Heavy Metal Removal from Soil by Complexing Reagents with Recycling of Complexing Reagents

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Abstract

Heavy metals in the environment are a source of some concern because of their potential reactivity, toxicity, and mobility in the soil. Soil contamination by metals is placing human and environmental health at risk through possible contamination of food chain.

Soil washing can be used to remove metals from the soil. Chemical treatment involves the addition of extraction agents that react with the contaminant and leach it from the soil. The liquid, containing the contaminants, is separated from the soil resulting in a clean solid phase. Six chelating reagents, EDTA, Citric acid, ADA, DTPA, SCMC, and DPTA, were employed to determine the relative extraction efficiencies of the six chelating reagents for the target metals. Recycling of chelating reagent was the main interest of this study. The experiments were divided into four parts: (1) preliminary studies on the preparation and characterization of soil that included grinding, sieving, soil texture measurements, total metals content post digestion and the distribution of metals in different soil fractions as well as (2) a comparison of the extraction efficiencies of six chelating reagents toward Cu, Pb, Zn, Fe, and Mn. Additionally, the chelating reagent was liberated and recycled by treatment of the metal-complexes with disodium diethyl dithiocarbomate (DEDTC). Additionally, supercritical CO_2 was used to extract metal-DEDTC complexes using various surfactants to maintain the metal-DEDTC complexes in suspension. Finally, (4) magnesium metal was evaluated as an alternative method for liberating the water-soluble chelating reagent from the complex so as to be able to recycle this reagent as well.

The different approaches were promising in terms of recycling the chelating reagents that suggests a means of optimizing the experimental conditions in future applications.

RÉSUMÉ

La présence de métaux lourds dans l'environnement est une source d'inquétude à cause de leur réactivité potentielle, leur toxicité,et de leur mobilité dans le sol. La contamination du sol par ces métaux met donc à risque non seulment l'environnement mais aussi la santé de l'homme.

Le lavage du sol peut être utilisé pour enlever les métaux contaminant du sol. Ce lavage se fait par le traitement chimique impliquant l'addition d'agents d'extraction qui réagissent avec le produit contaminant en l'extrayant du sol. Le liquide contaminé est alors séparé de la phase solide, le sol, dit propre. Six agents connus sont utilisés pour l'extraction de ces métaux: EDTA, Acid citrique, DTPA, SCMC, ADA et DPTA. Le recyclage de ces agents dit de chélation est l'intérêt pricipal de cette étude. Les expériences ont été divisées en quatre parties: (1) L'étude préliminaire sur la préparation et la charactérisation du sol, incluant le 'griding', le 'sieving', la texture du sol, le contenu total des métaux post-digestion, et la distribution de ces métaux dans les différentes fractions du sol. (2) La comparaison de l'efficacité d'extraction des six agents de chélation face aux éléments suivants: le plomb, le cuivre, le zinc, le fer et le manganèse. Les agents de chélation ont été recyclés en traitant les complexes-métaux avec du DEDTC (disodium diethyldithiocarbomate). (3) L'utilisation du CO_2 supercritique pour l'extraction des complexes-métaux en utilisant des surfactants pour maintenir les complexes métaux/DEDTCen suspension. (4) L'évaluation de l'utilisation du magnésium comme méthode alternative pour la libération de l'agent de chélation soluble dans l'eau et permettre son recyclage.

Ces différentes approches ont démontré des résultats prometteurs pour le recyclage des agents de chélation, ce qui suggère la possibitité d'optimiser ces conditions expérimentales pour des applications futures.

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CHAPTER I INTRODUCTION AND LITERATURE REVIEW

Over the past decades, soil contamination has emerged as a key global environmental issue. It has become increasingly apparent that soil contamination is placing human and environmental health at risk principally through contaminating our food chain. The reasons for soil contamination are diverse. Coal tar pits, mine tailing wastes, landfill sites, accidental waste water discharges and the addition of excess fertilizers and sewage sludge to arable lands and pesticide usage all contribute to soil contamination. In addition, atmospheric deposition also represents an important source of contamination. The array of contaminants to be addressed (toxic trace metals, excess nutrients, volatile and non-volatile organic toxicants and radioactive isotopes is both large and diverse in scope.

Heavy metals in the environment are a source of concern because of their potential reactivity, toxicity, and mobility in the soil. Some heavy metals (e.g., Cu and Zn) are essential for plant and animal health. Other metals (including Fe and Mg), are not considered to pose a threat since both elements are already present, in much larger amounts in the soil, than are added in wastes. However, at environmental concentrations above that necessary to sustain life, toxic effects can occur. Other heavy metals (e.g., Cd and Pb) are not considered to be essential to plants. Toxic effects can become apparent when these metals become concentrated above background levels in the environment.

Definition of heavy metals

The term "heavy metals", which is in common use, refers to metals with a density greater than a specific value, usually 5 or 6g cm^{-3} (Wild, 1993). Often, it refers to metals discharged by industry of which the metalloid arsenic, As; cadmium, Cd; chromium, Cr; copper, Cu; lead, Pb; mercury, Hg; nickel, Ni; and zinc, Zn, are listed by a European Commission directive as representing the greatest hazard to plants or animals. As used in this thesis, the term heavy metals refers to hazardous metals, usually of high density, whatever their source. The term "hazardous elements" is used where both metals and non-metals are to be described.

Hazardous elements in soils

The concentrations in the Earth's crust (including soils) of elements considered to a hazard are provided in Table 1.1. Metal concentrations differ greatly between different rock types; because these parent materials influence soil properties; their concentrations in soils also vary greatly.

Table 1.1 Average Concentrations of Some Hazardous Metals

Metal	Earth's crust (μg/g)	Rocks with highest concentration	Soils (μg/g)	Soils[a] (kg/ha)
As	1.5	shales and clays	0.1-50	0.2-100
Cd	0.1	shales and clays	0.01-2.4	.02-4.8
Cr	100	ultrabasic	5-1500	10-3000
Cu	50	basic	2-250	4-500
Hg	0.05	sandstones	0.01-0.3	0.02-0.6
Ni	80	ultrabasic	2-1000	4-2000
Pb	14	granite	2-300	4-600
Zn	75	Shales and clays	10-300	20-600

[a]Quantity of metal per hectare calculated for a soil depth of 15 cm and a bulk density of 1.3 (approximate mass 2000 t).

Source: Adapted from Alloway, B.J. (ed.) 1990. *Heavy Metals in soils*. Blackie, Glasgow.

The effects of emissions from industry (Table 1.2) depend on their chemical nature. Solid waste from the mining of metal ores and processing operations has a local effect whereas emissions into the atmosphere from metal refineries can contaminate large areas of land. Similarly, the metals in sewage sludge become more widely distributed on agricultural lands than if the same sludge is disposed within landfill sites.

Table 1.2 Annual Release of Metals into the Environment in the United Kingdom

	Cd	Cu	Ni	Pb	Zn
Total release (t/a)	754	15800	14800	51700	85000
Contribution to total release(%) from industry	25	23	27	33	31
Municipal waste disposal	67	65	71	65	64
Domestic	1	4	<1	<1	1
Urban run-off	<1	<1	<1	<1	<1
Agriculture	5	5	<1	<1	1
Dredging soil	1	3	1	1	2
Total release received in land fill sites (%)	83	84	91	81	88

Source: data of Critchley and Agg, quoted by Beckett, P.H.T. 1989. In *Inorganic Contaminants in the Vadose Zone* (eds b. Bar-Yosef, N.J. Barrow and J. Goldschmidt), pp. 159-75, Springer-Verlag, Berlin.

1.1 Metal Speciation and Metal Fractions In Soil

It was indicated that metals are present in soil in an extremely wide range of different forms. Factors affecting heavy metal retention by soils include solution pH, soil type and horizon, cation exchange capacity (CEC), natural organic matter, age of contamination, and the presence of other inorganic contaminants. Metal mobility is also influenced by the organic fraction in the soil as well as the clay and metal oxide content in the subsoil because these soil constituents have appreciable CECs.

A vast amount of effort has been expended in attempting to quantify metals held in different soil fractions, particularly those fractions that are thought to be mobile and bioavailable, since these fractions can potentially leach to pollute groundwater or can be transferred into food chains as a result of plant uptake.

A. Characterization by the physical properties of soil

Particle size distribution can influence the level of metal contamination in a soil. Fine particles, such as silts and clays, (<100 μm) have a greater surface area than coarser materials. Somewhat coarser soil particles are often characterized by surface irregularities enhanced by weathering, inorganic salt precipitation, and oxide formation. This uneven and somewhat porous surface can provide a favorable environment for surface deposition. As a result, the fine fraction of a soil often contains the majority of the total contamination. The distribution of particle sizes with which a metal contaminant is associated can determine the effectiveness of a number of metal remediation technologies, e.g., soil washing (Dzombak *et al.*, 1994)

Soil moisture influences the chemistry of contaminated soil. The amount of dissolved minerals, pH and redox potential of the soil water system depends on the soil's moisture content. Soil structure describes the size, shape, arrangement and degree of development of soils into structural units. Soil structure can influence contaminant mobility by limiting the degree of contact between groundwater and contaminants.

B. Characterization by physical or chemical reaction principles

The heavy metals in soil can occur in any of the following forms:

a. Soluble: as free ions, or as soluble complexes with inorganic anions or organic ligands. Note that chloride and sulphate ions tend to complex more strongly than does nitrate ion, and soluble organic anions complex more strongly with cation than does chloride ion. Among organic ligands, there are certain sites that interact with trace metals or simple cations with comparable affinities, and other sites where the metal complexation is appreciably stronger.
b. Exchangeable: held by predominantly electrostatic forces to negatively charged sites on clays, other minerals or organic matter, or to amorphous materials with a low pH of zero net charge. Apparently, the activation energy of exchange must be low, because this exchange reaction is usually rapid and complete.
c. Specific adsorption: held at sites (usually presumed to be inorganic) at which one element, or transition elements more generally, is retained relatively strongly by

predominantly covalent or co-ordinate forces. An ion held in this way is taken up and released more slowly than the same ion that interacts with solid materials via exchange processes.

d. Retained on insoluble organic materials: this category includes trace metal cation(s) in, or immobilized on biological or inactivated materials. It consists mainly of cations complexed to or chelated with organic materials, which have been either synthesized recently or represent recalcitrant residues from microbial metabolism.

e. Retained on or occluded within, oxides of iron, aluminium, or manganese: these oxides are rarely pure. They usually exist as a mix of oxides of these cations and probably other cations as well. Iron and manganese oxides have also been further sub-classified into "easily", "moderately", or "difficultly reducible" fractions according to the reagents that are required to dissolve them. The ease of release of occluded heavy metal cations is considered to depend on the solubility of the oxide(s) that contain them.

The chemical form and speciation of some important metals found at contaminated sites are discussed below. The influence of the chemical form on the fate and mobility of these compounds is also discussed.

Lead

The primary industrial sources of lead (Pb) contamination include metal smelting and processing, secondary metals production, and lead battery manufacture, pigment and chemical manufacture and lead-contaminated wastes. Widespread contamination resulting from the former use of lead as a gasoline additive is also of concern. Lead released to groundwater, surface water and land is usually in the form of elemental lead, lead oxides and hydroxides (Smith et al.1995). Lead occurs most commonly with an oxidation state of 0 or +2. Pb(II) is the more common and reactive form of lead and forms mononuclear and polynuclear oxides and hydroxides. Under most conditions, Pb^{2+} and lead-hydroxy complexes are the most stable forms of lead (Smith et al., 1995). Low solubility compounds are formed by complexation with inorganic ions (Cl^-, CO_3^{2-}, SO_4^{2-} or PO_4^{3-}) and organic ligands (humic and fulvic acids, EDTA, amino acids). Lead carbonate solids form above pH6 and PbS is the most stable solid when elevated sulfide concentrations are present under reducing conditions. Most lead that is released to the environment is retained in the soil (Evans, 1994). The primary processes that influences the fate of lead in soil include adsorption, ion exchange, precipitation and complexation with sorbed organic matter. These processes limit the amount of lead that can be transported into the surface water or groundwater. The relatively volatile organolead compounds, tetraalkyl leads, may form in anaerobic sediments as a result of methylation mediated by microorgnanisms (Smith et al., 1995).

Zinc

Zinc (Zn) does not occur naturally in its elemental form. It is usually extracted from mineral ores to form zinc oxide. The primary industrial use for Zinc is as a corrosion-resistant coating for iron or steel (Smith et al. 1995). Zinc usually occurs in the +2 oxidation state and forms complexes with a variety of anions, amino acids and organic acids. Zn may precipitate as $Zn(OH)_2$, $ZnCO_3$, ZnS, or $Zn(CN)_2$

Copper

Copper (Cu) is mined as a primary ~~ore~~ product from copper sulfide and oxide ores. Mining activities are the major source of copper contamination. In aerobic, sufficiently alkaline systems, $CuCO_3$ is the dominant soluble copper species. The cupric ion, Cu^{2+}, and hydroxide complexes, $Cu(OH)_2$, are also species that are commonly present. Copper forms strong complexes in solution with humic acids. The affinity of Cu for humates is increased as the pH is increases and the ionic strength is decreased. In anaerobic environments, if sufficient sulfur is present, CuS is formed. Copper mobility is decreased by sorption to mineral surfaces. Cu^{2+} sorbs strongly to mineral surfaces over a wide range of pH values (Dzombak and Morel, 1990). The cupric ion (Cu^{2+}) is the most toxic species of copper. Copper toxicity has also been demonstrated for $CuOH^+$ and $Cu_2(OH)^{2+}$ (Lagrega et al., 1994).

Iron (Fe) and Manganese (Mn)

Iron and manganese do not constitute a problem, since both elements are already present much larger amounts in the soil than are added in wastes. If the added manganese were to present a problem by becoming soluble, then so would the native manganese under the same conditions (G.W.Leeper,1985).

1.2 Influence of Soil Properties on Mobility

McBride (1989) suggested that a valuable approach to assess the mobility of metals in soils would be with a clear understanding of the soil properties and condition that affect their long- and short-term fates in soils. Chemical and physical properties of the contaminated matrix influence the mobility of metals in soil. Contamination exists in three forms in the soil matrix: solubilized contaminants within the soil solution phase, adsorbed contaminants on soil surfaces, and contaminants fixed chemically as solid compounds.

Soil pH values generally range between 4.0 and 8.5 with buffering by Al at low pH and by $CaCO_3$ at high pH (Wild, 1988). Metal cations are most mobile under acidic conditions whereas anions tend to sorb to oxide minerals in this pH range (Dzombak and Morel, 1987). At higher pHs, cations precipitate or adsorb to mineral surfaces and metal anions are mobilized. The presence of hydrous metal oxides of Fe, Al, Mn can influence metal concentrations appreciably because these minerals can remove cations and anions from solution by ion exchange, specific adsorption and surface precipitation (Ellis and Fogg, 1985; Dzombak and Morel, 1987). Sorption of metal cations onto hydrous oxides generally increases sharply with increasing pH and is most appreciable at pH values above the neutral range, while sorption of metal anions is greatest at low pH and decreases as pH is increased. Cation exchange capacity (CEC) refers to the concentration of readily exchangeable cations on a mineral surface and is often used to indicate the affinity of soils for uptake of cations such as metals. Anion exchange capacity (AEC) indicates the affinity of soils for uptake of anions, and is usually appreciably lower than the CEC of the soil. In addition to hydrous oxides, clays are also important ion exchange materials for metals (Sposito, 1989). The presence of natural organic matter (NOM) has been demonstrated to influence the sorption of metal ions to mineral surfaces. NOM has been observed to enhance sorption of Cu^{2+} at low pH, and suppress Cu^{2+} sorption at high pH (Tipping et al., 1983; Davis, 1984). Organic matter, particularly humic materials, can complex metals and affect their removal from solution (Ali and Dzombak, 1996). Humic materials contain carboxylic and phenolic functional groups that can complex with metal ions.

1.3 Experimental Methods for Determining Metal Speciation by Metal Fractionation of Soils

A vast body of literature exists that describes procedures/techniques designed to characterize the different fractions in soil; their main purpose is to assess the different bonding or retention strengths of heavy metals present in soil, and hence to infer their potential mobility and bioavailability.

Tessier, et al. (1979) have examined the merits of the method of sequential "selective" extractions on a sediment sample. This method has been used to fractionate heavy metals in soils as well. In the choice of reagents for the sequential extraction, particular emphasis was placed on the potential selectivity of each leaching solution.

1. *For the exchangeable fraction of the metals*, the soil (1.0 g) was extracted at room temperature for 1 h with 8 ml of either magnesium chloride solution (1 M $MgCl_2$, pH 7.0) or sodium acetate solution (1.0 M NaOAc, pH 8.2) with continuous agitation (Tessier et al. 1979).
2. *For metals bound to carbonates*, the residual soil from step (1) was leached, for 5h at room temperature, with 8 ml of 1 M NaOAc adjusted to pH 5.0 with acetic acid (HOAc). Continuous agitation was maintained (Tessier et al. 1979).
3. *For metals bound to Fe-Mn oxides*, the residual soil from step (2) was extracted with 20 ml 0.04M$NH_2OH \cdot HCl$ in 20% (v/v) HNO_3. The experiment was performed at 96±3°C with occasional agitation and the time needed to completely dissolve the free iron oxides was evaluated (Tessier et al. 1979).

4. *For metal bound to organic matter.* The residual soil from step (3) was mixed with 1ml of 0.02M HNO_3 and 5 ml of 30% H_2O_2, adjusted to pH1 with HNO_3, then heated to 85±2°C for 2 hours with occasional agitation. A second 3ml aliquot of 30% H_2O_2 was then added and the sample was heated again to 85±2°C for 3 hours with intermittent agitation. After cooling, 5 ml of 3.2M NH_4OAc in 20% (v/v) HNO_3 was added and the sample was further diluted to 20 ml with water then agitated continuously for 30 minutes.
5. *For residual metals*, the procedures for dissolving primary and secondary minerals usually involve either alkaline fusion or dissolution with mixtures of hydrofluoric acid and some other strong acid to ensure complete dissolution of the silicates, a large excess of fusion salt must be used, resulting in high salt concentrations in the solution to be analyzed for trace metals.

The above method, developed by Tessier and coworkers (1979) is the seminal procedure. There are numerous methods that are less time consuming or more practical, such as method proposed by the BCR (Community Bureau of Reference) (Perez-cid et al 1996). I.Maiz (1997) presented an attempt to divide the metal fraction in soil into two categories: a mobile fraction that is extracted with $CaCl_2$ or a complexing reagent and residual fraction that can not be mobilized with this reagent. Although soil sequential extraction can provide a measure of the metal concentrations in different fractions of the soil, there are at least three serious problems that must be considered when using sequential extraction procedures:

- Labile metal phases can be exchanged during sample preparation.
- Re-adsorption or precipitation processes can occur during extraction.
- Both the duration of the extraction and the soil/solution ratio can play an important role in the amount of metals that are extracted.

