraient pas dans les eaux de surface. Ces amendements de sol pourraient aussi fournir des nutriments et améliorer la croissance des arbres. Ainsi une étude a été entreprise pour évaluer l'efficacité du biochar et du compost à retenir les métaux potentiellement toxiques présents dans les fosses en présence de sels de déglaçage. Utilisant un design statistique, le sol employé par la Ville de Montréal dans ses fosses de plantation pour les arbres de rue a été amendé avec 9 combinaisons différentes de compost (0-15% m/m) et biochar (0-10% m/m). L'adsorption/désorption de Na, Cu, Zn, Cd et Pb ont été évaluées sur tous ces mélanges de sols. Ces deux types d'amendements ont montré des potentiels différents à retenir les métaux potentiellement toxiques dans les sols de fosses affectées par les sels de déglaçage. Le sol amendé avec 7.5% de compost a montré la meilleure adsorption de Zn et Pb. L'effet positif du compost sur la rétention de métaux peut être expliqué par sa grande capacité d'échange cationique et son effet positif sur le pH. En ce qui concerne le Na, Cu et Cd, le sol individuel (non amendé) semble être le meilleur adsorbant. Le biochar utilisé dans la présente étude n'a pas contribué à améliorer la capacité du sol à retenir les contaminants. Les propriétés de biochar varient grandement en fonction du matériau et des conditions de pyrolyse utilisés à la source du procédé donc les résultats obtenus dans cette étude pourraient être spécifiques à celle-ci.

Pour faire suite aux tests d'adsorption/désorption, un essai de phytotoxicité a été développé pour évaluer la biodisponibilté des métaux dans les mélanges de sols comprenant 0, 5, 10 % de compost. Des combinaisons de sol et compost amendés avec des concentrations convenues (niveaux nuls, moyens et élevés) de Na, Cu, Zn, Cd et Pb ont été utilisées dans une étude de croissance de 14 jours avec de l'orge (*Hordeum vulgare* L.). Basés sur la mesure des paramètres d'émergence, de croissance et de concentrations des métaux potentiellement toxiques sur les racines et les pousses d'orge, les sols amendés de compost montrent moins de Cu, Zn, Cd et Pb absorbés par les plants d'orge qu'avec les sols non-amendés. Ceci pourrait être attribué au fait que le compost est riche en Ca et Mg et que les métaux y sont complexés de manière spécifique; ces macronutriments pourraient entrer en compétition avec les métaux traces dans leur absorption par la plante. L'ajout de compost a aussi diminué l'absorption de Na et Cd par les plants d'orge possiblement à cause d'un processus indirect impliquant ses effets sur la CEC et le pH. La contamination des sols avec du Na de même qu'avec les métaux potentiellement toxiques affecte aussi leur biodisponibilité pour la plante et ce, possiblement à cause de la compétition entre tous ces métaux pour les sites d'échange. L'amendement des sols avec du

compost a aussi augmenté la disponibilité de Ca, Mg, K et P mais n'a pas eu d'effet sur NH_4^+ et NO_3^- disponible pour les plants d'orge.

A court terme, l'ajout de compost a significativement diminué la biodisponibilité des métaux potentiellement toxiques et a amélioré la fertilité des sols. Néanmoins, des études plus approfondies sont nécessaires pour évaluer les effets à long terme de l'ajout de compost sur la rétention et la biodisponibilté des contaminants avant de pouvoir recommander son utilisation comme traitement contre les impacts des contaminants urbains sur les sols des fosses de plantation. Même si le biochar parait être inefficace dans les conditions de cette étude, ses propriétés sont tellement spécifiques à son matériau initial ou à ses conditions de production qu'il faut souligner que nos conclusions quant à son utilisation ne s'appliquent qu'aux mélanges utilisés dans ce projet. D'autres types de sols, compost ou biochar pourraient montrer des propriétés différentes de sorption et rétention des métaux.

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Dedication

This thesis is dedicated to my parents and my sister, with much love. Thank you for your endless support and inspiration.

Thesis format and contribution of authors

Following the Guidelines Concerning Thesis Preparation presented by McGill University, this thesis is written in manuscript format by the candidate. The thesis consists of four manuscripts. Dr. O. Grant Clark, as thesis supervisor, Dr. William H. Hendershot, as thesis co-supervisor and Dr. Pierre Jutras and Dr. Shiv O. Prasher, as academic advisors, co-authored all the manuscripts. The first three manuscripts (Chapters 4, 5, and 6) are published and are reproduced with the permission of the publishers, whereas the fourth manuscript (Chapter 7) is currently under review for publication. The candidate was fully responsible for conducting all the experimental work (experimental design and chemical analyses), statistical analysis of the data and discussion of the results, and manuscript preparation. Dr. O. Grant Clark, Dr. William H. Hendershot, and Dr. Pierre Jutras were involved in the design and data interpretation of the experiments and editorial assistance of all written manuscripts and the thesis. Dr. William H. Hendershot also provided all the lab space and the equipment for chemical and growth tests, with the technical assistance of Hélène Lalande. Dr. Shiv O. Prasher provided scientific advice for experimental design and data interpretation. The City of Montreal Transport Department financially supported this project.

Publications related to the thesis are listed as follows:

- Kargar, M., P. Jutras, O.G. Clark, W.H. Hendershot, and S.O. Prasher. 2013. Trace metal contamination influenced by land use, soil age, and organic matter in Montreal tree pit soil. Journal of Environmental Quality 42:1527–1533.

- Kargar, M., P. Jutras, O.G. Clark, W.H. Hendershot, and S.O. Prasher. 2015. Macronutrient availability in urban tree pit soil influenced by land use, time and organic matter. Urban Ecosystems, DOI: 10.1007/s11252-015-0439-7.

- Kargar, M., O.G. Clark, W.H. Hendershot, P. Jutras, and S.O. Prasher. 2015. Immobilization of trace metals in contaminated urban soil amended with compost and biochar. Water, Air, and Soil Pollution, DOI: 10.1007/s11270-015-2450-2.

- Kargar, M., O.G. Clark, W.H. Hendershot, P. Jutras, and S.O. Prasher. 2015. Direct and indirect effect of compost on bioavailability of Na and trace metals in urban soils. Chemisorption. Under review.

Scientific presentations related to the thesis are listed as follows:

- Kargar, M., O.G. Clark, P. Jutras, W. Hendershot, S.O. Prasher. 2012. Bioretention systems in Montreal tree pits. NABEC-CSBE/SCGAB Annual International Meeting. July 15-18.Orillia, Ontario, Canada.

- Kargar, M., W.H. Hendershot, O.G. Clark, P. Jutras, and S.O. Prasher. Dynamics of trace metals and deicing salt in compost-biochar amended soil. 2013. ASABE Annual International Meeting. July 21-24. Kansas City, Missouri, USA.

- Kargar, M., O.G. Clark, W.H. Hendershot, P. Jutras, and S.O. Prasher. 2014. Designing a healthier soil for Montreal street trees. Urban Environmental Pollution, Climate Change and Urban Environment. June 12-15. Toronto, Ontario, Canada.

- Kargar, M., O.G. Clark, W.H. Hendershot, P. Jutras, and S.O. Prasher. 2014. Adsorption of trace metals and deicing salt in soil amended with compost or biochar. ASABE and CSBE | SCGAB Annual International Meeting. July 13-16. Montreal, Quebec, Canada

Contributions to knowledge

Urban soil problems, including contamination with potentially toxic metals such as trace metals and Na derived from de-icing salt, and nutrient deficiency, are increasingly recognized as significant reasons for the short life span of street trees (Jim, 1998a). Therefore the main objective of this study was to improve the sorption and retention ability of tree pit soil for trace metals and de-icing salt and to provide adequate content of available nutrients for street trees. Compost and biochar were considered as two possible organic amendments for tree pit soil. Chemical experiments and statistical analysis were conducted on the soil samples collected in a prior study from Montreal tree pits in commercial and residential land use zones and also on the newly designed soil mixtures. The following contributions to knowledge were made:

1. In conjunction with prior studies done on tree pit soils in the City of Montreal, this study determined that significant quantitative relationships exists among urban environmental factors, soil chemical parameters and the abundance of trace metals and de-icing salt, as well as nutrient availability in tree pit soil. The results of this study provide a baseline assessment, which can be used as a guideline for future studies on soil chemistry and urban environmental factors.
2. A soil mixture combined with 7.5% (w/w) of compost was proposed as the mixture best able to decrease the mobility and bioavailability of metals in tree pit soils and to provide plant-available nutrients.
3. Compost showed both direct and indirect effects on metal bioavailability. The direct effects of compost were likely due to the formation of relatively insoluble organo-metallic complexes, which bound metals like Cu, Zn and Pb. Compost also provided macronutrients such as Ca^{2+} and Mg^{2+} which compete with metals like Cd for absorption by barley plants. Compost indirectly affected the uptake of metals by barley plants through its influence on soil pH and CEC.
4. This study indicated that biochar did not improve the ability of soils to retain contaminants. However, as previous studies indicated, the properties of biochar vary widely depending on the feedstock from which it is produced and its production process. It must be noted, therefore, that these results are specific to the soil mixtures used in this study. Other types of soil, compost, and biochar could have different abilities in terms of metal sorption and retention.

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Nomenclature

ACPL	*Acer platanoides*
ACSA	*Acer saccharinum*
Al	Aluminum
ANOVA	Analysis of variance
As	Arsenic
ATP	Adenosine triphosphate
BC	Biochar
$B_m(x)$	The m^{th} basis function
Ca	Calcium
Cd	Cadmium
CEC	Cation exchange capacity
CEOC	*Celtis occidentalis*
c,c_0	The constant
c_m	Coefficient of the m^{th} basis function
CO_2	Carbon dioxide
Conc	Concentration of metals in runoff water
CP	Compost
Cu	Copper
CV	Coefficient of variation
DBH	Diameter at breast height
DisSt	Distance (of the tree pit) from the curb (street)
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
EC	Electrical conductivity
EDTA	Ethylene-diamine-tetra-acetic acid
EF	Efficiency (of model)
exg	Exchangeable
Fe	Iron
FRPE	*Fraxinus pennsylvanica*
GLTR	*Gleditsia triacanthos*
K	Potassium
K_d	Partitioning coefficient
MARS	Multivariate adaptive regression splines
Mg	Magnesium
Mn	Manganese
N	Nitrogen
Na	Sodium
NaCl	Sodium chloride
NH_4^+	Ammonium
NO_3^-	Nitrate
Mo	Molybdenum
$\overline{O}$	Mean of observed values
O_i	Observed value
OM	Organic matter
P	Phosphorus

P_i	Predicted value
p-value	Probability of an observed result assuming that the null hypothesis is true
Pb	Lead
PitV	(Tree) pit volume
r	Correlation coefficient
R^2	Coefficient of determination
S	Steady-state concentration
SD	Standard deviation
SL	Soil
SOM	Soil organic matter
StW	Street width
TICO	*Tilia cordata*
U	Error variance
ULPU	*Ulmus pumila*
y	Year
Z	Standard score
Zn	Zinc
δ	Standard deviation
μ	Average of the data

Chapter 1. Introduction

1.1. General introduction

Urban trees play important roles in maintaining the viability of urban ecosystems and enhancing the welfare of urban society. Depending on species and age, trees provide different services, *e.g.,* absorbing carbon dioxide (CO_2), generating oxygen through photosynthesis, improving air quality, ameliorating microclimate, serving to reduce noise, retaining rainwater, providing recreational and aesthetic services, and reducing energy consumption by lowering the temperature in the buildings that the trees shade (Chen and Jim, 2008; Donovan and Butry, 2009). Donovan and Butry (2010) estimated the annual value of the ecosystem services provided by street trees in Portland, Oregon at around \$54 million, as compared to the associated maintenance costs (such as pruning and leaf removal), which was \$4.61 million annually. However, street trees have shorter life spans than trees growing in non-urban areas. In a survey of 20 American cities, Skiera and Moll (1992) found the mean lifespan of downtown street trees to be 13 years, compared to 150 years for trees in a rural setting.

The urban environment imposes difficult conditions on street trees grown in tree pits, such as soil compaction and the attendant exclusion of air and water from the soil pore space (Gregory et al., 2006), trace metal contamination (Li et al., 2013b), contamination with de-icing salt (Cunningham et al., 2008), and nutrient deficiency (Černohlávková et al., 2008). These soil problems are increasingly identified as contributors to the poor health or death of many street trees (Jim, 1998a).

The soil of street tree pits can infiltrate runoff from surrounding paved areas. The movement of water through the soil is affected by the presence of a thin layer of silt and clay particles, and organic matter at the soil's surface as well as the underlying soil's characteristics. The thin soil layer on top of street tree pits may cause a surface seal, thereby decreasing the water infiltration rate. The infiltration capacity of the underlying soil depends on the soil moisture content and porosity. Different factors including soil texture, root development, structure, and presence of organic matter can affect the porosity of the soil (Pit et al., 1999). Compaction of the tree pit soil reduces infiltration, thereby increasing run-off and decreasing groundwater recharge (Haynes et al., 2013).

Amending soil with organic material is one cost-effective way to improve contaminated urban soil and improve urban runoff water quality. Derived from biological matter, compost and biochar usually need little pre-treatment before they can serve as direct soil amendments (Beesley et al., 2011). The amendment of urban soil with compost and/or biochar may provide important benefits such as binding pollutants originating from urban runoff water and also improving the availability of nutrients for tree growth (City of Montreal, 1995).

The use of compost as a soil amendment has been shown to have multiple benefits such as controlling soil erosion by bonding soil particles into larger, water-stable aggregates; increasing pore space and air circulation in the soil; reducing soil compaction; increasing trace metal adsorption in the soil; and, enriching the soil with micro- and macronutrients (Lakhdar et al., 2009). The benefits of adding compost to soil can, however, be negated by the mobilization of some trace metals such as Cu along with dissolved organic carbon (DOC) in the soils amended with compost (Beesley and Dickinson, 2011).

To compensate for the negative effect of compost on the mobility of some contaminants, the addition of biochar could prove effective. Biochar is produced from biomass by combustion under low-oxygen conditions, resulting in a porous, low-density carbon-rich material. Owing to its large charged surface area and cation exchange capacity (CEC), biochar has the potential to immobilize trace metals and prevent the leaching of nutrients (Beesley et al., 2011).

Over and above its soil amending function, applying organic matter such as compost in the improved soil mixtures for street trees can support the Montreal waste management master plan (Department of the Environment and Sustainable Development, 2009). While roughly 47% of Montreal’s municipal solid waste in 2008 was organic matter, only 8% of this organic fraction was recovered. The City of Montreal is trying to increase the recovery rate for organic waste to at least 60% by 2025 (Communauté métropolitain de Montréal, 2015). Making use of organic material as compost will help the City of Montreal to move closer to this goal.

Amending tree pit soil with compost and biochar may also decrease the susceptibility of urban trees to invasive insects such as emerald ash borer (*Agrilus planipennis* Fairmaire) and help urban trees recover their ecological services (Doten, 2014). Emerald ash borer has been observed to kill mature ash trees within 3 to 5 years of infestation by boring into the xylem (or bark on larger trees) to build a pupal cell and thereby disrupting transportation of water and nutrients in the tree trunk (Baranchikov et al., 2008). Recent surveys have revealed that roadside trees have experienced greater damage from the emerald ash borer than trees in natural forests, probably because they experience greater stress such as soil compaction and contamination (Liu et al., 2003).

1.2. Research objectives

The overall goal of this research was to improve the ability of tree pit soil to retain trace metals and de-icing salt and to render nutrients more available to tree roots. In this case, tree pit soil can provide a medium for efficient percolation of runoff water and for growth of healthy street trees. Given the lack of local information on urban soil, we sought to complete a baseline assessment, which can serve as a guideline for future studies on improved selected soil attributes. This research contained three main studies, with specific objectives as follows:

i. Study I: determine the effect of the urban environment (*e.g.*, urban land use), soil chemical properties (*e.g.*, soil organic matter (SOM)), and the time elapsed after tree transplanting from nursery to tree pits (soil age), on trace metal abundance and nutrient availability in the tree pit soils of Montreal sidewalks.

ii. Study II: determine the effects of soil amendment (*e.g.*, compost and biochar), used both singly and in combination, on sorption and retention ability of the soil for potentially toxic metals (de-icing salt and trace metals).

iii. Study III: determine the direct and indirect effects of soil amendments on plant growth and the bioavailability of trace metals and nutrients at different levels of soil contamination.

1.3. Thesis outline

This thesis is manuscript based and covers 10 chapters. Chapter 1 presents a general overview of the problem and the objectives of this research. Chapter 2 provides a comprehensive literature review on limiting factors for street trees and the possible solutions for improving these limiting factors. Chapter 3 briefly reviews the methods applied in each study, concentrating more on the experimental design for sample selection and treatment combinations.

Chapters 4 and 5 focus on the relationship among trace metal (copper (Cu), zinc (Zn), cadmium (Cd), and lead (Pb)) abundance and nutrient (calcium (Ca), magnesium (Mg), potassium (K), phosphorus (P), and total mineral nitrogen (N)) availability and urban environmental factors and chemical parameters of soil samples exposed to de-icing salt and collected from street tree pits in a prior study in Montreal. Papers based on results presented in Chapters 4 and 5 are published in *Journal of Environmental Quality* and *Journal of Urban Ecosystems*.

Chapter 6 compares the ability of compost and biochar to improve the sorption capacity of soil mixtures for trace metals and Na as a component of de-icing salt. The paper based on the results presented in this chapter has been published in *Journal of Water, Air, and Soil Pollution*. Considering the results of chapter 6, chapter 7 specifically assesses the ability of compost in either directly or indirectly affecting Na or trace metal (Cu, Zn, Cd, and Pb) bioavailability in tree pit soil with different levels of contamination. The paper based on the results presented in this chapter has been submitted to the *Chemosphere Journal.* Chapter 8 presents a summary of the study's important results and conclusions. Chapter 9 suggests some directions for future research. Chapter 10 displays the literature cited.

Chapter 2. Literature review

2.1. Urban soil

As a category of anthropic soils, urban soils are classified into three main classes: (i) soils heavily transformed by human activity and composed of a mixture of materials (*e.g.*, street tree pit soil) distinctly different than that of less transformed soil (*e.g.,* agricultural soil) or natural soil (*e.g.,* forest soil); (ii) soils in parks and gardens that are closer to less transformed soil (*e.g.,* agricultural soil) but have different composition, use, and management than them; and (iii) soils resulting from various construction activities in urban areas and that are often sealed (Morel et al., 2005). Compared to forest or agricultural soils, urban soils have different physical and chemical characteristics such as a greater heterogeneity and compaction, restricted aeration and water drainage, interrupted nutrient cycling and modified soil organism activity, modified soil temperature regimes and the presence of anthropogenic contaminants (Craul, 1985). These characteristics of urban soils can be affected by the urban environment (Pouyat et al., 2007) and may significantly influence plants and soil organisms (Morel et al., 2005).

The functionality of urban soils in providing an adequate and healthy belowground medium for tree growth is one of the main concerns related to urban soil. Moreover, given the relatively large area of sealed earth surfaces in the urban environment, urban soil can play a crucial role in moderating flooding risk by storing infiltration water, and in sorption and retention of contaminants from urban runoff water (Yang and Zhang, 2011).

2.2. General characteristics of urban soil

Different soil characteristics can affect urban soil function as a medium for tree growth and runoff water treatment as follows:

2.2.1 Soil physical characteristics

The physical properties of a soil influence the amount of nutrients that the soil holds, and also the availability of the nutrients to plants. As a soil becomes finer in texture, it will hold more nutrients and water. The nutrient and water holding reservoir available to a plant can vary according to the soil depth. The more deeply and widely a plant can root, the more nutrients and water it will reach (Harris et al., 1999c).

In an urban environment, street trees live in "pot-like confinements" named tree pits (Fig. 2.1) (Wang, 2004). Limited tree pit volume and the intensive traffic of vehicles and pedestrians on the street and sidewalks can physically interfere with tree root growth. This occurs mainly through soil compaction (Harris et al., 1999c), a soil densification process which results from dynamic load application, and the attendant change in relative position of soil particles and the resultant decreases in air voids (Fang and Daniels, 2006). Soils under pavements are also highly compacted to meet engineering load-bearing requirements (Bassuk et al., 2009). Soil compaction depends on different factors including the type of the soil, the nature of the pore fluid, the temperature, and the type and concentration of exchangeable ions in the electrolyte solution (Fang and Daniels, 2006). Soil compaction affects different soil properties including water holding capacity, plant-availability of the nutrients, aeration, rate of water percolation and drainage through the soil, as well as the ease of root penetration (Harris et al., 1999a).

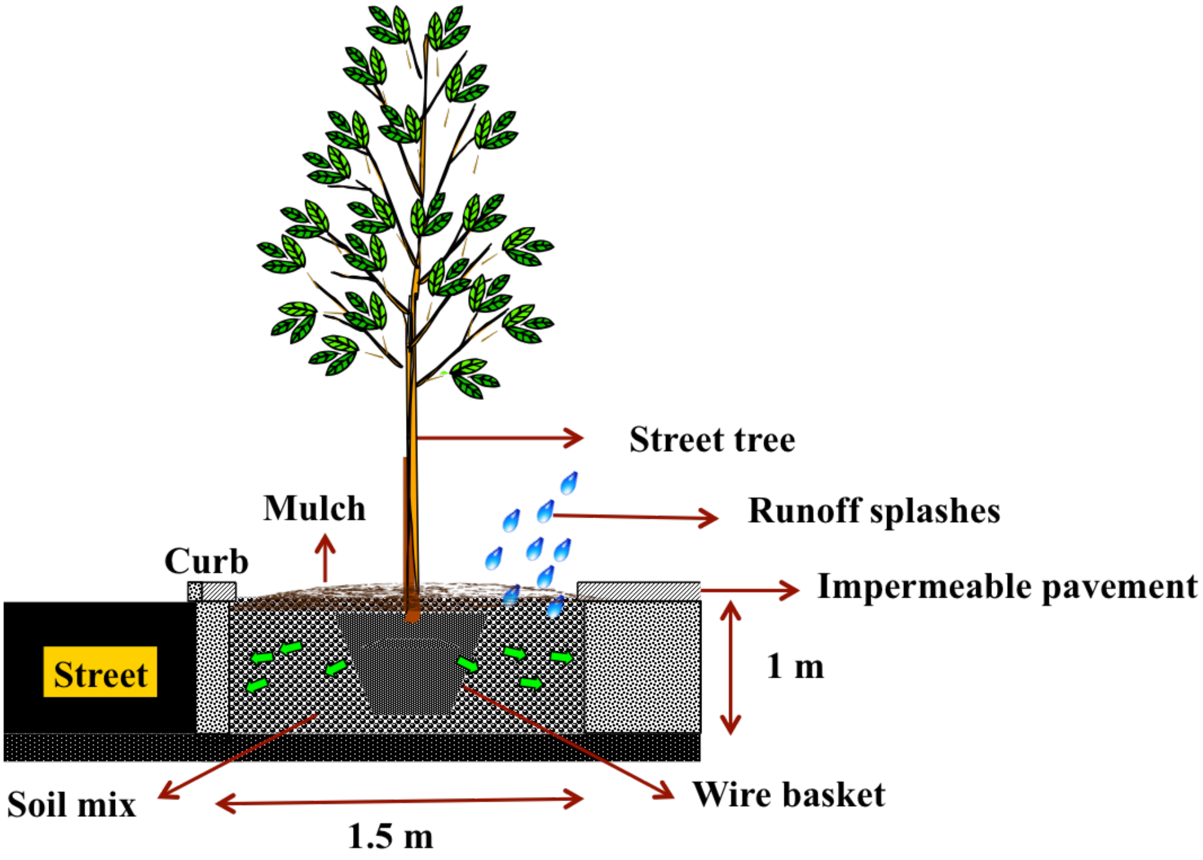

Fig.2.1. Typical tree pit in Montreal

High soil compaction can cause physiological dysfunctions in trees and can induce changes in the quantity and balance of growth hormones. As soils become increasingly compacted, respiration of tree roots shifts toward an anaerobic state and the absorption of water and major mineral nutrients is reduced, leading, in turn, to a decrease in trees' leaf area and rate of photosynthesis (Kozlowski, 1999).

2.2.2 Soil chemical characteristics

Interrupted organic matter cycling and nutrient dynamics

As plant litter is generally collected or swept away in urban locales, organic matter cycling in urban soils is greatly inhibited or altogether lacking (Meuser, 2010). Considering that organic matter is the primary source of nutrients such as nitrogen and phosphorus; one would expect low quantities of these nutrients in urban topsoil compared to that in natural ecosystems (Li et al., 2013c). Moreover, most urban soils such as tree pit soil do not rest on parent material, and thus do not receive the nutrients released from mineral weathering. Hence, in urban soil environments nutrients are slowly depleted from the limited soil volume (Craul, 1985).

Release of nutrients from the soil solid phase to the soil solution is generally controlled by soil physicochemical processes including desorption and dissolution, mass flow, diffusion and mineralization, which are controlled by soil and tree root–mycorrhizal characteristics (Comerford, 2005). Different soil characteristics such as soil pH, organic matter content, texture, temperature, and moisture content affect nutrient bioavailability in the soil (Prescott, 2005).

Trees need macronutrients for their growth and health. Nitrogen, as a macronutrient, is available in the soil mostly as nitrate (NO_3^- as an oxidized form of N) and ammonium (NH_4^+, a reduced form of N) ions. Nitrogen may become available to street trees through different processes such as mineralization of organic matter, addition of fertilizers, and fixation of atmospheric N by bacteria (Scharenbroch and Lloyd, 2004). Soil N availability affects the physiological state of trees, for example, high levels of available N stimulate growth and biomass production as a result of increasing leaf area, leaf chlorophyll concentration, and phytosynthetic rates (Li et al., 2012).

Absorption of soil N by other plants in the tree pits (*e.g.*, weeds) or by microorganisms during the decomposition of organic matter low in N, can reduce soil N levels, as can denitrification by soil organisms, leaching and volatilization (Harris et al., 1999b). Lowered available soil N can result in a significant decrease in plant photosynthesis, accumulation of carbohydrates (sugars and starch) in the leaves, higher levels of carbon allocated to the roots and an increase in root-to shoot biomass ratio (Boussadia et al., 2010).

The availability of P, another macronutrient, is affected by the relative quantity of soil components (*e.g.*, clay, organic matter, and hydrous oxides of iron (Fe) and aluminum (Al)), the background electrolyte concentration and valence of cations, as well as soil pH. Unlike N, which can be recycled to the soil by fixation from the air, once P is lost through a number of different pathways (*e.g.*, soil erosion, runoff, or leaching) it cannot be replenished except from external sources such as fertilizers (Sanyal and Datta, 1991). Phosphorus can also be released to the soil by weathering of P-bearing minerals. However, low amounts of plant-available P still remains as a limiting factor for plant growth in many situations because of the shortage of soil-forming rocks that contain P-bearing minerals, the strong dependence of P compound solubility on soil pH, and the possibility of P fixation in the soil (Craul, 1992a).

Almost all P is taken up by plants in either of two orthophosphate anion forms ($H_2PO_4^-$ or HPO_4^{2-}); however, most soil P remains unavailable to plants (Evans and Johnston, 2004). As a macronutrient, P plays different roles in the plants including as a component of nucleoproteins and phospholipids. High-energy bonds associated with phosphate groups are the main medium for energy transfers in plants. Phosphorus occurs in both organic and inorganic forms and maybe translocated in plants in both forms. Deficiencies in P can cause severe stunting of young trees without other visible symptoms (Kramer and Kozlowski, 1979a, 1979b).

As with other soil macronutrients, a number of soil physicochemical characteristics affect K availability. These include types of clay minerals in the soil, CEC, soil temperature, soil moisture, soil aeration, soil pH, and the relative quantities of other nutrients (Tisdale et al., 1993b). Potassium, available as K^+, can provide a number of benefits to plants. It can hasten plant maturity; increase root growth and provide resistance to drought, cold, and disease (Harris et al., 1999b). Potassium deficiency results in low protein synthesis and a higher rate of respiration. Considering the multiple functions of K in enzyme systems, K deficiency can have different effects on different plant species depending on the intensity of the deficiency, age of plants, and availability of other elements (Chatterjee and Dube, 2004).

Calcium, as a macronutrient, is available for plants as Ca^{2+} in the soil solution and as exchangeable Ca^{2+} on soil colloids. In general, different factors determine Ca availability to plants, including total Ca supply, soil pH, percent of Ca^{2+} saturation on CEC, type of soil colloids, and the ratio of Ca^{2+} to other cations in the soil solution (Tisdale et al., 1993c). Calcium plays different roles in plants including regulating plant structure and functioning as a constituent of cell walls and a stabilizer of membrane structure, as an activator of enzymes, and as a modulator of plant growth hormones (Hepler, 2005). Calcium increases cell wall strength and thickness, controls permeability of cell membranes and regulates movement of ions and metabolites in plants. Calcium also enhances NO_3^- uptake. Calcium is not usually a limiting nutrient, but there are several defects that can be related to Ca deficiency, including poor root development, leaf necrosis and curling. Calcium has few direct toxic effects on plants, most problems caused by excess soil Ca being the result of secondary effects of high soil pH, including reduced uptake of other nutrients such as P, K, Mg, Cu and Zn (Osman, 2013).

Like Ca^{2+}, Mg occurs mainly as exchangeable or dissolved Mg^{2+}. Magnesium availability to plants depends on the concentration of dissolved Mg^{2+}, soil pH, type of clay, the percentage of soil cation exchange sites occupied by Mg^{2+}, and the concentration of other exchangeable cations (Tisdale et al., 1993c). The physiological roles of Mg in plants include the absorption of solar energy by occupying the central position in the chlorophyll molecule, as a modulator for enzymes, in the chelation to nucleotidyl phosphate forms, and in the process of protein synthesis (Verbruggen and Hermans, 2013). Magnesium deficiency in woody plants is often difficult to control. Because Mg has a large hydrated radius and sorbs weakly to soil colloids, it is exposed to leaching especially in soils with low pH and CEC. Magnesium availability and its retention in soils can be increased by liming acid soils with dolomitic limestone (Mg and Ca carbonates) and thereby raising their pH to between 5.5 and 6.5, and also by supplementing the soil's organic matter content (Harris et al., 1999b).

Copper and Zn can be counted as two of the most important micronutrients absorbed by plants. Plants need Cu and Zn for their association with enzymatic activities (Tisdale et al., 1993a). Copper and Zn deficiency in trees may decrease leaf size and lead to the development of necrotic spots in the leaves. Shoots may die back as a result of Cu and Zn deficiency, resulting in trees having a stunted appearance (Harris et al., 1999b).

Soil contamination with de-icing salt

Providing safe driving conditions in urban areas located in cold regions is of primary concern during winter months. Hence, large quantities of de-icing chemicals are applied in order to clear the pavement and allow a normal traffic flow. While de-icing salt may dissolve in the melting snow and run off directly, moving traffic may also splash salt into the roadside environment and cause the salt to penetrate through the soil and become available to plant roots or groundwater, or be deposited directly on roadside vegetation (Ramakrishna and Viraraghavan, 2005).

In general, the presence of de-icing salt has negative effects on soil properties, roadside tree growth and groundwater quality (Wang, 2004). Sodium chloride (NaCl) is the preferred de-icing compound. Since Na^+ and Cl^- are quite soluble, they can be transported by runoff water into soil situated near the street. As soil particles and Cl^- are both negatively charged, and the Cl^- is fairly small, it is very mobile through the soil profile. Comparatively, Na^+ is positively charged and thus less mobile in the soil than Cl^-. When Na^+ is present in high concentrations, it displaces naturally occurring Ca^{2+} and Mg^{2+}. High concentration of Na^+ also disperses the organic and inorganic colloids of the soil and allows them to leach down through the soil profile (Ramakrishna and Viraraghavan, 2005). Exchange of Ca^{2+} and Mg^{2+} with Na^+ on soil exchange sites and deflocculation of soil particles in roadside soils can increase colloid and associated trace metal mobility, reduce hydraulic conductivity, change soil and soil solution pH, change ion concentrations in soil solution, and alter the microbial community (Green et al., 2008a).

