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REMEDIATION OF TRACE METAL CONTAMINATED SOILS

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ABSTRACT

Ph.D. **Raden Sri Tejowulan** **Natural Resource Sciences**

Remediation of Trace Metal Contaminated Soils

A series of laboratory experiments was conducted with the objectives of: determining the feasibility of a soil washing technique with chelating agents as a means of removing trace metal contaminants from soils, investigating exchange resins as a means of removing metals from the resulting extracts, applying the techniques for reducing trace metal concentrations in contaminated urban soils, and estimating the metal speciation and retention in the soils through computer modeling.

The chelating agent ethylene diamine tetraacetic acid (EDTA) is promising. The ligand is more effective in removing the metal contaminants from soils than HCl. In a batch experiment, EDTA released a large portion of metals from soils to soil extracts. A batch method was also developed for recovering the metal contaminants in the resulting EDTA soil-extracts. Using an anion exchange resin (AER) AG 3-x4, up to 99% of the Cd, Cu, Pb, and Zn were removed from the leachates.

To increase the efficacy of the extraction method we tested different reagent, amount, and technical application strategies using soil columns. Mixing the reagent with the whole soil column was found to be the most efficient method for the application of the chelating agent for the purpose of metal extraction from soils. It was found that EDTA was superior to citric acid in removing Cd, Cu, Pb, and Zn from the soils investigated. Up to 27% more Cd, 23% more Cu, 42% more Pb, and 21% more Zn were removed by the EDTA and the removal was further increased with the addition of an acid/salt solution (1.0 M HCl and 1.0 M KCl) to the columns. Other promising results are that the AER in columns is an effective method for extracting metals from EDTA soil-extracts with different properties. The resin column method was found to be more efficient than the resin batch procedure.

The most efficient metal extraction technique that was developed in the preceding experiment was tested in the laboratory using larger soil samples. The results of the simulated field experiment confirmed that the remediation of contaminated soils can be achieved using EDTA. The majority of the contaminated soils were decreased to the point that they could be reused for commercial and/or residential use. The results also indicated that no metal enrichment was observed in the lower sections of the soil column after leaching the column with an EDTA solution. The fractionation of the soils before and after leaching revealed that much of the metals in the soils was retained in the carbonate and oxide fractions and much of the metals mobilized by the leaching come from these two fractions. Although an increase in the amount of metals was observed in the exchangeable fraction of some of the cleaned soils, in general, less metals are found in every fraction after the washing.

Metal speciation and retention by soil surfaces influence the fate of the freed metals in the soils, and therefore, they determine the degrees of success of metal leaching in soils. Computer models can be used to predict the possible metal speciation and interaction with solid surfaces in soils. Using the MINEQL$^+$ program, the models estimated that most of the metal species in the soil extracts (in the presence of EDTA, chloro, hydroxo, and carbonato ligands and humate and hydrous ferric oxide (HFO) solid phases) were present as soluble metal-EDTA complexes. The findings were in close agreement with the results obtained from the experiment using the AER. It appears that the metal-EDTA complexes found in the systems are very stable over a wide range of soil pH. The results indicated that computer modeling, in part, can be a valuable tool to describe the potential chemical reactions in the soil solution. Our surface complexation models also indicated that the EDTA is much stronger than the humate and the HFO solid phases in forming complexes with the metals. As a consequence, the adsorption of the Cd, Cu, Pb, and Zn by the solid surfaces was negligible in the presence of EDTA.

RÉSUMÉ

Ph.D. **Raden Sri Tejowulan** **Sciences des Ressources Naturelles**

Remédiation des sols contaminés par les métaux lourds

Une série d'expériences de laboratoire a été menée afin de répondre aux objectifs suivants: 1) déterminer la faisabilité de nettoyer des sols contaminés en utilisant des agents chélatants pour en extraire les métaux traces, 2) évaluer les résines d'échanges anioniques pour retirer les métaux des extraits de sol et 3) appliquer ces techniques sur des sols urbains contaminés.

L'agent chélatant EDTA (l'acide éthylène diamine tétraacétique) est très prometteur. Ce ligand est plus efficace pour extraire les métaux traces des sols que le HCl. Le sol contaminé a été agité dans une solution de EDTA. L'agent chélatant a extrait des sols un grande proportion des métaux. Nous avons ensuite développé une méthode de récupération des métaux extraits par le EDTA. Une résine d'échange anionique (AG 3-x4) a permis de retirer jusqu'à 99% du Cd, du Cu, du Pb et du Zn lorsqu'elle a été mélangée aux lixiviats.

Afin de rafiner notre méthode d'extraction, nous avons testé en colonnes de sol, différents reactifs utilisés en différentes quantités et selon différentes stratégies d'application. La meilleure façon d'appliquer le ligand a été de le mélanger dans toute la colonne de sol. Le EDTA s'est avéré supérieur à l'acide citrique pour extraire le Cd (27% de plus), le Cu (23% de plus), le Pb (42% de plus) et le Zn (21% de plus) dans les sols étudiés. En remplaçant l'eau par une solution acide/sel (1.0 M HCl et 1.0 M KCl), la lixiviation des métaux des colonnes de sol a été significativement améliorée. Par ailleurs, la résine d'échanges d'anioniques semble plus efficace lorsqu'elle est employée en colonne plutôt que dans une procédure de mélange en vrac.

La méthode qui a donné les résultats les plus prometteurs a été testée en laboratoire en utilisant des volumes de sol contaminé plus grands. L'expérience de simulation des conditions de terrain confirme que le EDTA peut servir à nettoyer de grands volumes de sols contaminés par les métaux lourds. Trois des quatre sols étudiés ont été améliorés au point d'être réutilisables dans des zones commerciales ou résidentielles. Nous n'avons observé aucun enrichissement en métaux traces de la zone inférieure des colonnes suivant le traitement au EDTA. L'examen de la colonne de sol à la fin de l'expérience révèle que les métaux traces du sol ont été extraits principalement de la fraction des carbonates et des oxydes. Dans la plupart des cas, on observe une diminution des métaux traces sous toutes leurs formes sauf en certaines occasions où l'on a noté une augmentation de la fraction échangeable.

La spéciation des métaux et leur rétention sur les surfaces influencent la quantité de métal lixiviée. Il est possible, à l'aide de modèles informatiques de prédire la spéciation des métaux et leurs interactions avec les surfaces du sol, sous differentes influences. Une étude de modélisation a donc été menée pour mieux comprendre les interactions entre les différentes espèces des métaux et l'EDTA, les acides humiques, les oxides de fer hydreux et d'autres ligands tel que les chloro, les hydroxo et les carbonato. A l'aide du logiciel MINEQL$^+$, il a été estimé que la plupart des espèces des métaux extraites du sol était complexée avec le EDTA. Ces résultats concordent avec ceux de l'essai d'extraction avec résines d'échanges anioniques. Il ressort de ces travaux que les complexes metal-EDTA des systèmes sont très stables et cela, sur un grand interval de pH. La modélisation s'est avérée être un outil valable pour étudier les réactions dans la solution du sol et a indiqué que le EDTA a une affinité pour les métaux qui est de beaucoup supérieure à celle des acides humiques ou des oxides de fer hydreux de la phase solide. Conformément aux prédictions du model, l'adsorption du Cd, du Cu, du Pb et du Zn par les surfaces solides a été négligeable en présence de EDTA.

PREFACE

Soils contaminated by trace metals have become common due to the release of solid wastes, gases and/or fly ash from residential, agricultural, industrial and mining activities. The contamination problem will probably become worse and negative impacts will occur for the environment and human health if prevention and remediation efforts are unsatisfactory. The pressure on scientists is great to come up with credible solutions to contain and remediate the contaminated soils, so that the unwanted impacts do not materialize. This thesis deals with soil contamination in the Montreal region by attempting to develop methods for the removal of trace metals from contaminated soils.

This thesis is composed of five Chapters preceded by a general introduction and ended by a Chapter of general conclusions and possible future research. Chapter 1 presents the theoretical background of trace metal contamination including the principles of metal-soil interactions, metal-chelate reactions, and metal-resin interaction which is intended to provide a review sufficient for understanding the concepts discussed in the following Chapters. Chapter 2 focuses on the extraction of trace metal contaminants from soils using acid and a chelating agent and on the removal of the metal contaminants from the resulting leachates using ion exchangers in batch experiments. Chapter 3 evaluates and improves the methods in Chapter 2 using column techniques. Varying methods of ligand applications, kind and form of ligands, kind of leaching solution, leaching speed, and extraction methods were investigated. Several resin trapping techniques for the metal in the leachates were also studied. Chapter 4 discusses the use of the most efficient method found in Chapter 3 to clean a large amount of contaminated soil to simulate a field experiment. Evaluation is made regarding the quality of the soils in general after the cleaning.

Chapter 5 uses computer modeling to describe the behavior of metals and EDTA molecules in soil systems. The MINEQL$^+$ program, for the reasons of simplicity and convenience, was chosen to model metal speciation in the EDTA soil-extracts and the potential retention of metals by the humate and the hydrous ferric oxide (HFO) surfaces. Such studies help determine the applicability of the extraction method for other soils. In Chapter 6, a general summary provides an overview of this thesis and some suggestions for future research. Connecting paragraphs are inserted between the different papers.

In accordance with the regulation of the Faculty of Graduate Studies and Research of McGill University, the following statement is included:

Candidates have the option of including, as part of the thesis, the text of one or more papers submitted or to be submitted for publication, or the clearly-duplicated text of one or more published papers. These texts must be bound as an integral part of the thesis.

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Additional material must be provided where appropriate (e.g. in appendices) and in sufficient detail to allow a clear and precise judgement to be made of the importance and originality of the research reported in the thesis.

In the case of manuscripts co-authored by the candidate and others, ***the candidate is required to make an explicit statement in the thesis as to who contributed to such work and to what extend****. Supervisors must attest to the accuracy of such statements at the doctoral oral defense. Since the task of the examiners is made more difficult in these cases, it is in the candidate's interest to make perfectly clear the responsibilities of all the authors of the co-authored papers.*

The candidate has been fully responsible for both conducting the original studies and for preparing the manuscripts. All the papers included in this thesis were co-authored by the candidate and his supervisor Dr. W.H. Hendershot. Dr. Hendershot's role was that of supervisor, to provide guidance through discussing my ideas and editorial assistance in the preparation of the thesis.

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CONTRIBUTION TO KNOWLEDGE

The experiments presented in this thesis contain new findings which expand further our knowledge in understanding the complex nature of soil-trace metal interactions and the problems associated with remediation. Major contributions to knowledge include the following.

1. Ethylene diamine tetraacetic acids (EDTA) is a suitable reagent for cleaning trace metal contaminated soils; it removes a large amount of metals from soils having high $CaCO_3$ and iron oxide contents. Using repeated washings with a low concentration of the ligand, or one single application with a high concentration, contaminated soils after washing can be reused for commercial and/or residential purposes. The fractionation studies revealed that much of the metals in the soils used in this experiment is retained in the carbonate and oxide fractions, and much of the metals found in the leachates after leaching with EDTA is removed from these two fractions. The treatment with the EDTA improves the quality of the contaminated soils by significantly reducing the trace metal content of the soils, improving pH for most living organisms, and increasing the CEC which permits better nutrient retention in the soils.
2. The dissolution of trace metals by EDTA is not rate limited. The rate of removal depends on amounts of EDTA used and not the contact time between EDTA and the soils. The findings suggest that quick and effective cleaning of metal contaminants is possible using EDTA once the recuperation method for the ligand is available to off set the cost of cleaning. One clear advantage of using EDTA for cleaning is that no enrichment of metals in the lower sections of the soil profiles was observed in our column leaching experiments.
3. The anion exchange resin (AER) AG 3-x4 is a strong sink for Cd, Cu, Pb, and Zn

from leachate generated from soil washing with chelating agents. It removes more metals from the leachates when higher concentrations of ligand are present in the leachates. We believe that AER attracts metals mostly in the form of metal-ligand complexes. Further studies revealed that the AER is effective in removing the metals from the extracts with a wide range of pH and salt contents. When the resin method is combined with the technique of metal extraction using high concentration of ligand (point No. 2), they together constitute a novel and effective method for soil remediation.

4. The forms of ligands and the methods of ligand applications and extractions affect the leaching rate of trace metals from soils. A nearly insoluble strong-chelate (e.g., H_4EDTA) is best applied in the form of solution as long as it can be kept soluble in the solution. In contrast, a very soluble weak-chelate (e.g., citric acid) is best applied as crystal or powder form. Also, mixing the ligands thoroughly with the soil sample removed more metals from the soils as compared with mixing the ligand with the upper portion of the soil column. As well, extraction using batch methods removed more metals from the contaminated soils than the column technique.
5. The $MINEQL^+$ program is a valuable tool for assessing the metal speciation in soils in contact with EDTA. The models support the results from the AER experiment which suggests the domination of the metal-EDTA complexes in the EDTA soil-extracts.

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GENERAL INTRODUCTION

Many soils throughout the world have been contaminated by a variety of organic and inorganic contaminants (Jones, 1991; Nriagu and Pacyna, 1988) due to increasing world population and the booming industrial and agricultural sectors. Some important activities that contribute to the problem include mining and related activities, agricultural and industrial operations, air emissions, and incineration, which release solid wastes, gases and/or fly ash to the soil environment (Tiller, 1992; Adriano, 1986). The problem will probably become worse, and the pressures on scientists are great to come up with credible solutions to contain and remediate contaminated soils.

In contrast to the numerous methods that exist for removing organic contaminants from soils, only few techniques are available for treating soils contaminated with trace metals (Davis and Singh, 1995). Among the methods frequently used for controlling metal pollutants in the field are soil excavation and landfills, phytoremediation, and metal immobilization. Technical barriers (e.g., separation and recuperation of metals from soils) have traditionally impeded the development of methods for metal contaminated soils and efficient and cost effective methods still have to be developed.

One of the most promising cleanup technologies for organic and inorganic contaminants in soils is soil-washing using extracting solutions (Gombert, 1994). Studies have shown that soils contaminated with a wide variety of organic contaminants can be effectively treated by soil washing using water or solutions containing chemical additives (Chawla et al., 1991). Many researchers have used in-situ soil washing to treat soils containing trace metal contaminants. Successful work has been reported particularly when chelating or complexing agents, acids or bases, or reducing or oxidizing agents were used in the remediation process. Apparently, the chemical treatments added to the extracting solution can mobilize trace metal contaminants that previously could not be effectively removed from the soil by water washing alone. Depending on the kind of chemical additives used, release of metal contaminants from the soil can take place through several physico-chemical processes including redox reactions, desorption and dissolution, ion pairing and complexation, and/or acid and base reactions.

Among the most widely studied chemical additives used for removing trace metals from soils, chelating agents have generated a great deal of interest owing to their strong reaction with metals to form stable metal-chelate complexes (Li and Shuman, 1996; Hong et al., 1995). Due to its effectiveness in mobilizing trace metals, ethylene diaminetetraacetic acid (EDTA) has received considerable attention. The applicability of each washing solution is site- and contaminant-specific and the effectiveness of the EDTA as a chemical additive in trace metal remediation deserves further study. Type of chemical additives, rates and methods of application, length and rate of extraction, batch versus column extraction, kinds and complexity of metal contaminants, and absence or presence of other chemical additives and salts are all variables which affect metal extraction from contaminated soil. In addition, metals along with the chemical additives removed from a contaminated site can pose a threat to the environment; hence, understanding their chemical speciation and behavior in the soil systems and finding suitable technologies for their recuperation are some very important tasks.

The present study was undertaken to investigate the role of chelating agents in trace metal remediation of contaminated soils. The objectives of the study were: 1) to develop in-situ and ex-situ remediation techniques using EDTA as a means of washing metal from contaminated soils, 2) to investigate exchange resins as a means of recovering metals from the resulting leachates, 3) to apply these techniques in the laboratory to reduce trace metal contamination of urban soils to acceptable levels for residential or industrial/commercial use, and (4) to use a computer model to investigate metal behavior in the EDTA soil systems.

Four major experiments were conducted in the study. In the first experiment (Chapter 2), EDTA was compared to HCl in batch experiments to determine the suitability of the two solutions for cleaning soils highly contaminated by trace metals. EDTA and HCl are known metal extractants capable of dissolving a large quantity of metals from mineral carbonates, sulfides and oxides as well as organic matter in the soil (Li and Shuman, 1996; Beckett, 1989). The use of the reagents in the experiments might serve the goal of removing metals for the purpose of soil remediation.

The use of exchange resins to remove metals from the resulting EDTA soil-extracts is also discussed in Chapter 2. Cation chelating resin Chelex-100 and anion exchange resin (AER) AG 3-x4 were tested for their ability to remove metals in the leachates.

In Chapter 3, experiments were conducted to see if higher amounts of Cd, Cu, Pb, and Zn were removed from the soil-column with the addition of more concentrated EDTA along with acid and salt solutions. Experiments with citric acid (a naturally available chelator) were also reported in this chapter. Methods of EDTA applications and leaching speeds were also tested in the experiments to find the best combination of methods for metal cleaning using a Centurion column extractor. Experiments were also conducted to see if the resin in columns was as effective as in the batch experiment in removing metal-EDTA complexes from the EDTA soil-extracts.

Our final goal was to develop methods that can be applied in the field to clean contaminated sites. Before we decided to do a full-scale field experiment, a small scale experiment using large soil columns was conducted in the laboratory. The method chosen was the most effective treatment that had been obtained in the previous experiment (Chapter 3). The focus of Chapter 4 was to examine if the removal of trace-metal contaminants increased with the application of ligands and acid/salt solution when a large quantity of soil was used. Also investigated was if the treatment altered the forms and amounts of the residual metals in the soil column and changed the chemical properties of the soils.

Because the success of metal remediation depends on the form of the metals in the soil systems, understanding the behavior of these pollutants in soil is important. Chapter 5 discussed this matter by focusing on the use of computer modeling (the MINEQL$^+$ program) to study the metal speciation and reaction with the surface charge of soils (e.g., humate and hydrous ferric oxide) in soil systems dominated by EDTA. Validation of the predicted results by the program was made by comparing with the results of the AER extraction obtained in the laboratory experiment. The thesis ends with a summary, conclusions, and suggestions for future research in Chapter 6.

CHAPTER 1

GENERAL LITERATURE REVIEW

In the following, a theoretical background of trace-metal contamination, principles of metal-soil interaction, metal extraction by chelating agents in soil and environmental studies, and resin retention of metal-chelate complexes are presented. The information is intended to provide a review sufficient for understanding the concepts discussed in the following Chapters.

1.1. Trace-Metal Contamination: General Remarks

Soil can be contaminated in a number of ways, but generally results from two major sources (Adriano, 1986). The first major source of pollutants is the build up of contaminants that result from human activities (as has been stated elsewhere in this thesis). The second source is the result of natural processes including metal accumulation from rock dissolution and volcanic activities. Of the two major sources, however, the anthropogenic source is dominant (Nriagu and Pacyna, 1988).

The trace-metal contaminants released to the environment are controlled by a complex set of processes. Consequently, contaminated soils can potentially have an impact on other components of the ecosystem. For example, groundwater may be polluted by the leaching of toxic chemicals from contaminated soils (Miller et al., 1983). Soils and water bodies of a neighboring contaminated site may become polluted from surface runoff or dust blowing from the contaminated site.

The existence of contaminated sites can result in contaminant releases and possible receptor exposure (Pierzynski and Schwab, 1993), resulting in both short- and long-term effects on living organisms including humans (Ernst, 1996; Tiller, 1989). The potential for adverse health effects on populations can involve several organ systems, depending on the specific metals contacted, the extent of exposure (e.g., dose and intake), the characteristic of the exposed individual (e.g., age, gender, susceptibility to toxins, etc.), the metabolism of the chemicals involved, and the presence or absence of confounding variables such as other diseases (Grisham, 1986). Typical health effects caused by trace-metal contamination include anemia, heart disease, and skin cancer for arsenic (As); kidney damage, fetal death, and lung and respiratory tract for cadmium (Cd); gastrointestinal and liver damage for copper (Cu); asthma, headache, and lung and respiratory tract for nickel (Ni); anemia, bone marrow depression, kidney damage, and seizures for lead (Pb) and; corneal and cell damage for zinc (Zn) (Majumdar et al., 1995). Human health problems and ecological damage due to contaminant exposures may cause huge economic losses in the long term.

Because contaminated sites may pose health risks (Kido et al., 1992), understanding the nature of contaminated sites becomes very important. Through assessment, the level of hazard a contaminated site presents (e.g., high, intermediate, or low) can be determined (Tiller, 1989). Thus, the assessment becomes an essential step for successful contaminated-site management programs. Among important factors affecting the degree of hazard posed by contaminants present in the environment are: physical form of contaminants, composition, quantity, reactivity, mobility, persistence, biological and ecological effects, indirect health effects, and local site conditions.

Since the protection of the environment can, at the same time, contribute to long-term economic progress, economic development and environmental protection should complement each other: improving one has the potential to enhance the other (World Bank, 1989). Several analysts have indeed concluded that environmental problems are generally inseparable from socioeconomic development problems, and that long-term economic growth depends on protecting the environment (World Bank, 1989). For these reasons, the need for establishing realistic corrective action for contaminated sites and credible legislative-regulatory controls is now even greater than before.

1.2. Trace Metal Behavior in Soil Systems

Solid phases tend towards equilibrium with the aqueous phase of soils. Ions are held by solids to reduce losses from leaching and released into soil solution to maintain availability for plants. Some important soil reactions involved in these balancing processes include ion exchange, adsorption/desorption, and precipitation/dissolution (Van Riemsdijk and Van der Zee, 1991). The metal ions held in soils by ion exchange processes minimize loss, but they remain generally available for plants (reversible). In contrast, metals held by the specific adsorption and precipitation processes are considered not to be readily available for plants (Wild, 1993). Understanding the behavior of metals in soils is useful in many aspects of soil and environmental studies including in making decisions about methods of remediation for metal contaminated soils.

1.2.1. Metal speciation in soil solutions

Soil solutions are composed of a variety of ionic species. Dissolved ions (or molecules) in soil solution do not exist as simple, free ions, but are surrounded by water molecules because of hydration (Winegardner, 1996; Tan, 1994). Water molecules are attached to the central metal ion and form single unit complex ions as represented by $M(H_2O)_x]^{n+}$, where n^+ refers to the formal oxidation state on the metal ion and x the coordination number.

The attraction of the central ion for water molecules in this $M(H_2O)_x]^{n+}$ ion complex structure is so strong that the cation's charge tends to repel hydronium ions or protons, of the water molecules (Bohn et al., 1985; Sposito, 1984). The process of hydrogen repulsion from the complex ions is known as hydrolysis or deprotonation; the general reaction is represented by

$$[M(H_2O)_x]^{n+} <===> [M(OH)_y (H_2O)_{x-y}]^{(n-y)+} + {}_yH^+$$

where y is the number of H^+ ions released to solution. When the solution is made more alkaline, more H^+ ions tend to dissociate from the hydration sphere (Bohn et al., 1985).

Many metal species in soil solutions result from the hydrolysis reaction. The hydrolysis of a hydrated Fe and Al, $Fe(H_2O)_6^{3+}$ and Al $(H_2O)_6^{3+}$, to form various metal species (e.g., MOH^{2+}, $M(OH)_2^+$, $M(OH)_4^-$) in soil solutions, is an example. The types and amounts of metal species present depend on the solution pH (Sposito, 1984).

Ions in soil solutions also interact with ligands of different types, forming complex ions or ion pairs. When a ligand attaches electrostatically to the outside solvation sphere of a hydrated ion, the outer-sphere complex (ion pair) is formed. The general complexation reaction between a hydrated metal, $[M(H_2O)_x]^{n+}$, and a ligand, L^{l-}, in soil solution to form an outer-sphere complex is represented by

$$a[M(H_2O)_x]^{n+} + bL^{l-} <===> [M(H_2O)_x]_aL_b$$

where a and b are stoichiometric coefficients. Association between a metal and a ligand through this mechanisms is considered to be weak and is exchanged readily.

Some ligands however penetrate deeply into the inner hydration sphere surrounding the central ion and replace one or more of the inner water molecules (Sposito, 1984), forming the inner-sphere complexes as illustrated in the following reaction

$$a[M(H_2O)_x]^{n+} + bL^{l-} <===> [M_aL_b(H_2O)_{x-y}] + {}_yH_2O$$

where y the number of water molecules released into solution. Many metal species in soil solutions result from these complex ion and ion pair reactions. Inner-sphere complexes of Cd and Zn with Cl in soil solution are some examples. The formation of such complexes may increase the total solubility of the metals in soils and influences the overall metal speciation in the soil solution (Doner, 1986; Dowdy and Volk, 1983).

The redox reaction (oxidation and reduction reaction) is another important process affecting the metal speciation in soil solutions. Some important trace elements (e.g., As, Cr, Cu, Fe, Mn, and Se) are sensitive to oxygen or CO_2 pressure in soils; they can undergo changes in oxidation state under the range of redox conditions found in soils (Florence, 1982; Bartlett, 1981; Lindsay, 1979). Selenium, for instance, can exist as selenide (Se^{2-}), elemental Se (Se^{o}), selenite [SeO_3^{2-}, Se (IV)], and selenate [SeO_4^{2-}, Se (VI)]. Selenate is more mobile than selenite and other reduced forms of Se, hence it is more available. Some elements, such as Cd are less mobile under "reduced" conditions. This may be due to the formation of CdS in a reducing environment (Pierzynski et al., 1994). Humic acid can act as a reducing agent and reduces Cr (VI), the more toxic form of chromium, to Cr (III) (Florence, 1982). Cr (III) will then form a stable complex with the carboxyl groups on the humic acid, and could change the Cr speciation in the soil solution.

1.2.2. Metal retention in soils

Ions or molecules in soil solutions also form inner- or outer-sphere complexes with surface functional groups of soils (Schindler, 1991). Outer-sphere complexes involve electrostatic coulombic interactions (Yu, 1997; Evans, 1989). It is usually a rapid process (μS or mS) and is inherently reversible. Absorption via this outer-sphere mechanism (or non-specific adsorption) is generally weak and greatly affected by ionic strength of the aqueous phase and occurs only on surfaces that are of opposite charge to the adsorbate (Wild, 1993; Abd-Elfattah and Wada, 1981). The inner-sphere mechanism (or specific adsorption), on the other hand, is covalent (Evans, 1989). It is a slow process (often increasing gradually over several days), not readily reversible, and modestly affected by the ionic strength of the aqueous phase. The inner-sphere complex can be monodentate or multidentate and such reactions can increase, reduce, neutralize, or reverse the charge of the surface (Stumm, 1992; Schindler, 1991). Inner-sphere adsorption often initiates precipitation (another form of ion retention in soils), and in some cases, there are no clear boundaries between them (Brummer et al., 1983). Outer- and inner-sphere complexation as well as precipitation can occur simultaneously in soils; they together influence the behavior of ions in soil systems.

1.2.2.1. Surface charge of soils

There are two distinct sources of negative surface charge in soils, the permanent or constant charge and the variable or pH-dependent charge. Soils obtain their surface charges from both inorganic and organic materials or solids. Constant charge is invariant with soil pH and results from the isomorphous substitution of layer silicates. The constant charge generated from layer silicates or silicate clays range from near zero in serpentine, halloysite and kaolinite to over 120 $\text{cmol}_c\ \text{kg}^{-1}$ in vermiculite and smectite minerals (McBride, 1994). Silicate clays with high constant charge usually have high cation exchange capacity (CEC), but it is not the case for some minerals such as micas and chlorites. Even though micas and chlorites have high structural constant negative charge, their CEC are relatively low because some of the charge sites in the minerals are inaccessible (Wild, 1993).

Besides the constant charge, the silicate clays also generate variable charge on their crystal edges. However, the magnitude of this charge on 2:1 layer silicates is low and relatively unimportant for cation exchange. For 1:1 layer silicates (e.g., serpentine, halloysite and kaolinite) which possess little constant charge, the role of crystal edges is very important with respect to cation exchange. As reported by Bohn et al. (1985), only 5 to 10% of the negative charge on 2:1 layer silicates is pH dependent, whereas more than 50% of the charge developed on 1:1 minerals can be pH-dependent.

For the variable charge surfaces, the primary source of charge is the protonation and deprotonation of surface functional groups, including hydroxyl (-OH), carboxyl (-COOH), phenolic ($-C_6H_4OH$), and amine ($-NH_2$), on the surfaces of soil solids

(Sposito, 1984). The soil materials that contain functional groups capable of developing variable charge include edged layer silicates, oxides and hydrous oxides, allophane, imogolite, and organic matter. The deprotonation of OH ions from the terminal OH groups (the OH bonded to a single metal ion such as Al, Fe, Mn, and Si on the mineral edges) is an example. According to Pauling's valence rule the charge of this terminal hydroxyl group is either +1/2 (for the protonated hydroxyl) or -1/2 (for the deprotonated group), as illustrated in the reaction below.

$$\underset{\text{(CEC)}}{>\mathrm{Fe\text{-}OH}]^{-1/2}} \quad \underset{+\,\mathrm{OH}^-}{\overset{+\,\mathrm{H}^+}{<\!\!==\!\!>}} \quad \underset{\text{(AEC)}}{>\mathrm{Fe\text{-}OH_2}]^{+1/2}}$$

The reaction shows that the surfaces of the variable charge minerals are amphoteric, behaving as both acids and bases. Because the degree of protonation and deprotonation of the functional groups is determined by the pH of the solution, the charge on the variable charge minerals is pH dependent; the net charge can be either negative or positive depending on the solution pH.

A 'term' used to indicate the zero net charge in soil is known as the point of zero charge (PZC), defined as the pH at which the colloidal particle has no net charge. Although many variable charge materials (e.g., oxides) usually have net negative charge at relatively high pH ($pH>6.0$), soils of variable charge in the tropics usually have a PZC of 4.5. The low PZC in tropical soils is usually attributed to the presence of kaolinite in the soils. Organic matter which is negatively charged at pH values greater than 3 can also contribute to the low PZC (White, 1987). (Please note that carboxyl and phenolic groups of the organic matter deprotonate at pHs common in many soils).

With the preceding discussion, it is obvious that the relative contribution of constant and variable charge on charge development in soils depends on the composition of soil colloids, the solution pH, and the ionic environment in which the soil has been formed. Most soils, however, should have a net negative charge because of the constant charge on layer silicates and negative charge on organic matter, but some highly weathered soils dominated by allophane or hydrous oxides, for example, can actually have a net positive charge at low pH.

1.2.2.2. Ion exchange

In nature, soils are always in some form of dynamic equilibrium. The negative charges on the constant and variable charge surfaces are balanced by the positive charges of ions in the soil solution; conversely, the positive charges of the variable charge materials are neutralized by the negative charges of other ions (Tan, 1998). The sorbed ions on the charged surfaces are exchangeable and the process is called 'cation exchange' (CEC) for the exchange between cations, and 'anion exchange' (AEC) for the exchange between anions. The ion exchange capacity is very important because it determines the capacity of a soil to hold ions in forms that are available for plant uptake but are not susceptible to leaching in the soil profile (Abd-Elfattah and Wada, 1981). This feature has important agronomic and environmental aspects.

Ion exchange involves electrostatic interactions between a counterion on a charged particle surface and counterions in a diffuse cloud around the charged particles. It is usually rapid, diffusion-controlled, reversible, stoichiometric, and selective (Wild, 1993). Exchange reversibility means that the adsorbed ions are readily desorbed back to the soil solution; whereas, stoichiometry refers to replacement of ion (or ions) by an equivalent (in terms of ion charge) amount of other ion(s). For example, to maintain stoichiometry, two Na^+ ions are necessary to replace one Ca^{2+} ion.

Since electrostatic forces are involved in ion exchange, Coulomb's law can be used to explain the selectivity of preference of the ion exchanger for one ion over the other. In general, for a given group of elements from the Periodic Table with the same valence, ions with the smallest hydrated radius will be preferred (Sposito, 1984). Thus, for the Group 1 elements the general order of selectivity would be: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+ > H^+$ (Yu, 1997). For ions of different valence, generally the higher charged ion will be preferred, for example, $Al^{3+} > Ca^{2+} > Mg^{2+} > K^+ = NH_4^+ > Na^+$ (Bohn et al., 1985). In addition, polarization (the distortion of the electron cloud about an anion by a cation) is also an important factor determining the selectivity. The smaller the hydrated radius of the cation (or the greater the valence) the greater is the polarizing power of the cation.

Although the ion exchange reaction is considered rapid, the rate of the ion exchange is not always the same for each element for every soil (Tan, 1998). The rate of ion exchange in soils is dependent on the type and quantity of inorganic and organic components, and the charge and radius of the ion being considered. For example ion exchange reactions usually occur more rapidly on clay minerals such as kaolinite and oxides than on clay surfaces such as vermiculite and mica (McBride, 1994). This is attributed to the external exchange sites on kaolinite and oxides versus the multiple types of exchange sites with vermiculite and mica. External planar, edges, and interlayer sites exist on the surfaces of vermiculite and micas with some of the latter partially collapsed. High rates of reactions are often observed for external sites, intermediate rates on edges sites, and low rates on interlayer sites (Jardine and Sparks, 1984).

The type of ion also has a pronounced effect on the rate of exchange (Tan, 1998). Exchange of ions like K^+, NH_4^+, and Cs^+ is often slower than that of ions such as Ca^{2+} and Mg^{2+}. This is related to the smaller hydrated radius of the former ions. The smaller ions fit well in the interlayer spaces of clay minerals, which cause partial or total interlayer space collapse. The exchange is thus slow and particle diffusion-controlled. The charge of the ion also affects the kinetics of ion exchange. Generally, the rate of exchange decreases as the charge of the exchanging species increases (Yu, 1997).

1.2.2.3. Specific adsorption of cations on variable charge materials

Cations are also adsorbed on soils through specific adsorption or chemosorption, an inner-sphere type of ion complexation in soils. The adsorption involves both physical (e.g. van der Waals attraction and the electrostatics outer-sphere complexation) and chemical forces (e.g., ligand exchange, covalent bonding, and hydrogen bonding) (Stumm and Morgan, 1996; Bolt and Van Riemsdijk, 1991). Specific adsorption affects the properties of soils, particularly the electrostatic charge of suspended particles and colloids (Stumm, 1992).

Amongst the important surface-site providers for specific adsorption of metal ions in soils are the oxides and hydroxides of Fe, Al, and Mn, the allophane and imogolite, and the edges of layer silicate clays (e.g., kaolinite) as well as soil organic matter (Alloway, 1995). These sites, as represented by an iron oxide surface ($>$Fe-OH]$^{-1/2}$), exhibit a valence-unsatisfied OH^- or H_2O ligand bound to a metal ion on the solid structure. They react with a trace metal, $M(H_2O)_6^{n+}$, forming strong surface complexes. The typical specific adsorption reaction between a trace metal, $M(H_2O)_6^{n+}$ and an iron oxide surface, $>$Fe-OH]$^{-1/2}$, is shown in the following reaction

$$>\mathrm{Fe\text{-}OH]}^{-1/2} + M(H_2O)_6^{n+} ===> \ >\mathrm{Fe\text{-}O\text{-}M}(H_2O)_5]^{(n-1/2)+} + nH_3O^+$$

The reaction is relatively slow (as compared to ion exchange) with several features as follows (McBride, 1994): (1) a number of hydrogen ions, *n* H^+, are released for each M^{n+} cation adsorbed, (2) the adsorbed cation is not readily reversible, (3) the metal ion adsorbed becomes an integral part of the resulting complex structure, (4) the adsorption is very selective (oxide minerals have high degree of preferences for particular metals), and (5) the adsorption changes the measured surface charge, shifting the PZC to higher pH. The features clearly distinguish the specific adsorption from the more simple reaction of ion exchange (non-specific adsorption).