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

1.4 Current Methods for Soil Remediation

There are many sites that are contaminated with heavy metals. The current baseline technology for remediation of soil contaminated with heavy metals is excavation, containerization, transportation, and final disposal at a permitted land disposal facility. The most widely used technology for remediating heavy metal contaminated soils is dig-and-haul or solidification/stabilization. Neither technology results in the removal and/or concentration of the heavy metals from the contaminated soils nor can either technique be implemented using in situ strategies. Also, both techniques have become more costly due to limited landfill space and processing costs. With increased facility closures and regulatory pressures on operating facilities to improve environmental conditions, innovative heavy metal remediation technologies are needed that can concentrate the metals and return the remediated soils back to the environmental, possibly while recovering the metals. The general approaches to remediation will be discussed briefly.

Isolation

Isolation technologies attempt to prevent the transport of contaminants by containing them within a designated area (Cynthia, 1997). These technologies can be used to prevent further contamination of groundwater when other treatment options are not physically or economically feasible for a contaminated site. The site can also be isolated temporarily in order to limit transport during site assessment and/or remediation. Included are several different treatments such as capping and sub-surface barriers.

Immobilization

Immobilization technologies are designed to reduce the mobility of contaminants by changing the physical and/or leaching characteristics of the contaminated matrix. Mobility is usually decreased by physically restricting contact between the contaminant and the surrounding groundwater or by altering the contaminant chemically to make it more stable with respect to dissolution in groundwater. The aqueous and solid phase chemistry of metals is conducive to immobilization with these techniques. A variety of methods are available for immobilization of metal contaminants, including those that use chemical reagents and/or thermal treatment to physically bind the contaminated soil or sludge. Most immobilization technologies can be performed either ex situ or in situ. In situ processes are preferred due to the lower labor and energy requirements, but implementation will depend on specific site conditions. Solidification, vitrification and stabilization/immobilization technologies are the most commonly selected treatment options for metals-contaminated sites (Conner, 1990).

Toxicity and /or Mobility reduction

Chemical and/or biological processes can be used to alter the form of the metal contaminants in order to decrease toxicity and/or mobility.

a. Chemical treatment

Chemical reactions can be initiated that are designed to decrease the toxicity or mobility of metal contaminants. The three types of reactions that can be used for this purpose are oxidation, reduction or neutralization reactions. Chemical treatment is often used as a pretreatment stage for other technologies. The reduction of Cr(VI) to Cr(III) is the most common form of chemical treatment.

b. Biological treatment

Biological treatment technologies are available for remediation of metals-contaminated sites. These technologies are commonly used for the remediation of organic contaminants and are beginning to be applied for metal remediation, although most applications to date have been either bench or pilot scale (Schnoor, 1997). Biological treatment exploits natural biological processes that allow certain plants and microorganisms to mediate transformations including adsorption, oxidation, reduction, or methylation reactions (Means and Hinchee, 1994).

Physical Separation

Physical separation is an ex situ process that attempts to separate the contaminated material from the rest of the soil matrix by exploiting certain characteristics of the metal and soil. Physical separation techniques are available that seperate based on particle size, particle density, surface and/or magnetic properties of the contaminated soil. These techniques are most effective when the metal is either in the form of discrete particles in the soil or if the metal is sorbed to soil particles that occur in a particular size fraction.

Physical separation is often used as a form of pretreatment in order to reduce the amount of material requiring subsequent treatment (Rosetti, 1993). Several techniques are available for physical separation of contaminated soils including screening, classification, gravity concentration, magnetic separation and froth flotation.

Extraction

Metals-contaminated sites can be remediated using techniques designed to extract, either in situ or ex situ, the contaminated fraction from the rest of the soil. Metal extraction can be achieved by contacting the contaminated soil with a solution containing extracting agents (either soil washing or in situ soil flushing) or by electro-kinetic processes. The contaminated fraction of soil and/or process water is separated from the remaining soil and disposed or treated. Recent advances in the washing or flushing of heavy metals from contaminated soils using chemical chelators within aqueous carrier solution have shown much promise as an alternative technology.

1.5 Soil Washing

Soil washing can be used to remove metals from the soil aqueous suspension by chemical or physical treatment methods. Soil washing is an ex situ process that requires soil excavation prior to treatment. Chemical treatment involves addition of extraction agents that react with the contaminant and leach it from the soil (Elliot and Brown, 1989; Ellis and Fogg, 1985; Tuin and Tels, 1990). The liquid, containing the contaminants, is separated from the soil resulting in a clean solid phase. Physical treatment is achieved by particle size separation techniques adapted from mineral processing to concentrate the contaminant within a particular size fraction (Allen and Torres, 1991).

Fine particles (<63µm) often contain the majority of contaminated material because they bind contaminants due to their large and reactive surface areas. Many current soil washing approaches attempt to separate the fine fraction from the remainder of the soil in order to reduce the amount of material for subsequent treatment or disposal (Rosetti, 1993). Particle size separation techniques might not be successful if coatings, (e.g. metal oxide) are present on particles within larger size fractions (Van Ben Schoten et al., 1994).

Chemical treatment can be used to solubilize contaminants from the most contaminated fraction of the soil. Chemical treatment is performed on aqueous slurry of the contaminated material to which an extracting agent has been added. The extraction is performed in a mixing vessel or in combination with the physical treatment stage. The choice of extractant depends on the contaminants that are present and the characteristics of the soil matrix. Many processes manipulate the acid/base chemistry of the slurry to leach contaminants from the soil (Tuin and Tels, 1990). However, if a very low pH is required, concerns about dissolution of the soil matrix can arise. Chelating agents (e.g., EDTA) selectively bind with certain metals and can be used to solubilize contaminants from the soil matrix (Elliot and Brown, 1989). Oxidizing or reducing agents (e.g., hydrogen peroxide, sodium borohydride) provide yet another option to aid in solubilization of metals since chemical oxidation/reduction can convert metals to more soluble forms (Assink and Rulkens, 1989; Tuin et al., 1987). Finally, surfactants can be used for the extraction of metals from soil (U.S.EPA, 1996b).

Factors affecting soil-washing processes include: (Peters, 1999)

- Clay content (which makes it difficult to remove contaminants);
- Complex waste mixtures (which affects formulation of suitable wash fluids);
- High humic content (which inhibits contaminant removal);
- Metals concentration (the technology does not remove insoluble metals, although other metals can be solubilized);
- Mineralogy (which can affect process behavior and contaminant binding);
- Particle size distribution/soil texture (which influences the efficiency of removal from the wash fluid. (Oversized debris requires removal);
- Separation coefficient (if the contaminant is tightly bound to the soil matrix, prolonged leaching is required);
- Wash solution (the solution might be difficult to recover from the soil matrix).

1.6 Surfactant Enhancements of Soil Remediation

Hessling et al. (1989) reported that a 0.5% anionic surfactant solution in soil washing enhanced Pb removal from contaminated soils from a battery-recycling facility. Based on their findings, the authors suggested that surfactants offer good potential as soil washing additives for enhancing the removal of lead. The characteristic of anionic surfactant complexation and association with metal cations has been applied to enhance the removal of metal ions (Scamehorn et al., 1989; Simons et al., 1992) as well as simultaneously to remove organic and divalent metal cations from water (Dunn et al., 1989). The process is known as micellar-enhanced ultrafiltration (MEUF). Dunn et al. (1989) demonstrated that an anionic surfactant solubilized organic solutes (phenol or *o*-cresol) within the hydrophobic cores of the micelles, while divalent metals (Zn^{2+} and Ni^{2+}) became bound to the anionic exterior surfaces of the micelle. A surfactant does not form micelles until the surfactant concentration is at or above a threshold concentration, which is defined as the critical micelle concentration (CMC). The CMC is a function of the structure of the surfactant, the temperature of the solution, the concentration of added electrolytes and the concentration of solubilizates (Harwell, 1992). At sub-CMC levels, little solubility enhancement is observed.

The goal of employing a surfactant is to mobilize and or solubilize nonaqueous liquid phases and/or to solubilize sorbed contamnants. These phenomena occur because the surfactant can:

1) Lower the nonaqueous phase liquid (NAPL)–water interfacial tension, thereby decreasing the strength of capillary forces within porous media
2) Create a Winsor type III middle phase microemulsion
3) Solubilize individual cotaminant molecules in surfactant micelles or single phase microemulsion (with added co-surfactant(s), usually alcohols)

Surfactant molecules possess both polar and nonpolar regions. The polar region is often a sulfate, sulfonate, carboxylate, or polyethoxylate group, and often, contains a succinate or sorbitan group. The nonpolar group is generally a linear hydrocarbon chain; however, it is sometimes branched and can contain a phenolic or other aromatic group. Surfactantant molecules are referred to as amphiphilic (both loving) because the polar group has a large affinity for polar solvents, such as water, whereas the nonpolar group has a high affinity for nonpolar or hydrophobic solvents including most organic liquids. Upon addition to water, the large energy requirement for solubilizing the nonpolar portion of the surfactant molecules in the water is minimized by: (1) transfer of the portion of the molecule to a nonpolar solvent through the liquid-liquid interface, or (2) self assembly of these groups, forming surfactant aggregates known as micelles (Jafvert, 1996).

Generally, surfactants can be divided into three categories based on the identity of their hydrophilic head groups: nonionic, anionic and cationic. For soil remediation applications, loss of surfactant is a major concern as it not only reduces the effectiveness of the process but also increases the operating cost with higher dose requirements. Sorption of surfactants depends on the nature of the soil surface and on the pH in the system (Harwell, 1992). However, the higher adsorption of anionic surfactant to soil usually is observed at lower pH because the solid/liquid interface is more positively charged at low pH (Harwell, 1992; Scamehorn et al., 1982). In contrast, the losses of cationic surfactant often are significant, making their use for remediation less favorable when compared with the use of anionic or nonionic surfactants.

1.7 Background for Chelatant Extraction

In the most recent twenty years, many soil and environmental scientists have dedicated much effort to removing heavy metals from contaminated soils by using various chelating agents or organic acid(s). Soil is a complex multi-component system that acts as a physical, chemical and biological reactor to render the behavior of pollutants difficult to predict. It has been demonstrated (Jafvert, 1996) that complexation of trace elements by organic matter can increase their mobility appreciably.

1.7.1 Chemistry of Metal Extraction Using Chelating Agents

a. Metal speciation in natural water.

In the presence of ambient ligands such as HCO_3^-, CO_3^{2-}, Cl^- or SO_4^{2-}, an aqueous divalent contaminant metal can equilibrate into various free and complex forms:

$$M_{aq} = M^{2+} + M(OH)_x^{(2-x)} + M_x(OH)_y^{(2x-y)} + M(H_nCO_3)_x^{2(1-x+n)} + MCl_x^{(2-x)} + M(SO_4)_x^{(2-x)}$$

In contaminated soils, the total amount of metals in the aqueous and solid phases is at levels much higher than those found in the solution phase. The solubility of the metal(s) is typically too small to generate satisfactory results by washing with water alone. The solubilities of contaminant metals are controlled by the dominant mineral phases that depend upon the pH and/or the ambient ligands available. Commonly observed metal mineral phases include oxide, hydroxide, carbonate, and hydroxy-carbonate phases.

b. Acid-base equilibria involving chelating agents.

Effective chelating agents typically have multiple coordination sites (i.e. electron donating sites) available for complexation with a metal center (electron deficient specie). They are often multi-protic acids (H_nL) capable of undergoing acid-base equilibrium reactions in the aqueous phase,

$$H_nL = H^+ + H_{n-1}L^-$$

And subsequently,

$$H_{n-m}L^{m-} = H^+ + H_{n-(m+1)}L^{-(m+1)}$$

c. Metals complexation with chelating agents.

Each conjugate acid/base of the chelating agent can form a strong complex with the metal, resulting in the formation of various complexes $M_x(H_{n-m}L)_y^{2x-my}$.

$$xM^{2+} + yH_{n-m}L^{m-} = M_x(H_{n-m}L)_y^{2x-my}$$

1.7.2 Chelating Agents' Selectivity toward Target Heavy Metal(s)

For extractions of target heavy metals, the chelating agents should satisfy the following criteria:

a. The chelating agent(s) (with and without the chelated metal) must be compatible with the soil and must display no adverse effects on the stability of the complex.

b. The ligands should possess high metal complexing abilities toward heavy and transition metals as opposed to hard sphere cations such as Ca or Mg. The ratio of the magnitudes of the equilibrium complexation constants for heavy metals relative to the constants for alkali metals can provide an indication of possible success.

c. Ligands that contain sulfur and nigrogen as donor atoms are generally preferred for their higher selectivity toward target metals [transition metals (e.g.Cu^{2+}, Ni^{2+}) and B-type (soft sphere) cations (Zn^{2+}, Cd^{2+}, Pb^{2+}, Hg^{2+})]. Ligands containing sulfur or nitrogen as donor atoms generally form more stable complexes with soft sphere metals, whereas ligands containing oxygen as the donor atom prefer hard sphere cations.

d. Multidentate ligands are preferred because they contain multiple coordinating sites capable of forming more stable complexes with metals.

1.8 Studies involving Chelating Extractions of Metals from Contaminated Soils

During the past twenty years, many soil and environment scientists have dedicated much effort to removing heavy metals from contaminated soils using chelating agents or organic acids. EDTA has been used extensively in soil science because of its ability to mobilize metal cations efficiently coupled with only minor impact on the physical and chemical properties of the soil.

Ghestem (1997) performed experiments on extractability of EDTA-heavy metal complexes in polluted soils. The reactivity of certain trace metals (Cd, Pb, Zn, Cu) present in three polluted soils was studied using a classical extractant (EDTA). The effects of the concentration of this reagent (from 0.0001M to 0.05M) as well as the pH of the extracting solution (from 2 to 8) on the amounts of mobilized metal were determined. The behavior of the cations seemed to depend strongly on the excess/lack of EDTA. For excess EDTA, the concentrations of extracted cations were pH-independent. On the contrary, when using insufficient EDTA, the quantities of extracted cations displayed a complex behavior versus pH, that varied with the type of cation and with the level of soil contamination. A competition phenomenon between minor and major cations of the soil was revealed. The major cations were Fe^{2+} and Ca^{2+} in neutral media. However, when present in excess, EDTA was a powerful extractant of trace metals from the soil: recovery rates in excess of 60% have been observed frequently.

Removal of trace metals from contaminated soils using EDTA incorporating resin-trapping techniques was developed by Tejowulan and Hendershot (1998). Their study showed that extraction of metal with EDTA is a promising approach even at a low concentration. The procedure to remove metal-EDTA complexes from the leachates using an anion exchange resin is able to trap up to 99% of the Cd, Cu, and Zn, and 93% of the Pb in the soil leachates.

Elliot et al. (1989) have studied the use of EDTA for the decontamination for a highly contaminated soil containing 210,000mg/kg lead from a battery reclamation site. They observed that EDTA could extract all of the non-detrial Pb, which amounted to ~80% of total Pb burden in this matrix. Recovery of Pb was generally greater at pH<5 but was decreased slightly as the pH became more alkaline. EDTA concentrations were studied in the range 0.02-0.08M. The authors observed that maximum Pb removal was obtained with an EDTA/Pb molar ration between 1.5 and 2.5. The same researchers have also studied the influence of electrolytes on EDTA extraction (Brown and Elliot, 1992). They reported that the presence of monovalent electrolytes, sodium, lithium and ammonium perchlorate increased Pb recovery (compared to simple EDTA leaching) over the entire pH range from 5 to 9. Divalent electrolytes, calcium and magnesium perchlorate caused a similar improvement in Pb recovery at acidic pHs, but suppressed Pb solubilization at more alkaline pHs. In the presence of electrolytes, a stoichiometric amount of EDTA was sufficient for the extraction of all the non-detrital Pb at pH 4-6.

Peters and Shem (1992) have also studied the performance of EDTA for the removal of Pb retained in soils with high clay and silt contents. Contamination, as $Pb(NO_3)_2$, was added artificially to a clean soil, at nominal Pb concentrations from 500 to 10000 mg/kg. For an initial Pb concentration of 10000 mg/kg, the maximum removal of Pb was 64.2%. The extraction of Pb with EDTA was found to be pH insensitive. They have also observed that the concentration of EDTA over the range 0.01 to 0.1M had little effect on the removal efficiency.

Very limited data exists concerning the behavior of soil matrices during EDTA leaching of contaminated soils. Elliot et al. (1989) found that the release of Fe increased with decreasing pH. Iron dissolution was rather limited however (12% at pH, 6) compared to the 86% dissolution of Pb.

Papassiopi (1999) evaluated the performance of EDTA for the treatment of calcareous soils, contaminated with heavy metals from mining and smelting activities. The effect of EDTA concentration was studied using four concentrations of the disodium EDTA (0.025,0.05,0.125 and 0.25M). It is observed that the improvement in metals removal mirrored almost linearly the increase of EDTA concentration, suggesting that the removal of all three metals, Pb, Zn and Cd might be improved with concentration greater than 0.25M. This behavior was quite different from previous results that had indicated that EDTA concentration had little effect on the removal efficiency of lead from contaminated soils.

In order to verify if more efficient overall extractions could be obtained with higher EDTA concentrations, additional leaching tests were performed with 1M solutions using the tetrasodium EDTA salt. It should be noted that disodium EDTA concentration can not exceed the value of 0.3M, due to its limiting solubility. The Na_4-EDTA was used in order to achieve concentrations as high as 1.2M (Hart,1987). The results indicated that Pb, Zn and Cd recoveries were decreased in the tetrasodium EDTA, even though the concentration of chelating anion was increased from 0.25 to 1M and the corresponding stoichiometric excess was increased from 23 to 90 mol/mol. The reduced performance of tetrasodium EDTA could be attributed to the alkaline conditions, which prevail in the leaching solution using the Na_4-EDTA.

Papassiopi (1999) also studied the effect of solid to liquid ratio and demonstrated that extraction efficiencies decreased for all three metals when the solid to liquid ratio increases from 10% to 36%. These results indicate that it is not possible to reduce the chelant dose, decreasing either the level of EDTA or the volume of leaching solution, without affecting the efficiency of metals removal from this particular soil sample.

It was also observed that calcium was the dominant dissolved element in the solution and bound almost 89% of the available EDTA, whereas Zn and Pb utilized only 5.7% of the chelant ions. These results indicate that EDTA is not selective for the target contaminants but interacts with Ca as well. Based on these results, it was concluded that prediction for EDTA consumption must be based on the Ca content of the soil, rather than only on the contamination level of heavy metals.

1.9 Recovery and Reuse of the Chelating Agents

Strong chelating agents such as EDTA extract heavy metals from contaminated soils more efficiently; however, an increasing challenge remains the recovery of both the extracted metals and the chelating agent so that it can be reused. Reuse of the chelator at least three to four times is necessary for the process to be economical. Thus, remediation by chelation-extraction with a focus on the recovery and reuse of the complexing reagent represents an attractive objective. Laboratory tests thus far have demonstrated that chelation extraction is viable for soil remediation but that only moderate-strength chelators can be recovered (Chen et al., 1995; Chen and Hong, 1995).

