Biogeochemical Studies of Metal Uptake and Transportation in Plants on an Urban Brownfield

Yu Qian
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BIOGEOCHEMICAL STUDIES OF
METAL UPTAKE AND TRANSPORTATION IN PLANTS
ON AN URBAN BROWNFIELD

A DISSERTATION

Submitted to the Faculty of
Montclair State University in partial fulfillment
of the requirements
for the degree of Doctor of Philosophy

by
YU QIAN
Montclair State University
Montclair, NJ
2015

Dissertation Chair: Huan Feng, PhD
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THE GRADUATE SCHOOL
DISSERTATION APPROVAL

We hereby approve the Dissertation

BIOGEOCHEMICAL STUDIES OF METAL UPTAKE AND TRANSPORTATION
IN PLANTS ON AN URBAN BROWNFIELD

of

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Soil metal contamination has been a concern due to the potential ecological and human health risks. In order to assist with the management and sustainable restoration of vegetated metal contaminated land, this dissertation targets at understanding the biogeochemical processes that control the assimilation of metals by plants on urban coastal brownfield soils. The dissertation includes: i) micro-scale measurement of metal spatial distribution and speciation using synchrotron techniques to investigate the mechanism of metal uptake and translocation in roots based on the association between metal localizations in plant roots, ii) study on the biogeochemical factors that control plant metal assimilation efficiency and metal distribution in plan, and iii) environmental assessment of the potential ecological risk of metal contaminated brownfield sites. The micro-scale study of metal uptake and transportation were conducted on the root sections of Typha latifolia L. The results indicated that iron plaque on root surface acted as a barrier for Pb root uptake and a buffer for Zn, Mn and Cu root uptake. The accumulation of Zn, Mn and Cu in the vascular bundles and dermal tissues might follow a similar mechanism. This study also identified metal uptake efficiencies by roots, stems and leaves, which varied with soil pH, soil TOC, metal element, metal concentration, growth season, and plant species. In an evaluation of potential ecological risk of metal
contaminated soil, criteria such as geoaccumulation index, enrichment factor, and ecological risk index were applied to assess metal enrichment and divided the contaminated sites into three regions with low, moderate, and high potential ecological risks. Overall, this research investigated the transport and behavior of metals in contaminated land at both the micro and macro scales. Results from this dissertation research could be used as a reference for land management agencies and environmental protection agencies in their decision-making efforts toward sustainable redevelopment and restoration of contaminated land.
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DEDICATION

In memory of my grandparents Xuemin, Ruiyun, and Liangsheng

and

To my loving parents, Xiaofan and Nanlan, and my lovely family
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# LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>BCF</td>
<td>Bioconcentration factor</td>
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<tr>
<td>SD</td>
<td>Standard deviation</td>
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<tr>
<td>AAS</td>
<td>Atomic absorption spectroscopy</td>
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<tr>
<td>ATSDR</td>
<td>Agency for Toxic Substances and Disease Registry</td>
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<tr>
<td>BCR</td>
<td>Community Bureau of Reference</td>
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<tr>
<td>CCME</td>
<td>Canadian Council of Ministers of the Environment</td>
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<tr>
<td>CRM</td>
<td>Common reed/mugwort</td>
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<td>CRRNJ</td>
<td>Central Railroad of New Jersey</td>
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<tr>
<td>EDTA</td>
<td>Ethylenediamine tetraacetic acid</td>
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<tr>
<td>EDS/EDX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<tr>
<td>EF</td>
<td>Enrichment factors</td>
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<td>EPA</td>
<td>Environmental Protection Agency</td>
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<tr>
<td>$E_r^{ij}$</td>
<td>Ecological risk index</td>
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<tr>
<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
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<tr>
<td>GPS</td>
<td>Global position system</td>
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<tr>
<td>HQ</td>
<td>Hazard quotients</td>
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<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
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<tr>
<td>$I_{geo}$</td>
<td>Geoaccumulation index</td>
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<tr>
<td>LA-ICP-MS</td>
<td>Laser ablation inductively coupled plasma mass spectrometry</td>
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<tr>
<td>LOI</td>
<td>Loss of ignition</td>
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<td>LSP</td>
<td>Liberty State Park</td>
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<td>LVRR</td>
<td>Lehigh Valley Railroad</td>
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<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>MEP</td>
<td>Ministry of Environmental Protection of the People’s Republic of China</td>
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<td>MDL</td>
<td>Minimum detection levels</td>
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<td>MG</td>
<td>Maritime grasslands</td>
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<td>MS</td>
<td>Maritime shrubland</td>
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<td>NIST SRM</td>
<td>National Institute of Standards and Technology Standard Reference Materials</td>
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<td>NJDEP</td>
<td>New Jersey Department of Environmental Protection</td>
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<tr>
<td>NJCA</td>
<td>New Jersey Administrative Code</td>
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<tr>
<td>OCT</td>
<td>Optimal cutting temperature</td>
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<tr>
<td>OLS</td>
<td>Ordinary least squares</td>
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<tr>
<td>PIXE</td>
<td>Micro-proton induced X-ray emission</td>
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<td>RI</td>
<td>Risk index</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SIMS</td>
<td>Secondary ionization mass spectrometry</td>
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<tr>
<td>SNH</td>
<td>Successional northern hardwood</td>
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<td>SOF</td>
<td>Successional old field</td>
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<tr>
<td>SQG</td>
<td>Sediment quality guideline</td>
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<tr>
<td>SSB</td>
<td>Successional shrubland</td>
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<td>SSC</td>
<td>Sediment chemical concentration</td>
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<td>SSL</td>
<td>Ecological soil screen level</td>
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<tr>
<td>SµXRF</td>
<td>Synchrotron micro X-ray fluorescence</td>
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*T. latifolia* L. *Typha latifolia* L.  

t | Tem | Transmission electron microscopy |
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<tr>
<td>TF</td>
<td>Translocation factor</td>
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<tr>
<td>Acronym</td>
<td>Description</td>
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<td>---------</td>
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<tr>
<td>TOC</td>
<td>Total organic content</td>
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<tr>
<td>UK</td>
<td>United Kingdom</td>
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</tr>
<tr>
<td>UMDNJ</td>
<td>University of Medicine and Dentistry of New Jersey</td>
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<tr>
<td>USA</td>
<td>United State</td>
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<tr>
<td>USACE</td>
<td>United State Army Corps of Engineers</td>
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<tr>
<td>XANES</td>
<td>X-ray absorption near-edge structure</td>
<td></td>
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<tr>
<td>XRS</td>
<td>X-ray spectroscopy</td>
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CHAPTER 1

INTRODUCTION

1.1 Metal biogeochemical cycle in terrestrial ecosystem

Metals are indispensable constituents in the earth system. They are retained in the heterogeneous soil matrix in various forms (Duffs, 2002; Tessier et al., 1979; Zimmerman and Weindorf, 2010). The fate, mobility, and behavior of metals in soil are governed by the soil geochemical properties (Wuana and Okieimen, 2011). Metal biogeochemical cycle is a pathway by which metals move through compartments of an ecosystem (Figure 1-1) (Mitsch and Gosselink, 2007). The exchange of metals between biosphere and pedosphere is a part of metal biogeochemical cycle. As shown in Figure 1-1, plant assimilation of metals can be simplified into the following steps: mobilization of solidified metals in soil into bioavailable metals in soil pore water, plant root uptake of bioavailable metals from soil pore water, root to shoot transportation of metals, and accumulation of metals in plant tissues (Clemens et al., 2002; Kramer, 2010; Salt et al., 1998; Weis and Weis, 2004). Figure 1-1 shows a natural terrestrial ecosystem with metals cycling between each compartment dynamically.

Plants in terrestrial environment can accumulate metals from soil effectively. When the metal concentrations in the plant tissues increase to a level that is hazardous to normal biological metabolism, the plants will apply strategies to protect themselves from
metal toxicity. Common strategies include reducing root metal sorption rate, increasing root tolerance to high soil metal concentration and isolating metal in vacuoles and leaf surface. There are two major outflows for metals accumulated in the plants. One is transportation to higher trophic level through food chain and the other is entering abiotic surrounding as detritus. When microorganisms decompose detritus in soil, metals are released back to the soil and a full metal biogeochemical cycle is completed (Adriano, 2001; Cheng, 2003; Weis and Weis, 2004). In summary, plant uptake and transportation of metals is an important ingredient of the dynamic exchange of metals between the biota and the abiotic environment. Therefore, studying metal uptake and transportation by plant is important in understanding metal biogeochemical cycle in urban ecosystem.

1.2 Metal contamination in urban brownfield sites

The biogeochemical cycle of metals in terrestrial ecosystems is influenced by anthropogenic activities (Vitousek et al., 1997). Among all the terrestrial ecosystems disturbed by human activities, urban ecosystem receives the highest degree of human disturbance than the others do (De Kimpe and Morel, 2000). Urban ecosystem receives metal influxes from a wide range of sources, including dust and aerosol particles from fuel combustion and solid or liquid waste depositions. As a result, soil metal concentrations in urban ecosystem are higher than that in the undisturbed natural
ecosystem. Consequently, the potential hazards and risks to human health and ecosystem are raised when human and organisms are exposed to contaminated urban soil (Underwood, 2012; Langston, 1990).

Brownfield is an “abandoned, idled or underused industrial and commercial facilities where expansion or redevelopment is complicated by real or perceived environmental contamination” (USEPA, 2002). Generally, brownfield has the following features: (i) diverse past history including residential, commercial and industrial use; (ii) soil and ground water contamination; (iii) potential risk to both local residents and the environment; and (iv) small area (<10 acres or 0.04 km²) with combined contaminants. Vegetations growing on the brownfield can assimilate metals in their biomass continuously (Figure 1-2). French et al. (2006) observed that trees planted on the resorted brownfield sites accumulated metals at high concentrations. Moreover, soil metal concentration impacted the assemblage trajectory of plant species growing on the urban brownfield (Gallagher et al., 2008a, 2008b; Gallagher et al., 2011). The previous studies suggest that metals accumulated in urban brownfields have relative high potential ecological risk and the metal contaminated soils in the urban brownfield should be mitigated properly.
1.3 Metal bioavailability in soil environment

Bioavailable metal is the portion of metals in the soil that is available for the biota to uptake (Alloway, 2010). Metals in soil minerals need to complete two steps before they finally become available to biota. Dissolution of soil mineral in water is the first step, which determines the total concentration of metals in the aqueous environment that is potentially available for plant root uptake. Common ion effect, ionic strength effect, and ion complexation effect in the solution can determine the dissolution rate of minerals by affecting the solubility of minerals. Generally speaking, when the solubility increases, more minerals can be dissolved in the water. Not all the metals that exist in the minerals are equally available for dissolution. There are five fractions of solid phase that metals can be partitioned in soil: exchangeable, carbonate, iron-manganese oxide, organic, and crystalline (Tessier et al., 1979). Metals in water-soluble and exchangeable fractions are the most bioavailable; metals precipitated with Fe-Mn oxides and metal organo-/inorgano- complex fractions are potentially bioavailable; metals bounded with insoluble sulfide and crystalline lattice fractions are not bioavailable (Gambrell, 1994). The relative partitioning of metals associated with each fraction is different (Alloway, 2010). Some metals mainly occur in bioavailable fractions, such as Zn and Cd, while the other metals tend to exist as less bioavailable form (Lasat, 2000). The second step is the speciation of the dissolved metals in soil pore water. Speciation describes the stable state that dissolved
metals in the solution exist as free ions and complexes (Sposito, 2008). Complex is a stable molecular association that comprises a central ion or molecule that is bound to one or more other ions or molecules. There are three different binding species that can help to form soluble complexes: proton complexes (proton bindings species bind with anion central species), ligands (anion or neutral molecule binding species), and chelates (two or more functional groups in a ligand bound to a metal cation) (Sposito, 2008). pH, redox potential, presence of organic and inorganic ligands, and metal type are all important factors affecting the availability of metals (Violante et al., 2010). The impact of pH on the dissolution of minerals relies on H\(^+\) ions competing with metal ions for binding spots. The lower the pH is, the more the metal ions are substituted by H\(^+\) ions and, hence, the higher the mineral dissolution is. Once the metal ions are released into the solution, pH plays an important role in the metal speciation. Free metal cations and protonated anions are favored in low pH (pH <6), while more carbonate or hydroxyl complexes are observed at high pH (pH > 7.4) (Sposito, 2008). Redox potential represents the availability of electrons in the solution. The presence of ligand determines the speciation of metal complexes in the water. The more soluble metal complex is formed, the more metal is potentially available for the biota (Driscoll, 1998). Both organic ligands such as humic acid, fulvic acid, and root exudates (Sauve et al., 2000; Halim et al., 2003; Laing et al., 2009; Violante et al., 2010), and inorganic ligands such as Cl\(^-\), HCO\(_3^-\), surfactants,
and EDTA (Soriano-Disla et al., 2011) can form coordination complex with metal ions and impact metal bioavailability. As a result, the availability of metal in soil solution is closely related to soil physical-chemical environment, and also varies with metal type. However, the major soil property that impacts the availability of metal always differs from case to case.

1.4 Metal root uptake and root to shoot transport in plants

A typical process of metal transfer in plant can be divided into the following steps: uptake of metal from soil into root, translocate metal from root tissue to aerial tissue, and finally accumulate metal in the aerial tissue (Weis and Weis, 2004) (Figure 1-3).

Root systems play important role in the plant uptake, transport, and accumulation of metals. At the interface between lithosphere and biosphere, the root system can actively concentrate nutrients and exclude toxins (Hinsinger and Courchesne, 2008; Mauseth, 2012). As indicated in Figure 1-4, the root epidermis, exodermis, and tissues between are considered as dermal tissue (Marschner, 2011; Taiz and Zeiger, 2010).

While protecting root internal tissues from the external toxins (Claus et al., 2012; Clemens et al., 2002), dermal tissues absorb metals from soil in the form of free ions or small organic-metal complex either through vacant spaces between cell walls (apoplast) or through plasmodesmata between cytoplasm (symplast) (Marschner, 2012). Driven by
the negative pressure generated by evapotranspiration, metal ions can be transported from root epidermis into vascular tissues by passing through root cortex and root endodermis (Mauseth, 2012). Cortex tissues compose of several unspecialized cells with thin cell walls that locate between root exodermis and endodermis. The main function of cortex is radial solution transport and nutrient storage (Marschner, 2012). Endodermis, however, restrict metals in the apoplast from entering the vascular bundles by forming the lignified Casparian strip. Metal complexes cannot enter the vascular bundles and further transported to the aerial tissues unless they are inside of the symplast. Nevertheless, transportation of metals in the symplast is not obstacle-free. Intracellular compounds delay or stop the movement of metals by forming metal-phytochelatin complexes and accumulate these compounds in the vacuoles of root cells, making the cytoplasm a reservoir of metals (Clemens et al., 2002). Vascular bundle is surrounded by the root endodermis. It consists of vascular tissues and pith, and regulates transportation of nutrient solutions between the root and the shoot (Marschner, 2012). In summary, metal radial transportation from the external soil solution into the center vascular bundles is the result of integrated interaction between factors including external bioavailable metal concentration, apoplast ion reserve capacity, membrane transporter selectivity, symplast mineral sequestration, and root to shoot solution flux (Brennan and Shelley, 1999; Clemens et al., 2002; Hall, 2003; Marschner, 2012; Puig and Penarrubia, 2009; Taiz and
Zeiger, 2010). Therefore, investigation of the association between the localization of metals in different tissue sections of the plant root can provide a comprehensive understanding of root metal transfer process.

1.5 Iron plaque and root metal uptake

An Fe-Mn enriched deposit on the surface of plant roots has been observed in many previous studies (Armstrong and Armstrong, 1988; St-Cyr and Crowder, 1989). It is named as iron plaque because it is mostly composed of iron hydroxides. The structures of Fe minerals in the iron plaque include ferrihydrite, goethite, lepidocrocite, siderite and amorphous oxide iron, and so on. Other metal(loid)s have been observed to associate with the iron plaque. For example, Mn and Zn existed as discrete, isolated mixed metal carbonate nodules on the plaque (Hansel et al., 2001). The formation of iron plaque depends on the availability of oxygen and metal ions in the soil. Both factors are related to the soil environment and plant physiological activities. According to the study by St-Cyr et al. (1989), high soil moisture and oxygen radiation are favorable for the formation of iron plaque because oxygen can oxidize reduced ferrous ions and produce ferric precipitations around the root. In addition, it is found that the ratio between carbonate-bounded Fe and Mn in the soil is similar to the ratio between Fe and Mn in the plaque (St-Cyr et al., 1989). Besides the soil environment, the formation of iron plaque is also
related to the root physiological activity. Wetland plant species develop special structures in order to adapt to saturated anaerobic environment. Wetland plants supply oxygen to the underground roots by aerating intercellular spaces in root tissues. Oxygen in the aerated root tissues tends to diffuse through the root surface into the external environment, and this process is named as the radial loss of oxygen. Armstrong et al. (1999) found that root dermal tissues determined the diffusion rate of radial loss of oxygen. For example, radial loss of oxygen decreased rapidly within 30 mm from the root tip to the root base area, where the root dermal tissues were developed (Armstrong et al., 1999). Several other studies also reached the similar conclusion (Peng et al., 2009). As soon as iron plaque precipitates on the surface of root, it becomes the inter-surface between soil solution and root tissues. Iron plaque has very strong adsorption capacity to cations and many metals are either adsorbed by or co-precipitated with the iron plaque (Povidisa et al., 2009; Liu et al., 2011). Whether or not iron plaque plays a role as barrier or buffer of root metal uptake have been studied in various metal species and plant species. Liu et al. (2011) identified iron plaque as a barrier of the uptake of Pb by rice root, which is the same as indicated by Peverly et al. (1995), who studied *Phragmites australis* (common reed). However, the work done by Zhong et al. (2010) based on *Iris pseudacorus* (yellow iris) and Ye et al. (1998) based on *Typha latifolia* (broadle cattail) indicated that iron plaque enhanced the uptake of Pb by root. They considered iron plaque as a buffer of root
uptake. Similar phenomenon was observed during the uptake of As by rice, in which iron plaque increased the uptake of As by increasing As adsorption around the root (Deng et al., 2010). In summary, the formation of iron plaque is a complicated biogeochemical process and the role iron plaque plays in root metal uptake processes varies with both plant species and metal speciation. A good understanding of the relationship between metal uptake and iron plaque in the root system is critical in exploration of metal uptake mechanism. Therefore, the knowledge of the function of iron plaque in the root metal uptake should be further explored.

1.6 Environmental assessment for metal contaminated soil

The stability of an ecosystem is inevitably impacted when it is exposed to the contaminated soil. Once metal present in organism reaches a threshold concentration, many key lifecycle metabolic activities such as photosynthesis, root growth, and reproduction will be hindered (Baker, 1981). At the same time, protection and damage repair of metabolic activities will be stimulated in order to neutralize metal toxicities (Alloway, 2010). Therefore, given the concern on potential ecotoxicological impact on the organisms living on the contaminated site, ecological risk assessment on urban brownfield sites are necessary in order to properly monitor, manage, and redevelop urban brownfield.
Various analytical chemistry approaches are developed to analyze soil metal concentrations in order to evaluate the impact of metal contamination on terrestrial ecosystem (Table 1-1). Pseudo total metal fraction in soil includes both the non-bioavailable and bioavailable metal fractions. It usually estimates the portion of total soil cation exchange capacity that is saturated by metals. Although Pseudo total fraction does not represent the fraction of metals that is bioavailable for plants and soil organism, it indicates potential ecological risks. It is known that mobilisable metal fraction includes both potentially bioavailable and bioavailable metal fractions, while mobile metal fraction in soil represents bioavailable fraction only. In order to evaluate the portion of metals that can be uptake by plant root and organisms in the soil, both mobilisable and mobile fractions should be measured (Gupta et al., 1996). Besides the establishment of different soil metal analytical methods, several ecosystem risk assessment indexes have also been developed to provide reference for the assessment of ecological risk of contaminated soils:

1) Enrichment factor (EF) and geoaccumulation index ($I_{geo}$): They are used to assess the anthropogenic metal pollution level in comparison with the background metal concentration in soil. These indexes help to identify areas with metal load from external sources. Total metal concentrations in the soil are required for the assessment;
(2) Potential ecological risk index (RI): The RI is used to assess the degree of potential ecological risk of metals in the soil. Different from EF and $I_{geo}$, the RI evaluates the overall toxicity of metals in the soil. The toxicity of each metal is transferred into individual toxic factor to be considered in calculating the overall potential ecological risk of the metals in the soil (Hakanson, 1980; Sun et al., 2010);

(3) Critical reactive metal concentration in the soil (Alloway, 2010): This approach estimates the critical reactive metal concentration in the soil (soil metal concentration determined by 0.43M HNO$_3$ or EDTA extraction) based on the soil physiochemical properties such as clay content, pH, and organic matter content. When the measured soil bioavailable metal concentration exceeds the established critical reactive metal concentration, ecotoxicological effects on soil organisms and plants might occur; and

(4) Soil metal concentration criteria: These are the values established by the government agencies. The values could be difference from state to state or from country to country around the world. Many countries have developed soil metal concentration standards for different purposes. In USA, the Environmental Protection Agency (EPA) developed the Ecological Soil Screen Levels (Eco-SSL) for metals based on references from scientific research (EPA, 2005). The New
Jersey Department of Environmental Protection (NJDEP) has developed clean up criteria for urban soil management (NJAC, 2012; NJDEP, 2012). In Canada, the Canadian Council of Ministers of the Environment (CCME) developed the Canadian Environmental Quality Guidelines for the protection of environmental health. The guideline has developed the maximum acceptable soil metal concentration for different land use such as agricultural, residential/parkland, commercial, and industrial (CCME, 2013). In Swiss, the Swiss Federal Council proposed the Ordinance Relating to Impacts on the Soil in order to maintain the fertility of soil. In this ordinance, the guide value, trigger value, and clean up value of soil metals are developed for both total soil metal concentration and soluble soil metal concentration. Guide value indicates possible negative effect from soil metals on soil quality. Trigger value indicates metals in soil pose possible danger for ecosystems. Clean up value indicates soil contamination is very likely to pose chronic hazard effect on ecosystem (Figure 1-5) (The Swiss Federal Council, 1998; Gupta et al., 1996). The Netherlands Ministry of Housing, Spatial Planning and Environment’s Circular has classified soil metal contamination into three levels: Dutch intervention, which is the maximum tolerable contaminant concentration for ecosystem; Dutch target, which is the contaminant concentration that has negligible risk for ecosystems; Dutch HC50
lies between Dutch Intervention and Dutch Target, indicated the contaminant is hazardous to 50% of the species in the ecosystem at the concentration (Swartjes, 1999). In China, the Ministry of Environmental Protection of the People’s Republic of China (MEP) established Environmental Quality Standard for Soil. The standard divided soil total concentration into three levels: background value that represents pristine lands, target value that poses no risk to ecosystem and human health, and critical value that is acceptable for agricultural production but may impact human health (MEP, 1996).

To evaluate the ecological risk of soil metal contamination, one should measure metal concentration in specific soil fraction and select soil metal ecological risk assessment criteria based on the purpose and target receptors in the ecosystem.

1.7 Application of advanced technologies in study of metal distribution and speciation in plants

Knowing how metals are acquired, transported, distributed, and accumulated in plants is important for regulating metal flux from abiotic soil environment to biota. Metals exist in plant tissues either by compartmentalization in specific subcellular compartments (e.g., cell wall, vacuolar), or chelating with various ligands (e.g., amino acid, peptides) (Wu and Becker, 2012). Both metal concentrations and metal chemical
speciations vary with plant tissue type (Zhao et al., 2014). Although wet chemistry total digestion of plant tissues for total metal concentration analysis can provide information on the uptake and translocation rate of metals in plants, it is well recognized that traditional chemical approaches cannot fully reflect metal spatial distributions in different types of plant tissues (Zhao et al., 2014). Metallomics, defined by Szpunar (2005) as “comprehensive analysis of the entirety of metal and metalloid species within a cell or tissue type” was established in order to address the localization and speciation of elements amongst a specific position in a system (Szpunar, 2005; Wu and Becker, 2012). Advanced techniques for analysis of metal distribution and speciation have been developed to meet the need of plant metallomics study. To achieve greater concentration sensitivity, lower detection limit and spatial resolution, the state-of-the-art synchrotron based techniques are attracting more and more beamline users in plant metalloid study (Wu and Becker, 2012). Currently, there are more than 40 synchrotron facilities around the world. These synchrotron facilities can generate high photon source brighter (>10 orders of magnitude) than conventional X-ray tubes and, hence, raise the sensitivity, resolution and element detection range. Only very small amount of sample is required for the analysis and in situ hydrated plant samples can be directly measured (Zhao et al., 2014).

Synchrotron X-ray fluorescence (XRF, or S-XRF) and X-ray absorption
spectrometry (XAS) are the two types of synchrotron techniques used for plant sample analysis. In the recent decades, scientists began to apply XRF and XAS techniques in plant to visualize metal distribution in plant tissues. Leigh Broadhurst et al. (2008) applied synchrotron based XRF and XANES techniques to study Ni accumulation mechanism in Ni-hyperaccumulating species *Alyssum corsicum*. In this study, full-sized XRF maps for Ni, Mn, and Ca were measured for *Alyssum corsicum* leaf and the XANES spectrum of Ni and Mn were measured at leaf trichome. The XRF maps showed that Ni and Mn in leaf were heterogeneously distributed but correlated at some specific locations above vascular tissue. Also, the XANES spectrum at trichome indicated that Mn(II) and Ni(II) were the dominant oxidation state of the elements. The results above indicated the Ni accumulation mechanism applied by *Alyssum corsicum* might be developed from Mn handling system (Leigh Broadhurst et al., 2008). Zimmer et al. (2011) applied XRF and scanning electron microscopy (SEM) to study the distributions of As, Ca, Cu, Fe, K, Mn, Ni, S and Zn in a root cross section of willow root collected from a contaminated floodplain. At the same time, the role iron plaque plays at the root surface in the uptake and immobilization of As were also analyzed. The concentrations of Ca, Cu, Ni, S and Zn were high in the internal part of the root section, where roughly correspond to the aerenchmatic tissue of the root according to SEM image. The correlation between As and Fe in the root section showed three sets of pixel patches in iron plaque, indicating that As
was possibly associated with Fe in three different sorption mechanisms (Zimmer et al., 2011). Rouff et al. (2013) applied XRF and XANES techniques to study metal distribution and speciation in fresh *Phragmites australis* whole roots collected from an urban contaminated wetland. Spatial correlation between Fe and Mn on root surface indicated the formation of iron plaque, and XANES spectrum of Cu and Zn in hot spots suggested that these two elements were associated with ligands phytate and cysteine (Rouff et al., 2013). Feng et al. (2013) applied XRF and XANES techniques to explore the speciation and distribution of Fe and Pb in the *Typha latifolia* L. root sections. Strong spatial correlation between Pb and Fe was observed on the root surface, and the major Pb and Fe species in root section were Pb(II) and Fe(III). The association and speciation of Pb and Fe on root surface indicated that iron plaque might sequestrate Pb and further influence Pb uptake (Feng et al., 2013). Lu et al. (2014) applied XRF and EXAFS techniques to investigate the distribution and speciation of Zn in the fresh leaves and stems of a Zn hyperaccumulator *Sedum alfredii*. XRF results indicated the distribution pattern of Zn in roots, stems, and leaves were age-depended. EXAFS analysis of the hot spots of Zn in leaves suggested Zn mainly associated with malate and formed Zn-citrate/Zn-cell wall complexes in the roots (Lu et al., 2014).
1.8 Goal and objective of this dissertation

The goal of this dissertation research is to understand the biogeochemical processes and mechanisms controlling the translocation of metals in dominant plants on an urban brownfield site. The objectives of this research are to:

1) Investigate the impact of the soil environment on the spatial distribution of metals in wetland plant root and study root metal uptake mechanisms based on micro-scale metal spatial distributions in root;

2) Determine the factors that control the soil metal bioavailability and metal accumulation in plant growing on a metal contaminated brownfield site;

3) Estimate the influence of soil metal concentrations and physiochemical properties on the uptake and root to shoot transportation rate of metals by plants; and

4) Evaluate the potential ecological risk of metal contaminated brownfield.

1.9 The structure of this dissertation

Chapter 1 is a general introduction of the research background and structure of this dissertation.

Chapter 2 describes a synchrotron study of metal localization based on the spatial distributions of Zn, Cu, Mn, Pb and Zn in Typha latifolia L. root investigated. Significant difference ($p<0.05$) of metal localization between the dermal tissues and the vascular
bundles was observed. Statistical analyses were performed on the data to explore internal relationships between the spatial accumulation of Cu, Mn, Pb, Fe and Zn in the dermal tissue and the vascular bundles. A simple linear regression analysis was applied to investigate the association between metal accumulations in different types of tissue. Factor analysis showed that there is a close association between Pb and Fe; and Cu and Zn in the dermal tissue, indicating these elements possibly associate to each other following different mechanisms. In the vascular bundles, high loadings of Zn, Mn, and Cu were found in the same factor, suggesting the localization of these three elements is controlled by the same factor. Cluster analysis was conducted based on the spatial distribution of Pb and Fe in the dermal tissue and divided dermal tissues into iron plaque region and regular dermal tissue region. The results of this study indicate that iron plaque possibly acts as a barrier for Pb and a buffer for Zn, Mn and Cu. The localizations of Zn, Cu and Mn are similar in dermal tissues and vascular bundles of *T. latifolia* L.

Chapter 3 presents a geochemical study of toxic metal translocation in an urban brownfield wetland. This chapter shows the study of metal translocation in rhizosphere soil and dominant plant samples collected at a brownfield site in New Jersey, USA, during summer 2005. The soil physiochemical properties and plant tissue metal concentrations were collected for the samples to evaluate plant metal uptake from the contaminated soils. Metal concentrations varied from 4.25 to 978 mg g\(^{-1}\) for As, 9.68-209
mg g\(^{-1}\) for Cr, 23.9-1870 mg g\(^{-1}\) for Cu, and 24.8-6502 mg g\(^{-1}\) for Zn. A wide range of metal uptake efficiencies in the roots, stems and leaves was found in this study. Data showed that (1) *Betula populifolia* has high Zn, Cu and As accumulations in the root, and high concentrations of Cu and Zn in the stem and the leaf; (2) *Rhus copallinum* has high accumulation of Zn and Cr in the leaf and Cu in the stem; (3) *Polygonum cuspidatum* has high accumulations of Cu and As in the root; and (4) *Artemisia vulgaris* shows high Cu accumulation in the leaf and the stem. This chapter has been published in Environmental Pollution (Qian et al. 2012).

*Chapter 4* presents a study of V uptake and translocation in dominant plant species on an urban coastal brownfield site. Factors that control metal V uptake and translocation in naturally assembled plant species in Liberty State Park were investigated. Six dominant species were collected from 22 stations in the study area. Vanadium concentration in the plants decreased in a sequence of root > leaf > stem. No significant differences were found among the six dominant plant species in terms of root V uptake efficiency (V BCF) and V root to shoot translocation (V TF). Although soil pH and TOC did not show significant impact on V accumulation in the roots, soil labile V content showed significant positive linear correlation \((p < 0.05)\) with plant root V. Nonlinear regression analysis indicates that V translocation efficiency decreases with increasing concentration in the soil, implying that excessive V in the soil might inhibit its sorption
by the plant roots. Leaf V concentration was constant in all the plant species regardless of
the variation in soil V concentration. The study shows that the six dominant plant species
on site had limited the amount of V translocated to the aerial part of the plant. This
chapter has been published in Science of the Total Environment (Qian et al., 2014).