Several factors affect the specific adsorption of metals in soils; the most important ones are the pH of the medium, the type of the adsorbent, the concentration of sorptive surface, the nature of the adsorbed metals (e.g., electronegativity, polarizability, hydration, etc.) and the accompanying metal species (Keizer and Bruggenwert, 1991). Specific adsorption of metal cations on charged surfaces is pH-dependent (Christensen, 1984); when the pH is raised the metal adsorption increases. A high pH is favorable to the hydrolysis of the ions, resulting in the increase of the hydroxo metal ions, MOH^{n+}. Because the hydrolyzed metal ions carry less electric charge, they are favorably adsorbed on the charged surface through short-range forces. The specific adsorption is characterized by a narrow pH range where adsorption increases to nearly 100%, known as the adsorption edge. The pH of the adsorption edge is dependent on the nature of the adsorbed cations.

The type of the absorptive surface, whether it is the >Si-OH, >Ti-OH, >Al-OH, or >Fe(III)-OH, affects the adsorption results (McBride, 1994). The key factor is the acid-base property of the absorptive surfaces, which are determined by the ratio between the valence and the coordination number of metal constituting the adsorption site. The smaller the ratio, the less acidic the group, the more effective is the metal adsorption (Yu, 1997). The >Si-OH surface bonding group having the valence:coordination number ratio of 1.0 should adsorb metals less effectively than the >Ti-OH (0.67) or the >Al-OH and >Fe(III)-OH (0.5) groups, because the >Si-OH group is more acidic than the other -OH groups (McBride, 1994).

The type of the mineral surface bonding group, whether it is a bridging hydroxyl, a terminal hydroxyl, H_2O molecule, or OH^+ ion also affects the adsorption results (McBride, 1994; Schindler, 1991). For example, a terminal OH^- type (e.g., an O atom bonded to one Al^{3+} and one H^+) of mineral surface bonding group is more likely to form a covalent bond with trace metals than a bridging OH^- group (e.g., an O atom bonded to two Al^{3+} and one H^+); because, when the two surface bonding groups are deprotonated, the terminal OH^- group ($Al\text{-}O^-$) forms a stronger Lewis base than the bridging OH^- group, which then reacts preferentially with trace metals (McBride, 1994; Schindler, 1991).

The specific adsorption of cations is caused by the negative surface charge of variable charge materials. Thus, the extent of adsorption is closely related to the concentration of the negatively charged surfaces (Bohn et al., 1985). For example, crystalline gibbsite [$Al(OH)_3$] adsorbs less metal as compared to the noncrystalline oxides and allophanes. Apparently, gibbsite contains no mineral surface bonding groups on its crystal faces and bonding probably occurs only at edges that posses a few OH^- or H_2O groups (McBride, 1994). In contrast, amorphous oxides and allophane (because of their structural disorder) possess larger numbers of valence-unsatisfied groups and, therefore, they can adsorb more trace metals.

The nature of the adsorbed metal also has to be considered in explaining differences in trace metal adsorption behavior (Norvell, 1980). The tendency of hydrolysis is one of the important cation properties determining the degree of adsorption; the greater the tendency for metals to hydrolyze the greater is their potential for being adsorbed onto the soils. Pb^{2+} ions, for example, (at a given pH) are more readily hydrolyzed than the Cd^{2+} ions (as indicated by their first hydrolytic constant value, pK_1, 7.7 for Pb^{2+} and 10.1 for Cd^{2+}). As a consequence, Pb^{2+} ions are adsorbed by the soils more strongly than the Cd^{2+} ions (Yu, 1997). Electronegativity is another important property of metal affecting adsorption, because it determines the strength of covalent bonding between metal and oxygen atoms on variable charge surfaces.

In the case of the accompanying ions, the electrolytes may influence the adsorption of metal through one or more of the following mechanisms (Yu, 1997). The electrolytes change the ionic strength of the solution systems which could affect the activity coefficient of the metal, the H^+, and the OH^- ions and thereby affect the rate of metal adsorption. The electrolytes can form complex ions or ion-pairs with other metal ions in solutions and thereby reduce the number of the adsorbed metals. The electrolytes may be adsorbed onto the surface solids, altering the charge composition of the surface and therefore alter the adsorbing capacity indirectly. The electrolytes induce the contraction of the electric double layer at the surface of the colloid, lower the electrokinetic potential at the immediate solid surface, thus alters the adsorption of metal ions (Sposito, 1984).

1.2.2.4. Ligand exchange of anions

As with metal cations, oxyanions such as $B(OH)_4^-$, CO_3^{2-}, $H_3SiO_4^-$, PO_4^{3-}, SO_4^{2-}, AsO_4^{3-}, SeO_3^{2-}, and MoO_4^{2-} can be adsorbed by a ligand exchange mechanism forming an inner-sphere complex with oxides or other variable charge materials. The OH^- or OH_2^+ groups in the mineral surface is displaced by an O of the oxyanions as simplified in the following reactions

$$>S\text{-}OH + L^{n-} \text{===>} >S\text{-}L^{(n-1)-} + OH^-$$

$$>S\text{-}OH_2^+ + L^{n-} \text{===>} >S\text{-}L^{(n-1)-} + H_2O$$

where L^{n-} is an inorganic oxyanion of valence n, and >S-OH is a surface hydroxyl group. The reaction (mostly) occurs at low pH with some distinct features as follows: the OH^- ion or H_2O molecule is released into solution, the adsorption is selective and not easily reversible, and the reaction increases net negative charge on variable charge surfaces (lower PZC) (Evans, 1989). The hydroxyl (OH^-) groups (>S-OH) and the water molecule (H_2O) groups ($>S\text{-}OH_2^+$) are believed to be the main reactive groups responsible in the reaction. Major minerals able to generate ligand exchange surfaces include noncrystalline aluminosilicates (e.g., allophanes and imogolite), the Fe, Al, Mn oxides and hydroxides, and the edge sites of layer silicate clays (Evans, 1989).

Because the ligand exchange reaction is pH dependent, the dominant factors affecting the reaction should include the pH, the characteristics of the variable charge surfaces, and the nature of the anions (Yu, 1997). The effect of pH is obvious; it directly affects the protonation and deprotonation of hydroxyl groups on the variable charge surfaces, leading to changes in the ratio between the hydroxyl and H_2O groups as well as the net charge of the soils. A decrease in pH, for example, will increase the concentration of positively charged H_2O groups ($>S\text{-}OH_2^+$) due to protonation of the -OH groups and will generally lead to an increase in anion adsorption (Sposito, 1984). Once an oxyanion (e.g., SO_4^{2-}) is adsorbed by a surface colloid (by replacing the surface -OH group), more negative charge is transferred to the surface. As a result, the PZC of the colloidal surface will decrease.

Because ligand exchange of anions is specific, it can be expected that only materials with desirable surface properties could perform such an exchange. As a result, different soils would experience different degrees of specific adsorption with anions. Goethite, for example, even though there are three types of -OH groups on the mineral, only the -OH bound with one iron ion (called A-type -OH group) is capable of performing ligand exchange, while B-type (with three iron ions) and C- type (with two iron ions) -OH groups can form only hydrogen bonds with the adsorbing anions (McBride, 1994). Other mineral surfaces such as Fe, Al, Mn, and Si hydroxides (amorphous and crystalline) and edges of clay minerals would undergo ligand exchange with oxyanions by forming one or more of the following complexes: monodentate complexes, bidentate complexes, or binuclear bridging complexes (Yu, 1997). The metal complexes are not easily reversible and their desorption into the soil solution will be determined by the characteristics of the soil (e.g., the pH and the nature of the anions) at a particular time.

The adsorption as has been cited earlier is also affected by the characteristics of the anion, most importantly, by its kind and its concentration (Yu, 1997). Phosphate can form a strong complex with mineral surfaces in soils; it is stronger than the bond with the sulphate complex so that the phosphate can displace the sulphate from the mineral surfaces. As a consequence of the strong adsorption, phosphate availability in soils is generally low. Although the phosphate can be displaced by high concentration of other strongly held anions, e.g., fluoride and silicate in natural soils, the displacement by the fluoride and silicate is less important than the release of phosphate generated by microorganisms (Bohn et al., 1985).

The fact that some anions are more preferentially adsorbed by mineral surfaces than others is not disputable, but the reasons for selectivity shown by particular anions for particular mineral surfaces are not very well understood. However, according to McBride (1994), there is a general rule that "if an anion shows a tendency to bond strongly with a particular metal ion in solution, it will show a comparably strong affinity for a surface >S-OH or >S-OH_2 site composed of the same metal". The "shared charge" (that is a measure of the positive charge that the oxyanion's central atom shares formally with each bonded O atom, e.g., PO_4^{3-} has 5/4 shared charge, SeO_3^{2-} (4/3), CrO_4^{2-} (6/4)), the ionic size, the electronegativity, and the anion acidity are some properties believed to influence the adsorption selectivity (McBride, 1994).

1.2.2.5. Metal adsorption on organic matter

As with the amorphous and inorganic minerals, soil organic matter is capable of binding many metal ions very strongly. This is as a result of highly reactive surfaces on soil organic matter in general and humic acid in particular (Norvell, 1980). The functional groups such as those of basic (e.g., -NH_2 amino, =O carbonyl, -OH alcohol, and -S- thioether) and acidic (e.g., -COOH carboxyl, -OH enolic or phenolic, and -SH thiol) properties are the source of the reactive sites, where metals coordinate directly to form inner-sphere complexes with the functional groups. The reaction is very selective and not readily reversible. However, because of the complexity (or mixture) of the soil organic matter composition and structure, it is believed that complexation with metals involves not a single but various binding mechanisms involving many functional groups (MacCarthy, 1991). The van der Waals attraction, strong ionic bond, hydrogen bond, and covalent bond are expected to take part in the formation of these complexes. The covalent bond however is believed to be the major force in the complex formation; hence the complexes should have the same properties as the specific adsorption of metals on inorganic mineral surfaces as outlined above.

A significant property of organic matter is its ability to form complexes with metals by chelation; the formation of a ring structure in which a metal is held by two or more electron-donating groups of ligands (Stevenson, 1991). The donor atoms are usually the O, N, and S that constitute the functional groups of the organic matter (Parfitt and Taylor, 1995; Norvell, 1980). These elements are Lewis bases and in metal bonding reactions, they would react with metals with Lewis acid properties. Because the O, N, and S have a different degree of hardness in Lewis bases (O > N > S), different metals would preferentially react with these donor atoms (Parfitt and Taylor, 1995). For example, Ca^{2+} (a hard acid) would preferentially complex with O-containing groups such as carboxylate and phenolate. Conversely, Cu^{2+} (a soft acid) would preferentially complex with the ligand containing N (a softer ligand) (Parfitt and Taylor, 1995).

Although numerous studies has been conducted to explain the extent of metal-organic matter retention, so far, no consistent rule of metal selectivity can be agreed upon. As the selectivity is determined both by the properties of the organic matter and the metal, unless the two components are well characterized, the extent of their reactions in soils will never be fully understood. It is believed that the shear complexity of organic matter, its composition and structure, has been the major constraint in establishing the extent of metal retention and selectivity by this substance (McBride, 1994).

The following are some important factors believed to affect the extent of metal-retention in soils by organic matters (McBride, 1994): (1) the nature of the organic matter or the type and concentration of functional groups, (2) the adsorption capacity of the organic matter, (3) the pH of the soil medium, and (4) the ionic strength of the solution.

Many studies have reported different series of relative complexing strength of metal by organic matter. The typical series according to Evans (1989) would be Hg = Fe = Pb = Al = Cr = Cu > Cd > Zn > Ni > Co > Mn. Based on this series, Evans (1989) concludes that the extent of metal retention by organic matter did not coincide with either the atomic radius, the hydration radius, the atomic weight, or the atomic number. The conclusion is in agreement with the argument given above that organic matter composition and structure are the major factors determining the extent of metal complexation reactions. Since the composition and structure of organic matter in soils vary widely from soil to soil and are not easily characterized, generalization about the order of complexing strength of metal retention by organic matter should be avoided. The following example mirrors the problem.

It was found that for low levels of Cd^{2+}, soil has preference for Cd^{2+} over Ca^{2+}, but at high levels of Cd^{2+}, after a certain amount of Cd^{2+} was adsorbed, the preference of the soil for Cd^{2+} over Ca^{2+} diminishes (McBride, 1994). It seems that the soil contains a limited number of soft base ligands, and once these ligands complex with Cd^{2+} the remaining base ligands, such as the harder carboxylic and phenolic groups, fail to show a similar selectivity for Cd^{2+} over Ca^{2+}. The example shows that the major factor is not the characteristic of the metals but the composition, the concentration, and the structure of the organic matter.

1.2.2.6. Precipitation and co-precipitation

Precipitation can be defined as the process of a three-dimensional growth of solids from the liquid phase(s). The important parameter for precipitation is the ratio between the ion activity product (IAP) and the solubility product (K_{SO}), which determines whether the solution phase is undersaturated, saturated, or supersaturated. A condition of undersaturation is indicated by the IAP/K_{SO} ratio less than one ($IAP/K_{SO} < 1$), saturation by the $IAP/K_{SO} = 1$, and supersaturation by the $IAP/K_{SO} > 1$. When solutions are supersaturated, precipitation can occur (Yu, 1997).

Precipitation however varies with different solutions. In a homogeneous solution, precipitation begins only with a large margin of supersaturation, because of a higher energy barrier for nucleation. In soils, the energy barrier for nucleation is small because of the catalytic effect of the organic and inorganic materials. As a result, precipitation can occur at a relatively small margin of supersaturation. For example, gibbsite does not precipitate in a solution supersaturated by this mineral, but the presence of smectite promotes gibbsite precipitation in the same solution (McBride, 1997).

Precipitation is common in soils. It is an important process that controls the solubility of abundant elements (e.g., Al, Fe, Si, Mn, Ca, and Mg) in normal soils, and trace metals in some contaminated soils. Amongst the most important precipitates in soils are the oxides, oxyhydroxides, hydroxides, carbonates, sulfides, silicates, and phosphates (De Boodt, 1991). Table 1.1 shows some of the precipitates and the solubility products of their metal precipitates. In soils, the Cd^{2+}, Cu^{2+}, Pb^{2+}, and Zn^{2+} solubilities are most likely to be limited by the three precipitates (carbonate, oxide/hydroxide, and sulfide precipitates); although other precipitates, such as phosphates, may occur in significant amounts in highly phosphate-fertilized croplands. Although carbonates have higher solubility constants than the (hydr)oxide and sulfide precipitates (as shown in Table 1.1), the determination of the most limited precipitates for metal release into soil solution should not be based solely on solubility constant values, but should consider other important factors such as the pH and redox in the soil.

Since the solubility of the precipitates is the result of the interactions between many determining factors (e.g., the acidity and the redox of the soil system), the extent of metal release by the precipitates will depend on a set of soil condition governed by these factors. In addition, the kind and composition of precipitates also determine the solubility of trace metals in soils (Lindsay, 1979). For example, metals would be more readily released from the carbonates than from the phosphates because of the lower solubility of the phosphate precipitates. Also, precipitates of more than one anion are sometimes less soluble than simple pure solids of one anion with cation(s). For example, the hydroxycarbonates of Cu and Zn can be less soluble than the simple Cu or Zn hydroxides or carbonates. The hydroxysulfates and hydroxyphosphates of Al are more stable precipitates than its sulfate or phosphate forms (Yu, 1997).

Besides, metals could also experience co-precipitation in soils. When spontaneous dissolution and recrystalization of minerals occur, metal co-precipitation can take place. Metal co-precipitation will readily take place on minerals with relatively high solubility products such as calcite and Fe and Al oxides. For example, soil reduction generates soluble Fe and Mn from Fe or Mn crystalline oxides, when the soil is reoxidized new crystal oxides are formed, entrapping trace metals. Similarly, calcite always undergoes a dynamic state of dissolution and recrystalization; trace metals (e.g., Mn^{2+}, Cd^{2+}, and Fe^{2+}) enter the calcite structure on precipitation and become entrapped within the crystal structure. As a result, the (toxic or trace essential) metals become inaccessible to desorption. These examples underline the importance of co-precipitation in controlling metal solubility and availability in soils.

1.2.2.7. Desorption and dissolution

Desorption/adsorption are important processes in soils because they control metal mobilities. Desorption is a more difficult process than adsorption. Adsorption reactions tend to be fast and diffusion controlled, whereas desorption is a slow process with a constant rate several orders of magnitude slower than the rate of adsorption (Barrow, 1987). Several reasons may explain the slow reaction of desorption. First, the metal cations adsorbed by charged mineral surfaces gradually lose much of their lability over time. The possible reasons include the increasing crystallinity of the metal-adsorbent complexes and the increasing surface coverage on adsorbed metals by surface precipitates. Second, adsorption may or may not require a significant activation energy. In contrast, desorption always requires an activation energy to at least overcome the adsorption energy. As a result, not all the adsorbed metals are desorbed and gradually the reaction becomes less reversible (Barrow, 1987).

The irreversibility of the adsorbed metals is not universal but depends on pH, the kind of adsorbents and the length of time over which the adsorption had occurred. For example, the irreversibility increases with the increase of pH. Apparently at higher pH, the multidentate ligands dominate over the monodentate. The multidentate ligand forms much stronger complexes with metal than the monodentate ligand; as a result, a very slow rate of desorption can be expected at higher pH because of the high energy required for metal separation. By the same rationale, adsorbents with more multidentate ligands can be anticipated to have slower desorption rates than those with fewer multidentate ligands (Yu, 1997).

For organic matter, a general rule can be summarized as follows; the most strongly bound metals are the most slowly desorbed because a larger activation energy is required to break the stronger bonds. Dissociation of adsorbed metals from organic surfaces are several orders of magnitude slower than their adsorption. In contrast to cation adsorption, anion adsorption seems to be more readily reversible. Anion desorption requires a lower activation energy and is therefore kinetically favorable (Bohn et al., 1985).

Dissolution is another important chemical reaction that determines the fate of metal contaminants in soils. Contaminant mobility is also affected by the dissolution-precipitation equilibria of the solid phases. When the soil solution is under-saturated or a strong complexing ligand is added, dissolution can occur.

Dissolution of minerals involves several steps including (1) mass transfer of dissolving reactants from the bulk solution to the mineral surfaces, (2) adsorption of solutes, (3) interlattice transfer of reacting species, (4) surface chemical reactions, (5) removal of reactants from the surface, and (6) mass transfer of products into the bulk solution. In normal soils, step 3, 4, and 5 are the rate limiting steps (Stumm, 1990); the detachment of metal species from the surface into the soil solution is a slow and rate limited process.

However, the addition of other ligands can overcome the rate limiting steps and therefore promotes dissolution (Schindler, 1991). Surface protonation, for example, increases dissolution by polarizing interatomic bonds close to the central surface ions, which promotes the release of a cation surface group. Ligands such as EDTA, NTA, and EGTA increase dissolution by polarizing the metal-oxygen bonds, causing detachment of the metal cation into the solution phase. Reductants decrease the redox potential of the soil system thereby promote metal dissolution from oxides.

A useful way of determining dissolution is to use stability diagrams which are constructed by converting a solubility relationship equation into log terms and rearranging terms to form a straight line relationship. As the diagram includes different solid phases with different stabilities, one can compare the solubility of the different solid phases at the same time and predict the presence of stable solid phases in different soil systems. Such diagrams are very useful and easy to use. The portion of straight line relationships closest to the origin of the x and y axes represents the most stable mineral phase (Lindsay, 1979).

1.3. Metal Reaction with Chelating Agents

One way of mobilizing metals from a soil is through complexation reaction with chelating agents. Many kinds of ligands are available commercially including diamino cyclohexane tetraacetic acid (DCyTA), ethylene glycol tetraacetic acid (EGTA), and nitrilo triacetic acid (NTA).

When a chelating agent is placed in contact with polyvalent metals in the soil, it releases its protons or counterions in preference to the metals. As a result, the soil-bound trace-metals are removed and transformed into soluble metal complexes (Peters and Shem, 1992). In general, the larger the number of protons donated the stronger the stability of the metal-chelate complexes. Thus, EDTA which has 6 donor atoms (hexadentate) should form more stable complexes with metals than NTA which has only 3 donor atoms (tridentate). However, chelating agents with more than 6 protons (e.g., DTPA, octadentate) often form less stable metal-chelate complexes due to their large size ring formation. The chelating agents having 5 or 6 proton donors are considered the strongest ligands in forming complexes with trace-metals.

Among the chelating agents available commercially, EDTA has received considerable attention because of its ability to form stable, low-biodegradable, water soluble complexes with many cations (Sundstrom et al., 1996; Borggaard, 1976). EDTA forms 1:1 complexes almost instantaneously with most cations, regardless of their oxidation state (Pribil, 1972). The most common cations involved in the reaction with EDTA include the metals of the transitional and lanthanide groups, and the alkaline earth metals, particularly the Ca and Mg. Such strong reactions with a wide range of metals makes EDTA a potentially interesting reagent for remediation of metal contaminated soil.

However, the fact that EDTA is expensive and toxic at high concentrations (Lee et al., 1996; Mazidji et al., 1992) may not satisfy the five criteria required for the safe and effective use of chelating agents in soil remediation. The criteria include (Anderson, 1993): 1) the chelating agent should form water soluble complexes over a wide pH range, 2) the complexes so formed should be non-adsorbable to soil surfaces, 3) should not be easily degraded biologically, 4) should have low toxicity or be harmless, and 5) should be cost-effective. Techniques that are able to recover and recycle the EDTA would reduce the cost and the potential hazard to the environment and living organisms. This would make EDTA more satisfactory for application in soil remediation.

1.4. Equilibrium Theory

1.4.1. Thermodynamic and conditional equilibrium constants

The formation of each metal-ligand complex in the soil solution can be described using a conditional stability or conditional equilibrium constant, K^{cond}. The determination of stability constants for metal-ligand complexes provides information on the affinity of the metal for the ligand, and they also provide valuable insights into the fate of metals in the environment (Farrah and Pickering, 1977). Because the conditions of the soil solution changes over time, the conditional stability constants vary with the composition and total electrolyte concentration of the soil solution.

For inorganic complexes, conditional stability constants can be related to thermodynamic stability or thermodynamic equilibrium constant (K^{o}) which are measured at a standard temperature and pressure and at zero ionic strength (independent of chemical composition of the soil solution). The relationship between thermodynamic and conditional equilibrium constant may be explained as follows.

For any reaction (Lindsay, 1979):

$$aA + bB <===> cC + dD \qquad (1)$$

a thermodynamic equilibrium constant, K^{o}, can be written as

$$K^{o} = \frac{(C)^{c}(D)^{d}}{(A)^{a}(B)^{b}} \qquad (2)$$

where the small superscript letters refer to stoichiometric coefficient and A, B, C, and D are chemical species. The parentheses in Eq. 2 refer to the chemical activity of each of the chemical species.

Thermodynamic equilibrium constants are independent of the electrolyte composition of soil solution because they are expressed in terms of activities, not concentrations (Lindsay, 1979). Unfortunately, the activities of ions in solutions generally cannot be measured directly as opposed to their concentration. The activity and concentration of an ion in solution can be related, however, through the expression

$$(B) = [B]\gamma_B \tag{3}$$

where [B] is the concentration of species B in mol L^{-1} and γ_B is a single ion activity coefficient for species B. Using the relationship in Eq. 3, Equation 2 can be rewritten in terms of concentrations rather than activities

$$K^{o} = \frac{[C]^{c}\gamma_{C}^{c}[D]^{d}\gamma_{D}^{d}}{[A]^{a}\gamma_{A}^{a}[B]^{b}\gamma_{B}^{b}} = \frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}} \times \frac{\gamma_{C}^{c}\gamma_{D}^{d}}{\gamma_{A}^{a}\gamma_{B}^{b}} = K^{cond}\,\frac{\gamma_{C}^{c}\gamma_{D}^{d}}{\gamma_{A}^{a}\gamma_{B}^{b}} \tag{4}$$

where K^{cond} is the conditional equilibrium constant. The ratio of the activity coefficients is the correction term that relates K^{cond} to K^{o}. The value of the activity coefficients, and therefore the value of the ratio of the activity coefficients, changes with changes in the electrolyte composition of the soil solution (Lindsay, 1979). In very dilute solutions, the value of the activity coefficients approaches 1, and the conditional equilibrium constant approaches the thermodynamic equilibrium constant.

1.4.2. Metal-EDTA equilibrium constants

When EDTA is added to the soil, equilibrium is established between the EDTA and the metal ions. The deprotonation of the EDTA takes place and is very pH dependent. Complete deprotonation of EDTA can only be achieved at very high pH. Consequently, the fraction of EDTA in deprotonated and protonated forms varies with time and soil conditions and can be computed from the α coefficients. For instance, the EDTA fraction present in the completely deprotonated form (L^{4-}) is:

$$\alpha_{L^{4-}} = \frac{K_1K_2K_3K_4}{[H^+]^4 + K_1[H^+]^3 + K_1K_2[H^+]^2 + K_1K_2K_3[H^+] + K_1K_2K_3K_4}$$

where K_1, K_2, K_3, and K_4 are the dissociation constants of the acid to yield H_3L^-, H_2L^{2-}, HL^{3-}, and L^{4-}, respectively, as described in the reactions below.

$$H_4L \Longleftrightarrow H_3L^- + H^+ \qquad K_1 = \frac{[H_4L]}{[H_3L^-] + [H^+]}$$

$$H_3L^- \Longleftrightarrow H_2L^{2-} + H^+ \qquad K_2 = \frac{[H_3L^-]}{[H_2L^{2-}] + [H^+]}$$

$$H_2L^{2-} \Longleftrightarrow HL^{3-} + H^+ \qquad K_3 = \frac{[H_2L^{2-}]}{[HL^{3-}] + [H^+]}$$

$$HL^{3-} \Longleftrightarrow L^{4-} + H^+ \qquad K_4 = \frac{[HL^{3-}]}{[L^{4-}] + [H^+]}$$

For other protonated complexes (HL^{3-}, H_2L^{2-}, and H_3L^-) the fractions can be expressed by the related α coefficient.

The EDTA has a double betaine structure containing four carboxymethyl groups attached to the nitrogen atoms of the ethylenediamine backbone. When deprotonation takes place, the first and second protons are removed from opposite ends of the molecule, which then approximates a dibasic ion. The third hydrogen atom will be removed from between the carboxyl-carboxyl linkage, and the fourth will migrate to the nitrogen atom (Pibril, 1972).

The reactions $M^{n+} + L^{4-} \Longleftrightarrow ML^{(n-4)+}$ and $ML^{(n-4)+} + H^+ \Longleftrightarrow MHL^{(n-3)+}$, illustrate the formation of deprotonated and protonated chelates that can occur when ligand is added to the soil. From these reactions stability constants are obtained. The formation constants of the ML and the MHL from the reactions can be calculated as:

$$K_{ML} = \frac{[ML^{(n-4)+}]}{[M^{n+}]\,[L^{4-}]} \quad \text{and} \quad K_{MHL} = \frac{[MHL^{(n-3)+}]}{[ML^{(n-4)+}]\,[H^{+}]}, \text{ respectively,}$$

and are conventionally presented as logarithmic values. Most of the chelates have high formation constants and high solubility (Hong and Pintauro, 1996ab). In most cases, the larger the value and the more positively charged, the greater is the tendency for the chelate to form, hence, a more efficient extraction (Wilson and Clark, 1994). This fact is of vital importance in soil cleanup because the formation of such complexes helps in mobilizing relatively insoluble metals. Table 1.2 shows the thermodynamic constants for some metal chelates (Stumm and Morgan, 1996).

As shown in the Table, the strength of the chemical bond between a metal and a chelating agent differs with different chelating agents and metal ions. Chelates formed between a natural chelator (e.g., citrate) and a metal ion are often weaker than those formed between a synthetic ligand (e.g., EDTA) and a metal ion. As well, metal chelates of an alkaline earth metals (e.g., Ca and Mg) are usually weaker than those chelates formed from reactions between a ligand and a trace (e.g., Cd, Cu, Pb, etc.) metal.

Table 1.3 shows the logarithmic conditional constants of some metal-EDTA complexes as functions of pH (Ringbom, 1963). The Table shows that the maximum values of many conditional constants differ greatly from the values of the stability constants. For example, the stability constant of Cu-EDTA, $K_{\text{Cu-EDTA}}$ (Table 1.2), is 20.5, but the maximum conditional constant for the metal is 16.6 at pH about 9 or 10 (Table 1.3). According to Ringbom (1963) "very high values of stability constants may be misleading because it is not possible in the majority of cases to prepare a solution in which all the metal is in the form of aquo ions and all the EDTA in the form of completely deprotonated forms." Only the alkaline earth metals can have conditional constants equal or close to their stability constants (Ringbom, 1963).

1.5. Release of Metals from Soils by Chelators

The ability to form extremely stable metal complexes makes chelating agents promising extracting reagents for treatment of metal polluted soils (Elliott and Brown, 1989). Although chelating agents have long been used to assess the bioavailable fraction of soil metals, their use for soil cleanup is a more recent application. In an early study, Kobayashi et al. (1974) treated paddy soils with four kinds of EDTA ($Na_2CaEDTA$ $2H_2O$; Na_2H_2EDTA $2H_2O$; Na_4EDTA $4H_2O$; H_4EDTA) and found that treatment with EDTA 4H was the most effective method for decreasing Cd content in the soil.

Elliott and Brown (1989) studied the effects of chelating agents on Pb solubilization of soil containing about 21% Pb. EDTA was reported to be more effective in removing Pb than the same amount of NTA. Because the EDTA forms a stronger water soluble complex with Pb ($PbEDTA^{2-}$, 19.8) over PbNTA complex ($PbNTA^{-}$,12.6) the result is not surprising. They also found that at higher EDTA concentrations Pb recovery was enhanced but an excess of NTA reduced Pb removal from the soil for pH values less than 8.5. The differences can be attributed to the adsorption properties of the resulting complexes. For the $PbEDTA^{2-}$ complex all six coordination sites of the Pb ion are involved in the complexation with EDTA leaving no coordination sites for bridging to the solid surfaces. In contrast, the PbNTA complex possesses two free metal coordination sites available for the formation of a ternary complex with solid surfaces of soils. As a result, the $PbEDTA^{2-}$ complexes tend to stay in solution whereas the $PbNTA^{-}$ complexes can be readsorbed onto the soil surfaces.

More recently, Brown and Elliott (1992) investigated the use of electrolytes to enhance Pb extraction by EDTA from soil and concluded that addition of 0.5 M perchlorate salts of monovalent cations (Na, Li, and NH_4) increased the total Pb recovery by 10%.

Samanidou and Fytianos (1990) extracted Cd, Cu, Cr, Mn, and Pb from river sediments using EDTA, NTA, and other chelators. Copper showed the greatest tendency for remobilization from the sediments and, of all the chelating agents examined, EDTA and NTA demonstrated the greatest ability to mobilize the metals. An increase in mobilization was noticed with the increase of agent concentration.

Yu and Klarup (1994) investigated the effects of pH and EDTA concentration on the mobilization of metals under equilibrium conditions. EDTA enhanced the rate of metal extraction from sediment particles. They concluded that the enhancement of the rate of extraction by EDTA is indirect, mainly caused by the drop in pH upon addition of EDTA. Complete removal of metal contaminants from the sediment was found to be a very difficult and slow process.

Abumaizar and Khan (1996) explored the use of low concentration solutions of sodium metabisulfite ($Na_2S_2O_5$, a reducing agent) and EDTA in removing Pb and Zn from contaminated soils. Sodium EDTA was superior to the $Na_2S_2O_5$ in removing Pb and Zn from silty clay soil and millpond sludge.

1.6. Resin Retention of Metal-Chelate Complexes

Synthetic ion exchange resins have previously been reported to be effective filters in removing metal contaminants from municipal wastes and industrial effluents (Sengupta et al., 1991; Grant et al., 1987; Anonymous, 1986). They have been used successfully in industrial waste cleaning, particularly with trace metal (Holl and Horst, 1987), including recovery of metals from organic solvents and hydrometallurgical liquid wastes (Diaz and Mijangos, 1987). They also removed Cu successfully from organic complexing agents such as carboxylic acid, tartaric acid, and alkanolamine type compounds (Spearot and

Peck, 1984). However, according to Spearot and Peck (1984), no resin materials were found that could successfully extract metals from EDTA-metal complexes. The main reason is that there are no resins that can bind metals more strongly than EDTA and attempts to remove metals with resins (using cation or chelating resins) are therefore often unsuccessful.

After an intensive search of the literature, we found no evidence that any research has been carried out using anion exchange resin to remove metals from the metal-EDTA or metal-chelate complexes in soil remediation. The fact is surprising to us as many researchers have been using the chelators to clean up trace metals from contaminated soils for at least the last two decades. Because the metal-chelate complex is anionic in nature attempts might be made to utilize the anion exchange resin to capture the metal-EDTA complexes as part of a soil remediation process.

Table 1.1. Solubility product constants of metal carbonates, oxides, and sulfides (McBride, 1994; De Boodt, 1991), expressed as *-log* of the solubility product.

Carbonates: $K_{so} = [M^{2+}][CO_3^{2-}]$

	Hg^{2+}	Pb^{2+}	Cd^{2+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}
$-\log K_{so}$	16.0	13.1	11.7	10.7	10.4	10.2	10.0	9.9	8.2

Oxides and hydroxides: $K_{so} = [M^{n+}][OH^-]^2$

	Hg^{2+}	Pb^{2+}	Cd^{2+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}
$-\log K_{so}$	25.4	15.3	14.4	15.2	12.8	16.9	14.9	20.3	14.0

Sulfides: $K_{so} = [M^{2+}][S^{2-}]$

	Hg^{2+}	Pb^{2+}	Cd^{2+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	Co^{2+}	Cu^{2+}	Ni^{2+}
$-\log K_{so}$	52.1	27.5	27.0	18.1	13.5	24.7	21.3	36.1	21.0

Table 1.2. The stability constants* for metal-ligand complexes (Stumm and Morgan, 1996)

Complexes	Cd	Cu	Pb	Zn	Fe(II)	Fe(III)	Mn	Ca	Mg
M-EDTA	18.2	20.5	19.8	18.3	16.1	27.7	15.6	12.4	10.6
M-HEDTA	21.5	23.9	23.0	21.7	19.3	29.2	19.1	16.0	15.1
M-NTA	11.1	14.2	12.6	12.0	9.6	17.9	8.7	7.6	6.5
M-$(NTA)_2$	15.1	18.1	-	14.9	13.6	26.3	11.6	-	-
M-CDTA	21.7	23.7	22.1	21.1	20.8	32.6	19.2	15.0	12.8
M-HCDTA	25.1	27.3	25.3	24.4	23.9	-	22.4	-	-
M-IDA	6.6	11.5	8.3	8.2	6.7	12.5	-	3.5	3.8
M-$(IDA)_2$	11.1	17.6	-	13.5	11.0	-	-	-	-
M-Acetate	1.9	2.2	2.7	1.6	1.4	4.0	1.4	1.2	1.3
M-$(Acetate)_2$	3.2	3.6	4.1	1.8	-	7.6	-	-	-
M-Citrate	5.0	7.2	5.4	6.1	5.7	13.5	5.5	4.7	4.7
M-HCitrate	7.2	10.7	8.1	6.8	9.9	-	9.4	9.5	9.2
M-Glutamate	4.8	8.8	-	5.8	4.6	13.8	-	2.1	2.8
M-$(Glutamate)_2$	-	15.0	-	9.5	-	-	-	-	-
M-Glycolate	1.9	2.9	2.5	2.4	1.9	3.7	1.6	1.6	1.3
M-$(Glycolate)_2$	2.7	4.7	3.7	3.6	-	-	-	-	-
M-Malonate	3.2	5.7	4.0	3.8	-	9.3	3.3	2.4	2.9
M-HMalonate	6.9	8.3	-	7.1	-	-	-	6.6	7.1
M-$(Malonate)_2$	4.0	8.2	4.5	5.4	-	-	-	-	-

* Constants are given as logarithms of the overall formation constant for the complexes, at zero ionic strength and 25°C.