Hong et al (1999) performed experiments on the separation of metals from EDTA with Na_2S, resulting in >99%, 70 to 74% and 93 to98% recovery of extracted Pb, Zn and Cu respectively. To aid in recovery, precipitating agents Na_2S and $Ca(OH)_2$ were added at 5mM each. $Ca(OH)_2$ was used as a cationic precipitant that provided Ca^{2+} ions to compete for EDTA replacing the chelated contaminant metal and encouraging its release from the chelator, whereas Na_2S was used as an anionic precipitant that provided HS^-/S^{2-} anions to compete with EDTA for the contaminating metal cations. The contaminating metals were recovered readily in the following decreasing order: Cu, Zn, and Pb. Each of these metal ions *was* recovered efficiently with appropriate chelator-to-precipitant ratios. The results demonstrated that:

1) Improved extraction performance can be achieved with higher EDTA concentration (e.g. 50mM) and with more washing cycles.

2) EDTA can be reclaimed using a slight excess of Na_2S precipitant at moderately alkaline condition*s* (e.g., pH 10), so that the chelant can be reused over several cycles.

Tamara and Gregory (1999) employed Fe powder to reduce the burden of dissolved heavy metals in acid rock drainage wastes. Possible removal reaction mechanisms were similar in that they depended on the surface characteristics of the zero-valent metal. Direct reaction with iron (Fe^0) results in an electrochemical reduction of the dissolved metal specie to the zero-valent state and it's subsequent sorption to the iron surface by a process termed cementation. The success of this cementation reaction can be predicted from the difference in the standard reduction potentials of the metals involved. When iron metal (Fe^0) corrodes in water, ferrous iron is produced at local anodic sites and acid is consumed by forming hydrogen gas at local cathodic sites. As protons are consumed during iron corrosion, the concentration of hydroxide increases causing metal hydroxides and hydroxide complexes to precipitate. Metallic ions and compounds can become adsorbed to the particle surface. Dissolved metals can also be exchanged with iron ions in iron oxides and hydroxides. The ability of a crystal lattice to undergo ion exchange is related to the ionic radius rather than the respective charge on the ions.

Iron has been used often as a remediation reagent because it has a high reduction potential and the reaction rates are limited by mass transport. The reaction steps with iron occur relatively rapidly; however, iron does not react as quickly with water at near neutral pHs. Other metals are less effective because the reaction rate is limited by the chemistry rather than diffusion or because water competes for reactive sites on the metal surface. Iron appears to be the best elemental material for environmental remediation because it is a strong reductant, nontoxic and inexpensive. Examples of contaminants that have been treated with zero-valent iron are halogenated hydrocarbons, such as carbon tetrachloride and other solvents, nitro aromatics, and heavy metals, such as chromium. Remediation of metal contaminated sites using the iron metal approach is becoming increasingly popular. Results have demonstrated that the concentration of Cd, As, Co, Cr and Cu are decreased rapidly (within several minutes) whereas the concentration of Zn and Pb are decreased only more slowly (taking several hours)(Tamara and Gregory, 1999).

Tunay and Kabdasli (1994) performed hydroxide precipitation of complexed metals. Hydroxide precipitation is the most common method on the basis of performance, ease of operation and cost. Although, sulfide precipitation has many advantages over hydroxide precipitation, including higher efficiencies and far less pH dependency, it finds limited application because of hazardous nature of the sludge produced, cost, and operational difficulties. In their study, the authors wished to evaluate the mechanism of ligand-sharing of metals that were added to wastewater to ensure efficient removal of complexed heavy metals. Different strengths of EDTA, NTA and succinic acid were selected as the organic complexants. Calcium was used as the ligand-binding agent. Model solutions were prepared for a single metal-single ligand system and several metal and ligand combinations in a closed system and single metal-single ligand in an open system. Model solutions were interpreted considering the relative magnitudes of the solubility, stability and ionization constants. Results indicated that at high pH, precipitation is applicable to those cases where organic ligand can be bound efficiently by calcium or any other coagulant or any pH adjustment agent thus freeing the heavy metal to form hydroxide or carbonate solids.

1.10 Supercritical Carbon Dioxide (Sc-CO_2) Extraction of Heavy Metals

1.10.1 Theoretical Principles

The principle of supercritical fluid extraction has been well described. If a gas such as carbon dioxide is compressed, certain distinct changes in the physical properties and behavior are observed below a certain temperature (termed the critical temperature, T_c), at which saturated liquid and vapor can exist together. Below a certain volume for a given pressure, the material must be liquid. If the volume is permitted to increase at the given pressure, at a particular volume all the given mass will be gasified. At temperatures above

T_c it is not possible to liquefy the gas no matter how much pressure is applied. The critical pressure of the gas, P_c, may be defined as the pressure required liquefying the vapor or gas at the critical temperature of the substance (Bott, 1982).

Carbon dioxide remains among the most desirable of compressable gases since it has a relatively low critical temperature (31°C) and a relatively low critical pressure (73 atm). Also carbon dioxide is: (1) inert and non-corrosive in a non-ionizing environment, (2) nonflammable and non-explosive, (3) abundant and inexpensive, (4) nontoxic, and (5) of low viscosity, low surface tension and high diffusivity (Bott, 1982). Carbon dioxide dissolves many toxic compounds, including polyaromatic hydrocarbons (PAHs), chlorinated hydrocarbons (including polychlorinated benzenes (PCBs), phenols, and many pesticides, and can be used for the extraction of these compounds from soil (Laitinen et al., 1994).

1.10.2 Supercritical Fluid Extraction of Metal Ions and Metal Chelates

The majority of quantitative SFE studies have focused on the extraction of relatively non-polar analytes. Polar and ionic and ionic analytes are more difficult to extract because of their low solubility in carbon dioxide and their potential for strong interactions with active sites within the matrix. Novel reagents have been added to various SCFs to provide enhanced yet selective extraction of target analytes. One of the most common methodologies for the extraction of metal ions from aqueous and solid matrices is the reaction of the target metal ion with a ligand to form a neutral metal complex followed by solvent extraction. The organic extraction solvent characteristically is toxic, and creates environmental concerns for both handling and safe disposal (Ager and Marshall, 1998).

However, because of the low solubility of metal ions and conventional metal chelating agents, there has been only limited progress in the use of CO_2 as a solvent for the extraction of metals. A number of researchers have explored the design of highly CO_2–soluble chelating agents to allow extraction of metal ions. Yazdi and Beckman (1995) generated highly carbon dioxide soluble chelating agents via functionalization of conventional chelating groups with a fluoroether or silicone tail (which are referred to as CO_2–philic) that provides the following advantages:

(1) There is no limitation in the length of the CO_2–philic portion of the molecule. The length of the tail can be arbitrarily varied in order to provide the desired solubility at the desired pressure.

(2) Once a method for the attachment of a chelating agent to a tail has been developed, a tail with any CO_2–philic functional group can be attached to the chelating agent, thus providing custom-tailored chelating agents for diverse applications according to the solubility and cost requirements.

(3) There is appreciable flexibility in choosing the chelating head when using the tail attachment method. If a chelating agent or a related compound can be synthesized with a reactive functional group somewhat removed from the chelating site, then a CO_2–philic tail can be attached.

The strategy of attaching a CO_2–philic tail to a conventional chelating head has been successful in producing chelated complexing agents that remain soluble at concentrations of 30-200 mmol/L at pressures less than 2000 psi. They remove metals from solid and liquid matrices efficiently. The capability of functioning at lower pressure and higher chelating agent loading is significant because these properties impact greatly on the economics of the process.

Li and Beckman (1998) proposed that the low pH of water in contact with SC-CO_2 (2.8-3.0) could result in poor extraction efficiencies with many common chelating agents. In their study, the CO_2-soluble compound perfluoropolyether piperazine dithiocarbamate, that represents an analogue of ammonium pyrrolidinedithiocarbamate (APDC), was synthesized. This dithiocarbamate was capable of extracting a variety of metal ions (except chromium) at pH's as low as 1.0. It is known that metal ions replace H^- during chelation so that low pH's can render the reaction less favorable. The chelating head-group used in their study, a dithiocarbamate, was chosen from the literature based on its affinity for target metals at low pHs. APDC is a member of the commonly used sulfur-containing chelating agents, one that forms stable complexes with ions having either partially filled d orbital fully filled d orbital and low positive charge.

1.11 Metal Analysis of Soil and/or Soil Extracts

In order to investigate the heavy metals content in the soil we expect to mobilize with a variety of treatments, it becomes very important to identify a method or technique that is less time consuming, economical and stable with time, so as to obtain relatively accurate and reproducible results.

1.11.1 Soil Digestion

Most methods currently used for metal analysis require that the sample be presented to the instrument as a liquid as is the case for atomic absorption spectrometry (AAS). For AAS analysis of most biological, environmental, or food samples, it is usually necessary to perform a digestion of the sample, in order to: (1) release the analyte element from the organic matrix into a form that is detectable by the AAS technique; (2) make a true solution of the sample.

The conventional method for soil digestion employs concentrated $HClO_4$ and HNO_3, and normally takes approximately 12 hours to complete depending on the soil type. This procedure is both time-consuming and laborious. Since the first report of using microwaves as a heat source for wet chemical digestion Abu-Samra (1975), the microwave digestion technique has gradually gained widespread acceptance as a rapid and efficient method of sample preparation. Using this technique has reduced the digestion time dramatically Other benefits include reduced contamination, less reagent and sample consumption, a reduction in the loss of volatile species and improved safety (Kinston and Jassie, 1988). In the early 90's, the introduction of high temperature/pressure digestion devices provided a further impetus to the evolution of the technique (Dunemann and Meinerling, 1992). The advantages of the microwave digestion technique have led to its application as an effective sample preparation method for a wide range of sample matrices.

Closed Microwave Digestion

The closed microwave digestion technique involves placing the sample in a sealed vial (or bomb), usually constructed of a fluorinated polymer, such as polytetrafluoroethylene or perfluoroalkoxy polymer. After adding the digestion reagents, the bomb is sealed tightly and placed in the microwave oven and irradiated with microwave energy. The major advantage of the closed microwave digestion is the high heating efficiency that can be achieved. Heating causes an increase in pressure, due to the evaporation of digestion acids and gases evolved during the decomposition of the sample matrix. This benefits the digestion process by increasing the boiling point of the liquid phase, which accelerates the breakdown of the sample matrix. However, the excessive build-up of pressure, especially during the digestion of samples with a high content of organic matter, can lead to the rupture of sealed vessels. For reasons of safety, most digestion bombs are fitted with pressure relief valves that are designed to open if the pressure becomes excessive. If venting does occur, sample losses are likely and a less active digestion can result from the loss of volatilized acid vapor.

Open Digestion Techniques

Open digestion systems operate at atmospheric pressure and so do not suffer from the problem associated with a rapid pressure build-up. However, they do require an effective fume removal system. The potential loss of volatile species is minimized by the re-condensation of vapors in a reflux column mounted above the digestion flask. The addition of digestion reagent at any stage during the procedure (which can increase the effectiveness of the digestion) is also facilitated. This is a distinct advantage over closed methods where the addition of reagents cannot be achieved without cooling and opening the vessels.

A disadvantage of the early open digestion system was that only one sample could be digested at a time. More recently, a two-or six-cavity open microwave digestion unit has become available commercially. Other features include the ability to program the power output/desired temperature to each sample independently (Prolabo, 1995).

More and more soil scientists are employing microwave digestion technique for sample preparation. Florian et al. (1998) made a comparison of microwave-assisted leaching techniques for the determination of heavy metals in sediments, soils, and sludges. Xing and Veneman (1998) performed microwave digestion for analyses of metals in soil. They compared digestion efficiencies with and without added hydrogen peroxide, and concluded that the analytical results obtained with nitric acid alone were not significantly different from the results obtained with a nitric acid and hydrogen peroxide mixture. Krishnamurti et al. (1994) utilized microwave digestion technique for the determination of total cadmium in soils. The soil samples and standard sediment samples were digested in a microwave oven using concentrated HNO_3 or by the conventional HF-$HClO_4$ digestion in platinum crucibles. Both digestion methods produced comparable quantitative values for total Cd in certified reference materials. Thus the microwave digestion technique was demonstrated to be an accurate and rapid method for digesting soil samples prior to total Cd determinations.

1.11.2 Metal Analysis

Atomic absorption spectrometry (AAS) is generally considered to be a mature technique, and at present is the most widely used technique for the determination of metals. The positive features of this technique remain the relative freedom for spectral interference and the modest purchase and operating costs. The approach is relatively simple and the instrumentation is widely available. It can be found in analytical trace metal laboratories and in a variety of biological, clinical, and environmental research, metallurgical and routine analytical establishments.

AAS involves the study and measurement of the absorption of radiant energy by free atoms. Free atoms are generated by an atomizer, which can be a flame or an electro-thermal (furnace) atomizer. Radiation from a suitable light source such as a hollow cathode lamp (containing the element to be determined) is directed through the resulting population of free atoms that attenuate the incident radiation. The degree of attenuation (absorption) of the incident radiation is proportional to the concentration of the analyte atoms within the light path. Absorption by free atoms at other (non-absorbing) wavelengths is essentially zero.

Atomic absorption detection limits depend on the type of atomizer used and on the sample matrix. Generally, the levels of analyte element are in the range of micrograms per milliliter to sub nanograms per milliliter, the latter being the case when a furnace atomizer is employed. These limits of detection are usually adequate to determine trace metals in a wide variety of samples.

Flame Atomization

A flame is formed using air, oxygen, or nitrous oxide as the oxidant gas and hydrogen, acetylene, coal gas, or butane as the fuel gas. Most often a mixture of air and acetylene provides the support gases to provide a stable flame that is maintained some3-7 mm above the burner head. A liquid sample is aspirated into the nebulizer where turbulent gas flows cause most of the sample droplets to coalesce and to deposit on the sides of the chamber. The larger droplets are discarded via a drain. Only the smallest liquid droplets are carried up through the nebulizing chamber and into the flame where the solvent is evaporated. The solid residue of micro-crystals is decomposed and free atoms are generated.

For each elemental analysis the best wavelength must be selected and the instrumental conditions must be optimized. These include the choice of flame type, fuel and oxidant flow rates, burner height, and slit width. Most manufacturers supply methods that represent a good starting point for establishing optimal operating conditions. The usual method of analysis entails the preparation of an analytical working curve by measuring the absorbance of a series of standard solutions of the elements of interest and plotting the graph of absorbance versus concentration. The element concentration in the sample solutions can then be obtained from the graph by interpolation.

1.12 Objectives of the Research

Based on the above review of the literatures, the project was focused on using chelating reagents to remove heavy metals from field contaminated soils. An additional objective was to identify and optimize conditions that would permit the chelating agent to be recycled. The recycled agent was to be added back to the soil to mobilize fresh toxicant. There are several complexing reagents that *were* of interest:

1. Disodium EDTA
2. Citric Acid
3. ADA (N-(2-acetamido)iminidiacetic acid)
4. DTPA (Diethylenetriamine pentaacetic acid)
5. SCMC (S-carboxymethylcysteine)
6. DPTA (1,3-Diamino-2-hydroxypropane-N,N,N,N-tetraacetic acid)

The target heavy metals included Cu, Fe, Mn, Pb and Zn. The studies were anticipated to provide the following information:

- Determine the relative extraction efficiencies of the six chelating reagents for the target metals.
- Identify and optimize a method to recycle the complexing reagents as many times as possible so as to minimize the possible costs of these operations.

CHAPTER II SOIL SAMPLE PREPARATION AND CHARACTERIZATION

2.1 Preparation of Soil Sample

Soil handling and preparation is the first important step for soil analysis, there are usually three major procedures:

Drying

Most soil samples for testing arrive at the laboratory in "field-moist" conditions. This means that the samples may range from air dry to saturated. Usually the first operation when moist samples are received is to dry them. For routine soil testing all Canadian provinces recommend drying of the samples before analysis. Analysis of undried samples is not recommended because of the effect of moisture content on soil to extractant ratio and the need to determine moisture content. A surprising range of drying temperatures has been used across Canada (Table 2.1), the best that can be done is to use the drying method recommended for the province from which the soils are taken.

Table 2.1 A Survey of Soil-Handling Methods for Routine Soil Testing (Bates, 1993)

	Drying	Grinding method	Sieve size	measuring
Newfoundland	40°C	Mortar and pestle	1 mm & 2 mm	Volume
P.E.I.	35°C	Mechanical	2 mm	Weight
Nova Scotia	35°C	Mortar and pestle	2 mm	Volume
New Brunswick	Air dry	Mortar and pestle	2 mm	Volume
Quebec	<37	Mortar and pestle	2 mm	Volume
Ontario	35°C	Flail	2 mm	Volume
Manitoba	<35°C	Heavy-duty grinder	2 mm	Volume
Saskatchewan	30°C	Flail (except for micro)	2 mm	Volume
Alberta	60°C	Flail	2 mm	Volume
British Columbia	55°C	Wood blocks	2 mm	Volume

Grinding and Screening

For routine soil tests almost all provinces grind samples to pass a 2-mm screen - there seems little reason to change from this. Use of a finer screen will remove the very coarse sand, 1.0-2.0 mm diameter, unless the particles are broken with grinding. Nylon or stainless steel screens are recommended for micronutrient samples.

Canadian laboratories use a range of grinding methods from a wood block or agate mortar and pestle to a flail-type and other mechanical grinder. The soil should not be subjected to sufficient force or abrasion to break up the individual sand, silt or clay particles. Where micronutrient and metal tests are to be conducted, particular care should be taken in the choice and use of grinder so as to prevent contamination. Stainless steel is the conventional choice where metal is used for screening and grinding. It seems to be generally satisfactory, but considering the range of metals used in stainless steel, this should not be taken for granted.

The soil sample used for the studies was an urban soil taken from a site that had been closed by Quebec government since it had been identified as being heavily contaminated with trace metals. The soil sample, which has been dried and properly stored in a container, was provided by the soil lab in the Department of Natural Resources, McGill University. The only subsequent preparation consisted of griding and passing the soil through 0.5mm screen prior to treatment/chemical analysis.

2.2 Determination of Soil Texture

Physically, the soil is a mixture of mineral matter, organic matter, water and air. The mineral matter is composed of inorganic and organic particles varying in size from stones to gravel to powder. The finest soil fractions often contain the highest concentrations of contaminants because this fraction has the highest surface area per unit volume and thus favors adsorption-type phenomena. In addition, the fine soil fraction usually contains appreciable quantities of natural organic matter that can serve as a sink for organic contaminants.

