# Recycling of Complexometric Extractant(s) to

# Remediate a Soil Contaminated with Heavy Metals

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# Abstract

A possible remediation strategy that involved washing with complexing reagents(s) [disodium ethylenediaminetetraacetate (Na$_2$EDTA) alone or in combination with bis-(2-hydroxyethyl)dithiocarbamate (HEDC)] was evaluated with an urban soil that had been field contaminated with excesses of heavy metal (HMs). Heavy metals (Cd, Cu, Mn, Ni, Pb and Zn) were targeted for removal. The aqueous solution that resulted from washing was treated with zero-valent (ZV) magnesium (Mg$^0$) or bimetallic mixture (Pd$^0$/Mg$^0$ or Ag$^0$/Mg$^0$) to release the chelating reagent(s) from their heavy metal complexes. During this reaction, the heavy metals were precipitated from solution as hydroxides or became plated on to the surface of the excess ZV reagent. Thus, an appreciable fraction of the mobilized Pb and Cu and a portion of Zn became cemented to the surface of the ZV metal whereas most of the Fe and Mn were removed from solution as insoluble hydroxides. After filtration and pH re-adjustment, the demetallized solution was then returned to the soil to extract more heavy metals. After three washing cycles with the same reagent, it was observed that the sparing quantity of EDTA (10 mmoles) had mobilized 32-54% of the soil burden heavy metals (5 mmoles), but only 0.1% of the iron had been removed.

A 1:1 (mol/mol) mixture of EDTA and HEDC proved to be approximately equally efficient at HM extraction despite more than a three-fold reduction (3 mmoles) in the quantity of reagents. Three washing with the same reagent mobilized some 49% of the Pb, 18% of the Zn and 19% of the Mn but only 7% of the Cu and 1% of the Fe from the test soil.

# Résumé

Une stratégie possible de remédiation qui a impliqué le lavage avec d'agents complexants: acide éthylène diamine tétra acétique disodique (Na$_2$EDTA) seul ou en combinaison avec du bi-(2-hydroxyéthyle)dithiocarbamate (HEDC)] a été évalué avec un sol urbain très contaminé avec des métaux lourds (MLs). Les métaux lourds, cadmium (Cd), cuivre (Cu), manganèse (Mn), nickel (Ni), plomb (Pb) et zinc (Zn) ont été ciblés pour cette étude. La solution aqueuse résultant du lavage a été traitée avec du magnésium (Mg$^0$) à valence zéro (VZ) ou avec un mélange bimétallique (Pd$^0$/Mg$^0$ ou Ag$^0$/Mg$^0$) afin de libérer l'agent complexant des métaux lourds. Durant la réaction, les métaux lourds ont été précipités de la solution aqueuse comme hydroxydes ou ont été plaqués à la surface des VZ. Ainsi, une fraction appréciable du Pb et du Cu a été mobilisée et une portion du Zn est devenue plaqué à la surface du VZ tandis que la majorité du Fe et du Mn a été enlevé de la solution aqueuse comme des hydroxydes insolubles. Après une filtration le pH fut réajusté et la solution fut ré-utilisée sur un nouvel échantillon de sol urbain contaminé afin d'extraire les métaux lourds. Après trois cycles avec le même agent complexant, la faible quantité de EDTA utilisé (10 mmoles) a mobilisé 32-54% des métaux lourds (5 mmoles), mais seulement 0.1% du fer a été enlevé.

Une proportion de 1:1 (mole/mole) de EDTA et HEDC s'est révélé presque qu'aussi efficace pour extraire les MLs et ce en dépit d'une réduction de plus de trois fois (3 mmoles) la quantité de d'agent complexant utilisé. Trois lavages avec le même agent complexant ont permit de mobiliser 49% du Pb, 18% du Zn et 19% du Mn mais seulement 7% du Cu et 1% du Fe sur l'échantillon de sol évalué.

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## 1. 1 Introduction

Soil is the thin skin at the earth's surface that supports life on this planet. It is the life sustaining pedosphere. This biologically active, porous and structured medium is an effective integrator and dissipater of mass flux and energy. It is the medium through which biomass productivity is sustained, the foundation upon which structures are built, the fabric on which organism are anchored and housed (habitat), the repository of solid and liquid wastes and a living filter for the bio-remediation of waste products and water supplies. Soil is a fundamental component of our ecosystem and one of the most vulnerable to contamination and degradation through accidental or deliberate mismanagement (7).

The exploitation of natural resources without sufficient protection during the last two centuries of industrialization has caused an appreciable deleterious environmental impact. This impact continues to be felt currently so that we have to pay the debt now for our past behaviors. If nothing is done, the cost in the future will be much higher. Soil contamination, when coupled with multimedia transport processes, can adversely impact the quality of water and air, thereby reducing overall environmental quality. The use of soil as a waste repository for cleanup can reduce environmental quality. Agricultural sustainability will then be impacted adversely. The effect of environmental contamination, has thus become one of the principal current global concerns. Industrialized societies have recognized the need to correct the past environmental degradations that were both legal and accepted by society when they occurred but violate current standards of the environmental protection (7).

### 1. 1. 2 Soil Chemistry

To increase our understanding of soil contamination by heavy metals, it is necessary to gain an insight into the behavior of trace metals within the soil matrix. Soils are heterogeneous mixtures of air, water, inorganic, and organic solids and microorganism. Soils are complex systems that contain varying quantities of these components. They can be divided into two subsystems, a biotic (biological) subsystem that includes many organisms and a second abiotic system that consists of non-living materials (1).

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The abiotic fraction of the soil consists of a mixture of all three phases: gas, liquid, and solid. The main components in the gas phase are similar to the air above the soil: $O_2$, $CO_2$, $N_2$. The only differences between the gas phase in soil and the atmosphere above it is the different proportion for each constituent gas. The liquid phase is referred to as the soil solution; it contains salts, low molecular weight organic compounds, and absorbed gases. The last phase of soil is the solid porous structure that retains the liquid and gas of the soil. It is composed of both crystalline, and amorphous minerals and organic substances (1).

Soil is a very complex structure, yet it is characterized by certain physical and chemical properties. The physical characteristics of soil include (2):

1.  Macro porosity; the soil is composed of pores with a mean diameter greater than 200 $\mu$m.

2.  Micro porosity; the soil also contains pores with micron diameters with a mean value that is less than 200 $\mu$m.

3.  Physical stability refers to the binding between individual soil particles to form aggregates.

4.  Soil geometry; the internal and external surfaces that collectively result in the soil's specific surface area in square meters per gram. This parameter can vary with depth.

The chemical properties of soil include:

1.  Permanent charges within the soil matrix that result in a cation exchange capacity (CEC) that is independent of pH.

2.  Variable charges, that results in a pH dependant CEC

3.  Point zero charge, PZC, is defined as the minimum net charge (approximately zero), or the point when CEC minus the anion exchange capacity (AEC) is minimized.

4.  The capacity to adsorb both hydrophobic, and hydrophilic compounds.

5.  The buffering capacity that is measured by its ability to resist pH changes (19).

### 1. 1. 3 Sources of Heavy Metals in Soil:

Soil contamination can be defined as any compound that was not originally present in the soil. Once these contaminants have been accumulated beyond the level that the soil can absorb/neutralize these contaminants become dangerous and can threaten the health of any organism that contacts them. These contaminants then become hazardous wastes. Based on numerous surveys, there were between 400,000 and 600,000 hazardous waste sites in the U.S. in 1991 (7). In the European Union, there were some 120,000 to 150,000 contaminated sites, containing 1,000,000,000 m$^3$ of waste and contaminated soil. In Italy alone, there were about 20,000 contaminated sites (11).

Many sources of metals can cause soil contamination. These sources range from industrial activities including coal tar pits, mine tailings, landfill sites, waste waters, discharge accidents and agricultural activities that use excesses of pesticides and/or fertilizers.

Mining represents the major source of metal salts. During mining activities, deep reservoirs of rock are brought to the surface and crushed. Huge surface areas of unextracted metal ores that have been under exposed to oxygen and water have become more bio-available. Sulfides in the residual one can be oxidized to sulfate and can release metal to aquatic system. Mine tailing can become weathered and can continue to release metals for several hundred years after the mining activity has ceased (13). The U.S. EPA (Environmental Protection Agency) has estimated that some 31 trillion kg of mine wastes and one trillion kg of tailings have been accumulated between the years 1910 and 1981, with over 80% of these wastes having been generated by the heavy metal (uranium, copper, iron, lead) mining segment (3). A summary of major wastes produced from mining in the U.S is presented in the Table 1.1. A second summary of the extent of land contamination in major industrialized nations is presented in Table 1.2 (7).

In addition to the contamination by heavy metals released from mining, contamination can also result from the regular daily life within our communities, and include the production of sewage sludge and municipal compost. The addition of municipal sewage sludge to agricultural land has been performed for many years. This practice was intended to exploit the high organic content in the sludge to fertilize the soil. Unfortunately, researches have observed that the addition of sewage waste as a soil

ammendment can add excesses of heavy metal that are deleterious to agricultural production. Concentrations of lead, nickel and cadmium have been reported to be much higher in food crops that have received sewage water (14). As a result, the application of sewage sludge to agricultural lands in South Africa has been severely restricted (12).

Table 1.1. Summary of major mining areas of environmental concern (3).

| Ore | No of Sites | Quantity of Wastes (million metric tons/years) | Environmental concern |
|---|---|---|---|
| Copper | 19 | 502 | Elevated metal, low pH |
| Gold and Silver | 117 | 100 | Radioactivity |
| Iron | 26 | 177 | Elevated metal, low pH |
| Lead and Zinc | 23 | 18 | Residual cyanide |
| Phosphate | 27 | 403 | Elevated metal, low pH |
| Other Metals | 24 | 62 | Elevated metal, low pH |
| Total | 226 | 1262 | |

Table 1. 2. The extent of land contamination (7) in selected industrialized countries.

| Country | No of contaminated sites |
|---|---|
| Denmark | 10,500 |
| France | 75,000 square kilometres |
| German | 144,000 |
| The Netherlands | 110,000 |
| United Kingdom | 50,000-100,000 |
| U.S.A | 400,000-600,000 |

Pollution can also be classified into two types. One type is the slow but continued degradation of soil quality by the excessive input of chemical from various sources. This type of contamination is often from agricultural and community activities. The other type of contamination is the more massive contamination of restricted areas, mainly by the intentional dumping or fugitive emissions of industrial waste materials. No matter the

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pattern of heavy metal accumulation (slow or more rapid), the degradative effects remain long lived.

### 1. 1. 4 Ecological and Biotic Health Impacts:

Improper management during the exploitation of natural resources has mobilized considerable quantities of hazardous wastes into our environment. These avtivities have created the impacts that have unbalanced nature. The accumulation of these wastes have contributed to an increase in serious irreversible, or incapacitating illnesses. Wastes have continued to pose a potential hazard to the health of humans and the environment when improperly managed, treated, stored or disposed of.

The pollution of soil by heavy metal compounds can inhibit microbial enzymatic activities and reduce the diversity among populations of soil flora and fauna. The transfer of metals to human can result from food chain transfers from contaminated plants or indirectly by consuming meat from animals that have ingested contaminated plants or soil (5).

Most heavy metals are essential for life, however only minuscule quantities are required. It is very easy to accumulate excessive amounts of these metals that render them poisonous. Normally trace metals maintain the function for GI tract, blood, growth and proper function of the central nervous system. The interactions of trace mineral with living organisms must be balanced. Exposure to an excess of one trace metal can result in deficiency of another (a slight manganese overload, can cause iron deficiency). Similarly, a deficiency of one metal can cause a second metal to become toxic. For example, iron deficiency can render the body vulnerable to lead poisoning (45).

Contaminated soil from an agricultural point of view can cause an adverse effect on food supplies. For example, it has been reported that crops (especially green leafy vegetables) grown in close proximity to industrial areas, rivers (that receive wastes from industry), mining areas and roadways have greatly increased heavy metal burdens (14). In addition to accumulation of heavy metals by plants that can threaten the food chains, cadmium, lead and mercury have been demonstrated to impede plant growth (5).

From an ecological point of view, heavy metal contamination can threaten the health of animals and birds. Several studies have demonstrated that elevated nesting

mortality and retarded brain development in birds that have been exposed to excesses of lead (15). There is also evidence indicating that cadmium (Cd) can reduce human calcium uptake and can cause Itai Itai disease. Moreover, heavy metal will eventually be leached to the ground water and contaminate the aquatic environment. Research has demonstrated that Cd can also affect heart development in the shark (16).

The impacts of heavy metals are not limited to adverse health and ecological effects, but also can be expensive to remediate. Two percent of the gross national product (GNP) in the USA is spent on remediating the environment and controlling pollution. This is about 50% of the amount that people normally spend on clothing. In the Netherlands, the costs of controlling pollution between 1987 to 2000 was estimated to be 26.7 - 44 billion for air pollution, 327 - 896 millions for radiation pollution, and 34.4 - 57.6 billions for water pollution (4).

## 1. 2 Interaction of Heavy Metal Ions with Soil

### 1. 2. 1 Definition of Heavy Metal:

Trace elements are natural constituents present in the environment at low concentrations, typically less than 0.1% (4). These elements can be toxic to living organisms if present at excessive concentrations. Trace elements include heavy metals, micronutrients (chemical substances that are require by plants at a level of less than 50 mg/g of plant dry weight). Heavy metals have also been categorized as those elements with densities that exceed $5.0 g/cm^3$ (4). The sources of heavy metals and their concentrations in soil depend on the underlying parental material (rocks), but concentrations in excess of background levels have resulted mainly from anthropogenic (human) activities associated with industrialization (2)

### 1. 2. 2 Characteristics of Heavy Metal in Soil:

Although, each heavy metal has its own unique set of reactions in soil, collectively they all have certain characteristics in common. With the exception of Mo that tends to be present in the soil in an anionic form ($MoO_4^{2-}$), the other heavy metal are primary cationic in soil. Cr might be present as chromate ($CrO_4^{2-}$) within discharge, but it

can't remain in such a highly oxidized state within a living system and is converted spontaneously to its cationic form ($Cr^{3+}$). The second feature of heavy metals is that they have the tendency to be retained by the soil. (6)

Contaminated soil can contain heavy metals in various forms, including combinations with oxides, sulfides and phosphates or adsorbed by soil colloids. With time, metal ions can be mobilized into soil solution. As an example, relatively insoluble oxide can be converted to a soluble bicarbonate or a sulfide can be converted to the corresponding sulfate by the action of microorganisms. The fates of heavy metals can be summarized as follows (6). They tend to:

1- Remain with soil solution and eventually drain to aquatic environment

2- Be taken up by plants, which can be harvested subsequently and enter the mammalian food chain.

3- Become volatilized into the gaseous phase. This activity is more prevalent with certain metalloids, including arsenic and selenium, because they are more susceptible to microbially mediated transformation that generate volatile organometallic compounds within certain biological systems.

4- Be retained by the soil in a relatively insoluble form either temporarily or permanently.


## 1. 2. 3 Effects of Soil Physical Properties on Heavy Metal Retention:

The solid phase of soil consists of various constituents of different sizes, shapes and densities. Most of the organic components within this phase are of colloidal dimensions, but there can be differences in the degree of dispersion of the mineral components. The mineral and rock particles that exceed 2 mm in diameter conventionally are classified as stone or gravel. The fraction between 0.2 and 2 mm in diameter represent coarse sand and the fine sand fraction are considered to be those particles that have diameters of 0.2-0.02 mm. Whereas the fraction between 0.02-0.002 mm is classified as silt, the mineral components smaller than 0.002 mm represent the clay fraction (1). Particle size distributions can influence the level of metal contamination in soil. Fine particles, such as silts and clays (<100 μm) have an increased surface area to volume ratio relative to the coarser materials. As a result, the fine fraction of soil frequently has been

observed to contain the majority of the total contamination. Coarse soil particles are often characterized by surface irregularities that have been enhanced by weathering, inorganic salt precipitation, and oxide formation. This uneven and porous surface can provide a favorable environment for surface deposition. The distribution of particle sizes with which a metal contaminant is associated can determine the success of a number of heavy metal remediation procedures (10).

## 1. 2. 4 Influence of Soil Chemical Properties on Heavy Metal Mobility:
### 1. 2. 4. 1 Adsorption:

The pH, Cation Exchange Capacity (CEC), and carbonate content in soil are important factors that determine the fate of heavy metal, since they influence adsorption (or retention) and mobility of heavy metals within the soil (10). In fact, the hazard associated with a heavy metal depends of its mobility or retention within soil, because adsorption determines the quantity of metal that is retained by soil surfaces and it is one of the dominant process that affect transport of contaminants within this medium (4). Several retention mechanisms can be operative within soil. Cation exchange capacity and specific adsorption are two mechanisms that control metal adsorption. Heavy metal can also be retained by solid state diffusion and precipitation reactions. Heavy metal retention has been observed to increase with increasing soil pH, CEC, organic content, clay content and metal oxide content within the soil. Generally, the strength of metal retention is increased, as the concentration of the contaminant is decreased. The average binding strength of a soil is decreased once the limited number of high energy binding sites have been filled (17). Moreover, an increase of redox potentials can also increase adsorption due to the formation relatively insoluble oxides. Reports have also demonstrated that metals within wet lands have been exposed to high relative redox potentials, so that heavy metals become strongly bound to oxides and they are very stable. However, decreases in the redox potential can result in dissolution of hydroxides and the release of the metal to the soil solution (28).

