

# **Heavy Metals in Urban Soils**

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## **Abstract**

Due to highly intensive human activity, urban soils are suffering from degradation. As a consequence, the quality of groundwater could be affected. Since more and more urban dwellers have come to recognize the close relationship between urban soils and their water and air, as well as the growing popularity of urban agriculture, concern regarding soil contamination is on the increase.

This thesis is focused on the investigation of heavy metal contaminated urban soils (especially lead and zinc). Soil samples from greater Montreal area were collected. The concentrations of lead and zinc of some soil samples were at elevated levels, with the highest concentration being 2000 mg/kg (the EPA standard limits for both metals is 300 mg/kg at residential soils). The physical and chemical properties of soils, including soil particle size distribution, soil cation exchange capacity (CEC), soil specific surface area (SSA), soil permeability coefficients, were determined. The majority of soil particles in the samples were found to have the texture of fine sand (loamy and silty sands). Selective sequential extraction (SSE) was performed to understand the affinities of heavy metals toward various fractions of soil. The results indicate that lead has the highest affinity toward soil fraction of organic matter, while zinc has the highest affinity toward soil oxides. Soil column leaching tests were carried out. SSE, together with soil leaching tests, explains the mobility of heavy metals. It shows that zinc has a higher mobility in soils than lead. With the knowledge of heavy metal mobility in soils, the soil decontamination scheme can be planned.

## **Acknowledgement**

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# Chapter 1

## Introduction

In modern societies, heavy metals are widely used in every aspect of industrial and human activities. The unavoidable subsequent deposition of heavy metals in our soil system can have a serious and long-term impact on the quality of environment. Soil, although highly important in our everyday activities, has not been understood thoroughly in terms of its role in retaining contaminants. It is mainly ignored by the general public despite its close relationship with contaminated water and air, both of which seem to gain more attention due to the outbreak of acute waterborne or airborne diseases. In some cases, soil could be the major culprit creating water and air pollution, such as the contamination of groundwater and the emission of volatile chemicals from soils.

This project was brought about by a group of urban dwellers, who were concerned about the soil quality in their communal backyard, which used to be the dumping ground of some industrial activities. Initial general investigation of the heavy metal levels at that garden revealed abnormally high levels of lead and zinc contamination. Further investigations were carried out to determine the soil properties to gain a basic knowledge of soil in terms of its role in heavy metals interaction mechanisms. Some

urban soil samples from other locations were also collected and analyzed in similar experiments.

The objectives of this thesis can be described as follows:

- To investigate heavy metal contamination of urban soils in downtown Montreal, with the focus on lead and zinc.
- To investigate soil properties, including its particle size distribution and surface properties such as specific surface area (SSA) and cation exchange capacity (CEC).
- To determine the relationship between the soil particle properties and the heavy metals that they retained.
- To determine the distribution of heavy metals among the various soil fractions.
- To determine the soil permeability coefficient and the mobilities of lead and zinc in the soil.

This thesis is divided into six chapters:

**Chapter One:** Introduction of thesis

**Chapter Two:** Introduction and literature review of the physical and chemical properties of soils

**Chapter Three:** Introduction and literature review of the interactions between soil and heavy metals

**Chapter Four:** Experimental methods

**Chapter Five:** Results and discussion

**Chapter Six:** Recommendations for future work

## Chapter 2

### Soil

Soil has been known to play an important role in the fate and transport of contaminants. Soils are very diverse in composition and behavior. Studying the properties and characteristics of soil would help us to understand the physical and chemical interactions regarding the attenuation of contaminants.

#### 2.1 Physical properties of soil

##### 2.1.1 Soil composition and characterization

A soil system is composed of soil minerals, soil organic matter, water and air. As can be seen from Fig. 2.1 (Reddi 2000), the fluid phases (water and air) contribute up to 50 % of the whole soil system; thus, they interact constantly with the soil particles and play an important role in the soil-contaminant interactions.

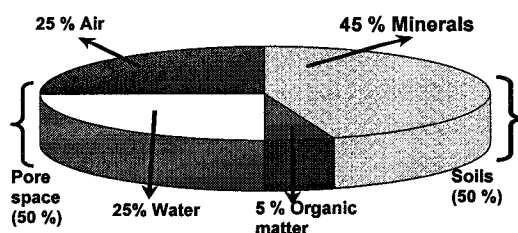


Fig. 2.1 Soil system (Reddi 2000)

The solid part of a soil system is formed from the disintegration of parent rock materials of the earth's crust; the mechanism of soil structure formation is extremely complex and mainly caused by several natural processes, including physical, chemical and biological processes and some man-made processes. The nature and origin of the parent materials are also important factors (Das 1985). Soil weathering is a combination of destruction and re-synthesis. Rocks are broken down to smaller fragments and eventually to various minerals, which subsequently undergo modification or change to completely new compounds by chemical reactions.

Some major weathering processes (Wild 1993) are: (a) Mechanical disintegration: wind, water and ice erosion; plant and animals influences (b) Chemical decomposition: oxidation and reduction; hydrolysis due to the large proportion of soil water; carbonation and other acidic processes due to the presence of hydrogen ions in soil water; chelation and complexion due to the metal ions existing within soil system. (c) The presence of microorganisms and soil organic matter cause the biological processes of soil formation. Soils inherit their structures from the parent materials. The nature of the weathering processes and the subsequent transportation and deposition by water and air results in huge variations of soil particle sizes, which range from 0.05 to 2.0 millimeter. Particle size distribution is one of the most common ways to characterize soils. Generally speaking, soils can be grouped into four broad categories of gravel, sand, silt, and clay-sized particles. Table 2.1 shows soil groupings based on particle diameters by various

organizations (Das 1985). It is also common to subgroup soils by their textures, which is the coarseness or fineness of a soil. Natural soil particles tend to be bonded together as aggregates, caused by their shrinking-expanding behavior under wetting or drying weather conditions, or by soil organisms.

**Table 2.1 Soil chemistry of hazardous material ( Das 1985)**

Soil particle		Equivalent diameter size (mm)
<b>Gravel</b>		> 2 mm
<b>Sand</b>		0.05 – 2 mm
	Very coarse	1 – 2 mm
	Coarse	0.5 – 1 mm
	Medium	0.25 – 0.5 mm
	Fine	0.1 – 0.25 mm
	Very fine	0.05 – 0.1 mm
<b>Silt</b>		0.002 – 0.05 mm
<b>Clay</b>		< 0.002 m (< 2 micrometer)

### 2.1.2 Inorganic soil minerals

The inorganic part of soil system is composed of numerous inorganic chemicals, commonly called soil minerals. Some elements in soil such as C, O, H, Si, Al, Ca, etc. and some trace metals (Fe, Pb, Zn, Cd, Cu, and Ni, etc) (Iskandar 2001) in limited amounts, are immobilized within soil mineral structures by the following mechanisms:

- (a) **Chemical adsorption:** covalent bonds between an element (ion) and the soil surface
- (b) **Solid state diffusion:** elements penetrating into some void spaces of clay mineral structure
- (c) **Precipitation:** dissolved minerals that become insoluble compounds on soil clay surfaces.

Minerals occur naturally; they have characteristic structures and chemical compositions. Soil minerals come in various sizes; some are as large as the smaller rock fragments, while others, such as colloidal soil clays, have to be observed with the aid of a microscope. Primary minerals such as quartz (the major component of sand and silt) inherit most of their composition from parent rock materials (Nagaraj 2001); secondary minerals such as clay minerals, oxides and carbonates do not resemble the original materials.


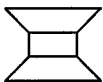
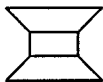
### **Clay minerals**

Clays are usually mica-like shapes and become highly plastic when wet. They expand and become sticky with suitable moisture and they shrink when dry (Nagaraj 2001). The coarse fractions of clay particles are particles such as quartz and gibbsite. It is the fine clay particles that attract more attention. Fine soil clay minerals contain mainly aluminosilicates, including elements like Si, Al, Mg, and Fe (Reddi 2000). They, together with soil organic matter, influence strongly the physical and chemical properties of soil because of their smaller particle sizes, large ion exchange structures, and large surface area. Clay minerals have crystalline structures and are composed of substructure unit layers (Reddi 2000), which appear sequentially throughout the entire mineral. In general, minerals with similar chemical compositions have similar chemical properties. Most clay minerals contain mainly silica layers (tetrahedral sheet), whose structure consists of four oxygens surrounding a silicon atom in tetrahedral positions and an alumina layer (octahedral sheet), whose structure is of cations (aluminum, magnesium, etc.) surrounded by oxygens in octahedral positions. Based on the chemical structures, three



groups, kaolinites, illites and montmorillonites, are shown by their simplified unit structures in Table 2.2 (Yong et al. 1992):

**Table 2.2 Categorization of clay minerals (Yong et al. 1992)**

Clay mineral	Kaolinites	Illites; Vermiculites	Montmorillonites
Crystal structure			

 → Silica layer (tetrahedral sheet)

 → Alumina layer (octahedral sheet)

**I. Kaolinites:** Each unit contains a silica layer and an alumina layer. Between units, there are strong oxygen-hydroxyl bondings (Das 1985). Therefore, their structure units are tightly held together; expansion or shrinking does not commonly occur when wetted or dried. Since all the surface interactions involve only the external surfaces and cations cannot easily enter between the units, kaolinites have the smallest specific surface area and cation exchange capacity among all the other clay minerals.

**II. Montmorillonites:** Each unit is made of two silica layers with one alumina layer bound in between; units are held loosely by weak oxygen-oxygen bondings (Das 1985). Consequently, montmorillonite expands and shrinks very easily. The flexibility of each unit makes its internal surface available for reaction. Thus, montmorillonites have the highest specific surface area as well as cation exchange capacity among clay minerals.

**III. Illites:** Illites (or mica-like minerals) have similar general structures as the montmorillonites and their physical and chemical properties lie between kaolinites and montmorillonites. The inter-unit positions are occupied tightly by potassium ions, which fit right in the hexagonal holes of the silica layer. Those ions are not exchangeable. Thus, illites do not expand like montmorillonites do.

**IV. Vermiculites:** Vermiculites have similar structures and characteristics to illites. The major difference between the two is the ions at the inter-unit positions. Magnesium ions occupy the inter-unit positions of vermiculites. Thus, they would expand when exposed to water due to the association of water layers with magnesium ions. The cation exchange capacity and specific surface area of vermiculites lie in between illites and montmorillonites.

#### **Soil oxides, hydroxides and oxyhydroxides minerals**

Oxides, hydroxides and oxyhydroxides are commonly referred to as oxides and are another common form of soil minerals. This type of soil minerals often dominates the tropical and semitropical regions (Wild 1993), where the soils show the color of red and yellow. When some of the cations—mainly Al, Fe and Mn-- are released from soil, they react with water to form oxides and hydroxides. This fraction of soil mineral has both crystalline (mineral) and non-crystalline (amorphous) forms. Among the crystalline oxides, *Gibbsite* ( $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ) is the most common aluminum hydroxide; *Goethite* ( $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ) and *limonite* ( $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ) are the most common iron oxides (Yong and Mulligan 2004). The crystalline oxides share some properties with clay minerals such as its definite crystalline structures and its ability to contain negative charges on its surfaces. Amorphous aluminum and iron oxides could form coatings among soil

particles (Roundhill 2001). These gel-like coatings can aggregate soil particles into microstructure units.

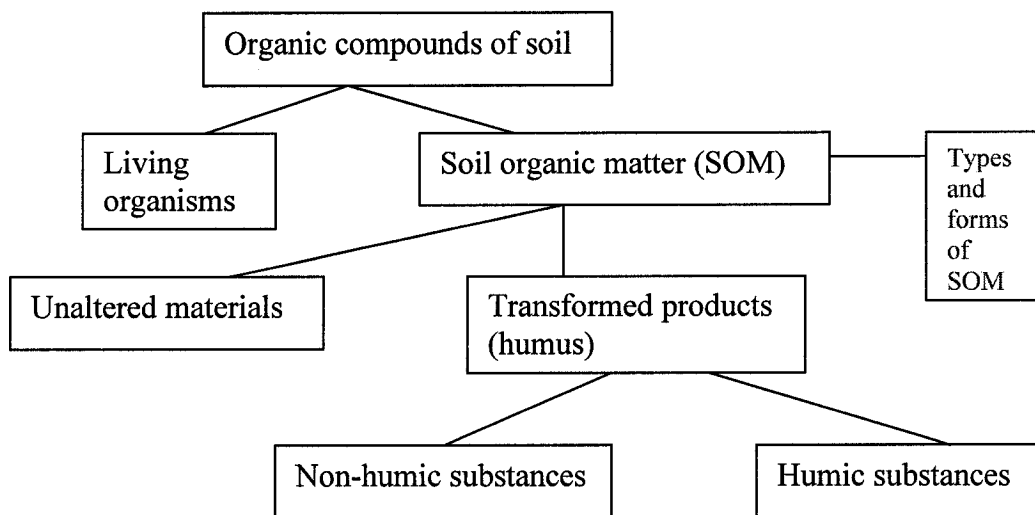
### **Soil carbonate minerals**

The most common soil carbonate minerals found are *calcite* ( $\text{CaCO}_3$ ) and *dolomite* [ $\text{CaMg}(\text{CO}_3)_2$ ] (Roundhill 2001). Since most of the bonds linking cations and anions in carbonate minerals are ionic in nature, in comparison to other soil minerals, carbonates are softer, more soluble and more subject leaching out from the soil. Therefore they are more abundant in arid and semi-arid regions (Das 1985) where leaching is limited. Carbonate minerals can react easily with the  $\text{H}_2\text{O}$  present in the soil, producing bicarbonate ions ( $\text{HCO}_3^-$ ). Thus they would affect the pH of the soil, which is one of the dominating factors affecting chemical and biological processes occurring in soil.

### **2.1.3 Soil organic matter**

Soils contain various organic compounds, which are an accumulation of partially decomposed plant and animal residues. They are easily subjected to attack by soil microorganisms. From the compound degradation degree, soil organic matter can be divided, as seen from Fig.2.3 (Dragun 1998), into residual organic matter that still preserves identifiable structures of its origin and decomposed colloidal particles (called “humus”). Humus can be further divided into (a) **non-humic substances**: Identifiable, well-defined, high-molecular-weight bio-polymers such as polysaccharides, proteins, and simpler substances such as sugars, amino acids, etc. (b) **humic substances**: they are unidentifiable, irregular organics that cannot be placed in any categories of non-humic

polymers. They account for 70 to 80 % of the humus and are usually brown to black in color.



**Fig. 2.2 Soil organic matter (Dragun 1998)**

Humus is a complex mixture of amorphous and colloidal compounds, which had been modified from the original parent materials by various soil microorganisms. Two functional groups, carboxyl (COOH) and hydroxyl (OH) groups, at its surface are the major sources of negative charges of soil organic matter (how functional groups contribute to the negative charges of soils will be discussed at Chap. 2.3.2).

In contrary to its stable crystalline counterpart - clay minerals - soil organic matter is susceptible to slow but continuous microorganism attack, which contributes to its surface interactions. The huge surface area of organic matter provides sites for cation exchange; the high metals affinity is due to the functional groups and ligands at its surfaces that will form complexes and chelates with metal cations (Petruzzelli 1993).

Colloidal soil organic matter has a strong affinity for heavy metals and the metal retention capacity of soil is usually well correlated with the amount of its organic matter. Although soil organic matter only makes up 0.5% to 5% of the total soil system, it plays an important role in maintaining good soil structure and stability. Among the benefits of soil organic matter are (Dragun 1998): (a) providing nutrients like nitrogen, phosphorus, sulfur and a food source for plants and microorganisms, (b) aggregating small soil particles and forming strong complexes between soil organic compounds and soil minerals to strengthen soil structure, (c) increasing soil's buffering capacity to resist acidity changes, (d) contributing to almost 50 % of soil's cation exchange capacity, (e) increasing the amount of soil water.

## **2.2 Water in soil**

Water is a simple molecule containing one oxygen atom and two hydrogen atoms. Since an oxygen atom has a higher electronegativity than a hydrogen atom, the electron distribution in water molecules is asymmetrical; the two bonding pairs of electrons are closer to oxygen atom than to hydrogen atoms. Although water molecules are neutral, the polarity (Wild 1993) (asymmetrical distribution of electron pairs) causes oxygen atom to possess partial negative charges and hydrogen atoms partial positive charges. It is the polarity that causes one water molecule to bond to another one by forming a hydrogen bond (which will be discussed in Chap. 3.3.1.1). Water is the most important solvent in the soil system and it makes up approximately 25 % of the whole soil system; the addition of water can come from rainfall, snowmelt and irrigation and the losses of

water from evaporation and plants' transpiration. The driving mechanisms for water migration in soil mainly come from thermal, osmotic, ionic gravitational and hydraulic forces (Logston 2003). Water in soil, generally known as soil solution, is a complex electrolytic solution, containing a wide variety of organic and inorganic ions and molecules. In regard to the fate and transport of contaminant leachates, water is the primary factor to consider. Most of the metal cations do not exist individually in water, the polarity of water molecules results in the hydration of these positive-charged ions by attracting the negatively charged side (oxygen atom) of water to them (Ross 1994). The negatively charged soil surface also becomes hydrated due to the same reason. The hydration of cations and soil surfaces is to release energy to achieve more stable compounds.

### **2.2.1 Maximum water retention capacity and field capacity**

Soil particles do not usually exist individually; they aggregate into a stable unit, known as a ped. Soil peds, together with other causes such as chemical weathering, plant roots, burrowing animals and human activities will create pore space inside soils, which are more visible in the topsoil (30% – 60% pore space) than in subsurface soils (Kramer 1995). Macropores usually allow the easy movement of percolating water; as for micropores, water movement is greatly restricted to slow capillary movement. During heavy rainfall, water is applied to the soil; all the pore space of the topsoil, including the part originally filled up with air, is saturated with water. Additional application of water will result in the downward movement of water. At this point, the upper part of soil is

said to be at its maximum water retention capacity (Kramer 1995). However, as the water supply stops, after a period of time, the water will stop moving downward. The water originally filled up all the pore space will move out of the macropores and settle in the micropores. The soil is then said to be at its field capacity (Kramer 1995), where the water moves slowly due to the capillary movement of water in micropores.

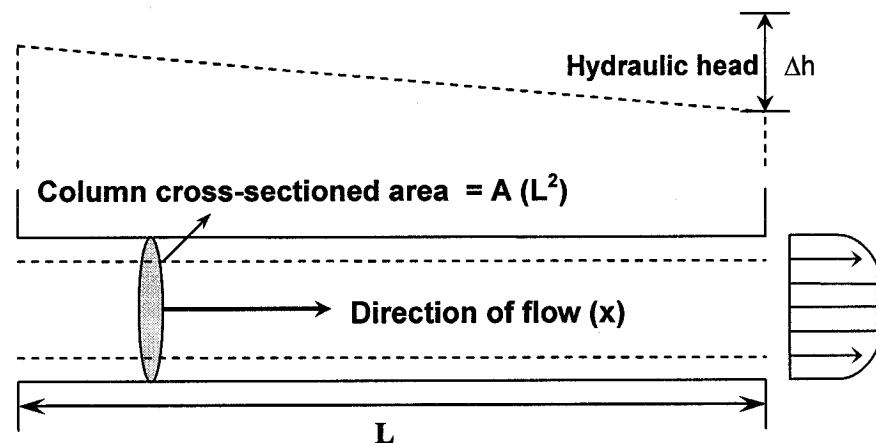
### **2.2.2 Soil permeability and Darcy's Law**

Soil structures have a tremendous impact in terms of how water moves in soil. The various pores within soil particle will conduct fluid transmission, which is termed soil permeability. Fluid, especially water, is an important phase in soil system. A study in the mechanism of the flow of fluid is essential in understanding how the contaminants fluid interacts with the soil particles. Permeability usually involved in the soil particle sizes as well as pore geometry. Porosity ( $n$ ) is defined as the percentage of pore volume or void space, or that volume within rock that can transport fluid. Soils with smaller particle sizes usually have narrower flow channels, thus smaller permabilities (as well as porosity). Therefore, clay-sized particles ( $< 2$  micron) are usually used as engineering soil barriers for containing contaminant leachates. To demonstrate the soil permeability, we can apply the principle of flow in a capillary tube, as is shown in Fig. 2.4 (Reddi 2000), within which, Darcy's law stated that hydraulic head gradient – hydraulic head ( $h$ , the gradient of the energy per unit volume possessed by the water) changes with distance – is proportional to the specific discharge (the amount of water flowing across a

unit area perpendicular to the flow per unit time) and it can be written as (Moriwaki 2003):

$$q = Q/A = -K \times dh/dx,$$

where  $q$  is the specific discharge [Length(L) / Time(T)],  $Q$  is the water flow rate ( $L^3/T$ ),  $K$  is the permeability coefficient [ $L/T$ ], and  $dh/dx$  is the head gradient [ $L/L$ ].