Increased soil salinity can decrease nutrient absorption by plants by affecting nutrient availability in the soil (Grattan and Grieve, 1999). Sodium derived from de-icing salt may lead to shortages in available N in street soil by flushing NH_4^+ ions from exchange sites. Long-term soil exposure to de-icing salt may also increase the competition of Na with naturally occurring Ca and Mg for the organic matter exchange sites and cause leaching out of Ca and Mg (Green et al., 2008a). In contrast to N, high levels of P were observed in street soils exposed to high concentrations of Na in Riga, Latvia (Cekstere and Osvalde, 2013). This high level of P was consistent with the high P concentrations measured in soils and trees in Riga approximately 40 years ago. Cekstere and Osvalde (2013) attributed the high P concentrations to the application of phosphate fertilizers to street soils over several decades, and the subsequent formation of barely soluble P compounds, mainly with Ca and Mg, in the neutral and alkaline greenery soils.

Salinity can also affect the competitive uptake of nutrients, transport or partitioning of nutrients within the plant or cause a decrease in the physiological activity of a given nutrient, resulting in an increase in the plant's internal requirement for that essential element (Grattan and Grieve, 1999). In general, when NaCl is absorbed into plants, the uptake of other nutrients, such as K and Ca is inhibited (Kayama et al., 2003). High concentrations of Na may interfere with K acquisition by the roots, disrupt the integrity of root membranes and alter their selectivity for the absorption of K over Na in order to meet the requirements of metabolic processes, the regulation of ion transport, and osmotic adjustment (Grattan and Grieve, 1999).

Soil contamination with trace metals

Trace metals such as Cu, Zn, Cd and Pb can be carried to urban soil by particles from sources such as vehicle exhaust and the wear of brakes and tires (Ajmone-Marsan and Biasioli, 2010; Wei and Yang, 2010). The fate of these trace metals in the urban soil is partially dependent on metal properties such as electronegativity, ionic potential and polarizability in acid-base reactions (Schwertfeger, 2010). Defining ionic potential as the ratio of charge to the radius of the ion, McBride (1994b) grouped metals and metalloids into hydrated cations, insoluble hydroxides and soluble oxyanions or hydroxyanions, based on their ionic potentials. Hydrated cations include metals with low ionic potential (*e.g.,* Na^+ and K^+) that tend to form soluble, weakly hydrating cations. Hydrated cations also include metals with slightly greater ionic potentials such as Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} which are still soluble, but can hydrate more strongly than metals with low ionic potential. These metals can be involved in ion exchange reactions. Metals with high ionic potential can promote hydrolysis through polarizing water sufficiently strongly to rupture the O - H bond and precipitate as hydroxides (of metals like Al^{3+}, Fe^{3+}, and manganese (Mn^{3+})), or form soluble oxyanions and hydroxyanions (of metalloids like arsenic (As^{5+}) and molybdenum (Mo^{6+})).

Metal solubility in the soil solution also depends on many processes, which are mainly controlled by soil pH and the type and amount of soil organic matter (SOM) (Kabata-Pendias, 2001a). Metal adsorption on soil adsorbing surfaces depends partially on their surface charge, which is strongly controlled by soil pH (Kabata-Pendias and Pendias, 2001). Overall, Cu solubility decreases to a minimum at about pH 7 to 8. At alkaline pH values, the high affinity of dissolved organic matter to Cu can inhibit Cu sorption in soils. Zinc is very mobile in most soils, however SOM can strongly hold Zn, especially at neutral and alkaline pH values of the soil. Cadmium sorption capacity of the soil is pH dependent (4.4–7.0) and involves competition between the metallic cation and protons for exchange sites on soil particles. Increasing pH ($pH>7$) results in increased sorption of Cd on humic substances or Cd precipitation. Lead is generally accumulated near the soil surface, mainly due to its sorption by SOM. Lead mobilization in soil solution is usually slow, but some parameters, such as decreasing pH and the formation of Pb-organo–metallic complexes may increase its solubility (Kabata-Pendias and Mukherjee, 2007).

Trace metal solubility in the soil solution can also depend on some ions present at high concentrations in the soil solution (*e.g.*, Na^+ originating from the use of de-icing salt on urban streets) which can mobilize trace metals in the soil (Cunningham et al., 2008). The effect of high soil solution Na^+ concentration on trace metal mobilization can be attributed in part to Na^+ exchange with Ca^{2+} and protons in the soil (Bäckström et al., 2004; Wang, 2004). Sodium cation exchange with Ca^{2+} leads to increasing competition for soil exchange sites between Ca^{2+} and trace metal cations such as Cd^{2+} and Zn^{2+}(Boekhold et al., 1993). Ion exchange can decrease trace metal sorption to the salt-affected soil. De-icing salt has also the potential to increase the mobility of trace metals as a result of SOM dispersion (Katip et al., 2012; Luoma and Davis, 1983; Peng et al., 2009). This dispersion may promote accumulated trace metals in the soil to enter into the soil solution via colloid-assisted transport (Wang, 2004). In a study of Cd, Cu, Pb, and Zn mobilization in soil under the effect of de-icing salt, Bäckström et al. (2004) observed an increase in Cd and Zn concentrations in the soil solution in response to ion exchange. In contrast, the mechanism of mobilization attributed to Cu and Pb involved the dispersion of organic matter that served as an important retention medium for these metals in the soil.

As different studies indicated, it is likely that many types of urban soils (including tree pit soil), as compared to agricultural and natural soils, contain elevated concentrations of trace metals (Ge et al., 2000; Lu and Bai, 2010; Wei and Yang, 2010). This excess concentration may have toxic effects on plants. The most common symptoms of Cu toxicity in plants include altered cell membrane permeability, immobilization of Cu in protein complexes and cell membranes, damage to deoxyribonucleic acid (DNA) in cells, and inhibition of photosynthetic electron transport (Kabata-Pendias and Mukherjee, 2007). Zinc toxicity can decrease photosynthesis, inhibit Adenosine triphosphate (ATP) synthesis and interrupt energy metabolism in plants (Reichman, 2002).

Plants have no metabolic requirement for Cd and Pb, and thus the availability of these metals to plants can cause serious health problems. The symptoms of Cd toxicity in plants generally are stunting and chlorosis. Cadmium can increase stomatal and mesophyll resistance to CO_2 uptake and inhibit photosynthesis (Kabata-Pendias and Mukherjee, 2007). Lead toxicity also may decrease plant growth and cause chlorosis. Lead toxicity in plants may change the membrane permeability, and disturb enzyme activity, water balance, and mineral nutrition (Sharma and Dubey, 2005).

2.3. Urban soil improvement

2.3.1. Compaction remediation

Different efforts such as application of structural soil, installing suspended pavements and using polymerized cubic structures beneath paving, and soil amendment with organic matter have been made to prevent or relieve soil compaction. Structural, skeletal, or engineered soil is made of coarse stone incorporated with the fine-textured mineral soil (Bartens et al., 2010). Structural soils have a high porosity and can bear the weight of the pavement and the load of heavy vehicular and pedestrian traffic on urban streets and sidewalks (Smiley et al., 2006). Grabosky and Bassuk (1996) observed that structural soil containing 80% (w/w) crushed stone and 20% (w/w) clay loam is more favorable for plant growth than the conventional soil used under pavements. Costello and Jones (2003) applied 80% (w/w) porous stone, a heat expanded-slate, mixed with 20% (w/w) sandy clay loam, as structural soil. The porous slate rock used in the structural soil mixture has approximately 30% void space. In this case, more space, air and water will be provided for tree root growth under a sidewalk as compared with the conventional soil or the structural soil with crushed stone (Urban, 2011).

As another solution to meet the dual needs of sidewalk stability and tree root growth, suspended pavements can be designed using polymerized cubic structures as the subsurface of pavements rather than compacted soil. Using polymerized cubic structures or “cells” as the subsurface of pavements can decrease soil compaction by supporting traffic loads (Bartens et al., 2010). These cells can accommodate nearly 100% uncompacted soil by volume as compared to structural soils that only contain approximately 20% soil by volume (Smiley et al., 2006) .

Placing polymerized cubic structures under the pavement begins with the excavation of the areas receiving the cells. Planting soil is placed inside the structures and is very lightly compacted to achieve optimum soil density for root growth. A geotextile and an aggregate are then laid over the soil and structures (Urban, 2011). The pre-cast concrete will be later lowered onto footers or concrete may be poured in place (Smiley et al., 2006).

Another method for decreasing soil compaction is to incorporate organic matter into the soils before they are installed in the tree pits. Most soils contain around 5% organic matter, but common incorporation rates range from 25% to 50% by volume. Given the decomposition of organic matter, in order to prevent damage to the roots a plant has developed throughout the soil, the amendment should be continuously replenished, particularly in the top 0.10 to 0.15 m of the soil (Harris et al., 1999a). Studying the effect on compaction of amending a sandy loam soil with 0%, 10%, 33%, 50%, or 75% (v/v) organic matter, Rivenshield and Bassuk (2007) found that the addition of an organic amendment at a rate of at least 33% (v/v) doubled macroporosity and reduced bulk density to below root growth restricting thresholds.

Although different methods of compaction remediation try to increase the rooting volume for street trees under pavement, the necessity to provide load-bearing capacity of the soil below the pavement and to meet the requirements for designing safe pavement structures must be accepted and realized (Grabosky and Basset, 1998).

2.3.2. Stabilization of soil contaminants

In general, amending soil with organic matter can affect the physicochemical characteristics and biological conditions of soil to make them more favorable for plant growth. As discussed previously, organic matter can also affect metal bioavailability in soils (Bernal et al., 2007; Pardo et al., 2011). Organic amendment can make soil aggregates more stable. It decreases soil compaction and improves the aeration of the soil. Organic amendment can also improve water holding capacity, water permeability, and porosity of the soil. It can retain up to 20 times its weight in water, which prevents drying and cracking of the soil (Bernal et al., 2007; Goecke et al., 2011).

Amending soil with organic matter also increases soil organic C content, which acts as the source of energy for the soil organisms (Bernal et al., 2007). According to Pardo et al. (2011), organic amendment of soil can increase the microbial activity, accelerating nitrification and improving the plant-availability of nutrients, therefore enhancing plant growth.

Different studies suggest that the addition of compost and/or biochar as organic amendments of soil can be a valuable tool in mitigating the negative effects of urban environment on soil and make some potential benefits to physicochemical characteristics of soil (Beesley et al., 2010). This change in soil characteristics can affect nutrient availability and trace metal mobility as explained below.

Effect of compost on nutrient availability in soil

Organic amendments such as compost can increase the CEC of the soil, which increases the sorption and retention of nutrients and releases them more slowly to the soil solution (Bernal et al., 2007). Compost can also cause macronutrients including N, P, Ca, Mg, and K to be released for plant growth by mineralization of organic matter (Bernal et al., 2007; Goecke et al., 2011; Planquart et al., 1999). The addition of compost can enhance nitrification in the soil (Walker et al., 2004). A 24-year study of long-term effects of compost applications in soil indicated an increase in total N content of the soil after compost addition (Werner et al., 1988). However, Herencia et al. (2008) reported a limited effect of compost on N availability for plants depending on such factors as soil properties, type of compost, environmental conditions and soil organisms.

Soil amendment with compost can increase the availability of P derived from phospho-humic complexes, which reduce the phosphate immobilization capacity of the soil. Humus can also decrease the fixing capacity of the soil for phosphate anions by coating clay and Fe/Al oxide particles (Stratton et al., 1995). Moreover, organic matter can affect K dynamics in soils. In compost-amended soils, K may not be immediately exchangeable and can be bound to clay minerals and organic matter. As a result of the dissociation of carboxylic and phenolic groups during compost decomposition and the action of organic colloids which possess negative charges, the residual K becomes more available (Lakhdar et al., 2009). The exchange sites of compost are also enriched with Ca^{2+} and Mg^{2+} which can be of specific importance for the reclamation of salt affected soil because exchangeable Ca^{2+} and Mg^{2+} can displace Na^{+} in the exchange complexes and cause Na^{+} leaching out of the soil (Lakhdar et al., 2009; Mahdy, 2011).

Different studies indicated significant amounts of a variety of essential trace elements for plants in compost (Fischer and Glaser, 2012; Herencia et al., 2008). Compost can increase the availability of nutrients including Cu, Fe, Mn and Zn in the soil by the formation of soluble metal chelates (Bernal et al., 2007). The quantity of other macro- and microelements derived from compost depends on the origin of the compost and the method of compost production. The availability of nutrients is also controlled by compost mineralization rate (Lakhdar et al., 2009).

Effect of compost on trace metal mobility in soil

The use of cost-effective and environmentally safe amendments such as organic matter derived from domestic refuse has been proposed as a promising method for improving metal–contaminated soil. It is commonly assumed that amending urban soil with organic materials can increase sorption capacity of soil for primary contaminants (such as trace metals and de-icing salts) and therefore decrease contaminant migration into the groundwater and uptake into street tree tissues (Wuana and Okieimen, 2011). The primary mechanisms for immobilization of potentially toxic metals by organic matter are adsorption, surface complexation, and precipitation (Karaca, 2004).

Different studies (*e.g.,* Angelova et al., 2013) attributed the increase in trace metal adsorption in compost-amended soils to the improved CEC of the soils following organic amendment. Cation exchange capacity is the quantity of negatively charged sites on compost functional groups for cation adsorption reversibly (McBride, 1994a; McLean and Bledsoe, 1992). The negative charges developed on compost functional groups must be balanced by cations at or near the surface. In compost amended soils, compost can increase CEC of soil from 20 to 70% (Lakhdar et al., 2009).

Organic amendments such as compost contain a high proportion of humic substances (mostly humus, humic acid and fulvic acid), which have a large capacity to bind with metal ions. Composts that are more mature and stable include a higher proportion of humic acids as compared to fulvic acids. Fulvic acids are the most mobile fraction of humic substances and a major component of dissolved organic matter in soil. Therefore, the presence of soluble organic matter, such as fulvic acids, may be responsible for the solubilization of trace metal (*e.g.,* Zn) in soils, whereas insoluble organic matter, such as humus and humic acids, may contribute to the immobilization of trace metals (*e.g.,* Pb). Indeed, fulvic acids are characterized by smaller molecular size fractions and a higher ability to form complexes with trace metals that are more mobile than those formed with humic acids (Hattab et al., 2014).

Amending soil with compost may also cause metal ions to be more soluble and thus more available to the plants, as compost decreases soil pH (Walker et al., 2004). Depending on soil pH, compost may decrease soil pH by increasing the CO_2 levels produced from the decomposition of organic matter (Mohammad and Athamneh, 2004). Dissolution of CO_2 to form H_2CO_3 can increase the concentration of H^+ ions in the soil solution (Bolan et al., 2003). This will increase the competition between H^+ ions and trace metals for sorption to compost-amended soil, and thus increase trace metal mobility.

Depending on soil pH, however, soil amendment with compost can decrease soil acidity due to the displacement of OH^- from Al/Fe Oxide surfaces by organic anions during the mineralization of compost. The increased concentration of OH^- in soil solution can result in trace metal precipitation as metal hydroxides and decrease their plant-availability (Bolan et al., 2014). Amending soil with compost can also decrease trace metal mobility by releasing basic cations, such as K^+, Ca^{2+}, and Mg^{2+} and increasing soil pH (Achiba et al., 2009). The released basic cations can decrease the amount of H^+ on cation exchange sites and increase the effective CEC of the soil (McBride, 1994c). As a result, higher sorption of trace metals can be observed in soils amended with compost.

The improvements in the soil quality as a consequence of amendment with compost may be short term because of the relatively short half life of compost compared with the lengthy stay of some soil contaminants such as trace metals (Fischer and Glaser, 2012). Therefore, metal immobilization as a result of soil amendment with compost cannot be regarded as a permanent solution. Longer term effects of compost amendments on soil properties could be achieved by preserving or increasing the stable organic matter by using materials such as biochar in the soil (Amlinger et al., 2007). Therefore there has been growing interest in the conversion of organic residues into biochar (Bolan et al., 2012).

Biochar

Effect of biochar on nutrient availability in soil

Biochar can increase nutrient retention in the soil through different mechanisms. Adding biochar to the soil can increase soil CEC because of its abundance of carboxyl groups. These carboxyl groups are able to form organo-metallic complexes and also increase nutrient retention in the soil (Glaser et al., 2002; Sohi et al., 2010). The effect of biochar on plant- availability of nutrients such as N can be attributed to the high C/N ratio of biochar which causes higher sorption of ammonium and biological N fixation (Sohi et al., 2010). Also biochar can increase nitrification by adsorbing inhibitory compounds in the soil environment (DeLuca et al., 2012).

Nutrients can also be retained in the soil solution in micro- and macropores of biochar. This mechanism is important for the nutrients that are very mobile and cannot normally be adsorbed to the soil, such as NO_3^- at high pH, or base cations at low pH. Consequently, fewer nutrients may be lost through leaching and nutrient use by plant roots grown in biochar-amended soils can be more efficient (Glaser et al., 2002). Biochar can also act as the direct source of nutrients and can add free basic cations such as K^+, Ca^{2+}, and Mg^{2+} to the soil solution (Glaser et al., 2002; Prendergast-Miller et al., 2013).

Some studies suggest that the addition of biochar to soils can partially help to solve soil fertility problems. For instance, Novak et al. (2009) observed that 67 days after the addition of biochar to soils of the Coastal Plains of the Southeastern U.S, the concentrations of Ca, K, Mn and P in soil were increased relative to non-amended soils. However, enhanced retention of plant nutrients can restrict plant growth on soils amended solely with biochars; therefore its use in combination with other amendments such as compost can result in a positive interaction between compost and biochar (Beesley et al., 2011). This interaction can increase plant-available nutrients through biological N fixation, reduced nutrient leaching, and increased nutrient supply (Liu et al., 2012).

Effect of biochar on trace metal mobility in soil

Depending on its physicochemical characteristics, biochar can sorb some environmental contaminants, such as trace metals (Park et al., 2011). A large negatively-charged surface area and a high CEC enable biochar to enhance sorption of trace metals and reduce their mobility when used to amend contaminated soils (Beesley et al., 2011). Trakal et al. (2011), investigating the sorption behavior of Cu, Pb, Cd, and Zn in a biochar-amended soil, attributed the high sorption of Cu and Pb in such soils to the high affinity of cations to organic matter. In contrast, no improved sorption of Cd or Zn was observed in biochar-amended soils, probably as a result of the predominant stabilization of Cd and Zn on to Mn and Fe oxyhydroxides and clay minerals and their lower sorption to organic matter as compared to Cu and Pb (Trakal et al., 2011).

Biochar normally has an alkaline pH. An increase in the soil pH after biochar addition, particularly to acidic soils, can result in a decrease in the mobility of cationic metals through the hydrolysis of trace metal cations and precipitation of metal oxyhydroxides (Jiang et al., 2012a; Novak et al., 2009). Higher pH can also increase the negative surface charge of the biochar-amended soil, which results in an increase in cation exchange capacity. Therefore, the affinity of the biochar-amended soil particle surfaces for cations will increase (Jiang et al., 2012a).

The other mechanism through which biochar reduces metal mobility is precipitation. For instance, P originally contained in biochar can react with soil Pb and immobilize it by forming insoluble hydroxypyromorphite ($Pb_5 (PO_4)_3 (OH)$) (Cao et al., 2011). Specific adsorption (inner-sphere surface complex formation) is another mechanism through which biochar decreases metal mobility. Specific adsorption causes strong and irreversible binding of trace metal ions with biochar containing organic matter (Bradl, 2004). According to Jiang et al. (2012a), biochar can increase the specific adsorption of Cu^{2+} and Pb^{2+} by the oxygen-containing functional groups such as -COOH and -OH on biochar, which can form stable complexes with the metals.

Different studies have indicated the positive effect of the application of organic materials such as biochar on immobilisation of metals in soils (*e.g.,* Kloss et al., 2014). However, biochar may conversely enhance the co-mobilisation of metals like Cu with dissolved organic carbon (DOC). These metals have high affinity to organic matter (Beesley et al., 2011). Also, over time, the capacity of biochar to immobilise contaminants will change as their sorption sites are occupied by native soil organic matter and competing contaminants (Beesley et al., 2011).

The capacity of biochar for metal sorption depends on the pyrolysis conditions (*e.g.,* pyrolysis temperature), the feedstock used in producing the biochar, and biochar age (Uchimiya et al., 2010). According to Nartey and Zhao (2014), the charged surface area and the pore volume of the biochar and therefore its metal sorption, increased with pyrolytic temperature. Also the stability of biochar toward microbial and abiotic degradation increases as a function of pyrolysis temperature (Uchimiya et al., 2011).

In a study by Mukome et al. (2013) on the effect of different feedstock on the surface area of biochar and its metal sorption, they observed a clear trend associating softwood-derived biochars with large surface area. Larger surface areas were observed in softwood (*e.g.,* pine and cedar) derived biochars and increased with pyrolysis temperature as compared with biochar derived from hardwoods (*e.g.,* maple and oak). Also depending on the feedstock, biochar contains different concentrations of elements such as P, S, Ca, and Na. These elements can affect metal availability in soils amended with biochar (Lima et al., 2014).

As Nartey and Zhao (2014) stated, the capacity of biochar for metal adsorption can increase as the biochar ages, because oxidation processes over time create hydroxyl and carboxylic acid functional groups on the surface of the biochar. These functional groups contribute to coordination between trace metals and the biochar surface.

2.4. Knowledge gap

Soil contamination with trace metals from traffic sources in urban environments has been studied in North America and Europe (Paul et al., 2014). Heavy traffic on urban streets in boreal and temperate regions may expose the soil adjacent to the streets to increased concentrations of de-icing salt (Ramakrishna and Viraraghavan, 2005). The presence of trace metals and de-icing salt in urban soil can impact the availability of nutrients for the tree roots (Roberts et al., 2006). Little quantitative knowledge is available on the dynamics of the trace metals and the availability of the nutrients in urban soils, subject to potential contamination with de-icing salt, in relationship with environmental factors. To close this knowledge gap, this research defined the quantitative relationships of trace metal abundance and nutrient availability with environmental factors. Defining these relationships is necessary in order to identify the limiting factors that might shorten the life span of street trees, and to use this understanding to define effective methods for urban soil improvement.

Previous studies indicated a dual effect of organic amendments, such as compost and biochar, on improving contaminated soil quality. While different studies indicated the positive effect of the application of organic materials on the immobilisation of metals in soils (*e.g.,* Kloss et al., 2014), compost or biochar may conversely result in the co-mobilisation of metals with DOC (Beesley et al., 2011). Gaps in knowledge remain about the optimum amount of these organic amendments to be added to contaminated soil, particularly with regard to improving nutrient supply and limiting contaminant absorption by plants. To help fill this gap, this research is mainly focused on comparing the sorption-retention capacity of organic amended soils with non-amended soils through sorption-desorption tests and phytotoxicity trials. The results of lab-scale experiments and statistical analysis can indicate which amendment at what percentage can significantly reduce metal mobility in the soil solution and decrease the bioavailability of those metals to plants in the short term. However, before the best amendment for moderating the impact of contaminants in urban soils can be conclusively identified, the long-term effects of soil amendments on the retention of contaminants should be investigated.

Connecting statement I

In chapters 1 and 2, we defined the main research questions and reviewed the available literature in order to identify the important variables for our studies. In chapter 3, we briefly explained the experimental design of the chemical and statistical analyses performed on these important variables in each of the three studies of this research.

Chapter 3. Methodology

3.1. Study I

3.1.1. Stratified random sample selection

The short life span of many street trees in downtown Montreal may be attributable in part to higher than average concentrations of potentially toxic metals (trace metals and de-icing salt) in the tree pit soils. An appropriate supply of nutrients and the chemical composition of the tree pit soil are other important factors affecting the growth and life span of trees in urban centers. The effects of land use, soil organic matter (SOM), and time since the tree was transplanted from the nursery to the tree pit (soil age) were studied with respect to the total concentration of trace metals (Cr, Ni, Cu, Zn, Cd, and Pb) and availability of nutrients (K, Ca, Mg, P, and total mineral N) and Na in soil collected from tree pits on commercial and residential streets.

The tree pit soil samples used for this study were selected from among 796 soil samples collected from Montreal tree pits in a prior study (Jutras, 2008). Four soil samples had been collected at the edges of each of 796 tree pits located beside selected streets in five land use zones: intensive commercial, commercial, institutional, intensive residential and residential. Following a stratified random sampling protocol to select samples for the current study, four criteria were initially considered including land use, SOM, soil age and tree species. All samples were initially stratified into exclusive classes, according to the attributes under study, and were then selected from each class randomly. Sample selection proceeded as described in detail in the following sections.

Land use

The desired samples for the current study were selected from commercial and residential zones due to the higher number of samples from those zones and the hypothesis that the differences between these two zones would be larger than those between any other pairing among the five land use zones. After this step, 302 samples remained, including 102 samples from commercial zones and 200 samples from residential zones.

Soil organic matter

Considering the acceptable range of organic matter for tree pit soil as 4 to 7% (rounded up to 10%) according to the City of Montreal's standards (City of Montreal, 1995), samples with SOM content higher than 10% were omitted from the study. The remaining samples were classified according to two levels of organic matter (SOM content < 5.5% and 5.5% ≤ SOM content ≤ 10%). After this step, 227 soil samples remained, including 61 samples from commercial zones and 166 samples from residential zones.

Soil age

Next, the samples were clustered according to four soil age classes (in years since transplantation), partitioned so as to achieve an adequate number of samples in each class (age < 12 y, 12 ≤ age < 17 y, 17 ≤ age < 28 y, and 28 y≤ age). The maximum soil age in the available dataset was 40 years. Each class boundary was defined in such a way that intergroup variance exceeded the intragroup variance. Table 3.1 shows the number of samples in each of the aforementioned classes of land use, SOM and soil age.

Table 3.1. Number of samples in each subclass of land use, SOM and time after tree transplanting (soil age)

Land use	SOM[†] (%)	Age (y [††])	Count	Sum
Commercial	≤5.5	x < 12	3	23
		12 ≤ x < 17	12	
		17 ≤ x < 28	5	
		28≤ x	3	
	5.5 < x ≤ 10	x < 12	11	38
		12 ≤ x < 17	17	
		17 ≤ x < 28	5	
		28≤ x	5	
Residential	≤5.5	x < 12	3	56
		12 ≤ x < 17	12	
		17 ≤ x < 28	29	
		28≤ x	12	
	5.5 < x ≤ 10	x < 12	15	110
		12 ≤ x < 17	29	
		17 ≤ x < 28	59	
		28≤ x	7	

[†] SOM=soil organic matter

[††] y =year

Tree species

Initially, tree species were considered as a classification criterion. The tree species represented in the selected sample set according to land use, SOM, and soil age, are shown in Table 3.2. However, because of an inadequate number of samples, the further subclassification of soil samples based on tree species was rejected (Table 3.3).

Table 3.2. Tree species represented in the selected sample set

Abbreviation	Name
ACSA	*Acer saccharinum*
ACPL	*Acer platanoides*
FRPE	*Fraxinus pennsylvanica*
GLTR	*Gleditsia triacanthos*
TICO	*Tilia cordata*
ULPU	*Ulmus pumila*
CEOC	*Celtis occidentalis*

Table 3.3. Number of existing soil samples in each subclass of land use, age, SOM, and tree species

	Commercial Zone SOM† Class 1				Commercial Zone SOM Class 2				Residential Zone SOM Class 1				Residential Zone SOM Class 2			
	Age Classes															
Tree Species Code‡	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
ACSA	0	0	2	0	0	0	0	0	0	3	4	0	0	2	5	0
ACPL	0	6	2	0	0	4	4	0	0	0	3	0	1	2	6	0
FRPE	1	8	0	0	2	3	0	0	0	4	13	2	0	3	16	2
GLTR	0	0	0	0	0	0	0	0	1	4	11	0	1	5	3	0
TICO	0	0	0	0	0	0	0	0	0	5	14	0	0	3	13	0
ULPU	1	2	4	1	3	8	1	4	0	0	0	0	0	0	0	0
CEOC	0	1	0	0	0	4	0	0	2	5	1	0	5	12	10	0

†SOM=soil organic matter

‡ACSA=*Acer saccharinum*, ACPL=*Acer platanoides*, FRPE=*Fraxinus pennsylvanica*, GLTR=*Gleditsia triacanthos*, TICO=*Tilia cordata*, ULPU=*Ulmus pumila*, CEOC=*Celtis occidentalis*

Random selection

Samples were randomly selected in each subclass, where necessary; to further reduce the number of samples, to reach a minimum of 3 and maximum of 5 replicates in every subclass. Finally, from the 796 existing soil samples, 73 samples were selected, including 35 samples from commercial zones and 38 samples from residential zones.

3.1.2. Chemical analysis and data treatment

Total concentrations of trace metals (Cr, Ni, Cu, Zn, Cd, and Pb) and macronutrients (K, Ca, Mg, P, and total mineral N) were analyzed in the selected soil samples. Contingency table analysis and multiple linear regression were applied in order to study how land use, SOM, and soil age of the selected samples were related to the total concentrations of Cr, Ni, Cu, Zn, Cd, and Pb in the soil. Other variables, such as soil pH, street width, distance of the tree pit from the curb, and tree pit volume, were also used as inputs for the statistical analysis to increase its explanatory power. Multivariate Adaptive Regression Splines (MARS) were applied in order to explore the relationships between Na, the availability of K, Ca, Mg, P, and the total mineral N with SOM, soil pH, land use, soil age, street width, and tree pit cover material. A more detailed explanation of the methodology for chemical analysis and data treatment will be presented in Chapters 4 and 5.

3.2. Study II

3.2.1. Central composite rotatable design

The ability of tree pit soil amended with compost and biochar for sorption and retention of Cu, Zn, Cd, Pb in the presence of de-icing salt (Na) was studied by conducting sorption and desorption tests on the soil mixtures containing different percentages of compost and biochar. The soil mixtures were based on a sandy loam, provided by the soil supplier of the Ville-Marie borough, Montreal, Quebec, Canada. Applying a central composite rotatable design, the percentages of compost and biochar in combination with soil were defined in order to obtain the maximum amount of information with the fewest number of experiments on mixing compost and biochar with soil.

A central composite rotatable design for two factors (*i.e.,* levels of compost and biochar) uses treatment combinations at points equally spaced around the circumference of a circle. In the case of two factors, there are nine treatment combinations (2^n+2n+1, where $n =$ number of factors). One treatment combination is the center point (0,0) that includes the mid-range of the treatments. The first set (factorial points) involves 2^n combinations of treatments ($-\lambda, -\lambda$; $\lambda, -\lambda$; $-\lambda$, λ; λ, λ), forming the main factorial design. The second set (star points) involved $2n$ treatment combinations ($-1, 0; 1, 0; 0, 1; 0, -1$). These four additional combinations of treatments include the extreme values for each variable combined with the mid-range of the other variable (Bowley, 2008) (Fig. 3.1).