Chapter 5 discusses ecological risk assessment of metal contaminated soil on an
abandoned urban brownfield site. In this study, soil samples were collected from 22 sites
in Liberty State Park, New Jersey, in 2005 for metal enrichment characterization and
potential ecological risk assessment. Geoaccumulation index ($I_{\text{geo}}$) showed the
enrichment level of metals followed an order of Cu>Pb>Zn>As>Cr>Hg while the
potential ecological risk factor ($E_P^i$) indicated the potential ecological risk of each metal
was in the order of Cu>Pb>As>Hg>Zn>Cr. Among these 22 sites, this investigation
identified 9 sites at moderate ecological risk, 3 sites at considerable ecological risk, and 4
sites at high ecological risk according to the potential ecological risk index (RI).
Hierarchical cluster analysis (CA) of soil metal concentrations separated the study sites
into four groups, which are supported by the significant difference in RI values.
Geographically, three regions in the Liberty State Park brownfield site were determined
based on the CA results and RI values. The first region was at the lowest ecological risk.
The second region was under the moderate ecological risk of elevated Cu, Pb, and Zn
concentrations and had a significant correlation between Cr and Pb. The third region was
under the highest ecological risk of the highest concentrations of Cu, Pb, Hg and Zn.

There was also a significant positive linear correlation between Pb and Zn in the third region. This chapter has been submitted to a journal for peer-review.

Chapter 6 summarizes metal (As, Cd, Cr, Cu, Hg, Fe, Mn, Ni, Pb and Zn) concentrations in 54 selected riverine, estuarine and coastal sites around the world and evaluated the sediment metal contamination in these selected sites. The study recommends that these areas need a better environmental management practice for restoration. This chapter has been published as a book chapter in Heavy Metal Sediment (Qian et al., 2011).

Chapter 7 states the environmental implication of this dissertation research and recommends the strategies for the future environmental research and management.
1.10 References


Langston, W., 1990. Toxic effects of metals and the incidence of metal pollution in marine ecosystems.


Table 1-1 Metal fractions in soils and commonly extraction media (Gupta et al., 1996).

<table>
<thead>
<tr>
<th>Fractions in soil</th>
<th>Characteristics of fraction</th>
<th>Commonly used extracting media</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo total</td>
<td>Non-active + Potentially active (Mobilisable)</td>
<td>Strong acid solutions: <em>aqua regia</em>, boiling HNO$_3$, HCl</td>
</tr>
<tr>
<td>Mobilisable</td>
<td>Potentially activ + Active</td>
<td>Complexing agent solution</td>
</tr>
<tr>
<td></td>
<td>Potentially bioavailable or potentially leachable</td>
<td>Buffered and unbuffered complexing and chelating reagents like HN$_4$OAc + EDTA, EDTA, Acetic acid, DTPA + CaCl$_2$</td>
</tr>
<tr>
<td>Mobile</td>
<td>Active (bioavailable and easily leachable)</td>
<td>Neutral unbuffered salt solutions like NaNO$_3$, CaCl$_2$, NH$_4$NO$_3$</td>
</tr>
<tr>
<td>Immobile</td>
<td>Pseudo total - Mobilisable</td>
<td>See pseudo total and mobilisable</td>
</tr>
</tbody>
</table>
Figure 1-1 Biogeochemical cycle of trace elements on a vegetated site.
Figure 1-2 Source, fate, and behavior of metal in urban ecosystem
Figure 1-3 Scheme of the process plant takes for metal uptake, transport and accumulation.
Figure 1-4 A schematic diagram of metal uptake and transport in plant root. Modified based on Taiz and Ziger (2010).
Figure 1-5 Risk assessment and management for contaminated soil using a three-level evaluation system considering mobile, mobilisable and pseudo total metal fractions in soil. All values imply soil metal concentrations (Gupta et al., 1996).
CHAPTER 2

SYNCHROTRON STUDY OF METAL LOCALIZATION IN

*Typha latifolia* L. ROOT SECTIONS

Abstract

This study investigated spatial distributions of Fe, Cu, Mn, Pb and Zn in *Typha latifolia* L. root. Statistical analyses were performed on the data to explore the differences in spatial distributions of Cu, Mn, Pb, Fe and Zn in the dermal tissue and the vascular bundles. Significant difference ($p<0.05$) in metal localization between the dermal tissues and the vascular bundles was observed. Simple linear regression was applied to investigate the association between metals from different types of tissue. Factor analysis showed that in the dermal tissue, Pb and Fe were closely associated together, and Cu and Zn were associated together, suggesting that metal localization mechanisms could be elemental dependent. In the vascular bundles, Zn, Mn, and Cu showed strong association, suggesting that the localization of these three elements is controlled by the similar mechanism. Cluster analysis was conducted to divide the dermal tissue into iron plaque region and regular dermal tissue region based on the spatial distribution of Pb and Fe in the dermal tissue. The results of this study indicate that iron plaque possibly acts as a barrier for Pb and a buffer for Zn, Mn and Cu. The localization of Zn, Cu and Mn is similar in the dermal and vascular tissues of *T. latifolia* L.
Keywords: Synchrotron µ-XRF, Root metal uptake, Iron plaque, *Typha latifolia* L., Brownfield wetland;
2.1 Introduction

Urban soil contamination has increased dramatically in recent decades due to anthropogenic activities (Desouki and Feng, 2012; Luo et al., 2012; Qian et al., 2011; Wuana and Okieimen, 2011). Lead (Pb), copper (Cu), manganese (Mn) and zinc (Zn) are contaminants commonly found in urban soil. Once they enter soil, these metals cannot be degraded and tend to accumulate in soil and pose potential risks to urban ecological stability and human health. Urban brownfields are concerned specifically because they are in densely populated areas and difficult to revitalize (French et al., 2006; Gallagher et al., 2008; Luo et al., 2012; McKenna, 1998). In recent decades, phytoremediation is becoming popular in contaminated soil remediation and restoration because it is an environmental friendly and cost-effective approach (Salt et al., 1998). Plants are transplanted in abandoned brownfields to mitigate soil metal contamination, improve urban ecosystem stability, and remediate soil metal contamination (Desouki and Feng, 2012; Dickinson et al., 2009; French et al., 2006; McKenna, 1998). Typha latifolia L. (broadleaf cattail) is a wetland plant that is widely used for wetland restoration, eutrophic lake clean up, and wastewater effluent treatment (Calheiros et al., 2009; Sasmaz et al., 2008; Ye et al., 1997; Ye et al., 1998). Previous field studies identified T. latifolia L. as a plant species that is capable of tolerating contaminated soil with extremely high metal concentration (McNaughton et al., 1974), which makes it an ideal candidate for
phytoextracting metals from the contaminated wetlands for remediation purpose (Brunham and Bendell, 2010; Grisey et al., 2011; Klink et al., 2012; McNaughton et al., 1974; Sasmaz et al., 2008; Ye et al., 1997, 2001).

Iron plaque is a layer of amorphous Fe hydroxide structure that commonly observed on the surface of wetland plant root. The negative surface charge of iron plaque makes it capable of adsorbing or co-precipitating metal(loid)s. Located at the interface between soil pore water and root surface dermal tissues, iron plaque plays a role either as a buffer that can enhance metal uptake efficiency, or as a barrier that restricts the transportation of metals at root surface (Tripathi et al., 2014). Metal ions in soil pore water enter apoplast freely at root epidermis through passive diffusion, which is driven by concentration gradient and evapotranspiration. At the same time, metals also enter symplast through cell membranes actively under the assistance of selective membrane transporters (Marschner, 2012; Taiz and Zeiger, 2010). When metals reach the vascular bundles, the Casparian strip blocks the transportation of substances in the apoplast and prevents them from entering the vascular bundles. Only metals in the symplastic system can enter the vascular tissue and transported to plant shoot (Brennan and Shelley, 1999; Clemens et al., 2002; Rascio and Navari-Izzo, 2011). Therefore, localization of metals in root tissues reflects root metal uptake and transportation processes (Marschner, 2012; Merchant, 2010).
Recently, micro-scale investigation on metal localization by means of advanced techniques has provided information on mechanisms of metal uptake and translocation in *T. latifolia* L. Lyubenova et al. (2012, 2013) applied micro-proton induced X-ray emission (micro-PIXE) to analyze the spatial distribution of 18 elements in tissues of *T. latifolia* L and observed tissue-specific distribution of these elements (Lyubenova et al., 2012; Lyubenova et al., 2013). Synchrotron X-ray absorption near-edge microstructure spectroscopy (XANES) measurement for identification of Pb and Fe speciation on *T. latifolia* L. roots surface showed that Pb(II) and Fe(III) are the major species in the iron plaque in the root epidermis (Feng et al., 2013). Because micro-scale analysis of metal spatial distributions can target the metal localization and speciation on the particular plant tissues, the synchrotron X-ray radiation measurement becomes a very good complement of bulk chemical analysis on plant metal uptake. In this study, we aim at investigating the mechanisms that control the localization of Cu, Fe, Pb, Mn and Zn in *T. latifolia* L. root tissues to provide information on metal spatial distribution in the root system of *T. latifolia* L. growing on contaminated wetland and tissue-specific association between metals in the root.
2.2 Methodology

2.2.1 Study Site

The study site is an urban brownfield within Liberty State Park, New Jersey, with an area of 1 km$^2$. This site was once used for railway transportation and coal storage for a century. As a result of previous industrial activities, high soil metal concentrations were found on site (Gallagher et al., 2008; Qian et al., 2012). The total soil metal concentrations of Cu, Pb and Zn in this wetland are $124 \pm 51 \mu g \ g^{-1}$, $453 \pm 266 \mu g \ g^{-1}$ and $309 \pm 125 \mu g \ g^{-1}$, respectively, which are all above the background levels in New Jersey (Cu: $14 \mu g \ g^{-1}$, Pb: $35 \mu g \ g^{-1}$ and Zn: $22 \mu g \ g^{-1}$; EPA, 2005) and indicate the site is highly contaminated.

2.2.2 Sample Collection and process

*Typha latifolia* L. samples were collected at Site TP-1 in the growing season in 2010 and 2011 along the edge of the storm water drainage ditch. During the growing season, the plant has the highest metabolism rate and root to shoot translocation rate (Tursun et al., 2011). After the collection, the samples were immediately transported to Montclair State University and Stony Brook University for laboratory treatment. Bulk soils on the plant roots were removed by hands initially, then rinsed gently with tap water
and finally with distilled-deionized water. To prepare the samples for synchrotron XRF analysis, fresh root samples were embedded in the Cryo-Embedding compound and then frozen to a solid at an optimal cutting temperature (OCT) of -20 °C. 30 µm thickness root sections were then cut from the frozen samples with a cryotome (Cryostat CM1950, Leica Microsystems). Two root sections were prepared for the samples collected from each year. These four root sections were then mounted on a 25 × 76 mm² quartz microscope slide (SPI Supplies®) and stored at 4 °C before synchrotron XRF analysis.

2.2.3 Synchrotron analysis

Synchrotron micro X-ray fluorescence (µXRF) analysis on the four root sections was conducted at X27A Beamline workstation in the National Synchrotron Light Source at Brookhaven National Laboratory (Upton, NY). The energy range was fixed at 13.5 keV to excite fluoresces of Cu, Fe, Pb, Mn and Zn simultaneously. Optical images of the root sections were collected with optical microscope before synchrotron XRF analysis. Before the analysis started, the slide mounted with the samples was oriented at 45° to the beam and a 13-element Canberra Ge array was used to collect elemental map with a step size of 10 µm and a dwell time of 7 seconds (Figure 2-1). The synchrotron XRF data collection was made at the beamline workstation, and then processed at Montclair State University. Reference material NIST 1832 and NIST 1833 were analyzed along with the
samples during each synchrotron XRF measurement. The concentration of each metal in the synchrotron map was calculated based on the element concentrations in the reference materials.

Longitudinal mapping of metal (Cu Fe, Mn and Zn) distributions in the root specimens were made at the NSLS X26A beamline using synchrotron µXRF microprobe. The X-ray energy was set at 13.5 keV. The beam size on the sample was $7 \, \mu m \times 10 \, \mu m$ with a step size of 15 $\mu m$. The attenuation of the incident X-rays and outgoing X-rays was relatively low so that the entire thickness of the root was sampled with varying efficiencies.

2.2.4 Root Anatomy

Two root sections were collected from the *T. latifolia* L. roots in both 2010 and 2011. Five different types of root tissue could be identified based on optical images of the root section: epidermis, exodermis, cortex, endodermis, and vascular bundles (Figure 2-1, a-d).
2.2.5 Data processing and statistical analysis

The original data of metal (Cu, Zn, Mn, Pb and Zn) distributions in each root section was saved as a matrix and presented as 2D map (Figure 2-1). Each pixel in the synchrotron XRF map represents metal concentration in the root section voxel with a resolution of 10×10×30 µm³ for the 2010 samples, or 20×20×30 µm³ for the 2011 samples. Based on root anatomy morphology observed in the optical images, the root dermal tissues and the vascular bundles (surrounded by endodermis) were identified (Appendix A) and the data was extracted from the original XRF map using MATLAB (The MathWorks Inc., version 7.1.0.246). The extracted matrix data were then transformed into linear data for further statistical analysis. Factor analysis was applied to identify the inherent association between the spatial distribution of Cu, Mn, Fe, Pb and Zn in both dermal tissues and vascular bundles. Hierarchical cluster analysis was applied to investigate the close association of metal distributions in the dermal tissues. The type of joining algorithm used to amalgamate clusters was Ward’s method and the metric for measuring distance between the metals in each case was Euclidean distance (Burns and Burns, 2008; McDonald, 2009). Simple linear regression analysis was performed to explore the relationship between metals.
2.3 Results

2.3.1 Root anatomy analysis

Figure 2-1 shows the anatomy structure of root sections of *T. latifolia* L. Five different types of root tissue could be identified, which are epidermis, exodermis, cortex, endodermis, and vascular bundles (Figure 2-1). Epidermis, exodermis and the tissue between are considered as dermal tissues (Figure 2-1, a-d, ep-ex). Cortex tissues include several layers of cells with thin cell walls (Figure 2-1, a-d, co). In the middle of the root is vascular bundle, surrounded by a layer of endodermis with the suberized Casparian strip (Figure 2-1, a-d, en and va).

It is well recognized that root tissues play different roles in root metal uptake and transportation. Dermal tissue maintains the selectivity of root uptake from soil by taking up water and nutrients and avoiding unwanted compounds like toxic substances and soil borne pathogens. The vascular bundles selectively transport substances from root cortex tissues and upload the substances to stems and shoots of the plant (Schreiber and Franke, 2011). Therefore, we examined the XRF maps of dermal tissues and vascular bundles to investigate how these tissues regulate root metal uptake based on the metal distributions in each type of tissue.
2.3.2 Metal localizations in dermal tissues and vascular bundles

As shown in Table 2-1, the coefficients of variance of metal concentrations are greater than 0.5, suggesting a highly heterogeneous spatial accumulation of metals in each part of all the tissues (Table 2-1). In order to reduce data skewness for further statistical analysis, a logarithm (log_{10}) transformation was applied to all the data (McDonald, 2009).

In the dermal tissues, Fe shows the highest accumulation among all the five elements (Figure 2-1). The average concentration of Fe ranges from 374 ± 836 µg g\(^{-1}\) to 3709 ± 4806 µg g\(^{-1}\), followed by Zn ranging from 23.7 ± 29.9 µg g\(^{-1}\) to 510 ± 260 µg g\(^{-1}\). The concentrations of Mn (22.4 ± 34.0 µg g\(^{-1}\) to 56.9 ± 39.9 µg g\(^{-1}\)), Pb (1.86 ± 6.46 µg g\(^{-1}\) to 62.2 ± 103 µg g\(^{-1}\)), and Cu (4.45 ± 5.19 µg g\(^{-1}\) to 44.2 ± 20.6 µg g\(^{-1}\)) are not as high as Fe and Zn (Table 2-1). The coefficients of variance of Pb and Fe are higher than other elements, indicating that these two metals have greater variations in spatial distribution than the others (Table 2-1). This is in consistent with the “hot spots” of Fe and Pb observed on surface of the dermal tissues. It can be inferred that the spatial accumulation of Cu, Mn and Zn in the root dermal tissues are more homogeneous relative to Pb and Fe.

In the vascular bundles, the accumulations of the five metals are different from the dermal tissue. The average concentration of Zn is the highest, ranging from 5.87 ± 5.30 µg g\(^{-1}\) to 964 ± 666 µg g\(^{-1}\), following by Fe (9.82 ± 5.55 µg g\(^{-1}\)to 128 ± 172 µg g\(^{-1}\)).
Mn (2.66 ± 3.95 µg g\(^{-1}\) to 50.8 ± 34.0 µg g\(^{-1}\)), Cu (4.56 ± 4.87 µg g\(^{-1}\) to 41.8 ± 15.6 µg g\(^{-1}\)) and Pb (0.08 ± 0.41 µg g\(^{-1}\) to 6.20 ± 7.82 µg g\(^{-1}\)) (Table 2-1). In particular, the concentrations of Fe and Pb in the vascular bundles are almost an order of magnitude lower than that in the dermal tissue, indicating that these two metals mainly accumulate in the dermal tissue of the root (Figure 2-1). As shown in Figure 2-1 (e, f, g, h; i, j, k, l; m, n, o, p) bright rings of Mn, Cu and Zn are observed around the vascular bundles, where the Casparian strip is likely located. In a study by Lyubenova et al. (2012), the same bright ring structure was observed in the root sections of *T. latifolia* L. Our results suggest that the bright rings of Mn, Cu and Zn observed around the vascular bundles are likely these metals from the apoplastic transportation that accumulate around the Casparian strip.

Synchrotron µXRF radiograph images (Figure 2-2) show the heterogeneity of metal (Cu, Fe, Mn and Zn) distributions along a 1 cm long root branch. Several “hot spots” of metals are scattering across the branch. Therefore, heterogeneous distribution of metals could be observed not only across root sections, but also along the root.
2.3.3 Relationship between the localization of metals in dermal tissues and vascular bundles

As the localization of metals is heterogeneous across the root sections, the mechanisms controlling the accumulation of metals in specific tissues should be examined. In order to investigate possible mechanisms governing the uptake and transportation of metals, the association among Pb, Fe, Mn, Cu, and Zn in their spatial distributions in both dermal tissues and vascular bundles were analyzed. Because all the four root samples were collected in the growing season, they should share the same mechanisms regulating the metal accumulations. Therefore, the spatial distributions of Pb, Fe, Mn, Cu and Zn from all the four samples were analyzed together without distinction. Factor analysis was performed to explore the internal relationships between the metal spatial accumulation in both dermal tissues and vascular bundles.

In the dermal tissue, three factors with eigenvalue greater than 0.5 are identified, which explain 92% of the total variance (Table 2-2). High loadings of Pb (0.95) and Fe (0.91) are observed in Factor 1 that explains 35.73% of the total variance, indicating close relationship between Pb and Fe in their spatial distribution in the root dermal tissues. Sequestration of Pb on wetland plant root surface with iron plaque have been observed in many studies (e.g., Feng et al., 2013; Liu et al., 2007; Liu et al., 2011). Therefore, Factor 1 represents the iron plaque in the dermal tissues. Factor 2, which has high loadings of Cu
(0.95) and Zn (0.93), explains 36.42% of the total variance. This factor indicates a close association between Zn and Cu in the localization in the dermal tissue as essential nutrients. Factor 3 accounts for 20.00% of the total variance with only one high loading element, Mn (0.95).

In the vascular bundles, three factors with eigenvalue greater than 0.5 are identified and explain 90.14% of the total variance (Table 2-2). Factor 1 explains 47.93% of the total variance. It has high loadings of Zn (0.92), Mn (0.87) and Cu (0.87), which are all essential nutrients for plant growth. The other two factors have high loading of only one specific metal in each factor. Factor 2 has high loading of Pb (0.97) and explains 21.89% of the total variance. Factor 3 has high loading of Fe (0.99) and explains 20.32% of the total variance.

The factor analysis suggests that the accumulations of metals in the dermal tissues and the vascular bundles are controlled by different mechanisms. In order to investigate the difference in the mechanisms, which control the metal localization, between the dermal tissues and the vascular bundles, the associations between the spatial distribution of Cu, Mn, Pb, Fe and Zn in each type of tissue were further investigated. Simple linear regressions between the localization of metals in each specific type of root tissue are conducted to explore the association between metals.
2.4 Discussion

2.4.1 Spatial distributions of metals in dermal tissue

Root dermal tissues locate at the interface between soil pore water and root tissues and play a key role in controlling the uptake of mineral elements. Accumulation of metals in the dermal tissues is determined by the following two factors: (i) biological metabolic regulation of dermal tissues in metals accumulation; and (ii) adsorption or co-precipitation of metal cations with iron plaque on the root surface (Marschner, 2012; Tripathi et al., 2014). In the dermal tissues, Zn, Mn and Cu can be transported in the root through apoplast as free cation ions or symplast as metal complexes. For Fe, however, this element is transported from the root surface to the vascular bundles mainly through the symplast as Fe$^{2+}$ complexes although Fe is essential to plant (Hell and Stephan, 2003). Iron plaque is formed around the root surface when soluble Fe$^{2+}$ diffuses through root apoplast of the root and oxidized under aerated condition (Hell and Stephan, 2003). Many studies have proved that iron plaque can effectively adsorb metals such as Pb, Mn, Zn and Cu (Greipsson and Crowder, 1992; St-Cyr and Campbell, 1996; Ye et al., 1997).

Although both iron plaque and regular dermal tissue can accumulate Pb, Mn, Zn, Cu and Fe, the processes may be governed by the different mechanisms. Therefore, it is
critical to separate the iron plaque region from the regular dermal tissue region in the
dermal tissues before analyze the relationship between the elements. High sorption of Pb
by iron plaque on *Iris pseudacorus* L. root surface has been already reported (Zhong et al.,
2010). Liu et al. (2011) also indicate that iron plaque can increase the sequestration of Pb
on *Oryza sativa* L. root surface. The similar spatial distribution of high concentration of
Pb (Figure 2-1, q, r, s, and t) and Fe (Figure 2-1, u, v, w, and x) in *T. latifolia* L. dermal
tissues is consistent with strong association between Pb and iron plaque. Therefore,
spatial distribution patterns of Pb and Fe in the dermal tissue are used as an indicator of
the existence of iron plaque in the dermal tissue.

Hierarchical cluster analysis was performed based on the spatial distributions of
Pb and Fe. Root dermal tissues are divided into two clusters: iron plaque (CA1) and
regular dermal tissues (CA2) (Figure 2-3). As shown in Figure 2-3, iron plaque (CA1)
scatters heterogeneously in the dermal tissues, indicating that iron plaque does not
accumulate in the dermal tissues uniformly. Also, as shown in Table 2-3, Fe
concentration in iron plaque (Figure2-3) is significantly higher than that in the regular
dermal tissue. This is consistent with the observation from a study by Becker et al. (1995),
who claimed that iron plaque comprised up to 95% of the total root iron content in the
apoplast.
Because of the high affinity of metal cations to Fe hydroxide, iron plaque plays a role as either buffer or barrier of metals in the root uptake process. Tripathi et al. (2014) suggests that iron plaque acts as a buffer of Ca and P, and a barrier of As in *T. latifolia* L. When iron plaque plays a role as a barrier of As in *T. latifolia* L., the spatial distribution of As is closely associated with iron plaque around the root surface and the accumulation of As is extremely low in root cortex and vascular bundles (Hansel et al., 2002). The role of iron plaque in the uptake of a metal can be judged based on the relationship between Fe and the metal in the iron plaque. If the correlation between Fe and the metal is strong in the iron plaque but weak in the regular dermal tissue, then iron plaque eliminates the uptake of this metal. If the correlation between Fe and the metal was weak in iron plaque but strong in regular dermal tissue, then iron plaque had no affinity to this metal. If the correlation between Fe and the metal was strong in both the iron plaque and the regular dermal tissue, it suggests that the iron plaque has strong affinity to the metal, but does not eliminate further transportation of the metal. In this case, the iron plaque might be a buffer of the metal. In this study, simple linear regressions are applied to compare the relationships offer with metals (Cu, Mn, Pb and Zn) between iron plaque and regular dermal tissues (Figure 2-4).

The results show that Pb has significant \((p<0.05)\) positive correlation with Fe in the iron plaque in all the four root samples (Figure 2-4, A, B, C, D) with \(r^2 > 0.5\).
suggesting a strong association between Fe and Pb in the iron plaque. However, the association between Fe and Pb is rather weak in the regular dermal tissue. As showing in Figure 2-1, the accumulation of Pb is rather low in the inner rim of the dermal tissue. This observation is consistent with the work by Feng et al. (2013), who indicated a strong association between Pb and Fe localization on the surface of *T. latifolia* L. root. In addition, extremely low accumulation of Pb is observed in the cortex tissues and the vascular bundles in this study (Figure 2-1), indicating that very limited amount of Pb was transported to rest part of the plant tissues. Very likely, iron plaque acts as a barrier for the uptake of Pb in *T. latifolia* L.

Similar to Pb, associations between Fe and Mn, Zn and Cu are significant (*p*<0.05) in the iron plaque, indicating that iron plaque can scavenge these metals (Figure 2-4). In the regular dermal tissues, however, the correlations between Fe and the three metals (Mn, Zn and Cu) are inconsistent. Both significant (Figure 2-4, E, F, H, I, J, L, M, and P) and insignificant (Figure 2-4, G, K, N and O) associations are observed. Moreover, the associations between Fe and the three metals (Mn, Zn and Cu) in the regular dermal tissues are rather weak (*p* > 0.05). The results suggest that Fe and the three other metals (Mn, Zn and Cu) do not share the same transport and accumulation mechanisms in the regular dermal tissues.
The association between Cu, Mn and Zn is further investigated by comparing the correlation among the three minerals in the iron plaque and the regular dermal tissues (Figure 2-5). Generally speaking, although the concentrations of Mn, Zn and Cu are higher in the iron plaque, there is no significant difference between the iron plaque and the regular dermal tissues with respect to associations of the three elements with Fe (Figure 2-5).

Root dermal tissues accumulate metals based on the cation exchange capacity in the cell wall (apoplast) and selective uptake of metals by cell plasma membrane (symplast). The association of metals with cell wall is determined by the concentration of metal cations in soil solution and the competition between metal cations. The accumulation of metals in cell plasma, however, is determined by the selective transportation of metals by cell membrane transporters (Cestone et al., 2012; Marschner, 2012). As shown in Figure 2-5, the association between essential metals (Mn, Fe and Cu) is similar no matter whether it is in iron plaque and or in the regular dermal tissues, suggesting that the accumulations of these metals is possibly controlled by the same mechanism. The only difference is iron plaque adsorbs higher concentration of Mn, Zn and Cu. These observations are consistent with previous studies conducted by St-Cyr and Campbell (1996) and Batty et al. (2000) who suggested that the adsorption and co-precipitation of Cu, Mn and Zn with iron plaque should not influence the further root
uptake of these metals. Therefore, iron plaque possibly acts as a buffer for the accumulation of Mn, Zn and Cu in *T. latifolia* L.

2.4.2 Spatial distributions of metals in vascular bundles

Vascular bundles bridge the exchange of nutrients between roots and shoots and upload mineral nutrients from roots to shoots through xylem. In order to enter the xylem, metals in soil pore water have to pass three obstacles: the suberized exodermis on the inner rim of dermal tissues, the Casparian strip around the vascular bundles, and the cell membrane. The exodermis and the Casparian strip inhibit substances transportation via apoplast pathway, while the membrane transporters decide the type and the amount of metals transported through symplast pathway (Brennan and Shelley, 1999; Clemens et al., 2002; Colangelo and Guerinot, 2006; Rascio and Navari-Izzo, 2011). In the dermal tissue, metal accumulation is determined by the combined effects of soil pore water, apoplast and symplast (Taiz and Zeiger, 2010). In the vascular bundles, however, metal accumulation is mainly determined by symplast.

In this study, high concentrations of Zn, Mn and Cu on the Casparian strip around the vascular bundles were observed (Figure 2-1). Similar rings with high metal concentrations around the endodermis were also observed by Yamaguchi et al. (2011).
They exposed *Solanum torvum* (Cd excluder) and *Solanum melongena* (Cd accumulator) to high concentration of Cd and found that Cd concentration around the endodermis was higher in *Solanum torvum* than that in *Solanum melongena* (Yamaguchi et al., 2011). Therefore, our results suggest that Casparian strip in the root may delay the transportation of Zn, Mn and Cu from apoplast to symplast.

Simple linear regression analysis was performed to investigate the relationship among Zn, Mn and Cu distributions in the root tissues. In order to examine the similarity or difference in metal (Zn, Mn and Cu) accumulation mechanisms between the dermal tissues and the vascular bundles, the relationships between these metals in both types of tissue were compared. Figure 2-6 shows the correlations between Zn and Mn, Zn and Cu, and Mn and Cu in the dermal tissue and the vascular bundles in each sample. Significant \( p<0.05 \) positive correlations are observed in most of the metal pairs.

The significant correlation between Mn and Zn can be attributed to the similar uptake and transport mechanisms between these two elements. It was found that Zn and Mn could be taken up by *T. latifolia* L. from the rhizosphere soil more effectively than Cu (Klink et al., 2012; Sasmaz et al., 2008), and Mn and Zn might share the same transporters, such as ZIP and IRT1 in the root tissue (Hall and Williams, 2003).
There is no difference observed in the metal relationships between the dermal tissues and the vascular bundles (Figure 2-6). In addition, the slopes of the metal regression lines show nearly no difference between the dermal tissues and the vascular bundles in most cases (Figure 2-6). The different trends in the regression lines between the two tissues are seen in a few cases (Figure 2-6 D, H, and L), which is possibly due to heterogeneous accumulation of metals in the tissues. Regardless of the difference in the slopes between the dermal tissues and the vascular bundles as shown in Figure 2-6 (D, H, L), no distinctive boundaries between the scatter plots from the two tissues are observed (Figure 2-6). It should be noticed that, in the vascular bundle, high accumulation of metals were mainly concentrated on the outer rim of the vascular bundle. This is where Casparian strip locates. Therefore, the similar relationships of Zn, Cu, and Mn between the dermal tissue and the vascular bundles is possibly due to the similar transport processes that caused these metals mainly accumulated in the apoplast of dermal tissue and the apoplast around the Casparian strip. It can be further suggested that these three metals are mainly accumulate in the apoplastic system before they enter the vascular bundles.
2.5 Conclusion

In this study, the spatial distributions of Fe, Cu, Mn, Pb and Zn in *T. latifolia* L. root system were investigated to explore possible mechanisms that govern metal localizations. The accumulation of metals in the root sections collected in the growing season varied spatially with the sample positions, the root tissue types, and the metal themselves. Factor analysis shows internal correlation in Cu, Mn, Pb, Fe and Zn spatial distributions in the dermal tissue and the vascular bundles. The significant correlations in the spatial distribution of Pb and Fe, Cu and Zn in the dermal tissue can be attributed to the function of Fe plaques in the metal scavenge. This study indicates that iron plaque possibly acts as a barrier of Pb and a buffer of Zn, Mn and Cu in metal transport in the dermal tissue. In the vascular bundles, Zn, Mn and Cu show significant correlations in their spatial distributions. The results suggest that Cu, Mn and Zn may share the similar transport mechanisms and accumulate in the vascular bundles. In addition, there is no difference in Zn, Mn and Cu accumulations between the dermal tissue and the vascular bundles, suggesting that these two types of tissues may accumulate the metals in a similar way.

This study demonstrates that synchrotron XRF technique provides an innovative approach to study metal assimilation in the plants and explore the mechanism of plant
metal uptake and transportation. The results suggest that *T. latifolia* L. can be used as an indicator of soil bioavailability of Zn, Cu, Mn and Fe, and an excluder of Pb.
2.6 References


St-Cyr, L., Campbell, P.G., 1996. Metals (Fe, Mn, Zn) in the root plaque of submerged aquatic plants collected in situ: relations with metal concentrations in the adjacent sediments and in the root tissue. Biogeochemistry 33, 45-76.