## 1. 2. 4 .2 Effect of Acidity:

Heavy metal solubilities are strongly dependant on soil acidity. Generally, soil pH values range from 4.0 to 8.5 and are buffered by Al as [$Al(OH)_3$] at low pH or $CaCO_3$ at alkaline pH (10). Most metals are present in their cationic forms, and their solubilities (or mobilization) into the soil solution is increased with decreasing pH levels in the soil. In contrast, the opposite is generally true for the anionic metal compounds. The solubilities of metallic anions increase with increased pH, whereas cationic species precipitate or become absorbed to mineral surface and lose mobility (27). Therefore, heavy metal can be sorbed both as cations ($Cr^{+3}$, $Pb^{+2}$, $Cu^{+2}$, $Zn^{+2}$, $Ni^{+2}$, $Cd^{+2}$) in neutral to high pH and as anions ($SeO_4^{2-}$, $CrO_4^{2-}$) in neutral to mildly acidic pH (56). For this reason, most cationic metals ($Pb^{+2}$, $Al^{+3}$ and $Mn^{+2}$) become increasingly soluble at lower pHs. Thus, they become more available for plant uptake (4). Acid rain and many additional industrial contaminants (acids) can modify the nature of soil by decreasing its pH and causing cationic metal compounds to become more available to contacting organisms or biological processes. In addition, the acidification of soil, as a consequence of oxidation, can cause the remobilization of heavy metals. In order to reduce plant uptake of excesses of heavy metals, it is essential to prevent the reduction of soil pH. There is abundant research that has demonstrated that the addition of liming materials to the soil can increase soil pH, and thereby reduce the availability of heavy metal (22).

## 1. 2. 4. 3 Effect of Carbonate and Sulphide contents:

The pH of the soil solution is strongly dependent on the carbonate and sulphide contents of the soil. The higher the carbonate content in soil, the higher the pH of the soil solution will be. In contrast, the higher the sulphide components, the lower the pH the soil solution will be. The sulphidic components, when exposed to atmospheric oxygen and moisture, can undergo a series of oxidations and hydrolysis reactions producing sulphuric acid and the more soluble metal sulfates (18, 22).

## 1. 2. 4. 4 Ions Exchange Capacities (CEC or AEC)

Ion Exchange Capacity is the interchange between an ion in solution and a second ion bound to a charged surface. This process can occur by the exchange of cations or by

exchange of anions. CEC and AEC are important because they determine the capacity of soil to retain ions in a form that remain available for plant uptake but are not susceptible to leaching within the soil profile. Since most metals are in cationic forms, Cation Exchange Capacity is the main parameter that determines the fate of metals in soil (and its bio-availability for plant uptake). The principal sources of CEC are clay minerals, organic matter and amorphours minerals (4). In general, a higher CEC increases metal retention within soil but decreases plant uptake (17).

### 1. 2. 4. 5 Lead (Pb):

The primary source of industrially mediated lead contamination include metal smelting and processing, secondary metal production, lead battery manufacture and chemical manufacture that all generate lead contaminated wastes. Most commonly, lead occurs with an oxidation state of 0 or +2. Pb(II) is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides. Under most conditions, $Pb^{2+}$ and lead hydroxide complexes are the most stable forms. Soluble compounds are formed by complexation with inorganic ions ($Cl^-$, $CO_3^{2-}$, $SO_4^{2-}$ or $PO_4^{3-}$) and organic ligands (EDTA, humic and fulvic acids). Lead carbonate solid forms above pH 6 and PbS is the most stable solid when elevated sulfide concentrations are present under reducing conditions. Most of the lead that is released to the environment is retained by the soil. The primary processes that influence the fate of lead within the soil are adsorption, ion exchange, precipitation and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into surface or groundwaters. The relatively volatile organo-lead compounds can form in anaerobic sediment by methylation mediated by microorganisms (10).

### 1. 2. 4. 6 Copper (Cu):

Copper is recovered as a primary product from copper sulfide and oxide ores. Under aerobic conditions, $CuCO_3$ is the dominat soluble copper species. The cupric ion, $Cu^{2+}$ and hydroxide complex, $Cu(OH)_2$, are also species that are commonly present. Copper forms strong complexes with humic acid. The $Cu^{2+}$ is the toxic species of copper and its mobility is decreased by sorption at mineral surface (10). Cu is strongly associated

with organic matter. In normal soil, it moves as a neutral molecule or as an anion in organic combination (as it does within plants). Chelated Cu is much less toxic than is the cation (6). As mentioned previously, most heavy metals are essential in that they are required by organisms to survive. Cu is one of the trace elements that is needed in small quantities, Cu serves as a constituent of several enzymes in the body and deficiencies can cause cardiovascular disease. However, elevated copper ingestion can lead to overt signs of copper toxicity including Wilson and Menkes diseases (45).

### 1. 2. 4. 7 Zinc (Zn):

Zinc does not occur naturally in its elemental form. It is usually extracted from mineral ores in the form of zinc oxide. The primary industrial use for zinc is as a corrosion resistant coating for iron and steel. Zinc usually occurs in the 2+ oxidation state and forms complexes with a variety of anions, amino acids, and organic ligands. Zinc can be precipitated as $Zn(OH)_2$, $ZnCO_3$, or $Zn(CN)_2$ (10).

### 1. 2. 4. 8 Nickel (Ni):

Nickel behaves similarly to Zn, although it forms stronger chelate links with organic functional groups. Its main characteristic is that it is sorbed to negative sites that are increased as the pH rises (6).

### 1. 3. 1 The Heavy Metal Fractions in Soil

Not all heavy metals present in soil are dangerous. It is not logical to determine the metal pollution based only on the total metal concentration present in the soil, since some heavy metals exist in soil naturally and come from the weathering of parental rock. They are not mobile and thus there is no hazard associated with these levels of these metals (19). Identification of the geochemical phases of metal and physiochemical properties of the soil are necessary to evaluate the availability (capacity of be mobilized) of heavy metals within the soil particulate fraction. For example, it is important to know the oxidation state of arsenic and chromium, since appreciable changes in toxicities are

associated with changes in their oxidation states. In general, trivalent arsenic is of increased environmental concern relative to As(V) compounds because it is more mobile (20, 27). The systematic investigation of metal fractions started in the early 1980s and aimed to evaluate the metal fractions available to plants for the estimation of phyto-toxicity, and/or nutrient uptake (23). The distribution of trace metal fractions in soil depends on several variables, including the nature and concentration of substrate solids, redox potential, and pH (33).

Many forms of heavy metals are available within the soil. Metals can be grouped into exchangeable, inorganically bound, organically bound, dissolved, and residual fractions. The geochemical forms of heavy metals in soil affect their solubilities which directly influence their mobilities and bio-availability. Soluble forms depend strongly on the relative contribution of solid soil components (silicates, carbonate, oxides, organic matter) to metal retention. The type and degree of adsorption capacity of these various metal fractions are very different (22). Their forms will change with time due to weathering and environmental changes caused by humans. For example, acid rain and exposure of sub-surface mineral ores (mining activities) or to oxygen can cause metals to become more mobile and change from one form to another. Mobility, and hence the availability of trace element is important for the assessment of trace element burdens in soil (19).

### 1. 3. 2 Sequential Heavy Metal Extraction:

The chemical properties of each metal fraction is explored in more detail below, together with the type of solution that has been used to extract them. However, the detailed laboratory procedures (material and experimental conditions of time and temperature) performed during this research is provided in the next chapter (entitled preliminary tests for soil characteristics).

There are several schemes for the determination of metal fractions in soil. Most of these schemes are based on the same principle. Examples include the use of a salt solution to remove the exchangeable metal fraction and the use of a reducing solution to mobilize the oxide metal fraction. There is a method that has been developed by the Measurement and Testing Programme (BCR) which requires only three steps to analyze

four metal fractions. The BCR method divides the total trace metals into four fractions: an acid soluble (exchangeable and carbonate fractions), a reducible (Fe/Mn oxide), an oxidizable (organically bound fraction) and a residual fraction (23). The original fractionation method was developed by Tessier et al. This procedure has an additional step that uses a salt solution to extract a more specific exchangeable fraction (25, 28). This method was used for the current research. Zerbe has also developed a scheme that uses two different reducing solutions (stronger and weaker) to extract the Mn and Fe oxides as separate fractions. The feature of this method is a more precise estimate for the oxidized metal fraction; the rest of the sequential procedure is similar to the Tessier scheme (26).

## 1. 3. 3 The exchangeable fraction:

Comprises metals that are held within the soil matrix mainly by electrostatic forces to negatively charged sites on clay, mineral, or on amorphours materials with a low pH of zero charge. Metals in this fraction are isotopically exchangeable and can be displaced by the basic cations that are commonly present in soil. The activation energy of exchange is low and in consequence, the exchange is usually rapid and virtually complete (10). The metals in this fraction are in their most mobile form. Certain salt solutions, including sodium acetate or magnesium chloride have been popular to extract this metal fraction (25).

## 1. 3. 4 The carbonate fraction:

Several researches have demonstrated that appreciable portions of the total heavy metal burden are contained within this fraction. Heavy metals of this form are associated with carbonate and are susceptible to changes of pH (22). The major carbonates found in soil include calcite ($CaCO_3$), and magnesite [$MgCO_3$, which is very unstable and is transformed to Mg $(OH)_2$] (4). The metals in this fraction are also referred to as the acid soluble form within the BCR method, since it is very soluble in mild acid solution. The most commonly used solution to mobilize this fraction is a buffer of sodium acetate with acetic acid (10, 25).

## 1. 3. 5 The Fe/Mn Oxide fraction:

It has been well established now that iron and manganese oxides exist as nodules, deposits that cement particles together, or simply as coating on particle. These oxides are efficient scavengers for trace metals and are thermodynamically unstable under anoxic conditions (22). Of the two, manganese oxide is the weaker oxide and it is quite common in soil. This fraction provides a source of Mn, an essential element for plants. This fraction can adsorb heavy metals, and is a natural oxidant for certain other metals ($As^{+3}$ and $Cr^{+3}$) (4). The solutions required to extract metals of this fraction are reducing reagents (e.g., $NH_2OH \cdot HCl$) to mobilize Mn and Fe from oxides or trace metals adsorbed or occluded on/within the surfaces of Mn/Fe oxide. Since Fe oxide has an increased ability to bind metals in general, Fe oxide requires a reducing reagent with a stronger reducing ability than does Mn oxide (24).

## 1. 3. 6 The organically bound fraction:

Trace metal can be bound to various forms of organic matter including living organisms, detritus and coatings on mineral particles. The complexation and peptization properties of natural organic matter (humic and fulvic acids) are widely recognized, as is the phenomenon of bio-accumulation within certain living organisms. Under oxidizing condition in natural waters, organic matter can be degraded slowly, leading to a release of the bound trace metals (26). Since this metal is organically complexed, the best way to release this fraction is to oxidize the organic matter. The most commonly used solution is the combination of hydrogen peroxide with diluted acid (10, 25).

## 1. 3. 7 The residual fraction:

The metals present in this fraction include the residual solid as primary and secondary minerals that are retained within the crystal structures. These metals are not anticipated to be released into solution over a reasonable time span under conditions of natural weathering (26). This metal fraction is the most stable fraction in soil since it forms part of soil structure. The one way to release these metals is by using strong acids to decompose the soil structure to release the metals within this fraction. The most commonly used acid solution is the combination of nitric acid with hydrochloric acid

(10). In fact, any solution that can destroy the soil structure and completely free these metals can be used.

As mentioned earlier, several different sequential extraction procedures are available. Although they are characterized by certain differences in the experimental conditions, they are all based on similar principles. The method used for the current studies was developed by Tessier and coworkers (25). There are other methods that are simpler and less time consuming such as method proposed by BCR (23). Despite the fact that soil sequential extractions can provide a measure of metal concentration in different fractions of soil, there are at least three serious problem that must be considered when evaluating the results from these schemes (10).

1- The metal within the labile metal phases can be exchanged during sample preparation.

2- Re-adsorption or precipitation processes can occur during extraction.

3- Both the duration of extraction and the soil/solution ratio can play an important role in the amount of metals that are extracted.

Despite the limitation of the sequential extraction technique, it remains the most popular approach to characterizing the different metal fraction in soil.

## 1. 4. 1 Soil Remediation

The treatment of contaminated soils represents a complex and challenging problem. Heavy metal contamination is more difficult to deal with than other contaminants, since metals don't degrade as is common with organic pollutants (17). The interactive nature of various parameters, that can affect the long-term mobility of metals, must be evaluated. For example, one should consider the effects of metal speciation (metal fractions) and the influence of parental material present at the contaminated sites for the elaboration of a soil remediation strategy.

## 1. 4. 2 Detoxification: remove or stabilize:

No matter which remediation strategy is used, it is always based either of two approaches to achieve the same goal: making the heavy metals less available to contacting organisms (48). The first option is to increase the stability of metals within soil matrix in order to reduce their availability for plants uptake while at same time, ensuring that these metals remain sorbed to the soil particulates. Movement into the soil solution and subsequent leaching to ground water must be minimized. There are many techniques/procedures to stabilize/limit heavy metal mobility. The most common technique is to increase the soil adsorption interactions with metals. This can be done by increasing pH and CEC and/or with the addition of lime (calcium carbonate) and organic compounds. Zeolite, laminar silicate, iron and aluminium oxides have been used to remove heavy metals from industrial waste waters and for the immobilization of metals within polluted soil (4, 22, 36, 48).

The second strategy to detoxify heavy metal pollution is to separate the heavy metals from the soil. Most of the remediation techniques are based on this approach. To extract heavy metals from the soil successfully, it is important to reduce their adsorption to soil particles (or increase metal mobility). This can be done with several strategies. As an example, soil pH can be decreased with acid (citric acid or phosphoric acid) to increase metal solubility to soil solution (31). Also the addition of salt (calcium chloride) (32,35) or organic chelators, including ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA) can reduce the metal adsorption to soil particulates (29, 30, 32).

## 1. 4. 3 Treatments for Heavy Metal contaminated soil:

To date, certain methods have been developed to remediate the contaminated soil. Remediation processes can be divided into two approaches. The first one is an *In Situ* treatment, in which the soil is treated in place, without excavation and subsequent transport to a second location. The second approach is referred to as *Ex-Situ*. It involves the removal of contaminated soil following excavation. The concern with this method remains the exposure to contaminants when soil needs to be treated at another site (4).

In order to mitigate the environmental problems that have been caused by the heavy metal contamination, many studies have evaluated potential remediation methods including treatment of the soil to remove these contaminants. Several treatments are available, including chemical techniques that remove heavy metals from the soil while others include bioremediation that employ suitable microorganisms to transform the mobile heavy metal into the less bio-available form (10). All of those techniques have certain advantages and limitations. Although the concepts behind each treatment is different, they all have the same goal: to remove contaminating metals from the damaged region and transform them to a less available form or area. To achieve the goal of the remediation, these treatments should be simple to perform, free of deleterious side effects, economical, and applicable to a wide variety of geographic and climatic areas (4).

## 1. 4. 4 Bio-Remediation

Bio-remediation is an immobilization technique that is based on use of genetically modified microorganisms to alter the heavy metals fraction so as to convert them from a toxic form(s) to a less available form(s). Relative to other strategies, this method can be applied in an extended area at the same time and it remains the economical approach. However, this technique has certain limitations, including the fact that it is time consuming to perform. Climate and geological conditions can also limit the suitability of this method. Moreover, high concentrations of toxicants can limit or completely inactivate microbial activity. It is not a permanent solution, since metals remain in the soil, and their availability can be altered by many environmental parameters including acid rain. Thus, this method is only suitable for a moderately contaminated soil and represents a temporary treatment (4, 10).

## 1. 4. 5 Phyto-Remediation

Phyto-remediation is another treatment to physically remove heavy metals from contaminated soil. This technique is based on the concept that certain plants require metals as nutrients; thus contaminants can be accumulated within their tissues, and can be removed at harvest. Certain plant species can hyper-accumulate certain heavy metals and the subsequent recovery of the contaminating metals from plant materials can be easier

than from the soil. This method can be applied to wide areas at the same time and it is also an inexpensive method to remove contaminants from soil. However, it remains a very time consuming method that can also be limited by geological and climate conditions. Another side effect is that hyper-accumulation does not work well when the degree of contamination is very high. Moreover, certain metals require a specific plant species for the efficient uptake. Hence, the ability to treat a variety of metals is decreased. For example, plants species capable of hyper-accumulating lead have not been identified to date (37).

Table 1. 3. Summary of *in situ* and *ex situ* treatments for contaminated soil

| Technology | Applicable Contaminants |
|---|---|
| *In Situ* | |
| Bioremediation | Petroleum hydrocarbons |
| | Chlorinated solvents |
| Vitrification | Petroleum hydrocarbons |
| | Chlorinated solvents |
| Stabilization | Petroleum hydrocarbons |
| | Chlorinated solvents |
| | Metal |
| Isolation / Containment | Petroleum hydrocarbons |
| | Chlorinated solvents |
| *Ex- situ* | |
| Land Treatment | Petroleum hydrocarbons |
| | Coal-tar residues |
| Thermal Treatment | Petroleum hydrocarbons |
| | Chlorinated solvents |
| | Coal-tar residues |
| Solidification | Petroleum hydrocarbons |
| | Chlorinated solvents |
| | Coal-tar residues |
| | Metal |
| Chemical Extraction | Petroleum hydrocarbons |
| | Chlorinated solvents |
| | Coal-tar residues |
| | Metal |
| Excavation/ disposal | Petroleum hydrocarbons |
| | Metal |
| | Coal-tar residues |

## 1. 4. 6 Excavation

This is a physical treatment to dilute the contaminated soil with regular soil. Although this method has been applied in Australia, there are many environmental concerns with this treatment, since it can cause migration of contaminants from polluted site to a less highly polluted area. The advantages of this method include the fact that it is simple to perform, fast and economical. But is not a permanent solution (4).