The United States Department of Agriculture recognizes three major groups of soil separates: sand (2.0-0.050mm), silt (0.050-0.002 mm), and clay (<0.002 mm). The relative proportions of the soil separates determines the soil texture. When clay is present in dominant proportions relative to silt and sand concentrations, the soil is described as having a fine or heavy texture. Fine textured soils are plastic and sticky when wet, and hard and massive when dry. They are very difficult to plow hence the term heavy texture. On the other hand, when sand is dominant, the soil exhibits a coarse or light texture. Coarse textured soils are loose and friable and are easy to plow hence the term light texture. In the presence of balanced concentrations of sand, silt, and clay, the soil is considered to have a medium texture.

Methodology

The laboratory method for soil texture determination, an indirect method, is conducted by the quantitative determination of soil separates. This type of analysis is conventionally referred to as particle size distribution or particle size analysis (Soil Survey Staff, 1975). Formerly called mechanical analysis, this procedure sorts out the inorganic soil particles into the sand, silt, and clay fractions. Two important steps in the analysis are dispersion and sedimentation.

Sample Dispersion

The dispersion of soils is accomplished by a combination of methods. The methods for dispersion can be classified as either chemical or physical.

Chemical Dispersion: Following the removal of cementing and flocculating agents, samples are maintained in a dispersed state until the sedimentation measurements are completed. A variety of dispersing chemicals has been used. These include Na-hexametaphosphate (HMP), Na_2PO_7, NaOH, Na_2CO_3, and NaOBr. Of these, HMP appears to be the most commonly used dispersant.

Physical Dispersion: Several methods of physical dispersion have been used in conjunction with pretreatment and chemical dispersion. The American Society of Testing

Materials recommends either an electric mixer with specially designed stirring paddles or an air-jet stirrer (Chu & Davidson, 1953; Theisen et al., 1968)

Ultrasonic Dispersion: The principle behind ultrasonic dispersion is the transmission of vibrating sound waves within the soil solution. The sound waves produce microscopic bubbles that collapse, producing cavitation. The release of intense energy of cavitation literally blasts the soil aggregates apart, causing dispersion even in highly aggregated soils.

Sedimentation

After the soil has been dispersed, the different particle size fractions are sorted out by sedimentation techniques using the Bouyoucos hydrometer or the pipette method. In the Bouyoucos hydrometer method, the amount of the different size fractions is determined with a soil hydrometer. In the pipette method, a pipette is used to withdraw an aliquot of the soil suspension at a predetermined time and depth, then dried and weighed. For quantitative collection of the various size fractions, the suspended material can be siphoned off at fixed time periods and dried. The hydrometer method was adopted for the current studies since it is a simple and rapid procedure for the analysis of soil texture through the measurement of total sand, silt and clay contents.

Dispersion Reagent

Sodium metaphosphate, $(NaPO_3)_x$ Na_2O (x~13), 40 g, was dissolved in 1 L of distilled water. A 10 mL aliquot was used for each determination. A 50.0 g sample of soil was mixed with 10 mL of sodium metaphosphate solution diluted with distilled water and transferred to a blender cup until the cup is 50% full. The suspension was blended mechanically for 15 min, then transfered quantitatively to an A.S.T.M. soil-testing cylinder. A hydrometer was placed into the suspension exactly 40 s after thorough mixing and the level was recorded to the nearest 0.5 scale division. The suspension was again stirred and a second reading was recorded after a subsequent 40s. The average of the two readings was considered to equal the temperature specific amount of silt plus clay. The suspension was stirred a third time and the hydrometer and temperature readings were recorded after 120 min of settling to obtain the amount of clay (g). The procedure was repeated in its entirety starting with 100g of soil.

The results obtained for the contaminated urban soil are recorded in Table 2.2:

Table 2.2. Soil Texture of Soil Sample

Soil sample	Sand (%)	Clay (%)	Silt (%)
100 g	61.5	5.0	33.5
50 g	64	1.6	34.4

2.3 Determination of Total Heavy Metal Burden in Soil

Before employing various soil remediation methods, it was necessary to determine how much heavy metals were associated with soil. With this data, one can then make an informed choice among workable strategies for remediating the contaminated material. The procedures followed to determine the total heavy metal content involved *a* digestion of the soil with strong acid followed by atomic absorption spectrophotometric determination of the quantities of analyte metals in the resulting aqueous solution. For these studies, both microwave digestion and conventional strong acid digestion were performed and the results were compared.

Method and Material

A. Nitric Acid Block Digestion (APHA, 1995)

A weighed aliquot (~1g that had been sieved to 0.5mm) was carefully combined with 15ml HNO_3 in a 100 ml digestion tube and permitted to stand overnight in a perchloric acid fume hood. The block was heated gradually to 150°C and permitted to digest until the evolution of NO_2 vapours had ceased then allowed to cool for 15 min. Perchloric acid (5ml) was added and the flask was returned to the block and again heated gradually over 2 hours to 150 °C. The digestion was considered to be complete when the evolution of white vapours had ceased. When cooled, the crude digest was diluted to 100 ml with distilled deionized (DD) water. After standing for some 18h, 70-80ml of supernatant solution was decanted into biotite plastic bottles (90 ml capacity) and stored to await analysis by flame atomic absorption spectrophotometer (AAS).

B. Microwave Digestion

Microwave digestions were performed using a focussed open digestion system with a Prolabo Type 3.6 Micro-digester. The digester features a focussed microwave source and an open digestion flask. The microwave frequency was 2.45GHz. The instrument was also equipped with a suction-scrubbing unit that was capable of aspirating the acidic volatiles away from the neck of each flask.

Procedure: Soil, 1g, was combined with 15ml of nitric acid (18M) in each of 3 microwave digestion flasks and digested using a program that successively added (15ml of nitric acid), heated under 30% of power (~145°C) for 20 minutes, cooled for 15 minutes then supplemented with 5mL perchloric acid and reheated with 25% power (~125°C) for 20 minutes. The digests were permitted to cool then diluted to 100ml with distilled deionized (DD) water. The supernatant fraction was recovered (70-80 ml) and stored in a plastic bottle to await analysis by flame-AAS.

C. Metal Analysis by Flame AAS

Heavy metals were solubilized by digestion with concentrated acids. AAS was then used to determine the metal contents in the digestion solutions to provide information about the heavy metal burdens in the soil samples (see Table 2.4). The flame-AAS used in these experiment was a GBC model 903 Single Beam Atomic Absorption Spectrophotometer. The optimum spectrophotometer operating conditions for each metal are provided in Table 2.3. The measurements for subsequent analyses were also performed with these operating conditions.

Calibrations were performed by diluting aqueous metal standard solutions [1,000µg/mL, traceable to NIST primary standard , SCP Chemical Co. St-Laurent, QC] with de-ionized distilled water to its corresponding optimum working range.

Table 2.3 Optimum Working Condition of Flame AAS

	Wavelength (λ)	Slit Width (nm)	Working Rang (μg/mL)	Sensitivity Range (μg/mL)
Cu	324.7	0.5	1-5	0.025
Fe	248.3	0.2	2-9	0.05
Mn	279.5	0.2	1-3.6	0.02
Pb	217.0	1.0	2.5-20	0.06
Zn	213.9	0.5	0.4-1.5	0.008

2.4 Determination of Metal Fractions in Soil by Sequential Extraction

As discussed in the first chapter, the fate of heavy metals in a contaminated soil is dependent on both the total amount of the metals and on the chemical forms in which they exist. Metal speciation in soils is commonly partitioned into the following five fractions: exchangeable, bound to carbonate, bound to Fe/Mn oxides, bound to organic matter, and residuals (considered to be bound mainly to clay minerals). The most widely used sequential extraction method was provided by Tessier et al. (1979) and is based on the fact that different forms of heavy metals retained in soils can be extracted selectively by a series of extracting reagents. Although the selective sequential extraction method is useful for obtaining information on the distribution of heavy metals, Romas et al.(1994) reported that there were three limitations: (1) the limited selectivity of extractants; (2) the redistribution of metals during the extraction process, and (3) the decreased efficiency of a reagent dose if metal content is excessively high. In this research, the procedures (Irene et al., 1998) based on the method developed by Tessier et al.(1979) with minor modifications was used to determine the heavy metal fractions in the soil (See Figure 2.1 that presents a flow diagram of the sequential extraction process).

The entire sequential extraction procedure was carried out by using 1g of soil during the extraction of each fraction because of liquid losses during each step. One gram of soil was placed in a polyethylene centrifuge tube (Nalgene, 100 mL) and the required chemicals were added following the procedure to isolate the different fractions. After extraction, the liquid supernatant fraction was isolated by centrifugation for 15 minutes. A suitable aliquot of the supernatant fraction was analyzed for metal concentrations. Table 2.4 summarizes the results of the metal fractionation associated with the soil.

From this table it can be concluded that the soil is highly contaminated with heavy metals; the concentrations of Zn, Pb and Cu are appreciably higher than tolerated levels. It should also be pointed out that the soil contains an appreciable amount of iron; iron is not a contaminant of serious concern because it is commonly presence, at high levels, in many soils. Therefore, an important property of the optimum chelating agent is one that minimizes the extraction of iron into solution, while maximizing the extraction of the other heavy metals of concern. It was observed that there was a large portion of heavy metals associated with the Fe/Mn oxide fraction. The organically bound heavy metal fraction was not detected even when strong nitric acid and hydrogen peroxide were employed. It is difficult to conclude that there was no organically bound forms present. The metals were probably bound strongly to or intercalated within the lattice where they were not accessible even to strong extractant chemicals. During the experiment, fresh soil sample was used for each extraction step to avoid the loss of sample, that might have resulted in the overlap of the fractions, although each step used a specific chemical to isolate the corresponding fraction.

Figure 2.1 Flow diagram of the sequential extraction process

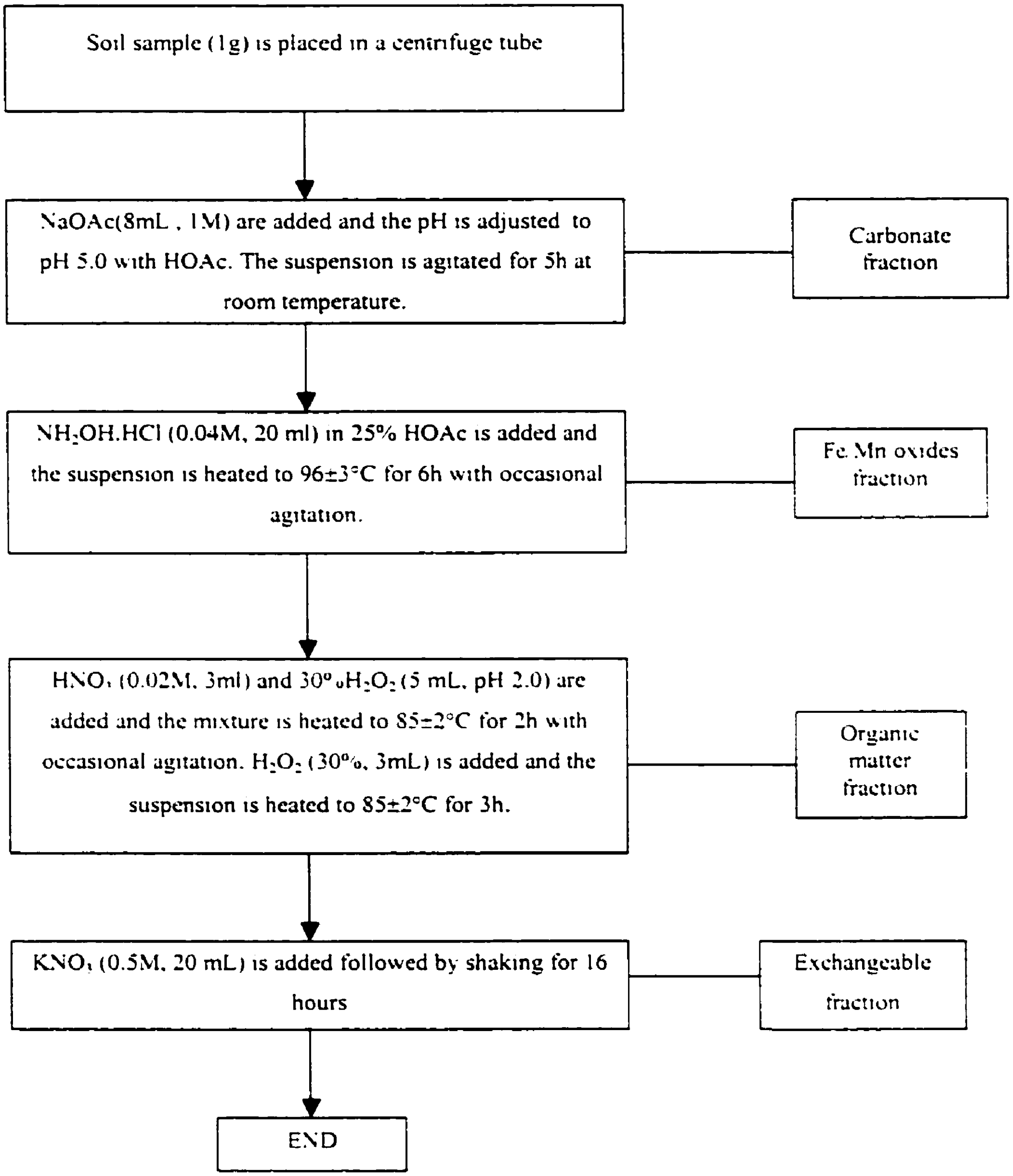


Table 2.4 Total Metal Content and Metal Fraction of Soil Sample

	Cu	**Fe**	**Mn**	**Pb**	**Zn**
Total Soil Metal Burden[a]	486±8%	32,098±7%	503±4%	596±7.6%	2028±12%
Carbonate Fraction	12%	0.01%	13%	13%	26%
Fe/Mn Oxides Fraction	21%	13%	55%	50%	75%
Organically Bound Fraction	N.D.	N.D.	N.D.	N.D.	N.D.
Exchangeable Fraction	N.D.	N.D.	N.D.	N.D.	N.D.

[a] *unit for the row of 'Total Metal Burden of Soil' is μg (metal)/g (soil)*

CHAPTER III SOIL REMEDIATION AND CHELANT RECYCLING

The general characteristics of the soil sample were described in Chapter 2. The current chapter focuses on approaches to the remediation of the metal contaminated soil by complexometric extraction and on methods to recycle chelating reagents.

3.1 Soil Cleaning by Complexometric Extraction and Reagent Recovery by substitution with diethyldithiocarbamate (DEDTC)

3.1.1 Introduction

There is an extensive literature concerning the complexometric extraction of soils. Ellis et al. (1985) reported the sequential treatment of a soil contaminated with cadmium, chromium, copper, lead, and nickel, using EDTA, hydroxylamine hydrochloride, and citrate buffer. The EDTA chelated and solubilized all of the metals to some degree; the hydroxylamine hydrochloride reduced the iron oxide-manganese oxide matrix of the soil that released bound metals, and also reduced insoluble chromates to chromium (II) and chromium (III). Steele and Pichtel (1998) also performed three sequential extractions on a soil. Lead extraction efficiency was independent of EDTA concentration and greater than 82% of the lead was removed. The mobilization of this element was significantly dependent on ADA concentration; extraction efficiencies were increased from 66% to 84% with increasing ADA concentrations. The selection of complexing reagents in the current studies was based on the previous literature reports and also on the widely recognized trend that ligands containing sulfur and nitrogen as donor atoms are generally preferred for higher selectivity toward the heavy metals of interests such as Cd, Cu, Mn Pb, and Zn.

3.1.2 Experimental Procedures

Reagents:

ADA (N-(2-acetamido)iminodiacetic acid, $C_6H_{10}N_2O_5$) 99%; EDTA (ethylenediaminetetraacetic Acid Disodium Salt $C_{10}H_{14}N_2Na_2O_8 \cdot H_2O$) P.A. grade and SCMC (s-carboxymethyl-L-cysteine) 98% were purchased from ACROS (U.S.A.).
citric Acid monohydrate, 99% [HOC (COOH)($CH_2COOH)_2 \cdot H_2O$], DPTA (1.3-diamino-2-hydroxypropane-N'N'N'N'-tetraacetic acid 99%, $C_{11}H_{18}N_2O_9$), DTPA (diethylenetriamine pentaacetic acid, $C_{14}H_{23}N_3O_4$) and DEDTC (sodium diethyldithiocarbamate trihydrate, $(C_2H_5)_2$ $NCS_2Na \cdot 3H_2O$) 99%, were purchased from Aldrich Chemical Company, Inc., Oakville ON

All chemicals used were ACS reagent grade or better. Working solutions were prepared from stock standards (1000μg/mL) purchased from BDH® (Montreal, Quebec, Canada) or Sigma-Aldrich® (Oakville, ON). All glassware was washed successively in a soap solution, soaked in nitric acid (20%, v/v), rinsed with copious quantities of distilled deionized water and dried in the oven.

Sample Preparation:

An accurately weighed aliquot of soil (~100g) was suspended in 0.1M EDTA (100mL) in a 100ml-centrifuge tube, shaken for 16 or 24h, then centrifuged and the supernatant fraction was filtered through Celite under suction to obtain a clear solution. The metal contents of the clarified solution were measured by flame-AAS (F-AAS). Subsequently, the pH of the solution was adjusted to approximately 3 then a 10-fold molar excess of DEDTC (based on heavy metal content) was added to result in an immediate precipitation. The precipitate was recovered by filtration and the filtrate was re-combined with the solids fraction from the first soil extraction. The metal content in the DEDTC precipitate was measures by F-AAS. Subsequent extractions of the soil were completed in identical fashion until further mobilization of metals from the particulate fraction of the soil became very small. Separate aliquots of the soil were treated with an equal volume (0.1M) of each of five other complexing reagents (ADA, citric acid, DPTA, DTPA and SCMC) and processed in identical fashion. By contrast, the concentration of the DTPA extractant was 0.022M.

Results and Discussion:

The most time consuming step of the experiment was the equilibration stage so the length of time required to achieve equilibrium was of primary concern. Twenty-four hours, that had been cited previously and 16 hours that was convenient in terms of the daily experient schedule were chosen for the experiment design. The results was summarized in Table3.1. Three replicates were performed for these two set times and the chelating reagent used was EDTA. From the data in Table 3.1, the quantity of Cu released from the ~~soil~~ during 24 hours is 119μg/g, which is quite close to the result recovered after 16 hour of equilibration. (121μg/g). Recoveries, after 24h or 16h of equilibration, were similar for the other metals (Fe, 65 and 72μg; Pb, 129 and 139μg; Zn, 482 and 471μg; Mn, 32and 32 μg). No appreciable differences in the quantities of extracted heavy metals were evident. The extractable fraction of the total metal burdens had been mobilized during the initial 16h; it was not necessary to extend the equilibration time further.. So the samples could be put on the shaker at 5:00 PM, stay over night, and be taken out at the next morning 9:00 AM for following treatment and analysis.