Table 1.3. The conditional constants* for metal-EDTA complexes (Ringbom, 1963).

Cations	pH													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Cd^{2+}	1.0	3.8	6.0	7.9	9.9	11.7	13.1	14.2	15.0	15.5	14.4	12.0	8.4	4.5
Cu^{2+}	3.4	6.1	8.3	10.2	12.2	14.0	15.4	16.3	16.6	16.6	16.1	15.7	15.6	15.6
Pb^{2+}	2.4	5.2	7.4	9.4	11.4	13.2	14.5	15.2	15.2	14.8	13.9	10.6	7.6	4.6
Zn^{2+}	1.1	3.8	6.0	7.9	9.9	11.7	13.1	14.2	14.9	13.6	11.0	8.0	4.7	1.0
Fe^{2+}	-	1.5	3.7	5.7	7.7	9.5	10.9	12.0	12.8	13.2	12.7	11.8	10.8	9.8
Fe^{3+}	8.2	11.5	13.9	14.7	14.8	14.6	14.1	13.7	13.6	14.0	14.3	14.4	14.4	14.4
Mn^{2+}	-	1.4	3.6	5.5	7.4	9.2	10.6	11.7	12.6	13.4	13.4	12.6	11.6	10.6
Ca^{2+}	-	-	-	2.2	4.1	5.9	7.3	8.4	9.3	10.2	10.6	10.7	10.4	9.7
Mg^{2+}	-	-	-	-	2.1	3.9	5.3	6.4	7.3	8.2	8.5	8.2	7.4	-

* Constants are given as logarithms of the overal formation constant, β ,for the complexes, at 0.1 ionic strength and 20°C.

CHAPTER 2

REMOVAL OF TRACE METALS FROM CONTAMINATED SOILS USING EDTA INCORPORATING RESIN TRAPPING TECHNIQUES

2.1. Abstract

A series of experiments was conducted using two urban soils from Montreal contaminated with high levels of trace metals. The experiments were aimed at removing and recuperating trace metals from the contaminated soils using EDTA and HCl. Acid washing with 1.0 mM HCl was found to be ineffective in removing trace metals from the soils. In contrast, the extraction with ethylene diamine tetraacetic acid (EDTA) is a promising approach; at a low concentration it removed large amounts of metals. In one soil we were able to decrease Cd concentration from 6.2 to 1.4 mg kg^{-1}; the corresponding results for Cu were 700 to 330 mg kg^{-1}, Pb 800 to 410 mg kg^{-1}, and Zn 2600 to 431 mg kg^{-1} after 12 times 24 h extraction with 2.74 mM EDTA. These represent decreases of 76% for Cd, 53% for Cu, 49% for Pb, and 84% for Zn. In a second, less contaminated soil, the Cu concentration was reduced from 130 to 85 mg kg^{-1} after 3 times 24 h extractions with 2.74 mM EDTA. We have also developed a procedure to remove metal-EDTA complexes from the leachates using an anion exchange resin (AER). With this technique we were able to trap up to 99% of the Cd, Cu, and Zn, and 93% of the Pb in the soil leachates.

2.2. Introduction

The rapid development of industry and the use of chemical substances in many industrial activities has caused a steady increase of trace-metal pollution in soils (Nriagu and Pacyna, 1988). Because soils which are contaminated with trace metals can pose a serious health threat to living organisms (humans included), reliable remediation techniques are required for site clean-up (Abumaizar and Khan, 1996). This has led to research to improve the available techniques for metal removal from contaminated soils.

At present, a variety of approaches have been suggested for remediating contaminated soils (Martin and Allen, 1996). However, no methods are available that give satisfactory results in dealing with the problem (Ho et al., 1995). The main constraints have been the technical difficulties in removing the contaminants from the soils and in collecting them once they are in the soil solution.

In our view, the washing-based techniques may be a practical approach to soil remediation, provided that the solubilization of metals can be dramatically increased and the flow of the mobilized metal contaminants in the drainage water (the leachates) can be adequately controlled. Since trace metals are sparingly soluble and occur predominantly in a sorbed state (Dowdy and Volk, 1983), washing the soils with water alone would be expected to remove too low an amount of metal to be used to clean up contaminated sites. To increase metal solubility and raise the concentration of cations in the leachates, chemical agents have to be added to the washing water (Davis and Singh, 1995). Ion exchange resins can then be used as ion sinks for the metal leached from the soils (Skogley and Dobermann, 1996).

The objectives of this study were: 1) to develop a technique to remove Cd, Cu, Pb, and Zn from contaminated soils by means of washing the soils with HCl and EDTA solutions and 2) to investigate exchange resins as a means of recovering metals from the resulting leachates.

2.3. Materials and Methods

2.3.1. Soils and resin materials

Two urban soils were collected from industrial sites on the Island of Montreal. The bulk soil samples from the surface horizons were air dried, and sieved through a 2 mm screen. Some characteristics of these soils are presented in Table 2.1. The total metal content was determined by flame atomic absorption spectrometry (AAS) following acid digestion (Cook, 1998), the carbonate content by a titrimetric method (Bundy and Bremner, 1972), pH with a 1:2 soil to water ratio (Hendershot et al., 1993), the organic carbon content by titrimetric dichromate wet oxidation (Nelson and Sommers, 1982), and cation exchange capacity (CEC) by unbuffered 0.1 M $BaCl_2$ (Hendershot and Duquette, 1986).

The resin exchangers used for the experiments were the synthetic chelating resin Chelex-100 and the anion exchange resin (AER) AG 3-x4 supplied by Bio-Rad Laboratories. Descriptions of the two resin exchangers are provided in Table 2.2.

2.3.2. Laboratory techniques for metal extractions

2.3.2.1. Preliminary experiment

Extraction of metals from soils was performed using hydrochloric acid (HCl) and EDTA solutions. The procedures involved the treatment of 6 g soil (<2.0 mm) with a 30 mL volume of the extracting solutions, giving a soil:solution ratio of 1:5. The mixtures of the soil and solution were placed in 50 mL nalgene centrifuge tubes and shaken using a reciprocating shaker at about 120 strokes per minute (s.p.m.) for 5 h. The soil suspensions were centrifuged at 500*g* for 30 min and the supernatant solutions were then passed through Whatman 42 filter paper into 30 mL vials for AAS determination of metal concentration.

2.3.2.2. Metal extraction experiment

Each soil was extracted for Cd, Cu, Pb, and Zn using EDTA extracting solutions at three different concentrations (0.68 mM, 1.37 mM, 2.74 mM). These extracting solutions had corresponding pH values of 3.08, 2.86, and 2.64. The extraction procedures were as follows. A mixture of 6 g of soil plus 30 mL of the extractant, after shaking by hand for about 30 s to disperse the soil particles, was shaken continually for 24 h; the tube was centrifuged and the supernatant was then filtered and saved for analysis by AAS. The procedure was repeated for 12 subsequent extractions on the same soil subsample. The procedures for centrifugation, filtration, and metal determination were all similar to those described above. The total of each metal removed from the soils, for each extraction period, was measured; the total metal removed from soils after 12 extractions was calculated as the sum of the metal in the 12 filtrates.

2.3.3. Laboratory procedures for trapping metals extracted

2.3.3.1. Preparation of soil solution

Soil solutions or EDTA soil-extracts were obtained as described above except that for larger volumes of soil, 100 mL or 250 mL tubes were used. The US1 soil sample was chosen because it contained higher levels of metal contaminants. The EDTA soil-extracts were analyzed and the results are presented in Table 2.3. These solutions were then used for experiments involving the resin exchangers.

2.3.3.2. Resin pretreatments

To convert the Chelex to H-form, a volume of the chelating resin saturated with Na (the original form) was rinsed with 4 volumes of 1.0 M HCl solution plus 5 volumes of deionized water. The AER was used in its original free-base form.

2.3.3.3. Trapping procedures

The metal-EDTA trapping procedures studied is still in its preliminary stage. Numerous experiments were conducted which would have taken considerable time and labor if we used column methods. For this reason, a batch technique was chosen for this experiment because it is simple, less time-consuming, reproducible, and less tedious (Allen et al., 1995). In our experiments, the Chelex and AER were tested for their capacity to extract Cd, Cu, Pb, and Zn from the EDTA soil-extracts. Mixtures with different ratios of the resins to the EDTA soil-extract (1:5 to 1:400) were shaken continuously for 2 h using a reciprocating shaker (120 s.p.m). Following the extraction, the solutions were passed through Whatman 42 filter paper and the filtrate retained for elemental analysis. The amounts of the metals retained by the resins was calculated from the differences in metal content of the solution before and after contact with the resins.

The data were tested statistically to determine the levels of significance using Mac StatView (Anonymous, 1988); for comparison purposes data were tested by the least significance differences (LSD) test.

2.4. Results and Discussion

Table 2.1 shows the metal contents of the two samples used in these experiments. Comparing the soils, it is obvious that US1 is more contaminated than US2. The Cd, Cu, Pb, and Zn concentrations in US1 are in excess of maximum permissible concentrations for a residential area (5.0 mg of Cd; 100 mg of Cu; 500 mg of Pb; and 500 mg Zn kg^{-1}) according to The Interim Canadian Environmental Quality Criteria for Contaminated Sites, and even exceeds the limits for a commercial or industrial use (500 mg Cu kg^{-1} and 1500 mg Zn kg^{-1}) (CCME, 1991). For US2, only the total Cu concentration is slightly above the limit for a residential area.

2.4.1. Washing solution and processes

The effectiveness of washing is closely related to the ability of the extracting solution to dissolve the metal contaminants in soils. However, the strong bonds between soil and metals make the cleaning process difficult (Gombert, 1994). Therefore, only extractants capable of dissolving large quantities of metals would be suitable for cleaning purposes. The realization that the goal of soil remediation is to remove the metal and preserve the natural soil properties, limits the choice of extractants that can be used in the cleaning process.

EDTA was chosen because it forms a strong bond with metals (Li and Shuman, 1996; Brown and Elliot, 1992), as reflected by their high equilibrium formation constants, log k (e.g. 18.3 for Zn, 20.5 Cu, 18.2 Cd, 19.8 Pb) (Stumm and Morgan, 1996; Hong and Pintauro, 1996a; Norvell, 1991), and is less destructive to soil properties, compared to those of acid washing (Yu and Klarup, 1994). According to Beckett (1989), EDTA, when it is placed in direct contact with the soil: (1) could complex any metals in the soil solution (though with a different degree of selectivity for different metals), (2) could desorb and complex loosely held metal ions and some more tightly held forms, and (3) could dissolve some minerals containing trace metals and complex the freed metals.

In this study, the EDTA washing solution was not buffered and its pH was altered by the natural acid-neutralizing capacity of the soil. Data from extract analyses showed that pH of the 2.74 mM EDTA solution increased significantly from 2.6 to 7.4 after being in contact with soil for 24 h. The 12 subsequent extracts obtained from US1 using the 2.74 mM EDTA solution gave pH values ranging between 7.42 at the beginning of the extraction and 7.85 at the 12th subsequent extraction. With US2, the pHs were between 7.55 and 8.02.

Upon introduction of the EDTA solution into the soil, metals were desorbed into the soil solution as a result of direct EDTA attack on soil particles. This EDTA attack results in a rapid increase of the metal concentration in the soil solution. Once the soil solution is removed and new EDTA solution is added, more metals can be released into the soil solution, and this likely includes portions of metals from more tightly held forms and from metal-containing solid phases that can be released into soil solution only by dissolution of the solid particles. Finally, a portion of metals would remain in solid particles that cannot be removed by EDTA at the tested concentrations.

2.4.2. Metal extraction

2.4.2.1. Preliminary experiment

Our initial studies showed that acid washing with 1.0 mM HCl solution did not remove significant amounts of trace metals (Table 2.4). The inefficiency of HCl may be due to the high buffering capacity of $CaCO_3$ in the soils (Table 2.1). Most of the HCl would be used to solubilize the carbonates and the pH of the solution would remain too high to increase trace metal solubility. The use of more concentrated acid washing solutions may increase the amount of metals extracted, but a dramatic increase would be unlikely before the carbonates dissolved. Also, concentrated acid washing is undesirable because of negative impacts on the properties of the soil.

In contrast, the extraction with 2.74 mM EDTA solution (having approximately the same amount of acidity as the 1.0 mM HCl solution) is a promising approach; it removes a large amount of metals from the contaminated soils. For this reason, subsequent experiments focus on the use of EDTA as an extractor of trace metals from soils.

2.4.2.2. Metal extraction experiment

Of the three EDTA extractants (0.68 mM, 1.37 mM, 2.74 mM EDTA) tested for Cd, Cu, Pb, and Zn, the 2.74 mM extract removed the most metal (Table 2.5). After 12 times 24 h extraction, about 75.9%, 52.8%, 49.0%, and 83.7% of the total Cd, Cu, Pb, and Zn in US1 were removed by this extractant (Figure 2.1). In US2, the amounts of Cd, Cu, Pb, and Zn extracted by the same molarity EDTA represent 60%, 34.9%, 72.6%, and 25.6% of the total contents, respectively. After the 12 times 24 h extraction with the 2.74 mM EDTA, the Cd (6.2), Cu (700), Pb (800), and Zn (2,650 mg Zn kg^{-1}) content of US1 decreased to 1.42, 331, 408, and 431 mg kg^{-1}, respectively. These new concentrations are all below the maximum concentrations permitted for commercial or industrial use. For US2, the copper concentration (130) has been reduced to 84.7 mg Cu kg^{-1}. This new level is below the 100 mg Cu kg^{-1} limit for a residential area. The concentrations of Cd (1.1), Pb (268), and Zn (360) were reduced to 0.49, 73.3, and 268 mg kg^{-1}, respectively. In this experiment, the lowest percentages of metals removed were observed in the lowest concentration of EDTA (0.68 mM).

The removal of metals in the soils by EDTA is ligand enhanced. Total removal is greater with higher concentration of EDTA. The result agrees with previous investigations found in the literature (Samanidou and Fytianos, 1990; Elliot and Brown, 1989). Since rate of removal depends on amounts of EDTA used and not the contact time between EDTA and the soils we can conclude that the dissolution of trace metals was not rate limited.

As is shown in Figure 2.1, continual removal of metals during the 12 times 24 h extractions is noted for all metals tested. With US2, the initial metal-removal rate is fairly rapid and the rate of removal diminishes abruptly. For instance, about 58% of Cu and Zn of the metals displaced during 12 times 24 h extraction (representing about 30% of the total) was removed in just two extractions. Since US2 is less contaminated, the results may be explained by the fact that the metals removed were largely those held in easily soluble complexes which comprised only a small portion of the total. Most of the metals presumably were held tightly in the soil.

For the US1 soil, in which the metal contamination is very high (e.g., 2,650 mg Zn kg^{-1}), the removal of metals is initially rapid and the rate of removal decreases gradually. This implies that large amounts of metals such as those held in the carbonate, oxide, and sulfide minerals, as well as organic matter are available for removal by EDTA

(Beckett, 1989).

2.4.3. Metal trapping techniques

Synthetic ion exchange resins have previously been reported to be an effective filter in removing metal contaminants from municipal wastes and industrial effluents (Anonymous, 1986). They removed Cu successfully from organic complexing agents such as quadrol, carboxylic, tartaric acid, and alkanolamine type compounds (Spearot and Peck, 1984). In a literature review by Spearot and Peck (1984), no resin materials were found to successfully extract metals from EDTA-metal complexes. Chelex-100 was not discussed in this review and may be the type of adsorbent that would be capable of removing metals from EDTA-metal complexes. This resin is specifically designed to bind with transition metals such as Cd, Co, Cr, Cu, Ni, Pb, and Zn. It has a high affinity for polyvalent metals and is effective over a wide pH range (2-14). A review of current literature shows that Chelex-100 has been used successfully in industrial waste cleaning, particularly with trace metals (Diaz and Mijangos, 1987), including recovery from organic solvents and hydrometallurgical liquid wastes.

Despite the positive results found in previous studies, our results with Chelex-100 were not satisfactory. The resin removed some metals from the EDTA soil-extracts, but the percentage of metal removed is not very high. As is shown in Table 2.6, on average, only about 55% of the metals were removed from the EDTA soil-extract with a resin to extract solution ratio of 1:5. When less resin was used, relative to the amount of EDTA soil-extract, (e.g., 1:20), the ability of the resin to remove the metals was dramatically reduced. For example when the ratio of resin to EDTA soil-extract is decreased from 1:5 to 1:20, only about 32% of the total Zn, 22% of the Cu, 16% of the Cd, and 21% of the Pb in the EDTA soil-extract was removed. The apparent ineffectiveness of metal extraction by Chelex-100 implies that the stability constant for the formation of metal-

EDTA complexes is stronger than for the metal-Chelex complexes.

We further investigated the ability of Chelex-100 in removing metals by lowering the pH of the EDTA soil-extract from pH 8.5 down to 4.0. We expected that at high pH most metal would be in the form of a metal-EDTA complex, a form that is not easily available to Chelex; by lowering the pH we hoped to break the metal-chelate bond and increase the amount of free metal cations, a form that is more available to the Chelex resin. However, there were no statistically significant differences between the amount of metal adsorbed at the two pH values. Although pH often has a strong influence in the mobilization of metals (Xue et al., 1995), it seems that the relative binding strength of EDTA and Chelex-100 is more important than the effect of pH in this particular experiment.

The data in Table 2.7 show that when the extraction conditions were kept similar, less metals were extracted by Chelex from solution obtained with 2.74 mM EDTA, than with 1.37 mM EDTA, when in fact, higher metal concentrations were available in the first EDTA soil-extract. This suggests that at higher EDTA concentration more metal is held by the ligand (Beveridge et al., 1989). In conclusion, although removal of metals was achieved with the Chelex, the low efficiency limits its use for remediation purposes.

The same procedures were used to test the ability of AER to extract the metal cations from the EDTA soil-extract. We hypothesized that most of the metal in the EDTA soil-extract would occur in the form of a metal-EDTA complex, which is anionic in nature. Introducing a positively charged surface such as an AER into the EDTA soil-extract was expected to attract the metal-EDTA complexes to form a resin-chelate-metal complex. It can be seen that AER is a strong sink for Cd, Cu, Pb, and Zn from EDTA soil-extracts (Table 2.6).

The results of the experiments with the AER in extracting Cd, Cu, Pb, and Zn cations from the EDTA soil-extract were very promising. In comparison to the Chelex-

100 (Table 2.6), much higher concentrations of metals were removed by the AER from the EDTA soil-extracts. For instance, at resin to EDTA soil-extract ratio of 1:20, 94% of total Cd, 90% of Cu, 91% of Pb, and 96% of Zn were removed by the AER whereas only 28% of Cd, 34% of Cu, 27% of Pb, and 32% of Zn were removed by Chelex-100. Even at a ratio of 1:100, the percentages of metal removed by the AER still exceeded the amounts removed by Chelex-100 at a ratio of 1:20. For copper, the results are very encouraging, the AER removed 79% of the total Cu at 1:200 ratio and 45% at 1:400.

An interesting result was obtained when the AER was examined for its ability to remove metals in the presence of different concentrations of EDTA. In contrast to the Chelex-100, the AER works best in the presence of EDTA (Table 2.7); it removed more metals at higher EDTA concentrations.

The time of extraction or contact between the AER and the soil-extract could be important in determining the effectiveness of metal removals. An experiment using 1:20 resin to EDTA soil-extract ratio was conducted for different times. The results are shown in Table 2.8. In general, there is statistically no significant differences among 2 h, 4 h, and 24 h extraction times. This means that the reaction between the AER resin with the metal-EDTA complexes is rapid.

2.5. Conclusions

Acid and chelate-wash were investigated as a means of removing trace metals from two urban soils contaminated by Cd, Cu, Pb, and Zn. Acid washing with HCl (1.0 mM) was found to be ineffective in removing trace metals from the soils. Higher concentrations of HCl may improve the metal removal, but would result in adverse effects to the soil. EDTA is more effective for washing the metals from the soils. A large portion of metals can be removed with EDTA at low concentrations (0.68 mM, 1.37 mM, 2.74 mM). In general, the higher the concentration of chelating agent used, the more metals are extracted.

We have also developed a procedure to remove metal-EDTA complexes from the leachates using an anion exchange resin. This procedures is simple and has the potential for in-situ or ex-situ use in the field once the separation and collection of the metals and EDTA from their complexes become possible.

Table 2.1. Selected characteristics and total metal content of the soils used in the experiments (0-20 cm top layer).

	Total Metals														
Soils	Cd	Cu	Pb	Zn	Mn	Fe	Ca	Mg	Sand	Silt	Clay	$CaCO_3$	Org.C	pH	CEC cmol (+) kg^{-1}
	mg kg^{-1}					%			%						
US1	6.3	700	800	2650	517	4.3	18	0.88	69	24	7	16.2	2.84	8.03	12.8
US2	1.1	130	269	360	827	6.1	22	2.1	53	39	8	23.7	3.11	8.49	14.7

Table 2.2. Properties of the synthetic ion exchangers used in the study.

	Chelex-100	AER AG 3-x4
Type	weakly acidic cation chelating resin	weakly basic anion exchange resin
Resin matrix	polystyrene	polystyrene
Functional group	$R\text{-}CH_2N(CH_2COO\text{-})_2$	$R\text{-}CH_2N^+H(CH_3)_2$
Density (kg L^{-1})	0.65	0.70
Exchange capacity (meq g^{-1} dry resin)	2.0	2.8
Moisture content (%)	65-75	40-45
Chemical form	Na^+	OH^-
Effective pH range	4-14	<7.0
Stability pH range	0-14	0-14
Wet mesh range (mm)	0.30-0.85	0.43-1.18

Table 2.3. Trace metal concentrations in different molarities of EDTA solutions after 24 h extraction.

Molarity-mM	Metal Concentration (mg L^{-1}) -- Average Value			
	Cd	Cu	Pb	Zn
0.68	0.15 a*	5.35 a*	2.20 a*	40.0 a*
1.37	0.25 b	11.5 b	5.70 b	80.0 b
2.74	0.34 c	20.5 c	18.6 c	128 c

* numbers followed by the same letter for the same element are not significantly different at p = 0.05 level.

Table 2.4. Amount (mg kg^{-1}) of trace metals removed from contaminated soils by HCl and EDTA solutions after 5 h extraction.

Soil	Molarity-mM	Metals -- Average Value			
		Cd	Cu	Pb	Zn
HCl extractant					
US1	1.0	0.055	0.30	0.20	4.90
US2	1.0	0.050	0.15	0.10	0.20
EDTA-chelator					
US1	2.74	0.525	8.03	3.88	72.5
US2	2.74	0.250	2.85	5.90	9.75

Table 2.5. Cumulative amount (mg kg^{-1}) of trace metals removed from soils after the 12 times 24 h extraction with different molarities of EDTA.

	0.68 mM				1.37 mM				2.74 mM			
	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
US1*	3.28 a	175 a	197 a	1050 a	4.15 b	259 b	281 b	1580 b	4.88 c	369 c	392 c	2220 c
US2*	0.40 a	32.8 a	78.0 a	65.8 a	0.56 b	36.7 b	141 b	72.1 b	0.66 c	45.3 c	195 c	92.1 c

* numbers followed by the same letter for the same element for each soil are not significantly different at $p = 0.05$ level.

Table 2.6. Percentages of trace metals removed by: 1) the Chelex-100 and 2) the AER from the EDTA soil-extract at two pH values (8.5 and 4.0) after 2 h extraction.

Ratio of resin to soil extract	% metals removed*							
	Cd		Cu		Pb		Zn	
	8.5	4.0	8.5	4.0	8.5	4.0	8.5	4.0
1) <u>Chelex-100</u>								
1 : 5	43	46	60	66	53	57	51	53
1 : 10	36	37	47	49	42	45	39	43
1 : 20	28	29	33	35	27	28	32	34
2) <u>AER</u>								
1 : 5	98		91		98		99	
1 : 10	96		90		97		98	
1 : 20	94		90		91		96	
1 : 50	70		89		57		73	
1 : 100	36		86		27		42	
1 : 200			79					
1 : 400			45					

* % from total metals (0.25 mg Cd L^{-1}, 11.5 Cu, 5.70 Pb, and 80.0 Zn) in the EDTA soil-extract (obtained from extraction of 6 g soil with 30 mL of 1.37 mM EDTA for 24 h).

Table 2.7. Amount (μg) of trace metals removed by: 1) Chelex-100 and 2) AER from two different EDTA soil-extracts (1:20 resin to solution ratio; 2 h extraction).

EDTA concentration	Cd		Cu		Pb		Zn	
	T*	TR†	T*	TR†	T*	TR†	T*	TR†
1) Chelex-100								
1.37 mM	5.0	2.2	230	138	114	60	1600	816
2.74 mM	6.8	1.7	410	98	372	63	2560	614
2) AER								
1.37 mM	5.0	4.7	230	207	114	104	1600	1540
2.74 mM	6.8	5.8	410	352	372	286	2560	2250

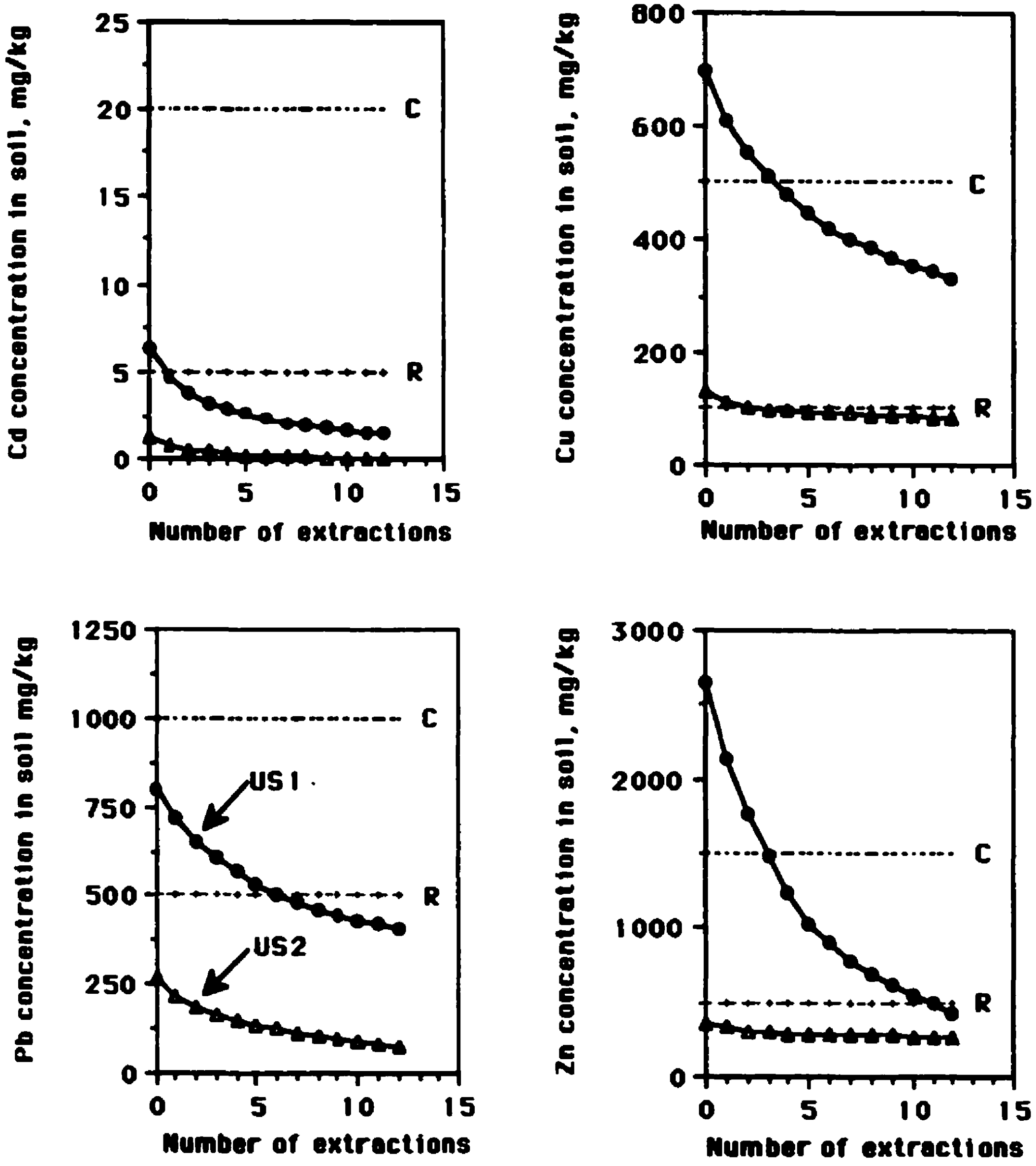
* Total in soil solution; † total removed by the Chelex-100 or AER.

Table 2.8. Percentages of trace metals removed by the AER for different extraction times from various EDTA-soil extracts (1:20 ratio; 120 s.p.m).

Extraction time (h)	Metal removal (%) -- Average Value			
	Cd	Cu	Pb	Zn
		0.68 mM EDTA soil-extract		
2	99.0 ^{NS}	98.7 ^{NS}	93.3 ^{NS}	98.3 ^{NS}
4	99.0	98.9	93.3	98.6
24	99.0	99.3	93.3	98.9
		1.37 mM EDTA soil-extract		
2	96.0 ^{NS}	89.1 ^{NS}	91.7 ^{NS}	95.8 ^{NS}
4	96.0	93.0	93.3	96.4
24	98.0	94.0	93.3	97.1
		2.74 mM EDTA soil-extract		
2	85.3 ^{NS}	91.4 ^{NS}	76.2 ^{NS}	91.4 ^{NS}
4	85.3	93.2	79.0	92.4
24	88.3	94.9	83.5	93.1

NS not significantly different at $p = 0.05$ level between 2, 4, and 24 h experiments.

Figure 2.1. Levels of trace metals during 12 times 24 h extraction with 2.74 mM EDTA as plotted against the maximum limits permitted for commercial/industrial (C) and residential use (R). US1 and US2 denotes urban soil number 1 and number 2, respectively.


Cd concentration in soil, mg/kg
25
20
15
10
5
0
C
R
0
5
10
15
Number of extractions
Cu concentration in soil, mg/kg
800
600
400
200
0
C
R
0
5
10
15
Number of extractions
Pb concentration in soil mg/kg
1250
1000
750
500
250
0
C
US1
R
US2
0
5
10
15
Number of extractions
Zn concentration in soil, mg/kg
3000
2000
1000
0
C
R
0
5
10
15
Number of extractions

CONNECTING PARAGRAPH

The experiments in Chapter 2 showed that the EDTA chelating agent was effective in removing Cd, Cu, Pb, and Zn from the contaminated urban soils. The results also showed that trace metals can be effectively removed by the AER from the resulting ligand soil-extracts. All the previous experiments were conducted in the laboratory using batch methods. The next experiment is to determine if higher amounts of metals can be removed from soil-columns by different forms and techniques of ligand application, leaching speed, and by the addition of an acid/salt solution and more concentrated EDTA; and if the AER in a column is as effective as it was in the batch experiment in removing trace metals from the EDTA soil-extracts.

CHAPTER 3

SOIL DECONTAMINATION: A LABORATORY COLUMN EXTRACTION OF TRACE METALS USING EDTA AND CITRIC ACID

3.1. Abstract

Laboratory studies were conducted to test the feasibility of a washing technique using chelating agents as a means of removing trace metals from contaminated soils. The objectives of the studies were to determine the effects of kind, rate and technique of ligand amendment, leaching speed, and extraction method on extraction rate of Cd, Cu, Pb, and Zn from contaminated soils. Studies were also conducted to determine the feasibility of resins as a means of removing the dissolved metals from the resulting leachates.

The EDTA molecules in dissolved form work better than the powder form at lower ligand concentrations. At higher ligand concentrations, EDTA in the form of solution generally removed less metals from the soils due to the precipitation of EDTA over the period of extraction. More metals were removed when either EDTA or citric acid were mixed thoroughly with the soil sample than when the chelating agent was mixed only with the upper 1.0 cm portion of the soil column through single or multiple applications. On average, 1% to 22% more metals were extracted from the soils using the single homogeneous application method with citric acid or EDTA than using the surface application methods.

The study showed that EDTA demonstrated superior performance compared to citric acid. Up to 27% more Cd, 23% more Cu, 42% more Pb, and 21% more Zn were removed by EDTA as compared to citric acid. The ability of the EDTA to form stronger metal chelates than the citric acid is the main reason for the superiority.

The benefit of adding acid and/or salts to soils in enhancing metal removal was confirmed in this study. The acid/salt solution treatment removed more metals from the

EDTA soil column than the water treatment. Up to 10% more Cd, 9% more Cu, 6% more Pb, and 9% more Zn were extracted by the acid/salt treatment as compared to the water treatment. Varying leaching speed apparently did not affect the extraction rate of metals from the soils.

Our study showed that the resin column retained more metals than the resin when used in the batch procedure. Nearly complete metal recovery (96%-100%) from the EDTA soil-extract was achieved with a column using 1:20 resin:extract ratio. The recovery remained high (87%-100%) for Cd, Cu, and Zn with a lower resin:soil extract ratio (1:50).

3.2. Introduction

Many soils have become contaminated with trace metals due to industrial activity (Sheppard and Thibault, 1992). If these soils are not contained or cleaned, they could pollute nearby groundwater and surface water systems and cause widespread contamination of the local ecosystem with negative effects on human health (Tiller, 1989). Considering the hazard that could result from soil contamination, remediation techniques are needed for site cleanup.

One of the techniques that can remove trace metals from soils is washing with chemical additives (Gombert, 1994). However, our knowledge of this technique is incomplete and we believe that more research into factors such as the kind of ligand amendment, rate and technique of ligand application, leaching speed, and the properties of extracting solution is needed (Merrill et al., 1987). In addition, the hazardous nature of the resulting complex drainage-water requires that the metals and additives in the spent washing fluid have to be separated from the body of the water. Current techniques for such separations are expensive and very limited (Dudzinska and Pawlowski, 1993). Improving the methods, particularly those which emphasize the recovery and recycling of the metals and the additives could provide economic advantages (Yin et al., 1995).