Table 2-1 Metal concentrations (Mean ± S.D.) (µg g⁻¹) and ranges (Min-Median-Max) (µg g⁻¹) of Cu, Fe, Mn, Pb and Zn in the root sections collected in the tip and middle of *T. latifolia* L. collected in 2010 and 2011.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>n</th>
<th>Min</th>
<th>Max</th>
<th>Median</th>
<th>Mean</th>
<th>C.V.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>µg g⁻¹</td>
<td>µg g⁻¹</td>
<td>µg g⁻¹</td>
<td>µg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>2010 (I)</td>
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<td>531</td>
<td>BDL</td>
<td>33464</td>
<td>2373</td>
<td>3709</td>
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</tr>
<tr>
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<td>Cu</td>
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<td>18.7</td>
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</tr>
<tr>
<td></td>
<td>Zn*</td>
<td></td>
<td>19.7</td>
<td>666</td>
<td>179</td>
<td>188</td>
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</tr>
<tr>
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<td>Mn*</td>
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<td>n.d.</td>
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<td>862</td>
<td>1.82</td>
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<td>Cu</td>
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<td>212</td>
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<td></td>
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<td>468</td>
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<td></td>
<td>1.33</td>
<td>203</td>
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</tr>
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<td></td>
<td>Pb*</td>
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<td>BDL</td>
<td>422</td>
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<td>65.80</td>
<td>13821</td>
<td>349</td>
<td>1710</td>
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<td>BDL</td>
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</tr>
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<td>BDL</td>
<td>70.0</td>
<td>BDL</td>
<td>1.86</td>
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<th>Mean</th>
<th>C.V.</th>
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<td></td>
<td></td>
<td>µg g⁻¹</td>
<td>µg g⁻¹</td>
<td>µg g⁻¹</td>
<td>µg g⁻¹</td>
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<td>BDL</td>
<td>41.8</td>
<td>9.46</td>
<td>11.1</td>
<td>0.74</td>
</tr>
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<td>BDL</td>
<td>453</td>
<td>73.7</td>
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<td>138</td>
<td>15.9</td>
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<td></td>
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<td>30.6</td>
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<td>59.0</td>
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<td>192</td>
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<td>6.20</td>
<td>1.26</td>
</tr>
<tr>
<td>2011 (II)</td>
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<td>BDL</td>
<td>26.3</td>
<td>10.2</td>
<td>9.82</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BDL</td>
<td>17.1</td>
<td>5.56</td>
<td>5.55</td>
<td>0.65</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BDL</td>
<td>27.5</td>
<td>5.14</td>
<td>5.87</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BDL</td>
<td>22.7</td>
<td>BDL</td>
<td>2.66</td>
<td>1.49</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BDL</td>
<td>3.51</td>
<td>BDL</td>
<td>0.08</td>
<td>5.05</td>
</tr>
</tbody>
</table>

* Significant difference between metal accumulation in the dermal tissue and the vascular bundle (Wilcoxon test, *p*<0.05).
Table 2-2 Results of factor analysis based on localization of Cu, Fe, Mn, Pb and Zn in the dermal tissue and vascular bundle (Rotated loading matrix, Varimax rotation, Gamma = 1.000).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Parameter</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
</tr>
</thead>
<tbody>
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<td>log_{10}(Fe)</td>
<td>0.95</td>
<td>-0.07</td>
<td>0.13</td>
<td>log_{10}(Zn)</td>
<td>0.92</td>
<td>-0.24</td>
<td>0.06</td>
</tr>
<tr>
<td>log_{10}(Pb)</td>
<td>0.91</td>
<td>0.17</td>
<td>0.22</td>
<td>log_{10}(Mn)</td>
<td>0.88</td>
<td>0.20</td>
<td>0.14</td>
</tr>
<tr>
<td>log_{10}(Cu)</td>
<td>0.01</td>
<td>0.95</td>
<td>0.09</td>
<td>log_{10}(Cu)</td>
<td>0.87</td>
<td>-0.22</td>
<td>-0.01</td>
</tr>
<tr>
<td>log_{10}(Zn)</td>
<td>0.08</td>
<td>0.93</td>
<td>0.14</td>
<td>log_{10}(Pb)</td>
<td>-0.12</td>
<td>0.97</td>
<td>0.15</td>
</tr>
<tr>
<td>log_{10}(Mn)</td>
<td>0.25</td>
<td>0.18</td>
<td>0.95</td>
<td>log_{10}(Fe)</td>
<td>0.09</td>
<td>0.14</td>
<td>0.99</td>
</tr>
<tr>
<td>Percent of total variance explained</td>
<td>35.7</td>
<td>36.4</td>
<td>20.0</td>
<td>Percent of total variance explained</td>
<td>47.9</td>
<td>21.9</td>
<td>20.3</td>
</tr>
</tbody>
</table>
Table 2-3 Accumulation (µg g\(^{-1}\)) of Fe in the iron plaque and regular dermal tissues from *T. latifolia* L. root sections collected in 2010 and 2011.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron plaque</th>
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<th></th>
<th>Regular dermal tissues</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n</td>
<td>Min µg g(^{-1})</td>
<td>Max µg g(^{-1})</td>
<td>Median µg g(^{-1})</td>
<td>Mean ± S.D. µg g(^{-1})</td>
<td>n</td>
</tr>
<tr>
<td>2010 (I)</td>
<td>404</td>
<td>187.00</td>
<td>33464</td>
<td>3720</td>
<td>4845 ± 4996</td>
<td>127</td>
</tr>
<tr>
<td>2010 (II)</td>
<td>320</td>
<td>BDL</td>
<td>14667</td>
<td>810</td>
<td>1499 ± 2035</td>
<td>336</td>
</tr>
<tr>
<td>2011 (I)</td>
<td>250</td>
<td>439.00</td>
<td>13820</td>
<td>2517</td>
<td>3446 ± 2814</td>
<td>282</td>
</tr>
<tr>
<td>2011 (II)</td>
<td>202</td>
<td>394.00</td>
<td>9021</td>
<td>856.0</td>
<td>1351 ± 1334</td>
<td>678</td>
</tr>
</tbody>
</table>
Figure 2-1 Optical images and concentration (µg g⁻¹) spatial distribution of Cu, Mn, Pb, Fe and Zn in *T. latifolia* L. root sections in the tip and the middle of roots collected in 2010 and 2011. ep: epidermis; ex: exodermis; co: cortex; en: endodermis ca: Casparian strip; va: vascular tissues (a-d, optical images of root tissue sections; e-h, spatial distribution of Zn; i-l, spatial distribution of Cu; m-p, spatial distribution of Mn; q-t, spatial distribution of Pb; u-x, spatial distribution of Fe).
Figure 2-2 Spatial accumulation of Cu, Fe, Mn and Zn in whole root collected in *T. latifolia* L. collected in 2010.
Figure 2-3 Iron plaque region and regular dermal tissue region identified by the cluster analysis in the dermal tissues of four root sections (A-D, iron plaque region; E-H, regular dermal tissue). The concentration scale bar indicated the concentration of Fe in the XRF map, the regions traced by white line indicate identified clusters.
Figure 2-4 Simple linear regressions between log\(_{10}\)(Fe) and the other four metals log\(_{10}\)(Pb), log\(_{10}\)(Cu), log\(_{10}\)(Zn) and log\(_{10}\)(Mn) in the iron plaque region and regular dermal tissue region of the dermal tissues in the root sections collected in 2010 and 2011 (open circle ◌: iron plaque region; solid circle ●: regular dermal tissue. A, E, I, M: root section collected from root (I) of 2010 *T. latifolia* L.; B, F, J, N: root section collected from the (II) of 2010 *T. latifolia* L.; C, G, K, O: root section collected from the (I) of 2011 *T. latifolia* L.; D, H, L, P: root section collected from the (II) of 2011 *T. latifolia* L.)
Figure 2-5 Simple linear regressions between essential nutrients $\log_{10}(\text{Cu})$, $\log_{10}(\text{Zn})$ and $\log_{10}(\text{Mn})$ in the iron plaque region and regular dermal tissue region of the dermal tissues in the root sections collected in 2010 and 2011 (open circle ○: iron plaque region; solid circle ●:regular dermal tissue. A, E, I: root section collected from root (I) of 2010 *T. latifolia* L.; B, F, J: root section collected from (II) of 2010; C, G, K: root section collected from the (I) of 2011 *T. latifolia* L.; D, H, L: root section collected from the (II) of 2011 *T. latifolia* L.).
Figure 2-6 Simple linear regressions between essential nutrients $\log_{10}(\text{Cu})$, $\log_{10}(\text{Zn})$ and $\log_{10}(\text{Mn})$ in the dermal tissues and vascular bundles of the root sections collected in 2010 and 2011 (open circle: ● dermal tissues; solid circle ◌:vascular bundles. A, E, I: root section collected from root (I) of 2010 *T. latifolia* L.; B, F, J: root section collected from (II) of 2010; C, G, K: root section collected from the (I) of 2011 *T. latifolia* L.; D, H, I: root section collected from the (II) of 2011 *T. latifolia* L.).
CHAPTER 3

A GEOCHEMICAL STUDY OF TOXIC METAL TRANSLOCATION IN AN URBAN BROWNFIELD WETLAND

[This chapter was published in Environmental Pollution 166(2012) 23-30; DOI: 10.1016/j.envpol.2012.02.027]

Abstract

Rhizosphere soil and dominant plant samples were collected at a brownfield site in New Jersey, USA, during summer 2005 to evaluate plant metal uptake from the contaminated soils. Metal concentrations varied from 4.25 to 978 mg g\(^{-1}\) for As, 9.68-209 mg g\(^{-1}\) for Cr, 23.9-1870 mg g\(^{-1}\) for Cu, and 24.8-6502 mg g\(^{-1}\) for Zn. A wide range of metal uptake efficiencies in the roots, stems and leaves was found in this study. Data showed that (1) *Betula populifolia* has high Zn, Cu and As accumulations in the root, and high concentrations of Cu and Zn in the stem and the leaf; (2) *Rhus copallinum* has high accumulation of Zn and Cr in the leaf and Cu in the stem; (3) *Polygonum cuspidatum* has high accumulations of Cu and As in the root; and (4) *Artemisia vulgaris* shows high Cu accumulation in the leaf and the stem.

**Keywords:** Brownfield, Bioconcentration factor (BCF), Plants, Rhizosphere, Metal bioavailability
3.1 Introduction

“Brownfields”, which are primarily located in urban industrial areas, have presented both economic and environmental concerns for decades. Numerous studies have shown that contaminated soils and sediments often contain mixed organic and inorganic contaminants (Feng et al., 1998; Feng et al., 2004; Feng et al., 2011; Gallagher et al., 2008; Onwueme and Feng, 2006; Yu et al., 2001a; Zhang et al., 2009; Zhang et al., 2001). Such contamination can pose both environmental and human health problems (Roy et al., 2005). To mitigate the risk associated with high soil metal concentration and foster sustainable development initiatives within the urban context, remediation of soil metals in brownfields has become an important and timely issue (Thornton et al., 2007). Previous studies have shown that the promising methods for soil metal removal include chemical/physical remediation, phytoremediation and micro remediation. Furthermore, bio-removal/stabilization approaches have the advantages of cost-effectiveness, environmental friendliness and fewer side effects, comparing to traditional chemical/physical remediation (Ferro et al., 1999; Glass, 1999; Wu et al., 2010). There are two basic approaches for plants to remediate brownfield, one is phytostabilization, which is the process of the absorption and catchment of pollutants within the rhizosphere (Berti and Cunningham, 2000); the other one is phytoextraction, where metals are translocated into plant tissue that can be harvested (Blaylock and Huang, 2000). An
efficient transfer and sequestration of metal within the plant tissue is essential to the application of phytoextraction as an economical and non-invasive method of remediation of contaminated sites. Accumulation of metals in plant tissue is mainly determined by metal uptake efficiencies by plants and metal bioavailability in the soil (Pilon-Smits, 2005).

As essential micro-nutrients metals play a critical role in plant metabolism. However, high concentrations of metals are toxic to plants and can inhibit metabolism growth and reproduction. It is well documented that plants are capable of absorbing metals from the soil and storing these metals into various tissues (Das et al., 2010; Gallagher et al., 2008; Lacerda et al., 1997; Martin et al., 2006; Martin et al., 2003; Naftel et al., 2002; Weis and Weis, 2004; Williams et al., 1994). Metal ions can form chelating compounds with chelators (e.g., nicotianamine, organic acids, glutathione, phytochelatin, and metallothionein protein) in plant tissue cells, so that metal toxicity is reduced within the cells (Cobbett and Goldsbrough, 2000; Pilon-Smits, 2005). These metal chelating compounds can be further sequestered in cell vascular in the roots (Pilon-Smits, 2005). However, metals can also pass through the root tissue cell wall and root xylem, become transported into stem xylem with assistance of transporter proteins, or chelators (Pilon-Smits, 2005). Then, the metals can further transfer from stem xylem into leaf tissue where metals can be bound by chelators and sequestered in leaf symplast vacuole or the
cell wall (Burken, 2003; Cobbett and Goldsbrough, 2000). Previous studies show that metal bioavailability and toxicity are dependent on soil pH, redox potential, biota, mineral and organic contents, and complicated by synergistic interactions between these variables (Martin et al., 2006; Martin et al., 2003; Morrissey and Guerinot, 2009; Naftel et al., 2002). Therefore, understanding the biogeochemical processes and mechanisms that control the mobility of metals in soils, sediments and their translocation to plants is a critical aspect of brownfield bioremediation and rehabilitation. This study defines the efficiencies of plant uptake of several soil metals found at elevated concentrations. The results will improve our understanding of the potential for phytoremediation and phytostabilization in naturally assembled plant communities that colonize in urban brownfields.

3.2 Materials and methods

3.2.1 Study area

This study was conducted at Liberty State Park (LSP), Jersey City, New Jersey, located on the west bank of Upper New York Bay (centered at 40_4201400N; 74_0301400W). Used as a railroad yard for over a century the Central Rail Road of New Jersey filed for bankruptcy and closed in 1969 (Gallagher et al., 2008). Since then, the 1
km² study site has remained isolated and undisturbed. Nevertheless, soil metal concentrations remain relatively high and unevenly distributed (Gallagher et al., 2008). Using a previously established vegetative assemblage survey (United States Army Corps of Engineers, 2004a, 2004b), 22 sampling stations were selected for this study by comparing assemblage boundary maps and aerial photography that give adequate representation of the represented assemblages. These included two sites from the successional old field assemblage, 4 each within the common reed/mugwort and the maritime shrub land assemblages, and 12 within the successional northern hardwood assemblage (Figure 3-1).

3.2.2 Plant materials

Plant tissue samples (root, stem and leaves) of eight (8) species, which include three woody species and five herbaceous species, were collected at the 22 stations within the park during the summer of 2005 (Figure 3-1). The coordinates were recorded with GPS (Corvallis Microtechnology MC-GPS, accuracy 1 m). The woody species include *Betula populifolia* (gray birch, n = 8), *Rhus copallinum* (winged sumac, n = 5), and *Populus deltoids* (eastern cottonwood, n = 3), and the five herbaceous species are *Artemisia vulgaris* (mugwort, n = 4), *Onoclea sensibilis* (n = 1), *Phragmites australis* (n = 1), *Solidago virgaurea* (n = 1), and *Polygonum cuspidatum* (n = 1). These plant
samples were collected randomly from the dominant species at each sampling site to investigate plant metal uptake efficiencies and the relationship between soil and plant tissue samples. Roots were visually traced from the bole and excavated using a hand spade. Root fibers were collected, loose soil was removed with distilled water, and 10-15 g (wet weight) samples were stored in clean polypropylene containers. Woody tissue was collected by cutting a cross sectional ‘cookie’ at approximately 1 m height, from which a wedge representing all growth years and of at least 25 g (wet weight) was taken from the specimen. Representative leaf samples were also collected from each specimen. With woody species, 5 g (wet weight) leaf samples were collected from the upper, middle, and lower sections of the plant to ensure that the samples were representative of the entire plant. Herbaceous plants were clipped above the ground and the entire plant was collected. Soil samples were also collected at the same stations in triplicate at 1 m spacing according to the depth of the greatest root penetration determined by visual examination and ranged from 4 cm to 15 cm with a mean of 9.2 cm. Gravel and visible plant material (roots and leaves) were removed from soil samples in the field. These soil samples were then placed in clean, new polypropylene containers, and stored at 4 °C. A LaMotte field soil pH meter was used for in situ soil pH measurement. Sample analyses for metal concentrations were transferred to the Environmental Toxicology Laboratory at
the University of Medicine and Dentistry of New Jersey (UMDNJ) with accompanying Chain-of-Custody sheets on the day of collection for further analysis.

3.2.3 Metal analysis

The analytical methods for metals were more fully described and explained in Gallagher et al. (2008). Briefly, after removal of organic detritus (twigs, roots, etc.), each soil sub-sample was mixed thoroughly in sufficient double-distilled water to create a slurry and sieved through nylon mesh to <125 µm, with the screen washed with additional distilled water to aid passage. The biological and soil sub-samples for metal analysis were oven-dried at 60 °C for ~48 h to constant weights. An aliquot of 0.5 g dried soil sample was weighed to the nearest milligram, treated with 10 ml trace-metal grade HNO₃, and acid extracted in Teflon bombs in a MARS-5 (CEM Corp.) programmed microwave instrument at >170 °C for 30 min. These acid extracts were reduced to a minimum volume on hot-plates and re-diluted with 1% HNO₃ for analysis by atomic absorption spectroscopy (AAS). A method blank and a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1944 were analyzed simultaneously with each set of 12 soil samples. These samples were analyzed for Cr, Cu, and Zn by Perkin-Elmer Model 603 flame AAS. Arsenic concentration was determined in the presence of a Mg(NO₃)₂/Pd(NO₃)₂ matrix modifier by Perkin-Elmer
Z5100 graphite furnace AAS with Zeeman background correction. Organic matter content in the soil samples was estimated by the “loss on ignition” method (Craft et al., 1991), ashing an aliquot of ~1 g dried soil sample in a crucible in a muffle furnace with temperature ramping overnight to 450 °C. It should be aware that LOI% represents the total amount of carbon in soil, including inorganic carbon like carbonated minerals and organic carbon like humic substances and organism detritus. Considering the study site had been used as a freight yard for coal storage, it is possible that carbon from historical coals also contributed to the LOI% in this study.

Plant materials for metal analysis were also dried at 60 °C for ~48 h to constant weights, weighed to the nearest milligram and distributed as 0.3 g sample of each triplicate. They were first treated with 30% H₂O₂ to mineralize cellulose, and then prepared similarly to soil samples (Gallagher et al., 2008). A method blank and a standard reference material (NIST SRM1573a, tomato leaves) were analyzed simultaneously with each set of 12 plant samples. Metals and metalloids in plant materials were analyzed similarly to the soil samples. However, when there was <1% absorption by flame AAS, a graphite furnace AAS with Zeeman Effect was employed to increase the sensitivity (Perkin-Elmer Z5100 instrument). Minimum detection levels (MDLs) were calculated for each metal by taking three times the standard deviation of the values measured for the blanks (Gallagher et al., 2008).
3.2.4 Evaluation of plant metal uptake efficiency

Bioconcentration factor (BCF), which is defined as the ratio of metal concentrations in the plant to that in the soil, is a useful indicator to measure metal uptake efficiency by plants (Audet and Charest, 2007; Dowdy and McKone, 1997; Kim et al., 2003; McGeer et al., 2003; Zhang et al., 2001). According to Dowdy and McKone (1997), BCF is defined as

\[
BCF = \frac{[\text{Metal}]_{\text{plant}}}{[\text{Metal}]_{\text{soil}}} \tag{1}
\]

where [Metal]_{plant} is the total metal concentration in the plant tissue, and [Metal]_{soil} is the total metal concentration in the soil. The relationship between metal uptake efficiency by roots and soil chemistry were examined by linear regression analysis (McBean, 1998). Based on the studentized residual values, which compares the data to the studentized range distribution, derived from an ordinary least squares (OLS) regression model performed on the raw data, several outliers were removed although there may still not exist statistically significant relationship between the parameters.
3.3 Results and discussion

The 22 sampling stations at the LSP all exhibit characteristic metal concentrations of brownfield soils. Concentrations of As (4.25-978 mg g\(^{-1}\)), Cr (9.68-209 mg g\(^{-1}\)), Cu (23.9-1870 mg g\(^{-1}\)) and Zn (24.8-6502 mg g\(^{-1}\)) are above most residential and ecological standards (Table 3-1). Although variations in the metal concentrations in the plants growing at the LSP may indicate the differences in metal uptake efficiency that are both metal and plant species specific, the results suggest that the metals are generally accumulated more in the roots than that in the aerial parts of the plants (Figure 3-2).

3.3.1 Metal uptake efficiency and plant species

To evaluate the plant metal uptake efficiency, BCF was used as an index to assess the amount of metal sequestered in a specific part of the plant. Results of the BCF for eight different plant species are tabulated in Table 3-2. Among eight plant species, *Betula populifolia* has the highest Zn BCF values in the root (2.84 - 2.40) and leaf (12.8 - 13.6) while *Rhus copallinum* has the highest Zn BCF value in the stem (1.20 - 1.27) (Table 3-2). *Polygonum cuspidatum* is found to have the highest Cu BCF value in the root (0.84), *Artemisia vulgaris* has the highest Cu BCF value in leaf (0.10 - 0.04), and *Artemisia vulgaris, Betula populifolia* and *Rhus copallinum* all have the highest Cu BCF value in the stem (0.030 - 0.02, 0.030 - 0.04 and 0.030 - 0.02, respectively) (Table 3-2). *Betula*
"Betula populifolia" has the highest Cr BCF value in the root (0.31 - 0.13), whereas "Rhus copallinum" has the highest Cr BCF value in both leaf (0.02 - 0.01) and stem (0.01 - 0.02) (Table 3-2). "Polygonum cuspidatum" has the highest As BCF value in the root (0.21) although "Betula populifolia", "Populus deltoides" and "Rhus copallinum" exhibit measurable concentrations of As in roots (Table 3-2). Among the metals studied for plant uptake, Zn is generally found to have higher BCF values than other metals (As, Cr and Cu) (Table 3-2). Zinc also exhibits higher concentration in leaf than that in root in "Betula populifolia" and "Populus deltoides" (Figure 3-2). As shown in Table 3-2 and Figure 3-2, the metals are absorbed by the roots in rhizosphere, accumulated in roots, and transported to stems and leaves in various quantities depending on the specific plant species. The value of root BCF is the highest in all plant species except for the accumulation of Zn in "Betula populifolia" and "Populus deltoides". These results suggest that the metals are mainly stabilized and stored in the underground biomass or the roots. This is especially true for As, whose storage is very low in the above ground biomass.

According to Michaelis-Menten kinetics, when metal concentrations in soil are the same, the species and quantity of each metal that stored in root tissue are determined by the number of specific metal ion transporter proteins residing on cell membrane (Abedin et al., 2002; Marschner, 2012; Pilon-Smits, 2005). Since the species and quantity of membrane transporter proteins are different, the BCF values from this study may be
indirect evidence supporting that transporter proteins in the cell membrane are responsible for selective sorption of individual metal, and the quantity of transporter proteins is controlling the efficiency of metal uptake in plants. Hall and Williams (2003) also pointed out that there are several toxic metal transporter families in a plant, of which each transporter protein family has preference on certain toxic metal element, and the expression of the metal transporters varies with plant species and plant tissues. Our results (Table 3-2) appear to be consistent with those observations of the previous studies.

In our study, *Betula populifolia*, *Rhus copallinum*, *Polygonum cuspidatum* and *Artemisia vulgaris* demonstrate their high capacity in accumulating certain toxic metal elements. Specifically, *Betula populifolia* has the highest Zn, Cr and As accumulations in the root, the highest Cu accumulation in the stem, and the highest Zn accumulation in the leaf. This suggests that *Betula populifolia* may have high quantity of Zn specific transporters in the root and the leaf. The BCF values of Zn and Cr in leaf and Cu in the stem of *Rhus copallinum* are relatively higher than that of other species (Table 3-2), suggesting that the aerial part of this plant may have exceptional amount of Zn, Cr and Cu transporters (Clemens, 2001). *Polygonum cuspidatum* has high root BCF values of Cu and As (Table 3-2), implying a high expression level of relevant toxic metal transporter family in its root (Hall and Williams, 2003). *Artemisia vulgaris* shows high BCF levels of Cu in the leaf and the stem (Table 3-2), which suggests a comparably high Cu transporter
expression in the aerial tissue of the plant (Hall and Williams, 2003). Identification of specific metal transporters is beyond the scope of this study, but the results from other studies (Abedin et al., 2002; Clemens, 2001; Hall and Williams, 2003; Marschner, 2012; McGeer et al., 2003; Pilon-Smits, 2005) are useful references. Our results support the concept that biological transport is one of the key factors controlling the accumulation of metals in specific parts of the plant and, when these factors are understood, soil metal load can be predictive of plant uptake potential.

3.3.2 Factors controlling soil metal uptake efficiency

Within this assemblage of plants we found that metal (As, Cr, Cu and Zn) concentrations in the plants show a significant (p < 0.05) increase with that in the soils although the absorption efficiencies of each metal vary from one to another (Figure 3-3). Metals accumulated in plant root determined the actual amount of metals that can be assimilated by plant biomass. Knowing how to control the uptake efficiency of metals by root under certain soil metal concentration level will provide valuable advices on the regulation of plant assimilation rate of soil metals (Alloway, 2010). The efficiency of root metal uptake is expressed as the ratio between metal concentrations in plant roots and soil (i.e., BCF). Many previous studies have proved that root metal uptake efficiency is determined by both the root selective metal uptake (plant species dependent) and metal
bioavailability (edaphic condition dependent) in the soil (Bolan et al., 2014; Marschner, 2012; Thornton et al., 2007). In this study, the edaphic factors that determine the metal uptake efficiency by root are explored by simple linear regression between metal BCF and various edaphic parameters.

Organic matter content in the soil affect metal bioavailability through the following approaches: create a reducing environment through microbial activities, enhance early diagenetic reaction in the soil, adsorb trace metal ions, and form organically-bound solid/dissolved complexes (Alloway, 2010; Calmano et al., 1993). In particular, the behavior of metal ion adsorption and complex formation mainly depends on the metal element (Alloway, 2010). Organic matter contents in the soils at Liberty State Park vary considerably, ranging from 8.81% to 52.6% with an average of 27.8 ± 13.1% (Table 3-1). Variations of metal (As, Cr, Cu and Zn) root BCF with organic matter content as expressed by LOI are shown in Figure 3-4. Cu shows a significant negative linear correlation ($r^2 = 0.283$, $p =0.011$) with organic content in soil (Figure 3-4). This could be attributed to the formation of very stable Cu chelate compound with organic matter. It is reported that in soil over 99% of the dissolved Cu was in the form of dissolved Cu organo-complex (Karlsson et al., 2006; Wells et al., 1998). However, there are no significant correlations between metal BCF values and organic matter contents for As, Cr, and Zn (Figure 3-4). Previous study indicates that very limited amount of As can
be found in organic complex forms, explained the insignificant correlation between soil organic matter content and As BCF value (Cullen and Reimer, 1989). It was reported that chromium solubility is mainly a function of soil pH and redox potential (Alloway, 2010). The insignificant relationship between soil organic matter content and Cr BCF value is possibly because organic matter in soil forms solid organic complex with Cr (Kotaś and Stasicka, 2000). For Zn, organic matter dose not directly related to the solubility of the metal as it mainly adsorb Zn in colloidal solid fraction, which is in consistent with the insignificant relationship between LOI% and Zn BCF value in Figure 3-4 (Alloway, 2010).

Besides soil organic matter content, soil pH is another important edaphic factor that is capable of influencing metal bioavailability. As indicated by previous studies, under low pH condition, high H⁺ concentration increases metal mobility by replacing metals from ligands such as OH⁻, CO₃²⁻, SO₄²⁻, Cl⁻, S²⁻ and phosphates (Gundersen and Steinnes, 2003; Zeng et al., 2011). It was also reported that metal mobility is high when pH is between 5.0 and 6.5, and low when pH is approaching 7 (Cappuyns et al., 2004). According to the work of Peng et al. (2009), decreases soil pH can increase the bioavailability of metals (BCF) in the soil. In this study, however, although the soil pH values in our study sites vary from 5.0 to 7.5 (Table 3-1), the metal (As, Cr and Cu) mobility do not demonstrate significant changes within the pH range except Zn (Figure 3-
As showed in Figure 3-6, Zn demonstrates a significant negative correlation with pH ($r^2 = 0.412, p = 0.002$) in the rhizosphere, while there exist no significant correlations between the other three metals (As, Cr and Cu) and the soil pH (Figure 3-6). Many researches have proved the solubility of Zn increases at decreasing pH (Alloway, 2010; EPA, 2007). At the same time, there are a number of specific transporters for Zn in root in order to accumulate sufficient essential mineral nutrients for plants, making Zn accumulation in root very sensitive to the change of Zn bioavailability in the soil (Marschner, 2012; Taiz and Zeiger, 2010). The insignificant correlation between soil pH and the other three metals is either because of lacking biological transporter (e.g., specific transporter for As and Cr does not exist ubiquitously in plant species) or due to insensitive to the change of pH (e.g., the solubility of Cu is more sensitive to the change of soil organic matter compared to soil pH) (Alloway, 2010).

Besides influencing the solubility of metals in soil, soil pH and organic matter content also interact with each other dynamically. One of the consequences of the organic matter mineralization is its influence on soil pH (Kelderman and Osman, 2007). In this study, pH and LOI show a less significant negative relationship ($r^2 = 0.148, p = 0.07$) (Figure 3-5), implying that the organic matter content in the soil of Liberty State Park is related to the change of soil pH, but other edaphic factor also contribute to soil pH change. When organic matter in soil is under early diagenesis effect, CO$_2$ is released into
soil and lower soil pH as the result of carbon oxidation. At the same time, redox reactions happened in soil under various Eh range consumes $H^+$ and buffers soil acidity effectively (Alloway, 2010). The relationship between soil pH and LOI in this study is possibly the result of interaction between carbon oxidation, redox reaction, and other $H^+$ consumption reactions.

Therefore, the uptake of metal from the soil by plant is a complicated process that is controlled by both geochemical reactions and biological metabolic processes. In addition to plant specific conditions, the weight of each factor on the controlling of metal uptake efficiency varies with element. As a brownfield site with high metal concentrations and different chemical, physical, vegetation assembling, and morphology characters in each study sites, the results from this study of the interaction between metal mobility and soil properties can be inconsistent with that from other studies (Cappuyns et al., 2004; Jones et al., 2002; Peng et al., 2009; Sauve et al., 2000; Sekaly et al., 1999; Zeng et al., 2011). It can be indicated from the results that except for referring to previous studies, it is still necessary to conduct on-site evaluation when estimating the influence of edaphic condition on metal bioavailability.
3.4 Conclusion

This investigation of metal (As, Cr, Cu, and Zn) concentrations in the soils and plants in an urban brownfield site indicates that the metal bioconcentration factors (BCFs) of plant roots, stems and leaves vary widely from plant to plant depending on each individual metal and plant species. The results show that metals mainly accumulate in the root system, and the metal accumulation levels in the aerial sections of the plants, such as stems and leaves, are relatively lower than that in the root tissue. In most cases, the concentrations between the stems and the leaves are comparable although these stems and leaves are found to have different responses with respect to different metals in some cases. *Betula populifolia, Rhus copallinum, Polygonum cuspidatum* and *Artemisia vulgaris* have comparably higher capacity in accumulation of specific metals in their tissues, suggesting a relatively high expression level of metal transporters. The study also shows that environmental factors, such as organic matter content and pH, in the rhizosphere are very important and critical to metal uptake by the plants as demonstrated by metal uptake efficiencies. In general, low pH condition and low organic matter content are favorable to increase metal uptake efficiency of all the four metals studied (As, Cr, Cu and Zn). These results demonstrate that metal bioavailability and uptake efficiencies by the roots in rhizosphere are complicated by many factors including pH, oxidation-reduction potential and organic content. Specifically, Cu bioavailability significantly decreases with
increasing organic matter content in the soil, whereas Zn uptake efficiency significantly decreases with increasing soil pH level.
3.5 References


Table 3-1 Metal concentrations, carbon content and pH in Liberty State Park soils along with the dominant species at each site.