Regarding the chelating extraction, six complexing reagents (see structures in Figure 3.6) were employed. For each chelating reagent, two or three cycles of extraction were applied to each soil sample which dependeded on the efficiency of the first extraction stage. Sodium diethyldithiocarbamate was used to strip the metal from the metal-complex. A number of dithiocarbamate (DTC) reagents have been used for chelation and solvent extraction of trace metals from aqueous solutions (Wyttenbach and Bajo, 1975). These reagents behave as bidentate univalent anionic ligands, offering two donor S atoms, and forming stable complexes with a large number of elements. Table3.3-3.8 sumarize the results of the extraction efficiency of both fresh and recycled six complexing reagents. Three replicates analysis for each complexing reagent were performed and the mean and the relative standard deviation were calculated as the final results.

As recorded in table3.3, the concentration of Cu that was released from the soil into the 0.1M EDTA extractant amounted to 119μg Cu/g of soil. The concentration of Cu was reduced to 'none detected' post treatment of the EDTA solution with DEDTC. The second equilibration of recycled EDTA with the soil particulate fraction mobilized a further 76μg/g of [Cu] that was again precipitated efficiently with the DEDTC (no Cu detected in filtrate). A third extraction mobilized a further 36μg/g of [Cu]. Fe is less efficiently mobilized (32098μg/g in soil). In the first EDTA equilibration, only 64μg/g is released and 4 μg/mL were detected in the filtrate after treatment with DEDTC. Second and third equilibration s with recycled EDTA extracted approximately the same amount of Fe from the soil as was mobilized by the extraction, DEDTC again stripped Fe from Fe-EDTA, and only 2μg Fe/mL remained in the filtrate. EDTA was inefficient at mobilizing Mn. When present initially 503μg/g in the soil, 0.1MEDTA removed 32μg/g in first extracion, but DEDTC did not precipitate Mn, which results in the increasing concentration of Mn in the later extraction. Pb that was present initially at 596μg/g in the soil was reduced by 113 μg/g with the equilibration with 0.1M EDTA. Post treatment with 2.0g DEDTC, the filtrate that contained 2μg/mL, was re-combined with the soil particulate fraction and re-equilibrated for a further 16h. The resulting solution had released a further 100μg/g from the soil. After precipitation with DEDTC, filtration and re-equilibration a further 53μg/g Pb was removed from the soil particulate fraction. For Zn, the first extraction removed 510μg/g of the 2028 μg/g soil burden. The filtrate, post precipitation with DEDTC, contained 52μg Zn/mL. The second equilibration mobilized a further 384μg/g from the soil. The concentration in the filtrate, after DEDTC treatment, was reduced to 8 μg/ml and when re-equilibrated with the particulates, a further 191μg/g was removed from the soil. Thus, the complexant was re-generated at each stage and mobilized more of the Zinc.

Table 3.4 records the extraction efficiency with DPTA. Apparently, DPTA was very selective to Zn and Cu, followed by Pb. There was almost no extraction of Fe and Mn. Total extraction efficiency of Cu, Zn and Pb are 32%, 41% and 11% respectively. The DEDTC retained its capacity to precipitate with metals from their metal-complexes and whereas Cu was not detected in the filtrate, 32μg/mL of Zn remained in solution.

Table 3.5 presents the extraction efficiency with DTPA. First extraction with this reagent, all of the analyte metals (97, 63, 27, 99, 360μg/g of Cu, Fe, Mn, Pb and Zn) were mobilized to some extent from the soil. Unfrotunately, the recycled DTPA was no longer effective during the second extraction. Table 3.6 records that SCMC mobilized both Cu and Zn. (72μg/g and 43μg/g respectively) but had no effect on the Fe, Mn and Pb burdens in the soil extraction. After DEDTC precipitation, no metal was detected, but the second equilibration with recycled SCMC extracted only Cu and Zn (4.26 μg/g and 57μg/g respectively) levels that were insignificant when compared to the initial soil burdens.

It can be observed from Table 3.7 that ADA behaved similarly to SCMC; it also complexed Cu and Zn, but was ineffective for the other three metals. After treatment with DEDTC the Cu and Zn were precipitated from their metal-ADA complexes and the liberated ADA solution was able to extract 37 μg/g of Zn, but no more Cu was mobilized. For this reason, it was not necessary to perform any subsequent DEDTC treatment or a third extraction. Table 3.8 summarizes the extraction efficiencies with citric acid. Citric acid was somewhat effective at mobilizing all metals, but, relative to the other extractants, the efficiency of this reagent was quite low. During DEDTC precipitation, analyte metals were stripped from their metal-citrate complexes. The recycled citrate was capable of mobilizing more heavy metals but the efficiency of Cu, Fe and Zn mobilization decreased. Even the third equilibration continued to mobilize more metal contaminants. The quantity of Zn actually increased from the second to the third extraction.

Comparison of the structures of the six chelating reagents (Figure 3.1) reveals that all six structures are polycarboxylates and many have a heteroatom in the beta position. These structures are quite similar. The reasons for their different avidities for metals in the soil, probably can be explained in three ways:

(1) The distance between two carboxylic group within the structure. The smaller the distance between two groups, the more strongly the metal is chelated. If they are too far separated, it becomes increasingly difficult to form a strong complex.

(2) pH, plays an important role during the extraction process. Since different chelating reagents have different numbers of COOH, NH_2 groups, which result in the variance

of solution pH, certain metals become more easily chelated under acidic condition and others under alkline condition.

(3) Ionized form. Metal exists in soil in different valence states (e.g. Cu^+ or Cu^{++} e.g.) and chelating reagents have different chelating affinities toward the different metals.

In order to determine whether the metals were mobilized primarily by combination with the complex reagent, a separate extraction with distilled water was performed in which 50g of soil was equilibrated with 50ml of distilled de-ionized water. Metal analyses of the supernatant fraction by flame AAS demonstrated that only traces of metals were mobilized. It was concluded that the metals content observed for extractions in the presence of complexing agents resulted only from chelation. Arbitarily, various concentrations of the chelating reagent was prepared (0.1M for EDTA, 0.05M for SCMC, ADA or DTPA, and 0.022M for DPTA). If it is asssumed that extraction efficiencies were proportional to the concentrations of complex reagents, certain conclusions can be drawn.

Conclusions

As evidenced in Figure 3.2, 3.3, 3.4, 3.5 and 3.6, the extraction efficiencies of various chelating reagents toward different metals can be compared.

For Cu, the extraction efficiency (in the presence of the metal mixture) decreased in the order of DPTA>EDTA >DTPA>SCMC>ADA>citric acid;

For Fe, the order of efficiency was EDTA>DTPA>citric acid>DPTA>ADA ~SCMC;

For Pb, the order was EDTA>DTPA>DPTA>ADA ~SCMC ~citric acid. By contrast, SCMC, citric acid and ADA were ineffective;

For Mn, the order was EDTA>DTPA>Citric Acid>DPTA~ADA ~SCMC; the latter three reagents were only modestly effective for Mn;

For Zn, the order was EDTA>DTPA>DPTA>ADA>SCMC ~citric acid

A. The precipitation efficiency of DEDTC

It was demonstrated that DEDTC stripped metal from the metal-complex efficiently. Metal was transposed to metal-$(DEDTC)_2$ and precipitated. The transformation was especially efficient for Cu and Pb. But traces of other metals, including Zn and Mn, remained in the filtrate. Table 3.9 presents the metal complex formation constants of both EDTA and DEDTC. The formation constants of Cu-DEDTC and Pb-DEDTC are higher than those of EDTA, but the other constants are close even lower than those of EDTA. Yet in this studies, the heavy-metal-EDTA complexes were transposed efficiently to their corresponding metal-$(DEDTC)_2$ complexes and precipitated. A possible explanation might lie in the relative metal selectivities of the two reagents. The soil also contained appreciable quantities of available Ca, Mg and Fe that don't combine with DEDTC (or form weak complexes in the case of Fe) but do combine with the EDTA (even if more weakly) because they are in vast excess. By contrast, the DEDTC reagent is selective for heavy metals and can compete with the EDTA.

B. The extraction efficiency of recycled chelating reagents

The chelating reagents that had been liberated from the metal complexes (by reaction with DEDTC) were returned to the soil particulate fraction to be equilibrated a second time. With certain exceptions, the liberated reagents were still somewhat effective, however the extraction efficiency decreased in most cases.

Presumably, not all of Zn and Mn was in the same form in the sample, and only a certain fraction of the complexing reagent is liberated by reaction with the DEDTC so that only a fraction remained available to complex more heavy metal(s).

By comparing the extraction efficiencies of fresh chelating solution *vs.* recycled solution, it was found that:

(I). EDTA, DTPA and DPTA were the most efficient complexing reagents toward the six metals.

(II). DPTA and EDTA could be recycled at least three times, although the efficiency continued to decrease. The DTPA reagent lost its ability to mobilize more metal from the particulate fraction after treatment with DEDTC.

It is found that although the total quantity of extractant added to the soil was less than the heavy metal burden in the soil, by adding less than the required amount, the recycling process still works to make the process more efficient. The results demonstrated that extraction efficiencies under the experimental conditions were quite low for Fe and Mn no matter which one of the chelating reagent was used, which is consistent with the result reported by Peters (1998) that Cu, Pb, and Zn have greater than 70% of their distribution in forms amenable to soil washing techniques, whereas Mn and Fe were somewhat less amenable to soil washing using chelant extraction. Fortunately, Fe and Mn were not of great concern in terms of soil pollution.

Table3.1 Equilibration of the soil with 0.1M EDTA[a] for 24h or for 16h of shaking

		0.1M EDTA (24h)				0.1M EDTA (16h)			
	Soil Burden	**S1**	**S2**	**S3**	**Means (24h)**	**S1**	**S2**	**S3**	**Means (16h)**
Cu	486 ± 8%	128	119	111	119 ± 5%	123	122	117	121 ± 2%
Fe	32,098 ±7%	73	64	59	65 ± 9%	69	72	76	72 ± 4%
Mn	503 ± 4%	33	32	32	32 ± 2%	31	35	31	32 ± 6%
Pb	596 ± 7.6%	150	113	125	129 ± 11%	136	148	132	139 ±5%
Zn	2028 ± 7.6%	445	510	486	482 ± 5%	492	455	467	471 ±3%

[a] ug (metal)/g (soil)

Table3.2 Metals[a] released from the soil with distilled de-ionized water

Cu	**Mn**	**Pb**	**Fe**	**Zn**	**Mg**	**Ca**
N.D.	N.D.	N.D.	N.D.	N.D.	1.85	344.7

[a]: µg/g of soil

Table 3.3 Sequential equilibrations of soil with EDTA regenerated prior to cycles two and three by DEDTC precipitation

	Cu	**Fe**	**Mn**	**Pb**	**Zn**
Soil Burden (ug/g)	486 ± 8%	32,098 ± 7%	503 ± 4%	596 ± 7.6%	2028±12%
1st 0.1M EDTA equilibration (µg/g)	119±8%	64±5%	32±8%	113±8%	510±5%
Filtrate post DEDTC (µg/ml)	N.D.	4± 1%	45± 0.5%	2± 0.5%	52± 0.4%
2nd EDTA equilibration (µg/g)	76±0.4%	73±1%	75±0.8%	100±2%	384±0.4%
Filtrate post DEDTC treatment (µg/ml)	N.D.	2±0.3%	50± 0.5%	1± 0.5%	8± 0.3%
3rd EDTA equilibration (µg/g)	36±0.6%	62±1.6%	53±3%	58±2.5%	191±1.5%
Total % mobilized	**47**	**0.1**	**32**	**45**	**54**

1ST eqyukubratuib 0.1M EDTA (100mL) +100g soil, shaken 16h/centrifugation, V=47ml @pH 8.0, 2.0 g (11.68mmloles) NaDEDTC followed by filtration

2ND equilibration, recycled EDTA 45ml+50g soil, shaken 16h, V=33ml @pH=7.45, 1.0g NaDEDT followed by filtration

3RD equilibration recycled EDTA+50g soil, shaken 16h, V=22ml@pH6.8

Table 3.4 Sequential equilibrations of soil with DPTA regenerated prior to cycles two and three by DEDTC precipitation

	Cu	**Fe**	**Mn**	**Pb**	**Zn**
Soil Burden (ug/g)	486 ± 8%	32,098 ± 7%	503 ± 4%	596 ± 7.6%	2028±12%
1st 0.022 M DPTA equilibration (µg/g)	67±18%	9±8%	2±20%	10±15%	290±15%
Filtrate post DEDTC precipitation (µg/ml)	N.D.	N.D.	3	N.D.	32
2nd DPTA equilibration (µg/g)	52	41	20	33	337
Filtrate post DEDTC precipitation (µg/ml)	N.D.	3	19	1	32
3rd DPTA equilibration (µg/g)	40	36	17	23	196
Total % mobilized	**32**	**~0**	**~0**	**11%**	**41%**

1ST equilibration 0.022M DPTA equilibration (100ml+100g soil), shaken 16h then centrifuged. V=45ml, pH. 7.NaDEDTC (1.19g) followed by filtration

2ND equilibration with DPTA (40ml+50g soil), shaken 16h, V=32ml pH 7. NaDEDTC (0.8g) followed by filtration

3RD equilibration with DPTA (30ml+50 g soil), shaken 16h, V=23ml pH 7.0

Table 3.5 Sequential equilibrations of soil with DTPA regenerated prior to cycles two and three by DEDTC precipitation

	Cu	**Fe**	**Mn**	**Pb**	**Zn**
Soil Burden (µg/g)	486 ± 8%	32,098 ± 7%	503 ± 4%	596 ± 7.6%	2028±12%
1st 0.05 M DTPA equilibration (µg/g)	97±8%	63±6%	27±8%	99±7%	360±13%
Filtrate post DEDTC precipitation (µg/ml)	N.D.	N.D.	29	N.D.	9
2nd DTPA equilibration (µg/g)	0.3	0.72	50	N.D.	85
Filtrate post DEDTC precipitation (µg/ml)	0.3	N.D.	55.6	N.D.	89
3RD DTPA quilibration (µg/g)	N.D.	5	27	N.D.	83
Total % mobilized	20	~0	5.4	17	21

1ST 0.05M DTPA (00ml)+100g soil, shaken 16h centrifugation, V=46ml @ pH8.3

2g Na DEDTC followed by filtration.

2ND recycled DTPA40ml +50g soil, shaken 16h, V=33ml@ pH7.0

0.18gNaDEDTC followed by filtration

3RD recycled DTPA30ml +50 g soil, shaken 16h, V=26 @pH7

Table3.6 Sequential soil equilibration with SCMC regenerated prior to stage two by precipitation with DEDTC

	Cu	Fe	Mn	Pb	Zn
Soil Burden (µg/g)	486 ± 8%	32,098 ± 7%	503 ± 4%	596 ± 7.6%	2028±12%
1st 0.05 M SCMC equilibration (µg/g)	72	N.D.	0.6	N.D.	43
Filtrate post DEDTC precipitation (µg/ml)	N.D.	N.D.	N.D.	N.D.	N.D.
2nd SCMC equilibration (µg/g)	4.26	N.D.	1.6	N.D.	57

1ST 0.05M SCMC equilibration (100ml+100g soil), shaken 16h then centrifuged.
V = 47 ml. pH. 7.9

NaDEDTC (0.4g) followed by filtration.

2ND equilibration with SCMC (48ml+50g soil), shaken 16h then centrifuged. V = 45 ml.
pH 7.4

Table 3.7 Sequential soil equilibration with ADA regenerated prior to stage two by precipitation with DEDTC

	Cu	Fe	Mn	Pb	Zn
Soil Burden (ug/g)	486 ± 8%	32,098 ± 7%	503 ± 4%	596 ± 7.6%	2028±12%
1st 0.05 M ADA equilibration (µg/g)	32	N.D.	N.D.	3	192
Filtrate post DEDTC precipitation (µg/ml)	N.D.	N.D.	N.D.	N.D.	N.D.
2ND ADA equilibration (µg/g)	N.D.	N.D.	6	N.D.	37

1ST 0.05M ADA equilibration (100ml+100g soil), shaken 16h then centrifugation.

V = 45 ml pH 7.8

NaDEDTC (0.7g) followed by filtration.