The objectives of this study were to determine, in column experiments, the effects of kind, rate and technique of ligand amendment and leaching speed on extraction rate of Cd, Cu, Pb, and Zn from contaminated urban soils, and to investigate an anion exchange resin (AER) as a mean of recovering the dissolved metals from the leachates.

3.3. Materials and Methods

Four urban soils collected from a Military Base (MB), two Railway Yards (RY1 and RY2), and a Zinc Foundry (ZF), highly contaminated with at least one of these elements (Cd, Cu, Pb, Zn) (Table 3.1), were used for the following experiments.

3.3.1. Metal extraction

All soil was air dried, passed through a 2 mm screen and used for experiments. Soil samples (10 g) were put into columns; care was taken to bring the soil up to slightly above the natural bulk density to ensure sufficient uniformity among different columns and to obtain acceptably reproducible leaching data. The columns were 15 cm in length and 15 mm inside diameter; the depth of the soil was about 4.0 cm with soils having bulk density of 1.4 g cm^{-3}. Filter pulp was placed into the tube below and above the soil column. Extractions were carried out using a Centurion column extractor (an automatic machine with adjustable speed designated for leaching experiment) at either 40 mL per 12 h or 10 mL per 12 h leaching speeds. After each extraction, the soil column was kept in contact with the air for 12 h to maintain the oxidation state of the soil. Cd, Cu, Pb, and Zn extracted from the experiments were determined using atomic adsorption spectrophotometry (AAS). The EDTA used in dissolved form was prepared by stirring the powder in hot water (60°C).

3.3.1.1. The forms of EDTA: solution vs powder

Two different groups of columns containing soil only or soil and EDTA powder (0.06 g, 0.12 g and 0.24 g H_4EDTA) were used. The first group of columns was leached with solution containing EDTA (200 μg mL^{-1}, 400 μg mL^{-1} and 800 μg mL^{-1}) until total amounts of 0.06 g, 0.12 g and 0.24 g EDTA were passed through the column. The second group of columns was leached with water only, using a 40 mL per 12 h leaching speed.

3.3.1.2. Methods of EDTA applications: single surface vs single homogeneous and multiple vs single

Single surface application of ligand was tested using 0.72 g EDTA mixed with the upper part of the soil column (approximately 1.0 cm in depth) and washed with water at 40 mL per 12 h speed, five times. The single homogeneous method was tested by mixing the same amount of the ligand thoroughly with the soil sample with similar washing. For comparison purposes, 0.52 g citric acid (having the same number of binding sites) was tested using the same procedures as an alternative ligand to EDTA.

Sixty mg or 120 mg of EDTA powder (corresponding to 0.6% or 1.2% of the soil weight) was placed into the soil column, mixed thoroughly with the upper 1.0 cm of the soil and leached with water using 40 mL per 12 h leaching speed. The procedure was repeated 12 or 6 times until the total amount of EDTA added equaled 7.2% of the soil weight (0.72 g EDTA). The technique is referred to as the multiple method. Similar procedures were repeated by replacing EDTA with 0.43 g and 0.86 g citric acid until the total amount of citric acid added reached 0.52 g.

3.3.1.3. Properties of the leaching solution

The single homogeneous method experiments using EDTA were repeated by washing the soil column with water containing 1.0 M HCl and 1.0 M KCl.

3.3.1.4. Leaching speed

Mixtures of soil and 0.72 g EDTA leached with water and acid/salt solution, and mixtures of soil and 0.52 g citric acid washed with water were tested with the slower leaching speed (10 mL per 12 h).

3.3.1.5. Extraction methods

Mixtures of soil and EDTA (0.24 g, 0.48 g, and 0.72 g) were leached with 200 mL of water by shaking using a reciprocating shaker at 120 strokes per minute (s.p.m) for 5 h and by leaching the mixtures in column with the same amount of water at 40 mL per 12 h leaching speed to see the relative extraction efficiencies between the two methods.

3.3.2. Metal retention on exchange resins

Columns, similar to the ones used in the soil column experiment were filled with a 0.40 g (1.12 meq), 0.80 g (2.24 meq), or 2.0 g (5.6 meq) dry weight of the anion exchange resin (AER AG 3-x4) sandwiched between filter pulp. Forty (40) mL EDTA soil-extracts (obtained from the batch extraction of 125 g soil-RY1 with 625 mL of 1.37 mM H_4EDTA solution for 24 h at 120 s.p.m.) were passed through the columns at a rate of 40 mL per 12 h using the Centurion column extractor. The same procedures were repeated using Chelex-100 (0.56 g, 1.12 g, and 2.8 g resin dry weight) and combination between Chelex-100 (top half) and AER (bottom half) (0.28 g and 0.20 g, 0.56 g and 0.40, and 1.4 g and 1.0 g resin dry weight for the Chelex and AER, respectively) of identical exchange capacity. The extract used for this experiment were obtained from the batch extraction of 125 g soil-RY1 with 1.25 g H_4EDTA and 625 mL 1.0 M HCl/KCl for 24 h at 120 s.p.m.). Effluents was collected and the concentration of Cd, Cu, Pb, and Zn determined.

For comparison purposes the same amounts of resin and EDTA soil-extract, as were used in the column technique, were put into a 50 mL centrifuge tube and shaken for 5 h using a reciprocating shaker (120 s.p.m.).

The data were tested statistically to determine the levels of significance. For comparison purposes data were tested by the least significance differences (LSD) test using Mac StatView (Anonymous, 1988).

3.4. Results and Discussion

3.4.1. Metal extraction

3.4.1.1. Solution vs powder experiment

The experimental investigation has shown that the physical form of EDTA affects the leaching rate of trace metals from soils. Adding EDTA to soil columns in the form of dissolved molecules (solution method), increased the removal rate of metals significantly from the column compared to applying EDTA as powder and subsequently washing with water (Table 3.2).

EDTA molecules in solution apparently complex metals readily during leaching whereas EDTA in powdered form requires time to dissolve before it can effectively react with metals in the soil. Consequently, areas in the soil column that can be penetrated by the EDTA solution have more chance of releasing the metals into the drainage water than the areas in contact with the powder. EDTA applied as powder may be left intact or undissolved if problems such as compaction or discontinuity of the soil pores prevent the water solution from reaching the powder.

Soils with high concentrations of metal contaminants, like the ones used in this experiment, often contain abundant amounts of non-detrital metals (Davis and Singh, 1995), metals which are released without dissolution of the mineral. This group of metals includes water soluble, exchangeable, specifically adsorbed, and organically bound fractions, and is considered EDTA extractable (Beckett, 1989). Consequently, the forms of EDTA that readily complex the metals will have more chances of successfully removing the metals from the soils.

At the highest EDTA concentration (2.4%), ligand in the form of solution generally removed less metals from the column compared to the powder form, apparently due to the precipitation of EDTA over the period of extraction times. H_4EDTA is nearly insoluble in water (Kobayashi et al., 1974), but its solubility can be enhanced by raising the temperature of the water. Although EDTA may be dissolved in heated water, H_4EDTA will precipitate over time. The time required for the precipitation to occur decreases as the concentration of the EDTA in the water increases. The occurrence of the precipitation in this experiment was indicated by the formation of a thin layer of very fine EDTA particles on the wall of the column (above the soil) and on the surface of the uppermost soil-column. Because of the reprecipitation problem with solution technique, the following experiments which involve the use of much higher EDTA concentrations focus on powder form.

It is apparent from Table 3.2 that as chelating reagent was increased, more metals were extracted from the soils, but extraction efficiency declined. For example, when the ligand concentration increased two folds the total metals extracted was not automatically double. The removal increments decreased markedly at the higher EDTA:soil ratios. At the end of the experiments with the EDTA powder, between 22% and 53% of the total soil Cd, 38% and 44% Cu, 28% and 64% Pb, and 26% and 48% Zn were removed from the soils using the 2.4% rate.

3.4.1.2. Single homogeneous vs single surface ligand application

More metals were removed when either EDTA or citric acid was mixed thoroughly with the soil sample than when the chelating agent was mixed only with the upper 1.0 cm of the soil column (Table 3.3). On average, the single homogeneous method using EDTA removed 6.5% more Cd, 8.0% more Cu, 11.3% more Pb, and 8.3% more Zn than the single surface method. Smaller differences were observed between the two methods when citric acid was used. On average, 2.3% more Cd, 4.0% more Cu, 2.5% more Pb, and 2.8% more Zn were extracted by the ligand with the single homogeneous than with the single surface method.

The primary reason for the lower extraction efficiency of the single surface method compared to the single homogeneous method is due to the varying solubility of the EDTA under different column conditions. The single surface method could remove larger amounts of metals from the soil if all the EDTA applied could be solubilized and reacted with the metals in the soil column. The considerable amount of EDTA added to the soil surface may have saturated the surface portion with the chelate; rinsed off most of the metals in the section; but left some EDTA undissolved. This reduced the total amounts of metals removed from the column. The presence of undissolved EDTA was clearly seen as a grayish-white color in the upper section of the column, which is the mixture of EDTA and heavily leached soil. On the other hand, EDTA added as single homogeneous method is less concentrated and distributes over the entire soil column allowing more EDTA contact with metals. Less concentrated EDTA allows faster solubilization of the chelate, keeps undissolved EDTA to a minimum, and, consequently, increases the metals that can be extracted from the column.

In contrast to EDTA, citric acid is soluble in water. When it was used in the single surface method, it was immediately solubilized and washed out of the column by the first or second leaching. It is possible an appreciable portion of the dissolved citric acid molecules does not come in contact with the metal contaminants in the soils during their downward movement through the column. On the other hand, the single homogeneous method of citric acid allows intimate contact between the ligand and the soil particles throughout the entire soil column. The well distributed position of the chelate between the soil particles would reduce or slow down the solubilization of the chelate allowing relatively longer contact between the chelate and the metal contaminants, and, therefore, increases metal leaching. The slight differences in how the citric acid solubilizes under the two column conditions may have contributed smaller variations in the amounts of total metals extracted by the ligand using the two techniques.

It is obvious that EDTA and citric acid have advantages and disadvantages when they are used for cleaning soils contaminated with trace metals. EDTA removed significantly more Cd, Cu, Pb, and Zn from the soil than did citric acid. The single homogeneous treatment using EDTA removed between 35% and 76% of the total Cd in soils, 60% and 74% of Cu, 72% and 84% of Pb, and 41% and 85% of Zn. In comparison, between 20% and 49% Cd, 37% and 57% of Cu, 32% and 42% of Pb, and 20% and 66% of Zn were removed from the soils by the citric acid (Table 3.3). Similar results were observed with the single surface method. Although much less metals were removed from the soils by this method, the efficiency of the EDTA over the citric acid was maintained throughout the experiment.

The superiority of EDTA over citric acid can be explained as follows. EDTA is a strong complexing agent; it forms very strong metal chelates with most cations particularly the metals in the transitional groups such as Cd, Cu, Fe, Mn, Pb, and Zn (Xue et al., 1995). As has been widely cited elsewhere, EDTA depresses the adsorption of metals to clay hydroxides, clay silicates, and quartz (Elliott and Brown, 1989); releases metals from some amorphous and crystalline oxides and silicates; and inhibits or prevent metals from precipitating with oxides, hydroxides, sulfides, or other ligands (Hong and Pintauro, 1996a; Davis and Singh, 1995). On the other hand, citric acid (like other natural chelating agents such as amino acids, cyanides, gluconic, humic acid, and tartrate) is a weak complexing agent and forms weak metal chelates (Holl, 1993) that are susceptible to hydrolysis; hence, it can reduce the number of metals that can be bound by the chelate. Weaker chelating agents may interact and form ternary complex with metals and clay particles and thereby reduce their ability to enhance contaminant removal (Ye and Lucy, 1995). As suggested by David and Singh (1995), the most efficient metal removal should result from the strongest complexing agent.

All these explanations emphasize the importance of choosing the right chelating agent for the purpose of cleaning soils contaminated by trace metals. Anderson (1993) suggested several important criteria for selecting a chelate suitable for remediation purposes: soluble in water, treatable, recyclable and reusable, low toxicity, safe, and easy handling. One clear advantage of using citric acid over EDTA in soil remediation is that it is safer compared to EDTA.

3.4.1.3. Multiple vs single ligand application

Lower amounts of metals were removed from the columns by the multiple method compared to the single homogeneous method (Table 3.3). Between 29% and 58% of the total soil Cd, 51% and 57% Cu, 52% and 64% Pb, and 26% and 62% Zn were removed by the surface multiple method using 0.6% EDTA increment as compared to between 35% and 76% Cd, 60% and 74% Cu, 72% and 84% Pb, and 41% and 85% Zn extracted with the single homogeneous method. For the EDTA, the problem of intact ligand, which exists in the single surface application (described previously), apparently persists with the multiple method. The greyish-white color of soil EDTA-mixture became more and more pronounced towards the end of the extraction. This phenomenon implied that the amount of undissolved EDTA powder may have increased with every addition of EDTA powder to the column and resulted in an accumulation of EDTA in the uppermost section of the soil column. The depletion of soil salts in the soil section where the EDTA powder is placed and the inability of water alone to solubilize the powder may be the main reasons for the build up of the EDTA.

It is important to note that when the same amount of ligand is added to the soil surface with single or multiple leaching, the fewest number of applications generally resulted in the most efficient metal removal (Table 3.3). For example, after receiving a total of 7.2% EDTA or 5.2% citric acid, the single surface method extracted more metals from the soils than the multiple method with 6 x 1.2% and 12 x 0.6% EDTA or 6 x 0.86% and 12 x 0.43% citric acid. The higher concentration in the single application apparently resulted in a greater extracting efficiency. The results from the multiple application also demonstrated that less metals were removed by the citric acid than by EDTA.

3.4.1.4. Properties of leaching solution: water vs acid/salt

Among the treatments investigated, the single homogeneous method with EDTA, was demonstrated to be the most efficient technique for extracting metals from the soils. Further tests were conducted to maximize the performance of the method by replacing the water with an acid-salt solution (1M HCl/KCl). The addition of acid and/or salts to soils has been reported to enhance the extractability of metals from the soils by the EDTA (Brown and Elliott, 1992). Our studies with acid and salt in this chapter and in chapter 4 and 5 corroborate this observation.

In general, the acid/salt solution treatment removed more metals from the EDTA soil columns than the water treatment (Figure 3.1). Up to 83% of Cd, 80% Cu, 90% Pb and Zn were removed by the acid/salt solution treatment as compared to 76% Cd, 74% Cu, 84% Pb, and 85% Zn removed by the water treatment. Further, the results showed that significantly greater amounts of metals were continuously being released in the subsequent extraction by the acid/salt solution than the water treatment (data not shown), indicating the important effects of the acid/salt solution in solubilizing metal ions from the water insoluble metal pools which will be discussed further in chapter 5.

3.4.1.5. Leaching speed

In this investigation, two different leaching speeds (40 mL per 12 h and 10 mL per 12 h) were compared for their ability to extract metals from columns containing: (i) mixtures of soil and EDTA leached with water and acid/salt solution, and (ii) mixtures of soil and citric acid washed with water. As shown in Table 3.4, no statistically significant differences are observed in the amount of Cd, Cu, Pb, and Zn extracted from the columns by the two different speeds of leaching.

Amounts of Cd, Cu, Pb, and Zn extracted from the soils may be more closely related to the speed of ions released by EDTA, EDTA plus HCl/KCl, or citric acid to the soil solution rather than the speed of leaching. In this regard, the EDTA, the EDTA plus HCl/KCl, or the citric acid is thought to be capable of mobilizing the metal cations from the soil and complexing them in soil solution in a relatively short time which is appreciably more rapid than either of the leaching speed that were evaluated in this experiment.

3.4.1.6. Batch vs column extraction methods

The batch technique is often used in preliminary studies as a suitable method for comparing various tests. It is an easy, rapid, simpler and more reproducible method than the column test (Allen et al., 1995; Grant et al., 1987) and provides a good estimate of the concentration of metals that can desorb from the soil. The column method however is more realistic in simulating the field situation and is often recommended as a mandatory step prior to any actual leaching experiments in the field (Environment Canada, 1986).

The results of the batch and column experiments showed that larger amounts of metals were extracted from the soils by the batch than the column method in almost all treatments (Table 3.5). The agitation method used in the batch experiment may have been too severe causing fragmentation of the solid particles, and leading to dissolution of the exposed metal compounds (Slavek et al., 1990). Such fragmentation would not have occurred in the column because of the relatively gentle flow of the extracting solution.

The agitation may have also caused complete dissolution of EDTA powder in soil suspension allowing widespread contact between the EDTA molecules, metal contaminants, and all soil particle surfaces. Consequently, in the batch experiment more metals would have dissolved and complexed with EDTA. In the columns, a portion of the EDTA powder may have been trapped between the soil particles and/or inhibited from contact with the leaching solution, as described previously, and consequently, less metals were removed.

3.4.2. Metal retention by exchange resin

In a previous batch experiment, the AER AG 3-x4 was found to be effective at extracting metals from the EDTA soil-leachate generated from the soil wash (Chapter 2). As summarized in Table 3.6, the amounts of metals retained in the resin column are more than that predicted by the batch method. Nearly complete metal recovery (98%-100%) from the EDTA soil-extract was achieved with a column using 1:20 resin:extract solution ratio. The recovery remained high (87-100%) for Cd, Cu, and Zn with a lower resin:soil extract ratio (1:50).

It is possible the agitation in batch method was too severe for the resin; it may have caused the break up of the weaker beads and reduced the ability of the beads to retain metals. Further, the agitation may have severed the bond linking the resin and the metals and caused the release of the metals from the resin. In contrast, the gentle moving of the fluid in a column allowed optimum contact and reaction between the metals and the resin functional group, and hence, increased metal retention onto the resin.

A comparison of the effectiveness of the AER, the Chelex-100, and both resins (half AER and half Chelex-100) in removing metals from the EDTA-acid/salt soil-extract demonstrated that the Chelex-100 removed the smallest quantities of Cd, Cu, Pb, and Zn from the metal-EDTA soil-extract, followed by the treatment combination, and the AER (Table 3.7). The findings imply that the metal-EDTA complexes in our experimental conditions are very stable. Even, the Chelex-100, a strong chelating agent for metal cations, is not effective in breaking the bonds between the metals and the EDTA. It is important to note that the low percentages of Cd, Pb, and Zn removed by the AER are not an indication of the poor resin performance, but are a result of metal levels in the leachate far exceeding the retention capacity of AER. The high percentage of Cu removal indicated the preference of the AER for Cu over other metal cations.

It is obvious from the results that the more AER in the EDTA soil-extract, the more metals were removed from the solution. Apparently, the AER is effective in removing the metal-EDTA complexes from the extracts over a wide range of pH (Chapter 2) and salt contents. The finding emphasizes the advantages of using a strong chelating agent like the EDTA as a means of removing metals from contaminated soils and using the positively charged matrices like the AER to trap the resulting negative charged molecules of the metal-ligand complex.

The results with citric acid were not particularly encouraging in this experiment because the poor efficiency of the reagent in removing metals from the soils, as compared to the EDTA results. However, the metal stripping experiment provided a promising result with regard to using the AER to trap the metals from the citric acid soil-extract. Using the citric acid extracts containing 0.11 mg Cd L^{-1}, 28 mg Cu L^{-1}, 22 mg Pb L^{-1}, and 147 mg Zn L^{-1}, removal of 97% Cd, 99% Cu, 93% Pb, and 64% Zn by the AER column were observed with 1:20 resin:solution ratio. When the 1:50 ratio was used, the percentages of the removal dropped to 62% for Cd, 69% for Cu, 37% for Pb, and 35% for Zn. The findings demonstrated that the anion exchange resin was a suitable tool for the removal of metals from the soil extract (Holl, 1993) of different properties .

3.5. Conclusions

A series of column tests were conducted to determine the extraction efficiency of complexing reagents in removing metals from contaminated soils. The use of dissolved reagents as metal extractants from soils was more efficient than the powder form only at lower reagent concentrations. At higher ligand concentrations, the method becomes less effective because of the difficulties in keeping the reagent dissolved. More metals were removed from the soil columns when the ligand was mixed with the whole soil column than when it was just mixed in the surface layer through single or multiple application. On average, 2.3% to 11.3% more metals were extracted from the soils using the single homogeneous method with citric acid and EDTA than using the surface application method.

It is obvious from the study that EDTA was superior to citric acid in removing Cd, Cu, Pb, and Zn from the soils investigated. On average, up to 27% more Cd, 23% more Cu, 42% more Pb, and 21% more Zn were removed by the EDTA. The ability of the EDTA to form stronger metal chelates than the citric acid is the main reason for the superiority. The findings emphasize the importance of choosing the right chelate for the purpose of cleaning soils contaminated by trace metals.

The benefit of added acid and/or salts to enhance the ability of the EDTA to remove metals from soils was confirmed in this study. Up to 83% of Cd, 80% Cu, 90% Pb and Zn were removed by the acid/salt solution treatment as compared to 76% Cd, 74% Cu, 84% Pb, and 85% Zn removed by the water treatment. Attempts to improve the amounts of metal extracted by leaching at a slower speed did not change the results.

The resin technique using the AER column was found to be more efficient than the resin batch, and is an effective method for extracting metals from the various metal-ligand soil-extracts. The finding is significant, confirming the advantages of using a strong chelating agent as a means of removing metals from contaminated soils and using the resin as a means of trapping the metal and the ligand.

Table 3.1. Selected characteristics and total metal content of the soils used in the experiments (0-20 cm top layer).

	Total Metals																	
Soils	Cd	Cu	Pb	Zn	Mn	Fe	Ca	Mg	Texture	Sand	Silt	Clay	$CaCO_3$	Org.C	BS	EC	pH	CEC
	mg kg^{-1}					%				%						µS		cmol(+) kg^{-1}
MB	3.0	60	980	180	655	3.1	9.1	0.78	SL	71	21	8	11	4.2	100	257	8.0	11.4
RY1	6.3	700	800	2650	517	4.3	18	0.88	SL	69	24	7	16	2.8	100	444	8.0	9.9
RY2	5.5	800	2200	400	629	6.5	19	0.92	SL	72	18	10	22	1.7	100	513	8.0	10.1
ZF	182	522	548	14500	5867	3.8	19	2.5	L	35	59	6	23	0.6	100	502	8.0	7.3

Table 3.2. Percentages of trace metals removed by EDTA added in solution or powder form.

Soils	Solution			Powder		
	% EDTA*			% EDTA*		
	0.6	1.2	2.4	0.6	1.2	2.4
			Cadmium			
MB	14 b	19 b	21 a	11 a	16 a	22 a
RY1	25 b	43 b	49 a	22 a	40 a	53 b
RY2	18 b	35 b	39 a	15 a	30 a	42 b
ZF	26 b	40 b	46 a	23 a	37 a	49 b
			Copper			
MB	15 b	33 b	41 a	12 a	29 a	43 b
RY1	23 b	34 b	40 a	19 a	31 a	43 b
RY2	15 b	31 b	35 a	12 a	27 a	38 b
ZF	22 b	37 b	41 a	20 a	34 a	44 b
			Lead			
MB	24 b	53 b	56 a	21 a	48 a	64 b
RY1	14 b	22 b	24 a	10 a	19 a	28 b
RY2	29 b	45 b	49 a	25 a	40 a	52 b
ZF	16 b	27 b	31 a	13 a	24 a	35 b
			Zinc			
MB	13 b	21 b	23 a	10 a	18 a	26 b
RY1	16 b	31 b	37 a	10 a	26 a	41 b
RY2	14 b	26 b	33 a	11 a	23 a	37 b
ZF	26 b	38 b	43 a	19 a	35 a	48 b

* % of the total weight of soil. Different letters indicate significant differences between powder and solution application at $p = 0.05$ level between the same rate of ligand application.

Table 3.3. Amount (mg kg^{-1}) of trace metals remaining in the soils after leaching 10 g soil column with various methods of ligand application.

Soils	Total Metals	EDTA (7.2%)*						Citric Acid (5.2%)*				CCME Standards†	
		HCl/KCl		Homogeneous	Surface	Multiple		Homogeneous	Surface	Multiple		Residential	Commercial
		Homogeneous	Surface			1.2%*	0.6%*			0.86%*	0.43%*		
						Cadmium						5.0	20
MB	3.0	1.44	1.86	1.95	2.04	2.04	2.13	2.40	2.46	2.49	2.52		
RY1	6.3	1.20	1.64	1.70	2.08	2.39	2.65	3.97	4.16	4.28	4.35		
RY2	5.5	1.32	1.76	1.87	2.15	2.31	2.42	3.41	3.47	3.58	3.69		
ZF	182	30.9	60.1	43.7	65.5	69.2	81.9	92.8	98.3	100	106		
						Copper						100	500
MB	60	21.6	26.4	24.0	27.6	28.2	29.4	37.8	39.6	40.1	41.4		
RY1	700	140	224	203	259	294	301	420	448	455	476		
RY2	800	232	296	288	328	336	376	488	504	520	560		
ZF	522	104	177	136	204	230	235	224	261	266	271		
						Lead						500	1000
MB	980	108	186	167	284	333	382	568	598	627	637		
RY1	800	120	200	160	240	280	296	504	520	528	531		
RY2	2200	220	440	352	616	660	792	1496	1540	1562	1606		
ZF	548	137	192	153	214	236	263	367	384	389	406		
						Zinc						500	1500
MB	180	99.0	117	106	121	124	133	144	148	149	153		
RY1	2650	504	663	742	875	1007	1087	1219	1325	1378	1458		
RY2	400	172	212	188	236	240	268	248	252	260	264		
ZF	14500	1450	2320	2175	3335	4640	5510	4930	5510	6380	6525		

* % from the total weight of soil; † the maximum metal concentration limits in soils for residential or commercial use.

Table 3.4. Cumulative percent (%) removal of trace metals from soils displaced by different leaching treatments at two leaching speeds.*

Soils	Cd		Cu		Pb		Zn	
	1[†]	2[#]	1[†]	2[#]	1[†]	2[#]	1[†]	2[#]
7.2% EDTA + 1.0 M HCl/KCl								
MB	42	43	64	66	89	89	45	46
RY1	81	82	80	81	85	87	81	83
RY2	76	78	71	69	90	91	57	57
ZF	83	84	80	82	75	76	90	90
7.2% EDTA + Deionized Water								
MB	35	36	61	62	83	85	41	42
RY1	73	75	71	70	79	79	73	74
RY2	66	66	64	66	84	86	52	52
ZF	76	77	74	76	72	73	81	83
5.2% Citric Acid + Deionized Water								
MB	19	20	37	38	42	44	19	19
RY1	34	35	40	42	37	37	54	56
RY2	37	36	39	39	32	34	38	40
ZF	49	50	57	58	33	34	66	66

* leaching speed not significantly different at $p = 0.05$ level for all data ([†] 40 mL per 12 h and [#] 10 mL per 12 h leaching speed).

Table 3.5. Cumulative percent (%) removal of trace metals from soils displaced by two leaching techniques (Batch vs Column) at various EDTA concentrations.*

Soils	EDTA (%)†	Batch Leaching				Column Leaching#			
		Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
MB	2.4	25	44 NS	69	28	22	43 NS	64	25
	4.8	34	57	79	37	31	54	75	34
	7.2	39	66	86	45	35	60	83	41
RY1	2.4	56	45	35	44	53	42	26	41
	4.8	70	65	66	69	67	58	61	66
	7.2	79	74	84	76	73	71	80	73
RY2	2.4	45	41	57	40	41	38	52	37
	4.8	65	57	74	49	57	54	71	46
	7.2	69	68	85 NS	56	66	64	84 NS	53
ZF	2.4	53	45	40	51	49	42	35	48
	4.8	69	63	64	75	65	60	60	70
	7.2	80	79	73 NS	86 NS	76	74	72 NS	85NS

* leaching methods significantly different at $p = 0.05$ level for all data except those with NS sign. † percent from the total weight of soil and # single homogeneous method.

Table 3.6. Percentages of trace metals removed by the AER from the EDTA soil-extract using: 1) batch and 2) column methods.*

Ratio of resin to soil extract	% metal removed†							
	Cd		Cu		Pb		Zn	
	1	2	1	2	1	2	1	2
1 : 20	94	98	90	100	91	98	96	100
1 : 50	70	87	90	100	57	68	73	95
1 : 100	36	49	89	96	27	36	42	58

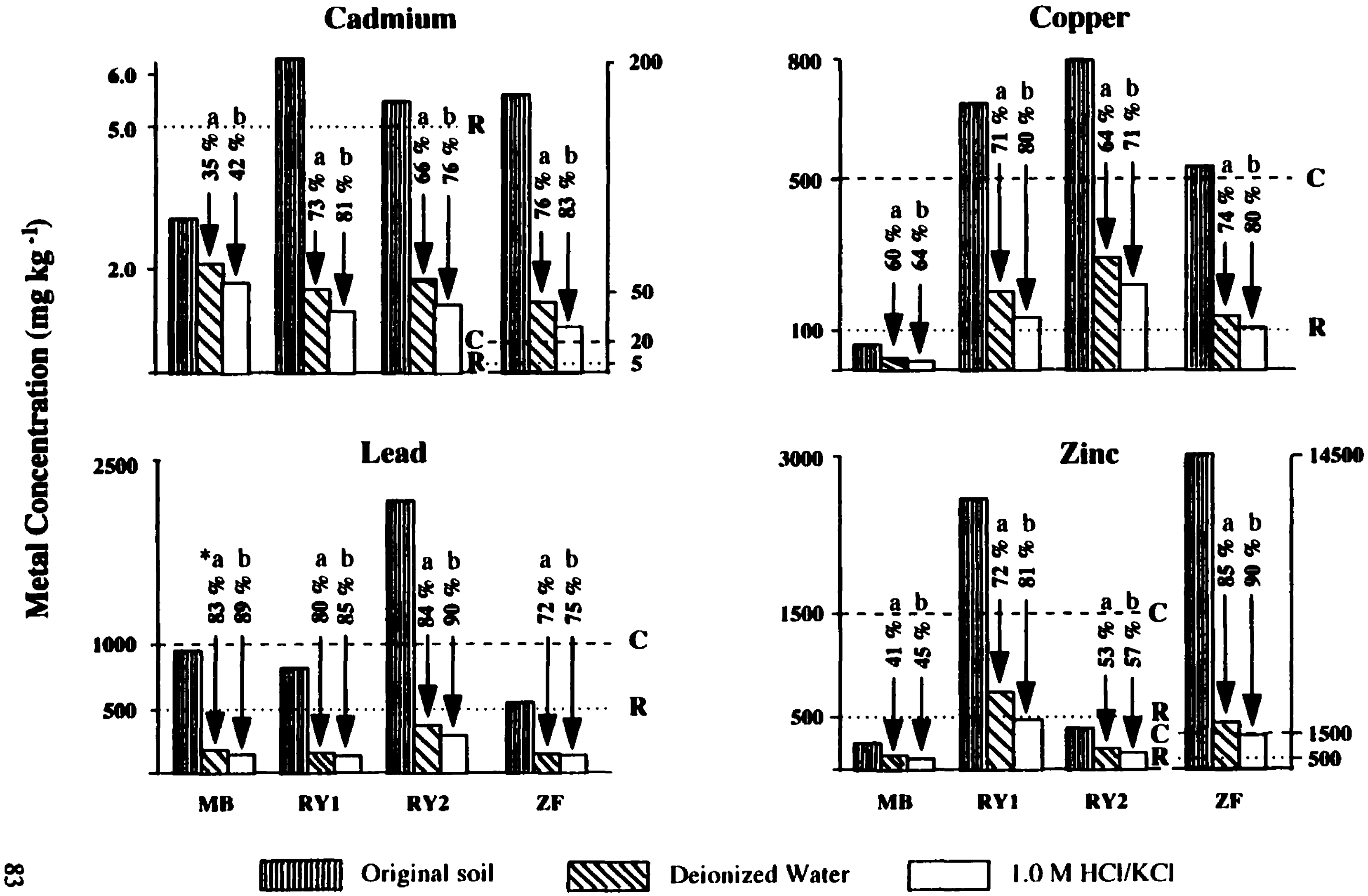
* trapping methods significantly different at $p = 0.05$ level for each element and resin to soil extract ratio. † % from total metal (0.25 mg Cd L^{-1}; 12 mg Cu L^{-1}; 5.7 mg Pb L^{-1}; and 80 mg Zn L^{-1}) in the EDTA soil extract obtained from the extraction of 125 g soil with 625 mL of 1.37 mM EDTA for 24 h at 120 s.p.m.

Table 3.7. Percentages of trace metals removed by: 1) the AER, 2) the Chelex-100, and 3) the combination of the AER and the Chelex-100 from the EDTA soil-extract using column method.

Ratio of resin to soil extract	% metal removed*											
	Cd			Cu			Pb			Zn		
	1	2	3	1	2	3	1	2	3	1	2	3
1 : 20	39 c	15 a	32 b	100 b	36 a	99 b	66 c	23 a	36 b	45 c	8 a	25 b
1 : 50	26 c	11 a	17 b	100 c	33 a	70 b	34 c	19 a	24 b	28 c	5 a	16 b
1 : 100	21 c	6 a	12 b	93 c	30 a	53 b	26 c	9 a	16 b	12 c	3 a	6 b

* % from total metal (0.66 mg Cd L^{-1}; 47 mg Cu L^{-1}; 42 mg Pb L^{-1}; and 240 mg Zn L^{-1}) in the EDTA soil extract obtained from the batch extraction of 125 g soil with 1.25 g EDTA-4H and 625 mL 1.0 M HCl/KCl extracting solution for 24 h. Different letters indicate significantly different at p = 0.05 level between the different resins for each element.

Figure 3.1. Levels of trace metals before and after leaching the EDTA-soil column with deionized water or acid/salt solution. C=commercial and R=residential limits. * different letters indicate significant differences at $p = 0.05$ level between the two treatments.



Cadmium
Copper
Lead
Zinc
Metal Concentration (mg kg⁻¹)
6.0
5.0
2.0
200
50
20
5
800
500
100
2500
1000
500
3000
1500
500
14500
1500
500
R
C
a
b
35 %
42 %
73 %
81 %
66 %
76 %
76 %
83 %
60 %
64 %
71 %
80 %
64 %
71 %
74 %
80 %
*a
83 %
89 %
80 %
85 %
84 %
90 %
72 %
75 %
41 %
45 %
72 %
81 %
53 %
57 %
85 %
90 %
MB
RY1
RY2
ZF
Original soil
Deionized Water
1.0 M HCl/KCl

CONNECTING PARAGRAPH

The experiments in Chapter 3 provided us valuable information concerning the removal of trace metal contaminants from the soil columns using chelating agent. Our concern is if the similar success can be obtained in larger columns using large amounts of soil. Since our final goal was to develop methods that can be applied in the field to clean contaminated soils, such laboratory experiments should precede any attempts of conducting a full-scale experiment in the field. Since washing may impose adverse effects on soils, determining the properties of soils after receiving washing treatment is important. Some factors that need to be addressed are the concentrations and the fractions of metals in the cleaned soils, the distribution of metals in the soil column/profile, and the quality of the soil in general. This discussion is the focus of Chapter 4.

CHAPTER 4

REMOVAL OF TRACE METAL CONTAMINANTS USING EDTA AND ACID/SALT SOLUTION IN A LABORATORY SIMULATED FIELD EXPERIMENT

4.1. Abstract

The ability of EDTA and washwater to mobilize trace metal ions from contaminated soil was evaluated by conducting column tests in the laboratory. Four urban soils highly contaminated with at least one trace metal were mixed with EDTA and subjected to 30-days of leaching with water or the mixture of 1.0 M HCl and 1.0 M KCl solution. The effects of the leaching on the chemical quality of soil and the fraction of the residual metal ions left in the soils were investigated by conducting tests on the soils post treatment.

