DEVELOPMENT OF AN ON-SITE *EX-SITU* UNSATURATED-FLOW REMEDIATION PROCESS FOR TRACE METAL CONTAMINATED SOILS

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Abstract

Innovative means and methods were tested to develop an economical, pragmatic and environmentally sustainable soil remediation process for heavy metal contaminated soils. An unsaturated-flow soil washing procedure was devised to dissolve the soil-bound toxic heavy metals; the latter were extracted by a chemical washing solution that percolated through the soil matrix. Subsequently, the leached toxic heavy metals were selectively concentrated, by a chemical precipitation process, into a solid waste. Thereby, a fraction of the spent ethylenediaminetetraacetic acid (EDTA), within the washing and rinsing leachate, was theoretically regenerated and recycle-ready.

The unsaturated-flow washing procedure was perfected by applying different treatments to a soil from a secure landfill. This soil was contaminated with Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, S and Zn. The major contaminants were Fe, Pb, Zn, S, Cu and Mn, making up 25, 1.9, 1.0, 0.4, 0.4 and 0.2% wt of the soil. The extraction responses of the contaminants and those of Al, Ca, Mg and P were established for citric acid (0.5 M) and different molarities of diammonium EDTA ($(NH_4)_2$EDTA). The DOW Chemical Company supplied the $(NH_4)_2$EDTA (*i.e.* VERSENE), a 1.37 M industrial cleaner, which roughly costs \$1.85 kg^{-1} in bulk. The affordability of VERSENE was a pre-condition for hoping to satisfy the economical feasibility of remediating trace metal contaminated soils.

Ultimately, the developed unsaturated-flow washing procedure was tested in a pilot-scale experiment, for its ability to remediate a soil from an abandoned car battery recycling facility. The latter soil was severely contaminated with Pb (3.9% wt). Drip irrigation was used to apply $(NH_4)_2$EDTA and water-rinsing solutions to the surface of soil heaps that rested atop an impermeable barrier, which permited the retrieval of the leachate. A cumulative EDTA input to the soil of 10.6% wt extracted 49.4% of the total Pb content of the soil. Alternatively, readily biodegradable citric acid barely extracted 2.2% of the total Pb content of the soil, for a cumulative input of 18.1% weight of soil. Different treatments were tested for their effectiveness in concentrating the leached toxic heavy metals into a solid waste. The Pb was best precipitated with Na_2S alone, as it provided the most concentrated solid toxic waste.

The environmental sustainability of remediating trace metal contaminated soils was thoroughly examined, as per the amounts of chemical entrants and toxic waste by-products, and per the post-treatment leaching of toxic levels of the remaining and potentially toxic trace metals. In addition, an analysis of costs compared the unsaturated-flow remediation process to a saturated process and to the STABLEX process, which stabilises, cements and disposes the solid waste in a secure cell within a landfill. Finally, management solutions for trace metal contaminated soils and environmental recommendations, for realistically assessing the threats posed by trace metal contaminated soils, are discussed.

Résumé

Des moyens et procédés innovateurs furent testés pour le développement d'un processus de remédiation pour des sols contaminés aux métaux lourds. Le processus devait être écologique, économique et pragmatique. Un protocole pour un lavage à écoulement insaturé pour sols à été conçu pour dissoudre les métaux toxiques. Les sols furent lessivés par la percolation d'une solution chimique lavante. Subséquemment, les métaux toxiques lessivés furent ciblés et concentrés, par un procédé de précipitation chimique, en un déchet solide. En ce faisant, une fraction de l'acide éthylènediamine tétra-acétique (EDTA) contenu dans les lixiviats provenant de la solution chimique lavante et de l'eau de rinçage, donc épuisée, fut théoriquement régénérée et prêt au recyclage.

Le procédé à écoulement insaturé de lavage de sols fut perfectionné en traitant un sol, provenant d'un site d'enfouissement sanitaire sécuritaire. Ce sol fut contaminé en Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, S et Zn. Les contaminants principaux furent Fe, Pb, Zn, S, Cu et Mn, constituant 25, 1.9, 1.0, 0.4, 0.4 and 0.2% du poids total du sol. Les comportements d'extraction des contaminants et de ceux de l'Al, Ca, Mg et P furent établis pour l'acide citrique (0.5 M) et pour différentes molarités de $(NH_4)_2EDTA$. La compagnie DOW Chemical a fourni le $(NH_4)_2EDTA$ (*i.e.* VERSENE), un produit industriel nettoyant de 1.37 M, qui coûte environ $1.85 kg^{-1} en gros. Précurseur à un tel projet, le faible coût du VERSENE fut nécessaire pour financièrement permettre d'espérer à accomplir la remédiation de sols contaminés aux métaux lourds.

Ultimement, le procédé de lavage de sols à écoulement insaturé fut testé dans une expérience à l'échelle pilote pour son habilité à remédier un sol provenant d'un site abandonné de recyclage de batteries de voitures. Ce dernier sol fut sévèrement contaminé en Pb (3.9% au poids). L'irrigation goutte-à-goutte fut utilisée pour appliquer les solutions de $(NH_4)_2EDTA$ et d'eau de rinçage en surface de piles de sols, placées au-dessus d'une barrière imperméable qui permit de collecter le lixiviat. Une addition de 10.6% de EDTA à extrait 49.4% du contenu total en Pb du sol. Contrairement à l'EDTA, l'acide citrique est biodégradable. Ainsi, l'acide citrique fut testé en tant qu'alternative plus environnementale. Malheureusement, l'acide citrique a extrait seulement 2.2% du Pb dans le sol, pour un ajout cumulatif de 18.1% au poids du sol.

Différents traitements furent testés pour leurs efficacités à concentrer les métaux lourds lessivés en un déchet solide. L'utilisatio n de Na_2S seul, pour précipiter le Pb hors du lixiviat, fut la meilleure approche, grâce à son habilité à concentrer le Pb en un déchet solide. Idéalement le résidu toxique solide serait recyclé; sinon il doit être stabilisé, solidifié et incorporé dans une cellule sécuritaire d'un site d'enfouissement.

L'aspect écologique de la remédiation de sols contaminés aux métaux lourds fut examiné pour l'ajout de produits chimiques, la production de déchets toxiques résiduels et la mobilité post-traitement des métaux lourds potentiellement toxiques. Aussi, une analyse des coûts associés au traitement à écoulement insaturé fut comparée à celle d'un processus saturé. Une analyse de coûts a comparé un procédé à écoulement insaturé à un procédé saturé et à l'enfouissement du sol dans des cellule sécuritaire. Finalement, des solutions de gestion pour les sites contaminés au métaux lourds et des recommendations environnementales, afin de bien cerner le risque réelle posé par les sols contaminés au métaux lourds, sont délibérées.

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I am appreciative to have had the opportunity to study and learn in a privileged place of learning, such as Macdonald Campus of McGill University. Beyond the wealth of learning, I was fortunate to have had two beautiful children during my Ph.D. studies, Naomi Maïa and Noa Laurier. Being a student graced me with the chance of having flexible hours, thus allowing me to spend cherished time with my children and nurture the tremendous love I harbour for them.

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List of Abbreviations

∅	Diameter
% wt	Percent Weight Ratio
% wt l^{-1}	Percent Weight Ratio as per Leachate
AAS	Atomic Absorption Spectrophotometer
AER	Anion Exchange Resin
$-C_6H_4OH$	Phenols
CaCO3	Calcium Carbonate
CEC	Cation Exchange Capacity
CER	Cation Exchange Resin
cmol kg^{-1}	CentiMoles per Kilogram
cn	Coordination Number
-COOH	Carboxyl Functional Group
$-NH_2$	Amine Functional Group
-OH	Hydroxyl Functional Group
EC	Electrical Conductivity
EDTA	Ethylenediaminetetraacetic Acid
EDTA:S	EDTA to Soil Ratio
Eh	Soil Redox Potential
Fe^{2+}	Ferrous oxide
Fe^{3+}	Ferric oxide
$Fe_2O_3 \cdot H_2O$	Iron Oxyhydroxide
$Fe_2(OH)_3 \cdot$	Iron(III) hydroxide
H_3O^+	Hydronium Ion
hr	Hour
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
iMc	Initial *M-soil* Content
ISLL	initial soil leachability level
J-soil	Soil from a the battery recycling plant in Saint-Jean-sur-Richelieu
K_f	Formation Constant
L:S	Liquid to Soil Ratio
LA, LB	Lewis Acid, Lewis Base
K_{SO}	Solubility Products of a Mineral
M	Molarity
MDDSEI	*M*aximum Daily Discharge Standards for the Electroplating Industry
mS cm^{-1}	milliSiemens per Centimetre
M-soil	Soil from a secure landfill in Montréal
NaOH	Caustic Soda
Na_2S	Sodium Sulphide
$(NH_4)_2EDTA$	Diammonium Ethylenediaminetetraacetic Acid
OH^-	Hydroxyl ion
OM	Organic Matter
pK_f	Formation Constant of Metal Complexes
pK_{SO}	Negative Logarithm of the Solubility Product
RSE	Relative Standard Error
ΣL:S	Cumulative Leachate to Soil Ratio
SOM	Soil Organic Matter
STD	Standard Deviation
µg L^{-1}	Microgram per Litre
USP	United States Pharmacopeia
V	Volts

1 Introduction

Heavy metals are metals that have a density greater than 5 g cm^{-3} (Pfafflin and Ziegler, 1998). Herein, the term <u>*toxic trace metal*</u> *refers to potentially toxic levels of trace metals within contaminated soils, which is in contrast to harmless and naturally occurring trace metal levels in soils.*

When heavy metals salts are spilt onto the soil, the metal cations sorb onto mineral and organic surfaces quickly. In general, these heavy metals remain immobile. Still, they could potentially leave the contaminated sites through surface runoff, leaching and wind erosion. Ideally, sites contaminated with heavy metals should be decontaminated to eliminate any health risk and provide an environmentally sustainable solution. Alas, this poses a great challenge, since heavy metals do not biodegrade. Thus, the remediation of a heavy metal contaminated soil requires a viable chemical recovery process that is able to extract and concentrate the contaminants in two steps. As a first step, a chelating agent is added to the soil as a washing solution to extract the heavy metals. In turn, the recovered leachate also needs to be decontaminated of its heavy metals. Sites containing heavy metal solids would need to be pre-treated to remove these solids via gravitational separation, before applying chelating agents. As a requisite, any remediation process that sets out to mobilize heavy metals with chelating agents requires a fully contained system, ruling out any *in-situ* approach. A saturated soil washing procedure which mixes soil and washing solution as a slurry in 20 000 L reservoirs has/is being examined (CRIQ, 2001). When treating large volumes of contaminated soils, this process becomes very costly and work intensive, since each small batch needs to be mixed/washed, stabilised and dried.

The most economical and common approach for decontaminating trace metal contaminated sites is excavation for secure landfill burial. However, new legislation requires the decontaminated of severely contaminated soils prior to their disposal in secure landfills. Such landfills that receive toxic waste may pose future risks to the environment, therefore require perpetual monitoring for assessing their state of impermeability (*i.e.* to quantify off-site leaching). Alternatively, immobilization techniques attempt to cement heavy metal to the soil particles in order to reduce the risk of their translocation by leaching. The applications of lime and soda ash have been previously used as cementing agents (Catalan and Li, 2000). The disadvantage of this technique is that the site maintains it high metal content and will require ongoing monitoring. To create a safe buffer zone, a site treated in this manner needs to be covered with >60 cm of pH-neutral soil containing little organic matter (EPA, 1999).

Researchers are still trying to phytoremediate heavy metal contaminated soils (Römkens *et al.* 2002). However, phytoremediation has several disadvantages that limit its utility for heavy metal contaminated soil: (i) solubilizing heavy metals; (ii) containing the solubilised heavy metals within the root zone; and (iii) harvesting and disposing of plant shoots and roots over several seasons (specialised plants accumulate <0.01% of Cd or Pb in aboveground biomass, based on dry weight; Römkens *et al.*, 2002).

Chemical soil washing for heavy metal removal would seem promising, if not for high costs and concerns about post-treatment leaching of toxic levels of trace metals. A more efficient and environmental sustainable alternative to the saturated procedure needs to be devised. The process must limit the use of chemical inputs for mobilizing the toxic trace metals, for precipitating them out of the metal-laden leachate and for stabilizing the treated soil. An on-site *ex-situ* unsaturated-flow approach is proposed to limit the soil handling costs and eliminate the mechanical mixing costs, by excavating and heaping the contaminated soil atop a geomembrane. As a single batch process, drip irrigation applies the washing and rinsing liquids atop a single soil heap. The leachate is collected by gravitational flow from the underlying geomembrane. The procedure also aims at producing the least amount of contaminated leachate.

1.1 Problem Assessment

Industrialisation has brought on the mining of heavy metals such as cobalt (Co), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn). The metalloid arsenic (As) and the heavy metal cadmium (Cd) are obtained as by-products from the processing of Cu, Pb and Zn ores (EPA, 1997). The aforementioned heavy metals are transformed and incorporated into various objects. Although Cr, Cu, Ni and Zn can be found in multimineral dietary supplements, As, Cd, Co, Hg and Pb are potentially toxic to humans even in small amounts.

The mineral tailings from the transformation of the ores are stockpiled and exposed to precipitation and wind. Hence, surface runoff, leaching and wind erosion occur, thereby threatening the health of mining communities. Unfortunately, this receives little attention, since the threat remains localised in remote areas. Treating wood for preservation is another raw material transformation that has contaminated soils, by careless use of creosote or chromate, copper and arsenate (CCA) (Mueller *et al.*, 1989). The practices of the wood preservation industries have also contaminated surface and underground water resources with polycyclic aromatic hydrocarbons, heavy metals and As (PWGSC, 1998).

In the 21st century, industrialised nations have established environmental regulations regarding the use and disposal of heavy metals, may it be for pulp and paper, metal plating and finishing operations, or for sewage and fertiliser applications. The guidelines are established to help sustain the quality of the environment, thereby protecting humans, fauna and flora against potentially adverse effects of heavy metals. Unfortunately, environmental regulations and awareness only started in the 1970's. Until then, anthropogenic activities took little care in the mining of heavy metal ores or in their importation into urban areas, where they were transformed for various uses. A mandatory ban on Pb-based paint was enacted in 1978, and incentive programs to limit the use of lead in plumbing were implemented in the 1980's. Restrictive use of leaded gasoline occurred in 1986. Most of the lead emissions from vehicles, 250 000 tons year^{-1} in the 1970's in the U.S., settled in the urban areas leaving elevated amounts of lead on soil surfaces (Nriagu, 1990).

Ports and railway yards are examples of sites contaminated with spillage from the unloading and loading of heavy metals from truckage. In most large cities, spillage and disposal of industrial waste from foundries, smelting industries, automobile battery plants and old paint factories have contaminated soils and waterway sediments with Cd, Cu, Pb, Zn and other heavy metals. As a result, prime real estate in large urban centres became contaminated with heavy metals that accumulated from the middle of the 19th century up until the 1970's. Many of these contaminated sites now stand abandoned and are referred to as Brownfields, contaminated sites with potential for redevelopment. This poses a threat to humans who work or live near sites contaminated with As, Cd, Co, Hg or Pb, since they are cumulative poisons. Beneficial trace metals (*i.e.* micronutrients) become deleterious to plants, when found in elevated concentrations within the soil solution. Hence, soils contaminated with Cu, Mn and Zn are not usually toxic to humans, but are rather phytotoxic (Nolan *et al.*, 2003). Le ministère de l'Environnement du Québec (MENV) regulates the maximum acceptable heavy metal concentrations in the soil of land used for agriculture, residences and industries, or for disposal in secure land fills (table 1.1).

Table 1.1 Regulatory Levels of Heavy Metal in Soils (μg g^{-1})*

Soil Usage	Criteria	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Agricultural	A-Level	1.5	15	85	40	0.2	770	50	50	110
Residential	B-Level	5	50	250	100	2	1000	100	500	500
Industrial	C-Level	20	300	800	500	10	2200	500	1000	1500
Secure Landfill	D-Level	100	1500	4000	2500	50	11000	2500	5000	7500

*MENV (2001)

Contaminated soil with trace metals in excess to the D-Level criterion cannot be excavated and sent to a secure landfill, unless it is treated chemically to remove 90% of the contaminants and is stabilized against trace metal leaching (*i.e.* decontaminated). The D-Level criterion was implemented in 2001 by the MENV to limit the dumping of highly contaminated soils imported from outside the province.

The regulatory levels are established with generic guidelines: very soluble forms of potentially toxic trace metals are added to soils, prior to bioassays (Cook and Hendershot, 1996). The tests are very conservative, as they do not take into account the immobility that characterizes weathered contaminated soils (Leita and DeNobili, 1991). Furthermore, they do not distinguish between phytotoxic or anthropotoxic attributes. For example, the regulatory levels consider soils as potentially toxic as soon as their Cu, Mn or Zn levels could be inhibitory to plant growth, even though the levels would not pose any danger to human health. Table 1.2, compares the nutritive trace metals found within a 1.3g multimineral daily dietary supplement to their C-Level criterion. The tablet has concentrations of Cu, Mn and Zn, which are 3.1, 1.7 and 7.7 times greater than the C-Level. Moreover, the Zn concentration of the multimineral daily dietary supplement is 1.5 times greater than the D-Level criterion.

Table 1.2 Concentration of Essential Minerals in a 1.3g Mineral Supplement* (μg g^{-1})

	Cr	Cu	Fe	Mg	Mn	Ni	Zn
1.3g Mineral Supplement (*i.e.* tablet)	19.2	1538	7692	3846	3846	3.85	11538
C-Level Soil Toxicity Criteria	800	500			2200	500	1500
Tablet to C-Level Concentration Ratio		3.1			1.7		7.7

* LOBLAWS INC.

Unlike organic contaminants, trace metals are not absorbed by and do not pass through the skin. However, over long periods, excessive inhalation or ingestion of trace metals can cause a variety of ailments (table 1.3). Alas, the conservatism of regulatory levels can induce unfounded fears in regards to the actual threats of trace metal contaminated soils.

Table 1.3 Symptoms of Trace Metal Poisoning (Waiyaki 2000; Majumdar et al., 1995)

Elements	Symptoms	Domestic Use
Cd	Edema, renal disfunction causing (excess protein in urine), emphysema	Utensils
Cu*	Gastrointestinal and liver damages	Plumbing, wiring, drugs, 1¢
Hg	Chest pain, dyspnea (difficulty in breathing), insomnia	Cosmetics
Mn*	Insomnia, hypersexuality, headache, speech disturbance, muscular pain	Dyes
Ni*	Headache, nausea, dry cough, dyspnea, visual impairment, sweating, weakness	Utensils, cigarettes, 5¢
Pb	Neurological and kidney disorder, cerebral edema, anemia, bone marrow depression	Drugs
Zn*	Corneal and cell damages	Shampoo, zinc oxide cream (15% wt), utensils, galvanised steel

* Essential mineral

1.2 Project Hypotheses

For large-scale decontamination, saturated soil washing for trace metal removal involves the mechanical mixing of one small batch at a time. Unfortunately, saturated soil washing is more costly than excavation for secure landfill burial. CINTEC (Lasalle, QC) charges \$75 ton^{-1} for the excavation and disposal of C-Level contaminated soil; this is for more than 5000 tons and does not include the cost to replenish the site with uncontaminated soil. The proposed research is based on the assumption that trace metal contaminated soils can be remediated under unsaturated flow conditions. This enables a remediation process design that reduces the expenses related to soil and leachate handling. Furthermore, the introduction of a cheaper and more efficient chelating agent, as well as optimal unsaturated application conditions must be sought. In addition, convective air exchange (forced ventilation) within remediation heaps could improve the dispersion of the washing solution and create an oxidising environment more favourable to trace metal extraction. The present research sought to develop an affordable and environmentally sustainable procedure for remediating soils contaminated highly elevated levels of trace metals (*i.e.* D-Level contaminated soils).

1.3 Project Objectives

The goal of this project was to develop an innovative on-site *ex-situ* soil washing process, for remediating trace metal contaminated soils quickly, effectively, economically and safely. The first innovative feature of this research is the use of an industrial grade compound as the chelating agent: *VERSENE* diammonium EDTA (ethylenediaminetetraacetic acid). At a fifth of the cost, $(NH_4)_2EDTA$ is proposed, instead of disodium EDTA (Na_2EDTA), the more commonly used chelating agent in laboratory research (Skoog *et al.*, 2000). The main uses of $(NH_4)_2EDTA$ are: (i) as an industrial cleaning product; (ii) for scale removal and prevention; and (iii) as a rust inhibitor.

Secondly, optimal conditions for the extraction of trace metals by EDTA will be determined. Thirdly, an unsaturated-flow soil extraction technique will be devised with the intention of using on-site drip irrigation to apply the washing and rinsing solutions atop of a single soil heap. This application process would treat the contaminated soil in a single batch, as an unsaturated-flow treatment, thereby reducing the cost related to soil handling. Drip-irrigation is retained as an economical means for applying the chelating agent to the excavated contaminated soil: costly corrosion resistant reservoirs and energy demanding mechanical mixers are avoided.

Fourthly, providing convective airflow within the soil heap would increase aeration. Hence, a convective air exchange process will be studied as it could provide a greater extraction of trace metals due an increase in the oxidative state of the soil. Finally, economic and environmental assessments will be made for both evaporation and Na_2S precipitation, in their ability to treat the process leachate by concentrating the contaminants in an end-of-process solid waste. Experiments will be conducted, at the laboratory, column and pilot-scale levels, to verify the efficiencies of the hypothesised procedures, as well as to determine the optimum process design.

More specifically, the objectives of this research project are as follows:

1. To establish the efficiency of $(NH_4)_2EDTA$ to form soluble metal complexes that can be leached from the soil, at the laboratory-scale;
2. To establish optimal EDTA concentration ratios for maximum trace metal removal, at the laboratory and column-scale;

3. To investigate the use of an unsaturated-flow soil washing technique for reclaiming trace metal contaminated soil, at the column-scale;
4. To compare the extraction efficiency of citric acid against that of EDTA, at the column-scale;
5. To study the oxidising ability of convective air exchange to better enhance $(NH_4)_2EDTA$ trace metal removal form soil, at the column-scale;
6. To investigate the feasibility of using drip-irrigation to provide unsaturated-flow conditions for the soil washing process, on small soil heaps at the pilot-scale level (1:10000); and
7. To establish the efficiency of leachate evaporation and Na_2S precipitation for concentrating the leachate contaminants.

These objectives were met by conducting a number of successive studies, for which each finding(s) was reapplied to the subsequent experiments. In addition an experimental decontamination platform, located on the Macdonald Campus, was constructed for six 75-ton heaps (Appendix 1 & 2). The uniformity of soil-moisture dispersion within the heaps (1:100 scale) under drip irrigation with/without convective airflow was examined. In the end, the feasibility of the proposed unsaturated-flow remediation process was assessed.

Using a flask-scale experiment (*i.e.* batch extraction), three different EDTA compounds were tested for their efficiency to remediate a sandy loam soil contaminated with Cd, Cu, Pb, S and Zn. The sandy loam soil was collected from the top 20 cm of an abandoned car battery recycling industry in Saint-Jean-sur-Richelieu (Québec), and is referred to hereafter as the *J-soil*.

Other flask experiments looked at the effect of time, shaking, molarities and liquid to soil (*L:*S) ratios on the extraction of trace metals from a loamy sand. The loamy sand was obtained from a secure landfill in Lasalle (Québec) and is referred to hereafter as the *M-soil*. The *M-soil* was contaminated with Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, S and Zn.

A column experiment compared an unsaturated-flow extraction, which mimicked the drip irrigation process, to a saturated extraction. In an unsaturated-flow experiment, the efficiency of citric acid was compared to that of EDTA. In addition, the effect of sequentially submitting unsaturated columns to convective airflow was examined for its oxidising effect on trace metal removal. The column experiments used the *M-soil*.

The pilot-scale experiment examined drip-irrigation as means for applying the reagent solution to 32.7 kg *J-soil* heaps. The extraction efficiency of citric acid was again compared to that of EDTA. The leachate from the EDTA soil washing of the *J-soil* heaps was also treated to concentrate the Pb into a solid waste, following which the upward scalability of the proposed decontamination process was assessed.

1.4 Scope of the Project

This study involves two soils with anthropogenic contamination. The *J-soil*, a sandy loam obtained from a car battery recycling facility, was severely contaminated with Pb in contents 39.1 times the level allowed by the C-Level criterion. In addition, the *J-soil* was contaminated with Cd and Zn in excess of the Québec B-Level criterion. The *M-soil*, a loamy sand obtained from a secure landfill, was contaminated with Cd, Cu, Mn, Pb and Zn in excess of the Québec D-Level criterion and with Co, Cr and Ni in excess of the Québec B-Level criterion. The contents in Cd Cu, Pb and Zn were very high and exceeded the C-Level criterion by 5.4, 7.5, 19.5 and 6.6 times, respectively. The secure landfill soil was also contaminated with 92.5 $\mu g\, g^{-1}$ of polychlorinated biphenyls (PCBs) (Valentin, M., 2000)[t].

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[t] Master's thesis: *Laboratory study of solvent extraction of polychlorinated biphenyls in soil.*, p. 3-2. McGill University, Montréal.

2 Literature Review

This chapter provides a general background for the understanding of the principles that influence metal-soil interactions. More specifically, it addresses the possible states of fixation of metal ions, whether adsorbed, chemisorbed, complexed or precipitated. A comprehensive assessment of the existing remediation technologies for trace metal contaminated soils is included. A constructive critique is done of the existing research, in their inability of being scaled up to site-scale applications. The theory of chelating agents and their efficiencies is reviewed. Finally, different treatment methods for the removal of trace metals from solutions are examined for their applicability to treat leachate with very large amounts of trace metals.

2.1 General Background

Soil particles are made of either organic particles or mineral particles with humic coatings. In general, the trace metal contaminants are co-precipitated or strongly sorbed onto soil particles. Hence, trace metals are stable and usually immobile. Nevertheless, they can still potentially leave the contaminated sites through surface runoff, leaching or wind erosion.

Soils are always in some form of dynamic equilibrium: the inorganic and organic particles of the soil interact with air, water, microorganisms and roots. Most of the soil dynamics are associated with water, through weathering and solute transport. Capillary water is the thin film of water on the surface of soil particle, which is rich in solutes. The capillary and the gravitational water make up the soil solution. Being ionic and dipolar, water dissociates into hydronium (H^+) and hydroxide (OH^-) ions. The solute composition of a soil solution is in equilibrium between the particle oxides and H^+, OH^- and H_2O. The negative charges on the surfaces of soil particles try to reach a balance with the cations found in the soil solution. The soil solution is the source of mineral nutrients and usually carries a net electropositive charge.

The high dielectric nature of water is responsible for the availability of the positive and negative charges in soil solution. When an ion interacts with a water molecule, it is said to hydrate. The reaction in which cations break up H_2O and react with OH^- is called hydrolysis.

The earth is rich in sediments and rocks, which supply wood, fibres, metals and fossil fuels that support our way of life. Soil retains nutrients and essential ions, and releases them slowly into soil solution in trace amounts. Because of theses sorption and desorption kinetics, arable land supplies humans with their main sources of food. Soil also acts as a buffer zone between the atmosphere and ground water, but unfortunately does not have the ability to mitigate all of the pollution stemming from anthropogenic activities. Furthermore, air pollution has reduced the ability of soil to buffer contamination by increasing the rate of soil acidification. As soil become more acidic, its fixation capacity of cations reduces. Hence, nutritive Ca^{2+} and Mg^{2+} are lost through leaching, along with other metals. The main sources of atmospheric depositions causing acidification are summarised in table 2.1.

Table 2.1 Atmospheric Sources of Soil Acidification in Order of Importance*

Acid Pollutants	Atmospheric Source	Anthropogenic or Natural Causes
Sulphurous acids	sulphur dioxide	combustion of coal is the principal cause combustion of fossil fuels smelting of metal sulphides volcanic eruptions
Nitrous acids	oxides of nitrogen	combustion of fossil fuels
Hydrochloric acid		combustion of coal
Carbonic acid	carbon dioxide	combustion of fossil fuels and coal
Ammonia		application of organic manures

* Wild (1993)

Most of the mineral structures of the earth are formed by bonds between O^{2-} and Si^{4+}, Al^{3+}, $Fe^{2+,3+}$ and Mg^{2+}. Respectively, their concentrations typically account for 49, 33, 7, 4 and 0.6%wt of the soil (Bohn et *al.*, 2001). Within theses oxides of silicon (Si^{4+}), aluminium (Al^{3+}) and iron ($Fe^{2+,3+}$), the oxyanion (O^{2-}) is large as compared to the generally much smaller metallic cations.

Usually, soils are negatively charged, due to colloidal clays and humus. On the other hand, soil water tends to be positively charged. The existence of variably charged solid and liquid media facilitates the influx of positively or negatively charged micro and macronutrients into the soil solution. From this is drawn the common term cation exchange capacity (CEC) of a soil, which involves electrostatic attraction of the excess electric charges between oppositely charged ions (*i.e.* Coulomb attraction).

The mobility of metals within the soil depends on the extent of fixation, the identities of formed complexes and reaction kinetics. Fixation of metals ions on soil minerals can occur by adsorption (electrostatic attraction) and chemisorption. Sorbed cations can become covered by mineral and humic coatings, thereby becoming less likely to diffuse into solution. Metal ions can also be retained by complexation with soil organic mater and immobilised within microbial cells. Complexation refers to the reaction that transforms a simple ion into a complex organic ion. In addition, precipitation of impure minerals can incorporate trace metals within a well-crystallised structure.

2.2 Fixation of Metal Ions in Soil

2.2.1 General conditions affecting mobility and sorption of metals ions

Generally, soils high in clays and humic material retain larger amounts of metals ions. Clay particles are $<2\mu m$ and provide a large numbers of sorption sites due to their high surface areas. Similarly, humic substances are polymers with high surface areas. Contrarily to humic substances, which may dissolve in solution depending on pH, clay particles are colloidal.

Within a given soil, the acidity, $[H^+]$, of the soil solution affects the protonation/ deprotonation of soil particle OH^- groups. Soil solution pH is the main factor governing metal fixation. The negative charge of a soil particles increases as the pH of the soil solution increases, thus increasing metal sorption through hydrolysis. Higher pH will trigger the more abundant metal cation to precipitate as oxides, carbonates, phosphates and/or sulphides. Exceptions however do exist; alkalinity may induce trace metal solubility by forming soluble metal-chloride complexes with Hg, Pb and Cd (McBride, 1994). The pH of the soil solution influences and is influenced by ionic concentrations.

Soil redox potential (*Eh*) is an indicator of the intensity of the reducing or oxidising conditions in the soil, thereby yielding information on the possible mobility/immobility of ions. Saturated soils have lower *Eh* values and reduced mobility of Cd, Cu, Pb, and Zn (McBride, 1994). In anaerobic soils, concentration of Fe^{2+}, and to a lesser extent Mn^{2+}, are high and tend to dominate the *Eh*. For a given soil, *Eh*-pH diagrams provide information on the fixation state of elements.

In parent rocks, Cd, Cu, Hg, Ni, Pb and Zn occur mostly as sulphide minerals. These minerals are highly insoluble in reducing environments, however upon weathering in oxidising conditions the parent rocks can dissolve and release theses chalcophilic (*i.e.* sulphur loving) metal cations into solution. The reluctance of sulphide minerals to dissolve also extends to their anthropogenic forms, for which the extent of solubility increases with acidity. Zinc and Pb reach their maximum solubility under both acidic and oxidising conditions (McBride, 1994). On the other hand, Co and Mn are most soluble in acidic and reducing conditions. Iron is mainly found in primary minerals as Fe^{2+}. In the presence of oxygen, Fe^{2+} dissolves, oxidises into Fe^{3+} and tends to precipitate as insoluble Fe^{3+} oxides (Shuman, 1991).

Sorption reactions tend to be rapid, exothermic in nature, and mostly governed by diffusion. Conversely, desorption reactions tend to be three orders of magnitude slower, since an activation energy is required to overcome the sorption energy (McBride, 1994). With time, the coating of sorbed metals by humates or surface precipitates renders desorption even more difficult. Bioavailability of soil trace metals depends on their degree of sorption with soil particles. In soils, the relative order of solubility of trace metals is: (i) water soluble; (ii) strongly adsorbed; (iii) chemisorbed; (iv) organically complexed; (v) precipitated; and (vi) held in primary minerals. Specific sorption processes of ions with soil particles are a function of the ion type, the composition of the soil solution and the inorganic and/or organic nature of the soil particle. The different physicochemical factors behind metal sorption are addressed in the following sections.

2.2.2 Adsorption

The adsorptive capacity of a soil provides plants with a steady supply of nutrients. Adsorption involves the exchange of ions, in which the soil particle selectively retains a cation. These ionic bonds are non-directional and relatively long-range. Ionic bonds are outer-sphere bonds exerted uniformly in all directions; they are also referred to as electrostatic bonds. Cation exchange capacity (CEC) of a soil is the ability of negatively charged minerals, like layer silicate clays, to adsorb cations based on ion exchange. Ion exchange is usually rapid, diffusion controlled, reversible and stoichiometric (Wild, 1993). The electrostatic nature of adsorption involves reactions that are governed by valence forces, which distribute the different ions relative to their concentration and attractive force.

The reactivity of a soil mineral surface depends on its coordination number (*cn*) and its number of valence-unsatisfied terminal groups. The *cn* represents the number of oxygen anions required to surround each of its terminal cations. The smaller the valence:*cn* ratio of the sorption site, the less acidic are the hydroxyl groups and the more effective is the site for metal adsorption (McBride, 1994). The Fe and Al oxides (3^+:6) are more effective in attracting cations than the Si oxides (4^+:4).

Multivalent metal cations will effectively displace or be preferred over monovalent cations. For elements of same valence, larger cations posses smaller hydrated radii, allowing them to be held closer and more strongly to the minerals. Based on electrostatic forces, the predicted adsorption of divalent cations to soil minerals is: Ni > Ca > Mg > Cu > Co > Zn > Cd > Pb (McBride, 1994).

2.2.3 Chemisorption

Chemisorption involves covalent bonds, which are directional, short-range and selective. Covalent bonds are inner-sphere bonds exerted at angles; they are also referred to as coordinated bonds. In chemisorption, the electrons are shared by the elements. As compared to an ionic bond, a covalent bond is less reversible, showing little tendency to ionise. Clay minerals, such as oxide and non-crystalline minerals, chemisorb metals proportionally to their structural disorder. A potential chemisorption site has a valence-unsatisfied OH^-, which is most commonly bound to Al^{3+}, Fe^{3+} or $Mn^{3+,4+}$ of the soil mineral (McBride, 1994). The OH^- ion releases H^+ to form a single covalent bond with a metal cation by sharing one pair of electrons, offered by the O^{2-} atom. The lone pair of electrons offered by OH^- makes it a unidentate ligand.

The ability of a metal cation to form a strong covalent bond with O^{2-} is mainly function of its electronegativity (power to attract electrons), and to a lesser extent of its ease of polarisation. Based solely on the theory of Pauling's scale, table 2.2 lists the theoretical (*i.e.* predicted) order for the chemisorption of some metal cations.

Table 2.2 Predicted Order of Affinity of Divalent Metal Ions for Minerals*

Affinity Sequence	Cu^{2+}	>	Ni^{2+}	>	Co^{2+}	>	Pb^{2+}	>	Cd^{2+}	>	Zn^{2+}	>	Mn^{2+}	>	Mg^{2+}	>	Ca^{2+}
Electronegativity	2		1.91		1.88		1.87		1.7		1.65		1.55		1.31		1

* Pauling (1960)

The latter theoretical sequence (table 2.2) tends to be observed for Mn oxide minerals, however Fe and Al oxide minerals, as well as layered silicates show different preferences (table 2.3). Amongst the listed elements, Pb and Cu are the cations that hydrolyse the most easily. Thus as seen by the ranking of Pb and Cu, hydrolysis may also play a role in chemisorption (McBride, 1994). The sequences do not consider the specific properties of a soil.

Table 2.3 Observed Order of Affinity of Divalent Metal Ions for Minerals*

Amorphous Fe Oxides	Pb^{2+}	>	Cu^{2+}	>	Zn^{2+}	>	Ni^{2+}	>	Cd^{2+}	>	Co^{2+}	>	Mg^{2+}	>	Ca^{2+}
Al Oxides	Cu^{2+}	>	Pb^{2+}	>	Zn^{2+}	>	Ni^{2+}	>	Co^{2+}	>	Cd^{2+}	>	Mg^{2+}	>	Ca^{2+}
Layered Silicates	Pb^{2+}	>	Cu^{2+}	>	Co^{2+}	>	Zn^{2+}	>	Ni^{2+}	=	Cd^{2+}	>	Mg^{2+}	>	Ca^{2+}

* Bohn *et al.* (2001)

2.2.4 Humus Complexation

Most mineral soils contain around 3% soil organic matter (SOM), of which only 5% is biomass (Bohn *et al.* 2001). Around 70% of SOM is stabilized humus, some of which date back hundreds or thousands of years (Schnitzer, 1995; Huang, 1995). The remainder of the SOM (~25%) is made of labile non-humidified organic materials. These are transitory structured plant residues and biochemical exudates involved in the cycling of nutrients. Approximately 4% of new humus is decomposed in the first year and the stability of humus increases over time (Martin *et al.*, 1986).

Humidified organic acids are brownish amorphous polymers such as humic acids (HA), fulvic acids (FA) and insoluble humin. Humus is predominantly comprised of HA, which mainly bonds with the clay fraction of the soil to form mineral-oxyhydroxides-HA colloids. Humic acids form inner-sphere complexes with variable-charged minerals, such as oxides and allophanes. Complexation involves ligand exchange, or chemical adsorption, which requires the displacement of a H_2O molecule in order to produce a covalent bond that resists decomposition. Exceptionally, hydrated Al^{3+} and Ca^{2+} on the surface of negatively charged clays tend to retain their H_2O molecules. Both Al^{3+} and Ca^{2+} each have a large valence and small hydration radius: hence they are strongly polarized (Schnitzer, 1986). In this case, the HA tend to form electrostatic bonds through H_2O molecules held in the primary hydration shell of the Al^{3+} and Ca^{2+} (*i.e.* water bridging). Even if H_2O bridging involves weaker outer sphere complexation, the HA are stabilized against decomposition.

In the heterogeneous matrices that present the A-horizons, there is a generalized coating of minerals particles with humates. These very thin amorphous polymeric coatings roughly represent 2% of the soil Humates are mostly associated with clays that have a heterogeneously oxidised surface, high surface area and a low inherent mass. The thin humate coatings play a major role in fixing trace metals due to their numerous functional groups.