## 1. 4. 7 Leaching

Leaching or soil flushing is an *in situ* treatment that can be relatively more costly to perform. It involves leaching the soil with water that often has been supplemented with a surfactant or chelating reagent to remove the contaminants. The leachate is then collected, down gradient from the site, using a collection system for subsequent treatment and disposal. The side effects of this method is that large quantities of water are needed to mobilize the pollutant, and consequently, the waste stream is very large and disposal cost can be very high (4).

## 1. 4. 8 Soil washing Treatment:

Among of available methods, chemical extraction or soil washing remains one of the more practical techniques used by industry. It is both a physical and chemical treatment based on a separation principle that brings a chelating reagent into contact with the polluting metals. The chelating reagent can increase the aqueous solubility of metals and remove them from the soil particulate fraction.

The most commonly used solutions to extract heavy metal from soil are water, acid solution, and solutions of organic complexants. Water and acid solutions have proven to be either too mild or too aggressive, which leaves organic complexant as the preferred option (32). For example, several researchers have demonstrated that ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA) and nitrilotriacetic acid (NTA) can be applied successfully to extract heavy metals from contaminated site (32, 39, and 41).

The advantage of the complexation method is that metals are removed permanently from soil within a short time, but processing is more expensive when

compared with many others treatments. At the same time, there are certain environmental concerns about the chemical additive used in this method (4). These concerns include the stability and toxicity of the reagent once released into the environment. For example NTA is considered to be a carcinogen. In addition, most chelating reagents are effective for the extraction of cationic metals, but the efficiency is reduced for the mobilization of anionic metals. For example arsenate ($AsO_4^{3-}$) and arsenite ($AsO_3^{3-}$) cannot be mobilized easily with EDTA (31). Moreover, the applications of certain chelating agents (EDTA and NTA) have demonstrated that they are relatively bio-stable and are degraded only very slowly. Their presence within soil can increase metal mobility and metal uptake by plant (29, 30).

## 1. 5. 1 Chemical Extraction in Soil Washing Treatment

The clean up of soil contaminated with heavy metals is one of the more difficult tasks for environment remediation. Several techniques have been developed that aim to remove heavy metals from the contaminated soil, including ex-situ soil washing with various physical-chemical methods (38).

### 1. 5. 2 Application of Soil Washing:

Soil washing is a treatment technique that combines both physical and chemical processes to produce an appreciable volume reduction of contaminated soil. It is widely regarded as a panacea for the huge inventory of contaminated soils. This environmental technique is based on the same principals used in hydrometallugy for ore processing (42).

This technique has received a great deal of attention in the United States. This recognition has been given additional impetus by the Superfund Amendment and Reauthorization Act (SARA). SARA has described remedial actions that permanently and significantly reduces the volume, toxicity, or mobility of contaminated material. The legislation has further recognized that remedial action should be a permanent solution and has advocated that alternative treatment technologies or resource recovery technologies be used to the maximum extent in practice (43).

Moreover, the EPA has recently completed a review of the potential markets for remediation technologies, including soil washing. This review concluded that: "There is a need for increased use of new separation technologies (such as soil washing) that reduce the quantity of waste requiring solidification/stabilization, or permit the recycling of valuable metals"(43). Because of the enormous quantities of contaminated soil that require treatment, EPA has estimated the potential market for soil washing techniques. This estimation indicated that over 20 million cubic yards of soil were contaminated with metals and the quantity continues to increase each year (43).

## 1. 5. 3 Principal of Chemical Extraction:

Chemical extraction has been used for the determination of the heavy metal concentrations in soil and sewage. This technique has a great potential to be improved and applied to the washing of soil to remove the metal contaminants. The principal of chemical extraction is based on the functioning of chelating reagent in the solution as surfactants to bind metal while soil is washed. Technically, any substance that does not cause side effect (or minimizes them) while, at same time, has the ability to mobilize the metals from the soil particulate fraction during the washing process can be applied to reduce the heavy metal contamination.

Desorption from organic matter, clay, minerals, metal oxides, and soil particles in general is the principal mechanism of heavy metal removal from the soil. Metal desorption from soil materials is influenced by the presence of inorganic and organic ligands capable of combining with the metals to form stable complexes and chelates. The role of inorganic complexation in metal retentions within the soil has been subject of extensive research. It has been demonstrated that inorganic ions do not reduce metal sorption appreciably. In contrast, organic ligands can suppress metal sorption within the soil-water system by competing with the specific solid surface sites for the free aqueo-metal ion. Alternately, these organic materials can be sorbed on particular surfaces and reduce the adsorptive capacity at these sites. Organic ligand can also enhance metal sorption by forming stable surface ligand adducts capable of complexing or chelating the metal ion while facilitating the simultaneous coordination of the metal to the particle surface (29).

## 1. 5. 4. Factors affecting soil-washing processes: (10)

1- Clay content; an increased clay content increases the total surface area per volume of soil. Therefore, it becomes more difficult to extract the metal pollutant.

2- Complex mixtures of metal waste can affect the selection/formulation of washing solutions that contain chelating reagent.

3- High humic content can decrease the mobilities of heavy metals.

4- Metal concentrations and fractionation. Not all metals are in a soluble form, they can be very strongly bound to minerals, organic matter, or oxides that can be very stable and very difficult to extract.

5- Mineralogy. The type and concentrations of various minerals appreciably influence contaminant binding processes.

6- Particle size distribution/soil texture, since oversize debris decrease the mean surface area of the soil.

7- Longer washing times can be required for metal that is strongly bound to soil.


## 1. 5. 5 Properties of Chelator:

The complex structures of soil and the complications associated with different metal characteristics make remediation treatments more difficult. The choice of chemical additive(s) for soil washing is therefore a critical decision that can determine the relative success of the treatment. It is essential to have a good understanding of the characteristics and properties of chemical additives, metal properties and their interactions with each other.

A metal complex is formed when there is an association between a metal ion (an electron deficient species) and electron rich ligand that is capable of donating electron density to form one or more coordinate bonds. If the interaction results in ring formation, the product is an especially stable adduct that is known as a chelate (from the Greek meaning clam like). The chelator or ligand (reducing agent) acts as an electron donor that behaves as Lewis base whereas the metal ion acts as an electron pair acceptor and behaves as a Lewis acid. In most cases, metal-complexes result from the electrostatic attraction between the metal ion and the anionic or polar ligand (8).

For chelation, the ligand must contain at least two separate donor sites that are capable of interacting with the same metal ion. Species that act as electron donors are typically the more electronegative elements or heteroatoms and include nitrogen, phosphorous, oxygen, and sulphur. Donor atoms can be part of an acidic or basic functional group. A basic group is one in which an atom carries a lone pair of electrons that can interact with a metal ion (or a proton). An acidic group can lose a proton and coordinates with a metal ions (8). A further condition for chelation is that the functional groups should be geometrically positioned within the ligand so that ring formation can include the metal ion. For example, in ethylenediamine the two amino groups are separated by an ethylenic carbon fragment. This carbon bridge confers some degree of flexibility to the molecule. It can easily adopt a conformation in which the nitrogen atoms occupy adjacent position in the coordination shell of a metal ion with only minimal distortion from the "natural" tetrahedral bond angles of tetravalent carbon (8).

The extent of interaction for a chelating ligand with metal ions in solution can be described as a general complex formation equilibrium. Each metal ion, $Mn^{+n}$, is hydrated and reacts with ligand, L, in a series of replacement reactions with water. If L is an uncharged unidendate ligand, the formation of complexes proceeds in a manner with successive replacements of water molecules:

$$M(H_2O)_x^{n+} + L \leftrightarrow M(H_2O)_{x-1} - L^{n+} + H_2O \quad (K_1)$$

$$M(H_2O)_{x-1}L^{n+} + L \leftrightarrow M(H_2O)_{x-2} - L_2^{n+} + H_2O \quad (K_2)$$
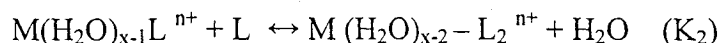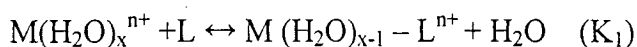
Successive reaction will continue until an equilibrium has been reached (8).

## 1. 5. 6. 1 Classification of Ligands:

There are several different types of ligands with different properties and abilities to react with metals. Certain ligands have multiple binding sites that enable them to bind multiple metal ions at once, whereas other have only two binding sites with lower binding efficiencies. Thus, ligands can be classified according to the number of donor atoms (binding sites) and sub-divided further in terms of the particular types of functional groups. This provides some information that can help to predict the properties of the ligand (8).

## 1. 5. 6. 2 Bidenate Ligands:

Conventionally, chelators are classified as bidenate, tridendate, or as multidenate ligands. Bidenate ligands can be classified further into 3 categories: one category contains 2 basic functional group, the second has one acidic and one basic group, whereas the last one has two acid groups.

The ligand with two basic groups functions as the neutral molecule and the resulting chelate has the same charge as the one originally on the metal ion. Example of the first category includes ligands that contain two nitrogen donor sites. They range from aliphatic (acyclic) compounds like ethylenediamine, to heterocyclic bases. Ligand with two acidic groups include inorganic acids as well as certain other organic ligand. The chelation by inorganic anions normally contains three or four oxygens , such as, $CO_3^{2-}$ $SO_4^{2-}$, and $PO_4^{3-}$. For example, the complex $[Co(NH_3)_4CO_3]$ contains a bidentate carbonate ion and the cobalt(III) ion achieves its customary coordination number of 6. The simplest organic dibasic acid is oxalic acid and the planar oxalate ion $C_2O_4^{2-}$ behaves as a bidentate ligand forming a five-membered ring. The stability of resulting complex is decreased as the number of spacer methylene groups within the ligand is increased (8).

A chelator with one acid and one basic group has many opportunities to be arranged in conformations of low energy so that chelation can occur. One reaction observed frequently with these ligands is that they form electrically neutral complexes. This happens if the process of chelation satisfies both the oxidation state and coordination number of metal ion. In general, if the coordination number is twice the oxidation state, chelation with this ligand can result in the formation of an uncharged complex. This type of complex formed by one acid and one basic group is commonly referred to as an "inner complexes".

## 1. 5. 6. 3 Multidentate Ligand:

Many molecules or ions contains more than one donor atom that can coordinate with a single metal ion at two or more positions within its primary coordinate shell. The ligand is said to behave in a multidenate fashion. Chelators with multidenate character are of special interest, since they commonly display higher avidity for metal cations. Many chelating reagents have more than two donor atoms that in most cases are oxygen or

nitrogen. With a greater number of potential binding sites, the ligand is able to occupy more positions of the primary coordination sphere of the metal ion. In order to provide an increased understanding of the characteristics of multidenate ligands, the basic structure of a simple bidenate ligand, ethylenediamine, will be described. In this molecule, the donor nitrogens are attached to adjacent carbon atoms, and when binding to a metal cation occurs, a five-member ring is formed. The process of chelation will spread the excess electron density over all five atoms. Therefore, one way to design multidenate ligands is to use a longer carbon spacer chain and continue with more substitutions of further primary amine groups on three, four, or more adjacent carbon atoms.

A favorable situation for multidenate ligands to react occurs when one or two donor functional groups act as linking atoms within the molecule, to facilitate the introduction of a side-chain carrying another donor atom. As examples, (Figure 1.1), the structure for *N*-(2-aminoethyl)-ethylenediamine and *N,N*–di–(2–aminoethyl) ethylenediamine are presented. Both molecules have flexibility and can assume an appropriate conformation without appreciable distortion. This ability enables them to wrap around the metal ion without difficulty. Complexes of *N,N*–di–(2–aminoethyl) ethylenediamine typically are very stable. It is quite feasible to synthesize penta-and hexadetate ligands of similar structure to provide complexes with increased stability (8).

### 1. 5. 7 Selectivity of Chelating Agent during Heavy Metal Extraction (10)

For successful extraction of heavy metals, there are certain criteria that must be considered during the selection of the chelating agent.

a.  The chelating agent should be toxicologically innocuous and unreactive with soil and not have adverse interactions with the environment post treatment.

b.  Ligands with multiple coordinating sites are preferred, since they are capable to forming more stable complexes with heavy metals.

c.  Ligands that contain sulfur and nitrogen groups are preferred, since they represent donor atoms that interact preferentially with transition metals (Cu, and Ni) and soft sphere cationic metals (Zn, Cd, Pb, and Hg). Ligands with sulfur or nitrogen atoms are more prone to react with soft sphere cations whereas ligands with oxygen react preferentially with hard sphere metal cations (10).

Figure 1.1 The structure of $N$-(2-aminoethyl)-ethylenediamine and $N,N$–di–(2–aminoethyl) ethylenediamine



N-(2-aminoethyl) ethylenediamine

$N,N'$-di-(2-aminoethyl) ethylenediamine
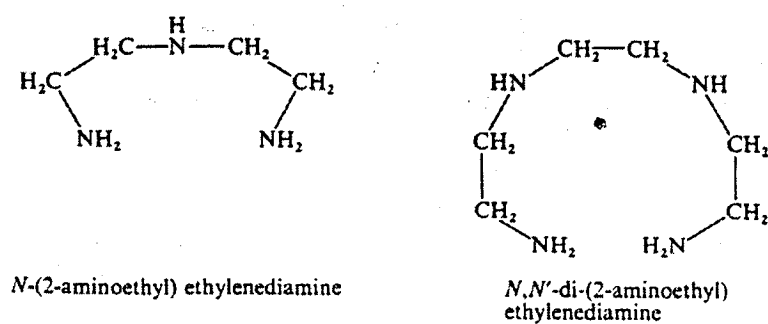
## 1. 5. 8. 1 Aminopolycarboxylic acids:

The aminopolycarboxylic acids are among the most effective chelating ligands. They are derived from the simple amino acid glycine that contains one amino (nitrogen group) and one carboxylate within its molecular structure. A five–membered ring is formed during the chelation process. This type of chelator can contain several carboxylate groups bound to one or more nitrogen atoms with the result that several chelate rings can be formed. With the nitrogen group present in this ligand, interactions with metal cation are characterized by a preference for soft sphere cation metal.

The most widely used aminopolycarboxylic acids are NTA and EDTA. The practical value of EDTA and NTA is based on their abilities to form stable, water soluble complexes with many metal ions. This property is stronger for ions such as magnesium and calcium, which is applied as the basis of an analytical method for the determination of the hardness in water caused by these two metal ions.

## 1. 5. 8. 2 EDTA

The tetra acid, EDTA, has a low water solubility (0.2 g per 100 cm$^3$ of water) and therefore this reagent is used commonly in the form of disodium salt $Na_2H_2Y \cdot H_2O$ (solubility = 10.8 g in 100 cm$^3$ at 22°C) (8). It is both an industrial and analytical reagent because of its ability to complex with many divalent and trivalent metal cations that are characterized by up to a hexadenate primary co-ordination sphere (six bonds). EDTA has been applied in various remediation treatments and has demonstrated a high affinity for both exchangeable and oxide metals within polluted soils (38, 40). It is currently scheduled by EPA for acute toxicity evaluation. This chelator has been used with both mammals and aquatic organisms to treat various heavy metal intoxications (2).

In general, the relative stability of a metal-EDTA complex in the presence of other metals can be predicted from the relative stability constants, the pH of the solution, and the concentrations of metal cations, EDTA, and other electrolytes. Figure 1.2 provides a comparison of the stability constants for various metal-EDTA complexes as a function of pH. At low pHs (<3.0), the tendency for metal-EDTA complexes to form can be assumed to follow the following sequence: $Fe^{3+}> Cu^{2+}> Pb^{2+}> Al^{3+}> Zn^{2+}> Mn^{2+}> Ca^{2+}> Mg^{2+}$ (47). The formation constants for metal-EDTA complexes are presented in Table 1.3 (48).

## 1. 5. 8. 3. NTA

Nitrilotriacetic acid (NTA) is structurally somewhat similar to EDTA, in that they both have N and COOH functional groups. This complexing reagent forms a maximum of four bonds with a metal cation. It has been demonstrated to increase metal mobility in soil. It has been used to reduce metal toxicity to mammalian, aqualtic and microbial life (2, 29). Although NTA has the ability to mobilize heavy metals, it has been demonstrated to be toxic and might not be a suitable reagent for environmental applications. Some studies have demonstrated that Fe-NTA is a potent nephrotoxic agent, that can enhance ornithine decarboxylase (ODC) activity and cause renal oxidative stress and decrease the renal antioxidant enzyme (59, 60).

Other aminopolycarboxylic acids, that have been synthesized and evaluated for metal-complexing properties, include 1,2-diaminocyclohexanetetraacetic acid (DCTA),

ethyleneglycolbis(2-aminoethylether)tetraacetic    acid    (EGTA),    and
diethylenetriaminepentaacetic acid (DTPA). These 3 chelator have imidodiacetate acid
groups that are linked together in various ways to provide variation in the stability
constants of their complexes with metals (8). DTPA possesses both amino and
carboxylate functional groups and can form octadentate complexes with heavy metals. It
can be used as an efficient chelator to estimate metal bio-availability in soils or sediment
(2).