EDTA is a suitable reagent to enhance the metal removal from the highly contaminated soils. Large amounts of metals were removed by the EDTA from the soils. The additions of the acid/salt solution significantly improved the amounts of metals removed by the EDTA. Approximately 7-23% more Cd, 2-6% more Cu, 2-9% more Pb, and 6-12% more Zn were removed from the EDTA-soil columns using the acid/salt solution treatment compared to the water treatment. After the cleaning, three of the four soils could be reused for commercial and/or residential purpose.

Fractionation studies revealed that most of the trace metals in the original soils were associated with the carbonate and oxide fractions and most of the metals removed from the soils originated from these two fractions. For Cd, the decrease in the carbonate and oxide fractions accounted for up to 88% of the decrease in total metal content following cleaning. For Cu and Zn, the equivalent decreases were up to 87% and 92%. The carbonate fraction accounted for up to 80% of the decrease in Pb content of the soils.

With regard to soil quality, treatment with EDTA and acid/salt solution improved the quality of the contaminated soils. The post treatment soils had lower metal concentrations, lower pH, and higher CEC which could provide a better environment for biota that inhabit the soil environment.

4.2. Introduction

The lack of reliable methods for the removal of trace metal contaminants has prompted the recent development of innovative techniques for remediation of contaminated soil (Abumaizar and Khan, 1996). A strategy frequently used encompasses the mobilization of the contaminants from the soil phase to the liquid phase (extraction technique). Soil washing is an existing technique which has been used commercially for decades to mobilize organic contaminants and has recently been modified to use for remediation of soils contaminated by trace metals (Anderson, 1993).

It is well established that the efficacy of the washing technique in removing trace metals from contaminated soils is determined by the aggressivity of the leaching solution (Environment Canada, 1986). Acidity, complexing ability, reagent concentration, and ionic strength are some of the important properties of leaching solutions which determine aggressivity. Most metallic cations are more soluble in acidic environments (Alloway, 1995) and the use of acidic solutions should enhance the removal of trace-metal ions from the soils. Complexing agents are well known for their ability to react with multivalent metal cations and the use of such ligands in soil remediation can accelerate trace metal removal from contaminated soils (Sundstorm et al., 1996). Since the efficacy of an extracting solution is largely determined by its concentration, the use of reagent at a reasonably high concentration can increase the effectiveness of trace metal removal. In addition, the effectiveness of acids and chelating agents can be enhanced or suppressed by the electrolytic amendment (Brown and Elliott, 1992). Understanding the behavior of the electrolytes could therefore help to optimize capabilities of the extracting solutions to remove trace metals from contaminated soils.

The EDTA is used extensively in the field of trace metal remediation for two major reasons. They react strongly with most metals in soils to form soluble EDTA-metal complexes and they lower the soil acidity thereby activating the metals in the soils. Since the EDTA acids are nearly insoluble in water (Kobayashi et al., 1974), particularly at high concentration, the present studies were carried out by mixing the EDTA powder with the soil samples. The objectives were to determine the effects of the extracting solutions, deionized water and acid/salt solution, on the rate of removal of Cd, Cu, Pb, and Zn ions from the EDTA-soil mixtures and, to investigate the effects of the extracting solutions on the forms and amounts of residual metals and on the chemical qualities of the post treatment soils.

4.3. Materials and Methods

Four urban soils collected from a Military Base (MB), two Railway Yards (RY1 and RY2), and a Zinc Foundry (ZF) which were highly contaminated with trace metals, were air-dried, passed through a 2-mm screen, and analyzed for total metal (Cd, Cu, Pb, Zn, Fe, Mn) content and selected soil characteristics (Table 4.1).

4.3.1. Leaching procedures

Soil washing was performed in packed columns to simulate field leaching or heap-leaching. Each soil sample (2.3 kg) was mixed thoroughly with 115 g EDTA and packed into a tube (50 cm length and 7.5 cm inner diameter) to form an approximately 40 cm thick soil column having a bulk density of 1.4 g cm^{-3}. The application of the high amount of EDTA used (5% of soil weight) was intended to accelerate the remediation process.

Four soils and two extracting solutions (deionized water and a 1.0 M HCl and 1.0

M KCl mixture) were each duplicated to give a total of 16 leaching columns. Filter pulp was placed into the tube above and below the soil. At the beginning of the extraction experiment, the soil sample was remoistened to approximately field capacity, from the bottom of the soil column with a quantity of the treatment solution. Each day 500 mL of washing solution was added to the column surface and extracted using a Centurion column extractor at a constant rate of 500 mL leachate per 12 h. Each extract, used to generate the data, was composed of two days of leachates. After each extraction, the soil-column was kept in contact with the air for 12 h to maintain the oxidation state of the soil.

The soil extract was then centrifuged for 20 minutes to separate the solid particles from the supernatant. Supernatants were stored in plastic vials for subsequent analyses using an Atomic Absorption Spectrometer (AAS) for Cd, Cu, Pb, and Zn determination. The procedure was repeated until 15 L of leachates had been collected (30 days). The total of each metal removed from the soils was calculated as the sum of the metals in the resulting leachates.

4.3.2. Metal fractionation

After completion of the leaching experiment, the soil-column was sampled at 10 cm intervals, air dried, weighed, and analyzed for the fractionation studies to quantify the amounts of residual metals and to identify their forms in the post treatment soils. The fractionation was conducted using non-sequential extraction as follows: (1) water-soluble and exchangeable (0.5 M KNO_3, 16 h) (Sposito et al., 1982), (2) carbonates (1.0 M NaOAc, pH 5.0, 5 h, continuous agitation) (Harrison et al., 1981), and (3) oxides (0.2 M ammonium oxalate + 0.2 M oxalic acid, pH 3.0, on the end-over-end shaker for 4 h in the dark) (Sheldrick, 1984). All metals were analyzed using the AAS.

4.3.3. Soil chemical quality determination

Samples of the column were also analyzed to determine the effects of the leaching treatment on chemical quality of soil. Total metals (i.e., Cd, Cu, Pb, and Zn and Ca, Mg, Fe, and Mn) were determined following nitric-perchloric (HNO_3-$HClO_4$) acid digestion (Cook, 1998). The pH and EC were determined with a 1:2 soil to water ratio (Hendershot et al., 1993), and the CEC was measured in unbuffered 0.1 M barium chloride ($BaCl_2$) (Hendershot and Duquette, 1986). The data were tested statistically to determine the levels of significance. Data were tested for comparison purposes by the least significance differences (LSD) test using Mac StatView (Anonymous, 1988).

4.4. Results and Discussion

The four soils under investigation were each highly contaminated with at least one of the trace metals measured (Table 4.1). The Mn, Fe, Ca, and Mg contents in the soils reflect the amounts found in the calcareous soils of the Canadian temperate region. The high Ca and Mg content in the soils could pose serious difficulties for remediation because of their role as competitor ions for the trace metals and their possible role as metal coprecipitators (Hong and Pintauro, 1996a). Trace metals in carbonate form could be released through acid dissolution but this process is highly impractical when there is more than 20% carbonate content in the soil. Similar problems could arise due to high Fe and Mn contents in the soils as Fe and Mn are both present in soils mainly as highly insoluble mineral oxides (Lavesque and Mathur, 1988). High content of the oxides in the soil system will undoubtedly retard the release of the adsorbed or occluded trace metals associated with the Fe and Mn oxides.

It is evident from Table 4.1 that the soils are alkaline, with a narrow pH range (7.97-8.03) and moderate to high carbonate content (11-26%), but they vary markedly in their texture (sandy loam to loam), organic matter content (0.6-3.5%), and cation exchange capacity (6.1-11.4 cmol(+) kg^{-1}). Analyses of the CEC revealed that the exchange sites of the four soils were dominated by base cations with the percentage base saturation of 100%.

4.4.1. Impact of leaching on total metal concentration

The impact of the leaching experiments on each soil sample is shown in Figure 4.1. Removal results are plotted against the maximum concentration limit for Cd, Cu, Pb, and Zn permitted for commercial/industrial (C), and residential use according to The Interim Canadian Environmental Quality Criteria for Contaminated Sites (CCME, 1991). The Cd (3.0 mg kg^{-1}), Cu (60), Pb (980) and Zn (180) content of MB site decreased to 2.1, 29, 251, and 117 mg kg^{-1}, respectively, for the water treatment, and to 1.4, 27, 190, and 95 mg kg^{-1}, respectively, for the acid/salt treatment. Although the MB soil sample was initially very contaminated with Pb, after leaching treatments the Pb content was reduced to the level permitted for the residential use.

Soil from the RY1 site contained Cd (6.3 mg kg^{-1}), Cu (700), Pb (800), and Zn (2,650). After washing tests, the new Cd concentrations (2.3 and 1.7 mg kg^{-1} for water and acid/salt solution treatment, respectively) and Pb (314 and 239 mg kg^{-1}) were below the level permitted for the residential use. The Cu and Zn concentration of the soil were substantially reduced from their original metal levels, but the Cu (305 and 291 mg kg^{-1}) and Zn (970 and 740 mg kg^{-1}) concentrations were still quite high and were only acceptable for commercial use.

The RY2 site was contaminated by Cd (5.5 mg kg^{-1}), Cu (800), and Pb (2,200). After leaching, the soil Cd content was reduced to concentrations of 2.5 and 1.7 mg kg^{-1} for water and acid/salt solution, respectively and was acceptable for residential use. The Cu levels remained high (403 and 362 mg kg^{-1}) and were acceptable only for commercial use. With acid/salt solution treatment, the Pb content of the original soil was reduced to

491 mg kg^{-1}, a level acceptable for both commercial and residential use. With the water treatment, the Pb concentration was lowered to 682 mg kg^{-1}, a level acceptable only for commercial use.

The ZF site was highly contaminated with Cd (145 mg kg^{-1}) and Zn (14,100). Although it responded well to the leaching treatments by releasing substantial amounts of Cd and Zn, the new metal levels of 56 and 47 mg Cd kg^{-1} and 3,483 and 3,288 mg Zn kg^{-1} for water and acid/salt solution, respectively, were still above levels required for the commercial and residential uses.

At the end of the experiment, 30 to 64% Cd, 50-58% Cu, 58-74% Pb, and 35-71% Zn of the total amount in the soil were removed from the soil columns after leaching the columns with 15 L volume of deionized water. The same procedures with the acid/salt solution removed 53 to 73% of the total Cd, 55-64% Cu, 60-81% Pb, and 48-77% Zn. The results showed approximately 7-23% more Cd, 2-6% Cu, 2-9% Pb, and 6-12% Zn were removed from the soil columns using the acid/salt solution compared to the water treatment. The percentage recoveries showed that the H_4EDTA alone or with acid/salt solution extracted considerable amounts of metal ions from the soil but the acid/salt treatment solubilized and mobilized more metal ions in the soils. Beneficial effects of the acid/salt treatment on metal removal from soils will be discussed in Chapter 5 in the study of metal speciation and retention in the EDTA/HCl-soil system.

The results demonstrate that each contaminated soil has unique characteristics and gives a particular response to the treatments imposed on it. In the experiments, some important soil factors that may be considered responsible for the different results may include: 1) the kind and amount of trace metal contaminants, 2) oxide and carbonate content, 3) organic carbon content, and 4) sand, silt, and clay content in the soils.

When more than one metal contaminant was present in the soil, competition between contaminants for adsorption sites in soils occurs (Christensen, 1987). The kind and amounts of metal, their ionic size along with other soil properties such as clay types and pH are among the important factors affecting competition (Elliott et al., 1989). Since most contaminants in soils usually reside in oxide, carbonate, and organic fractions (Xing et al., 1995; Gombert, 1994; Chang et al., 1984), the effective extraction of metal contaminants by EDTA largely depends on the level of Fe, Mn, Ca, Mg, and organic carbon content in the soils. High concentration of the constituents in soils is usually related to low extraction of metal contaminants from the soils due to low solubility and/or high interference by Fe, Mn, Ca, and Mg ions. Many studies found the presence of appreciable amounts of Ca and Mg (Hong and Pintauro, 1996a; Doepker, 1991; Tessier et al., 1979) and Fe and Mn (Kobayashi et al., 1974) in soil suppressed the solubilization of soil bound Cd, Cu, Pb, and Zn for removal by EDTA. Further, the solubility of metals is also related to the particle size. Metals are associated more with clay than silt or sand and attach strongly to the clay; hence, the metals in soils rich in clays are usually less accessible for removal.

4.4.2. Mode of metal removal

Of the total trace metals extracted with 15 L of water solution, 37 to 56% of the Cd, 59-64% of the Cu, 46-53% of the Pb, and 51-66% of the Zn were recovered in the first 1 L volume of water. Subsequent leaching with the second 1 L volume of water significantly increased the percentage recoveries of the Cd (54-80%), Cu (80-88%), Pb (69-83%), and Zn (73-87%) but the actual amounts of the metal removed with this second 1 L volume were much less compared to the first 1 L volume leaching. The subsequent trace metal extractions by the EDTA with each additional 1 L volume of water became less significant, except for the Cd (excluding the ZF soil sample), where reasonable quantities of trace metals were continuously removed by EDTA until the fifth 1 L volume of water, when approximately 80% of the Cd percentage recovery was reached. Similar trends were observed with the acid/salt solution, where the first leaching with 1 L volume of the solution extracted the bulk of the Cd (29-54%), Cu (55-61%), Pb (47-58%), and Zn (51-61%). Percentage values were comparable to the results obtained from the first leach of the water test, with exception for Cd of the RY2 sample which extracted relatively less metal.

Lower pH of initial leachates together with the high concentration of EDTA molecules contributed to the rapid extraction by removing the water soluble and easily exchangeable Cd, Cu, Pb, and Zn from the soil and dissolving the trace metals from some solid particles of carbonates, oxides, and organically bound fraction. The later group of metal fractions is insoluble but relatively readily dissolved by EDTA extraction (Sheppard and Thibault, 1992; Beckett, 1989). The metals of these relatively mobile pools would likely contribute the major part of metals removed by the rapid extraction.

Although H_4EDTA is nearly insoluble in water (Kobayashi et al., 1974) the high recovery of trace metals at the initial stage of the leaching process indicated a rapid reaction of H_4EDTA in the soil solution. This suggests that when H_4EDTA is in direct contact with the salt solution of the soil, reactions between H_4EDTA and metal ions in the soil solution take place and result in solubilization of the EDTA. Pribil (1972) states that the reaction between the EDTA and metal ions in the soil has been shown to be spontaneous.

The slow release which followed the fraction that was rapidly extracted may result from the diffusion or slow dissolution of relatively insoluble minerals (Yu and Klarup, 1994). The remainder was bound in the discrete mineral particles of oxide and silicate mineral pools and other insoluble secondary minerals. The metal in the later groups of the mineral pools would be expected to be released more slowly as it is mainly controlled by diffusion and mineral weathering.

Among the four soils under study, the ZF soil sample responded most efficiently to the treatments, with over 80% of the Cd, Cu, Pb, and Zn recovered after leaching with only 2 L of water. Based on our current treatments, it seems that leaching with 2 L or 3 L volume of water was sufficient for the Cu, Pb, and Zn extraction by EDTA in soil columns. For Cd, leaching might have to be continued to 4 L or 5 L volume of water to obtain adequate metal removal. The findings suggest that metal removal from a contaminated soil system is affected by the behavior of the metal contaminants and the environmental characteristics of each soil.

4.4.3. Metal distribution as a result of treatment

The results of chemical analyses (Figure 4.2) demonstrated that there was no enrichment of any metal under investigation in the lower sections of the soil column/profile. For water treatment, the amounts of remaining metals generally decreased with increased soil depth. By contrast, more metals remained at the bottom sections of the soil column when the acid/salt solution treatment was applied.

Two different scenarios are proposed to explain the results of the water and acid/salt solution treatments. First, when the homogeneous mixture of soil and EDTA in a column was leached with the deionized water, the extent of metal removal was governed by the concentration, or the acidifying and complexing force, of the EDTA (Environment Canada, 1986). Upon the introduction of water, the EDTA in the upper part of the column dissolved into the soil solution and reacted with trace metal ions in the soil. However, because of the high concentration of EDTA used in this experiment (5%), probably not all the EDTA dissolved in the initial leaching, and not all the dissolved EDTA complexed the trace metals in the soils. As the non-complexed (dissolved) EDTA moved downward because of leaching, ligand concentration increased in the lower part of the column and increased the EDTA strength in solubilizing and removing trace metals ions in this section.

A different scenario prevailed when the acid/salt solution (pH 1.0) was used as a washing solution. In addition to the effect of EDTA, two other important factors, the acid effect of HCl and the presence of the salt solution of KCl, were involved in the metal removal process. Continuous acidification of the overlying sections along with the salt effect, enhanced the liberation and dissolution of metals from the solid phases of soils into the soil solution from the surface section. The acidification may also have maintained a more gradual release of the H_4EDTA into the soil solution because lower pH suppresses the dissolution of the EDTA molecules. The gradual release of the EDTA may have reduced the numbers of the free-EDTA molecules being washed out of the soil columns and improved the EDTA leaching efficiency in the upper sections.

Because of relatively high concentrations of metals and inorganic ligands being washed out of soil in the upper part of the column, and the relatively high pH in the lower sections of the column, redeposition of metals in the bottom part of the column is possible. The likely mechanism of the redeposition is through the formation or the precipitation of secondary minerals. The formation of the secondary minerals in the lower section of the column undoubtedly increased the metal concentration relative to that in the upper column.

4.4.4. Metal fractionation

The data for the trace metal fractionation of the untreated and treated soils are presented in Table 4.2. The data show that EDTA removes considerable amounts of metals from the carbonate and oxide fractions. Please note that these are operationally defined fractions with names used for conveniences; hence, care should be taken in interpreting the data. For example, the amount of metals in the oxide fraction may not originate exclusively from the oxide fraction. It could include the metals in the exchangeable fraction and some metals from the carbonate fraction.

Cadmium. The Cd in the untreated soils was found mainly in the carbonate (14-48%) and oxide (6-28%) fractions. Only a small percentage of the trace metals in the soils resided in the exchangeable fraction (<4%). After leaching the soils with water or acid/salt solutions, large amounts of Cd in the original soils were removed from the carbonate and oxide fractions. Although the acid/salt treatment removed significantly more Cd from the soils than the water treatment did, no general trends were observed that the acid/salt treatment removed more Cd from the carbonate or oxide fraction compared to the water treatment. In the cleaned soils, a large percentage of the remaining Cd was associated with carbonate (5-71%) and oxide (3-16%) fractions. The Cd concentration in the exchangeable fraction remained small; and in most cases, smaller than the concentrations in the untreated soils.

Copper. The Cu in the original soils was mainly found in the oxide (36-64%) followed by the carbonate (3-17%) fraction. Only a small percentage of the trace metals in the soils was associated with the exchangeable fraction (<0.5%). After treatment applications with water or acid/salt solutions, the total Cu in the oxide and carbonate fractions of the cleaned soils remained dominant but much less than in the original soils. Enrichment in the exchangeable fraction was found in the cleaned soils with the water treatment, where the concentrations of exchangeable Cu in the soils increased to 0.54-3.7 mg kg^{-1} from their original concentrations (0.16-2.5 mg kg^{-1}). The results were variable with the acid/salt solution treatment in which only two of the four soils experienced an increase in their exchangeable fraction after the treatment.

Lead. Similar to the trend observed with the Cd and Cu, the Pb carbonate fraction constituted a large percentage (6.3-16%) of Pb concentration in the original soils as compared to the Pb exchangeable fraction which constituted less than 0.8% of the total Pb in the soils. Data were not available for Pb in the oxide fraction; the amount of Pb in the fraction could not be measured because of the low solubility of Pb-oxalate. After washing the soils with water or acid/salt solution, less Pb was retained in the carbonate fraction, but the relative amount to the total Pb concentration in the treated soils remained high (3-26%). Significantly higher ($p=0.05$) Pb concentrations were found in the exchangeable fraction of the treated soils compared to the untreated soils. The exchangeable Pb concentrations increased from 0.080-7.7 mg kg^{-1} in the original soils to 2.4-18 mg kg^{-1} and 0.80-11 mg kg^{-1} after treatment applications with water and acid/salt solution, respectively.

Zinc. Similar to the trend observed with the Cd and Cu, the Zn concentration in the untreated soils resided mostly in the oxide (27-56%) and carbonate (5-38%) fractions with small amounts associated with the exchangeable fraction (<0.6%). After washing with water or acid/salt solution treatment, the Zn concentrations in the oxide (60-3850 mg kg^{-1}) and carbonate (11-3440 mg kg^{-1}) fractions of the untreated soils were significantly reduced to the much lower Zn concentrations 32-500 mg kg^{-1} and 4.3-241 mg kg^{-1} for oxide and carbonate fractions, respectively. For the Zn exchangeable fraction, all the cleaned soils experienced an increase in the amounts of Zn, except for the ZF sample.

The results showed that large percentage of the Cd, Cu, Pb, and Zn in the soils resided in the carbonate and oxide fractions and much of the metals removed from the soils originated from these two fractions. For Cd, the decrease in the carbonate and oxide fractions accounted for up to 88% of the decrease in total metal content following cleaning. For Cu and Zn, the equivalent decreases were up to 87% and 92%. The carbonate fraction accounted for up to 80% of the decrease in Pb content of the soils.

4.4.5. Soil quality

Although there are varied views about what constitutes soil quality, the common goal of soil remediation is usually to avoid widespread ecological damage (Fuller and Warrick, 1985). In urban areas, attempts to reuse contaminated soils which would otherwise be unusable, is one of the main reasons behind the soil remedial effort. After leaching the soil-EDTA mixture with water or acid/salt solutions, three of the contaminated soils, MB, RY1, and RY2, had sufficiently low total metal concentrations they could now be used either as residential or commercial area. The ZF sample is still considered contaminated with metals but the much lower total metal concentrations have improved its quality.

The pH, EC, and CEC influence the soil quality through their impact on soil characteristics (i.e., fertility, salinity, degree of contaminant, and biological activity) which, in turn, determine the ability of a soil to function or maintain a healthy ecosystem (Pierzynski et al., 1994). Soil pH decreased slightly after treatment with water or acid/salt solution and in general, lower pH was observed with the acid/salt solution than the water treatment (Table 4.3). The drop of the soil pH closer to the neutral value definitely provides better soil quality, thereby better environmental conditions for plants and soil organisms.

The EC of the soils (Table 4.3), in contrast to pH, increased significantly after the treatments. On average, the EC values increased between 140 μS and 874 μS for the water treatment and between 2,799 μS and 3,361 μS for the acid/salt solution. The EC increase after water leaching was mainly a result of the Ca and Mg released from the dissolution of carbonates caused by the EDTA attack on the soil particles. In the case of the acid/salt solution, both the carbonate dissolution and the constant addition of neutral salt KCl into the soil were two important forces responsible for the EC increase. High concentration of neutral soluble salts could interfere seriously with the growth of most plants particularly when the soil pH is high (Brady and Weil, 1996). Despite the higher EC, CEC analyses showed the domination of Ca, Mg, and K on the exchange sites. The Ca, Mg, and K cations form relatively harmless soluble neutral salts and contribute to relatively moderate soil pH. The domination of Na salt in exchange sites, in contrast, results in higher pH values and is detrimental to most plants due to Na toxicity (Brady and Weil, 1996).

In trace metal management, the role of CEC is very important because it acts as one of the transitory media for metal retention and release from soils (Fuller and Warrick, 1985). In contaminated soils, high CEC provides more sites for metal retention, and reduces the amount of metal lost from the soils through leaching. With time, some of the metals retained by the exchange sites will diffuse into internal lattices of minerals or be further adsorbed through specific adsorption on solid compartments of soil. The process reduces the amount of metals available in soil solution at any time, and reduces the toxicity threat for plants and living organisms in the soil.

The CEC in all soils increased after leaching treatment (Table 4.3). On average, an increase between 0.20 cmol(+) kg^{-1} and 1.9 cmol(+) kg^{-1} for the water and between 3.7 cmol(+) kg^{-1} and 6.0 cmol(+) kg^{-1} for the acid/salt solution treatment was observed. The increased CEC indicated that treatment with EDTA or EDTA plus acid/salt solution had caused dissolution of carbonates and oxides in the soils and freed the exchange sites once blocked by these materials. Alternatively, the treatments may have exposed the internal surface layers of some clay silicate minerals, thereby increasing the number of exchange sites.

4.5. Conclusions

The remediation of contaminated soils can be achieved using EDTA. The presence of EDTA in the soil enhances the solubilization of soil-bound metals into the soil solution, and the addition of acid/salt solution further improves metal removal by the EDTA method. Approximately 7-23% more Cd, 2-6% more Cu, 2-9% more Pb, and 6-12% more Zn were removed from the EDTA-soil columns using the acid/salt solution compared to the water treatment. Most of the metals were removed from the soil in the first leaching. This finding shows that H_4EDTA alone or with acid/salt solution is a suitable reagent for the extraction of metal ions from the soil. The desirable characteristic of the EDTA method is that no metal enrichment in the soil profile was observed after leaching.

The fractionation studies revealed that the quantities of different trace metal ions in soil are not alike for various soil fractions, and differences exist between soils of different properties. Most of the metals in the soils used in this study were found in the carbonate and oxide fractions, and most of the metals found in the extract solution were removed from these two fractions.

Treatment with EDTA and acid/salt solution appreciably improved the quality of contaminated soils. Among the significant result were: (1) decreased metal contents of the soils to concentrations that are acceptable for residential and/or industrial use, (2) adjustment of the pH towards conditions that are more amenable to supporting growth of plants or other soil living organisms, and (3) increased the CEC which permits better metal retention in soil.

Table 4.1. Selected characteristics and total metal content of the soils used in the experiments (0-20 cm top layer).

Soils	Total Metals								Texture	Sand	Silt	Clay	$CaCO_3$	Org. C	BS	EC	pH	CEC
	Cd	Cu	Pb	Zn	Mn	Fe	Ca	Mg										
	mg kg^{-1}					%				%						μS		cmol(+) kg^{-1}
MB	3.0	60	980	180	655	3.1	9.1	0.78	SL	71	21	8	11	4.2	100	257	8.0	11.4
RY1	6.3	700	800	2650	517	4.3	18	0.88	SL	69	24	7	16	2.8	100	444	8.0	9.9
RY2	5.5	800	2200	400	629	6.5	19	0.92	SL	72	18	10	22	1.7	100	513	8.0	10.1
ZF	145	340	490	14100	4900	2.3	22	5.5	L	38	57	4	26	0.5	100	520	8.0	6.1

Table 4.2. Amounts (mg kg^{-1}) of cadmium, copper, lead, and zinc in soil fractions before and after leaching with water or acid salt/solution.

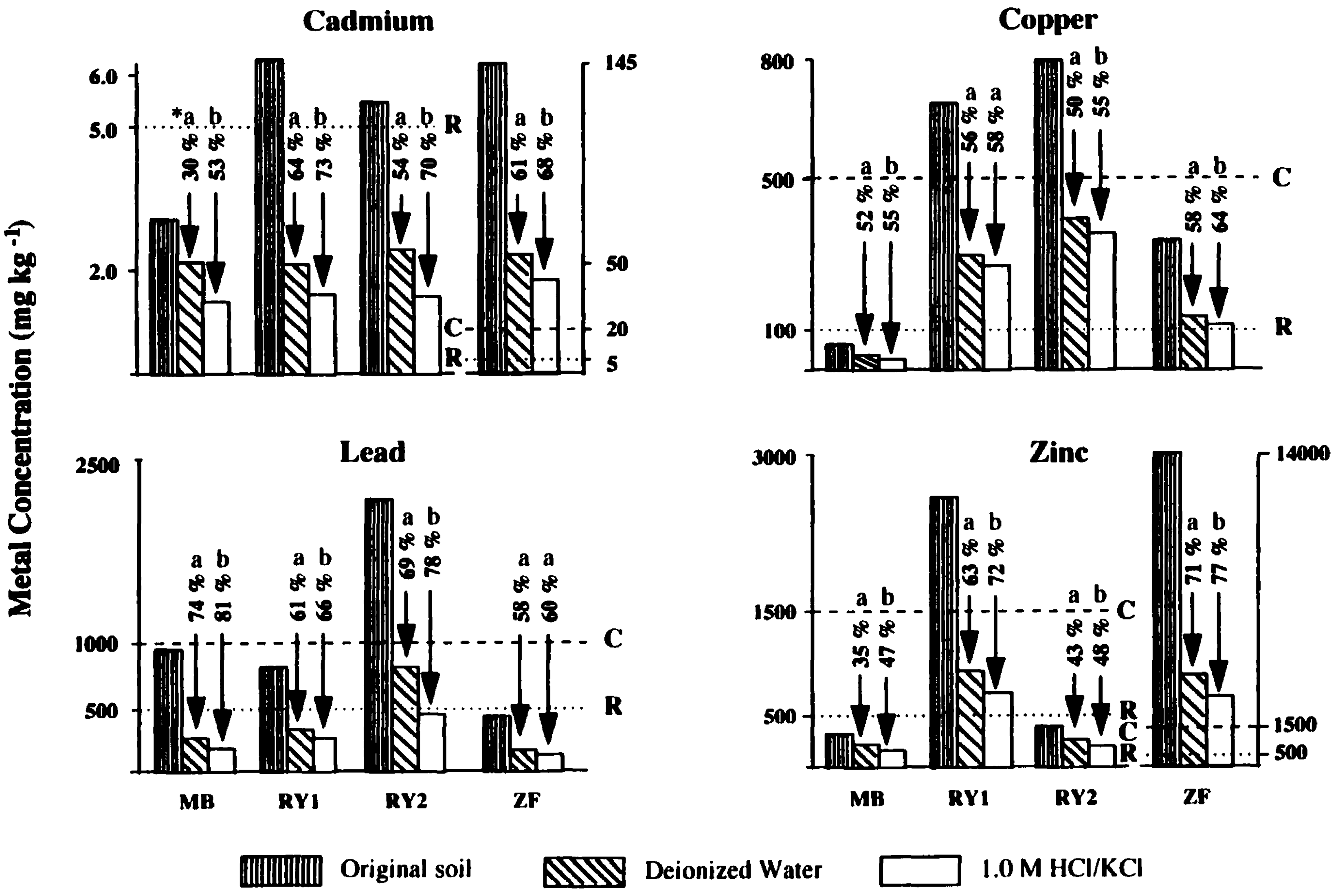
	Soil Samples											
Fractions	MB	RY1	RY2	ZF	MB	RY1	RY2	ZF	MB	RY1	RY2	ZF
	Original				Deionized Water				1M HCl/KCl			
						Cadmium						
Exchangeable	0.033 b*	0.09 c	0.020 b	3.5 c	0.016 a	0.063 b	0.020 b	1.3 b	0.030 b	0.018 a	0.010 a	0.87 a
Carbonate	0.83 c	3.0 b	0.77 c	28 c	0.40 b	1.5 ab	0.62 b	5.0 b	0.32 a	0.99 a	0.46 a	2.2 a
Oxide (amorph.)	0.32 b	0.6 c	0.32 b	41 b	0.068 ab	0.19 b	0.11 ab	8.7 ab	0.051 a	0.15 a	0.08 a	5.7 a
Total	3.0 c	6.3 c	5.5 c	145 c	2.1 b	2.3 b	2.5 b	56 b	1.4 a	1.7 a	1.7 a	47 a
						Copper						
Exchangeable	0.24 a	2.5 b	1.5 a	0.16 a	0.54 b	2.6 b	3.7 c	2.0 c	0.22 a	1.3 a	2.2 b	1.7 b
Carbonate	1.9 b	116 c	46 c	41 b	1.4 ab	72 b	38 b	4.9 ab	1.1 a	41 a	30 a	2.9 a
Oxide (amorph.)	28 b	449 c	413 c	121 b	12 a	180 b	277 b	22 a	11 a	144 a	235 a	18 a
Total	60 b	700 c	800 c	340 c	29 a	305 b	403 b	144 b	27 a	291 a	362 a	123 a
						Lead						
Exchangeable	7.7 a	0.08 a	10 ab	0.08 a	14 c	2.4 c	18 b	11 c	11 b	0.80 b	8.3 a	7.2 b
Carbonate	143 c	83 c	354 c	31 b	60 b	53 b	173 b	5.3 a	30 a	34 a	85 a	5.0 a
Oxide (amorph.)	--	--	--	--	--	--	--	--	--	--	--	--
Total	980 c	800 c	2200 c	490 b	251 b	314 b	682 b	204 a	190 a	269 a	491 a	195 a
						Zinc						
Exchangeable	0.96 a	13 a	0.96 a	39 b	1.2 ab	28 c	3.0 c	21 a	5.9 c	18 b	1.4 b	18 a
Carbonate	11 c	600 c	20 b	3440 c	5.6 b	241 b	11 a	172 b	4.3 a	203 a	11 a	138 a
Oxide (amorph.)	60 c	1210 c	225 c	3850 c	43 b	450 b	144 a	428 a	32 a	370 a	153 b	500 b
Total	180 c	2650 c	400 c	14100 b	117 b	970 a	229 a	3480 a	95 a	739 a	307 b	3290 a

* different letters indicate significant differences at $p = 0.05$ level for the same fraction and element for each soil.

Table 4.3. The pH, EC, and CEC of the soils before and after leaching with water or acid salt/solution.