Humic and fulvic acids are multidentate ligands with multiple electron-donating sites: they have numerous O-containing carboxylic (-COOH) and -OH functional groups. The HA are base-soluble and are responsible for metal-soil fixation through the formation of insoluble metal-organic complexes. The FA are acid-soluble and form soluble metal-organic complexes which behave like biochemical exudates, which are non-humidified organic acids, such as citric acid (Stevenson and Fitch, 1986).

Metal-humus complexation is very selective; it fulfills the strongest covalent bonds then the weaker electrostatic bonds (McBride, 1994). As a priority, the trivalent ions, Fe^{3+} and Al^{3+}, are complexed through the formation of chelate rings; then the HA selectively complex the strongest divalent cations. The weaker divalent cations and the monovalent cations tend to form soluble covalent or ionic bonds with FA. Table 2.4 lists the observed selectivity of divalent cations for complexing with humic substances.

Table 2.4 Observed Order of Affinity of Divalent Metal Ions for Humus*

Bonding Tendency				← Inner-Sphere							Outer-Sphere →								
Affinity Sequence (pH 5)	Cu^{2+}	>	Ni^{2+}	>	Pb^{2+}	>	Cd^{2+}	>	Co^{2+}	>	Ca^{2+}	>	Zn^{2+}	>	Fe^{2+}	>	Mn^{2+}	>	Mg^{2+}
Electronegativity (Pauling)	2.0		1.91		1.87		1.7		1.88		1.0		1.65		1.8		1.55	3	1.31

* McBride (1994)

As compared to the sequence based on electronegativity (table 2.2), this sequence differs in the displacement of Co^{2+} and Ca^{2+}. The first cations listed tend to form insoluble covalently bonded complexes or chelate rings, whereas the latter cations tend to form ionic bonds and remain freely exchangeable. The sequence does not take into account the specific properties of each soil.

The *Lewis acid-base* concept deals with the transfer of an electron pair and predicts the attraction between different elements. This concept is more general than the more familiar *Brönstead-Lowry acid-base* concept, which deals with the transfer of a proton, namely H^+. *Lewis acids* (*LA*) are electron-pair acceptors and *Lewis bases* (*LB*) are electron-pair donors. The *Pearson Hardness Concept* (1963) classifies the *Lewis acids* and *bases* from hard to soft. A *Hard LA* preferentially bonds with a *Hard LB* and a soft *LA* preferentially bonds with a Soft *LB*. Organic acids are *LB*, for which the composition of their functional groups determines their degree of hardness, such $O > N > S$. The alkali, alkaline and trivalent metals are *Hard LA*, hence oxygen-loving, and they tend to forms ionic bonds between -COOH and -OH functional groups. The chalcophiles (Cd^{2+}, Cu^{2+}, Pb^{2+} & Zn^{2+}) are *Soft LA*, which tend to form covalent bonds with sulphhydryl functional groups (-SH). *Intermediate LA* are nitrogen loving and tend to form covalent bonds with amine groups ($-NH_2$). They are transition metals, of which Cu^{2+} is the most stable (Bohn, 2001; McBride, 1994).

The formation of an organic-metal complex is dependant on: (i) the humic substance (*i.e.* organic ligand); (ii) the metal cation; (iii) pH; and (iv) *Eh*. The speciation of the organic-metal complex determines whether it forms an insoluble or soluble complex, which enhances metal mobility of an otherwise insoluble metal. *Soft* bonds are more insoluble than *Hard* bonds.

2.2.5 Precipitation

Precipitation is the formation of a crystal nucleus in the soil solution. Nucleation involves the joining of a few ions, atoms or molecules. Nucleation forms a stable solid (*i.e.* precipitate) when the soil solution is saturated, otherwise the tiny crystal nuclei tend to re-dissolve due to their high surface energies. The formation of a precipitate is the formation of a zero-charged, water insoluble complex (Basalo and Johnson, 1964). Precipitation of the more abundant elements (Al, Fe, Si, Mn, Ca, Mg & S) into mineral forms is common and helps controls their bio-availability (McBride, 1994). In comparison to sorption, which is a two-dimensional soil surface reaction, precipitation products occupy a small volume (*i.e.* solid) within the soil solution.

Usually in soils, heavy metals (with the exception of Mn and Fe) are found in trace amounts and are strongly sorbed (*i.e.* immobile). Soils containing excessive amounts of trace metals could be potentially toxic, since otherwise insoluble metal carbonates, oxides, sulphides or phosphates could be more likely to dissolve. Table 2.5 lists the negative logarithms of the solubility products (pK_{SO}) of some pure minerals.

Table 2.5 Solubility Products of Pure Metal Minerals (pK_{SO})*

			← Insolubility Tendency					Solubility Tendency →					
Carbonates	Hg^{2+}	Pb^{2+}	Cd^{2+}	Fe^{2+}	Mn^{2+}	Zn^{2+}	Co^{2+}	Cu^{2+}	Ca^{2+}	Ni^{2+}			
$(M^{2+})(CO_3^{2-})$	16	13.1	11.7	10.7	10.4	10.2	10	9.9	8.42	8.2			
Oxides	Fe^{3+}	Al^{3+}	Hg^{2+}	Cu^{2+}	Zn^{2+}	Pb^{2+}	Fe^{2+}	Co^{2+}	Cd^{2+}	Ni^{2+}	Mn^{2+}	Mg^{2+}	Ca^{2+}
$(M^{n+})(OH^-)$	39.1	31.2	25.4	20.3	16.9	15.3	15.2	14.9	14.4	14	12.8	11.2	5.2
Sulphides	Hg^{2+}	Cu^{2+}	Pb^{2+}	Cd^{2+}	Zn^{2+}	Co^{2+}	Ni^{2+}	Fe^{2+}	Mn^{2+}				
$(M^{2+})(S^{2-})$	52.1	36.1	27.5	27	24.7	21.3	21	18.1	13.5				
Phosphates	Pb^{2+}	Zn^{2+}	Al^{3+}	Fe^{3+}	Mg^{2+}	Ni^{2+}	Ca^{2+}						
$(M^{n+})(PO_4^{3-})$	43.5	35.3	30.5	26.4	24.2	16.2	16						

* McBride (1994), De Boodt (1991), Ringbom (1979)

The solubility products of a mineral (K_{SO}) represents the equilibrium between a slightly soluble mineral and its ions within a saturated solution. These values offer a theoretical guidance for assessing the solubility of metals precipitates within the soil. The minerals most likely to dissolve into soil solution are the ones that have a high K_{SO} (*i.e.* low pK_{SO}). Trace metals salts co-precipitated within impure minerals become entrapped within structures of growing crystals. Due to a larger array of anions and cations, impure minerals precipitates are usually more stable (*i.e.* higher pK_{SO}) than pure minerals.

2.3 Soil Remediation Technologies

In soil, anthropogenic influxes of trace metals undergo a variety of reactions such as oxidation-reduction, sorption-desorption and precipitation-dissolution. Primarily, trace metals are co-precipitated or become tightly bound to soil particles through chemisorption or complexation. When bound to oxides, carbonates, sulphides, phosphates and/or humus, trace metals become sparingly soluble or exchangeable. However, over time, environmental conditions or changes in landscaping can affect the physical, mineralogical and chemical properties of the soil, and can lead to the release of potentially toxic levels of trace metals into surface and subsurface water resources. To maximize environmental sustainability, contaminated sites should be treated carefully for the removal of tightly bound trace metal ions, even if they do not pose immediate hazards. Yet, this strategy remains impossible due to pragmatic, environmental and economical restraints of the existing remediation treatments.

Four methods are frequently mentioned when considering the remediation of trace metal contaminated sites: (i) excavation for landfill burial; (ii) phytoremediation; (iii) chemical immobilisation; and (iv) soil washing. Electrokinetic and electrodialectic methods, and microorganism fixation and are under exploration and will remain unfeasible for real life applications.

Excavation for landfill burial is simple but costly. It has expenses related to excavation, transportation, refilling and landfill dues, which roughly tally \$85 ton^{-1}. Although secure landfills are designed for theoretical impermeablility, the trace metals from contaminated soils could eventually seep out and induce translocated groundwater contamination (Kaoser *et al.*, 2000). Furthermore, secure landfills require periodic monitoring, even long after the shut down of such a site. Hence, secure landfills offer limited environmental sustainability.

Phytoremediation aims to extract potentially toxic trace metals with hyper-accumulating plants. However, these plants can only potentially extract the trace metals within their root zone, given that the trace metal are in the aqueous phase; this requires that the trace metals be water soluble or exchangeable, which is seldom the case. Plants can only incorporate up to 1.5% of their weight in trace metals. Hence, it can take many cropping years to attempt to decontaminated, while producing large amounts of biomass that needs to be disposed of.

In chemical immobilisation, alkali-releasing materials are added to contaminated soils, in order to reduce the solubility/mobility of the trace metals (Selim and Sparks, 2001). Alkaline amendments reduce metal solubility by increasing soil pH thus resulting in increased chemisorption and precipitation. *In situ* chemical immobilisation with lime or soda ash has low inherent costs. However, it does not eliminate the threat of wind or water erosion of colloid-bound trace metals. In addition, immobilisation may lead to future leaching problems caused by biological activities or soil acidification, hence periodic monitoring is required.

Soil washing for trace metal removal is designed to extract the contaminants by increasing their solubility and mobility. The first large-scale soil washing took place at a Superfund site in New Jersey (Anderson, 1993). The site was contaminated with polynuclear aromatic hydrocarbons (PAH). The excavated soil was sieved with 5-cm screens, humidified into a slurry and vigorously mixed in a hydroclone in order to separate out the fine soil particles. An air floatation tank, with the appropriate dose of surfactant, was used to remove the contaminants from the fine soil particles. Since, soil washing has been infrequently used as an *ex-situ* technique for remediating sites contaminated with organic and inorganic pollutants, due to its high operation costs. In 1995, the Canadian Armed Forces awarded a $28.3 M contract to TALLON METAL TECHNOLOGIES INC. to remediate a section of the Longue Pointe Military Base in Montréal (Project Ploughshares, 1996). The West end of the base was contaminated with spillage and particulate Pb downfall from a neighbouring car battery crushing industry. The *ex-situ* acid-leaching soil washing technique, while removing a fraction of the Pb, adversely increased the mobility of the remaining Pb, even after caustic neutralisation. Ultimately, treated soil became environmentally unsafe and was sent to a secure landfill in Grandes-Piles (Québec).

In-situ mobilisation of soil contaminants with simultaneous extraction and injection of aqueous solutions through horizontal wells is known as soil flushing. This process requires that natural vertical and lateral barriers to flow be present, in order to prevent any off-site percolation of the solubilised contaminants: an unrealistic scenario. Microorganisms immobilisation of metal ions is another method, but has methodological and economical constraints for outdoor cultivation and harvesting (Magna *et al.*, 1998). The electrokinetic method has the limitation of using electrodes to create an electric field for the removal of metal ions from saturated soils with high permeability and nearly static groundwater flow. Another limitation, electrolysis reactions at the electrodes can affect pH of water and consequently limit the extent of metal ion migration (Acar and Alshawabkeh, 1993).

2.4 The Use of Chelating Agents to Reclaim Trace Metal Contaminated Soils

2.4.1 General Background and Theory

Chelating agents have long been used as titrants, for the determinations of a broad range of analytes. In agriculture, titrimetry is used to assess the bioavailable fraction of soil trace metals. In addition, chelating agents are used as soil amendments for delivering nutrients to cultivated land (FeNaEDTA) and as anti-oxidising preservatives for food and biological samples (Na_2EDTA). The pulp and paper industry uses EDTA to remove metal ions from mechanical pulps in order to increase the efficiency of hydrogen peroxide bleaching (Ager and Marshall, 2001).

For soil remediation, chelating agents have been studied for their ability to dissolve and extract soil-bound trace metal contaminants. Chelating agents polarise the metal-oxygen bonds of the soil particles, thus causing the detachment of the metal cations and the formation of a soluble metal complex. The chelating agent must furnish a strong enough activation energy to overcome the metal-soil particle sorption energy. Dissolution of a metal occurs when the metal has a greater affinity for the chelating agent than for its soil-binding site. For soil reclamation, the ideal complex-forming reagent would be: (i) soluble; (ii) strongly complexing over a wide range of pH; (iii) biodegradable; (iv) non-toxic or ecologically safe; and (iv) cost-effective.

Chelation forms a five- or six-membered heterocyclic ring (chelate), in which a cation bonds to two or more electron donating sites of a single ligand. Hence, a ligand with two or more electron-donating sites is referred to as a chelating agent or multidentate ligand. Different chelating agents have different functional groups, with varying numbers of electron donor sites, which are capable of complexing with trace metals. Chelating agents having four or six electron donor groups (tetra and hexadentate) are most effective in extracting metal ions, since they react more completely and within a single-step (Skoog *et al.*, 2000).

In 1945, Gerold Schwarzenbach first recognised the ability of aminocarboxylic acids to form remarkably stable chelates with metal ions. Aminocarboxylic acids are synthesised by combining into a single molecule both amino and carboxylate functional groups. The most common and one of the most versatile aminocarboxylic acid is the hexadentate EDTA, it has four carboxylic groups and two amine groups. As noted by Schwarzenbach, the synthesis of a more powerful complexing agent is limited (Ringbom, 1979). Still today, EDTA is one of the most important and widely used reagents in titrimetry (Skoog *et al.*, 2000). Hereafter, the focus will be on EDTA for its reclamation of soils contaminated with trace metals.

The EDTA molecule has four dissociable protons, two on carboxyl groups and one with each amine group. In aqueous solutions at approximately neutral pH, EDTA is a dianion, two of its four dissociable hydrogens having ionized. Even though EDTA has six ligand atoms, it forms water-soluble stoichiometric 1:1 complexes with metal ions regardless of their charge (Skoog *et al.*, 2000). Theses dissolved metal-EDTA complexes are negatively charged.

For a homogenous solution, the *formation constant* (K_f) indicates the direction and completeness of the chemical reaction at equilibrium. The K_f of a metal-ligand complex hints to the tendency of a chelating agent to bind that given metal ion. Larger K_f values denote more stable chelates and indicate a better ability for binding metals. Table 2.6 lists the formation constants of metal ions with EDTA, citric acid and two stronger aminocarboxylic acids. These values can be used in a semi-quantitative fashion for soil remediation. The *formation constant* is also known as the equilibrium or stability constant.

Table 2.6 Formation Constants of Metal Complexes (pK_f)*

Ligand	Fe^{3+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Co^{2+}	Al^{3+}	Fe^{2+}	Mn^{2+}	Ca^{2+}	Mg^{2+}
DCTA[c]	29.3	24.3	21.3	19.4	19.7	18.7	19.2	18.9	17.6	18.2	16.8	12.5	10.3
DTPA[f]	27.5	27	20.5	20	18.9	18	19	19	-	16	15.5	10	9.3
EDTA	25.1	21.8	18.8	18.6	18.0	16.5	6.5	16.3	16.1	14.3	13.8	10.7	8.7
Citric Acid	10.9	-	6.1	4.8	5.2	4.5	4	4.4	7.4	3.1	3.4	3.5	2.8

* Ringbom (1979), *Skoog et al.* (2000), values for 0.1 ionic strength and 20°C

[c] DCTA: *1,2-diaminocyclohexane tetraaidic acid*

[f] DTPA: *diethylenetriamine tetraacidic acid*

Conditional formation constants (K_f'), also known as the effective formation constant, is a pH-dependant equilibrium constant of a homogenous solution at a specific pH. Soil pH can range from 5.5 to 8, but soils are generally acidic. Extremely acid soils may have a pH as low as 4 and extremely alkaline soils may have a pH as high as 10 (Winegardner, 1996). Table 2.7 lists the conditional formation constants of metal-EDTA complexes. Although the strengths of the EDTA-metal complexes increase with solution pH, the strengths of metal-soil bonds also tend to increase. Hence, greater extraction efficiency is expected for a soil solution of lower pH.

Table 2.7 Conditional Formation Constants of Metal-EDTA Complexes (pK_f')*

pH	Fe^{3+}	Hg^{2+}	Cu^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}	Cd^{2+}	Co^{2+}	Al^{3+}	Fe^{2+}	Mn^{2+}	Ca^{2+}	Mg^{2+}
10	24.7	21.3	18.3	18.2	17.6	16.0	16.0	15.8	15.7	13.9	13.3	10.2	8.2
9	23.8	20.5	17.5	17.3	16.8	15.2	15.2	15.0	14.8	13.0	12.5	9.4	7.4
8	22.8	19.5	16.5	16.4	15.8	14.2	14.2	14.0	13.8	12.1	11.5	8.4	6.4
7	21.8	18.5	15.5	15.3	14.7	13.2	13.1	13.0	12.8	11.0	10.5	7.4	5.4
6	20.5	17.1	14.1	14.0	13.4	11.8	11.8	11.6	11.5	9.7	9.1	6.0	4.0
5	18.7	15.3	12.3	12.2	11.6	10.0	10.0	9.8	9.7	7.9	7.3	4.2	2.2
4	16.7	13.4	10.4	10.2	9.6	8.1	8.0	7.9	7.7	5.9	5.3	2.3	0.2

* Ringbom (1979), values for 0.1 ionic strength and 20°C

2.4.2 Experimental Effectiveness of Chelating Agents

Determining the effectiveness of a chelating agent for soil washing has commonly been done in batch extractions at the laboratory-scale (*i.e.* flask studies). The flask studies shake the soil within a washing solution, usually for 24 hours. The washing solution and the contaminated soil are habitually mixed in *L:*S ratios ranging from 10:1 to 25:1. Although the molarity (M) of the washing solution may be small, high *L:S* ratios can submit the soil to large amounts of chelating agent relative to the amount of soil, while producing excessive amounts of leachate. For a large-scale treatment, mimicking the vigorous shaking of a flask-scale extraction would be limited to mechanical mixing, which would incur great expenditures. Thus reducing the *L:S* ratio and increasing the concentration of the washing solution would be more pragmatic for scaling-up.

Batch extractions can help understand the approaches that need to be taken towards the decontamination of soils, but require modifications to become pragmatic and environmentally sustainable for a site-scale process. On another note, many have used soils artificially contaminated with toxic levels of trace metals. Artificially contaminated soils lack the hardening of the sorbed trace metals, as possess field-contaminated soils through their weathering and subsequent mineral and organic coating. Thus, the % removal results obtained from artificially contaminated soils are inflated and are not representative of the extraction efficiency of trace metals from field contaminated soils. As an example, Cline and Reed (1995) found that shaking EDTA 0.1 M in a 25:1 *L:S* ratio, with eight different artificially contaminated soils, removed 91.2% of the Pb. Their overall results showed that the extractions tended to be independent of soil type and washing solution concentration, which is not the case for field-contaminated soils. The results from artificially contaminated soils can still provide some insight into the challenge of reclaiming field-contaminated soils.

Plants exude various organic acids, which form nutritive plant available complexes through the chelation of essential elements. Natural organic acids are readily biodegradable and provide a transient transport of micronutrients. Concentrated forms of these natural chelating agents have been considered for soil remediation.

Wasay *et al.* (2001) evaluated natural and synthetic chelating agents for their ability to remove trace metal ions from artificially contaminated soils at variable levels of pH. The soils were mixed for 24 hrs with the chelating agents in a 25:1 *L:S* ratio. Citric acid, 0.2 M and pH 5.3, removed Cr, Hg and Pb to the extent of 38, 89 and 60%. At pH

4.5, Na_2EDTA 0.02 M removed 10, 18 and 85% of Cr, Hg and Pb. Diethylenetriamine pentaacetic acid (DTPA) 0.02 M and pH 4.5 removed 12, 40 and 85% of Cr, Hg and Pb. Even at a one tenth the molarity, both synthetic organic acids proved to be more efficient in removing Pb, than citric acid. However, the larger amounts of citric acid (10 **x** that of EDTA) removed more Cr and Hg.

In an earlier work, Farrah and Pickering (1978) examined the abilities of seventeen different chemical solutions to displace Cd, Cu, Pb and Zn from artificially contaminated clays (kaolinite, illite & montmorillionite). After stirring the different clay-extractant mixtures in a 2:1 *L:S* ratio, only Na_2EDTA (0.001 M, pH 7.0) quantitatively removed all four ions, but after three days of equilibration. Of the organic acids, oxalic acid (0.1 M, pH 3.3) totally displaced Cd, Cu, and Zn, whereas 0.01 M sodium citrate effectively removed Cd and Zn. The natural oxalic acid and sodium citrate were used in 100-fold and 10-fold excess of that of synthetic Na_2EDTA, with less overall effectiveness. In comparison to EDTA, larger bulk requirements of natural organic acids would tend to limit their utility for soil decontamination. Other reagents, such as ammonium oxalate, ammonium nitrate, nitric acid and ammonium acetate displaced moderate quantities of one or more metal ions from the clays.

Brown and Elliot (1989) treated soil from a car battery recycling facility with a washing solution. The soil contained 21% wt of Pb and was equilibrated by shaking the mixture for 5 hrs in a 25:1 *L:S* ratio. By using a large EDTA to soil ratio (*EDTA:S*) of 37% wt, 65% removal was achieved.

Ting and Marshall (2001) opted for a more pragmatic 1:1 *L:S* ratio extraction of a soil with 596 and 2028 $\mu g\,g^{-1}$ of Pb and Zn. A 16-hour mixing with Na_2EDTA 0.1 M removed 19% Pb and 25% Zn, while DTPA 0.05 M extracted similar amounts of 17 and 18%. Although half the amount of DTPA was as effective as Na_2EDTA, the former costs 40 times more making it unaffordable. The EDTA treatment was repeated on a soil with 6.6 $mg\,g^{-1}$ of Pb, it removed 22% of the Pb (Lee and Marshall 2002). In comparison to previous works, reducing the *L:S* ratio reduced the ensuing amount of liquid waste; however, greater molarities would have been required to decontaminate the soil.

Papassiopi *et al.* (1999) mixed soil containing 10.2% Ca, 1.25% Pb and 1.02% Zn with Na_2EDTA washing solutions for 22 hrs. While using a *L:S* ratio of 10:1, increasing the molarity of Na_2EDTA tenfold, from 0.025 M to 0.25 M, extracted merely 3 times the amounts of Cd, Pb and Zn. For a 0.25 M washing solution, lowering the *L:S* ratio to 5:2 (*i.e.* by 400%) only reduced the amount of extracted Pb g^{-1} of soil by 50%. After rinsing the soil 3 times with 20 ml of deionised water, a second extraction was performed. The post-extraction Ca concentration in the leachate was 8.5 times that of Pb, similarly to their initial soil ratios, and 14.4 times that of Zn. In a study by Parfitt and Taylor (1995), 89% of the EDTA binding sites were assumed to be occupied by Ca^{2+}. Hence, within a contaminated soil, larger intrinsic amounts of easily and abundantly exchangeable alkali and alkaline elements would negatively influence the extraction of trace metals.

Effectiveness of EDTA in removing trace metals, like Pb, from soils with high organic matter (25%) was also observed (Abumaizar and Khan, 1996). Ghestem and Bermond (1998) found that upon using an EDTA washing solution in excess of 0.1 M, the extraction became less pH dependent. For soils contaminated predominantly with Pb, an *EDTA:Pb* molar ratio of 2:1 was recommend for remediation (PEI, 1986).

The use of monovalent electrolytes, $NaClO_4$ or NH_4ClO_4, along with Na_4EDTA improved Pb extractability by 10% (Brown and Elliot, 1992). Conversely, divalent electrolytes, such Ca^{2+} and Mg^{2+} perchlorates, were observed to suppress the extraction of Pb. The co-addition of EDTA and strong acids, such HCl, HNO_3 and H_2SO_4, enhanced the dissolution of metal ions (Tejowulan, 1999; Neale *et al.*, 1997; Van Benschoten *et al.*, 1997). However, the use of strong acids can further disturb the physical, chemical and biological properties of the soil.

2.5 Treatment of Metal-Laden Leachate

Soil washing produces a leachate rich in metal-ligand complexes. The treatment of such a metal-rich leachate involves the removal of the toxic metals and the disposal of a concentrated dehydrated waste. Within a land reclamation endeavour, perhaps the precipitation process could also regenerate the spent EDTA for its reuse. However, the main goal of the precipitation process remains the treatment of the leachate for the concentration of the toxic metals. In regards to the precipitation process, no information concerning the concentration factor of the contaminants was found in the literature, as the intents were to regenerate the spent EDTA. Existing methods for removing toxic metal ions from municipal and industrial wastewater include precipitation, cation exchange resins (CER) and electrodialysis.

Precipitation is a standard method for removing trace metals from wastewaters; it involves the adsorption and co-precipitation of trace metals on and within mineral precipitates. Within a solution, the formation of mineral precipitates is triggered by the addition of oxides, sulphides or carbonates. Precipitation is a low-cost technology that is effective in quickly removing large quantities of metal ions. The precipitation process involves the addition of a precipitating agent and the dehydration of the solid waste (to be sent for recycling or secure landfill disposal). Precipitation may also involve (i) pH adjustment; (ii) addition of a flocculent; and (iii) filtration of the supernatant to recover small unsettled particles.

Ferric oxide is commonly used for removing the metalloid arsenic (As) from drinking water. When added to a solution, amorphous iron oxyhydroxides ($Fe_2O_3 \cdot H_2O$) form, in which As and the potentially toxic trace metals become entrapped. The reactivity of the ironbound hydroxyl sites can be increased by adding caustic soda (NaOH), thereby increasing the trace metal co-precipitation. When hydroxides of Fe^{3+} are formed by direct addition of a base, a bulky gelatinous mass is formed. The voluminous suspension, which entraps the contaminants, is difficult to filter out. However, a gradual and homogenous addition of NaOH limits the relative saturation and forms colloidal and crystalline precipitates, which are denser and much easier to filter (Skoog *et al.*, 2000). Therefore, optimizing the addition of Fe^{3+} and NaOH can reduce the volume of sludge and the need for flocculent (*e.g.* Al oxide).

Banerjee (2002) treated effluent from a steel making facility, with ferric iron (Fe^{3+}) and NaOH (to maintain an operating pH of 8). For a high 10:1 Fe:Cu weight ratio dosage, low Cu, Pb and Zn levels (510, 33 & 160 $\mu g\,L^{-1}$) were reduced below 5 $\mu g\,L^{-1}$. Macchi *et al.*, 1993 collected wastewaters from three battery industries containing approximately 4 $mg\,L^{-1}$ of Pb. By using a 1:2 Fe:Pb weight ratio dosage and adjusting the pH to 8, the concentration of Pb was reduced below 0.2 $mg\,L^{-1}$ within 30 min. Similar results were also obtained for artificial solutions containing 10 $mg\,L^{-1}$ of Pb. The Fe requirements for precipitating out Pb is less than for solutions contaminated in Cu or Zn. Adding inexpensive and non-toxic scavenger ions like Fe^{3+} to spent EDTA solutions might de-complex Pb from the EDTA, however a greater amount of solid waste is formed as compared to Na_2S precipitation

Sulphide precipitation is more effective than oxide precipitation for concentrating contaminants and lowering wastewater Cd, Cu, Pb and Zn levels below 0.1 $mg\,L^{-1}$, especially for solutions containing highly stable metal-EDTA complexes (Bhattacharyya *et al.*, 1979; Skoufadis *et al.*, 1997). However, ferric oxides are usually used for common daily applications, since inorganic sulphides, although more efficient, release toxic hydrogen sulphide gas (H_2S). On the other hand, organic sulphide compounds do not releases H_2S, but they are costly.

With the intention of recycling the EDTA washing solution, Hong *et al.* (1999) used Na_2S as an anionic precipitating agent and $Ca(OH)_2$ to increase the pH to 9, as well as to supply Ca^{2+} as an exchange ion for the EDTA-bound metals. A 100 ml 20 mM spent EDTA washing solution was amended with 5 mmol of Na_2S. The recovery of Cu, Pb and Zn from the leachate, with ~8, 160 & 20 mg L^{-1}, reached 95%, 99% and 72%. When reapplying the regenerated washing solutions to the same soil in a 20:1 *L:S* ratio as previously, a sharp decrease in the extractions ability of Cu, Pb and Zn was reported for the regenerated washing solution.

Zeng *et al.* (2001) regenerated a 720 ml spent 20 mM Na_2EDTA washing solution by adding 0.4 g of $Ca(OH)_2$, 7.5 mmol of Na_2S and 7.8 ml of HNO_3 10%. The first leachate that was recovered contained 17, 34 and 15 mg $L^{-1}$of Cu, Pb and Zn. The1st and 2nd reapplications to the same soil, in a 2:1 *L:S* ratio as previously, extracted 12.2 and 56.5% less Pb than initially. Conversely by the 6th soil-reapplication, the Fe extraction increased by 51.3%. After having recycled the EDTA six times, an average of 21% of the EDTA was estimated to have been retained in the soil. To what extent did the regenerated EDTA contribute to further extract the trace metals is unknown, since large amounts of residual metal-EDTA complexes could have been released subsequent to the initial fresh-addition of EDTA. Furthermore, to what extent the increased dissolution resistance and/or a less efficient EDTA extraction potential were responsible for successively reducing the extraction of the trace metals is also unknown.

The 2 Volt reduction potential of magnesium metal, $Mg^0 \rightarrow Mg^{2+}$, is much stronger than the 0.4 V reduction of iron metal $Fe^0 \rightarrow Fe^{2+}$. Lee and Marshall (2002) hypothesised that the use of zero-valent magnesium flakes (Mg^0) could cause the washing solution to liberate sufficient OH^- to co-precipitate the trace metals. A Mg^0:Pb weight ratio dosage of 3:2 was used to regenerate a 0.1 M EDTA washing solution applied in a 1:1 *L:S* ratio. The leachate contained 1464 $\mu g\, mL^{-1}$. The 30-min reaction precipitated 81% of Pb while the 24-hr reaction precipitated 92% of Pb. The initial batch extraction removed 22% of Pb from the soil, to which the regenerated EDTA was re-added. Together, the residual EDTA in the soil and the regenerated EDTA extracted 19% of the initial Pb content, which represents 85.4% of the initial extraction. Recycling and re-adding the washing solution to the soil for a second time extracted 17% more Pb, which represented 78.3% of the initial extraction.

The recycling and re-extraction results for the Mg^0-regenerated EDTA were greater than those reported by Zeng *et al.* (2001) for Na_2S regeneration. However, the amount of Pb in the soil was also greater (*cf.* 6555 to 509 $\mu g\, g^{-1}$) as was the amount of added EDTA (*cf.* 0.1 M in 1:1 *L:S* ratio to 0.02 M in 2:1 *L:S* ratio), thereby a greater amount of leachable residual metal-EDTA complexes would have also been left behind in the soil. In any event, Mg^0 is much more costly than Na_2S, and produces more solid waste.

Tejowulan and Hendershot (1998) stripped the leachate from the metal-EDTA as a whole with an anion exchange resin (AER). For an *AER:EDTA* weight ratio of 25:4, the removals of Cd, Cu, Pb and Zn all surpassed 90%, regardless of solution pH. However, large amounts of solid toxic waste resulted, due to the large amount of AER that was required. Moreover, the heavy EDTA molecule was lost during the process and there was little concentration of the contaminants, which were part of an EDTA-metal-polymer waste product. Polymeric ion exchange resins are costly to buy and operate.

Cation exchange resins (CER) are polymeric cation exchangers that extract cations from a surrounding solution (*e.g.* chelex 100). Although CER do not remove the EDTA from solution, they still produce a large amount of waste product. These resins are placed, in the form of beads, within exchange columns, or are moulded into macroporous composite membranes. The former technique is used for water softening and demineralisation, and the later is used to strip contaminated sludge (Sengupta, 2002). For the removal of toxic trace metal ions, the CER has to be highly selective to avoid its saturation with the abundant non-toxic alkali and alkaline metals present in the wastewater. Polymeric cation exchange processes are costly and would only be effective for polishing solutions with small quantities of heavy metals. For leachate solutions with metal-EDTA complexes, highly selective polymeric cation exchangers are ineffective in stripping the trace metals away from the EDTA.

Lime ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) are inexpensive, but produce excessive amounts of sludge (Macchi *et al.*, 1993). Similarly, when activated carbon, peat and biopolymers, such as alginates and chitin derivatives, are used as cation exchange materials, they produce enormous amounts of solid waste, thereby making them environmentally unsustainable.

In metal electrodialysis, an anion exchange membrane of very low porosity filters cations by blocking their passage. The membrane systems can lower toxic level of metals to non-toxic trace levels; however, they are expensive and sophisticated. Furthermore, the membrane filters clog rapidly and need to be regenerated frequently.

2.6 Summary and Conclusions

Successful removal of trace metal contaminants from soils has been reported in various batch extraction studies. However, theses successes are deceiving, since large amounts of washing solution were used to extract the soil, making up scaling environmentally unsustainable and non-economical. Hence, small *L:S* ratios should be used in order to produce small volumes of contaminated leachate, as in turn the leachate requires treatment.

Chelating agent extraction efficiencies reported for the treatment of laboratory-contaminated soils are greater than the extraction efficiencies reported for the treatment of field-contaminated soils. The more labile nature of trace metals in laboratory-contaminated soils is not representative of the difficulties of dissolution that characterise weathered field-contaminated soils. Hence, the high chelating agent extraction efficiencies reported for the treatment of laboratory-contaminated soils are misleading, whether they were obtained with natural or synthetic organic acids.

Batch extraction is difficult to reproduce on a site-scale level. The scaling up as proposed by the CRIQ would require that the soil be mixed with the washing solution within ~20 000 L corrosion resistant reservoirs (CRIQ, 2001). This is still being examined by the CRIQ, however the procedure is very costly, as per the equipment, mechanical energy and labour expenditures. The site-scale mixing of saturated soil can only treat small amounts of soil at a time, thereby requiring the manipulation of several successive batches.

The trace metal contaminants that are removed from the soil need to be substantially concentrated into an end-of-process waste product. Unfortunately, the studies that have looked at precipitating out heavy metals from EDTA leachate have focused on the regeneration of the EDTA and have omitted to address the magnitude of the resulting toxic by-products. Furthermore, theses studies have not considered the contribution of the residual soil-retained EDTA in extracting trace metals during successive washings.

Based on the traditional laboratory studies that have been conducted and through innovative approaches, an economical, pragmatic and environmentally sustainable remediation process was sought. In doing so, an unsaturated on-site *ex-situ* process was proposed as it would provide a pragmatic and economical way to treat all the contaminated soil in one batch. Such a process would also limit the volume of contaminated leachate and provide substantial cost savings in regards to soil manipulation, labour and mechanical energy required for mixing the slurry. The soil would be made into a single heap atop an impermeable geomembrane, drip irrigation would apply the washing solution to the surface of the heap and the washing solution would percolate through the heap.

As a pre-condition to developing an economically feasible remediation process, a more economical alternative to Na_2EDTA needed to be found. Following which, the environmental sustainability of the whole process needed to be established, as per the EDTA requirements per kg of soil, the ability of the leachate treatment to provide a small volume of concentrated toxic waste, and the innocuous nature of the treated soil.

3 Characteristics of the Experimental Soils

Two soils were used in this research. One soil was taken from the top 20 cm layer of an abandoned lead battery plant in Saint-Jean-sur-Richelieu (Québec). This soil, referred to as the *J-soil*, was used in the first flask experiments and in the pilot-scale experiment. The other soil was obtained from a secure landfill in Montréal (Québec), the *M-soil*, and was used in flask and column experiments.

3.1 Soil Characterisation Methods

The soils were sieved to determine their sand content. A hydrometer analysis was performed on a soil-water mixture to determine the silt and clay content. Soil organic matter was determined by a wet dichromate oxidation technique (Jackson, 1958). Soil pH was measured in an equilibrated 1:2 soil to water suspension. The CEC was calculated by exchanging cations with unbuffered $BaCl_2$ 0.1 M and the EC was calculated in a 1:2 soil:water ratio (Hendershot *et al.*, 1993).

The soils were digested with a MILESTONE Ethos Plus Microwave Labstation, according to the EPA Method 3052, without the addition of hydrofluoric acid (HF). Thus, 9 ml of concentrated nitric acid (HNO_3) and 3 ml of concentrated hydrochloric acid (HCl) were added to 0.5 g of soil. The #2710 certified interference soil material with highly elevated trace metals from the NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY (NIST) was digested for quality control (table 3.1). Soil digestion solutions and soil extractions were analysed with a VARIAN *VISTA-MPX*, a radial ICP-OES. Fractionation results from a sequential extraction procedures represent no more than the soil's equilibrium response to the use of severe chemicals under extreme conditions, and do not determine the speciation of the trace elements (Nolan *et al.*, 2003). Thus, sequential extractions of the soils were not performed.

Table 3.1 Characteristics of the NIST #2710 Soil

	Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	S	Zn
Specifications (µg g^{-1})	64400	12500	21.8	10*	39*	2950	33800	8530	10100	14.3	1060	5532	2400	6952
Wavelengths (nm)	394.4	317.9	226.5	230.8	267.7	324.8	259.9	280.3	257.6	230.3	213.6	220.4	182.0	213.9
Results (µg g^{-1})	28182	11528	23.1	72.3	19.6	3347	32245	6503	9999	54.6	549	5891	2474	6850

* Values are not certified

3.2 *J-soil* Characteristics

The *J-soil* was determined to be a sandy loam and was sieved to 2 mm for the analyses. The results for the *J-soil* analyses are presented in tables 3.2 to 3.4. The reader might want to refer to table 1.1, it lists the regulatory levels of trace metals in soils. Initially, the *J-soil*'s amount of water-leachable Pb was more than 230 times the allowable drinking water standards (table 3.5)

Table 3.2 Characterisation of the *J-soil*

Sand %	Silt %	Clay %	Organic C %	pH in water	pH in $BaCl_2$	CEC cmol kg^{-1}	EC mS cm^{-1}
64.6	16.8	18.6	0.7	7.2	6.6	17.1	2.8

Table 3.3 Potentially Toxic Trace Metal Content of the *J-soil* (μg g^{-1} ± RSE)

Cd	Cu	Pb	Zn
[b]6.0 ± 1.2%	[a]43.7 ± 3.7%	[d]39101 ± 3.4%	[b]788 ± 24%

[a] A-Level criterion, [b] B-Level criterion, [d] D-Level criterion

Table 3.4 Micro/Macronutrient and Al Contents of the *J-soil* (μg g^{-1})

Al	Ca	Co	Cr	Fe	Mg	Mn	[a]Ni	P	S
47323	107138	5.2	59.0	20812	8839	243	52.2	408	4935

[a] A-Level criterion

Table 3.5 Concentration of Trace Metals in the Leachate obtained from *J-soil* Saturated with Deionised Water

	Cu	Pb	Zn
μg g^{-1} of soil	43.7[a]	39101[d]	788[b]
μg L^{-1} of leachate	102	2316	895
MENV (2001) Drinking Water Standards (μg L^{-1})	1000	10	5000

[a] A-Level criterion, [b] B-Level criterion, [d] D-Level criterion

3.3 *M-soil* Characteristics

The *M-soil* was determined to be a loamy sand and was sieved with a 1.5mm screen prior to the experiments. The results for the analysis of the *M-soil* are presented in tables 3.6 to 3.9. The reader might want to refer to table 1.1, it lists the regulatory levels of trace metals in soils. The *M-soil's* amounts of water-leachable elements are presented in table 3.10.