Fig 1.2. Variation in the stability constant for various metal-EDTA complexes as
function of pH (2).
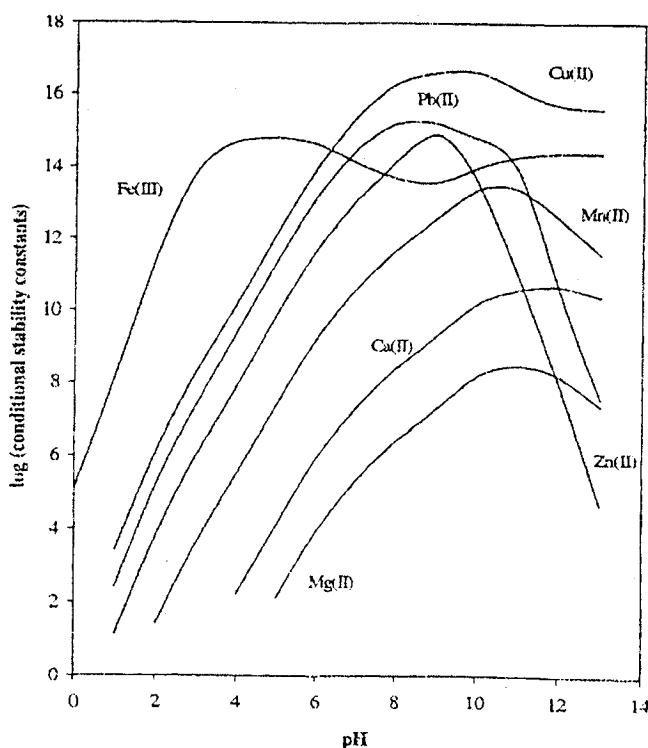
Table 1.4. Log of stability constants for metal-EDTA complexes (48)

| Ele ment | Cation | LogK$_{(M-EDTA)}$ | logK$_{(M-HEDTA)}$ |
|---|---|---|---|
| Cadmium | Cd$^{+2}$ | 16.5 | 2.9 |
| Calcium | Ca$^{+2}$ | 10.7 | 3.1 |
| Chromium | Cr$^{+3}$ | 23.0 | 2.3 |
| Copper | Cu$^{+2}$ | 18.8 | 3.0 |
| Iron | Fe$^{+2}$ | 14.3 | 2.8 |
| | Fe$^{+2}$ | 25.1 | 1.4 |
| Lead | Pb$^{+2}$ | 18.0 | 2.8 |
| Magnesium | Mg$^{+2}$ | 8.7 | 3.9 |
| Manganese | Mn$^{+2}$ | 14.0 | 3.1 |
| Mercury | Hg$^{+2}$ | 21.8 | 3.1 |
| Nickel | Ni$^{+2}$ | 18.6 | 3.2 |
| Zinc | Zn$^{+2}$ | 16.5 | 3.0 |

Fig 1.3. Chemical structures of NTA, EDTA and N-(2-aminoethyl)ethylenediamine at neutral pH (2).
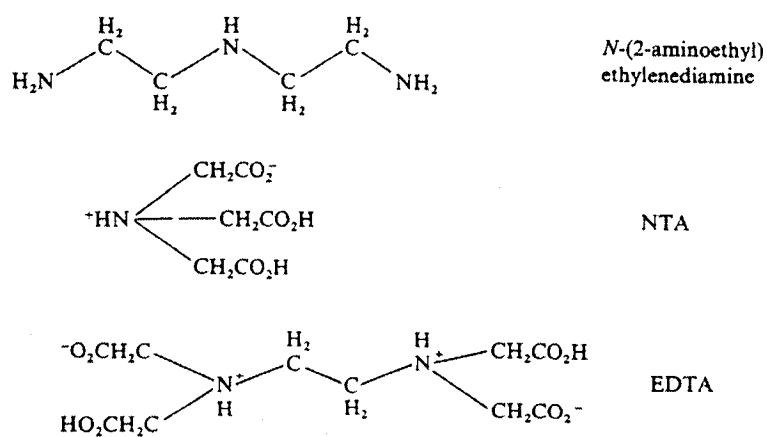
### 1. 5. 9 Dithiocarbamate ligands (HEDC):

Bis(2-hydroxyethyl)dithiocarbamate (HEDC) is a complexing reagent that has been described in the technical literature on several occasions. This ligand has become a focus of current research because of its behavioral similarity to diethyldithiocarbamate (DEDTC) in its reaction with metals. HEDC has 2 sulfur groups that provide the potential to interact with transition metals as well as to reduce certain other metal cations from their oxidized form to reduced forms [e.g., Cr(IV) to Cr(III)]. This chemical has been used as titrant to determine nickel. An interesting feature of this compound is that both the starting reagent ($Na_2HEDC$) and the heavy metal complexes [M-(HEDC)$_2$] are somewhat soluble in water. This contrasts the non-polar nature of most M-(DEDTC)$_2$ complexes. Moreover, this chemical has also been applied to pre-concentrate metals from seawater using solid phase extraction (9).

### 1. 6 Recycling of Chelating Reagent

Soil washing techniques with chemical reagents (chelators) have proven to be an efficient strategy to mobilize heavy metals from contaminated soil. This treatment can result in the permanent removal of heavy metal from the polluted site if the aqueous extract is separated from the soil particles. Strong chelating reagents, such as EDTA (47, 48), can extract heavy metals more completely however, there are 2 main difficulties with this technique. The first limitation is that the technique remains an expensive treatment because of the huge amounts of chelating reagent required to mobilize heavy metals from polluted sites (47). The second perceived difficulty results from the environmental concerns that the chemical additive (chelating reagent) is recalcitrant within the soil environment. The challenge remains to recover and recycle the chelating reagent. The improvement for soil washing using a chelometric extractant that is recycled several time represents a further improvement for chemical extraction (40). Reuse of the chelator for at least three to four time is necessary for the process to become more economical and environmentally accepted.

Research has demonstrated that chelating extraction is viable for soil remediation but that only moderate strength chelators can be recovered (46). However, there are also a

limited number of studies that have indicated that strong chelating reagents, like EDTA, that are not biodegradable, can be recovered and recycled (38, 40).

One reported recycling method was the application of electrolysis in conjunction with a cation exchange membrane to recover metals from solutions of metal-EDTA complex (47, 48, 49). Although results demonstrated that the recovery of metals and EDTA could be as high as 99 and 91%, respectively, the recovered EDTA was not reused for further treatment of contaminated soil. Moreover, the high pH (>10) in the cathode compartment resulted in the degradation of the membrane, and precipitation of EDTA on the membrane surface that resulted in a diminished EDTA recovery and a diminished current efficiency (47). Thus, several operating problems must be addressed before the electro-membrane system can become a practical and feasible treatment for recycling EDTA.

Other recycling methods are based on the concept of ligand release from its metal complex by precipitating the metals as their insoluble hydroxides. Other researches have used salts that compete with the heavy metals for the ligand (10). Additional studies have demonstrated that addition of $Na_2S$ can separate metals from EDTA complexes efficiently, since $Na^+$ competes with the heavy metal for the ligand and the heavy metal forms insoluble sulphides. This method has been improved with addition of $Ca(OH)_2$; the added $OH^-$ reacts with metal to form metal hydroxides that is precipitated when the pH is increased further (10).

In addition of $Na_2S$ and $Ca(OH)_2$, several similar researches have been performed. Metal-ligand complexes were separated and precipitated with several other chemicals, including phosphate and sulfate (47). Studies have demonstrated further that precipitation of lead ion, as lead hydroxide or as lead sulfide, can be performed at high pH. Furthermore, addition of ferrous sulfate, at pH 6-9, was found to be effective in treating Cu-EDTA complex in metal finishing wastewaters. Ferrous ions from ferrous sulfate were able to displace $Cu^{+2}$ in the Cu-EDTA complex by forming a more stable Fe-EDTA complex. Still other research has demonstrated that the addition of calcium hydroxide to a Fe-EDTA solution resulted in the precipitation of more than 99% of ferric ions from Fe-EDTA complex (47). Similar studies have reported that calcium ion was effective in binding with EDTA at high pH, freeing the heavy metal from the metal-EDTA complex

by forming hydroxide or carbonate precipitate (47). Experiments were performed based on the above strategy that demonstrated that the EDTA recycle could be achieved with either phosphate and sulfate precipitation to separate Pb from its EDTA complex. The liberated EDTA was reused several times (47).

The addition of zero–valent Mg and/or Fe metal flakes can also separate metal-EDTA complexes based on heavy metal hydroxide precipitation. Zero-valent Mg and Fe particles can be hydrolyzed spontaneously by water to generate $OH^-$ that can react, in turn, with heavy metals to form insoluble $M(OH)_n$. A second redox reaction associated with this procedure has been referred to as cementation. Zero-valent Mg or Fe can be oxidized spontaneously, while certain heavy metal ions are reduced to their elemental form. In this reaction, electron transfer occurs at the zero-valent metal surfaces so that the reduced heavy metal becomes plated right at the surface of the excess zero-valent metal. The net effect is that the heavy metal is removed from solution. This technique was performed originally with Fe powder to remove dissolved heavy metals from acid rock drainage waste (10). However, dissolving metal reduction has been popular in organic and organometallic chemistry for many years.

### 1. 7 Research Objectives: Chemical Extraction in Soil Washing Treatment

The search for improvements to the soil washing technique has been the main focus of this research. The goal was to improve the efficiency of metals extraction during soil washing by increasing the interaction and binding strength between metals and chelator to form water soluble complexes. Another objective of this research was to recycle the chelating reagent. It was anticipated that less chemical would have to be released post treatment and at the same time, treatment costs would be reduced correspondingly. Since previous research had demonstrated that certain iminodiacetate chelating reagents (EDTA analogs) were not very toxic but were not degraded rapidly in the environment (30), recycling these reagents to perform multiple extractions seemed to be a prudent objective. The selectivity of the chelating reagents, a consideration of the type of soil, the type of contaminating metal, and the ways that heavy metals are bound up within the soil are all important factors that determine the success of the method.

Therefore, the objective of the studies described in this thesis were to evaluate and optimize a possible remediation procedure for an urban soil that had been burdened with excess heavy metals. These objectives were to be accomplished by

1- Performing a metal fractionation of the soil to demonstrate that an appreciable portion of the total metal burden was in a form that could be mobilized by complexometric extraction.

2- Removing the mobilized heavy metals by precipitation from their aqueous metal complex(es) so as to be able to recycle the liberated complexing reagent back to the soil to extract more heavy metals.

3- Comparing the efficiencies of mobilization using EDTA versus a mixture of EDTA with a water soluble bis-(2-hydroxyethyl)- dithiocarbamate (hydroxyethyl-dithiocarbamate).

4- Monitoring the relative extraction efficiencies with increasing quantities of the contaminated soil.

5- Determining the fate of any complexing reagent(s) that was lost during processing.


It was anticipated that, with these procedures, a sparing quantity (less than a stoichiometric equivalent) of complexing reagent(s) could be used to mobilize the dislodgeable fraction of the total heavy metal burden.

# Chapter II

## Preliminary Tests – Soil Sample preparation and Characterization

### 2. 1 Introduction:

The requirement to remove heavy metals from contaminated lands results from the potential deleterious impacts that excesses of these compounds can have on biota. In order to generate accurate estimates of the soil's properties, sample preparation is the first important step for soil analysis; it is important to provide precise information on the quantities of heavy metals present in the soil as well as other characteristics of the soil matrix.

Before applying chemical extractions in soil washing treatments, there are four major preliminary procedures that are required to condition and characterize the soil. These include: soil handling, soil characterization, soil fractionation and total heavy metals determination. Soil handling involves drying, screening and homogenizing the soil to provide a uniform sample. The process of soil characterization involves tests to determine the relative proportions (percentages) of soil particle sizes (conventionally soil texture is grouped into clay, silt and sand), carbonate content, pH, organic content and the cation exchange capacity (CEC) of the soil sample. Soil fractionation studies evaluate the quantities of the different metal fractions in soil and include exchangeable, carbonate, Fe/Mn oxide, organically bonded and residual metal fractions.

### 2. 2 Sample Handling: Drying and Screening:

Drying, screening and homogenization are the common steps for all soil analyses prior to analytical determinations. Most soils arrive at the laboratory in a "field-moist" condition. This means that the sample may range from air dry to water-saturated. Since virtually all soil parameters are expressed on a per weight basis, the soil samples must be dried to some constant and repeatable level. For routine soil testing, all Canadian provinces recommend drying the sample before analysis. Analyses of un-dried samples is not recommended because of the influence of moisture content on soil properties.

A surprising range of drying temperature are recommended across Canada; the conditions of drying vary from province to province. Critical parameters for soil handling

procedures in Canada are summarized in Table 2.1. The degree of drying has an important influence on the amount of potassium extracted from soil containing micaceous clay or vermiculite. There are numerous studies that have demonstrated that the amount of potassium released by drying increases with the drying temperature (50).

Table 2.1. Summary of the recommended methods for routine soil studies from various Canadian provincial governments (50).

|  | Drying | Grinding method | Sieve size | Measuring |
|---|---|---|---|---|
| Newfoundland | 40°C | Mortar & pestle | 1mm or 2mm[a] | Volume |
| PEI | 35°C | Mechanical | 2mm | Weight |
| Nova Scotia | 35°C | Mortar & pestle | 2mm | Volume |
| New Brunswick | <37°C | Mortar & pestle | 2mm | Volume[b] |
| Quebec | 35°C | Mortar & pestle | 2mm | Volume |
| Ontario | 35°C | Flail | 2mm | Volume |
| Manitoba | <35°C | Heavy duty grinder | 2mm | Volume |
| Saskatchewan | 30°C | Flail, except for micro | 2mm | Volume |
| Alberta | 60°C | Flail | 2mm | Volume[c] |
| British Colombia | 55°C | Wood Block | 2mm | Volume |

[a] 1mm for mineral soil, 2mm for organic.

[b] Organic soil weight

[c] Alberta permits a choice of whether laboratory weight or measured volume of sample is used in calculations.

For routine soil tests, almost all Canadian provinces grind the sample to pass a 2-mm screen so as to remove the very coarse sand fraction (1.0-2.0mm diameter). There are different methods/techniques available for the grinding process, ranging from a wood block or agate mortar and pestle to a flail-type device or other mechanical grinder. The soil should not be subjected to force sufficient to fragment the sand, silt and clay particles. Particular care should be taken in the choice of a grinder to prevent contamination if metals quantitations are to be performed. Certain provinces avoid the use of a metal grinder for either metal or micro-nutrient studies (50).

## 2. 3 Soil Characterization:

### 2. 3. 1 Particles Size Distribution Analysis:

The second part of the preliminary testing regimen is soil texture analyses (sometime referred to as particle size distribution analyses). The goal of these experiments is to determine the proportions of different soil particles within the sample. Soil can be classified on the basis of particle size. Conventionally, fractions are grouped into three categories: sand 2.0-0.050mm, silt 0.05-0.002mm, and clay <0.002mm (10). It is important to estimate the size of soil particles, because the smaller soil particles (clay) have an increased surface area to volume ratio. Thus, the ability for this fraction of small soil particle to adsorb metal contaminants is increased. If a higher percent of smaller particles are present in the soil, it is described as having a fine texture. Fine texture soils are plastic and sticky when wet and hard and massive when dry. They are more difficult to plow. In contrast, if the soil is dominated by coarse sand particles, the soils tend to be loose, and friable and are easier to plow (10). The methods and materials used in this research were based on a book edited by Martin R. Carter for the Canadian Society of Soil Science (50).

### 2. 3. 2 Method and Materials:

There are various methods available to determine the soil size distribution. The hydrometer method is a commonly used approach that was used for the determination of particle size in this research.

A hydrometer can be used to measure the density of the soil solution after various settling time to achieve estimates of the particles size distributions. This approach is based on the concept that coarse particles (sand) settle more rapidly than fine particles (clay). Thus, dispersions of soil particles after various times of settling is the indication of particle size that can be measured with a hydrometer.

## 2. 3. 3 Calibration for Hydrometer:

1- Add 100 mL of Calgon solution to the cynlinder and make the volume up to 1 L with distilled water. Mix thoroughly with plunger and let stand until the temperature of the solution has been equilibrated (20°-25°C).

2- Lower the hydrometer into the solution carefully, and determine the scale reading, $R_L$, at the upper edge of the meniscus surrounding the stem.

## 2. 3. 4 Hydrometer Procedure:

1- Weigh 40.0 g of soil into a 600-mL beaker, add 100 mL of Calgon solution and approximately 300 mL distilled water, and permit the sample to soak overnight.

2- Weight another aliquot of the same soil (10g) for determination of oven-dried weight. Dry sample overnight at 105°C, cool, and weigh.

3- Transfer the Calgon-treated sample to a dispersing cup and mix for 5 min with the electric mixer (milkshake machine).

4- Transfer the suspension to a cylinder and add sufficient distilled water to increase the volume to 1 L.

5- Allow sufficient time for the suspension to become equilibrated at room temperature (between 20 and 25°C).