**Fig. 2.3 Illustration of a capillary tube containing soil in permeability testing (Reddi 2000)**

Different soil columns contain various soil permeabilities and porosities. When a fluid is conducted through a soil column, not all surfaces of the soil particles' are exposed to the fluid. Therefore, only a small fraction of the interactive surfaces (soil specific surfaces area, SSA, see next section) is contacted with the fluid. This fraction of surface area is called the "wetted surface area,  $S_w$ ". In considering the wetted surface area, one can express the relationship for permeability coefficient in the form of Poiseuille and Kozeny-Carman (K-C) model (Yong and Mulligan, 2003):



$$k = (C_s n^3 \gamma) / (\eta T^2 S_w^2)$$

, where

- $k$  is the permeability coefficient that considers permeant and soil structure properties
- $C_s$  is the shape factor, or the cross-sectional face of soil pore space, usually takes on a value of 0.4.
- $n$  is the soil porosity (percentage of pore volume to total soil volume)
- $\gamma$  and  $\eta$  are the density and viscosity of the permeating fluid, respectively; with  $\gamma$  of  $1 \text{ g/cm}^3$  for water and  $\eta$  of  $10^{-2} \text{ g/cm}\cdot\text{s}$  for water
- $T$  is the tortuosity, usually takes on the value of  $\sqrt{2}$

The relationship between soil permeability coefficient ( $k$ ), soil porosity ( $n$ ) and soil wetted surface area ( $S_w$ ) will be demonstrated according to the Poiseuille and Kozeny-Carman (K-C) model in section 5.2.1 and Figs. 5.10 and 5.11.

## 2.3 Chemical properties of soil

### 2.3.1 Specific surface area

Since soil is a colloidal system, the interfaces, which are the boundary regions between two homogeneous phases: solid/liquid or solid/gas. are essential factors controlling the behavior of a colloidal system (Mansour 1993). The soil surface is the part that participates the partitioning of contaminants. Thus, the soil's physical and chemical properties are highly correlated with its surface area. The surface area per gram of soil

( $\text{m}^2/\text{g}$ ) is termed specific surface area (SSA) of soil. The smaller the particle size, the bigger the SSA. Therefore, clay particles and soil organic matter contain the largest specific surface area among all the soil particles. Some clay minerals, such as montmorillonites and illites, possess internal surface area as well. The internal surface area occurs between the layered crystal units. Table 2.3 is a list of the SSA for different soil particles (Reddi 2000).

**Table 2.3 Specific surface areas for various soil particles (Reddi 2000)**

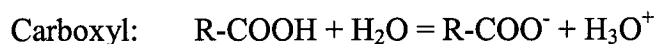
	Soil			Soil clay minerals		
	Loamy sand	Silt loam	Clay	Kaolinites	Illites	Montmorillonites
SSA ( $\text{m}^2/\text{g}$ )	10-40	50-150	150-250	5-39	65-200	600-800

### 2.3.2 Soil surface properties

#### pH-dependent charges

We have mentioned the reactive soil surfaces, where the interactions with contaminants take place. For most of the inorganic soil minerals, during the formation of crystalline structures, broken bonds (between S and O and between O and Al) on the edges of silica and alumina sheets would result due to disruption of the processes (Wild 1993). Thus, the positive or negative charges would result from the unsatisfied valences at these edges. Depending on the pH of the surrounding environment, soil edge broken bonds would contain positive charges when the pH is low and negative ones at high pH.

Some chemical groups associated with external soil surface substances called surface functional groups are another factor contributing to the pH-dependent charges of soil surfaces. Although as little as 5% of the whole soil-water system is organic matter, its surfaces are the most popular sites for the coordination of surface functional groups. Carbon structures combine with nitrogen, oxygen or hydrogen to form most of the functional groups associated with soil organic matter. Some common functional groups are carboxyl (-COOH), hydroxyl (-OH) [phenolic and alcoholic], carbonyl (C=O), amino (-NH<sub>2</sub>) and sulfhydryl (-SH) (Dragun 1998). Their ability to deprotonate (giving protons, when the soil pH is greater than its pKa) and protonate (receiving protons, when the soil pH is smaller than its pKa), depending on the pH of soil system, would develop charges on the soil surface. One of the examples of deprotonation of surface functional group is that as the pH of the environment increases, the hydrogen of a common weak acid functional group, carboxylic acid, would dissociate slightly and the colloidal surface would be left with a negative charge (Petruzzelli 1993):



However, as the pH of the system decreases, such as in moderately acidic to strongly acidic soils, the hydrogen is held tightly and not subject to easy dissociation. Thus the surface negative charge is not apparent. These groups bind hydrogen by covalent bonding. The presence of these functional groups gives the soil surfaces some negative charges. They also control a significant proportion of the activities between the soil surface and contaminants.

### **Permanent charges**

Soil surfaces also contain charges through isomorphous substitution that are associated with the silicate clay minerals. The replacement of cations of similar sizes would take place without disrupting the crystal structure of the minerals. The replacing cations are usually less positive than the replaced cations. Therefore, isomorphous substitution usually results in net negative charges at the soil surfaces. Isomorphous substitution primarily occurs in the internal surfaces of soil clay minerals, the substitution of  $Mg^{2+}$  and  $Al^{3+}$  or  $Si^{4+}$  in the octahedral or tetrahedral layers by ions of smaller valences, such as  $Li^+$ ,  $Mg^{2+}$ ,  $Fe^{2+}$ , and  $Al^{3+}$  (Yong 2001). These charges do not depend on the pH of the soil system and are permanent charges. The net charges of soil surface would combine with the various contributions made by the above mechanisms, including broken edge bonds, surface functional groups, and isomorphous substitution.

### **2.3.3 Cation exchange capacity**

Negative charges existing on the soil surfaces, charge-compensation cations must be held in order to satisfy the electroneutrality. Several locations where cations can be held are: external surfaces of clay minerals and soil organic matter, internal surfaces and structural holes of clay minerals (Reddi 2000). These cations are called exchangeable cations because they can be exchanged by cations of the same valence or twice the amount of cations of half the original valences. Depending on the amount of negative charges that the soil surfaces contain, cation exchange capacity (C.E.C) is a quantitative measurement of the amount of exchangeable cations that the soil surfaces could hold per

unit weight or volume. It is usually expressed as milligram equivalents per 100 gram of soil (meq/100 g soil). The C.E.C for some of the soil types are shown in Table 2.4 (Lines-Kelly 1993):

**Table 2.4 C.E.C for different soil types (Lines-Kelly 1993)**

<b>Soil Textures</b>	<b>C.E.C Range (meq/100 g soil)</b>
<b>Coarse sand</b>	5 – 15
<b>Medium silts</b>	8 – 30
<b>Fine clay minerals</b>	10 – 150
<b>Soil organic matter</b>	> 200

We can recognize from Table 2.4 that different soil textures contain huge variations of C.E.C values. Even within the same area of soils, C.E.C could exhibit wide variations. We can also see from Table 2.4 that soil organic matter and soil clay minerals contribute greatly to the soil C.E.C. The surface functional groups that exist extensively on the surfaces of soil organic matter are the primary reason contributing to its high C.E.C. Therefore, the amount of soil organic matter and what type of soil minerals (C.E.C: 2-5 meq/100g for kaolinites compared to 80–100 meq/100g for montmorillonites) are two major determining factors of C.E.C (Alloway 1993). In agriculture, C.E.C is usually used as an indicator of the soil's storage capacity of positive charged plant nutrients (Kramer 1995), such as calcium ( $\text{Ca}^{2+}$ ), magnesium ( $\text{Mg}^{2+}$ ), potassium ( $\text{K}^+$ ) and ammonium ( $\text{NH}_4^+$ ), with calcium and magnesium being the predominant exchangeable cations. A large cation exchange capacity usually means that this soil can retain a greater amount of nutrients for plant uptake for longer fertilization periods.

The ease of a cation that is held on the soil surface or replaced by another one is mainly dependent upon its valence and hydrated ion size, and is called ion exchange selectivity (Alloway 1990). Since physical adsorption (section 3.3.1.1) of ions onto soil surfaces is mainly from electrostatic forces; according to Coulomb's law, we can say that cations' replacing power will get higher with the increase of ions' valences and with the decrease of hydrated ion sizes. With the exception of hydrogen ion ( $H^+$ ), which behaves like a trivalent ion (Alloway 1993). In addition to ionic charges and hydrated ion sizes, another reason for ion exchange selectivity for soil clay minerals is how well the ions fit in the structure holes (e.g. the hexagonal "holes" between the tetrahedral layers) (Yong et al. 1992). For individual soil fractions, the order of cation replacing powers will vary, but mostly they obey the rules above.

#### **Soil pH and cation exchange capacity**

Soil cation exchange capacity depends strongly on the pH of soil system. From the previous soil surface charge session (section 2.3.2), when the pH of soil system is low ( $pH < 6$ ), most of the pH-dependent charges will not contribute significantly to the soil CEC<sup>1</sup>, because the hydrogen on the exchange sites of both soil organic matter and some inorganic minerals are held strongly. Thus some of the negative exchange sites will be blocked, which results in the reduction of soil CEC. At low pH values, the permanent-charge will be the major CEC contributor. On the other hand, while the soil pH is high, both pH-dependent and permanent charges contribute to the soil CEC. Thus the CEC is high.

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<sup>1</sup> Carboxyl (-COOH) has pKa of 2.34, it would continue deprotonating until soil pH gets lower than 2.34.

### 2.3.4 Diffuse Double Layer (DDL) model

We have shown that the soil reactive surfaces contain charges (section 2.3.2). When they are placed in a soil solution with different contaminants, the various ions in the solution would interact with the surface charges. Since the net charges on soil surfaces are usually negative, there will be a greater concentration of positive ions e.g. cations such as heavy metals accumulating adjacent to the clay surface and an area farther away where there is a greater concentration of anions. The rearrangement of both positive and negative ions near the soil surface will generate an electric double layer or diffuse double layer (DDL) as shown in Fig. 2.5. The Guoy-Chapman model (Yong et al. 1992) assumes that all ions are point charges, and the planar colloid surfaces are infinite; the surface charges, which are involved only in electrostatic forces, are distributed uniformly of the entire surface. The Stern model (Yong et al. 1992) improved it by assuming that some cations were held tightly next to colloid surfaces in a layer of specifically adsorbed cations, which is called the Stern layer (Fig. 2.5). The highest concentration of cations lies within the Stern layer and it decreases in the Gouy-Chapman DDL layer. The lowest concentration of cations is in the bulk soil solution.

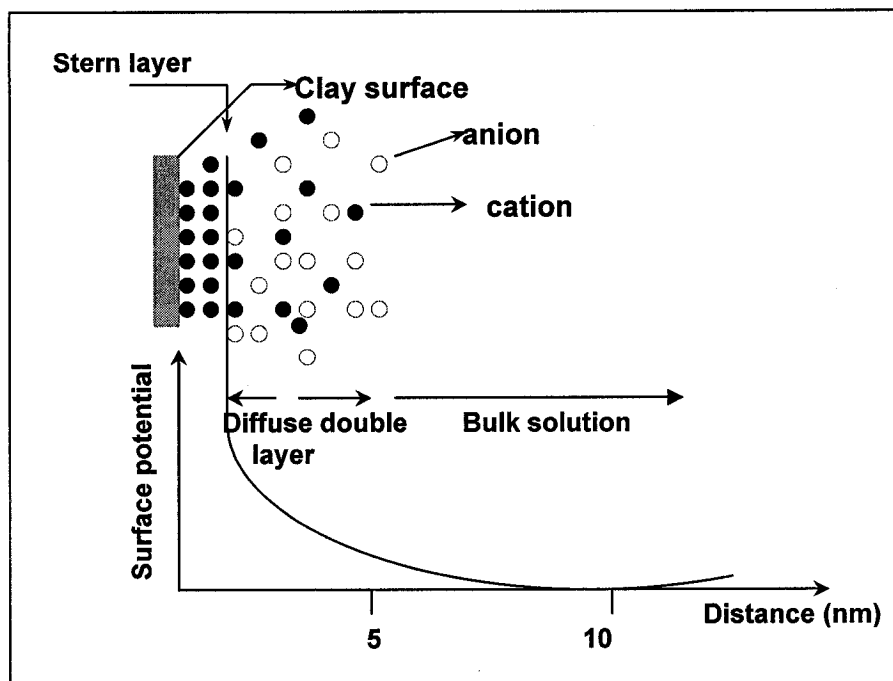


Fig. 2.4 Diffuse double layer (Yong, 2003)

## 2.4 Soil acidity and buffering capacity

The adsorbed cations have different effects on soil acidity and alkalinity. Hydrogen (directly) and aluminum (indirectly) contribute to the increasing concentration of  $H^+$  ion in the soil (Wild 1993), resulting in acid soils, while most of other cations move the soil towards alkalinity. In a humid region, organic and mineral acids are formed naturally as the organic matter decompose. The most commonly found organic acid in soil is carbonic acid ( $H_2CO_3$ ) from the reaction of  $CO_2$  and water. Some other inorganic acids in soil include  $H_2SO_4$  and  $HNO_3$  (Beegle 1995). The generated hydrogen ions will tend to replace other adsorbed cations. In addition, the high precipitation of rain tends to dissolve considerable amount of exchangeable bases, such as calcium and to a lesser extent magnesium, potassium and sodium, from the topsoil. These bases will form



complexes with ligands within the soil solution. Therefore, the great loss of lime (bases) explains why soils in a humid region tend to be more acid (pH ~ 5.6 to 5.8) compared to pH values of 7 and over for semiarid region soils.

In the soil system, there exists a resistance to a change in pH, which is the soil buffering capacity. In an equilibrium soil system, the hydrogen ion concentration controlled by the soil surface force (called “reserve acidity”) is balanced with the one in the bulk soil solution, outside of surface diffuse double layer (called “active acidity”) (Beegle 1995). Whenever H-ions are added to the soil, the temporary increase of H-ions in the soil solution will disrupt equilibrium. Therefore it will force the extra H-ions to be adsorbed onto the soil surface. The soil pH will be retained under a new equilibrium. The higher the soil cation exchange capacity, the better is its buffering capacity due to the fact that there will be more neutralizing bases adsorbed on soil surfaces to combat the added hydrogen ions.

## Chapter 3

### Heavy metals in urban soils

With the increase of human population, more and more cities expand into rural areas. We are surrounded by urban soils, which are located within cities in park areas, recreation areas, community gardens, lawns, and etc. Due to the frequent and intense human activities, urban soils tend to suffer from quality degradation. Among them are soil contamination by heavy metals, atmospheric depositions, organic contaminants, excess fertilizer and herbicide and chemical spills; soil acidification; loss of vegetation and soil erosion due to land development; infections by pathogenic microorganisms. Urban soils are tied closely to the purification of groundwater, which subsequently affects the quality of our drinking water. Thus, the importance of maintaining the quality of urban soils cannot be overemphasized.

Heavy metals, unlike other organic contaminants, tend to remain in the soil system for a long period of time due to their low biodegradation degree. Their presence in soils would persist even after the removal of the pollution sources. Several studies have

reported the elevated levels of heavy metal (Pb and Zn) contents in urban soils at some major cities around the world (Imperato et al., 2002; Murray et al., 2002; Finster et al., 2003; and Mielke et al., 2004). They are shown in Table 3.1 below.

**Table 3.1 Pb and Zn concentration for some major cities in the world**

Cities	Chicago (USA)	Miami (USA)	New Orleans (USA)	Naples city (Italy)	Denizli (Turkey)	Pearl river delta (China)	Montreal (Canada)
<b>Pb (mg/kg)</b>	Min: 27 Max: 4580 Mean: 800	Min: 3 Max: 1088 Mean: 426	Min: 163 Max: 4500 Mean: 656	Min: 4 Max: 3420 Mean: 262	Mean: 337±26	Mean: 335	Min: 90 Max: 973 Mean: 505
<b>Zn (mg/kg)</b>	n/a	n/a	Min: 83 Max: 4818 Mean: 373	Min: 30 Max: 2550 Mean: 251	Mean: 506±20	Mean: 836	Min: 203 Max: 934 Mean: 546

Table 3.1 shows that urban soils suffer degradation by moderate to high heavy metal contents of Pb and Zn (the EPA standard for the Pb and Zn concentrations for residential soils is 300 mg/kg for both metals). Among them, Murray (1999) showed (Table 3.2) the heavy metal contents of some urban contaminated sites in Montreal, Canada.

**Table 3.2 Heavy metal contents of Montreal urban soils (mg/kg soil) (Murray, 1999)**

Sites	Pb	Zn	Cd	Cu	Ni
<b>Area I</b>	Min: 90 Max: 973 Mean: 505	203 934 546	1.9 13.3 7.2	59 417 236	26 116 64
<b>Area II</b>	Min: 233 Max: 764 Mean: 472	209 1350 509	1.0 5.4 2.9	93 476 245	42 243 97
<b>Area III</b>	Min: 234 Max: 1190 Mean: 515	203 701 410	2.8 10.6 6.2	81 196 170	37 114 64

The Quebec residential soil quality criteria ABC - A being the background level of heavy metals in soils, B being the heavy metal levels requiring monitoring, C being the levels requiring soil remediation – are shown in Table 3.3.

**Table 3.3 Quebec residential soil quality criteria**

Classification	Pb (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	Cu (mg/kg)	Ni (mg/kg)
A	50	100	1.5	50	50
B	400	400	5	100	100
C	1000	1500	20	500	500

The data in Table 3.2 shows that the average value of heavy metal contents in Montreal urban soils lies within Quebec soil quality criteria B – C (requiring monitoring, but no remediation planning needed). However, the maximum values for some of the heavy metals exceed (e.g. Pb) or close to (e.g. Zn and Cu) the criteria C threshold.

### 3.1 Impacts of heavy metals

Heavy metals are defined as the metals with an atomic number higher than 38 in their elemental forms (Alloway 1990); there are 38 elements in total. When heavy metals are in trace concentrations, some may be essential as micronutrients. Some heavy metals, called trace elements, are essential in building living tissues in trace amounts, such as Co, Cu, Fe, Mn, Zn, Ni, etc. (Ross 1994). However, we are concerned with those that originated from anthropogenic activities, such as from landfills, chemical waste leachates and sludges. They are generally considered to be pollutants. The heavy metals that we are concerned with are lead (*Pb*), cadmium (*Cd*), chromium (*Cr*), copper (*Cu*), iron (*Fe*), mercury (*Hg*), zinc (*Zn*) and nickel (*Ni*). Most heavy metals can be found widely in our environment including air, water, soil and a limited amount in the tissues of plants and animals.

In aqueous solutions and soil-water systems, heavy metal cations ( $M^{n+}$ ) cannot exist individually, they are generally chemically bonded to water molecules as hydroxy complexes,  $M(H_2O)_x^{n+}$  (Samiullah 1990). In the natural state of soils, most of them contain background levels of heavy metals concentrations; however, in areas with higher agricultural, industrial, and municipal activities, soils might contain excessive levels of concentrations, which could pose a serious threat to human, animals and plants. Most of the heavy metals are found to be toxic in both of their elemental forms and compounds. While the majority of the metals were sorbed onto the soil surfaces by different mechanisms, which we will discuss over the next section, some of them would be released (desorbed) to the ground water owing to some natural changes in the environment, e.g. pH changes and redox chemical reactions. The desorption of heavy metals might impact the environment such as by the further contamination of groundwater.

### **Lead (Pb)**

Lead in mining districts is most found in the ore galena (or lead sulfide.  $PbS$ ) in its 2+ oxidation state (Yong and Mulligan 2004). However, in urban soils, they are found in greater amounts adsorbed onto soil surfaces, especially soil organic matter, in the forms of cerussite (lead carbonate), anglesite (lead sulfate), lead halides, (e.g.  $PbBrCl$ ) and massicot (lead oxide) (Davis 1988). The background concentration of lead on soil is less than 50 mg/kg and it could get as high as 1000 mg/kg or over in some urban areas. Environmental Protection Agency (EPA) uses a limit of 300 mg/kg as the standard limit for lead contamination for soil (Sittig 1994). In general, the mobility of lead in soil is

slow. In urban soils, there are two primary sources of lead contamination: (a) Peeled paint chips from old buildings, which were painted with lead-based paint, mixing with soils adjacent to the houses. (b) Lead from vehicle emissions. The most serious form of exposure to lead is through direct ingestion. Harper (2002) showed that the blood Pb levels of the children living in South African's urban area is much higher than those from other developed countries. This is due to the heavy metal contaminated urban soils and the still large number of vehicles using leaded gasoline. For young children, the internal absorption of lead is approximately five times more efficient than for adults.

### **Cadmium (Cd)**

Compared to other heavy metals, cadmium is relatively rare in nature with its normal background levels of 0.01–1.0 mg/kg (Sittig 1994). The mineral compounds of cadmium are usually in the forms of greenockite (cadmium sulfide, CdS) and otavite (cadmium carbonate, CdCO<sub>3</sub>) (Petruzzelli 1993). It is usually generated from the industrial waste of metal plating, nickel-cadmium batteries, pesticides, etc. It is most toxic in its ionic form, which can form various stable complexes and dissolve easily in water with high mobility at lower pH ranges between 4.5 and 5.5 (Petruzzelli 1993). Soil contamination with cadmium is a serious growing concern since it is a highly toxic and carcinogenic metal. Consumption of contaminated plants containing over 3.0 mg/kg (Angel 1998) of cadmium would threaten the health of humans and animals.

### **Arsenic (As)**

Soils can contain natural levels of arsenic in the range of 3–12 mg/kg (Sittig 1994) or through waste spills and leachates from chemical and manufacturing plants. Most

arsenic in soil exists primarily in its oxidized forms, with both arsenite (+3) and arsenate (+5) the most common valence states (Dragun 1998). Inorganic arsenic compounds are arsenic hydrides (e.g. arsine  $\text{AsH}_3$ ), arsenic halides (e.g. arsenic trifluoride  $\text{AsF}_3$ ), arsenic oxides (e.g. arsenic trioxide  $\text{As}_2\text{O}_3$ ), and arsenic acid ( $\text{H}_3\text{AsO}_4$ ) (Soil Quality Institute 2000). Arsenic could combine with carbon easily to form various organo-arsenic compounds, which were once used as an ingredient as pesticides and wood preservatives, but now are largely replaced by metal-free compounds (Ross 1994). Because arsenic is naturally present in groundwater due to minerals dissolving from soils, we are all exposed to low doses of arsenic. However, these levels are generally safe. Some recent studies (Parvez et al 2001 and Islam 2000) show that arsenic contamination of groundwater has caused millions of wells to produce unsafe drinking water in countries such as Bangladesh, China and Vietnam.