Table 3.6 Characterisation of the *M-soil*

Sand	Silt	Clay	Organic C	pH		CEC	EC
%	%	%	%	in water	in $BaCl_2$	cmol kg^{-1}	mS cm^{-1}
78.2	10.0	11.8	7.4	7.4	6.5	9.8	0.59

Table 3.7 Potentially Toxic Trace Metals, Fe and Sulphur Contents of the *M-soil* (μg g^{-1})

Cd^d	Co^b	Cr^b	Cu^d	Fe	Mn^c	Ni^b	Pb^d	S	Zn^d
107	103	344	3768	248826	2368	317	19466	4432	9917

[b] B-Level criterion, [c] C-Level criterion, [d] D-Level criterion

Table 3.8 Relative Excess of the *M-soil* in Heavy Metals to Natural Amounts as Found in North American Soils (times)*

Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	S	Zn
97.7	6.1	1.6	130	4.9	2.8	10.6	749	7.4	118

* McBride(1994), Bohn *et al.* (2001)

Table 3.9 Micro/Macronutrient and Al Contents of the *M-soil* (μg g^{-1} ± RSD)

Al	Ca	Mg	P
58251 ± 2.3%	23109 ± 2.6%	5569 ± 9.0%	333 ± 10%

Table 3.10 Concentration of Elements in the Leachate obtained from *M-soil* Saturated with Deionised Water (μg ml^{-1})

S	Ca	Mg	Zn^d	Mn^c	P	Ni^b	Cu^d
643	646	93	0.95	0.17	0.06	0.10	0.10

[b] B-Level criterion, [c] C-Level criterion, [d] D-Level criterion

Preface to Chapter 4

The comprehensive literature review revealed the need for the development of an economical, pragmatic and environmentally sustainable solution for remediating trace metal contaminated soils. In keeping with previous work, which involved the batch extraction technique, chapter 4 looked at different modifications to the more general saturated extraction approach. Diammonium EDTA was tested as a cheaper alternative to Na_2EDTA. With the intention of reducing the extraction time and omitting the mechanical shaking, the importance of both factors was examined. In order to increase the extraction efficiency and reduce the volume of the contaminated leachate, high molarity washing solutions in low liquid to soil ratios were evaluated.

4

Saturated Extraction Experiments to verify Feasibility Preconditions for this Research Project and to Optimise the Use of EDTA

A major obstacle in the implementation of soil washing for the reclamation of trace metal contaminated soil is the high cost of synthetic chelating agents. In the literature, the most frequently cited chelating agent for trace metal extraction from soils is Na_2EDTA, for its efficiency, availability and low cost, relative to other synthetic aminopolycarboxylic acids. For the same reasons, Na_2EDTA is the most commonly used reagent for titrimetry (Skoog *et al.*, 2000). In bulk, Na_2EDTA, made by the DOW CHEMICAL COMPANY, costs roughly $\$11.50\,kg^{-1}$ (UNIVAR, Montréal), which would be too costly for large-scale decontamination projects; the lowest available purity for Na_2EDTA is a USP (United States Pharmacopeia) grade.

On the other hand, VERSENE diammonium EDTA chelating agent, a technical-grade 1.37 M solution of $(NH_4)_2EDTA$, only costs around $\$1.85\,kg^{-1}$ (DOW, Midland). The 1.37 M $(NH_4)_2EDTA$ solution has a salt content of 45 % wt; on a dry basis, $(NH_4)_2EDTA$ ends up costing roughly $\$4.10\,kg^{-1}$. Thus, assuming an equal extraction efficiency, as compared to Na_2EDTA, the $(NH_4)_2EDTA$ could potentially afford a 64.3% savings. The lower $(NH_4)_2EDTA$ molecular weight (326 g) would also provide an additional 12.4% savings, as compared to Na_2EDTA (372 g).

Without the affordability of $(NH_4)_2EDTA$, the economics of the proposed process would not be conducive for large-scale land reclamation. Still, the chelating ability of $(NH_4)_2EDTA$ needed to be proven, as different EDTA chemicals can react differently within the soil. Papassiopi *et al.* (1999) reported that Na_4EDTA was less effective than Na_2EDTA. Thus, the 1st flask experiment compared the extraction efficiency of $(NH_4)_2EDTA$ to those of Na_2EDTA and FeNaEDTA.

The transfer of trace metals into the soil solution, during an extraction procedure, varies with time. Most often, the laboratory batch extractions involve a 24-hour equilibration time. However, the proposed engineering design intends to use drip irrigation to apply the washing/rinsing solutions atop a soil heap. Hence, the effect of a reduction of the equilibration time, during an unsaturated-flow extraction, needed to be measured. The 2nd flask experiment looked at the effect of extraction times that were shorter than 24 hrs.

Batch extractions usually entail vigorous shaking of a quantity of soil within a larger volume of washing solution. Attempts are being made to scale-up this common laboratory procedure (CRIQ, 2001). However, large-scale mixing procedures are too costly, costing more than \$200 ton^{-1} (Project Ploughshares, 1996). As an alternative, a non-mechanized unsaturated-flow procedure is explored. To mimic the state of heap leaching, the 3rd flask experiment compared a still-saturated extraction (*i.e.* unshaken extraction) to the common laboratory batch extraction.

The effectiveness of regenerating and recycling the EDTA washing solution has displayed certain limitations and might not help reduce the amount of EDTA inputs nor the amount of leachate (Lee and Marshall, 2002; Zeng *et al.*, 2001). Reducing the *L:S* ratio could increase the environmental sustainability of the process by reducing the volume of cumulative leachate, which in turn requires treatment. The 4th and 5th experiments investigated the effects of extracting metals from the *M-soil* with small *L:S* ratio additions of highly concentrated washing solutions. The contribution of the post-wash soil-retained EDTA on ensuing water-rinse extractions was also examined. This washing and rinsing sequence is referred to as a washing cycle

4.1 General Methodology (specific methodologies are given within each section)

Unless otherwise specified, the generic term EDTA is used specifically to abbreviate the use of $(NH_4)_2EDTA$. A saturated EDTA extraction describes the physical state of a submerged soil. A washing cycle consisted of a one-step addition of an EDTA wash and of subsequent rinses with deionised water. A liquid to soil ratio is abbreviated by L:S ratio.

All the experiments dealt with EDTA extractions of trace metal contaminated soils under saturated conditions. The *J-soil* was used in the 1st experiment and the *M-soil* was used in the remaining ones. The first three experiments were performed as flask extractions with a 1:1 *L:S* ratio, where 25 g of soil were saturated with 25 ml of washing solution. After the designated equilibration times, the soil-solution mixtures were centrifuged and the supernatants were collected.

The 4th and 5th experiments involved column-scale extractions, which computed the cumulative extraction of metals during a washing cycle. The soil columns were made by packing 25 g of dry *M-soil* between polyethylene frits in 60 ml capacity syringes. Prior to the experiment, the columns were saturated with 15 ml of deionised water; the *M*-soil retained a residual moisture content of approximately 29% wt. Within a washing cycle, the wash and deionised water rinses were consistently added at a specific *L:S* ratio; washing and rinsing solutions were introduced into the columns through the bottom. Following a 24-hour equilibration time, the leachate solutions were collected by compressing the air in the top of the syringe (*i.e.* pressure-aided drainage). The ensuing deionised water rinses extracted the EDTA-complexed metals that remained in the soil following the washing solution addition.

The *J-soil* batch extractions were carried out in triplicate and the extraction solutions were analysed with a GBC 903 Single Beam AAS. The *M-soil* batch extractions were carried out in quadruplicate and the extraction solutions were analysed with a VARIAN *VISTA-MPX*, a radial ICP-OES. The results are presented as averages. The CoStat *6.2* software was used for the regression analysis. For the statistical analysis, the STATGRAPHICS®*PLUS 4.0* software was used to compute the t-tests between the end-extraction results from two treatment populations. STATGRAPHICS®*PLUS 4.0* was also used to assess the equality of the variances between the two treatment populations, as well as the normality of each population's distribution.

4.2 Saturated Extraction Efficiencies of Different EDTA Compounds

The 1st experiment compared three different EDTA compounds for their efficiencies in extracting Cd, Cu, Pb and Zn from the *J-soil*, against those of $(NH_4)_2EDTA$. DOOSAN SERDARY RESEARCH LABORATORIES (Toronto) provided a FeNaEDTA salt and two Na_2EDTA salts, one from Korea and one from Germany. The soil was mixed with 0.2 M washing solutions (*c.a.* the saturation of Na_2EDTA) and shaken for 16 hrs (table 4.1).

Table 4.1 Sixteen-Hour Extractions with 0.2 M EDTA Compounds (mg L^{-1} ± RSE[t])

Chelating Agent	Cd	Cu	Pb	Zn
$(NH_4)_2EDTA$	0.18 ± 4.6%	5.79 ± 6.9%	6712 ± 8.1%	26.2 ± 2.0%
Na_2EDTA^G (Germany)	0.22 ± 0.6%	4.97 ± 1.2%	6870 ± 2.9%	16.1 ± 2.8%
Na_2EDTA^K (Korea)	0.20 ± 5.2%	4.42 ± 8.1%	5713 ± 5.6%	14.2 ± 4.6%
FeNaEDTA	0.13 ± 2.9%	2.17 ± 2.7%	1244 ± 8.7%	11.4 ± 12.7%

[t] Relative Standard Error

In theory, the EDTA molecule has its strongest affinity for Fe^{3+} (table 2.7), thereby reluctantly exchanging it for other cations. Accordingly, the least amount of metals was extracted by FeNaEDTA, which is used as a fertiliser/chelating agent in hydroponics and on nutrient-depleted European farmland. On the other hand, $(NH_4)_2$EDTA and Na_2EDTA^G extracted the greatest amounts of the potentially toxic trace metals. At the 99.9% level, $(NH_4)_2$EDTA extracted significantly more Zn than Na_2EDTA^G (fig. 4.1). This represented a 60% increase in the removal of Zn. Both $(NH_4)_2$EDTA and Na_2EDTA^G were found to remove equivalent amounts of Cu and Pb, whereas Na_2EDTA^G removed significantly more Cd than $(NH_4)_2$EDTA (at the 99.9% level).

The 68.8% chelating agent cost savings, as compared to Na_2EDTA, favoured $(NH_4)_2$EDTA as the synthetic chelating agent most suited for the development of a large-scale decontamination process, even though $(NH_4)_2$EDTA extracted 1.2 times less Cd. When considering the economic feasibility of reclaiming soils contaminated with trace metals, one of the major obstacle was the extreme cost of the chelating agent. The savings offered by $(NH_4)_2$EDTA encouraged the development of a cost effective site-scale remediation procedure. Hence, throughout this study, synthetic $(NH_4)_2$EDTA was used as the chelating agent.

4.3 Effect of Time on Still-Saturated Extractions of Trace Metals

This 2nd experiment measured the impact of equilibration time on the extraction of potentially toxic trace metals from the *M-soil*, under still conditions (*i.e.* unshaken). The still conditions in this flask-scale experiment intended to be representative of a non-mechanically mixed site-scale remediation process. The washing solution was poured onto the soil within the flask and both were permitted to equilibrate.

At the 90% confidence level, the extraction of Cd, Cu, Pb and Zn significantly increased with time up to 12 hours, and stabilised thereafter (fig. 4.2). There seems to have been no need to extend still-saturated extractions beyond 12 hours. However, a soil-EDTA interaction time of at least 12 hrs is required to better utilise the extraction potential of EDTA. Similarly, Xie and Marshall (2001) previously reported no difference in the removal of Cu, Fe, Mn, Pb and Zn between a 16 and 24-hour batch extraction.

FIGURE 4.1 Saturated Extractions from Shaking 25 g of *J-soil* in a 1:1 *L:S* Ratio with $(NH_4)_2EDTA$ or Na_2EDTA with 99.9% Confidence Intervals

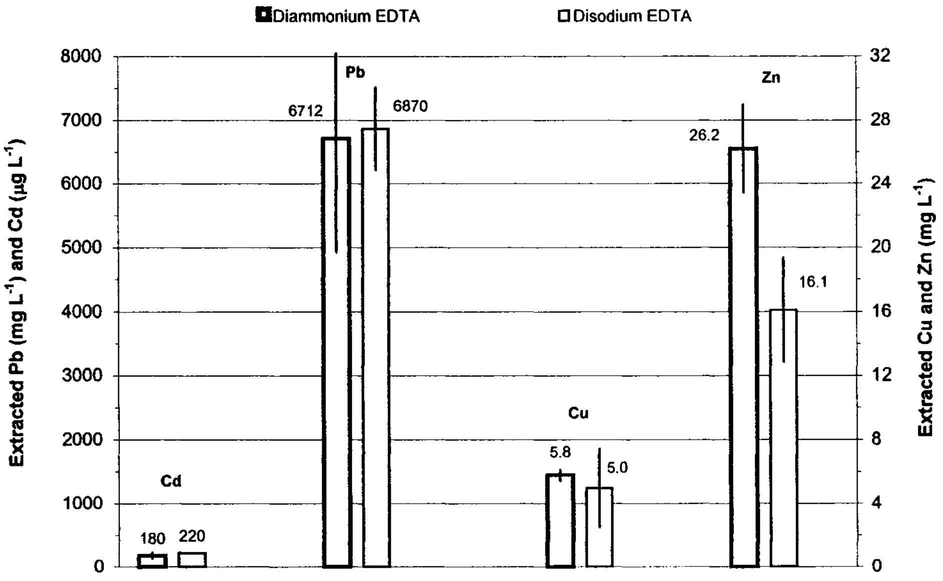
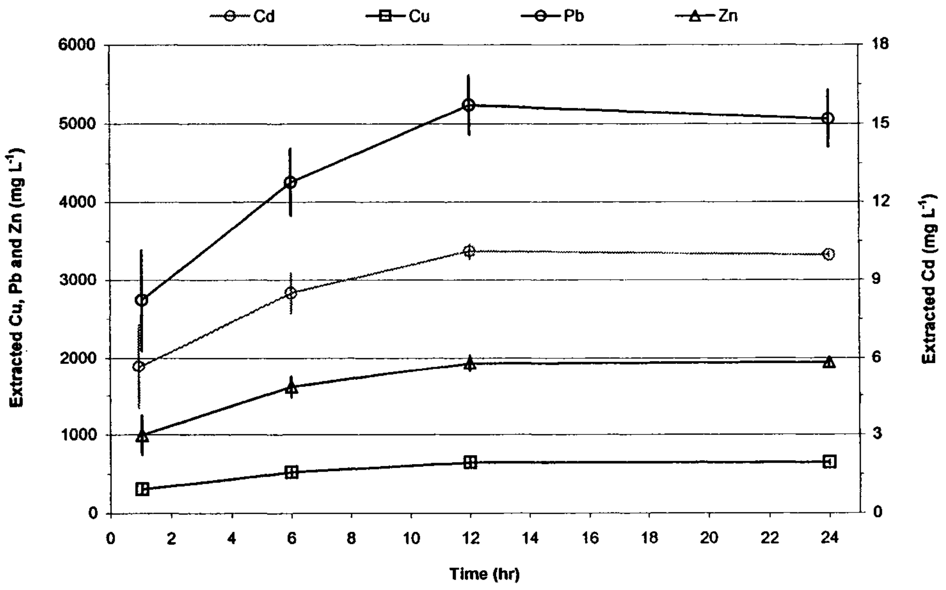


FIGURE 4.2 Time Response of Still 25 g 1:1 *L:S* Ratio 0.2 M $(NH_4)_2EDTA$ Extractions with 90% Confidence Intervals



To ensure a 12-hour extraction time, the proposed unsaturated process will need to limit the rapid leaching of the added EDTA. The added washing solution volume will need to be optimized to merely displace the old soil solution, thereby giving the new EDTA a longer soil residency time (*i.e.* ~12 hrs). Therefore, the overall addition of the washing solution will be divided into wash sequences, which will be given in small *L:S* ratios and in intervals of at least 12 hrs. The impact of further reducing the *L:S* ratio, on the extraction of potentially toxic trace metals, is examined later in sections 4.5 and 4.6

4.4 Effect of Shaking Soil Slurries on the Extractions of Trace Metals

For the EDTA still-saturated extraction, it was found previously that time did not have a significant effect on extracting Cd, Cu, Pb or Zn beyond 12 hrs. To establish the impact of contact time and shaking, a 3rd experiment compared a still (unshaken) extraction to a shaken one. The experiment was conducted for 1-hour and 12-hour extraction times (fig. 4.3). The shaken procedure was performed by a rotary shaker at 250 rpm. These batch extractions were performed on the *M-soil.*

There was no difference between the still and shaken procedures, at the 90% level of significance. Still, the 1-hour shaken experiment showed a tendency to extract 50% more Cd, Cu and Zn, and 40% more Pb, as compared to the still extraction. Overall, the extraction results for the shaken experiment showed less variation than the still experiment. Shaking physically provided a more uniform soil-solution mixture. For example, in the 12-hour experiment, the coefficients of variation (C_v) for Pb were 8.3% (still) and 3.9% (shaken). The C_v also diminished with increasing equilibration time. In the still experiment, the C_v for Zn diminished from 33.7% to 3.4%, when comparing the 1-hour experiment to the 12-hour one.

Neither the greater uniformity of the soil-solution mixture nor the abrasions between the particle surfaces, both provided by the dynamic energy from the shaking, increased the extraction of the trace metals, as compared to the still experiment. The shaken procedure was not used in the remaining experiments, as the still saturated extraction procedure was more representative of the proposed unsaturated procedure.

FIGURE 4.3 a One-Hour Shaking Response of a 1:1 *L:S* Ratio 0.2 M $(NH_4)_2$EDTA Extraction with 90% Confidence Intervals

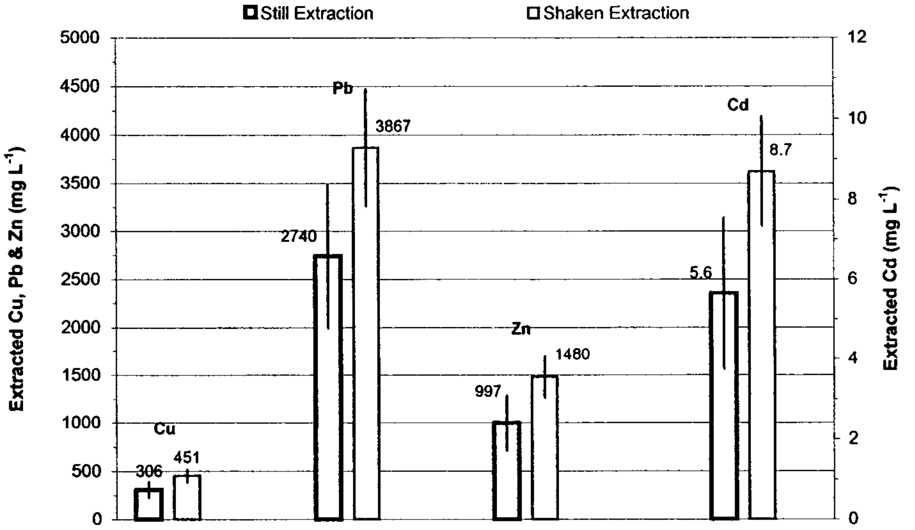
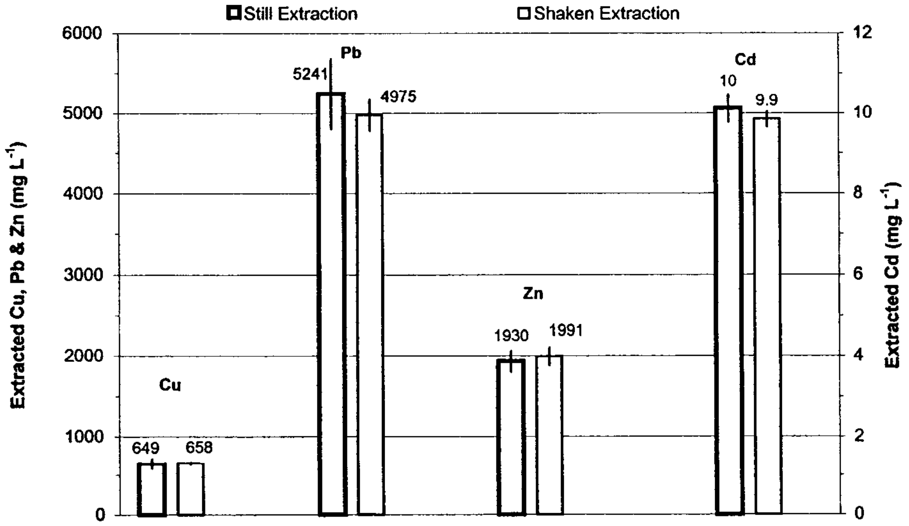


FIGURE 4.3 b Twelve-Hour Shaking Response of a 1:1 *L:S* Ratio 0.2 M $(NH_4)_2$EDTA Extraction with 90% Confidence Intervals



4.5 Saturated Extractions with High Molarity EDTA Washes in Low *L:S* Ratios

The 1.37M EDTA solution and its derivatives were abbreviated by 1.4M, 0.7M etc. *The mmol quantities of added EDTA represent the amounts added to 25g of soil, and are not to be confused with the molarity of the washing solutions. The term macroelement is used to describe an analysed element that was abundantly found in the soil, in the order of mg* g^{-1}.

Performed in soil columns, the 4th experiment was conducted to examine the benefits of applying the washing solution with a higher molarity and in a lower *L:S* ratio. The concentrations of the washes were increased substantially and the *L:S* ratio was reduced to 2:5. This was done with the objective of increasing the EDTA extraction efficiency. Following the washing solution addition sequence, the contribution of the soil-retained EDTA towards rinse-extracting metals was also evaluated over several rinse sequences.

In order to determine the scope of the impact of EDTA on the *M-soil*, the leachate solutions were tested for 14 analytes: 12 metals, P and S. As a reference, the initial mole contents of the *M-soil*'s 14 elements are presented in table 4.2. No distinction was made for the different sources of the elements, whether from parent minerals, weathered products or contaminated spills.

Table 4.2 Ranking of the 14 Elements in mmoles as per 25g of Soil of *M-soil*

Rank	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Fe	Al	Ca	Mg	Zn[d]	S	Pb[d]	Cu[d]	Mn[c]	Cr[b]	P	Ni[b]	Cd[d]	Co[b]
mmoles	111	54	21	5.7	3.8	3.5	2.3	1.5	1.1	0.17	0.27	0.14	0.02	0.04

[b] B-Level initial criterion, [c] C-Level initial criterion, [d] D-Level initial criterion

Prior to the washing cycle, the 25g *M-soil* columns were saturated for 24hrs with 15ml of deionised water. The sieved *M*-soil retained a residual moisture content of approximately 29%wt. In order to establish the soil's initial water-leachable levels, the leachate was collected and its elemental content was determined. The results for the main water-leached elements are presented in table 4.3.

Table 4.3 Concentration of Elements in the Leachate from *M-soil* Columns Saturated with Deionised Water

	S	Ca	Mg	Zn[d]	Mn[c]	P	Ni[b]	Cu[d]
Soil Ranking (moles)	6th	3rd	4th	5th	9th	11th	12th	8th
mM	20.0	16.1	3.82	0.015	0.003	0.002	0.002	0.002
$\mu g\ ml^{-1}$	643	646	93	0.95	0.17	0.06	0.10	0.10

[b] B-Level initial criterion, [c] C-Level initial criterion, [d] D-Level initial criterion

Within a washing cycle, the EDTA wash and deionised water rinses were consistently added as 10 ml. The washing solutions added either 0.7, 3.5, 7 or 14 mmol of EDTA per 25 g of soil. With the exception of the 0.7-mmol addition of EDTA, the washing solutions had high molarities (*i.e.* 3.5, 0.7 & 1.4 M), in accordance with the findings of section 4.5. The cumulative extractions from the washing cycle, as calculated from the wash and ensuing rinses are presented in figure 4.4. In order to evaluate the overall stoichiometric 1:1 selectivity of the EDTA for the soil metals, the extraction results are presented in mole quantities. The metals are presented in a decreasing order of extraction, as obtained with the 7-mmol addition.

The extraction of metals increased for greater inputs of EDTA, remaining very specific to each element and treatment. However, the efficiency in extracting the trace metals diminished with increasing inputs of EDTA. As the soil was depleted of its more easily dissolvable trace metal fractions, the remaining potentially toxic trace metals, which were more strongly sorbed onto or within soil particles, were less mobile and more difficult to extract.

The post-wash deionised water rinses largely contributed towards the extraction of elements. Table 4.4 lists the ratios of the amounts extracted by the 1st rinse relative to the amounts extracted by the wash. The first rinse of the 14, 7, 3.5 and 0.7-mmol EDTA washing cycles removed on average 94, 43, 50 and 34% equivalents of the amounts of the D-Level contaminants that had been removed by the wash.

Table 4.4 Ratios of the 1st Rinse-extracted Amounts to the Wash-extracted Amounts from Saturated 25 g Columns (%)

	Al	Ca	Cd[d]	Co[b]	Cr[b]	Cu[d]	Fe	Mg	Mn[c]	Ni[b]	P	Pb[d]	S	Zn[d]
14 mmol	80	66	90	81	66	102	122	220	82	98	44	102	113	83
7 mmol	12	43	40	30	15	43	19	28	35	29	28	48	73	39
3.5 mmol	10	44	46	63	42	53	37	48	59	44	57	54	68	48
0.7 mmol	-	51	41	124	-	38	3.9	51	35	5.0	88	26	75	31

[b] B-Level initial criterion, [c] C-Level initial criterion, [d] D-Level initial criterion

FIGURE 4.4 a Cumulative Saturated Column Extractions from a Single EDTA Washing Cycle with 2:5 L:S Ratio Additions to 25 g of Soil

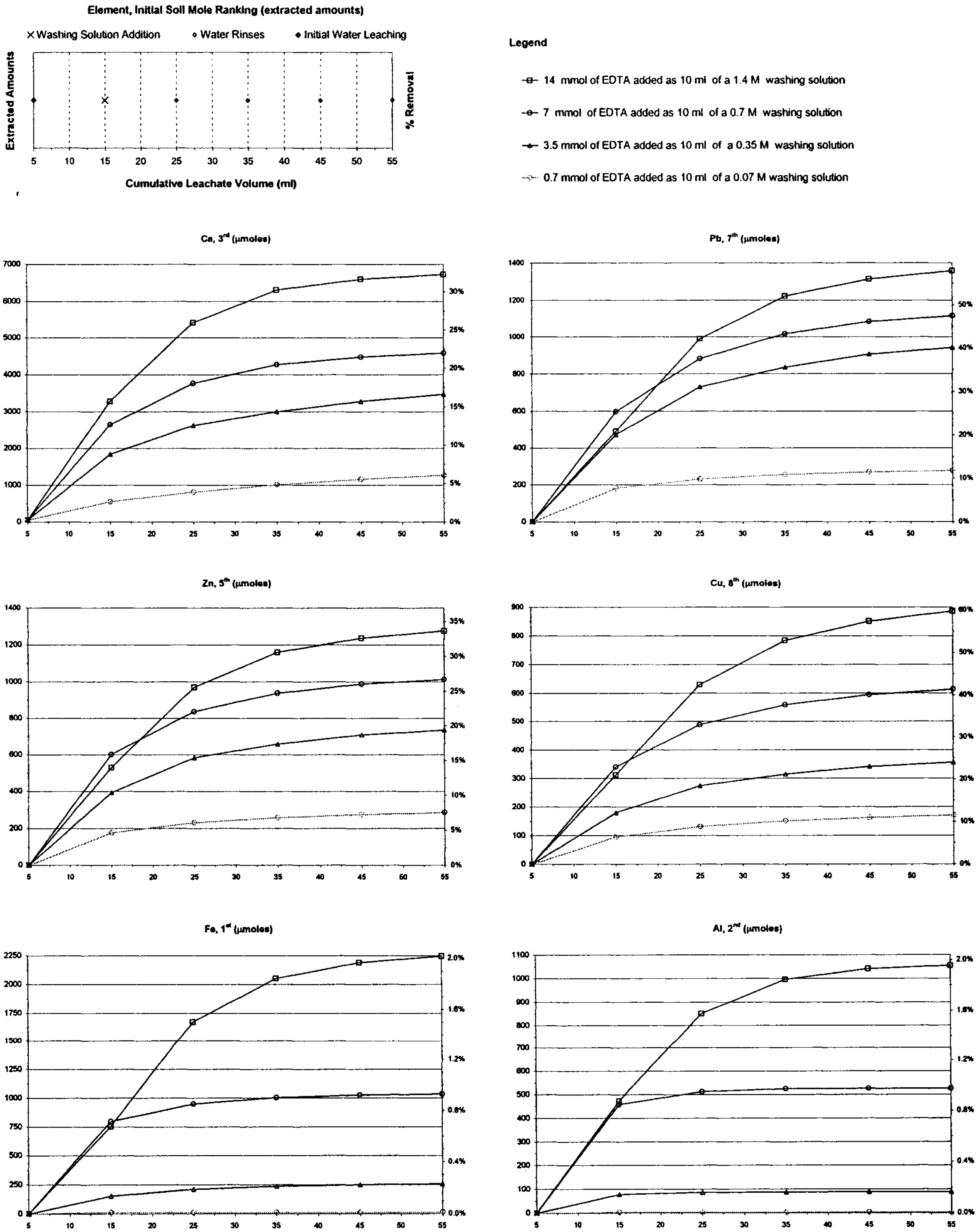
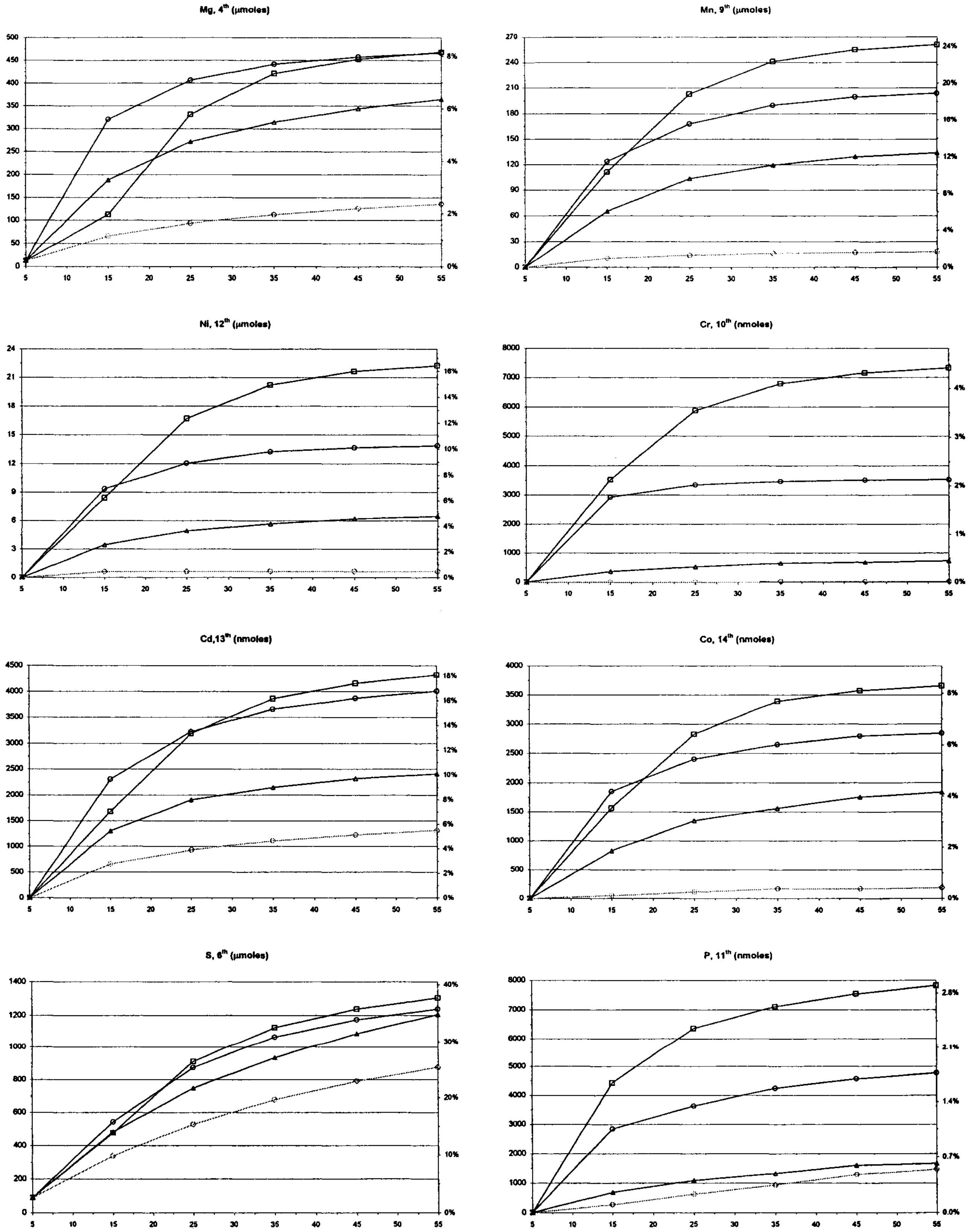


FIGURE 4.4 b Cumulative Saturated Column Extractions from a Single EDTA Washing Cycle with 2:5 L:S Ratio Additions to 25 g of Soil



For the 14-mmol washing cycle, the B, C and D-Level contaminants, as well as the other elements with the exception of P, were extracted in greater amounts during the post-wash rinses than during the wash itself (table 4.5). This is attributed to large amounts of post-wash residual EDTA, which were retained in the soil. The amounts of soil-retained EDTA following the 7, 3.5 and 0.7-mmol washes contributed towards rinse-extracting half to equal the amounts of the D-Level contaminants that had been wash-extracted. This new insight affects the interpretation of the extraction ability of regenerated-EDTA. In previous EDTA recycling studies, the soil-retained EDTA was not taken into account for its contribution towards the extraction of the potentially toxic trace metals (Lee and Marshall, 2002; Zeng *et al.*, 2001; Hong *et al.*, 1999).

Table 4.5 Ratio of the Rinse-extracted Amounts to the Wash-extracted Amounts from Saturated 25 g Columns (times)

	Al	Ca	Cd^d	Co^b	Cr^b	Cu^d	Fe	Mg	Mn^c	Ni^b	P	Pb^d	S	Zn^d
14 mmol	1.2	1.1	1.6	1.3	1.1	1.8	2.0	3.6	1.3	1.6	0.8	1.8	2.2	1.4
7 mmol	0.1	0.7	0.7	0.5	0.2	0.8	0.3	0.5	0.6	0.5	0.7	0.9	1.5	0.7
3.5 mmol	0.1	0.9	0.8	1.2	1.0	1.0	0.7	1.1	1.1	0.9	1.4	1.0	2.4	0.9
0.7 mmol	-	1.4	1.0	2.6	-	0.8	0.04	1.3	0.7	0.05	4.4	0.5	2.1	0.6

^{b} B-Level initial criterion, ^{c} C-Level initial criterion, ^{d} D-Level initial criterion

Even though the theoretical formation constant value for Ca is quite low (pK_f 10.7), EDTA extracted Ca in the greatest amounts (fig 4.4). Calcium is among the most abundant and exchangeable cations in soils and is generally found in moderately soluble parent or precipitated carbonates minerals (Donor and Lynn, 1989). Initially, Ca was the third most abundant in the soil and the second most leachable of the 14 analysed elements. Magnesium followed Ca in soil abundance and leachability, but was extracted in much smaller quantities; Mg has a theoretical pK_f value of 8.7. The 14-mmol extraction removed similar amounts of Mg as the 7-mmol extraction, thus limiting the extraction of Mg.

Amongst the heavy metals, Pb and Cu had the greatest % removal, both having relatively high theoretical pK_f (18, 18.8). Still, the extracted amounts of Zn, ranked 5th in mole abundance in the soil, surpassed those of Cu, ranked 8th. With the exception of the 14-mmol extraction, the extraction of Pb, ranked 7th, surpassed the extractions of Fe and Al, ranked 1st and 2nd. For the lower strength treatments (*i.e.* 3.5 and 0.7 mmol), the extractions of Zn and Cu also surpassed the extractions of Fe and Al.

In soils, the bulk of Fe and Al are usually found in minerals from parent rocks, *e.g.* Fe oxides and Al silicates and hydroxides. The *M-soil* was contaminated with 5 times the normal Fe level, thus elevating it past Al as the most abundant of the analysed elements. The contaminating Fe, which accounted for 80% of the total Fe, was most likely in the form of precipitated Fe oxide minerals. These precipitated Fe oxides were anticipated to be more prone to dissolution than the minerals from parent rocks, however this was not the case. The % removal of Fe and Al were almost equivalent for each EDTA addition. Thus, the Fe and Al minerals, whether precipitated or from parent rocks, would have resisted dissolution in the same manner and without discrimination on their origin.

With increasing inputs of EDTA, fewer chemisorbed metals were left on Fe and Al oxide surfaces. As a result, less available metals and more exposed oxide surfaces led to the dissolution of theses minerals. Upon doubling the EDTA addition to 14 mmol, the extractions of Fe and Al more than doubled (*i.e.* 2.3 and 2.1 times). With the exception of the generally abundant extraction of Ca, the 14 mmol of EDTA was found to have mainly scavenged for Fe and Al. The previously described extraction behaviour of an element, tending to indicate that its main provenance is from the dissolution of its minerals, was referred to as *mineralution*.

The *M-soil* was contaminated with 7 times the normal level of S, thus making S the most leachable of the 14 elements. For the lowest 0.7 mmol of EDTA, the 25% removal for S was the greatest of the 14 elements. However, increasing EDTA beyond 3.5 mmol, minutely increased the extraction of S which had already reached 35% removal. It is believed that this 35% removal accounted for the mobile sulphates and that the remaining S was found in insoluble sulphides.