6- Insert the plunger and move it up and down to mix the contents thoroughly. Dislodge sediment with strong upward strokes of the plunger near the bottom and by spinning the plunger while the disk is just above the sediment. Complete the stirring with 2 or 3 slow, smooth strokes. Record the time required for complete stirring. Add a drop of amyl alcohol if the surface of the suspension becomes covered with foam.

7- Lower the hydrometer carefully into the suspension and record the reading after 40 seconds ($R_{40s}$).

8- Remove the hydrometer after 40 second, rinse it and wipe it dry.

9- Reinsert the hydrometer carefully and record a second reading at 7 hours ($R_{7h}$).

## 2. 3. 5 Calculation:

Sand % = $(R_{40s} - R_L)$ * 100/oven dried soil Wt. in g

Clay % = $(R_{7h} - R_L)$ * 100/oven dried soil Wt. in g

Silt % = 100 − (sand % + clay %)

The result indicated that the soil under this study was a sandy loam. Details concerning the other soil tests, including organic content, CEC and soil pH have been summarized in the Table 2.2

**Table 2.2 Summary of Sample Soil Characteristics**

| | |
|---|---|
| Sand (%) | 17.1 |
| Clay (%) | 6.2 |
| Silt (%) | 76.6 |
| CaCO3 (%) | 18.5 |
| PH | 7.0 |
| Organic Content (%) | 0.9 |
| CEC [cmol(+) kg$^{-1}$] | 9.7 |

## 2. 4. 1 Cation Exchange Capacity:

Soil posseses electrostatic charges that result from atomic substitutions within the lattices of soil minerals and (as result of hydrolysis) reaction on broken edges of the lattices and at the surface of oxides, hydroxides, and organic matter. The charges attract counter (exchangeable) ions and form an exchange complex. The principle of the methods for exchangeable ions is to saturate the exchange complex with some cation that can be bound preferentially to the exchangeable sites that are already present on the charged surface. Cation Exchage Capacity is a measure of the amount of ions that can be adsorbed, in exchangeable fashion, to the negative sites within the soil matrix (50).

Many methods are available to determine the CEC of soil. The $BaCl_2$ method is one such method that rapidly can provide effective CEC measurement for a wide range of soil types. This method is based on the measurement of exchangeable cations: Ca. Mg, K, Al, Fe and Mn. For a soil with a large amount of pH-dependent cation exchange sites, the

capacity measured at pH 7 will be considerably greater than the capacity determined with this method (50).

## 2. 4. 2 Materials and Method: The BaCl₂ Method

The materials required for this method include:

(1) Barium chloride, 0.1M.

(2) Standard solution of Ca, Mg, K, Na, Al, Fe and Mn that is used for the measurement by Atomic Absorption Spectrometry (AAS).

(3) Lanthanum solution (100g $L^{-1}$ or 53.49g of $LaCl_3 \cdot 7H_2O$ dissolved in 200 mL DD water)


The procedures to be performed for this method are:

1- Place 0.5g of dried, organic, or fine texture soil (or 3.0g of coarse textured soil) into a 50 mL centrifuge tube. Record the exact weight of each soil sample, including blanks, duplicates, and quality control standards.

2- Add 30.0 mL of 0.1M BaCl₂ to each tube and shake, in end over end fashion, for 2 h.

3- Centrifuge (700 X g for 15 min) and filter to recover the supernatant (SN) fraction.

4- Analyze the cation concentrations of Ca, Mg, K, Na, Al, Fe and Mn by AAS.


The CEC content can be calculated with the following equation:

$$M^+ \text{ cmol } (^+) \text{ kg}^{-1} = C \text{ cmol } (^+) \text{ L}^{-1} * (0.03 \text{ L/wt. Soil g}) * 1000\text{g kg}^{-1} * DF$$

Where,

$M^+$: concentration of an adsorbed cation, cmol $(^+)$ kg$^{-1}$

C: concentration of the same cation measured in BaCl₂ extract

DF: Dilution factor (if applicable)


Effective CEC (or total CEC): CEC cmol $(^+)$ kg$^{-1}$ = $\Sigma$ M$^+$ cmol $(^+)$ kg$^{-1}$

The conversion value corresponding to cmol $(^+)$ are as following:

$$1 \text{ mg L}^{-1} \text{ Ca} = 4.99 * 10^{-3} \text{ cmol } (^+) \text{ L}^{-1}$$
$$1 \text{ mg L}^{-1} \text{ Mg} = 8.23 * 10^{-3} \text{ cmol } (^+) \text{ L}^{-1}$$
$$1 \text{ mg L}^{-1} \text{ K} = 2.56 * 10^{-3} \text{ cmol } (^+) \text{ L}^{-1}$$

$$1 \text{ mg L}^{-1} \text{ Na} = 4.35 * 10^{-3} \text{ cmol } (^+) \text{ L}^{-1}$$

$$1 \text{ mg L}^{-1} \text{ Al} = 11.12 * 10^{-3} \text{ cmol } (^+) \text{ L}^{-1}$$

$$1 \text{ mg L}^{-1} \text{ Fe} = 5.37 * 10^{-3} \text{ cmol } (^+) \text{ L}^{-1}$$

$$1 \text{ mg L}^{-1} \text{ Mn} = 3.64 * 10^{-3} \text{ cmol } (^+) \text{ L}^{-1}$$

## 2. 4. 3 Carbonate Content: Empirical Standard Curve:

Carbon occurs within the soil in both organic and inorganic forms. The greater part of the soil carbon is usually found in the organic matter fraction and among carbonate minerals. While organic carbon occurs in all soils, carbonate only occurs in certain soil. Inorganic carbon commonly occurs as calcite. A variety of methods are available for the determination of carbonate content, and include chemical determination based on an empirical standard curve. This method is based on the principal that the pH of the soil is related to its carbonate content when treated with acid. When a known quantity of acetic acid is consumed by reaction with carbonate, the final pH can be correlated with the dissolution of $CaCO_3$. This is a rapid method that has been used as a routine analytical procedure when large number of samples were involved (51).

## 2. 4. 4 Materials and Methods:

The procedures were performed as follows (51):

1- Prepare calcite ($CaCO_3$) standards in the range of 5 to 500 mg into separate 50 mL centrifuge tubes.

2- Add 25 mL of 0.4 mol $L^{-1}$ acetic acid, a quantity sufficient to neutralize all of $CaCO_3$ in the most concentrated standard (500 mg of calcite). The neutralization reaction has been formulated as:

$$CaCO_3 + 2CH_3COOH \rightarrow Ca^{+2} + 2CH_3COO^- + H_2O + CO_2 \text{ (g)}$$
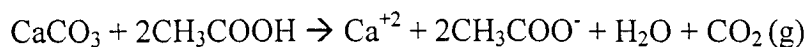
3- Shake solution intermittently during 8 hours and permit the tubes to stand overnight with loosened caps to permit the escape of $CO_2$.

4- Use an ultrasonic probe at low setting to degas the sample and prevent excessive splashing.

5- Centrifuge the incubated solutions and the record pH value.

6- Plot a standard curve of pH versus. Log $[CaCO_3/(T - CaCO_3)]$. T represents the weight of $CaCO_3$ (mg) used to neutralize acetic acid, depending on whether volume or the concentration was used.

7- The identical procedural steps (1 to 6) are repeated using 2g of soil sample (<100 mesh size).

Calculation:

From the observed pH, determine the values of log $[CaCO_3/(T - CaCO_3)]$ and by means of the standard curve, calculate the weight of $CaCO_3$ (mg) in the soil sample.

The % $CaCO_3$ equivalent = mg of $CaCO_3$ / Mg sample *100

## 2. 5 Soil pH determination:

Soil pH remains a critical measurement for routine soil analysis, because many chemical and biological properties of soil are controlled by the pH of the soil solution. Soil pH is normally measured with water, but less frequently it can also be determined using dilute salt solution for certain agricultural soils.

The procedures to measure pH for this research was performed with an aqueous soil suspension 1:2 (m/v). The procedures were performed as follows: 10g of soil sample were mixed with 20 mL DD water. The resulting suspension was shaken for 30 minutes and then permitted to settle for 1 h and then the pH of the supernatant fraction was recorded (51).

## 2. 6 Total Organic Content:

Several important soil properties, including adsorption and retention of water, reserve exchange base, nitrogen supply capacity and soil structural stability all depend, to some degree, on the quantity of organic matter within the soil (52). Analysis of soils for their contents of organic matter has become an important routine procedure for soil characterization.

Several methods are available to determine the content of organic matter in soil, including determinations of organic carbon using wet and dry combustion procedures or

measurement of $CO_2$ evolved or by determining the consumption of a strong oxidizing agent by the sample (52). Chromic acid has been used extensively to measure oxidizable organic content in soil testing laboratories within the USA. However, there are concerns regarding the disposal of Cr wastes. Other replacement reagents, such as humic acid also have been reported to provide an irreproducible result for certain types of soil. Thus, the development of an improved method for measurement of organic content was required (53).

A promising method to determine the organic content of soil is based on the weight loss on ignition. Heating soil sample at temperatures below 500°C can burn off (combust) the organic matter in soil. The difference in weight before and after ignition can provide an indication of the organic matter content of the soil. This method can be performed only at temperatures below 500°C; otherwise errors can be introduced by volatilization of components of the inorganic fraction. For example, the loss of $CO_2$ from carbonate, structural water from clay minerals, oxidation of $Fe^{2+}$. This method has been evaluated many times and proven to be less error prone than comparable wet oxidation techniques (53).

## 2. 6. 2 Method and Material:

The weight loss on ignition was used for the present research. The procedure to determine the total organic content proved to be simple and straight forward. Five replicate determinations were performed. The sequential steps for each determination were (53):

1- Record the weight (about 1g) of each sample.

2- Dry each sample for 2 h at 105 °C.

3- Re-weigh each sample accurately.

4- Maintain the sample at 360°C for 2 h.

5- Permit the sample to cool to room temperature and re-measure the weight.

6- Determine the % of loss on ignition (LOI) and convert to organic content:

$$\% \text{ organic matter (OM)} = 0.973 \text{ LOI} - 0.33$$

The soil contained a high percentage of silt in the 0-20cm layer within the upper horizon of a former battery fabrication facility that had been abandoned for many years. The soil was thus a neutral silty loam with a relatively low organic content and a moderate cation exchange capacity.

## 2. 7. 1 Total Heavy Metal Concentration Analysis:

The total quantity of heavy metals present in the contaminated soil can provide relevant information before the actual extraction is performed. It provides an estimate of the quantities of heavy metals present but without regard to how these analytes are bound up within the soil matrix.

The total heavy metal burden in soil can be determined with numerous different analytical techniques, including nitric acid in combination with microwave or block digestion or with combinations of nitric acid with hydrogen peroxide. The fundamental processing techniques behind these methods are similar; they all use strong acids (normally mineral acid) or mixtures of strong acids to digest the soil sample. Acid digestion is frequently termed wet oxidation. Subsequent determinations are performed on the digest frequently by Atomic Absorption Spectrometry (AAS) or by Optical Emission Spectroscopy (OES) (51). Differences between various recommended acid digestion procedures frequently involve the combination and the type of acids used and the duration of processing.

Commonly used acids include the mineral acid, such as, sulphuric, hydrochloric, hydrofluoric, nitric or perchloric acid (51). In certain cases, surphuric acid is not recommended for the simultaneous extraction of different metals, because of the formation of insoluble sulphate salts. Hydrofluoric and perchloric acids also have certain limitations and they are not recommended for routines metal analyses. Hydrofluoric acid is especially corrosive and can be difficult to contain whereas perchloric acid can form explosive salts with certain metal cations, especially if the vapors are trapped in a wooden or plastic housing of the fume exhaust system. Both acids require special handling procedures because of their corrosive/explosive nature and generally, they are not suitable for routine analyses. To date, nitric acid remains the most widely recommended acid for soil digestions. Many researches have reported that the use of hot

concentrated nitric acid alone or a mixture of hot nitric-perchloric acid has provided comparable results. Therefore, the use of either concentrated nitric, or a mixture of nitric-perchloric acid remains a common digestion practice for metal determinations in many accredited routine laboratories (51).

There are two principal acid digestion methods available: microwave accelerated digestion and nitric acid block digestion (51). Each digestion technique has certain advantages and limitations. Microwave accelerated digestions are rapid, but require more sophisticated and expensive equipment, whereas block digestions are, in general, more time consuming but can be easier to perform.

### 2. 7. 2 Microwave Assisted Digestion:

Microwave digestion is a process that treats the sample with nitric acid in a Microwave Sample Preparation System. The characteristics of this process include the application of an intense microwave energy source at elevated (sealed vessel) or ambient pressure (open focused system) to heat the nitric acid suspension in a short time. This digestion procedure typically requires only 40 minutes to generate a clear solution of digest in a single cycle, which is time efficient compared to other techniques (10). The general procedure of this method is to add the sample in a Teflon-coated vessel together with nitric acid. As soon as acid is added, the vessel is shaken to release all carbon dioxide from any carbonate that was present in the sample. The vessel is then closed tightly using the capping station and a disc seal. The vessel is then heated at 95 % power with pressure of 60 psi for 20 minutes. In order to completely digest the soil sample, the sample is frequently heated for a second time (the total digestion cycle around 40 minutes, 51). Alternately, the digestion can be effected at ambient pressure in an open focused microwave system.

### 2. 7. 3 Nitric Acid Block Digestion:

The second common digestion technique for soil analysis is the nitric acid block digestion. This method is more time consuming but remains a very simple technique to perform. Heat is used to accelerate the conversion of soil suspended in nitric acid into a clear solution. Certain parameters can be modified as required to suit the needs of each

sample matrix. The duration of heating can be modified as needed to dissolve the soil completely. Block digestion was the method followed to prepare soil sample for total metal determinations in this research.

**2. 7. 4 Material and Method for Acid Block Digestion (10,51):**

The digestion method was performed as follows:

1- Concentrated nitric acid, 15 mL, mixed with 1 gram of soil in a glass digestion tube.

2- The sample was heated with a block digestor at $180^{\circ}C$ until nitric acid had evaporated virtually completely (approximately one hour).

3- The acid digest was permitted to cool for 15 minutes.

4- Perchloric acid, 5 mL, was added to the digest.

5- The sample was then re-heated at $150^{\circ}C$ for a further 2 h. The digestion was considered to be complete when the evolution of white vapors had ceased.

6- The resulting crude acid digest was then filtered and diluted to volume with DD water prior to analysis by Atomic Absorption Spectrometry.

The result of experiments to determine the total heavy metal concentrations ($\mu g \; g^{-1}$) present in the soil sample are summarized in the Table 2.3, together with data for the different metal fractions.

## 2. 8. 1 Soil Sequential Extraction – Heavy Metal Fraction

Heavy metals in soil are present in several different forms. The various metal species can be present in a soluble ionic, exchangeable, organically bound or a residual form. Certain of these forms are more mobile, while other forms are very stable and are not converted readily from one form to another. Different metal fractions within soil require different methods to separate them from the soil matrix. The most common technique employs chemical extraction with different reagents to mobilize analyte metals selectively from soil. The various metal fractions behave differently toward different chemical reagents.

## 2. 8. 2 Material and Methods:

Several different procedures have been developed for the determination of metal fractions in soil. The underlying concepts of soil fractionation were presented in the first chapter. This research followed the sequential extraction procedures developed by Tessier et al. (10, 25). The procedures to isolate each fractions are outlined below. The strategy in sequential analysis was to extract the most mobile metal fraction (exchangeable) first and then to proceed to each subsequent fraction in stepwise fashion using increasingly less selective chemical reagents. The extracting procedures started with the weakest salt solution and increased in solvent strength for each successive fraction.

## 2. 8. 3 Exchangeable:

The exchangeable metal fraction is retained within the soil matrix mainly by electrostaic forces of negatively charged sites on clays, minerals, organic matter, or and amorphous materials (at low pH). Based on this electrostatic model, cations of this fraction are isotropically exchangeable and can be replaced by the common cations that are normally present in soil. Since the rate of exchange is rapid, the activation energy for exchange must be relatively low. The binding of the exchangeable metals is considered to begin with electrovalent forces but with time, they can be converted very slowly to covalent binding.

The conventional procedure to determine the exchangeable metal fraction in soil is to treat one g of soil with 8 mL of magnesium chloride solution (1M $MgCl_2$ at pH 7) or sodium acetate solution (20 mL of 1M KOAc, pH 8.2) with continued agitation at room temperature for one hour. Numerous other reagents, including ammonium acetate, sodium acetate, and magnesium chloride have been used to mobilize exchangeable metals from soil. Certain of these reagents have a limitation in that they also extract a portion of other metal fractions. For example, carbonate ($CaCO_3$) has a lower solubility in sodium acetate at pH 8.2. The consequence for the low carbonate solubility is that it will enable other metal fractions to be removed as well and cause an overlap of different metal fractions. For this research, potassium nitrate (0.5M, pH 7, 20 mL) was mixed with one g of soil during 1 hour. The suspension was centrifuged and filtered. The supernatant

fraction was diluted to100ml then stored to await analysis by AAS. The particulate fraction from this procedure was retained for further fractionation experiments (21).