### **Chromium (Cr)**

Chromium is most often found in soils in the oxidation states of Cr (III) and Cr (V) with the hexavalent form being the most toxic (Alloway 1990). They are commonly used in some industrial activities like the manufacture of steel, leather tanning, textile dyeing, etc., and they are essential for man and animals at trace concentration. The background concentration level of chromium in soils is 1.5 – 40 mg/kg (Sittig 1994).

### **Copper (Cu) and Zinc (Zn)**

Copper and zinc can occur both naturally in air, water and in some food and from some industrial activities. They are essential plant nutrients by low level of concentrations. The background concentration for zinc is 15 – 30 mg/kg with 300 mg/kg regarded as the

threshold concentration in soil contamination (Sittig 1994). As with all other heavy metals, they can be adsorbed onto soil surfaces when the concentration is high and their motilities will increase at low pH.

## **3.2 Environmental fate and transport of heavy metals**

### **3.2.1 Interactions of heavy metals**

When heavy metals are released into soils, their initial mobility depends upon the original forms that they are discharged into soil, which in turn depends on the discharge sources. For example, industrial sludges contain a large proportion of organic matter associated heavy metals, while vehicle emissions have greater amounts of metal oxides (Roundhill 2001). The subsequent retention by soil is however controlled by the physical-chemical properties of soil particles, such as soil pH, soil organic matter content and composition, type of soil mineral surfaces, and by the environmental factors such as soil temperature and moisture content (Phadungchewit 1990). All these factors are not independent from each other.

Some common characteristics of soil-metal interactions are (Yong and Mulligan 2004): (1) at high pH, they tend to be retained by the soil system more easily (2) most metals cations accumulate at topsoil and migrate down to groundwater (3) metal cations form complexes with organic and inorganic molecules and get hydrated when surrounded by



water molecules (4) metals can be removed by precipitation with oxides and carbonates. Nevertheless, since under natural conditions, a mixture of heavy metals and other organic and inorganic pollutants are present in the soil solution, the competition between the various compounds for the soil reaction sites also plays an important role in terms of heavy metal retention.

### 3.2.1.1 Physisorption and chemisorption

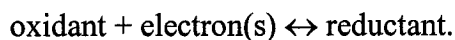
During the processes involving the interactions between soil and contaminant leachates, contaminants would be physically or chemically attracted to the surfaces of soils due to the attraction forces from the soil surfaces. Physical adsorption (or “physisorption”) is a rapid, non-activated process (no activation energy involved) and it is a relatively weak bonding. Physisorption usually involves electrostatic forces. Two common physisorptions are: **(1) Hydrogen bonds:** hydrogen bond can be built between two polar molecules; it is an attraction force between a hydrogen atom in one molecule and an atom with high electronegativity such as O, F or N in another molecule (Das 1985). Hydrogen bonds play an important role in the soil-water system. They are responsible for the cohesion of water molecules and the adhesion of water molecules to soil surfaces by holding the hydrogen in water molecule onto the oxygen in clay surface. They are also responsible for holding layers of clay minerals together (Kramer 1995). **(2) van der Waals:** a very weak force compared to other bonding mechanisms. van der Waals bonding results from the dipole-dipole attractions (Yong and Mulligan 2004), which are

created when some electrons are sifted slightly to one side of the an atom, leading to a net negative charge on this side. Chemical sorption (or “chemisorption”) involves activation energy and the energy level is of the same order of magnitude as in a chemical reaction. Two major types of chemisorption are **(1) Ionic**: the transfer of electrons between two opposite charged ions **(2) Covalent**: the sharing of a pair of valence electrons by two atoms. Covalent bonds usually create more stable molecules, due to the noble gas electron configuration.

### 3.2.1.2 Oxidation - reduction (redox) reactions and hydrolysis

#### Oxidation-reduction (redox) process

The oxidation – reduction (redox) process involves the transfer of electrons between two participants. When two redox couples are placed together, the one with the greater affinity for electrons plays the oxidizing agent (that is reduced), while the other one is oxidized. A general redox equation can be expressed as (Das 1985):



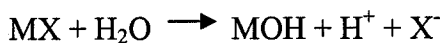
To understand the process of oxidation and reduction in a soil system requires knowledge of the movement and content of water and O<sub>2</sub> in the soil. Since oxygen is one of the most common elements within soil, together with its high electron affinity, it is almost always the electrons receptor in any soil redox reactions. The abundantly present microorganisms in soil are usually required as catalysts in a soil redox process. The

bacteria can extract energy from the reactions or utilize the carbon sources for their growth.

The redox status is an indication of the electron activity in soil-water system. It is commonly expressed as Eh, the redox potential (Dragun 1998). The values of Eh result from a combination of complex oxidation and reduction reactions, participating compounds and the pH of the system. Redox processes aim at lowering the free energy of the whole system for achieving a more stable system (Yong et al. 1992). Most metal cations in soil-water system have more than one oxidation states, of which state they exist mainly depends on the redox status of the soil system. The one state that is the most stable depends on the electronic configuration in the atom's d orbital. One of the impacts of redox reactions in the environmental fate of heavy metals is that they will result in the oxidation state changes of most of the heavy metals and will directly affect the binding properties and reactivity of heavy metals (Yong 2001).

### **Hydrolysis**

Soil minerals are composed of cations and anions. Thus in an aqueous solution, they can ionize to produce various pH values for the soil-water system. Hydrolysis is the reaction of  $H^+$  and  $OH^-$  ions in water with various contaminant components. Taking the example of heavy metals, the hydrolysis reaction can be expressed as (Samiullah 1990):



Since hydrolysis involves  $\text{H}^+$  and  $\text{OH}^-$  ions, it will depend strongly on the pH of the soil-water system and also on the types of metal ions and their oxidation states.

### 3.2.1.3 Ligands and heavy metals complexation

The process of a cation, usually metal ions, combining molecules or anions, which contain free pair of electrons, is known as complexation (Petruzzelli 1993). These chemical combinations known as complexes with the molecules or anions are referred to as ligands. Complexation occurs by building covalent bonds between the cations and ligands. The presence of ligands in soil solution usually leads to an increase of the solubility of metal cations by building complexes (Ross 1994). Wastewater leachates usually contain all kinds of ligands; some common inorganic ligands are  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{CO}_3^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{PO}_3^{3-}$ ,  $\text{CN}^-$ , etc.; functional groups such carboxyl, phenolic, alcoholic and carbonyl groups are common organic ligands (Yong and Mulligan 2004). In general, organic ligands will form more stable complexes with metal ions than inorganic ones and the stability of these complexes will increase with increasing pH due to the increasing deprotonation of the functional groups (Dragun 1998).

Ligand molecules have one or more atoms that are responsible for the chemical composition of ligands, because these atoms contain the free pair of electrons that coordinate with metal cations. In general, the ligands with more than one atom

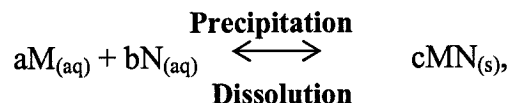
containing free pair of electrons, the more stable complexes they will form with metal cations; these complexes are called chelates. Complexation is important in heavy metal retention in the soil system, because the anionic ligands will compete with the soil surfaces for the sorption of heavy metals cations (Petruzzelli 1993). Therefore, the soil retention capacity will be affected due to the presence of ligands in soil solution.

The kinds of ligands existing in soil solution also influence the stability of complexes they form or the degree it affects the soil retention capacity. Some category of ligands will easily coordinate with cations to form soluble complexes, which subsequently have a high affinity for soil surfaces (Dragun 1998). This type of ligands, such as the most commonly found hydroxide ion in soil organic matter surfaces, will increase the extent that metal cations retained by soil surfaces. While another category of ligands will form soluble complexes with cations, those complexes will not easily be adsorbed onto soil surfaces, as they will flow with the water instead. The examples of this type of ligands are some organic acids, and amino acids, etc.

#### **3.2.1.4 Precipitation and dissolution**

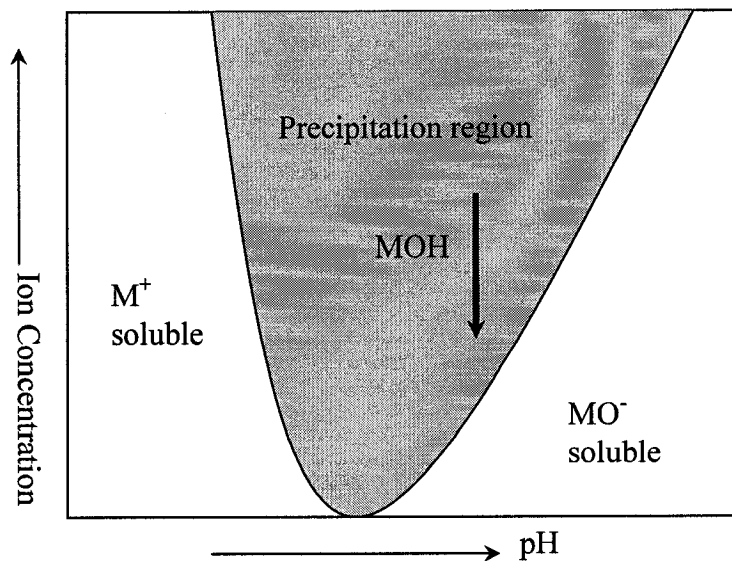
When the metal ion activities (concentrations) in slightly alkaline water are in excess of the solubility product ( $K$ ), precipitation will begin (Kramer 1995). Sorption and precipitation processes all end up removing metal ions from soil solution to solid soil phase. However, in the case of precipitation, new solid compounds will form.

Precipitation is the converse reaction of dissolution. One example of a precipitation-dissolution reaction of AB compounds is expressed as follows:



with  $K$  (solubility product constant) =  $[M]^a[N]^b$ , which will allow us to estimate the concentrations of ions in solution for precipitation to occur. When the rates of both directions are equal, equilibrium is reached.

Some important anions in water that control the precipitation process are carbonates ( $\text{CO}_3^{2-}$ ), hydroxides ( $\text{OH}^-$ ), sulfates ( $\text{SO}_4^{2-}$ ), chlorides ( $\text{Cl}^-$ ), sulfides ( $\text{S}^{2-}$ ), etc.; with  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  forming soluble solid compounds with metals cations and the rest forming insoluble compounds (Nagaraj 2001). The pH of the soil system is one of the primary factors influencing the precipitation process. Fig. 3.1 (Dragun 1998) shows that only at certain ranges of pH that precipitation would start; the onset pH of precipitation is different among different metals and it also depends on if there are other metal cations present in the solution. We can see from the precipitation-dissolution diagram that when pH is low (the left area), the metal cations would be either hydrated or form positive-charged complexes, which will subsequently adsorbed by soil surfaces. When pH increases up to the end of the precipitation, the metal cations will form negatively charged complexes, which will migrate with the water flow (Yong 2001).



**Fig. 3.1 Precipitation-dissolution diagram (Dragun 1998)**

Dissolution will occur when the ionic activity (concentration) is lower than the solubility product. Water is the primary and constant force controlling the dissolution process owing to its polarity (see section 2.2). When water molecules surround a heavy metal compound; the negative-charge part of water (oxygen) will be attracted to the cation while the positive-charge part to the anion. If the bonding between metal cation and anion or the attraction from other elements of the same crystal is not strong enough, water molecules will dissolve the metal compounds by pulling them into solution (Dragun 1998). Some other factors responsible for the dissolution of metal compounds are the addition of inorganic or organic acid or base solvents.

### 3.3 Selective sequential extraction

The toxicity of heavy metals depends not only on their total metal content on soils, but on their mobility and speciation with soil fractions and contaminants. Several studies (Imperato et al., 2002; Murray et al., 2002; Finster et al., 2003; and Mielke et al., 2004) show the total heavy metal contents in urban soils. Only few studies (Yong et al., 1993; Murray, 1999) actually further investigated the speciation of the heavy metals with different soil fractions. As we discussed in Chap. 2 that soil is made up of various fractions, so metals can be retained in the form of exchangeables, oxides, carbonates, or bound to soil organic matter. Each soil fraction with different chemical structure is responsible for adsorbing heavy metals by different mechanisms. Determining the distribution percentages of heavy metals on various soils fractions will provide useful information on the mobility and bioavailability of heavy metals in soils since the heavy metal activities in soils is well correlated to the soil chemical properties.

Selective Sequential Extraction (SSE) is a technique for understanding how metals contaminants being distributed over soil fractions. By destroying the bonding between heavy metals and soil fractions using a series of reagents, metal ions will be released into solution and can be further analyzed with atomic adsorption spectrophotometer (AAS). Appropriate reagents must be used for the sequential extraction for successful analysis. There are five sequential steps with increasingly aggressive reagents. The reagents involved can be categorized as: concentrated inert electrolytes, weak acids,



reducing and oxidizing agents, complexing agents and strong acids (Yong et al. 1992).

These five steps are as follows:

### **1. Exchangeable metals**

Metals that are physically (non-specifically) adsorbed onto soil fractions like clay minerals or soil organic matter by electrostatic forces are ion-exchangeable. Any cation with higher soil affinity can be used to replace targeted metal cations. Some neutral salts such as  $MgCl_2$ ,  $CaCl_2$  and  $KNO_3$  can be used to release the exchangeable metal (Mulligan and Dahr Azma 2003)

### **2. Carbonate bonded metals**

Since soil carbonates usually become more soluble in acidified solution, a weak acidified acetate reagent (e.g. NaOAc, pH adjusted with acetic acid) (Yong et al. 1992) can be applied to dissolve soil carbonates like calcite and dolomite, releasing the metals associated with this fraction of soil.

### **3. Oxides and hydroxides bonded metals**

There are several mechanisms that metals can be bonded to soil oxides and hydroxides. Depending on their crystallization degree (soil oxides have both crystalline and non-crystalline structures, see chap. 2.1.2), metals can be bonded by complexation with the surface functional groups or precipitation. A reducing agent is commonly used for extraction (Yong et al. 1992).

### **4. Soil organic matter bonded metals**

As discussed in section 2.1.3, soil organic matter is the most active soil fraction in terms of interaction with heavy metal contaminants. The soil-metal interactions involving soil

organic matter include: complexation, sorption and chelation (Kumada 1987). The general reagent for releasing metals from this soil fraction is an oxidizing agent.

### 5. Residual fraction

This is a fairly small percentage of metal fraction. It completes the mass balance. A strong acid such as aqua regia is usually applied to destroy the metal bonding within the lattice of silicate minerals (Mulligan and Dahr Azma 2003).

Yong et al. (2004) collected the soil samples from a site adjacent to an active landfill site around South Wales, UK. More than 50 % of the soil particles are in the soil clay range with a high percentage of carbonates (> 18 %) but a low percentage of organic matter (< 5%). The soil solution pH was measured to be 8.6. The result is shown in Table 3.4.

**Table 3.4 Heavy metals affinity for various soil fractions (Yong et al., 2004)**

<b>Heavy Metal</b>	<b>Affinity towards soil fraction</b>
<b>Lead (Pb)</b>	Carbonates > oxides > Soil organic matter > Residual > Exchangeable
<b>Zinc (Zn)</b>	Carbonates > Oxides > Exchangeable > Residual > Soil organic matter

Table 3.4 shows that most of the heavy metals in tested soil samples were precipitated by both soil carbonates and soil oxides. This is consistent with the high soil pH and high carbonate fractions. Mulligan and Dahr Azma (2003) used metal-contaminated sediment samples from a canal area located in a metal and steel industry. The components of these samples were determined to be in the silt fraction with a small percentage of soil clay. The result for the sequential extraction is shown at Table 3. 5.

**Table 3.5 Heavy metals affinity for various soil fractions (Mulligan and Dahr Azma, 2003)**

<b>Heavy metal</b>	<b>Affinity towards soil fraction</b>
<b>Lead (Pb)</b>	Soil organic matter > Oxides > Carbonates > Residual > Exchangeable
<b>Zinc (Zn)</b>	Oxides > Soil organic matter > Carbonates > Residual > Exchangeable

The high percentage of metals retained by the organic matter is due to the high content of organic matter of sediment. Ying Lu (2003) did an interesting comparison of the sequential extraction results for both urban and non-urban soils. It showed that both metals were mostly associated to the soil residual fraction at the non-urban soils; while at the urban soils, they are highly associated with the soil organic matter and soil oxide. This result can be explained from the sources of these heavy metal contaminants at urban soils. Since anthropogenic activities and atmospheric deposition account for the majority of the urban soil pollution. Thus metals would be more associated with the soil oxides and soil organic matter. On the other hand, the less contaminated non-urban soils would have the heavy metals presence at the most immobile form (the soil residual fraction).

Selective sequential extraction analysis can give an indication of the mobility and reactivity of heavy metals in soils and subsequently their availability and potential harmful effects to the environment. When the majority of heavy metals are in higher mobility forms, then some precautions must be taken to prevent the mobile heavy metals from contaminating groundwater.

### 3.4 Heavy metal contents in plant tissues

Recently, urban gardening has become increasingly popular. Many urban dwellers use it as a way of ensuring fresh, pesticide-free produce. Nevertheless, the danger of the accumulation of contaminants from the soils by the garden crops has sometimes been ignored. Due to their smaller areas, urban gardens could easily become the targets of pollution sources from human and industrial activities. The accumulation of heavy metals at urban soils has been reported by several studies (Imperato et al., 2002; Murray et al., 2002; Finster et al., 2003; and Mielke et al., 2004). The correlation between the soil quality and the garden crops was discussed in the studies of Finster (2003), Kang (1995), and Murray (1999).

Attention has been focused on the accumulation of heavy metals (especially Pb) by the plant tissues. Some plants have high tolerance to the toxicity of heavy metal; therefore, they could accumulate higher metal contents. Some reports (Finster, 2003; Kang, 1995) showed the accumulation of Pb by the edible parts of some leafy and roots plants. Children are especially the victims of the direct ingestion of metal-contaminated crops, since the correlation between children's blood lead levels and the direct ingestion of Pb of any form has been proven high (Kang, 1995).

Some studies (Breward, 2003) also pointed out the low correlation of the "total" heavy metal contents in soils and the metal levels being accumulated by plants. They argued that heavy metals are often present in soils by different forms; depending on which soil

fraction they are absorbed by. Some forms of heavy metals are more mobile and bioavailable than others, such as those retained by soil exchangeable and carbonate fractions. The metals absorbed by the soil oxides, organic matter and residual fractions tend to be more stable. It is only the soluble fractions of metals in soils that are highly correlated to the metal levels in plant tissues.

## **Chapter 4**

### **Experimental Methods**

#### **4.1 Sample collection and preparation**

##### **4.1.1 Urban soils and soil sampling procedure**

Conventional way of analyzing the impact of heavy metals in soils system based on a total-control method with prepared, decontaminated soils (most of them soil clays, some with pre-decided fraction of several soil particle sizes). Several tests are carried out after the soils being artificially contaminated with different heavy metal solutions for certain period of time (several days to several months). The contamination period is usually insufficient for the fully acclimation of heavy metals to various soil fractions. Therefore, the heavy metals retained are usually more soluble. As a result, these heavy metals would usually have higher mobilities than those in natural soils (high percentage would be retained by the soil exchangeable fraction). In addition, the contaminating solutions are usually composed of one or several concerned heavy metals, unlike at the natural condition, a multi-metal contaminant is usually present. Thus, the competition from other metals is not usually taken into consideration at the laboratory setting.

Thirty-four soil samples were collected in greater Montreal area. Seven of the soil samples were collected in a communal backyard garden, where nearby heavy traffic has been a concern of the residents; twenty-seven samples were collected near three major streets in downtown Montreal as well as the Westmount (Metro Vendome) area. Fig. 4.1 shows a simple sketch of soil sample locations. Table 4.1 shows a list of sample locations.

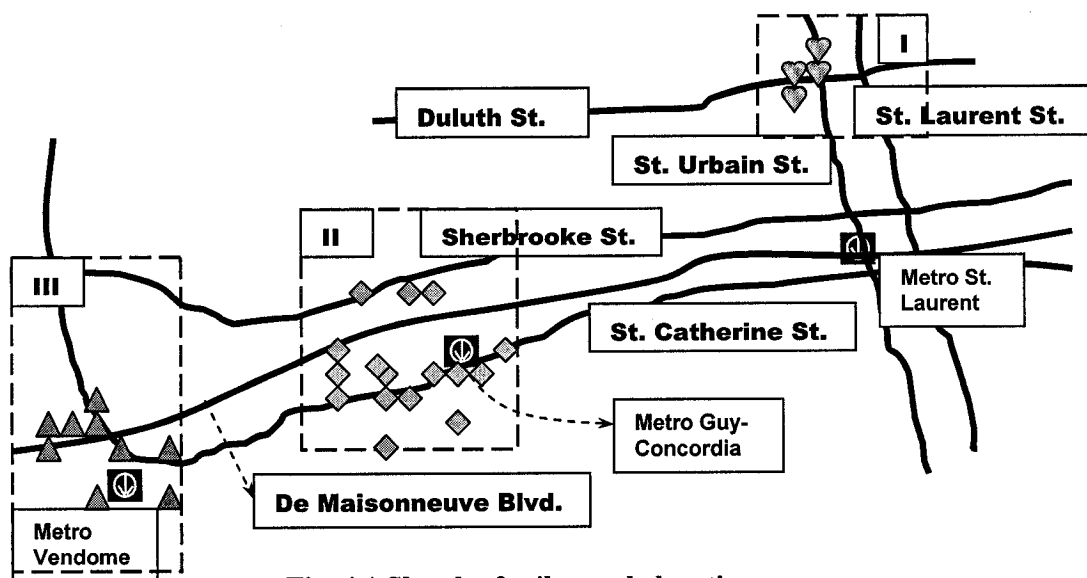


Fig. 4.1 Sketch of soil sample locations

At Fig. 4.1, heart-shaped dots at the upper right corner of the figure represent the soil sample locations for area I (communal garden), diamond-shaped dots at the centre of the figure represent the soil sample locations for area II (near Concordia University) and triangle-shaped dots at the lower left corner of the figure represent the soil sample locations for area III (near Vendome metro).