<table>
<thead>
<tr>
<th>Site</th>
<th>Dominant species</th>
<th>Type of species</th>
<th>As (µg g⁻¹)</th>
<th>Cr (µg g⁻¹)</th>
<th>Cu (µg g⁻¹)</th>
<th>Zn (µg g⁻¹)</th>
<th>TOC (%)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP-21</td>
<td>Artemisia vulgaris</td>
<td>Herbaceous</td>
<td>37.4 ± 7.9</td>
<td>38.2 ± 2.6</td>
<td>345 ± 40</td>
<td>1058 ± 327</td>
<td>28.4</td>
<td>6.6</td>
</tr>
<tr>
<td>TP-40</td>
<td>Artemisia vulgaris</td>
<td>Herbaceous</td>
<td>13.2 ± 2.1</td>
<td>20.3 ± 7.5</td>
<td>153 ± 44.5</td>
<td>159 ± 48</td>
<td>17.3</td>
<td>6.6</td>
</tr>
<tr>
<td>TP40C</td>
<td>Artemisia vulgaris</td>
<td>Herbaceous</td>
<td>14.2 ± 6.8</td>
<td>20.2 ± 12.5</td>
<td>229 ± 87.7</td>
<td>304 ± 315</td>
<td>14.9</td>
<td>6.8</td>
</tr>
<tr>
<td>TP-8</td>
<td>Artemisia vulgaris</td>
<td>Herbaceous</td>
<td>11.9 ± 0.4</td>
<td>38.4 ± 2.9</td>
<td>168 ± 18</td>
<td>207 ± 54</td>
<td>47.4</td>
<td>6.0</td>
</tr>
<tr>
<td>TP-16</td>
<td>Onoclea sensibilis</td>
<td>Herbaceous</td>
<td>35.1 ± 14.9</td>
<td>53.4 ± 7.9</td>
<td>67.0 ± 27.7</td>
<td>38.7 ± 20.5</td>
<td>13.6</td>
<td>6.2</td>
</tr>
<tr>
<td>TP-16</td>
<td>Phragmites australis</td>
<td>Herbaceous</td>
<td>35.1 ± 14.9</td>
<td>53.4 ± 7.9</td>
<td>67.0 ± 27.7</td>
<td>38.7 ± 20.5</td>
<td>13.6</td>
<td>6.2</td>
</tr>
<tr>
<td>TP-28/17</td>
<td>Polygonum cuspidatum</td>
<td>Herbaceous</td>
<td>12.5 ± 4.6</td>
<td>43.4 ± 11.5</td>
<td>48.3 ± 11.9</td>
<td>963 ± 13.8</td>
<td>9.7</td>
<td>5.4</td>
</tr>
<tr>
<td>TP-8</td>
<td>Solidago virgaurea</td>
<td>Herbaceous</td>
<td>11.9 ± 0.4</td>
<td>38.4 ± 2.9</td>
<td>168 ± 18</td>
<td>207 ± 54</td>
<td>47.4</td>
<td>6.0</td>
</tr>
<tr>
<td>TP-14</td>
<td>Betula populifolia</td>
<td>Woody</td>
<td>87.4 ± 41.3</td>
<td>37.8 ± 33.4</td>
<td>103 ± 37</td>
<td>49.9 ± 12.6</td>
<td>52.6</td>
<td>5.2</td>
</tr>
<tr>
<td>TP-14/16</td>
<td>Betula populifolia</td>
<td>Woody</td>
<td>42.8 ± 9.0</td>
<td>209 ± 59.4</td>
<td>129 ± 11</td>
<td>157 ± 51</td>
<td>34.9</td>
<td>5.2</td>
</tr>
<tr>
<td>TP-18</td>
<td>Betula populifolia</td>
<td>Woody</td>
<td>33.3 ± 3.9</td>
<td>27.6 ± 17.0</td>
<td>238 ± 6</td>
<td>491 ± 473</td>
<td>23.7</td>
<td>6.0</td>
</tr>
<tr>
<td>TP-28</td>
<td>Betula populifolia</td>
<td>Woody</td>
<td>22.5 ± 2.0</td>
<td>68.5 ± 5.19</td>
<td>44.3 ± 10.4</td>
<td>72.5 ± 13.2</td>
<td>45.5</td>
<td>5.0</td>
</tr>
<tr>
<td>TP-41</td>
<td>Betula populifolia</td>
<td>Woody</td>
<td>13.3 ± 3.7</td>
<td>9.7 ± 4.43</td>
<td>68.4 ± 23.7</td>
<td>198 ± 103</td>
<td>10.0</td>
<td>6.0</td>
</tr>
<tr>
<td>TP-43</td>
<td>Betula populifolia</td>
<td>Woody</td>
<td>21.0 ± 2.0</td>
<td>10.2 ± 3.0</td>
<td>166 ± 72</td>
<td>63.7 ± 15.6</td>
<td>28.3</td>
<td>5.4</td>
</tr>
<tr>
<td>TP-43/14</td>
<td>Betula populifolia</td>
<td>Woody</td>
<td>17.6 ± 4.1</td>
<td>11.4 ± 2.5</td>
<td>69.9 ± 12.2</td>
<td>49.0 ± 14.9</td>
<td>21.1</td>
<td>5.0</td>
</tr>
<tr>
<td>TP-48</td>
<td>Betula populifolia</td>
<td>Woody</td>
<td>10.7 ± 5.9</td>
<td>16.7 ± 20.0</td>
<td>76.4 ± 18.0</td>
<td>24.9 ± 12.3</td>
<td>19.8</td>
<td>6.1</td>
</tr>
<tr>
<td>TP-10</td>
<td>Populus deltoids</td>
<td>Woody</td>
<td>193 ± 11.2</td>
<td>61.6 ± 39.2</td>
<td>257 ± 31</td>
<td>131 ± 90</td>
<td>32.3</td>
<td>5.4</td>
</tr>
<tr>
<td>TP-24</td>
<td>Populus deltoids</td>
<td>Woody</td>
<td>23.6 ± 1.7</td>
<td>44.0 ± 3.5</td>
<td>249 ± 35</td>
<td>718 ± 219</td>
<td>29.8</td>
<td>6.6</td>
</tr>
<tr>
<td>TP-25</td>
<td>Populus deltoids</td>
<td>Woody</td>
<td>270 ± 18.4</td>
<td>40.4 ± 26.1</td>
<td>1527 ± 219</td>
<td>1586 ± 1358</td>
<td>30.7</td>
<td>6.2</td>
</tr>
<tr>
<td>TP-1</td>
<td>Rhus copallimum</td>
<td>Woody</td>
<td>12.5 ± 7.1</td>
<td>41.3 ± 19.1</td>
<td>124 ± 51</td>
<td>309 ± 125</td>
<td>8.81</td>
<td>6.0</td>
</tr>
<tr>
<td>TP-21/40</td>
<td>Rhus copallimum</td>
<td>Woody</td>
<td>15.7 ± 1.8</td>
<td>32.1 ± 2.5</td>
<td>224 ± 46</td>
<td>603 ± 8</td>
<td>32.7</td>
<td>6.2</td>
</tr>
<tr>
<td>TP-3</td>
<td>Rhus copallimum</td>
<td>Woody</td>
<td>38.9 ± 11.4</td>
<td>70.1 ± 12.6</td>
<td>379 ± 356</td>
<td>168 ± 167</td>
<td>28.5</td>
<td>5.8</td>
</tr>
<tr>
<td>TP-40 B</td>
<td>Rhus copallimum</td>
<td>Woody</td>
<td>24.8 ± 4.6</td>
<td>46.6 ± 5.0</td>
<td>212 ± 28.4</td>
<td>232 ± 40</td>
<td>31.0</td>
<td>7.4</td>
</tr>
<tr>
<td>TP7/8</td>
<td>Rhus copallimum</td>
<td>Woody</td>
<td>57.1 ± 17.3</td>
<td>50.6 ± 3.8</td>
<td>199 ± 24</td>
<td>218 ± 73</td>
<td>51.0</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Table 3-2 Metal bioconcentration factor (BCF) of roots, stems and leaves relatively to soils for different plant species.

<table>
<thead>
<tr>
<th>Plant species</th>
<th># of samples</th>
<th>Ratio</th>
<th>Statistics</th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Artemisia vulgaris</em></td>
<td>4</td>
<td>Root/Soil</td>
<td>mean ± s.d.</td>
<td>0.09 ± 0.07</td>
<td>0.19 ± 0.09</td>
<td>0.32 ± 0.13</td>
<td>0.90 ± 0.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>0.04–0.19</td>
<td>0.10–0.31</td>
<td>0.24–0.51</td>
<td>0.36–1.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.01 ± 0.01</td>
<td>0.10 ± 0.04</td>
<td>0.34 ± 0.21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>n.a.</td>
<td>0.00–0.03</td>
<td>0.06–0.15</td>
<td>0.09–0.59</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.01 ± 0.00</td>
<td>0.03 ± 0.02</td>
<td>0.84 ± 0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>n.a.</td>
<td>0.00–0.01</td>
<td>0.01–0.06</td>
<td>0.62–1.33</td>
</tr>
<tr>
<td><em>Betula poplifolia</em></td>
<td>8</td>
<td>Root/Soil</td>
<td>mean ± s.d.</td>
<td>0.11 ± 0.12</td>
<td>0.31 ± 0.13</td>
<td>0.41 ± 0.11</td>
<td>2.84 ± 2.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>0.01–0.41</td>
<td>0.19–0.57</td>
<td>0.23–0.52</td>
<td>0.93–6.79</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf/Soil</td>
<td>mean ± s.d.</td>
<td>0.00 ± 0.00</td>
<td>0.01 ± 0.01</td>
<td>0.06 ± 0.03</td>
<td>12.8 ± 13.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>0.00–0.01</td>
<td>0.00–0.04</td>
<td>0.03–0.12</td>
<td>1.5–41.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.00 ± 0.00</td>
<td>0.03 ± 0.04</td>
<td>0.40 ± 0.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>n.a.</td>
<td>0.00–0.01</td>
<td>0.00–0.13</td>
<td>0.04–0.89</td>
</tr>
<tr>
<td><em>Onoclea sensibilis</em></td>
<td>1</td>
<td>Root/Soil</td>
<td>mean ± s.d.</td>
<td>0.08</td>
<td>0.25</td>
<td>0.72</td>
<td>0.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.01</td>
<td>0.07</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td><em>Phragmites australis</em></td>
<td>1</td>
<td>Root/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.01</td>
<td>0.08</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td><em>Polygonum cuspidatum</em></td>
<td>1</td>
<td>Root/Soil</td>
<td>mean ± s.d.</td>
<td>0.21</td>
<td>0.29</td>
<td>0.84</td>
<td>1.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.01</td>
<td>0.09</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.00</td>
<td>0.01</td>
<td>0.02</td>
</tr>
<tr>
<td><em>Populus deltoids</em></td>
<td>3</td>
<td>Root/Soil</td>
<td>mean ± s.d.</td>
<td>0.05 ± 0.05</td>
<td>0.10 ± 0.05</td>
<td>0.18 ± 0.12</td>
<td>1.04 ± 0.90</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>0.01–0.10</td>
<td>0.07–0.15</td>
<td>0.07–0.30</td>
<td>0.38–2.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf/Soil</td>
<td>mean ± s.d.</td>
<td>0.00 ± 0.00</td>
<td>0.00 ± 0.00</td>
<td>0.02 ± 0.02</td>
<td>4.47 ± 4.83</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>0.00–0.00</td>
<td>0.00–0.01</td>
<td>0.01–0.03</td>
<td>1.04–10.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>0.30 ± 0.29</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>n.a.</td>
<td>0.00–0.01</td>
<td>0.10–0.62</td>
<td></td>
</tr>
<tr>
<td><em>Rhus copallinum</em></td>
<td>5</td>
<td>Root/Soil</td>
<td>mean ± s.d.</td>
<td>0.02 ± 0.02</td>
<td>0.04 ± 0.05</td>
<td>0.05 ± 0.07</td>
<td>1.22 ± 1.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>0.00–0.05</td>
<td>0.00–0.10</td>
<td>0.00–0.18</td>
<td>0.10–4.47</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf/Soil</td>
<td>mean ± s.d.</td>
<td>0.01 ± 0.00</td>
<td>0.02 ± 0.01</td>
<td>0.04 ± 0.03</td>
<td>0.20 ± 0.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>0.00–0.01</td>
<td>0.01–0.04</td>
<td>0.01–0.08</td>
<td>0.06–0.44</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.01 ± 0.02</td>
<td>0.03 ± 0.02</td>
<td>1.20 ± 1.27</td>
</tr>
<tr>
<td></td>
<td></td>
<td>range</td>
<td></td>
<td>n.a.</td>
<td>0.00–0.06</td>
<td>0.01–0.05</td>
<td>0.05–2.80</td>
</tr>
<tr>
<td><em>Solidago virgaurea</em></td>
<td>1</td>
<td>Root/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
<td>n.a.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Leaf/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.01</td>
<td>0.06</td>
<td>0.34</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stem/Soil</td>
<td>mean ± s.d.</td>
<td>n.a.</td>
<td>0.00</td>
<td>0.06</td>
<td>1.92</td>
</tr>
</tbody>
</table>

Note: n.a. = Not available.
Figure 3-1 Map of Liberty State Park, New Jersey with the vegetation assembling patterns for each sampling site. SNH, successional northern hardwood; SSB, successional shrub land; SOF, successional old field; MS, maritime shrub land; MG, maritime grasslands; CRM, common-reed-dominated wetland.
Figure 3-2 Comparisons of metal (As, Cr, Cu and Zn) uptake by plant leaves, stems and roots of selected predominant plant species in the study site. The results indicate the metals are mainly accumulated in the plant roots.
Figure 3-3 Significant correlations of metal (As, Cr, Cu and Zn) concentrations between the soils and the plant roots. The results indicate the ability of plant uptake of metals from the metal contaminated soils. Data were expressed in logarithmic-based scale to address the general trends between each parameter.
Figure 3-4 Effect of organic matter on metal (As, Cr, Cu and Zn) bioconcentration factors of the plant roots. The results suggest that the low organic matter content is generally in favor of bioaccumulation of metals in the roots with significant influence on Cu but less or no influence on As, Cr and Zn.
Figure 3-5 pH changes as a function of organic matter in the soils. Data in the circle is a statistical outlier and excluded from the regression analysis. The results suggest that high organic matter content is in favor of producing more H$^+$ ions due to early diagenesis of organic matter.
Figure 3-6 Effect of pH on metal (As, Cr, Cu and Zn) bioconcentration factors of the plant roots. Data in the circles are statistical outliers and excluded from the regression analysis. The results suggest that the low pH is generally in favor of bioaccumulation of metals with significant influence on Zn but less or no influence on As, Cr and Cu.
CHAPTER 4

VANADIUM UPTAKE AND TRANSLOCATION IN DOMINANT PLANT SPECIES ON AN URBAN COASTAL BROWNFIELD SITE

[This chapter was published in Science of the Total Environment 476-477(2014) 696-704;
DOI: 10.1016/j.scitotenv.2014.01.049]

Abstract

This study, conducted at a brownfield site in New Jersey, USA, investigated factors controlling V uptake and translocation in naturally assembled plant species. Six dominant species were collected from 22 stations in the study area. We found that V concentration in the plants decreased in a sequence of root>leaf>stem. No significant differences were found among the six dominant plant species in terms of root V uptake efficiency (V BCF) and V root to shoot translocation (V TF). Although soil pH and TOC did not show significant impact on V accumulation in the roots, soil labile V content showed significant positive linear correlation ($p<0.05$) with plant root V. Non-linear regression analysis indicates that V translocation efficiency decreases with increasing concentration in the soil, implying that excessive V in the soil might inhibit its absorption by the plant roots. Leaf V concentration was constant in all the plant species regardless the variation
in soil V concentration. The study shows that the six dominant plant species on site had limited amount of V translocated to the aerial part of the plant.

Keywords: Vanadium, Brownfield, Plant, Uptake, Translocation, Toxic effect
4.1 Introduction

Urban brownfields are abandoned, idle or under-used commercial and industrial sites where on-site contamination has inhibited redevelopment due to potential environmental and social risks (Alker et al., 2000). In addition, soil metal contamination in urban brownfields has aroused great environmental and public health concerns (Gallagher et al., 2008; Thums et al., 2008). Remediation of the urban brownfield is becoming increasingly important in post-industrial landscapes. Compared to the traditional chemical/physical remediation approaches for metal-contaminated soils, phytoremediation/phytostabilization offers a cost-effective and environmental friendly solution (Desouki and Feng, 2012; Ferro et al., 1999; Glass, 1999). Previous studies indicate that there are several processes involved in metal uptake by plants from soils and metal translocation within the plants. These processes include uptake of bioavailable metals, metal chelation and compartmentation in roots, metal translocation from root to shoot, and metal chelation and compartmentation in leaves (Pilon-Smits, 2005; Qian et al., 2012; Weis and Weis, 2004). While soil metal bioavailability determines the potential uptake, soil pH, redox potential, and total organic matter content control the release of metal from different fractions of the soil metals (Driscoll et al., 1994; Sposito, 2008; Violante et al., 2010). Plant uptake of bioavailable metal ions occurs at the interface between rhizosphere soil and root surface. Metals are then accumulated in the root or
further translocated to the aerial tissue through vascular tissue (Pilon-Smits, 2005). It has been observed that high metal concentrations in the contaminated brownfield can have negative impact on metabolism of the plants (Larsson et al., 2013). When the concentrations of soil metals exceed the tolerance threshold, metabolism is impacted and the plant will likely be excluded from the vegetation assemblage (Gallagher et al., 2008). Many species however, can tolerate excessive amount of metals in the environment with strategies such as exclusion and detoxification/isolation (Baker, 1981; Ehlken and Kirchner, 2002; Remon et al., 2013). The tolerance strategy further determines metal concentrations in different tissue parts of a plant. As an excluder, a plant is capable of inhibiting the uptake of certain metals. In contrast, a as an accumulator a plant is capable of detoxifying or isolating certain metals and accumulating high concentration of the metals in the aerial tissue (Ehlken and Kirchner, 2002; Tangahu et al., 2011). Due to biological magnification, high metal concentrations in the aerial plant tissue can potentially result in both ecological and public health risks. It is therefore crucial to understand how soil properties and plant species impact metal assimilation when evaluating brownfield bioremediation, mitigation and restoration.

Vanadium (V) is a trace element ranking as the 22\textsuperscript{nd} most abundant element in the earth’s crust. Excessive amount of V in human body can increase the possibility of lung cancer occurrence. It can also cause nausea, mild diarrhea, and stomach cramps in human
body (ATSDR, 2012). Naturally, V co-exists with minerals and fossil fuels in oxidation states of V(III) and V(V), yet naturally-occurring V enrichment is rarely found (ATSDR, 2012). It was reported that approximately $2.30 \times 10^8$ kg of V was annually introduced to the environment through human activities, of which $1.32 \times 10^8$ kg was deposited on the land and resulted in elevated soil V concentration (Hope, 1997). Fuel combustion is one of the most important anthropogenic V sources in the environment because V can be found in most of coal and crude oil products (Chouparova et al., 2004; Hope, 1994, 1997; Nadal et al., 2004; Soldi et al., Peloso, 1996; Teng et al., 2011). As a result, soil V concentration in the fuel combustion venues (i.e. areas close to oil refineries, fuel powered facilities, and heavy automobile traffic) is usually much higher than natural abundance (Al-Surrayai, et al., 2009; Khan et al., 2011; Nadal et al., 2004; Soldi et al., 1996; Teng et al., 2011). Vanadium flux from soil to land biota approximately ranges from $8.14 \times 10^7$ kg y$^{-1}$ to $2.58 \times 10^8$ kg y$^{-1}$ (Hope, 1997). In areas with high soil V concentration, assimilation of V by plants is considered as the major V flux from soil to biota because plants have the highest direct exposure to the soil (ATSDR, 2012). The role of soil properties and plant species in V assimilation in the plant has been studied and the results vary from case to case. Both soil pH and TOC have been shown to have a significant effect on V bioavailability in the soil (Agnieszka and Barbara, 2012; Poledniok and Buhl, 2003; Teng et al., 2011). The accumulation of V in plant tissue also
depends on plant species and soil V content. For example, V concentration in vegetable and grass tissues around a thermal power plant ranged from $2.95 \pm 0.02 \mu g \ g^{-1}$ to $13.98 \pm 0.11 \mu g \ g^{-1}$, which has the potential to impact human health (Khan et al., 2011). Potedniok and Buhl (2003) found that V concentrations were $65 \pm 20 \mu g \ g^{-1}$ and $22 \pm 4 \mu g \ g^{-1}$ in the bush bean (*Phaseolus vulgaris* L.) root and aerial tissue, respectively, even though the extractable V concentration in the soil was $0.6 \pm 0.05 \mu g/ g$. A study on plants growing in an industrial city in China revealed that V concentrations ranged from $2.6 \mu g \ g^{-1}$ to $42.8 \mu g \ g^{-1}$ in the leaf tissue of 36 plant samples and $88.2 \mu g \ g^{-1}$ to $868.4 \mu g \ g^{-1}$ in the soil, respectively (Teng et al., 2011).

The interior section of Liberty State Park contains a brownfield and is located in the densely populated city of Jersey City close to the borough of Manhattan, New York. Until its acquisition by the State of New Jersey in 1969, the site had been used for railroad transportation and coal storage for over a century. The historical coal combustion caused V enrichment in the soil, a condition typical of many post-industrial sites of from that era. A better understanding of the assimilation of V within the novel vegetative assemblages of such sites is critical to the assessment of the ecological risk associated with the use of phytostabilization as a mitigation strategy. In this study we explore V plant assimilation by characterizing the roles of soil properties, seasonal variations, and plant species in V root uptake and root to shoot translocation. We hypothesized, based on
our previous work with other metals that V would be restricted primarily to the root system of the targeted species and that translocation to the aerial section of the plant would occur at significantly reduced concentrations.

4.2 Methodology

4.2.1 Study Site

Liberty State Park in northern New Jersey consists of approximately 5 km$^2$ (1156 acres) of protected land and water areas. It was originally a saltmarsh mud flat and shellfish bed under the water, which was later filled with municipal, commercial and industrial waste. By 1836 the Central Railroad of New Jersey (CRRNJ) began operations on the site. The site was used as the railroad center and freight yard for transportation and goods storage until the late 1960s when New Jersey Department of Environmental Protection began to acquire the land, and transformed it into a public park. Our study site was an area of ~1 km$^2$ (251 acre) within the center of the Liberty State Park (Figure 4-1). Due to the nature of the fill materials, the previous use as a coal storage facility, coal transport and incomplete combustion of fossil fuels, the freight yard was contaminated by various metals. The metals are unevenly distributed on this site and the concentrations of most metals are above the New Jersey Residential Soil Cleanup Criteria (EPA, 1999).
Therefore, the study site has been isolated from public and left undeveloped since it was transferred to the New Jersey Division of Parks and Forestry in 1970 (Gallagher et al., 2008).

4.2.2 Sample collection

The first sampling campaign was conducted in June 2005 with twenty-two sampling sites selected based on the species dominance and vegetation assemblage patterns. Six dominant plant species growing on site, including three perennial herbaceous species (*Artemisia vulgaris* L., *Polygonum cuspidatum* and *Phragmites australis* (Cav.) Trin. ex Steud.) and three deciduous woody species (*Rhus copallinum* L., *Betula populifolia* and *Populus deltoides*), were chosen for this study. The dominant plant species at each sampling site were identified and triplicate root, stem and leaf samples of each were collected and stored in clean polypropylene containers. Soil samples around the plants from each of the 22 sampling sites were also collected in the area of the greatest root density. Detritus such as gravels and roots/leaves were removed from the soil samples before the soils were stored in labeled polypropylene containers and kept at 4°C for further treatment and analysis. Soil pH was measured using a LaMotte field soil pH meter. A detailed description of the sampling procedures can be found in Gallagher et al. (2008).
The second sampling campaign was conducted in May and November 2011 and *P. australis* root tissue samples were collected in triplicates from two (Sites TP-1 and TP-25) out of 22 sampling sites based on the metal concentration levels in the soils determined by previous studies (Gallagher et al., 2008). *Phragmites australis* roots were dug out of the ground with the soil around it and stored in clean Ziploc bags. Soil core samples (approximately 10 cm in length) around the sampled plants were also collected. The core samples were capped on both ends of the core containers after the cores were recovered. Both plant and soil samples were temporarily stored in the coolers, transported to the laboratory and stored at 4°C before the further treatment. During the sample treatment, bulk soils on the surface of root samples were initially removed by hand. The root samples were then rinsed with tap water. Finally, the clean root samples were rinsed with Milli-Q water and stored at 4°C in a refrigerator. Soil core samples were sectioned in the laboratory at 0.5 cm interval from 1 to 2 cm and then at 1 cm interval for rest of the cores. Then, both soil and root tissue samples were oven-dried at 80°C for three days or till samples were completely dry, sealed in labeled polypropylene bags and stored at 4°C for future analysis.
4.2.3 Laboratory analysis

Detailed laboratory analytical procedures for the samples collected in June 2005 were described in Gallagher et al. (2008). In brief, soil samples were homogenized thoroughly, sieved to <125 μm, and oven-dried at 80°C for 48 h. For samples collected in May and November 2011, soil and plant samples were dried in an oven at 60°C for 48 hours. The dried soil samples were grounded with a pestle and a mortar to fine powders. Microwave digestion was used for the soil samples collected in June 2005 to analyze potential leachable V concentration in the soil. Concentrated HNO$_3$ was used as a matrix to release metals from exchangeable fraction, carbonate fraction, iron-manganese oxides fraction, and organic matter bounded fraction in the soil (Tessier et al., 1979). In brief, an aliquot of 0.5g from each soil sample was weighted for metal analysis. The sample was then treated with 10 ml concentrated trace-metal grade HNO$_3$ in Teflon bombs and heated at >170°C for 30 min in a MARS-5 (CEM Corp.) microwave. National Institute of Standard Technology (NIST) Standard Reference Material (SRM) 1944 was analyzed along with every 12 soil samples in order to monitor the quality of soil digestion. The method blanks were also analyzed to monitor the contamination during the digestion. The sample solutions were then reduced to minimum volume and diluted with 1% HNO$_3$ for analysis on atomic absorption spectroscopy (AAS). In the meantime, plant samples were dried at 60°C for 48 h and weighed to approximately 0.3 g for metal concentration.
analysis, followed by treatment with 30% H_2O_2 and acid digested in Teflon bombs in a MARS-5 (CEM Corp.) programmed microwave instrument. During the course of sample digestion, a method blank and NIST SRM1573 reference materials (tomato leaves) were treated exactly as same as every 12 plant samples for the quality assurance and quality control purpose. The solution were then diluted to a certain volume using 1% HNO_3, and analyzed for metal concentrations similar to soil metal analysis.

Teflon beaker total digestion was used to analyze total soil V concentration for the samples collected in 2011. By applying HF along with HNO_3 to the samples in the digestion process, the metals that bound to crystal structure in the residual fraction were released (Tessier et al., 1979). Therefore, comparing to HNO_3 microwave digestion, Teflon beakers were used for soil sample digestion for total V concentration. During the analysis, an aliquot of 0.25g of soil sample or 0.4 g of plant sample was weighted in a Teflon beaker for acid total digestion. Then, a three-step (HNO_3-HClO_4-HF) total digestion method was applied to the soil samples (Feng et al., 1998; Feng et al., 2011; Windom et al., 1989). Briefly, each soil sample was first digested at 120°C for 2 hours with addition of 5 ml trace-metal grade HNO_3 and 5ml trace-metal grade HF in each Teflon beakers placed with a Teflon cover. Then, 5 ml HNO_3 and 2 ml HClO_4 were added to the Teflon beaker and each soil sample was digested at 180°C until the solution was condensed to a viscous paste. Finally, the paste was dissolved in 10 ml of 10% trace-
metal grade HNO$_3$ and the sample solution was sealed in a pre-cleaned plastic bottle.

Each plant sample was digested at 180°C with addition of trace metal grade 5ml HNO$_3$ + 1ml HClO$_4$ in a Teflon beaker with a Teflon cover. When the solution became condensed pastes, 10 ml of 10% trace metal grade HNO$_3$ was added to each beaker to dissolve the paste. The solution was then transferred to pre-cleaned plastic bottles and stored for further analysis. To remove black carbon and other precipitates in the solution, each solution was filtered through a 20 µm filter before the instrument analysis. All the samples were analyzed for metal concentrations on Element 2 Finnigan MAT Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

In order to monitor the quality of the soil and plant digestion processes, two standard reference materials (SRM), SRM 8704 Buffalo River Sediment and SRM 1515 Apple Leaves issued by National Institute of Standards and Technology (NIST) were analyzed along with the soil and plant samples, respectively. The analytical values of V concentration in Apple Leaves and Buffalo River Sediment were 0.19 ± 0.03 µg g$^{-1}$ and 94 ± 8 µg g$^{-1}$, respectively, within the range of the NIST certified reference values. The results demonstrated the accuracy and precision of the chemical analysis. Organic content in the soils was determined by loss on ignition (LOI) method (Davies, 1974). The dried soil samples were heated at 450°C in a muffle furnace for 8 hours and the percentage of the weight loss was used as the percentage of organic matter in the soils.
4.2.4 Evaluation of V enrichment and plant uptake efficiency

Vanadium concentration in the soils collected from two sites (Sites TP-1 and TP-25) in May 2011 was used to evaluate V pollution level. Geoaccumulation index ($I_{geo}$), which is an indicator of the soil quality and metal enrichment, was applied to distinguish anthropogenic sourced metals from natural origin metals (G. Müller, 1979; Zhang et al., 2009). $I_{geo}$ is mathematically defined as:

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n}$$

where $C_n$ is the metal concentration of interest and $B_n$ is the metal background value that derived from metal concentration in the upper continental crust, sampling site, or regional record (Martin and Whitfield, 1983; Müller, 1979; Taylor and McLennan, 1995). Factor 1.5 is a matrix constant that corrects the lithogenic effects. In this study, V background concentration ($V = 30 \mu g \, g^{-1}$) was adopted from the New Jersey State mean soil metal background concentrations reported by US Environmental Protection Agency (EPA, 2003). Plant metal accumulation efficiency was measured by metal bioconcentration factor (BCF), which is a ratio of metal concentration in plant tissue to that in the soil (Audet and Charest, 2007b; Dowdy and McKone, 1997; Kim et al., 2003):
where $[\text{Me}]_{\text{plant}}$ is the total metal concentration in the plant tissue, and $[\text{Me}]_{\text{soil}}$ is the total metal concentration in the soil. In this study, root V uptake efficiency was evaluated by BCF based on V concentrations in the plant roots and soils collected in June 2005. Another indicator used to evaluate the efficiency of metal transport from the root tissue to the aerial parts of the plant is translocation factor (TF) and expressed as (Marchio et al., 2004):

$$TF = \frac{[\text{Me}]_{\text{aerial}}}{[\text{Me}]_{\text{root}}}$$

where $[\text{Me}]_{\text{aerial}}$ is metal concentration in the aerial part of the plant and $[\text{Me}]_{\text{root}}$ is metal concentration in the root tissue of the plant (Bose and Bhattacharyya, 2008; Bose et al., 2008; Soda et al., 2012). In this study, V concentration in the leaf tissue was used to estimate V translocation rate between the root and the leaf because V concentration in the stem was much lower than that in the leaf (Table 4-1).