## 2. 8. 4 Carbonate:

Metals bound to carbonate represent a separate metal fraction that is susceptible to changes of pH. The extraction method to mobilize this fraction was to treat the particulate fraction with sodium acetate (8 mL, 1M) adjusted the pH to 5 with acetic acid (HOAc). Some agitation was necessary during this procedure, the time required for carbonate dissolution was dependent on particle size, percentage and the type of carbonate present. To evaluate the optimum time for carbonate metal mobilization, the soil sample was first treated with 1M NaOAc for one hour to remove the exchangeable metal fraction then the supernatant fraction was assayed for calcium concentration at different time intervals. As detailed in several previous reports, the optimum time to extract carbonate bound metals is 5 hours of agitation. Post equilibration, the resulting suspension was centrifuged, filtered and the filtrate was retained for metal determinations by AAS. The soil particulate fraction was retained for further extraction stages (21).

## 2. 8. 5 Fe/Mn Oxide:

Metal fractions bound to iron and manganese oxides occur principally as nodules, or as cement between the soil particles. These oxides are excellent scavengers because of their strong affinities for heavy metal. The most efficient method to extract Mg and Fe oxides involves a combination of different reagents to reduce the metals to their more soluble ferrous and manganous forms. In order to mobilize metals bound to oxides, dilute mineral acids were required. The soil particulate fraction from the previous step was mixed with hydroxylamine hydrochloride [0.04 M, 20 mL in nitric acid, 1+4 (v/v)]. The experiment was performed at elevated temperature (96 ± 3°C) with occasional agitation. For certain soils, the addition of ammonium acetate (NH₄OAc) was desirable to minimize adsorption of extracted metals onto oxidized soil particulates.

The optimum reaction time to reduce/dissolve the Fe and Mn oxides in soil can be evaluated by measuring the Fe concentration in the centrifuged supernatant fraction at various time intervals. Research has demonstrated that the optimum time to extract the

oxide bound metals fraction is 6 hours. Prolonged treatment at this stage can cause attack of the reagent on the metal fraction that is bound to organic matter, as well as metals in the residual fraction (21).

### 2. 8. 6 Organically Bound:

After processing to remove metals bound to iron manganese oxyhydroxides, the fraction of metal bound to organic matter was determined. Trace metals bound to various forms of organic matter included living organisms, detritus, and coatings on mineral particles. Under oxidizing conditions in natural water, organic matter can be degraded resulting in the release of metals in a soluble form.

The next step in the sequential extraction procedure aimed to release the organically bound metals from the soil particulates fraction that resulted from the previous treatment. The particulate fraction was added to a mixture of nitric acid (3 mL, 0.02M) and hydrogen peroxide (5 mL, 30% v/v), and then the pH level was adjusted to 2 with nitric acid. The mixture was heated to 85°C for two hours with intermittent agitation. A second aliquot of hydrogen peroxide (3 mL, 30% v/v) was added to the suspension and the heating was continued for a further three hours at the same temperature. The sample was then permitted to cool. Ammonium acetate [3.2M, 5 mL in 1+4 (v/v) $HNO_3$] was then added. The addition of $NH_4OAc$ was designed to prevent adsorption of extracted metals on to the oxidized particulates. The sample was then centrifuged and filtered as in the previous stages. More efficient methods are available to destroy the organic matter and release organically bound metals, but those techniques require the use of strong and concentrated acids, such as, nitric acid alone or in combination with perchloric acid. Unfortunately the use of the strong acid can dissolve soil particles resulting in the release metal bound up within the residual fraction (21).

### 2. 8. 7 Residual:

The final metal fraction that can to be removed from soil is the residual metal fraction. The residual metals are difficult to remove, since they comprise mainly the primary and secondary minerals that retain trace metals within their crystalline structures. These metals therefore require prolonged treatment to cause release. For this research, the

residual metal fraction was considered to be the difference between the total metal burden in the soil and the sum of the other four fractions (exchangeable, carbonate, Fe/Mn oxide and organic bound). Therefore, no specific procedure was performed to isolate this metal fraction. The relative proportion of the various metal fractions in the urban soil is presented in Table 2.3 and permissible maximal are reported in Table 2.4.

## 2.1. Flow diagram of the Sequential Extraction Procedure (21).

### Exchangeable Particulates

20 mL of $KNO_3$ (0.5M) at pH 7 – agitate 1 g of soil sample during 1 h

### Carbonate Particulate

NaOAc , 8 mL, 1M, adjusted the pH to 5 with acetic acid (HOAc) agitate the soil suspension for 5 h.

### Fe/Mn Oxide Particulate

20 mL, 0.04M $NH_2OH \cdot HCl$ in 20 % (v/v) $HNO_3$ – agitate the sample suspension for 6 h at $96 \pm 3 °C$

### Organic bound Particulate

3 mL $HNO_3$ (0.02M) and 5 ml of 30% $H_2O_2$ of solution was adjusted to pH 2 with $HNO_3$.
The mixture is heated to $85 °C$ for 2 h with intermittent agitation.
$H_2O_2$, 3 mL, 30% is added, and heating is continued for three hours at the same temperature.
The sample is then allowed to cool and $NH_4OAc$, 5 mL, 3.2M in 20% (v/v) $HNO_3$ is added

### Residual Particulates

Total heavy metal burden obtained from nitric acid block digestion minus to the sum of the other four fractions.

Table 2.3 Total heavy metal burden and concentration ($\mu g\ g^{-1}$) of the various metal fractions in the soil sample.

| Analyte | Total HM burden | Exchangeable | Carbonate | Fe/Mn Oxide | Organically bound | Residual |
|---|---|---|---|---|---|---|
| Cd | 6.2±0% | 2.7 | N.D. | 1.8 | N.D | 1.7 |
| Cu | 15.5±7% | 2.2 | N.D. | 11 | N.D. | 2.6 |
| Fe | 10753±3% | 12 | 26 | 7234 | 241 | 3239 |
| Mn | 188±9% | 4 | 45 | 109 | 3 | 28 |
| Ni | 53±9% | 16 | 29 | 12 | N.D. | -4 |
| Pb | 6555±12% | 734 | 3383 | 2101 | 53 | 283 |
| Zn | 160±5% | 6 | 32 | 59 | 1 | 63 |

N.D. = none detected, > 0.01 $\mu g\ g^{-1}$ for Cd, Cu and Ni

Table 2.4. Total heavy metal concentration in the soil sample ($\mu g\ g^{-1}$) and the maximal burden permitted in Quebec (58).

| Analyte | Total Concentration HM burden | Quebec Permissible Maximal | | |
|---|---|---|---|---|
| | | A | B | C |
| Cd | 6.2±0% | 1.5 | 5 | 20 |
| Cu | 15.5±7% | 50 | 100 | 500 |
| Fe | 10753±3% | N.A. | N.A. | N.A. |
| Mn | 188±9% | N.A. | N.A. | N.A. |
| Ni | 53±9% | 50 | 100 | 500 |
| Pb | 6555±12% | 50 | 500 | 1000 |
| Zn | 160±5% | 100 | 500 | 1500 |

N.D. = none detected

A = Heavy metal maxima in soil that is considered to be at natural concentration

B = Heavy metal in soil at critical level that require close monitoring.

C = Heavy metal present in soil beyond the acceptable level and requiring immediate treatment.

Based on the data contained in Tables 2.3 and 2.4, the soil sample was judged to be heavily contaminated with Pb. It contained a level of Pb that was six times greater than the minimum level considered by Quebec government to require immediate treatment. It also contained elevated levels of Cd that were sufficient to warrant close monitoring. Since Pb was the major contaminant in this soil, emphasis was placed on this metal. There were some 4000 ppm of Pb in the sum of the exchangeable and carbonate fractions that were considered to be available for uptake by plants. Therefore, the removal of Pb in these fractions became a primary goal.

# Chapter III

## Recycling of Complexometric Extractant(s) to Remediate a Soil Contaminated with Heavy Metals

### 3. 1 Exploitation of Chelating Reagents:

The application of chemical extraction for soil washing has been studied extensively to evaluate the potential to remediate soils that have been burdened with excesses of heavy metals.

Among the numerous chelators that are available commercially, the application of disodium ethylenediamineacetate (EDTA) has remained among the most promising of reagents on the basis of cost and efficiency. More recent studies have focused on increasing the ability of this chemical to mobilize heavy metals from contaminated soil and on the reuse of this chemical for multiple extraction cycles. Studies have been performed to analyze the efficiency of EDTA at different concentrations and pH levels to mobilize heavy metal from soil. The results demonstrated that if present in excess, EDTA behaved independently of pH, since it was able to mobilize about the same quantities of heavy metal over a range of pHs (40). Another report evaluated the efficiency of EDTA, at 0.0001-0.05M to remove metals for pHs between 2-8 (55). It concluded that excess EDTA was able to extract heavy metals independently of pH, but that limited concentrations of EDTA displayed a complex behaviour versus pH that varied with the identity of target metal cation.

Another study applied EDTA to remediate soil contaminated with 210,000 mg kg$^{-1}$ of Pb from a battery reclamation site. EDTA was able to extract up to 80 % of total Pb burden (or all of the non-detritus Pb). The extraction efficiency was evaluated at different concentrations between 0.02 to 0.08 M. Lead recovery was more efficient at pHs less than 5, but was decreased as the extracting solution became more alkaline. The study also reported that the addition of electrolyte increased the extraction rate. As examples, the addition of sodium, lithium or ammonium perchlorate together with EDTA increase the removal of Pb relative to the same concentration of EDTA alone (21). Divalent electrolytes, such as calcium or magnesium perchlorate were also demonstrated to

increase Pb mobilization and improve EDTA extraction at acidic conditions. With the support of electrolyte, a stoichiometric amount of EDTA at pH of 4 to 6 was sufficient to recover all of non-detrital Pb. This reagent was also demonstrated to be effective at extracting metal from high clay and silt soils (55).

### 3. 2. 1 Recycling of Chelating Reagents:

Because the application of chelating reagent(s) to wash contaminated soil can be very expensive, recycling the chelating reagent(s) becomes an important objective to improve the technique. However, to date, the limited number of reports have indicated that only the moderate-strength chelators or electrochemically mediated reduction of metal-EDTA complexes have been successful.

In the electrochemical approach, cationic metals were reduced and deposited onto the cathode surface while the complexing reagent was released into solution during the process of electrochemical reduction. Research has been performed to study the reaction of metal precipitation (as insoluble metal hydroxide) from different types of iminodiacetate analogs, nitriloacetic acid (NTA), and succinic acid solutions. Calcium was added as a ligand binding agent, metals were precipitated at high pH and the chelator was liberated after binding with Ca (or other coagulant). This phenomenon could also have been achieved with any pH adjustment reagent capable of reacting with free metal to form insoluble hydroxide or carbonate (61).

Another study indicated that the separation of metal from EDTA complex by formation of metal hydroxide was not efficient, in part because EDTA remained a very stable chelating agent. It was reported that the separation of metal from metal-EDTA complexes by metal precipitation with sulfide was more efficient (62).

In addition to the precipitation of metals as hydroxides or sulfides, the addition of $Na_2S$ and $Ca(OH)_2$ were also useful chemicals to free ligand from metal complexes. This method was also performed to investigate the effect of sulfide precipitation with $Na_2S$ as a chemical treatment for heavy metal polluted waste waters. The results demonstrated that sulfide precipitation was an efficient method to precipitate Cd, Zn, Pb and Cu (57). This procedure was based on the strategy that $Na_2S$ was used as an anionic precipitant to provide $HS^-$ or $S^{-2}$ anions to compete with the chelating reagent for the contaminating

metal cations. Calcium hydroxide [Ca(OH)$_2$] enhanced this reaction by providing Ca$^{+2}$ to compete for EDTA ligand by displacing metal from its chelator complex. Other research was performed to separate Pb, Zn and Cu from their EDTA complexes, with the result that >99%, 70-74%, and 93-98% respectively of these metals were recovered after this treatment (40). This research also demonstrated that higher concentrations of EDTA improved soil washing performance because more washing cycles could be performed with reclamation of EDTA after addition of Na$_2$S and Ca(OH)$_2$ at a pH of 10. At present, metal precipitation as hydroxide is the most commonly used approach on the basis of ease of operation, performance and cost. Even though sulfide precipitation has advantages of less pH dependency and increased efficiency, it is toxicologically hazardous and appreciably more expensive.

### 3. 2. 2 Cementation Reaction:

Iron powder has been used to reduce the dissolved heavy metal ions in acid rock drainage wastes to their elemental forms. This technique could also have been performed to recover heavy metal and recycle chelating reagents. The removal mechanisms involved in this technique were considered to include both cementation and hydroxidation. For cementation reactions, zero valent Fe powder represented the electron source for metal cations (mainly Cu and Cd), and the reduced metals become plated onto the surface of Fe powder. With hydroxide formation, the Fe powder reacts with water to produce OH$^-$ and H$_2$ gas. The OH$^-$ can then react with metal cation (mainly Al, Zn and Ni) to form metal hydroxide precipitate and the pH was increased. Metalloids like As and Sb could also co-precipitate with Fe.

Iron powder and other zero valent metals were also used to decrease the Uranium level in sub-surface leachate. Another study has reported that metals extracted with an organic complexing reagent can be treated with a reactive metal powder (Zn, Al, Cu, Cd, Mn, Fe, Mg) as the reducing agent (63). The mechanisms were those mentioned above, causing the reduction of cations and their separations from the organic complexing reagent by cementation on the surface of the metal powder. The results indicated that the organic chelating reagent was purified and separated from metal contaminants. Fe seemed to be a promising metallic material for this process because it has strong reducing

properties ($E^o$, -0.4V), is nontoxic, and inexpensive. The cementation technique has demonstrated that Cd, Co, Cr, Cu can be separated rapidly from solution requiring only a few minutes of reaction to separate them from their organic complexes, whereas Zn and Pb took longer, and requiring a few hours.

Based on reports that Fe powder can separate metal cations from their EDTA complexes via a redox reaction, it becomes necessary to develop a deeper understanding concerning reduction potentials and to compare this thermodynamic potential with the corresponding potentials of zero valent metal powders. The standard reduction potential ($E^o$) for the $Fe^{2+}/Fe^o$ is approximately -0.47V, whereas $Mg^{2+}/Mg^o$ couple is much higher (approximately -2.V). Based on thermodynamic considerations, the higher reducing potential (of $Mg^o$) should have the capacity to reduce a greater number of metal cations and cement them onto the $Mg^o$ surface during the metal mediated corrosion process. A study evaluated $Mg^o$ to separate metals from their complexes with the cementation technique. The result demonstrated that an excess of HEDC [bis(2-hydroxyethyl) dithiocarbamate] was capable of removing appreciable quantities of heavy metals (19-57%) and retained its complexing activity when recycled. Appreciable portions of the Pb, Cu, and Zn were cemented on the surface of the excess $Mg^o$ (10).

In addition to Fe powder and Mg flakes, combinations of $Mg^o$ with $Pd^o$ or $Ag^o$ have been investigated. It was observed that these bimetallic mixtures can increase the rate of reaction and improve cementation process to separate metals from organic chelators. Studies have reported that $Mg^o/Pd^o$ removed Mn, Cu and Fe rapidly from metal-diethylenetriaminepentaacetic acid (DTPA) complexes. However, DTPA was not released efficiently for further recycling. Other chelating reagents were evaluated as DTPA replacements in the same research (55). These workers found that N-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) and ethylenenebis (oxyethylenenitrilo) EGTA were possible chelating reagent for both efficient metal removal of Mn, Cu, and Fe from solution and the efficient release of chelating reagent (46). During this cementation reaction, the zero valent metal was oxidized and released so that the utility of the process can be compromised by the toxicity of the liberated cation.

Concurrently, the zero-valent metal can be anticipated to react spontaneously with water to produce hydroxide ion and molecular hydrogen. The focus of this research was to attempt to recycle the chelating reagent by freeing the chelator from their metal complexes. It was anticipated that large amount of Fe, Ca, and Mg within soil matrix might serve to increase the efficiency of ligand release from their metal complexes. Alternately, liberating the chelator might be archived by precipitating of the metal cation with hydroxide.

In the present research, EDTA or EDTA-dithiocarbamate (HEDC) mixture were to be released from their complexes and recycled to mobilize more heavy metal from field contaminated soil. The chemicals were to be studied both separately and in combination. Whereas EDTA can form a tetra anion so that six electron rich donor sites are available on each molecule, HEDC has two anionic sites but this molecule can also reduce certain metal to a more mobile form.

## 3. 3 Experimental Procedures:

### 3. 3. 1 Atomic Absorption Spectrometer:

AAS determinations of the quantities of analyte metals in aqueous solution were performed with a GBC model 903 single beam Atomic Absorption Spectrometer. The operating conditions were optimized based on the recommendation provided by the instrumental manufacturer.

### 3. 3. 2 Chemical Reagent:

Bis(2-hydroxyethyl)-dithiocarbamate (HEDC) was synthesized following the method of Fritz and Sutton (10). Details are provided below. Disodium Ethylenediaminetetraacetic acid (EDTA) was purchased from Sigma Aldrich Chemical Co., Oakville, On, Canada. All other chemicals used for this project were ACS reagent grade or better. Standard solutions of seven analyte metals (Cd, Cu, Fe, Mn, Ni, Pb, and Zn) were prepared from stock standard solutions (1000 $\mu g\ mL^{-1}$) purchased from BDH (Montreal, Qc, Canada) or Sigma-Aldrich. Stability constants and conditional formation constants have been documented (54). Glassware was washed in a soap solution, soaked in diluted HCl acid (20% v/v), rinsed with double distilled water and dried in an oven at 110°C.