**Table 4.1 Soil sample locations****Area I:**

<b>Sample numbers</b>	<b>Sample locations</b>
No.1 – no. 7	Communal garden at the corner of St. Urbain St. and Duluth St.
No. 8	Parking lot, corner of St. Urbain St. and Bagg St.
No. 9	Du Parc St.
No. 10	Corner of St. Urbain St. and Duluth St.

**Area II:**

<b>Sample numbers</b>	<b>Sample locations</b>
No. 11	Corner of St. Catherine St. and St. Marc St. –(1)
No. 12	Corner of St. Catherine St. and St. Marc St. –(2)
No. 13	Corner of St. Catherine St. and St. Marc St. – (3)
No. 14	Corner of St. Catherine St. and Fort St.
No. 15	Corner of St. Catherine St. and Chomedey St.
No. 16	Corner of St. Catherine St. and Lamber-closse St.
No. 17	Corner of St. Catherine St. and Mackay St.
No. 18	Corner of St. Catherine St. and St. Mathieu St. – (1)
No. 19	Corner of St. Catherine St. and St. Mathieu St. – (2)
No. 20	Corner of Maisonneuve Blvd. W and Bishop St.
No. 21	Corner of Maisonneuve Blvd. W and Crescent St.
No. 22	Corner of Maisonneuve Blvd. W and Guy St. – (1)
No. 23	Corner of Maisonneuve Blvd. W and Guy St. – (2)
No. 24	Corner of Maisonneuve Blvd. W and Guy St. – (3)
No. 25	Corner of Maisonneuve Blvd. W and Guy St. – (4)

**Area III:**

<b>Sample numbers</b>	<b>Sample locations</b>
No. 26	Corner of Maisonneuve Blvd. W and Bulmer St. – (1)
No. 27	Corner of Maisonneuve Blvd. W and Bulmer St. – (2)
No. 28	Corner of Maisonneuve Blvd. W and Bulmer St. – (3)
No. 29	Corner of Sherbrooke St. and Bulmer St.
No. 30	Corner of Sherbrooke St. and Grey St.
No. 31	Corner of Sherbrooke St. and Vendome St.
No. 32	Corner of Sherbrooke St. and Narlowest St.
No. 33	Corner of Sherbrooke St. and Northcliff St.
No.34	Bulmer St.



All of the samples were taken within a 20-cm depth (topsoil). Two ways of collecting soil samples are random sampling and systematic sampling (Jacobsen 1998). We adopted the systematic sampling scheme; every sampling location (usually a plot of 170 cm × 125 cm) was divided into 4 to 6 sub-areas. A standard steel hand auger was used for the collection of soil sample here. After samples were collected from each sub-area, they were mixed thoroughly to get a uniform soil sample representing each specific sample location. These moist, well-mixed soil samples were stored in several plastic centrifuge tubes before being transferred to the laboratory for various analyses. Drying is crucial before soil analysis, because natural, moist soil particles were hydrated (surrounded by water molecules). This layer of water molecules would prevent reagents from contacting the soil surface, which would subsequently stop the reaction from occurring. Soil samples were left dried at an oven at 105 C for 24 hour; then a series of sieves were utilized for analyzing soil particle size distribution. The aperture opening of each sieve utilized is listed in Table 4.2.

**Table 4.2 Sieve aperture opening**

<b>Sieve No.</b>	<b>No.16</b>	<b>No.20</b>	<b>No.30</b>	<b>No.50</b>	<b>No.100</b>	<b>No.200</b>
<b>Aperture opening</b>	1.18 mm	0.85 mm	0.6 mm	0.3 mm	0.15 mm	0.075 mm

Particle size distribution of our soil samples will be discussed at Chap. 5. As later shown in Table 5.2, most of the soil samples have the majority of the particle sizes ranging from 0.6 mm (sieve No. 30) to 0.15 mm (sieve No. 100); the fractions of soil particles bigger than 0.6 mm (those would not pass sieve No. 30) were discarded.

The fraction of soil particles smaller than 0.15 mm (those pass through sieve No. 100) was kept because small-size particles, especially clay-size particles, influence greatly the soil surface properties. From then on, all the experiments were performed on soil fractions that pass through sieve No. 30.

## **4.2 Batch Tests**

In batch tests, soil particles (air-dried or oven dried) were dispersed into various reagents. Since soil surface properties are the dominating factors influencing the interaction between soil and contaminants, batch tests were used, which assume that all the soil particle surfaces are exposed to reagents and available for interaction, for measuring soil physical and chemical properties. For analyzing soil heavy metal contamination levels of lead and zinc and understanding how they are distributed over various soil fractions, batch tests were also carried out. A general procedure for soil batch tests is depicted in Fig. 4.2; 1.5-5 g of soil was used depending on different experiments.

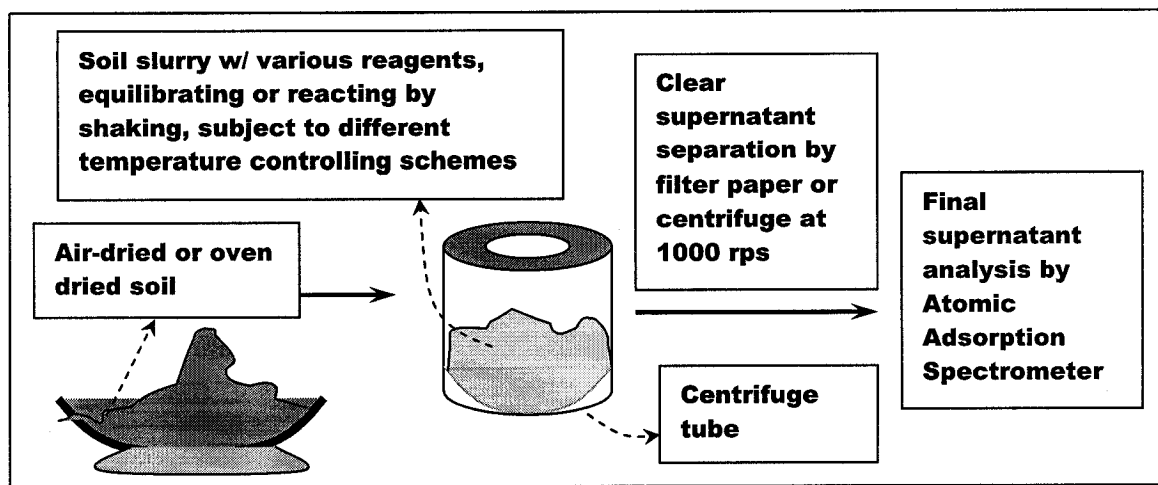


Fig. 4.2 Soil batch procedure

#### 4.2.1 Soil digestion

Soil samples were analyzed for its adsorbed metals content. Different kinds of reagents are responsible for extraction of various fractions. 4 M of hydrochloric acid (HCl) was used here for heavy metals extraction (Rounhill 2001). Because of the strong acidity of HCl, it will extract the most firmly held metals. 20 ml of 4 M HCl was added in each oven-dried soil sample of 2 g. The acid-soil slurry containing centrifuge tubes were placed in a shaker for 24-h shaking. After shaking, all samples were filtered by No. 41 filter paper; the clear supernatants were analyzed by Atomic Adsorption Spectrometer (AAS) for its heavy metal concentrations.

#### 4.2.2 Cation Exchange Capacity (CEC)

There are various ways of measuring soil cation exchange capacity (Polemio 1977); most of them based on the principle of replacing all the cations already existing on soil surface with another cation whose amount will be measured subsequently to determine the concentration of soil cations. Potassium ion ( $K^+$ ) and ammonium ion ( $NH_4^+$ ) are normally used for the determination of soil CEC (Gelderman 1997). The main reason based on the ion exchange selectivity list (section 2.3.2), they are among the medium to high preference, coupled with their extremely weak hydration and the perfect sizes to fit in the structure holes of clay minerals; all of which make them perfect candidate ions for CEC determination. The CEC measurement procedure used as well as the materials is shown as follows (Chapman 1965):

##### **Materials**

1. 5 g oven dry soil
2. Plastic centrifuge tubes with stopper
3. 100 ml beakers
4. 1 M potassium acetate ( $KC_2H_3O_2$ )
5. Methyl alcohol ( $CH_3OH$ )
6. 1 M ammonium acetate ( $NH_4C_2H_3O_2$ )
7. PERKIN ELMER AAnalyst 100/300 Atomic Absorption Spectrophotometer (AAS)
8. Standard potassium solutions (5, 25, 100 ppm) for AAS

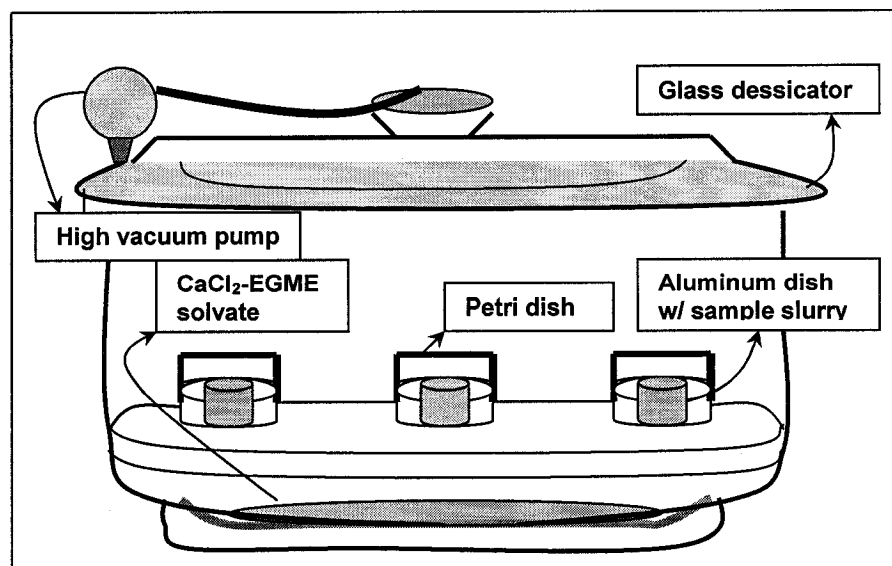
## Procedures

1. 5 g of soil was weighed into each centrifuge tube
2. 20 ml of potassium acetate ( $\text{KC}_2\text{H}_3\text{O}_2$ ) was added to each tube; all tubes were capped and shaken continuously for 5 minutes. This step is to flood the soil and replace the soil cations with  $\text{K}^+$  cations.
3. The sides of the tubes were rinsed with distilled water to wash down the soil particles remaining on the sides to the soil solution.
4. The tubes were centrifuged at 1000 rps for 15 min (or until the supernatant on top of the soil is clear enough for decanting out of the tubes); the clear supernatant was discarded. This step is to pour off the displaced cations.
5. Step 2 to 4 were repeated to make sure that all the soil cations are replaced and discarded.
6. 20 ml of methyl alcohol ( $\text{CH}_3\text{OH}$ ) was added to each tube, which was shaken by hand until all the soil particles are suspended in the solution. The tubes were centrifuged at 1000 rpm for 15 minutes (or until the supernatant is clear enough for decanting out of the tubes); the clear supernatant was discarded. Step 6 can be repeated a couple of times. This step is to wash off the remaining  $\text{K}^+$  that is still at the soil solution (not being adsorbed by soil surface) by an electrically neutral solvent, which will not replace any cation.
7. 25 ml of 1 M ammonium acetate ( $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ) were added to each tube; the tubes were capped and shaken until all the soil particles are suspended in the solution.

8. The sides of the tubes were rinsed to wash down all the soil particles remaining on the sides to the solution; the tubes were then centrifuged at 1000 rpm for 15 min (or until the supernatant on top of the soil is clear enough for decanting out of the tubes).
9. The clear supernatant was poured into a clean 100 ml beaker and steps 7 to 9 were repeated. Steps 7 to 9 are to replace  $K^+$  adsorbed by the soil surface with  $NH_4^+$ , so we can utilize AAS to measure the concentration of the displaced  $K^+$  ions in the solution to know quantitatively how many cations originally present on the soil surface.

#### **4.2.3 Specific Surface Area (SSA)**

The SSA measuring methods are based on wetting soil samples with a polar reagent (Ethylene Glycol Monoethyl Ether (EGME) was used here) and equilibrating them (Heilman 1965). Excess liquid was removed until only a monomolecular layer of reagent adsorbed by soil surface.



**Fig. 4.3 Soil specific surface area measurement**

Periodical measurements (every 1 hour 45min, see step 6 at procedure below) were taken until a constant weight was reached. The apparatus for measuring soil SSA is depicted in Fig. 4.3 above. The reason for choosing EGME over other polar reagents (e.g. ethylene glycol) is that it has a higher vapor pressure at room temperature; thus, the evaporation takes place quickly (Cerato 2002). The whole equilibrium time takes less than 24 h. SSA was calculated by converting the mass of retained liquid to surface area by the following two formula (Cerato 2002):

$$2.86 \blacktriangleright 10^{-4} \text{ g EGME} = \text{monolayer of } 1 \text{ m}^2 \text{ surface area}$$

$$\begin{aligned} [\text{wt. of EGME retained (mg)} / \text{wt. of dry soil (g)}] \blacktriangleright [1 \text{ m}^2 / 0.286 \text{ mg EGME}] \\ = \text{surface area (m}^2/\text{g)} \end{aligned}$$

The materials and procedures for SSA measurements are as follows (Cerato 2002):

**Materials**

1. 2.0 g of air-dry soil
2. Phosphorous pentoxide ( $P_2O_5$ )
3. Ethylene glycol monoethyl ether (EGME)
4. 40 mesh calcium chloride ( $CaCl_2$ )
5. Glass dessicator
6. High vacuum pump

**Procedures**

1. 2.0 g of air-dry soil samples were weighed precisely into aluminum weighing dishes.
2.  $P_2O_5$  was spread over the bottom of the glass dessicator; the weighed soil samples were left in the evacuated dessicator to dry for a period of 24-hour (longer if necessary) while they were measured periodically to obtain a constant weight.
3. Enough EGME was added just to cover the dried soil samples and this was left to equilibrate for around one hour.
4. 130 g  $CaCl_2$ -EGME solvate was prepared: 120 g  $CaCl_2$  was weighed and dried in oven (100 C) for 1 hr. 100 g of the hot, dry  $CaCl_2$  was added to 30 g EGME; they were mixed thoroughly. After cooling, the  $CaCl_2$ -EGME solvate was spread over the bottom of the dessicator after the  $P_2O_5$  was removed.
5. Sample-EGME slurry was placed in Petri dishes and the cover was laid loosely over.



6. Samples were placed in the dessicator and evacuated with a high vacuum pump for 45 min. The dessicator was left close for 1 h before weighing the samples. This last step was repeated for several times until a constant weight is obtained.

#### **4.2.4 Selective Sequential Extraction**

The sequential extraction by Yong et al. (1993) was adopted here. The procedure is listed in Table 4.3. 1.5 g of soil was used for each step. After each digestion, the supernatant was filtered and the clear supernatant was collected from each fraction. These supernatants were analyzed with AAS (as suggested by the AAS user's manual on standard atomic absorption conditions, an operational parameter of wavelength of 283.3 nm for lead and 213.9 nm for zinc were chosen).

Table 4.3 Selective Sequential Extraction Procedure

Order of sequence	Procedure and chemical reagents	Fraction
1	Extraction of metals w/ 8 ml of 1 M $MgCl_2$ (pH 7) for 1 hr	Exchangeable
2	Extraction of metals w/ 8 ml of 1 M $NaOAc$ adjusted to pH 5 w/ acetic acid for 5 hr	Carbonates
3	Extraction of metals w/ 20 ml of 0.04 M $NH_2OH.HCl$ in 25 % (v/v) acetic acid (pH 2.5) at 96° C for 6 hr	Oxides and hydroxides
4	(i) Extraction of metals w/ 3 ml of 0.02 M $HNO_3$ and 5 ml of 30 % $H_2O_2$ (pH 2) for 2 hr at 85 ° C (ii) 3 ml of 30 % $H_2O_2$ (pH 2) at 85 ° C for 3 hr (iii) 5 ml of 3.2 M $NH_4OAc$ in 20 % (v/v) $HNO_3$ , diluted to 20 ml at room temperature for 30 min	Soil organic matter
5	Digestion at 90 ° C w/ 25 ml of dilute aqua regia (50 ml $HCl$ , 200 ml $HNO_3$ and 750 ml water) for 3 hr	Residual fraction

Ac = acetate

#### **4.2.5 Micro-digestion of plants**

Three regular garden plants and grass were taken from the communal garden, where abnormally high concentrations of Pb and Zn were found. They were quickly transported back to the laboratory and thoroughly washed, first with tap water to clean off any attached soil particles, and then with still water. Plant roots and leaves were separated and both were dried in an oven at 105 C for three days, until they reached their final equilibrium weights. Each plant sample was ground to powder separately. 0.5 g of each sample were weighed out and put into microwave digestion vials with 10 ml of concentrated HNO<sub>3</sub>. Because of the high organic matter of plant tissue, pre-digestion is needed before all vials were put into the microwave to prevent the build up of NO<sub>2</sub> - gas which remains inside the microwave vials during the digestion process. All vials were left in a fume hood for three days before being microwave digested. The program of microwave plant digestion suggested by a study of Kang and Mcpherson (1995) was implemented here. After the digestion, the vials were left in the microwave overnight until the pressure inside the vials was released. The filtered supernatants were analyzed with AAS to determine the concentrations of Pb and Zn.

#### **4.3 Soil column tests: permeability tests and leaching tests**

To cause minimal disturbance with soil structure, soil columns, also called leaching cells, were utilized with intact soil samples. Similar to field conditions, only a limited amount of soil particles in a column come in direct contact with the leachates, thus

participating in the soil-contaminant interaction. The leachate is usually composed of a highly complex mixture of organic and inorganic compounds. Soil pore geometry, which conducts the passage of contaminant fluids, along with the physical and chemical properties of both soil and contaminants, plays an equally crucial role in soil-contaminant interaction. Permeability tests and soil leaching tests were carried out in a soil column, which is depicted in Fig. 4.4.

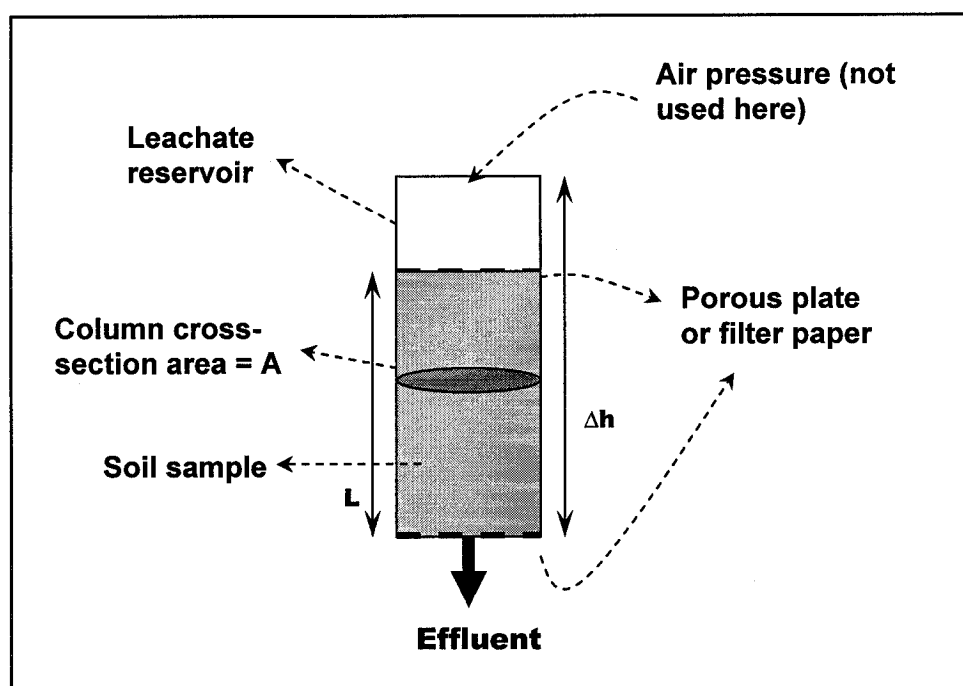


Fig. 4.4 Soil leaching cell

Water was leached through soil columns for permeability tests; the flow of effluent was measured. From Fig. 4.4 and Darcy's law, the permeability coefficient for the soil samples was calculated by:

$$q = Q/A = -K \triangleright \Delta h/ L$$

For the leaching tests, three types of leachates were leached through soil columns: a 300-mg/L solution of lead chloride, a 300-mg/L solution of zinc nitrate and a solution of mixed lead and zinc with each of equal concentration of 300 mg/L. Pore volume (pv) is a useful measuring unit for leachate passing through soil column. One pore volume is defined as the volume of leachate filled up the void space of each soil column. Continuous leachate was leached through soil column, effluents were collected every 2 to 10 pv of solution passing through the column and their concentrations were analyzed with atomic adsorption spectrophotometer. The relative concentration of effluent to influent was plotted versus number of pore volumes in a breakthrough curve.