For Cd, doubling the addition of EDTA from 7 mmol to 14 mmol provided a small increase in extraction. After the extractions of its complexed and chemisorbed forms, the extraction of Cd was considered to have been strongly limited by co-precipitation within sulphide minerals. This would imply that 80% of Cd was found in insoluble sulphide minerals. Unlike Cd, chalcophilic Cu, Pb and Zn were further extracted upon doubling the EDTA addition from 7 to 14 mmol at the 14 mmol level. The % removal of Pb, Zn and Cu improved to 58, 34 and 60%, from 48, 26 and 40%. After the dissolution of their complexed and chemisorbed forms, Cu, Pb and Zn were still readily extracted, likely from Fe oxide co-precipitates, hydroxy-carbonate precipitates and/or their own oxide and hydroxide precipitates.

In soils, Mn is cycled between solution and Mn nodules, which are Mn oxides with impurities of Fe and of trace metals like Co, Cr and Pb (McKenzie, 1989; McBride, 1994). The removal of this C-Level contaminant was likely due to the dissolution such nodules. For Ni and P, their 1.7-fold increases in extraction approached the 2-fold EDTA increase from 7 to 14 mmol. The similar behaviour of Ni to Fe may be explained by its tendency to readily co-precipitates in Fe-oxides (McBride,1994).

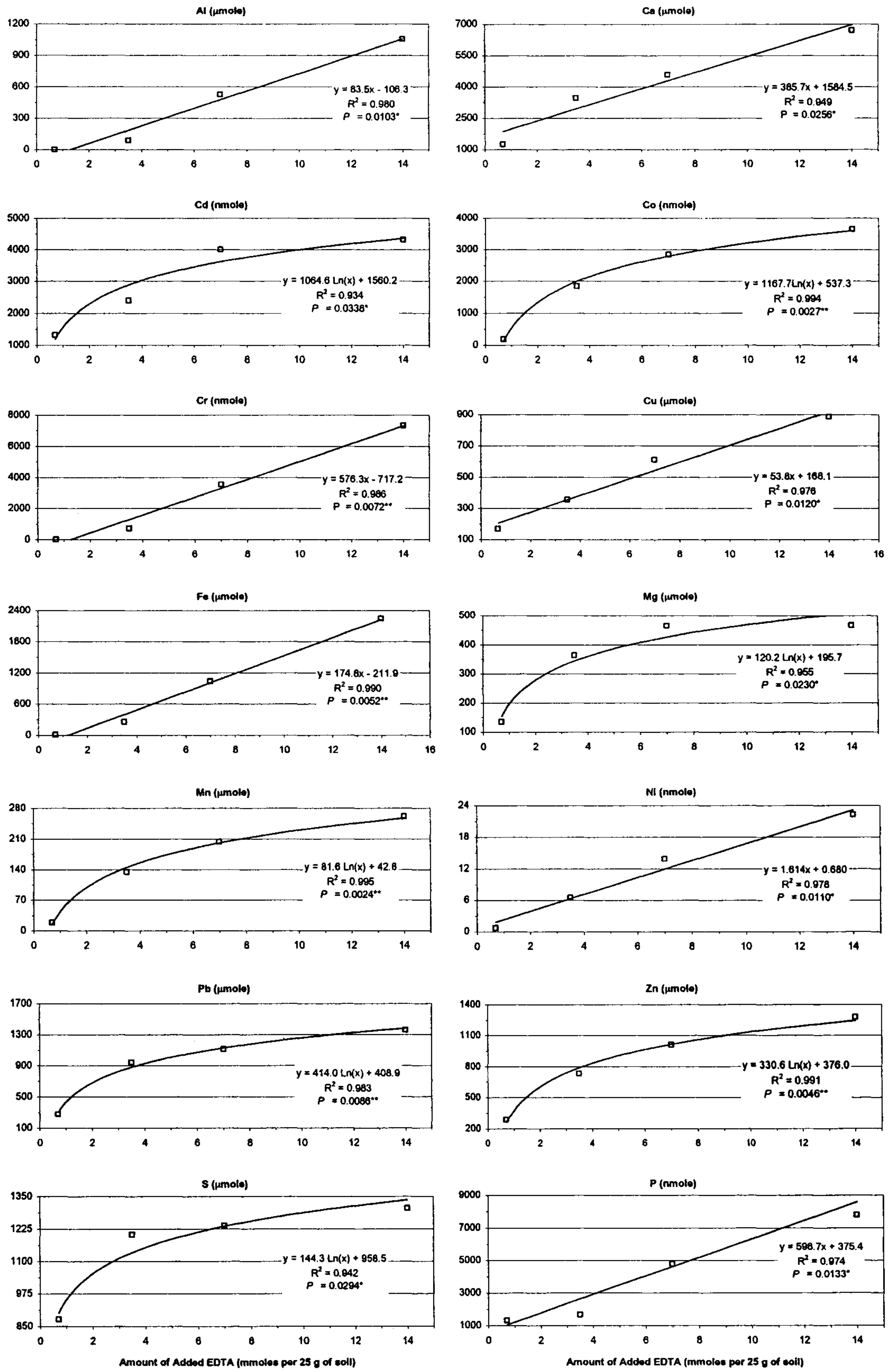
Even at the nanomole level, Cr and P behaved much like Al and Fe. Upon doubling EDTA to 14 mmol, Cr was the lone trace element for which the extraction more than doubled (*i.e.* 2.1 times). Chromium usually occurs in soils as the immobile Cr^{3+} and could be found in replacement of Fe^{3+} in Fe oxides (McBride, 1994). This could explain its similar behaviour to that of Fe. In soil, undissolved P is chemisorbed or precipitated as phosphates (McBride, 1994). It is assumed that the 0.7 and 3.5 mmol of EDTA would have extracted the metals that were chemisorbed along with P on the surface of the soil particles, causing P to dissolve as well. For the 7 and 14 mmol inputs, the larger extractions of P suggest phosphate *mineralution.*

To establish extraction trends of the cumulative amounts of extracted elements in regards to the additions of EDTA, regression and ANOVA analyses were performed (fig. 4.5). Small 2:5 *L:S* ratios were used for all the additions of EDTA, which included one low and three high-molarity additions. The lower boundary of the regression models (*i.e.* 0.7-mmol addition) was equivalent to 28 μmol g^{-1} of *M-soil.*

Of the analysed elements, the three most abundant in the soil (Fe, Al & Ca) exhibited linear extraction responses to the different amounts of added EDTA. A linear response indicated that the extraction of an element was not dissolution-limited over the range of the washing solution concentrations. Of the D-Level contaminants, Cu was the only one to have a linear extraction response. The only B-Level contaminants that exhibited linear extraction responses were Cr and Ni.

A logarithmic response indicated the occurrence of an extraction limitation, arising from the very low addition (*i.e.* 0.7 mmol) and/or the very high addition (*i.e.* 14 mmol). The very weak EDTA ionic strength offered by the 0.07 M washing solution would have limited the dissolution of Mn and Co, whereas the very high 14-mmol EDTA addition would have limited the dissolution of Mg. However, the extraction limitations of Pb, Cd and S were attributed to the soil's stronger retention of the remaining elements; the next experiment in section 4.6 verified this hypothesis.

FIGURE 4.5 Regression Models between EDTA added in excess of 28 µmol g^{-1} of *M-soil* and Extracted Levels of Each Element



4.6 Saturated Extractions of Like Amounts of EDTA in High or Low Molarities

The 5th experiment studied the effects of increasing the molarity of the washing solution and adding it in a smaller 1:5 *L:S* ratio, for equivalent amounts of added EDTA. This was done with the objective of increasing the EDTA extraction efficiency, and in contrast to adding a more dilute washing solution in a larger *L:S* ratio. The comparative results for two 7 and two 3.5-mmol EDTA additions are presented in figure 4.6 while the statistics are shown in table 4.6.

Figure 4.6 illustrates how the very concentrated 1.4 M EDTA washing solution had a limiting effect on the dissolution of Mg, but did not adversely affect the extractions of Cd, Pb nor S. Moreover, in the other experiment (*i.e.* 7-mmol addition of EDTA), the treatment with the 1.4 M wash, applied in a lower *L:S* ratio, extracted significantly more Pb (at the 99% level) than the 0.7 M treatment. Therefore, the 14 mmol-limited extractions as seen in section 4.5 were attributable to the soil's stronger retention of the remaining metals.

In the experiment that added 3.5 mmol of EDTA, the treatment with the more concentrated 0.7 M wash, applied in a lower *L:S* ratio, extracted significantly more Al (at the 99.9% level), Cr and Ni (at the 99% level), and Cu, Fe and Zn (at the 95% level) than the treatment with the more dilute 0.35 M wash. However, the latter, which was applied in a higher *L:S* ratio, extracted significantly more Ca and Mg (at the 99.9 and 95% levels) than the 0.7 M wash. As compared to the 0.35 M wash, the more concentrated 0.7 M wash provided the soil with a solution of greater EDTA ionic strength, in which the EDTA was more selective towards Al and the heavy metals and less selective towards Ca and Mg. Thus, concentrating the washing solution and applying it and the ensuing rinses in a smaller *L:S* ratio increased the dissolutions of the potentially toxic trace metals, with the exception of Cd, Co and Mn.

The use of a very concentrated wash could perhaps reduce the generation of leachate by riding the soil more quickly of its contaminants. The high solubility of $(NH_4)_2$EDTA (45% wt) allows the use of very concentrated 1.4 M washing solutions, which increase the efficiency of trace metal removal. This is greatly advantages $(NH_4)_2$EDTA over Na_2EDTA, which has a water solubility of 7% wt and for which the molarity of a pure solution is limited to ~0.2 M (DOW Chemical Company, 2002).

FIGURE 4.6 a Cumulative Saturated Column Extractions from a Single EDTA Washing Cycle with either 2:5 or 1:5 L:S Ratio Additions to 25 g of Soil

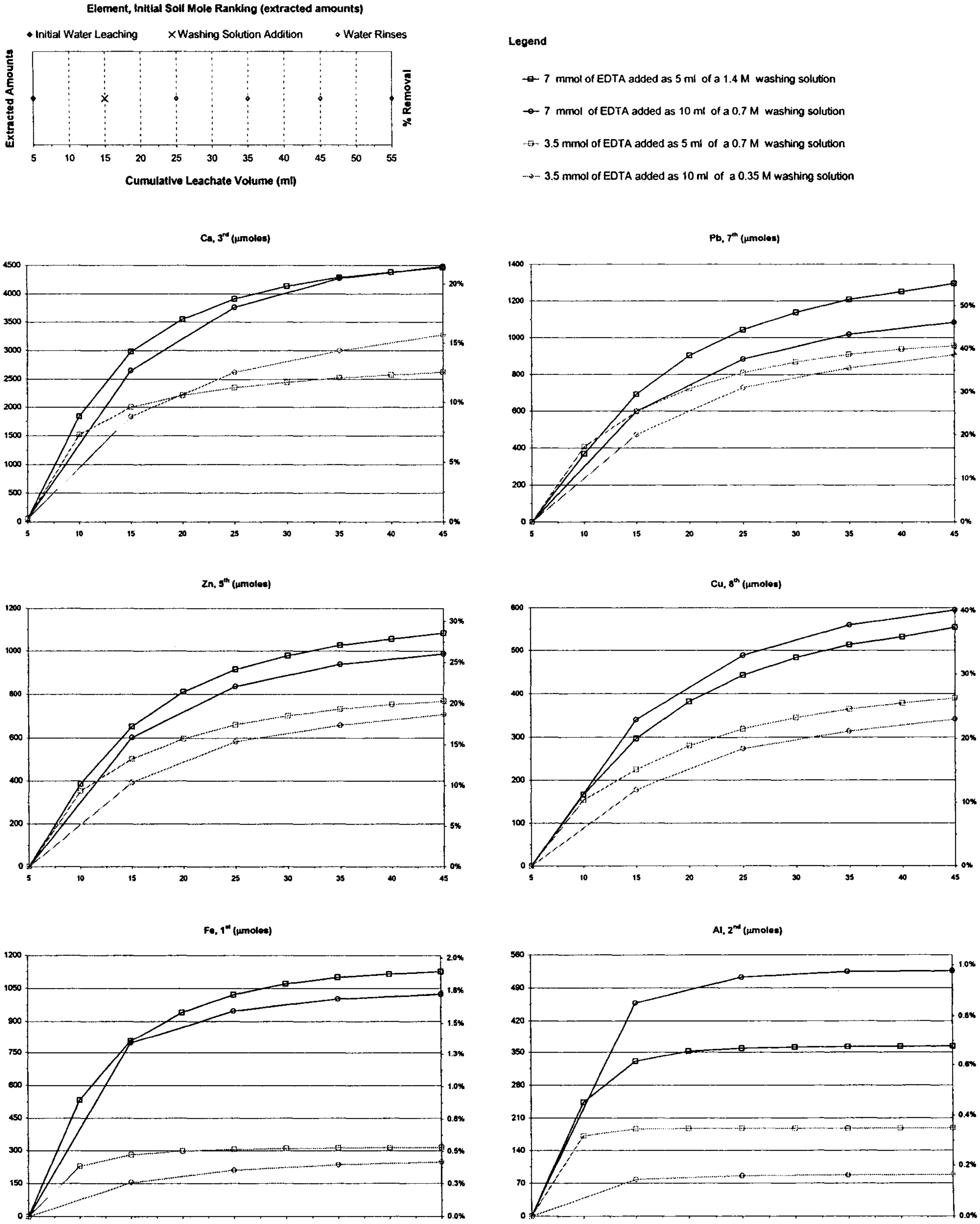


FIGURE 4.6 b Cumulative Saturated Column Extractions from a Single EDTA Washing Cycle with either 2:5 or 1:5 L:S Ratio Additions to 25 g of Soil

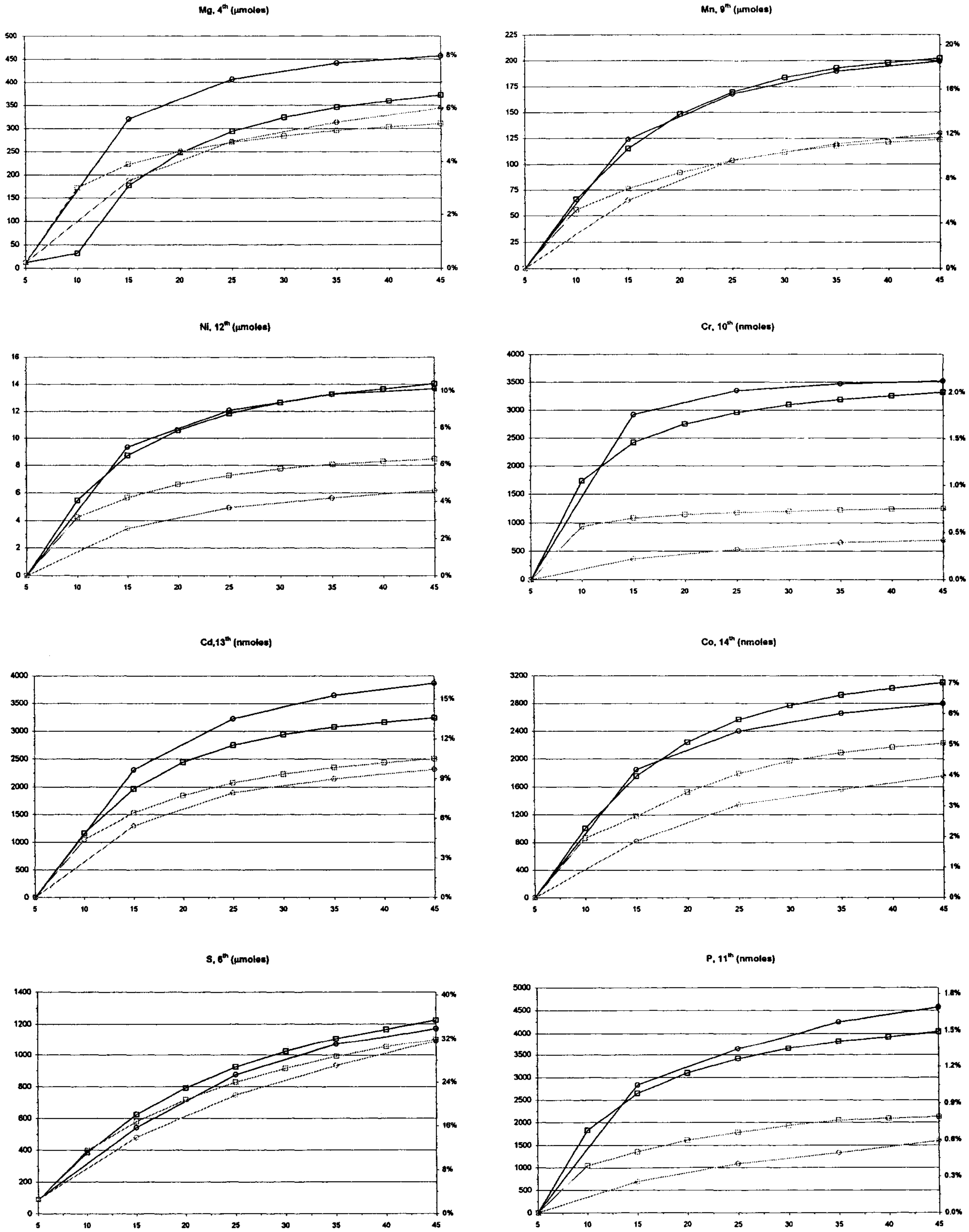


Table 4.6 t-test of the Cumulative Washing Cycle Extractions of a 1:5 *L:S* to a 2:5 *L:S* Ratio for Equal EDTA Amounts

Element	1:5 *L:S* x 2:5 *L:S* (Molarities)	t	*P*	Unequal Variances*	Departure from Normality^{K}
Al	1.4 x 0.7	-2.34	0.0580	yes	0.7 M
	0.7 x 0.35	11.21	0.0000 ***		
Ca	1.4 x 0.7	-0.04	0.9681	yes	0.7 M
	0.7 x **0.35**	-7.37	0.0003 ***		
Cd	1.4 x 0.7	-1.78	0.1248	yes	
	0.7 x 0.35	1.46	0.1950		
Co	1.4 x 0.7	1.93	0.1013	yes	
	0.7 x 0.35	2.38	0.0545		
Cr	1.4 x 0.7	-0.43	0.6813		
	0.7 x 0.35	4.45	0.0043 **		
Cu	1.4 x 0.7	-1.51	0.1821		
	0.7 x 0.35	2.57	0.0423 *		
Fe	1.4 x 0.7	0.96	0.3755		
	0.7 x 0.35	2.73	0.0341 *		
Mg	1.4 x **0.7**	-2.68	0.0368 (*)	yes	1.4 & 0.7 M
	0.7 x **0.35**	-2.88	0.0280 *		
Mn	1.4 x 0.7	0.26	0.8052		
	0.7 x 0.35	-0.61	0.5618		
Ni	1.4 x 0.7	0.42	0.6894		
	0.7 x 0.35	5.21	0.0020 **		
P	1.4 x 0.7	-0.75	0.4788		
	0.7 x 0.35	2.24	0.0662		
Pb	**1.4** x 0.7	5.60	0.0014 **		
	0.7 x 0.35	1.86	0.1120		
S	1.4 x 0.7	0.40	0.7038		
	0.7 x 0.35	1.74	0.1315		
Zn	1.4 x 0.7	1.68	0.1440	yes	0.7 M
	0.7 x 0.35	3.08	0.0217 *		

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

$^{(***)}$, $^{(**)}$ or $^{(*)}$ The significant difference is overruled by unequal population variances or non-normal population distributions

^{K} Kurtosis was the only factor, as no skewness was present

4.7 Comparison of the Current Results to Those of Previous Studies

A comparative assessment was performed to distinguish this study from previous studies and highlight the author's resolve to provide an economical, pragmatic and environmentally sustainable solution for remediating trace metal contaminated soils. In order to compare the extraction efficiency of this study to those of other studies, an added EDTA to initial soil-Pb molar ratio (*EDTA*:*Pb*) was used. Hence, our 2.9 *EDTA*:*Pb* and cumulative 1:1 *L:S* ratio was compared to those of other studies (table 4.6).

Table 4.7 Comparison of the Results Obtained in the Present 7 mmol Study against those of Previous Studies

	EDTA:S (%wt)	*EDTA:Pb* (mol:mol)	*L:S*	Cycles[c]	Cd Removal ($\mu g\,g^{-1}$)[i]		Cu Removal ($\mu g\,g^{-1}$)[i]		Pb Removal ($\mu g\,g^{-1}$)[i]		Zn Removal ($\mu g\,g^{-1}$)[i]	
Andrade (2004)	8.9%	2.9	1:1	1 + 2	16%	107	36%	3768	54%	19466	24%	9917
Lee & Marshall (2002)	3.7%	3.2	1:1	1 + 0	0.6%	6.2	9.0%	15.5	22%	6555	11%	160
Tejowulan & Hendershot (1998)	1.0%	43	60:1	12 + 0	76%	6.3	53%	700	49%	800	84%	2650
Papassiopi *et al.* (1997)	186%	83	80:1	2 + 6	48%	80	-	-	57%	12500	45%	10200
Barona *et al.* (2001)	19%	222	>10:1	1 + >1	-	-	-	-	33%	466	14%	772

[c] Number of washes and rinses

[i] Initial soil content

Our results were obtained from an initial 7-mmol wash followed by two deionised water rinses (*i.e.* a saturated washing cycle). The other studies used Na_2EDTA as a chelating agent, or H_4EDTA in the case of Tejowulan and Hendershot. The conclusions from the comparisons are not absolute in nature, since the forms and amounts of each potentially toxic trace metal within the soils were different.

With an *EDTA*:*S* of 186%wt, Papassiopi *et al.* obtained a slightly better extraction of Pb, as compared to this study. The former experiment is environmentally unsustainable and uneconomically, since almost two times more EDTA than soil was used. Furthermore it produced a cumulative *L:S* ratio 80 times greater than that of this study. Papassiopi *et al.* did triple and almost doubled the Cd and Zn extractions, as compared this study, but this was achieved with a 28 times greater *EDTA*:*Pb*. As compared to Papassiopi *et al.*, Tejowulan and Hendershot improved the extraction of Cd and Zn by roughly 1.7 times, by reducing the *EDTA*:*Pb* and the cumulative *L:S* ratio by roughly two-fold. However, their extraction of Pb was reduced by 14%. Barona *et al.* used an *EDTA*:*Pb* two orders of magnitude greater than this study, yet extracted less Pb and Zn.

With an equivalent *L:S* ratio to that of Lee and Marshall, the present 7 mmol study extracted 2.4 times more Pb with a slightly lower *EDTA*:*Pb*. The former was the most environmentally sustainable procedure of the previous studies. However, the present study still achieved a higher % removal for Cd, Cu, Pb and Zn. As was first ascertained in section 4.5, this success was attributed to the addition of the EDTA washing solution in a higher molarity within a smaller *L:S* ratio. This methodology was retained, reused and improved, in the experiments of the following chapters.

4.8 Summary and Conclusions

Diammonium EDTA is more than five times cheaper than Na_2EDTA and extracted significantly more Cu and Zn, as much Pb but less Cd. The relative low cost of $(NH_4)_2EDTA$ and its efficiency in extracting trace metals were necessary precursors for developing a pragmatic approach for remediating soils contaminated with trace metals. The high solubility of $(NH_4)_2EDTA$ in water also allowed highly concentrated washing solutions, which reduced the volume of liquid waste by extracting more trace metals within smaller cumulative leachate volumes.

Extending the saturated extraction from 12 hours to 24 hours did not increase the extraction of Cd, Cu, Pb or Zn. Furthermore, unshaken slurries extracted as much of Cd, Cu, Pb or Zn as the shaken ones. Therefore, the development of a non-shaken 12-hour equilibration process seems feasible.

The treatment of a soil with an EDTA wash leaves behind considerable amounts of residual EDTA. Upon rinsing the treated soil with deionised water, the residual EDTA caused a considerable water extraction of trace metals. The 1st rinse extracted trace metal in slightly smaller amounts to those of the wash extraction. With each additional rinse sequence the soil was being depleted of its residual EDTA, hence the rinses successively extracted fewer amounts of metals. For equal additions of EDTA, concentrating the saturated washing solution and applying it and the ensuing rinses in smaller *L:S* ratios increased significantly the extraction of Cd, Cu, Pb and Zn.

The two largest increases in extractions occurred upon doubling the EDTA addition to 14 mmol; these were attributed to Fe and Al and likely associated to their *mineralution*. In contrast, the smallest increases in extracted amounts were for Pb and Cd, which also occurred when doubling the EDTA to 14 mmol. Therefore, the precipitated Fe oxides, stemming from the Fe contamination, seemingly contained few impurities of Cd, Cu, Pb and Zn. Thus, it is hypothesised that a large fraction of the latter trace metals were co-precipitated within sulphate and sulphide minerals. The extraction cap for S, observed when adding 14 mmol of EDTA, seemed to indicate that the sulphate minerals would have mostly been dissolved, while the remaining S, in the form of sulphide minerals, would have resisted dissolution. Thus, the limiting factor for the extraction of the remaining chalcophiles could have been the dissolution of the sulphide minerals.

The linear regression models demonstrated that the extraction efficiencies of some macroelement and microelements (Al, Ca, Fe & Cu; and Cr & Ni) were not limited by the concentration of the washing solution, which was applied in a small 2:5 *L:S* ratio. Conversely, logarithmic regression models indicated that the low-concentration washing solution (0.07 M) limited EDTA's extraction potential towards Mn and Co. Otherwise, the logarithmic regression models indicated a diminished extraction efficiency for the highly concentrated washing solutions. This was attributed to the increasing difficulty of dissolving the residual amounts of the soil-bound trace metals, with the exception of Mg.

The measurements of pH and redox potentials could have provided useful information towards understanding the governing chemical reactions in the above experiments. However, these measurements were not carried out nor were investigations on the forms of metal complexes resulting from the experimental processes, as this study focused on the feasibility of using a chemical soil washing procedure on a site-scale level. The post-treatment soil-retained EDTA was not measured, yet it was witnessed as a result of the extraction of metals by subsequent deionised water rinses. In chapter 5, the experiments attempt to improve the previous findings vis-à-vis the chemical extraction of trace metals with EDTA and to reduce the cumulative leachate volume. An unsaturated-flow extraction procedure was tested to fulfill the requirements for a pragmatic implementation of a site-scale remediation process.

Preface to Chapter 5

In chapter 4, the application of high molarity washing solutions in low *L:S* ratios increased the extraction efficiency and reduced the volume of the contaminated leachate. This approach was applied to the following experiments. The experiments examined unsaturated-flow extractions from soil columns and compared them to still-saturated extractions. The experiments were carried out as single and multiple washing cycles. A washing cycle consisted of adding a single wash, which was followed by sequential additions of deionised water for rinsing.

5

Extraction of Potentially Toxic Trace Metals from Soils with $(NH_4)_2EDTA$ Washing Cycles under Unsaturated-Flow Conditions

Large-scale removal of trace metals from contaminated soils has been carried out as a chemical washing process of soil slurries, which involved mechanical mixing of small batches of sieved soil with a washing solution (CRIQ, 2001). This approach costs > \$200 ton^{-1} (Project Ploughshares, 1996). Hence, landowners of C-Level contaminated soils would be more inclined to excavate their soil and send it to a secure landfill. For example, to dispose of 5000 tons of soil would cost \$90 ton^{-1} (*i.e.* \$60 ton^{-1}for the landfill (CINTEC, Lasalle), \$15 ton^{-1} for excavation and local transport, and \$15 ton^{-1} for refilling the site). For D-Level contaminated soils, STABLEX (Blainville) charges \$165 ton^{-1} to transport (*i.e.* for 50 km) the soil to their site, neutralise it, stabilise it, solidify it with cement, and deposit the solidified soil in secure cells on adjacent governmental land.

The proposed engineering design assumes that D-Level contaminated soils could be heaped and remediated under unsaturated flow conditions. Heap leaching has been used to extract precious metals (*i.e.* gold & silver) from ores with NaCN solutions (Matlock *et al.*, 2002). An on-site *ex-situ* unsaturated approach reduces the soil handling costs and eliminates the mechanical mixing costs, by excavating and heaping the contaminated soil atop a geomembrane. As a single batch process, drip irrigation applies the washing and rinsing liquids atop the soil heap. The leachate is collected by gravitational flow from the underlying geomembrane. Thus, the soil is moved only twice (*i.e.* before and after treatment). Drip irrigation tape is inexpensive, costing around ¢8 m^{-1} (HARNOIS, Joliette). An EPDM geomembrane costs around \$3.50 m^2 (FIRESTONE, Brussels) and could be reused on more than one site. An unsaturated-flow process provides substantial reductions in expenses related to multiple handlings of the soil and is estimated to cost \$100 ton^{-1}, about half that of a saturated process (appendix 3).

In order to reproduce the intended design of an unsaturated-flow remediation process, unsaturated column studies were undertaken. From the observations of section 4.6, washing solutions were applied in high-molarities and in a low 1:5 *L:S* ratio. The unsaturated column extractions were performed in conjunction with saturated column extractions. The saturated and unsaturated-flow procedures were compared to establish the extraction ability of the proposed unsaturated process.

5.1 General Methodology

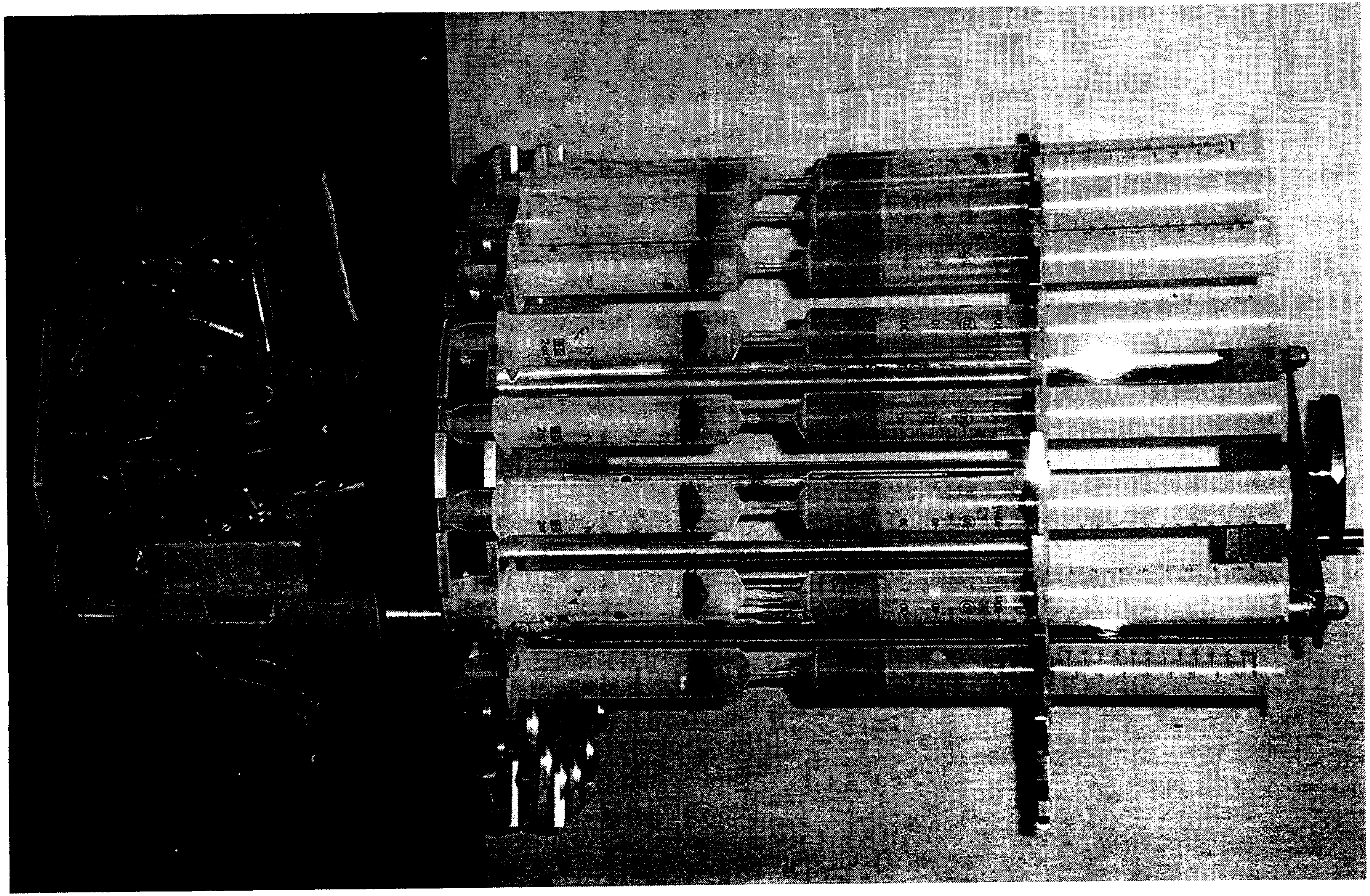
The generic term EDTA specifically abbreviates our experimental use of diammonium EDTA. A washing cycle consisted of a one-step EDTA wash and subsequent rinses with deionised water. A <u>*saturated extraction*</u> *describes the physical state of a waterlogged soil. An unsaturated-flow extraction is abbreviated by unsaturated extraction. The 1.37*M *EDTA washing solution and its derivatives are abbreviated by 1.4*M*, 0.7*M etc. *The mmol quantities of added EDTA represent the amounts that were added to 25g of soil, and are not be confused with the molarity of the washing solutions in which they were found. A liquid to soil ratio is abbreviated by L:S ratio.*

The experiments dealt with unsaturated EDTA extractions of soil columns, made by packing 25g of *M-soil* between polyethylene frits in a 60ml capacity syringe. The VERSENE EDTA was obtained from the DOW Chemical Company (Midland). To provide the columns with unsaturated flow conditions, they were installed in a CENTURION column extractor (picture 1). The top syringe acted as the vacuum barrier when filled with the washing or rinsing solution. The washing and the rinsing solutions were supplied at a rate of 0.5ml hr^{-1}, over 10hours. Once the last of the liquid had been drawn through the column, the water seal was broken and the system was open to the atmosphere. The extraction ran for an extra 8 hours to remove remaining gravitational water. The leachate was recovered and analysed.

Prior to the unsaturated experiment, the soil was moistened with 15ml of deionised water at a rate of 1ml hr^{-1}. This was performed to optimise the distribution of the percolating EDTA washing solution throughout the soil. The soil retained a moisture content of roughly 29% wt. The washing solution was then added in a 1:5 *L:S* ratio to the moist soil (*i.e.* 5ml). The subsequent rinses also added 5ml volumes for each 24-hour sequence.

The extractions were performed in quadruplicates. The extraction solutions were analysed with a VARIAN *VISTA-MPX* radial ICP-OES. The results are presented as averages of the quadruplicate extracts. To establish the scope of the impact of EDTA on the soil, the extraction solutions were tested for 14 analytes: 12 metals, P and S. In order to evaluate the stoichiometric 1:1 selectivity of EDTA for the soil metals, the results for the extracted elements are presented in mole quantities. The extraction results are presented as cumulative amounts for each element.

PICTURE 1 Unsaturated Flow Column Extraction Set-up



For the statistical analysis, the STATGRAPHICS®*PLUS 4.0* software was used to compute the t-tests between the end-extraction results from two treatment populations. STATGRAPHICS®*PLUS 4.0* was also used to assess the equality of the variances between the two treatment populations, as well as the normality of each population's distribution.

5.2 Unsaturated Extractions with High Molarity EDTA Washes in 1:5 *L:S* Ratios

This 1st experiment was designed to assess how well an unsaturated-flow extraction would measure up to a still-saturated extraction for a single washing cycle. Three washing solutions of different EDTA concentrations were used in a small 1:5 *L:S* ratio. The unsaturated column extractions results were compared to saturated column extractions for equivalent EDTA additions.

A first dissimilarity between the saturated and unsaturated extractions was that the former were done under stagnant reducing conditions and the latter were performed under oxidising conditions with vacuum-induced flow. When adding the washing solution through unsaturated flow, a part of the EDTA remained in the soil and part leached out. Depending on the percolation route, the leached EDTA would have been in contact with the soil for anywhere between 4 to 12 hours. This differs from the saturated experiment, where all of the EDTA was retained in the soil for a full 24 hours.

Figure 5.1 presents the cumulative extractions from respective washing cycles. The leachate collected from the saturated washing solution addition contained the greatest amount of elements of all the individually collected leachate volumes during its washing cycle. In contrast, it was the first rinse that extracted the most elements during the unsaturated washing cycle; this stemmed from the large amount of residual EDTA that was left in the soil following the unsaturated-flow application of the washing solution.

As in section 4.6, the extraction of metals from soils increased with increased additions of EDTA, remaining specific to each element and treatment. As well, the efficiency of the mobilisation of trace metals diminished with increasing amounts of EDTA, due to increasing immobility of the remaining metals. Calcium and Pb were first and second in extraction abundance on a mole basis; whether submitted to saturated or unsaturated conditions, the extracted quantities remained similar for Ca and Pb.