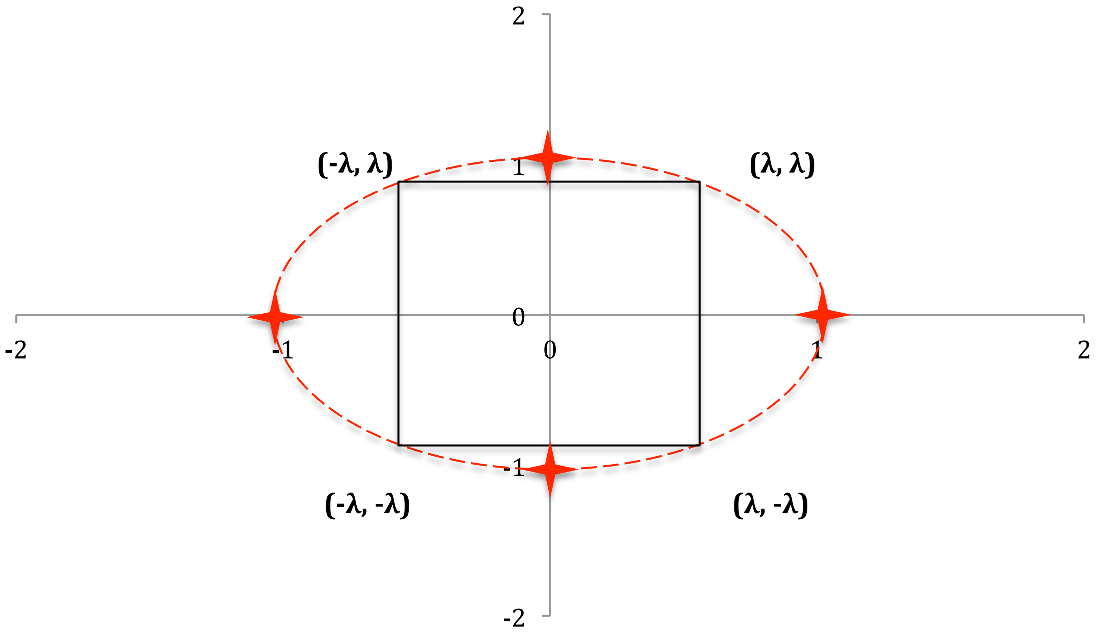

Fig. 3.1. Schematic diagram of a two factor central composite rotatable design. Treatment combinations include center point (0,0), 2^n factorial points ($-\lambda, -\lambda;\ \lambda, -\lambda;\ -\lambda,\ \lambda;\ \lambda, \lambda$), and 2n star points ($-1, 0; 1, 0; 0, 1; 0, -1$) (n=number of factors)

In order to create a central composite rotatable design, the radius adjustment factor should equal to $2^{n/4}$. To obtain the variable level equivalent to the $-\lambda$ and λ values on the coded scale, equation 3.1 is used (Bowley, 2008):

$$\pm\lambda = \boldsymbol{range\ midpoint} \pm \left[\frac{\boldsymbol{range}}{2\times\boldsymbol{radius\ adjustment\ factor}}\right] \qquad \text{Eq.[3.1]}$$

Considering the maximum percentage of compost as 15% by weight and maximum percentage of biochar as 10% by weight in combination with non-amended non-contaminated soil, the factorial points, the star points, and the center point in central composite rotatable design can be summarized as follows (Table 3.4):

Table 3.4. Factorial points, star points, and center point of compost and biochar percentages required for central composite rotatable design

Treatment combination	Compost (% w/w)	Biochar (% w/w)
Factorial points	2.2	1.5
	12.8	8.5
	12.8	1.5
	2.2	8.5
Star points	7.5	0
	7.5	10
	0	5
	15	5
Center point	7.5	5

3.2.2. Chemical analysis and data treatment

The nine soil mixtures were flushed with a contaminating solution including Na, Cu, Zn, Cd, and Pb. The partitioning coefficient (K_d), defined as the ratio of the total contaminant (mg kg^{-1}) bound to the solids to that found in the solution phase (mg L^{-1}), was calculated for Na, Cu, Zn, Cd, and Pb based on the amount of each of these metals that was retained by the soil mixtures. To identify the importance of compost and biochar in modifying the K_d values of the metals of interest in the soil mixtures, multiple linear regression was applied. Using the K_d values and the mean concentration of the contaminants in the runoff water in urban areas with heavy traffic, the steady state concentrations of potentially toxic metals were estimated. It was assumed that at the steady state concentrations of metals in the soil, the concentration of metals in the soil leachates equals their concentration in runoff water.

In order to find the improved soil mixture for the sorption and retention of Na, Cu, Zn, Cd, and Pb, the mean values of the steady state concentrations of the metals were compared in different soil mixtures using the Tukey test. A more detailed methodology for the sorption and desorption tests and statistical analysis is presented in Chapter 6.

3.3. Study III

3.3.1. Factorial experiment

Based on the results of the second study, compost was selected as the best soil amendment. In order to determine how soil amended with compost could modify the bioavailability of Na, Cu, Zn, Cd, and Pb, a phytotoxicity test was designed. Three percentages (0, 5 and 10 % (w/w)) of compost were added to the soil. The soil mixtures were then spiked with three contamination levels (control, medium, and high concentrations) of Na, Cu, Zn, Cd, and Pb.

A factorial design was used for the phytotoxicity test that considered 5 and 10% w/w percentages of compost added to the city soil that were then spiked with the medium and high levels of contamination as compared to the non-contaminated, non-amended soil mixtures. The factorial design is a type of research methodology that allows for the investigation of the main and interaction effects between two or more independent variables (% compost by weight and contamination level) on a response variable (metal absorption by plants). In this design, the term factor refers to an independent variable (Nordstokke and Colp, 2014). Each factor must have two or more levels (values) so that the effect of a change in the value of the factor can be estimated (Mukerjee and Wu, 2006). Considering two factors with three levels for each (compost percentages: 0, 5 and 10% w/w and contamination levels: control, medium and high), the factorial design of phytotoxicity test included nine soil mixtures. Each soil mixture was replicated six times.

3.3.2. Chemical analysis and data treatment

After drying and then leaching the spiked soil mixtures with 400μM $CaCl_2$-$CaSO_4$ and with the modified dilute Hoagland's solution, a 14-day plant growth assay was conducted with barley plants (*Hordeum vulgare* L.) grown in the spiked leached soil mixtures. The phytotoxicity test followed the procedure outlined in Environment Canada's Biological Test Method for the emergence and growth of terrestrial plants (Environment Canada, 2005).

In order to characterize the interactions between the percentage compost and contamination levels in the soil mixtures, a general linear model was applied using analysis of variance. Multiple linear regression was used to explore the relationships between percentage compost, soil contamination level, and the chemical characteristics of soil (*i.e.,* pH and CEC), with the absorption of Na, Cu, Zn, Cd, and Pb by barley plants. Path analysis also was used to determine the direct effect of the predictor variables (percentage compost and contamination levels) on the amount of Na and trace metals absorbed by barley plants. Path analysis also estimates the indirect effects of the predictor variables on the response variables through their effect on intermediate variables (pH and CEC) (Bradham et al., 2006). A more detailed explanation of the methodology for soil spiking and leaching, the phytotoxicity test, and data treatment is presented in Chapter 7.

Connecting statement II

In chapter 4, we hypothesized that there are specific trace metals with significantly higher concentrations than the standards determined by the Canadian Council of Ministers of the Environment (1999). Following chemical and statistical analyses described briefly in chapter 3, in chapter 4 we tried to determine which of the abiotic factors affecting street tree growth (Jutras et al., 2010) also had a significant interaction with each other and had a potential influence on trace metal content in tree pit soil. The abiotic factors included as input to the analysis were land use category, soil age, SOM, pH, street width, distance of the tree pit from the curb, and tree pit volume. The results of this study can provide an understanding of the type and rate of the accumulation of trace metals in the tree pit soil, which is of great concern for future measures of urban soil improvement.

Chapter 4

Trace metal contamination in surface soil of urban tree pits influenced by land use, soil age and organic matter in Montreal tree pit soil

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4.1. Abstract

The short life span of many street trees in the Montreal downtown area may be due in part to higher than standard concentrations of trace metals in the tree pit soils. The effects of land use, soil organic matter, and time since tree planting in a given tree pit (soil age) were studied with respect to the total concentration of trace metals (Cr, Ni, Cu, Zn, Cd and Pb) in soil collected from tree pits on commercial and residential streets. Contingency table analysis and multiple linear regression were applied to study how these independent variables were related to the total concentrations of trace metals in soil. Other variables such as pH, street width, distance of the tree pit from the curb, and tree pit volume were also used as inputs for statistical analysis in an attempt to increase the explanatory power of the resulting statistical model. Significantly higher concentrations of Cu, Zn, Cd, and Pb were observed in soils from commercial streets possibly as a result of heavier traffic as compared to residential streets. Soil organic matter was positively correlated with the concentrations of Cu and Pb probably due to the high ability of organic matter to retain these trace metals. Nickel, Cu, Zn, Cd and Pb were positively correlated with the soil age presumably because trace metals accumulate in the tree pit soil over time. This knowledge will be helpful in providing soil quality standards aimed at improving the longevity of downtown street trees.

Keywords: Tree pit, urban soils, land use, soil chemistry, street trees

4.2. Introduction

In urban environments, there are often trees planted in sidewalk tree pits along downtown streets. The environmental and social benefits provided by the large number of public trees in the City of Montreal are valued at around $648 million (Jutras, 2008). However, these trees face conditions which threaten their health and shorten their life expectancy as compared to forest trees (Quigley, 2004). Little is known about the effects of urbanization on soil properties and processes in reference to tree health (Hagan et al., 2012; Wei and Yang, 2010). Hence, identifying the limiting factors for tree health in urban environments can be crucial for urban tree management. Compacted soil and exclusion of air and water from the soil pore space are common problems affecting tree health in sidewalks (Harris et al., 1999b), as is trace metal pollution (Chen et al., 2010; Li et al., 2013b), and contamination with de-icing salt (Bäckström et al., 2004; Cunningham et al., 2008; Czerniawska-Kusza et al., 2004). The presence of these contaminants in tree pit soil can impact the availability of nutrients for the tree roots (Roberts et al., 2006). According to Day et al. (2010), this can happen because of changes in the cation exchange capacity of the soil or alterations to the population of mycorrhizal species which help make the nutrients available to the tree roots.

Potential health risks and the disturbance of geochemical cycling in urban ecosystems are other important issues on which urban soil contaminants, such as trace metals, have a direct influence (Xia et al., 2011). Much attention has therefore been given during recent decades to issues related to urban soil contamination. In addition, the soil in tree pits can play a significant role in filtering contaminants from urban runoff water and in improving urban runoff water quality, which is one of the broadly stated goals of stormwater management (National Research Council (U.S.): Committee on Reducing Stormwater Discharge Contributions to Water Pollution, 2009).

Land use, as a measure of anthropogenic influence, is a governing factor which influences the chemical properties of tree pit soil. Its effect on tree pit soil can be direct (*e.g.,* physical disturbance) or indirect (*e.g.,* soil hydrophobicity as a result of deicing salt application) (Pouyat et al., 2007). According to the type of urban land use (*e.g.,* commercial vs. residential), the direct or indirect effects of land use on the physical and chemical properties of urban soils will be different (Harris et al., 1999c; Park et al., 2010).

In terms of the effect of land use on trace metal concentration in urban soil, different studies indicated different results. Pouyat et al. (2007) did a study on the effects of land use on the trace metal concentrations in soils in Baltimore, Maryland. The land use categories considered were: commercial, industrial, institutional, transportation rights-of-way, high- and medium-density residential, golf course, park, urban open, unmanaged forest, and wetland. The results indicated that trace metal concentrations (Cu, Cr, Ni, Pb, and Zn) were not related to land use. The lack of statistically significant differences in that study may have been due to the scale of observation and the sampling intensity. In contrast, Guo et al. (2012) observed significantly higher concentrations of trace metals (Pb, Zn, and Cu) in commercial zones as compared with residential zones in Yibin City, Sichuan Province, China. In commercial zones, the vehicular traffic led to increased concentrations of trace metals, such as Pb, Cd and Cu, in the soil along the street (Czarnowska, 1999), since the metals are deposited in particles from vehicle exhaust, the wear of brakes and tires, etc.(Wei and Yang, 2010).

The fate of the trace metals in the soil depends on many soil processes, which are mainly controlled by pH and the type and amount of soil organic matter (Kabata-Pendias, 2001a). The soil pH is an important parameter affecting trace metal sorption-desorption, precipitation-dissolution, complex formation and oxidation-reduction reactions (McLean and Bledsoe, 1992). Organic matter also has an important effect on trace metal transportation and accumulation in soil contaminated with trace metals (Kabata-Pendias, 2001b). However, tree pit soil does not generally have rich top soil (Jim, 1998b). Limited organic matter additions to the tree pit soil over time (Roberts et al., 2006), and also organic matter dispersion under the effect of de-icing salt in the urban environment (Green et al., 2008b) may cause a decrease in the organic matter content of the soil over time.

The heterogeneity of urban soil chemistry cannot be attributed only to the differences in land use. Researchers who previously examined soils under similar land use regimes found that key soil chemical properties can also have significant relationship with the soil age (Park et al., 2010). In the current study, the age of the tree pit soil is considered as the time since the trees were transplanted from the nursery to the tree pit. At the end of the lifespan of a street tree, the dead tree will be removed and the previous soil in the tree pit will be excavated. Then, fresh soil will be added when the new young tree is planted in the tree pit. Over time, trace metal concentrations in the soil can increase due to traffic emissions and runoff water (Peltola et al., 2005).

The main objective of this study is the chemical characterization of soil samples from Montreal tree pits, exposed to urban runoff for 4-40 years. The results of this study can improve our understanding of the impact of different environmental and soil chemical characteristics on trace metal concentrations in tree pit soil. It is likely that most types of urban soils, including tree pit soils, will contain higher than background levels of trace metals (Craul, 1992c). Therefore, the intent in this study was to answer the following questions:

1. What is the trace metal (Cr, Ni, Cu, Zn, Cd, and Pb) concentration present in the soil of sidewalk tree pits in Montreal?
2. Do these trace metal concentrations exceed standards recommended by the Canadian Council of Ministers of the Environment (1999) for urban soil in commercial and residential zones and, if so, what factors are correlated with these excessive concentrations?
3. Do land use, soil organic matter (SOM), and soil age have significant relationships with trace metal (Cr, Ni, Cu, Zn, Cd and Pb) concentrations in tree pit soils?

4.3. Materials and methods

4.3.1. Study site description

The study was conducted in the City of Montreal (Quebec, Canada), which lies at latitude 45°30’ north and longitude 73°34’ west with a humid continental climate characterized by hot summers and cold winters. The mean annual precipitation and snowfall from 1971 to 2000 were 106 cm and 226 cm, respectively (Environment Canada, 2012a). The average summer and winter temperatures from 1981 to 2010 are around 19˚C and -8˚C, respectively (Environment Canada, 2012b). The study area was classified into two land use zones: commercial and residential. The criteria for land use classification included the importance of vehicular and pedestrian traffic, the size of the tree pits, the level of exposure to de-icing salts, and the width of the streets (Jutras et al., 2010). Five streets in this study were categorized as lying in commercial zones, and eleven streets in residential zones.

4.3.2. Soil sampling

During a prior study, Jutras et al. (2008) collected four soil samples at the edges of each of 796 tree pits (at a depth of 0–20 cm) on the selected streets in five land use zones (intensive commercial, commercial, institutional, intensive residential and residential) in the City of Montreal, then mixed them to form a composite for each tree pit. The samples were dried at room temperature for 14 days, sieved through a 2-mm metal sieve to remove large particles and stored in closed plastic bags until analysis. In the current study, land use, SOM and soil age were considered as the three most important independent variables affecting the chemistry of the tree pit soil. Seventy-three samples were selected randomly from the original stratified sample set, including 35 samples from commercial zones and 38 samples from residential zones.

4.3.3. Independent variable classes for sample selection

For the current study, samples were selected only from commercial and residential zones as they were more numerous and were expected to show greater contrast. The samples were then sorted according to SOM and soil age classes. At this step, considering the acceptable range (4-7% rounded up to 10%) of SOM in the standard recipe for Montreal tree pit soil, samples with SOM content higher than 10% were omitted from the sample set, while the rest were classified into two groups: samples with SOM content<5.5% and samples with 5.5≤SOM content≤10%. The samples in each SOM class were then clustered into four age classes, partitioned so as to achieve an adequate number of samples in each class: age < 12 y, 12 ≤ age < 17 y, 17 ≤ age < 28 y, and 28 y≤ age (maximum 40 years). Every class contains from 3 to 5 samples, for a total of 73 samples.

4.3.4. Analysis

Chemical analysis

After sample selection, different chemical characteristics of the soil samples were measured. Soil pH was measured by pH meter (Accumet AR10; Fisher Scientific Inc., Pittsburgh, PA) in water using a 1:2 (7 g soil: 14 mL H_2O) soil-to-solution ratio (Hendershot et al., 1993b). Total concentrations of trace metals, including Cr, Ni, Cu, Zn, Cd and Pb, were estimated by hot nitric acid digestion. In this protocol, 2 mL of concentrated nitric acid (16 M) was added to a 0.2 g soil sample, heated for 5 hours on a block heater set at 130 °C, cooled, diluted up to 50 mL with nanopure water and left to settle overnight. The total concentrations of trace metals were then quantified in the extracts using an inductively coupled plasma-mass spectrometer (820-MS, Varian, Melbourne, Australia)(Hendershot et al., 2008). Quality control of the analysis of total concentration of trace metals was assured by analysis of certified reference material (SED 90-4 and SED 94-3 provided by the Environment Canada Proficiency Testing program). Recovery percentage of the SED 90-4 and SED 94-3 were as follows: 99.08, 105.99% for Cr; 108.83, 98.17% for Ni; 106.82, 100.36% for Cu; 101.12, 101.67% for Zn, 97.46, 99.05% for Cd, and 105.50, 101.20% for Pb.

Statistical analysis

Contingency table analysis and multiple linear regression were done using SPSS Statistics (V.21, IBM). The data were normalized using a base-10 logarithmic transformation, and normality was confirmed with the Kolmogorov-Smirnov test. Multiple linear regression was used to determine the relationships between dependent variables (trace metal concentrations: Cr, Ni, Cu, Zn, Cd, and Pb) and independent variables (land use category, SOM and soil age). It was also applied to explore whether the inclusion of other variables (pH, street width, distance of the tree pit from the curb, and tree pit volume, measured in Jutras et al., 2008) could increase the explanatory power of the statistical model.

A backward elimination method was used to find out which independent variables were important. This method starts with all candidate independent variables and then eliminates the variables that contribute the least to explain the variation of the dependent variable. This process is repeated until all the remaining independent variables in the model have a significant partial regression coefficient (Legendre and Legendre, 1998).

In order to exclude collinearity between the regression factors, the variance inflation factor was computed; generally a value greater than 10 indicates collinearity between variables (O'Brien, 2007). The coefficient of determination (R^2) was calculated to indicate the overall predictive accuracy of the multiple linear regression model.

Analysis of variance using the general linear model was applied to characterize the interactions between land use classes and other independent variables. Hierarchical cluster analysis (Ward's minimum variance method) was used to categorize the dependent variables for contingency table analysis (Table 4.1), which was then employed to show the effect of land use (a categorical variable) on the total concentration of trace metals. Ward's minimum variance method is used to group data by minimizing the total inter-cluster variance while maximizing the intra-cluster variance (Brown and Martin, 1996).

Table 4.1. Classes of trace metal concentrations (mg kg $^{-1}$ soil) for contingency table analysis

Trace metals	Upper class boundary [†]			
	Class 1	Class 2	Class 3	Class 4
Cr	33	54	66	100
Ni	16	22	34	100
Cu	53	80	216	-
Zn	123	255	950	-
Cd	0.4	0.8	6.2	-
Pb	100	290	670	2150

[†] Each class includes the range of trace metal concentrations smaller or equal to the upper class boundary (the first class range starts at 0).

4.4. Results and discussion

4.4.1. Descriptive statistics

As descriptive statistics of the soil chemical parameters indicated (Table 4.2), Cd and Pb in commercial zones and Pb in residential zones demonstrated coefficients of variation (CV) higher than 1. The soil Zn and Cu also indicated high CV values in commercial zone. This can be attributed to the non-homogeneous distribution of metals in tree pit soils (Li et al., 2013b) or their anthropogenic source, such as vehicle emissions, oxidation of car lubricants, and gradual deterioration of vehicle mechanical parts (Chen et al., 2012).

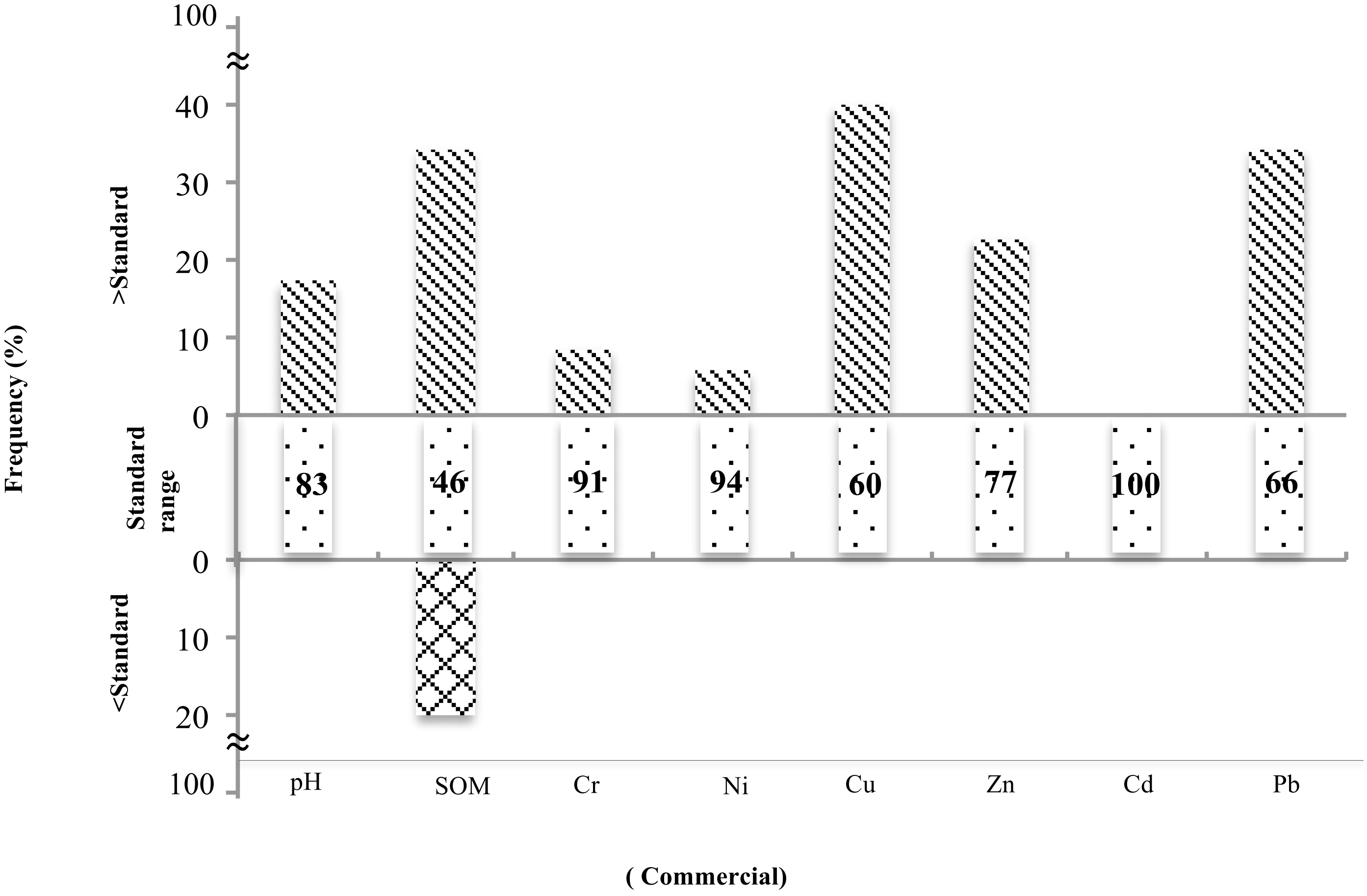
The results of the Kolmogorov-Smirnov test ($p<0.05$) of data from both commercial and residential zones showed that Cd and Pb concentrations were not normally distributed. Hence, all the data were normalized with a base-10 logarithmic transformation.

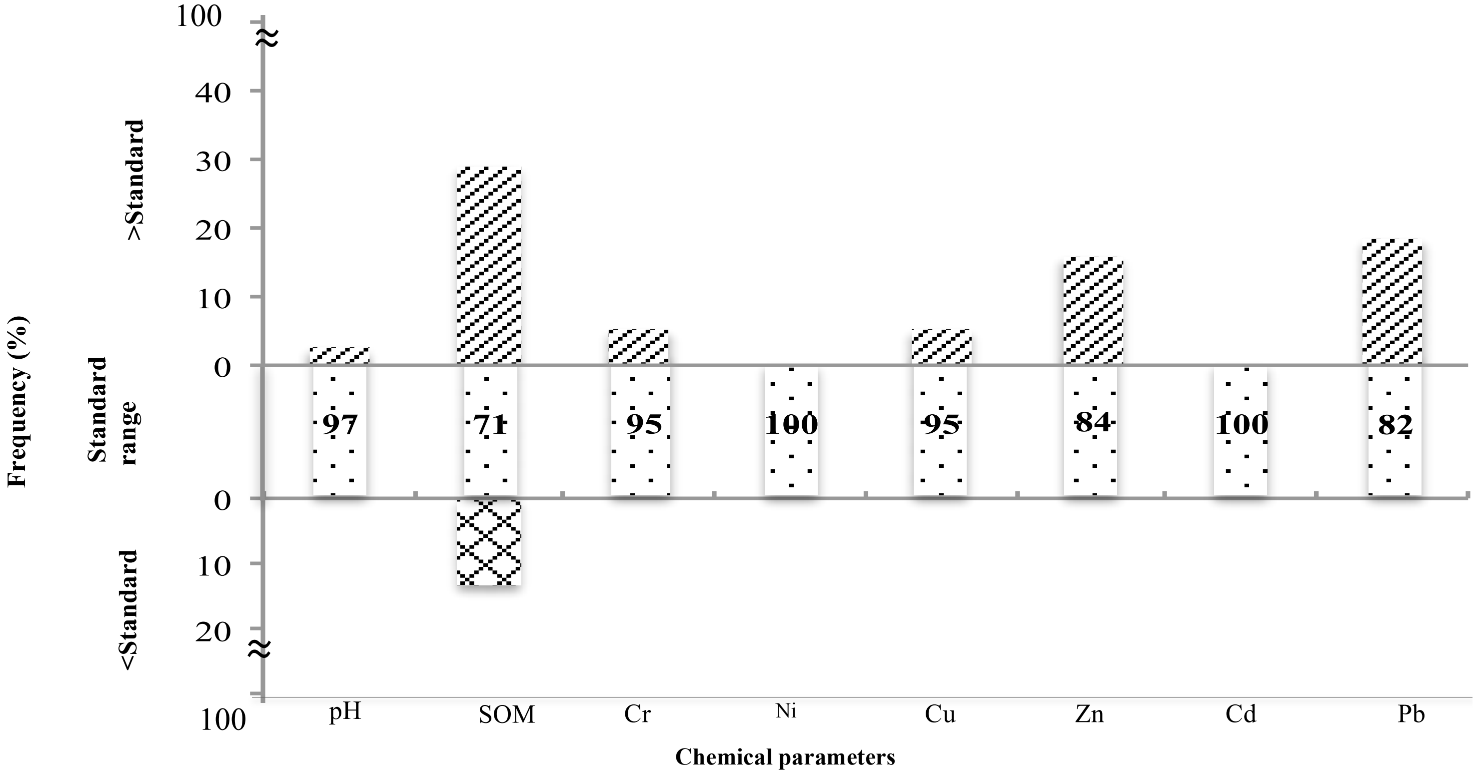
Table 4.2. Descriptive statistics of the soil chemical properties in commercial and residential zones

	Commercial zone (n=35)						**Residential zone (n=38)**					
Variable	Min.	Max.	Mean	SD[£]	CV [†]	Standard [‡]	Min.	Max.	Mean	SD	CV	Standard [§]
pH	6.73	8.41	7.55	0.39	0.05	6-8	6.52	8.1	7.44	0.35	0.05	6-8
SOM[€] (%)	2.16	9.71	5.91	2.06	0.35	4-7 [¶]	3.31	9.55	5.98	1.8	0.3	4-7 [¶]
Cr (mg kg^{-1})	14.5	98.6	42	24.2	0.58	87	16.2	66.3	31.7	12.4	0.39	64
Ni (mg kg^{-1})	8.94	97.6	24.6	17.6	0.72	50	9.44	37.3	20.2	6.25	0.31	50
Cu (mg kg^{-1})	9.83	216	72.7	57.8	0.79	91	9.93	81.6	31.2	15.4	0.5	63
Zn (mg kg^{-1})	33.9	948	262	222	0.85	360	51.7	395	127	71.6	0.56	200
Cd (mg kg^{-1})	0.13	6.13	1.08	1.32	1.22	22	0.19	1.28	0.48	0.27	0.56	10
Pb (mg kg^{-1})	13.7	2150	357	516	1.44	260	15.7	678	93.2	119	1.28	140

[€] SOM= soil organic matter
[£] SD= standard deviation
[†] CV= coefficient of Variation
[‡] Canadian soil quality guidelines for protection of the environment and human health in a commercial zone (Canadian Council of Ministers of the Environment, 1999)
[§] Canadian soil quality guidelines for protection of the environment and human health in a residential zone (Canadian Council of Ministers of the Environment, 1999)
[¶] City of Montreal's recipe for the soil mixtures used in tree pits (City of Montreal, 1995)

Figure 4.1 indicates the sample frequency percentage across chemical parameters, which falls below, equal, or exceed the standard values in commercial and residential zones. These standard values were derived from Canadian soil quality guidelines for protection of the environment and human health in commercial and residential zones (Canadian Council of Ministers of the Environment, 1999). The soil Cd concentration in both commercial and residential zones and the soil Ni concentration in the residential zone did not exceed the standard values. In commercial zones, Cr and Ni concentrations were not significantly different from the standard values while pH, SOM, Cu, Zn, and Pb concentrations were significantly higher than the standard values.





(Residential)

Fig. 4.1. Frequency (%) of soil samples, which were below, within, or above the recommended range of values for a number of chemical parameters in commercial and residential zones. The recommended range of values (standards) refer to the Canadian soil quality guidelines for protection of the environment and human health in commercial and residential zones (Symbol ≈ shows the Y axis scale break in order to illustrate the small frequencies more clearly)

As Wei and Yang (2010) mentioned, in general trace metals such as Cu, Pb, and Zn show the highest contamination in urban soil in comparison with other trace metals such as Cr and Ni. In the residential zone, pH, Cr and Cu were not significantly different from the standards. Among different soil chemical parameters, only SOM fell significantly below the recommended value for Montreal tree pit soils in both commercial ($p<0.01$) and residential zones ($p<0.05$). According to Jim (1998b), the inadequacy of organic matter is a common problem for urban soils and may be attributed to different factors such as the low amount of litter returned to the soil (Roberts et al., 2006), and also organic matter dispersion (Green et al., 2008b) and leaching from the soils exposed to de-icing salt (Green and Cresser, 2008).

4.4.2. Effect of land use

According to the measured chemical parameters of the soil samples (Table 4.3) and the result of contingency table analysis (Table 4.4), Cu, Zn, Cd, and Pb concentrations were significantly higher in commercial zones than in residential zones, as corroborated by other studies. Considering the traffic emissions as one of the main possible sources of these trace metals in urban soil (Wei and Yang, 2010), this significantly higher concentration of trace metals in the commercial zones can be attributed to the heavier traffic on the commercial streets in comparison to the residential ones (Mingkui and Hao, 2009).