## Chapter 5

### Results and Discussion

#### 5.1 Batch Tests

Soil particles were dispersed in solutions (reagents) for measuring their physical and chemical properties, such as specific surface area (SSA) and cation exchange capacity (CEC). Heavy metals contamination levels in the soils were tested. A further measurement of how metal cations being distributed onto different fractions of soil was carried out by subjecting soil particles to sequential reagents, which aims at destroying the bondings between metals and soil surfaces. This measurement is called selective sequential extraction.

##### 5.1.1 Specific Surface Area and Cation Exchange Capacity

The cation exchange capacities (CEC) as well as specific surface area (SSA) for some selected soil samples is shown in Table 5.1 below. For those soil samples with both the SSA and CEC measured, the values of CEC divided by SSA (the underlined numbers) were also calculated for later analysis.

**Table 5.1 Cation exchange capacity and specific surface areas for soil samples**

Sample no.	No.1	No.2	No.3	No.4	No.5	No.6	No.7	No.8
CEC (meq/100g)	54.4	63.5	70.5	60.6	68.4	n/a	63.7	63.2
SSA (m <sup>2</sup> /g)	n/a	n/a	n/a	11.7	13.8	7.1	n/a	18.28
CEC/SSA (meq/100g)/(m <sup>2</sup> /g)	n/a	n/a	n/a	<u>5.2*</u>	4.96	n/a	n/a	<u>3.46*</u>

Sample no.	No.9	No.10	No.12	No.15	No.16	No.17	No.18	No.20
CEC (meq/100g)	20.0	64.7	51.4	66.3	30.9	87.4	22.8	27.1
SSA (m <sup>2</sup> /g)	N/a	n/a	11.1	n/a	n/a	18.32	27.2	10.12
CEC/SSA	N/a	n/a	<u>4.63*</u>	n/a	n/a	<u>4.77*</u>	<u>0.84*</u>	<u>2.68*</u>

Sample no.	No.21	No.25	No.26	No.28	No.29	No.30	No.31	No.32
CEC (meq/100g)	34	76.9	29.9	39.7	20.6	40.6	18.3	27.2
SSA (m <sup>2</sup> /g)	N/a	10.9	23.43	7.25	30.16	26.6	20.5	n/a
CEC/SSA	N/a	<u>7.06*</u>	<u>1.28*</u>	<u>5.48*</u>	<u>0.68*</u>	<u>1.53*</u>	<u>0.89*</u>	n/a

\* The underlined numbers (CEC/SSA) were calculated for later analysis

Table 5.1 shows that the SSA of the collected soil samples ranged from 7.1 m<sup>2</sup>/g to 30.16 m<sup>2</sup>/g. This is in the range of loamy sand according to Table 2.3.

### 5.1.2 Heavy metals concentrations in soils

Seven soil samples from the communal garden in area I, locations shown in Fig. 5.1, were digested with acid to test six concerned heavy metals concentrations: lead (Pb), zinc (Zn), chromium (Cr), cadmium (Cd), copper (Cu) and nickel (Ni). The results are shown in Fig. 5.2.

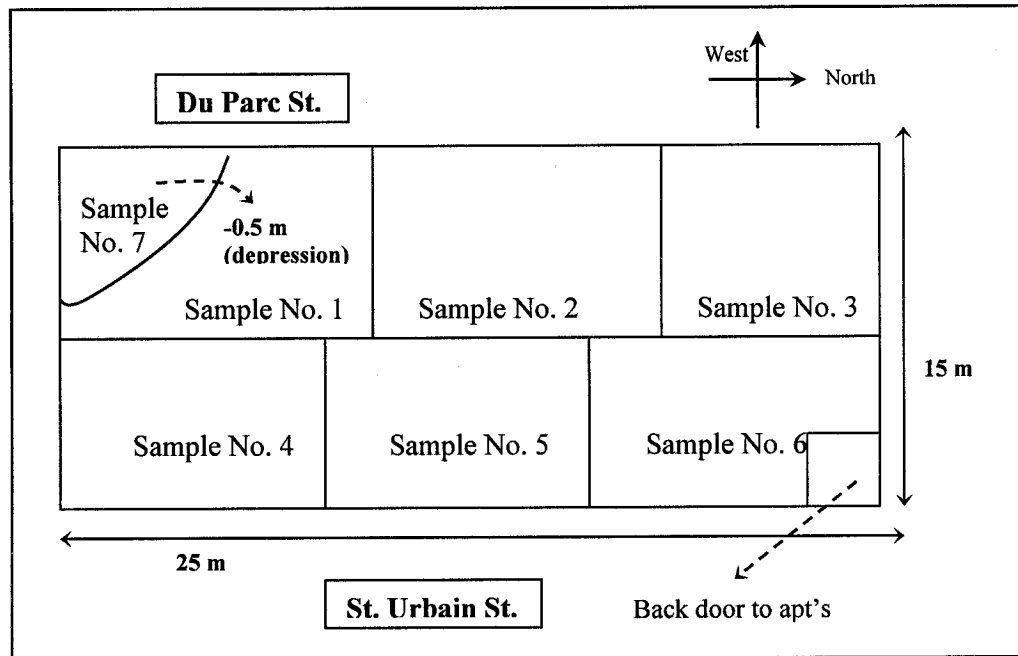
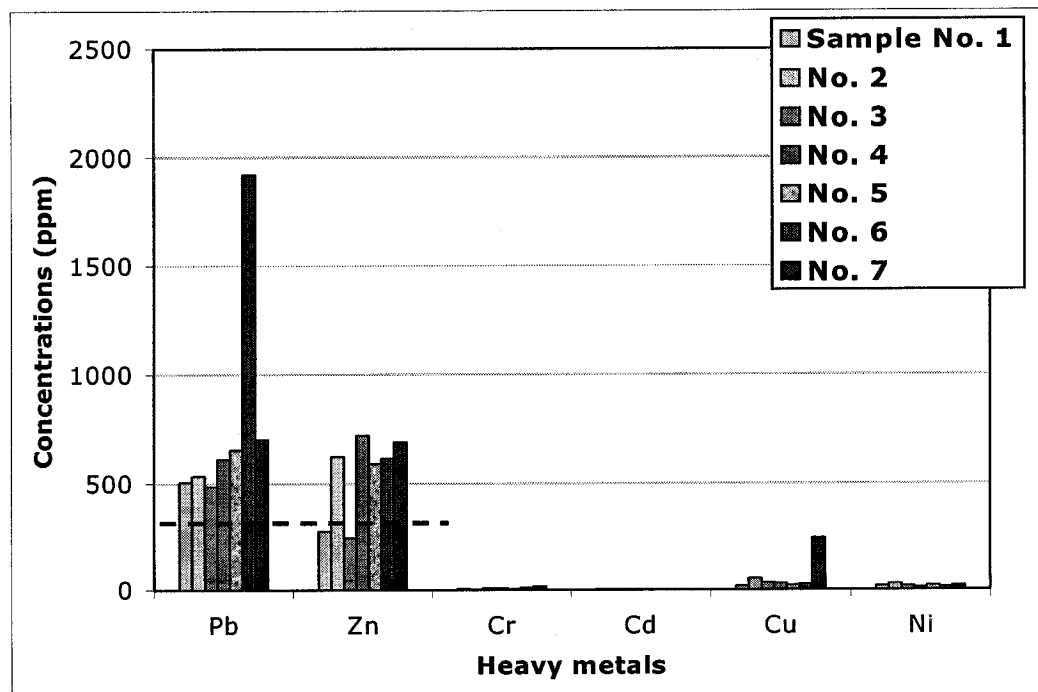


Fig. 5.1 Soil sample location map for communal garden

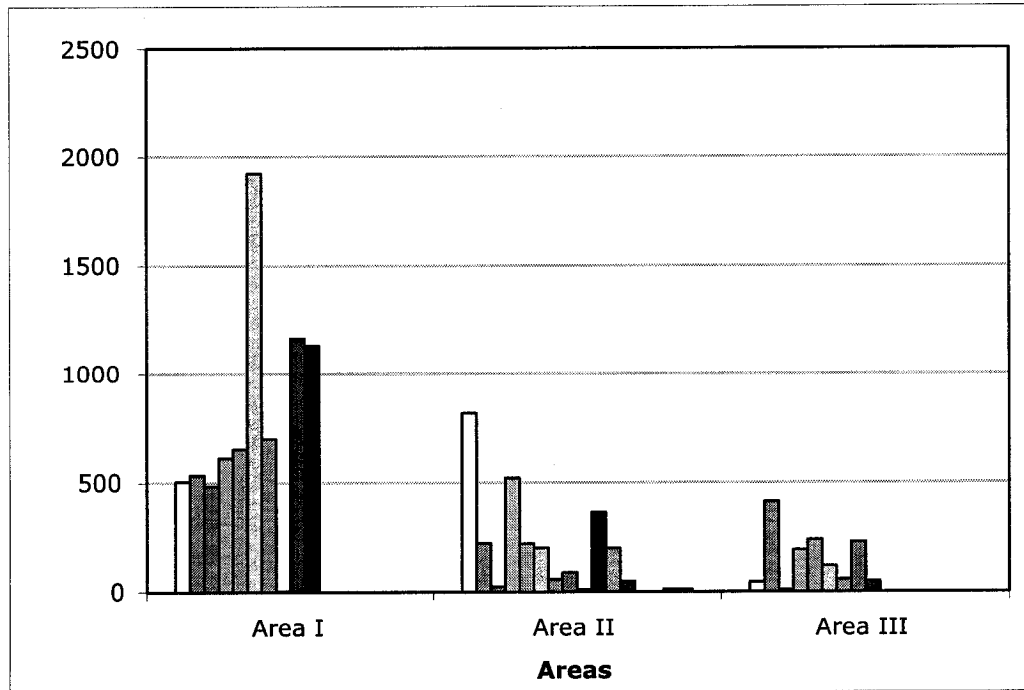


\* Two dash lines indicate the acceptable concentration for both Pb and Zn

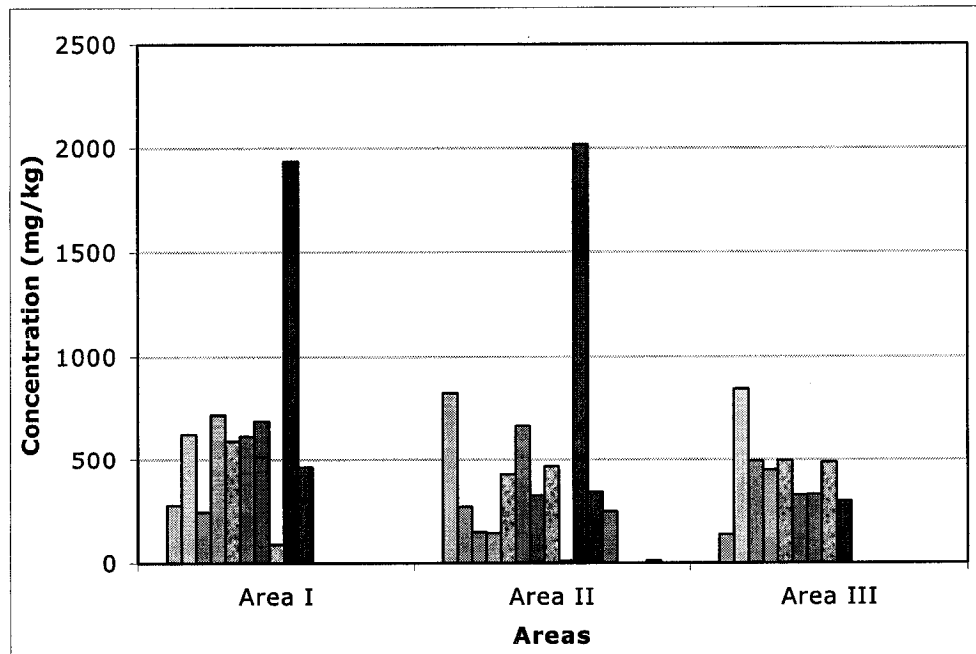
Fig. 5.2 Acid digestion of six heavy metals on soil samples taken from communal garden



From Fig. 5.2, it can be seen that four out of the six heavy metals tested are within their background concentration levels, thus they do not pose a threat to human health by the standard posed by Environmental Protection Agency (EPA) and Quebec soil quality criteria. However, lead and zinc concentrations, especially at sample No. 6, were significantly higher than the threshold concentrations (the acceptable concentration for both Pb and Zn is between two dash lines) (Sittig 1994). The rest of the experiments were focused on these two heavy metals in terms of their fate and transport in soil. The Pb and Zn concentrations on these soil samples are shown in Fig. 5.3 and 5.4:



**Fig. 5.3 Lead concentrations on soil samples taken from various locations of three areas (Area I: 7 samples from communal garden and 3 samples from locations near it, Area II: 15 samples from near Concordia University. Area III: 9 samples from near Metro Vendome; detailed map of each soil sample location shown in Fig. 4.1)**



**Fig. 5.4 Zinc Concentrations on soil samples taken from various locations of three areas**

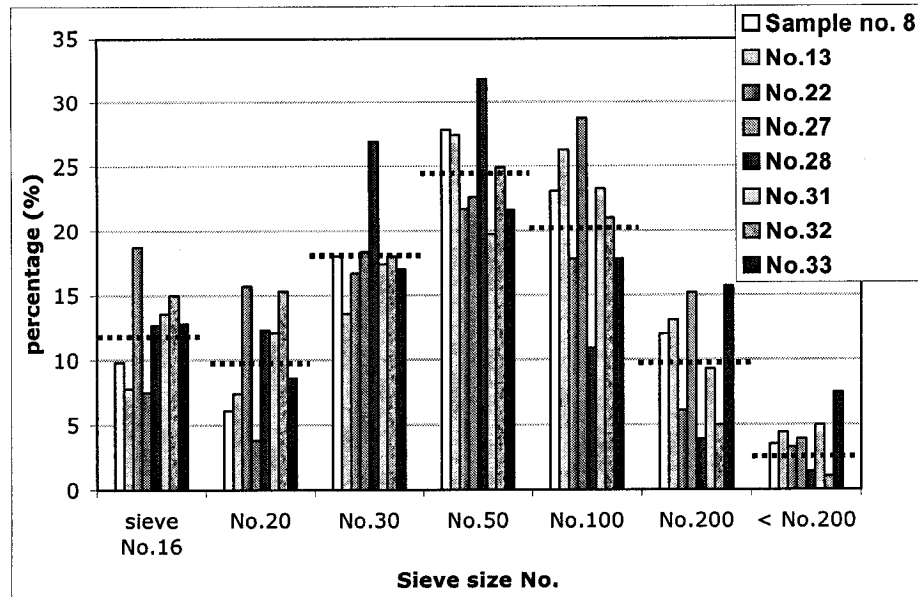
It can be seen from Fig. 5.3 and Fig. 5.4 that the concentration of lead and zinc in urban soils varies greatly. The lead concentration ranges from almost zero (5 mg/kg) to almost 2000 mg/kg; the zinc concentration ranges from 100 mg/kg to over 2000 mg/kg. According to the Quebec soil quality criteria (chap. 3), the Pb and Zn contents of the collected soil samples are within B – C range (requiring monitoring, but no remediation planning needed). The results show the same level of heavy metal contamination at urban soils from Montreal area as those reported by Murray (1999).

As discussed in Section 3.1, the sources of heavy metal contamination come from all kinds of natural and human activities. Depending on the history of land uses and the degree of leaching by rainfall and urban runoff in the areas, huge variations of heavy metal concentrations are expected. The concentrations of both lead and zinc in the communal garden and locations near it in area I are substantially higher than the rest of the samples (zinc concentrations in area II are also high). Urban communal gardens are relatively small compared to agricultural land, but they are likely to be subjected to more concentrated pollution, since all of the gardens are easily contaminated from atmospheric and particulate material deposition. Sometimes, the garden soil contamination problem can be associated with the housing being established on previously contaminated sites. The area where the communal garden situated used to be the dumping ground for some industrial activities and it is situated a few blocks away from two major traffic streets, St. Urbain St. and Du Parc St. (seen from Fig. 5.1), with old buildings surrounding it and some garden furniture scattered around. The metals deposited from the industrial waste, the emissions deposit and other contamination

sources such as paint chips, the disposal of bonfire ash, and the lead lost from children toys all contribute to the higher concentrations of lead and zinc. The high soil organic matter, which generally adsorbed greater amounts of heavy metals due to its active surface reactions compared to other soil fractions (see soil organic matter in Section 2.1.3), present at the communal garden also account for the high levels of heavy metals contents.

### **5.1.3 Particle size distribution**

Eight samples from both area II and III were collected for particle size distribution analysis using the sieving technique. The available sieves in the environmental laboratory ranged from sieve No. 10 (aperture opening: 2.0 mm) to sieve No. 200 (aperture opening: 75  $\mu\text{m}$  ( $10^{-3}\text{mm}$ )). Every particle size portion of each sample was digested with acid to determine the lead and zinc concentrations. The particle size distribution for some soil samples is shown at Fig. 5.5 and 5.6; the heavy metal concentration for each soil particle size range is presented in Table 5.2.



\* Dashed lines representing the mean values for each sieve size group

Sieve No.	16	20	30	50	100	200	< 200
% Mean ( $\bar{m}$ )	12.2	10.2	18.3	24.7	21.1	10.0	3.8
Standard deviation ( $\alpha$ )	3.5	4.1	3.6	3.8	5.2	4.4	1.9

Fig.5.5 Particle size distribution of various soil samples

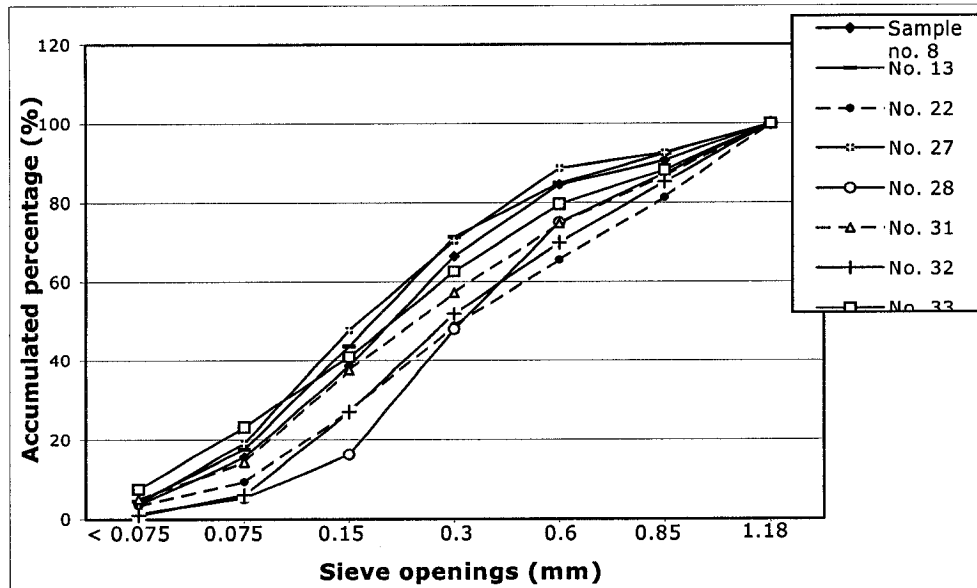


Fig. 5.6 The accumulated percentage of soil particles passing through various sieves

Table 5.2 Heavy metal content of each soil particle size range

Sample No. 8	Pb concentration (mg/kg)	Zn concentration (mg/kg)	Sample No.13	Pb concentration (mg/kg)	Zn concentration (mg/kg)
Sieve no.			Sieve no.		
No.16	n/a	n/a	No.16	n/a	n/a
No.20	2	84	No.20	3	91
No.30	1	76	No.30	12	147
No.50	2	80	No.50	15	88
No.100	0	71	No.100	16	109
No.200	0	56	No.200	12	106
< No.200	23	133	< No.200	29	173

Sample No.22	Pb concentration (mg/kg)	Zn concentration (mg/kg)	Sample No.27	Pb concentration (mg/kg)	Zn concentration (mg/kg)
Sieve no.			Sieve no.		
No.16	n/a	n/a	No.16	n/a	n/a
No.20	44	185	No.20	358	858
No.30	36	157	No.30	406	968
No.50	39	167	No.50	400	961
No.100	39	158	No.100	418	1013
No.200	45	194	No.200	396	942
< No.200	57	263	< No.200	422	1030

Sample No.28	Pb concentration (mg/kg)	Zn concentration (mg/kg)	Sample No.31	Pb concentration (mg/kg)	Zn concentration (mg/kg)
Sieve no.			Sieve no.		
No.16	n/a	n/a	No.16	n/a	n/a
No.20	0	46	No.20	94	320
No.30	9	53	No.30	163	396
No.50	6	67	No.50	185	382
No.100	29	163	No.100	263	484
No.200	84	339	No.200	122	375
< No.200	131	451	< No.200	112	356

Sample No.32	Pb concentration (mg/kg)	Zn concentration (mg/kg)	Sample No.33	Pb concentration (mg/kg)	Zn concentration (mg/kg)
Sieve no.			Sieve no.		
No.16	n/a	n/a	No.16	n/a	n/a
No.20	46	316	No.20	85	316
No.30	39	327	No.30	113	337
No.50	48	333	No.50	131	329
No.100	59	357	No.100	108	343
No.200	56	350	No.200	248	510
< No.200	65	n/a	< No.200	260	522

From Table 5.2, Fig. 5.5 and 5.6, most of the samples chosen for analysis have the majority of soil particles ranging between sieve no. 30 (aperture opening: 0.6 mm) and no. 100 (aperture opening: 0.15 mm), which are in the range of coarse sand to fine sand. All of the samples have a small percentage (< 7.5 %) of particles passing sieve no. 200 (aperture opening: 0.075 mm); these portions of soils are either silt or clay-size particles. We can conclude that the soil samples collected can be categorized as sand or loamy sand according to the textural classification (Fig. 2.2). This result is consistent with the one from section 5.1.1. It was shown in section 5.1.1 that the specific surface area (SSA) for the collected soil samples is in the range of loamy sand. We have shown that soil particles with smaller diameters accumulate heavy metals more easily due to their higher specific surface area and cation exchange capacity. From the Pb and Zn concentrations absorbed in each particle size range shown in Table 5.2, the fraction of soil particles with diameters smaller than 0.075 mm (< sieve no. 200), which makes up less than 10 % of the whole particle size ranges, does show a stronger retention capacity for lead and zinc over larger particle sizes in most of the samples. However, the differences in heavy metal accumulation over different particle size ranges are not significant. We can conclude that among the sandy soil particles, heavy metals such as lead and zinc will generally absorb onto soil particles of different size ranges with preference absorption on smaller particle sizes.