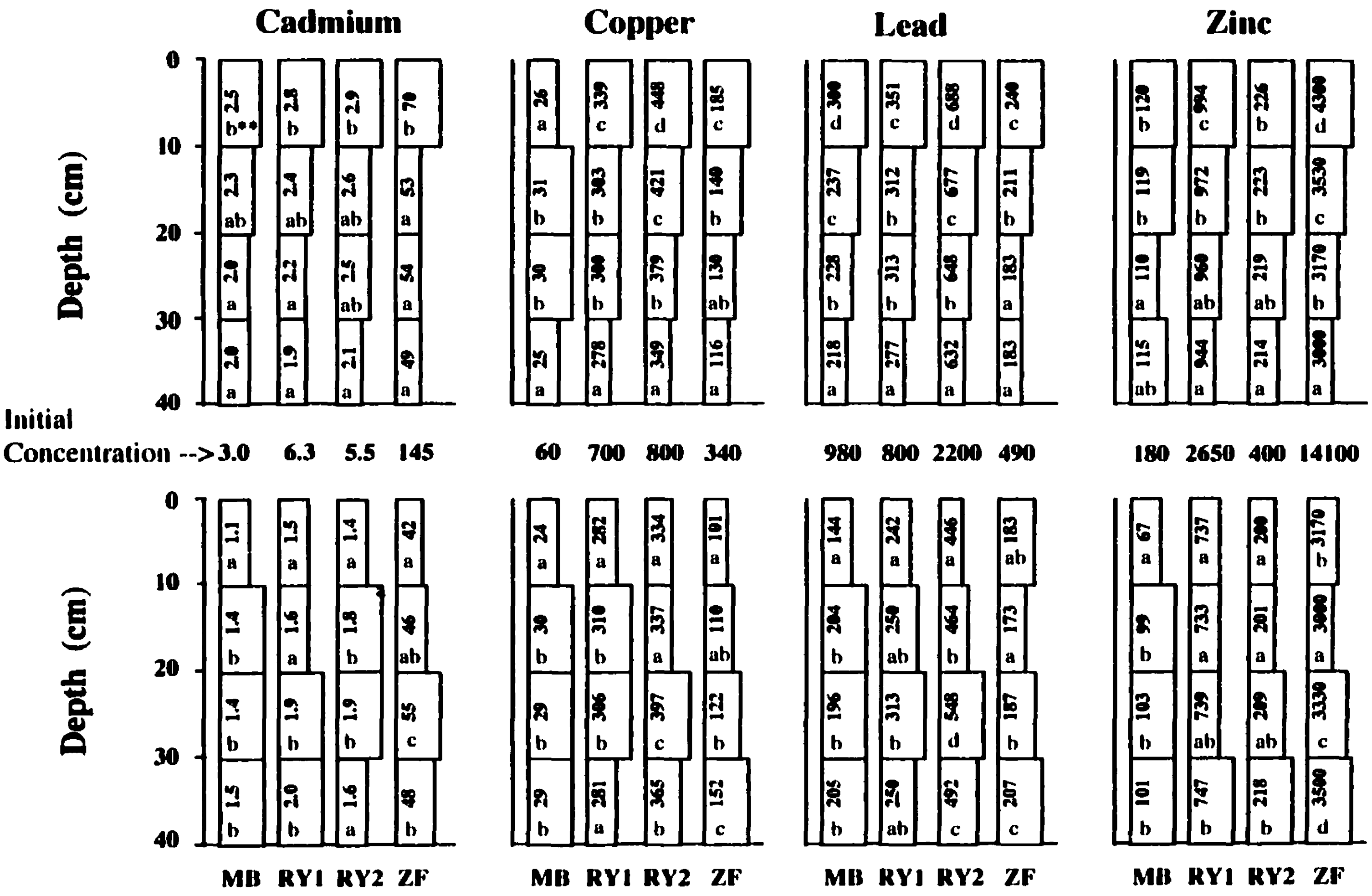
	pH			EC (μS)			CEC (cmol(+) kg^{-1})		
Soils	Original	Water	HCl/KCl	Original	Water	HCl/KCl	Original	Water	HCl/KCl
MB	7.99	7.76	7.46	257	1130	3110	11.4	11.8	17.4
RY1	8.03	7.83	7.49	444	584	3810	9.9	12.1	15.6
RY2	7.97	7.88	7.73	513	1120	3310	10.1	12.0	14.8
ZF	8.01	7.93	7.68	520	671	3400	6.1	6.3	10.1

Figure 4.1. Levels of trace metals before and after leaching the EDTA-soil column with deionized water or acid/salt solution. C=commercial and R=residential limits. * different letters indicate significant differences at $p = 0.05$ level between the two treatments.



Cadmium
Copper
Lead
Zinc
Metal Concentration (mg kg⁻¹)
6.0
5.0
2.0
145
50
20
5
*a b
30 % 53 %
a b
64 % 73 %
a b
54 % 70 %
a b
61 % 68 %
R
C
R
800
500
100
a b
52 % 55 %
a a
56 % 58 %
a b
50 % 55 %
a b
58 % 64 %
C
R
2500
1000
500
a b
74 % 81 %
a b
61 % 66 %
a b
69 % 78 %
a a
58 % 60 %
C
R
3000
1500
500
14000
1500
500
a b
35 % 47 %
a b
63 % 72 %
a b
43 % 48 %
a b
71 % 77 %
C
R
C
R
MB
RY1
RY2
ZF
MB
RY1
RY2
ZF
Original soil
Deionized Water
1.0 M HCl/KCl

Figure 4.2. Distribution of trace metals in columns containing homogeneous mixtures of soil and EDTA after leaching with water (Upper Panels) and acid/salt solution (Lower Panels). Number in the boxes indicates the metal concentrations (mg kg^{-1}) in the section of the column after leaching. ** different letters indicate significant differences at $p = 0.05$ level between layers in the same column.


Cadmium
Copper
Lead
Zinc
Depth (cm)
0
10
20
30
40
2.5 b**
2.3 ab
2.0 a
2.0 a
2.8 b
2.4 ab
2.2 a
1.9 a
2.9 b
2.6 ab
2.5 ab
2.1 a
70 b
53 a
54 a
49 a
26 a
31 b
30 b
25 a
339 c
303 b
300 b
278 a
448 d
421 c
379 b
349 a
185 c
140 b
130 ab
116 a
300 d
237 c
228 b
218 a
351 c
312 b
313 b
277 a
688 d
677 c
648 b
632 a
240 c
211 b
183 a
183 a
120 b
119 b
110 a
115 ab
994 c
972 b
960 ab
944 a
226 b
223 b
219 ab
214 a
4300 d
3530 c
3170 b
3000 a
Initial
Concentration -->3.0 6.3 5.5 145
60 700 800 340
980 800 2200 490
180 2650 400 14100
Depth (cm)
0
10
20
30
40
1.1 a
1.4 b
1.4 b
1.5 b
1.5 a
1.6 a
1.9 b
2.0 b
1.4 a
1.8 b
1.9 b
1.6 a
42 a
46 ab
55 c
48 b
24 a
30 b
29 b
29 b
282 a
310 b
306 b
281 a
334 a
337 a
397 c
365 b
101 a
110 ab
122 b
152 c
144 a
204 b
196 b
205 b
242 a
250 ab
313 b
250 ab
446 a
464 b
548 d
492 c
183 ab
173 a
187 b
207 c
67 a
99 b
103 b
101 b
737 a
733 a
739 ab
747 b
200 a
201 a
209 ab
218 b
3170 b
3000 a
3330 c
3500 d
MB RY1 RY2 ZF
MB RY1 RY2 ZF
MB RY1 RY2 ZF
MB RY1 RY2 ZF

Connecting Paragraph

The preceding chapters demonstrated that EDTA can be used successfully to clean contaminated soils in the laboratory, using either small or large volumes of soil with batch and column techniques. The results also indicated that application of HCl improved the extractions of metal from the soils. Since only four soils were studied in the laboratory, the applicability of the technique to other metal contaminated soils can only be speculated on. Computer modeling can be used to predict the behavior of EDTA and other ligands (e.g., chloro, hydroxo, and carbonato) in soil. This opens the way to modeling the behavior of other soils in the presence of EDTA. In this chapter the results obtained in the laboratory will be used to verify the output from a chemical speciation model.

CHAPTER 5

METAL SPECIATION AND RETENTION IN THE EDTA/HCl-SOIL SYSTEM: A MODELING APPROACH

5.1. Abstract

The MINEQL$^+$ program was used to model metal speciation and adsorption in soil systems in contact with HCl and EDTA. The goals were: (1) to describe the metal speciation in the soil systems containing high concentration of EDTA (1.2%, 2.4%, and 4.8% of the soil weight), (2) to validate the model using experimental data, and (3) to estimate the metal retention by humate and hydrous ferric oxide (HFO) surfaces. The model indicated that the metal-EDTA complexes are the dominant forms of the metal species present in the soil-extracts. Treatments with salt concentrations up to 1.0 M KCl or with HCl at a low concentration (0.1 M) generally increased the amount of metal extracted from the soils, but did not change the domination of the metal-EDTA complexes in the systems. Nearly 100% of the Cd, Cu, Pb, and Zn in the systems were present as EDTA complexes. Addition of 1.0 M HCl significantly decreased the pH of the soil extracts, for example from pH 8.0 to 3.5, and increased the number of chloride species, particularly for Cd, but the most abundant species in the system remained the metal-EDTA complexes. When the amounts of metals extracted by the anion exchange resin (AER) was plotted with the amounts of EDTA metal complexes predicted by the models, a strong correlation (r=0.99) was observed between the two values. The results suggest that the model is a useful tool for predicting the metal speciation in soil solutions. When charged surfaces of soils such as humate and HFO were included in the program, through a surface-complexation model using the two-layer approach, the metal-EDTA complexes remained the dominant species in the soil system over a wide range of soil pH. The results suggested that EDTA is much more efficient than the humate or the HFO surfaces in forming complexes with the metals.

5.2. Introduction

Computer-models are gaining wide acceptance as an assessment tool to forecast, describe, or predict metal speciation, transport, retention and adsorption in soil and plant systems. The fundamental principles that underlie equilibrium computations are well described by Zachara and Westall (1999), Stumm and Morgan (1996), Parker et al. (1995), Morel (1983), Westall and Hohl (1980), and Lindsay (1979). In general, models are reasonably accurate in predicting chemical interactions that can take place in a system (Westall and Hohl, 1980); nevertheless, they share common limitations in thermodynamic data and interferences from rate dependent reactions (Schecher and McAvoy, 1994).

The MINEQL$^+$ program can be used for chemical equilibrium modeling of laboratory and environmental systems. It is "an integrated software package that has a solid theoretical foundation superimposed on advanced data management tools" (Schecher and McAvoy, 1994). Since 1976, the original MINEQL program has continuously been improved and used successfully to predict chemical speciation in aquatic systems and surface adsorption of ions onto mineral and organic surfaces of the terrestrial systems. In the laboratory, the model predicts successfully the metal speciation in solutions and those bound to the mineral and organic surfaces of solid particles (Hendershot, 1998; Westall, 1981; Westall et al., 1976).

In soils, trace metals of various kinds (ions and molecules) interact intimately through the soil solution with heterogeneous organic and inorganic materials that vary in surface functional groups and affinity for the metals. Specific adsorption of cations can occur on mineral surfaces for those metals that are involved in hydrolysis reactions with water such as Cd, Cu, Pb, Zn, Mn, Ni, and Co. The adsorption reaction involves the formation of an inner-sphere complex between the metallic cation and the negatively charged surface oxides, hydroxides, and oxyhydroxides of Al, Fe, and Mn or by forming ternary surface complexes between ligand, metal, and soil minerals. In addition, some metals can be specifically adsorbed at organic surfaces through various complexation reactions with the functional groups of the organic matter (e.g., -COOH carboxyl, -OH phenolic, -SH thiol, $-NH_2$ amino, =O carbonyl, -OH alcohol, and -S- thioether).

Given this information, any attempt to remove trace metals from soils using acids and ligands should not overlook the adsorption phenomena. The application of the ligands EDTA and Cl to soils could increase or decrease metal retention in the soils (Lumsdon et al., 1995; Garcia-Miragaya and Page, 1976; Hahne and Kroontje, 1973) depending on the formation constant for the complexes, the kind and concentration of the metal and ligand, and the pH of the solution.

This study was intended to see the performance of HCl and EDTA on metal mobilization in some contaminated soils, by taking into account the important role of humate and HFO surfaces as metal adsorbents, through computer modeling using the $MINEQL^+$ program. The objectives were: (1) to calculate the speciation of extracts from four metal contaminated soils, (2) to compare the results of the speciation calculation with measured values of EDTA-metal complexes adsorbed on AER, and (3) to use a surface complexation model to examine the relative binding strength of trace metals with EDTA and surface charge sites of HFO and organic matter.

5.3. Materials and Methods

5.3.1. Soils

Four soil samples (MB, RY1, RY2, ZF) from the surface layer (0-20 cm) were chosen for the study. The soils represent sites in the Greater Montreal region that have been contaminated with trace metals from various sources (industrial, railway, and military activities). The selected soils varied in texture and contained high concentrations of at least one of the following metals: Cd, Cu, Pb, and Zn. The metal contents and the detailed characteristics of the four soil samples are presented in Table 5.1. The total metal analysis was carried out by digestion of soils in concentrated $HNO_3/HClO_4$ (Cook, 1998). The soil texture was determined using the hydrometer method described by McKeague (1976). The soil pH and the electrical conductivity (EC) were determined in a 1:2 soil to water ratio (Hendershot et al., 1993), the carbonate content by a titrimetric method (Bundy and Bremner, 1972), the organic carbon content by titrimetric dichromate wet oxidation (Nelson and Sommers, 1982), and the cation exchange capacity (CEC) by the unbuffered 0.1 M $BaCl_2$ method (Hendershot and Duquette, 1986). The oxide contents of the soils were estimated using the dithionite-citrate (DC) extraction method (Ross and Wang, 1993).

5.3.2. Laboratory procedures of metal extraction

Each soil was extracted using the following methods. The soil (5 g), extracting solution (25 mL), and the EDTA (1.2%, 2.4%, and 4.8% of the soil weight) were mixed on a reciprocating shaker at a low speed (120 stroke per minute) for 48 h. The extracting solutions varied from water (alone) to water containing HCl (0.1 M and 1.0 M), KCl (0.1 M and 1.0 M), or combinations of the HCl and KCl. The extracts were centrifuged and the supernatants were decanted, filtered and stored for pH and metal concentration determination. The metal concentrations (Appendix I Part A-G) obtained were then used for the input metal concentration in modeling.

For validation of the model, 10 g of soils (RY1 or RY2) containing 0.1%, 0.2%, 0.4%, 0.6%, 1.0%, 1.2%, and 2.4 % of EDTA were shaken with 50 mL of deionized water for 24 h, centrifuged, and filtered for metal determination. The EDTA soil-extracts were then passed through the anion exchange resin (AER) AG 3-x4 to remove the Cd-, Cu-, Pb-, and Zn-EDTA from the soil-extracts. The amounts of the metal-EDTA complexes retained by the AER were determined and the values were then compared with the concentrations that were estimated by the models.

5.3.3. Metal speciation in soil solution

Thirteen components (H_2O, H^+, CO_3^{2-}, $EDTA^{-4}$, Ca^{2+}, Mg^{2+}, Fe^{3+}, Mn^{2+}, Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cl^-) were chosen to model the chemical speciation in the soil solutions. Table 5.2, part A, indicates the thermodynamic data used in the calculation. For the sake of reliability and consistency of the data, the complexation constants were taken from Stumm and Morgan (1996) (if they were available). Since the MINEQL$^+$ program using H^+ as the computed species, all of the equilibrium constants for OH^- species taken from Stumm and Morgan (1996) were recalculated to satisfy the input requirements. Some data for the ionic strengths larger than zero were recalculated to zero ionic strength. These data conversions and recalculations are indicated in the Table. Other constants were taken from Turner et al. (1981) for $FeCO_3^+$ and $MnCO_3$ (aq) and from Nordstrom et al. (1990) for $FeCl_3$ (aq) and $MnCl_2$. A carbon dioxide partial pressure (P_{CO_2}) equal to a value of -3.5 was chosen for the model since the solutions were assumed to be in equilibrium with the atmosphere. After the metal and EDTA concentrations (Appendix I Part A-G) of the components were added into the program, the model was run at the fixed pH of the soil solution or as pH titration between 2.0 and 8.5. It is assumed that all EDTA added is in solution. The MB, RY1, RY2, and ZF samples were used in this experiment. Appendix II Part A shows the input data for the metal speciation as a function of pH in soil solutions with water treatment using RY2 and 4.8% EDTA. Figure 5.1a is the result of the model calculation using the input.

5.3.4. Metal complexation with humate and HFO

The components for the surface complexation model included humate, $>Fe^sOH^o$ and $>Fe^wOH^o$ oxide surfaces ("s" for strong sites and "w" for weak sites), "Coul." for the coulombic factor, and all the components that were used previously in the soil solution metal-speciation experiment. In all, there were as many as seventeen components considered in this surface-complexation calculation involving 8 metal elements, humate and HFO. The important species from the interaction reactions between the components were indicated in Table 5.2, part A and B. The RY2 sample was used in this experiment. This soil contained moderate amount of organic matter and high amount of oxide materials.

Humic materials. Studies involving the measurement of the equilibrium constants for natural humic materials and trace metals are relatively scarce (Bolton et al., 1996; Lumsdon et al., 1995; Tipping, 1993; Tipping and Hurley, 1992; Brezonik et al., 1991; Gunneriusson and Sjoberg, 1991; Lovgren and Sjoberg, 1989; Tipping et al., 1988; Ephraim et al., 1986; Sunda and Hanson, 1979). None of these studies provides a consistent set of values for the eight metals (Cd, Cu, Pb, Zn, Ca, Mg, Fe, and Mn) we need to include in the model. Several authors have stated that oxalate has a similar binding strength with trace metals as natural humic substances (Gunneriusson and Sjoberg, 1991; Lovgren and Sjoberg, 1989; Evans, 1998, personal communication-class notes), and a well-developed database for oxalate is available (Martell and Smith, 1989, 1982, and 1977; Perrin, 1979). As a first approximation of the binding of trace metals to the humic material in our soils we decided to use the constants for oxalate. These prediction could be improved if we were to measure the properties of the humic material in these soils; however this is outside the scope of the present study.

The complexation constants for the metal-humate species and the H- and H_2-humate (using the oxalate data) were taken from Martell and Smith (1989, 1982, and 1977). The values for the H, Ca and Mg constants were taken from the data of the 1989 reference, the Cd and Cu from the 1982 reference, and others from the 1977 source. We assume that all of the soil organic matter was in the solid phase and that the organic materials carried homogeneous simple diprotic complexation sites.

Values of the concentration of the humic substance in the soils were calculated according to the calculation method described by Gunneriusson and Sjoberg (1991). The authors stated that each gram of organic carbon contains 0.00278 moles H_2L group. The laboratory procedures of metal extraction in our experiment were performed with the equivalent of 200 g soil per liter of solution. Using the Gunneriusson and Sjoberg's approach, the RY2 sample which contains 3.4 g C per 200 g soil carried 0.00945 moles H_2L organic binding group. This value was used for the model calculations.

Hydrous ferric oxide. The MINEQL$^+$ program is a convenient tool to estimate the adsorption of metals on HFO surfaces because it formally incorporates into its program the two-layer surface complexation approach for the reactions between metal and HFO (Schecher and McAvoy, 1994; Dzombak and Morel, 1990). Input parameters such as the total surface area of sorbing surface (600 m^2/g HFO), the HFO intrinsic acidity constants (-7.29 and -8.93), and the surface site densities (0.005 and 0.2 mol/mol Fe for the "high or strong affinity" ($>Fe^sOH^o$) site and for a "low or weak affinity" ($>Fe^wOH^o$) site, respectively) have all been incorporated into the program.

The important parameter associated with the HFO that need to be calculated and entered into the program was the total concentration of the ferric ions in the soil which was estimated from the soil extraction using the dithionate-citrate procedure. The laboratory analysis indicated a total amount of 0.1128 moles ferric ions per 200 g soil in RY2 soil. This value was used for the input data in the modeling calculations. Other required parameters were the complexation constants for the metal/HFO surface reactions. Conveniently, all the required constants for Cd, Cu, Pb, Zn, Ca, Mg, and Mn metal reactions with HFO were available in the book written by Dzombak and Morel (1990).

The parameters of the humate and HFO were entered together into the program;

the evaluation was made based on the two-layer approach as described by Dzombak and Morel (1990). Detailed instructions on how to run this program are in the MINEQL$^+$ handbook by Schecher and McAvoy (1994). Our research objective was to evaluate the competing effects between EDTA, humate, HFO, and other ligands (e.g., Cl^-, OH^-, CO_3^{2-}) on metal retention in soils. The program was evaluated using titration calculation type at pH range between 2.0 and 8.5. Appendix II part B is the input data for the metal speciation as a fuction of pH in soils in the presence of EDTA, humate (SOM), and hydrous ferric oxide (HFO) with water treatment using sample RY2 and 4.8% EDTA. Figure 5.3a shows the result of the calculation using the input.

5.3.5. Statistical analysis

The data were tested statistically to determine the levels of significance. For comparison purposes data were tested by the least significance differences (LSD) test using Mac StatView (Anonymous, 1988). Simple linear correlation was employed to examine the relationships between the amounts of the metal-EDTA complexes retained by the AER and the concentrations that were estimated by the models.

5.4. Results and Discussion

5.4.1. Effects of treatments on total metal removal

Our experimental results indicated the extractabilities of the Cd, Cu, Pb, and Zn from the four soils varied with the properties of the extracting solution. The acid (HCl), salt (KCl), or the combination acid/salt (HCl/KCl) treatment removed more metals from the EDTA soil mixture than did water alone (Table 5.3). The combination acid/salt treatment (1.0 M) proved to be the most efficient technique for extracting metals from the soils. Up to 77% of Cd, 72% Cu, 86% Pb, and 79% Zn were removed by the acid/salt solution treatment as compared to 70% Cd, 65% Cu, 79% Pb, and 69% Zn removed by the water treatment. In general, the rate of metal release from the soils by the treatments increased in the order water treatment < 0.1 M KCl < 1.0 M KCl < 0.1 M HCl < 0.1 M HCl/KCl < 1.0 M HCl < 1.0 M HCl/KCl. The beneficial effect of the acid, salt, or the combination acid/salt treatment over the water can be explained by the direct effect of the pH of the solution (or the proton effect), and/or by the effects of the electrolytic ions (K^+ and Cl^- ions), on the solubilization and mobilization of metal ions in the soil.

Acidification is one of the most important processes controlling metal solubility and mobility in soils (Boekhold et al., 1993). In calcareous soils, for example, the hydrogen ion attacks the carbonate materials and frees the metals associated with them. Protons are also sorbed onto oxides which weakens the metal-lattice bonds, increases the dissolution rate of metals, and improves the chance for mineral weathering (Davis and Singh, 1995). Metal adsorption/desorption and precipitation/solubilization are all pH dependent with metal adsorption and precipitation predominant at higher pH and metal desorption and solubilization greatest at lower pH.

In our experiment with the 1.0 M HCl/KCl solution, the low pH may have increased the trace metal desorption and solubility. Results (data not shown) indicated increased concentrations of Ca, Mg, Fe, and Mn in the leachates from the acid/salt compared to the water treatment. Increased amounts of the metals may be related to the dissolution of mineral carbonates and oxides in the soils. The dissolution of the carbonates and oxides undoubtedly resulted in more Cd, Cu, Pb, and Zn in the soil solution.

The addition of monovalent potassium chloride (KCl) salts might have enhanced the Cd, Cu, Pb, and Zn removal. Although definitive results are unavailable from this experiment, it is probable that KCl enhanced the release of metals through activity coefficient effects, which would elevate the solubility of the metal bearing solid phases and thereby release adsorbed and occluded metal (Brown and Elliott, 1992). The addition of KCl might have liberated metals from the soil exchange sites through direct displacement of the metal cations by K^+ ions. The exchange sites which normally prefer metals or other cations of high valence could lose their selectivity to K^+ when the ratio between the K^+ and metals increased. Some monovalent cations like K^+, because of their size and steric effects, can also displace specifically sorbed metal ions.

Further, the Cl^- ions of the KCl may have formed a weak complex with metal ions and enhanced the dissolution of the metals (Gaita and Al-Bazi, 1995; Boekhold et al., 1993; Yong and Sheremata, 1991; Doner, 1986). The model indicated that Cl^- ion forms more complexes with the Cd, Cu, Pb, and Zn with the addition of the HCl (Figure 5.1 and 5.3). Also, the non-specific adsorption of Cl^- may have lowered the charge of the oxide surfaces and hence reduced the number of sites available for metal adsorption (Gunneriusson, 1994; Gunneriusson et al., 1994). Since K^+ ions complex poorly with EDTA, the positive effects of K^+ as well as Cl^- and H^+ effects, contributed to greater metal removal from the soils under the acid/salt treatment.

5.4.2. Effects of treatments on metal speciation

5.4.2.1. Metal speciation of the EDTA soil-extracts

Based on the MINEQL$^+$ output, the chemical speciation for the Cd, Cu, Pb, and Zn in the EDTA soil-extracts were exactly the same for all treatments, except the 1.0 M HCl and 1.0 M HCl/KCl treatments (Table 5.4). Nearly 100 percent (>99%) of the Cd, Cu, Pb, and Zn were calculated to be present as metal-EDTA forms (Cd-EDTA and Cd-HEDTA, Cu-EDTA and Cu-HEDTA, Pb-EDTA and Pb-HEDTA, Zn-EDTA and Zn-HEDTA). The results indicated the strong bond between the EDTA molecules and the metal ions in the soils as has been suggested in many studies (Martin and Allen, 1996; Lavesque and Mathur, 1988; Burridge and Hewitt, 1987; Lindsay and Norvell, 1969). The introduction of 1.0 M KCl into the EDTA soil system did not change the metal speciation. Similarly, no variations in metal speciation were observed with the use of 0.1 M HCl. Apparently, at this concentration, the pH of the soil solution was not noticeably decreased and the reaction between the metals, the Cl^-, and the EDTA were unaffected.

With HCl solutions at 1.0 M concentration, the pH dropped dramatically from 8.0 to a new pH level (between 3.54 and 4.72) (Table 5.4). At these pH values, some chloride species, particularly those of Cd (e.g., $CdCl^+$, $CdCl_2$ (aq), $CdCl_3^-$) were formed in significant concentrations (Table 5.4). The results indicated the important effect of the H^+ ions (at this concentration level) in lowering the pH of the systems, which, in turn, changed the chemical equilibrium and the metal speciation of the system. Although the metal chlorides were formed, the dominant species of the Cd, Cu, Pb, and Zn in the 1.0 M HCl system remained the metal-EDTA complexes. The results confirmed the widely cited argument that metals form stable complexes with EDTA molecules in a relatively wide range of soil pH. No differences were observed between the 1.0 M HCl and 1.0 M HCl/KCl treatments with regards to the Cd, Cu, Pb, and Zn speciation.

5.4.2.2. Metal speciation of EDTA soil extracts as a function of pH

Figure 5.1a and 5.1b illustrate the influence of pH on metal speciation in the EDTA/water and EDTA/HCl systems. To simplify the figures all of the metal complexes with the same ligand were combined (i.e., Cd-OH is the sum of the $CdOH^+$ and $Cd(OH)_2$ (aq) species and Cd-Cl is the sum of the $CdCl^+$, $CdCl_2$ (aq), and $CdCl_3^-$). Obviously, there are no other dissolved ligands that compete effectively with EDTA (under the EDTA/water system) in forming complexes with metal Cd, Cu, Pb, and Zn over the pH range between 2.0 and 8.5. Only the free ion species (at lower pH) and the metal-OH of Cu and Pb (at higher pH) are present in appreciable concentrations; but their concentrations are considerably lower than the EDTA species. It seems that the chloro-, hydroxo-, and carbonato-metal species play an unimportant role in metal speciation of soil extracts in the presence of high EDTA concentrations (Figure 5.1a).

The applications of the 1.0 M HCl influenced markedly the metal speciation in the EDTA soil system. As summarized in Figure 5.1b, the extent of complex formation depends on pH. Although Cl forms less stable complexes with metals than EDTA, it efficiently competes with this ligand in forming metal complexes at lower pH. However, the EDTA dominates metal speciation as long as the pH is higher than 3.5. This suggests that a relatively large excess of HCl would have to be added to reduce the domination of the metal-EDTA complex in the system. Similar to the results under the EDTA/water system, the hydroxo- and carbonato-metal complexes are negligible in this EDTA/HCl system. Their concentrations are low throughout most of the pH range and are not affected by the addition of HCl.

5.4.3. Validation of the models using the resin experimental data

When a solution containing metal-EDTA complexes is passed through a column of anion exchange resin (AER), the metal-EDTA complexes in the solution should be retained by the resin. If we assume that the adsorption by the AER is a quantitative indicator of the amount of metal in an EDTA complex, then the MINEQL$^+$ model output can be tested.

The extraction of metals from the soil using different concentrations of the EDTA removed as little as 0.055 mg Cd L^{-1} and as much as 0.66 mg Cd L^{-1}. For the Cu, Pb, and Zn, the corresponding values were 5.4 and 47, 3 and 63, and 3 and 122 mg L^{-1}. Since the models estimated that nearly 100% of the metals in the EDTA soil-extracts are in the form of the metal EDTA complexes, these concentration values were therefore used as our predicted metal values by the models. Although the AER did not remove all of the dissolved metals in the extracts (89-96%), the percent removal for each metal was highly correlated ($r = 0.99$) with the metal concentrations predicted by the models (Figure 5.2).

Discrepancies between the predicted percent of metal-EDTA complexes and the amount actually retained by the AER can be explained by either the overestimation made by the models or incomplete removal of the metals by the resin.

The results corroborate that EDTA, as we have seen, has a high affinity for the metals. Most of the Cd, Cu, Pb, and Zn in soil extracts with or without HCl (Table 5.4) were present in the metal-EDTA forms as they were predicted by the models or corroborated by the extraction using the AER. Only at a very low pH values (pH < 3.0), the concentration of the metal EDTA species diminished in the presence of high Cl^- ions (Figure 5.1a and 5.1b). Again, the results explained why the removal of Cd, Cu, Pb, and Zn from the EDTA soil extracts is more successful with the anion exchange resin than with the cation exchange resin (e.g., Chelex-100) as observed by Tejowulan and Hendershot (1998) in their attempt of removing metals using anion and cation exchange resins from the EDTA soil-extracts. Since the metal reaction with EDTA formed anionic complex molecules, the introduction of the AER (which is positively charged) provides an excellent sink for the complexes.

5.4.4. Metal complexation with humate and HFO surfaces

Ion sorption in soil occurs through chemical interactions between active ions with various soil solids (both organic and inorganic). In normal soils, minute amounts of trace metals dissolve and are available for uptake by living organisms. The majority of the metals are retained strongly by the soils because of the strong reactions between the metals and the solid phases. Because of these reactions, the removal of metals from soils for the purpose of remediation is potentially difficult. The role of the synthetic chelating agents (e.g., EDTA) and HCl in enhancing the metal removal from soils is well understood; however, the use of such ligands for remediation purposes should not ignore the role of the solid phases in retaining the metals.

5.4.4.1. Effects of humate on metal retention

No appreciable amounts of metals were held by the humate surfaces under the EDTA/water system at higher pH (Figure 5.3a). The metal humates, at pH higher than 4.0, were present only at very low concentrations ($<10^{-7.0}$) as compared to the concentrations of metals in the EDTA form ($>10^{-5}$). When the percentage calculations were performed, the model indicated that more than 99% of the Cd, Cu, Pb, and Zn metals in the system were present as metal-EDTA complexes. It seems that, over the common pH range in soils, the humate was not an efficient competitor for the metals in the solution system dominated by EDTA chelates. However, the humate proved to be stronger than other ligands such as the chloro, hydroxo, and carbonato in retaining metals from the same solution system. At pH lower than 3.0 (the pH range uncommon in soils), the humate along with the free-metal species exceeded the concentration of EDTA-metal species.

Similarly, virtually no metal complexes were predicted to be retained from the EDTA/HCl system by the humate at pH higher than 3.0 (Figure 5.3b). According to the model, the addition of 1.0 M HCl solution did not increase the bonding between the humate and the metals, either by their pH or Cl^- ion effects. Rather, at the lower pH values, the opposite was true; the concentrations of Cd-, Cu-, Pb- and Zn-humate complexes were somewhat decreased with the addition of HCl (Figure 5.3b). More metals were converted to the metal-Cl form from the humate, as well as from the EDTA and free-metal forms. In this EDTA/HCl system, the role of humate as a metal adsorbent was inferior as compared to the EDTA, chloride, and the free-metal ions. The metals (particularly Cu) are well known to strongly interact with the organic matter in many soils. However, the results from the models (with or without HCl treatments) indicated only insignificant amounts of Cu existed in the form of humate in pH range common in soils.

5.4.4.2. Effects of HFO on Metal Retention

The models indicated that the strongest reactions between metal and the HFO were generally found at higher pH values (pH > 6.5) (Figure 5.3a and 5.3b). However, the strong reaction between the metal and the surface oxides were still not an efficient competitor for the reactions between the metal and the EDTA molecules. The metal-EDTA complexes seem to be the only dominant species in the soil systems dominated by the EDTA.

The additions of 1.0 M HCl into the EDTA/water system generally did not change the concentrations of the metal-HFO complexes, except at very low pH values, where noticeable decreases were observed for the complexation reactions between the HFO with the Cd and Pb. Although the HFO was inferior to the EDTA molecules in bonding metal cations, its important role as a sink for metals at higher pH systems was not disputable. As was indicated in the models, the HFO exceeded the role of the chloro, hydroxo, and carbonato in bonding metals from the soil solutions at higher pH systems. Among the metals investigated in the present study (Cd, Cu, Pb, and Zn), the Pb appeared to form the strongest reaction with the HFO (Figure 5.3a and 5.3b). Finally, although it was not a definitive result, the abundant concentrations of metals found in the EDTA-forms in comparison to the minute amounts of metals in humate and HFO suggested that metal desorption might have occurred in both solid surfaces of the soils. Large amounts of metals removed from the soils by the EDTA extraction were one indicator supporting the suggestive idea.

The results presented were need to be interpreted in light of the limitations of the input data. Assumptions were made regarding: (1) the bonding strength of the humic substances (we used the complexation constants for oxalate), (2) the amount and strength of the bonds to HFO (values from Dzombak and Morel (1990) were used rather than measured values for our soils), (3) that no other surfaces in the soils (i.e., Al, Mn crystalline and amorphous materials) adsorbed trace metals, and (4) that no ternary complexes between soil surfaces and metal were considered since no data were available. The modeling results give a first-approximate of the likely behavior of a soil in contact with concentrated EDTA.

5.5. Conclusions

When all the required inputs are available, modeling can be satisfactorily used to estimate the chemical equilibrium reactions in soil systems and to compare predictions with the observed experimental data. The MINEQL$^+$ program predicted that the metal EDTA was the dominant form of metal in the EDTA soil extracts. More than 99% of the Cd, Cu, Pb, and Zn were in the form of Cd-EDTA, Cu-EDTA, Pb-EDTA, and Zn-EDTA. The estimations were in a close agreement with the amounts of Cd, Cu, Pb, and Zn retained by the AER from the same soil extracts. The results proved that modeling can be a valuable tool for estimating the potential chemical reactions in soils.

The addition of the 1.0 M HCl dramatically decreased the pH of the EDTA soil-extracts, but it did not significantly affect the Cu, Pb, and Zn-EDTA complexes. Although Cd is the most affected by HCl, its major form remained Cd-EDTA. The output agreed with the widely cited argument that EDTA forms a stable/soluble complex with metal, over a wide range of soil pH. The surface complexation models predicted somewhat unsurprising results. No appreciable amounts of metals were adsorbed by the humate and HFO surfaces.

Table 5.1. Selected characteristics and total metal content of the soils used in the experiments (0-20 cm top layer).

	Total Metals																	
Soils	Cd	Cu	Pb	Zn	Mn	Fe	Ca	Mg	Fe-DC*	Sand	Silt	Clay	$CaCO_3$	Org. C	BS	EC	pH	CEC
	mg kg^{-1}					%				%						µS		cmol(+) kg^{-1}
MB	3.0	60	980	180	655	3.1	9.1	0.78	1.1	71	21	8	11	4.2	100	257	8.0	11.4
RY1	6.3	700	800	2650	517	4.3	18	0.88	1.9	69	24	7	16	2.8	100	444	8.0	9.9
RY2	5.5	800	2200	400	629	6.5	19	0.92	3.2	72	18	10	22	1.7	100	513	8.0	10.1
ZF	182	522	548	14500	5867	3.8	19	2.5	1.1	35	59	6	23	0.6	100	502	8.0	7.3

* Fe extracted by dithionate-citrate method.

Table 5.2. Thermodynamic data used in the calculation.