FIGURE 5.1 a Cumulative Unsaturated Column Extractions from a Single EDTA Washing Cycle with 1:5 L:S Ratio Additions to 25 g of Soil

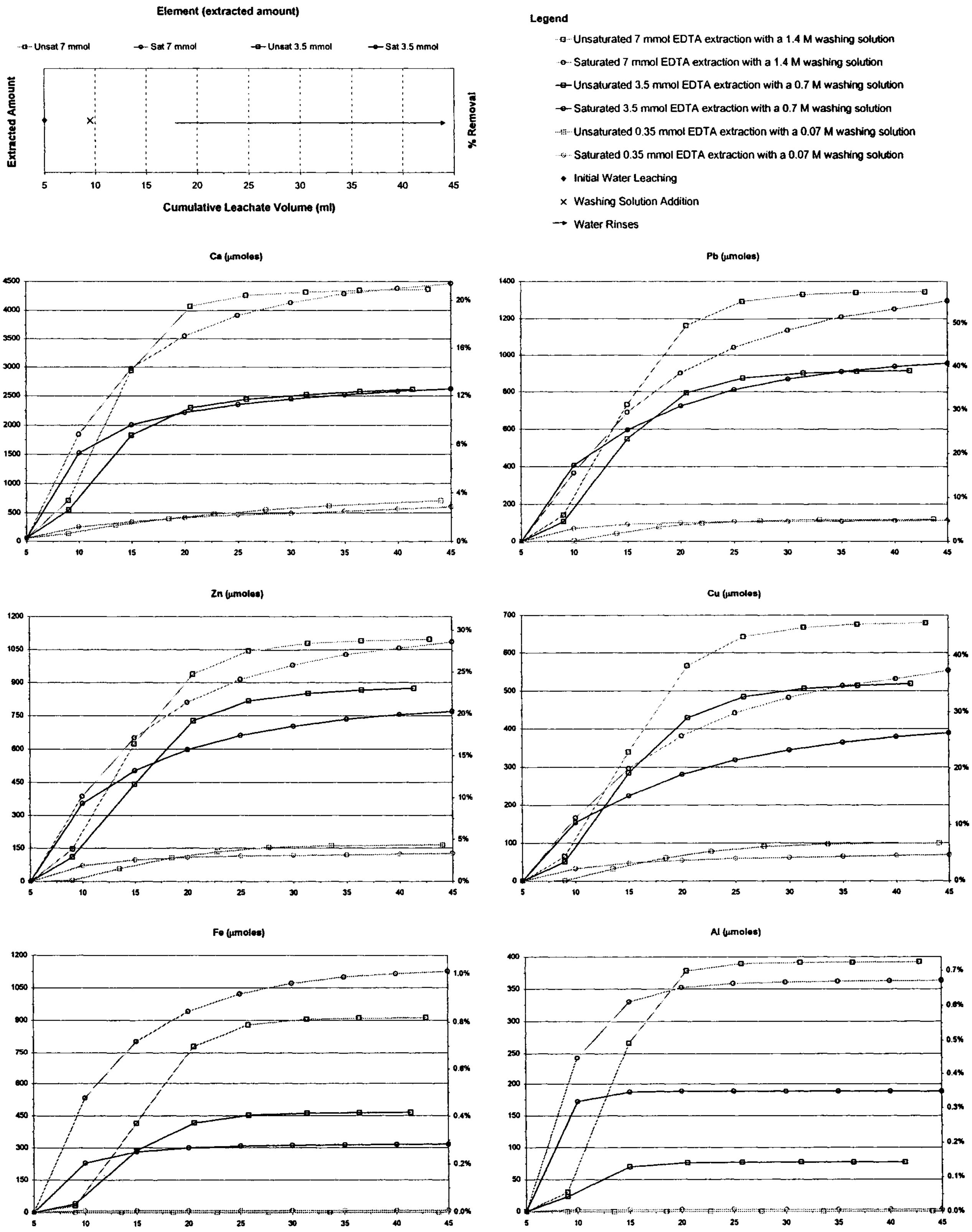
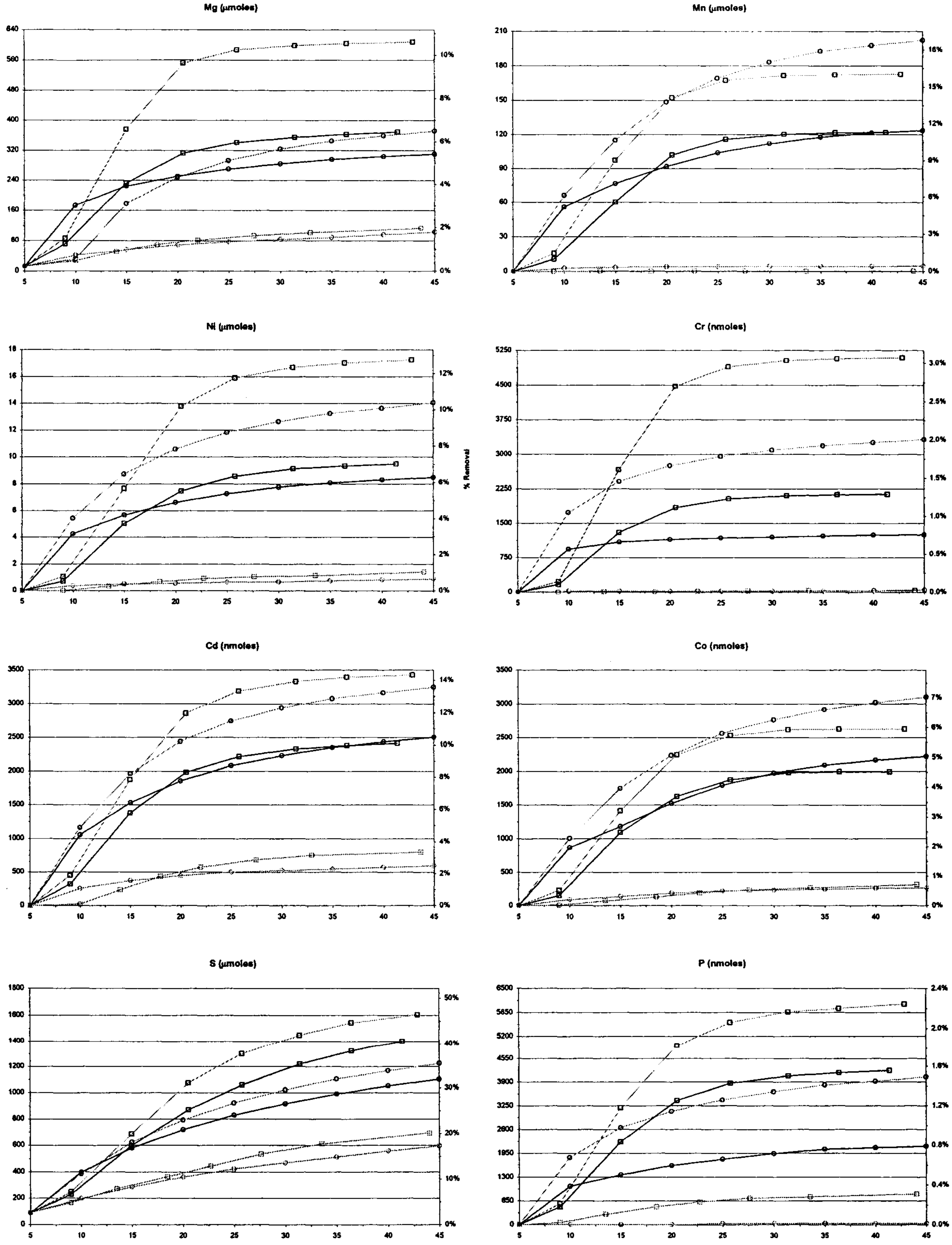


FIGURE 5.1 b Cumulative Unsaturated Column Extractions from a Single EDTA Washing Cycle with 1:5 L:S Ratio Additions to 25 g of Soil



For both 0.35-mmol extractions, EDTA was overwhelmingly consumed by Ca (*i.e.* 58.6%). This correlates with the fact that Ca is the most abundantly exchangeable cation in the soil environment. The relative impact of the exchangeable Ca fraction diminished with higher molarities. Still, in the 3.5 and 7-mmol extractions, Ca complexed with 45.5% of the EDTA. Thus, Ca played a major part in limiting the EDTA extraction of trace metals. Even higher amounts of Ca have been reported to have consumed the available binding sites of Na_2EDTA (Papassiopi *et al.*, 1997; Zeng *et al.*, 2001).

As compared to its 3.5-mmol saturated counterpart, the unsaturated extraction increased the extractions of Cr and Cu by 72 and 37% (table 5.1). These differences were significant at the 95 and 99% levels (table 5.2). The 3.5-mmol unsaturated extraction also increased the removal of Fe, Mg and S by 47, 22 and 33% (at the 99% level), and P by 101% (at the 99.9% level). As a result, the 3.5-mmol unsaturated extraction extracted significantly less Al (at the 99.9% level); together the greater 162, 149 and 47-mmol extractions of Cu, Fe and Mg largely exceeded the 111-mmol reduction in the extraction of Al. The 3.5-mmol extractions of the other contaminants (Pb, Mn, Ni, Cd & Co) showed no significant difference between the saturated and unsaturated treatments. The 3.5 mmol saturated % removal of Fe and Al were comparable (~0.3%). In contrast, the 3.5-mmol unsaturated % removal of Fe was triple that of Al. This surplus might be attributable to the fact that the Fe^{2+} were able to oxidise to Fe^{3+}, which is preferred by EDTA (pK_f 25.1), whereas Al cannot be oxidised beyond its Al^{+3} valence (pK_f 14.3).

Table 5.1 Increase of an Unsaturated to a Saturated Extraction after 40 ml of a 3.5-mmol Washing Cycle in a 1:5 *L*:*S* Ratio

Ca	Pb^{d}	Zn^{d}	Cu^{d}	Fe	Al	Mg	Mn^{c}	Ni^{b}	Cr^{b}	Cd^{d}	Co^{b}	S	P
1.3%	(-2.5%)	15.8%	36.8%**	47.3%**	(-58.9%)***	21.5%**	0.4%	14.2%	71.6%**	(-1.0%)	(-8.0%)	33.3%**	101.1%***

^{b} B-Level initial criterion, ^{c} C-Level initial criterion, ^{d} D-Level initial criterion

The 7-mmol unsaturated treatment removed significantly more P and S (at the 99.9% level) and significantly less Fe and P (at the 95% level), as compared to its saturated counterpart. The unsaturated 7-mmol washing cycle had comparable % removals for Al and Fe (~0.77%). However, upon doubling the EDTA addition from 3.5 mmol, the saturated 7-mmol washing cycle over proportionally increased the extraction of Fe by 3.6 times, while the extraction of Al proportionally increased by 1.9 times. When doubling the EDTA to 7 mmol, the increase in the extraction of S was modest for both treatments (*i.e.* ~12% on average). This hinted to a complete removal of the more

Table 5.2 t-test of the Cumulative Extractions of a Saturated to an Unsaturated-Flow Single Washing Cycle

Element	Unsaturated x Saturated (EDTA mmol Additions)	t	*P*	Unequal Variances	Departure from Normality^{K}
Al	7 x 7	2.26	0.0647		
	3.5 x **3.5**	-11.11	0.0000 ***		
	0.35 x **0.35**	-5.85	0.0011 **	(yes)^{y}	
Ca	7 x 7	-0.77	0.4711		
	3.5 x 3.5	0.39	0.7041		
	0.35 x 0.35	1.92	0.1028		Saturated
Cd	7 x 7	0.84	0.4328		
	3.5 x 3.5	-0.15	0.8885		
	0.35 x 0.35	3.03	0.0230 *		
Co	7 x **7**	-3.94	0.0076 $^{(**)}$	yes	
	3.5 x 3.5	-1.00	0.3566		
	0.35 x 0.35	-0.14	0.8927		
Cr	7 x 7	2.09	0.0819	yes	
	3.5 x 3.5	3.11	0.0209 *		
	0.35 x 0.35	-0.80	0.4522		Both
Cu	**7** x 7	3.21	0.0183 $^{(*)}$	yes	
	3.5 x 3.5	4.32	0.0050 **		
	0.35 x 0.35	3.97	0.0074 **		
Fe	7 x **7**	-3.02	0.0234 *		
	3.5 x 3.5	4.47	0.0043 **		
	0.35 x **0.35**	-4.98	0.0025 **	(yes)^{y}	
Mg	**7** x 7	34.95	0.0000 $^{(**)}$		Saturated
	3.5 x 3.5	4.81	0.0030 **		
	0.35 x 0.35	0.58	0.5807		Saturated
Mn	7 x **7**	-3.88	0.0082 *		
	3.5 x 3.5	0.40	0.7046		
	0.35 x **0.35**	-15.02	0.0000 ***		
Ni	7 x 7	1.93	0.1019	yes	
	3.5 x 3.5	2.07	0.0829		
	0.35 x 0.35	3.98	0.0073 $^{(**)}$		Unsaturated
P	**7** x 7	6.12	0.0009 ***		
	3.5 x 3.5	11.18	0.0000 ***		
	0.35 x 0.35	2.37	0.0556		
Pb	7 x 7	0.7983	0.4551		Unsaturated
	3.5 x 3.5	-0.72	0.4965		
	0.35 x 0.35	0.58	0.5817		
S	**7** x 7	8.93	0.0001 ***		
	3.5 x 3.5	5.18	0.0021 **		
	0.35 x 0.35	1.64	0.1519		Saturated
Zn	7 x 7	0.65	0.5347		
	3.5 x 3.5	1.77	0.1272		
	0.35 x 0.35	2.78	0.0322 *		

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

$^{(***)}$, $^{(**)}$ or $^{(*)}$ The significant difference is overruled by unequal population variances or non-normal population distributions

^{y} The near zero variance of the unsaturated extraction was due to near zero extractions, thus was different from the saturated variance

^{K} Kurtosis was the only factor, as no skewness was present

soluble sulphates and to the onset of having to dissolve the highly insoluble sulphide minerals, as first observed in section 4.6.

For the 0.35-mmol additions, the unsaturated procedure increased significantly the extraction of the contaminants Cd, Cu and Zn (at the 95%, 99% and 95% levels). In contrast, Mn was extracted more efficiently by the 0.35-mmol saturated extraction (significant at the 99.9% level). In addition, the saturated extractions of Al and Fe were significantly greater than those of the unsaturated ones (at the 99% level).

The complete submersion of the soil in the saturated treatment likely increased the diffusion of the washing solution into the mineral structures. This would explain the greater metal leachability in the rinses at the end of the saturated washing cycle. Nevertheless, with the exception of the 0.35-mmol extraction of Mn, the unsaturated treatment achieved equivalent or even greater extractions of potentially toxic trace metals, as compared to the saturated treatment. These results would favour the unsaturated remediation procedure, which is better positioned to provide site-scale feasibility. The oxidising state of the soil under the unsaturated extraction is hypothesised as the main reason for the greater efficiency in extracting certain trace metals, as compared to the reducing state of the saturated extraction.

The fluid dynamics of the unsaturated-flow experiment are such that the extraction conditions submitted the soil particles to a small slow-moving surface flow, which yielded a very minute *L:S* ratio interaction. The effect of renewing, by flow, this minute *L:S* ratio remains undefined, although it is assumed to have been positive. The unsaturated washing conditions might have provided high redox potential conditions that accelerated the oxidation of the ammonium, added as $(NH_4)_2EDTA$. Thus, a rapid decrease in soil pH might have favored the removal of trace metals. The unsaturated washing cycle reduced the amounts of Cd, Cu and Mn by one regulatory level. However, it did not reduce the amounts of Cd, Cu, Pb or Zn below the C-Level criterion for industries (table 5.3). The *M-soil* required further EDTA additions for it to become decontaminated; this is examined in the next section.

Table 5.3 % Removal of C and D-Level Metal Contaminants by an Unsaturated 0.7 M Washing Cycle Added in a 1:5 *L:S* Ratio

	Pb^d	Zn^d	Cu^d	Mn^c	Cd^d
Target Extraction for B-Level Criterion	94.9%	84.9%	86.7%	7.1%	81.4%
Cumulative Extraction from One Washing Cycle	38.9%	23.1%	35.0%	11.3%	10.1%
Soil Criteria After One Washing Cycle	*d*	*d*	*c*	*b*	*c*

[c] C-Level initial criterion, [d] D-Level initial criterion

5.3 Unsaturated Extractions from Three 0.7 M EDTA Washing Cycles

In order to extract more of the potentially toxic trace metals, two additional 3.5-mmol washing cycles were added to the previous 3.5 mmol treatment. This was done instead of supplementing the 7 mmol treatment with an additional washing cycle, which would have amounted to an excessive total EDTA to soil ratio (*EDTA:S*) of 17.8% wt. Three 0.7 M washing cycles permitted a total addition of a smaller *EDTA:S* of 13.4% wt. The extractions from three 0.7 M unsaturated washing cycles were compared to saturated ones (fig. 5.2).

The 2nd and 3rd washing cycles extracted less and less metals, except for Fe and Al, which increased by larger and larger amounts. As the soil was being depleted of its more dissolvable fractions of trace metals, the EDTA scavenged the more abundant Fe and Al. After two washing cycles, the previously lower unsaturated extraction of Al surpassed the saturated one and reached a 99% significant difference after three washing cycles (table 5.4). Aluminium's unsaturated % removal grew closer to that of Fe's at the end of the three washing cycles. The difference between the saturated and unsaturated extraction of Fe was no longer significant at the end of three washing cycles.

Table 5.4 t-test of the Cumulative Extractions of Three 0.7 M Saturated to Three 0.7 M Unsaturated Washing Cycles

Element	Unsaturated x Saturated # of Washing Cycles·(Molarity)	t	*P*	Unequal Variances	Departure from Normality^{K}
Al	**3·(0.7)** x 3·(0.7)	-5.63	0.0013 **		
Ca	**3·(0.7)** x 3·(0.7)	-4.34	0.0049 $^{(**)}$		Saturated
Cd	3·(0.7) x 3·(0.7)	-0.56	0.5942		
Co	3·(0.7) x **3·(0.7)**	5.06	0.0023 $^{(**)}$	yes	
Cr	**3·(0.7)** x 3·(0.7)	-13.43	0.0000 ***		
Cu	3·(0.7) x 3·(0.7)	-2.07	0.0836		
Fe	3·(0.7) x 3·(0.7)	-1.75	0.1302		
Mg	**3·(0.7)** x 3·(0.7)	-4.04	0.0068 **		
Mn	3·(0.7) x 3·(0.7)	-0.34	0.7484		
Ni	**3·(0.7)** x 3·(0.7)	-4.03	0.0069 **		
P	3·(0.7) x 3·(0.7)	0.09	0.9292		
Pb	3·(0.7) x 3·(0.7)	-0.33	0.7517		
S	3·(0.7) x 3·(0.7)	-0.75	0.4793		
Zn	**3·(0.7)** x 3·(0.7)	-2.66	0.0376 *		

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

$^{(***)}$, $^{(**)}$ or $^{(*)}$ The significant difference is overruled by unequal population variances or non-normal population distributions

^{K} Kurtosis was the only factor, as no skewness was present

FIGURE 5.2 a Cumulative Unsaturated Column Extractions from Three 0.7 M EDTA Washing Cycles with 1:5 L:S Ratio Additions to 25 g of Soil

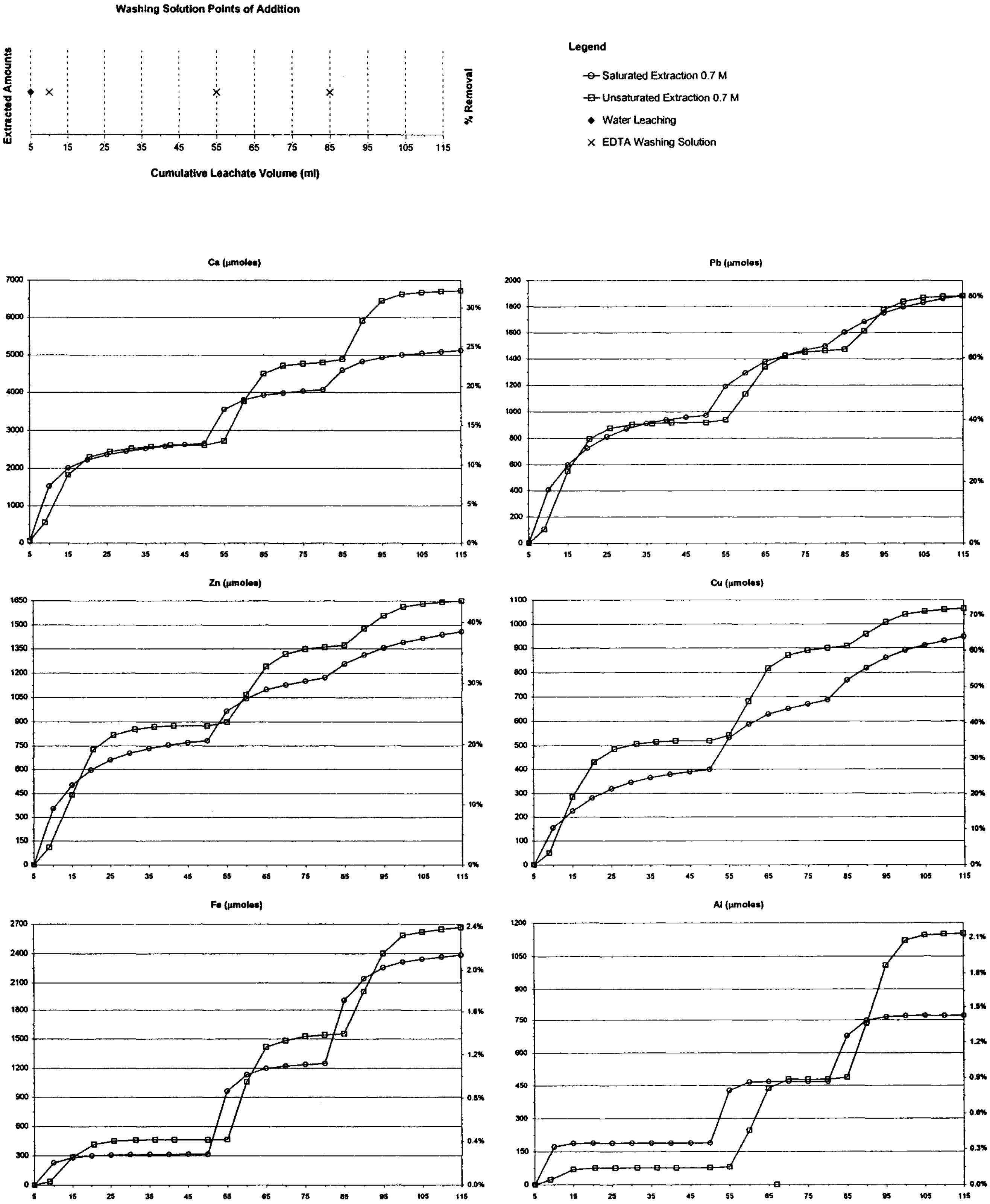
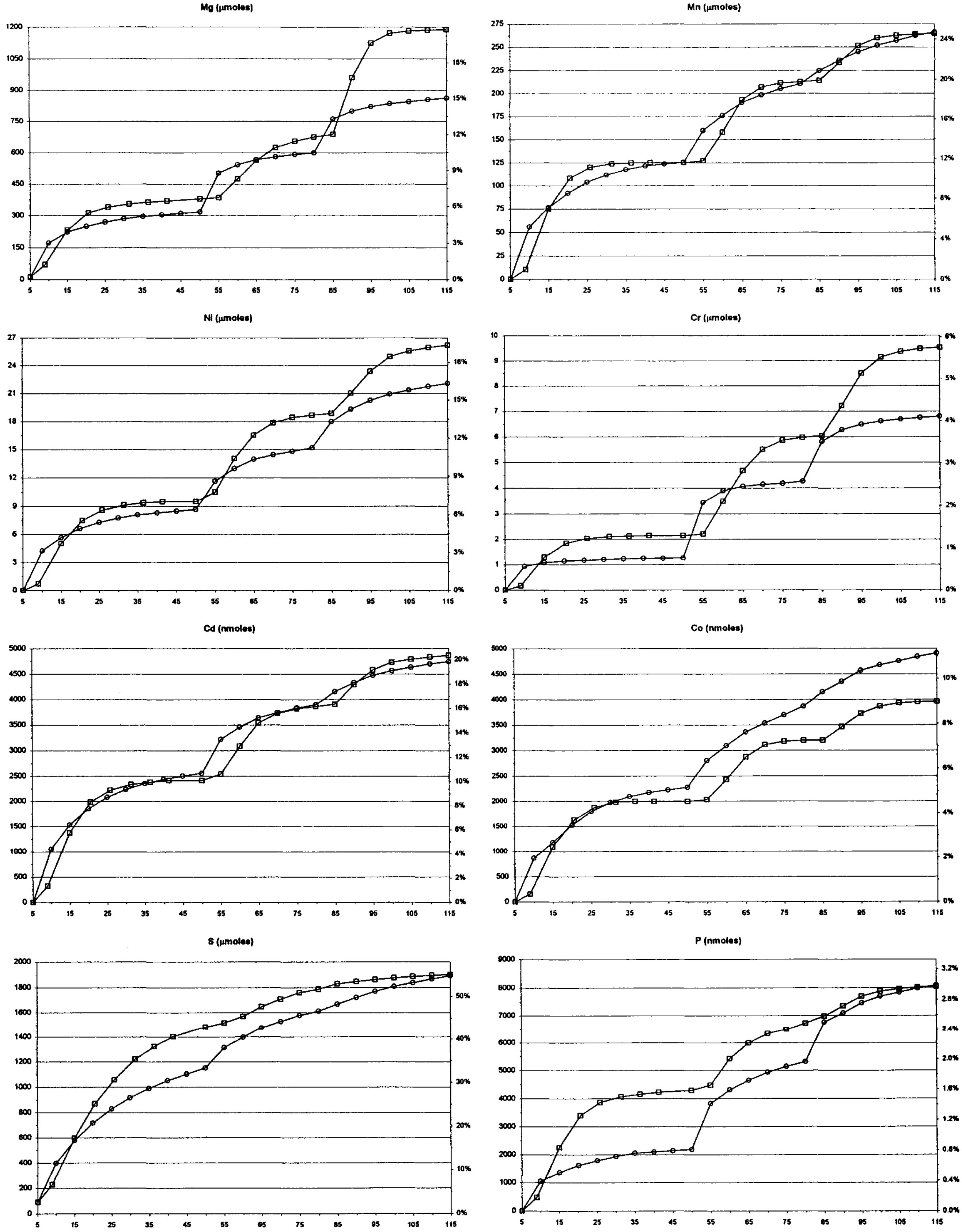


FIGURE 5.2 b Cumulative Unsaturated Column Extractions from Three 0.7 M EDTA Washing Cycles with 1:5 L:S Ratio Additions to 25 g of Soil



Chromium and Mg also did not follow the general decreasing extraction trend. The extraction of Cr increased during the 2nd washing cycle and the extraction of Mg increased during the 3rd washing cycles. The increased extractions of Mg in the 3rd cycle was similar to those of Fe and Al, thus suggesting the presence of Mg precipitates and/or co-precipitates within the contamination-formed Fe oxides. After the three washing cycles, significantly more Mg (at the 99% level) was extracted under the unsaturated treatment.

The three unsaturated washing cycles permitted Ni and Cr to build on their differences with the saturated washing cycles, reaching the 99% and 99.9% levels at the end of the three cycles. Zinc and Cu maintained their higher unsaturated extractions, as provided by the 1st cycle; after the three washing cycles, their unsaturated extractions were significantly higher, at the 95 and 90% levels. Both treatments extracted similar amounts of Pb, Mn, Cd and Co throughout the cycles. However, the saturated extraction showed a tendency to extract more Co than the unsaturated extraction, due to a more persistent post-wash leachability.

With each additional washing cycle, the difference between Ca's unsaturated and saturated extractions increased. Conversely, the difference between the unsaturated and saturated extractions diminished for S and P. Following three washing cycles, the majority of the EDTA was consumed by complexing with Ca (40.4%) and Fe (16.1%), whereas less than 30% of the added EDTA complexed with the potentially toxic trace metals (table 5.5).

Table 5.5 Extractions Relative to the Total of Extracted Metals from Three 0.7 M Unsaturated Washing Cycles (mol mol^{-1})

Ca	Fe	Pb^{d}	Zn^{d}	Cu^{d}	Al	Mg	Mn^{c}	Ni^{b}
40.4%	16.1%	11.3%	9.9%	6.4%	6.9%	7.1%	1.6%	0.2%

[b] B-Level initial criterion, [c] C-Level initial criterion, [d] D-Level initial criterion

5.4 Trace Metal Levels after Three and Five 0.7 M Unsaturated Washing Cycles

The excessive D-Level contaminants, Pb, Zn and Cu, exhibited the highest % removals amongst the trace metals (table 5.6). As compared to a single washing cycle, three unsaturated washing cycles added 3 times more EDTA, yet they only extracted twice as much Pb, Zn, Cu and Cd. This unproportional extraction response to the addition of

EDTA denoted an increased difficulty in dissolving the remaining amounts of the trace metals.

Table 5.6a % Removal of D-Level Metals by Three 0.7 M Unsaturated Washing Cycles in a 1:5 *L:S* Ratio

	Pb	Zn	Cu	Mn	Cd
Original Criterion Levels	*d*	*d*	*d*	*c*	*d*
Target Extraction for B-Level Criteria	94.9%	84.9%	86.7%	7.1%	81.4%
Cumulative Extraction from Three Washing Cycles	80.1%	43.5%	71.9%	24.6%	20.4%
Soil Criterion Levels After Three Washing Cycles	*c*	*c*	*c**	*b**	*c**

* achieved after one washing cycle

Table 5.6b % Removal of B-Level and Other Elements by Three 0.7 M Unsaturated Washing Cycles in a 1:5 *L:S* Ratio

Ca	Fe	Al	Mg	Ni^b	Cr^b	Co^b	S	P
32.2%	2.4%	2.1%	20.6%	19.4%	5.8%	9.0%	55.7%	2.9%

^{b} B-Level initial criterion

The *M-soil* was contaminated with large quantities of Fe and trace metals, which made it difficult to meet the criterion for industries. The *EDTA:S* of 13.4%wt, from the three washing cycles reduced the amounts of Pb and Zn by one regulatory level. However, their amounts, as well as those of Cu and Cd were not reduced below the C-Level criterion. Adding three 0.7 M unsaturated washing cycles produced close to 5 times more leachate than the volume of the contaminated soil.

For the purpose of assessing the resilience of the *M-soil* towards decontamination, five 0.7 M washing cycles were added, representing an *EDTA:S* of 22.3 %wt (table 5.7). Collectively, the five unsaturated 0.7 M washing cycles reduced the levels of Pb and Cu below the C-Level criterion; both levels remained slightly in excess of the B-level criterion for residences. Yet, Zn and Cd levels were still well above the C-Level criterion.

Table 5.7a % Removal of D-Level Metal Contaminants by five Unsaturated 0.7 M EDTA Washing Cycles in a 1:5 *L:S* Ratio

	Pb	Zn	Cu	Mn	Cd
Cumulative Extraction from Five Washing Cycles	96.4%	53.5%	93.5%	30.3%	25.5%
Soil Criterion Levels After Five Washing Cycles	*b*	*c***	*b*	*b**	*c**

* achieved after one washing cycle, ** achieved after three washing cycles

Table 5.7b % Removal of Non-targeted Elements by Five Unsaturated 0.7 M EDTA Washing Cycles in a 1:5 *L:S* Ratio

Ca	Fe	Al	Mg	Ni^b	Cr^b	Co^b	S	P
40.3%	4.0%	3.2%	28.8%	27.4%	8.1%	12.0%	60.9%	3.5%

^{b} B-Level initial criterion

Without substantial improvements to the extraction process, the *M-soil* would likely require environmentally unsustainable additions of EDTA in order to fall below the C-Level criterion for all trace metals. The next section examines the benefit of further concentrating the washing solution, to reduce the leachate volume.

5.5 Extractions by a 1.4 M Cyclic Washing and Two 0.7 M Cyclic Washings

The present experiment tried to verify if multiple washing cycles could benefit EDTA extractions. The extractions of a single 1.4 M washing cycle were compared to those of two 0.7 M washing cycles. The two 0.7 M EDTA washing cycles increased significantly the extraction of Zn, Cu, Mn, Cd and Co, at the 99.9, 99, 95 and 95% levels as compared to the single 1.4 M washing cycle (table 5.8). The two 0.7 M EDTA washing cycles also increased significantly the extraction of Fe, Mg and S (at the 99.9, 95 and 99.9% levels). Although the two 0.7 M washing cycles extracted more trace metals, they also produced twice the leachate volume.

Table 5.8 t-test of the Cumulative Extractions of One 1.4 M Washing Cycle to Two 0.7 M Washing Cycles

Element	EDTA x EDTA Additions·(Molarities)	t	*P*	Unequal Variances
Al	2·(0.7) x 1.4	1.92	0.1033	yes
Ca	**2·(0.7)** x 1.4	3.74	0.0096 $^{(**)}$	yes
Cd	**2·(0.7)** x 1.4	2.60	0.0408 *	
Co	**2·(0.7)** x 1.4	2.98	0.0245 *	
Cr	2·(0.7) x 1.4	1.12	0.3073	yes
Cu	**2·(0.7)** x 1.4	5.02	0.0024 **	
Fe	**2·(0.7)** x 1.4	8.02	0.0002 ***	
Mg	**2·(0.7)** x 1.4	3.57	0.0118 *	
Mn	**2·(0.7)** x 1.4	3.13	0.0203 *	
Ni	2·(0.7) x 1.4	0.74	0.4857	
P	2·(0.7) x 1.4	1.48	0.1891	
Pb	2·(0.7) x 1.4	1.40	0.2094	
S	**2·(0.7)** x 1.4	7.60	0.0003 ***	
Zn	**2·(0.7)** x 1.4	6.74	0.0005 ***	

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

$^{(***)}$, $^{(**)}$ or $^{(*)}$ The significant difference is overruled by unequal population variances or non-normal population distributions

The two 0.7 M EDTA washing cycle increased the extraction of Fe by the largest amount (68.8%), as compared to the single 1.4 M EDTA washing cycle (table 5.9). The increase in mineral dissolution of Fe (*e.g.* oxides) was 3 times more than Al (*e.g.* silicates & hydroxides) and Mn (*e.g.* oxides nodules), and 7 times more than Ca (*e.g.* carbonates). The second 0.7 M EDTA washing cycle extracted supplemental Fe, which most likely oxidised to ferric oxides as a result of the first cycle. Thus, EDTA would have selectively complexed Fe^{3+}, for which it has the strongest affinity amongst the metals (table 2.6).

Table 5.9 Increase in Unsaturated Extraction by Dividing a 1.4 M Washing Cycles into Two 0.7 M Washing Cycles

Ca	Pb[d]	Zn[d]	Cu[d]	Fe	Al	Mg	Mn[c]	Ni[b]	Cr[b]	Cd[d]	Co[b]	S	P
9.9%	8.7%	24.1%	32.2%	68.8%	22.1%	11.0%	23.2%	8.2%	17.2%	12.6%	21.7%	11.4%	10.6%

[b] B-Level initial criterion, [c] C-Level initial criterion, [d] D-Level initial criterion

Several factors contributed to the increased extractions of the two successive 0.7 M EDTA washing cycles, as compared to the single 1.4 M EDTA washing cycle. It is assumed that, following the 1st wash, the residual soil-retained EDTA had time to complex surfaces cations, oxidise mineral and organic surfaces, and weaken the soil particles' hold of surface cations. The addition of a 2nd fresh wash, at the onset of the 1st washing cycle, created a large concentration gradient between the soil solution and the soil surface for a second time. Furthermore, the impact of the second EDTA wash was compounded with the residual EDTA left in the soil following the first washing. In addition, the two successive 0.7 M EDTA washing cycles, in total, added twice the volume of washing solution and deionised water required for rinsing.

5.6 Comparison of the Obtained Results to Those of a Previous Study

This section was designed to verify that the proposed developments provided a more economical, pragmatic and environmentally sustainable solution for remediating trace metal contaminated soils. The results of this study were compared to those of a similar work, in which a dry mixture of contaminated soil and H_4EDTA were column-leached. A total of 0.72 g of H_4EDTA was mixed in with 10 g of soil. In order to compare the efficiency of both experiments in extracting their main contaminant, an added EDTA to initial soil-Pb molar ratio (*EDTA:Pb*) was used. Hence, the emphasis was to compare our 4.5 *EDTA:Pb* and cumulative 4:1 *L:S* ratio, as added in three 0.7 M unsaturated washing cycles, to those of Tejowulan (1999) (table 5.10).

Table 5.10 Comparison of the Results of the Present Study (3 x 0.7 M cycles) against those of a Previous Column Study

	EDTA:S (%wt)	*EDTA:Pb* (mol:mol)	*L:S*	Cycles[c]	Cd Removal (μg g^{-1})[i]		Cu Removal (μg g^{-1})		Pb Removal (μg g^{-1})		Zn Removal (μg g^{-1})	
Andrade (2004)	13%	4.5	4:1	1 + 5	20%	107	72%	3768	80%	19466	44%	9917
Tejowulan (1999)	7.2%	23	20:1	0[d] + 5	66%	5.5	64%	800	84%	2200	53%	400
Superior amount of *M-soil* contaminants (times)						19		5		9		25
Excess of the % removal of the present to past study (times or %)					-3.2*t*		12%		-5%		-1.2*t*	

[c] Number of washes and rinses

[i] Initial soil content

[d] Dry soil and H_4EDTA mixture

Even though a 5 times greater *EDTA:Pb* was used and that 5 times more leachate was produced, the % removal of Pb was only slightly higher, as compared to this study. Moreover, the initial *M-soil* content (*iMc*) in Pb was 9 times greater than the Pb content of the other soil. Even with a 5 times greater *iMc* in Cu, this study had a greater % removal. The *iMc* in Cd and Zn were 19 and 25 times greater, but our study resulted in % removals that were merely 3.3 and 1.2 times less.

These results indicate that an EDTA washing solution with a high molarity added in a low *L:S* ratio is more conducive for the extraction of trace metals, as compared to leaching a dry soil-EDTA mixture. This compliments the findings of section 4.7, in which EDTA washing solutions with high molarities added in low *L:S* ratios were found to be more efficient in extracting potentially toxic trace metals under saturated conditions.

5.7 Summary and Conclusions

Regardless of the saturated or unsaturated treatment, each successive washing cycle extracted less of each element, with Fe and Al as exceptions. As the soil was being depleted of its easily dissolvable fractions of potentially toxic trace metals, the EDTA scavenged the more abundant Fe and Al. Calcium used up the most EDTA, as it represented more than 40% of the total amount of extracted metals.

The oxidising conditions of the unsaturated experiment are likely responsible for the significant increases in the extractions of Cd, Cr, Cu, Ni and Zn, as compared to the reducing conditions of the saturated experiment. These findings encourage the development of an unsaturated remediation process, knowing that it would be, as a minimum, as effective in extracting potentially toxic trace metals. A site-scale unsaturated-flow heap-leaching remediation process for trace metal contaminated soils would be more affordable than its saturated batch-mixing counterpart.

For the soil columns, applying two 0.7 M washing cycles to soil columns, instead of a single washing cycle of 1.4 M, extracted more Zn, Cu, Mn, Cd and Co. As compared to the 1.4 m single-cycle extraction, the 0.7 m two-cycle extraction benefited from two equilibrations, compounded strength of fresh and residual EDTA, and doubled cumulative liquid volume additions. Even though multiple EDTA inputs into multiple washings might extract more of the targeted metals, the washing solution should still have the highest possible molarity in order to create a strong concentration gradient between the particle surfaces and the soil solution. By doing so, this would increase the EDTA extraction efficiency and limit the production of leachate.

Applying a total *EDTA:S* of 13.4% wt, as per three 0.7 M washing cycles, did not decontaminate the *M-soil*. At the end of the third 0.7 M washing cycle, the post-treatment leaching of toxic levels of trace metals exceeded the original soil's levels. Moreover, post-treatment leaching of toxic levels of trace metals exceeded the discharge standards that regulate the electroplating industry. In the following chapter, the post-treatment leachability of metals is further examined.