### 5.1.4 Selective Sequential Extraction

The soil sample originally contaminated with higher concentrations of Pb and Zn (> 300 mg/kg) was further investigated to determine how these heavy metals cations are distributed within soil fractions. Selective sequential extraction was performed on thirteen soil samples and Table 5.3 shows the results of the extractions.

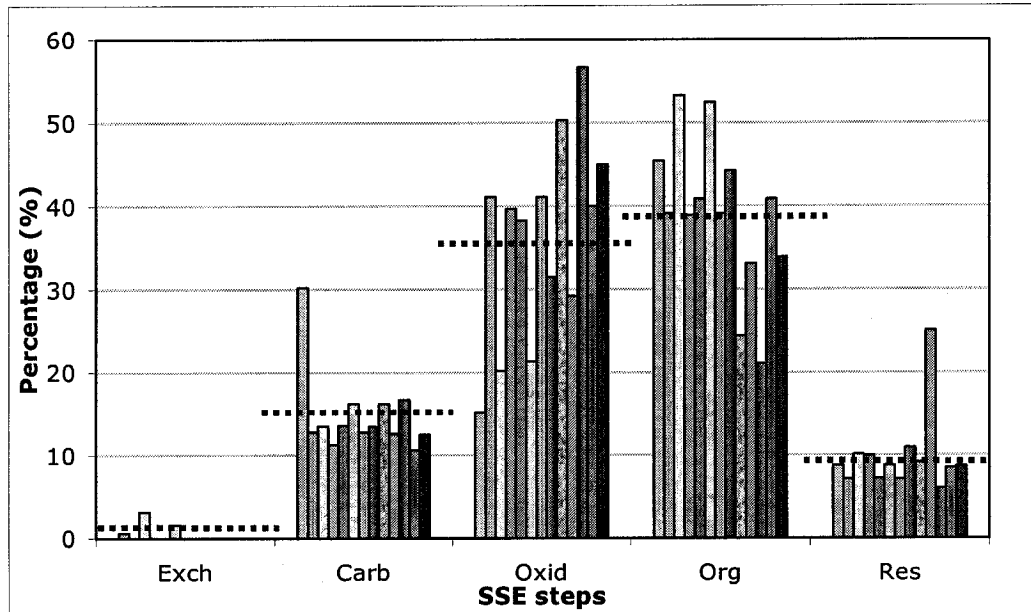
**Table 5.3 Selective Sequential Extraction of Pb and Zn of various soil samples with the total Pb and Zn concentrations analyzed by AAS after acid digestion**

<b>Sample No. 1</b> (Soil heavy metal content: Pb = 506 mg/kg; Zn = 279 mg/kg)		
<b>Step</b>	<b>Percentage (%) of the total concentration, Pb</b>	<b>Percentage (%) of the total concentration, Zn</b>
1—exchangeable	0.61	0.66
2 – carbonate	30.2	13.6
3 – oxides	15.1	44.37
4 – O.M.	45.45	21.9
5 – residual	8.78	19.4
<b>Sample No. 2</b> (Soil heavy metal content: Pb = 534 mg/kg; Zn = 623.5 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0.43
2 – carbonate	12.7	13.4
3 – oxides	41.1	58.5
4 – O.M.	39.1	12
5 – residual	7.1	15.6
<b>Sample No. 3</b> (Soil heavy metal content: Pb = 486 mg/kg; Zn = 248 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	3.16	1.4
2 – carbonate	13.38	15.0
3 – oxides	20.19	42.84
4 – O.M.	53.2	27.58
5 – residual	10.08	13.16



<b>Sample No. 4</b> (Soil heavy metal content: Pb = 610.5 mg/kg; Zn = 720 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0.4
2 – carbonate	11.3	9.1
3 – oxides	39.7	58.9
4 – O.M.	38.92	11.7
5 – residual	9.94	19.9
<b>Sample No. 5</b> (Soil heavy metal content: Pb = 653.5 mg/kg; Zn = 590.5 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0.48
2 – carbonate	13.5	22.2
3 – oxides	38.3	50
4 – O.M.	40.9	10.7
5 – residual	7.2	16.6
<b>Sample No. 6</b> (Soil heavy metal content: Pb = 1923 mg/kg; Zn = 615 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	1.62	1.09
2 – carbonate	16.19	17.64
3 – oxides	21.28	46.0
4 – O.M.	52.14	22.78
5 – residual	8.77	11.77
<b>Sample No. 7</b> (Soil heavy metal content: Pb = 703 mg/kg; Zn = 690.5 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0.43
2 – carbonate	12.7	13.4
3 – oxides	41.1	58.5
4 – O.M.	39.1	12
5 – residual	7.1	15.6
<b>Sample No. 9</b> (Soil heavy metal content: Pb = 1166.25 mg/kg; Zn = 1937.5 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0
2 – carbonate	13.35	7.06
3 – oxides	31.5	50.68
4 – O.M.	44.21	23.88
5 – residual	10.94	18.39

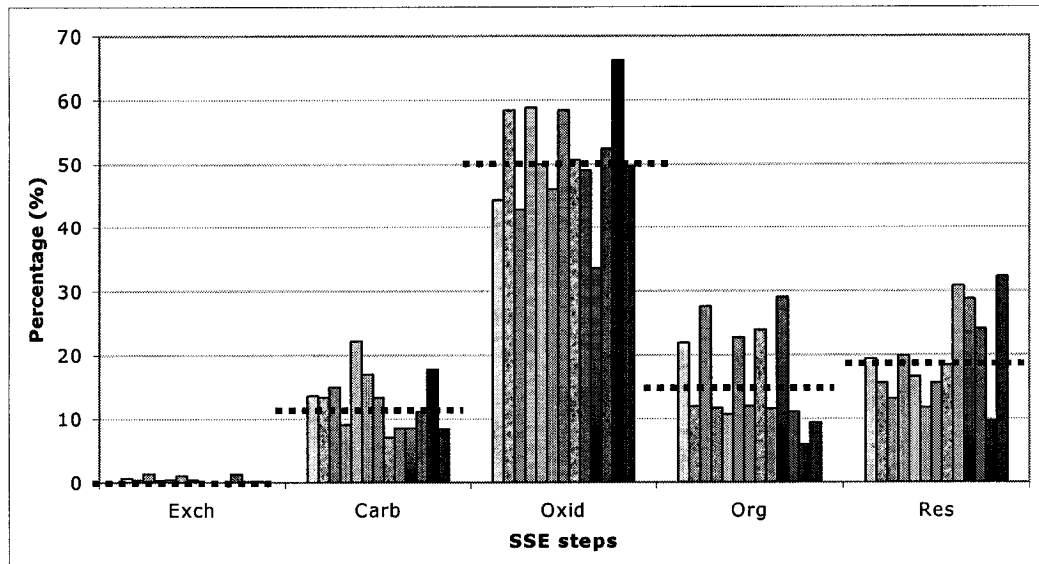
<b>Sample No. 10</b> (Soil heavy metal content: Pb = 1132.5 mg/kg; Zn = 462.5 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0
2 – carbonate	16.21	8.55
3 – oxides	50.23	49.03
4 – O.M.	24.41	11.55
5 – residual	9.15	30.88
<b>Sample No. 11</b> (Soil heavy metal content: Pb = 820 mg/kg; Zn = 824 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0
2 – carbonate	12.54	8.54
3 – oxides	29.24	33.6
4 – O.M.	33.14	29.05
5 – residual	25.08	28.81
<b>Sample No. 20</b> (Soil heavy metal content: Pb = 363.3 mg/kg; Zn = 2018.5 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0.2
2 – carbonate	16.7	17.8
3 – oxides	56.4	66.4
4 – O.M.	21	6
5 – residual	6	9.7
<b>Sample No. 27</b> (Soil heavy metal content: Pb = 413 mg/kg; Zn = 843.5 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	1.3
2 – carbonate	10.6	11.1
3 – oxides	40	52.5
4 – O.M.	40.9	11.1
5 – residual	8.5	24
<b>Sample No. 30</b> (Soil heavy metal content: Pb = 240 mg/kg; Zn = 494 mg/kg)		
<b>Step</b>	<b>Percentage (%), Pb</b>	<b>Percentage (%), Zn</b>
1—exchangeable	0	0.2
2 – carbonate	12.4	8.4
3 – oxides	45	49.8
4 – O.M.	33.9	9.4
5 – residual	8.7	32.3



(a)

\* Dashed lines representing the mean values for each step group

Step	Exch	Carb	Oxid	Org	Res
% Mean ( $\bar{x}$ )	0.41	14.75	36.09	38.95	9.8
Standard deviation ( $\alpha$ )	0.91	4.8	11.62	8.98	4.61



(b)

\* Dashed lines representing the mean values for each step group

Step	Exch	Carb	Oxid	Org	Res
% Mean ( $\bar{x}$ )	0.5069	12.75	50.86	16.13	19.7
Standard deviation ( $\alpha$ )	0.46	4.37	8.13	7.41	6.99

**Fig. 5.7** Five selective sequential extraction steps on 10 different soil samples for (a) Pb and (b) Zn , different patterns representing various soil samples (sample No. 1 to No. 30 from left to right).

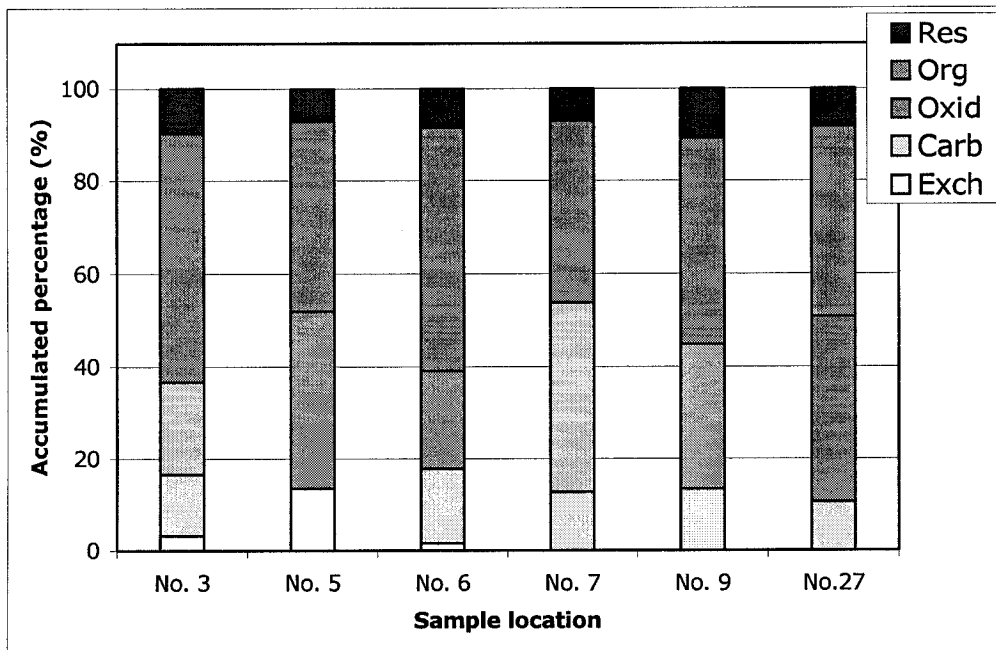


Fig. 5.8 Selective sequential extraction of Pb for six representative soil samples versus the accumulated percentage of each extraction fraction

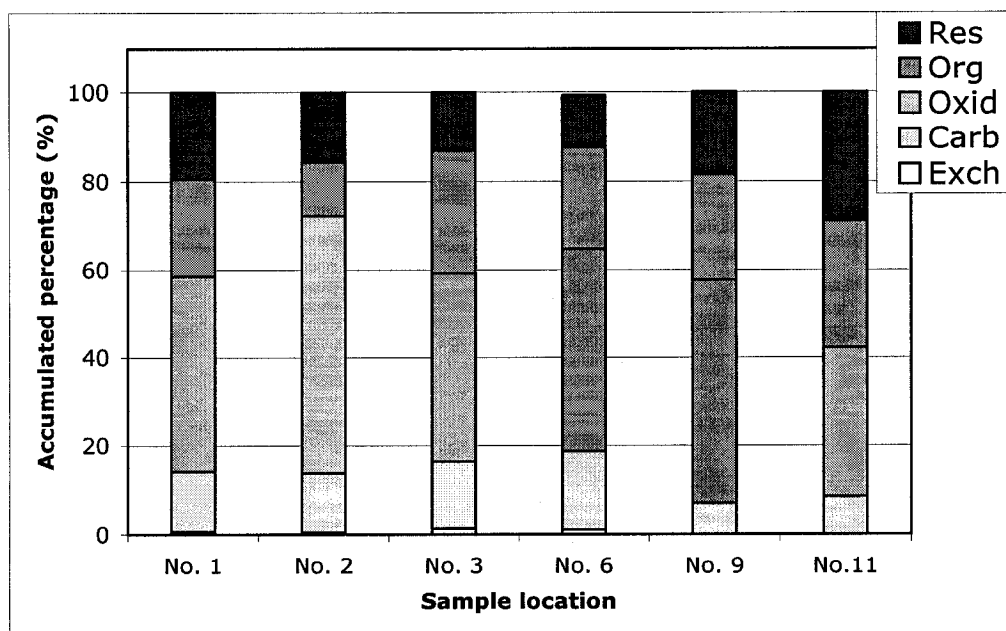


Fig. 5.9 Selective sequential extraction of Zn for six representative soil samples versus the accumulated percentage of each extraction fraction

From Table 5.3, Fig. 5.7, 5.8, and 5.9 it can be seen that both lead and zinc have different affinities towards different soil fractions, the order of the affinity is detailed as Table 5.4 below.

**Table 5.4 Heavy metals affinity for various soil fractions**

<b>Heavy Metal</b>	<b>Affinity towards soil fraction</b>
<b>Lead (Pb)</b>	Soil organic matter $\approx$ Oxides > Carbonate > Residual > Exchangeable
<b>Zinc (Zn)</b>	Oxides > Residual $\approx$ Soil organic matter > Carbonate > Exchangeable

We can see that both Pb and Zn have higher affinity towards soil fractions of soil organic matter and oxides; while little of both metals are attached to the exchangeable fraction. The humus in soil organic matter has large specific surface area and various functional groups attached; therefore, a series of chemical and physical interactions between metals cations and soil organic surfaces, including complexation, adsorption and chelation, take place there. Therefore, heavy metals would be bound to soil organic matter more easily than other soil fractions. Metals bound to the exchangeable fraction of soil are mostly physically adsorbed (by electrostatic force) to the soil surfaces, thus the bonding is weaker compared to other binding mechanisms. The moderate to high degree of leaching by rainfall and the competition from other cations present in the leachate solution possibly explains why only a limited amount of Pb and Zn were retained by this soil fraction. The results agree with the ones of Lu's paper (2003) (discussed at section 3.3), the highly association of Pb and Zn with soil oxides and organic matter is partially due to the sources of these heavy metals. It is also important to point out that these results are highly operationally defined, since the redistribution of

metals would happen during the extraction processes. Therefore, the data only shows the relative speciation of metals by soil fractions.

In comparison to Mulligan and Dahr Azma (2003) shown in Table 3.5, for lead (Pb), the affinity order agrees completely. As for zinc (Zn), oxide is the most abundant soil fraction that contains zinc for both results. Another example of sequential extraction is by Yong (2001). A prepared illite soil artificially contaminated with Pb before the sequential extraction test showed the highest affinity towards the soil exchangeable fraction, followed by the soil carbonates, the residual fraction is at the bottom of the Pb affinity. The sequential extraction test for Zn is not specified. This result showed that due to the insufficient of metal acclimation time over the soils, artificially contaminated soils usually retain metals with less strong bonding. Thus, the heavy metal mobility is usually higher in these types of soils in comparison to the natural soils.

#### **5.1.5 Microwave digestion of plants**

Some recent studies (Günthardt-Goerg 2003, Boominathan 2003) indicate the retention capacity of plant tissues. According to section 5.1.2, the concentrations of both Pb and Zn of all the soil samples in area I of the communal garden are at abnormally higher levels. Therefore, some common plants, such as grass, crinum lily, and other unknown plants, grown at this garden were extracted with a spade and transported to the laboratory for analysis. Table 5.6 below shows the result of microwave digestion of plants taken from the communal garden.

**Table 5.5 Concentrations of Pb and Zn of communal garden plants after microwave digestion**

Plants	# 1 (leaf)	# 1 (root)	# 2 (leaf)	# 2 (root)	# 3 (leaf)	# 3 (root)
<b>Lead (mg/kg)</b>	40	16	44	Not detectable	Not detectable	Not detectable
<b>Zn (mg/kg)</b>	65	78	82	91	82	67

As seen in Fig. 5.2 and Fig. 5.3, most of the Pb and Zn concentrations at the communal garden soil are well above 500 mg/kg with some samples above 1000 mg/kg. The microwave digestion of communal garden plants (Table 5.6) shows that the amount of Pb and Zn retained by plant tissues (leaves and roots). Zn is one of the essential elements (Mylavarapu 2002) for the metabolism of plants, typically ranging from 20 – 100 mg/kg in plant tissues, depending on the given plant. Pb is not required for plant growth, thus the amount of Pb in plant tissue is usually low (< 50 mg/kg). Therefore, the level of Pb and Zn detected from the collected plant tissues is within their typical range in plants. The low heavy metal contents at the collected plant tissues can be explained from the result of selective sequential extraction. Table 5.4 shows that the soil exchangeable fraction retained the least levels of Pb and Zn, which indicates the low bioavailability of these both metals in our soil samples.

## 5.2 Column Tests

To mimic field conditions, soil samples were packed into a column to maintain intact soil structures. Both permeability tests (section 5.2.1) and leaching tests (section 5.2.2) were carried out in the soil columns.

### 5.2.1 Permeability Tests

Permeability tests were performed on ten soil samples. Table 5.7 indicates the permeability coefficients calculated from Darcy's Law. They all range from  $10^{-3}$  to  $10^{-1}$  cm/sec, which is within the range of silty (fine) sand.

**Table 5.6 Soil permeability tests**

Sample no.	No. 10	No.11	No.17	No.23	No.24	No.25	No.26	No.28	No.30	No.31
Permeability coefficient (cm/sec) $\times 10^{-2}$	2.3	2.4	0.875	3.9	2.1	1.6	0.63	1.9	0.61	3.5

In section 2.2.2, it was mentioned that by considering soil permeating fluids as well as soil structural properties, the permeability coefficient ( $k$ ) can be expressed according to the Poiseuille and Kozeny-Carman (K-C) model:

$$k = (C_s n^3 \gamma) / (\eta T^2 S_w^2)$$

From this model, Fig. 5.10 can be obtained. The soil permeability tests resulting from Table 5.7 can be plotted (as shown by  $\otimes$  signs) in this graph to determine the



corresponding wetted surface area for each soil column test. In comparison a study results of Yong and Mulligan (2003), which are shown in Fig. 5.11, these soil samples have a much higher soil permeability coefficient than those in that study. In this study it was in the range of  $10^{-4}$  to  $10^{-6}$  compared to the range of  $10^{-9}$  to  $10^{-6}$ . A much smaller soil wetted surface area is thus expected.