4.2.5 Statistical analysis

Factor analysis was used to determine the inherent relationships among many analyzed elements (Dragon, 2006; Reimann et al., 2001). New groups of variables (the
factors) are generated from the initial sets of variables based on their linear correlations. The percentage of total variance explained by each factor indicates the capacity of each factor that explains the variance related to whole matrix of variables. The factor tends to be better explained by those variables that have loading close to 1 or -1 (Davis, 1973). When the loading of a variable is between 0.7 and 1, it is considered as highly relevant to the factor; when the loading of a variable ranges from 0.4 to 0.7, the factor is considered to have a moderate control on the variable; and when the loading of a variable is less than 0.4, it is unlikely relevant to the factor. To better discern the major factors, Varimax rotation technique was used in factor analysis to rotate the variable matrix to a simple orthogonal structure (Davis, 1973). In addition to factor analysis, Wilcoxon nonparametric test was applied to determine the hypothetical existence of a significant difference between the means and the medians in different groups when the distribution of data did not follow normal distribution (Hajek, 1969). Linear regression and nonlinear regression analyses were also performed on the measured data to estimate the model parameters that can fit the relationship between different pairs of variables (Qian et al., 2012).
4.3 Results

For the samples collected in June 2005, soil properties varied among the 22 sampling sites (Table 4-1). Soil TOC ranged from 9% to 53% and soil pH from 5.0 to 7.4 (Table 4-1). Soil labile V content, from the 2011 samples, varied from not detectable (n.d.) to 118 ± 21 µg g⁻¹ (Table 4-1). Vanadium concentration in plant samples varied with plant tissue parts and between the two sites. It ranged from 25.7 µg g⁻¹ to 280 µg g⁻¹ in roots, n.d. to 0.46 µg g⁻¹ in stems, and 2.06 µg g⁻¹ to 12.1 µg g⁻¹ in leaves (Table 4-1). Similar to previous studies (Martin and Kaplan, 1998; Teng et al., 2011), V concentration in the leaves was lower than that in the roots. The stems had the lowest V concentration of all. Root BCF varied from 0.88 ± 0.91 to 10.8 ± 18.9 while the root to shoot V TF was between 0.01 ± 0.00 and 0.45 ± 0.01. The result indicates a much lower root to shoot translocation rate of V in these dominant plant species.

Based on the total metal load determination from a previous study (Gallagher et al., 2008), two sampling sites were used for V soil contamination analysis in 2011. Site TP-1 had the lowest total metal load, while Site TP-25 had the highest total metal load (Gallagher et al., 2008). Analytical results of soil samples collected in May 2011 at Sites TP-1 and TP-25 showed that total V concentration in the soil in the upper 10 cm ranged from 71.1 µg g⁻¹ to 83.1 µg g⁻¹ with an average of 77.2 ± 6.0 µg g⁻¹ at Site TP-1, and 84.2 µg g⁻¹ to 227 µg g⁻¹ with an average of 144 ± 74 µg g⁻¹ at Site TP-25, respectively (Table
In comparison with soil labile V content measured for the 2005 samples from the two sites, i.e., 19.6 ± 17.0 µg g⁻¹ at Site TP-1 and 40.6 ± 29.4 µg g⁻¹ at Site TP-25, respectively (Table 4-1), the total V concentration is significantly ($p<0.05$) higher (Table 4-2). The portion of labile V in the soil accounted for 20 - 30% of the total soil V concentration, which is consistent with another study on V fractioning in the soil (Teng et al. 2011b). We used a geoaccumulation index ($I_{geo}$) to characterize soil V contamination. $I_{geo}$ calculated for V at site TP-1 and site TP-25 were 0.78 and 1.68, respectively (Table 4-2). As shown in Table 4-1, there are 10 sites, which have labile V in the soil above 40.6 ± 29.4 µg g⁻¹. It is reasonable to assume that the $I_{geo}$ for V at these 10 sites is above 1.68, which is similar to the case at Site TP-25. Vanadium concentration in *Phragmites australis* roots collected in late spring/early summer (May 2011) and winter (November 2011) were measured separately. As shown in Table 4-3, V concentration in the roots collected in May 2011 ranged from 1.72 ± 0.03 µg g⁻¹ to 1.65 ± 0.03 µg g⁻¹, while the root collected in November 2011 had V concentration between 2.83 ± 0.59 µg g⁻¹ to 9.43 ± 0.74 µg g⁻¹. While root concentration remain well below soil concentrations, there is a significant ($p<0.05$) increase of V root concentration from May to November, indicating that the root accumulated more V in winter than that in late spring/early summer. In addition, in November 2011, root V concentration at Site TP-25 was significantly higher than that at Site TP-1 (Table 4-3).
4.4 Discussions

4.4.1 Soil Vanadium contamination assessment

It is generally accepted that coal combustion and storage leachate are major anthropogenic sources of V (Chouparova et al., 2004; Hope, 1994, 1997; Nadal et al., 2004; Soldi et al., 1996; Teng et al., 2011). Vanadium concentration in coal and oil products ranges from 15 to 125 µg g⁻¹ (ATSDR, 2012). Because our study site had been used as a freight yard for coal transportation and stocking for over a century (NJDEP, 1995), carbon combustion and onsite coal storage were the anthropogenic sources of V to the study site. The enrichment of V in the soil from Liberty State Park was measured by $I_{geo}$. According to Müller (1979), $0 < I_{geo} < 1$ indicates the site is unpolluted, while $1 < I_{geo} < 2$ means the site is moderately polluted. The result of this study showed that Site TP-25 had moderate V contamination, while Site TP-1 was not polluted by V. Based on this result, it is possible that 10 out of 22 sampling sites may have V contamination. In other words, approximately half of the total sampling sites might have been moderately polluted by V due to past anthropogenic activities on the site. If so, the V polluted sites have potential risk to both environment and public health. Further study is needed to confirm the potential risk of V contamination.
4.4.2 Seasonal variation in V concentration in Phragmites australis roots

*Phragmites australis* is a perennial herbaceous wetland species, whose growth follows a seasonal dynamic cycle. Therefore, seasonal variation in root V concentration could be attributed to the dynamic growth cycle of the plant that forms new shoots from April to May, establishes foliar structure from June to July, blooms in August and September, and finally the aboveground parts start senescence and transporting nutrients from shoot to root after October. From winter (November) to early spring (May), the plant is under dormancy and only minimal heterotrophic metabolism can be observed in plant rhizomes (Lippert et al., 1999; Tursun et al., 2011). In this study, root V concentration in November 2011 was higher than that in May 2011, indicating that the root accumulated more V in winter than that in late spring/early summer (Table 4-3) or that accumulation in the root tissue over the growing season is a cumulative process. Since May is early in the growth cycle of *P. australis* and the soluble fraction of V is low, there is limited uptake at this time (Tursun et al., 2011). High root V concentration in November 2011 and little V root to shoot translocation indicate a sequestration mechanism within the root tissue. This is consistent with previous studies that indicated that metal accumulation was relevant to the seasonal dynamics of the plant (Weis and Weis, 2004). Higher V concentration in roots collected at Site TP-25 in November 2011 demonstrates that the amount of V accumulated in the root is positively related to V
concentration in the soil, which is consistent with the results from other studies (Martin and Kaplan, 1998; Teng et al., 2011; Tham et al., 2001; Yang et al., 2011).

4.4.3 Vanadium uptake and translocation in the dominant species

A wide variation in V concentration in the plant tissues (Table 4-1) indicates that uptake and translocation is the result of complex interaction of chemical, biological and physical factors (Ehlken and Kirchner, 2002). In other words, these processes can be different between perennial, herbaceous, and deciduous woody species even though the amount of metal assimilated from the soil is the same (Pulford and Watson, 2003). For example, deciduous trees have deep and extensive root systems that can avoid heavily contaminated soil by root redistribution. Also, deciduous trees can translocate metals from root to shoot more efficiently than herbaceous species as they have higher transpiration rates creating a large volume of xylem sap flow from root to shoot (Pulford and Watson, 2003; Taiz and Zeiger, 2006). Moreover, the aerial biomass of the deciduous tree is larger than the herbaceous species. This can dilute the concentration of V in aerial tissue and protect the plant from the toxic effect caused by high V concentration (Pulford and Watson, 2003). In this study, root BCF and TF varied from 0.56 to 10.8 and 0.01 to 0.45, respectively (Table 4-1). However, the results from the Wilcoxon test indicate that unlike several of the studies cited above there was no significant difference (p>0.05) in V
root accumulation and translocation efficiency between the two types of plant species (i.e., perennial herbaceous plants and deciduous woody plants).

Previous studies have shown that accumulation and translocation rate of pollutants from a contaminated site can be species specific (Ehlken and Kirchner, 2002; Pulford and Watson, 2003; Tangahu et al., 2011; Weis and Weis, 2004). Several plants have been reported as V accumulators, such as *Astragalus*, *Castillejo*, and *Chrysothamnus* while the others had been identified as V excluders, i.e. *Betula*, *Salix*, and *Pinus* (Baker, 1981; Cannon, 1963; Reimann et al., 2001). In our previous study, we found significant difference in root metal (Zn, Cu, and Cr) accumulation efficiency (BCF) among the six dominant plant species (i.e., *Artemisia vulgaris*, *Polygonum cuspidatum* and *Phragmites australis*, *Rhus copallinum*, *Betula populifolia* and *Populus deltoides*) growing in Liberty State Park (Qian et al., 2012). In this study, we further tested the difference in root BCF and TF of V among the six plant species from the study site. The result from the Wilcoxon test indicates that there is no significant difference (p>0.05) in BCF and TF among the six plant species (Figure 4-2).
Factor analysis of V root uptake and translocation

In this study, we performed factor analysis on the data to identify the factors controlling V root uptake and translocation efficiency. Variables used for factor analysis include soil pH, soil TOC, soil labile V content, root V concentration, leaf V concentration, root V BCF, and V TF. The results showed that four factors (eigenvalue > 0.5) explained 89.8% variance of the data (Table 4-4). Factor 1 has high loadings of root V concentration (-0.96) and soil labile V content (-0.84); and moderate loadings of the V TF (0.64) and soil pH (0.45). Factor 1 accounts for the highest total variance (32.3%) and indicates that V uptake by the roots from the soils is affected by soil pH and soil labile V content (Table 4-4). It is likely that there is a positive relationship between soil labile V content and root V concentration and there is also a negative relationship between soil pH and root V concentration. In addition, the V TF is weakly and negatively coupled with root V concentration. The relationship indicates high V concentration in the soils inversely impacts the root to shoot V translocation efficiency within the plants (Table 4-4). Factor 2 has high loadings of soil TOC (-0.91) and soil pH (0.69), and accounts for 20% of the total variance (Table 4-4). This factor specifically indicates the inverse relationship between soil TOC and soil pH, indicating that organic matter mineralization in the soil decreases the soil pH (Kelderman and Osman, 2007). Similar trend between soil pH and soil TOC was also observed in the soils at Liberty State Park in our previous
work (Qian et al., 2011). Factor 3 has high loadings of leaf V concentration (-0.94) and the V TF (-0.66). It accounts for 20.1% of the total variance and implies that the accumulation of V in the leaves is positively correlated with the root to shoot translocation rate. Factor 4 accounts for 17.3% of the total variance. It has a high loading of the root V BCF (0.97) and a moderate loading of the soil labile V content (-0.39) (Table 4-4). This factor indicates a slightly negative correlation between the soil labile V content and the root V BCF.

4.4.5 Root V uptake and V root to shoot translocation efficiency

Root uptake and accumulation of V is a complicated process that involves release of V ions from the bulk soil into soil pore water (Teng et al., 2011), uptake of V ions from the soil pore water by the plant root (Kim et al., 2003), and accumulation of V in the plant root tissues. In addition, V accumulated in the root can also be translocated to plant aerial part (Pilon-Smits, 2005; Weis and Weis, 2004). It is known that V accumulation and translocation are the results of a series of biogeochemical factors, such as plant species, V soil fractions, and soil properties including pH and TOC (Khan et al., 2013; Pilon-Smits, 2005; Teng et al., 2011; Weis and Weis, 2004). Although the study site has diverse dominant plant species, the scenario is simplified by as plant species does not
impact the assimilation of V (Figure 4-2). Therefore, the impact on V uptake by root and root to shoot translocation mainly relies on soil labile V content, soil pH, and soil TOC.

As indicated by the factor analysis, soil TOC is not relevant to the accumulation and the translocation of V, which is further evidenced by the insignificant correlation between soil TOC and root V concentration ($p>0.05$). To further understand the relationship between the different variables, regression analysis was performed. Linear regression analysis indicates that there is a significant ($p<0.05$) positive correlation between soil potentially available V concentration and root V concentration (Figure 4-3). The result is consistent with that from the factor analysis, indicating that V concentration in the plant roots is primarily related to soil labile V content. This result is also consistent with other studies which reported that V concentration in root increased with V concentration in the media around the root (Al-Surrayai et al., 2009; Martin and Kaplan, 1998; Teng et al., 2011; Tham et al., 2001; Yang et al., 2011).

It has been known that when soil metal concentration exceeds the plant tolerance, growth and metabolism will be inhibited and eventually the species will be excluded from the site vegetation assemblage even though there is a seed existing in the regional pool (Gallagher et al., 2008). The vegetation assemblage in Liberty State Park has been developing for more than fifty years and is characterized by dominant species capable of tolerating high soil metal concentration. The correlation between soil labile V content and
root V accumulation efficiency (V BCF) indicates a close relationship between soil V concentration and root metabolism, which should be further examined to understand how soil V concentration can impact root V accumulation efficiency. However, these data indicate that the concentration of V in the soils of the site does not significantly contribute to the soil metal threshold effect on plant productivity observed in previous studies (Gallagher et al., 2008).

It appears that root V BCF is high under low soil V concentration, and then decreases dramatically as soil V concentration increases (Figure 4-4). A similar pattern was also observed in another study (Olness et al., 2005), which showed exponential decreases in root length, root weight, and shoot dry weight with increasing V concentration in the solution. In this study, we applied a non-linear exponential function to describe the relationship between root V BCF (BCF (V)_{root}) and soil V concentration ([V]_{soil}) (r^2=0.868):

\[
BCF(V)_{root} = 72.62e^{-0.279[V]_{soil}} + 1.99
\]

(4)

This exponential function describes the proportional change of a dependent variable with the change of an independent variable. Although root V concentration increases with soil V concentration, the proportional increase of root V concentration is less than that in soil V concentration (Equation 4), i.e., V accumulation efficiency
decreases with increasing soil labile V content (Figure 4-4). The results indicate that excess V is actively excluded and supports previous work that an internal mechanism which inhibits plant V absorbance capacity (Furukawa, 2001; Larsson et al., 2013; Smith et al., 2013; Tham et al., 2001).

Since Liberty State Park provides a green refuge in the middle of high density human development and is used by both local and migrating species, the trophic transfer and biomagnification of V has the potential for both human and ecological risk. However, the decrease in V TF with increasing labile V concentration (Figure 4-5) significantly reduces such risks. While there is a sharp increase in the TF with increasing soil V concentration until the concentration reaches 20 µg g⁻¹, there is then a dramatic decrease until soil V concentration increases to 50 µg g⁻¹ with a continued decrease afterwards (Figure 4-5). In addition, while the V concentration in leaves fluctuates between 4 µg g⁻¹ and 12 µg g⁻¹ with an average of 8.0±2.7 µg g⁻¹ (Table 4-4) there is no obvious change in leaf V concentration with soil V concentration. Hence, leaf V concentration is constant regardless soil V concentration change. Apparently these dominant species have developed strategies to exclude excess V ions from assimilation. Such exclusion mechanisms have been demonstrated in several other plant species (Baker, 1981; Chakraborty et al., 2011; Dahmani-Muller et al., 2000; Deng et al., 2004). Perhaps as V is not a nutrient element, and excessive V in plant tissue inhibits the metabolism of plant
(Lin et al., 2013; Taiz and Zeiger, 2006), the limited translocation of V to aerial parts of the plant provides a selective advantage during colonization and establishment. Moreover, the limited root to shoot translocation of V greatly reduced the potential ecological and public health risk caused by the urban brownfield.

4.5 Conclusion

Vanadium contamination was found in the soil at Liberty State Park brownfield site. Analysis of six dominant plant species growing on site showed no significant difference in root V uptake efficiency and V root to shoot translocation between perennial herbaceous species and deciduous woody species. The results suggest that the differences in plant species do not play a major role in determining plant V assimilation and the dominant plant species growing in Liberty State Park. Root V concentration showed significant positive linear correlation ($p<0.05$) with soil labile V content. Soil pH and TOC had no significant impact on root V accumulation. The results suggest that soil V concentration is the primary factor affecting V root accumulation. However, non-linear regression analysis shows that V root accumulation efficiency decrease with increasing soil V concentration, indicating that excessive V in the soil is toxic to the plant growth and can inhibit plant V absorbance capacity. This is supported by constant V concentration in the leaf regardless the variation in soil V concentration. The result
indicates a limited root to shoot translocation. A decrease of V TF with increasing soil V concentration (> 20 µg g⁻¹) also supports this conclusion that V ion entering the aerial tissue may be restricted. Higher V accumulation in *Phragmites australis* root collected in winter season than that collected in later spring/early summer suggests that V accumulation in *Phragmites australis* roots is related to the plant seasonal dynamics.

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4.6 References


Agency for Toxic Substances and Disease Registry (ATSDR), 2012. Toxicological profile: vanadium. Atlanta, GA.


Environmental Protection Agency (EPA), 2003. Ecological soil screening levels for vanadium.


Table 4-1 Physical and chemical parameters and vanadium concentrations (Mean ± S.D.) in soils and plant tissues of dominant species at the sampling sites in Liberty State Park.

<table>
<thead>
<tr>
<th>Site</th>
<th>Family</th>
<th>Plant species</th>
<th>TOC (%)</th>
<th>pH</th>
<th>Soil potentially leachable content (μg g⁻¹)</th>
<th>Root (μg g⁻¹)</th>
<th>Stem (μg g⁻¹)</th>
<th>Leaf (μg g⁻¹)</th>
<th>Root BCFb</th>
<th>TFc</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP-21</td>
<td>Herbaceous</td>
<td><em>Artemisia vulgaris</em></td>
<td>28</td>
<td>6.6</td>
<td>8.28 ± 14.30</td>
<td>89.4 ± 26.6</td>
<td>0.46 ± 0.22</td>
<td>11.5 ± 2.3</td>
<td>10.8 ± 18.9</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>TP-8</td>
<td>Herbaceous</td>
<td><em>Artemisia vulgaris</em></td>
<td>47</td>
<td>6.0</td>
<td>44.2 ± 6.7</td>
<td>113 ± 81</td>
<td>n.d.</td>
<td>11.6 ± 1.5</td>
<td>2.56 ± 187</td>
<td>0.10 ± 0.03</td>
</tr>
<tr>
<td>TP-40</td>
<td>Herbaceous</td>
<td><em>Artemisia vulgaris</em></td>
<td>17</td>
<td>6.6</td>
<td>29.0 ± 14.3</td>
<td>86.0 ± 25.1</td>
<td>n.d.</td>
<td>6.98 ± 0.43</td>
<td>2.97 ± 170</td>
<td>0.08 ± 0.00</td>
</tr>
<tr>
<td>TP-40C</td>
<td>Herbaceous</td>
<td><em>Artemisia vulgaris</em></td>
<td>15</td>
<td>6.8</td>
<td>20.7 ± 14.3</td>
<td>25.7 ± 3.7</td>
<td>n.d.</td>
<td>11.5 ± 1.0</td>
<td>1.24 ± 0.88</td>
<td>0.45 ± 0.01</td>
</tr>
<tr>
<td>TP-28-17</td>
<td>Herbaceous</td>
<td><em>Polygonum cuspidatum</em></td>
<td>10</td>
<td>5.4</td>
<td>79.8 ± 14.6</td>
<td>225 ± 167</td>
<td>n.d.</td>
<td>9.40 ± 0.70</td>
<td>2.82 ± 2.16</td>
<td>0.04 ± 0.01</td>
</tr>
<tr>
<td>TP-16</td>
<td>Herbaceous</td>
<td><em>Phragmites australis</em></td>
<td>14</td>
<td>6.2</td>
<td>72.3 ± 21.9</td>
<td>218 ± 42</td>
<td>n.d.</td>
<td>2.06 ± 0.84</td>
<td>3.02 ± 1.08</td>
<td>0.01 ± 0.00</td>
</tr>
<tr>
<td>TP-3</td>
<td>Woody</td>
<td><em>Rhus copallinum</em></td>
<td>28</td>
<td>5.8</td>
<td>118 ± 57</td>
<td>116 ± 68</td>
<td>0.08 ± 0.13</td>
<td>7.49 ± 2.46</td>
<td>0.98 ± 0.75</td>
<td>0.06 ± 0.01</td>
</tr>
<tr>
<td>TP-7/8</td>
<td>Woody</td>
<td><em>Rhus copallinum</em></td>
<td>51</td>
<td>5.4</td>
<td>58.0 ± 7.3</td>
<td>32.5 ± 5.4</td>
<td>n.d.</td>
<td>4.28 ± 0.60</td>
<td>0.56 ± 0.12</td>
<td>0.13 ± 0.00</td>
</tr>
<tr>
<td>TP-40B</td>
<td>Woody</td>
<td><em>Rhus copallinum</em></td>
<td>31</td>
<td>7.4</td>
<td>24.9 ± 21.6</td>
<td>118 ± 66</td>
<td>n.d.</td>
<td>6.19 ± 0.59</td>
<td>4.74 ± 4.90</td>
<td>0.05 ± 0.01</td>
</tr>
<tr>
<td>TP-1</td>
<td>Woody</td>
<td><em>Rhus copallinum</em></td>
<td>9</td>
<td>6.0</td>
<td>19.6 ± 17.0</td>
<td>61.2 ± 3.3</td>
<td>n.d.</td>
<td>8.71 ± 0.57</td>
<td>3.12 ± 2.71</td>
<td>0.14 ± 0.00</td>
</tr>
<tr>
<td>TP-21A0</td>
<td>Woody</td>
<td><em>Rhus copallinum</em></td>
<td>33</td>
<td>6.2</td>
<td>27.0 ± 20.1</td>
<td>39.4 ± 15.2</td>
<td>n.d.</td>
<td>4.94 ± 0.13</td>
<td>1.46 ± 1.22</td>
<td>0.13 ± 0.01</td>
</tr>
<tr>
<td>TP-2B</td>
<td>Woody</td>
<td><em>Betula populifolia</em></td>
<td>46</td>
<td>5.0</td>
<td>118 ± 21</td>
<td>165 ± 34</td>
<td>n.d.</td>
<td>5.96 ± 0.53</td>
<td>1.40 ± 0.38</td>
<td>0.04 ± 0.00</td>
</tr>
<tr>
<td>TP-41</td>
<td>Woody</td>
<td><em>Betula populifolia</em></td>
<td>10</td>
<td>6.0</td>
<td>9.31 ± 16.10</td>
<td>57.8 ± 20.0</td>
<td>n.d.</td>
<td>8.09 ± 1.41</td>
<td>6.21 ± 10.95</td>
<td>0.14 ± 0.01</td>
</tr>
<tr>
<td>TP-43</td>
<td>Woody</td>
<td><em>Betula populifolia</em></td>
<td>28</td>
<td>5.4</td>
<td>7.37 ± 12.80</td>
<td>79.2 ± 11.2</td>
<td>n.d.</td>
<td>9.38 ± 3.02</td>
<td>10.7 ± 18.7</td>
<td>0.12 ± 0.01</td>
</tr>
<tr>
<td>TP-13A4</td>
<td>Woody</td>
<td><em>Betula populifolia</em></td>
<td>21</td>
<td>5.0</td>
<td>0 ± 0</td>
<td>106 ± 61</td>
<td>n.d.</td>
<td>7.30 ± 1.31</td>
<td>4.61 ± 0.40</td>
<td>0.07 ± 0.01</td>
</tr>
<tr>
<td>TP-48</td>
<td>Woody</td>
<td><em>Betula populifolia</em></td>
<td>20</td>
<td>6.1</td>
<td>18.1 ± 15.9</td>
<td>39.8 ± 3.3</td>
<td>n.d.</td>
<td>12.1 ± 1.6</td>
<td>2.20 ± 1.94</td>
<td>0.30 ± 0.00</td>
</tr>
<tr>
<td>TP-14</td>
<td>Woody</td>
<td><em>Betula populifolia</em></td>
<td>53</td>
<td>5.2</td>
<td>37.8 ± 24.3</td>
<td>33.1 ± 16.7</td>
<td>n.d.</td>
<td>9.63 ± 0.09</td>
<td>0.88 ± 0.91</td>
<td>0.29 ± 0.04</td>
</tr>
<tr>
<td>TP-4415</td>
<td>Woody</td>
<td><em>Betula populifolia</em></td>
<td>35</td>
<td>5.2</td>
<td>193 ± 113</td>
<td>280 ± 53</td>
<td>0.24 ± 0.24</td>
<td>11.1 ± 0.9</td>
<td>1.45 ± 0.89</td>
<td>0.04 ± 0.00</td>
</tr>
<tr>
<td>TP-18</td>
<td>Woody</td>
<td><em>Betula populifolia</em></td>
<td>24</td>
<td>6.0</td>
<td>66.9 ± 19.5</td>
<td>106 ± 10</td>
<td>0.04 ± 0.08</td>
<td>9.08 ± 0.40</td>
<td>1.58 ± 0.48</td>
<td>0.09 ± 0.00</td>
</tr>
<tr>
<td>TP-10</td>
<td>Woody</td>
<td><em>Populus deltoides</em></td>
<td>32</td>
<td>5.4</td>
<td>54.0 ± 32.2</td>
<td>119 ± 0</td>
<td>n.d.</td>
<td>8.24 ± 0.61</td>
<td>2.20 ± 1.31</td>
<td>0.07 ± 0.00</td>
</tr>
<tr>
<td>TP-24</td>
<td>Woody</td>
<td><em>Populus deltoides</em></td>
<td>30</td>
<td>6.6</td>
<td>39.0 ± 31.2</td>
<td>67.3 ± 22.9</td>
<td>n.d.</td>
<td>5.35 ± 2.19</td>
<td>1.73 ± 1.50</td>
<td>0.08 ± 0.01</td>
</tr>
<tr>
<td>TP-25</td>
<td>Woody</td>
<td><em>Populus deltoides</em></td>
<td>30</td>
<td>6.2</td>
<td>40.6 ± 29.4</td>
<td>88.7 ± 72.4</td>
<td>0.05 ± 0.09</td>
<td>4.86 ± 0.35</td>
<td>2.18 ± 2.38</td>
<td>0.05 ± 0.02</td>
</tr>
</tbody>
</table>

b. Root bioconcentration factor (BCF) is calculated for the plant that grows on each site based on vanadium concentration in root and soil.
c. Translocation factor (TF) is calculated for the plant that grows on each site based on vanadium concentration in root and leaf.
Table 4-2 Total vanadium concentration and geoaccumulation index (Mean ± S.D.) in the soils collected in May 2011 at Sites TP-1 and TP-25.

<table>
<thead>
<tr>
<th>Site</th>
<th>V (µg g⁻¹)</th>
<th>I_{geo}</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP-1</td>
<td>77.2 ± 6.0</td>
<td>0.78 ± 0.02</td>
</tr>
<tr>
<td>TP-25</td>
<td>144 ± 74</td>
<td>1.68 ± 0.72</td>
</tr>
</tbody>
</table>
Table 4-3 Comparison of seasonal variations in vanadium concentration (Mean ± S.D.) in *Phragmites australis* root at Sites TP-1 and TP-25. Plant samples were collected in May 2011 and November 2011, respectively.

<table>
<thead>
<tr>
<th>Site</th>
<th>May 2011</th>
<th>November 2011</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>V (µg g⁻¹)</td>
<td>V (µg g⁻¹)</td>
</tr>
<tr>
<td>TP-1</td>
<td>1.72 ± 0.03</td>
<td>2.83 ± 0.59</td>
</tr>
<tr>
<td>TP-25</td>
<td>1.65 ± 0.03</td>
<td>9.43 ± 0.74</td>
</tr>
</tbody>
</table>
Table 4-4 Results of factor analysis based on the rotated loading matrix (VARIMAX, Gamma = 1.000).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Factor 1</th>
<th>Factor 2</th>
<th>Factor 3</th>
<th>Factor 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Root V concentration</td>
<td>-0.96</td>
<td>0.07</td>
<td>0.08</td>
<td>0.03</td>
</tr>
<tr>
<td>Soil potentially leachable V content</td>
<td>-0.84</td>
<td>-0.27</td>
<td>0.00</td>
<td>-0.39</td>
</tr>
<tr>
<td>Vanadium TF</td>
<td>0.64</td>
<td>0.07</td>
<td>-0.66</td>
<td>-0.26</td>
</tr>
<tr>
<td>Total organic content (TOC)</td>
<td>0.10</td>
<td>-0.91</td>
<td>0.13</td>
<td>-0.12</td>
</tr>
<tr>
<td>pH</td>
<td>0.45</td>
<td>0.69</td>
<td>0.21</td>
<td>0.08</td>
</tr>
<tr>
<td>Leaf vanadium concentration</td>
<td>-0.01</td>
<td>-0.01</td>
<td>-0.94</td>
<td>0.18</td>
</tr>
<tr>
<td>Root V BCF</td>
<td>0.08</td>
<td>0.14</td>
<td>-0.10</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Percent of total variance explained: 32.3 20.1 20.07 17.33
Figure 4-1 Map showing Liberty State Park, New Jersey, with the vegetation assembling patterns for each sampling site. SNH: successional northern hardwood; SSB: successional shrub land; SOF: successional old field; MS: maritime shrub land; MG: maritime grasslands; CRM: common reed/mugwort; FFW: floodplain forested wetlands; SSW: shrub swamp wetland; SEM: shallow emergent marsh; and CRW: common-reed-dominated wetland.
Figure 4-2 Root V bioconcentration factor (BCF) (a); and V translocation factor (TF) (b) for six plant species. Both root V BCF and V TF show no significant (p>0.05) variation among the plant species.
Figure 4-3 Significant correlation ($p<0.05$) between soil V concentrations and root V concentrations. The results indicate the ability of plant uptake of V from the soils.
Non-linear exponential function shows the change of root V BCF with soil V concentration. Root V BCF shows an increase at low soil V concentration (<20 μg g\(^{-1}\)), but decreases when soil V concentration is >20 μg g\(^{-1}\).
Figure 4-5 Non-linear exponential function shows the change of V TF with soil V concentration.
CHAPTER 5

ECOLOGICAL RISK ASSESSMENT OF METAL CONTAMINATED SOIL ON AN ABANDONED URBAN BROWNFIELD SITE

Abstract

In this study, soil samples were collected at 22 sites in Liberty State Park, New Jersey, in 2005 for metal enrichment and potential ecological risk assessment. Geoaccumulation index ($I_{geo}$) showed the enrichment level of metals followed an order of Cu>Pb>Zn>As>Cr>Hg while the potential ecological risk factor ($E_i^f$) indicated the potential ecological risk of each metal was in the order of Cu>Pb>As>Hg>Zn>Cr. Among these 22 sites, this investigation identified 9 sites at moderate ecological risk, 3 sites at considerable ecological risk, and 4 sites at high ecological risk according to the potential ecological risk index (RI). Hierarchical cluster analysis (CA) of soil metal concentrations separated the study sites into four groups, which are supported by the significant difference in RI values. Geographically, three regions in the Liberty State Park brownfield site were determined based on the CA results and RI values. The first region was at the lowest ecological risk. The second region was under the moderate ecological risk of elevated Cu, Pb, and Zn concentrations and had a significant correlation between Cr and Pb. The third region was under the highest ecological risk of the highest
concentrations of Cu, Pb, Hg and Zn. There was also a significant positive linear correlation between Pb and Zn in the third region.