Table 4.3. Trace metal concentrations in the soil as related to independent variables. Values are the mean (standard error) of the number of samples (n) shown

Land use	SOM[†]	Age	n	pH	Cr	Ni	Cu	Zn	Cd	Pb
	%	y[††]					mg kg^{-1}			
Commercial	≤5.5	x < 12	3	7.47(0.34)	31.0(7.2)	17.5(1.8)	36.9(20.8)	96.5(27.9)	0.31(0.09)	40.2(6.4)
		12 ≤ x < 17	5	7.56(0.19)	26.4(5.2)	15.9(1.8)	36.5(11.9)	155(48)	0.49(0.18)	211(100)
		17 ≤ x < 28	5	7.81(0.16)	40.8(7.2)	23.1(2.1)	96.3(7.6)	466(132)	2.05(0.88)	592(309)
		28≤ x	3	7.96(0.14)	75.2(8.3)	30.0(0.9)	153(19)	441(30)	3.01(1.56)	1060(199)
	5.5 < x ≤ 10	x < 12	5	7.42(0.10)	45.0(12.0)	18.5(2.5)	68.8(23.7)	177(44)	0.62(0.14)	106(21)
		12 ≤ x < 17	5	7.19(0.14)	22.5(4.2)	11.5(1.1)	15.6(3.0)	72.1(15.3)	0.26(0.07)	29.2(5.9)
		17 ≤ x < 28	5	7.58(0.11)	34.8(7.9)	23.4(3.9)	47.0(14.3)	312(151)	0.92(0.36)	147(74)
		28≤ x	4	7.54(0.26)	75.9(11.1)	63.9(13.1)	163(18)	409(36)	1.55(0.08)	945(403)
Residential	≤5.5	x < 12	3	7.60(0.26)	20.8(2.5)	18.3(5.6)	18.7(4.5)	71.0(11.8)	0.25(0.05)	29.9(7.5)
		12 ≤ x < 17	5	7.57(0.09)	28.8(4.0)	17. 8(1.6)	34.1(9.7)	165(65)	0.60(0.15)	104(36)
		17 ≤ x < 28	5	7.42(0.23)	36.0(3.3)	24.8(1.9)	33.9(3.6)	121(14)	0.45(0.06)	58.0(7.3)
		28≤ x	5	7.61(0.01)	27.2(3.3)	18.6(2.0)	17.8(1.1)	80.2(5.3)	0.30(0.01)	36.4(3.0)
	5.5 < x ≤ 10	x < 12	5	7.13(0.13)	23.0(3.1)	14.2(1.4)	26.6(3.4)	83.5(6.9)	0.31(0.02)	26.8(4.8)
		12 ≤ x < 17	5	7.40(0.08)	41.4(7.7)	24.2(3.6)	35.2(6.4)	146(29)	0.64(0.18)	209(121)
		17 ≤ x < 28	5	7.18(0.15)	40.3(8.1)	23.9(3.4)	41.3(5.6)	166(18)	0.60(0.09)	118(21)
		28≤ x	5	7.69(0.16)	31.8(4.2)	19.2(1.2)	36.5(11.3)	159(34)	0.58(0.15)	138(54)

[†] SOM=soil organic matter

[††] y= year

Table 4.4. Significance of relationship between trace metal concentration and land use category in contingency table analysis, as indicated by Pearson X^2

Trace metals	No. of classes[†]	X^2
Cr	4	7.26
Ni	4	6.03
Cu	3	16.1**
Zn	3	17.4**
Cd	3	9.18*
Pb	4	10.8*

* Significant at $p<0.05$

** Significant at $p<0.01$

[†] Number of classes of trace metal concentrations

4.4.3. Effects of other independent variables

Analysis of variance for Zn did not show any significant interactions between land use and any of the other independent variables (organic matter, pH, age, street width, distance of the tree pit to the curb and tree pit volume) (Table 4.5). Concentrations of Cr and Ni, however, were significantly influenced by land use × street width, land use × distance of the tree pit to the curb, and land use × tree pit volume. The concentration of Cu was significantly influenced by land use × SOM and land use × street width. The concentration of Cd was influenced by land use × SOM and that of Pb was influenced by land use × SOM and land use × tree pit volume. Therefore, samples from commercial and residential zones were examined separately.

Table 4.5. The significance of the effect of the interactions between land use and other independent variables on the concentration of trace metals in soil. The values in the table are *p*-values gained from analysis of variance using the general linear model

Interactions	Cr	Ni	Cu	Zn	Cd	Pb
Land use × SOM[¶]	0.61	0.43	0.03*	0.12	0.05*	0.03*
Land use × pH	0.99	0.68	0.92	0.55	0.91	0.92
Land use × Age	0.66	0.22	0.6	0.67	0.44	0.91
Land use × StW[†]	0.00**	0.00**	0.03*	0.23	0.26	0.67
Land use × DisSt[‡]	0.00**	0.04*	0.14	0.97	0.69	0.29
Land use × PitV[§]	0.02*	0.02*	0.09	0.3	0.17	0.01**

[¶] SOM=soil organic matter

[†] StW= street width

[‡] DisSt= distance (of the tree pit) from the curb (street)

[§] PitV =(tree) pit volume

Multiple linear regression was applied to evaluate how the other independent variables played a role in determining how the values of the dependent variables changed in the commercial and residential zones (Table 4.6). All the variance inflation factor values were below 10, which negate the possibility of collinearity among the independent variables in every model.

Table 4.6. Predictive models for concentrations of trace metals in commercial and residential zones. The numbers in the cells represent significant partial regression coefficients, which indicate the importance of the relationship between the corresponding dependent and independent variables. Blank cells indicate insignificant relationships

	Commercial zone (n=35)								Residential zone (n=38)							
	Intercept	**Log SOM[¶]**	**Log Age**	**Log pH**	**Log StW [†]**	**Log DisSt [‡]**	**Log PitV [§]**	**R^2 [£]**	**Intercept**	**Log SOM**	**Log Age**	**Log pH**	**Log StW**	**Log DisSt**	**Log PitV**	**R^2**
Log Cr					1.56	-1.69		0.65***	2.62		0.2		-1.05	0.94	-0.69	0.48***
Log Ni	-0.74		0.36		1.53			0.65***	2.3				-0.77	0.71	-0.46	0.31**
Log Cu	-3.02		0.32		4.07			0.82***	-0.22	0.45			1.48	0.54	-0.35	0.39**
Log Zn	-4.07		0.5	4.27	1.88			0.62***	1.75		0.37				-0.5	0.23**
Log Cd	-4.09		0.55		3.07			0.63***	-0.61		0.31				-0.46	0.20*
Log Pb	-7.84		0.83	9.88			1.16	0.55***	-6.19	1.24	0.72	7.43			-1.09	0.44***

* Significant at $p<0.05$

** Significant at $p<0.01$

***Significant at $p<0.001$

[¶] SOM= soil organic matter

[†] StW= street width

[‡] DisSt= distance (of the tree pit) from the curb (street)

[§] PitV =(tree) pit volume

[£] R^2= coefficient of determination

It seems that variations in environmental factors such as tree pit volume or distance to the curb can result in spatial heterogeneity of the tree pit soil and might obscure expected relationships between the other variables of interest in the tree pits. However, there are general identifiable patterns of the effect that urban environments have on concentrations of trace metals in the soil.

Organic matter showed a positive relationship with concentrations of Cu and Pb in the residential zone (Table 4.6). This positive relationship may be due to the high affinity of these trace metals for organic ligands in the soil (Kabata-Pendias, 2001a; McLean and Bledsoe, 1992), agreeing with work elsewhere (*e.g.,* Bäckström et al., 2004) . In general, organic matter plays a crucial role in relationship with trace metals because it tends to form soluble or insoluble complexes with trace metals. Therefore these complexes can be bioavailable in the soil profile or be retained in the soil (Vega et al., 2004).

Organic matter did not show a significant effect on trace metal concentrations in the commercial zone. Kumar and Edward (2009) related this to the adsorption of trace metals to other adsorbents in the soil, such as Fe and Mn oxyhydroxides and the formation of Cu and Pb precipitates (McBride, 1994e). In addition, the insignificance of the relationship between organic matter and trace metals may be ascribed to other factors. These factors include competition among trace metals and other cations for complexing sites on SOM (Katip et al., 2012; Luoma and Davis, 1983; Peng et al., 2009), such as Na from de-icing salt, which is more heavily used in the commercial zone, and Ca from the weathering of concrete in buildings and sidewalks (Cunningham et al., 2008). Another factor is the dispersion of organic matter due to high concentration of de-icing salt (Bäckström et al., 2004; Green et al., 2008b). These reasons presumably explain the insignificance of the relationships between SOM and trace metal concentrations in the commercial zone.

There is a positive relationship between trace metals in the soil (Ni, Cu, Zn, Cd and Pb) and soil age. According to Pezzente (1997), this relationship can be attributed to the continual input of these metals to the tree pit soil over time.

Wider streets in the commercial zone can correspond to higher traffic volumes which might be associated with higher concentrations of trace metals (Jutras et al., 2009). This may explain the significant positive relationship between street width and Cr, Ni, Cu, Zn, and Cd concentrations in the commercial zone (Table 4.6 and Fig. 4.2). There is a negative relationship, in the residential zones, between street width and the concentrations of some trace metals such as Cr and Ni (Table 4.6). These relationships may be attributed to the manner in which cars in the residential zone are parked next to the sidewalk, resulting in less splashing, a mechanism by which significant loads of trace metals would otherwise be transported into the tree pit soils (Sabin et al., 2005).

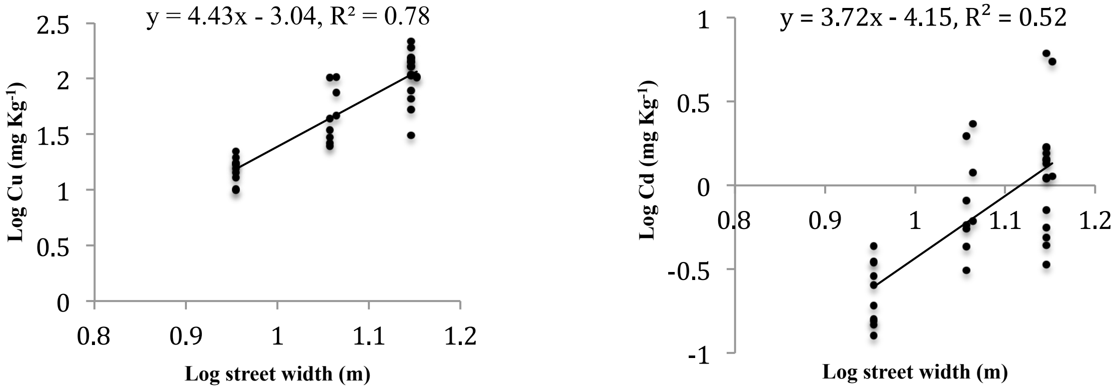


Fig. 4.2. Change in Cu and Cd concentrations as related to street width in commercial zones

There is also a positive relationship between pH and both Pb and Zn concentrations in the soil (Table 4.6 and Fig. 4.3), as confirmed by Yobouet et al. (2010). In general, maximum retention of cationic metals (*e.g.*, Pb^{2+} and Zn^{2+}) by the soil particles occurs in pH>7 (McLean and Bledsoe, 1992). As trace metals are retained in the soil solid phase due to an increase in pH, trace metal bioavailability in the soil solution may decrease. In alkaline and neutral environments, Pb and Zn solubility in the soil solution decreases markedly owing to chemisorption on oxides and aluminosilicates, complexation with organic matter, and precipitation as carbonates (McBride, 1994e; Takáč et al., 2009). Therefore, increasing pH may result in higher Pb and Zn concentrations in the soil solid phase.

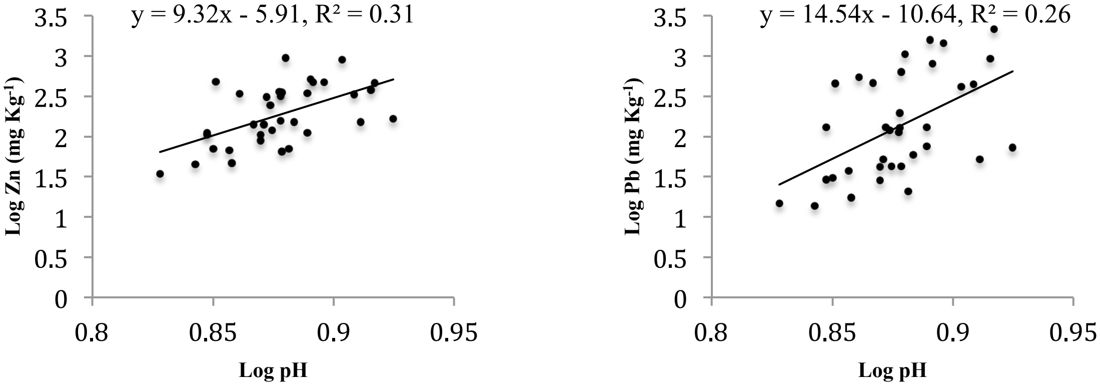


Fig. 4.3. Change in Zn and Pb concentrations as related to pH in commercial zones

4.5. Conclusion

Copper, Zn, and Pb concentrations in soils from commercial zones and Zn and Pb concentrations in soils from residential zones were significantly higher than standard values recommended in the Canadian soil quality guidelines for protection of the environment and human health in commercial and residential zones. Heavy vehicular traffic on wider streets in commercial zones and continual input of trace metals to the tree pit soil over time are some of the mechanisms presumed to result in these elevated values. Some soil chemical characteristics, such as SOM and pH, also impacted the concentrations of trace metals in the tree pit soil. The results of this study provide an understanding of the type and rate of the accumulation of trace metals in the tree pit soil. A step forward would be to conduct lab and field trials with various soil improvement methods aimed at attenuating excessive trace metal concentrations in the tree pit soil, as compared with urban soil quality guidelines. Meeting these guidelines can provide a healthier soil medium for the street trees, while increasing soil capacity for runoff infiltration and trace metal retention.

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Connecting statement III

In previous research, Jutras et al. (2010) appraised land use, street width, pH, exposure to light, and soil compaction as significant abiotic factors affecting the growth of different species of street trees in Montreal. In chapter 4, we described chemical and statistical analyses on Cu, Zn, Cd, and Pb concentrations in soil samples collected from tree pits in relationship with environmental factors and soil chemical characteristics. The results revealed land use, street width, and soil age as environmental factors, and SOM and pH as soil chemical factors, which significantly affected trace metal content in tree pit soils. In chapter 5, it is hypothesized that some of the environmental factors may affect the street tree growth indirectly by limiting the plant-availability of nutrients. A characterization was performed of the plant-availability of Ca, Mg, K, P, total mineral N, and Na in relationship with abiotic factors such as land use, street width, distance of the tree pit from the curb, tree pit volume, SOM, pH, type of cover material, underlying surficial geologic material, and soil age.

Chapter 5

Macronutrient availability in surface soil of urban tree pits influenced by land use, soil age, and soil organic matter in Montreal tree pit soil

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5.1. Abstract

An adequate supply of plant-available nutrients and an appropriate chemical composition of soils in tree pits are important factors affecting the health and life span of trees in urban environments. We used Multivariate Adaptive Regression Splines (MARS) to explore relationships between nutrient availability, soil organic matter (SOM), soil pH, land use, soil age (time since tree transplanting from nursery to the tree pit), street width, and tree pit cover material in Montreal, Quebec, Canada. Soil was collected to a depth of 20 cm from tree pits along commercial and residential streets and analyzed for concentrations of plant-available K, Ca, Mg, P, and N, concentration of Na, SOM content and soil pH. Mulching with wood chips and soil age influenced the availability of K, P, and N in the tree pit soils. Sodium concentration was positively correlated with soil pH, possibly due to the displacement of H^+ by Na^+ originating from de-icing salt. Soil organic matter content was positively correlated with Mg and Na concentrations in tree pit soils in commercial zones, and with K and Ca concentrations in those of residential zones. Soil from tree pits located along wide streets in commercial zones had high concentrations of Na and Ca, possibly due to higher volumes of traffic on those streets splashing more de-icing salt, and increased weathering of buildings and sidewalk by de-icing salt. The information presented here can be a valuable baseline for managing nutrients in tree pits, in order to mitigate the stresses that can shorten the life of street trees.

Keywords: Tree pit, nutrients, street trees, multivariate adaptive regression splines, cation exchange capacity

5.2. Introduction

Poor soil conditions in urban ecosystems limit the growth and life expectancy of street trees (Jim, 2004; Li et al., 2013c). Stressors include deficiency of plant-available nutrients and disrupted nutrient cycling, low organic matter content, elevated soil pH, and prolonged exposure to de-icing salt especially in the wide streets of commercial zones in boreal and temperate regions (Roberts et al., 2006; Zainudin et al., 2003). Wide streets undergo heavy vehicular traffic, which causes more splashes of de-icing salt as compared to the narrower streets in residential zones. These factors may degrade tree pit soil and dampen tree growth in commercial zones (Jutras et al., 2010).

Deficiency of essential plant nutrients makes street trees susceptible to the sometimes-harsh urban environment. Nitrogen (N) is one such nutrient, the lack of which limits tree growth in urban ecosystems (Jim, 1998b). Mineralization of organic matter and fixation of atmospheric N by some bacteria are two ways that N may become available as NO_3^- in soil solution or as NH_4^+ adsorbed on soil particles (Scharenbroch and Lloyd, 2004). Plant-available N as a component of amino acids, nucleic acids, proteins, and enzymes can affect the formation and activity of hormones and therefore may reduce or increase plant growth (Li et al., 2013a). Nitrogen deficiency can cause allocation of higher levels of carbon (C) to the roots, increase in root-to-shoot biomass ratio, decrease in photosynthesis, and failure to synthesize normal amounts of cholorophyll (Boussadia et al., 2010).

The availability of P, another essential nutrient, is low in many naturally-occurring soils. Phosphorus in plants forms part of the phosphorylated sugars necessary for energy transfer and photosynthetic systems, and is a component of nucleoproteins and phytin. Phosphorus also plays a role in protein metabolism and respiration (Craul, 1992d). Phosphorus deficiency in young trees often results in growth stunting (Fageria et al., 2010).

In addition to N and P, K, Ca, and Mg are also necessary for tree growth and health. Most soils contain enough available K for tree growth. Potassium plays an important role in enzyme activation, osmotic regulation in roots, and production of high-energy phosphate molecules (ATP) in plants (Tisdale et al., 1993a). Potassium deficiency can inhibit the translocation of carbohydrates from the leaves to other parts of the plant and also affect N metabolism (Kramer and Kozlowski, 1979a). Calcium, usually abundant, is a component of plant cell walls and also controls physiological processes in the cells, root growth, and elongation (Craul, 1992d). Soils that lack Ca may become so acidic that they become toxic for trees. Low plant-availability of nutrients together with Ca in an acidic soil can be more serious to tree growth and health than Ca deficiency alone (Harris et al., 1999b). Also, in acid soils, elevated concentrations of Al and Mn can become toxic to trees. Soil acidification can increase trace metal mobilization in soils and increase metal uptake by plants (Bolan et al., 2003).

Calcium deficiency results in serious injury to meristematic regions, especially root tips (Kramer and Kozlowski, 1979a). Magnesium is sufficient in most soils but may be deficient in strongly acidic sandy soils, where it can be easily leached away (Harris et al., 1999b). Magnesium is necessary for plants as part of the chlorophyll molecule and enzyme activity, formation of carbohydrates, proteins, and cell division (Craul, 1992d). Magnesium deficiency may result in chlorosis (Beets et al., 2004).

Nutrient availability in urban soils may be low because of limited cycling of nutrients and organic matter (Pulford, 1991). Soil in tree pits usually is neither derived from nor rests directly on the underlying parent material, and so might not receive nutrients released by mineral weathering (Pezzente, 1997). Organic matter, therefore, is often the main source of nutrients in tree pit soils. Leaf litter, a potentially important source of organic matter, is often returned to tree pit soil only in small quantities. The resulting limited cycling of organic matter can further reduce soil fertility (Roberts et al., 2006). This lack of organic matter can also destabilize structural aggregates, progressively reducing macroporosity, increasing soil compaction, and decreasing water-holding capacity. The paucity of SOM as an energy source also decreases the activity of soil fauna (Craul, 1992b). Microorganisms (mainly bacteria and fungi) promote soil aggregation via humification and by exuding colloidal polysaccharides that can hold the soil particles together (Buscot, 2005). Decreased microbial activity, therefore, can further degrade the structure of soil aggregates.

Soil properties, including soil nutrient concentrations, can also vary among urban land use zones (*e.g.,* commercial vs. residential) (Li et al., 2013c; Scharenbroch et al., 2005). Heavier traffic in commercial zones of boreal and temperate regions may expose the soil adjacent to the street to increased concentrations of de-icing salt, which can then percolate downward into deeper soil horizons or the groundwater (Ramakrishna and Viraraghavan, 2005). Previous studies have indicated that approximately 75-90% of de-icing salt enters the soil within 10 m of the curb by runoff, splashing or aerosol deposition (Green et al., 2008a). Moreover, salt spread directly on the sidewalk can be carried by runoff water to concentrate in tree pit soil (Hootman et al., 1994). Sodium from the de-icing salt can displace metal cations, including nutrients such as K, from exchange sites in the tree pit soil and thus affect nutrient availability for the street trees (Bäckström et al., 2004; Czerniawska-Kusza et al., 2004; Roberts et al., 2006). Furthermore, Na from de-icing salt and carbonate released by weathering of buildings and concrete structures can increase soil pH (Roberts et al., 2006). Alkalinity of tree pit soil can also be attributed to Ca originating from $CaCl_2$ as de-icing salt and from the weathered Ca-rich cement of curbs and sidewalks (Sutherland and Tolosa, 2001). However, in Montreal $CaCl_2$ is not commonly used as a de-icing agent due to its higher cost as compared to NaCl.

Heavy traffic on commercial streets can also contaminate the tree pit soil with trace metals. Contamination of tree pit soil with trace metals can affect the availability of nutrients by changing the cation exchange capacity of the soil or altering the population of mycorrhizal species which liberates nutrients (Kargar et al., 2013; Roberts et al., 2006).

Nutrient content can also be related to soil age (*i.e.* the time since the tree was transplanted from the nursery) (Park et al., 2010). The availability of some nutrients, like N, is often limited in young soils while other nutrients, like P, decrease in older soils from which nutrients have been leached or lost due to erosion. Accumulation of N in soil over time is also a function of SOM turnover, although SOM is more important as a source of N than of P (Lambers et al., 2008).

In previous research, Jutras et al. (2010) appraised land use, street width, pH, solar radiation levels, and soil compaction as significant abiotic factors affecting the growth of different species of street trees in Montreal. In the current study, it is hypothesized that some of these abiotic factors may affect street tree growth indirectly by limiting the plant-availability of nutrients in tree pit soil. We therefore characterized the plant-availability of Ca, Mg, K, P, total mineral N, and Na in relationship with abiotic factors such as land use category, street width, distance of the tree pit from the curb, tree pit volume, SOM content, pH, type of cover material, underlying surficial geologic material, and soil age.

This study is a part of a larger research program in tree pit soils focusing on trace metal abundance (Kargar et al., 2013) and nutrient availability as affected by other factors in the urban environment. The ultimate aim of the research is to improve tree pit soil for immobilization of trace metals and provision of adequate plant-available nutrients.

5.3. Material and Methods

5.3.1. Soil sampling

The study was conducted in Montreal, Quebec, Canada, which lies at 45°30' N and 73°34' W. Montreal has a humid continental climate with hot summers and cold winters. The average summer and winter temperatures from 1981 to 2010 were 19 and -8°C, respectively (Environment Canada, 2012b). The mean annual precipitation and snowfall from 1971 to 2000 were 106 and 226 cm, respectively (Environment Canada, 2012a).

In a previous study (Jutras, 2008), four soil samples were collected from the edges of each of 796 tree pits on selected streets of five land use zones including intensive commercial, commercial, institutional, intensive residential, and residential zones. Soil samples were collected only from 0–20 cm because the high compaction made deeper samples impractical. The soil samples were then mixed to form a composite sample for each tree pit. The average opening size of the tree pits was 1.5m × 1.5m. The criteria for street selection included the land use zone, height of buildings, geographic orientation, importance of vehicular and pedestrian use, size of tree pits, and width of street.

The soil samples were air-dried and sieved through a 2-mm metal screen. Seventy-three soil samples were selected from the original sample set by considering land use zone, SOM, and soil age as the three independent factors most likely to affect nutrient availability.

Soils from commercial and residential zones were included in this study because they showed the greatest contrast in the variables of interest and there was an adequate number of samples for statistical analysis. Five of the streets from which the selected soils were sampled were located in commercial zones, with heavy pedestrian and vehicular traffic and tree growth rates that were slow to fair. In the previous study (Jutras et al., 2010), growth rates in each land use zone were classified for each tree species considering diameter at breast height (DBH), crown diameter, height, crown diameter/DBH, crown volume/DBH, height/DBH, crown volume, annual DBH increment, crown diameter increment, height increment, and crown volume increment.

Eleven of the streets included in the study were located in residential zones, with less intensive vehicular and foot traffic and typically healthy trees (Jutras et al., 2010). The soil samples from those streets were further classified by SOM content and soil age. The standard recipe for tree pit soil in Montreal stipulates 4-7% (rounded up to 10%) SOM. Samples with SOM content > 10% were therefore excluded and the remaining samples were categorized into those with SOM content ≤ 5.5% and those with 5.5% < SOM content ≤ 10%. Samples in each category of land use and SOM were then sorted according to soil age: age < 12 y, 12 ≤ age < 17 y, 17 ≤ age < 28 y, and 28 ≤ age (maximum 40 years). The partition values between the age classes were chosen to balance the number of samples in each class. A total of 73 soil samples were analyzed in this study, including 35 samples from commercial zones and 38 samples from residential zones.

5.3.2. Soil analysis

Soil pH was measured with an Accumet AR10 meter (Fisher Scientific Inc., Pittsburgh, PA) at 1:2 soil-to-solution ratio (7 g soil/14 mL H_2O) (Hendershot et al., 1993b). Total mineral N (NH_4^+ and NO_3^-) was extracted with KCl (Maynard and Kalra, 1993) and measured by colorimetry on a multi-channel auto-analyser (Lachat Instruments, Milwaukee, WI). Available nutrients (P, Ca, Mg, K) and Na were extracted according to the Mehlich-III procedure using a mixture of acetic acid, ammonium nitrate, ammonium fluoride, ethylene-diamine-tetra-acetic acid (EDTA), and nitric acid (Tran and Simard, 1993). Colorimetry was used to determine the concentration of available P (Quick Chem FIA+, Lachat Instruments). Available Ca and Mg, and available Na and K were measured by flame atomic absorption spectroscopy and flame atomic emission spectroscopy, respectively, on the same Varian SpectAA 220FS. Soil organic matter content (%) was measured following the loss-on-ignition method (Schulte et al., 1991).

5.3.3. Statistical analysis

All the quantitative dependent (concentrations of Ca, Mg, K, P, total mineral N, and Na) and independent variables (SOM content, soil age, street width, distance of the tree pit from the curb and tree pit volume) in this study were normalized using a base-10 logarithmic transformation, as confirmed with the Kolmogorov-Smirnov test. The records were then separated according to land use zones (commercial and residential). An independent-samples t-test was done to determine if land use zone was significantly correlated with nutrient availability in the soil. A bivariate correlation analysis (Pearson correlation coefficient) was done between the Na and macronutrient concentrations in the soil samples and all the independent variables. The coefficient of variation (CV) was also calculated, defined as the ratio of the standard deviation to the mean. If the CV value of plant-availability of a nutrient is higher than 1, it can refer to an anthropogenic factor, which causes a high variation in the plant-availability of that nutrient as compared to the mean.

In order to find and model the relationships between the dependent variables (Ca, Mg, K, Na, P, and total mineral N concentrations) and independent factors (*e.g.*, soil age, and SOM content), bivariate correlation analysis (Pearson correlation coefficient) and Multivariate Adaptive Regression Splines (MARS) were done using SPSS statistics (V.21, IBM) and STATISTICA (V.12, StatSoft), respectively. Other independent variables were included in the model to investigate their effects on its explanatory power, including soil pH, street width, distance of the tree pit from the curb, tree pit volume, and type of soil cover (bare soil, grass, wood chips, flower bed, gravel, or bricks). The type of underlying surficial geologic deposit (clay, sand, sand/gravel, silt/sand/gravel, till, or rock) was also considered (Prest and Keyser, 1962).

MARS is a non-parametric adaptive regression technique which divides the solution space according to various intervals of the predictor variables, and then fits a basis function to each interval (Friedman, 1991). Equation 5.1 is a generic MARS model of a dependent variable y with M basis functions:

$$\widehat{Y}=\hat{f}_M(x)=c_0+\sum_{m=1}^{M} c_m B_m(x) \qquad \text{Eq.[5.1]}$$

$\widehat{Y}$ is the value of the dependent variable predicted by the MARS model, c_0 is the intercept, $B_m(x)$ is the m^{th} basis function, and c_m is the coefficient of the m^{th} basis function (Fernández et al., 2014). Considering x as the input variable and c as the constant indicating the threshold value, the basis functions in MARS are defined as follows (Eq. 5.2 and 5.3):

$$B_m(x)=\max(0, x-c)=\begin{cases} x-c & \text{if} \quad x\geq c \\ 0 & \text{otherwise} \end{cases} \qquad \text{Eq.[5.2]}$$

$$B_m(x)=\max(0, c-x)=\begin{cases} c-x & \text{if} \quad x<c \\ 0 & \text{otherwise} \end{cases} \qquad \text{Eq.[5.3]}$$

Generalized cross validation was applied in order to balance goodness-of-fit with model complexity (Chen et al., 1999). The correspondent-stopping threshold of the splines, which prevents over-fitting of the splines, was set at 0.0005. The efficiency (EF) of the model was then calculated in order to check the performance of the model (Eq. 5.4). The EF evaluates the variation in predicted values as compared with the observed ones (Singh, 2012).

$$EF=\frac{(\sum_{i=1}^{n}(O_i-\bar{O})^2-\sum_{i=1}^{n}(P_i-O_i)^2)}{\sum_{i=1}^{n}(O_i-\bar{O})^2} \qquad \text{Eq.[5.4]}$$

$\bar{O}$ is the mean of the observed values, O_i is the observed value, P_i is the predicted value, and *n* is the number of observations (Bera et al., 2006).

5.4. Results and discussion

5.4.1.Results

Descriptive statistics

Descriptive statistical parameters such as coefficient of variation (CV), and the recommended values in urban soils were demonstrated for K, Ca, Mg, P, total mineral N and Na concentrations, and for the soil chemical parameters (pH and SOM) associated with the nutrient variation (Table 5.1). Table 5.2 summarizes nutrient concentrations and the chemical parameters measured in soil samples from different classes of independent variables (land use zone, SOM and soil age). The concentrations of K and Na in the soils of commercial zones indicated CV values higher than 1. The CV value was also higher than 1 for total mineral N in soils from tree pits located both in commercial and residential zones.

Table 5.1. Descriptive statistics and test of significance for the soil chemical properties (pH, SOM, and nutrient concentrations (n=73)) between commercial and residential zones

Variable	Commercial zone (n=35) Min.	Max.	Mean	SD[€]	CV[£]	Residential zone (n=38) Min.	Max.	Mean	SD	CV	Standards	t-student *p* values[¶¶]
pH	6.8	8.7	7.71	0.39	0.05	6.6	8.29	7.52	0.36	0.05	6-8 [‡-‡‡]	0.54
SOM [¥](%)	2.16	9.71	5.91	2.03	0.34	3.31	9.55	5.98	1.77	0.3	4-7[¶]	0.39
K (mg kg $^{-1}$)	48.8	1570	259	345	1.33	63.5	561	220	104	0.47	74-150[†]	0
Ca (mg kg $^{-1}$)	1760	6930	4320	1080	0.25	2970	7830	4740	1130	0.24	300-1000[†]	0.99
Mg (mg kg $^{-1}$)	56.8	362	136	74.3	0.55	62.2	290	126	45	0.36	100-500[†]	0.1
Na (mg kg $^{-1}$)	0	639	192	196	1.02	18.1	610	116	111	0.96	250[§]	0.02
P (mg kg $^{-1}$)	16	218	66	42.5	0.65	19.6	336	124	87.1	0.7	30-60[†]	0.26
Total Mineral N (mg kg $^{-1}$)	10	173	24.3	26.4	1.09	10.5	303	41.7	58.2	1.4	2.5-25[†]	0.64

[¥] SOM= soil organic matter

[€] SD= standard deviation

[£] CV= coefficient of variation

[†] Recommended concentration of available nutrients in horticultural soils (Whitcomb, 1987)

[§] Threshold concentration considered as excessive for most trees (Hootman et al., 1994)

[‡] Canadian soil quality guidelines for protection of the environment and human health in commercial zones (Canadian Council of Ministers of the Environment, 1999)

[‡‡] Canadian soil quality guidelines for protection of the environment and human health in residential zones (Canadian Council of Ministers of the Environment, 1999)

[¶] City of Montreal's recipe for soil mixtures used in lawns and tree pits (City of Montreal, 1995)

[¶¶] Significance of difference between nutrient availability and soil chemical properties measured in soils collected from commercial zones as compared with the ones sampled from residential zones

About 43% of the samples taken in commercial zones and 73% of the samples from residential zones significantly exceeded ($p<0.01$) the recommended concentrations of available nutrients (Whitcomb, 1987). The soil available P also significantly exceeded ($p<0.01$) the recommended value for horticultural soils in the majority of samples from both the commercial (54%) and residential (71%) zones. The total mineral N significantly exceeded ($p<0.01$) the recommended value for horticultural soils in 34% of the soil samples from residential zones. Calcium exceeded the maximum recommended value for horticultural soils in all samples from both commercial and residential zones.