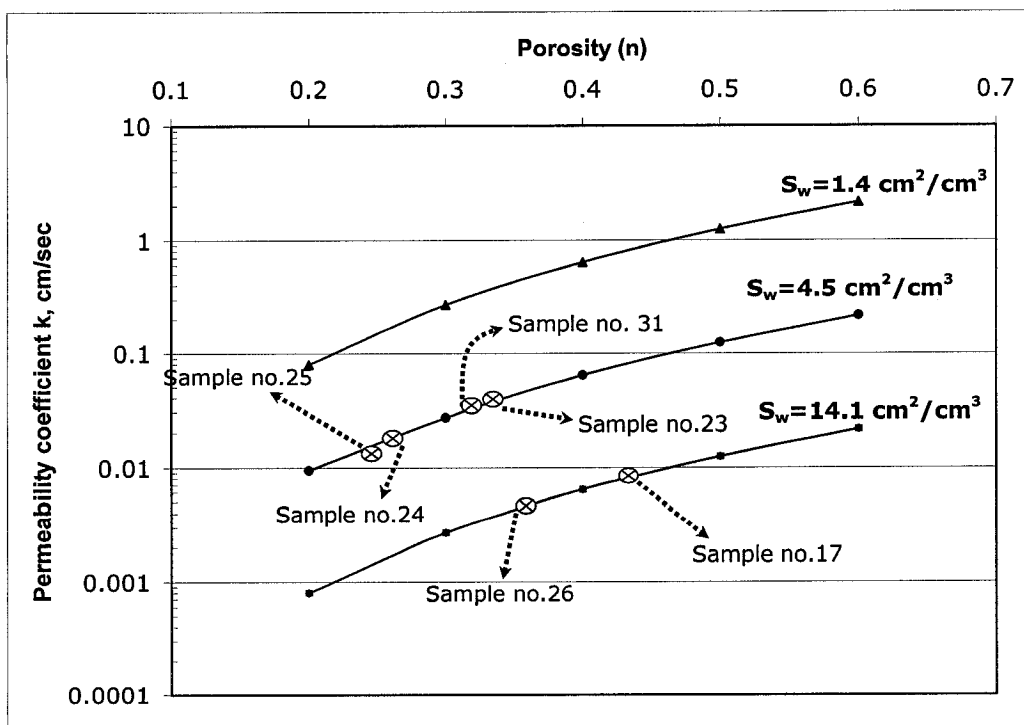


Fig. 5.10 Soil wetted surface area ( $S_w$ ) in relation to the permeability coefficient ( $k$ , cm/sec) and porosity of the soil columns

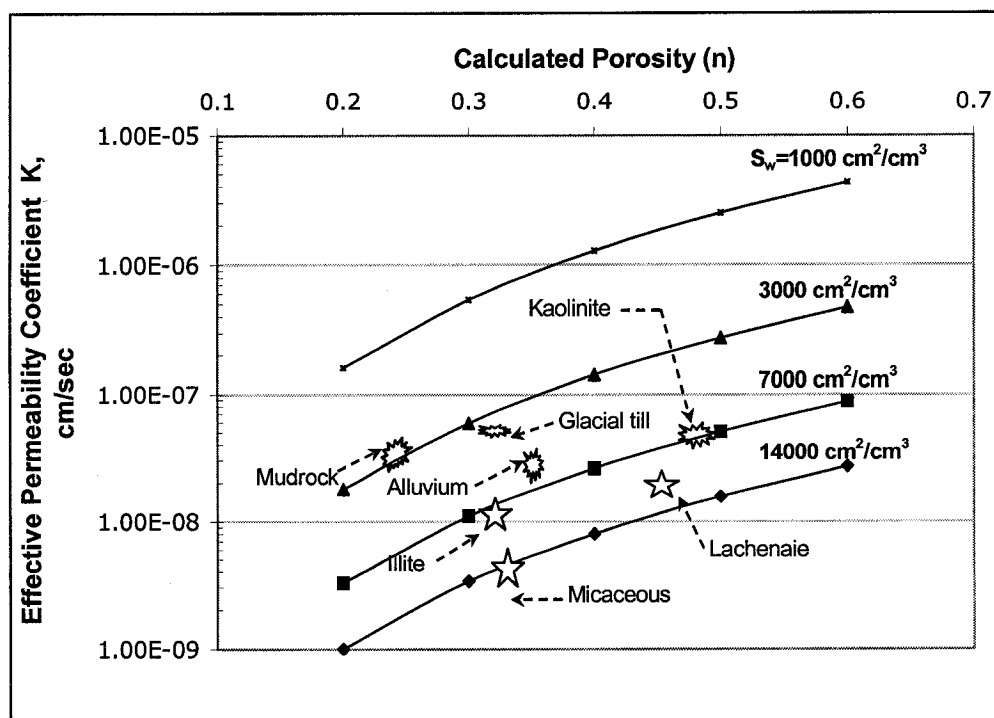
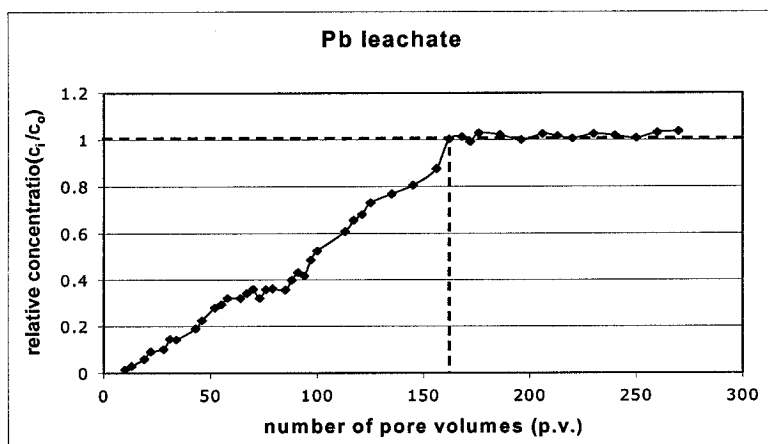


Fig. 5.11 Wetted surface area ( $S_w$ ) of soils in relation to the effective permeability coefficient and porosity of the soil (Yong and Mulligan, 2003)

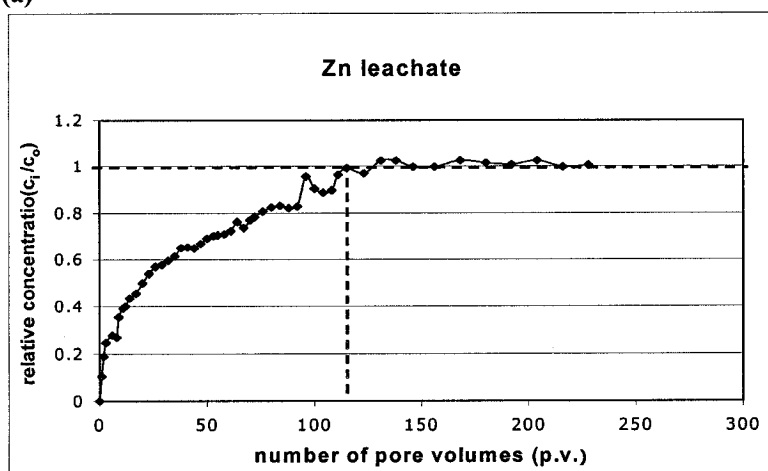
### 5.2.2 Leaching Tests

Five soil samples with low initial heavy metal contents were chosen for the performance of leaching tests. A sixth sample (sample no. 10) was also chosen for comparison purpose. They were divided into two sessions: (I) soils were leached with single heavy metal solutions, e.g. lead and zinc, of concentration of 300 mg/(L water) (II) soils were leached with mixed lead and zinc solution with each heavy metal of the same concentration of 300 mg/L. Figs. 5.12 to 5.17 exhibit the breakthrough curves of each leaching test.

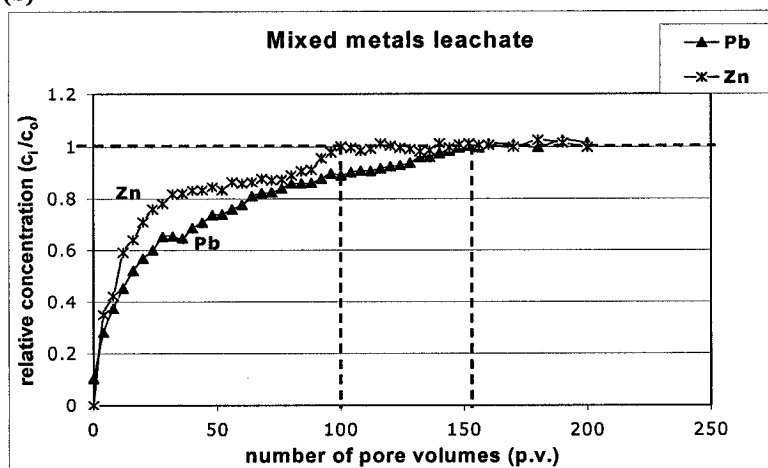
I. Sample no. 8; initial metal content: Pb (5 mg/kg), Zn (89 mg/kg)



(a)



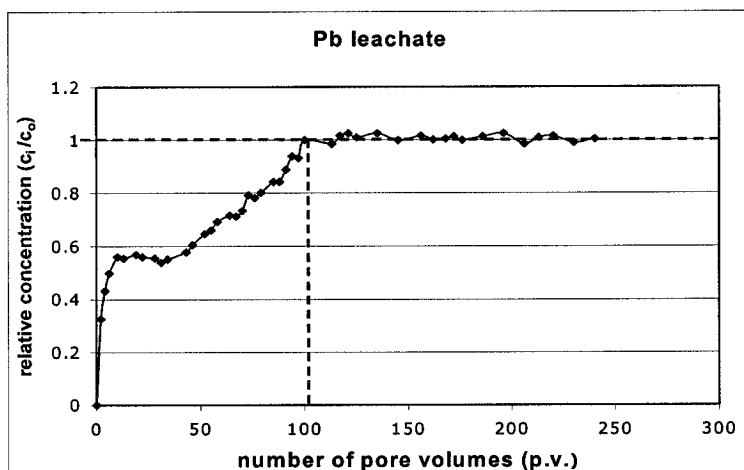
(b)



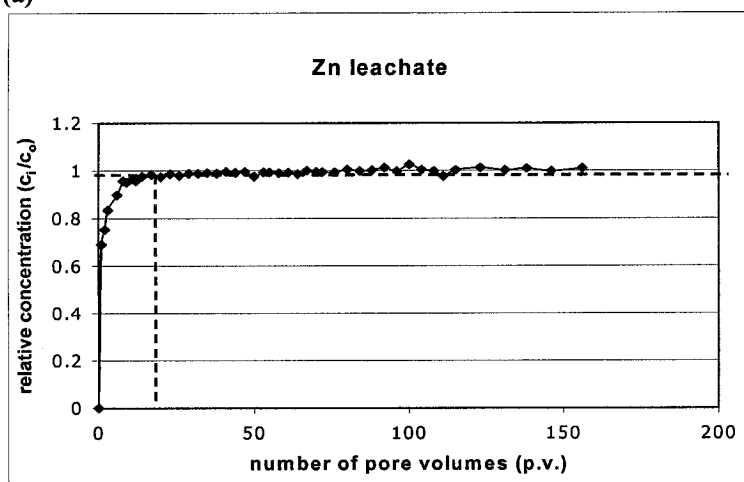
(c)

Fig. 5.12 Breakthrough curves for lead and zinc leachate, the dashed lines indicate the breakthrough pore volumes for (a) single Pb leachate - 162 pv (b) single Zn leachate - 115 pv (c) mixed Pb and Zn leachate - Pb (156 pv), Zn (100 pv)

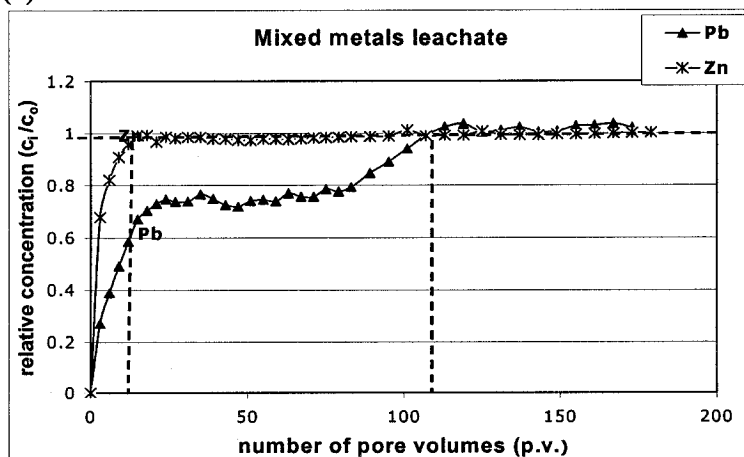
II. Sample no. 10; initial metal content: Pb (1132 mg/kg), Zn (462 mg/kg)



(a)



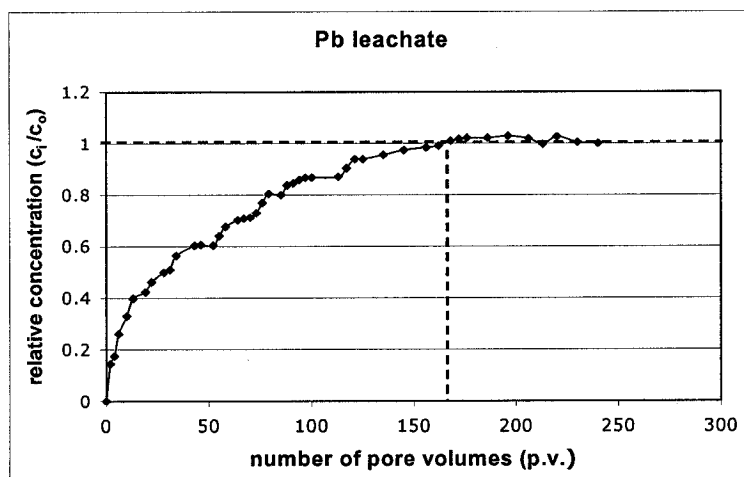
(b)



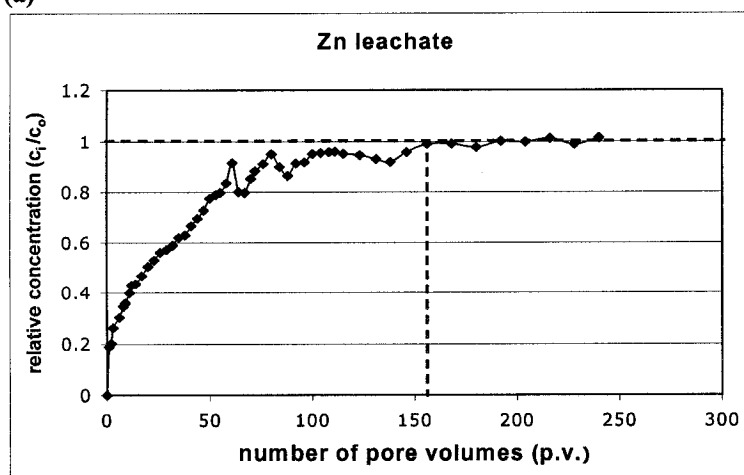
(c)

Fig. 5.13 Breakthrough curves for lead and zinc leachate, the dashed lines indicate the breakthrough pore volumes for (a) single Pb leachate - 100 pv (b) single Zn leachate - 17 pv (c) mixed Pb and Zn leachate - Pb (107 pv), Zn (15 pv)

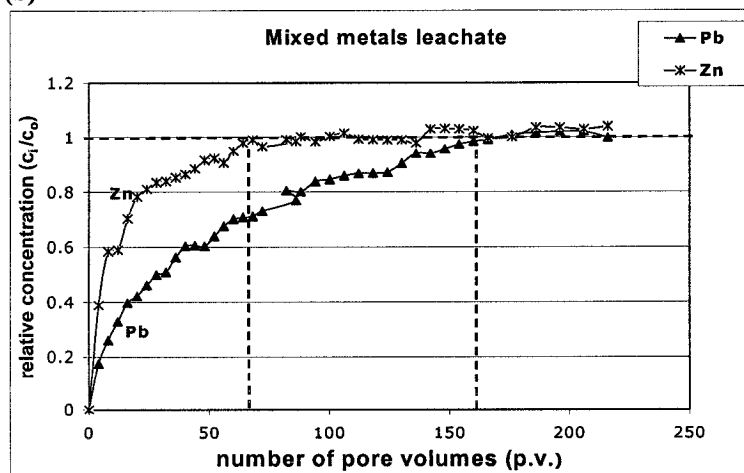
III. Sample no. 19; initial metal content: Pb (10 mg/kg), Zn (10 mg/kg)



(a)



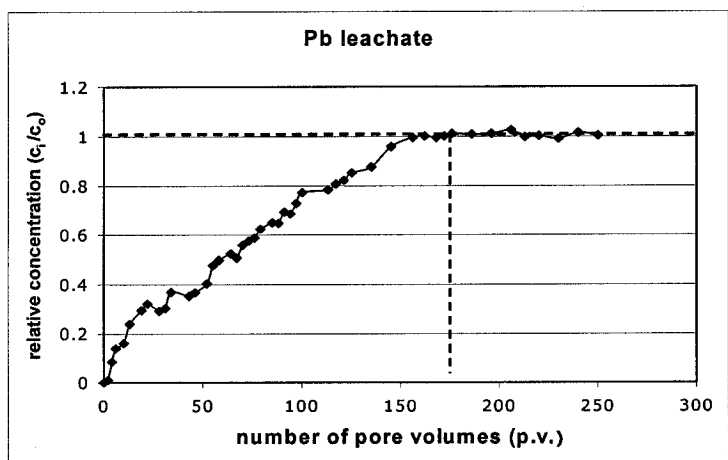
(b)



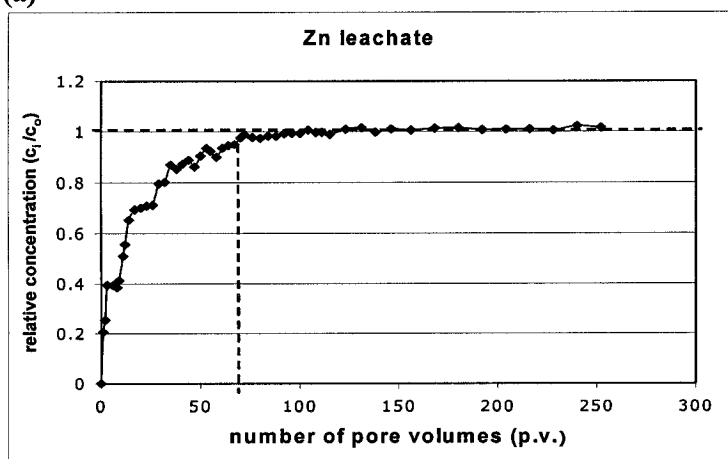
(c)

**Fig. 5.14 Breakthrough curves for lead and zinc leachate, the dashed lines indicate the breakthrough pore volumes for (a) single Pb leachate - 168 pv (b) single Zn leachate - 156 pv (c) mixed Pb and Zn leachate - Pb (160 pv), Zn (68 pv)**

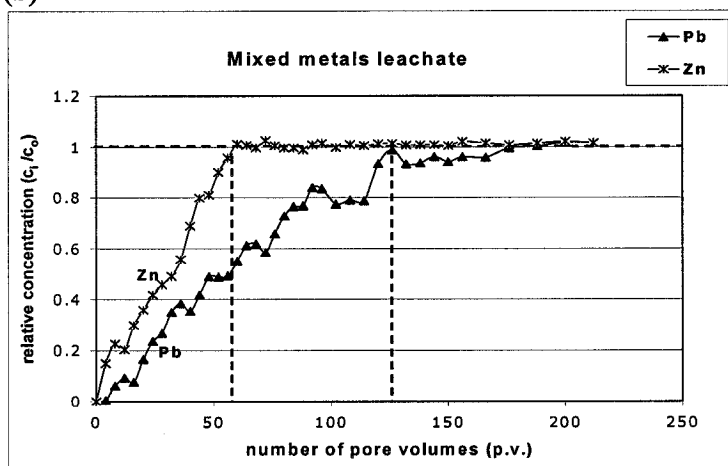
IV. Sample no. 22; initial metal content: Pb (45 mg/kg), Zn (250 mg/kg)



(a)



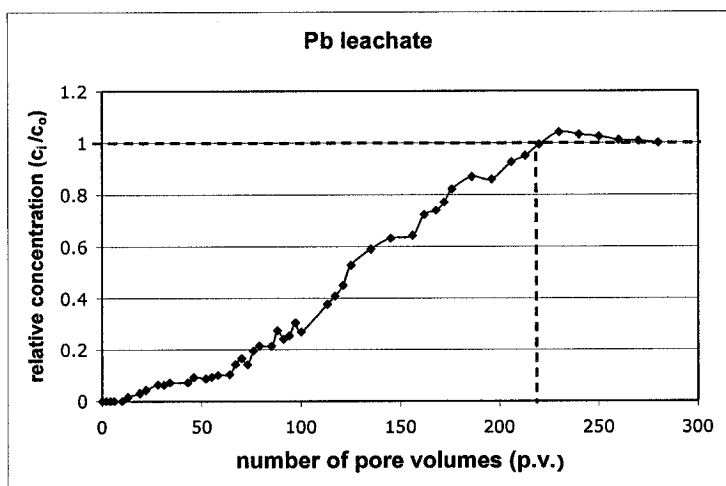
(b)



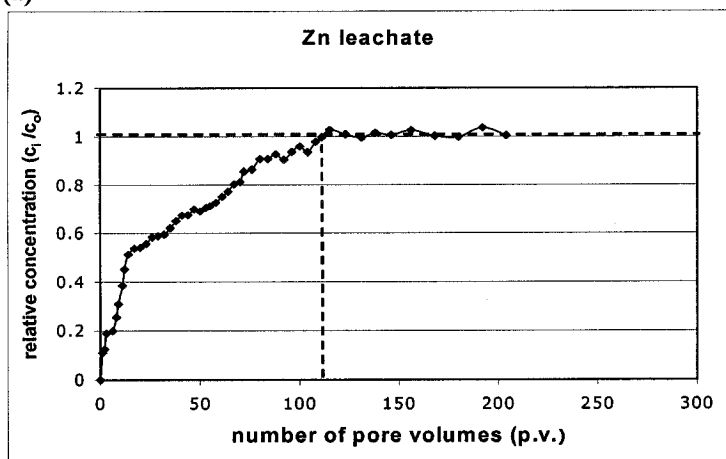
(c)