2ND ADA equilibration (38ml+50g soil), shaken 16h then centrifuged, V = 45 ml, pH 8.0

Table 3.8 Sequential soil equilibration with citric acid regenerated prior to stages two and three by precipitation with DEDTC

	Cu	Fe	Mn	Pb	Zn
Soil Burden (µg/g)	486 ± 8%	32,098 ± 7%	503 ± 4%	596 ± 7.6%	2028±12%
1st 0.05 M DTPA equilibration (µg/g)	31	57	9	N.D.	85
Filtrate post DEDTC precipitation (µg/ml)	N.D.	4	N.D.	N.D.	N.D.
2ND 0.05 M DTPA equilibration (µg/g)	15	25	18	N.D.	53
Filtrate post DEDTC precipitation (µg/ml)	N.D.	3	12	N.D.	N.D.
3RD 0.05 M DTPA equilibration (µg/g)	6	9	9	N.D.	110
Total % mobilized	11%	~0	7%	0	12%

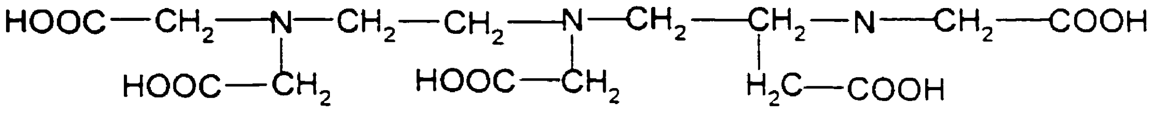
1ST 0.1M citric acid equilibration (100ml+100g soil). shaken 16h then centrifuged. V =47ml. pH 6.6 NaDEDTC (1g) followed by filtration

2ND equilibration with citric acid (40ml +50g soil). shaken 16h then centrifuged. V=19ml. pH 9NaDEDTC (0.48g) followed by filtration

3RD equilibration with citric acid (15ml+50 g soil). shaken 16h then centrifuged. V=15 ml pH 7

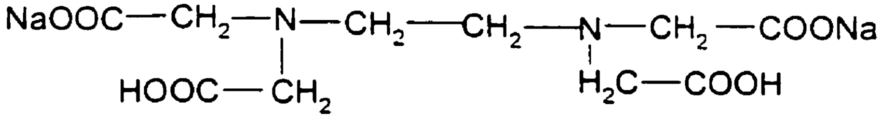
Figure 3.1 Structures of Chelating Reagents

DTPA:



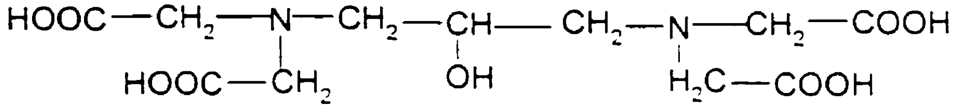
$\mathrm{HOOC{-}CH_2{-}N(CH_2{-}COOH){-}CH_2{-}CH_2{-}N(CH_2{-}COOH){-}CH_2{-}CH_2{-}N(CH_2{-}COOH){-}CH_2{-}COOH}$

EDTA



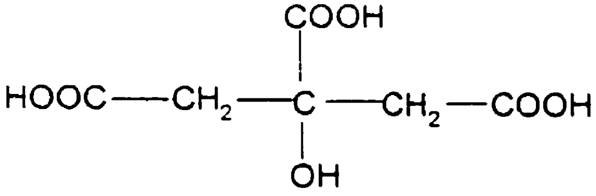
$\mathrm{NaOOC{-}CH_2{-}N(CH_2{-}COOH){-}CH_2{-}CH_2{-}N(CH_2{-}COOH){-}CH_2{-}COONa}$

DPTA



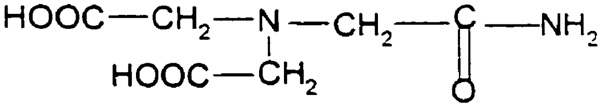
$\mathrm{HOOC{-}CH_2{-}N(CH_2{-}COOH){-}CH_2{-}CH(OH){-}CH_2{-}N(CH_2{-}COOH){-}CH_2{-}COOH}$

CITRIC ACID



$\mathrm{HOOC{-}CH_2{-}C(COOH)(OH){-}CH_2{-}COOH}$

ADA



$\mathrm{HOOC{-}CH_2{-}N(CH_2{-}COOH){-}CH_2{-}C({=}O){-}NH_2}$

SCMC

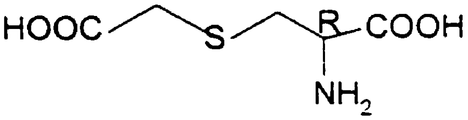
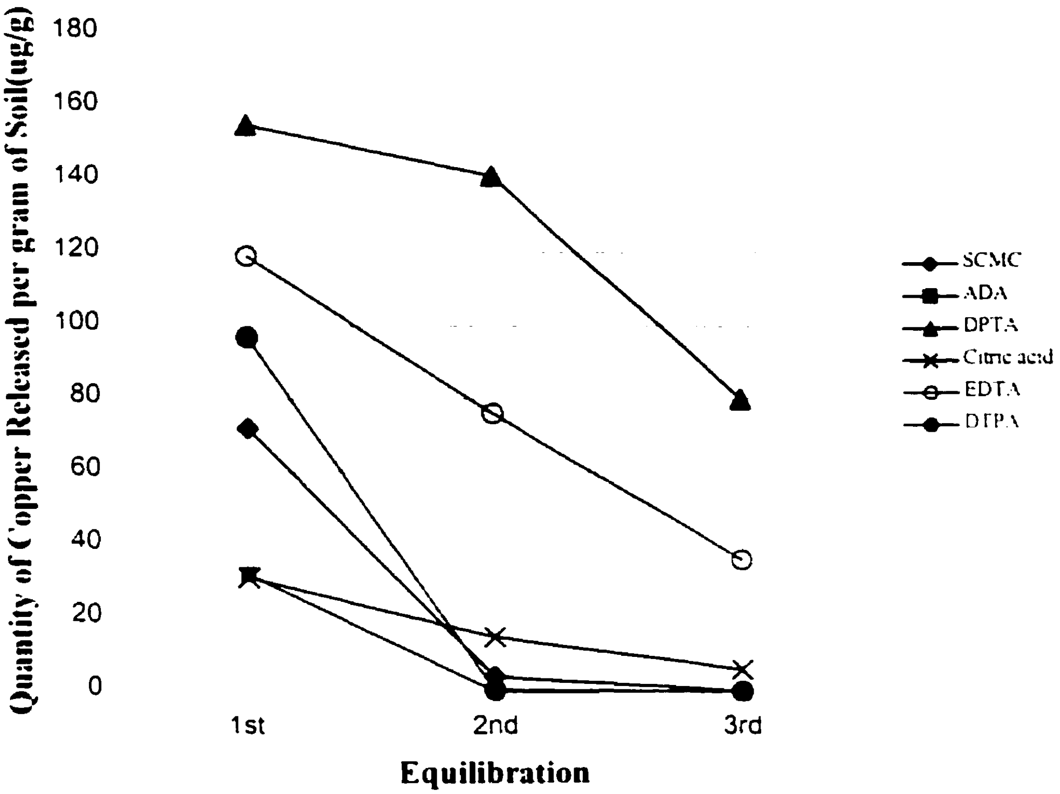
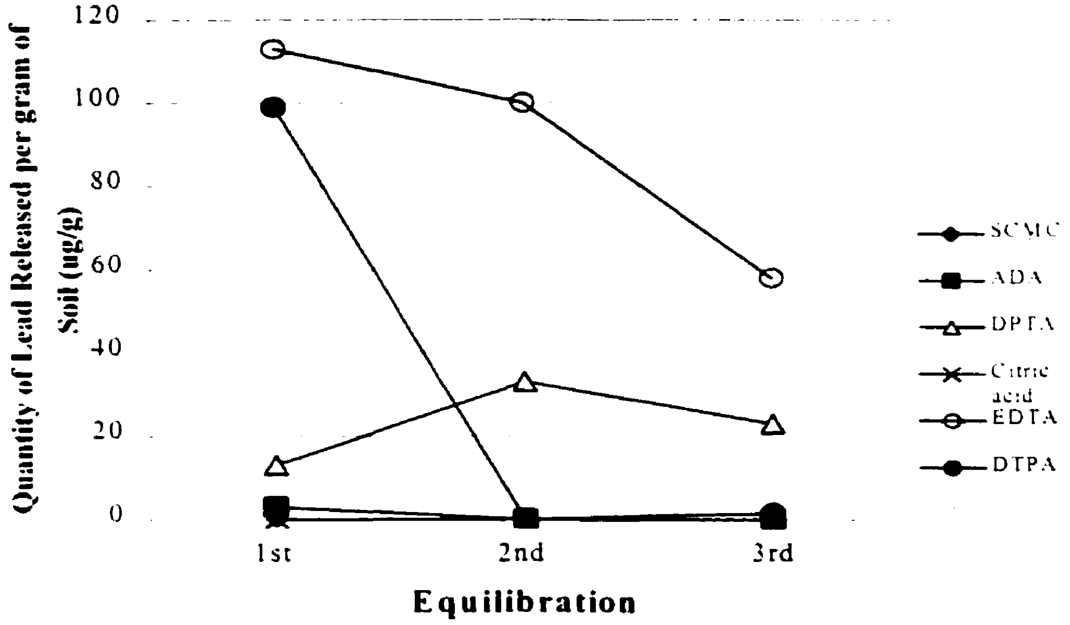


Figure 3.2 Sequential Extraction Efficiency for Cu



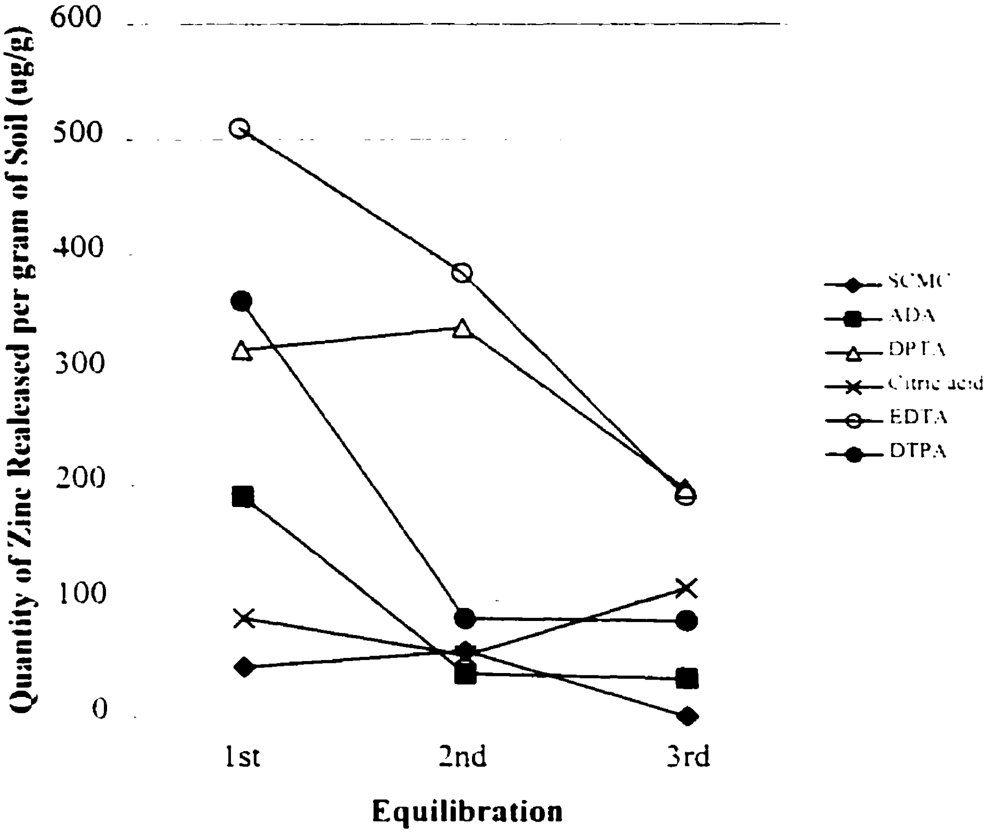
Notes: Each data point represents the mean of the replicates of the analysis.

Figure 3.3 Sequential Extraction Efficiency for Pb



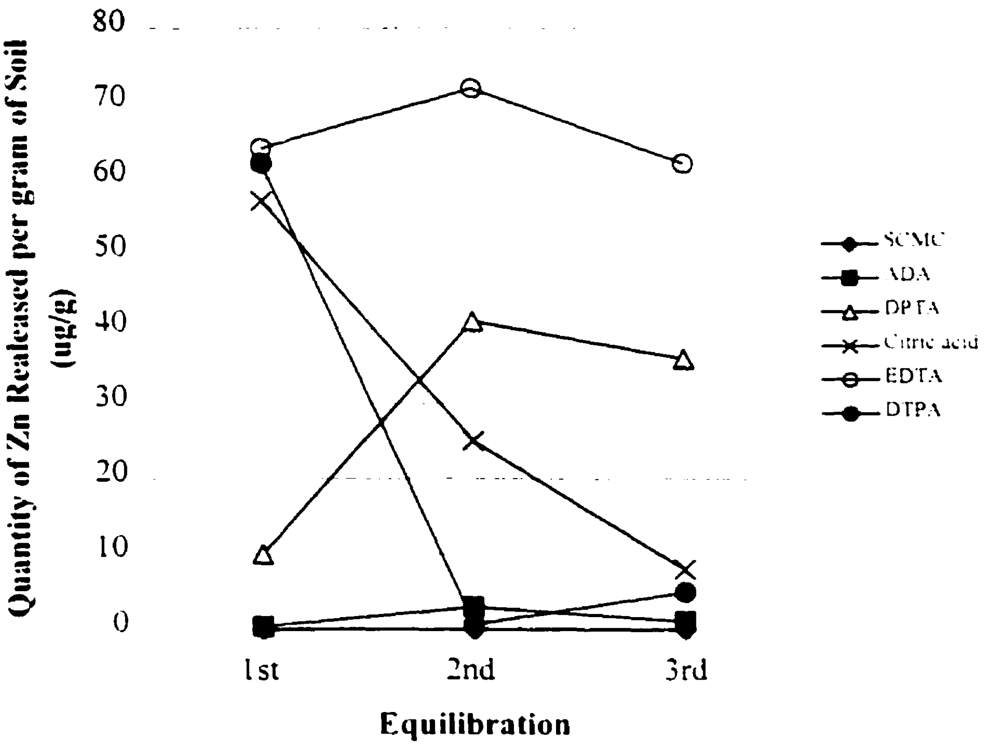
Notes: Each data point represents the mean of the replicates of the analysis.

Figure 3.4 Sequential Extraction Efficiency for Zn



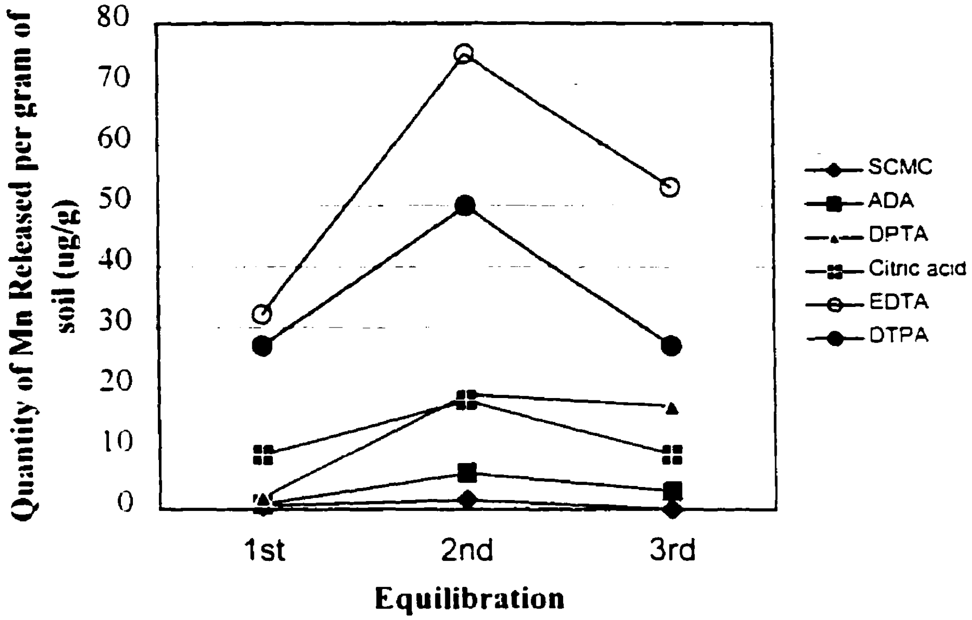
Notes: Each data point represents the mean of the replicates of the analysis.

Fugure3.5 Sequential Extraction Efficiency for Fe



Notes: Each data point represents the mean of the replicates of the analysis.

Figure 3.6 Sequential extraction efficiency for Mn



Notes: Each data point represents the mean of the replicates of the analysis.

3.2 Supercritical Carbon Dioxide Extraction of Metal Complex Enhanced by Surfactant

3.2.1 Introduction

A previous study (Ager, 1995) had demonstrated that metal ions can be removed from aqueous medium by complexometric extraction with supercritical carbon dioxide (Sc-CO_2). When coupled with supercritical fluid extraction, metals can be removed from aqueous media then accumulated efficiently on a trapping material consisting of granules of metallic iron (Fe^0). The zero-valent (ZV) iron is considered to be oxidized and solubilized while other more electro-active metal cations are reduced to their elemental form(s) and become plated on to the surfaces of the iron particles. The net reaction becomes one in which certain electro-active metal cations are spontaneously replaced by iron ions. It was of interest to determine whether the analogous reaction took place with metal-complexes. A Preliminary study was conducted by evaluating the recovery of Pb from Pb-DEDTC complex that had been suspended in an aqueous medium with the help of a surfactant. The non-ionic surfactant was added to the aqueous medium to generate a quasi-stable suspension of the metal-dithiocarbamate complex. Sc-CO_2 was then used to mobilize the metal-dithiocarbamate complex from the micelle suspension. At the same time, the mobilization of the surfactant into the Sc-CO_2 was also to be measured for the each extraction period.

Since metal-DEDTC complexes are only sparingly soluble in water, several problems can result when metal-dithiocarbamate (metal-DTC) complexes are extracted from aqueous medium with Sc-CO_2. Solid particles can block the capillary restrictors of the extractor and the presence of solids can cause the rates of mobilization purging of the solute(s) to become erratic. The concept was to maintain the dithiocarbamate (DTC) complexes as a finely divided suspension in the aqueous medium by generating surfactant spheres (micelles) that would retain the metal-DTC complexes in their lipophilic interior while the more polar functional groups on the exterior of the micelles would impart some water solubility. Provided that the surfactant concentration exceeds a certain critical concentration (critical micelle concentration, CMC) the layers of surfactant molecule reorganize spontaneously to form micelles. However, it was unclear whether the micelles would be mobilized in-tact or whether the Sc-CO_2 could strip the metal-DTC complex from the micelle leaving the empty micelle behind. It was hoped that the complexes would be mobilized into the Sc-CO2 while the surfactant molecules would be left behind and might be re-used.

The surfactants used in this study were Triton DF-16, TritonX-100 and Triton X-405, which are members of the most important class of commercial nonionic surfactants (polyoxyethylene alcohols), and Triton 770 was used as an example of an anionic surfactant. The physical properties of polyoxyethelene alcohols define their use in various applications. The most important physical properties of these materials are cloud point, foam profile, solubility, and wettability. The most common application of these materials is in emulsification and detergency. The properties and applications of polyoxyethylene alcohols are dependent on the molecular weight and structure of the hydrophobe (R in the structure below), the number of moles of ethylene oxide (n) per mole of hydrophobe contained in the chain, and the chain length.

$$\mathbf{RO\,(CH_2CH_2O)nOH}$$

The hydrophobe R is the oil soluble region of the surfactant. It can be either a linear or branched hydrocarbon chain obtained from synthetic or natural petrochemical sources. The hydrophobe is the basic "building block" of the surfactant molecule. The ethylene oxide chain is the hydrophile, or water-soluble portion, of the surfactant. In general, the larger the *n* values of the molecule, the more water-soluble is the molecule becomes.

3.2.2 Experiment

Reagents:

Pb^{2+} solution was prepared by dissolving $Pb(NO_3)_2$ (Aldrich Chemical Company, Inc., Milwaukee, WI) in de-ionized distilled water and diluting to the appropriate concentration. Nonionic surfactants Triton DF-16, Triton X-100, Triton X-405 and ionic surfactant Triton 770 were purchased from Sigma Chemical Co.(USA). $Co(NO_3)_2$. Ammonium thiocyanate (NH_4SCN) methylene chloride, methyl isobutyl ketone (MIBK) and methanol were purchased from Aldrich (Canada).

Sample preparation:

A solution containing 3ml Pb^{2+} (500 μg/ml) prepared from stock $Pb(NO_3)_2$ solution was mixed with 24ml surfactant solution [4% (w/v)] and 3ml MIBK, followed by a 5-fold excess (~0.008g) of DEDTC. The suspension was well mixed then transferred to the 40ml capacity extraction vessel. A stirrer bar was used within the vessel to maximize the homogeneity of the sample suspension.