Table 5.2. Nutrient concentrations in the soil as related to independent variables. Values are the mean (standard error) of the number of samples (n) shown

Land use	SOM†	Age	n	pH	K	Ca	Mg	Na	P	Mineral N
	%	y††			mg kg^{-1}					
Commercial	≤5.5	x < 12	3	7.47(0.34)	108(18.8)	3740(692)	89.6(9.55)	222 (179)	105(50.4)	18.5(2.34)
		12 ≤ x < 17	5	7.56(0.19)	113(20.0)	3450(659)	78.7(8.27)	38.2(11.0)	88.9(13.6)	19.0(0.45)
		17 ≤ x < 28	5	7.81(0.16)	144(34.3)	3980(300)	103(14.5)	156(114)	27.6(4.18)	12.8(1.05)
		28≤ x	3	7.96(0.14)	277(65.1)	4150(40.9)	98.6(1.91)	202(83.4)	33.4(3.26)	18.9(5.62)
	5.5 < x ≤ 10	x < 12	5	7.42(0.10)	130(12.8)	3630(309)	92.9(9.44)	354(81.8)	71.2(14.2)	22.7(3.56)
		12 ≤ x < 17	5	7.19(0.14)	79.6(17.9)	3010(398)	70.2(11.3)	34.8(10.4)	89.8(17.8)	16.6(2.57)
		17 ≤ x < 28	5	7.58(0.11)	197(32.6)	4340(494)	226(36.6)	162(32)	61.5(7.34)	25.2(3.30)
		28≤ x	4	7.54(0.26)	882(250)	3860(162)	214(34.7)	296(116)	60.3(17. 6)	64.3(36.4)
Residential	≤5.5	x < 12	3	7.60(0.26)	175(27.4)	3360(496)	119(29.9)	70.4(25.8)	135±70.7	84.5(66.9)
		12 ≤ x < 17	5	7.57(0.09)	136(11.6)	3270(224)	86.4(13.7)	35.3(5.54)	53.4±9.24	16.3(1.69)
		17 ≤ x < 28	5	7.42(0.23)	191(23.5)	3590(293)	96.6(6.23)	112(41.5)	98.1±30.9	47.6(16.2)
		28≤ x	5	7.61(0.01)	158(9.0)	3280(228)	78.3(7.37)	46.3(7.19)	63.7±27.2	15.5(3.73)
	5.5 < x ≤ 10	x < 12	5	7.13(0.13)	153(316)	3350(325)	94.1(7.53)	82.5(22.9)	230(40.9)	20.7(4.39)
		12 ≤ x < 17	5	7.40(0.08)	238(35.6)	4200(319)	149(29.5)	118(40.5)	150(22.1)	30.2(10.9)
		17 ≤ x < 28	5	7.18(0.15)	248(20.1)	4280(104)	155(9.92)	134(54.5)	174(35.9)	53.6(18.1)
		28≤ x	5	7.69(0.16)	206(26.1)	4740(114)	140(23.5)	106(21.1)	107(34.9)	81.9(56.1)

† SOM=soil organic matter
†† y= year

Modeling nutrient concentrations in land use zones

The results of independent-samples t-tests indicated significantly higher concentrations of Na in commercial zones ($p<0.05$) and of K in residential zones ($p<0.01$) as compared with the other land use zone. According to the MARS models (Table 5.3), the concentrations of some nutrients, like P, in tree pit soils from commercial zones were not significantly correlated with any of the independent variables. However, the concentrations of other nutrients (K, Ca, Mg and total mineral N) and Na in commercial zones were significantly related to different independent factors. Potassium concentration in the tree pit soils of commercial zones was positively correlated with soil age (r=0.66, $p<0.01$) and the use of wood chips as the cover of tree pit soil (r=0.36, $p<0.05$). Soil age, the use of wood chips to cover the tree pit soil, and surficial deposits of clay explained around 84% of the variation in K concentration (Table 5.3). Calcium concentration in the tree pit soils from commercial zones was positively correlated with pH (r=0.54 for pH<7.56, $p<0.01$). There were also positive correlations between Ca concentration in soils from commercial zones and the SOM content of the soil ($r=0.60$ for log $SOM^3 < 0.43$, $p<0.01$). Overall, soil pH, distance of the tree pit from the curb, and SOM content explained around 70% of the variation of Ca concentration in tree pit soils from commercial zones (Table 5.3). Magnesium concentration in tree pit soils from commercial zones was positively correlated with SOM content ($r=0.48$ for log $SOM>0.77$, $p<0.01$). Also, there was a positive correlation between Mg concentration and soil age in tree pit soils ($r=0.50$ for log $Age^3<2.09$, $p<0.01$). Soil organic matter content and soil age accounted for 69% of the variation of Mg in tree pit soils from commercial zones (Table 5.3). There was a positive relationship between Na concentration in tree pit soils from commercial zones and the street width ($r=0.84$, $p<0.01$), SOM content ($r=0.47$, $p<0.01$), and soil pH ($r=0.41$ for $pH^3>432.08$, $p<0.05$). These variables explained around 91% of the variation in Na concentration in the tree pit soil (Table 5.3).

Table 5.3. Predictive basis functions for nutrients in tree pit soils from commercial zones

Variable†	Basis functions‡	EF††
Log K	$-0.59 + 1.43 \times \max(0, 1.86-\mathrm{LogAge}^3) + 0.31 \times \max(0, \text{wood chips}-0) + 3.84 \times \max(0, \mathrm{logAge}-0.60) - 0.24 \times \max(0, \text{Clay}-0)$	0.84
Log Ca	$8.65 + 7.64 \times \max(0, \mathrm{pH}-7.56) - 6.46 \times \max(0, 7.56-\mathrm{pH}) - 0.59 \times \max(0, 0.43-\mathrm{LogSOM}^3) - 0.004 \times \max(0, \mathrm{pH}^3-304.82) + 2.35 \times \max(0, \mathrm{logDisSt}+0.10)$	0.70
Log Mg	$2.08 + 1.88 \times \max(0, \mathrm{logSOM}-0.77) - 0.17 \times \max(0, 2.09-\mathrm{LogAge}^3)$	0.69
Log Na	$1.44 + 3.89 \times \max(0, \mathrm{logStrW}-0.95) + 1.12 \times \max(0, \mathrm{LogSOM}^3-0.43) - 0.80 \times \max(0, 0.43-\mathrm{LogSOM}^3) + 0.004 \times \max(0, \mathrm{pH}^3-432.08)$	0.91
Log P	NA	-
Log Mineral N	$0.94 + 1.04 \times \max(0, 0.74-\mathrm{logSOM}) + 2.61 \times \max(0, \mathrm{logAge}-1.28) + 1.01 \times \max(0, 1.28-\mathrm{logAge}) + 0.55 \times \max(0, \mathrm{pH}-7.56) - 0.33 \times \max(0, \text{Silt/Sand/Gravel}-0)$	0.69

† All logarithms are base-10

‡ DisSt = distance (of the tree pit) from the curb (street); SOM = soil organic matter; StW = street width; NA = not applicable

†† EF= efficiency of model

Total mineral N (NH_4^+ and NO_3^-) concentration in tree pit soils from commercial zones was negatively correlated with soil age in soils younger than 19 years ($r=-0.53$ for log age<1.28, $p<0.05$). However, this correlation was reversed in older soils ($r=0.41$ for log age>1.28, $p<0.05$). Total mineral N indicated positive correlation with SOM content ($r=0.36$ for log SOM<0.74, $p<0.05$). Overall, SOM content, the type of surficial geologic deposit, soil pH, and soil age were associated with around 69% of the variation of total mineral N in tree pit soils from commercial zones (Table 5.3).

MARS models indicated that the concentrations of the nutrients in residential zones were significantly related to different independent factors. Potassium concentration was positively correlated with the SOM content of the tree pit soil (r=0.44 for log SOM<0.76, $p<0.01$). However, K concentration was negatively correlated with street width (r=-0.45 for log $\text{StW}^2>1.02$, $p<0.01$). Soil organic matter content, street width, tree pit cover material (bare soil or flowerbeds), and tree pit volume were associated with around 68% of the variation of K concentration in residential zones (Table 5.4). Calcium concentrations in the tree pit soils from residential zones were positively correlated with SOM content (r=0.42 for logSOM<0.76 $p<0.05$). Soil organic matter content, soil age, and sand/gravel as the surficial deposit were correlated with almost 43% of the Ca variation in the tree pit soil in residential zones (Table 5.4).

Table 5.4. Predictive basis functions for nutrients in tree pit soils from residential zones

Variable[†]	Basis functions [‡]	EF[††]
Log K	2.65 - 1.41 × max(0, LogStW^2-1.02) - 0.19 × max(0, bare soil-0) - 0.87 × max(0, 0.76-logSOM) - 0.22 × max(0, flower bed-0) - 0.50 × max(0, logPitV-0.08)	0.68
Log Ca	3.73- 0.57 × max(0, 0.76-logSOM) - 0.38 × max(0, 1.25-logAge) + 0.25 × max(0, Sand/Gravel-0)	0.43
Log Mg	2.15 - 1.06 × max(0, 0.76-logSOM)	0.38
Log Na	2.05- 0.36 × max(0, Clay-0)	0.22
Log P	1.84- 0.25 × max(0, LogAge^3-2.20) + 1.81× max(0, -0.12-logDisSt)	0.29
Log Mineral N	1.44 - 1.38 × max(0, 0.02-LogDisSt^2) + 0.24 × max(0, bare soil-0) - 0.27 × max(0, Clay-0)	0.51

[†] All logarithms are base-10

[‡] DisSt = distance (of the tree pit) from the curb (street); PitV = (tree) pit volume; SOM = soil organic matter; StW = street width

[††] EF= efficiency of model

The variation of other nutrients in residential zones was partially accounted for in MARS models. Magnesium concentration in tree pit soils from residential zones was positively correlated with SOM (r=0.62 for log SOM<0.76, $p<0.01$). This relationship explained around 38% of the Mg variation in the tree pit soil from residential land use zones (Table 5.4). The presence of surficial clays accounted for around 22% of the variation of Na in tree pit soil from residential land use zones (Table 5.4). Phosphorus was negatively correlated with the age of tree pit soils (r=-0. 50 for log $\text{Age}^3>2.20$, $p<0.01$). Soil age and the distance of the tree pit from the curb explained around 29% of the variation of P concentration in tree pit soils from residential land use zones (Table 5.4). Bare soil surfaces in tree pits, the presence of surficial clay deposits, and the distance of the tree pit from the curb in residential zones explained around 51% of the total mineral N variation in the tree pit soil from residential land use zones (Table 5.4).

5.4.2. Discussion

Soils in urban tree pits are very heterogeneous in terms of characteristics such as concentration of soil nutrients, due to direct effects of the urban environment (*e.g.,* physical disturbances), indirect effects (*e.g.,* atmospheric deposition of pollutants such as potentially toxic metals and organic chemicals), and the interacting processes that relate them (Pouyat et al., 2010). We excluded some variables from this discussion, such as the distance of the tree pit from the curb, the nature of the surficial geologic deposit, and the tree pit volume, because they did not have a highly significant statistical relationship ($r<0.35$) with the concentrations of Na or the soil nutrients of interest. Other factors, however, such as soil age, soil pH, SOM content, tree pit cover type and street width in different land uses were significantly correlated with differences in soil chemical properties. The high CV that were observed might be associated with anthropogenic processes (Zhang et al., 2009) including the use of de-icing salt on the street (as a possible source of Na), deposition of residues from fossil fuel combustion (as a possible source of mineral N), or the application of cover materials to tree pit soils (as a possible source of K) (Li et al., 2013b).

Land use

According to Szombathová et al. (2009), land use type (*e.g.,* commercial vs. residential zones) can affect soil properties in urban areas. Similar results were found in Montreal by Jutras et al. (2010). High EF values for MARS models of soils in commercial zones indicated effects of SOM, soil pH, soil age and street width on nutrient availability in commercial zones (Table 5.3) stronger than those in residential zones (Table 5.4). The results of independent-samples t-tests showed that the concentrations of Na in tree pit soils from the commercial zone were significantly higher ($p<0.01$) than in those from residential zones. These results corroborate those of Pouyat et al. (2007) in Baltimore, MD who observed significantly higher concentrations of Na in soils next to constructed elements such as roads and construction zones in comparison with other land use zones. On the other hand, the results of independent-samples t-tests indicated significantly ($p<0.05$) lower concentrations of K in tree pit soils from commercial zones as compared to those from residential zones. According to Norrström and Bergstedt (2001), high concentrations of Na can displace K adsorbed between the layers of 1:2 type clays in the soil and can therefore result in K leaching from the soil.

Our results did not indicate any significant differences in other variables (Ca, Mg, total mineral N, and P) between tree pit soils from commercial and residential zones. As the results of our study indicated (Table 5.1), nutrients in both commercial and residential zones exceeded the values recommended by Whitcomb (1987) for horticultural soils. Pouyat et al. (2007) also found that, although some of the soil chemical and physical properties were significantly different among various land use zones in Baltimore, most sites had sufficient available soil nutrients to support tree growth.

Soil age (time after tree transplanting)

In general, nutrient availability was positively related to soil age. According to Davies et al. (2010), the gradual dissolution of concrete from impervious surfaces such as buildings and sidewalks can be responsible for high levels of bicarbonate, Ca and other ions associated with concrete in urban runoff water. The exposure of tree pit soil to this runoff water can cause the accumulation of Ca. This process might explain the positive association between soil age and available Ca in soils from residential zones and also the significantly higher concentration of Ca (p<0.01) in both commercial and residential zones as compared to the maximum recommended value.

The availability of other nutrients such as K and Mg also increased with soil age in our study. Scharenbroch et al. (2005) observed significantly higher K concentrations in older urban landscapes (age of 64 years) as compared to newer ones (age of 9 years). They attributed the higher concentration of nutrients in older urban soils to decreased soil disturbance. According to Scharenbroch et al. (2005), as time passes, the associated impacts of the urban environment on soil may be reduced and therefore the physical, biological, and chemical properties of soil can be improved and the plant-availability of nutrients such as K may increase.

Soil age may be negatively correlated with the availability of some other nutrients such as total mineral N and P in tree pit soils. The decrease in total mineral N until 19 years (Log age<1.28) and P concentrations in the tree pit soils in our study might be attributable to limited cycling of SOM (Lambers et al., 2008). Organic matter is lost in urban soils through litter removal and by oxidation, erosion, and soil removal (Scharenbroch and Lloyd, 2004). The decrease in total mineral N and P can also be attributed to the accumulation of de-icing salt and trace metals in tree pit soil over time. According to Green et al. (2008a), the use of road salts can inhibit nitrification in the roadside soil because of the higher sensitivity of nitrifiers to salinity in comparison to the ammonifiers, and therefore a shortage of NO_3^- and an accumulation of NH_4^+ may occur. Cation exchange competition from Na^+ can also increase NH_4^+ leaching from the roadside soil. In samples of soils older than 19 years, however, the total mineral N began to increase. Lambers et al. (2008) attributed increased amounts of mineral N in some situations to N deposition from airborne particles over time.

The accumulation of trace metals such as Cu and Zn in the tree pit soils over time (Kargar et al., 2013) can inhibit the growth of the fungi which make nutrients such as P available for tree roots (Pezzente, 1997). Also, gradual binding of P with carbonates from the weathering of buildings can limit the availability of P in the tree pit soil as time passes (Li et al., 2013c). These mechanisms might explain the P concentrations in our study which, in 20% of the soil samples from commercial zones ($p<0.01$), were lower than the values recommended by Whitcomb (1987) for horticultural soils.

Soil pH

The pH values of urban soils can be higher than their natural counterparts. These elevated pH values can originate from the application of NaCl as de-icing salt (Craul, 1992b). The use of NaCl to melt winter ice on streets and sidewalks introduces Na^+ into the soil, displacing H^+ from cation exchange sites so that H^+ is flushed from the soil and the pH value of the soil will increase (Roberts et al., 2006). The positive relationship observed in our study between pH and Na in commercial zones corroborates this possibility. The weathering of buildings made of bricks and cements can also increase the amount of Ca and carbonate in the soil and elevate the soil pH (Howard and Olszewska, 2011). This is in agreement with the positive relationship between pH value and Ca concentrations that we observed in commercial zones ($r=0.54$, $p<0.01$).

Soil pH is one of the factors that control nitrification. At low pH, the ability of nitrifiers to absorb N is very limited (Ste-Marie and Paré, 1999), while nitrification rates have been found to increase with soil pH (Nugroho et al., 2007). The positive relationship between total mineral N and pH in commercial zones in our study supports this hypothesis.

Soil organic matter

Retention of Ca^{2+}, Mg^{2+}, and K^+ by cation exchange in the soil and the release of N and P by mineralization are two of the many beneficial functions of SOM (McBride, 1994d). The statistical models developed in this study demonstrated a significant positive relationship between SOM content and the plant-available K and Mg concentrations in commercial and residential zones, total mineral N concentrations in commercial zones, and Ca concentrations in residential zones. Other studies have shown positive correlation between tree growth and concentrations of nutrients like K, Ca, and Mg in the soil, depending on the amount and the quality of organic matter input (*e.g.,* litter quality) (Clarholm and Skyllberg, 2013; Zerpa et al., 2010). Mack et al. (2014) studied the effect of organic matter removal on nutrient availability by litter from forest floors during 15 years. After 15 years, N and P were less available in the treatments from which organic matter was removed. In spite of the removal of the residues, Mack et al. (2014) did not observe significant reductions in below- or above-ground productivity of forest trees. They attributed the lack of difference in tree productivity before and after organic matter removal to increased soil moisture and temperature immediately after organic matter removal, which resulted in higher mineralization rates of labile pools of nutrients (including root residuals) as well as higher rates of nutrient translocation from senescing tissues.

Considering the positive relationship of total mineral N with SOM content only in the samples with SOM content <5% (or log SOM<0.74) and the negative correlation of total mineral N with soil age less than 19 years (Log age<1.28), it appears that in younger soils the total mineral N originates mainly from decomposition of SOM. The importance of this source of N decreased with time, until around 19 years after transplanting, because of the limited cycling of SOM (Lambers et al., 2008). This limited cycling of SOM in urban tree pits can be attributed to the small return of leaf litter to the soil (Roberts et al., 2006). Conjointly, the gradual input of Ca from the weathering of buildings and the formation of bonds between major organic functional groups (carboxyls and phenols) and Ca in the soil might fortify the tertiary structure of SOM, increasing its resistance to degradation by microorganisms, and thereby reducing the availability of N over time (Clarholm and Skyllberg, 2013). However, after around two decades, the availability of total mineral N started to increase again, possibly due to the deposition of N as airborne particles (Lambers et al., 2008).

Apart from leaf litter, repeated application and decomposition of the tree pit cover material such as wood chips can also increase SOM content and promote biological activity in tree pit soils (Urban, 2008). The resulting increase in microbial activity can make nutrients more available in the soil over time (Fraedrich and Ham, 1982; Holtz et al., 2004). In our study, the positive relationship between the abundance of available K in soils collected from tree pits in commercial zones and the application of wood chips as the tree pit cover corroborates this possibility.

Street width

Tree pits located beside wide, heavily traveled streets may be subject to higher salt levels than those adjacent to narrower streets with less vehicular traffic specifically in commercial zones (Berrang et al., 1985). The high coefficient of variation of Na concentration (CV=1.02) in the soil samples, 26% of which significantly exceeded the threshold for trees in commercial zones recommended by Hootman et al. (1994), might be related to variability in street width. The positive correlation of Na concentrations with street width in the tree pit soils in commercial zones confirmed this relationship. The variability of Na concentrations in soil can affect the availability of nutrients such as K and P in the tree pit soil. Deficiency of K (as in 9% of the soil samples from commercial zones ($p<0.01$)) as compared to the values recommended for horticultural soils by Whitcomb (1987) might be related to displacement of K by Na from de-icing salt. Norrström and Bergstedt (2001) observed that high Na^+ concentrations from de-icing salt increased leaching of base cations, including K^+, from the soil of a roadside infiltration trench.

5.5. Conclusion

Despite the heterogeneity among urban soils, there are discernible patterns relating nutrient availability in the surface soils of tree pits with SOM, soil age, and soil pH, as well as with environmental factors such as land use and street width. We hypothesized that these relationships might be attributable to factors such as litter input and the use of wood chips on the surface of the tree pits, as possible sources of nutrients including K and Mg. Long-term exposure to de-icing salt may increase soil pH and decrease soil nutrient retention capacity. The splashing of de-icing salt, accumulation of trace metals from heavy traffic on wider streets in commercial zones, and weathering of buildings can all increase concentrations of Na, Ca, and trace metals such as Cu and Zn in tree pit soils and therefore decrease the availability of nutrients like K, total mineral N, and P. In general, nutrients in both commercial and residential zones exceeded the recommended values for horticultural soils. Stronger relationships between environmental conditions, soil chemical factors, and nutrient availability were observed (higher EF values of MARS models) in soils from commercial zones as compared to those from residential zones. Based on our results, future research should examine the effects of environmental conditions and soil properties on nutrient availability across various spatial and temporal scales. Further research should evaluate how different measures for managing limiting factors, such as soil contamination with de-icing salt and trace metals, can affect nutrient availability. This would provide specific information to help develop appropriate strategies for urban design planning. One of these strategies could be to develop an optimized soil mixture for use in Montreal tree pits that would buffer the detrimental effects of the urban environment and would provide the nutrients required for healthy, long-lived trees.

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Connecting statement IV

In chapters 4 and 5, we found higher than recommended concentrations of trace metals in some tree pit soils sampled in Montreal, however, no deficiency was observed in plant-available nutrients in the soils. In chapter 6, we tried to increase the capacity of tree pit soil for sorption and retention of trace metals, by amending the soils with organic matter. Two types of organic matter, compost and biochar, were added to the tree pit soil. The improved mixture was identified through sorption and desorption tests on soil mixtures containing different percentages of compost and biochar.

Chapter 6

Immobilization of trace metals in contaminated urban soil amended with compost and biochar

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6.1. Abstract

Urban soil amendment with organic matter can increase the steady state concentration of trace metals in urban soil. Different types of organic matter have different abilities to sorb and retain trace metals. The potential of urban soil amended with compost derived from mixed green and table waste and with maple wood-derived biochar to retain trace metals (Cu, Zn, Cd, Pb) in the presence of de-icing salt (Na) was studied in a leaching test. Soil amended with compost retained significantly higher concentrations of Zn and Pb, as compared to soil amended with biochar, possibly due to the high cation exchange capacity of compost and its positive effect on soil pH. Indicating high ability for retaining trace metals, compost can bind contaminants originating from urban runoff water percolating through urban soil and provide a healthier medium for street tree growth.

Keywords: Sorption capacity, de-icing salt, organic matter, trace metals, urban soil

6.2. Introduction

6.2.1. Contaminants in urban soil

Urban soils are specifically threatened by contaminants such as trace metals (Li et al., 2013b) and de-icing salt (Cunningham et al., 2008). These contaminants in urban soil can be toxic to soil microbes and invertebrates, trees, and human (Jim, 1998a; Luo et al., 2012). Mobile metals in urban soil can also contaminate the underlying groundwater (Clark and Pitt, 2007).

The mobility of trace metals in the soil is a function of metal characteristics, total concentration of metals in the soil, and various soil properties (Brümmer, 1986; Linde et al., 2007; Waterlot et al., 2013). Some authors found a positive correlation between Cu retention and pH, soil organic matter (SOM), cation exchange capacity (CEC), and the sum of basic cations (mainly exchangeable Ca) (Covelo et al., 2007; Matos et al., 2001; Sherene, 2010).

Zinc retention can be dependent on soil pH and SOM. According to Güngör and Bekbölet (2010), an increase in Zn release to the soil solution at high pH values can be attributed to the decrease in intra and inter molecular hydrogen bonds in humic acid molecules that make them more open and linear in shape and increase in repulsive forces between the dissociated functional groups. Zinc dissolution can also increase at low soil pH. The reason might be the dissolution of Zn bound to different soil constituents, such as calcite, Fe/Al oxides, which are positively charged and probable H^+–Zn^{2+} exchange processes occurring on the mineral surfaces. For a given pH, soils with higher SOM content can provide a greater sorption capacity than soils with less content of SOM (Díaz-Barrientos et al., 2003).

According to Rashti et al. (2014), soil features including pH, SOM and CEC are negatively associated with Cd desorption. Various studies (Covelo et al., 2007; Matos et al., 2001) reported that Pb desorption from soil was negatively related to clay content, pH, and the content of organic matter. According to Strawn and Sparks (2000), by increasing SOM content, the rate of Pb sorption decreases. With higher levels of SOM in soils, there is often an increase in DOC. Dissolved organic carbon has the ability to form Pb-complexes (Shahid et al., 2012). However, Strawn and Sparks (2000) observed a decrease in Pb desorption as the amount of SOM increased. They attributed the slow desorption reaction to the SOM fraction of the soil, and to the larger activation energy that the desorption reaction requires as compared with that required for sorption.

Many studies indicated the high vulnerability of leaching trace metals in urban soils as a consequence of exposure to high concentration of NaCl as de-icing salt (Li et al., 2015). According to Nelson et al. (2009), the mobilization of trace metals under the effect of de-icing salt can happen through three main mechanisms including cation exchange, colloid dispersion, and Cl-complex formation. When Na^+ is present at high concentrations, it displaces naturally occurring Ca^{2+} and Mg^{2+}. Exchange of Ca^{2+} and Mg^{2+} with Na^+ in soil exchange sites and deflocculating soil particles can increase colloid mobility and therefore associated trace metal mobility (Green et al., 2008a).

6.2.2. Organic amendment of urban soil

It is commonly assumed that amending urban soil with organic materials such as compost can help the soil adsorb contaminants including trace metals and de-icing salts (Wuana and Okieimen, 2011). Owing to a spontaneous microbial oxidation of numerous raw sources such as green wastes, compost can be produced as a biologically stable, humified organic matter end-product (Beesley et al., 2014). Pardo et al. (2014) indicated that amending soil with compost prepared from solid olive-mill waste significantly decreases the mobile concentrations of Cd, Cu, Pb and Zn in contaminated mining loamy sand. Compost retains metals by raising soil pH, cation exchange, complexation, sorption, the presence of P, Al compounds, and other inorganic minerals or a combination of them (Bolan et al., 2014; Karami et al., 2011; Paradelo et al., 2011).

The application of biochar, as a porous, low-density carbon rich material produced from biomass combustion under low-oxygen conditions, can also reduce the mobility of trace metals in contaminated soils and therefore decrease the risk of these metals being taken up by plants (Beesley and Dickinson, 2011; Beesley et al., 2010). The potential of biochar for metal sorption can be related to the large surface area, CEC and porosity of biochar and an increase in the soil pH after biochar addition (Houben et al., 2013b; Kloss et al., 2014; Park et al., 2011). Also, Biochar carries a negative charge on its surface; therefore incorporation of biochar with soil can make the negative surface charge of the variable charge soils more negative. As a result, the adsorption affinity of the soil surface for cations such as trace metal cations will increase (Jiang et al., 2012b).

Conversely, there is indication that biochar might not immobilize trace metals as efficiently as some other amendments. For instance, Hanauer et al. (2012) studied the sorption of Cd, Cu, and Zn in mining soil with neutral pH level and high content of clay amended with iron grit, natural zeolite, biochar, and Divergan®[1] for 12 months. In this study, biochar was derived from peanut hull residues pyrolyzed at 480 ºC and indicated the least effect on the sorption of the trace metals. The feedstock and pyrolysis conditions used for biochar production likely affect its trace metal sorption capacity (Cao et al., 2011; Uchimiya et al., 2010).

6.2.3. Sorption capacity of urban soil

The mobility of metals in the soil environment is directly related to their partitioning between soil and solution, which is known as distribution coefficients (K_d) (Evans, 1989). The K_d values indicate the capability of a soil for sorption and retention of a contaminant and the extent of its movement to the liquid phase (Reddy and Dunn, 1986). A high K_d value indicates high metal retention by soil solid phase, which results in low metal bioavailability. Similarly, a low K_d value indicates that a higher proportion of the metal will be released to the soil solution (Shaheen, 2009). According to Buchter et al. (1989), soil pH and CEC are the most important characteristics affecting log K_d values of cation species. In general, high pH and high CEC soils retained greater quantities of the cation species than did low pH and low CEC soils.

This study is focused on determining how compost and biochar, used both singly and in combination, affect the chemical characteristics of urban soil (tree pit soil as a case study) and its sorption and retention of Cu, Zn, Cd and Pb in the presence of de-icing salt (Na). The null hypothesis in this research is that neither compost nor biochar increased the tree pit soil sorption capacity for trace metals under the effect of de-icing salt. The objective of this research is related to the broader goal of designing a soil medium that can reduce groundwater pollution and promote a healthier and longer life for street trees.

6.3. Materials and methods

6.3.1. Soil, compost and biochar

In order to compare the ability of compost with biochar for decreasing the mobility of Na, Cu, Zn, Cd and Pb in tree pit soil, sorption and desorption tests were conducted using soil mixtures with different percentages of compost and biochar. The fresh soil used as the basis for

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[1] As a scavenger and a product of BASF, Divergan is usually used as a fining agent in the beverage industry. It has nitrogenous heterocyclic compounds and high inner surface, which result in metal-complexing properties for Divergan (Hanauer et al., 2012).

the soil mixtures was a sandy loam provided by the borough of Ville-Marie, Montreal, Quebec, Canada. The compost was derived from mixed green and table waste from the West Island region of Montreal. The biochar was made from maple wood pyrolyzed at 450°C.

6.3.2. Preliminary analysis of soil, compost, and biochar

A preliminary analysis (pH, CEC, organic matter content, and texture) of the soil was compared with the standards for tree pit soil for the City of Montreal (Table 6.1) (City of Montreal, 1995) and the analysis results of compost and biochar. Measurement of pH was done with an Accumet AR10 meter (Fisher Scientific Inc., Pittsburgh, PA) in a 1:2 soil-to-solution ratio (7 g soil/14 mL H_2O) (Hendershot et al., 1993b). Exchange capacity for cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) was measured in soil mixtures, compost, and biochar extracted with 0.1 M $BaCl_2$ following Hendershot et al. (1993a). Soil organic matter was measured by loss on ignition (Schulte et al., 1991). Soil texture was determined using a hydrometer, following Bouyoucos (1936).