Increasing the *EDTA:S* to 22.3%, by submitting the soil to five 0.7 M washing cycles, was not considered to be viable economically or environmentally. The next step focused on improving the unsaturated extraction process and reducing the cumulative leachate volume. A flash washing procedure was used as an alternative to the multiple washing cycle procedure, it is studied in the next chapter. Although recycling and reusing the leachate for its EDTA contents might reduce the EDTA inputs, this approach was not considered herein; chronologically, we had to first examine and conclude on the feasibility of remediating the *M-soil* by using fresh washing solutions.

Preface to Chapter 6

In order to reduce the volume of leachate and increase the extraction efficiency, a flash washing procedure was investigated. The unsaturated-flow flash washing procedure sequentially added three washes, which were followed by sequential additions of water rinses. The efficiency of the flash washing to extract potentially toxic trace metals was compared to that of cyclic washing (*i.e.* multiple washing cycles). In parallel to the $(NH_4)_2$EDTA extractions, citric acid was tested for its ability to extract trace metals. The main reason for testing citric acid was to measure its post-wash leachability of potentially toxic trace metals.

6

Extraction of Potentially Toxic Trace Metals from Soils under Unsaturated-Flow Flash Washings of $(NH_4)_2$EDTA and Citric Acid

The previous unsaturated remediation procedure, although more efficient than its saturated counterpart, still required an improvement of the extraction efficiency of the D-Level contaminants. In addition, the modification(s) needed to produce a smaller amount of cumulative leachate. Finally, the treated soil must be left with a reduced leachability of its residual trace metals, as compared to the original untreated soil. An unsaturated-flow flash washing procedure was examined to address all three of the aforementioned challenges.

The flash washing consisted of three consecutive washing solution additions, which were followed by rinses. This was done as an alternative to the washing cycles, which followed each washing solution addition by the additions of several rinses (*i.e.* cyclic washing). The flash washing, with its back-to-back additions of the washing solution, intended to increase incrementally the concentration of EDTA in the soil solution over the three successive wash additions. This would improve the trace metal extraction efficiency and reduce the cumulative leachate volume by reducing more rapidly the post-treatment leaching of toxic levels of trace metals.

Citric acid is regarded as the strongest complexing natural organic acid (Wasay *et al.*, 2001). It was tested for its extraction abilities and for its affect on the post-treatment leaching of toxic levels of trace metals. Even though citric acid is not as strong a chelating agent as the synthetic EDTA, it is readily biodegradable, which could favour the reduction of the post-treatment leaching of toxic levels of trace metals. The efficiency of citric acid was compared to that of EDTA on an equimolar basis. In bulk, citric acid is 50% cheaper than $(NH_4)_2$EDTA, costing around $\$2\,kg^{-1}$ (UNIVAR, Montréal).

6.1 General Methodology

A flash washing consisted of three consecutive washing solution additions, followed by deionised water (DW) rinses. A washing cycle consisted of a one-step EDTA wash and subsequent DW rinses. Three washing cycles are equivalent to a cyclic washing.

Unsaturated extractions of the *M-soil* were conducted in 25g columns. The experimental design, the general unsaturated extraction procedure and the analytical methods were as described in section 5.1. However, the chelating agents were applied in a different molarity (0.5 M) and as a flash washing. The VERSENE EDTA was obtained from the DOW Chemical Company (Midland) and the citric acid anhydrous USP was purchased from Fisher Scientific (Whitby). A flash washing added 5 ml day^{-1} of washing solution on three consecutive days, followed by sequential 5 ml day^{-1} rinses with deionised water. For the statistical analysis, the STATGRAPHICS®*PLUS 4.0* software was used to compute the t-tests between the end-extraction results of the populations of two treatments. STATGRAPHICS®*PLUS 4.0* was also used to assess the equality of the variances between the two treatment populations, as well as the normality of each population's distribution.

6.2 Extractions from Unsaturated Flash Washings with 0.5 M Washes

The extraction results from the flash washing procedure were compared to those of three cyclic washings (fig. 6.1). In the EDTA flash washing, the peak extraction coincided with the 3rd and last washing solution addition, at which point the soil solution had the highest EDTA concentration. The soil solution of the initially moist soil had been gradually concentrated with EDTA following the successive additions of the three washes. Following this, the addition of the first rinse diluted the concentration of EDTA in the soil and in the leachate, which led to a reduction in extracted amounts. For the citric acid flash washing, the peak extractions of the trace metals were delayed until the 1st rinse that followed the three consecutive washes. This difference likely arose since citric acid is less soluble and more labile than EDTA (*i.e.* less mobile).

During the citric acid cyclic washing, the peak extractions of trace metals occurred during the 1st rinse of each cycle. For the EDTA cyclic washing, the peak extractions of

FIGURE 6.1 a Cumulative Unsaturated Column Extractions from a 0.5 M EDTA Flash Washing with 1:5 L:S Ratio Additions to 25 g of Soil

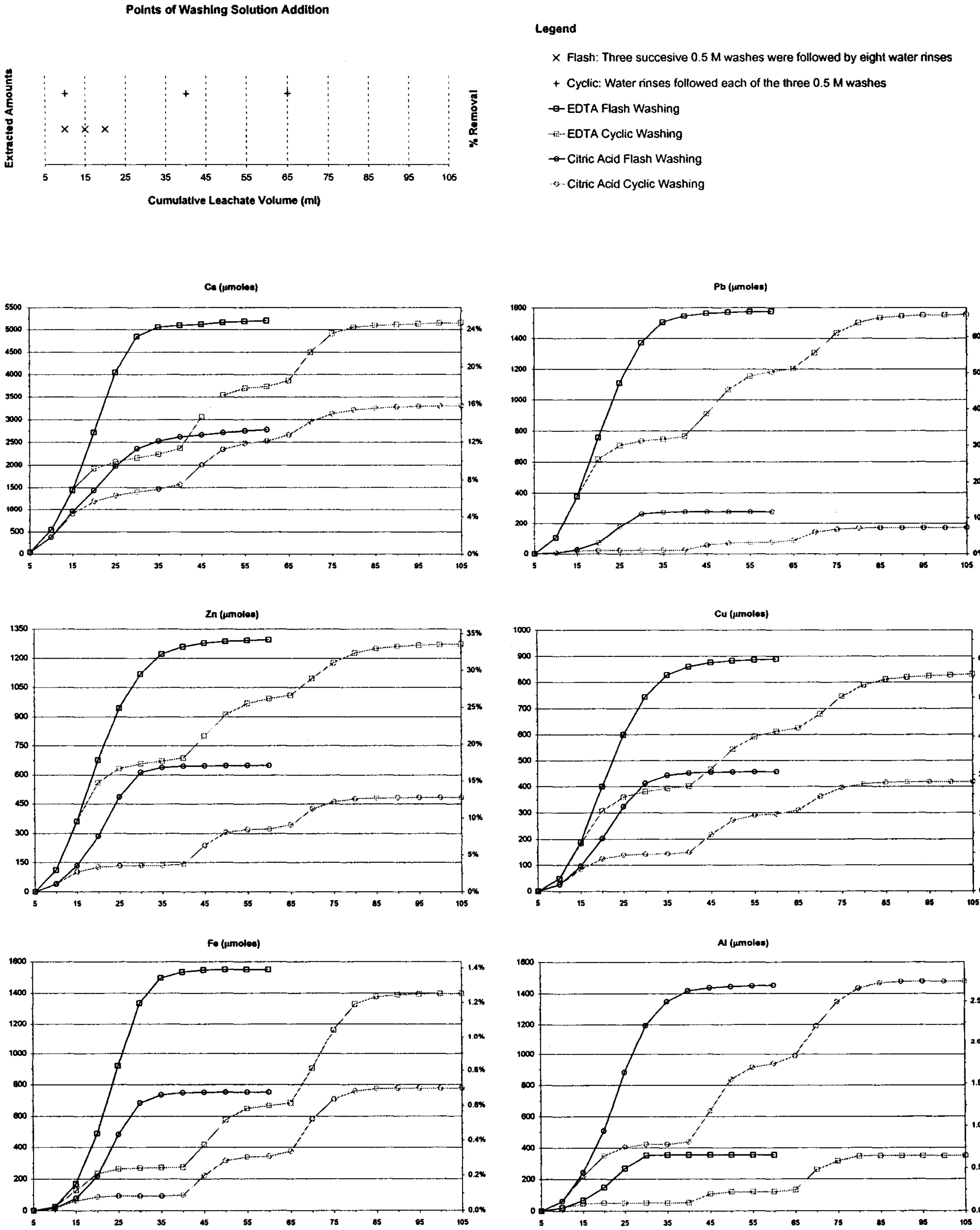
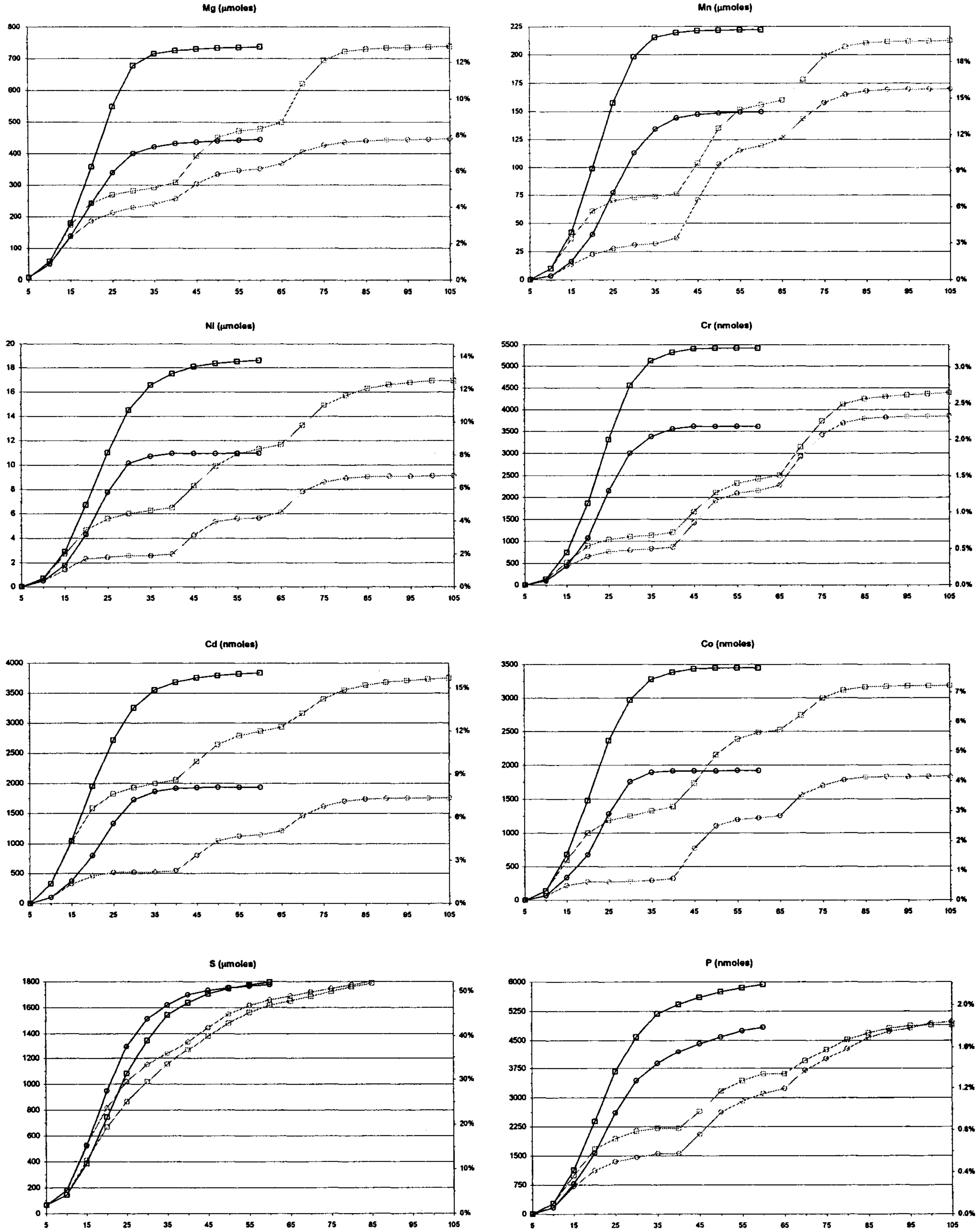


FIGURE 6.1 b Cumulative Unsaturated Column Extractions from a 0.5 M EDTA Flash Washing with 1:5 L:S Ratio Additions to 25 g of Soil



trace metals also occurred during the 1st rinse following each wash, with the exception of Cu, Fe and Pb. Their peak extractions were delayed until the 2nd rinse of the 2nd and 3rd washing cycles. After the 2nd washing solution addition, an increasingly smaller diversity of elements coated the mineral particles. Of the soil-abundant metals, Cu, Fe and Pb form the three most stable EDTA chelates. Hence, the soil-retained EDTA was likely selectively bound with Fe, Cu and Pb. In the 2nd washing cycle, the 2nd rinse extracted 19, 9 and 10% more Cu, Fe and Pb than the 1st rinse. This phenomenon accentuated for the 3rd washing cycle: its 2nd rinse extractions were 30, 27 and 15% greater than those of its 1st rinse.

The overall trace metal extraction potential of the chelating agents were utilised more efficiently in the flash washing than in the cyclic washing, with the exception of the citric acid extractions of Mn and Cr (table 6.1); however, the flash extractions of Mn and Cr were not significantly different from their cyclic extractions (table 6.2). As compared to the cyclic washing, the flash washing increased citric acid's extractions of Pb, Zn and Ni by 61, 34 and 20%. These differences were significant at the 99, 99.9, and 95% levels. As for EDTA, Cr was the lone element to have benefited significantly from the flash washing (at the 95% level). The EDTA flash washing extracted 23.3% more Cr than the cyclic washing.

Table 6.1a Relative Increase in Trace Metal Extractions by a Flash Washing over a Cyclic Washing as 3×0.5 M in 1:5 *L:S* Ratios

	Pb[d]	Zn[d]	Cu[d]	Mn[c]	Ni[b]	Cr[b]	Cd[d]	Co[b]
EDTA	1.2%	1.7%	6.9%	4.4%	9.8%	23.3%	2.3%	8.2%
Citric Acid	60.8%	34.0%	8.9%	(-11.8%)	20.3%	(-6.1%)	10.3%	4.7%

[b] B-Level initial criterion, [c] C-Level initial criterion, [d] D-Level initial criterion

Table 6.1b Relative Increase in Element Extractions by a Flash Washing over a Cyclic Washing as 3×0.5 M in 1:5 *L:S* Ratios

	Ca	Fe	Al	Mg	S	P
EDTA	0.9%	11.0%	1.6%	(-0.2%)	(-3.0%)	21.2%
Citric Acid	(-16.0%)	(-3.6%)	(-2.0%)	(-0.3%)	(-3.2%)	(-3.0%)

Following a single wash with several rinses immediately diluted the chelating agent's ionic strength in the soil solution. Conversely, building on the residual chelating agent, already left in the soil, the 2nd and 3rd flash washes consecutively increased the chelating agent concentration in the soil solution, thus increasing the extraction potential. The flash washing also permitted to reduce the cumulative leachate volume.

Table 6.2 t-test of the Cumulative Extractions of a 0.5M Flash to a 0.5M Cyclic Washing for Citric Acid and EDTA Washes

Element	Chelating Agent (Treatment)	t	*P*	Unequal Variances*	Departure from Normality^{K}
Al	Citric Acid: (Cyclic) x (Flash)	0.32	0.7593		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-0.13	0.8995		
	(Flash): $(NH_4)_2$EDTA x **Citric Acid:**	26.02	0.0000 ***		
Ca	Citric Acid: (Cyclic) x (Flash)	3.70	0.0101 *		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-0.13	0.8983		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-8.34	0.0002 $^{(***)}$	yes	
Cd	Citric Acid: (Cyclic) x (Flash)	-1.88	0.1088		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-0.39	0.7110		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-8.58	0.0001 ***		
Co	Citric Acid: (Cyclic) x (Flash)	-0.58	0.5797		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-1.15	0.2916		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-7.25	0.0004 ***		
Cr	Citric Acid: (Cyclic) x (Flash)	1.62	0.1552		
	$(NH_4)_2$EDTA: (Cyclic) x **(Flash)**	-5.86	0.0011 **		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-11.42	0.0000 ***		
Cu	Citric Acid: (Cyclic) x (Flash)	-1.40	0.2109		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-0.99	0.3584		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-7.67	0.0002 ***		
Fe	Citric Acid: (Cyclic) x (Flash)	0.32	0.7563		Flash
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-1.65	0.1494		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-8.02	0.0002 $^{(***)}$		Citric Acid
Mg	Citric Acid: (Cyclic) x (Flash)	0.01	0.9942		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	0.04	0.9682		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-7.52	0.0003 ***		
Mn	Citric Acid: (Cyclic) x (Flash)	1.64	0.1523		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-0.66	0.5354		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-5.12	0.0022 **		
Ni	Citric Acid: (Cyclic) x **(Flash)**	-2.97	0.0249 *		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	1.53	0.1770		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-7.50	0.0003 ***		
P	Citric Acid: (Cyclic) x (Flash)	0.22	0.8369		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-2.38	0.0547		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-3.29	0.0166 *		
Pb	Citric Acid: (Cyclic) x **(Flash)**	-4.77	0.0031 **		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-0.27	0.7960		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-38.62	0.0000 ***		
S	Citric Acid: (Cyclic) x (Flash)	0.94	0.3827		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	0.84	0.4348		
	(Flash): $(NH_4)_2$EDTA x Citric Acid:	-0.27	0.7946		
Zn	Citric Acid: (Cyclic) x **(Flash)**	-6.49	0.0006 ***		
	$(NH_4)_2$EDTA: (Cyclic) x (Flash)	-0.31	0.7684		
	(Flash): **$(NH_4)_2$EDTA** x Citric Acid:	-9.61	0.0001 ***		

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

$^{(***)}$, $^{(**)}$ or $^{(*)}$ The significant difference is overruled by unequal population variances or non-normal population distributions

^{K} Kurtosis was the only factor, as no skewness was present

The trace metal extractions from an EDTA flash washing were much higher than those of citric acid. These differences were all significant at the 99.9% level, except for Mn (at 99% level). The EDTA flash washing increased the trace metal extraction efficiency from 148% for Mn up to 570% for Pb, relative to the citric acid flash washing (table 6.3). The extractions of Mg and P were also increased significantly under the EDTA flash washing, at the 99.9 and 95% levels.

Table 6.3a % Removal of Contaminants from 25g Columns with an Unsaturated 0.5 M Flash Washing in a 1:5 *L:S* Ratio

	Pb[d]	Zn[d]	Cu[d]	Mn[c]	Ni[b]	Cr[b]	Cd[d]	Co[b]
EDTA	67.1%	34.2%	59.9%	20.6%	13.8%	3.3%	16.1%	7.8%
Citric Acid	11.8%	17.1%	30.9%	13.9%	8.1%	2.2%	8.1%	4.4%
Δ in extractions (times)	5.7	2.0	1.9	1.5	1.7	1.5	2.0	1.8

[b] B-Level initial criterion, [c] C-Level initial criterion, [d] D-Level initial criterion

Table 6.3b % Removal of Other Elements from 25g Columns with an Unsaturated 0.5 M Flash Washing in a 1:5 *L:S* Ratio

	Ca	Fe	Al	Mg	P	S
EDTA	36.1%	1.4%	0.7%	12.9%	2.2%	52.0%
Citric Acid	19.3%	0.7%	2.7%	7.8%	1.8%	51.4%
Δ in extractions (times)	1.9	2.1	(-4.1)	1.7	1.2	1.0

With 3 carboxylic groups, the tridentate citric acid demonstrated its highest affinity for Al^{3+} amongst the metals, and significantly extracted more Al than EDTA, at the 99.9% level. Similarly, maleic acid is selective towards Al^{3+}, even though it is a bidentate ligand with two carboxylic groups. In soils, maleic acid is exuded by roots for complexation with Al^{3+}, in order to reduce Al-rhizotoxicity (Jones, 1996).

Citric acid (192 g mol^{-1}) was added at a lesser amount of 5.8% wt soil^{-1}, as compared to the *EDTA:S* of 9.8% wt. Nevertheless, citric acid is not likely strong enough to reclaim soils severely contaminated with Pb as it removed close to 6 times less Pb than EDTA. In this study, a flash washing comprising of six citric acid washes would have been required, as a minimum, to achieve trace metals extraction levels similar to those of EDTA. This would have entailed a citric acid to soil ratio of >11.5% by weight. This estimate does not account for subsequent reductions in extraction efficiency that would occur with each successive wash; therefore, in practice, a much larger input is expected. Still, a larger input of biodegradable citric acid might be more environmentally sustainable than a lesser amount of EDTA, since citric acid is biodegradable and its post-treatment leaching of toxic levels of trace metals levelled off more quickly than for EDTA (fig. 6.1).

6.3 Unsaturated Extractions from Multiple 0.5 M and 0.7 M Cyclic Washings

The 0.7 M EDTA wash is an abbreviation of the 0.685 M wash that was used.

This section examines the benefit of using a more concentrated washing solution over several washing cycles. In figure 6.2, cumulative extractions from six 0.5 M washing cycles (*i.e.* 19.6% wt *EDTA:S*) were compared to those of four 0.7 M washing cycles (*i.e.* 17.9% wt *EDTA:S*). A t-test was done between the extracted amounts from six 0.5 M and four 0.7 M washing cycles. Although the six 0.5 M washing cycles used 9.5% more EDTA, the four 0.7 M washing cycles extracted significantly more Cr (at the 99.9% level) and as much of the other trace metals (table 6.4).

Table 6.4 t-test of the of Cumulative EDTA Extractions of Six 0.5 M to Four 0.7 M Washing Cycles

Additions (EDTA Molarity) x Additions (EDTA Molarity)
6·(0.5 M) x 4·(0.7 M)

	Al	Ca	Cd	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Pb	S	Zn
t	0.11	-1.08	0.30	0.67	7.23	-0.10	1.25	-0.24	0.85	1.05	2.13	-0.49	-1.64	0.85
P	0.92	0.32	0.77	0.53	0.00***	0.93	0.26	0.82	0.43	0.33	0.08	0.64	0.15	0.42

*** The 4·(0.7 M) extracted more Cr than the 6·(0.5 M), at the 99.9% Significance Level

In section 4.6, the single washing cycle that added equal amounts of EDTA in a more concentrated wash was more efficient in extracting trace metals than the washing cycle that added a more dilute wash. In this experiment, greater amounts of EDTA were added by the six 0.5 M washing cycles. Still, the four 0.7 M washing cycles had a greater extraction efficiency, as it produced a soil solution with a higher EDTA concentration. Furthermore, the shorter and more concentrated 0.7 M treatment produced a smaller cumulative leachate volume.

FIGURE 6.2 a Cumulative Unsaturated Column Extraction from Six 0.5 M and Four 0.7 M EDTA Washing Cycles with 1:5 L:S Ratio Additions to 25 g of Soil

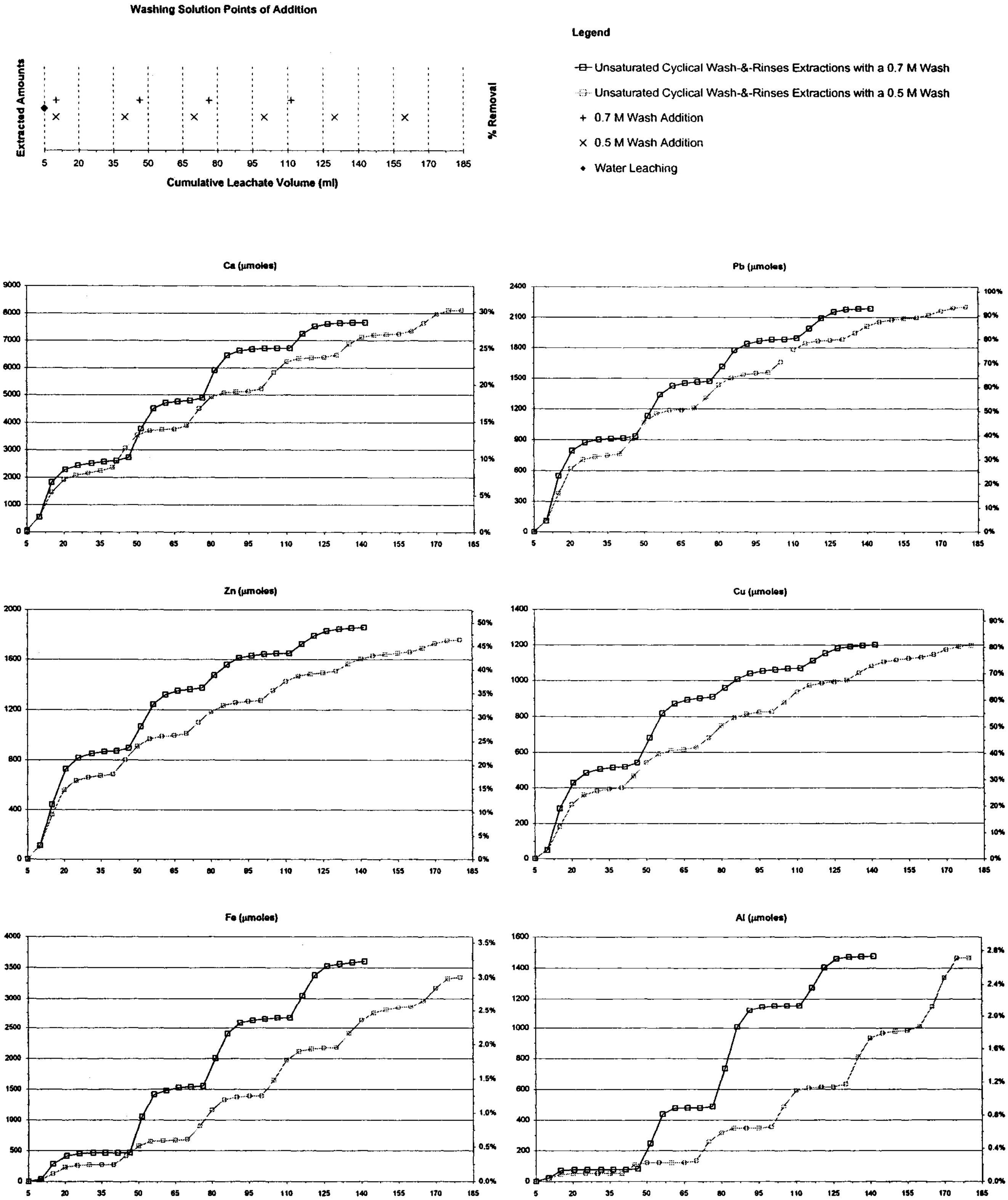
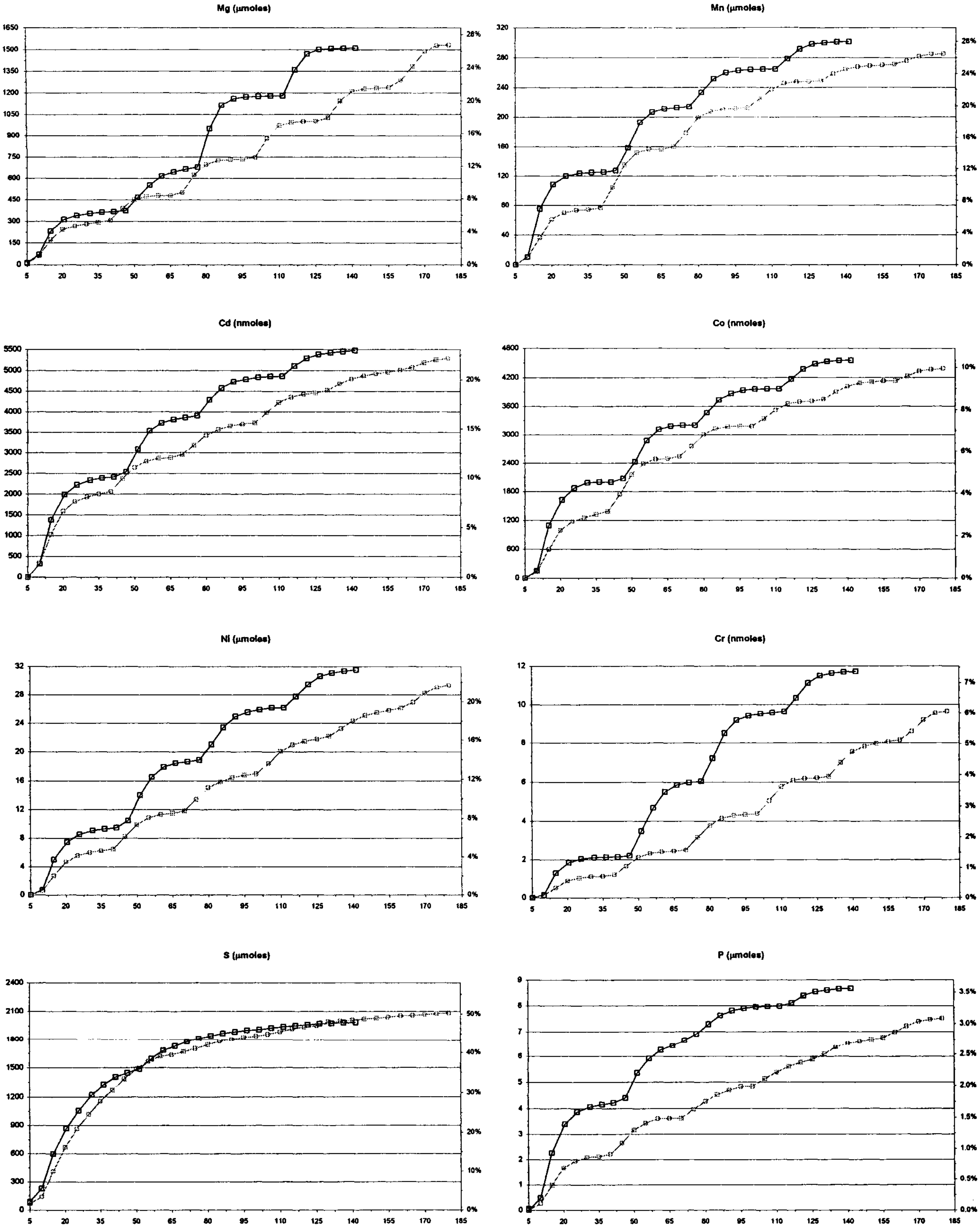


FIGURE 6.2 b Cumulative Unsaturated Column Extraction from Six 0.5 M and Four 0.7 M EDTA Washing Cycles with 1:5 L:S Ratio Additions to 25 g of Soil



6.4 Consumption of the Chelating Agents in the Cyclic and Flash Washings

Citric acid is a tridentate molecule which can complex more than one cation at a time. For instance, citric acid could complex 3 monovalent cations or 3 divalent cations between two molecules. In contrast, the hexadentate $EDTA^{-4}$ forms a stoichiometric 1:1 complex with a metal regardless of it valence (*i.e.* in a 1:1 mole ratio). Unlike $EDTA^{-4}$ which complexes metal cations *pro rata*, citric acid had the possibility to complex metal cations in excess of its number of molecules. In this section, the extents of the EDTA and citric acid extractions of cations were assessed by measuring the cumulative mole ratios for each treatment (*i.e.* moles of added chelator to the sum of the moles of the multivalent cations that were extracted).

With its 4 carboxylic groups and 2 amine groups, EDTA readily exchanges its complexed monovalent cations, like Na^+, K^+ and NH_4^+, for preferred multivalent metal cations (M^{n+}) (Harris, 1999). Accordingly, although initial deionised water leachabilities of Na and K were high, their extractions remained low. The peak Na extraction occurred during the EDTA flash washing and was less than 2½ times its initial leachability of 22.4 μmol. Similarly, the initial leachable amount for K was 5.9 μmol and its peak extraction was 26.7 μmol. The extracted amounts of Na and K were slightly less for the EDTA cyclic washing. Citric acid's extraction results for Na and K were similar to those of EDTA. Hence, both chelating agents were disinclined to complex monovalent cations in large amounts. Moreover, a portion of the extracted monovalent cations was not complexed, but rather displaced from their cation exchange sites by NH_4^+. Thus, Na and K would have leached uncomplexed from the soil, as were S and P. However, the extracted amounts of S and P were likely a consequence of the complexation of their sorbed/co-precipitated metals by the chelating agents.

Table 6.5 presents the ranking of the extracted M^{n+} under both washing conditions. The term macroelement was used to describe the analysed elements that were abundant in the soil (*i.e.* in the order of $mg\,g^{-1}$). Sulphur, a chacogen, was also included in the table, since each mole of leached S could likely account for the dissolution and extraction of a chalcophilic cation in similar proportions. To the contrary, the monovalent Na and K are not included in the table; both were likely not complexed by the chelating agents. Based on the results (not shown), the extracted amounts of Na and K could be roughly ranked within the table by dividing the Mg amounts by 4 and 9.

Table 6.5 a Extracted Macroelements for Each Sequence of 0.5 M Cyclic and Flash Washings with 1:5 L:S Ratio Additions to 25 g of Soil (μmol)

Ranking of Extracted Elements Appended with Initial Soil Ranking

* Addition of 0.5M washing solution equivalent to 2.5 mmol

Leachate (ml)												
5	$H_2$0			S-7 90.2	Ca-2 55.7	Mg-6 12.6	Zn-5 0.14	Cu-8 0.018	Al-3 0.012	Mn-9 0.004	**Pb-4** 0.003	Fe-1 0.002
10	Citrate		*	Ca-2 382	S-7 181	Al-3 61.2	Mg-6 50.6	Zn-5 39.5	Cu-8 25.9	Fe-1 15.1	**Pb-4** 6.9	Mn-9 3.5
	EDTA		*	Ca-2 546	S-7 145	Zn-5 112	**Pb-4** 107	Mg-6 56.6	Cu-8 48.7	Fe-1 24.9	Al-3 21.0	Mn-9 10.1
15	Citrate	Cyclic		Ca-2 461	S-7 267	Al-3 159	Zn-5 60.6	Mg-6 73.1	Cu-8 57.3	Fe-1 47.5	**Pb-4** 12.6	Mn-9 10.0
		Flash	*	Ca-2 564	S-7 305	Al-3 181	Zn-5 96.8	Mg-6 84.6	Cu-8 71.4	Fe-1 64.8	**Pb-4** 23.4	Mn-9 12.6
	EDTA	Cyclic		Ca-2 852	**Pb-4** 270	Zn-5 251	S-7 245	Cu-8 135	Fe-1 111	Mg-6 105	Al-3 32.1	Mn-9 27.5
		Flash	*	Ca-2 852	**Pb-4** 269	Zn-5 250	S-7 242	Cu-8 140	Fe-1 139	Mg-6 112	Al-3 42.5	Mn-9 30.5
20	Citrate	Cyclic		Ca-2 290	S-7 267	Al-3 130	Mg-6 52.0	Cu-8 40.7	Fe-1 24.4	Zn-5 24.4	Mn-9 8.8	**Pb-4** 4.0
		Flash	*	Ca-2 473	S-7 424	Al-3 267	Zn-5 152	Fe-1 137	Cu-8 106	Mg-6 102	**Pb-4** 43.8	Mn-9 24.0
	EDTA	Cyclic		Ca-2 471	S-7 257	**Pb-4** 243	Zn-5 198	Cu-8 125	Fe-1 103	Mg-6 69.8	Mn-9 25.0	Al-3 4.3
		Flash	*	Ca-2 1286	**Pb-4** 381	S-7 357	Fe-1 320	Zn-5 315	Cu-8 211	Mg-6 180	Al-3 81.1	Mn-9 57.0
25	Citrate	Cyclic		S-7 199	Ca-2 133	Al-3 56.2	Mg-6 25.9	Cu-8 14.5	Fe-1 6.4	Zn-5 5.9	Mn-9 5.6	**Pb-4** 1.3
		Flash		Ca-2 540	Al-3 372	S-7 352	Fe-1 266	Zn-5 200	Cu-8 122	**Pb-4** 106	Mg-6 98.2	Mn-9 37.6
	EDTA	Cyclic		S-7 197	Ca-2 151	**Pb-4** 88.9	Zn-5 73.4	Cu-8 53.5	Fe-1 31.0	Mg-6 25.2	Mn-9 9.1	Al-3 -
		Flash		Ca-2 1325	Fe-1 431	**Pb-4** 352	S-7 337	Zn-5 268	Cu-8 198	Mg-6 191	Al-3 118	Mn-9 58.5
30	Citrate	Cyclic		S-7 134	Ca-2 81.0	Al-3 17.1	Mg-6 15.5	Cu-8 3.8	Mn-9 2.8	Zn-5 1.7	Fe-1 0.61	**Pb-4** 0.24
		Flash		Ca-2 386	Al-3 312	S-7 217	Fe-1 203	Zn-5 128	Cu-8 89.7	**Pb-4** 82.3	Mg-6 61.3	Mn-9 35.5
	EDTA	Cyclic		S-7 152	Ca-2 89.7	**Pb-4** 28.3	Zn-5 25.9	Cu-8 20.9	Mg-6 13.3	Fe-1 6.9	Mn-9 2.7	Al-3 -
		Flash		Ca-2 801	Fe-1 414	S-7 266	**Pb-4** 260	Zn-5 175	Cu-8 145	Mg-6 129	Al-3 82.2	Mn-9 40.7
35	Citrate	Cyclic		S-7 87.2	Ca-2 56.6	Mg-6 11.9	Al-3 1.3	Mn-9 1.1	Cu-8 0.82	Zn-5 0.26	**Pb-4** 0.016	Fe-1 -
		Flash		Ca-2 166	Al-3 154	S-7 105	Fe-1 50.6	Cu-8 29.7	Zn-5 24.2	Mg-6 21.3	Mn-9 21.2	**Pb-4** 10.9
	EDTA	Cyclic		S-7 137	Ca-2 74.0	Zn-5 12.6	Cu-8 10.7	**Pb-4** 10.6	Mg-6 10.5	Mn-9 0.88	Fe-1 0.60	Al-3 -
		Flash		Ca-2 204	S-7 198	Fe-1 164	**Pb-4** 135	Zn-5 102	Cu-8 85.1	Mg-6 37.5	Mn-9 17.2	Al-3 4.0
40	Citrate	Cyclic	*	Ca-2 104	S-7 97.3	Mg-6 16.9	Al-3 14.8	Zn-5 8.3	Cu-8 7.0	Mn-9 5.2	Fe-1 4.7	**Pb-4** 1.2
		Flash		Ca-2 95.2	S-7 77.3	Al-3 68.3	Fe-1 13.1	Mg-6 10.6	Mn-9 9.9	Cu-8 8.8	Zn-5 6.6	**Pb-4** 3.1
	EDTA	Cyclic	*	Ca-2 133	S-7 117	**Pb-4** 18.8	Mg-6 15.7	Zn-5 14.4	Cu-8 8.9	Fe-1 2.7	Mn-9 2.3	Al-3 0.57
		Flash		S-7 93.6	Ca-2 44.2	**Pb-4** 40.6	Zn-5 38.0	Fe-1 37.9	Cu-8 32.3	Mg-6 9.6	Mn-9 4.0	Al-3 -
45	Citrate	Cyclic		Ca-2 437	Al-3 197	Fe-1 122	S-7 111	Zn-5 98.2	Cu-8 65.7	Mg-6 46.2	Mn-9 33.9	**Pb-4** 30.4
		Flash		Ca-2 43.5	S-7 33.7	Al-3 19.1	Mg-6 4.4	Mn-9 2.9	Cu-8 2.5	Fe-1 2.4	Zn-5 1.8	**Pb-4** 0.78
	EDTA	Cyclic		Ca-2 691	Fe-1 145	**Pb-4** 144	Zn-5 116	S-7 109	Mg-6 84.8	Cu-8 65.2	Al-3 55.7	Mn-9 27.6
		Flash		S-7 69.4	Ca-2 25.8	Zn-5 18.6	**Pb-4** 18.1	Cu-8 15.0	Fe-1 11.6	Mg-6 4.9	Mn-9 1.7	Al-3 -