HEDC was synthesized as follows: sodium hydroxide (40.0 g) was combined with 105.1g of di-ethanolamine in methanol (400 mL) in a 1L round bottom flask. The solution was cooled to 10 °C in an ice bath under a blanket of $N_2$ then 114g of carbon disulfide were added dropwise. After 2 hours of reaction, methanol was removed on a rotary evaporator at 35 °C. The resulting viscous liquid was induced to crystallize by adding 400 mL of 1-propanol accompanied by vigorous mixing. The yellow crystals were recovered by filtration and dried under vacuum at room temperature. The crystalline HEDC, approximately 150g, were stored in the refrigerator.

### 3. 3. 3 Soil Equilibration:

The first part of this research was directed to improving the extraction efficiency of heavy metals from the contaminated soil. EDTA and HEDC were the two chelating reagents used. They were studied under various conditions of pH and concentration. All the tests were performed with three replicates and the general procedures were the following.

An accurately weighed aliquot of dried sieved soil (100g) was suspended in 0.1M EDTA or other test complexant solution (100 mL) in a centrifuge tube. The suspension was shaken for 16 hours and then centrifuged. The supernatant fraction was filtered through Celite under gentle suction to obtain a clear filtrate.

Since the total concentration of heavy metals in this soil sample was approximately 0.03 mol, the quantity of chelator represented a stoichiometric equivalent. The parameters used to equilibrate the soil were 10 mmol EDTA, 3 mmol EDTA, 3 mmol HEDC, and combination of 1+1 EDTA and HEDC (each or 1.5 mmol) at pH 5, 6, or 7. The evaluation of the combination of the 2 chemicals to extract heavy metal were performed for the first time to our knowledge, there have been no previous reports of the efficacy of this combination to mobilize heavy metals from soil. It was not clear if the combination of two chelators (nitrogen and sulfur based) might interact synergistically, antagonistically or simply as the sum of the components.

The pHs of the soil suspensions were adjusted to 5 – 7. Certain heavy metals can be predicted to display increased mobility at lower pH. However, the pH should not be decreased too much, since other nutrients can be co-mobilized and the soil fertility can be

affected adversely. Soil washing can alter the soil fertility, but these effects should be minimized as much as possible. Arbitrarily, equilibrations were performed for 16 hours, since previous studies with 16 or 24 hours of equilibration had demonstrated no significant differences in the quantities of heavy metals mobilized at each time interval (10). Equilibration with water [absence of chelator(s)] was also performed for 16 hours for comparison.

### 3. 3. 4 Cementation and Recycling Process:

After soil equilibration, solutions of filtrate were analyzed for their content of heavy metals. The solutions were then treated with 0.1g of $Mg^0$ flakes to separate metal from chelator complexes. Although the initial quantity of solution was 100 mL, it was reduced to about 50 mL after soil washing due to absorption of liquid by the dry soil. Double distilled (DD) water was added to re-adjust the volume of filtrate to 100 mL. After addition of 0.1g of $Mg^0$ and reaction for up to 24 hours, the pH and the metal concentrations were measured at different time intervals. The concentration of metals in solution and pH were recorded after 0.16, 0.5, 1, 3 and 24 hours. Acetate buffer was added to the filtrate to adjust its pH to 4 before the addition of Mg flakes.

Certain procedures were also performed with $Mg^0/Pd^0$ or $Mg^0/Ag^0$ bimetallic mixture. The main difference with reaction with $Mg^0$ alone was that the bimetallic treatment was capable of separating metals from complexes more rapidly. Thus, metal concentrations in solution from reactions with bimetallic mixture were tested at shorter reaction intervals (0.05, 0.16, 0.5 h).

The same chelators (EDTA and/or HEDC) were recycled during the soil washing treatments to evaluate their efficacies during extended operation. During prolonged treatment, solutions were treated 5 successive times and each time the demetallized filtrate was recycled back to extract fresh contaminated soil. The results are presented in Table 3.6.

### 3. 4. 1 Result and Discussion – Soil equilibration:

The results of soil equilibrations are presented in Tables 3.1 to 3.4. Numerous trials were performed, but only the most striking results are reported and

discussed here. The results present here are metals extraction with a relatively high concentration of EDTA (0.1M, 10.0 mmol) and lower concentration of extractant, EDTA (0.03M, 3.0 mmol) and HEDC (0.03M, 3.0 mmol). As well, the result of mixed chelating agents EDTA with HEDC [(1+1, 0.03M each, 6.0 mmol total at pH 7) and (1+1, 0.015 M each, 3.0mmol total at various pHs)] are presented.

Table 3.1. Comparison of heavy metals ($\mu g\ g^{-1} \pm RSD^a$) in soil (100g) post equilibration for 16h with 10.0 mmol or 3.0 mmol EDTA at pH 7.

| Analyte | Soil Burden | 0.1M EDTA | 0.03M EDTA |
|---|---|---|---|
| Cd | 6.2±0% | N.D. [b] | N.D. |
| Cu | 15.5±7% | 1.4±3% | 0.6 |
| Fe | 10753±3% | 45±8% | 1±33% |
| Mn | 188±9% | 17±7% | 2±16% |
| Ni | 53±9% | 0.6±1% | 0.1 |
| Pb | 6555±12% | 1510±5% | 711 |
| Zn | 160±5% | 22±3% | 15±24% |

[a] RSD = one relative standard deviation

[b] N.D. = none detected, $> 0.01 \mu g\ mL^{-1}$ Cd

From the result presented in Table 3.1, it is clear that 0.1M EDTA removed appreciably more heavy metals from the soil than did the 0.03M EDTA. The higher quantity of EDTA (10.0 mmol) mobilized 1510 ppm (or 24%) of the total Pb burden whereas only 711 ppm (or 12%) of Pb was recovered with the 0.03M EDTA (3.0 mmol). Although 0.1M EDTA was capable of extracting more metal, the quantity of chelator was represented in a stoichiometric equivalent. For economic consideration and environmental concerns, it was considered to be important to minimize the amount of chelating reagent as much as possible (less than a stoichiometric equivalent). It became expedient to improve the extraction efficiency further when the concentration was 0.03M.

Table 3.2. Concentrations of heavy metals ($\mu$g g$^{-1}$±RSD[a]) in extracts generated with 0.03M EDTA, 0.03M HEDC, or mixed EDTA HEDC (1+1, 0.03M each, total 6.0 mmol) at pH 7.

| Analyte | Soil Burden | 0.03M EDTA | 0.03M HEDC | Mixed EDTA/HEDC (total 0.06M) |
|---------|-------------|------------|------------|-------------------------------|
| Cd | 6.2±0% | N.D.[b] | N.D. | N.D. |
| Cu | 15.5±7% | 0.6 | 0.4 | 1.2±22% |
| Fe | 10753±3% | 1±33% | 0.2±15 | 11±22% |
| Mn | 188±9% | 2±16% | N.D. | 20±12% |
| Ni | 53±9% | 0.1 | N.D. | 0.5±14% |
| Pb | 6555±12% | 711 | 8±28% | 1329±20% |
| Zn | 160±5% | 15±24% | N.D. | 18±19% |

[a] RSD = one relative standard deviation

[b] N.D. = none detected, > 0.01$\mu$g mL$^{-1}$ Cd

Many other chelators were evaluated at a concentration of 0.03M. For example, the results in Table 3.2 summarize the behavior of the water soluble bis-(2-hydroxyyethyl)-dithiocarbamate (HEDC) that was compared with 0.03M EDTA. The result indicated that none of tested chemicals was capable of extracting more than EDTA at the same concentration. The mobilization efficiency with HEDC alone was poor. This reagent mobilized only 8 ppm of Pb. This behavior was changed appreciably when the two chelating chemicals, each at 0.03M (total of 0.06M) were mixed together. The mixed EDTA/HEDC extractant mobilized twice as much metals as the sum of two separate treatments. The mixed EDTA/HEDC with total concentration of 0.06M (6.0 mmol) mobilized 1329 ppm of Pb, whereas the 0.03M EDTA or HEDC separately removed only 720 ppm of Pb (711 ppm Pb mobilized with 0.03M EDTA + 8 ppm Pb recovered with 0.03M HEDC). Moreover, mixed EDTA with HEDC (total of 6.0 mmol) mobilized almost the same quantity of Pb that 0.1M of EDTA (10.0 mmol).

To improve the extraction efficiency at low chelating concentration, further tests with mixed EDTA - HEDC chelants were performed. A mixed extractant, 0.03M EDTA

and HEDC in a 1:1 molar ratio (1.5 mmol each) also mobilized metal efficiently after minor pH adjustment. Despite approximately a three-fold reduction in the total chelant concentration, the 0.03M mixed solution mobilized almost as much heavy metal as 0.1M EDTA extractant (Tables 3.1 and 3.3). Table 3.3 demonstrates that at very low concentration of complexing reagents, pH can play an important role. Heavy metals can be more mobile at lower pH and presumably metal extraction is facilitated. Smaller quantities of heavy metals were removed from soil at pH 6 (853 ppm of lead), but increased quantities of metal were extracted if the pH was decreased to 5 (1420 ppm of Pb).

Table 3.3. Concentration of heavy metal ($\mu g \ g^{-1} \pm RSD^a$) extracted with mixed EDTA and HEDC at (0.03M each, 6.0 mmol total) pH 7, or mixed EDTA and HEDC (0.015 M each, 3.0 mmol total) at pH 5 or 6.

| Analyte | Soil Burden | EDTA/HEDC (6.0 mmol total) at pH 7 | EDTA/HEDC (3.0 mmol total) at pH 6 | EDTA/HEDC (3.0 mmol total) at pH 5 |
|---------|-------------|------------------------------------|------------------------------------|------------------------------------|
| Cd | 6.2±0% | N.D.[b] | 0.56±14 | N.D |
| Cu | 15.5±7% | 1.2±22% | 0.4±11 | 0.5±0 |
| Fe | 10753±3% | 11±22% | 1.6±12 | 10±4 |
| Mn | 188±9% | 20±12% | 16.31±12 | 15±3 |
| Ni | 53±9% | 0.5±14% | 0.2±9 | 0.6±0 |
| Pb | 6555±12% | 1329±20% | 852.6±10 | 1420±1 |
| Zn | 160±5% | 18±19% | 53.5±13.24 | 21±0 |

[a] RSD = one relative standard deviation

[b] N.D. = none detected, > 0.01μg mL$^{-1}$ Cd

### 3. 4. 2. Result and Discussion

### 3. 4. 2. 1. Cementation:

Cementation reactions were performed during several trials that included the demetallization of extract generated with 0.1M EDTA, and/or with mixed EDTA - HEDC (0.03M). After the cementation process, filtrates were recycled back to the soil to extract

more heavy metals. Multiple recycles were performed with demetallization between each successive extraction to liberate the reagents from their metal complexes.

### 3. 4 .2. 2 Mg⁰ cemented 0.1M EDTA:

In initial trials, reaction with $Mg^0$ were investigated with the view to recycle the 0.1M EDTA. The results of three successive equilibrations of 100g soil with EDTA extractant (initially 100 mL, 0.1M) are recorded in Table 3.4. After 16 hours of equilibration, the filtrate (47 mL) was analyzed for Cu, Fe, Mn, Pb, Zn and Cd content. A single equilibration mobilized 24% of the Pb, 14% of the Zn and 8.7% of the Mn. However, three successive equilibration mobilized a total of 59% of the lead, 24% of the zinc and 20% of the manganese burden from the soil, but only small quantities of cadmium, copper, and nickel (1.4%, 8.4%, and 1.1% respectively).

Before equilibrations two and three, the filtrate was diluted to 100 mL with water then treated with 0.1g magnesium metal ($Mg^0$) for 24 hours. As had been observed previously, the EDTA was released from metal complexes efficiently and the solution regained the ability to mobilize more heavy metal when re-combined with the same soil.

Table 3.4. Metal concentrations in soil ($\mu g\ g^{-1}$) extracted post equilibration (16 hours) of soil (100 g) with an equal volume of 0.1M EDTA that had been treated with $Mg^0$ between equilibration.

| Analyte | Soil Burden | 1st equilibration | 2ND equilibration | 3RD equilibration | Sum | % Mobilized |
|---------|-------------|-------------------|-------------------|-------------------|-----|-------------|
| Cd | 6.2±0% | 0.04±8 | 0.002±23 | 0.13±7 | 0.2 | 3 |
| Cu | 15.5±7% | 1.4±9 | N.D.[b] | N.D. | 1 | 6 |
| Fe | 10753±3% | 37±4 | 537±4 | 505.0±7 | 1079 | 10 |
| Mn | 188±9% | 11±6 | 27±5 | -1. ±18 | 37 | 20 |
| Ni | 53±9% | 0.5±11 | 2.1±9 | 0.2±7 | 3 | 6 |
| Pb | 6555±12% | 1464±5 | 1251±9 | 1146±15 | 3861 | 59 |
| Zn | 160±5% | 18±9 | 20±6 | 0.2±11 | 38 | 24 |

[a] RSD = one relative standard deviation

[b] N.D. = none detected, > 0.01μg mL⁻¹ Cu

A more detailed study was conducted to analyze the influence of $Mg^0$ on the release of chelating reagent during and after reaction with the metal-EDTA complex. The investigation was performed to monitor the changes of metal concentrations in solution during the demetalization process. The result demonstrated that metal concentrations decreased gradually after the addition of $Mg^0$. Both redox mediated cementation, in which heavy metal would be deposited on the surfaces of the excess $Mg^0$ and precipitate formation, as insoluble hydroxide were anticipated. Some 85% of Pb had been removed from solution after 0.5 h. However, the Mn and Zn were lost from solution only more slowly and required several hours (Table 3.5) of treatment.

After the cementation process, the filtrate was recycled to treat different forms of the soil. In one case, contaminated soil that had not been treated with chelating reagent served as the substrate whereas in the second case the particulate fraction from soil that has been washed once was the sample to be cleaned. The result indicated that recycled EDTA solutions (0.1M) retained the ability to extract more heavy metal in the subsequent equilibration. This behavior was not changed appreciably when the liberated extractant was returned to the soil to mobilize more toxicant (A vs. B, Table3.5).

### 3. 4. 2. 3 $Mg^0$ reaction with 0.03M EDTA-HEDC extractant:

In addition to evaluating the cementation reaction on the supernatant fraction from 0.1M EDTA, $Mg^0$ was also applied to the supernatant fraction from equilibrations with mixed EDTA - HEDC (0.015M each, 30 mmol total). Bearing in mind that the focus of this research was to identify a more efficient procedure to extract heavy metal using the minimum concentration of reagents. In this case, the mixed EDTA-HEDC extractant was capable of removing three times more metals than was the equivalent concentration of EDTA alone. It was important to evaluate the effect of zero valent metals on EDTA-HEDC mixtures.

The mixed extracting solution was apparently re-generated efficiently by treatment with 0.1g of $Mg^0$. As summarized in Table 3.6, approximately 86% of the Pb was removed from solution with 0.1g $Mg^0$, but a fraction of Mn and Zn remained in the solution post treatment. None the less, much of the complexing activity was restored to the extractant solution so that the extract post a second equilibration with the soil

particulate was very similar (in both heavy metal distribution and content) to the extract from fresh soil.

Table 3.5. Metal concentration ($\mu g\ g^{-1} \pm RSD^a$) in recycled soil extract (prior or post $Mg^0$ treatment) equilibrated with fresh soil (A) or soil that had been extracted once (B) with 0.1M EDTA.

**A**

| Analyte | Prior to $Mg^0$ add'n | 0.5h post add'n | 1h post add'n | 3h post add'n | 24 post add'n |
|---|---|---|---|---|---|
| Cd | N.D.[b] | N.D. | N.D. | N.D. | N.D. |
| Cu | 0.5±34% | N.D | N.D. | N.D | N.D. |
| Fe | 8±40% | 8±23% | 6±40% | 2±30% | 0.3±24% |
| Mn | 26±7% | 26±1% | 23±4% | 6±17% | 6±20% |
| Ni | 0.3±13% | N.D. | N.D. | N.D. | N.D. |
| Pb | 1552±17% | 220±18% | 340±20% | 269±51% | 61±31% |
| Zn | 84±6% | 87±11% | 84±14% | 12±14% | 4±12% |
| pH | 5.7 | 9.3 | 9.8 | 9.8 | |

**B**

| Analyte | Prior to $Mg^0$ add'n | 0.5h post add'n | 1h post add'n | 3h post add'n | 24 post add'n |
|---|---|---|---|---|---|
| Cd | N.D. | N.D. | N.D. | N.D. | N.D. |
| Cu | 0.8±0.8% | N.D | N.D. | N.D | N.D. |
| Fe | 101±5% | 101±5 | 57±21% | 43±27% | 0.5±44% |
| Mn | 21±3% | 18±9% | 17±7% | 13±16% | 5±24% |
| Ni | 0.5±10% | N.D. | N.D. | N.D. | N.D. |
| Pb | 1600±6% | 301±10% | 203±4% | 279±43% | 126±58% |
| Zn | 79±2 | 78±3 | 74±4 | 39±53% | 5±74% |
| pH | 5.7 | 9.3 | 9.4 | 9.8 | |

[a] RSD = one relation standard derivation based on 3 separate trials.