Table 6.1. Preliminary results of soil analysis as compared to the standards for tree pit soil for the City of Montreal and the analysis results for compost and biochar

Variable	Na	Cu	Zn	Cd	Pb	EC† (µs cm^{-1})	pH	CEC‡ (cmol$_{(+)}$ kg $^{-1}$)	Organic matter (%)	Soil texture (%) (clay/silt/sand)
	mg kg^{-1}									
Standard	_	_	_	_	_	_	6.00-7.00	10.0-20.0	4.00-7.00	_
Ville-Marie soil	131	18.1	87.9	0.53	16.8	1.38	7.66	17.7	6.3	12.3/9.7/78.0
Compost	308	33.7	106	0.49	16.1	1.56	8.07	74.7	57	_
Biochar	109	10	129	1.43	4.33	1.44	7	12.3	71.8	_

†EC= electrical conductivity

‡CEC= cation exchange capacity

6.3.3. Soil mixture preparation

To prepare the soil mixtures for the sorption and desorption test, the unamended, uncontaminated soil was dried at room temperature for 14 days and passed through a 2-mm metal sieve to remove large particles. Different percentages of compost (maximum 15% by weight) and biochar (maximum 10% by weight) were combined with the uncontaminated soil. A total of nine combinations of soil, compost, and biochar were used in triplicate in this study (Table 6.2) according to a central composite rotatable design.

Table 6.2. Compost and biochar percentages (by weight) in soil mixtures defined according to central rotatable composite design

Treatment	Soil (%)	Compost (%)	Biochar (%)
T1	96.3	2.2	1.5
T2	78.7	12.8	8.5
T3	85.7	12.8	1.5
T4	89.3	2.2	8.5
T5	92.5	7.5	0
T6	82.5	7.5	10
T7	95	0	5
T8	80	15	5
T9	87.5	7.5	5

6.3.4. Sorption and desorption test

The sorption test was performed on the soil mixtures for ten days in order to provide the soil mixtures sufficient time to equilibrate with the contaminants, as indicated by stable electrical conductivity (EC) values in the leachate measured by CDM 83 conductivity meter (Radiometer, Copenhagen, Denmark). Using a programmable vacuum extractor, columns containing 15 g of soil each were gradually leached at a constant rate (2-3 mL h^{-1}) with 20 mL of solution per day. The solution used for contaminating the soil mixtures contained the concentrations shown in Table 6.3. For the desorption test, the leached soils obtained from the sorption test were dried at room temperature, weighed and re-leached with 400 μM $CaCl_2$-$CaSO_4$ following the same procedure as in the sorption test.

Table 6.3. The component concentration of percolating solution in sorption and desorption tests

Type of test	Na	Cu	Zn	Cd	Pb	$CaCl_2$	$CaSO_4$
	mg L^{-1} day^{-1}						
Sorption	66	21.4	90.63	3.91	82.3	29.4	34.43
Desorption	-	-	-	-	-	29.4	34.43

6.3.5.Chemical analysis

The contaminated soil mixtures (after sorption test) and the soil leachates (collected on the tenth day of desorption test) were analyzed for Na, Cu, Zn, Cd and Pb using an inductively coupled plasma–mass spectrometer (820-MS, Varian, Melbourne, Australia) (Hendershot et al., 2008). The certified reference material used as the quality control of the analysis of total concentration of trace metals was SED 98-4 provided by the Environment Canada Proficiency Testing program. The recovery percentages of the SED 98-4 were as follows: 165% for Na, 107% for Cu, 100% for Zn, 126% for Cd, and 107% for Pb. Exchangeable base cations (Ca^{2+}, Mg^{2+}, K^+ and Na^+) of soil mixtures after adsorption test were extracted with 0.1 M $BaCl_2$ following Hendershot et al. (1993a).

The pH values and electrical conductivity of the soil leachates after desorption test were determined using an Accumet AR10 meter (Fisher Scientific Inc., Pittsburgh, PA) and CDM 83 conductivity meter (Radiometer, Copenhagen, Denmark), respectively. Dissolved organic carbon (DOC) was also determined in the soil leachates after desorption test using a Sievers Innovox TOC analyzer (GE Analytical Instruments Inc., CO, US).

6.3.6. Statistical analysis

Using the concentrations of $CaCl_2$-$CaSO_4$ extractable metals in the soil treatments, a bivariate correlation analysis (Spearman correlation coefficient) was done between Na, Cu, Zn, Cd, and Pb in the soil samples and some selected soil characteristics (*e.g.*, pH, CEC, EC, and DOC). The partitioning coefficient (K_d), defined as the ratio of the total bound contaminant (mg kg $^{-1}$) to that in soil leachate after equilibrium (mg L^{-1}), was calculated for the studied metals. To identify the importance of compost and biochar in modifying the partitioning coefficients of the metals of interest in the soil mixtures, multiple linear regression was applied using SPSS statistics (V.21, IBM). The regression input data were first standardized using standard score (Z-scores) following Eq. 6.1, where x is the data value, μ is the average of the data and δ the standard deviation of the data. The normality of the dataset was then confirmed using the Kolmogorov - Smirnov test.

$$Z=\frac{x-\mu}{\delta} \qquad \text{Eq.[6.1]}$$

The k_d values were then used for calculating the steady state concentration of metals in the soil. The steady state concentration is the maximum concentration of metals retained in soil mixture, as the concentration of the metals in the soil leachates equals the concentration of the metals in runoff water. In this case, steady state concentration of metals can be calculated following Eq.6.2:

$$S=K_d\times Conc \qquad \text{Eq.[6.2]}$$

Where S is the steady-state concentration retained in soil mixture (mg kg^{-1}), K_d is the distribution coefficient (L kg^{-1}), and Conc is the concentration of metals in run-off water (mg L^{-1}). Because of the lack of the measurements for trace metal and de-icing salt concentrations in runoff water collected from streets in downtown Montreal in existing studies, the average concentration of the metals in runoff water collected from traffic areas in Germany, U.K, Netherland, and U.S derived from Göbel et al. (2007) was used as Conc in Eq. 6.2 (Table 6.4). In order to find the optimum percentage of compost and biochar in soil mixture for sorption and retention of these metals, the mean values of the steady state concentrations of the metals in different soil mixtures were compared using the Duncan test in SPSS statistics.

Table 6.4. Average concentrations of metals in runoff water of traffic areas (Göbel et al., 2007)

Metal	Average concentration
Na (mg L^{-1})	108
Cu (μg L^{-1})	97
Zn (μg L^{-1})	407
Cd (μg L^{-1})	1.9
Pb (μg L^{-1})	170

6.4.Results and Discussion

6.4.1. Metal immobilization in amended soil mixtures

The comparison of sorption capacity (K_d values) (Table 6.6), calculated from total metal concentration in soil and in soil solution (Table 6.5), in different soil mixtures indicated the following order for mobility of metals: Na>Zn≥Cu>Pb>Cd. This result contradicts Öborn and Linde (2001), who observed higher mobility for Cd as compared with Zn, Cu and Pb in urban soil leachates. The mobility of metals can be dependent on total metal concentration in the soil (Adhikari and Singh, 2003; Luo et al., 2012) and their properties such as their electronegativity and charge-to-radius ratio (Paradelo et al., 2011). Mainly originated from de-icing salt (NaCl), Na has low electronegativity and low charge-to-radius ratio, which results in higher mobility of Na in soil leachates as compared to Cu, Zn, Cd and Pb. Different studies observed high susceptibility of roadside soils to leaching of trace metals as a result of exposure to high concentration of NaCl as de-icing salt (Li et al., 2015). One of the mechanisms through which Na makes the roadside soil vulnerable to the leaching of trace metal such as Zn and Cd is cation exchange (Li et al., 2015; Norrström, 2005). This can be confirmed by negative correlation of Na with Cd and Zn in the soil leachates collected after the desorption test (Table 6.7).

In soils exposed to high Na concentrations, soil aggregates break up. Dispersion of soil aggregates can release the organic matter and clay that complex with metal species. This in turn promotes the mobility of metals such as Cu via colloid assisted transport (Kluge et al., 2014; Nelson et al., 2009). The significant positive correlation between EC and Cu (Table6. 7) in the leachate of the soil mixtures also corroborates this possibility. The positive correlation of high EC values of soil solution and the use of de-icing salts and elevated leaching concentrations of trace metals such as Cu in roadside soils is in line with other studies (Kluge and Wessolek, 2012).

Table 6.5. Chemical characteristics (pH, CEC, DOC, EC), sorbed metal concentrations, $CaCl_2$-$CaSO_4$ extractable metal concentration from control soil (SL), compost (CP), biochar (BC), and soil mixtures (T1 to T9). Values are the mean (standard error) of sample replications.

Sample ID	Chemical characteristics				Sorbed metal concentration					$CaCl_2$ –$CaSO_4$ extractable metals				
	pH	CEC[†]	DOC[‡]	EC[§]	Na	Cu	Zn	Cd	Pb	Na	Cu	Zn	Cd	Pb
		$cmol_{(+)}$ kg^{-1}	%	µs cm^{-1}	mg kg^{-1}					mg L^{-1}				
SL	7.06	17.7	0.91	120	574	93	466	21	428	2.65	0	0.05	0	0.01
	(0.02)	(0.27)	(0.05)	(0.00)	(16.2)	(11.5)	(62.3)	(3.58)	(64.8)	(0.74)	(0.00)	(0.00)		(0.00)
CP	7.91	74.7	11.2	241	1314	114	474	20	446	9.62	0.01	0.03	0	0
	(0.00)	(0.71)	(0.60)	(0.01)	(53.7)	(11.2)	(29.5)	(1.42)	(95.2)	(0.20)	(0)	(0.00)		(0.00)
BC	7.64	12.3	29.5	213	215	49.1	223	10	273	1.26	0.07	0.13	0	0.09
	(0.03)	(0.85)	(2.00)	(0.00)	(8.94)	(8.60)	(1.58)	(0.58)	(57.0)	(0.11)	(0.01)	(0.01)		(0.00)
T1	7.39	19	1.47	128	553	100	450	21	479	1.22	0.01	0.06	0	0.01
	(0.00)	(0.19)	(0.13)	(0.02)	(29.7)	(3.04)	(31.8)	(1.28)	(2.58)	(0.02)	(0)	(0.00)		(0.00)
T2	7.6	25.5	2.47	153	636	164	650	35	906	1.61	0.01	0.03	0	0.01
	(0.02)	(1.36)	(0.28)	(0.00)	(3.98)	(74.3)	(96.4)	(7.57)	(50.3)	(0.55)	(0.00)	(0.00)		(0.00)
T3	7.54	25.9	2.57	149	726	126	540	26	622	1.6	0.01	0.04	0	0.01
	(0.00)	(1.31)	(0.60)	(0.01)	(53.7)	(11.2)	(29.5)	(1.42)	(95.2)	(0.20)	(0.00)	(0.00)		(0.00)
T4	7.21	20.4	3.62	135	564	103	435	21	500	1.2	0.02	0.09	0	0.01
	(0.03)	(0.23)	(2.00)	(0.00)	(8.94)	(8.60)	(1.58)	(0.58)	(57.0)	(0.11)	(0.01)	(0.01)		(0.00)
T5	7.29	23.6	2.13	138	616	97	453	20	461	1.46	0.01	0.05	0	0.01
	(0.01)	(0.40)	(0.20)	(0.01)	(36.2)	(15.2)	(90.9)	(4.91)	(83.8)	(0.40)	(0.00)	(0.00)		(0.00)
T6	7.32	20.5	2.37	145	628	121	548	26	637	1.49	0.01	0.05	0	0.01
	(0.03)	(1.29)	(0.50)	(0.02)	(13.8)	(5.85)	(2.22)	(0.74)	(77.8)	(0.52)	(0.00)	(0.01)		(0.00)
T7	7.23	17.8	1.13	130	575	105	465	22	552	1.27	0.01	0.07	0	0.01
	(0.01)	(0.36)	(0.06)	(0.01)	(22.7)	(20.0)	(14.4)	(1.34)	(156)	(0.22)	(0.00)	(0.00)		(0.00)
T8	7.58	23.9	2.68	151	686	182	758	39	1018	1.53	0.03	0.06	0	0.01
	(0.03)	(0.82)	(0.20)	(0.02)	(30.4)	(19.6)	(107.4)	(6.23)	(73.1)	(0.34)	(0.00)	(0.02)		(0.00)
T9	7.49	21.7	1.99	142	650	155	619	31	883	1.22	0.01	0.04	0	0.01
	(0.00)	(0.76)	(0.25)	(0.00)	(31.5)	(37)	(152.4)	(8.73)	(253)	(0.22)	(0.00)	(0.00)		(0.00)

[†] CEC= cation exchange capacity

[‡] DOC= dissolved organic carbon

[§] EC= electrical conductivity

Table 6.6. K_d values of control soil (SL), compost (CP), biochar (BC), and soil treatments (T1 to T9) for Na, Cu, Zn, Cd, and Pb

Sample ID	K_d † (L Kg^{-1})				
	Na	Cu	Zn	Cd	Pb
SL	236	19400	8720	928000	51600
CP	137	7870	13900	847000	92500
BC	171	670	1670	125000	3180
T1	452	16600	7400	648000	50400
T2	448	26600	22600	810000	80100
T3	465	14600	12300	855000	69700
T4	472	7710	5090	519000	37900
T5	447	14700	9220	491000	53300
T6	476	11800	11300	503000	58300
T7	471	15600	6720	524000	51300
T8	465	7240	14700	1050000	100000
T9	546	21100	13900	583000	90000

† K_d= distribution coefficient

Soil conditions (Tables 6.5 and 6.7) play a crucial role in determining the mobility of metals. According to Strobel et al. (2001) and Shaheen (2009), the release rate of metals like Cu and Pb into the soil solution can be related to pH, as the positive correlation between Cu and Pb and pH in our results also confirmed that (Table 6.7). If the mechanism of holding Cu and Pb in the soil is associated with exchange sites on soil particles, they will be easily extractable and sensitive to pH, because of the solubility of Cu and Pb hydroxide species (Li, 2006). Increase in soil pH, however, can increase the retention of cationic metals such as Cd to soil surfaces via adsorption, inner-sphere surface complexation, and/or precipitation (Shaheen, 2009). The negative correlation between soil pH and Cd concentration in soil solution (Table 6.7) also validates the increased Cd sorption with increased soil pH.

The mobility of metals like Cu and Pb in the soil leachates might also be attributed to the formation of soluble complexes with oxygen-containing functional groups of dissolved organic matter (Beesley and Dickinson, 2011). This was corroborated by the positive correlation between Cu and Pb concentrations and DOC in the soil leachates (Table 6.7). The lower mobility of Pb as compared to Cu may be attributed to stronger Pb fixation onto soil organic matter and Pb affinity to other adsorbing surfaces such as Mn and Fe oxyhydroxides and clay minerals in the soil mixtures (Moreno et al., 2006; Trakal et al., 2011).

The negative correlation of Zn and Cd concentrations with exchangeable cations, such as Ca and Mg, in the soil leachate (Table 6.7) supported the idea that cation exchange was the main mechanism controlling Zn and Cd mobility (Cavallaro and McBride, 1978). Positive correlation between exchangeable Ca and Mg and compost percentages in the soil mixtures (Table 6.7) corroborates that exchangeable Ca and Mg originate from organic amendments such as compost in the soil.

Our results indicated a low mobility for Cd. According to Kluge and Wessolek (2012), the low mobility of Cd in roadside soil can be related to high sorption capacity of soil and high pH values of roadside soil under the effect of de-icing salt, the influence of road building materials and alkaline dust from road surface abrasion. However, our result is in contrast to several other studies that indicated high mobility of Cd in urban roadside soil. Li et al. (2015) attributed the mobility of Cd to the formation of Cd-Cl complexes, which can penetrate to ground and surface water in areas exposed to de-icing salt.

Table 6.7. Spearman correlation coefficients between trace metal concentrations in soil leachates and soil chemical characteristics after desorption test

	Na	Cu	Zn	Cd	Pb	DOC	pH	EC	Ca_{exg}	Mg_{exg}	K_{exg}	Na_{exg}	CEC	CP	BC
Na	1														
Cu	-0.016	1													
Zn	-.687**	0.192	1												
Cd	-.692**	-0.022	.907**	1											
Pb	0.099	.841**	0.126	0.033	1										
DOC[†]	0.203	.852**	-0.104	-0.225	.852**	1									
pH	0.451	0.533*	-0.489	-.604*	.593*	.720**	1								
EC[¶]	0.5	.665*	-0.5	-.604*	.637*	.841**	.923**	1							
Ca_{exg}[‡]	.621*	0.137	-.874**	-.890**	0.209	0.396	.571*	.621*	1						
Mg_{exg}	.588*	0.066	-.841**	-.863**	0.198	0.33	.566*	.555*	.978**	1					
K_{exg}	0.357	.709**	-0.368	-0.429	.720**	.934**	.791**	.912**	0.549	0.456	1				
Na_{exg}	.577*	0.39	-.780**	-.841**	0.423	.621*	.786**	.841**	.934**	.901**	.736**	1			
CEC[§]	.599*	0.203	-.841**	-.896**	0.253	0.423	.610*	.654*	.989**	.962**	.577*	.945**	1		
CP[£]	.599*	0.318	-.777**	-.908**	0.309	0.49*	.685**	.719**	.947**	.919**	.605*	.942**	.969**	1	
BC[∂]	-0.226	0.385	0.215	0.195	0.41	0.457	0.34	0.384	-0.195	-0.301	0.46	0.022	-0.139	-0.056	1

* Significant at $p<0.05$

** Significant at $p<0.01$

[†] DOC= dissolved organic carbon

[¶] EC= electrical conductivity

[‡] exg=exchangeable

[§] CEC= cation exchange capacity

[£] CP= compost

[∂] BC=biochar

6.4.2.Comparison of the ability of compost and biochar to improve trace metal sorption in soil mixtures

The coefficients of determination (R^2) of multiple linear regression (Table 6.8) based on the K_d values (Table 6.6) indicated that the variation in partitioning of Zn and Pb between soil and soil solution was dominantly related to compost percentages in the soil mixtures. Different studies indicated the positive effect of compost on trace metal sorption in the soil. For instance, Paradelo et al. (2011) added compost from municipal solid waste at the rates of 3% or 6% dry weight to a cropped soil artificially contaminated with Pb and Zn. They observed the reduction for 99% of Pb and for 80% of Zn solubility in 0.01 M $CaCl_2$ extracts of soil amended with compost (6% dry weight).

The decrease in Pb and Zn availability in the soil amended with compost can be attributed to different factors. Increasing the strength of metal bonds to the soil matrix by displacing Pb from exchange sites to less labile forms such as metal complexes with humic and fulvic acids provided by organic matter in the soil can decrease Pb availability (Paradelo et al., 2011). This can be corroborated with the observed positive correlation between DOC and Pb in the soil solution after desorption test and also positive correlation between DOC and compost percentages in the soil mixtures (Table 6.7). According to Karaca (2004), the positive effect of compost on metal sorption may also be due to the high CEC of compost. The positive correlation of compost with CEC and negative correlation of CEC and Zn concentration in the soil leachates (Table 6.7) can confirm the results of Karaca's study (2004).

Steady state concentrations of Zn (Fig. 6.1-c) and Pb (Fig. 6.1-e) were measured in different soil mixtures (T1 to T9), control soil (SL), compost (CP), and biochar (BC). These measurements demonstrated that CP, T2, T3, T6, T8, and T9 had higher sorption capacities for Zn than did the other treatments, and CP, T2, T3, T8, and T9 had higher sorption capacities for Pb. Soil mixtures with 7.5% (w/w) or more compost (CP (100%), T2 and T3 (12.8%), T8 (15%), T6 and T9 (7.5%)) retained significantly more Zn and Pb than did the other treatments. However, no significant difference in sorption capacity was observed between treatments containing compost higher than 7.5% w/w. Therefore, it was concluded that 7.5% w/w can be selected as the optimum percentage of compost in a soil mixture in order to increase sorption capacity of the soil for Zn and Pb.

The use of compost did not significantly increase the retention of Na, Cu and Cd in the soil mixtures (Table 6.8). Comparing the steady state concentrations of Na and Cd in different soil mixtures after desorption tests (Fig. 6.1-a and Fig. 6.1-d) with the Duncan test indicated that there was no significant difference between soil mixtures (T1 to T9) and the control soil (SL). This suggested the soil was the main adsorbent of Na and Cd in the soil mixtures.

The wide range of compost percentages (2.2% to 12.8% w/w) in the treatments with highest sorption capacity for Cu (T1, T2, T3, T5 and T9) and the lack of significant difference between the steady state concentration of Cu in these treatments and control soil (SL) indicated that the soil may be a more important adsorbent of Cu as compared to compost (Fig. 6.1-b).

Table 6.8. The relationship of compost and biochar percentages with the partitioning coefficients of Na, Cu, Zn, Cd and Pb in soil mixtures, based on Z-scores

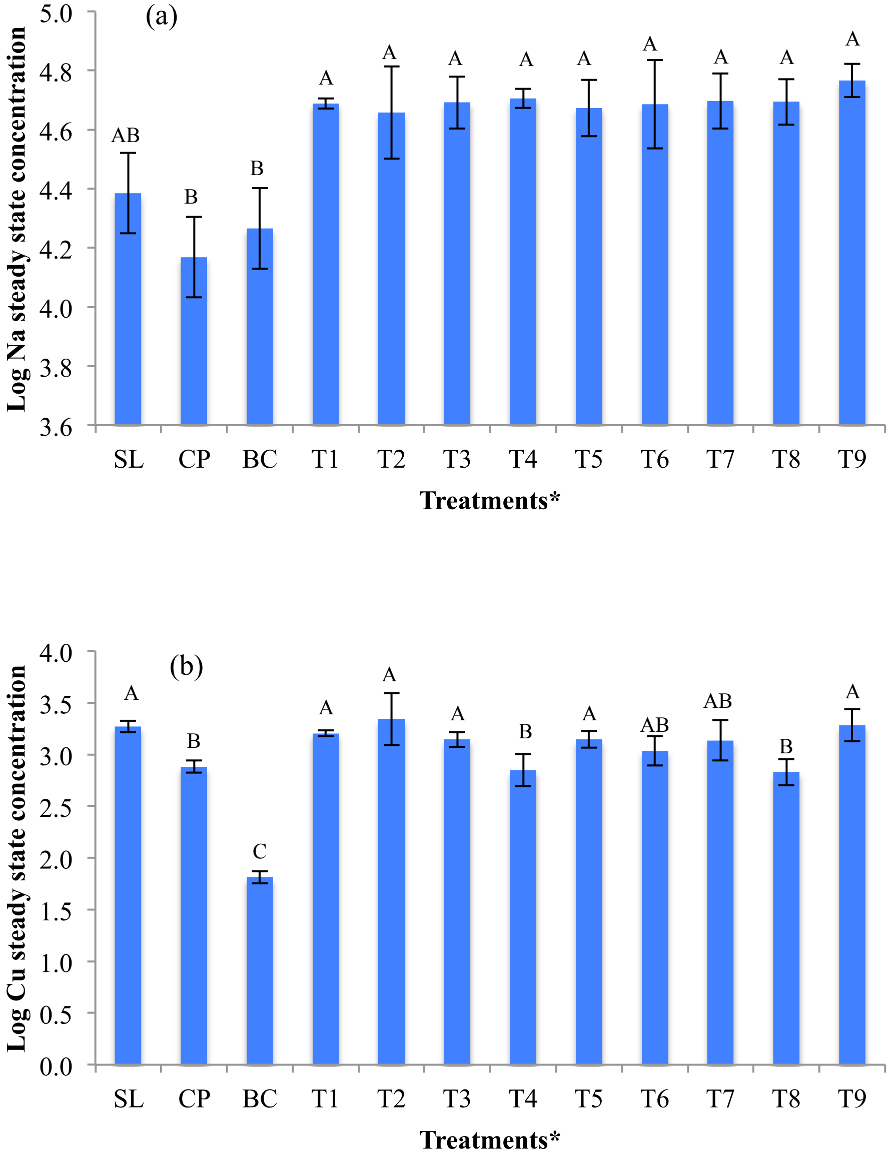
Z K_d	Intercept	Z compost	Z biochar	R^2
Na	-	NS[†]	NS	-
Cu	-	NS	NS	-
Zn	1.41**	3.57**	-	0.44
Cd	-	NS	NS	-
Pb	1.12**	2.76**	-	0.34

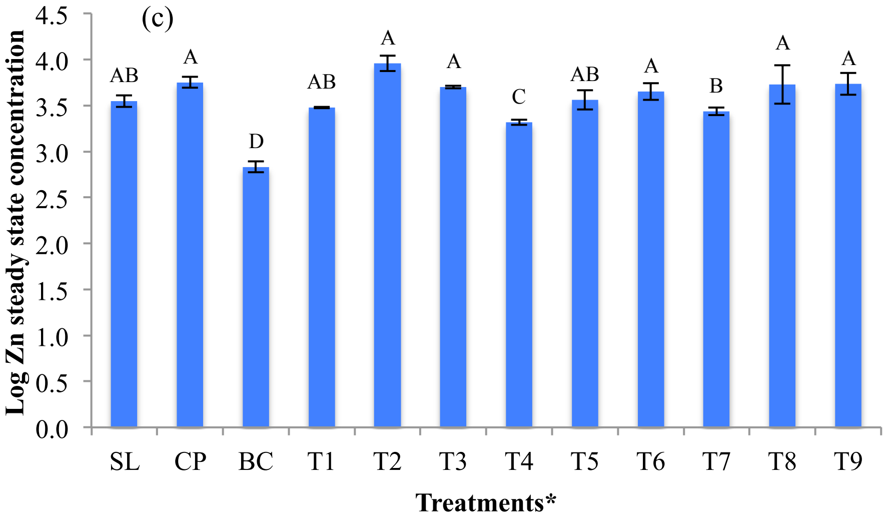
[†] NS: Not significant

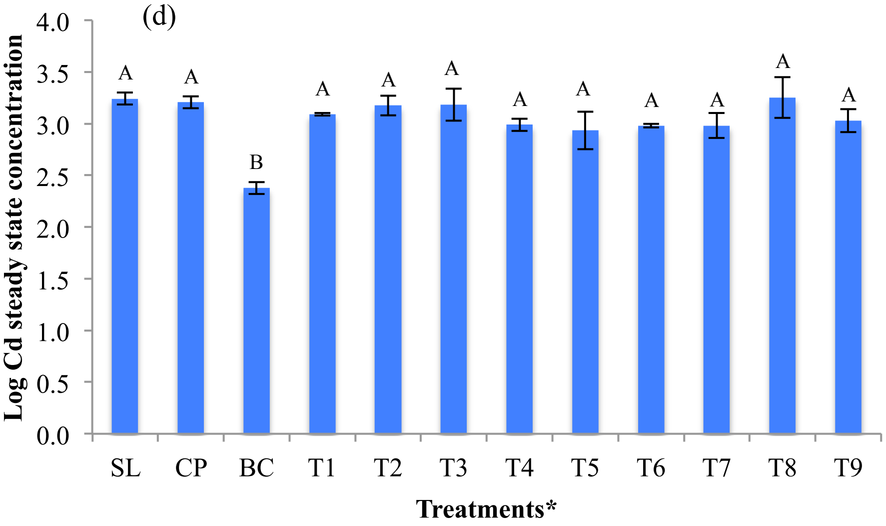
**Significant at $p<0.01$

Our results did not indicate any significant relationship between Na, Cu, Zn, Cd, and Pb partitioning coefficients and biochar percentages in the soil. Comparing steady state concentrations of Na, Cu, Zn, Cd, and Pb (Fig. 6.1) in soil mixtures (T1 to T9), control soil (SL), compost (CP), and biochar (BC) indicated significantly lower concentration of all the studied metals in biochar (BC). This finding contrasts with studies in which leachate concentrations of Cu, Zn, Cd and Pb decreased in biochar-amended soils (Beesley et al., 2010; Houben et al., 2013a; Karami et al., 2011; Trakal et al., 2011).

A few studies have indicated that biochar may not always decrease the mobility of trace metals. For instance, Kelly et al. (2014) showed that in mine tailings with high concentrations of toxic elements, biochar made from pine wood did not reduce the leachate concentrations of Cu, Zn, Cd, and Pb. Kloss et al. (2014) also reported that the application of woodchip-derived biochar had no impact on Cu, Cd, and Pb concentrations in leachates from agricultural soils. According to Hanauer et al. (2012), the sporadic behavior of biochar in retaining trace metals might be related to the feedstock and conditions of manufacture. Kloss et al. (2014) attributed the increase of metals in leachates from biochar-amended soils to the possibility of non-homogeneity of physicochemical properties of the soil-biochar mixture in the interaction with the percolating solution in the leaching process.


(a)
Log Na steady state concentration
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
AB
B
B
A
A
A
A
A
A
A
A
A
SL
CP
BC
T1
T2
T3
T4
T5
T6
T7
T8
T9
Treatments*
(b)
Log Cu steady state concentration
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
A
B
C
A
A
A
B
A
AB
AB
B
A
SL
CP
BC
T1
T2
T3
T4
T5
T6
T7
T8
T9
Treatments*


(c)
Log Zn steady state concentration
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
AB
A
D
AB
A
A
C
AB
A
B
A
A
SL
CP
BC
T1
T2
T3
T4
T5
T6
T7
T8
T9
Treatments*


(d)
Log Cd steady state concentration
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
A
A
B
A
A
A
A
A
A
A
A
A
SL
CP
BC
T1
T2
T3
T4
T5
T6
T7
T8
T9
Treatments*

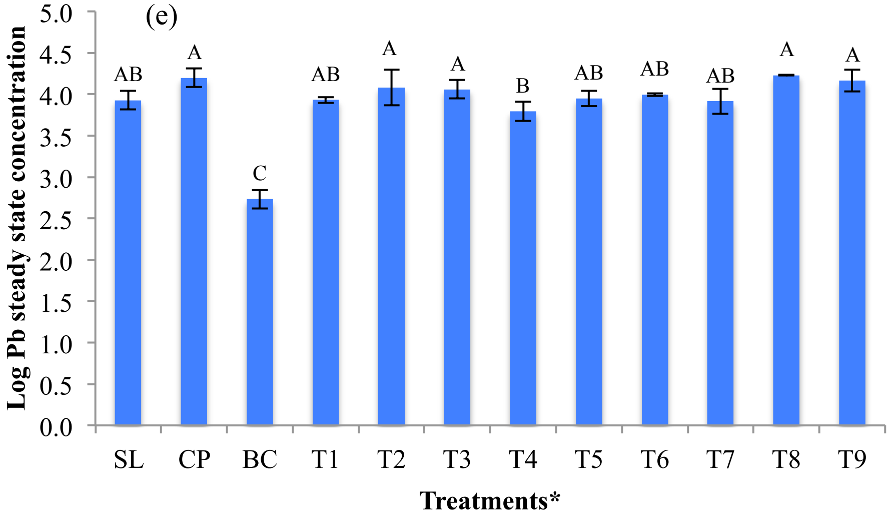


Fig. 6.1. Steady state concentrations of Na (a), Cu (b), Zn (c), Cd (d) and Pb (e) in contaminated soil mixtures. The y-axis is scaled logarithmically. *SL: 100% control soil, CP: 100% compost, BC: 100% biochar, T1: 2.2% compost and 1.5% biochar; T2: 12.8% compost and 8.5% biochar; T3: 12.8% compost and 1.5% biochar; T4: 2.2% compost and 8.5% biochar; T5: 7.5% compost, T6: 7.5% compost and 10% biochar; T7: 5% biochar; T8: 15% compost and 5% biochar; T9: 7.5% compost and 5% biochar (the percentages are by weight). Different letters on bar graphs indicate a significant difference.

6.5. Conclusion

This study demonstrated that Na, Cu, Zn and Pb in tree pit soils are vulnerable to leaching when exposed to a high NaCl concentration. In order to increase the sorption and retention of these metals in tree pit soil, compost and biochar indicated different functions. The results revealed that soil amended with compost (7.5 weight percentage as an optimum percentage) had a significantly higher capacity for sorption of Zn and Pb than did biochar-amended soil. The positive effect of compost on metal sorption and retention may be attributed to its high cation exchange capacity and positive effect on the soil pH. For Na, Cu, and Cd, the soil appeared to have the higher sorption capacity as compared to compost. The presence of biochar did not improve the ability of the soils to retain contaminants. The properties of biochar vary widely depending on the feedstock from which it is produced and the pyrolysis conditions. Although compost indicated a positive effect on sorption and retention of some trace metal during short-term sorption-desorption tests, long-term field studies would help to understand the functional sustainability of compost by monitoring the quality of the soil, the soil solution and the groundwater.