**Keywords:** Ecological risk, Metal contaminated soil, Geoaccumulation index, Risk index, Brownfield
5.1 Introduction

Urban brownfields are abandoned lands previously contaminated by anthropogenic development and not suitable for immediate use (Alker et al., 2000). Since land use in densely populated urban areas usually include transportation and other industrial activities, most brownfield lands are contaminated by metals and/or organics (Thornton et al., 2008). Metals are not degradable and tend to accumulate in soil. Under natural conditions metals are indispensable constituents of soil, however their concentrations are low. For example, metal(loid)s such as arsenic (As), lead (Pb), chromium (Cr), mercury (Hg), copper (Cu) and zinc (Zn) together constitute less than 1% of the total weight of the earth crust (Underwood, 2012). Human activities have been introducing metals into the soil in large volume. In addition, somewhere between 30% and 50% of the earth land surface have been impacted by anthropogenic activities over the past 100 years (Vitousek et al., 1997). Urban areas are some of the most artificially disturbed landscapes. As a result, metal concentrations in urban soils tend to be considerably higher than that in the undisturbed natural soils.

There are different sources of metals to urban soil. Industrial operation, railroad, traffic transportation and other anthropogenic activities can introduce metals into soils (Reimann and de Caritat, 2005; Wei and Yang, 2010; Ren et al., 2014). When an ecosystem is exposed to metal contaminated soil, metal ions can translocate to higher
trophic levels. Once the metal concentration within organisms exceeds the threshold concentrations, the regular metabolism activities will be adversely affected (Alloway, 2010). It is therefore critical to assess the enrichment level and potential ecological risk of metals in contaminated soils in order to properly monitor, manage, and redevelop urban brownfield sites.

Several soil risk assessment indexes have been developed that focus on either soil metal enrichment levels or potential ecological risks. For example, geoaccumulation index ($I_{geo}$) assesses the contamination level of each metal by comparing the onsite soil metal concentration to the background metal concentration (Ghrefat et al., 2011; Müller, 1969; Srinivasa Gowd et al., 2010). To the aspect of potential ecological risk, a potential ecological risk index (RI) is used to assess the potential adverse biological effect of metals within the soil. Different from $I_{geo}$, the RI evaluated the potential ecological risk of soil metal contamination by considering the overall toxicity of metals in soil (Hakanson, 1980; Sun et al., 2010). The goal of this study is to examine the contamination level and potential ecological risk associated with an urban brownfield from multiple perspectives. We believed that by considering a broader suite of indices, a more holistic understanding of the site, the mechanisms of contaminant transfer and the potential risks could be acquired. Such understandings are critical for the future management and redevelopment of this site.
5.2 Materials and methods

5.2.1 Study site

Liberty State Park is located in Jersey City, New Jersey, along the shore of New York Harbor (Figure 5-1). It is within New York Metropolitan area next to Manhattan, New York, one of the most populated urban areas in the world. Liberty State Park was a coastal wetland area which was transformed into marine port between 1860s and 1930s by the Central Railroad of New Jersey (CRRNJ). The rail yard was operational for over a century and included traffic from both the CRRNJ and Lehigh Valley Railroad (LVRR). Operations slowed over the decades following World War II, the CRRNJ declared bankruptcy and ceased operations in 1969. Due to its unique position and historical value, the area was acquired by the State of New Jersey and officially announced as Liberty State Park in 1976 (NJDEP, 1995; LSP, 2008). Nevertheless, soils in the park were contaminated due to the original fill materials and the long-term railway operation. A soil survey conducted in 1990 by the NJDEP indicated high levels of polynuclear aromatic hydrocarbons, pesticides, and metals (NJDEP, 1995). The State conducted several mitigation projects, such as clean soil capping and asphalt isolation on several areas of the park and much of the park was then opened to the public. However a 251 acre interior section was left unmitigated (Figure 5-1). Through natural colonization a highly diverse
and productive vegetative assemblage has been gradually developing on the area since 1976 (NJDEP, 1995; LSP, 2008). Over the years, this novel system consisting of a mix of both native and non-native species, and flora and fauna has become well established on the site (Gallagher 2008). However, as the location of this brownfield within the park is very close to a residential area and accessible to many organisms, the ecological and human health risks have been questioned.

5.2.2  Field work and Sample analysis

Based on vegetation assemblage boundaries map created from a vegetative inventory conducted in 2005 (Gallagher et al., 2008), 22 sites were selected from Liberty State Park for this study in 2005 (Figure 5-1). On each site, three soil samples were collected at 10 to 25 cm depth below the surface within 1m space and their GPS coordinates were recorded at the same time with MC-GPS (Corvallis Microtechnology, Inc. Corvallis, OR, USA) at 1 m accuracy (Gallagher et al., 2008). Soil samples for metal analysis were first sieved through <125 µm nylon mesh to remove organic detritus and gravels then thoroughly mixed. Then, the soil samples were oven-dried at 60 °C for approximately 48 hours to a constant weight. An aliquot of 0.5g soil was weighted for each sample and treated with 10 ml trace-metal grade HNO₃ in a Teflon bomb for microwave digestion using Mars-5 microwave digester (CEM Corp.). The digestion was
conducted at >170 °C for 30 minutes. Once the digestion was finished, acid extracts were then placed on a hot-plat and dried up to its minimum volume and re-diluted with 1% HNO₃ to 10 ml for the AAS analysis. For the quality control purpose, method blank and standard reference material (SRM) 1944 from the National Institute of Standards and Technology (NIST) was digested along with the soil samples. Each set of analysis contained 12 soil samples. Arsenic concentration was determined using Perkine Elmer Z5100 graphite furnace AAS with Zeeman background correction in the presence of Mg(NO₃)₂/Pd(NO₃)₂ as a matrix modifier. A cold-vapor AAS with a MAS-50D mercury analyzer (Bacharach, Inc.) was used for Hg concentration measurement (Gallagher et al., 2008).

5.2.3 Data analysis

5.2.3.1 Geoaccumulation index (I_{geo}) assessment

Geoaccumulation index (I_{geo}) compares the metal concentration in soil samples with its background concentration. The index was originally applied for sediment contamination assessment (Ghrefat et al., 2011; Müller, 1969; Srinivasa Gowd et al., 2010), and then further be used for soil contamination evaluation (Srinivasa Gowd et al., 2010). It is expressed as
\[ I_{\text{geo}} = \log_2 \left( \frac{C_n}{1.5B_n} \right) \]  

where \( C_n \) is metal concentration in the soil sample and \( B_n \) is background metal concentration. In this study, the New Jersey soil metal background concentrations were selected from the average concentration values reported by EPA (EPA, 2005). There is no reference value of Hg available in the soil metal background concentration developed by EPA. Therefore, the background concentration of Hg was referred from the work of Sanders (2003), who collected 284 natural soil samples from urban Piedmont region, urban coastal plain and rural areas of New Jersey. Liberty State Park locates in the urban Piedmont region, therefore we selected the median Hg concentration (0.18 µg g\(^{-1}\)) in this region as background concentration. Factor ‘1.5’ was used to adjust potential variations of the background data caused by lithological variations. Seven accumulation categories are defined according to the \( I_{\text{geo}} \) values: \( I_{\text{geo}} < 0 \) indicates no contamination; \( 0 < I_{\text{geo}} < 1 \), no contamination or moderate contamination; \( 1 < I_{\text{geo}} < 2 \), moderate contamination; \( 2 < I_{\text{geo}} < 3 \), moderate or strong contamination; \( 3 < I_{\text{geo}} < 4 \), strong contamination; \( 4 < I_{\text{geo}} < 5 \), strong or extreme contamination; and \( 5 < I_{\text{geo}} \), extreme contamination (Ghrefat et al., 2011).

5.2.3.2 Ecological risk assessment
Risk index (RI) assesses the degree of metal ecological risk in soil and evaluates the overall toxicity when metals are combined together. The toxicity of one specific metal can be determined by toxic factor \( T_r^i \) (Hakanson, 1980; Sun et al., 2010). According to Hakanson (1980),

\[
C_j^i = \frac{c_j^i}{c_k^i} \quad (2)
\]

\[
E_r^i = T_r^i \times C_j^i \quad (3)
\]

\[
RI = \sum_{i=1}^{m} E_r^i \quad (4)
\]

where \( E_r^i \) is the potential ecological risk index, \( RI \) is the sum of potential risk of individual metal, \( T_r^i \) is the toxic-response factor for a given metal, \( C_j^i \) is the contamination coefficient, \( c_j^i \) is the metal concentration of soil sample, and \( c_k^i \) is the background concentration of the metal in soil. Based on Hakanson’s approach, the toxic-response factor for As, Cr, Cu, Pb, Hg and Zn are 10, 2, 5, 5, 40, and 1, respectively. It should be noted that, in the original approach (Hakanson, 1980), bioproduction index (BPI) was used to estimate the real value of toxic-response factor. However, this toxic-response factor is also widely accepted in many studies as a substitution for the real toxic-response factor (Hakanson, 1980; Xu et al., 2008).
For a single metal, Hakanson (1980) created five classification categories, i.e., the ecological risks are low ($E_r^i<40$), moderate ($40<E_r^i<80$), considerable ($80<E_r^i<160$), high ($160<E_r^i<320$) and very high ($E_r^i>320$). When considering the summation of all metal potential ecological risk, the overall ecological risks RI can be divided into four categories based on the RI value, i.e., the ecological risks are low (RI<150), moderate (150<RI<300) considerable (300<RI<600) and very high (RI>600) (Zhu et al., 2012).

5.2.3.3 Statistical analysis

Shapiro-Wilk method was used to test the normality distribution of the data. The result indicated that the data failed the test ($p<0.01$). Therefore, the nonparametric method was applied to the data sets. Cluster analysis is an approach of data analysis that classifies the blended data into subgroups based on internal relationships between variables while maximizing the dissimilarity between those subgroups.

In this study, hierarchical cluster analysis was applied to investigate the closeness of soil metal concentrations among the 22 sites. The type of joining algorithm used to amalgamate clusters was Ward’s method and the metric for measuring distance for the raw and standardized data was Euclidean distance. In brief, Ward’s method assesses the relationship between each cluster by calculating the total sum of squared deviations from
the mean of a cluster, while Euclidean distance is determined by the actual arithmetic
difference between two values (Burns and Burns, 2008). Nonparametric Wilcoxon
method was applied to test the significance of differences between the data groups. A
correlation matrix was conducted to identify relationship between soil metal
concentrations in study sites. Least square linear regression was applied to test the linear
correlation between metals in each subgroup. All the statistical data analysis was
conducted using SYSTAT, while spatial analysis of metal distributions and site potential
ecological risks was performed using ArcGIS.

5.3 Results

5.3.1 Soil contamination in the Liberty State Park

The majority of the 22 sites had a coefficient of variance for each metal greater
than 20%, indicating uneven metal distributions at each site. In addition, a few sites had
relatively higher metal concentrations than rest of the sites (Figure 5-2). For example,
sites TP10, TP14, and TP25 had relatively higher As concentration, whereas site TP14/16
had higher Cr concentration, and sites TP17 and TP25 had higher Cu concentration. Lead
concentration was extremely high at site TP25 (4640 ± 1210 µg g⁻¹), while sites TP10,
TP18 and TP7/8 showed higher level of Hg (0.96 ± 1.48µg g⁻¹, 3.62 ± 5.95 µg g⁻¹ and
1.57 ± 0.77 µg g\(^{-1}\), respectively) than the other sites. Zinc concentration at site TP25 (1586 ± 1358 µg g\(^{-1}\)) was higher than rest of the sites. In addition, the range of each metal concentration varied widely. The concentrations ranged from 10.7 - 270 µg g\(^{-1}\) for As, 10.9 - 335 µg g\(^{-1}\) for Cr, 53.6 - 2200 µg g\(^{-1}\) for Cu, 96.6 - 6670 µg g\(^{-1}\) for Pb, n.d. - 3.62 µg g\(^{-1}\) for Hg, and 10.9 - 2330 µg g\(^{-1}\) for Zn (Figure 5-2). It is obvious that the distributions of the six metals (As, Cr, Cu, Hg, Pb and Zn) at the 22 sites are heterogeneous with considerable spatial variations.

### 5.3.2 Soil metal accumulation evaluation

To further evaluate the level of metal enrichment, the metal geoaccumulation indexes (\(I_{\text{geo}}\)) were calculated for the 22 sites. The magnitude of \(I_{\text{geo}}\) in Liberty State Park followed the order of: Cu>Pb>Zn>As>Cr>Hg. The geoaccumulation index of Cu (\(I_{\text{geo}}(\text{Cu})\)) in all sites was greater than 1.0, indicating that all the sites were contaminated by Cu. As shown in Figure 5-3, 46% sites were strongly or extremely contaminated and 54% sites were contaminated moderately or strongly. The \(I_{\text{geo}}\) of Pb in each site mostly fell in the categories between moderate contamination and strong contamination: 23% sites were moderately contaminated by Pb, 32% of the sites were moderately or strongly contaminated, and 36% of the sites were strongly contaminated. Geoaccumulation index of Zn ranged from -0.41 to 5.59, spreading over all the 7 categories of \(I_{\text{geo}}(\text{Zn})\) from no
contamination to extreme contamination. Soils contaminated by Zn moderately to strongly were found on 59% sites, of which 18% sites were considered as strongly to extremely Zn contaminated sites. According to the geoaccumulation index of As ($I_{geo}^{(As)}$), 77% of the total sites were classified as uncontaminated or moderately contaminated; only three sites were considered strongly or extremely contaminated. For both Cr and Hg, more than 60% sites had negative $I_{geo}$ values and 18% sites were between no contamination and moderate contamination, indicating these two metals were not major contaminants in this urban brownfield. The results show that the most enriched contaminants in the study area were Cu, Pb, and Zn.

5.3.3 Ecological risk evaluation

The potential ecological risk ($E_r^i$) of the six metals decreases in the order of Cu>Pb>As>Hg>Zn>Cr. As shown in Figure 5-4, the ecological risk of each individual metal is evaluated as follows:

(1) Cu – 9% sites were under extremely high ecological risk of Cu, 59% sites were at moderate or considerable ecological risk, and only 32% sites were immune from ecological risk caused by Cu;

(2) Pb – Majority (59%) of the sites were considered as moderate ecological risk.
However, only 10% sites were under considerable or extremely high ecological risk of Pb;

(3) As – More than 60% of the sites fell into the class of low ecological risk caused by As. Only a few sites were under considerable (9%), high (5%) and extreme (5%) ecological risk of As;

(4) Hg – Although 64% sites were not considered as contaminated by Hg according to the geoaccumulation index of Hg, the risk analysis based on Igeo showed that 55% sites were still considered at low Hg ecological risk, 14% sites at moderate ecological risk, 18% sites at considerable ecological risk, 5% sites at high ecological risk, and 5% sites at extremely high ecological risk. Compared to relative low metal enrichment suggested by Igeo, Hg had caused high ecological risk as indicated by $E^I$;

(5) Zn – This element fell into two categories, i.e., low ecological risk and moderate ecological risk. Although 59% sites were moderately or strongly contaminated by Zn, only 9% sites were considered as moderate ecological risk, implying that high Zn enrichment was not equivalent to high ecological risk; and

(6) Cr – The ecological risk caused by Cr was considered low at all the sites, implying that Cr did not caused significant ecological risk in this brownfield ecosystem.
Risk Index (RI), represents by the summation of the individual $E_i^r$ of As, Cr, Cu, Pb, Hg, and Zn, indicates to what extent the urban brownfield ecosystem was suffering from the soil contaminated by the above six metals (Sun et al., 2010). The RI of the 22 sites in this study ranged between 65.3 and 1693, suggesting that the potential ecological risk in the investigated sites ranges from low to high. Among the 22 sites, six sites were classified as low ecological risk; nine sites as moderate ecological risk; and three sites as considerable ecological risk. It should be noted that sites TP10, TP17, TP18 and TP25 were at very high ecological risk (Figure 5-5). At moderately risky sites, the $E_i^r$ of Cu took the highest weight of the RI in each site, followed by Pb and As. In the considerably risky sites, the $E_i^r$ of Cu contributed the most to the RI, followed by the $E_i^r$ of As and Hg. Finally, the $E_i^r$ of Pb followed by that of Cu and Hg contributed the most to the RI of the greatest risk.

5.3.4 Cluster Analysis

Hierarchical cluster analysis was performed on metal concentration data from the 22 urban brownfield sites. As Figure 5-6 illustrates, the sampling sites are divided into four clustering groups (Cluster 1, 2, 3 and 4) based on soil metal (As, Cr, Cu, Hg, Pb and Zn) concentrations. Cluster 1 includes six sites, which are sites TP41, TP28, TP28/17, TP43/14, TP16 and TP48, locate at the southern part of the study area. Cluster 2 consists
of ten sites, sites TP14, TP43, TP40, TP8, TP1, TP40C, TP40B, TP7/8, TP10 and TP14/16, distribute at the periphery of the park. Cluster 3 contains five sites, sites TP21, TP24, TP21/40, TP18 and TP17, locate at the northeast and center of the brownfield. Cluster 4 has only one site, site TP25 (Figure 5-6). The mean concentrations of all metals except Cr at the sites in Cluster 1 were lower than those in the other three clusters (Table 5-1). However, it was reported that the mean concentrations of As and Pb in the soil for plant growth were above the ecological soil screen level (SSL) set by USEPA (Gallagher et al., 2008), suggesting that these two elements may have adverse effect on the terrestrial plants growing at these sites in Cluster 1 (EPA, 2005). The maximum As concentration at the sites in Cluster 1 exceeded the NJ non-residential clean up criteria (Table 5-1), indicating that at least one of the Cluster 1 sites needed proper treatment to meet the non-residential use of the sites. In Cluster 2, the mean concentrations of metals in soils were higher than that in Cluster 1 (Table 5-1). Except Cr, the mean concentrations of all metals in the soils at the Cluster 2 sites were above plant SSL, suggesting possible toxic effect on vegetation. Therefore, the sites in Cluster 2 had potential toxic effects on plants. The sites in Cluster 3 had relatively high concentrations of Cu, Pb, Hg and Zn than that in the Cluster 1 and Cluster 2 sites (Table 5-1). As shown in Table 5-1, not only mean concentrations of these metals exceeded the SSL limit, but also the concentrations of As and Cu at several sites in Cluster 3 were above the NJ non-residential criteria. Therefore,
the potential risk of As and Cu was especially high at the sites in Cluster 3. The mean concentrations of As, Cu, Pb and Zn were the highest at site TP25, the only site in Cluster 4. Table 5-1 shows the mean concentrations of As, Cu, Pb, Hg and Zn at this site exceeded both plant SSL level and non-residential NJ limit. Therefore, site TP25 is theoretically not favorable for terrestrial plant growth, nor suitable for non-residential land use for public.

To further investigate the difference in potential ecological risk among the sites in the four clusters, a nonparametric paired test was performed to compare RI values between each cluster. Cluster 4 was excluded from this exercise because there was only one site (TP25) in this cluster, making it not appropriate for statistical analysis. According to the results from Wilcoxon paired test, significant differences were found between Cluster 1 and Cluster 2 ($p = 0.0014 < 0.05$), Cluster 2 and Cluster 3 ($p = 0.04 < 0.05$), and Cluster 1 and Cluster 3 ($p = 0.01 < 0.05$) (Figure 5-7).

5.4 Discussion

The accumulation of metals in urban soil has chronic impact on urban ecosystem through either direct exposure or indirect trophic transfer. In order to minimize the potential risk of metals from the contaminated soil, land use management and
remediation are required. Figure 5-8 shows the four clusters of study sites with RI levels labeled. These cluster groups correlated well with the RI levels. All the sites with the low ecological risk were found in Cluster 1 and located in the southeast corner of the study site. This area will be identified as Subarea 1 from now on to distinguish from the whole study area. Sites belonged to Cluster 2 were mostly at moderate ecological risk and a few at considerable ecological risk. These sites distributed at the rim of the study area (Figure 5-8) and are identified as Subarea 2. Finally, sites with considerable or extreme ecological risk belonged to Cluster 3. These sites are located in the northern section of the study area and identified as Subarea 3. Cluster 4 contained only one site (site TP25) that had extreme ecological risk and is also located in the north. For the purpose of this discussion, it is merged with Subarea 3 because it is surrounded by Subarea 3.

The patchy distribution of metals (As, Cr, Cu, Hg, Pb and Zn) within the subareas indicates the extreme heterogeneous metal accumulation. Since several deeper samples (up to 8 m) taken during earlier (NJDEP 1995, NRCD 2010) soil characterization efforts indicate little or no metal contamination at depth, most of the surficial contamination was probably the result of the rail yard operations.

The Pearson multiple linear correlation analysis that was conducted to test the relationship among the metals within each subarea indicates little correlation between
metals. The Subarea 1 sites (Table 5-1 and Figure 5-8) were mostly at low ecological risk and the average metal concentrations were the lowest compared to the sites from the other two subareas. In addition, we found no significant correlation between the six metals in Subarea 1 (Table 5-2), indicating that the metals at these sites were not likely sharing the same contaminant sources. Figure 5-8 shows the sites in Subarea 1 are now successional hardwoods, but were originally low lying areas between the rail road tracks (Figure 5-1), where the anthropogenic disturbance should be much less than that in the rest of the freight yard. However, the concentrations of As, Cr, Cu, Hg, Pb and Zn at most of the sites in Subarea 1 were still above the background levels for New Jersey, implying at least an indirect contaminant loading.

The sites in the Subarea 2 exhibited larger standard deviations of As, Cr, and Hg (Table 5-1) indicating large spatial variations of metal concentrations. It is possibly that the spatial variations in the source filling materials, or specific industrial activities resulted in the insignificant correlations between As, Cr, and Hg (Table 5-2). More importantly, the mean concentrations of Cu, Pb, and Zn in this subarea were greater than that in Subarea 1, suggesting that the sites in Subarea 2 all received and accumulated Cu, Pb, and Zn from additional sources besides the original filling material. According to Figure 5-1, the sites in Subarea 2 were originally covered by railway tracks; hence railway track might be one of the sources of these three metals. Previous studies on soil
contamination showed significant elevated concentrations of Cu, Zn, Cd and Mn in the soils close to railways in Sichuan, China, and high concentrations of Zn, Cd, and Pb in the soils near railway transport in the Qinghai-Tibet railway (Liu et al., 2009; Zhang et al., 2012). Hence, concentrations of Cu, Pb, and Zn in this study area might also be contributed from the historic railway transportation. However, there were no significant correlations observed between these three metals. One possible explanation is that anthropogenic activities after 1930s had disturbed the original soil composition and introduced the metals to this area from other places. In other words, besides railway operation, the operation of railway center over one century had introduced these metals from cargo or maintenance activities. Another explanation is plants uptake metals as nutrients at different rates and extracted the mobile fraction of metals from the soil to biomass, resulting in a change from the original metal concentrations (Smolders et al., 2009; Qian et al., 2012). For example, both Zn and Cu are essential nutrients for plants, but Zn is more bioavailable while the bioavailability of Cu is partly restricted by soil organic matter concentration. As a result, plant assimilates more Zn than Cu in the biomass (Imperato, 2003; Qian et al., 2012). On the contrary, most of Pb is in insoluble mineral phases and Pb is not an essential nutrient for plant (Imperato, 2003). As the result, the assimilation efficiency of Pb by plants is very limited (French et al., 2006; Qian et al., 2012). Interestingly, a significant ($p = 0.018<0.05$) correlation between Cr
and Pb was observed in this subarea. It is known that major industrial sources of Cr in soil include electroplating, tannery, wood preservation, chromium chemical production, stainless steel, and so forth (Alloway, 2010). While there is no record of the industrial activities mentioned above on the study according to the published documentations (NJDEP, 1995; LSP, 2008), the site did receive fill material from an electroplating plant in Jersey City (NJDEP, 1995). While the areas of high concentration were mitigated by removal, it is probable that the transport of the material created accidental enrichment.

In Subarea 3, the concentration of As and Cr remained at a relatively low level that is close to Subarea 1, suggesting limited additional sources of these two elements on site besides the original filling materials. The average concentrations of Hg were the highest among all the three subareas (Table 5-1). As shown in the historic map of the study area (Figure 5-1), sites in Subarea 3 are located in an area that was previously heavily covered by the railways for transportation. This area was where the trains uploaded and downloaded passengers, luggage, and cargos. Compared to other area in the park, this area appears to have the greatest contaminant loading. The major anthropogenic activities that release Hg to the environment include mining and smelting of ores, combustion of coal fuels, cement production, and gold production (Alloway, 2010). In view of the intense transportation activities on sites in Subarea 3 area, and the fact that the rail yard served as a major coal transfer hub and the early steam train engines were
coal fired, combustion of coal is the likely source of Hg in this area. Although the mean concentration of Pb at the sites in Subarea 3 were close to that in Subarea 2, the concentrations of Cu and Zn were much higher at the sites in Subarea 3 (Table 5-1). In addition, a significant ($p = 0.04<0.05$) linear correlation between Pb and Zn was found, suggesting that Pb and Zn may share the same pollution sources. It was mentioned early that Pb and Zn were two contaminants particularly from railway (Liu et al., 2009; Zhang et al., 2012). Therefore, railroad was very possibly the major contaminant source of soil around sites in Subarea 3.

5.5 Conclusion

In this study of elevated soil metal levels, all twenty-two sites demonstrated heterogeneous distributions of As, Cr, Cu, Hg, Pb, and Zn concentrations with large variations. The enrichment level of these metals, as indicated by $I_{geo}$ follows an order of Cu>Pb>Zn>As>Cr>Hg, while the contribution by each metal to the potential ecological risk is characterized by RI, which is the sum of potential risk of each individual metal ($E^{i}_{f}$) (Hakanson, 1980), was in an order of Cu>Pb>As>Hg>Zn>Cr. Hierarchical cluster analysis corresponded well to the site’s potential ecological risk levels based on the calculated risk index (RI) at each site.
Three subareas with distinct contamination levels and pollution sources were identified based on the RI value and the cluster analysis result of the 22 sites. The first subarea was wet depressed area and the contamination sources were not as great as the remainder of the site. The second and the third subareas had relatively high concentrations of Cu, Pb, and Zn and were in an area where the railway track was laid a century ago. The concentrations of Hg, Cu and Zn in the third subarea were higher than that in the second subarea. Pearson multiple correlation analysis conducted in each individual subarea showed significant correlations between Cu and Pb in Subarea 2 and between Pb and Zn in Subarea 3. The elevated Cu, Pb and Zn concentrations on site suggest the impact of the railway tracks and operations in the past. Subarea 3 was especially enriched in Hg probably due to the past combustion of coal as fuels.

According to the metal enrichment levels, potential ecological risks, and spatial distributions in the study area, a management plan for the restoration of this brownfield site can be developed with different emphases in each subarea that has been indicated in this study. The sites in Subarea 1, which have relative low metal concentration and low ecological risk, need regular monitoring on metal concentrations in the soils and organisms. The sites in Subarea 2, which have moderate metal enrichment and are at considerable ecological risk, need further assessment of ecological risk and metal mobility as well as monitoring groundwater metal concentration. Finally, as to the sites in
Subarea 3, which have the highest metal concentrations and exhibit the highest ecological risk, restriction of public access and remediation of groundwater and soil are recommended.

**Acknowledgments**

This work was supported in part by China Scholarship Council (Y.Q.), and Margaret and Herman Sokol Faculty Award (H.F.). We wish to thank Dr. Peddrick Weis, Theodore Proctor, and Francis Kemp of the Department of Preventive Medicine and Community Health, University of Medicine and Dentistry of New Jersey for soil metal analysis. In addition, we would like to thank Dr. Ildiko Pechmann for her invaluable assistance in chemical analysis and interpretation of the results.
5.6 References


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Environmental Protection Agency (EPA), 2005b. Ecological soil screening levels for lead. Washington, DC.

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Environmental Protection Agency (EPA), 2007a. Ecological soil screening levels for copper. Washington, DC.

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Table 5-1 Descriptive statistics of metal concentrations of urban brownfield soils in the four group sites in Liberty State Park.

<table>
<thead>
<tr>
<th>Sites</th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Hg</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Group 1 n=6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>18.6</td>
<td>33.9</td>
<td>62.4</td>
<td>149</td>
<td>0.16</td>
<td>79.9</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>9.13</td>
<td>24.7</td>
<td>12.9</td>
<td>40.4</td>
<td>0.23</td>
<td>63.2</td>
</tr>
<tr>
<td>Minimum</td>
<td>10.7</td>
<td>9.70</td>
<td>44.3</td>
<td>86.1</td>
<td>0.00</td>
<td>24.9</td>
</tr>
<tr>
<td>Maximum</td>
<td>35.1</td>
<td>68.5</td>
<td>76.4</td>
<td>196</td>
<td>0.60</td>
<td>198</td>
</tr>
<tr>
<td>Group 2 n=10</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>47.8</td>
<td>53.6</td>
<td>174</td>
<td>415</td>
<td>0.39</td>
<td>183</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>56.6</td>
<td>56.8</td>
<td>49.5</td>
<td>77.0</td>
<td>0.50</td>
<td>88.6</td>
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<tr>
<td>Minimum</td>
<td>11.9</td>
<td>10.2</td>
<td>103</td>
<td>303</td>
<td>0.06</td>
<td>50.0</td>
</tr>
<tr>
<td>Maximum</td>
<td>193</td>
<td>209</td>
<td>257</td>
<td>552</td>
<td>1.57</td>
<td>309</td>
</tr>
<tr>
<td>Group 3 n=5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean</td>
<td>24.6</td>
<td>33.4</td>
<td>487</td>
<td>420</td>
<td>0.98</td>
<td>658</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>10.7</td>
<td>7.77</td>
<td>500</td>
<td>122</td>
<td>1.48</td>
<td>250</td>
</tr>
<tr>
<td>Minimum</td>
<td>12.8</td>
<td>25.0</td>
<td>224</td>
<td>236</td>
<td>0.21</td>
<td>421</td>
</tr>
<tr>
<td>Maximum</td>
<td>37.4</td>
<td>44.0</td>
<td>1377</td>
<td>563</td>
<td>3.62</td>
<td>1058</td>
</tr>
<tr>
<td>Group 4 n=1</td>
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</tr>
<tr>
<td>Mean</td>
<td>270</td>
<td>40.4</td>
<td>1527</td>
<td>4640</td>
<td>0.18</td>
<td>1586</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>184</td>
<td>26.1</td>
<td>219</td>
<td>1210</td>
<td>0.19</td>
<td>1358</td>
</tr>
<tr>
<td>Minimum</td>
<td>69.8</td>
<td>23.1</td>
<td>1277</td>
<td>3249</td>
<td>0.02</td>
<td>739</td>
</tr>
<tr>
<td>Maximum</td>
<td>440</td>
<td>70.5</td>
<td>1685</td>
<td>5442</td>
<td>0.39</td>
<td>3153</td>
</tr>
<tr>
<td>Plant soil scree level¹</td>
<td>18.0</td>
<td>N/A</td>
<td>70.0</td>
<td>120</td>
<td>0.30*</td>
<td>160</td>
</tr>
<tr>
<td>New Jersey Background Concentration²</td>
<td>7.00</td>
<td>13.9</td>
<td>14.0</td>
<td>35.0</td>
<td>0.18**</td>
<td>22.0</td>
</tr>
<tr>
<td>Non-residential clean up³</td>
<td>20.0</td>
<td>6100</td>
<td>600</td>
<td>600</td>
<td>270</td>
<td>1500</td>
</tr>
</tbody>
</table>

1. EPA Ecological soil screen level (EPA 2005a;2005b;2005c;2007a;2007b;2008)
2. EPA Guidance for developing ecological soil screen levels (2005)

*Swartjes, F.A. (1999), Dutch target soil screening value of Hg, which have negligible risk for ecosystems.

**Sanders, P.F. (2003), ambient levels of metals in New Jersey soils. Median concentration of Hg for soil samples collected in urban piedmont.
Table 5-2 Pearson correlation matrix among different metal concentrations in urban soils in three group sites in Liberty State Park.