		Stability constants*							
Species		Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}	Ca^{2+}	Mg^{2+}	Fe^{3+}	Mn^{2+}
Part (A)									
OH^-	-14.00								
HCO_3^-	10.33								
H_2CO_3 (aq)	16.68								
HEDTA	11.12								
H_2EDTA	17.8								
H_3EDTA	21.04								
H_4EDTA	23.76								
H_5EDTA	24.76								
M-EDTA		18.2	20.5	19.8	18.3	12.4	10.6	27.7	15.6
M-HEDTA		21.5	23.9	23.0	21.7	16.0	15.1	29.2	19.1
M-OHEDTA		-	8.6**	-	-	-	-	19.8**	-
MCl		2.0	0.5	1.6	0.4	-	-	1.5	0.6
MCl_2 (aq)		2.6	-	1.8	0.2	-	-	2.1	0.25##
MCl_3		2.4	-	1.7	0.5	-	-	1.13##	-
MOH		-10.1**	-7.7**	-7.7**	-9.0**	-12.85**	-11.44**	-3.2**	-10.6**
$M(OH)_2$ (aq)		-20.4**	-16.2**	-17.1**	-16.9**	-	-	-5.7**	-22.2**
$M(OH)_3$ (aq)		-	-	-	-	-	-	-12.0	-
MCO_3 (aq)		4.5	6.7	6.7***	5.04***	3.2	3.4	9.72 #	4.10 #
$M(CO_3)_2$ (aq)		-	10.2	10.1***	-	-	-	-	-
$MHCO_3$		-	-	-	-	11.59	11.49	-	12.1
Part (B)									
H- & H_2-Humate	4.27 & 1.25								
M-Humate		3.89	6.23	4.91	4.87	3.19	3.42	7.74	3.95
$>Fe^sOH_2^+$ & $>Fe^wOH_2^+$	-7.29								
$>Fe^sOH^o$ & $>Fe^wOH^o$	-8.93						-	-	-
$>Fe^sOM$		0.47	2.89	4.65	0.99	4.97	-	-	-0.4
$>Fe^wOM$		-2.90	0.6	0.3	-1.99	-5.85	-4.6	-	-3.5

* Constants are given as logarithms of the overall formation constant, β, for the complexes. Part A, data are taken from Stumm and Morgan (1996), except for (#) which are taken from Turner et al. (1981) and (##) from Nordstrom et al. (1990). ** Constants are recalculated from OH to H^+ species. *** Constants are recalculated to zero ionic strength. Part B, all humate (or oxalate) data are taken from Martel and Smith (1989, 1982, 1977) and for the HFO, data are taken from Dzombak and Morel (1990). M denotes metal, "s" for strong and "w" for weak.

Table 5.3. Amounts (mg kg^{-1}) of trace metals remaining in the soils after batch extraction of 5 g soil containing 4.8%* EDTA with various properties of extracting solutions.

Soils	Total Metal	1 M HCl/KCl	1 M HCl	0.1 M HCl/KCl	0.1 M HCl	1 M KCl	0.1 MKCl	Water	CCME Standards†	
									Residential	Commercial
					Cadmium				5	20
MB	3.0	1.91 b	1.92 b	1.96 ab	1.96 ab	1.96 ab	1.98 a	1.99 a		
RY1	6.3	1.43 d	1.51 c	1.64 bc	1.67 b	1.72 b	1.85 ab	1.89 a		
RY2	5.5	1.46 cd	1.55 c	1.67 bc	1.71 bc	1.75 b	1.89 a	1.93 a		
ZF	182	46.5 c	47.8 bc	50.8 b	51.3 ab	52.3 ab	55.8 a	56.5 a		
					Copper				100	500
MB	60	20 b	21 b	24 ab	25 a	25 a	26 a	26 a		
RY1	700	194 cd	01 c	220 bc	222 bc	227 b	243 a	245 a		
RY2	800	301 cd	308 c	323 bc	325 bc	330 b	342 a	344 a		
ZF	522	165 cd	171 c	180 b	181 b	183 b	192 a	193 a		
					Lead				500	1000
MB	980	139 d	154 c	176 bc	177 bc	183 b	202 ab	208 a		
RY1	800	236 c	246 bc	53 b	254 b	256 b	270 a	272 a		
RY2	2200	394 e	443 d	476 c	481 c	505 b	564 ab	572 a		
ZF	548	171 bc	177 b	186 ab	187 ab	189 ab	197 a	197 a		
					Zinc				500	1500
MB	180	108 b	109 b	111 ab	111 ab	112 a	113 a	113 a		
RY1	2650	559 e	643 d	710 cd	721 c	765 b	811 a	822 a		
RY2	400	189 b	192 b	197 ab	198 ab	199 a	204 a	206 a		
ZF	14500	6880 e	7030 d	7230 c	7260 bc	7380 b	7510 ab	7540 a		

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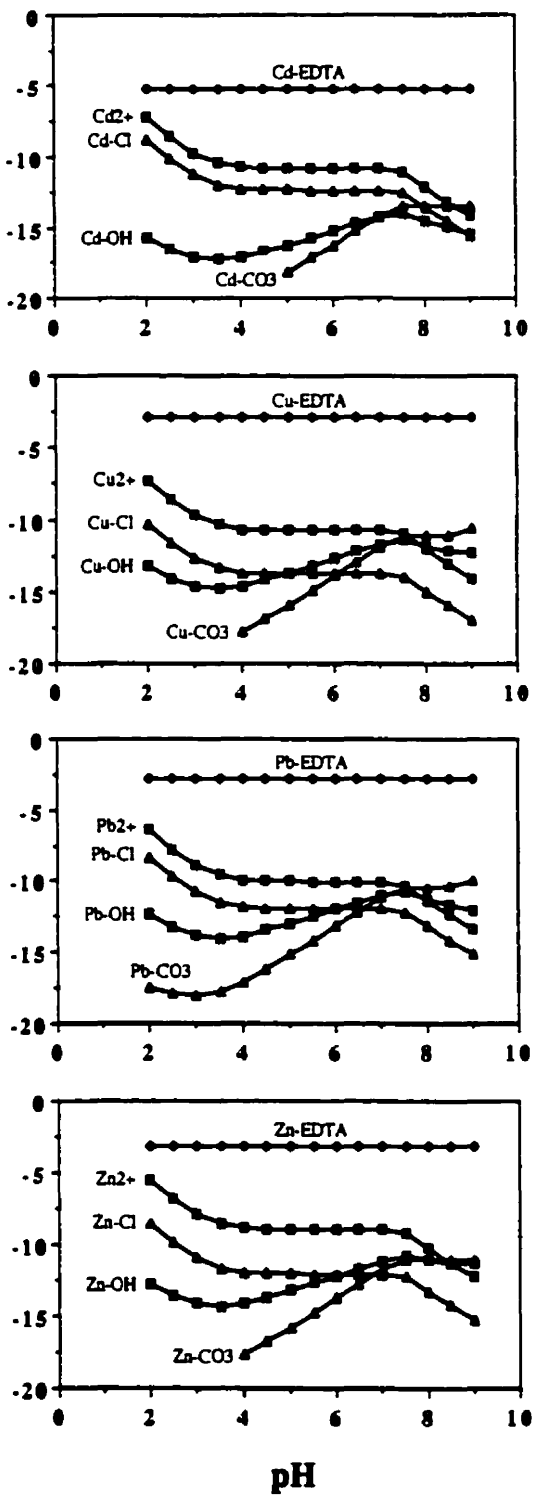
* % from the total weight of soil; † the maximum metal concentration limits for residential or commercial use established by the Canadian Council of Ministers of the Environment (CCME); different letters in the same line indicate significant differences at $p = 0.05$ level.

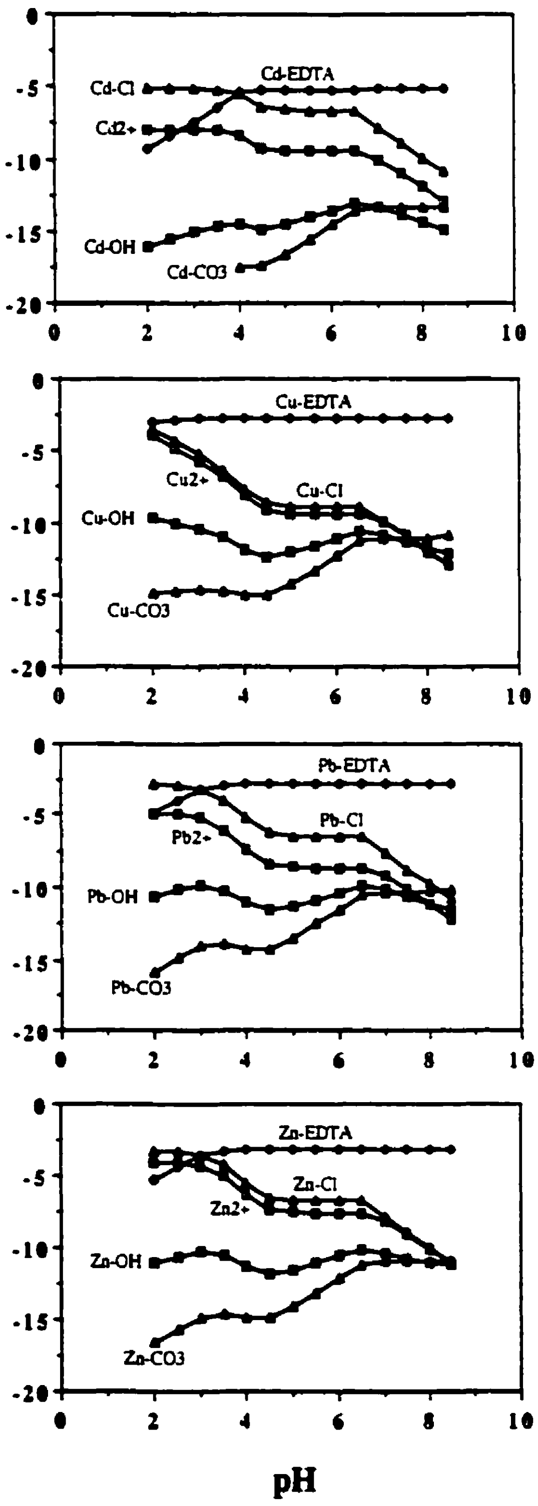
Table 5.4. The dominant metal species (%) of the EDTA soil leachates extracted using two different leaching solutions.

			WATER					1.0 M HCl				
Soils	EDTA (%)	Forms	pH	Cd	Cu	Pb	Zn	pH	Cd	Cu	Pb	Zn
MB	1.2	EDTA	7.90	-------- >99 --------				4.14	80	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							20			
	2.4	EDTA	7.87	-------- >99 --------				4.07	83	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							17			
	4.8	EDTA	7.64	-------- >99 --------				3.54	94	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							6			
RY1	1.2	EDTA	7.96	-------- >99 --------				4.39	81	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							19			
	2.4	EDTA	7.92	-------- >99 --------				4.25	81	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							19			
	4.8	EDTA	7.65	-------- >99 --------				4.11	81	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							19			
RY2	1.2	EDTA	8.01	-------- >99 --------				4.27	72	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							28			
	2.4	EDTA	7.97	-------- >99 --------				4.17	73	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							27			
	4.8	EDTA	7.89	-------- >99 --------				4.14	78	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							22			
ZF	1.2	EDTA	7.95	-------- >99 --------				4.72	60	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							40			
	2.4	EDTA	7.91	-------- >99 --------				4.66	58	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							42			
	4.8	EDTA	7.86	-------- >99 --------				4.52	78	--------- >99 ---------		
		CdCl$_n^{(2-n)}$							22			

Figure 5.1. The log concentrations (molar) of Cd, Cu, Pb, and Zn metal species in the EDTA soil-extracts as predicted by the models. (a) EDTA/Water and (b) EDTA/HCl system.



(a) EDTA/Water



(b) EDTA/HCl

Figure 5.2. Relationships between metal-EDTA complexes adsorbed on the resin and predicted by the MINEQL$^+$ program.

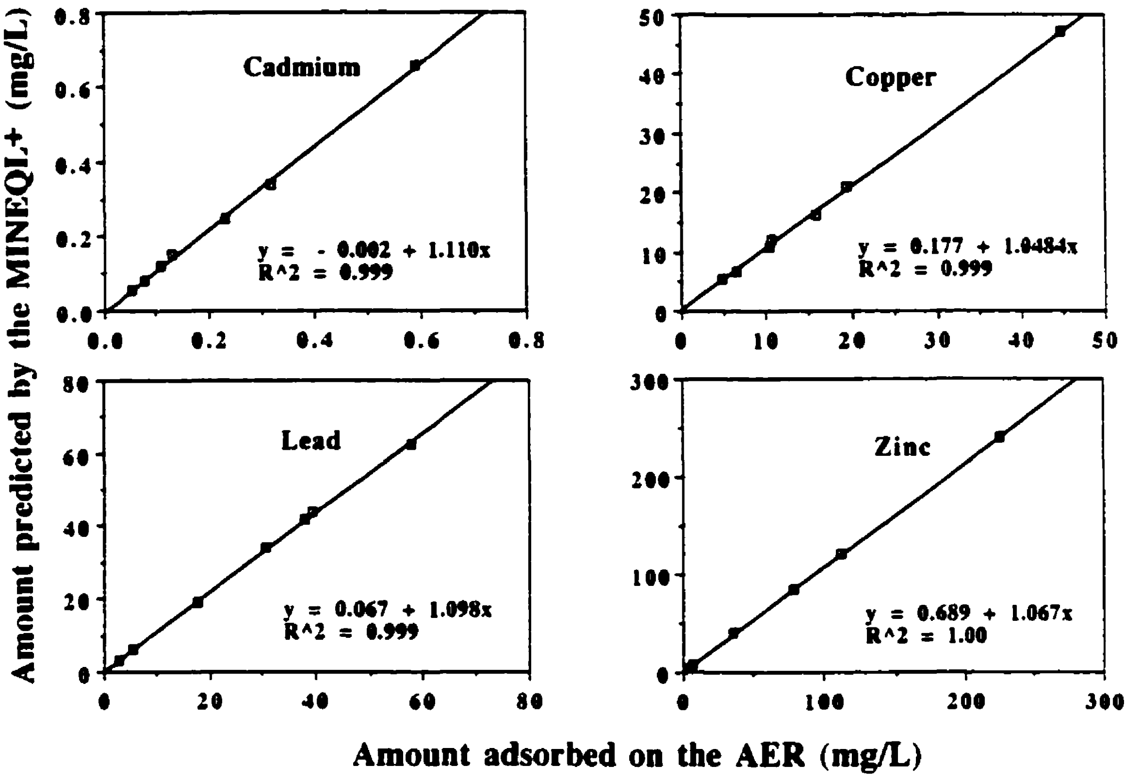
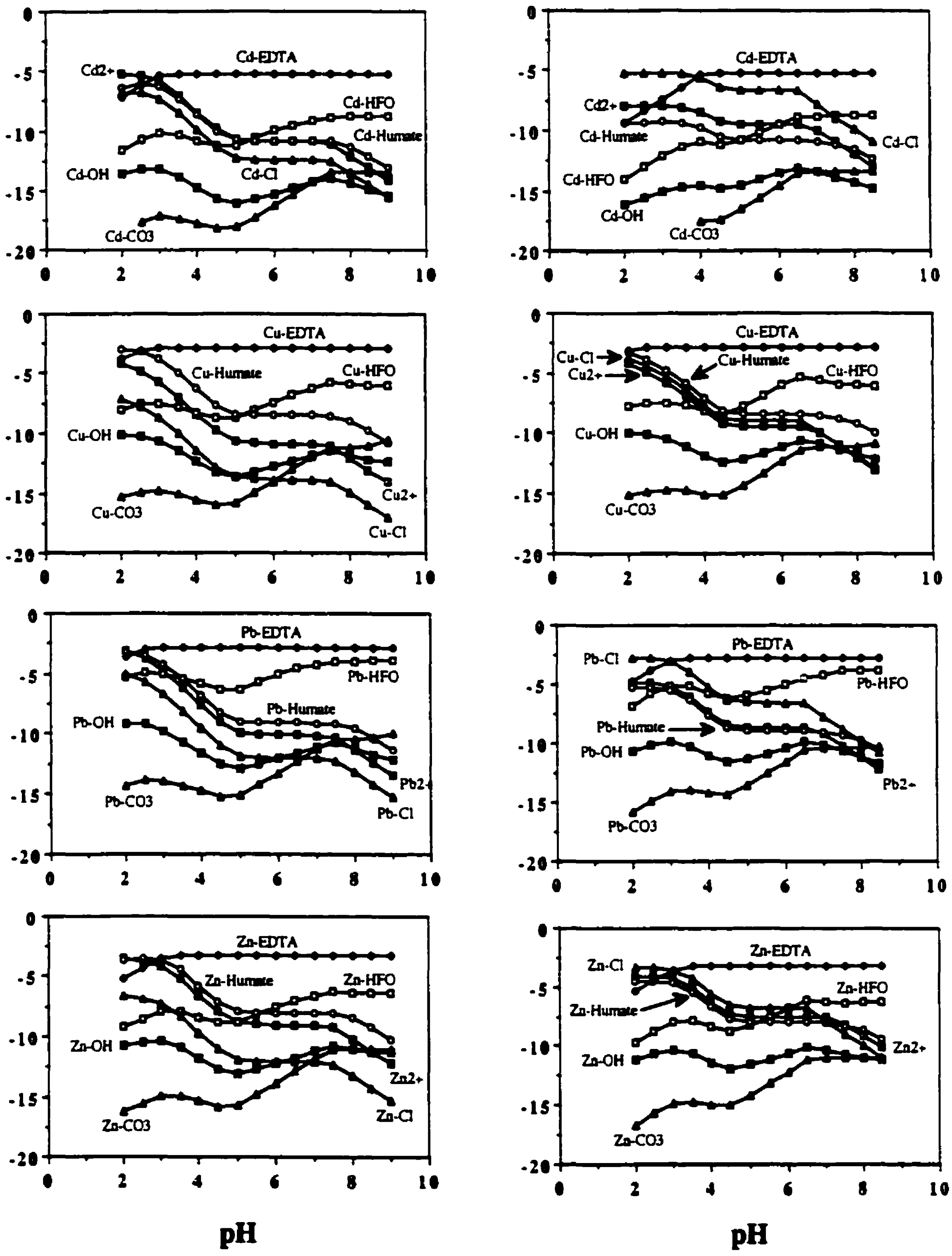

Cadmium
y = - 0.002 + 1.110x
R^2 = 0.999
Copper
y = 0.177 + 1.0484x
R^2 = 0.999
Lead
y = 0.067 + 1.098x
R^2 = 0.999
Zinc
y = 0.689 + 1.067x
R^2 = 1.00
0.0
0.2
0.4
0.6
0.8
0
10
20
30
40
50
0
20
40
60
80
0
100
200
300
Amount predicted by the MINEQL+ (mg/L)
Amount adsorbed on the AER (mg/L)

Figure 5.3. The Cd, Cu, Pb, and Zn metal speciation and reactions with solid surfaces of humate and hydrous ferric oxide (HFO) as predicted by the two-layer model under: (a) the EDTA/water and (b) the EDTA/HCl system (expressed in log concentration, molar).



(a) EDTA/Water

(b) EDTA/HCl

CHAPTER 6

GENERAL CONCLUSIONS AND FUTURE RESEARCH

6.1. Summary and General Conclusions

Metal contaminants in soils can pose a threat to humans and environmental health if they are not remediated satisfactorily. With this reason in mind, a series of experiments was conducted in the Environmental Chemistry Laboratory, McGill University-Macdonald Campus, with the objectives as follows: 1) to determine the feasibility of using a soil washing technique with chelating agents as a means of removing trace metals from contaminated soils, 2) to investigate exchange resins as a means of removing metals from the resulting ligand soil-extracts, and (3) to apply the technique developed for reducing metal contaminants to urban soils so that they can be reused for commercial or residential purposes.

Chapter 1 presented the general literature review, and is intended to provide sufficient review necessary for understanding the concepts discussed in this thesis. This chapter includes a discussion of the theoretical background of trace metal contamination, principles of metal-soil interaction, metal reaction with chelating agents, and resin retention of metal-chelate complexes.

Chapter 2 discusses the ability of the extracting solution to dissolve the metal contaminants in soils. Given that only extractants capable of dissolving large quantities of metals would be suitable for cleaning purposes, HCl and the chelating agent EDTA were chosen and used for the experiment. Our preliminary studies using a batch technique concluded that acid washing with the HCl solution did not remove significant amounts of metals from the soils, therefore, it is not useful in soil remediation. The high buffering capacity of the $CaCO_3$ in the soils may cause the acid washing to be inefficient. The use of more concentrated HCl could increase the amount of metal extracted, but a dramatic increase seems unlikely until the carbonate has been neutralized. Since the goal of soil remediation is to preserve the natural soil properties, the use of concentrated acid in soil washing is undesirable because of negative impacts on the properties of the soil.

In contrast to the hydrochloric acid, batch extraction with EDTA solution (at the same total acidity as the HCl) removed a large amount of metals from the contaminated soils. Up to 10 time more Cd, 27 time more Cu, 59 time more Pb, and 49 time more Zn were removed by the ligand. After leaching two urban soils 12 times with 2.74 mM EDTA, the metal concentrations of urban soil number one (US1) was reduced by 76%, 53%, 49%, and 84% of its total concentrations of Cd, Cu, Pb, and Zn, respectively. The Cu concentration of urban soil number two (US2) was reduced by 35% of its total concentration after leaching with the same amounts of EDTA for 3 times. At the end of the experiment, the US1 is suitable for commercial use whereas the US2 is suitable for both the commercial and residential use.

Chapter 2 also discussed the use of synthetic ion exchange resin to mobilize the dissolved metals from the leachates of EDTA soil-extracts. The chelating resin Chelex-100 was compared to the anion exchange resin AER AG 3-x4 for their ability to remove metal contaminants from the leachates using a batch technique. In contrast to what was expected, Chelex-100 removed less metals from the leachates. However, the results of the experiments with the AER in extracting trace-metals from the EDTA soil-extract were more promising; much higher concentration of metals were removed by the AER from the leachate. For instance at a resin to extract ratio of 1:20, 94% of total Cd, 90% of Cu, 91% of Pb, and 96% of Zn were removed by the AER whereas only 28% of Cd, 34% of Cu, 27% of Pb, and 32% of Zn were removed by the Chelex-100. The apparent ineffectiveness of metal extraction by Chelex-100 results from the relatively higher stability constants for the formation of the metal-EDTA complexes compared to the metal-Chelex complexes. We believed that at the pH value of the extract (8.5) most metals would be in the form of a metal-EDTA complex, a form that is more available for the AER than the Chelex.

Chapter 3 was undertaken to see if the results obtained using the batch method, in removing and recovering metals from contaminated soils, could be repeated using a column. Two chelating agents, EDTA and citrate, were used; different techniques of ligand applications were tested in this experiment. It appears that mixing the chelating agent with the whole soil column and subsequently washing the column with water was found to be the most efficient technique for the addition of reagents to extract trace metals from soils. This method permits the distribution of ligand over the entire soil column insuring more contact between ligand and metals and surfaces of solid particles. Distributing the powder makes the EDTA less concentrated; permits faster solubilization of the reagent (which is only slightly soluble in water), keeps undissolved EDTA to a minimum, and consequently, increases the amounts of metals that can be removed from the column. Mixing citric acid through the soil column retarded the solubilization of the chelate (which is readily soluble in water); allows increased contact between the chelate and the metals and surface solid particles, and, therefore increases metal leaching. It is found that EDTA was superior to citric acid in removing metal contaminants. Up to 27% more Cd, 23% more Cu, 42% more Pb, and 21% more Zn were removed by the EDTA using the technique. The ability of the EDTA to form stronger metal chelates than the corresponding complexes with citrate is the main reason for its superiority. The findings emphasize the importance of choosing the right chelate for the purpose of cleaning soils contaminated by trace metals.

It appears that the addition of the acid/salt solution (1.0 M HCl and 1.0 M KCl) to the EDTA-soil columns enhanced the ability of the EDTA to remove metals from soils. Up to 83% of Cd, 80% Cu, 90% Pb, and 90% Zn were removed by the acid/salt solution treatment as compared to 76% Cd, 74% Cu, 84% Pb, and 84% Zn removed by the water treatment. The beneficial effect of the acid/salt treatment results from the direct effect of the pH of the extracting solution and the effect of the electrolytic ions of K^+ and Cl^- on the solubilization and mobilization of metal ions in the soil (which have been discussed in detail elsewhere).

The use of AER for extracting the metals from the ligand soil-extract is also discussed in Chapter 3. The AER column appears to be an effective method for removing metals from the leachates, and is found to be more effective than the resin batch method discussed earlier. The AER was able to remove metals from both EDTA and citrate metal-ligand complexes and from the extracts with a wide range of pH and salt contents. The findings in this Chapter emphasize the advantages of using a strong chelating agent like EDTA as a means of removing metals from contaminated soils and using the positively charged matrices like the AER to trap the resulting negative charged molecules of the metal-ligand complexes.

The results in Chapter 3 confirmed that metal contaminants can be removed effectively from soils using the column technique. The question remains, however, if removal can also be achieved using larger volumes of soil. To judge this, 2.3 kg samples of soil were mixed thoroughly with 115 g EDTA powder, packed into a column, and washed with water and acid/salt solutions. The objective was to reduce the metal concentrations of the soils to acceptable levels for commercial and/or residential use. This is the focus of the Chapter 4.

The column experiment indicated that the remediation of contaminated soils can be achieved using H_4EDTA alone or with acid/salt solution. Up to 73% Cd, 64% Cu, 81% Pb, and 77% Zn were removed by the EDTA from the soil columns with the acid/salt solution treatment. After undergoing leaching with the acid/salt procedure, the MB, the RY1, and the RY2 sites can be reused for a commercial and/or residential area. However, because of its extremely high Cd and Zn content, the ZF site remains contaminated and remained unsuitable for either commercial or residential use.

Our fractionation studies of the cleaned soils revealed that leaching caused considerable loss of metals from the carbonate and oxide fractions. The findings corroborated that EDTA is a strong extractor for metals in soils; it successfully removes metals from strongly held metal pools in soils. The EDTA technique was advantageous in that: (1) no metal enrichment was observed in the lower sections of the soil profile, (2) the CEC was increased which permitted improved nutrient cation retention in the soil, and (3) the soil pH was improved to the level that is more suitable for plants and soil living organisms.

The preceding chapters focused on qualitative aspects of metal removal by EDTA from four contaminated soils. The usefulness of the technique for other soils can only be speculated on. A quantitative study is necessary to find a way of predicting the behavior of metal and EDTA in other soils. One way of doing this is to use computer modeling, which is the focus of the experiment in Chapter 5.

The results of modeling experiment indicated that the MINEQL+ program can be used as a tool to estimate the possible metal reactions in the soil solution and as an indicator for detecting the presence of chelates in the soil system. The model estimates that the dominant species in the EDTA soil-extracts were in the form of metal-EDTA complexes (in most cases nearly 100%). The estimated amounts were in close agreement with the amount of metals retained by the AER from the same soil extracts.

The model also indicated that the addition of HCl decreased the pH but it did not significantly affect the metal-EDTA species in the system. In addition, the model suggested that the extent of the metal sorption by the humate and hydrous ferric oxide surfaces were insignificant (in comparison to metal-EDTA complexes) so that we consider that metals might be desorbed from these solid surfaces. The high metal concentrations of Cd, Cu, Pb, and Zn (65-86%) removed from the four soils supports the suggestive idea.

6.2. Suggested Future Research

Significant findings have been made in this research. Further studies on the use of the chelating agent and resin techniques for the purpose of leaching metals from contaminated soils should consider the following:

1. Batch and column experiments in the laboratory showed promising results of using EDTA for removing metals from soils and resin for removing metals from the resulting leachate. A small-scale field experiment should be carried out to determine the potential use of the methods for in-situ soil washing.
2. The importance of choosing the right chelate for the right metal is recognized in the experiment. Tests should be carried out using different ligands to identify reagents that can perform more efficiently than EDTA in removing metals from various contaminated soils.
3. The AER removes metals in the form of metal-ligand complexes. Further studies are necessary to separate the complex for recuperation and reuse of the metal and ligand.
4. The successful use of the resin technique in removing metals from ligand soil-extracts is influenced by the forms of metals in the extracts (e.g., free cation or metal-ligand complex). Experiments on the forms of metals in the ligand soil-leachate are necessary to clearly explain the behavioral differences among resins in removing the metals.
5. In our view the best technique to remove metals from soil extracts (containing metal-ligand complexes) is through the complexation with a strong cation exchange resin. The technique removes metals and keeps the ligand in solution for reuse in repeating washing. Research is needed to find resins stronger than the Chelex-100. Also needed are experiments to determine the formation constants of different metal-resin and metal-chelate complexes to enable researchers to choose the right resin for removing metal cations from a particular metal-ligand complex.

6. Chelating agents may adsorb to soil or be lost into the environment through the drainage water. Since the accumulation of chelates could pose a hazard to the environment, future experiments should evaluate the fate of the chelate in the soil and drainage water, and their effects on biota raised in the treated soils.

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APPENDICES

APPENDIX I. EDTA and Metal concentrations* (molar) used in modeling experiments.

Appendix I Part A. EDTA + 1.0 M HCl + 1.0 M KCl treatment.

Soils	pH**	EDTA	Cd	Cu	Pb	Zn	Ca	Mg	Fe	Mn
MB	4.16	8.21E-03	9.34E-07	6.00E-05	4.90E-04	1.07E-04	4.60E-01	3.79E-02	1.58E-02	2.18E-03
	4.05	1.64E-02	1.50E-06	9.00E-05	7.15E-04	1.74E-04	4.93E-01	4.44E-02	2.27E-02	2.73E-03
	3.64	3.28E-02	1.95E-06	1.20E-04	8.12E-04	2.20E-04	5.26E-01	4.81E-02	2.91E-02	3.00E-03
RY1	4.29	8.21E-03	4.94E-06	7.70E-04	1.59E-04	2.37E-03	7.66E-01	4.61E-02	1.88E-02	1.91E-03
	4.28	1.64E-02	7.20E-06	1.13E-03	3.10E-04	4.15E-03	7.76E-01	5.14E-02	2.69E-02	2.46E-03
	4.13	3.28E-02	8.67E-06	1.59E-03	5.45E-04	6.40E-03	7.88E-01	5.64E-02	4.21E-02	2.91E-03
RY2	4.24	8.21E-03	3.25E-06	7.40E-04	9.45E-04	3.02E-04	7.81E-01	4.98E-02	3.58E-02	1.82E-03
	4.19	1.64E-02	5.04E-06	1.15E-03	1.37E-03	5.29E-04	8.43E-01	6.13E-02	5.91E-02	2.28E-03
	4.18	3.28E-02	7.20E-06	1.56E-03	1.74E-03	6.44E-04	9.61E-01	6.87E-02	7.52E-02	2.73E-03
ZF	4.71	8.21E-03	1.31E-04	6.00E-04	1.36E-04	6.49E-03	2.95E-01	8.75E-02	2.78E-02	2.21E-02
	4.67	1.64E-02	1.88E-04	8.00E-04	2.33E-04	1.28E-02	3.19E-01	1.23E-01	3.58E-02	2.57E-02
	4.55	3.28E-02	2.41E-04	1.12E-03	3.64E-04	2.20E-02	3.81E-01	2.30E-01	4.30E-02	2.89E-02

* Metal concentrations in EDTA soil-extracts; ** pH of EDTA soil extracts.

Appendix I Part B. EDTA + 1.0 M HCl treatment.

Soils	pH**	EDTA	Cd	Cu	Pb	Zn	Ca	Mg	Fe	Mn
MB	4.14	8.21E-03	9.08E-07	6.00E-05	4.84E-04	1.04E-04	4.54E-01	3.66E-02	1.42E-02	2.09E-03
	4.07	1.64E-02	1.44E-06	9.00E-05	6.96E-04	1.64E-04	4.83E-01	4.32E-02	1.97E-02	2.55E-03
	3.54	3.28E-02	1.92E-06	1.10E-04	7.97E-04	2.16E-04	5.15E-01	4.69E-02	2.60E-02	2.82E-03
RY1	4.39	8.21E-03	4.88E-06	7.50E-04	1.56E-04	2.32E-03	6.99E-01	4.20E-02	1.43E-02	1.82E-03
	4.25	1.64E-02	7.03E-06	1.09E-03	2.99E-04	3.96E-03	7.49E-01	4.98E-02	2.51E-02	2.18E-03
	4.11	3.28E-02	8.53E-06	1.57E-03	5.35E-04	6.14E-03	7.56E-01	5.43E-02	3.22E-02	2.46E-03
RY2	4.27	8.21E-03	3.17E-06	7.30E-04	9.17E-04	2.96E-04	7.63E-01	4.65E-02	3.04E-02	1.73E-03
	4.17	1.64E-02	4.89E-06	1.12E-03	1.32E-03	5.20E-04	8.21E-01	5.80E-02	4.30E-02	2.28E-03
	4.14	3.28E-02	7.03E-06	1.55E-03	1.70E-03	6.37E-04	9.23E-01	6.25E-02	5.28E-02	2.55E-03
ZF	4.72	8.21E-03	1.29E-04	6.00E-04	1.34E-04	6.44E-03	2.90E-01	8.55E-02	1.79E-02	4.55E-03
	4.66	1.64E-02	1.86E-04	7.90E-04	2.26E-04	1.25E-02	3.10E-01	1.11E-01	2.51E-02	1.45E-02
	4.52	3.28E-02	2.39E-04	1.11E-03	3.58E-04	2.16E-02	3.68E-01	2.12E-01	2.87E-02	2.08E-02

* Metal concentrations in EDTA soil-extracts; ** pH of EDTA soil extracts.

Appendix I Part C. EDTA + 0.1 M HCl + 0.1 M KCl treatment.

Soils	pH**	EDTA	Cd	Cu	Pb	Zn	Ca	Mg	Fe	Mn
MB	7.86	8.21E-03	8.81E-07	6.00E-05	4.72E-04	1.03E-04	6.80E-02	2.63E-03	6.40E-04	8.00E-04
	7.75	1.64E-02	1.40E-06	9.00E-05	6.78E-04	1.60E-04	8.90E-02	3.21E-03	1.06E-03	1.09E-03
	7.56	3.28E-02	1.86E-06	1.10E-04	7.76E-04	2.11E-04	1.17E-01	3.66E-03	1.34E-03	1.29E-03
RY1	7.93	8.21E-03	4.74E-06	7.20E-04	1.52E-04	2.23E-03	8.40E-02	3.33E-03	8.10E-04	5.28E-04
	7.75	1.64E-02	6.81E-06	1.04E-03	2.82E-04	3.79E-03	1.04E-01	3.70E-03	1.24E-03	6.92E-04
	7.60	3.28E-02	8.28E-06	1.51E-03	5.28E-04	5.93E-03	1.65E-01	4.32E-03	1.50E-03	9.28E-04
RY2	7.93	8.21E-03	3.11E-06	7.10E-04	9.00E-04	2.91E-04	8.60E-02	4.77E-03	9.50E-04	8.01E-04
	7.84	1.64E-02	4.72E-06	1.09E-03	1.28E-03	5.06E-04	1.06E-01	5.23E-03	1.24E-03	1.04E-03
	7.81	3.28E-02	6.82E-06	1.50E-03	1.66E-03	6.21E-04	1.70E-01	6.42E-03	1.63E-03	1.16E-03
ZF	7.77	8.21E-03	1.25E-04	5.80E-04	1.31E-04	6.27E-03	6.30E-02	1.50E-02	1.40E-04	1.73E-03
	7.55	1.64E-02	1.80E-04	7.70E-04	2.19E-04	1.23E-02	9.90E-02	1.85E-02	5.90E-04	2.44E-03
	7.53	3.28E-02	2.34E-04	1.08E-03	3.50E-04	2.14E-02	1.42E-01	2.86E-02	1.67E-03	5.02E-03

* Metal concentrations in EDTA soil-extracts; ** pH of EDTA soil extracts.