Supercritical Fluid Extractor:

The supercritical fluid extractor (Figure 3.7) a CCS Instrument Systems Model 3100, Avondale, PA, USA consisted of 50ml capacity, temperature and pressure equilibration vessel (TPEV) connected in series with a 40ml capacity extraction vessel (EV). Each vessel was mounted vertically within a separate compartment of the extractor and enclosed within a thermostatted heating jacket that permitted isothermal operation between ambient and 150°C over the course of the extraction. In operation, the aqueous sample was pressurized to the desired operating pressure by opening pneumatically controlled needle valves 4,2,7,6 and 1 while closing valves 3 and 5. Once the operating pressure had been achieved, valve 5 was opened and valve 6 was closed to reverse the flow of fluid to the extraction vessel. The TPEV acted as a supplementary dampener to smooth the pressure pulses generated by the air driven high pressure pump. Frequently, the TPEV was permitted to remain filled between extractions. Liquid mobile phase modifier was added by means of a high performance liquid chromatography (HPLC) pump located between the TPEV and the EV. The programmed run consists of 2 minute static equilibration followed by 30 minute of dynamic extraction followed by a further 20 minute of polishing in which only Sc-CO2 served as the mobile phase. The extractor effluent was trapped in solvent by dipping the exit tip of the capillary restrictor (0.5mm silica capillary tube) into 25 ml of methanol contained in a 40ml test tube.

Sample analysis:

1. Metal analysis

Metal analyses were performed by evaporating the methanolic trapping solution and dissolving the residues in 3 ml of 20% HNO_3, and 6ml of de-ionezed distilled water and 1ml methanol. The sample was analyzed by flame AAS.

2. Surfactant Analysis

Color developed with cobalt thiocyanate (Tabak and Bunch, 1981) was modified/optimized to determine the content of nonionic surfactant. The method was adopted in this study to measure linear primary alkyl ethoxylate alcohol nonionic surfactant (12-18 carbon atoms). The sample from either the methanolic trap or the extraction vessel was extracted with ethyl acetate (EtOAc) to concentrate the nonionic surfactant, and then died over sodium sulfate (Na_2SO_4) followed by evaporation to dryness on a steam bath aided by a gentle stream of clean dry nitrogen. The nonionic residue was dissolved in 15 ml of methylene chloride (CH_2Cl_2). An aliquot, 10.0 ml, was pipetted into a 125-ml capacity separatory funnel. Five ml of the cobalt thiocyanate solution was added and the phases vigorously mixed by shaking for 1 minute. After the layers had separated, the CH_2Cl_2 layer was filtered into a graduated 10-ml capacity, glass stoppered receiving tube until 7ml volume had been collected. The spectrometric analysis was performed with a model Novaspec 4049 (LKB, BIOCHEROM).

Results and Discussion:

Pressured CO_2 was transported through the extraction vessel where it solubilized non-polar solutes that were accumulated in the head-space above the aqueous sample. The Sc-CO_2 phase was replaced continuously by fresh solvent and solutes were entrained to the exit of the extractor that was terminated with a capillary restrictor. It was anticipated to be helpful to the extraction process to concentrate the solute materials in a water immiscible organic solvent that additionally was lighter than water. In preliminary studies, MIBK proved to be more efficient than ethyl acetate.

In further studies, three conditions were evaluated. Either (i.) 3ml MIBK was added into the starting sample; (ii) 3 ml MIBK was added into the starting sample followed by 0.25ml/min of purging with MIBK during 20 minutes or (iii) no MIBK was added. The surfactant chosen for this trial was Triton X-100 since it has been used previously for soil treatment (Huang et al., 1997). It was demonstrated (Table 3.10) that the Pb mobilization efficiency depended greatly on the addition of MIBK. The efficiency (40%) obtained without the addition of MIBK was only approximately one half of the efficiency (~80%) when MIBK was added. The organic modifier enhanced the metal mobilization- it helped CO_2 to strip the metal complex from the aqueous suspension. There were no large differences in efficiencies between condition (i) and (ii). Approximately 75% mobilization efficiency was obtained for both conditions. It was concluded that 3 ml MIBK was sufficient to enhance the metal mobilization into the Sc-CO_2. The major portion of the metal had already been mobilized during the transfer of the 3ml MIBK. It was not necessary to add any more organic phase modifier during the extraction period. The quantity of Pb that remained in the extraction vessel plus the quantity of Pb in the methanolic trap did not account for the total Pb that had been added initially to the sample. A possible explanation is that some of the metal analyte became stuck to the walls of the transfer lines. The possibility that some of the metal complex might have been trapped inefficiently from the Sc-CO_2 stream, seemed less likely based on previous experiments

Four different surfactants were evaluated to test their influences on metal mobilization. The surfactants were Triton DF-16, Triton X-100, Triton X-405 and Triton 770. They were available commercially and were characterized as "low foam forming" (Triton DF-16) or had been used previously for soil treatment (Triton X-100, Huang et al., 1997). Arbitrarily, the concentration of the surfactant for each trial was fixed at 4% (w/v) which exceeded the critical micelle concentration (CMC). Micelle formation was thus assured. Table 3.11 summarizes the efficiency of metal mobilization in the presence of each of the four test surfactants. Pb was not mobilized efficiently if Triton DF-16 or Triton770 were used (the efficiency was only 48 or 49%) whereas Triton X-100 and Triton X-405 performed more efficiently (74 and 77% respectively). More of the Pb-complex became attached to the nonpolar groups of Triton X-100 and Triton X-405 than to the Triton DF-16 and Triton 770. The HLB (hydrophile-lipophile balance) is an important parameter for surfactants. It is the expression of the relationship between size and strength of the polar (water-soluble) and nonpolar (oil-soluble) groups of the surfactant. Water-soluble surfactants have high HLBs. Among the four surfactants, Triton DF-16 and Triton 770 have higher HLBs than the other two surfactants, resulting in more of the Pb being attached to water soluble groups and would not be mobilized with the nonpolar mobile phase carbon dioxide. The Triton X-100 and Triton X-405 have lower HLBs, and more of the Pb became bound to nonpolar groups and would mobilized more readily.

Approximately 78% of $Pb(DEDTC)_2$ complex was mobilized from the Triton X-405 micelle suspension. The other aspect of interest was the quantity of surfactant that was also co-extracted. The less surfactant that is lost, the more economical the process would become. Any surfactant that remained could be re-used. The loss of surfactant under different conditions is summarized in Table 3.12. The quantity of surfactant that had been accumulated in the effluent during successive five-minute intervals (either with or without 3ml MIBK having been added to the starting sample) is recorded. The results demonstrated that whether MIBK was added or not, little surfactant was mobilized during the initial 10-minutes of extraction. However, the quantities of surfactant accumulated in the methanolic trap between the 10 and 15-minute intervals amounted to 11.97mg, 12.63mg, 12.8mg, and 15.2mg in four separate runs. For the interval between 15 and 20 minutes, 16.18mg, 17.09mg, 20.18mg, and 34mg of surfactant were accumulated in the trap. During the final ten-minute interval, surfactant continued to be mobilized. Similar quantities of surfactant were observed for both experimental conditions. The maximum quantity of surfactant was observed in the 15-20 minute interval.

It was observed that the surfactant loss was approximately 25% when 3ml MIBK was added to the sample, which was appreciably greater than the 14% loss in the absence of added MIBK. Seemingly, the added MIBK affected the surfactant mobility as well. Figure 3.7 illustrates the tendencies of the $Pb(DEDTC)_2$ complex to become mobilized as well as the mobilization of surfactant during successive 5- minute intervals over the course of the 30-minute of extraction. No metal was extracted during the initial 5 minutes, but Pb was observed in the ten-minute trap. The Pb content was increased at subsequent intervals and reached a maximum at the 20-minute interval then decreased subsequently. At the 30-minute interval most of the Pb had been mobilized. Interestingly, the mobilization maximum for both Pb and Triton X-405 occurred at the same time interval (20-minutes). It was concluded that 30 minutes of extraction was sufficient for the mobilization.

Conclusions:

When combined with diethyl dithiocarbamate, metals form water insoluble complexes that can be recovered by filtration. In this study, supercritical fluid extraction was coupled with a surfactant to decontaminate the metal-precipitated suspension. Pb was chosen for this preliminary study and MIBK was used as mobile phase modifier. Four surfactants were tested as aids to mobilize Pb. Concurrently, the loss of surfactant to the mobile phase was also evaluated.. The results can be summarized as follows:

- MIBK is an effective co-mobilization solvent that helps to transfer Pb (form unknown) from the extractor to the outlet trap. It was not necessary to supplement the mobile phase Sc-CO_2 with MIBK during the 30-minute extraction period: MIBK, 3ml, added directly to the aqueous sample, was sufficient to maximize the recovery of Pb from the aqueous suspension.

- The greatest Pb mobility was obtained when Triton X-405 or Triton X-100 surfactant was used to generate the cloudy micelle suspension.

- The recovery of Pb from the Triton X-405 suspension during 30-minute of extraction reached 82% while the surfactant loss amounted to approximately 27%. The maximum mobility for both Pb and surfactant was observed at the fifteen-twenty minute interval.

Table 3.10 Extraction efficiencies in the presence or absence of MIBK added as a mobile phase modifier

Experimental condition	Sample	Initial Pb (μg)	Residual Pb in sample suspension (μg)	Pb in the methanolic trap (μg)	Extraction Efficiency (%)
3ml MIBK added to the initial sample	S1	774	209	420	73
	S2	936	228	534	76
3ml MIBK + 0.25ml/min MIBK purging for 20 minutes	S1	936	214	587	77
	S2	852	180	550	79
No MIBK added	S1	926	557	60	40
	S2	879	490	80	44

Note: For this trial, Triton X-100 surfactant was used to form micelle. The extraction time was 30 minutes followed by 20 minutes of polishing.

Table 3.11 Pb recovery by extraction with SC-CO_2 in the presence of various surfactants

Surfactant	Initial Pb in the aqueous suspension * (μg)	Pb[a] remaining in the sample post extraction (μg)	Mobilized[b] Pb (μg)	Extraction Efficiency[c] (%)
Triton DF-16	774	394	128	49
Triton X-100	852	219	525	74
Triton X-405	1119	247	654	78
Triton 770	705	368	191	48

Note: experimental conditions for the above trials were 3ml Pb^{2+} + 24ml of 4% surfactant solution + 3ml MIBK. No supplementary MIBK was added during the extraction stage.

The extraction time was 30 minutes followed by 20 minutes of polishing.

* Quantity of Pb added initially to the aqueous sample.

[a] Quantity of Pb that remained in the extraction vessel post extraction

[b] Quantity of Pb detected in the methanol trap

[c] The extraction efficiency was calculated based on the quantity of unextracted Pb and the quantity added initially.

Table 3.12 Triton X-405 mobilization during the Sc-CO_2 extraction

Time (min)	Surfactant Amount (mg)				Pb amount (μg)
	Without MIBK		With MIBK		
	S1	S2	S1	S2	S1
5min	0	0	0	0	14.10
10 min	0	0	0	2.80	90.20
15 min	11.97	12.63	12.80	15.20	95.58
20 min	16.18	17.09	20.18	33.95	135.39
25 min	10.63	12.18	39.26	32.50	52.81
30 min	11.08	12.09	35.81	30.60	41.18
20min polishing	54.36	39.45	46.34	34.07	110.25
Total	104.22	93.44	154.39	179.17	525.41
Mobility (%)	**15.51**	**13.90**	**22.97**	**26.66**	**81.91**
Mean	**14.71%**		**24.82%**		**81.91%**

Figure 3.7 Supercritical Fluid Extractor System

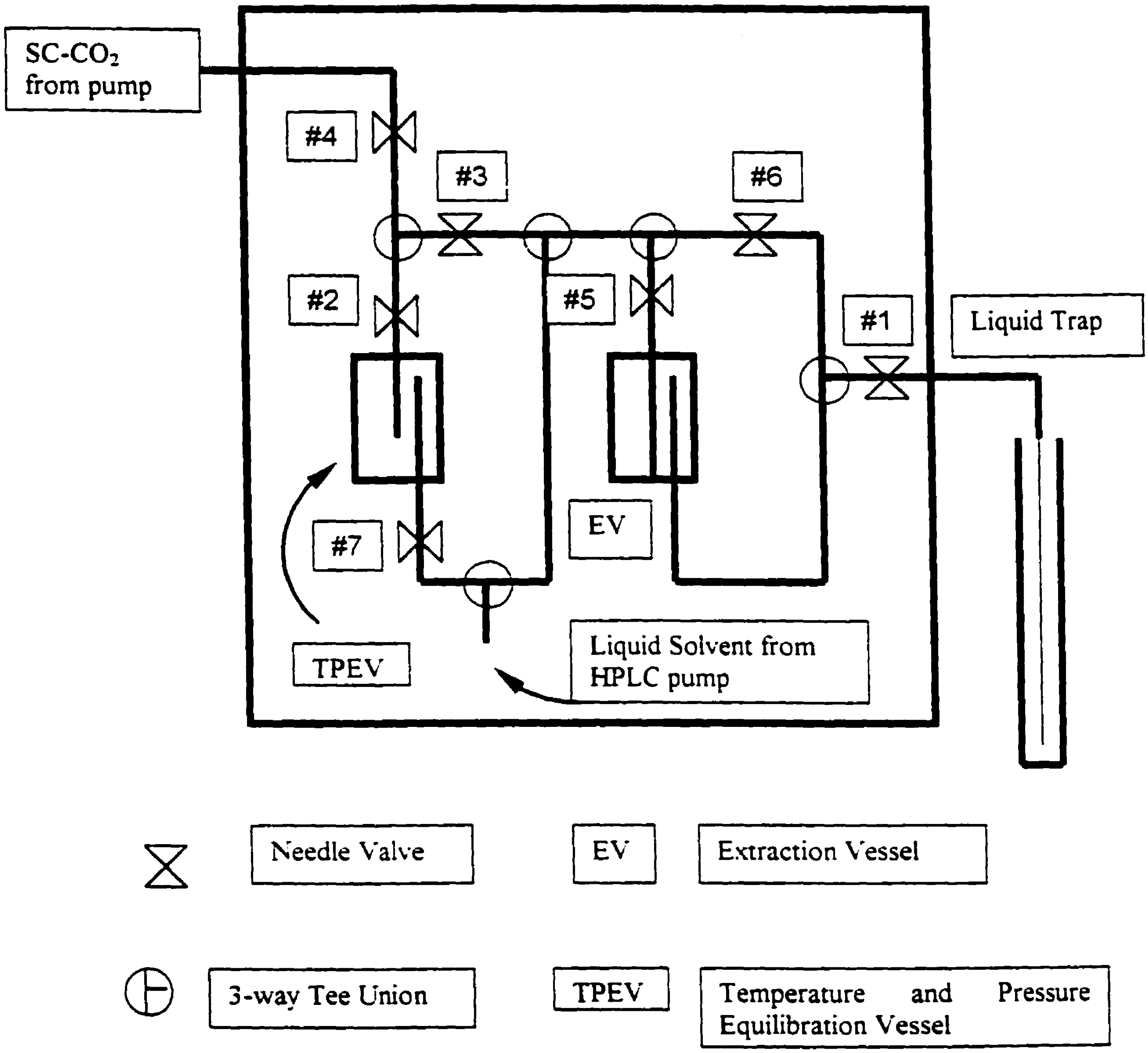
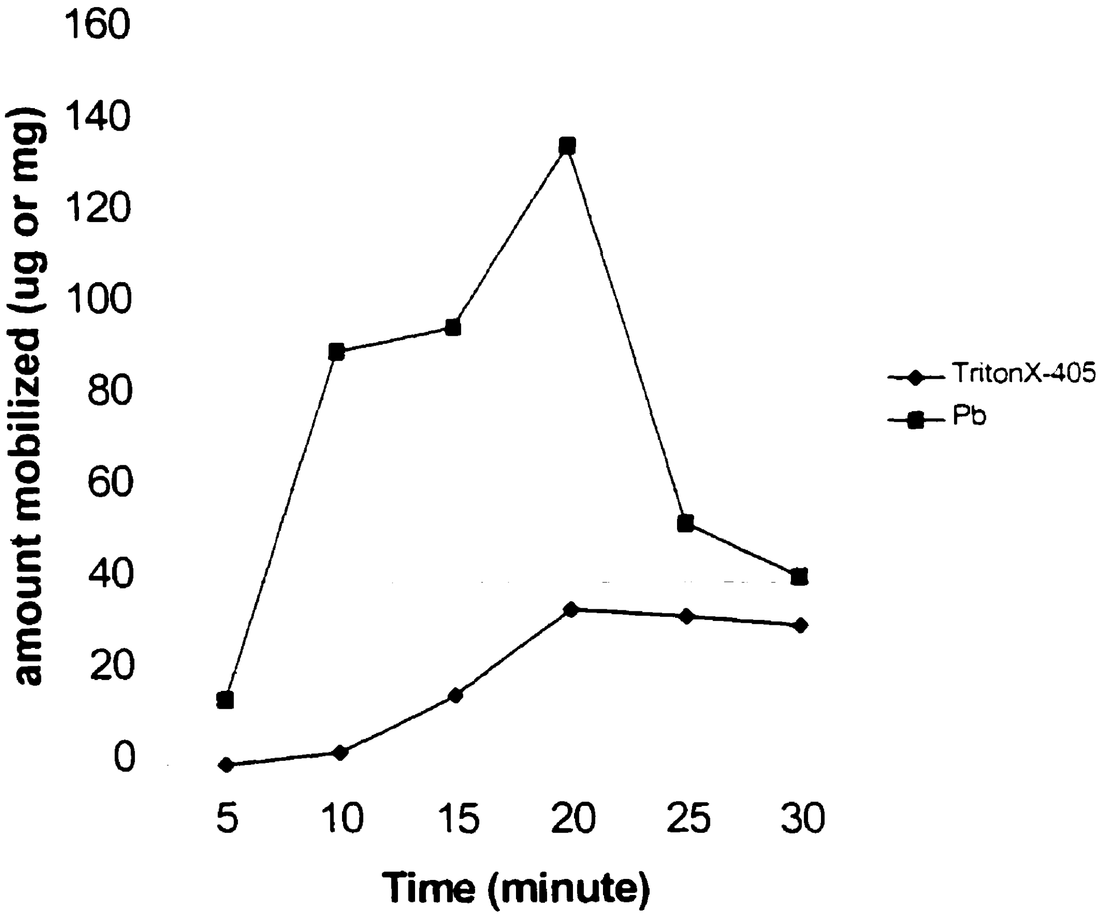


Figure 3.8 Mobilization of Triton X-405 and Pb observed in successive 5-minute fractions during 30 minutes of extraction



EDTA), and EDTA, which is a widely used but less selective chelating agent were selected for the following trials.