Fig. 5.15 Breakthrough curves for lead and zinc leachate, the dashed lines indicate the breakthrough pore volumes for (a) single Pb leachate - 156 pv (b) single Zn leachate - 72 pv (c) mixed Pb and Zn leachate - Pb (126 pv), Zn (60 pv)

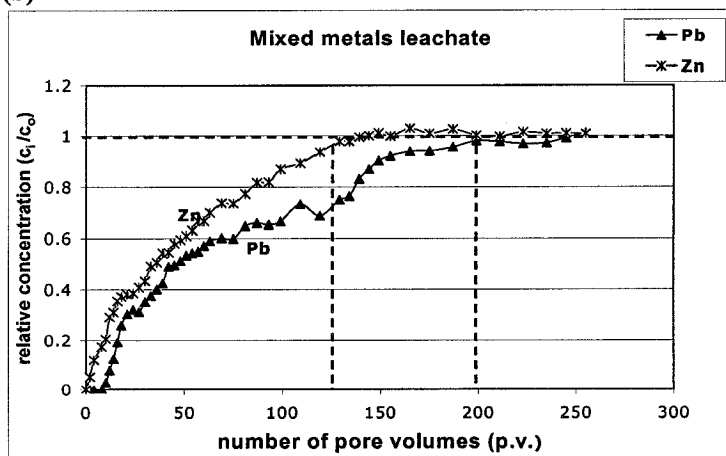
V. Sample no. 25; initial metal content: Pb (10 mg/kg), Zn (10 mg/kg)



(a)



(b)

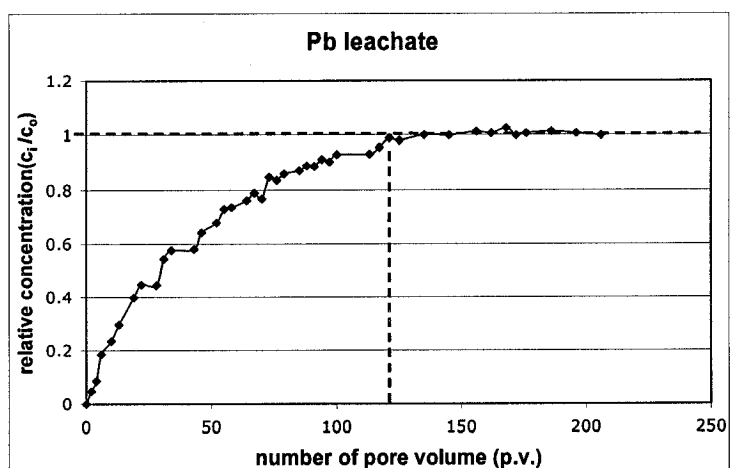


(c)

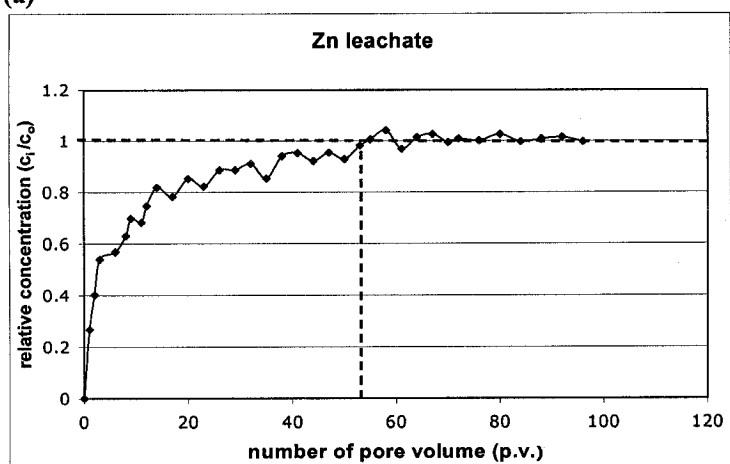
Fig. 5.16 Breakthrough curves for lead and zinc leachate, the dashed lines indicate the breakthrough pore volumes for (a) single Pb leachate - 220 pv (b) single Zn leachate - 115 pv (c) mixed Pb and Zn leachate - Pb (199 pv), Zn (129 pv)



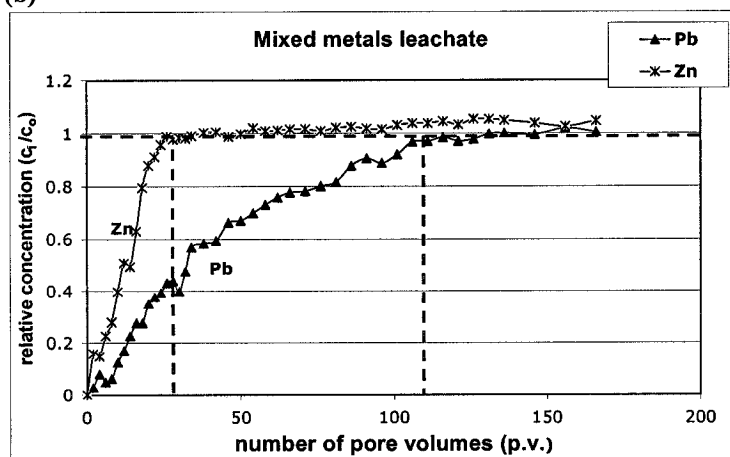
VI. Sample no. 26; initial metal content: Pb (42 mg/kg), Zn (138 mg/kg)



(a)



(b)



(c)

**Fig. 5.17 Breakthrough curves for lead and zinc leachate, the dashed lines indicate the breakthrough pore volumes for (a) single Pb leachate - 121 pv (b) single Zn leachate - 53 pv (c) mixed Pb and Zn leachate - Pb (116 pv), Zn (26 pv)**

From Fig. 5.12 to Fig. 5.17, Table 5.8 shows the summary of the breakthrough pore volumes for each sample, under each condition (single or mixed metal leachate).

**Table 5.7 Summary of breakthrough curve results**

Sample No.	No. 8	No.10	No. 19	No. 22	No. 25	No. 26
Initial heavy metal content before leaching (mg/kg)	<b>Pb</b> (5) <b>Zn</b> (89)	<b>Pb</b> (1132.5) <b>Zn</b> (462.5)	<b>Pb</b> (10) <b>Zn</b> (10)	<b>Pb</b> (45) <b>Zn</b> (250)	<b>Pb</b> (10) <b>Zn</b> (10)	<b>Pb</b> (42) <b>Zn</b> (138)
Single <b>Pb</b> leachate breakthrough p.v.	162 pv	100 pv	168 pv	156 pv	220 pv	121 pv
Single <b>Zn</b> leachate breakthrough p.v.	115 pv	17 pv	156 pv	72 pv	115 pv	53 pv
Mixed metals leachate breakthrough p.v.	<b>Pb</b> (156) <b>Zn</b> (100)	<b>Pb</b> (107) <b>Zn</b> (15)	<b>Pb</b> (160) <b>Zn</b> (68)	<b>Pb</b> (126) <b>Zn</b> (60)	<b>Pb</b> (199) <b>Zn</b> (129)	<b>Pb</b> (116) <b>Zn</b> (26)

Some graphs, such as the single-Pb leachate (Fig. 5.13 (a)) and the Pb-curve of the mixed-metal leachate ((Fig. 5.13 (c)) for sample no. 10, show two plateaus. This could be explained by the different interactions between soil and Pb. At the beginning of the leaching, Pb was absorbed by the soil exchangeable fraction; then the absorption by other soil fractions (carbonate, oxide or soil organic matter) follows.

We can see that for all of the soil samples, it takes fewer pore volumes of zinc solution to saturate the soils in comparison to the lead solution. This is consistent with the study of Phadungchewit (1990), which concluded that in soil solution, zinc has a higher mobility than lead. From sections 3.4 and 5.1.4 (Table 5.4) regarding selective sequential extraction, it was shown that heavy metals in the soils in the forms of organic matter would be held more tightly (lower mobility) than in the form of oxides (higher mobility). It also shows that lead has the highest affinity towards the soil organic matter

fraction, while zinc towards the soil oxides fraction. Therefore, zinc would be more mobile in soils than lead, this is also consistent with the result obtained in Table 5.8.

When a mixed zinc and lead solution was leached through the soil columns, the pore volumes for breakthrough to occur were reduced for both Pb and Zn, due to the competition of adsorption sites on soil surfaces, but the reduction was not substantial. Table 5.8 also shows that although sample no. 10 contains high concentrations of Pb (1132.5 mg/kg) and Zn (462.5 mg/kg) before leaching test, it is still able to accumulate more heavy metals. However, soil sample no.10 became saturated more easily as it took less pore volumes of leachates (100 pv of Pb and 17 pv of Zn) for breakthrough to occur compared to other soil samples. For the soil samples with lower concentrations of Pb and Zn, the pore volumes for breakthrough ranged from 121 pv to 220 pv for Pb, and 53 pv to 156 pv for Zn.

Three soil samples originally contaminated with the same degree of Pb and Zn concentrations were chosen for comparison of their heavy metal retention capacities and to demonstrate the dominant factors for the breakthrough pore volumes. Sample no. 8 (Pb -- 5 mg/kg; Zn – 89 mg/kg), sample no. 25 (Pb – 10 mg/kg; Zn -- 10 mg/kg) and sample no. 26 (Pb -- 42 mg/kg; Zn -- 138 mg/kg) were chosen. The breakthrough curves of both lead and zinc were compared and are shown in Fig. 5.18 and Fig. 5.19.

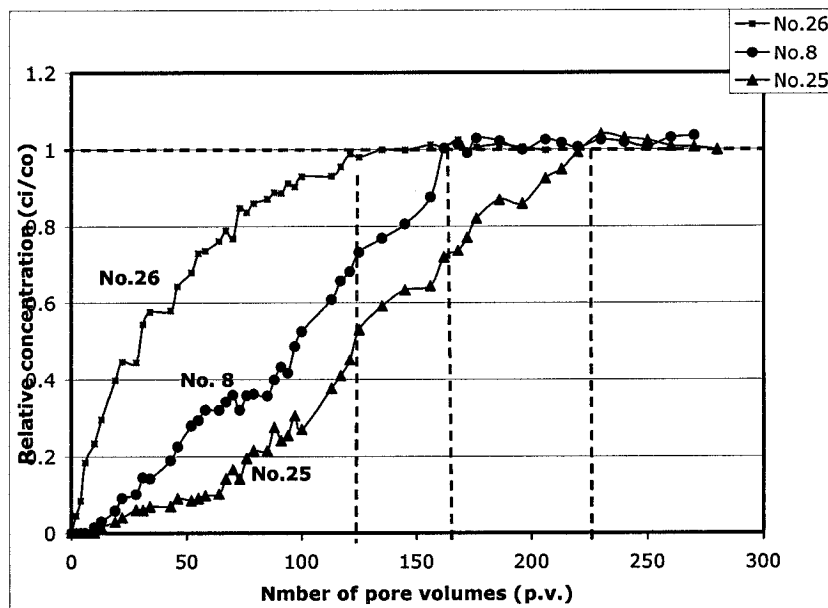


Fig. 5.18 Comparison of breakthrough curves from three soil samples originally contaminated with a similar degree of Pb concentrations.

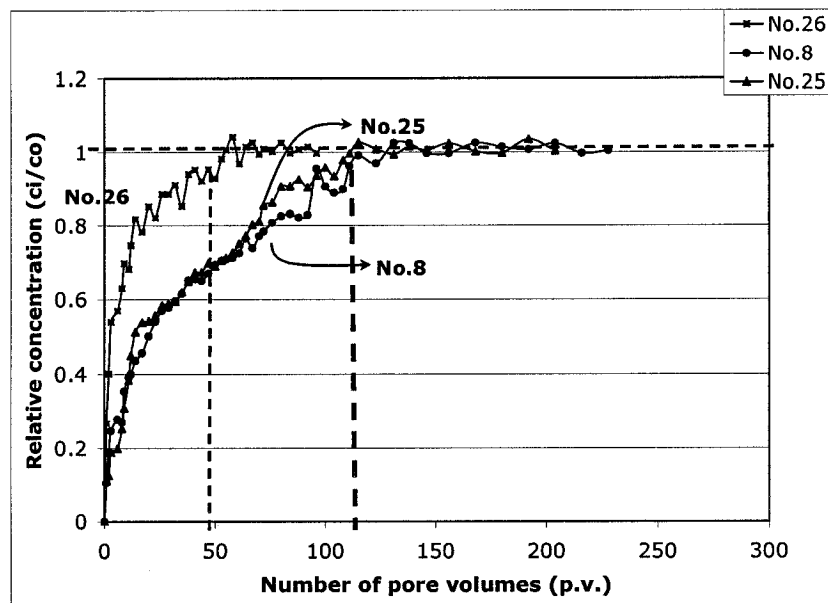


Fig. 5.19 Comparison of breakthrough curves from three soil samples originally contaminated with a similar degree of Zn concentrations.

In Fig. 5.18, it can be seen that for the lead leaching tests, sample no. 25 has the highest Pb retention capacity, with breakthrough pore volumes of 220 pv, compared to 162 pv for sample no. 8 and 121 pv for sample no. 26. Zinc leaching tests can be seen from Fig. 5.19. Sample no. 25 as well as sample no. 8 has the same Zn retention capacity of the breakthrough pore volume of 115 pv; while sample no. 26 has a lower retention capacity of 53 pv. These two figures indicate that, among these three soil samples, soil sample no. 25 shows the highest metal accumulation capacity for both lead and zinc, while soil sample no. 26 has the lowest capacity.

As seen in section 2.3 (the chemical and surface properties of soils) which shows that both cation exchange capacity (CEC) and specific surface area (SSA) contribute greatly to soil metal retention capacity (breakthrough pore volume). CEC and SSA can be related through the equation below (Yong and Mulligan 2003):

$$CEC = 10^5 \sigma_s (SSA)$$

where CEC is in the unit of meq/100 g soil;  $\sigma_s$  (soil surface charge density)– keq/m<sup>2</sup> and SSA – m<sup>2</sup>/kg soil. Taking the values of both CEC and SSA for these three soil samples from Table. 5.1, Table 5.9 shows that soil sample no.25 has the highest value of CEC/SSA (7.06), while soil sample no. 26 has the lowest value (1.28).

Table 5.8 CEC and SSA of three soil samples

Sample no.	No. 25	No. 8	No. 26
Cation Exchange Capacity (CEC) (meq/100 g soil)	76.9	63.2	29.9
Specific Surface Area (SSA) (m <sup>2</sup> /g soil)	10.9	18.28	23.43
CEC (meq/100 g soil) / SSA (m <sup>2</sup> /g soil)	7.06	3.46	1.28
Breakthrough pore volumes (pv)	Pb (220 pv) Zn (115 pv)	Pb (162 pv) Zn (115 pv)	Pb (121 pv) Zn (53 pv)

Fig. 5.18, Fig. 5.19 and Table 5.9 link the soil surface properties with its metal retention capacity. The soil sample with the highest retention capacity has the highest CEC/SSA value, which is shown at Fig. 5.20. It further demonstrates the essential role of soil surface properties in retaining heavy metal contaminants.

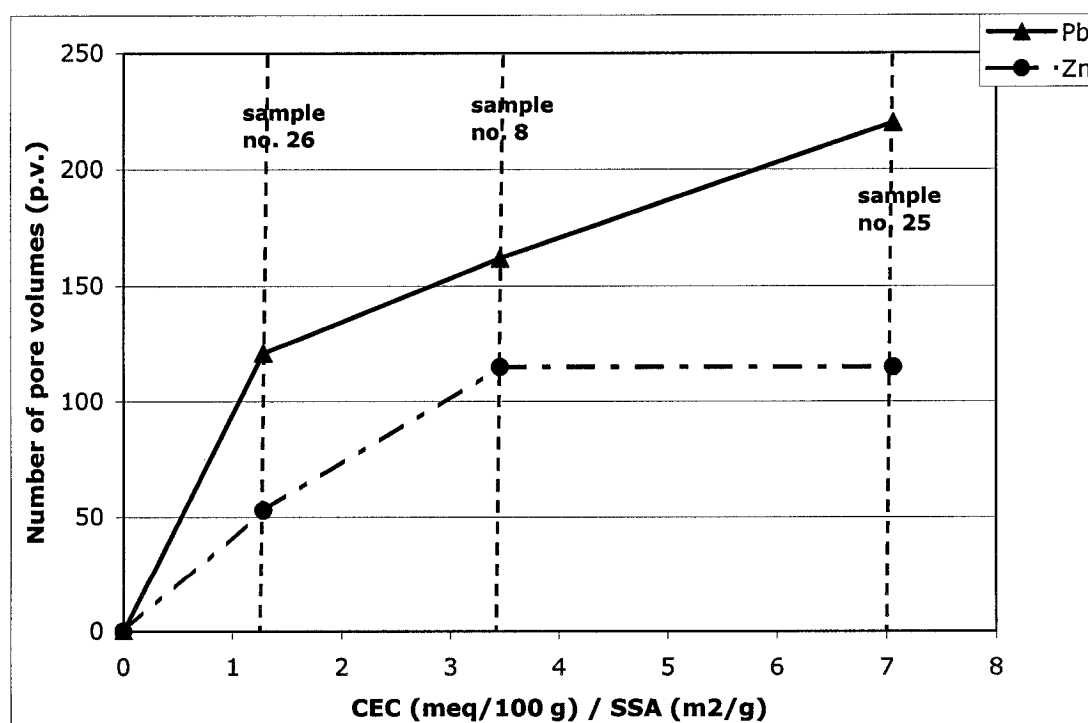


Fig. 5.20 Number of breakthrough pore volumes v.s. CEC / SSA

## Chapter 6

### Final Conclusions and Recommendations for future work

Urban soil properties in relation to heavy metal contamination were investigated in this project. A brief summary of the final results is listed as follows:

- Elevated lead and zinc concentrations were found in some urban soil samples. Urban soil Pb concentrations ranged from almost zero (5 mg/kg) to almost 2000 mg/kg. Urban zinc concentration ranged from 100 mg/kg to over 2000 mg/kg. The standard limit for both metals is 300 mg/kg.
- The majority of soil particles have the texture of fine sand (loamy and silty), as determined from the consistent results of the Specific Surface Area (SSA) tests, particle size distributions tests, and their permeability coefficients.
- The fraction of soil particles smaller than 0.075 mm (< sieve no. 200) has a stronger retention capacity for both lead and zinc compared to larger particle sizes.
- From selective sequential extraction, it can be determined that Pb has the highest affinity toward the organic soil fraction. Zn has the highest affinity toward soil oxides. The result agrees with previous studies.
- From leaching tests, it can be seen that zinc has a higher mobility in soil than lead. Thus, lead is retained preferentially in the soil in comparison to zinc. When

both metals are leached through soil columns, it took fewer pore volumes for both lead and zinc solutions to saturate the soil columns, due to the competition of retention sites.

The heavy metal contamination in urban soils has a long-lasting and serious impact on our environment. Heavy metals are not biodegradable and their different degrees of mobility in soil possess threats to the groundwater. This thesis provides fundamental knowledge of the soil properties and their retention ability on heavy metals. Since soils act as a reservoir for chemical compounds from either natural or human activities, a variety of other organic and inorganic compounds potentially pose a certain degree of danger in our soil environment. The different chemical properties of various soil contaminants result in different interaction mechanisms with soils. Some of these compounds will eventually make their journeys into underground aquifers and groundwater, creating groundwater contamination. While others (mainly organic contaminants) will be degraded or transformed into different compounds, which could be even more toxic than the parent compounds. Thus, the importance of soil quality cannot be over emphasized.

To further understand the soil properties and impact soils have on our daily lives, here are some recommendations for future study:

- Investigations on the aspect of phytoremediation (the use of plants to remediate environmental toxicity). Some studies (Günthardt-Goerg 2003; Boominathan 2003) have indicated that some hyperaccumulator plants show promising results



in terms of accumulation of various heavy metals. Afterwards, those plants can be harvested and destroyed; or recycled if sufficient amount of metals are accumulated. Using plants for soil remediation purposes is not only natural but provides several benefits, such as low maintenance, operational costs and the public acceptance due to its superior aesthetics.

- Further investigation into the interaction mechanisms between soil particles and contaminants. The role of soil is involved in the retardation, dilution, and accumulation processes for contaminants.
- Soil buffer-liner or barrier systems were built as an effective solution for preventing contaminants further degrade our groundwater quality. Thus, some mechanical properties of soil, such as soil clay properties, soil compactibility and soil shear strength should be investigated further in the future.
- Organic compounds, such as hydrocarbon compounds (PAH-Polycyclic Aromatic Hydrocarbon, BTEX- benzene, toluene, ethylbenzene, and xylene, and some VOCs) and organohalide compounds (TCE-trichloroethylene, and PCB-polychlorinated biphenyls) are also major soil pollutants. They possess different properties from their inorganic counterparts, and they are in general higher mobilities in soils, less stable and easier to break down compounds result in their different interaction with soils. Organic contaminants in soil, being more complex in nature, show more unpredictable properties than heavy metals. Some further studies can be done in terms of their behavior in soil.

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