Sequence Number				Sum of Metals	Cumulative Sum	**Excess Chelator to Extracted Metals** Σ(mmol)	Σ(%)
	$H_2$0			68.5			
1	Citrate		*	585	585	1915	327%
	EDTA		*	928	928	1572	169%
2	Citrate	Cyclic		881	1466	1034	70%
		Flash	*	1099	1684	3316	197%
	EDTA	Cyclic		1783	2711	-211	(-8%)
		Flash	*	1835	2763	2237	81%
3	Citrate	Cyclic		574	2040	460	23%
		Flash	*	1305	2989	4511	151%
	EDTA	Cyclic		1239	3950	-1450	(-58%)
		Flash	*	2831	5594	1906	34%
4	Citrate	Cyclic		249	2289	211	9%
		Flash		1743	4732	2768	59%
	EDTA	Cyclic		432	4382	-1882	(-75%)
		Flash		2943	8537	-1037	(-14%)
5	Citrate	Cyclic		123	2412	88	4%
		Flash		1298	6030	1470	24%
	EDTA	Cyclic		188	4570	-2070	(-83%)
		Flash		2046	10582	-3082	(-41%)
6	Citrate	Cyclic		72	2484	18	1%
		Flash		583	6613	887	13%
	EDTA	Cyclic		120	4690	-2190	(-88%)
		Flash		947	11529	-4029	(-54%)
7	Citrate	Cyclic	*	162	2646	2354	89%
		Flash		216	6829	671	10%
	EDTA	Cyclic	*	197	4886	114	2%
		Flash		207	11736	-4236	(-59%)
8	Citrate	Cyclic		1031	3677	1323	36%
		Flash		77	6906	594	9%
	EDTA	Cyclic		1329	6215	-1215	(-24%)
		Flash		96	11831	-4331	(-58%)

Table 6.5 b Extracted Macroelements for Each Sequence of 0.5 M Cyclic and Flash Washings with 1:5 L:S Ratio Additions to 25 g of Soil (μmol)

Ranking of Extracted Elements Appended with Initial Soil Ranking

* Addition of 0.5M washing solution equivalent to 2.5 mmol

Leachate (ml)											
50	Citrate	Cyclic	Ca-2 344	Al-3 203	S-7 103	Fe-1 95.5	Zn-5 64.5	Cu-8 56.4	Mn-9 32.4	Mg-6 32.3	**Pb-4** 14.6
		Flash	Ca-2 45.9	S-7 20.9	Al-3 9.3	Mg-6 3.5	Cu-8 1.4	Mn-9 1.4	Zn-5 1.3	Fe-1 0.57	**Pb-4** 0.28
	EDTA	Cyclic	Ca-2 482	**Pb-4** 159	Fe-1 158	Zn-5 108	S-7 103	Cu-8 77.7	Mg-6 59.4	Mn-9 31.2	Al-3 14.3
		Flash	Ca-2 40.4	S-7 39.3	Zn-5 9.5	**Pb-4** 7.3	Cu-8 6.6	Mg-6 3.0	Fe-1 2.9	Mn-9 0.55	Al-3 -
55	Citrate	Cyclic	Ca-2 126	Al-3 77.9	S-7 65.4	Fe-1 22.6	Cu-8 17.4	Zn-5 13.9	Mn-9 12.4	Mg-6 11.3	**Pb-4** 3.2
		Flash	Ca-2 42.4	S-7 13.7	Al-3 4.20	Mg-6 2.8	Zn-5 1.05	Mn-9 0.76	Cu-8 0.75	**Pb-4** 0.14	Fe-1 0.06
	EDTA	Cyclic	Ca-2 158	**Pb-4** 86.2	S-7 81.5	Fe-1 72.0	Zn-5 57.6	Cu-8 47.5	Mg-6 20.8	Mn-9 16.3	Al-3 0.66
		Flash	S-7 28.4	Ca-2 24.3	Zn-5 5.0	Cu-8 3.9	**Pb-4** 3.6	Mg-6 2.2	Fe-1 0.7	Mn-9 0.24	Al-3 -
60	Citrate	Cyclic	Ca-2 47.8	S-7 42.5	Al-3 23.2	Cu-8 5.0	Mg-6 4.75	Fe-1 4.2	Mn-9 4.1	Zn-5 3.1	**Pb-4** 0.63
		Flash	Ca-2 26.5	S-7 10.2	Al-3 2.4	Mg-6 2.2	Zn-5 0.61	Cu-8 0.58	Mn-9 0.4	**Pb-4** 0.07	Fe-1 -
	EDTA	Cyclic	S-7 53.1	Ca-2 39.9	**Pb-4** 29.5	Zn-5 23.2	Cu-8 19.7	Fe-1 16.5	Mg-6 6.4	Mn-9 4.6	Al-3 -
		Flash	S-7 21.6	19.3	Zn-5 3.3	Cu-8 2.6	**Pb-4** 2.0	Mg-6 1.7	Mn-9 0.12	Fe-1 0.10	Al-3 -
65	Citrate	Cyclic *	Ca-2 146	Al-3 48.2	Fe-1 30.9	S-7 30.4	Zn-5 21.9	Mg-6 18.1	Cu-8 15.7	**Pb-4** 13.1	Mn-9 6.6
	EDTA	Cyclic *	Ca-2 125	S-7 35.3	**Pb-4** 20.0	Mg-6 20.2	Zn-5 18.3	Fe-1 16.0	Cu-8 14.0	Al-3 12.8	Mn-9 3.9
70	Citrate	Cyclic	Ca-2 266	Fe-1 207	Al-3 202	Zn-5 80.8	Cu-8 51.6	**Pb-4** 52.6	Mg-6 37.4	S-7 31.5	Mn-9 17.5
	EDTA	Cyclic	Ca-2 629	Fe-1 221	Al-3 124	Mg-6 122	**Pb-4** 101	Zn-5 66.3	Cu-8 52.3	S-7 33.4	Mn-9 16.4
75	Citrate	Cyclic	Ca-2 176	Al-3 158	Fe-1 127	Zn-5 36.4	Cu-8 33.5	S-7 27.8	Mg-6 20.1	**Pb-4** 19.7	Mn-9 13.9
	EDTA	Cyclic	Ca-2 416	Fe-1 257	**Pb-4** 126	Zn-5 81.5	Mg-6 72.7	Cu-8 68.4	Al-3 57.9	S-7 39.4	Mn-9 20.7
80	Citrate	Cyclic	Ca-2 88.3	Al-3 85.6	Fe-1 53.2	S-7 27.3	Zn-5 15.64	Cu-8 15.61	Mg-6 9.4	**Pb-4** 7.5	Mn-9 7.3
	EDTA	Cyclic	Fe-1 167	Ca-2 147	**Pb-4** 67.2	Zn-5 49.9	Cu-8 43.4	S-7 33.4	Al-3 28.9	Mg-6 28.6	Mn-9 8.1
85	Citrate	Cyclic	Ca-2 30.0	Al-3 26.1	S-7 19.9	Fe-1 11.2	Cu-8 4.4	Zn-5 3.7	Mg-6 3.5	Mn-9 2.4	**Pb-4** 1.6
	EDTA	Cyclic	Fe-1 47.0	Ca-2 42.3	**Pb-4** 34.2	S-7 29.2	Zn-5 23.4	Cu-8 21.1	Mg-6 7.3	Mn-9 3.5	Al-3 1.5
90	Citrate	Cyclic	Ca-2 22.2	S-7 12.6	Al-3 9.2	Fe-1 2.7	Mg-6 2.1	Cu-8 1.6	Zn-5 1.3	Mn-9 1.0	**Pb-4** 0.44
	EDTA	Cyclic	S-7 20.6	Ca-2 17.3	Fe-1 13.7	**Pb-4** 12.3	Zn-5 10.6	Cu-11 9.2	Mg-6 3.0	Mn-9 1.1	Al-3 0.16
95	Citrate	Cyclic	Ca-2 16.5	S-7 10.3	Al-3 2.3	Mg-6 1.4	Cu-14 0.5	Fe-1 0.42	Zn-5 0.36	Mn-9 0.33	**Pb-4** 0.11
	EDTA	Cyclic	S-7 17.5	Ca-2 17.3	Zn-5 5.9	Cu-16 5.00	**Pb-4** 4.96	Fe-1 4.6	Mg-6 1.8	Mn-9 0.40	Al-3 -
100	Citrate	Cyclic	Ca-2 7.4	S-7 6.9	Mg-6 1.2	Al-3 0.43	Zn-5 0.26	Cu-8 0.19	Mn-9 0.12	**Pb-4** 0.06	Fe-1 -
	EDTA	Cyclic	S-7 15.4	Ca-2 15.0	Zn-5 4.2	Cu-8 3.3	**Pb-4** 2.9	Fe-1 2.0	Mg-6 1.7	Mn-9 0.21	Al-3 -
105	Citrate	Cyclic	Ca-2 4.5	S-7 2.7	Mg-6 0.450	Zn-5 0.10	Cu-8 0.06	Mn-9 0.03	**Pb-4** 0.02	Al-3 -	Fe-1 -
	DTA	Cyclic	S-7 10.3	Ca-2 8.1	Zn-5 2.4	Cu-8 2.1	**Pb-4** 1.5	Mg-6 1.3	Fe-1 0.92	Mn-9 0.11	Al-3 -

Sequence Number			Sum of Metals	Cumulative Sum	**Excess Chelator to Extracted Metals** Σ(mmol)	Σ(%)
9	Citrate	Cyclic	843	4519	481	11%
		Flash	64	6970	530	8%
	EDTA	Cyclic	1091	7306	-2306	(-46%)
		Flash	70	11902	-4402	(-59%)
10	Citrate	Cyclic	285	4804	196	4%
		Flash	52	7022	478	7%
	EDTA	Cyclic	459	7766	-2766	(-55%)
		Flash	40	11942	-4442	(-59%)
11	Citrate	Cyclic	93	4897	103	2%
		Flash	35	7056	444	6%
	EDTA	Cyclic	142	7907	-2907	(-58%)
		Flash	29	11971	-4471	(-62%)
12*	Citrate	Cyclic *	300	5197	2303	44%
	EDTA	Cyclic *	230	8137	-637	(-8%)
13	Citrate	Cyclic	935	6132	1368	22%
	EDTA	Cyclic	1354	9492	-1992	(-27%)
14	Citrate	Cyclic	708	6840	660	10%
	EDTA	Cyclic	1104	10595	-3095	(-41%)
15	Citrate	Cyclic	263	7123	377	5%
	EDTA	Cyclic	540	11135	-3635	(-48%)
16	Citrate	Cyclic	83	7206	294	4%
	EDTA	Cyclic	180	11316	-3816	(-51%)
17	Citrate	Cyclic	41	7246	254	3%
	EDTA	Cyclic	67	11383	-3883	(-52%)
18	Citrate	Cyclic	22	7268	232	3%
	EDTA	Cyclic	40	11423	-3923	(-52%)
19	Citrate	Cyclic	10	7278	222	3%
	EDTA	Cyclic	29	11452	-3952	(-53%)
20	Citrate	Cyclic	5	7283	217	3%
	DTA	Cyclic	16	11469	-3969	(-53%)

The EDTA washes not only complexed large amounts of M^{n+}, but also stripped the soil particles and exposed their surfaces to the extent that the M^{n+} were being extracted beyond the EDTA 1:1 complexing ability. The 1st rinse of the cyclic washing immediately extracted M^{n+} in excess of the amount of added EDTA. This excess then persisted throughout the 3 washing cycles. At the end of the first washing cycle, the amount of extracted M^{n+} exceeded the EDTA by 2.2 mmol or 88%. This was the largest M^{n+} extraction excess and it was 32 times the initial leachable M^{n+} amount. Uncomplexed leaching of Ca is assumed to have caused this huge surplus of extracted M^{n+}. The EDTA flash washing started to extract more M^{n+} than the amount of added EDTA during the 1st rinse (*i.e.* 16%), this amount kept on growing with each subsequent rinse to attain 62% after the 8th and final rinse.

Citric acid had its best chelator:ΣM^{n+} ratio in its last rinse of the first washing cycle. However, unlike EDTA, this amount of extracted M^{n+} remained less than the amount of added citric acid (*i.e.* by 1%). As for the citric acid flash washing, the M^{n+} deficit reached 6%. Therefore, even if citric acid had the potential to multi-complexed divalent cations, it did not extract a greater amount of M^{n+}, as compared to its own added amounts.

6.5 Post-Extraction Leachability Following Three 0.5 M Washing Cycles

In the unsaturated experiments of the previous chapter, large amounts of trace metals were still coming out after several rinses of the EDTA treated soil. A citric acid treatment would likely have a smaller post-treatment leaching of toxic levels of trace metals. To demonstrate this, citric acid's post-treatment leaching of toxic levels of trace metals was compared to those of EDTA. Figure 6.3 presents the deionised water extracted elements, as obtained onward from the 2nd rinse of the 3rd 0.5 M washing cycle. In total, 22 rinses were applied during the 3rd washing cycle, alone these rinses yielded a 4:1 cumulative *L:S* ratio.

The initial soil leachability level (*ISLL*) of S, Ca and Mg were, by far, the highest amongst the elements (table 4.3). However, their leachable amounts were the first to recede below the *ISLL*. Independently of the chelating agent, the 2nd rinse extracted an S level below its *ISLL*, and the 5th rinse extracted Ca and Mg below their *ISLL*. Iron and Al were the only elements for which the extractions became null. It took 7 rinses for the

Figure 6.3 a Average Column Extractions from Rinsing 25 g of Soil after a Third Unsaturated Cyclic Addition of a 0.5 M Wash given in a 1:5 L:S Ratio

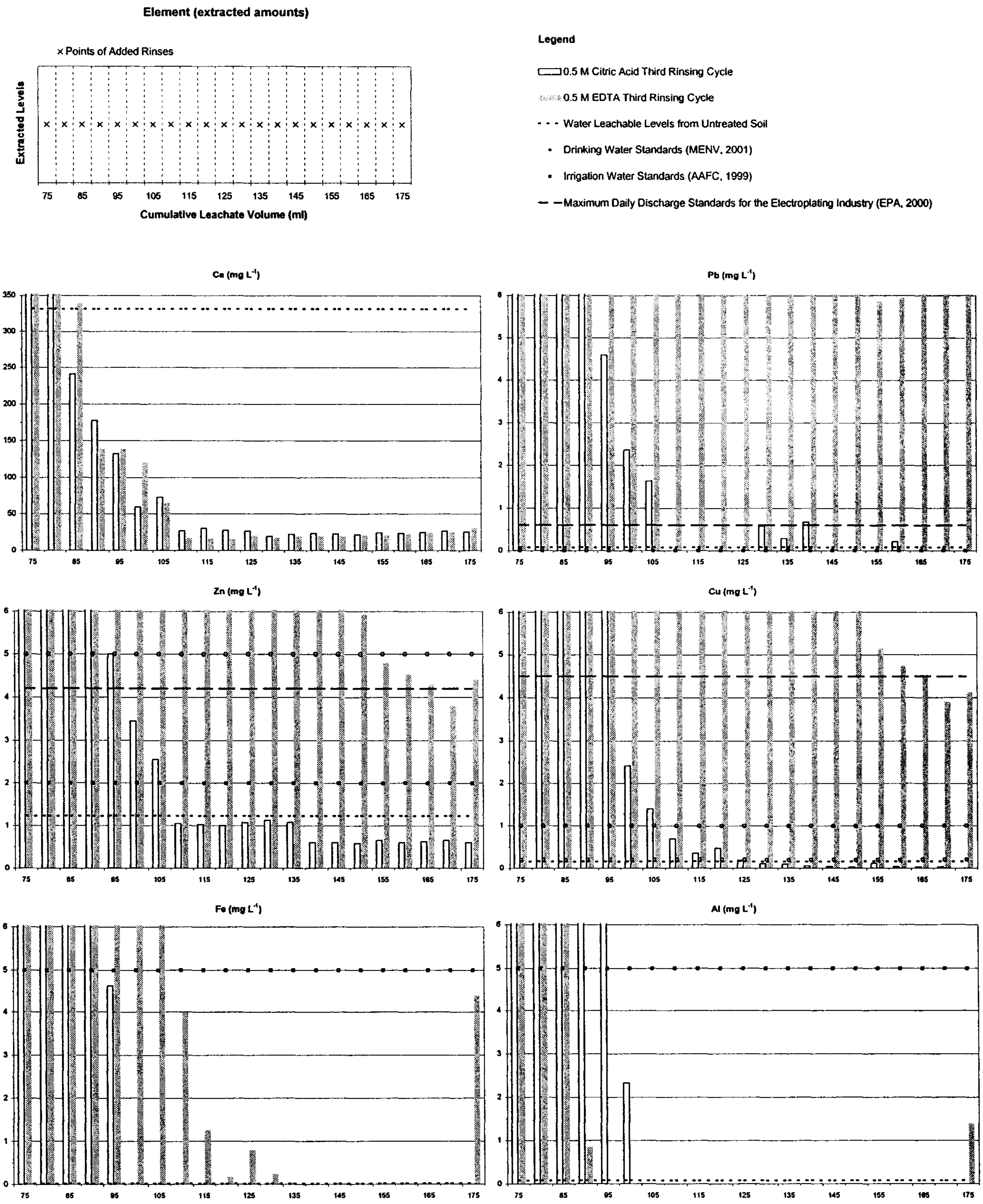
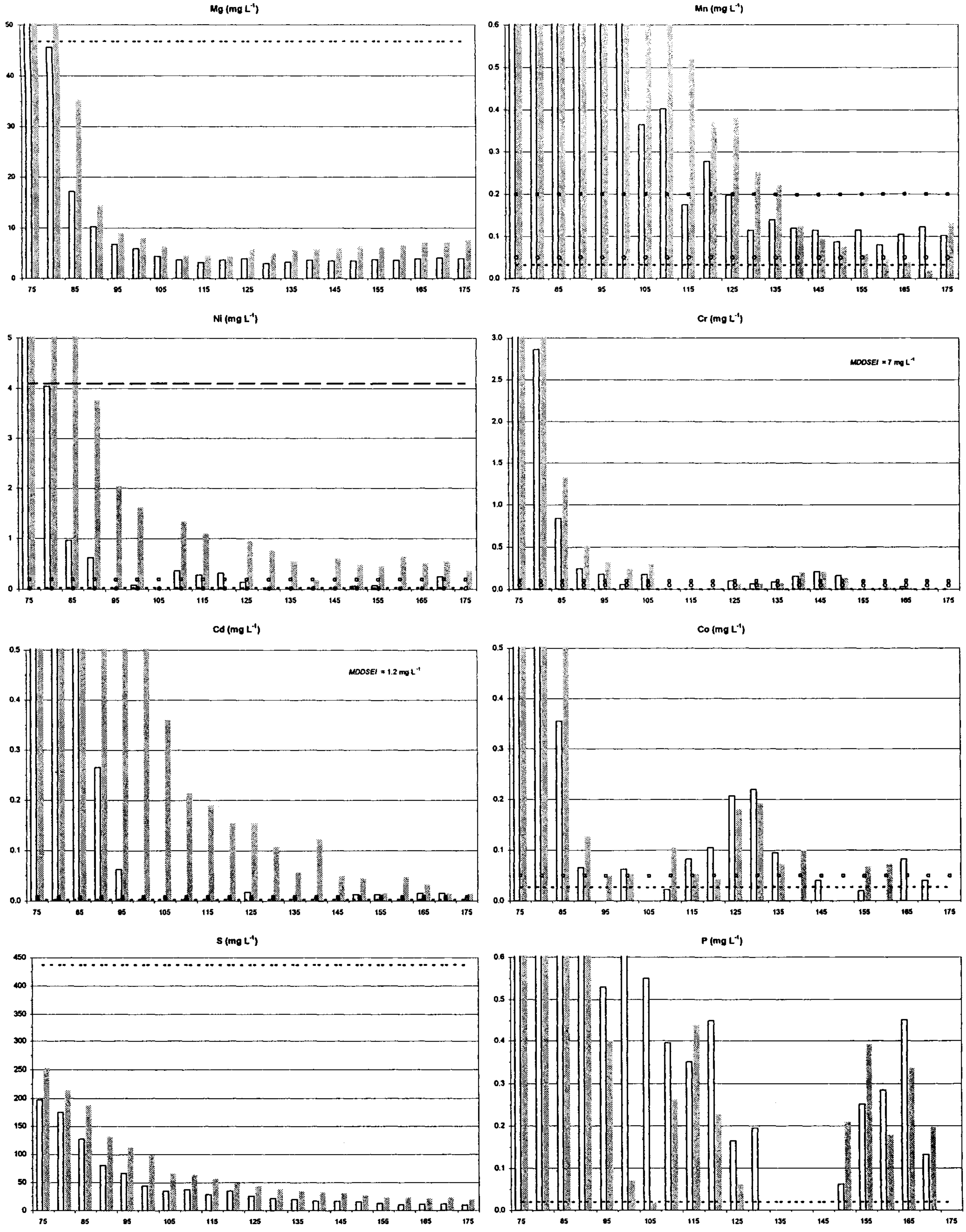


Figure 6.3 b Average Column Extractions from Rinsing 25 g of Soil after a Third Unsaturated Cyclic Addition of a 0.5 M Wash given in a 1:5 L:S Ratio



citric acid washing cycle to no longer extract Fe and Al; whereas it took 14 and 6 rinses for the EDTA washing cycle.

The other elements had undesirably prolonged post-treatment leachability, all remaining above their *ISLL* for both chelating agents. The addition of the chelating agents induced a chemical chaos within the soil. Although each additional rinse attenuated this chaos, the soil was still far from achieving its initial state of modest ion exchange. Aluminium, Mn^c, Co^b and P were the only four elements for which citric acid provoked post-treatment leachabilities that were sometimes greater than those of EDTA. For the D-Level chalcophilic contaminants (Pb, Zn, Cu & Cd), EDTA caused a much larger post-treatment leachability, as compared to citric acid.

By the 10th rinse of the 3rd citric acid washing cycle, the leachate met the maximum daily discharge standards for the electroplating industry (*MDDSEI*) for all potentially toxic trace metals, of which Pb was the most limiting. This indicated that the leachate collected after the 10th rinse could have been discharged in municipal sewers without treatment. This would reduce the site-scale cost associated with the leachate treatment.

Even after the 22nd rinse of the 3rd EDTA washing cycle, the rinse-extracted Pb in the leachate did not satisfy the *MDDSEI*. Though the Zn and Cu EDTA post-treatment leachate levels were tardy in meeting the *MDDSEI*, they still met them by the 22nd rinse. For the B-Level trace metals, their rinse-extractions met the *MDDSEI* by the 5th rinse (*e.g.* Ni, Cr, Cd & Co).

6.6 Comparison of the Citric Acid Results to Those of a Previous Study

A comparative assessment was done to distinguish this study from a previous column leaching study by Tejowulan (1999), in which 0.52g of citric acid were mixed with 10g of soil. Since the capacity of citric acid to decontaminate the *M-soil* of its Pb content was unlikely, the comparison focused on the removal of Cu, for which the soil content was the least different amongst the trace metals of both studies. Therefore, an added citric acid to an initial soil Cu molar ratio (*Citric*:*Cu*) was used to compare the results of the two studies (table 6.6).

Table 6.6 Comparison of the Citric Acid Results of this Study (Flash Washing) against those of an Other Column Study

	Citric : *S* (% wt)	*Citric* : *Cu* (mol:mol)	*L* : *S*	Cycles[c]	Cd Removal ($\mu g\,g^{-1}$)[i]		Cu Removal ($\mu g\,g^{-1}$)		Pb Removal ($\mu g\,g^{-1}$)		Zn Removal ($\mu g\,g^{-1}$)	
Andrade (2004)	6%	5	1:1	3 + 3	8%	107	30%	3768	12%	19466	17%	9917
Tejowulan (1999)	5.2%	22	20:1	0[d] + 5	38%	5.5	39%	800	32%	2200	38%	400
Superior amount of *M-soil* contaminants (times)					-	19	-	5	-	9	-	25
Deficiency of the % removal of the present to past study (times)					4.8	-	1.3	-	2.7	-	2.2	-

[c] Number of washes and rinses

[i] Initial soil content

[d] Dry soil and Citric Acid mixture

With a 4.4 times greater *Citric*:*Cu*, the other study merely achieved a 1.3 times greater % removal of Cu. Moreover, the initial *M-soil* content in Cu was 5 times greater. The other study also provided larger % removals for Cd, Pb and Zn; however given the much smaller amounts of initial contaminants, these increases were relative low. Thus, the flash washing procedure might seem advantageous, when considering the initial contamination of the soils. Even though citric acid could remove trace metals efficiently as a solution or as a dry additive, a homogenous site-scale mixture of citric acid powder and soil would be laborious. Hence, the dry additive is deemed unpractical for site-scale applications.

6.7 Summary and Conclusions

On a molar basis, the extraction of trace metals with EDTA was much higher than with citric acid. However, this large extraction difference is lessened by 58.9% when considering a more pragmatic weight basis comparison, as citric acid is a lighter molecule than EDTA. Compared to the EDTA cyclic washing, the EDTA flash washing increased the extraction of Cr and extracted similar amounts of other trace metals. The citric acid flash washing significantly increased the extraction of Pb, Zn and Ni, as compared to its cyclic washing counterpart. For similar amounts of added EDTA, reducing the concentration of the EDTA washing solution from 0.7 M to 0.5 M reduced the mobilisation of Cr. The less concentrated 0.5 M washing solution provided a lower EDTA concentration in the soil solution, which would have reduced the extraction potential of the EDTA.

One advantage of using citric acid was the shorter-lived post-treatment leachability of toxic levels of trace metals, which quickly met the *MDDSEI* standards. In contrast, the prolonged EDTA post-treatment leachability of Pb would not have allowed the disposal of untreated leachate into municipal sewers, even after 21 rinses that amounted to a cumulative 4:1 *L:S* ratio. Perhaps if the *M-soil* had been decontaminated in Pb, to the point of fulfilling the C-Level criterion, the post-treatment leachability of Pb would have dropped quickly enough to allow us to envision an eventual discharge of the rinses into municipal sewers. However, the post-treatment leachability of successfully EDTA-reclaimed soil needed to be established.

Treating the soil with EDTA extracted more moles of multivalent cations as compared to the added moles of EDTA. By using five 0.7 M unsaturated EDTA washing cycles, the C-Level criterion for Pb and Cu were met. However, the five cycles did not reduce the Zn and Cd levels below the C-Level criterion for industries, even though they amounted to an *EDTA:S* of 22.3% wt. Roughly 48 and 69% more Zn and Cd needed to be extracted, for the soil to be decontaminated. The economical and environmentally sustainable decontamination of the extremely contaminated landfill soil seemed unlikely. Still, means to further improve the EDTA extraction process were sought in chapter 7. In chapter 8, the long-term post-treatment leaching of toxic levels of trace metals from EDTA and citric acid treatments were examined in a pilot-scale treatment of a soil from an abandoned car battery recycling facility.

Preface to Chapter 7

In chapter 6, five washing cycles were unable to decontaminate the *M-soil*. Hence, modifications were made to the $(NH_4)_2EDTA$ unsaturated-flow extraction procedure, with the intent of improving the extraction efficiency.

7

Modifications to Improve the $(NH_4)_2$EDTA Unsaturated-Flow Extraction of Potentially Toxic Trace Metals from Soils

In our previous study, the use of EDTA in a proportion of 22.3% wt soil^{-1} was unable to lower the Zn and Cd contents, originally in excess of the D-Level criterion, of the extremely contaminated *M-soil* below the C-Level criterion. Increasing the inputs of EDTA beyond 22.3% wt soil^{-1} would have been environmentally unsustainable and was disregarded as a possibility. Modifications were done to the generic EDTA unsaturated cyclic washing procedure, in order to improve the extraction efficiency of the EDTA.

Four modifications to the unsaturated process were tested: (i) adding the EDTA washing solution to an initially unmoistened soil; (ii) sequentially wetting and drying the soil during a washing cycle; (iii) insertion of a citric acid cycle within EDTA washing cycles; and (iv) increasing the retention time of EDTA within the soil. The results of these modifications were compared to those of previous experiments.

7.1 General Methodology

The generic term EDTA specifically abbreviates our experimental use of diammonium EDTA. A washing cycle consisted of a one-step EDTA wash and subsequent rinses with deionised water. A saturated extraction describes the physical state of a waterlogged soil. An unsaturated-flow extraction is abbreviated by an unsaturated extraction. The 0.685 M EDTA washing solution and its derivatives are abbreviated as 0.7 M, etc. *A liquid to soil ratio is abbreviated by L:S ratio.*

All the modified unsaturated EDTA extractions were performed in soil columns, which were filled with 25 g of *M-soil*. The experimental design, the general unsaturated extraction procedure and the analytical methods were as described in section 5.1. The specific changes in the general methodology of the unsaturated experiment are addressed within their respective sections.

For the statistical analysis, the STATGRAPHICS®*PLUS 4.0* software was used to compute the t-tests between the end-extraction results from two treatment populations. STATGRAPHICS®*PLUS 4.0* was also used to assess the equality of the variances between the two treatment populations, as well as the normality of each population's distribution.

7.2 Addition of the EDTA Washing Solution to an Initially Unmoistened Soil

Adding the chelating agent to a dry soil would alter the chemical kinetics within the soil, perhaps in favour of the dissolution of the potentially toxic trace metals. To compare accurately an extraction of a dry soil to that of a moist soil, equal additions of EDTA and of recovered washing solution leachate were required. To compensate for the hydration of the dry soil, the dry-soil washing solution was supplemented with an additional 9.6 ml, as compared to its wet-soil counterpart. To ensure a better equivalence between the moist-soil and dry-soil experiments, namely the uniform wetting of the dry 25 g soil columns, the experiment were performed as saturated extraction procedures. Both treatments were done as per the extraction procedure of section 4.1.

It was assumed that increasing the volume of the dry-soil washing solution addition would yield a soil solution of similar EDTA concentration to that of the moist-soil extraction, upon the hydration of the dry soil. The dry-soil washing solution molarity was adjusted to 0.33 M and 21 ml were added. The latter treatment was compared to a 10 ml moist-soil addition of a 0.7 M washing solution. The recovered leachate volumes of the dry and moist 7-mmol EDTA additions both amounted to roughly 8 ml. Thereby, the initial requirement of equal leachate, which was intended to produce similar EDTA concentrations within their respective soil solutions, was satisfied. The results are presented in figure 7.1. Another moist-soil treatment (*i.e.* 5 ml addition of a 0.7 M washing solution) was also presented for comparative purposes; this washing cycle added half the amount of EDTA and is referred to as the 3.5-mmol moist-soil cycle.

FIGURE 7.1 a Cumulative Saturated Column Extractions from an EDTA Washing Cycle with a Dry-Soil Addition of the Washing Solution to 25 g

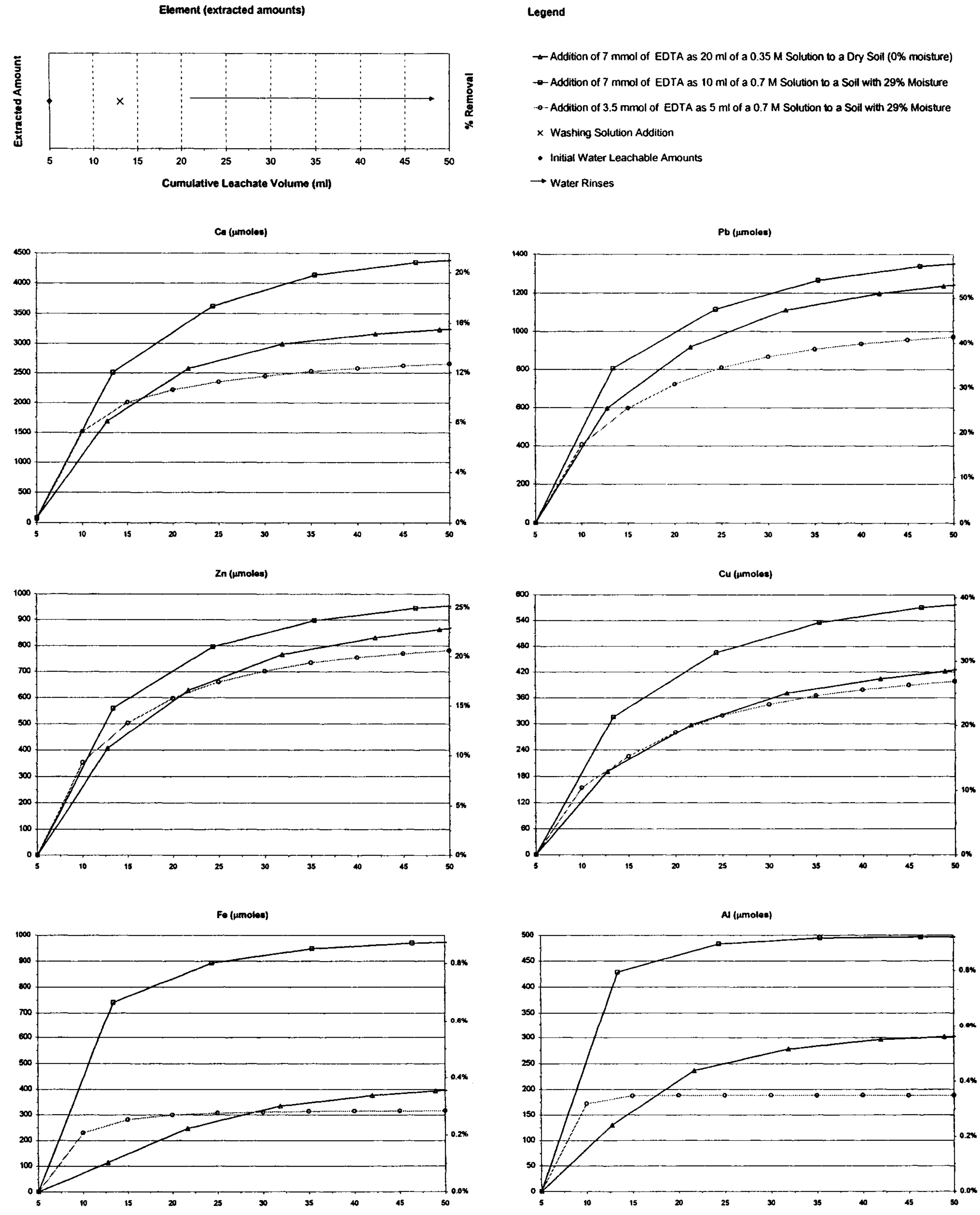
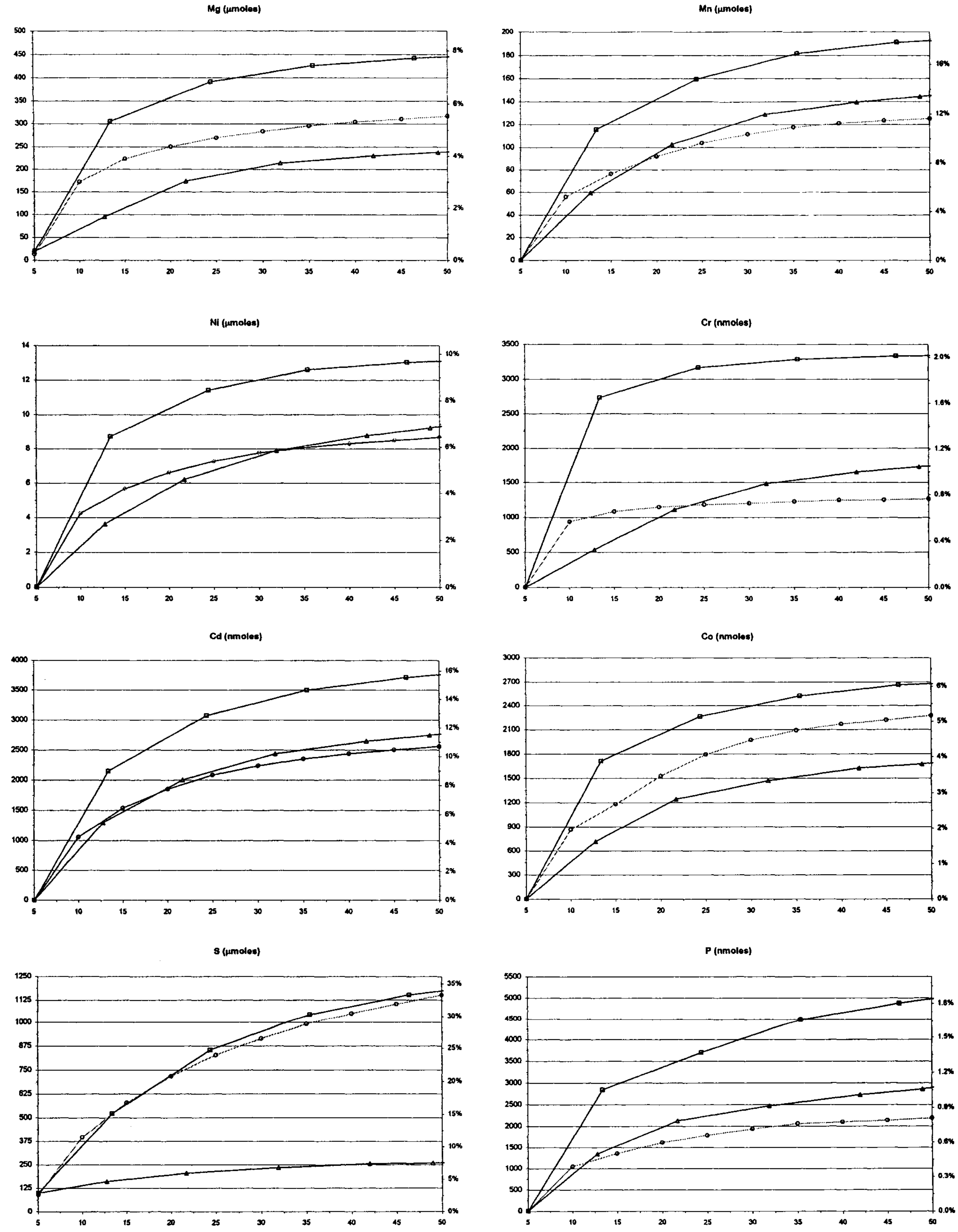


FIGURE 7.1 b Cumulative Saturated Column Extractions from an EDTA Washing Cycle with a Dry-Soil Addition of the Washing Solution to 25 g



As compared to the 7-mmol moist-soil treatment, the dry-soil application of 7 mmol of EDTA significantly impeded the extractions of Cu, Mn, Cd and Co, at the 99, 95, 95 and 99% levels (table 7.1). For the other elements, the dry-soil treatment showed a slight tendency to extract them in fewer amounts. The 7 mmol of the dry-soil treatment even tended to extract less Mg and Co than the 3.5 mmol moist-soil cycle that was obtained from the 5 ml addition of a 0.7M wash.