<table>
<thead>
<tr>
<th></th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Pb</th>
<th>Hg</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Group 1</strong></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.608</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>-0.099</td>
<td>-0.767</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.194</td>
<td>0.541</td>
<td>-0.155</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>-0.21</td>
<td>0.213</td>
<td>-0.351</td>
<td>0.321</td>
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<td></td>
</tr>
<tr>
<td>Zn</td>
<td>-0.337</td>
<td>-0.272</td>
<td>-0.142</td>
<td>-0.773</td>
<td>-0.089</td>
<td>1</td>
</tr>
<tr>
<td><strong>Group 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>As</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.149</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>0.392</td>
<td>-0.222</td>
<td>1</td>
<td></td>
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</tr>
<tr>
<td>Pb</td>
<td>0.412</td>
<td><strong>0.741</strong>*</td>
<td>0.193</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.484</td>
<td>-0.01</td>
<td>0.437</td>
<td>0.073</td>
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<td></td>
</tr>
<tr>
<td>Zn</td>
<td>-0.417</td>
<td>-0.061</td>
<td>0.271</td>
<td>0.263</td>
<td>0.005</td>
<td>1</td>
</tr>
<tr>
<td><strong>Group 3</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.333</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>-0.557</td>
<td>-0.573</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>0.707</td>
<td>0.815</td>
<td>-0.793</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>0.491</td>
<td>-0.371</td>
<td>-0.317</td>
<td>-0.077</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.641</td>
<td>0.718</td>
<td>-0.451</td>
<td><strong>0.895</strong>*</td>
<td>-0.337</td>
<td>1</td>
</tr>
</tbody>
</table>

* Correlation is significant at 0.05 level.
Figure 5-1 Map showing the study area and sampling sites in Liberty State Park (Adopted from Qian et al., 2012).
Figure 5-2 Comparisons of metal (As, Cr, Cu, Pb, Hg and Zn) concentration in the 22 study sites. The results indicated the soil metal concentration have significant spatial variation.
Figure 5-3 Percentage distribution of seven levels of $I_{geo}$ for As, Cr, Cu, Pb, Hg and Zn at 22 sites.
Figure 5-4 Percentage distribution of five levels of $E_r^I$ for As, Cr, Cu, Pb, Hg and Zn in 22 sites.
Figure 5-5 Risk Index of As, Cr, Cu, Pb, Hg and Zn in 22 sites. The lines represented different level of ecological risk: low ecological risk (RI<150); moderate ecological risk (150<RI<300); considerable ecological risk (300<RI<600); very high ecological risk (RI>600).
Figure 5-6 Hierarchical dendogram for 22 sites obtained by Hierarchical Cluster Analysis (Linkage: Ward; Distance: Euclidean).
Figure 5-7 Nonparametric paired test of RI values between the sites from four clusters.
Figure 5-8 Spatial distribution of site cluster groups (Cluster 1, 2, 3 and 4)) and ecological risk categories (Extreme high ecological risk, moderate ecological risk, considerable ecological risk and low ecological risk) in the Liberty State Park.
CHAPTER 6

ENVIRONMENTAL ASSESSMENT OF METAL CONCENTRATIONS IN
SELECTED RIVERINE, ESTUARINE AND COASTAL SEDIMENTS

[This chapter was published as a book chapter in Heavy Metal Sediments (2011) 59-85;
ISBN:978-1-67470-690-8]

Abstract

Riverine, estuarine and coastal environment are important ecosystem for aquatic and
marine life. However, long-term industrial developments with economic growth in coastal
regions have resulted in environmental degradation, habitat loss and geomorphologic
alteration in riverine, estuarine and coastal ecological systems globally. Due to coastal
development such as new industrial facilities and commercial port expansion, anthropogenic
metals are introduced near the construction sites and dispersed and transported to the
adjacent areas. Consequently, metal concentrations in riverine, estuarine and coastal
sediments are one of the focused environmental concerns. Sediment quality reflects the
long-term health status and the stability of the ecosystem of a riverine, estuarine and coastal
environment. The function of ecosystem as a pathway for the transport and exchange of
substances between different reservoirs is closely related to the stability of the ecosystem.
In this study, we summarize and report metal concentrations in the sediments of 43 selected
sites around the world to expand our knowledge in understanding the environmental quality.
We also assessed how metal concentration in the sediment influences the ecological
function of coastal ecosystem, particularly in the aspect of assisting the biogeochemical
circulation of metal elements. The results from this study could be applicable to science-based policy formulation, and ecological restoration/rehabilitation practices in an integrated coastal management framework to meet the urgent need for integrated coastal management planning and environmental protection.

**Keywords:** Sediment, Metal contamination assessment, Enrichment factor, Hazardous quotient, Biogeochemical circulation
6.1 Introduction

Metals are natural elements widely distributed in our environment in different speciation forms and oxidation state (Hill, 2010). Depending on the rock type, geophysical condition and geographical location around the world, metal concentrations present in sediments, soils, and water as naturally weathered products from the earth crust are different from place to place (Martin and Whitfield, 1983; Taylor and McLennan, 1995). Therefore, metal background concentrations could be very different. In general, trace amount of metals is essential micronutrients for growth of many organisms and necessary to organism metabolism (Underwood, 2012). However, metals in excessive amount can be toxic and cause pollution problem (Langston, 1990; Underwood, 2012). Because of human activities associated with the urbanization and industrialization in the twentieth century, anthropogenic input of metals has increased dramatically in the environment (Feng et al., 2005; Feng et al., 2008). For example, toxic metal pollution in estuary and coastal areas has been drawing increasing attention around the world because about 80% of the pollutants from human activities are introduced into estuary and coastal environment (Hill, 2010). Therefore, metal pollution in the estuarine and coastal sediments has become a major environmental problem because these areas are important habitats for aquatic life.
Riverine, estuarine and coastal environment are complex systems involving physical, chemical, and biological processes that play important roles in biogeochemical cycle of metals, and behavior, transport and fate of metal contaminants. Anthropogenic sources of metal pollution to the estuaries and coastal areas include mining, metal product fabrication, solid waste disposal, fossil fuel combustion, and municipal and industrial waste effluent (Hill, 2010). It is reported that acid mine drainage and erosion of waste dumps and tailings deposits introduce toxic metal in particulate form into water system; smelting of ore introduce metals to atmosphere, which end up as diffuse pollutants in soils and sediments (Salomons, 1995). Industrial wastewater is mostly from plants within the drainage area. Industries, such as foundry, paper-processing, laundry, tannery and dye works, can emit toxic metal particles and discharge wastewater to the adjacent estuaries and coastal areas (Feng et al., 1998; Hunt et al., 1994; Reddy et al., 2004; Salomons, 1995). Acid rain can leach metals and increase the mobility of toxic metals from pollutant sources to the environment (Müller et al., 2000). Once entered aquatic environment, toxic metals will be partitioned between dissolved phases and particulate phases with dominance in particulate phases due to their particle reactive nature. Most of these toxic metals will be ended in the sedimentary phases because of particle scavenging and settling. Therefore, high concentration of toxic metals are often found in sediments in many industrialized estuaries and coastal areas around the world because the major
sources of anthropogenic metals are originated from industrialization and urban
development with population growth in the areas (Bothner et al., 1998; Feng et al., 2004;
Forstner and Wittmann, 1979; Santos et al., 2005). In the sediment, the existence of
metals can be further classified as association with exchangeable, carbonates, Fe-Mn
oxides, organic matter, and residual phases as a result of the binding behavior between
toxic metal and surficial sediment matrices (Filgueiras et al., 2004). For example, it is
reported that depending on the metal chemical properties Zn and Cu are primarily bound
to organic matter while Cr is primarily to Fe-oxides (Yu et al., 2001). It is also found that
there exist significant correlations between Ni and carbonates, Cr and carbonates, Ni and
Fe-oxides, Cu and Mn-oxides, and Cr and Mn-oxides, respectively (Yu et al., 2001). It is
well known that fine-grained sediments are the main carriers of the toxic metals because
of its higher specific surface area (Che et al., 2003). Many studies have shown that
estuarine and coastal sediments are repository for metal pollutants and provide time-
integrated records of pollution history (Bopp and Simpson, 1989; Feng et al., 2004; Feng et
al., 2011; Goldberg et al., 1979; Trefry and Shokes, 1981; Valette-Silver, 1993). Therefore,
how the biogeochemical circulation of metals in these sediments can be influenced by the
ecological risk of metals is highly concerned.

Ecotoxicity and biogeochemical circulation of metals in an ecosystem is
determined by the metal concentration that organisms are exposed to. When the
concentration of metals in sediment exceeded certain threshold level, adverse biological effects frequently occur (Harikumar and Nasir, 2010). At molecular level, excessive metal accumulation in the organism might stimulate biological counter stress processes such as induction of antioxidant enzymes, physiological impairment, and extra energy consumption (Luoma, 1996). As the result, organism mortality raises continuously when sediment metal concentration increases (Long et al., 1995). In addition, the dynamic physiochemical ecological processes mediated the transportation of substances within the ecosystem can redistribute metals concentration by concentrating, permanently depositing, and transporting metals to various mediums. Therefore, the dynamic biogeochemical circulation of metals in sediments is also affected by the ecotoxicity of metals in sediments. For example, phytoplankton bloom can concentrate metal in sea water into biomass and increase bioaccumulation of metals in clams, eventually introduce significant amount of metals into food chain (Luoma, 1996).

This article summarizes the metal concentrations in the sediments in selected estuaries and coastal areas around the world based on our literature review. It aimed at reflecting the ecological hazardous impact in the biogeochemical circulation of metals associated with the urbanization and economic development.
6.2 Metal concentrations in estuarine and coastal sediments

In this study, metal concentrations in the riverine, estuarine and coastal sediments were derived from the published literature covering five continents including 43 selected sites around the world. The publications are based on the field studies in many countries, such as France (Audry et al., 2004), Spain (Bermejo et al., 2003; Caliani et al., 1997; DelValls et al., 2002), Greece (Galanopoulou et al., 2009; Pazi, 2011), Turkey (Topcuoğlu et al., 2004), Albania (Celo et al., 1999), Italy (Buccolieri et al., 2006; Spagnoli et al., 2008), United States (Feng et al., 1998; Hwang et al., 2006; Kim et al., 2004; Shumilin et al., 2002), French Guiana (Marchand et al., 2006), Mexico (Villaescusa-Celaya et al., 2000), China (Feng et al., 2011; Hong et al., 2003; Li et al., 2000), India (Jonathan and Ram Mohan, 2003; Reddy et al., 2004), Korea (Hyun et al., 2007), Azerbaijan (de Mora et al., 2004), Iran (de Mora et al., 2004), Kazakhstan (de Mora et al., 2004), Russia (de Mora et al., 2004), Fiji (Maata and Singh, 2008) and Australia (Liaghati et al., 2004) as well as Africa (El Nemr et al., 2006) and Antarctica (Andrade et al., 2001). As shown in Table 6-1, the sediment metal concentrations vary widely from place to place within these 43 selected study areas. The recorded metal concentrations range from 0.096% - 14.4% for Al, 0.038% - 6.21% for Fe, 0.01-1763 mg kg\(^{-1}\) for Cd, 1.00-1038 mg kg\(^{-1}\) for Cr, 0.50-4280 mg kg\(^{-1}\) for Cu, 0.01-11.6 mg kg\(^{-1}\) for Hg, 0.40-32600 mg kg\(^{-1}\) for Mn, 1.20-221 mg kg\(^{-1}\) for Ni, 0.69-5778 mg kg\(^{-1}\) for Pb, and
1.0-10000 mg kg\(^{-1}\) for Zn, respectively (Table 6-1). The wide variations in metal concentrations reflect the different natural mineral compositions in the sediments and significant anthropogenic toxic metal input in some of these coastal areas.

6.3 Sediment quality assessment

The environmental hazardous materials (e.g., toxic metals) can cause sediment contamination in estuaries and coastal areas. Therefore, metal enrichment factor has been widely used as the assessment criteria to study the sources and contamination of toxic metals in estuarine and coastal environment to prevent and control environmental pollution, protect marine life, ensure natural resource sustainable uses, maintain ecological equilibrium, and protect human health (Feng et al., 1998; Feng et al., 2004; Feng et al., 2011; Willem Salomons and Förstner, 1984; Sinex and Helz, 1981; Windom et al., 1991; Windom et al., 1989; Zhang and Liu, 2002; Zhang et al., 2009). In this section, estuarine and coastal sediment quality is evaluated by metal enrichment factor (EF). Metal enrichment factors (EF) are commonly used to identify metal concentrations of environmental concern. It is widely used in sediment quality assessment (Feng et al., 1998; Feng et al., 2004; Feng et al., 2011). Based on the EF values, natural metal concentrations can be distinguished from those of anthropogenic origin (Schropp et al., 1990; Sinex and Helz, 1981; Windom et al., 1989; J. Zhang and Liu, 2002). Therefore,
EF is a very useful indicator to evaluate sediment quality and metal contamination. Metal EF is mathematically defined by the following equation (Sinex and Helz, 1981):

\[
EF = \frac{(\frac{Me}{Re})_{\text{Sample}}}{(\frac{Me}{Re})_{\text{Background}}} \tag{1}
\]

where Me is the metal concentration of concern, Re is the concentration of either Al or Fe that are the most abundant element in the earth crust (Martin and Whitfield, 1983; Taylor and McLennan, 1995), \((\frac{Me}{Re})_{\text{Sample}}\) is the ratio in the sample, and \((\frac{Me}{Re})_{\text{Background}}\) is the ratio of the background. Ideally, the metal background concentration should be derived from the sampling site (Covelli et al., 2006; Kersten and Smedes, 2002; Liu et al., 2003). In most of the cases, however, the background data are not readily available. In this case, metal concentrations in the upper continental crust (Taylor and McLennan, 1995) are alternatives for the background values. The same approach has been used in our previous studies (Feng et al., 2004; Zhang et al., 2007; Zhang et al., 2009). For metal enrichment factor calculation performed in this study, we used the metal background values wherever they were available in the local study area. When the local metal background values were not available, we adopted the upper continental crust value as the background. Also, we had to use either Al or Fe in the EF calculation because Al data were not always available. However, our method is still valid because Al and Fe are commonly used for EF calculation (Bergamaschi et al., 2002; Conrad and Chisholm-
Based on the available Al and Fe data found in this study there exists a significant correlation 
(r=0.7745, n=13) between Al and Fe in the sediments (Figure 6-1), which supports our adoption.

Metal EFs provide an indication of the metal sources of and enrichment stage in the sediments. The assessment criteria using EF are generally based on the EF values (Klerks and Levinton, 1989; Loska and Wiechula, 2003; Willem Salomons and Förstner, 1984; Sinex and Helz, 1981; Sutherland et al., 2000; Yongming et al., 2006; Zhang and Liu, 2002). In a simple classification, EF ≈ 1 indicates natural crustal origin, whereas EF > 10 suggests anthropogenic source (Nolting et al., 1999). Zhang and Liu (2002) also recommended that 0.5 < EF < 1.5 suggest that the metals may be entirely from natural crustal weathering processes, whereas EF > 1.5 suggests that a significant portion of the metal is delivered from non-crustal materials. In a more detail classification, metal EF values can be divided into five categories based on the degree of enrichment, i.e., 1) EF < 2 suggests deficiency to minimal enrichment; 2) EF = 2–5, moderate enrichment; 3) EF = 5–20, significant enrichment; 4) EF = 20–40, very high enrichment; and 5) EF > 40, extremely high enrichment (Yongming et al., 2006).
Our calculation of metal enrichment factor (EF) has to depend on the data availability in the area. Therefore, there may be some unintentional bias in our dataset during the screen and selection. Nevertheless, the results from 24 selected estuaries and coastal areas for this study show that metal EF values vary widely from location to location from deficiency to extremely high enrichment (Figure 6-2). Specifically, the enrichment factors range from 0.2 – 2741 for Cd, 0.10 – 84 for Cr; 0.08 – 125 for Cu, 0.10 – 19 for Mn, 0.08 – 76 for Ni, 0.06 – 317 for Pb and 0.2 – 128 for Zn, respectively (Figure 6-2). Further analysis shows that among the metals in the study areas, some of them show different degree of enrichment as summarized below:

1. Cd – 9 out of 13 sites show unnatural enrichment, of which Suez Gulf, Alang-Sosiya coast and Odiel River show extremely high enrichment;

2. Cr – also 9 out of 20 sites show enrichment accumulation, of which Suez Gulf and Gulf of Mannar show significant enrichment level;

3. Cu – 8 out of 20 sites show sign of toxic metal enrichment, of which Suez Gulf and Odiel River show very high enrichment;

4. Ni – 7 out of 19 sites show metal enrichment, of which only Suez Gulf shows extremely high enrichment;

5. Pb – 13 out of 22 sites show unnatural enrichment, of which Suez Gulf and Odiel River show extremely high enrichment while Oyster Rock Landing salt marsh in
Delaware shows significant enrichment; and

(6) Zn – 8 out of 24 sites show Zn enrichment, of which Odiel River shows extremely high enrichment while Suez Gulf shows very high enrichment.

As shown in Table 6-2, cases of moderate to high enrichment (EF > 2) accounts for 33% - 69%. Relatively high percentages of enrichment occur to Cd (69%) and Pb (59%). Our study shows that metal enrichment factors reflect the sediment quality and the influence of local point sources of contaminants. Although we are not able to identify specific sources of these contaminants, we are certain that these contaminations are caused by local anthropogenic activities related to economic development.

6.4 Metal ecotoxicological assessment

Several approaches have been often used to assess the metal hazard potential to organisms, causing adverse biological effects (Long et al., 1998; Long et al., 1995; Urban and Cook, 1986). The potential ecotoxicological risk on organisms in the sediments can be evaluated using sediment guidelines (Ingersoll et al., 1996; Long et al., 1998; Long et al., 1995; Long and Morgan, 1990; Sundaray et al., 2011). Long et al. (1995) defined the effect range-low (ERL) and effect range-median (ERM) system based on the compilation of matching biological and chemical data from numerous modeling, laboratory, and field measurement in marine and estuarine sediments in order to better predict the toxicity of
contaminants. According to Long et al. (1995), ERL is defined based on the calculation of the 10th percentiles of organism influenced by the toxicity of a specific contaminant, while ERM value is based on the 50th percentiles of organism influenced by the toxicity of that contaminant. Three effect ranges of contaminant level could be set up by ERL and ERM. When the contaminant concentration is below ERL, a rarely biological adverse effect is anticipated, while the concentration is between ERL and ERM, occasional biological adverse effect is anticipated. However, when the concentration is greater than ERM value, a frequent biological adverse effect (> 50% chances) could occur (Ingersoll et al., 1996; Long et al., 1998; Long et al., 1995). To evaluate the potential biological adverse effect, hazard quotient (HQ) is one kind of single-value estimate, and is also the simplest method to estimate toxicity potential of the selected contaminant in the sediments (Urban and Cook, 1986; Wang et al., 2002). According to Urban and Cook (1986), the HQ is estimated by the following equation:

$$\text{HQ} = \frac{\text{SCC}}{\text{SQG}}$$  \hspace{1cm} (2)

where SCC is the sediment chemical concentration while SQG stands for the concentration defined by the sediment quality guideline. Both SCC and SQG are in mg kg\(^{-1}\). Since ERL is more reasonably predictive of non-toxic condition (SQGs), the SQG is set at ERL levels: Cd=1.2, Cr=81, Cu=34, Ni=20.9, Pb=46.7 and Zn=150 (Long et al.,
1995). In fact, HQ indicates the potential risk to organisms. If HQ<0.1, no adverse effects are expected; at 0.1 < HQ < 1, low potential hazards are expected; in the range of 1.0<HQ<10, some adverse effects or moderate hazards are probable; and when HQ>10, high hazard potential is anticipated (Filgueiras et al., 2004; Wang et al., 2002)

As shown in Figure 6-3, we found in this study that HQ values range from 0.04 – 832 for Cd (n=22), 0.08 – 5.7 for Cr (n=24), 0.38 – 17.8 for Cu (n=31), 0.14 – 1.6 for Ni (n=22), 0.08 – 50.7 for Pb (n=33), and 0.29 – 29.5 for Zn (n=34). The percentages of the estuaries and coastal areas facing various degree of hazard potential from no adverse effects (HQ < 0.1) to high hazard potential (HQ > 10) are shown in Figure 6-4. In most of the areas, only low hazard potentials (0.1 < HQ < 1) caused by these selected metals are expected. Except for Cd, high hazard potentials (HQ > 10) caused by Cr, Cu, Ni, Pb and Zn are expected in <10% of the study areas (Figure 6-4). Specifically, cases of potential adverse biological effect caused by each individual metal are described below:

(1) Cd – 8 out of 22 sites have Cd concentrations that exceed the ERL value and suggest moderate to high hazard potential, of which Suez Gulf, Cajarcite, Lot River, Keratsini Harbor and Alang-Sosiya coast show high hazard potential caused by Cd (Figure 6-3);

(2) Cr – 5 out of 24 sites (i.e., Adriatic Albanian coast, Keratisini Harbor, Alang-Sosiya coast, Gulf of Mannar, and Baja California) have Cr concentration
exceeding the ERL value and show moderate hazard potential (Figure 6-3);

(3) Cu – In addition to 2 out of 31 sites (i.e., Estuary of Huelva and Odiel River) have high hazard potential, another 16 out of 31 sites have moderate hazard potential (Figure 6-3);

(4) Ni – only 1 out of 22 sites (i.e., Adriatic Albania coast) has Ni concentration exceeding ERL value and has moderate hazard potential (Figure 6-3);

(5) Pb – 14 out of 33 sites have Pb concentration exceeding ERL value, of which 3 sites have high hazard potential while another 11 sites have moderate hazard potential (Figure 6-3); and

(6) Zn – 12 out of 34 sites have Zn concentration exceeding ERL value, of which 2 sites have high hazard potential while another 10 sites have moderate hazard potential (Figure 6-3).

6.5 Discussion and Conclusion

Toxic metal concentrations in the sediments from the most areas selected in this study are within the range of the natural levels. However, industrial activities, harbors, mining, wastewater and other anthropogenic sources are the main sources of toxic metal pollutants. Compositions of the sediments also play an important role in controlling the total amount of toxic metal pollutants (e.g., Cr, Cd, Pb and Cu) accumulating in the
sediments. As shown in this study, the concentrations of toxic metals in sediment are highly related to the water source and surrounding environment. For example, Suez Gulf received inputs of toxic metals mostly from municipal, dock and industrial activities (El Nemr et al., 2006). There is very high toxic metal enrichment in Suze Gulf but only Cd had exceeded ERL value, this is because the capacity of absorbing toxic metals of sandy texture bottom is limited (El Nemr et al., 2006). Odiel River received toxic metal inputs from industrial and mining activities (Bermejo et al., 2003). There is both very high toxic metal enrichment and biological toxicity of Cu, Pb and Zn. It is because the acidity of pH of sediment controlled the toxic metal presence in this area. The accumulation of toxic metals increases significantly with the increasing pH (Bermejo et al., 2003). It was also found that Pb and Zn concentrations increase with the increasing carbonate concentration in the estuary although the dominant texture of sediments is sandy (Bermejo et al., 2003). Keratsini Harbor and Saronikos Gulf receive toxic metal from sewage outfall, industrial and ship contaminants (Galanopoulou et al., 2009). Toxic metals (Cu, Cd, Zn, Pb and Cr) were highly enriched in the sediments and exceeded the ERL value (Figure 6-2 and Figure 6-3), suggesting this area could be highly toxicity to organism (Galanopoulou et al., 2009). Lot River water system gets toxic metal pollution from mining and smelting activity 50 years ago (Audry et al., 2004). Even though the pollution source was no longer there later, the residual Cd, Pb and Zn concentrations in the sediments were still
higher than the ERL values and this river system was classified as a severely polluted area because toxic metals were still being leached out from the former smelting sites (Audry et al., 2004). As one of the largest ship scrapping work in the world, Alang-Sosiya stretches about 14 km² and received pollutants including toxic metals, petroleum hydrocarbons, domestic wastes and bacterial contaminants (Reddy et al., 2004). The enrichment factors and HQs of Cd and Zn in this area were both above natural level (Figure 6-2 and Figure 6-3). High Cd and Zn concentrations in the sediments could be mainly attributed to the ship scrapping industry in this area (Reddy et al., 2004). The Gulf of Mannar is located in a high marine fauna production area, and received pollutants from industrial area, Tuticorin Harbor and River Tambraparani during the past three decades (Jonathan and Ram Mohan, 2003). The EF and HQ of Cr show significant enrichment and moderate hazard potential in this area (Figure 6-2 and Figure 6-3). High Cr concentration in the sediments could be attributed to heavy industrial activities in this area as well as carbonate and skeletal fragment being the main carrier phase (Jonathan and Ram Mohan, 2003). In Adriatic Albanian coast, pollutants were transported from industrial activities such as mining, commercial harbor and chlor-alkali plant, causing high Cr and Ni concentrations (Celo et al., 1999). Both Cr and Ni have moderate hazard potential to the organisms in this area (Figure 6-3).
Based on the analysis of the information collected for this study, our results suggest that the toxic metal contaminations should continue to raise our concern. It is not new that metal contaminations are currently still present in the world’s estuaries and coastal areas. The current issues are how we can effectively exercise the environmental protection, ecosystem restoration, and sustainable development of the coastal areas. These are also the worldwide issues. They are not just restricted in any localized area although the focuses could be different to a certain extent.
6.6 References


Langston, W., 1990. Toxic effects of metals and the incidence of metal pollution in marine ecosystems.


Liaghati, T., Preda, M., Cox, M., 2004. Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchment, southeast Queensland, Australia. Environ. Int. 29, 935-948.


Table 6-1 Metal concentrations in riverine, estuarine and coastal sediments from the selected areas around the world (Unit: mg kg$^{-1}$).

<table>
<thead>
<tr>
<th>Country/Region</th>
<th>Location</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
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<th>Zn</th>
<th>Pb</th>
<th>Sr</th>
<th>Reference</th>
</tr>
</thead>
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<td>Caribbean Sea</td>
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<td>2090</td>
<td>1680</td>
<td>1430</td>
<td>1030</td>
<td>820</td>
<td>620</td>
<td>Men et al., 2004</td>
</tr>
<tr>
<td>Range</td>
<td>1070 - 3180</td>
<td>1630 - 4600</td>
<td>1500 - 3800</td>
<td>1280 - 3560</td>
<td>1230 - 3210</td>
<td>1110 - 3060</td>
<td>980 - 2860</td>
<td>730 - 2460</td>
<td>140</td>
</tr>
<tr>
<td>Africa</td>
<td>Suez Gulf</td>
<td>2120</td>
<td>2120</td>
<td>1680</td>
<td>1430</td>
<td>1030</td>
<td>820</td>
<td>620</td>
<td>Men et al., 2004</td>
</tr>
<tr>
<td>Range</td>
<td>1070 - 3180</td>
<td>1630 - 4600</td>
<td>1500 - 3800</td>
<td>1280 - 3560</td>
<td>1230 - 3210</td>
<td>1110 - 3060</td>
<td>980 - 2860</td>
<td>730 - 2460</td>
<td>140</td>
</tr>
<tr>
<td>Antarctica</td>
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<td>2120</td>
<td>1680</td>
<td>1430</td>
<td>1030</td>
<td>820</td>
<td>620</td>
<td>Men et al., 2004</td>
</tr>
<tr>
<td>Range</td>
<td>1070 - 3180</td>
<td>1630 - 4600</td>
<td>1500 - 3800</td>
<td>1280 - 3560</td>
<td>1230 - 3210</td>
<td>1110 - 3060</td>
<td>980 - 2860</td>
<td>730 - 2460</td>
<td>140</td>
</tr>
<tr>
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<td>930</td>
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<td>910</td>
<td>900</td>
<td>890</td>
<td>Men et al., 2004</td>
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<tr>
<td>Range</td>
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<td>920 - 930</td>
<td>910 - 920</td>
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<td>880 - 890</td>
<td>870 - 880</td>
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<td>1680</td>
<td>1430</td>
<td>1030</td>
<td>820</td>
<td>620</td>
<td>Men et al., 2004</td>
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<td>1630 - 4600</td>
<td>1500 - 3800</td>
<td>1280 - 3560</td>
<td>1230 - 3210</td>
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<td>980 - 2860</td>
<td>730 - 2460</td>
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<td>4300</td>
<td>4200</td>
<td>4100</td>
<td>4000</td>
<td>3900</td>
<td>3800</td>
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<td>3900 - 3800</td>
<td>3800 - 3700</td>
<td>3700 - 3600</td>
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<tr>
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<td>3030</td>
<td>2930</td>
<td>2830</td>
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<td>2630</td>
<td>2530</td>
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<td>2430 - 2330</td>
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<td>Cuiroule, Loire</td>
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<td>135</td>
<td>145</td>
<td>155</td>
<td>165</td>
<td>175</td>
<td>185</td>
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<tr>
<td>Greece</td>
<td>Ceffi Gulf</td>
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<td>1014</td>
<td>1004</td>
<td>994</td>
<td>984</td>
<td>974</td>
<td>964</td>
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<td>1004 - 994</td>
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<td>970 - 960</td>
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Table 6-1 Metal concentrations in riverine, estuarine and coastal sediments from the selected areas around the world (Unit: mg kg\(^{-1}\)) (Continued).

<table>
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<tr>
<th>Country/Region</th>
<th>Location</th>
</tr>
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<tr>
<td><strong>India</strong></td>
<td>Alang-Sorara coast</td>
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<tr>
<td>Mean±SD</td>
<td>2130 ± 740</td>
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<td>Range</td>
<td>150 - 260</td>
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<td><strong>Italy</strong></td>
<td>Gulf of Mannarino</td>
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<tr>
<td>Mean±SD</td>
<td>120 ± 60</td>
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<tr>
<td><strong>Southern Italy</strong></td>
<td>Tarento Gulf</td>
</tr>
<tr>
<td>Mean±SD</td>
<td>29.5 ± 7.5</td>
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<td>Range</td>
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<td>Munyang Bay</td>
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<tr>
<td>Mean±SD</td>
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<td>Range</td>
<td>200 - 300</td>
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<td>Puget Sound, California</td>
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<tr>
<td>Mean±SD</td>
<td>5.500 ± 2400</td>
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<td>Ebro River and adjacent Atlantic shelf</td>
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<tr>
<td>Mean±SD</td>
<td>2370 ± 1165</td>
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<td>Range</td>
<td>200 - 2500</td>
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<td><strong>Turkey</strong></td>
<td>Marmara Sea</td>
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<td>Mean±SD</td>
<td>10909 ± 4540</td>
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<td>Range</td>
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<td><strong>U.S.</strong></td>
<td>Boise River</td>
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<td>Mean±SD</td>
<td>31.29 ± 343</td>
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<td>Range</td>
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<tr>
<td><strong>Upper Gulf of California</strong></td>
<td>Colorado River Delta</td>
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<tr>
<td>Mean±SD</td>
<td>354 ± 219</td>
</tr>
<tr>
<td>Range</td>
<td>100 - 500</td>
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<td><strong>Pacific Rock Lobster estuaries in Delaware</strong></td>
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<td>Range</td>
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<td><strong>Upper Gulf of California</strong></td>
<td>17500 ± 10340</td>
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<tr>
<td>Range</td>
<td>17000 ± 10870</td>
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Table and data source from: Taylor and McLennan, 1995.
Table 6-2: Statistical analysis of metal enrichment factor in the selected estuaries and coastal areas around the world, and the percentages of the cases with EF>2.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Pb</th>
<th>Zn</th>
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<td>n of cases studied</td>
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<td>20</td>
<td>20</td>
<td>19</td>
<td>22</td>
<td>24</td>
</tr>
<tr>
<td>Minimum EF value</td>
<td>1.5</td>
<td>0.39</td>
<td>0.57</td>
<td>0.23</td>
<td>0.82</td>
<td>0.88</td>
</tr>
<tr>
<td>Maximum EF value</td>
<td>1582</td>
<td>15</td>
<td>27</td>
<td>56</td>
<td>130</td>
<td>44</td>
</tr>
<tr>
<td>% of case with EF&gt;2</td>
<td>69</td>
<td>45</td>
<td>40</td>
<td>37</td>
<td>59</td>
<td>33</td>
</tr>
</tbody>
</table>
Figure 6-1  A significant correlation ($p < 0.001$) between Al and Fe in the sediments. Data are selected from 13 sites where both Al and Fe concentrations are available.
Figure 6-2 Enrichment factors (EF) of Cd, Cr, Cu, Ni, Pb and Zn in the sediments. The wide variations in metal enrichment factors among these sites reflect the different sources and enrichment of metals. High enrichment (EF > 2) suggests various degrees of metal pollution.
Figure 6-3 Hazard quotients (HQ) of Cd, Cr, Cu, Ni, Pb and Zn in the sediments. Moderate ($1 < HQ < 10$) to high ($HQ > 10$) hazard potential to cause adverse biological effect are anticipated in some riverine, estuarine and coastal areas.
Figure 6-4 Percentage of riverine, estuarine and coastal areas that have no (HQ < 0.1), low (0.1 < HQ < 1), moderate (1.0 < HQ < 10) and high (HQ > 10) potential hazards based on calculated HQ values of Cd, Cr, Cu, Ni, Pb and Zn. Cases vary from metal to metal due to the availability of the metal data. Total cases of each individual metals are $n_{Cd} = 22$, $n_{Cr} = 24$, $n_{Cu} = 31$, $n_{Ni} = 22$, $n_{Pb} = 33$, and $n_{Zn} = 34$, respectively.
CHAPTER 7
ENVIRONMENTAL MANAGEMENT IMPLICATIONS

Rapid urbanization and industrialization in the recent decades have introduced metals pollution in the ecosystem. The sustainable development of urban-coastal areas is threatened by the environmental contamination due to human activities and industrial activities (Feng et al., 2005, 2008). Brownfield sites are the sites with real or potential contamination and most of them are abandoned and located in the center of cities. Brownfield challenges the environmental protection agencies by increasing the potential ecological hazard and the health risk of residents living nearby. In addition, the difficulty of the redevelopment of the brownfield results in the uncertainty of land use, which will raise social issues for the local government managers such as the sluggish of local economy development and degeneration of the community (Litt et al., 2002). Toxic metal is one of the major contaminants in brownfield. Major sources causing soil metal enrichment include natural sources (e.g., rock outcropping), agricultural sources (e.g., fertilizers, fungicides, manures and pesticides), industrial sources (e.g., mining, refinement and fuel combustion), and domestic sources (e.g., wastewater, urban runoff, waste, landfill and transportation) (Nagajyoti et al., 2010). For example, soil metal contamination in mining areas, urban soils, urban road dusts and agricultural soils is very serious in China (Li et al., 2014; Wei and Yang, 2010). According to a recent survey, National Wide Survey of Soil Contamination in China (2014), agricultural lands, mining
areas, and urban brownfields are heavily contaminated. The major contaminants in the soils found in 82.8% of the contaminated sites in China are metal(loid)s, such as As, Cd, Hg and Pb.