Reagents:

HEDC was synthesized from reagent grade chemicals following the method of King and Fritz (1985). Sodium hydroxide (40.0g) and di-ethanolamine (105.1g) were dissolved in methanol (400 ml) contained in a 1 L round bottom flask. The solution was cooled to below 10°C in an ice bath and the head space was purged with N_2 while 114g of carbon disulfide was added dropwise. After 2 h, the methanol was removed on a rotary evaporator at a bath temperature of 35°C. The resultant viscous liquid was induced to crystallize by adding 400 ml of 2-propanol accompanied by vigorous mixing. The yellow precipitate was recovered by filtration and dried under vacuum at room temperature. The recovery of sodium (2-hydroxy-ethyl) dithiocarbamate was ~150g. HEDC stock solution (0.2 M) was prepared. Magnesium granules were purchased from Alfa Aesar (Ward Hill, MA) and EDTA, trace metal grade was purchased from ACROS (Montreal, QC).

Experimental Procedures:

A. HEDC

Three accurately weighed soil samples (~1g) were mixed with 0.2 M HEDC (25ml), shaken for 13h centrifuged, filtered and the heavy metals content in the supernatant fraction was determined (**1st extraction**). Mg flakes (0.5g) were added to the solution that was shaken for 2h, filtered and the content of heavy metals in the filtrate was measured. The filtrate, containing the liberated HEDC, was combined with 1g fresh soil and equilibrated by shaking for 13h. Post centrifugation and filtration, the metals content in the filtrate was again measured (**2nd extraction**). Mg flakes (0.2g) were added to the filtrate fraction and the resulting suspension was shaken for 2h, filtered then analyzed for heavy metals. The filtrate was combined with Mg flakes (0.2g) and fresh soil (~1g) shaken for 2h then centrifuged, filtered and analyzed for heavy metals (**3RD extraction**).

B. Kinetics of Stripping of Heavy Metals by Mg

Soil (~1g) was added to 0.1M EDTA (25ml) in each of six Nalgene centrifuge tubes The tubes were shaken for 16h, centrifuged, filtered and the supernatant fraction was assayed for heavy metals. A second set of six tubes was prepared similarly. Each tube was then amended with 1 g Mg then shaken for varying times (0.5, 1.0, 1.5, 2.0, 2.5 or 3.0h). Post filtration, heavy metals were determined in the filtrate. The filtrates, from the 2.5h and 3h equilibration, were amended with 0.5g of fresh soil shaken for 16h, centrifuged and filtered prior to heavy metal determinations.

Results and Discussion:

The results, recorded for the extraction of 1g soil with 0.2M HEDC (25ml), are summarized in Table 3.13 The mobilization of Cu, Pb, Zn, Fe, and Mn accounted for 56.8, 47.8, 35.7, 1.03 and 19% respectively of the initial burdens in the soil. When 0.5g of Mg flakes were added to this supernatant fraction from the soil and shaken for 2 hours, the metal contents plunged to trace levels for Cu, Pb and Zn and were non-detectable for Fe and Mn. This decline presumably was the result metal cementation reactions and or hydroxide induced precipitation. In order to characterize the process, the experiment was repeated but the residual Mg granules were rinsed with nitric acid after they had reacted with metal complexes. The HNO_3 washes were followed by several washes with distilled water. The metal contents in the solution were 199.5μg of Cu, 271μg of Pb, 233μg of Zn, 37μg of Fe, and 9μg of Mn, which were comparable to the metals content in the solution before treatment with Mg (268.8μg Cu, 297.6μg Pb, 696μg Zn, 345.6μg Fe, and 96μg Mn). Thus, an appreciable portion of Cu and Pb was transferred from metal complexes in solution to the surfaces of the Mg, as well as a portion of the Zn was transferred. By contrast, the decrease of Fe and Mn was due principally to precipitation since we were unable to detect much of them on the Mg surfaces.

The recycled HEDC solution was returned to a 1g aliquot of fresh soil. The reason for using a fresh soil sample was that it was suspected that the HEDC extractable fraction of the total metal burdens would have been almost completely released from the soil during the initial extraction. Table 3.13 documents the ability of recycled HEDC to mobilize Cu, Pb, Zn and Fe (but not Mn) although the quantities that were released were lower (48.7%, 34.3%, 17.7%, 0.86% and 2.8%) in comparison to the first extraction. The resulting solution was treated with Mg flakes, filtered, then combined with fresh soil (1g) to generate the third extraction. In the third extraction, the efficiency for Cu, Pb, Zn, Fe and Mn were 34.1%, 39.9%, 3.5% 0.74% and 0%, respectively. Whereas the extractant had become ineffective for Zn, Fe and Mn, it continued to mobilize some Cu and Pb.

When compared to other chelating reagents, EDTA is much less selective towards different metals but very efficient. It was chosen for further experiments to determine the kinetics of Mg-mediated heavy metal stripping from the EDTA-metal complex in order to optimize the length of time for the Mg treatment. Table 3.14 records that after being treated with Mg for 0.5 hour, the quantity of Cu had been decreased from 342 µg to 20 µg, Pb from 380 µg to 152 µg, Zn from 1596 µg to 960 µg, Mn from 296 µg to 191 µg and Fe from 2204 µg to 8 µg. It is apparent that Cu and Fe were stripped efficiently by the Mg in a short time. Further, approximately 50% of the Pb, Zn and Mn were transferred within 0.5 hour. With increased reaction times, the contents of Cu, Pb and Fe did not change appreciably whereas the quantities of Zn and Mn in the solution continued to decrease gradually. The final content of Zn and Mn in the solution were 284.8 µg and 83.2 µg respectively, which indicates that approximately 82% of Zn and 72% of Mn had been eliminated from solution after 3h of treatment with Mg flakes. Figure 3.9 illustrates the kinetics of stripping for the five metals during three hour of reaction with 0.5 g Mg flakes.

Conclusions:

The synthetic HEDC possessed characteristics similar to DEDTC, although it did not form precipitates with heavy metals. It was generally able to extract Cu, Pb, Zn, and Fe from soil, but had little effect on the soil-bound Mn. Mg flakes were demonstrated to strip heavy metals efficiently from their metal complexes presumably because this reagent has a higher redox potential relative to Fe^0. Metals were transferred from aqueous solution to the solid phase through cementation on Mg surfaces (Cu, Pb and part of Zn) and by hydroxide induced precipitation (Fe, Mn and part of Zn). Virtually complete stripping of Cu and Fe and 50% of stripping of Zn, Mn and Pb were achived in the first one-half hour and the remaining Zn and Mn were eliminated more gradually during the next two and half hours. By contrast, the quantity of lead remained constant after the first one-half hour.

Table 3.13 Metal extraction efficiencies with HEDC regenerated in stages two and three by treatment with Mg

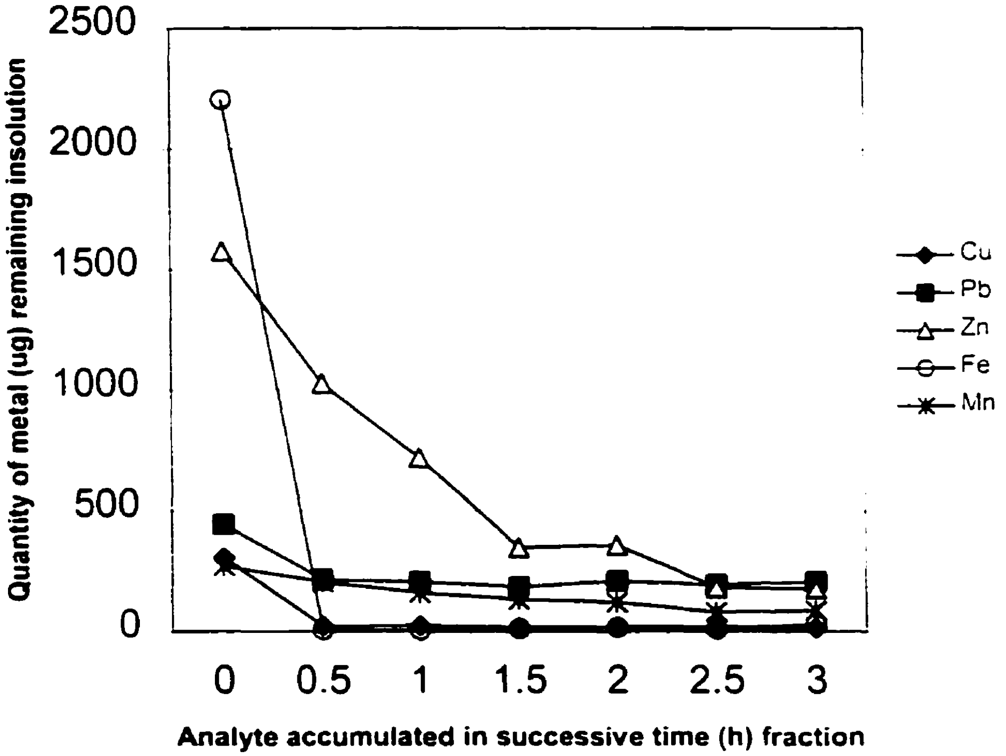
	Sample	**1st. E. E.* µg (%)**	**recycled sol'n (µg)**	**2nd. E.E.* µg (%)**	**recycled sol'n (µg)**	**3rd. E.E.* µg (%)**
Cu	S1	286.8 (58.9%)	9.5	200.25 (41.1%)	N.D.	69.5 (28.5%)
	S2	274.8 (56.5%)	6.8	249.3 (51%)	N.D.	90.3 (37%)
	S3	268.8 (55.0%)	5.1	264.1 (54.0%)	N.D.	91.5 (37.6%)
	Mean	**56.8%**		**48.7%**		**34.1%**
Pb	S1	262.8 (44%)	16.34	186 (31.1%)	8.28	102 (34%)
	S2	296.4 (49.6%)	15.45	223.2 (37.4%)	11.25	144.2 (48.3%)
	S3	297.6 (49.8%)	14.06	206.15 (34.5%)	12	111.75 (37.4%)
	Ave.	**47.8%**		**34.3%**		**39.9%**
Zn	S1	792 (39%)	7.22	333 (16%)	3.74	24 (2.4%)
	S2	684 (33.7%)	7.03	394.2 (19.4%)	2.85	38.58 (3.8%)
	S3	696 (34.3%)	8.36	359.1 (17.7%)	3.04	42.75 (4.2%)
	Ave.	**35.7%**		**17.7%**		**3.5%**
Fe	S1	358.2 (1.1%)	N.D.	320.25 (0.99%)	N.D.	118.57 (0.7%)
	S2	327.6 (1.0%)	N.D.	384.3 (0.99%)	N.D.	107.8 (0.67%)
	S3	345.6 (1.0%)	N.D.	206.15 (0.6%)	N.D.	138 (0.86%)
	Ave.	**1.03%**		**0.86%**		**0.74%**
Mn	S1	96 (19%)	N.D.	13.24 (2.6%)	N.D.	N.D
	S2	96 (19%)	N.D.	13.39 (2.6%)	N.D.	N.D.
	S3	96 (19%)	N.D.	16.34 (3.2%)	N.D.	N.D.
	Ave.	**19%**		**2.8%**		**0%**

Note: E.E. refers to extraction efficiency*

Table3.14 Kinetics of Stripping of Heavy Metals by Mg

Time (hour)	Cu (ug)		Pb (ug)		Zn (ug)		Fe (ug)		Mn (ug)	
	S1	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**	**S1**	**S2**
16h ext.	305	342	443	380	1577	1596	2204	1980	270	296
0.5 h	21	20	214	152	1028	960	5	8	205	191
1.0 h	24	20	205	169	720	672	5	7	161	175
1.5 h	17	20	184	173	348	416	12	11	133	138
2.0 h	17	15	208	170	357	348	17	12	121	126
2.5 h	19	16	194	172	182	300	11	15	81	109
3.0 h	14	12	206	156	178	284	30	16	87	83

Figure 3.9 Kinetics of Stripping of Metal by Mg



CHAPTER IV GENERAL CONCLUSIONS

The remediation of soil that has been contaminated with excessive levels of heavy metals has become the goal for many scientific disciplines including soil and environmental sciences in recent years. Of the various techniques, containment of the contaminated material continues to be perceived as being cost-effective in the short term but does not remedy the situation. The heavy metals continue to be bio-available to organisms. A variety of physical and chemical treatments have been evaluated to decrease the availability of heavy metals within the soil. Yet, the options remain somewhat limited. One can moderate toxicity by changing the oxidation state(s) of selected metal contaminants or one can make the toxicant(s) less available to organisms. Most of the remediation studies have used the latter approach. Soil washing (or in-situ soil flushing) have focused mainly on (*i.*) the application of chelating reagents to separate metals from the soil and (*ii.*) optimizing the conditions (such as pH) to maximize the extraction efficiency. In the current studies, efforts were directed to the recycling of the complex reagent(s) in an effort to minimize processing costs.

The experiments were divided into four parts: (1) preliminary studies on the preparation and characterization of soil that included grinding, sieving, soil texture measurements, total metals content post digestion and the distribution of metals in different soil fractions as well as (2) a comparison of the extraction efficiencies of six chelating reagents toward Cu, Pb, Zn, Fe, and Mn. Additionally, the chelating reagent was liberated and recycled by treatment of the metal-complexes with disodium diethyl dithiocarbamate (DEDTC). Additionally, supercritical CO_2 was used to extract metal-DEDTC complexes using various surfactants to maintain the metal-DEDTC complexes in suspension. Finally, (4) magnesium metal was evaluated as an alternative method for liberating the water-soluble chelating reagent from the complex so as to be able to recycle this reagent as well.

In initial experiments, the soil sample was characterized with respect to texture and heavy metal burdens indicated that the soil was heavily contaminated by heavy metals, especially Zn, Pb and Cu that appreciably exceeded tolerable levels. Additionally, the soil contained an appreciable amount of iron. However, the quantity was similar to levels in many pristine soils. Therefore, an important property of the optimum chelating agent is one that minimizes the extraction of iron into solution, while maximizing the extraction of the heavy metals of concern. For this soil, it was observed that a large proportion of heavy metals were associated with the Fe/Mn oxide fraction. The organically bound heavy metals were probably bound strongly or intercalated within the crystalline/amorphous lattice and were not accessible even to strong chemicals. Thus, this fraction was essentially devoid of extractable metals.

When the extraction efficiencies of the six chelating reagents were compared, EDTA, DTPA and DPTA seemed to possess a stronger ability to mobilize heavy metals from the soil. Possible reasons include their polydendate character, the pH value of the aqueous solution during the extraction and their affinity for specific metals. More detailed information would have been available if the trials had been conducted using a buffer to maintain the same pH condition for each chelant solution.variations in extraction efficiencies might have resulted from differences in the chemical structures of these extractants. Other studies in which the same reagent was evaluated at different pH conditions would indicate which of the factors is dominant. In these initial feasibility studies, the focus was mainly on the recycling of the complexing reagent(s). The soil and chelating solution were mixed in a 1:1 ratio without any special effort to regulate other potentially confounding variables.

Regarding the recycling of the chelating reagent, there has been little work reported in this area. EDTA has been recovered by hydroxide precipitation or by sulfide precipitation. In the current studies diethyl dithiocarbamate was evaluated as a means of stripping heavy metals from their metal-complexes so as to release the chelating reagent for reuse. The product metal-dithiocarbamate complexes were recovered by filtration. It was observed that most of the six chelating reagents could be recylced two or even three times (especially EDTA, and DPTA) although the extraction efficiency decreased to the each successive cycle. The loss of liquid filtrate was appreciable in all cases (from 100 ml solution initially to 50 ml after the first equilibration and 20-30 ml after three cycles).

Regardless of the number of times that the chelating reagents can be recycled and/or the declination of extraction capability, the preliminary experiment on recycling via DEDTC precipitation demonstrates the feasibility and simplicity of the approach.

Since DEDTC displayed a stronger affinity for heavy metals within the soil and readily formed a precipitate in the presence of EDTA and the other chelants, it became of interest to evaluate the use of DEDTC to extract metals directly from soil. The addition of a surfactant was anticipated to overcome the precipitation problem by forming a quasi-stable suspension of micelles. Preliminary experiments were performed by supercritical fluid extraction using a standard Pb solution complexed with DEDTC in surfactant suspension. A variety of surfactants were tested and the Pb mobilization efficiency was evaluated. Metal mobilization depended appreciably on the type of surfactant and the mobile phase modifier that were used. It was observed that approximately 82% of Pb was transferred from the complex micelle suspension into the final trap through silica capillary system. However, during the process there was a loss of 27% of Triton X-405 surfactant. It would appear that this approach is promising for surfactant reuse as well. To optimize the extraction conditions the choice of a surfactant with low foaming tendency and high metal mobilization ability. The choice of an organic co-solvent that is totally miscible with Sc-CO2, preferably lighter than water and that is capable of concentrating the metal complexes into the organic phase should be of most concern.

When DEDTC aqueous solution was equilibrated directly with the soil in the presence of surfactant, the anticipation that more metals would be extracted than had been mobilized with EDTA wasn't achieved (only 17.5μg of Zn, 7.5μg of Cu, 37.5μg of Pb were mobilized from 1.0 gram of soil and Mn was even not detected). It is possible that many of the metals were precipitated despite the presence of the surfactant. The complicating components of the soil might have contributed to the differences between the standard heavy metal solution and the actual soil sample.

An alternate approach was to employ a reagent that formed water-soluble complexes with heavy metals. HEDC, a DEDTC mimic, was synthesized in our laboratory and efficiently mobilized Zn, Pb, Cu, Fe but not Mn. Yet another method to recycle the chelating reagent(s) was to employ magnesium metal (Mg^0) that possesses a high redox potential and proved to react rapidly with several heavy metal ions. The net reaction was to cause the heavy metal ions to become cemented to the surfaces of the excess Mg^0 flakes. A kinetic study was designed to monitor the different forms (hydroxide precipitate vs. zero-valent) of the heavy metals that had been deposited on the surfaces of the magnesium metal. The results indicated that the virtually all of the Cu, Pb and part of Zn were transferred to Mg surfaces whereas the other metals were precipitated as their hydroxides. The source of the hydroxide was presumed to result from the reaction of Mg and water. The net reaction was essentially complete within three hours and certain metals were eliminated from solution within one-half hour. Other metals that might have mediated the redox reaction with heavy metals include potassium, calcium, sodium and aluminum all with high redox potentials. However, some of these candidates (K, Na and Ca) are too reactive with water to be controlled readily and aluminum forms aluminum hydroxides that can be hydrolyzed in acidic or alkline media. A further advantage of the Mg^0 system is the apparent lack of toxicity of the product Mg^{2+} cation that is a major common component of uncontaminated soils.

In the current studies, experiments on recycling chelating reagent using three different approaches were investigated:

- Diethyl dithiocarbamate precipitation
- Supercritical carbon dioxide extraction coupled with surfactant micelle formation
- Mg^0 flake cementation

Each of these approaches possessed certain advantages and disadvantages depending on the different applications. Regarding the application of these methods, it will be necessary to systematically investigate and optimize the working conditions, including the chemical dose, solution pH, and reaction time. I hope that these preliminary investigations have provided the basic information and suggestions for further fruitful studies.

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