Appendix I Part D. EDTA + 0.1 M HCl treatment.

Soils	pH**	EDTA	Cd	Cu	Pb	Zn	Ca	Mg	Fe	Mn
MB	7.85	8.21E-03	8.81E-07	6.00E-05	4.70E-04	1.02E-04	6.60E-02	2.51E-03	5.90E-04	7.65E-04
	7.76	1.64E-02	1.40E-06	9.00E-05	6.75E-04	1.59E-04	8.70E-02	3.00E-03	9.80E-04	1.02E-03
	7.56	3.28E-02	1.86E-06	1.10E-04	7.73E-04	2.10E-04	1.15E-01	3.50E-03	1.29E-03	1.18E-03
RY1	7.90	8.21E-03	4.72E-06	7.20E-04	1.52E-04	2.22E-03	7.70E-02	3.09E-03	6.60E-04	4.55E-04
	7.77	1.64E-02	6.78E-06	1.04E-03	2.79E-04	3.76E-03	9.90E-02	3.33E-03	1.22E-03	6.37E-04
	7.62	3.28E-02	8.24E-06	1.50E-03	5.27E-04	5.90E-03	1.45E-01	3.99E-03	1.45E-03	8.19E-04
RY2	7.94	8.21E-03	3.10E-06	7.10E-04	8.97E-04	2.90E-04	7.70E-02	4.65E-03	7.90E-04	7.28E-04
	7.84	1.64E-02	4.68E-06	1.08E-03	1.28E-03	5.05E-04	1.01E-01	4.90E-03	1.18E-03	1.00E-03
	7.79	3.28E-02	6.75E-06	1.50E-03	1.66E-03	6.18E-04	1.52E-01	6.21E-03	1.50E-03	1.09E-03
ZF	7.78	8.21E-03	1.25E-04	5.80E-04	1.31E-04	6.25E-03	6.10E-02	1.44E-02	1.30E-04	1.64E-03
	7.58	1.64E-02	1.80E-04	7.70E-04	2.18E-04	1.20E-02	9.70E-02	1.81E-02	4.70E-04	2.37E-03
	7.54	3.28E-02	2.33E-04	1.07E-03	3.49E-04	2.11E-02	1.40E-01	2.78E-02	1.45E-03	4.64E-03

* Metal concentrations in EDTA soil-extracts; ** pH of EDTA soil extracts.

Appendix 1 Part E. EDTA + 1.0 M KCl treatment.

Soils	pH**	EDTA	Cd	Cu	Pb	Zn	Ca	Mg	Fe	Mn
MB	7.95	8.21E-03	8.72E-07	6.00E-05	4.68E-04	1.02E-04	5.10E-02	8.60E-04	3.40E-04	4.73E-04
	7.89	1.64E-02	1.39E-06	9.00E-05	6.72E-04	1.58E-04	5.90E-02	1.36E-03	6.30E-04	6.92E-04
	7.71	3.28E-02	1.85E-06	1.10E-04	7.69E-04	2.09E-04	6.80E-02	2.18E-03	8.60E-04	8.74E-04
RY1	8.03	8.21E-03	4.66E-06	7.10E-04	1.51E-04	2.17E-03	6.50E-02	1.17E-03	5.60E-04	3.64E-04
	7.99	1.64E-02	6.71E-06	1.03E-03	2.79E-04	3.68E-03	8.40E-02	1.60E-03	7.50E-04	4.55E-04
	7.76	3.28E-02	8.15E-06	1.49E-03	5.25E-04	5.77E-03	9.00E-02	2.49E-03	1.04E-03	5.46E-04
RY2	8.00	8.21E-03	3.07E-06	7.00E-04	8.84E-04	2.88E-04	6.20E-02	2.59E-03	5.90E-04	5.46E-04
	7.99	1.64E-02	4.63E-06	1.07E-03	1.26E-03	5.01E-04	7.30E-02	3.00E-03	8.10E-04	6.37E-04
	7.93	3.28E-02	6.68E-06	1.48E-03	1.64E-03	6.15E-04	9.00E-02	4.44E-03	1.13E-03	8.19E-04
ZF	7.96	8.21E-03	1.23E-04	5.80E-04	1.30E-04	6.21E-03	4.70E-02	5.35E-03	5.00E-05	2.73E-04
	7.93	1.64E-02	1.77E-04	7.60E-04	2.16E-04	1.13E-02	7.10E-02	7.20E-03	3.20E-04	1.09E-03
	7.88	3.28E-02	2.31E-04	1.07E-03	3.46E-04	2.03E-02	9.00E-02	1.16E-02	1.31E-03	3.64E-03

* Metal concentrations in EDTA soil-extracts; ** pH of EDTA soil extracts.

Appendix I Part F. EDTA + 0.1 M KCl treatment.

Soils	pH**	EDTA	Cd	Cu	Pb	Zn	Ca	Mg	Fe	Mn
MB	7.90	8.21E-03	8.54E-07	6.00E-05	4.56E-04	9.96E-05	2.80E-02	7.00E-04	2.50E-04	2.91E-04
	7.88	1.64E-02	1.36E-06	8.00E-05	6.54E-04	1.55E-04	3.80E-02	1.24E-03	5.40E-04	4.55E-04
	7.70	3.28E-02	1.82E-06	1.10E-04	7.51E-04	2.04E-04	4.40E-02	1.57E-03	6.80E-04	5.64E-04
RY1	7.97	8.21E-03	4.52E-06	6.90E-04	1.47E-04	2.12E-03	5.50E-02	1.09E-03	5.00E-04	2.73E-04
	7.92	1.64E-02	6.50E-06	1.00E-03	2.71E-04	3.59E-03	6.800E-02	1.34E-03	7.00E-04	3.64E-04
	7.70	3.28E-02	7.91E-06	1.44E-03	5.12E-04	5.63E-03	7.800E-02	2.24E-03	9.80E-04	5.10E-04
RY2	8.02	8.21E-03	2.95E-06	6.80E-04	8.53E-04	2.83E-04	5.30E-02	2.27E-03	4.80E-04	3.64E-04
	7.96	1.64E-02	4.46E-06	1.04E-03	1.22E-03	4.92E-04	6.70E-02	3.00E-03	6.80E-04	5.46E-04
	7.90	3.28E-02	6.42E-06	1.44E-03	1.58E-03	6.01E-04	7.80E-02	4.20E-03	9.80E-04	6.37E-04
ZF	7.95	8.21E-03	1.20E-04	5.60E-04	1.27E-04	6.17E-03	3.30E-02	4.53E-03	2.00E-05	2.00E-04
	7.90	1.64E-02	1.73E-04	7.40E-04	2.12E-04	1.10E-02	5.50E-02	6.17E-03	2.70E-04	9.65E-04
	7.88	3.28E-02	2.25E-04	1.04E-03	3.39E-04	2.02E-02	7.20E-02	9.79E-02	1.24E-03	3.46E-03

* Metal concentrations in EDTA soil-extracts; ** pH of EDTA soil extracts.

Appendix 1 Part G. EDTA + Water treatment.

Soils	pH**	EDTA	Cd	Cu	Pb	Zn	Ca	Mg	Fe	Mn
MB	7.90	8.21E-03	8.54E-07	5.00E-05	4.54E-04	9.91E-05	2.20E-02	6.40E-04	2.50E-04	2.73E-04
	7.87	1.64E-02	1.35E-06	8.00E-05	6.53E-04	1.54E-04	3.10E-02	1.18E-03	5.20E-04	4.55E-04
	7.64	3.28E-02	1.80E-06	1.10E-04	7.47E-04	2.04E-04	3.50E-02	1.50E-03	6.60E-04	5.46E-04
RY1	7.96	8.21E-03	4.48E-06	6.80E-04	1.47E-04	2.11E-03	5.00E-02	1.03E-03	5.20E-04	2.73E-04
	7.92	1.64E-02	6.45E-06	9.90E-04	2.70E-04	3.57E-03	6.00E-02	1.30E-03	7.00E-04	3.64E-04
	7.65	3.28E-02	7.84E-06	1.43E-03	5.10E-04	5.59E-03	6.70E-02	2.12E-03	9.50E-04	4.55E-04
RY2	8.01	8.21E-03	2.92E-06	6.80E-04	8.49E-04	2.81E-04	4.70E-02	2.08E-03	4.70E-04	3.64E-04
	7.97	1.64E-02	4.40E-06	1.04E-03	1.21E-03	4.89E-04	6.40E-02	2.63E-03	6.40E-04	4.55E-04
	7.89	3.28E-02	6.36E-06	1.44E-03	1.57E-03	6.00E-04	7.20E-02	4.11E-03	9.30E-04	5.46E-04
ZF	7.95	8.21E-03	1.20E-04	5.60E-04	1.27E-04	6.00E-03	2.60E-02	3.60E-03	1.00E-05	1.82E-04
	7.91	1.64E-02	1.72E-04	7.40E-04	2.12E-04	1.15E-02	4.50E-02	5.35E-03	2.30E-04	9.10E-04
	7.86	3.28E-02	2.23E-04	1.03E-03	3.39E-04	2.01E-02	6.50E-02	9.52E-03	1.18E-03	3.46E-03

* Metal concentrations in EDTA soil-extracts; ** pH of EDTA soil extracts.

APPENDIX II. MINEQL$^+$ input data for the metal speciation in soils and soil solutions.

Appendix II Part A. MINEQL$^+$ input data for the metal speciation in soil solutions (RY2) in the presence of EDTA (4.8% or 0.0328 M), water treatment, and pH titration.

TEMPERATURE=25.0 CELSIUS EPS = 1.0E-04

ID	X	LOGX	T	COMPONENTS
2	1.00D-20	-20.00	1.00E-18	H_2O^+
3	1.00D-19	-19.00	1.00E-18	H^+
16	7.24D-04	-3.14	7.20E-02	Ca^{2+}
17	6.31D-08	-7.20	6.36E-06	Cd^{2+}
19	1.00D-05	-5.00	1.00E-03	Cl^-
23	1.00D-20	-20.00	1.00E-18	CO_3^{2-}
30	1.45D-05	-4.84	1.44E-03	Cu^{2+}
33	9.33D-06	-5.03	9.30E-04	Fe^{3+}
41	4.07D-05	-4.39	4.11E-03	Mg^{2+}
42	5.50D-06	-5.26	5.46E-04	Mn^{2+}
53	1.58D-05	-4.80	1.57E-03	Pb^{2+}
84	6.03D-06	-5.22	6.00E-04	Zn^{2+}
93	3.31D-04	-3.48	3.28E-02	$EDTA^{4-}$

ID	Name	LOGK	DELH	SPECIES	TYPE I-COMPONENTS
2	H_2O^+	0.00	0.00	H_2O^+	1
3	H^+	0.00	0.00	H^+	1
16	Ca^{2+}	0.00	0.00	Ca^{2+}	1
17	Cd^{2+}	0.00	0.00	Cd^{2+}	1
19	Cl^-	0.00	0.00	Cl^-	1
23	CO_3^{2-}	0.00	0.00	CO_3^{2-}	1

(Continued)

ID	Name	LOGK	DELH	SPECIES		TYPE I-COMPONENTS
30	Cu^{2+}	0.00	0.00	Cu^{2+}	1	
33	Fe^{3+}	0.00	0.00	Fe^{3+}	1	
41	Mg^{2+}	0.00	0.00	Mg^{2+}	1	
42	Mn^{2+}	0.00	0.00	Mn^{2+}	1	
53	Pb^{2+}	0.00	0.00	Pb^{2+}	1	
84	Zn^{2+}	0.00	0.00	Zn^{2+}	1	
93	$EDTA^{4-}$	0.00	0.00	$EDTA^{4-}$	1	

ID	Name	LOGK	DELH	SPECIES		TYPE II-COMPLEXES					
3800	OH^-	-14.00	13.34	H_2O	1	H^+	-1				
7300	$CaOH^+$	-12.85	14.54	H_2O	1	H^+	-1	Ca^{2+}	1		
7600	$CdOH^+$	-10.10	13.10	H_2O	1	H^+	-1	Cd^{2+}	1		
7700	$Cd(OH)_2AQ$	-20.40	0.00	H_2O	2	H^+	-2	Cd^{2+}	1		
13400	$CuOH^+$	-7.70	0.00	H_2O	1	H^+	-1	Cu^{2+}	1		
13500	$Cu(OH)_2AQ$	-16.20	0.00	H_2O	2	H^+	-2	Cu^{2+}	1		
13600	$CuOHEDTA^{3-}$	+8.60	0.00	H_2O	1	H^+	-1	Cu^{2+}	1	$EDTA^{4-}$	1
14300	$FeOH^{2+}$	-3.20	10.40	H_2O	1	H^+	-1	Fe^{3+}	1		
14400	$Fe(OH)_2^+$	-5.70	0.00	H_2O	2	H^+	-2	Fe^{3+}	1		
14600	$Fe(OH)_3AQ$	-12.00	0.00	H_2O	3	H^+	-3	Fe^{3+}	1		
15000	$FeOHEDTA^{2-}$	+19.80	0.00	H_2O	1	H^+	-1	Fe^{3+}	1	$EDTA^{4-}$	1
17900	$MgOH^+$	-11.44	15.94	H_2O	1	H^+	-1	Mg^{2+}	1		
18000	$MnOH^+$	-10.60	14.40	H_2O	1	H^+	-1	Mn^{2+}	1		
400004	$Mn(OH)_2$	-22.20	0.00	H_2O	2	H^+	-2	Mn^{2+}	1		
18700	$Pb(OH)_2AQ$	-17.10	0.00	H_2O	2	H^+	-2	Pb^{2+}	1		
18800	$PbOH^+$	-7.70	0.00	H_2O	1	H^+	-1	Pb^{2+}	1		
24800	$ZnOH^+$	-9.00	13.40	H_2O	1	H^+	-1	Zn^{2+}	1		
24900	$Zn(OH)_2AQ$	-16.90	0.00	H_2O	2	H^+	-2	Zn^{2+}	1		

(Continued)

ID	Name	LOGK	DELH	SPECIES		TYPE II-COMPLEXES			
28400	$CaHCO_3^+$	+11.59	1.79	H^+	1	Ca^{2+}	1	CO_3^{2-}	1
29100	$CaHEDTA^-$	+16.00	0.00	H^+	1	Ca^{2+}	1	$EDTA^{4-}$	1
29900	$CdHEDTA^-$	+21.50	0.00	H^+	1	Cd^{2+}	1	$EDTA^{4-}$	1
31700	H_2CO_3AQ	+16.68	-2.25	H^+	2	CO_3^{2-}	1		
31800	HCO_3^-	+10.33	-3.62	H^+	1	CO_3^{2-}	1		
32000	$MgHCO_3^+$	+11.49	-2.43	H^+	1	CO_3^{2-}	1	Mg^{2+}	1
32100	$MnHCO_3^+$	+12.10	0.00	H^+	1	CO_3^{2-}	1	Mn^{2+}	1
34800	$CuHEDTA^-$	+23.90	0.00	H^+	1	Cu^{2+}	1	$EDTA^{4-}$	1
36300	FeHEDTA	+29.20	0.00	H^+	1	Fe^{3+}	1	$EDTA^{4-}$	1
37800	$MgHEDTA^-$	+15.10	0.00	H^+	1	Mg^{2+}	1	$EDTA^{4-}$	1
38500	$MnHEDTA^-$	+19.10	0.00	H^+	1	Mn^{2+}	1	$EDTA^{4-}$	1
40700	$PbHEDTA^-$	+23.00	0.00	H^+	1	Pb^{2+}	1	$EDTA^{4-}$	1
45300	$ZnHEDTA^-$	+21.70	0.00	H^+	1	Zn^{2+}	1	$EDTA^{4-}$	1
46800	$HEDTA^{3-}$	+11.12	0.00	H^+	1	$EDTA^{4-}$	1		
46900	H_2EDTA^{2-}	+17.80	0.00	H^+	2	$EDTA^{4-}$	1		
47000	H_4EDTA	+23.76	0.00	H^+	4	$EDTA^{4-}$	1		
47100	H_5EDTA^+	+24.76	0.00	H^+	5	$EDTA^{4-}$	1		
47200	H_3EDTA^-	+21.04	0.00	H^+	3	$EDTA^{4-}$	1		
71800	$CaCO_3AQ$	+3.20	4.03	Ca^{2+}	1	CO_3^{2-}	1		
72700	$CaEDTA^{2-}$	+12.40	0.00	Ca^{2+}	1	$EDTA^{4-}$	1		
74100	$CdCl^+$	+2.00	0.59	Cd^{2+}	1	Cl^-	1		
74200	$CdCl_3^-$	+2.40	3.90	Cd^{2+}	1	Cl^-	3		
74300	$CdCl_2AQ$	+2.60	1.24	Cd^{2+}	1	Cl^-	2		
74800	$CdCO_3AQ$	+4.50	0.00	Cd^{2+}	1	CO_3^{2-}	1		
78900	$CdEDTA^{2-}$	+18.20	0.00	Cd^{2+}	1	$EDTA^{4-}$	1		
89300	$CuCl^+$	+0.50	8.65	Cl^-	1	Cu^{2+}	1		
89700	$FeCl_2^+$	+2.10	0.00	Cl^-	2	Fe^{3+}	1		

(Continued)

ID	Name	LOGK	DELH	SPECIES		TYPE II-COMPLEXES	
89800	$FeCl_3AQ$	+1.13	0.00	Cl^-	3	Fe^{3+}	1
89900	$FeCl^{2+}$	+1.50	5.60	Cl^-	1	Fe^{3+}	1
90100	$MnCl^+$	+0.60	0.00	Cl^-	1	Mn^{2+}	1
90300	$MnCl_2AQ$	+0.25	0.00	Cl^-	2	Mn^{2+}	1
90600	$PbCl_2AQ$	+1.80	1.08	Cl^-	2	Pb^{2+}	1
90700	$PbCl^+$	+1.60	4.38	Cl^-	1	Pb^{2+}	1
90800	$PbCl_3^-$	+1.70	2.17	Cl^-	3	Pb^{2+}	1
91700	$ZnCl_3^-$	+0.50	9.56	Cl^-	3	Zn^{2+}	1
91800	$ZnCl^+$	+0.40	7.79	Cl^-	1	Zn^{2+}	1
92000	$ZnCl_2AQ$	+0.20	8.50	Cl^-	2	Zn^{2+}	1
95100	$CuCO_3AQ$	+6.70	0.00	CO_3^{2-}	1	Cu^{2+}	1
95200	$Cu(CO_3)_2^{2-}$	+10.20	0.00	CO_3^{2-}	2	Cu^{2+}	1
95300	$MgCO_3AQ$	+3.40	2.02	CO_3^{2-}	1	Mg^{2+}	1
95700	$PbCO_3AQ$	+6.72	0.00	CO_3^{2-}	1	Pb^{2+}	1
95800	$Pb(CO_3)_2^{2-}$	+10.06	0.00	CO_3^{2-}	2	Pb^{2+}	1
96200	$ZnCO_3AQ$	+5.04	0.00	CO_3^{2-}	1	Zn^{2+}	1
400001	$FeCO_3^+$	+9.72	0.00	CO_3^{2-}	1	Fe^{3+}	1
400002	$MnCO_3$	+4.10	0.00	CO_3^{2-}	1	Mn^{2+}	1
106900	$CuEDTA^{2-}$	+20.50	0.00	Cu^{2+}	1	$EDTA^{4-}$	1
121400	$FeEDTA^-$	+27.70	0.00	Fe^{3+}	1	$EDTA^{4-}$	1
134100	$MgEDTA^{2-}$	+10.60	0.00	Mg^{2+}	1	$EDTA^{4-}$	1
137200	$MnEDTA^{2-}$	+15.60	0.00	Mn^{2+}	1	$EDTA^{4-}$	1
155100	$PbEDTA^{2-}$	+19.80	0.00	Pb^{2+}	1	$EDTA^{4-}$	1
168400	$ZnEDTA^{2-}$	+18.30	0.00	Zn^{2+}	1	$EDTA^{4-}$	1

Appendix II Part B. MINEQL$^+$ input data for the metal speciation in soils (RY2) in the presence of EDTA (4.8% or 0.0328 M), humate (SOM), and hydrous ferric oxides (HFO), under water treatment and at pH titration.

TEMPERATURE = 25.0 CELCIUS; SOLID CONCENTRATION (g/L) = 9.79E+00; SURFACE AREA (m^2/g) = 6.00E+02; EPS = 1.0E-04

ID	X	LOGX	T	COMPONENTS
2	1.00D-18	-18.00	1.00E-16	H_2O^+
3	1.00D-17	-17.00	1.00E-16	H^+
16	7.24D-04	-3.14	7.20E-02	Ca^{2+}
17	6.46D-08	-7.19	6.36E-06	Cd^{2+}
19	1.00D-05	-5.00	1.00E-03	Cl^-
23	1.00D-18	-18.00	1.00E-16	CO_3^{2-}
30	1.41D-05	-4.85	1.44E-03	Cu^{2+}
33	1.10D-03	-2.96	1.10E-01	Fe^{3+}
41	4.07D-05	-4.39	4.11E-03	Mg^{2+}
42	5.50D-06	-5.26	5.46E-04	Mn^{2+}
53	1.58D-05	-4.80	1.57E-03	Pb^{2+}
84	6.03D-06	-5.22	6.00E-04	Zn^{2+}
93	3.31D-04	-3.48	3.28E-02	EDTA$^+$
98	9.55D-05	-4.02	9.50E-03	Humate
139	1.00D-01	-1.00	1.00E-16	Coul.
140	5.50D-06	-5.26	5.50E-04	Fe(st)OH
141	2.19D-04	-3.66	2.20E-02	Fe(wk)OH

(Continued)

ID	Name	LOGK	DELH	SPECIES	TYPE I-COMPONENTS
2	H_2O^+	0.00	0.00	H_2O^+	1
3	H^+	0.00	0.00	H^+	1
16	Ca^{2+}	0.00	0.00	Ca^{2+}	1
17	Cd^{2+}	0.00	0.00	Cd^{2+}	1
19	Cl^-	0.00	0.00	Cl^-	1
23	CO_3^{2-}	0.00	0.00	CO_3^{2-}	1
30	Cu^{2+}	0.00	0.00	Cu^{2+}	1
33	Fe^{3+}	0.00	0.00	Fe^{3+}	1
41	Mg^{2+}	0.00	0.00	Mg^{2+}	1
42	Mn^{2+}	0.00	0.00	Mn^{2+}	1
53	Pb^{2+}	0.00	0.00	Pb^{2+}	1
84	Zn^{2+}	0.00	0.00	Zn^{2+}	1
93	$EDTA^{4-}$	0.00	0.00	$EDTA^{4-}$	1
98	Humate	0.00	0.00	Humate	1
141	Fe(wk)OH	0.00	0.00	Fe(wk)OH	1
140	Fe(st)OH	0.00	0.00	Fe(st)OH	1

ID	Name	LOGK	DELH	SPECIES		TYPE II-COMPLEXES					
168400	$ZnEDTA^{2-}$	18.30	0.00	Zn^{2+}	1	$EDTA^{4-}$	1				
400016	Fe(wk)OH-MgOH$^+$	-4.60	0.00	H^+	-1	Mg^{2+}	1	Coul.	1	Fe(wk)OH	1
400015	Fe(wk)OH-OHMn$^+$	-3.50	0.00	H^+	-1	Mn^{2+}	1	Coul.	1	Fe(wk)OH	1
400014	Fe(st)OH-MnOH$^+$	-0.40	0.00	H^+	-1	Mn^{2+}	1	Coul.	1	Fe(st)OH	1
400013	MnHumate	+3.95	0.00	Mn^{2+}	1	Humate	1				
400012	MgHumate	+3.42	0.00	Mg^{2+}	1	Humate	1				
400011	CaHumate	+3.19	0.00	Ca^{2+}	1	Humate	1				

(Continued)

ID	Name	LOGK	DELH	SPECIES		TYPE II-COMPLEXES					
400010	ZnHumate	+4.87	0.00	Zn^{2+}	1	Humate	1				
400009	PbHumate	+4.91	0.00	Pb^{2+}	1	Humate	1				
400008	H_2Humate	+1.25	0.00	H^+	2	Humate	1				
400007	$FeCO_3^+$	+9.72	0.00	CO_3^{2-}	1	Fe^{3+}	1				
400006	$MnCO_3$	+4.10	0.00	CO_3^{2-}	1	Mn^{2+}	1				
400005	$Mn(OH)_2$	-22.2	0.00	H_2O	2	H^+	-2	Mn^{2+}	1		
3800	OH^-	-14.00	13.34	H_2O	1	H^+	-1				
7300	$CaOH^+$	-12.85	14.54	H_2O	1	H^+	-1	Ca^{2+}	1		
7600	$CdOH^+$	-10.10	13.10	H_2O	1	H^+	-1	Cd^{2+}	1		
7700	$Cd(OH)_2$AQ	-20.40	0.00	H_2O	2	H^+	-2	Cd^{2+}	1		
13400	$CuOH^+$	-7.70	0.00	H_2O	1	H^+	-1	Cu^{2+}	1		
13500	$Cu(OH)_2$AQ	-16.20	0.00	H_2O	2	H^+	-2	Cu^{2+}	1		
13600	$CuOHEDTA^{3-}$	+8.60	0.00	H_2O	1	H^+	-1	Cu^{2+}	1	$EDTA^{4-}$	1
14300	$FeOH^{2+}$	-3.20	10.40	H_2O	1	H^+	-1	Fe^{3+}	1		
14400	$Fe(OH)_2^+$	-5.70	0.00	H_2O	2	H^+	-2	Fe^{3+}	1		
14600	$Fe(OH)_3$AQ	-12.00	0.00	H_2O	3	H^+	-3	Fe^{3+}	1		
15000	$FeOHEDTA^{2-}$	+19.80	0.00	H_2O	1	H^+	-1	Fe^{3+}	1	$EDTA^{4-}$	1
17900	$MgOH^+$	-11.44	15.94	H_2O	1	H^+	-1	Mg^{2+}	1		
18000	$MnOH^+$	-10.60	14.40	H_2O	1	H^+	-1	Mn^{2+}	1		
18700	$Pb(OH)_2$AQ	-17.10	0.00	H_2O	2	H^+	-2	Pb^{2+}	1		
18800	$PbOH^+$	-7.70	0.00	H_2O	1	H^+	-1	Pb^{2+}	1		
24800	$ZnOH^+$	-9.00	13.40	H_2O	1	H^+	-1	Zn^{2+}	1		
24900	$Zn(OH)_2$AQ	-16.90	0.00	H_2O	2	H^+	-2	Zn^{2+}	1		
28400	$CaHCO_3^+$	+11.59	1.79	H^+	1	Ca^{2+}	1	CO_3^{2-}	1		
29100	$CaHEDTA^-$	+16.00	0.00	H^+	1	Ca^{2+}	1	$EDTA^{4-}$	1		
250600	Fe(wk)OCa^+	-5.85	0.00	H^+	-1	Ca^{2+}	1	Coul.	1	Fe(wk)OH	1
29900	$CdHEDTA^-$	+21.50	0.00	H^+	1	Cd^{2+}	1	$EDTA^{4-}$	1		

(Continued)

ID	Name	LOGK	DELH	SPECIES		TYPE II-COMPLEXES					
251400	$Fe(st)OCd^+$	+0.47	0.00	H^+	-1	Cd^{2+}	1	Coul.	1	Fe(st)OH	1
251500	$Fe(wk)OCd^+$	-2.90	0.00	H^+	-1	Cd^{2+}	1	Coul.	1	Fe(wk)OH	1
31700	H_2CO_3AQ	+16.68	-2.25	H^+	2	CO_3^{2-}	1				
31800	HCO_3^-	+10.33	-3.62	H^+	1	CO_3^{2-}	1				
32000	$MgHCO_3^+$	+11.49	-2.43	H^+	1	CO_3^{2-}	1	Mg^{2+}	1		
32100	$MnHCO_3^+$	+12.10	0.00	H^+	1	CO_3^{2-}	1	Mn^{2+}	1		
34800	$CuHEDTA^-$	+23.90	0.00	H^+	1	Cu^{2+}	1	$EDTA^{4-}$	1		
251000	$Fe(st)OCu^+$	+2.89	0.00	H^+	-1	Cu^{2+}	1	Coul.	1	Fe(st)OH	1
251100	$Fe(wk)OCu^+$	+0.60	0.00	H^+	-1	Cu^{2+}	1	Coul.	1	Fe(wk)OH	1
36300	FeHEDTA	+29.20	0.00	H^+	1	Fe^{3+}	1	$EDTA^{4-}$	1		
37800	$MgHEDTA^-$	+15.10	0.00	H^+	1	Mg^{2+}	1	$EDTA^{4-}$	1		
38500	$MnHEDTA^-$	+19.10	0.00	H^+	1	Mn^{2+}	1	$EDTA^{4-}$	1		
40700	$PbHEDTA^-$	+23.00	0.00	H^+	1	Pb^{2+}	1	$EDTA^{4-}$	1		
252200	$Fe(st)OPb^+$	+4.65	0.00	H^+	-1	Pb^{2+}	1	Coul.	1	Fe(st)OH	1
252300	$Fe(wk)OPb^+$	+0.30	0.00	H^+	-1	Pb^{2+}	1	Coul.	1	Fe(wk)OH	1
45300	$ZnHEDTA^-$	+21.70	0.00	H^+	1	Zn^{2+}	1	$EDTA^{4-}$	1		
251600	$Fe(st)OZn^+$	+0.99	0.00	H^+	-1	Zn^{2+}	1	Coul.	1	Fe(st)OH	1
251700	$Fe(wk)OZn^+$	-1.99	0.00	H^+	-1	Zn^{2+}	1	Coul.	1	Fe(wk)OH	1
46800	$HEDTA^{3-}$	+11.12	0.00	H^+	1	$EDTA^{4-}$	1				
46900	H_2EDTA^{2-}	+17.80	0.00	H^+	2	$EDTA^{4-}$	1				
47000	H_4EDTA	+23.76	0.00	H^+	4	$EDTA^{4-}$	1				
47100	H_5EDTA^+	+24.76	0.00	H^+	5	$EDTA^{4-}$	1				
47200	H_3EDTA^-	+21.04	0.00	H^+	3	$EDTA^{4-}$	1				
47800	$HHumate^-$	+4.27	0.00	H^+	1	Humate	1				
250100	$Fe(st)OH_2^+$	+7.29	0.00	H^+	1	Coul.	1	Fe(st)OH	1		
250300	$Fe(st)O^-$	-8.93	0.00	H^+	-1	Coul.	-1	Fe(st)OH	1		
250200	$Fe(wk)OH_2^+$	+7.29	0.00	H^+	1	Coul.	1	Fe(wk)OH	1		

(Continued)

ID	Name	LOGK	DELH	SPECIES		TYPE II-COMPLEXES			
250400	$Fe(wk)O^-$	-8.93	0.00	H^+	-1	Coul.	-1	Fe(wk)OH	1
71800	$CaCO_3AQ$	+3.20	4.03	Ca^{2+}	1	CO_3^{2-}	1		
72700	$CaEDTA^{2-}$	+12.40	0.00	Ca^{2+}	1	$EDTA^{4-}$	1		
74100	$CdCl^+$	+2.00	0.59	Cd^{2+}	1	Cl^-	1		
74200	$CdCl_3^-$	+2.40	3.90	Cd^{2+}	1	Cl^-	3		
74300	$CdCl_2AQ$	+2.60	1.24	Cd^{2+}	1	Cl^-	2		
74800	$CdCO_3AQ$	+4.50	0.00	Cd^{2+}	1	CO_3^{2-}	1		
78900	$CdEDTA^{2-}$	+18.20	0.00	Cd^{2+}	1	$EDTA^{4-}$	1		
79400	CdHumate	+3.89	0.00	Cd^{2+}	1	Humate	1		
89300	$CuCl^+$	+0.50	8.65	Cl^-	1	Cu^{2+}	1		
89700	$FeCl_2^+$	+2.10	0.00	Cl^-	2	Fe^{3+}	1		
89800	$FeCl_3AQ$	+1.13	0.00	Cl^-	3	Fe^{3+}	1		
89900	$FeCl^{2+}$	+1.50	5.60	Cl^-	1	Fe^{3+}	1		
90100	$MnCl^+$	+0.60	0.00	Cl^-	1	Mn^{2+}	1		
90300	$MnCl_2AQ$	+0.25	0.00	Cl^-	2	Mn^{2+}	1		
90600	$PbCl_2AQ$	+1.80	1.08	Cl^-	2	Pb^{2+}	1		
90700	$PbCl^+$	+1.60	4.38	Cl^-	1	Pb^{2+}	1		
90800	$PbCl_3^-$	+1.70	2.17	Cl^-	3	Pb^{2+}	1		
91700	$ZnCl_3^-$	+0.50	9.56	Cl^-	3	Zn^{2+}	1		
91800	$ZnCl^+$	+0.40	7.79	Cl^-	1	Zn^{2+}	1		
92000	$ZnCl_2AQ$	+0.20	8.50	Cl^-	2	Zn^{2+}	1		
95100	$CuCO_3AQ$	+6.70	0.00	CO_3^{2-}	1	Cu^{2+}	1		
95200	$Cu(CO_3)_2^{2-}$	+10.20	0.00	CO_3^{2-}	2	Cu^{2+}	1		
95300	$MgCO_3AQ$	+3.40	2.02	CO_3^{2-}	1	Mg^{2+}	1		
95700	$PbCO_3AQ$	+6.72	0.00	CO_3^{2-}	1	Pb^{2+}	1		
95800	$Pb(CO_3)_2^{2-}$	+10.06	0.00	CO_3^{2-}	2	Pb^{2+}	1		
96200	$ZnCO_3AQ$	+5.04	0.00	CO_3^{2-}	1	Zn^{2+}	1		

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ID	Name	LOGK	DELH	SPECIES		TYPE II-COMPLEXES	
106900	$CuEDTA^{2-}$	+20.50	0.00	Cu^{2+}	1	$EDTA^{4-}$	1
107300	CuHumate	+6.23	0.00	Cu^{2+}	1	Humate	1
121400	$FeEDTA^{-}$	+27.70	0.00	Fe^{3+}	1	$EDTA^{4-}$	1
121600	$FeHumate^{+}$	+7.74	0.00	Fe^{3+}	1	Humate	1
134100	$MgEDTA^{2-}$	+10.60	0.00	Mg^{2+}	1	$EDTA^{4-}$	1
137200	$MnEDTA^{2-}$	+15.60	0.00	Mn^{2+}	1	$EDTA^{4-}$	1
155100	$PbEDTA^{2-}$	+19.80	0.00	Pb^{2+}	1	$EDTA^{4-}$	1