As a major sink of the metals, soil is a major reservoir accumulating the metals. Unlike most organic contaminants, metals tend to persist in soil for a long time once they are introduced into the soil. Long-term exposure of living organism to metal contaminated soil will result in hazards and risks to both ecosystem and human community (Wuana and Okieimen, 2011). Ecological risk stemmed from soil contamination is highly concerned because terrestrial ecosystem stability is an integral part of sustainable development of modern society. It also secures the general public wellness (Perrodin et al., 2011; Shackelford et al., 2013). Plant-soil interaction is the foundation for studying terrestrial ecosystem species composition, ecosystem function, and ecosystem stability (Krumins et al., 2015). Therefore, understanding the interaction between plant and contaminated soil is critical to maintain soil quality, stabilize ecosystem, and advise decision-making efforts toward sustainable redevelopment and restoration of contaminated ecosystem (Bolan et al., 2014; Peng et al., 2009; Perrodin et al., 2011).

This dissertation research is an integration of macro scale study with micro scale study. In this dissertation, the interaction between plant and soil in a terrestrial ecosystem
developed upon a legacy urban brownfield site was investigated from a biogeochemical perspective. Both micro scale synchrotron technique and macro scale traditional geochemical analysis were applied to investigate the uptake and transportation of metal from soil to plant biomass. In the micro scale, the mechanism of the iron plaque intermediated root metal uptake and root to shoot translocation will be investigated. In the macro scale, the factors that control the metal bioavailability to plants in the brownfield soil environment and the formation of iron plaque around the plant roots will be explored.

Synchrotron \( \mu \)-XRF technique was applied to investigate the spatial distribution of Pb, Cu, Mn, Fe and Zn in different types of the root tissues in *Typha latifolia* L. root. Differences in the relationship between elements in each type of tissue indicate that iron plaque acts as a barrier for the uptake of Pb and a buffer for Zn, Mn and Cu. It also indicates that Cu, Mn and Zn share similar transport mechanism in root tissues. This study proposes an innovative perspective in the investigation of the root metal uptake mechanism and provides the valuable information for artificial manipulation of plant metal uptake efficiency by demonstrating the tissue-specific relationships between metals in the plant root. It also provides insights for the development of phytoremediation strategies.
Metal concentration in the root, stem and leaf of the dominant plant species on a legacy urban brownfield site were studied. The role of soil pH and organic matter content in the biogeochemical cycling of metals in this terrestrial ecosystem was investigated in this dissertation research. This study identified the dominant plant species as excluder of As and Cr, and indicated that a passive accumulation strategy by the plants could be applied to control the assimilation rate of Cu and Zn. In addition, Betula populifolia, Populus tremuloides and Polygonum cuspidatum were identified as accumulator of Zn. Soil pH and organic matter content significantly influences the bioavailability of Zn and Cu, respectively. The results of this study can be used to advise the modification of bioavailability of Zn and Cu in the study site, and to provide valuable reference for the selection of plant species in future brownfield site restoration projects.

The potential ecological risk of contaminated site was evaluated in this study based on the different contamination indexes. Cluster analysis was applied to study the potential contamination sources based on the data collected from the 22 study sites. Four different regions with distinct ecological levels were identified from these 22 sites. This study recommends a combined statistical approach to divide the contaminate area into several sub-regions based on their pollution sources and potential ecological risk. Land remediation and management can be conducted more cost-efficiently according to the
different levels of the ecological risks for remediation/restoration of the contaminated sites.

The outcomes of this dissertation research make contributions to the development of metal ecological hazard risk assessment criteria for brownfield environmental restoration and management. Understanding the metal translocation in wetland plants can also provide information on plant selection for bioremediation and knowledge of how to develop hyperaccumulator plant through bioengineering modification. Locally, the outcomes of this research will be useful for developing environmental management strategies for New Jersey urban coastal development and environmental restoration and management. Finally, the outcome of this research can assist in developing a new cost-effective and environmentally-friendly approach for the mitigation and remediation of brownfield site and will certainly benefit federal, state and local government and environmental managers in their decision making for coastal environmental protection and restoration. In the meantime, the results from this research can be used as a part of New Jersey coastal environmental study and the project can serve as a model that can be applied elsewhere in the region and throughout the United States because it addresses a specific issue of urban environmental contamination and restoration.
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LIST OF APPENDICIES

Appendix A: Supplementary information for Chapter 2

Appendix B: Experimental data for Chapter 3

Appendix C: Experimental data for Chapter 5
Figure A-1, root tissue groups separation based on the optical images of root samples from inundated and low water level samples. Green: dermal tissues; Blue: Endodermis surrounded vascular bundles.
Appendix B

Experimental data for Chapter 3

Table B-1, metal concentrations (Mean ± SD) in roots of dominant species at the sampling sites in the Liberty State Park.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Plant species</th>
<th>As Mean ± SD</th>
<th>Cr Mean ± SD</th>
<th>Cu Mean ± SD</th>
<th>Zn Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP-21</td>
<td>Artemisia vulgaris</td>
<td>1.68 ± 0.49</td>
<td>5.93 ± 1.77</td>
<td>81.9 ± 17.4</td>
<td>377 ± 53.0</td>
</tr>
<tr>
<td>TP-40</td>
<td>Artemisia vulgaris</td>
<td>1.08 ± 0.68</td>
<td>6.38 ± 3.35</td>
<td>46.3 ± 14.0</td>
<td>59.8 ± 14.0</td>
</tr>
<tr>
<td>TP40C</td>
<td>Artemisia vulgaris</td>
<td>0.55 ± 0.24</td>
<td>2.06 ± 0.62</td>
<td>57.0 ± 15.9</td>
<td>374 ± 43.5</td>
</tr>
<tr>
<td>TP-8a</td>
<td>Artemisia vulgaris</td>
<td>2.29 ± 0.70</td>
<td>6.63 ± 1.82</td>
<td>85.4 ± 44.2</td>
<td>339 ± 147</td>
</tr>
<tr>
<td>TP-14</td>
<td>Betula populifolia</td>
<td>0.90 ± 0.69</td>
<td>9.34 ± 4.04</td>
<td>24.1 ± 3.98</td>
<td>320 ± 291</td>
</tr>
<tr>
<td>TP-14/16</td>
<td>Betula populifolia</td>
<td>3.34 ± 1.03</td>
<td>52.8 ± 23.9</td>
<td>51.4 ± 10.3</td>
<td>153 ± 17.6</td>
</tr>
<tr>
<td>TP-18</td>
<td>Betula populifolia</td>
<td>1.77 ± 0.49</td>
<td>10.7 ± 2.20</td>
<td>120 ± 16.8</td>
<td>458 ± 76.4</td>
</tr>
<tr>
<td>TP-28</td>
<td>Betula populifolia</td>
<td>1.64 ± 0.65</td>
<td>13.7 ± 3.87</td>
<td>20.1 ± 2.66</td>
<td>145 ± 10.3</td>
</tr>
<tr>
<td>TP-41</td>
<td>Betula populifolia</td>
<td>0.91 ± 0.17</td>
<td>1.83 ± 0.82</td>
<td>28.6 ± 2.58</td>
<td>303 ± 68.2</td>
</tr>
<tr>
<td>TP-43</td>
<td>Betula populifolia</td>
<td>1.56 ± 0.62</td>
<td>3.86 ± 1.61</td>
<td>40.6 ± 18.5</td>
<td>81.3 ± 20.5</td>
</tr>
<tr>
<td>TP-43/14</td>
<td>Betula populifolia</td>
<td>7.16 ± 5.61</td>
<td>2.83 ± 0.83</td>
<td>36.0 ± 9.24</td>
<td>135 ± 2.70</td>
</tr>
<tr>
<td>TP-48</td>
<td>Betula populifolia</td>
<td>1.26 ± 0.35</td>
<td>9.44 ± 2.51</td>
<td>38.7 ± 7.33</td>
<td>169 ± 22.7</td>
</tr>
<tr>
<td>TP-16a</td>
<td>Onoclea sensibilis</td>
<td>2.91 ± 0.34</td>
<td>13.4 ± 2.25</td>
<td>48.0 ± 3.14</td>
<td>37.5 ± 3.99</td>
</tr>
<tr>
<td>TP-28/17</td>
<td>Polygonum cuspidatum</td>
<td>2.56 ± 0.23</td>
<td>12.7 ± 0.10</td>
<td>40.3 ± 0.51</td>
<td>131 ± 9.06</td>
</tr>
<tr>
<td>TP-24</td>
<td>Populus sp.</td>
<td>0.95 ± 0.19</td>
<td>3.18 ± 1.54</td>
<td>43.6 ± 9.88</td>
<td>487 ± 32.3</td>
</tr>
<tr>
<td>TP-25</td>
<td>Populus sp.</td>
<td>3.25 ± 2.60</td>
<td>2.76 ± 2.03</td>
<td>113 ± 58.0</td>
<td>604 ± 229</td>
</tr>
<tr>
<td>TP-10</td>
<td>Populus tremuloides</td>
<td>20.2 ± 9.47</td>
<td>9.16 ± 2.44</td>
<td>78.4 ± 16.6</td>
<td>270 ± 26.5</td>
</tr>
<tr>
<td>TP-1</td>
<td>Rhus sp.</td>
<td>0.75 ± 0.07</td>
<td>4.92 ± 0.31</td>
<td>126 ± 44.9</td>
<td>694 ± 63.6</td>
</tr>
<tr>
<td>TP-21/40</td>
<td>Rhus sp.</td>
<td>0.52 ± 0.09</td>
<td>2.67 ± 0.91</td>
<td>40.6 ± 13.6</td>
<td>239 ± 29.9</td>
</tr>
<tr>
<td>TP-3</td>
<td>Rhus sp.</td>
<td>0.92 ± 0.70</td>
<td>10.1 ± 3.17</td>
<td>35.7 ± 5.82</td>
<td>147 ± 22.9</td>
</tr>
<tr>
<td>TP-40 B</td>
<td>Rhus sp.</td>
<td>1.21 ± 0.61</td>
<td>6.66 ± 4.56</td>
<td>53.5 ± 27.4</td>
<td>49.2 ± 18.8</td>
</tr>
<tr>
<td>TP7/8</td>
<td>Rhus sp.</td>
<td>1.24 ± 0.22</td>
<td>2.42 ± 0.23</td>
<td>17.3 ± 1.62</td>
<td>165 ± 20.1</td>
</tr>
</tbody>
</table>
Table B-2, metal concentrations (Mean ± SD) in leaves of dominant species at the sampling sites in the Liberty State Park.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Plant species</th>
<th>As</th>
<th>Cr</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
<td>Mean ± SD</td>
</tr>
<tr>
<td>TP-21</td>
<td>Artemisia vulgaris</td>
<td>BDL ± BDL</td>
<td>0.38 ± 0.26</td>
<td>19.0 ± 4.37</td>
<td>95.4 ± 14.7</td>
</tr>
<tr>
<td>TP-40</td>
<td>Artemisia vulgaris</td>
<td>BDL ± BDL</td>
<td>0.09 ± 0.00</td>
<td>23.3 ± 2.06</td>
<td>54.8 ± 3.62</td>
</tr>
<tr>
<td>TP40C</td>
<td>Artemisia vulgaris</td>
<td>BDL ± BDL</td>
<td>0.62 ± 0.15</td>
<td>21.4 ± 0.17</td>
<td>107 ± 27.5</td>
</tr>
<tr>
<td>TP-8a</td>
<td>Artemisia vulgaris</td>
<td>BDL ± BDL</td>
<td>0.40 ± 0.11</td>
<td>20.0 ± 0.96</td>
<td>122 ± 39.2</td>
</tr>
<tr>
<td>TP-14</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.25 ± 0.13</td>
<td>4.32 ± 1.15</td>
<td>256 ± 12.7</td>
</tr>
<tr>
<td>TP-14/16</td>
<td>Betula populifolia</td>
<td>0.05 ± 0.01</td>
<td>0.57 ± 0.15</td>
<td>5.57 ± 0.11</td>
<td>824 ± 49.3</td>
</tr>
<tr>
<td>TP-18</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.06 ± 0.06</td>
<td>6.93 ± 0.76</td>
<td>1284 ± 272</td>
</tr>
<tr>
<td>TP-28</td>
<td>Betula populifolia</td>
<td>0.01 ± 0.02</td>
<td>0.03 ± 0.05</td>
<td>5.45 ± 0.16</td>
<td>109 ± 53.0</td>
</tr>
<tr>
<td>TP-41</td>
<td>Betula populifolia</td>
<td>0.08 ± 0.01</td>
<td>0.13 ± 0.06</td>
<td>6.11 ± 0.06</td>
<td>1617 ± 70.3</td>
</tr>
<tr>
<td>TP-43</td>
<td>Betula populifolia</td>
<td>0.02 ± 0.02</td>
<td>0.37 ± 0.19</td>
<td>5.29 ± 0.16</td>
<td>1051 ± 13.3</td>
</tr>
<tr>
<td>TP-43/14</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.19 ± 0.11</td>
<td>6.15 ± 0.24</td>
<td>1062 ± 143</td>
</tr>
<tr>
<td>TP-48</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.48 ± 0.16</td>
<td>5.14 ± 0.16</td>
<td>1034 ± 66.1</td>
</tr>
<tr>
<td>TP-16a</td>
<td>Onoclea sensibilis</td>
<td>BDL ± BDL</td>
<td>0.72 ± 0.12</td>
<td>4.62 ± 0.41</td>
<td>2.69 ± 0.28</td>
</tr>
<tr>
<td>TP-28/17</td>
<td>Polygonum cuspidatum</td>
<td>BDL ± BDL</td>
<td>0.51 ± 0.24</td>
<td>4.29 ± 0.60</td>
<td>98.4 ± 23.5</td>
</tr>
<tr>
<td>TP-24</td>
<td>Populus sp.</td>
<td>BDL ± BDL</td>
<td>0.20 ± 0.19</td>
<td>8.62 ± 0.61</td>
<td>1693 ± 140</td>
</tr>
<tr>
<td>TP-25</td>
<td>Populus sp.</td>
<td>0.04 ± 0.01</td>
<td>0.16 ± 0.12</td>
<td>8.05 ± 0.12</td>
<td>1657 ± 34.7</td>
</tr>
<tr>
<td>TP-10</td>
<td>Populus tremuloides</td>
<td>BDL ± BDL</td>
<td>0.33 ± 0.00</td>
<td>8.99 ± 0.36</td>
<td>1309 ± 46.4</td>
</tr>
<tr>
<td>TP-1</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.37 ± 0.13</td>
<td>5.14 ± 1.10</td>
<td>54.7 ± 7.13</td>
</tr>
<tr>
<td>TP-21/40</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.28 ± 0.08</td>
<td>3.13 ± 0.26</td>
<td>1.81 ± 0.04</td>
</tr>
<tr>
<td>TP-3</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.58 ± 0.24</td>
<td>5.58 ± 0.42</td>
<td>29.1 ± 4.62</td>
</tr>
<tr>
<td>TP-40 B</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.04 ± 0.06</td>
<td>2.98 ± 0.08</td>
<td>1.06 ± 0.04</td>
</tr>
<tr>
<td>TP7/8</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.31 ± 0.01</td>
<td>4.44 ± 0.10</td>
<td>2.51 ± 0.27</td>
</tr>
</tbody>
</table>

*BDL: Below detection limit.
Table B-3, metal concentrations (Mean ± SD) in stems of dominant species at the sampling sites in the Liberty State Park.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Plant species</th>
<th>As Mean ± SD</th>
<th>Cr Mean ± SD</th>
<th>Cu Mean ± SD</th>
<th>Zn Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP-21</td>
<td>Artemisia vulgaris</td>
<td>BDL ± BDL</td>
<td>0.37 ± 0.03</td>
<td>8.18 ± 1.14</td>
<td>172 ± 47.7</td>
</tr>
<tr>
<td>TP-40</td>
<td>Artemisia vulgaris</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>10.7 ± 1.20</td>
<td>50.7 ± 3.24</td>
</tr>
<tr>
<td>TP-40C</td>
<td>Artemisia vulgaris</td>
<td>BDL ± BDL</td>
<td>0.15 ± 0.25</td>
<td>6.62 ± 2.42</td>
<td>118 ± 31.1</td>
</tr>
<tr>
<td>TP-8a</td>
<td>Artemisia vulgaris</td>
<td>BDL ± BDL</td>
<td>0.07 ± 0.11</td>
<td>7.42 ± 1.69</td>
<td>154 ± 17.5</td>
</tr>
<tr>
<td>TP-14</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>1.34 ± 0.01</td>
<td>66.6 ± 5.97</td>
</tr>
<tr>
<td>TP-14/16</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>2.18 ± 0.19</td>
<td>118 ± 17.8</td>
</tr>
<tr>
<td>TP-18</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>1.34 ± 0.21</td>
<td>241 ± 26.5</td>
</tr>
<tr>
<td>TP-28</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>1.28 ± 0.10</td>
<td>64.2 ± 4.26</td>
</tr>
<tr>
<td>TP-41</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>1.60 ± 0.56</td>
<td>243 ± 73.0</td>
</tr>
<tr>
<td>TP-43</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>1.32 ± 1.69</td>
<td>1.62 ± 0.35</td>
<td>70.0 ± 8.98</td>
</tr>
<tr>
<td>TP-43/14</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.64 ± 0.57</td>
<td>3.24 ± 0.14</td>
<td>112 ± 35.5</td>
</tr>
<tr>
<td>TP-48</td>
<td>Betula populifolia</td>
<td>BDL ± BDL</td>
<td>0.12 ± 0.21</td>
<td>1.31 ± 0.37</td>
<td>69.6 ± 3.53</td>
</tr>
<tr>
<td>TP-16a</td>
<td>Onoclea sensibilis</td>
<td>BDL ± BDL</td>
<td>0.51 ± 0.08</td>
<td>4.17 ± 0.96</td>
<td>25.5 ± 2.55</td>
</tr>
<tr>
<td>TP-28/17</td>
<td>Polygonum cuspidatum</td>
<td>BDL ± BDL</td>
<td>0.06 ± 0.10</td>
<td>6.51 ± 0.47</td>
<td>59.1 ± 3.90</td>
</tr>
<tr>
<td>TP-24</td>
<td>Populus sp.</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>3.26 ± 0.05</td>
<td>127 ± 16.2</td>
</tr>
<tr>
<td>TP-25</td>
<td>Populus sp.</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>3.02 ± 0.59</td>
<td>152 ± 35.6</td>
</tr>
<tr>
<td>TP-10</td>
<td>Populus tremuloides</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>2.49 ± 0.05</td>
<td>81.8 ± 44.1</td>
</tr>
<tr>
<td>TP-1</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>1.30 ± 0.40</td>
<td>14.8 ± 1.61</td>
</tr>
<tr>
<td>TP-21/40</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.07 ± 0.12</td>
<td>1.81 ± 0.24</td>
<td>21.5 ± 2.98</td>
</tr>
<tr>
<td>TP-3</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>1.59 ± 0.77</td>
<td>11.3 ± 3.78</td>
</tr>
<tr>
<td>TP-40 B</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.12 ± 0.21</td>
<td>2.66 ± 0.20</td>
<td>4.19 ± 0.47</td>
</tr>
<tr>
<td>TP7/8</td>
<td>Rhus sp.</td>
<td>BDL ± BDL</td>
<td>0.00 ± 0.00</td>
<td>2.90 ± 0.62</td>
<td>23.5 ± 3.08</td>
</tr>
</tbody>
</table>

*BDL: Below detection limit.
Appendix C

Experimental data for Chapter 5

Table C-1, metal (As, Cr and Cu) concentrations (Mean ± SD) in soils at the sampling sites in the Liberty State Park.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Coordination X</th>
<th>Coordination Y</th>
<th>As Mean ± SD</th>
<th>Cr Mean ± SD</th>
<th>Cu Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1</td>
<td>615359</td>
<td>682551</td>
<td>12.5 ± 7.14</td>
<td>41.3 ± 19.1</td>
<td>124 ± 51.0</td>
</tr>
<tr>
<td>TP10</td>
<td>616078</td>
<td>682643</td>
<td>193 ± 112</td>
<td>61.6 ± 39.2</td>
<td>257 ± 30.5</td>
</tr>
<tr>
<td>TP14</td>
<td>614905</td>
<td>681021</td>
<td>87.4 ± 41.3</td>
<td>37.8 ± 33.4</td>
<td>103 ± 36.9</td>
</tr>
<tr>
<td>TP14/16</td>
<td>615126</td>
<td>681157</td>
<td>42.8 ± 9.01</td>
<td>209 ± 59.4</td>
<td>129 ± 11.2</td>
</tr>
<tr>
<td>TP16</td>
<td>615418</td>
<td>681389</td>
<td>35.1 ± 14.9</td>
<td>53.4 ± 7.88</td>
<td>67.0 ± 27.7</td>
</tr>
<tr>
<td>TP17</td>
<td>615878</td>
<td>682044</td>
<td>12.8 ± 2.50</td>
<td>25.0 ± 5.50</td>
<td>1377 ± 2142</td>
</tr>
<tr>
<td>TP18</td>
<td>616122</td>
<td>682370</td>
<td>33.3 ± 3.94</td>
<td>27.6 ± 17.0</td>
<td>238 ± 5.87</td>
</tr>
<tr>
<td>TP21</td>
<td>616825</td>
<td>683332</td>
<td>37.4 ± 7.90</td>
<td>38.2 ± 2.60</td>
<td>345 ± 40.2</td>
</tr>
<tr>
<td>TP21/40</td>
<td>617192</td>
<td>683295</td>
<td>15.7 ± 1.85</td>
<td>32.1 ± 2.54</td>
<td>224 ± 45.5</td>
</tr>
<tr>
<td>TP24</td>
<td>616687</td>
<td>683055</td>
<td>23.6 ± 1.70</td>
<td>44.0 ± 3.53</td>
<td>249 ± 35.1</td>
</tr>
<tr>
<td>TP25</td>
<td>616633</td>
<td>682735</td>
<td>270 ± 184</td>
<td>40.4 ± 26.1</td>
<td>1527 ± 219</td>
</tr>
<tr>
<td>TP28</td>
<td>615695</td>
<td>681435</td>
<td>22.5 ± 1.95</td>
<td>68.5 ± 5.19</td>
<td>44.3 ± 10.4</td>
</tr>
<tr>
<td>TP28/17</td>
<td>615670</td>
<td>681804</td>
<td>12.5 ± 4.63</td>
<td>43.4 ± 11.5</td>
<td>48.3 ± 11.9</td>
</tr>
<tr>
<td>TP40</td>
<td>617570</td>
<td>683389</td>
<td>13.2 ± 2.12</td>
<td>20.3 ± 7.52</td>
<td>153 ± 44.5</td>
</tr>
<tr>
<td>TP40B</td>
<td>617476</td>
<td>683313</td>
<td>24.8 ± 4.59</td>
<td>46.6 ± 5.05</td>
<td>212 ± 28.4</td>
</tr>
<tr>
<td>TP40C</td>
<td>617359</td>
<td>683151</td>
<td>14.2 ± 6.78</td>
<td>20.2 ± 12.5</td>
<td>229 ± 87.7</td>
</tr>
<tr>
<td>TP41</td>
<td>616025</td>
<td>681197</td>
<td>13.3 ± 3.73</td>
<td>9.70 ± 4.43</td>
<td>68.4 ± 23.7</td>
</tr>
<tr>
<td>TP43</td>
<td>615483</td>
<td>680618</td>
<td>21.0 ± 1.99</td>
<td>10.2 ± 3.00</td>
<td>166 ± 72.1</td>
</tr>
<tr>
<td>TP43/14</td>
<td>615385</td>
<td>680898</td>
<td>17.6 ± 4.08</td>
<td>11.4 ± 2.52</td>
<td>69.9 ± 12.2</td>
</tr>
<tr>
<td>TP48</td>
<td>615998</td>
<td>680484</td>
<td>10.7 ± 5.94</td>
<td>16.7 ± 20.0</td>
<td>76.4 ± 18.0</td>
</tr>
<tr>
<td>TP7/8</td>
<td>616525</td>
<td>683508</td>
<td>57.1 ± 17.3</td>
<td>50.6 ± 3.80</td>
<td>199 ± 23.7</td>
</tr>
<tr>
<td>TP8</td>
<td>616543</td>
<td>683298</td>
<td>11.9 ± 0.41</td>
<td>38.4 ± 2.91</td>
<td>168 ± 18.0</td>
</tr>
</tbody>
</table>
Table C-2, metal (Pb, Hg and Zn) concentrations (Mean ± SD) in soils at the sampling sites in the Liberty State Park.

<table>
<thead>
<tr>
<th>Site ID</th>
<th>Coordination X</th>
<th>Coordination Y</th>
<th>Pb Mean ± SD</th>
<th>Hg Mean ± SD</th>
<th>Zn Mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>TP1</td>
<td>615359</td>
<td>682551</td>
<td>453 ± 266</td>
<td>0.12 ± 0.07</td>
<td>309 ± 125</td>
</tr>
<tr>
<td>TP10</td>
<td>616078</td>
<td>682643</td>
<td>500 ± 122</td>
<td>0.96 ± 1.48</td>
<td>131 ± 89.5</td>
</tr>
<tr>
<td>TP14</td>
<td>614905</td>
<td>681021</td>
<td>383 ± 228</td>
<td>0.13 ± 0.06</td>
<td>50.0 ± 12.6</td>
</tr>
<tr>
<td>TP14/16</td>
<td>615126</td>
<td>681157</td>
<td>552 ± 73.6</td>
<td>0.15 ± 0.03</td>
<td>157 ± 51.5</td>
</tr>
<tr>
<td>TP16</td>
<td>615418</td>
<td>681389</td>
<td>168 ± 60.9</td>
<td>0.17 ± 0.17</td>
<td>38.7 ± 20.5</td>
</tr>
<tr>
<td>TP17</td>
<td>615878</td>
<td>682044</td>
<td>236 ± 19.0</td>
<td>0.21 ± 0.13</td>
<td>421 ± 117</td>
</tr>
<tr>
<td>TP18</td>
<td>616122</td>
<td>682370</td>
<td>393 ± 94.5</td>
<td>3.62 ± 5.95</td>
<td>491 ± 473</td>
</tr>
<tr>
<td>TP21</td>
<td>616825</td>
<td>683332</td>
<td>563 ± 31.0</td>
<td>0.37 ± 0.21</td>
<td>1058 ± 327</td>
</tr>
<tr>
<td>TP21/40</td>
<td>617192</td>
<td>683295</td>
<td>421 ± 45.0</td>
<td>0.29 ± 0.06</td>
<td>603 ± 8.08</td>
</tr>
<tr>
<td>TP24</td>
<td>616687</td>
<td>683055</td>
<td>486 ± 38.0</td>
<td>0.40 ± 0.39</td>
<td>718 ± 219</td>
</tr>
<tr>
<td>TP25</td>
<td>616633</td>
<td>682735</td>
<td>4640 ± 1210</td>
<td>0.18 ± 0.19</td>
<td>1586 ± 1358</td>
</tr>
<tr>
<td>TP28</td>
<td>615695</td>
<td>681435</td>
<td>173 ± 23.2</td>
<td>0.00 ± 0.00</td>
<td>72.5 ± 13.2</td>
</tr>
<tr>
<td>TP28/17</td>
<td>615670</td>
<td>681804</td>
<td>156 ± 43.2</td>
<td>0.60 ± 0.30</td>
<td>96.3 ± 13.8</td>
</tr>
<tr>
<td>TP40</td>
<td>617570</td>
<td>683389</td>
<td>303 ± 66.3</td>
<td>0.50 ± 0.36</td>
<td>159 ± 48.4</td>
</tr>
<tr>
<td>TP40B</td>
<td>617476</td>
<td>683313</td>
<td>421 ± 75.1</td>
<td>0.21 ± 0.03</td>
<td>232 ± 40.1</td>
</tr>
<tr>
<td>TP40C</td>
<td>617359</td>
<td>683151</td>
<td>449 ± 238</td>
<td>0.07 ± 0.06</td>
<td>304 ± 315</td>
</tr>
<tr>
<td>TP41</td>
<td>616025</td>
<td>681197</td>
<td>86.1 ± 27.6</td>
<td>BDL ± BDL</td>
<td>198 ± 103</td>
</tr>
<tr>
<td>TP43</td>
<td>615483</td>
<td>680618</td>
<td>333 ± 132</td>
<td>BDL ± BDL</td>
<td>63.7 ± 15.6</td>
</tr>
<tr>
<td>TP43/14</td>
<td>615385</td>
<td>680898</td>
<td>117 ± 39.6</td>
<td>0.00 ± 0.00</td>
<td>49.0 ± 14.9</td>
</tr>
<tr>
<td>TP48</td>
<td>615998</td>
<td>680484</td>
<td>196 ± 83.8</td>
<td>0.17 ± 0.18</td>
<td>24.9 ± 12.3</td>
</tr>
<tr>
<td>TP7/8</td>
<td>616525</td>
<td>683508</td>
<td>409 ± 21.3</td>
<td>1.57 ± 0.77</td>
<td>218 ± 73.2</td>
</tr>
<tr>
<td>TP8</td>
<td>616543</td>
<td>683298</td>
<td>349 ± 50.3</td>
<td>0.15 ± 0.10</td>
<td>207 ± 53.9</td>
</tr>
</tbody>
</table>
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