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Connecting statement V

Chapter 6 described how compost can significantly increase the sorption and retention capacity of soil for contaminants like Pb and Zn as compared to biochar. Following the results of chapter 6, chapter 7 explains how phytotoxicity tests were conducted on compost-amended soils in order to quantify the effect of different amounts of compost and different levels of contamination on metal absorption by plants.

Chapter 7

Direct and indirect effects of compost on bioavailability of Na and trace metals in urban soils

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7.1. Abstract

The contamination of urban soils with Na and trace metals can be one of the major concerns for groundwater contamination and street tree health. The bioavailability of Na, Cu, Zn, Cd, and Pb in soil amended with 0, 5 and 10% compost was evaluated at zero, medium, and high contamination levels of soil mixtures. The relationship among soil properties, compost addition, contamination level and metal uptake by barley (*Hordeum vulgare* L.) was determined using multiple linear regression and path analysis. The results indicated the direct negative effect of compost on metal absorption possibly through specific complexation for Cu, Zn, Cd, and Pb. Compost can also affect the absorption of Na and Cd indirectly by means of CEC and pH. The degree of soil contamination with Na and trace metals can affect the competition of cations for the complexing sites of the soil mixtures and therefore can induce changes in metal availability for plants. Compost addition to the soil also increased nutrient availability, except for NH_4^+ and NO_3^- .We concluded that in the short term, the addition of compost significantly reduced metal bioavailability and improved nutrient availability. However, more studies are required to monitor the long-term ability of the compost to reduce Na and trace metal availability in urban soil.

Keywords: Metal bioavailability, compost, path analysis, nutrients

7.2. Introduction

The wide use of de-icing salt (NaCl as most commonly used), heavy vehicular traffic on the wide streets in commercial land use zones in urban environment and the continual input of trace metals (Cu, Zn, Pb and Cd) to the urban soil adjacent to the streets (like tree pit soil) over time possibly are the main reasons of the elevated values of metals in urban soil (Kargar et al., 2013). Metal persistence in the environment, potential to bioaccumulate, and the mobility of Na and trace metals can make the contamination of urban soils with de-icing salt and trace metals as an urban environmental problem (Richards et al., 2012).

Metals like Cu and Zn are counted as nutrients for plants. Plants need Cu in different physiological functions such as photosynthesis and respiration, carbohydrate and nitrate metabolism, water permeability, reproduction, and disease resistance (Kabata-Pendias and Mukherjee, 2007). Zinc forms a structural component of a large number of proteins with catalytic or regulatory functions in plants (Sharma, 2006). Plants require some Na to replace K in the case of a K deficiency, to facilitate the conversion of pyruvate into phosphoenolpyruvate in mesophyll cells, as an osmoticum during rapid growth, and to enhance nitrate uptake in roots and nitrate assimilation in leaves (Kronzucker et al., 2013).

An overabundance of elements like Cu, Zn, and Na, however, is a limiting factor to plant growth (Blumwald et al., 2000). At high concentrations of Cu in soil, it may cause toxicity by interfering with photosynthesis, the respiratory processes, and protein synthesis (Ali et al., 2004). The accumulation of Zn in excess in the plant tissues can result in physiological alterations and plant growth inhibition through changing carbohydrate metabolism and photosynthetic activity, preventing the synthesis of photosynthetic pigments, and reducing the content of essential nutrients such as Fe, Cu, and Mn (Barrameda-Medina et al., 2014). High concentrations of Na^+ in cells can limit membrane function, decrease chlorophyll concentration and the activity of several enzymes, and interrupt various metabolic processes such as gas exchange and photosynthesis (Cekstere et al., 2008). Water stress can also occur for plants grown in a saline medium.

Some trace elements like Cd and Pb are toxic and not needed by plants even at low concentrations. Depending on the exposure time, Cd can inhibit photosynthesis by increasing the resistance of stomatal and mesophyll to CO_2 uptake. Cadmium can also decrease water stress tolerance of plants, reduce water transport, and therefore degrade cell walls in xylem (Kabata-

Pendias and Mukherjee, 2007). Lead phytotoxicity in plants inhibits enzyme activities, causes disturbed nutrition and water imbalance, makes changes in hormonal status and membrane permeability, and possibly leads to cell death at high Pb concentrations (Sharma and Dubey, 2005). The visual symptoms of Cd and Pb toxicity in plants generally are stunting and chlorosis (Kabata-Pendias and Mukherjee, 2007; Sharma and Dubey, 2005).

Apart from differences among various plant species, soil physical characteristics such as soil texture and numerous chemical properties including pH, oxidation–reduction potential, organic ligands, and the ionic composition of the soil solution affect the metal mobility in the soil and the rate and the extent of the metal uptake by plants (Ali et al., 2004). Among above factors, pH and organic matter content or cation exchange capacity (CEC) play the most crucial role in determining the bioavailability and toxicity of metals to biota (Lakhdar et al., 2009; Lock et al., 2000). Increase in pH values of the soil can increase the adsorptive capacity of the soils and consequently, decrease metal bioavailability. Organic matter can also decrease the bioavailability and uptake of metals by plants by re-distributing trace metals from soluble and exchangeable forms to fractions associated with anionic functional groups of organic matter (Son et al., 2007).

Considering the negative effect of organic matter on bioavailability of trace metals, in situ application of organic material such as compost as an amendment is one cost-effective way to improve contaminated urban soil. The negative effect of compost on bioavailability of trace metals can partially be attributed to the increase in pH value of the soil by compost addition, which is usually proportional to the percentage of compost added, the pH of the compost and of the native soil (Shiralipour et al., 1992). The increase in the pH of soil may be due to the mineralization of carbon and the subsequent production of OH^- ions by ligand exchange as well as the introduction of basic cations, such as K^+, Ca^{2+}, and Mg^{2+} following compost incorporation with soil (Hargreaves et al., 2008). Depending on compost pH, soil amendment with compost can also increase the CEC of the soil from 20% to 70%. High CEC of the soil after compost addition can reduce the bioavailable fraction of metals (Lakhdar et al., 2009).

The high content and release of phosphate and other anions during mineralization of the organic matter such as compost can also limit metal solubility possibly due to the formation of insoluble salts. For instance, one of the key processes of Pb immobilization as a result of organic amendment of the soil is related to the formation of pyromorphite ($Pb_5(PO_4)_3Cl$) or other compounds with low solubility (Zhu et al., 2004). Organic matter can also decrease exchangeable or even organic matter-bound portion of metals in the amended soil, likely due to the formation of insoluble carbonates of trace metals with the CO_2 produced during mineralization of the organic matter (Walker et al., 2003).

Metal bioavailability also depends on the metals and their concentration in the soil (Waterlot et al., 2013). Murray et al. (2011) observed that depending on the Cd, Cu, Pb and Zn concentrations in the soil amended with compost in three urban gardens in Montreal, the metal bioavailability, and their uptake by plants grown in that soil, can alter, meaning that the complexation of metals with dissolved organic matter increases their bioavailability under micronutrient deficiency conditions, while complexation of highly available metals results in a sequestering effect where soil metal is high.

Simultaneously with reducing the metal mobility as a result of organic amendment of the contaminated soils, organic matter can create conditions that promote plant growth in amended soils. In a study conducted by Zhang et al. (2000) on wheat (*Triticum aestivum*), barley (*Hordeum vulgare*) and canola (*Brassica rapa*), compost applications generated positive yield responses in all three crops because of the improvement in nutrient availability. Alburquerque et al. (2007) also pointed out the positive impact of urban waste compost application on the growth of ryegrass plants and uptake of K, Cu, and P. However, they did not observe a significant effect of compost on increasing the N availability in the soil. Depending on the feedstock of compost, the small effect of compost on N availability in the soil can be related to the slow rate of mineralization of compost organic N and therefore the high microbial competition for available soil nitrogen (Alburquerque et al., 2007). Organic matter can also impact soil fertility by improving soil structure, and water-air ratio in the rhizosphere and increasing the populations of beneficial soil microorganisms (Chen, 1996).

The main purpose of this study was to determine if compost amendment of the soil can either directly or indirectly affect Na or trace metal (Cu, Zn, Cd, and Pb) bioavailability in urban soils with different levels of contamination.

7.3. Materials and methods

7.3.1. Preparation of soil mixtures

In order to determine how compost amendment of the soil can modify the bioavailability of Na and trace metals in urban soil, a phytotoxicity test was designed. Based on previous studies of urban soils in Montreal, Quebec, Canada (Jutras, 2008; Kargar et al., 2013), Cu, Zn, Cd, and Pb were selected as the main trace metals with which tree pit soils are usually contaminated. In the present study, the soil mixture, used in the phytotoxicity test, was based on a sandy loam soil, hereafter referred to as "city soil", provided by the tree pit soil supplier of the Ville-Marie borough, Montreal. Before preparing the soil mixtures, the soil was dried at room temperature for 14 days and passed through a 2-mm metal sieve to remove large particles. Three dry weight percentages (0, 5 and 10 %) of compost were added to the city soil. The compost was derived from mixed green and table waste from the West Island region of Montreal.

7.3.2. Spiking and leaching process

After the preparation of soil mixtures, they were spiked with three contamination levels including a control, medium, and high levels in small plastic bags. The high level of contamination equaled to the highest concentration of the studied metals measured in the soil samples collected from the street tree pits in a prior study in Montreal (Jutras, 2008; Kargar et al., 2013). The half value of the high contamination level was considered as the medium level. Following factorial design and considering the three weight percentages of compost addition to the city soil in three different contamination levels, the phytotoxicity test ended up with nine treatments with six replications per treatment. The percentages of soil and compost in each treatment and the contamination levels including the concentrations of Na, Cu, Zn, Cd, and Pb are summarized in Table 7.1.

After addition of the spiking solution to the soil in the plastic bags and mixing the soil with solution, the soils were left for one week to equilibrate. Soil aging, including gradual formation of precipitates and metal diffusion into micro pores, takes place under the effect of abiotic factors in the soil such as temperature, soil moisture content, pH, and total metal concentration (Lock and Janssen, 2003; Smolders et al., 2009). This fixation and diffusion result in reducing metal desorption and extractability (Schwertfeger, 2010). After one week, the soils were leached for one day with a 400μM $CaCl_2$-$CaSO_4$ solution in order to help remove the counter ions such as Ca^{2+}, Mg^{2+}, K^{2+} and Na^{+}.

During the last two days of soil preparation, samples were leached with a dilute nutrient solution (*i.e.,* modified dilute Hoagland's solution) containing 200 μM $Ca(NO_3)_2$, 80 μM

$Mg(SO_4)$, 200 µM KNO_3, and 40 µM KH_2PO_4 as will be explained later. Adding the nutrient solution to the soil helps the soil recover its fertility status that may have been reduced during contamination additions and the initial leaching process (Schwertfeger, 2010). Following Schwertfegera and Hendershot (2013), for leaching, 500 mL of the leaching solution was added to an approximately 450 g (dry weight) soil sample contained in a 500-mL perforated pot fitted to a Buchner funnel attached to the leaching apparatus. The leaching solution was passed through the soils in the pots at a rate of 100 mL h^{-1} over 5 hours. After leaching, the soils were dried for three days at room temperature and re-homogenized. The dried spiked leached soil samples were then hydrated up to approximately 70% of the soil water holding capacity after measuring the moisture content of the soil samples.

Table 7.1. Concentration of Na, Cu, Zn, Cd, and Pb in control, medium, and high level of contamination with different percentages of compost

Treatment No.	Treatment Code	City soil (% w/w)	Compost (% w/w)	Level of contamination	Na (mg kg $^{-1}$)	Cu (mg kg $^{-1}$)	Zn (mg kg $^{-1}$)	Cd (mg kg $^{-1}$)	Pb (mg kg $^{-1}$)
1	S-Ctrl	100	0	Control	0	0	0	0	0
2	SC-Ctrl	95	5	Control	0	0	0	0	0
3	SCC-Ctrl	90	10	Control	0	0	0	0	0
4	S-Mid	100	0	Medium	306	108	474	3	1075
5	SC-Mid	95	5	Medium	306	108	474	3	1075
6	SCC-Mid	90	10	Medium	306	108	474	3	1075
7	S-Hig	100	0	High	613	216	948	6	2150
8	SC-Hig	95	5	High	613	216	948	6	2150
9	SCC-Hig	90	10	High	613	216	948	6	2150

7.3.3. Phytotoxicity test

Following the procedure outlined in Environment Canada's Biological Test Method for the emergence and growth of terrestrial plants (Environment Canada, 2005), the spiked leached soil mixtures were used for a 14-day plant growth assay conducted with barley plants (*Hordeum vulgare* L.). The seeds were first pre-germinated for three days; the seedlings with approximately equal root length were then selected for planting in the cones containing around 100 g of the spiked leached soil mixtures. The height of the cone was 13.5 cm, and its diameter was 4 cm. The cones containing the seedlings and the soil mixtures were kept in a Conviron E15 plant growth chamber for 14 days with full spectrum fluorescent light averaging 370 µmol $(m^2.s)^{-1}$ per µA at a day/night average temperature of 24°C/15°C and a 16h photoperiod. The relative humidity was kept at $\geq 50\%$.

The cones were watered every day with double deionized water to maintain 70% water holding capacity. Test cones were assigned new random positions in the growth chamber daily. At the end of the growth period of 14 days, the barley seedlings were harvested. Loose soil was shaken from roots. The roots were then rinsed with deionized water, further cleaned by spraying them with double deionized water until roots were visibly free of soil. Roots were removed from shoots just above the root crown. After drying the roots and shoots at 65°C for 48h, the biomass of dry roots and shoots were recorded.

Dried roots and shoot samples were ground with a mortar and pestle, and subsamples weighing ≤0.200 g were placed in 10-mL Pyrex tubes and digested with 2 mL concentrated HNO_3 overnight (20°C) followed by a 5-h digestion at 120°C in a block digestion unit. Samples were cooled, diluted to 50 mL with double deionized water, and analyzed for Na, Cd, Cu, Zn, and Pb by inductively coupled plasma mass spectrometer (820-MS, Varian, Melbourne, Australia)(Hendershot et al., 2008). A certified reference material, NIST 1547 (peach leaves) was included as the quality control. The recovery percentages for NIST 1547 were as follows: 167% for Na, 100% for Cu, 99% for Zn, 100% for Cd, and 121% for Pb. The soil samples collected from the cones after harvesting the seedlings were also analyzed for Na, Cd, Cu, Zn, and Pb content following the same protocol for barley roots and shoots. A certified reference material, SED 98-04 provided by the Environment Canada Proficiency Testing program, was used as the quality control for soil analysis. The recovery percentages for SED 98-04 were as follows: 113% for Na, 97% for Cu, 88% for Zn, 128% for Cd, and 99% for Pb. The quantity of trace metal uptake by barley was estimated by multiplying the barley plant biomass (root plus shoot dry mass) by the metal concentrations in root and shoot tissues (Gandois et al., 2010; Wuana and Okieimen, 2011).

Soil pH was measured with an Accumet AR10 meter (Fisher Scientific Inc., Pittsburgh, PA) at 1:2 soil-to-solution ratio (7 g soil/14 mL H_2O) (Hendershot et al., 1993b). Cation exchange capacity (CEC) was determined by sum of the cations including Ca^{2+}, Mg^{2+}, K^+, Al^{3+}, Fe^{2+}, and Mn^{2+} extracted with 0.1 M $BaCl_2$ and analyzed by AA220-FS atomic absorption spectrometer-varian (Hendershot and Duquette, 1986). Available nutrients (P, Ca, Mg, K) of the soil after the phytotoxicity test were extracted according to the Mehlich-III procedure using a mixture of acetic acid, ammonium nitrate, ammonium fluoride, ethylene-diamine-tetra-acetic acid (EDTA), and nitric acid (Tran and Simard, 1993). Colorimetry was used to determine the concentration of available P (Quick Chem FIA+, Lachat Instruments, Milwaukee, WI). The available Ca and Mg and the available K were measured by flame atomic absorption spectroscopy and flame atomic emission spectroscopy, respectively on the same Varian SpectAA 220FS. Total mineral Nitrogen (NH_4^+ and NO_3^-) was extracted with KCl (Maynard and Kalra, 1993) and measured by colorimetry on a multi-channel auto-analyser (Lachat Instruments, Milwaukee, WI).

7.3.4. Data analysis

Analysis of variance using general linear model was applied to characterize the interactions between compost weight percentages and contamination levels in the soil mixtures. In order to evaluate the effect of compost weight percentages, contamination levels, and soil chemical properties (pH and CEC) on the metals absorbed by barley plants, multiple linear regression was done using a backward elimination method by SPSS statistics (V.21, IBM). However, multiple linear regression alone may not be useful for predicting trace metal bioavailability, because strong inter-correlations between predictor variables can result in apparent correlations of the absorbed metals (Na, Cu, Zn, Cd, and Pb) with compost and soil chemical properties (Bradham et al., 2006). Therefore, path analysis was used as a complementary analysis after backward regression analysis, using SmartPLS (2.0 M3, available at www.smartpls.de developed by Ringle et al. (2005)).

Path analysis partitions simple correlations into two types of relationships: the effect of the predictor variables (compost weight percentages and contamination levels) on response variable (the content of absorbed metals in barley plants), referred to as a direct effect, and the effect of predictor variables on the response variables as mediated by their effect on other predictor variables (pH and CEC), referred to as indirect effects (Bradham et al., 2006). The direct (standardized partial regression coefficients calculated as path coefficients) and indirect effects of predictor variables on response variables are illustrated in Fig. 7.1 and Table 7.2. A pathway was also considered for error variance (U) of the metal absorption as the response variable not measured by the direct and indirect effects of predictor variables. Considering R^2 as the determination coefficient, the error variance in pathway analysis can be calculated following Eq. 7.1 (Richards et al., 2012):

$$U=\sqrt{1-R^2} \qquad \text{Eq.[7.1]}$$

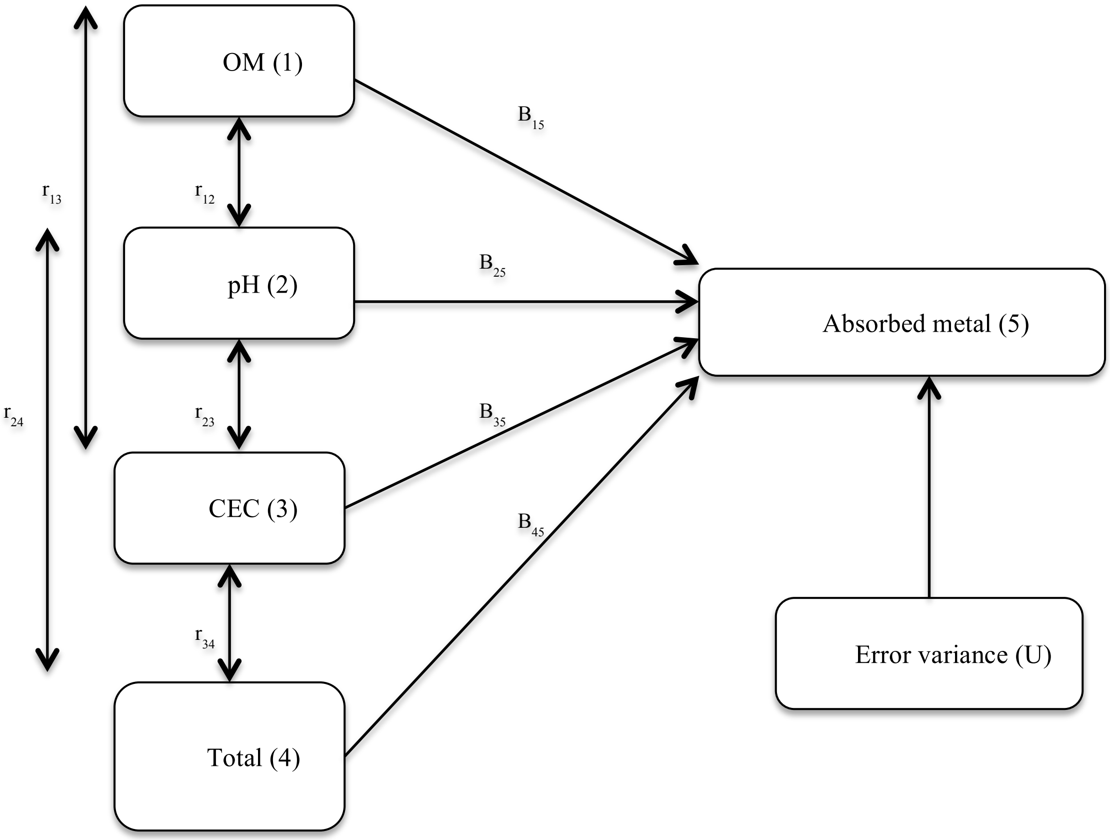


Fig. 7.1. Path diagrams including direct and indirect effects of compost weight percentages (OM) and contamination level (Total) on metal absorption by barley plants using the path coefficients between compost weight percentages (OM) and metal absorption (B_{15}), pH and metal absorption (B_{25}), CEC and metal absorption (B_{35}), and contamination level (Total) and metal absorption (B_{45}) and the Spearman correlation coefficients between compost weight percentages (OM) and pH (r_{12}), compost weight percentages (OM) and CEC (r_{13}), contamination level (Total) and pH (r_{24}) and contamination level (Total) and CEC (r_{34}). The error variance of the metal absorption is indicated as U. Subscript designations are: 1 for compost weight percentages (OM); 2 for pH; 3 for CEC, 4 for contamination level (Total), and 5 for metal absorption by barley plants. The direct effects are presented as single-headed arrows, while the inter-correlations between predictor variables are represented by double headed arrows (Basta et al., 1993).

Table 7.2. Direct and indirect effects of compost weight percentages and contamination levels on metal uptake by barley plants

	Direct effect	Indirect effect		Total effect
		via pH	via CEC[†]	
Compost	B_{15}	$r_{12}* B_{25}$	$r_{13}* B_{35}$	$B_{15}+ r_{12}* B_{25}+ r_{13}* B_{35}$
Contamination level	B_{45}	$r_{24}* B_{25}$	$r_{34}* B_{35}$	$B_{45}+ r_{42}* B_{25}+ r_{43}* B_{35}$

[†] CEC=cation exchange capacity

Before using multiple linear regression and path analysis, the data were checked for normality. Data were log-transformed where appropriate. The normality of the data distribution after transformation was checked with Kolmogorov-Smirnov test.

7.4. Results and discussion

The detailed discussion on the direct and indirect effects of compost weight percentages and contamination levels of the soil mixture on the studied metal bioavailability is as follows:

7.4.1. Direct effect of compost on metal uptake by barley plants

The addition of compost to the soil contaminated at different levels led to changes in soil chemical characteristics (Table 7.3) and the bioavailability of Na and trace metals (Cu, Zn, Cd, and Pb) as compared to the contaminated un-amended soil (city soil) (Tables 7.4 and 7.5). The results of the general linear model indicated no significant interaction between compost weight percentages and contamination levels in the soil mixtures. According to the results of multivariate regression (Table 7.6) and path analysis (Table 7.7), different factors affect the absorption of metals by barley plants in amended soil mixtures through different mechanisms. The results of path analysis indicated no significant direct effect of compost on Na absorption. Compost, as confirmed by the results of multivariate regression analysis (Table 7.6) and path analysis (Table 7.7), indicated a direct negative effect on the absorption of Cu and Zn (Table 7.7, B_{15}=-0.20 and -012 $p<0.01$ and 0.05) by barley plants. The direct negative effect of compost can be partially associated with complexation reactions of Cu and Zn with humic substances, which constitutes a major part of the organic matter of compost, and therefore the formation of low-solubility organo-metallic complexes (Basta et al., 1993; Paradelo et al., 2011).

Table 7.3. Chemical characteristics (pH and CEC) and total metal concentration in amended soils with different weight percentages of compost as compared with non-amended soil at different contamination levels. Values are the mean (standard error) of treatment replications.

Treatment Code	pH	CEC†	Na	Cu	Zn	Cd	Pb
		$cmol_{(+)}$ Kg^{-1}			mg kg^{-1}		
S-Ctrl	7.53	12.1	144	14.3	34.0	0.79	9.16
	(0. 1)	(0.34)	(25.3)	(0.99)	(2.00)	(0.26)	(0.63)
SC-Ctrl	7.81	13.3	132	13.4	34.4	0.42	9.13
	(0. 1)	(0.86)	(6.47)	(0.58)	(3.02)	(0.02)	(0.53)
SCC-Ctrl	8.06	15.7	139	15.1	37.5	0.42	9.48
	(0. 1)	(0.64)	(6.76)	(0.48)	(1.36)	(0.01)	(0.40)
S-Mid	7.54	13.0	311	88.3	364	2.36	791
	(0.1)	(0.30)	(5.29)	(2.51)	(9.67)	(0.09)	(22.7)
SC-Mid	7.58	14.3	320	105	397	2.94	880
	(0.1)	(0.64)	(7.36)	(1.90)	(6.75)	(0.06)	(18.4)
SCC-Mid	8.11	17.1	327	111	424	3.53	899
	(0.1)	(0.39)	(11.0)	(5.15)	(17.8)	(0.30)	(30.0)
S-Hig	7.87	13.6	594	191	767	5.92	1680
	(0.1)	(0.36)	(25.5)	(3.58)	(14.0)	(0.07)	(25.5)
SC-Hig	7.96	14.9	627	197	807	5.74	1855
	(0. 1)	(0.67)	(34.8)	(5.21)	(29.8)	(0.18)	(72.8)
SCC-Hig	7.99	17.2	617	203	817	5.70	1842
	(0.1)	(0.71)	(31.2)	(5.94)	(25.2)	(0.14)	(56.2)

†CEC= cation exchange capacity

Compost can also indicate a direct negative effect on the Pb absorption (Table 7.7, B_{15}= -0.06, $p<0.05$) by barley plants. According to Karami et al. (2011), the reduction of Pb solubility in the pore water of compost amended soils can be attributed to the humified complexes and also high P concentration in compost which results in the formation of pyromorphite ($Pb_5(PO4)_3Cl$) and diminution of Pb availability. Our results also indicated higher P availability in soils amended with compost as compared with ones measured in unamended soil (city soil) (Fig. 7.2). The binding of phosphate ions with Pb can decrease the solubility of Pb and make it unavailable for uptake by roots. Therefore, as Hardiman and Banin (1984) indicated, only Pb fractions that are easily dissociated or ionic forms of Pb can be absorbed by roots.

Table 7.4. Root biomass and metal concentration absorbed by barley roots. Values are the mean (standard error) of treatment replications.

Treatment Code	Biomass	Na	Cu	Zn	Cd	Pb
	g			mg kg^{-1}		
S-Ctrl	0.04	981	28.4	117	1.50	13.0
	(0.01)	(71.2)	(13.6)	(22.4)	(0.28)	(5.06)
SC-Ctrl	0.04	398	12.8	60.0	1.03	7.63
	(0.00)	(50.2)	(0.71)	(2.74)	(0.31)	(0.76)
SCC-Ctrl	0.05	300	11.5	54.0	0.45	5.00
	(0.00)	(47.3)	(1.22)	(6.21)	(0.08)	(1.18)
S-Mid	0.06	9600	85.6	308	14.0	227
	(0.01)	(578)	(8.75)	(21.6)	(1.07)	(11.9)
SC-Mid	0.04	7100	99.0	322	13.3	225
	(0.00)	(413)	(9.51)	(24.8)	(0.77)	(12.5)
SCC-Mid	0.05	5910	96.5	351	9.76	226
	(0.00)	(292)	(5.92)	(14.4)	(0.35)	(8.33)
S-Hig	0.04	11300	247	640	28.6	566
	(0.00)	(393)	(8.09)	(16.0)	(0.69)	(12.2)
SC-Hig	0.04	9260	209	580	20.1	457
	(0.00)	(411)	(17.8)	(37.9)	(1.27)	(29.2)
SCC-Hig	0.04	9710	191	615	19.5	496
	(0.00)	(443)	(13.5)	(46.6)	(0.94)	(29.4)

Compost decreases the bioavailability of trace metals such as Cd^{2+} (Table 7.7, $B_{15}=-0.29$, $p<0.01$) by increasing the available macronutrient ions such as Ca^{2+}, $Mg^{2+,}$ and K^{+} for barley plants (Fig. 7.2), therefore blocking uptake of trace metal ions (Farrell et al., 2010). According to Waterlot et al. (2013), plants take up Cd^{2+} through channels for Ca^{2+} and Mg^{2+}. Therefore, low availability of Ca^{2+} in the soil can result in low Ca/Mg ratios and, consequently, higher accumulation of Cd^{2+} in plants. Our results also indicated negative correlation between Ca^{2+} and Cd^{2+} bioavailability and Mg^{2+} and Cd^{2+} bioavailability in compost-amended soils ($r_{\text{Ca and Cd}}=-0.25$ and $r_{\text{Mg and Cd}}=-0.18$, $p<0.1$).

Trace metals can also be partially washed out of the soil by the initial leaching treatment. Leaching of the metals is more pronounced in compost-amended soils because of the increased aggregation of soil particles, which increases porosity (Farrell et al., 2010; Mahmoud and Ibrahim, 2012).

Table 7.5. Shoot biomass and metal concentration absorbed by barley shoot. Values are the mean (standard error) of treatment replications.