[b] N.D. = non detected, > 0.01 $\mu g\ g^{-1}$ Cd, Cu, Ni

Table 3.6. Metals concentrations ($\mu g\ g^{-1} \pm RSD^{a}$) in mixed 0.03M EDTA-HEDC extractant from soil post regeneration with $Mg^0$

| Analyte | Extract post $Mg^0$ | Soil that had been extracted once Post 2$^{nd}$ extraction | Net | Fresh soil Net |
|---|---|---|---|---|
| Cd | N.D.[b] | N.D. | N.D. | N.D. |
| Cu | N.D | 0.8±6% | 0.8±6% | 0.4±34% |
| Fe | 6±23% | 10±5% | 4±5% | 8±40% |
| Mn | 5±11% | 21±3% | 16±3% | 6±7% |
| Ni | N.D. | 0.5±10% | 0.5±10% | 0.3±13/5 |
| Pb | 198±23% | 1600±6% | 1420±6% | 1429±17% |
| Zn | 71±2 | 79±2% | 8±9% | 38±6% |

[a] RSD = one relative standard deviation

[b] N.D. = none detected, > 0.01μg mL$^{-1}$ Cd, Cu

### 3. 4. 2. 4 Five consecutive recycles of the 0.03M EDTA-HEDC extracting solution:

The same extraction solution was used to remediate the soil with five successive washes using regeneration of the extractant solution with $Mg^0$ between washes. The results of metal analyses are summarized in Table 3.7. As reported in this table, some 56% of the Pb, 21% of the Zn and ~20% of the Mn in this soil were mobilized by the five washes, but only18% and 13% of total Ni and Cu, respectively, were recovered. The heavy metals were extracted mainly during the first three washings. The first three washes with the mixed extracting solution removed ~49% of the Pb, ~18% of the Zn and ~19% of the Mn burdens, but only 7% of the Cu, 4% of the Ni and 1% of the Fe were removed from this soil sample. A possible explanation for this gradual but continued loss of mobilisation efficiency was sought by determining the residual complexant concentration in the solution after five successive washes with the mixed EDTA-HEDC solution.

Table 3.7. Heavy metal extracts ($\mu g \ g^{-1} \pm RSD^a$) post 16h equilibration of soil (100g) with an equal volume of mixed chelant (0.015M EDTA+0.015M HEDC) that had been treated with $Mg^0$ between equilibrations.

| Analyte | Cd | Cu | Fe | Mn | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|
| 1st equilib [c] | N.D.[b] | 0.5±0.6 | 10±4 | 15±3 | 0.6 | 1420±1 | 21 |
| 2nd equilib | N.D. | 0.4 | 55 | 21 | -0.7 | 1243 | 3 |
| 3rd equilib | N.D. | 0.2 | 85 | -1 | -0.2 | 545 | 4 |
| 4th equilib | N.D. | N.D. | 134 | 1.2 | 0.5 | 235 | 5 |
| 5th equilib | N.D. | N.D. | 97 | 1 | 0.9 | 220 | 0.4 |
| Sum | 0 | 1.1 | 284 | 36.9 | 0 | 3663 | 33 |
| % mobilized | 0 | 7 | 4 | 20 | 2 | 56 | 21 |

[a] RSD = one relative standard deviation

[b] N.D. = none detected, > 0.01$\mu g \ mL^{-1}$ Cd, Cu

[c] equilib = equilibration

### 3. 4. 2. 5 Zero Valent Bimetallic Cementaion:

The separation of metal from chelating reagents (EDTA or HEDC) required prolonged reaction with $Mg^0$ (several hours) - it represented a time consuming process. A more rapid and efficient reaction to remove metal from their EDTA complexs was sought in an effort to accelerate the rate of reaction with zero-valent metal. Zero valent bimetallic mixtures have removed metal efficiently from wood pulp extracts containing complexes of metal-iminodiacetate (EDTA-type) analogs. The time course of reactions of a mixture of palladium (0.2% w/w) or silver (1% w/w) with magnesium were evaluated. As evidenced in Table 3.8, both reactions with bimetallic mixture proved to be more rapid than with $Mg^0$ alone. Thirty minutes of reaction with $Pd^0/Mg^0$ resulted in residual metal contents in solution that were approximately equal to the levels that had been achieved after 24 h of reaction with $Mg^0$ alone (Table 3.5). The $Ag^0/Mg^0$ mixture proved to be less efficient after 0.5 hours, possibly due to the decreased hydroxide content after this time. The use of zero valent mixtures to reduce the metal content in

solution is considered to be promising. Although extended reaction times were not evaluated, it is anticipated that 1 hour of reaction would be sufficient to reduce the metal concentration to level below those observed for $Mg^0$ alone after 24 hours.

Table 3.8. Metal ($\mu g\ g^{-1} \pm RSD^a$) remaining in solution post treatment of M-EDTA complexes solution with $Pd^0/Mg^0$ or $Ag^0/Mg^0$ bimetallic mixture.

| Analyte | M-EDTA solution | Treatment with $Pd^0/Mg^0$ | | | Treatment with $Ag^0/Mg^0$ | | |
|---|---|---|---|---|---|---|---|
| | | 3 min | 10 min | 30 min | 3 min | 10 min | 30 min |
| Cd | N.D. | N.D.[b] | N.D. | N.D. | N.D. | N.D. | N.D. |
| Cu | 0.8±3 | 0.1±19 | N.D. | N.D. | N.D. | N.D. | N.D. |
| Fe | 36±8 | 30±3 | 27±13 | 12±57 | 31±12 | 26±4 | 26±11 |
| Mn | 12.4±3 | 10.2±6 | 10.2±9 | 9.7±7 | 11.3±10 | 11.0±11 | 11.2±13 |
| Ni | 1.3±6 | 1.3±8 | 1.0±12 | 1.0±9 | 1.3±4 | 1.0±9 | 1.0±29 |
| Pb | 1551 | 1216±17 | 630±30 | 93.9±39 | 1545±2 | 1398±4 | 474±39 |
| Zn | 20.4 | 17.9±9 | 16.6±12 | 3.6±40 | 18.2±2 | 18.6±2 | 18.0±11 |
| Total | | 1276 | 684.5± | 120.5 | 1606.5 | 1454.1 | 530.0 |
| PH post rx'n | | 7.94 | 8.26 | 9.28 | 7.81 | 7.98 | 8.28 |

[a] RSD = one relative standard deviation

[b] N.D. = none detected, > 0.01$\mu g\ mL^{-1}$ Cd, Cu

## 3. 5 Fate of EDTA and HEDC:

The fates of EDTA and HEDC were then investigated to provide further insight into their decreased ability to continue to extract more heavy metals. The EDTA, both free and complexed, was converted to the corresponding Cr-EDTA complex and determined spectrophotometrically at $\lambda = 545$ nm. The residual dithiocarbamate (HEDC) was first hydrolyzed to $CS_2$, volatilized and trapped in $Cu^{2+}$/diethylamino ethanol/methanol. The intensity of the color was measured spectrophotometrically at $\lambda = 435$nm. The results of analyses indicated that only about 27% of the EDTA and only ~0.13% of the dithiocarbamate (HEDC) remained in the solution and virtually none of

the dithiocarbamate was detected within the soil particulate fraction. These chelating reagents might have been lost to the solid metal hydroxides during the reaction with $Pd^0/Mg^0$ and filtration to remove this precipitate. This adsorption/occlusion phenomenon had not been anticipated and limited the utility of the recycling approach with this mixed extractant.

Figure 3.1. Comparison of Pb concentrations in extracting solutions that were prepared from EDTA, HEDC or mixed EDTA+HEDC at various concentration and pH.
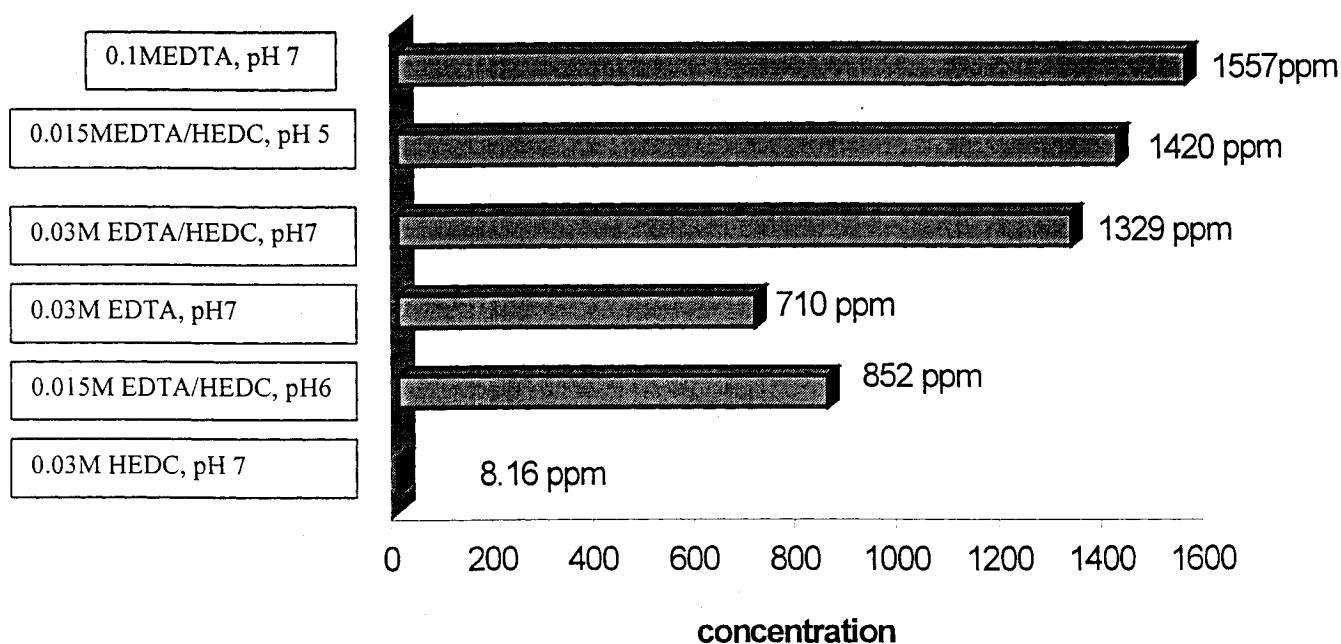


3. 6 Conclusion:

It was observed that the mixture of chelating reagents was more efficient at removing heavy metals than were the sum of the individual component chelators. With minor pH adjustment, mixtures of EDTA - HEDC mobilized quantities of heavy metals that were approximately equivalent to quantities mobilized with an EDTA solution that was three times more concentrated. The demetalization process was capable of liberating the chelating reagents from heavy metal complexes so that the solution could be recycled

three times. However, the extraction efficiency was decreased by losses of reagents possibly the result of adsorption or occlusion on/within the precipitated metals. The HEDC complexant could also be recycled but in this case losses to the solid phase were more extensive.

# Chapter VI

# General Conclusion and Future Research

## 4. 1. Summary and General Conclusions

Soil contamination has continued to receive increased attention because of concerns about the adverse impacts of heavy metals on soil fertility. The accumulation of trace metal contaminants in soil can pose a threat to the human health and to the environment if they are not treated.

The first chapter of this thesis summarized some general concerns regarding the continued accumulation of heavy metals in the environment as well as certain tenets of soil science together with an abridged review of techniques to remediate heavy metals pollution in soil.

As discussed in the first chapter, heavy metals are inorganic substances that result in contaminations that behave very differently from other types of pollution (organic forms). The threat of heavy metals continues even if the source of heavy metal pollution has been eliminated. For example, the main source of heavy metal contamination comes from mining activities, so that trace metals continue to be released into the environment (once the ores have been exposed to the atmosphere) even if the active mining operations have stopped. Thus, problems of trace metal contaminations that are already present in the environment continue to threaten human health even when preventive actions have been taken to avoid further contamination.

A further difference between heavy metals and organic contaminants is that they can not be degraded readily like other organic substances. A heavy metals consists of one basic element. By contrast, organic materials are made up of molecules that can be degraded or converted readily from one form to another in the environment. For example, complete combustion can convert hydrocarbon to $CO_2$ and $H_2O$. Heavy metals cannot be degraded with the same method because they don't have the tendency to catenation, and they only combine with a few other atoms to form small ions or molecules. Combustion of inorganic ions can convert them to oxides, which in certain cases can also be toxic. The most common conversion of inorganic ions is to cause a change of oxidation state to

a less toxic form, but many heavy metal are equi-toxic after the change of oxidation state. For instance, Cr(III) is innocuous whereas Cr(VI) is acutely toxic. Thus, it can be important to prevent oxidation of certain heavy metals into a more toxic form.

The only method to treat heavy metals is to make them less available to contacting organisms or to isolate biological processes. For contaminated soil, this can be done by solidification within the soil or by removing them from the soil matrix. Heavy metal solidification reduces its mobility and avoids plant uptake, but it is not a permanent solution because of the environmental processes that can re-mobilize them. Heavy metal extraction becomes the one attractive approach to treat this problem and is considered to be a permanent solution to controlling exposure.

Soil washing coupled with complexometric extraction appears to be an attractive method for efficient heavy metal removal with only minor environmental impacts that can be attenuated appreciably. The main concerns associated with chemical extraction are the costs of the chelating reagents required to treat the huge areas of contaminated site(s) and the second concern is for the environmental persistence of the chemical additive(s) once they are released post treatment. This research has focused on improving the efficiency of the chemical extraction process to minimize these two concerns. The search for new chemicals that can provide greater mobilization efficiencies remains attractive, since it can reduce the quantity of chemical required and decreasing the eventual cost to the environment. Moreover, recycling the chemicals where possible is another approach that can help to reduce the cost of processing.

Chapter two of this thesis focussed on characterization of the soil. This research was conducted on a soil sample from St-Jean, Quebec. Preliminary tests demonstrated that this soil was heavily contaminated with trace metals. The challenge for this investigation was to reduce the lead content because the burden of this metal was six times greater than the maximum level permitted by Quebec legislation. In addition to lead, six other metals were also studied; the cadmium burden was also sufficiently high to require close monitoring.

The results of this research have demonstrated that combinations of chelating reagents can interact synergistically to remove heavy metals. In this case, the combination of EDTA-HEDC was capable of extracting approximately as much metal as

EDTA alone but with a three-fold reduction in the required quantities of chemicals. An explanation why the combination of EDTA-HEDC was capable of removing more heavy metals was not available. With more trials, this experiment might help to reduce the cost of soil extraction further. Environmental concerns regarding these chemical additives can be anticipated to be reduced correspondingly.

In addition to the new combination of chemicals (EDTA-HEDC) that extracted heavy metal efficiently, the recycling of these chelating reagents was evaluated. It was demonstrated that that the chemical could be recycled up to five times. The treatment with zero valent magnesium was demonstrated to be effective for demetallization. This treatment permitted the chelating solution to be reused. Although the final two washings were not as efficient as the first three washing cycles (total of five equilibrations), the chemical combination continued to retain complexing activity over several cycles.

After the demetalization process with zero valent magnesium, heavy metals that were recovered by filtration, can also be recycled or can be confined to an isolated location. It might not be economically viable to recycle these metals due to cost of reprocessing the precipitate into useful products. However, these metals precipitate can be concentrated, stabilized and confined to avoid any further contamination. The recycling process evaluated in this research was designed to reuse the chelating reagent. The goals were to reduce the operating costs and to minimize the environmental concerns associated with soil washing. The objectives were to maximize the efficiency of the complexing reagent(s) for as many cycles as possible. Efforts were not made to recycle the heavy metal extracted from the polluted soil.

Modifying the oxidation state of heavy metals and converting the product to insoluble oxides/ sulfides/ carbonates, would seem to be economically feasible, but it probably isn't a final solution from an environmental point of view. As mentioned above, reducing the oxidation states of one metal might not cause a comparable decrease in toxicity of a second metal. Certain metals become even more toxic after reduction. Moreover, environmental processes such as weathering can re-oxidize the reduction product making them more acutely toxic.

The demonstration that equilibration with a combination of complexing reagents can increase the efficiency of mobilization together with ability to recycle the chelating

reagent have provided new techniques/procedures for the remediation of soil contamianted with heavy metals. Although more studies are required to explain the synergy observed with these complexing reagents, this alternative procedure should be of value to future restoration efforts.

## 4. 2 Suggestion for future work

Even though the combination of EDTA-HEDC can result in more efficient heavy metal extraction, no clear explanation has been proposed for this behaviour. Further studies are needed to explain the interactions between these two chemicals. Some suggestions for future research:

1- Investigate the interactions between EDTA and HEDC to identify the reasons why the combination can extract more heavy metals than equivalent quantities of the separate chemicals.

2- Search for an improved approach to retain the efficiency of chelation/mobilization during multiple recycle processing. The reasons why less heavy metals were extracted in the final two soil equilibrations should be identified.

3- Evaluate other combinations of chelating reagents. Reagents should be chosen based on an understanding of their complexing properties. For example, EDTA has four nitrogen donor groups whereas HEDC has two sulfur donor groups. An understanding of the properties of different chelators can help to identify more efficient combinations of extractants.

4- Extend this combination of chemicals to other types of contaminated soils. No two soils are identical: they have different pH, CEC, texture and burden of contaminating metals. These factors can affect the interactions of chelating reagents with heavy metals. It is important to evaluate the new combination with other contaminated soils.

Since no two soils are the same, it does not seem logical to search for a universal chelating reagent to treat all contaminated soils. The application of any treatment typically is site specific; one reagent might not be suitable at one site but efficient in another case. It is considered prudent to attempt to identify a group of common

chelating reagents with high extracting abilities that can remove heavy metal efficiently and can be applied in most cases.

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