Treatment Code	Biomass	Na	Cu	Zn	Cd	Pb
	g			mg kg^{-1}		
S-Ctrl	0.06	348	5.99	31.7	0.128	0.50
	(0.01)	(20.5)	(0.47)	(3.00)	(0.01)	(0.21)
SC-Ctrl	0.06	189	5.29	37.9	0.107	0.39
	(0.00)	(13.8)	(0.43)	(4.13)	(0.01)	(0.07)
SCC-Ctrl	0.06	211	5.31	38.0	0.079	0.39
	(0.00)	(16.5)	(0.33)	(2.11)	(0.00)	(0.07)
S-Mid	0.07	1220	19.1	413	5.53	51.3
	(0.00)	(544)	(1.18)	(24.4)	(0.73)	(2.78)
SC-Mid	0.05	8030	16.7	342	4.20	26.4
	(0.01)	(289)	(1.00)	(33.8)	(0.51)	(1.33)
SCC-Mid	0.06	6840	20.1	348	3.23	21.8
	(0.00)	(307)	(3.38)	(16.2)	(0.14)	(1.00)
S-Hig	0.05	11600	21.5	540	9.55	100
	(0.00)	(413)	(1.01)	(27.9)	(0.39)	(5.32)
SC-Hig	0.04	10100	20.7	420	5.45	74.3
	(0.00)	(318)	(1.05)	(18.3)	(0.22)	(4.08)
SCC-Hig	0.04	7670	18.1	417	5.65	58.1
	(0.00)	(371)	(0.98)	(33.5)	(0.48)	(3.26)

Table 7.6. Multiple linear regression and coefficient of determination (R^2) for relationship between soil properties and metal absorption by barley plants

Metal absorption[†]	Multiple linear regression	R^2
Na	5.32+2.25 (Total)-1.15(pH)+1.64 (CEC[‡])	0.85
Cu	0.40+0.91 (Total[¶])-0.01 (OM[§])	0.93
Zn	1.12+0.69 (Total)-0.01 (OM)	0.96
Cd	(-2.46)+0.45 (Total)-0.05 (OM)+3.41 (CEC)	0.66
Pb	(-0.097)+0.85 (Total)	0.97

[†] Metal absorption = the absorbed metal concentration measured in root and shoot in total

[‡] CEC=cation exchange capacity

[¶] Total=concentration of metals assumed as contamination level measured in the soil mixtures

[§] OM=organic matter of the soil including compost weight percentage

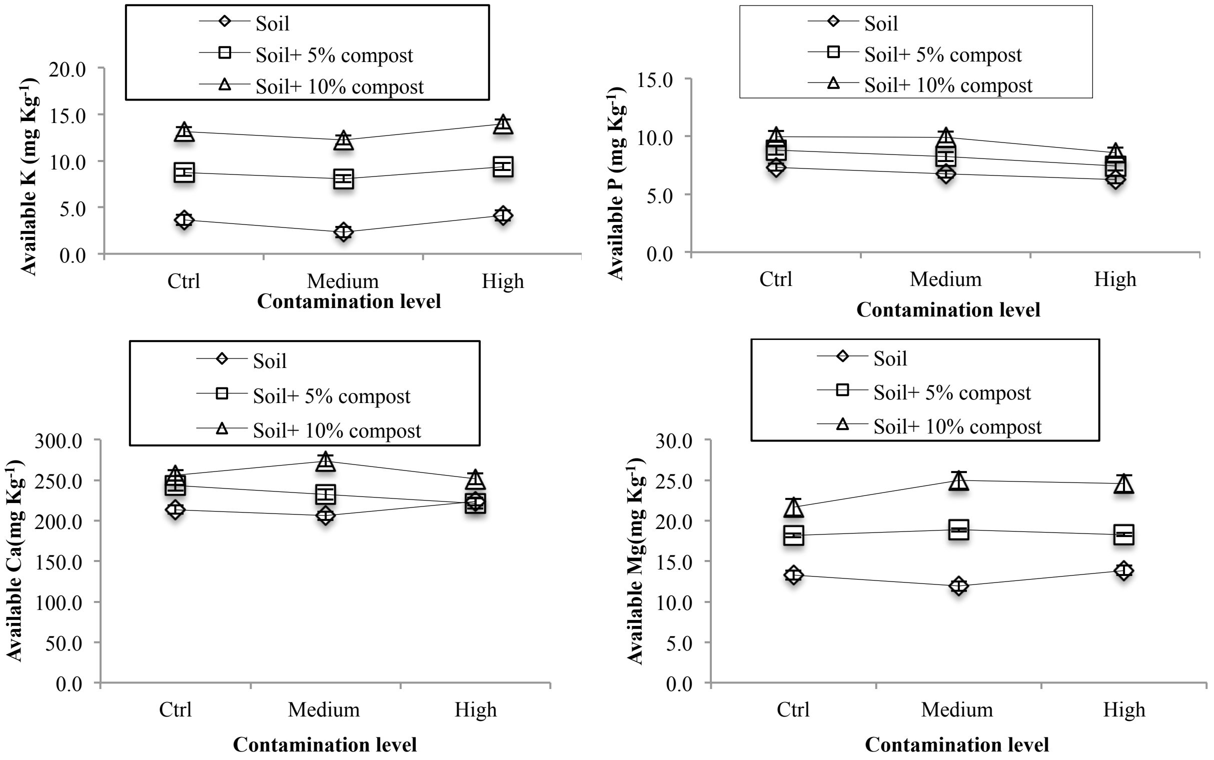


Fig. 7.2. The availability of P, K, Ca, and Mg in compost-amended soil as compared with non-amended soil at different contamination levels

7.4.2. Indirect effect of compost on metal uptake by barley plants

The positive effect of compost on pH and CEC of the soil mixtures ($r=0.84$ and 0.75, $p<0.01$) can result in the indirect effect of compost on metal uptake by barley plants. The results of multivariate regression (Table 7.6) indicated the negative effect of pH on Na uptake by barley plants. The results of path analysis (Table 7.7) demonstrated an increase in soil pH after compost addition and, therefore, a decrease in Na solubility and Na uptake by barley plants (Paradelo et al., 2011). The increase in pH of soil amended with compost is related to the consequent increase in the Ca^{2+} ion pool in the soil solution after compost addition to the soil ($r_{\text{pH and Ca}}= 0.61$, $p<0.01$) and thereby displacing Al^{3+} and H^+ ions, and binding Al^{3+} ions tightly to form insoluble Al^{3+} complexes (Farrell et al., 2010). The indirect effect of organic matter via CEC on absorption of some metals (Na and Cd) by barley plants (Tables 7.6 and 7.7) is related to the displacement of the exchangeable metals with high mobility like Na^+ and Cd^{2+} with continuous supply of Ca^{2+} and Mg^{2+} that compost provides in the soil ($r_{\text{Na and Ca}}= -0.39$ and $r_{\text{Na and Mg}}=-0.38$, $p<0.01$).

Table 7.7. Path analysis, coefficient of determination (R^2), and error variance (U) for direct and indirect effects (via pH and CEC) of compost weight percentages and contamination levels on metal uptake by barley plants

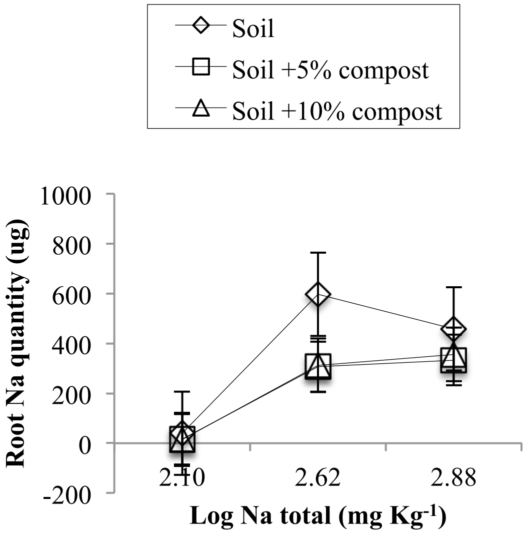
Variables	Direct effect	Indirect effect via.		Correlation coefficient	R^2	U
		pH	CEC[†]			
			Na uptake			
Compost	-0.07	-0.29**	0.14**	-0.48**	0.88	0.35
Contamination level	0.91**	-0.10**	0.05**	0.73**		
			Cu uptake			
Compost	-0.20**	0.02	0.06	-0.14	0.94	0.24
Contamination level	0.93**	0.01	0.03	.89**		
			Zn uptake			
Compost	-0.12*	0	0.02	-0.16	0.96	0.2
Contamination level	0.96**	0	0.006	0.92**		
			Cd uptake			
Compost	-0.29**	0.03	0.20*	-0.31*	0.68	0.57
Contamination level	0.73**	0.01	0.06*	0.86**		
			Pb uptake			
Compost	-0.06*	0.02	0.02	-0.19	0.98	0.14
Contamination level	0.98**	0	0.003	0.92**		

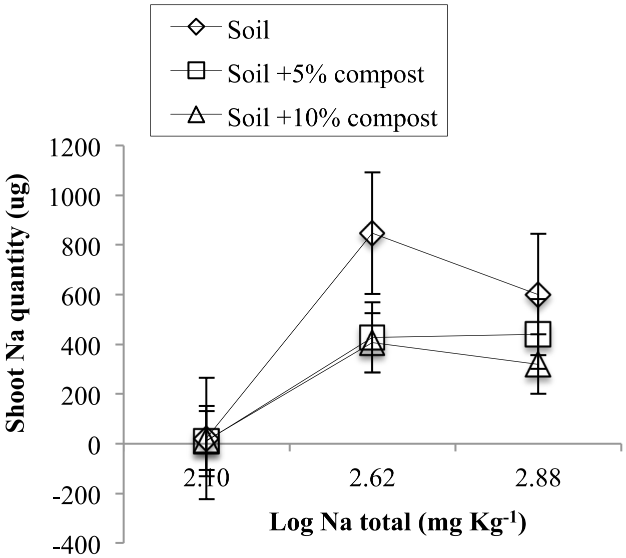
* Significant at $p<0.05$

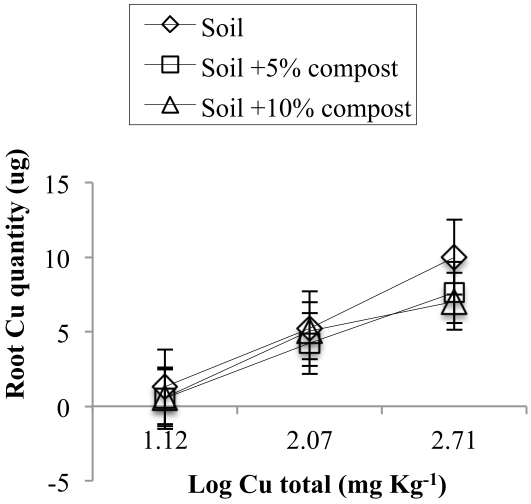
** Significant at $p<0.01$

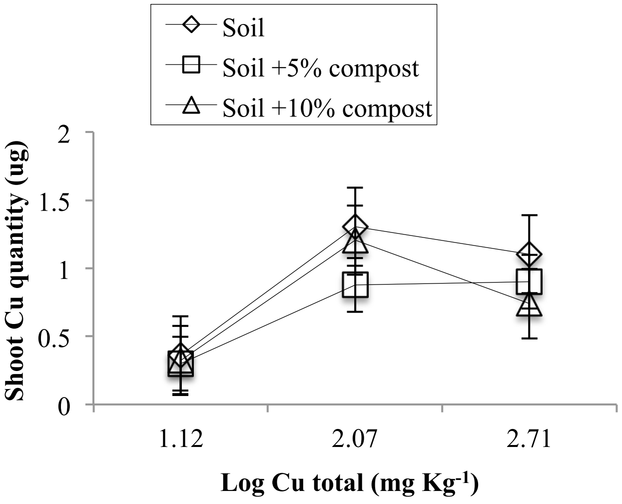
[†] CEC= cation exchange capacity

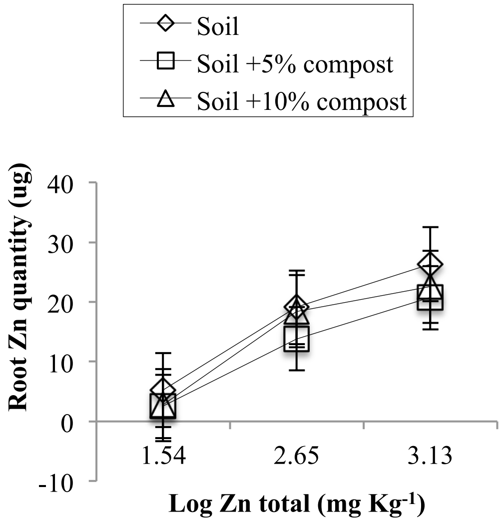
Considering the negative and positive direct and indirect effects of compost, in general, compost correlated negatively to metal bioavailability (Table 7.7). Consequently, significantly less metal in barley plants (roots and shoots), grown in compost-amended soils, was observed as compared with those grown in non-amended soils (Fig. 7.3). However, in general, no significant difference was observed between the absorbed metals in roots and shoots of barley grown in soil amended with 5% w/w compost as compared with the ones measured in the roots and shoots of barley grown in soil amended with 10% w/w compost.


Soil
Soil +5% compost
Soil +10% compost
Root Na quantity (ug)
1000
800
600
400
200
0
-200
2.10
2.62
2.88
Log Na total (mg Kg-1)

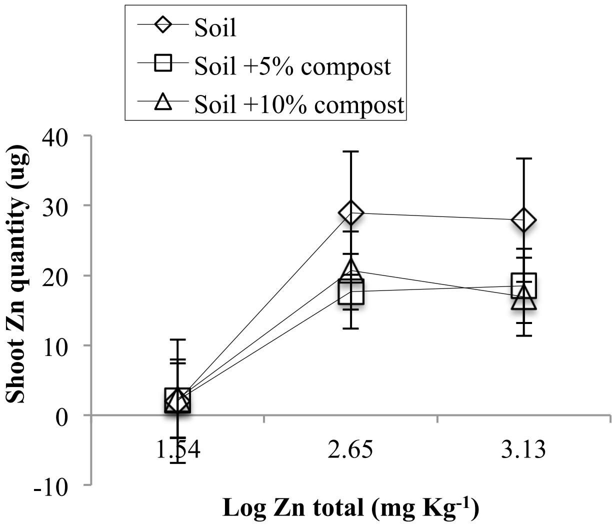

Soil
Soil +5% compost
Soil +10% compost
Shoot Na quantity (ug)
1200
1000
800
600
400
200
0
-200
-400
2.10
2.62
2.88
Log Na total (mg Kg-1)


Soil
Soil +5% compost
Soil +10% compost
Root Cu quantity (ug)
15
10
5
0
-5
1.12
2.07
2.71
Log Cu total (mg Kg-1)

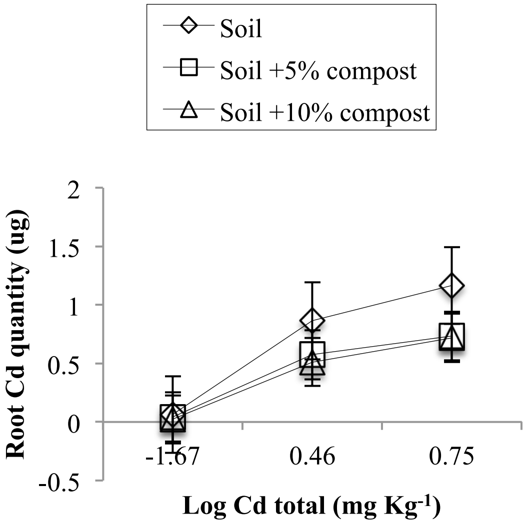

Soil
Soil +5% compost
Soil +10% compost
Shoot Cu quantity (ug)
2
1.5
1
0.5
0
1.12
2.07
2.71
Log Cu total (mg Kg-1)



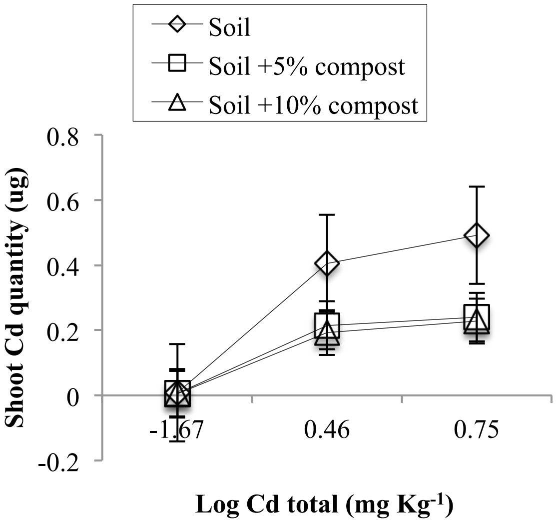
Soil
Soil +5% compost
Soil +10% compost
Root Zn quantity (ug)
40
30
20
10
0
-10
1.54
2.65
3.13
Log Zn total (mg Kg^{-1})



Soil
Soil +5% compost
Soil +10% compost
Shoot Zn quantity (ug)
40
30
20
10
0
-10
1.54
2.65
3.13
Log Zn total (mg Kg^{-1})



Soil
Soil +5% compost
Soil +10% compost
Root Cd quantity (ug)
2
1.5
1
0.5
0
-0.5
-1.67
0.46
0.75
Log Cd total (mg Kg^{-1})



Soil
Soil +5% compost
Soil +10% compost
Shoot Cd quantity (ug)
0.8
0.6
0.4
0.2
0
-0.2
-1.67
0.46
0.75
Log Cd total (mg Kg^{-1})

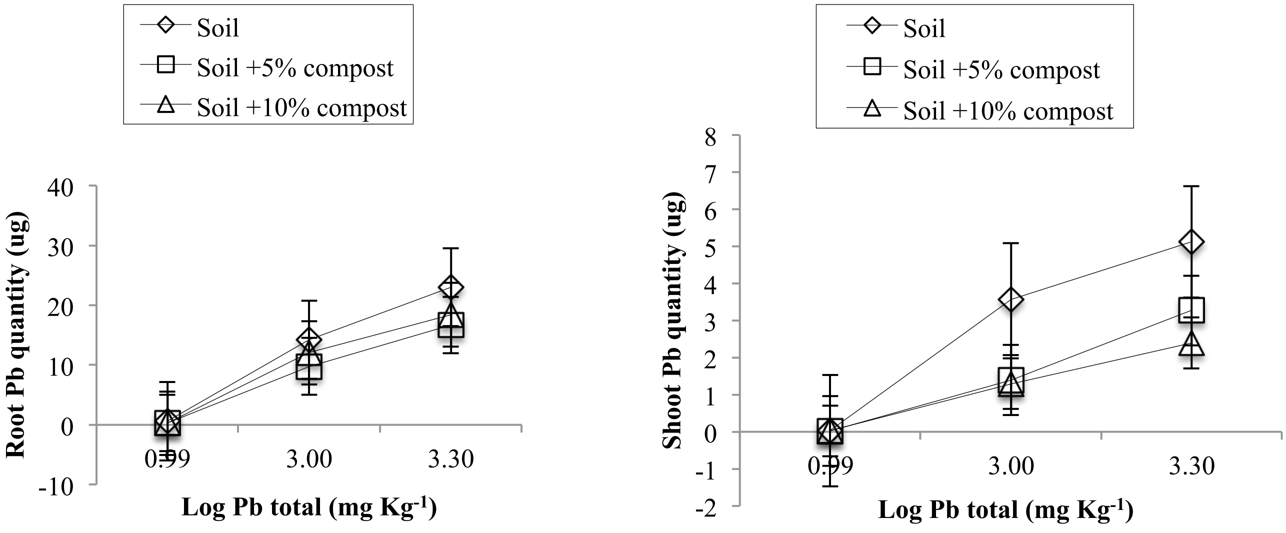


Fig. 7.3. Barley roots and shoots quantity of Na and trace metals (Cu, Zn, Cd, and Pb) grown in spiked leached soils showing increased level of contamination in soil mixtures

7.4.3. Contamination levels

Path analysis indicated a direct positive effect of the soil contamination level on metal accumulation in barley plants (Table 7.7), meaning that the higher the contamination level, the more Na and trace metals were taken up. Different studies indicated that the metal ions are more strongly adsorbed at lower ionic strengths, while any increases in electrolyte concentration results in a decrease in metal adsorption because of the competition by other cations for adsorption sites in the soil (Sherene, 2010). Therefore, higher concentration of metals can be available for absorption by plants.

Through CEC, contamination level indicated a positive indirect relationship with Cd and Na accumulation in barley plants. According to Zenteno et al. (2013), Cd can be initially adsorbed to the soil particles because of electrostatic attraction between Cd and charged adsorbing surfaces in the soil. The electrostatic attraction is positively related to the CEC of the adsorbents. However, because of the low affinity of the adsorption sites for Cd, it has a tendency to move down the soil profile and become available for plants after its immobilization. Vega et al. (2009) also referred to the reversibility of Cd adsorption in organic amended soils. That might explain the high availability of Cd for barley plants grown in compost amended soils despite the high CEC values of the soil as shown in the results of path analysis (Table 7.7) and multivariate regression (Table 7.6).

At high contamination levels, competition from cations like Cu^{2+} and Pb^{2+} can result in the preferential adsorption of these cations by the major sorbent components of the soil mixtures, organic matter, clay and Fe oxides as compared with cations with lower electronegativity such as Cd^{2+} (Vega et al., 2009) or Na^{+}. Therefore, at high contamination levels, more Na^{+} and Cd^{2+} can be available for absorption by barley plants.

7.4.4. Nutrient availability in compost amended soils

Our results indicated a significant compost-induced increase in nutrient availability including P, Ca, Mg, and K for barley plants (Fig. 7.2). In corroboration with our results, Farrell and Jones (2010) also observed an increased nutrient level in a soil heavily contaminated with Cu, Pb, and Zn after compost addition. However, we did not observe a significant effect of compost on increasing NH_4^+ and NO_3^- availability for barley plants. The N availability in composts depends on the stability of their organic matter and on their physicochemical characteristics. According to Chalhoub et al. (2013), composts with high C/N values (>15) usually limit N availability due to immobilisation of N in the soil. Compost, which is mostly C can result in the active growth of microorganisms. Therefore, an increase in biomass can occur in a soil without sufficient N. This will cause microorganisms to acquire N from the soil environment and decrease the availability of N for plants (Geisseler et al., 2010). Some studies also reported NO_3^- leaching from compost amended soils (Amlinger et al., 2003). The N dynamics in soil after compost incorporation can also be affected by environmental conditions such as soil type, moisture and temperature (Chalhoub et al., 2013).

7.5. Conclusion

The role of compost in the immobilization of Na, Cu, Zn, Cd, and Pb in urban soil was investigated through a phytotoxicity test. Adding compost as an amendment to the soil affects metal absorption by plants directly and indirectly. The direct effect of compost can occur through specific complexation, providing macronutrients such as Ca^{2+} and Mg^{2+}, and P binding to trace metals for metals like Cu, Zn, Cd, and Pb. Compost also affects metals like Na and Cd absorption by plants indirectly through CEC and pH. The contamination level of soil with Na and trace metals can affect the competition of cations for the complexing sites of the soil mixtures and therefore can induce changes in metal availability for plants. Compost addition to the soil also increased nutrient availability, except for NH_4^+ and NO_3^-. In short term, we observed a significant reduction in metal availability and increase in nutrient availability as a result of the addition of compost. However, before recommending compost for mitigating the impact of urban contaminants in urban soils, more studies are required on the long-term effect of compost on the retention and release of contaminants.

Acknowledgement

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Chapter 8. General summary and conclusions

8.1.General summary

Contamination with trace metals and de-icing salt and nutrient deficiency in tree pit soil represent two of the limiting factors for street tree health and for groundwater quality in an urban environment. In order to find if these limiting factors exist in Montreal tree pit soils, and if so how to improve them, three studies were designed:

Study I) The effects of environmental and soil chemical factors were studied with respect to both trace metals abundance (Cr, Ni, Cu, Zn, Cd and Pb) and nutrient availability (Ca, Mg, K, P, and total mineral N) in soils collected from tree pits on commercial and residential streets in Montreal, Quebec, Canada. Contingency table analysis, multiple linear regression, and Multivariate Adaptive Regression Splines (MARS) were applied to study how environmental and soil chemical factors were related to the total concentrations of trace metals and nutrient availability in tree pit soil.

Study II) The potential of urban soil amended with compost derived from mixed green and table waste and/or maple wood derived biochar in retaining Cu, Zn, Cd, Pb in the presence of de-icing salt (Na) was studied in sorption and desorption test. Multiple linear regression was applied in order to discover if either compost, biochar or both could significantly affect the partitioning of Na, Cu, Zn, Cd, and Pb between the soil matrix and soil solution. A comparison was made of the steady state concentrations of trace metals in different mixtures of soil, compost, and biochar in order to determine an optimum soil mixture for use in tree pits.

Study III) Based on the results of study II, the bioavailability of trace metals (Cu, Zn, Cd, and Pb), Na as well as nutrients (K, Ca, Mg, P, and total mineral N) in soil amended with 0, 5 and 10% (w/w) compost was evaluated in a phytotoxicity test for soil mixtures spiked with medium or high contamination levels and in the absence of any added contamination. The relationships among soil properties, compost percentage, contamination level and metal uptake by barley (*Hordeum vulgare* L.) were determined using multiple linear regression. Also because of the possibility of strong correlation between predictor variables, path analysis was used as a complementary analysis after regression analysis.

8.2. Conclusions

The results of the chemical and statistical analyses on the soil samples, previously collected from tree pits in commercial and residential land use zones, indicated that Cu, Zn, Cd, and Pb concentrations were significantly higher in commercial zones than in residential zones. The significantly higher concentrations of trace metals in the commercial zones might be attributed to the heavier traffic on commercial streets as compared to residential ones (Mingkui and Hao, 2009). Heavy vehicular traffic on wider streets in commercial zones resulting in an elevated input of contaminants to the tree pit soil over time is one mechanism presumed to result in these elevated values of Na and trace metals (Jutras et al., 2009; Sabin et al., 2005).

Some soil chemical characteristics, such as SOM and pH, also had an impact on the concentrations of trace metals in the tree pit soil. As different studies indicated (Kabata-Pendias, 2001a; McLean and Bledsoe, 1992), the positive relationship between SOM and the concentrations of trace metals such as Cu and Pb in tree pit soil of residential zones can be attributed to the high affinity of these trace metals for organic ligands in the soil. However in the commercial zone, SOM did not show a significant effect on trace metal concentrations. The lack of relationship between SOM and trace metal content in the commercial soils may be related to the sorption of trace metals to other adsorbents in the soil, such as Fe and Mn oxyhydroxides (Kumar and Edward, 2009), the formation of Cu and Pb precipitates (McBride, 1994e), and competition among trace metals and other cations, such as Na from de-icing salt and Ca from the weathering of concrete in buildings and sidewalks, for complexing sites on SOM (Cunningham et al., 2008; Katip et al., 2012). Increasing soil pH may also result in higher concentrations of metals like Pb and Zn in the soil solid phase likely through metal chemisorption on oxides and aluminosilicates, complexation with organic matter, and precipitation as carbonates (McBride, 1994e; Takáč et al., 2009).

An appropriate supply of soil nutrients is another important factor affecting the life span, health and growth of trees. Our results did not indicate any significant differences in Ca, Mg, P or total mineral N between tree pit soils from commercial and residential zones. The nutrient concentrations in both commercial and residential zones generally exceeded the values recommended for horticultural soils (Whitcomb, 1987). A significant positive relationship was observed between SOM and the available K, Ca, Mg, and total mineral N. Leaf litter and the repeated application and decomposition of the tree pit cover materials (*e.g.*, wood chips) can increase SOM content, promote biological activity in the soil (Urban, 2008), and thereby augment nutrient availability in the soil over time (Fraedrich and Ham, 1982; Holtz et al., 2004). This could be one mechanism that would account for the positive relationship between SOM and nutrient availability. The availability of K was also correlated with Na concentrations in the tree pit soil. Sodium can be derived from de-icing salt. According to Norrström and Bergstedt (2001), high concentrations of Na can result in K leaching from the soil through displacing K adsorbed between the layers of 1:2 type clays in the soil. The decrease in total mineral N can also be attributed to the accumulation of de-icing salt in tree pit soil over time. According to Green et al. (2008a), the high sensitivity of nitrifiers to salinity can result in a shortage of NO_3^- in roadside soil. Cation exchange competition from Na^+ can increase NH_4^+ leaching from the roadside soil.

The decrease in the availability of P over time can be attributed to the accumulation of trace metals such as Cu and Zn in the tree pit soils over time (Kargar et al., 2013). According to Pezzente (1997), the accumulation of these trace metals can inhibit the growth of the responsible fungi for making P available for tree roots. Also, the availability of P may decrease gradually through binding of P with carbonates from the weathering of buildings as time passes (Li et al., 2013c).The results of our leaching test on tree pit soil amended with compost and biochar indicated that soil acted as the main adsorbent of Na in the soil mixtures, and neither compost nor biochar significantly increased Na retention in soil mixtures. Our results did not indicate any significant relationship between the Cu, Zn, Cd, and Pb partitioning coefficients and biochar percentages in the soil. This lack of effect due to biochar was unexpected, given reports from other studies, but it is speculated that it might be related to the feedstock and the conditions used in the manufacture of the biochar. Therefore the subsequent phytotoxity test was designed without including biochar in the soil mixtures.

The results of the sorption and desorption tests and the phytotoxicity assay indicated that compost can decrease the mobility and bioavailability of Zn and Pb. It is generally thought that the increased CEC of compost-amended soil provides more bonding capacity for these metals, and that the humic and fulvic acids provided by compost result in the incorporation of metal ions into less labile metal complexes.

Copper showed high mobility, as it was abundantly present in the leachates from the desorption tests. High concentrations of Cu in pore water from non-amended soil, in contrast to the compost-amended soil, might be expected because of the strong association between Cu and DOC (Beesley et al., 2010).

The phytotoxicity test indicated that compost has the potential to decrease Cu and Cd bioavailability. This is in accordance with other studies which suggested that compost can decrease Cu bioavailability through complexation reactions with humic substances (Basta et al., 1993; Paradelo et al., 2011). This complexation results in very complicated compounds that are resistant to degradation by microorganisms. Also because of their large size, these complexes are not easily taken up by plants (Zhu et al., 2004). Farrell et al. (2010) suggest that compost may decrease the bioavailability of Cd by increasing the available macronutrient ions such as Ca^{2+}, Mg^{2+}, and K^+ and thereby blocking the uptake of Cd ions.

Our phytotoxicity study showed that compost also caused a significant increase in the availability of P, Ca, Mg, and K for barley plants. However, no significant increase was observed in NH_4^+ or NO_3^- availability. Chalhoub et al. (2013) explained that the N availability in soil after compost incorporation depends on the stability of the organic matter, the physicochemical characteristics of the compost, and on the environmental conditions such as soil type, moisture and temperature.

To conclude, the quantitative relationships among trace metal abundance, nutrient availability and environmental factors that were observed in this research can provide a valuable baseline for soil quality. Applying this baseline can help environmental specialists and city managers to plan future management strategies aimed at improving the longevity of downtown street trees.

Using compost to increase metal sorption and retention in amended soils and decrease metal absorption by plants can provide city managers with a cost-effective and environmentally friendly method for improvement of metal–contaminated tree pit soils. Compost increases soil fertility and so its use is presumed to generally increase street tree growth and life span and consequently to decrease tree replacement costs. The dual role of compost as a metal adsorbent and fertilizer should encourage city managers to recycle more biodegradable municipal solid waste as compost and therefore decrease the amount of organic waste deposited in landfills. There are processing costs associated with large-scale municipal composting that could make it more expensive than landfilling, depending on the circumstances of the municipality in question. However, it is widely accepted that landfilling is ultimately an unsustainable waste management strategy and options such as composting are gaining favor because they are considered to be more environmentally acceptable (Chiras, 2012).

Chapter 9. Suggestions for future research

The addition of compost significantly reduced the bioavailability of metals to plants and improved nutrient availability in our experiments. However, these experiments were run over the course of a few weeks, and the long-term effects of compost on the retention of contaminants could not be directly observed. It would be wise to investigate the potential long-term effects of mixing compost with soil for street tree pits. Therefore, as the next step to this research, a two-year study will monitor the actual function of the recommended soil mixture in newly designed, instrumented tree pits in the Hochelaga-Maisonneuve neighbourhood of Montreal, Quebec. The results of the monitoring study will be used to plan the large-scale deployment of the improved soil mixture in tree pits in the City of Montreal in order to buffer the stresses that lead to the premature death of street trees.

Biochar did not show any significant ability to retain Cu, Zn, Cd, and Pb in our experiments. As mentioned, the properties of different types of biochar vary greatly, and other researchers report that the use of biochar in soil improves soil properties and plant health. Further research might be needed to improve the ability of biochar to retain Na and trace metals. Effective conditioning of biochar as a soil amendment would increase the value of deadwood that might otherwise be discarded, for instance, from trees killed by insects such as emerald ash borer.

Compost affected neither the retention of Na in soil nor Na absorption by plants. It might be interesting, therefore, to investigate the use of other de-icing salts, such as $CaCl_2$ or $MgCl_2$, which have more affinity to organic matter, or a combination of these with NaCl. Lab-scale and field-scale experiments can show the effects of alternative types of de-icing salt on tree species such as little-leaf linden (*Tilia cordata* Mill.), which are widely planted but are known to be salt intolerant (Jutras, 2008).

It is often thought that urban soils are deficient in nutrients for tree growth. Our study indicated that there is no nutrient deficiency in soils sampled from urban tree pits. Other studies have indicated that changes in nutrient availability in the soil may not correspond directly to changes in the amounts of nutrients absorbed by plants (Noguchi et al., 2005). We recommend a study to monitor nutrient availability on a per-site basis over time, using methods such as tree xylem sap sampling, chemical analysis of foliage and tree pit soil, while also monitoring the growth of street trees. This monitoring study could reveal whether changes in tree growth are indeed related to nutrient concentrations in tree pit soils.

Soil sorption capacity for metals can be different depending on whether the soil is single-metal- or multi-metal-contaminated. Future studies could focus on sorption and desorption tests and phytotoxicity trials in order to compare soil sorption capacity in single and multi-metal contamination. The results of these experiments could help to predict the synergetic and antagonistic relationships between different contaminating metals, which affect metal mobility and bioavailability.

Chapter 10. References

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