Table 7.1 t-test of the Cumulative Extractions from a Saturated EDTA Washing Cycle of Initially Dry to Initially Moist Soil

Element	Dry x Moist Additions (Molarities)	t	*P*	Unequal Variances*	Departure from Normality^{K}
Al	0.7 x 0.7	2.19	0.0714	yes	Non-moist
Ca	0.7 x **0.7**	2.50	0.0464 $^{(*)}$	yes	
Cd	0.7 x **0.7**	2.50	0.0466 *		
Co	0.7 x **0.7**	4.39	0.0046 **		
Cr	0.7 x **0.7**	2.87	0.0282 $^{(*)}$	yes	
Cu	0.7 x **0.7**	3.71	0.0099 **		
Fe	0.7 x **0.7**	4.33	0.0049 $^{(**)}$	yes	
Mg	0.7 x **0.7**	5.14	0.0021 $^{(**)}$		Non-moist, Moist
Mn	0.7 x **0.7**	2.96	0.0251 *		
Ni	0.7 x **0.7**	3.11	0.0206 $^{(*)}$	yes	
P	0.7 x 0.7	2.22	0.0677	yes	
Pb	0.7 x 0.7	1.51	0.1826		
S	0.7 x **0.7**	21.44	0.0000 $^{(***)}$	yes	Non-moist, Moist
Zn	0.7 x 0.7	1.37	0.2380	yes	

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

$^{(***)}$, $^{(**)}$ or $^{(*)}$ The significant difference is overruled by unequal population variances or non-normal population distributions

^{K} Kurtosis was the only factor, as no skewness was present

Hydration of oxides and hydroxides result in a physical or chemical adsorption of water on the surfaces of the soil particles. When H_2O is chemically adsorbed, it is split into H^+ and OH^- to form hydroxylated surfaces on the soil particle (Gast, 1989). In the dry-soil extraction, the lack of initial soil moisture was unfavourable for the kinetics of metal dissolution. In the moist-soil extraction, prior to the wash addition, the hydrated surfaces of the particles were already in a chemical balance with the capillary water. The hydrated surfaces of the particles had previously liberated solutes into the capillary solution, thus were more exposed/vulnerable to the washing solution. Thereby, a greater extraction resulted from the addition of the washing solution to a moist soil, as compared to a dry soil.

7.3 Sequentially Wetting and Drying the Soil during a Washing Cycle

During the course of a washing cycle, soil columns sequentially underwent convective air exchange, in an attempt to enhance EDTA's trace metal removal by creating fully oxidising conditions within the soil matrix. The convective air exchange was achieved by applying vacuum airflow to the columns during the last quarter of the 24-hour interval between sequences. The vacuum airflow gradually resulted in the drying out of the soils, thereby causing the crystallization of the salts that were in the soil solutions. The convective air exchange was first performed following the washing solution extraction, after which rinsing and drying were carried out alternately for the remainder of the treatment (hereafter referred to as the drip-dry treatment. To collect quasi-equivalent leachate volumes as compared to their drip counterparts, the drip-dry columns were rinsed with additional amounts of water, which served to re-hydrate the soil. The results are presented in figure 7.2.

The 1.4 M extractions of Ca and the 0.7 M extraction of Al were enhanced significantly by the fully oxidising conditions of the 6-hour airflow drying, at the 95 and 99.9% levels (table 7.2). Both of these metals have a single valence state that cannot have been further oxidised. The airflow likely oxidised parts of the SOM, thus causing it to breakdown and release Ca and Al in solution. These were the only increases in extraction provided by the drip-dry treatment. The 1.4 M drip-dry treatment extracted significantly less Fe (at the 95% level); this was the only significant difference between both 1.4 M treatments. Under vacuum drying, the mineral stability of Fe^{3+} was likely increased, thereby its reduced extraction for the drip-dry treatment.

The 0.7 M drip-dry treatment suppressed significantly the extraction of S, Mn and Co (at the 95, 99 and 99.9% levels). The behaviour of Mn was similar to that of Co, for either the drip or drip-dry treatments. It is assumed that the airflow drying favoured the oxidation of Co^{2+} to Co^{3+}, which could have co-precipitated with Mn and formed insoluble Mn nodules; this would have reduced the extractions of Mn and Co during the 0.7 M drip-dry treatment. The association of Co^{3+} with Mn would be in agreement with the natural chemical behaviour of uncontaminated soils (McBride, 1994). Thus, initial hypothesis, which anticipated that the fully oxidising conditions and the crystallization of the drying soil solution could favour the extraction of trace metals, was disproved.

FIGURE 7.2 a Cumulative Column Extractions with Alternating Unsaturated Wetting and Convective Drying Within a Washing Cycle with 1:5 L:S Ratio Additions to 25 g

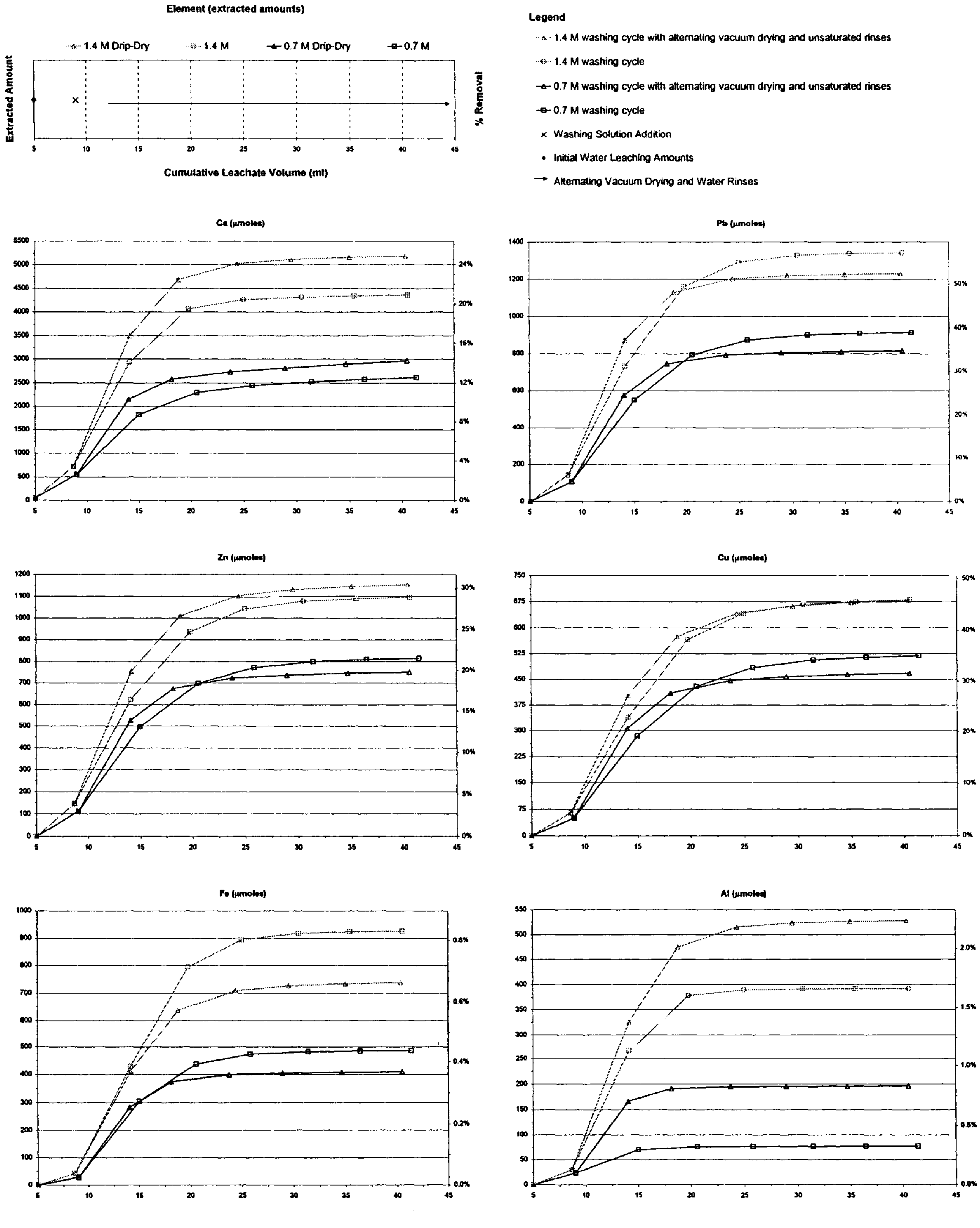


FIGURE 7.2 b Cumulative Column Extractions with Alternating Unsaturated Wetting and Convective Drying Within a Washing Cycle with 1:5 L:S Ratio Additions to 25 g

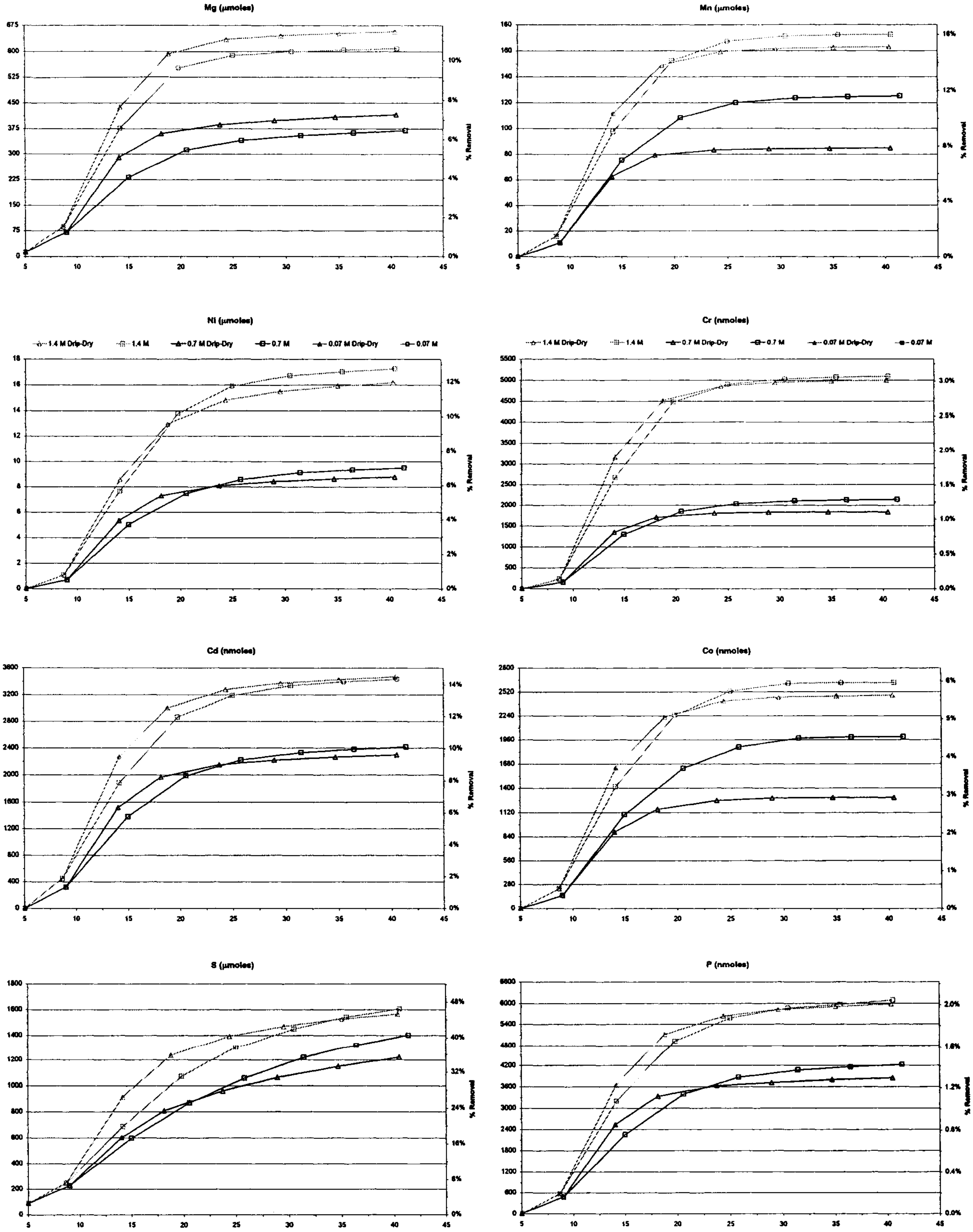


Table 7.2 t-test of the Cumulative Extractions of Alternately Dried to Non-Dried Unsaturated Washing Cycles

Element	Drip-Dry x Drip (EDTA Molar Additions)	t	*P*	Unequal Variances*	Departure from Normality^{K}
Al	**0.7** x 0.7	-8.24	0.0002 ***		
	1.4 x 1.4	-5.04	0.0024 $^{(**)}$	yes	
Ca	0.7 x 0.7	-1.49	0.1873		
	1.4 x 1.4	-3.23	0.0180 *		
Cd	0.7 x 0.7	0.83	0.4367		
	1.4 x 1.4	-0.12	0.9109		
Co	0.7 x **0.7**	6.45	0.0007 ***		
	1.4 x 1.4	0.95	0.3799		
Cr	0.7 x 0.7	1.09	0.3184		Drip-Dry
	1.4 x 1.4	0.10	0.9228		
Cu	0.7 x 0.7	1.20	0.2764		
	1.4 x 1.4	0.02	0.9827		
Fe	0.7 x 0.7	2.03	0.0877		
	1.4 x **1.4**	3.38	0.0147 *		
Mg	0.7 x 0.7	-1.62	0.1554		Drip-Dry
	1.4 x 1.4	-1.23	0.2636	yes	
Mn	0.7 x **0.7**	5.54	0.0015 **		
	1.4 x 1.4	1.08	0.3226		
Ni	0.7 x 0.7	1.25	0.2553		
	1.4 x 1.4	0.60	0.5684	yes	
P	0.7 x 0.7	1.06	0.3309		
	1.4 x 1.4	0.28	0.7893		
Pb	0.7 x 0.7	1.89	0.1077		
	1.4 x 1.4	1.33	0.2316		Drip
S	0.7 x **0.7**	2.96	0.0252 *		
	1.4 x 1.4	1.88	0.1096		
Zn	0.7 x 0.7	1.83	0.1166		Drip-Dry
	1.4 x 1.4	-1.32	0.2350		

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

$^{(***)}$, $^{(**)}$ or $^{(*)}$ The significant difference is overruled by unequal population variances or non-normal population distributions

^{K} Kurtosis was the only factor, as no skewness was present

7.4 Insertion of a Citric Acid Cycle within Three EDTA Washing Cycles

This experiment investigated the use of citric acid as a partial substitute for EDTA and citric acid's ability to help increase the EDTA extraction of trace metals. A cyclic washing procedure was used to establish an extraction response for each washing solution addition, whether EDTA or citric acid. A citric acid (0.5 M) washing cycle was inserted after the 1st of three 0.7 M EDTA washing cycles. The extractions from these four cycles (*i.e.* EDTA+CA) were compared to those of three EDTA cycles (fig. 7.3).

As compared to the three EDTA cycles, the only significant extraction increases generated by the EDTA+CA were for Al and Cr, at a 95% level (table 7.3). The additional citric acid washing cycle increased the extractions of Al and Cr by 26.0 and 13.6% (table 7.4). On the other hand, the extractions of Fe and Pb were impeded significantly at the 99.9 and 95% levels; their extractions were reduced by 35.1 and 8.0%.

Table 7.3 t-test of the Cumulative Extractions of Three EDTA to Three EDTA + Citric Acid Unsaturated Washing Cycles

Element	EDTA + Citric Acid x EDTA (Molar Additions)	t	P	Unequal Variances*	Departure from Normality^K
Al	**3·(0.7) + 0.5** x 3·(0.7)	3.59	0.0115 *		
Ca	3·(0.7) + 0.5 x 3·(0.7)	-1.24	0.2623		EDTA + Citric Acid
Cd	3·(0.7) + 0.5 x 3·(0.7)	-0.31	0.7658		
Co	3·(0.7) + 0.5 x 3·(0.7)	0.23	0.8283	yes	
Cr	**3·(0.7) + 0.5** x 3·(0.7)	3.10	0.0212 *		
Cu	3·(0.7) + 0.5 x 3·(0.7)	0.51	0.6284		
Fe	3·(0.7) + 0.5 x **3·(0.7)**	-7.04	0.0004 ***		
Mg	3·(0.7) + 0.5 x 3·(0.7)	0.32	0.7595		
Mn	3·(0.7) + 0.5 x 3·(0.7)	0.19	0.8526		
Ni	3·(0.7) + 0.5 x 3·(0.7)	-0.57	0.5918		
P	3·(0.7) + 0.5 x 3·(0.7)	1.69	0.1413		
Pb	3·(0.7) + 0.5 x **3·(0.7)**	-3.00	0.0239 *		
S	3·(0.7) + 0.5 x 3·(0.7)	-2.32	0.0593		
Zn	3·(0.7) + 0.5 x 3·(0.7)	-0.05	0.9624		

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

^{K} Kurtosis was the only factor, as no skewness was present

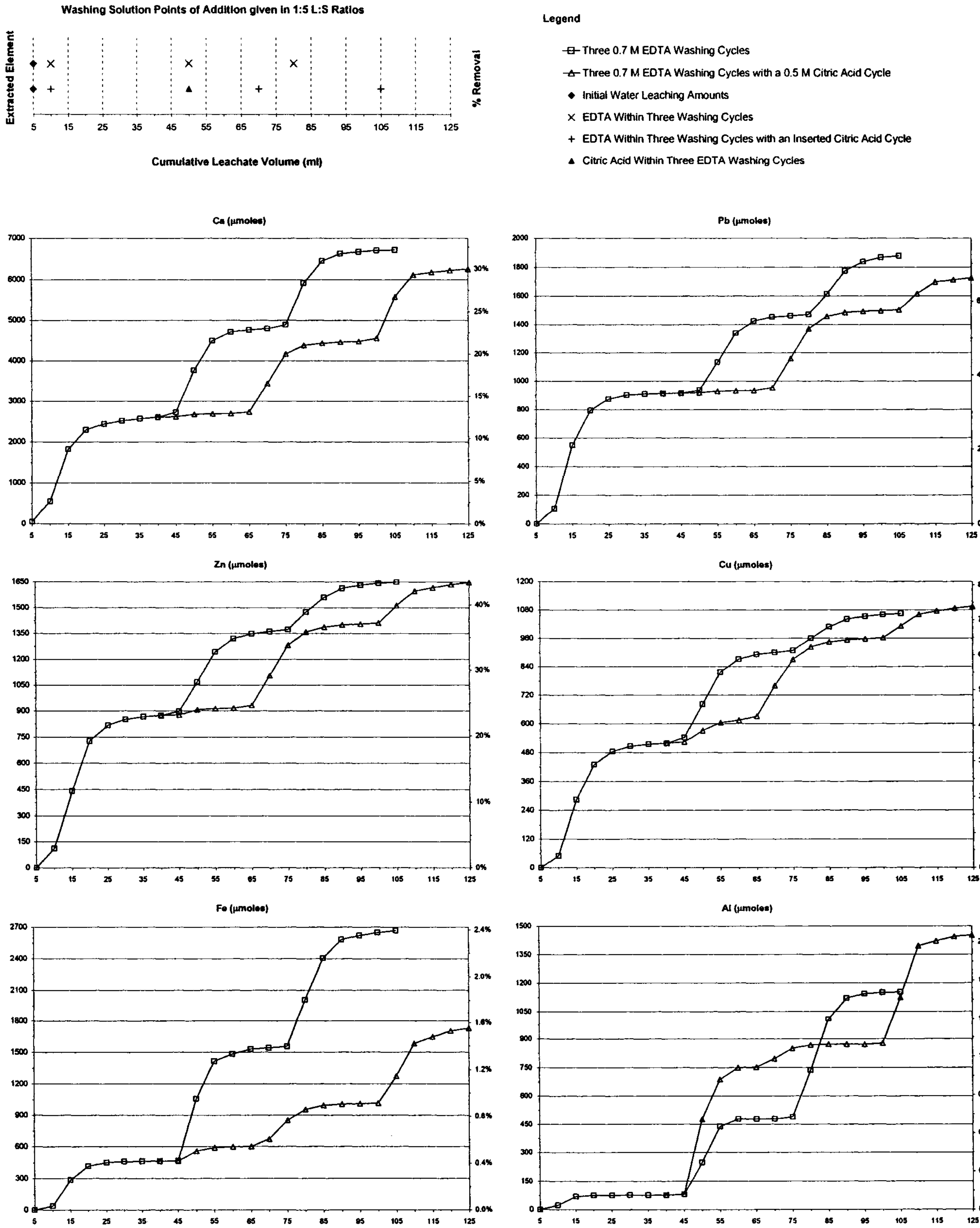
Table 7.4 Increase in Extractions from Inserting a Citric Acid Cycle within Three Unsaturated EDTA Washing Cycles

Ca	Pb^c	Zn^d	Cu^d	Fe	Al	Mg	Mn^c	Ni^b	Cr^b	Cd^d	Co^b	S	P
(-6.8%)	(-8.0%)*	(-0.2%)	2.8%	(-35.1%)***	26.0%*	2.9%	3.4%	(-3.7%)	13.6%*	(-0.1%)	2.1%	(-0.6%)	17.9%

^{b} B-Level initial criterion, ^{c} C-Level initial criterion, ^{d} D-Level initial criterion

*** 99.9%, ** 99% or * 95% Significance Level

FIGURE 7.3 a Cumulative Unsaturated Column Extractions from Inserting a Citric Acid Washing Cycle within Three EDTA Washing Cycles



Washing Solution Points of Addition given in 1:5 L:S Ratios

Ca (µmoles)

Pb (µmoles)

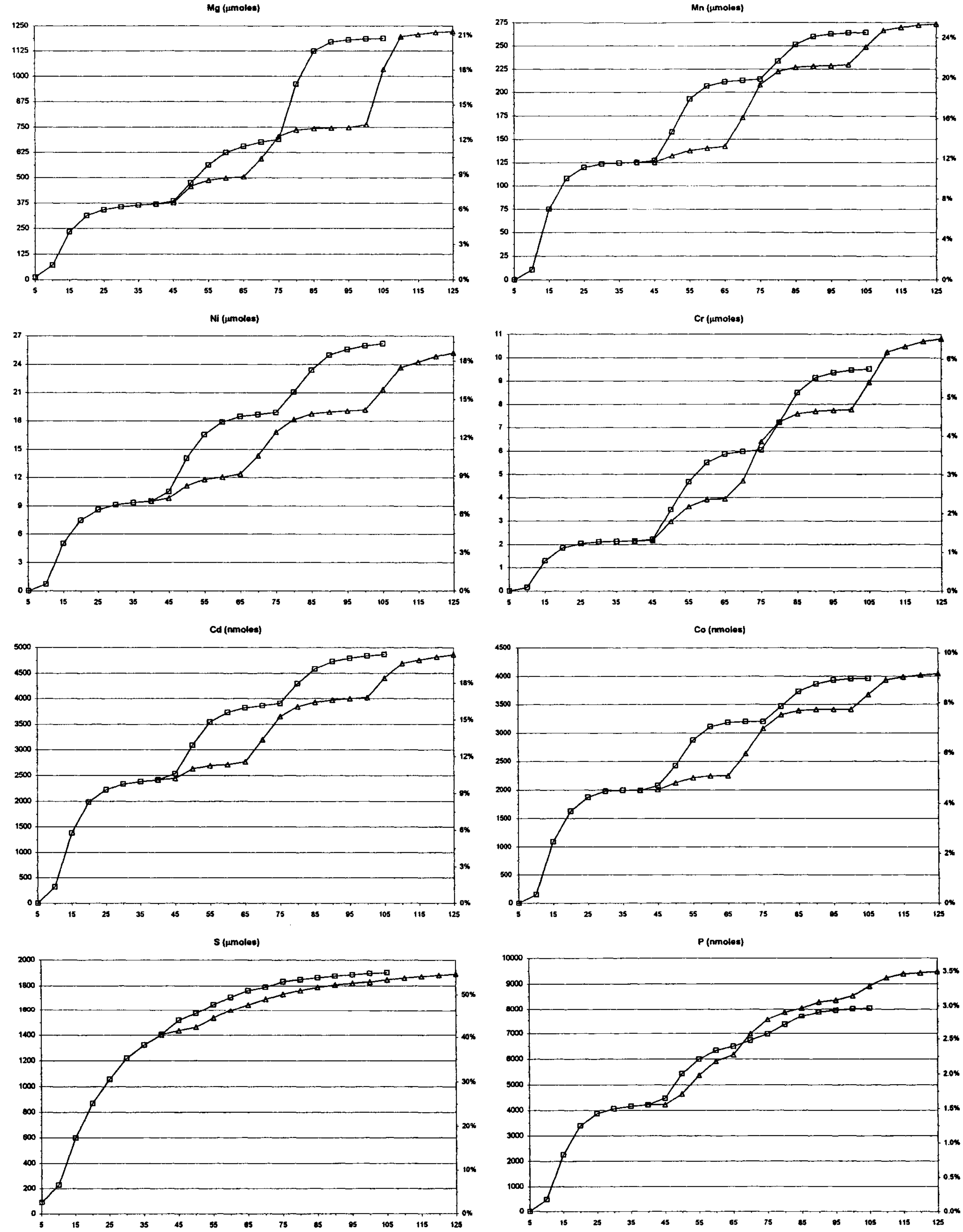
Zn (µmoles)

Cu (µmoles)

Fe (µmoles)

Al (µmoles)

FIGURE 7.3 b Cumulative Unsaturated Column Extractions from Inserting a Citric Acid Washing Cycle within Three EDTA Washing Cycles



Overall, EDTA+CA reduced the extraction of potentially toxic metals by 115 mmol, as compared to the three EDTA cycles. Although EDTA+CA increased the extraction of Cr, this increase was likely much smaller than the increase that would have been provided by a 4th EDTA washing cycle, inserted instead of the citric acid one. Thus, inserting a citric acid washing cycle within three EDTA cycles was counterproductive.

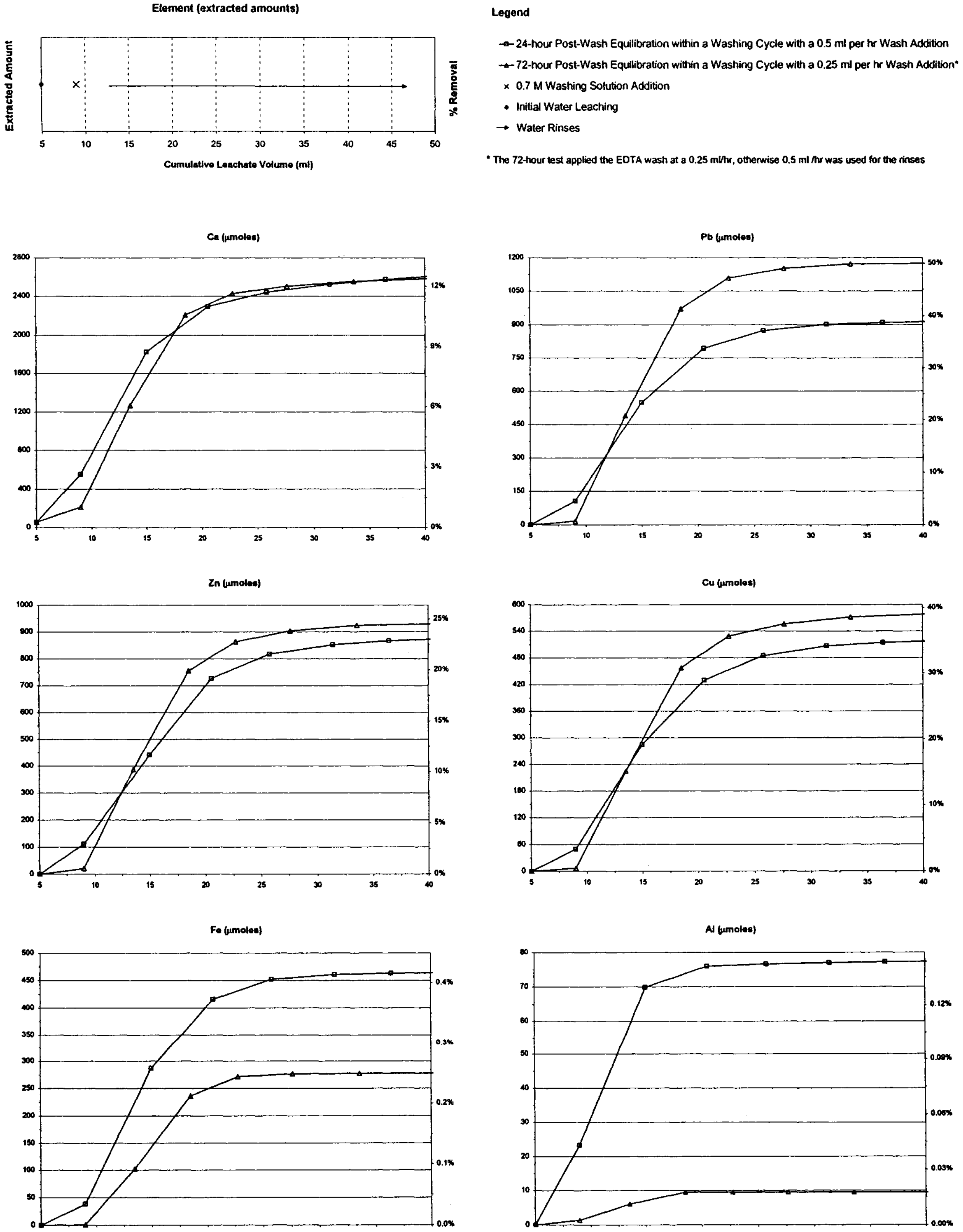
At the end of the EDTA+CA washing cycles, the leachability of the potentially toxic metals was greater than that of the three EDTA washing cycles. This perhaps resulted from the resorption of trace metals, previously complexed with citric acid, onto soil particles following citric acid's biodegradation. These trace metals would have gradually leached, due to ongoing EDTA dissolution kinetics within the soil, rather than remaining immobile as in the citric acid treatment of section 6.3. Hence, residual EDTA in the soil would have likely complexed and rinse-extracted these metals.

7.5 Increasing the Equilibration Time of the EDTA during an Unsaturated Wash

An increased equilibration time was sought by: (i) increasing the post-wash residual EDTA within the soil; and (ii) giving post-wash residual EDTA within the soil more time to extract the targeted metals. The soil's residual post-wash EDTA, was increased by applying the 0.7 M washing solution at half the flow rate (0.25 ml hr^{-1}). The lower flow rate slowed the passage of the wash through the soil and would have reduced the portion of EDTA that exited in the leachate. Furthermore, the soil-retained EDTA was given 72 hours to equilibrate instead of the previously used 24 hours (fig. 7.4). The modified treatment is referred to as the 72-hour extraction.

Cutting the washing solution flow rate in half reduced the amounts of extracted metals within washing solution leachate; the EDTA levels in the washing solution leachate would have been reduced proportionately. Therefore, more EDTA would have remained in the soil following the washing solution addition. Together, the increase in the post-wash residual EDTA and the 72-hour equilibration time extracted significantly more Pb (at the 95% level), as compared to the 24-hour treatment (table 7.5); the extraction of Pb increased by 28% or 259 mmol (table 7.6). In contrast, the 72-hour extraction decreased significantly the extractions of Fe, Al, Mg and S (at the 95, 99.9, 99 and 99.9% levels); the extractions of Fe, Al and Mg decreased by 187, 68 and 100 mmol, while that of S decreased by 27%.

FIGURE 7.4 a Cumulative Unsaturated Column Extractions from a 0.25 ml/hr Wash Addition within an EDTA Washing Cycle as a 1:5 L:S Ratio to 25 g



* The 72-hour test applied the EDTA wash at a 0.25 ml/hr, otherwise 0.5 ml /hr was used for the rinses

FIGURE 7.4 b Cumulative Unsaturated Column Extractions from a 0.25 ml/hr Wash Addition within an EDTA Washing Cycle as a 1:5 L:S Ratio to 25 g

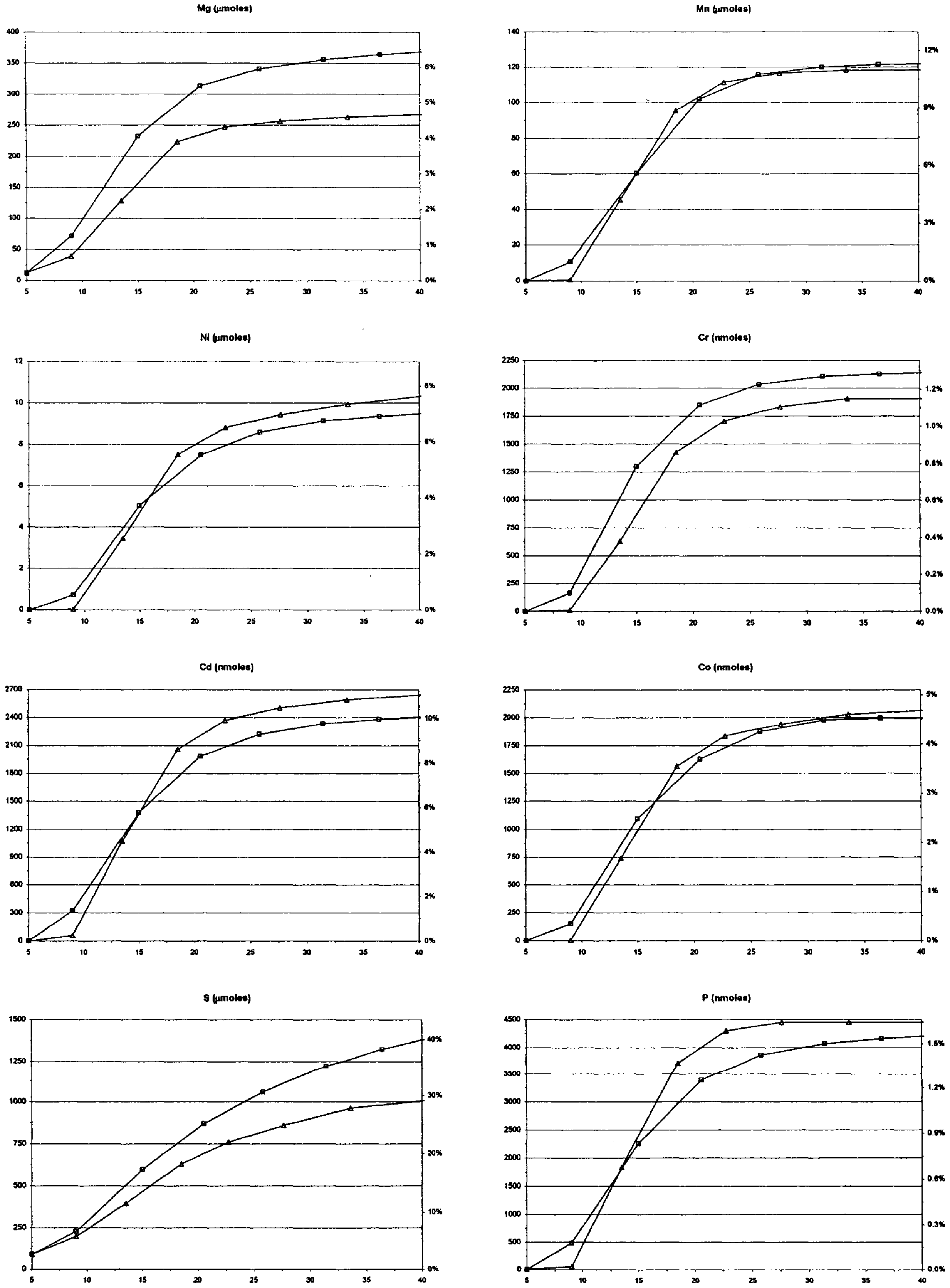


Table 7.5 t-test of the Cumulative Extractions of a 72-hour to a 24-hour Post-Wash Equilibration within a Washing Cycle[5]

Element	Long Time x Short Time Hours (ml per hour)	t	*P*	Unequal Variances*
Al	72 (0.25) x **24 (0.5)**	-6.87	0.0005 ***	
Ca	72 (0.25) x 24 (0.5)	-0.82	0.4443	
Cd	72 (0.25) x 24 (0.5)	1.03	0.3436	
Co	72 (0.25) x 24 (0.5)	0.21	0.8383	
Cr	72 (0.25) x 24 (0.5)	-0.55	0.6000	
Cu	72 (0.25) x 24 (0.5)	0.87	0.4194	
Fe	72 (0.25) x **24 (0.5)**	-3.31	0.0163 *	
Mg	72 (0.25) x **24 (0.5)**	-3.91	0.0078 **	
Mn	72 (0.25) x 24 (0.5)	-0.85	0.4279	
Ni	72 (0.25) x 24 (0.5)	0.31	0.7691	
P	72 (0.25) x 24 (0.5)	0.42	0.6911	yes
Pb	**72 (0.25)** x 24 (0.5)	3.32	0.0160 *	
S	72 (0.25) x **24 (0.5)**	-6.52	0.0006 ***	
Zn	72 (0.25) x 24 (0.5)	1.84	0.1147	

Bold numbers identify the treatment with the higher extraction

*** 99.9%, ** 99% or * 95% Significance Level

[5] The wash that was given a 72-hour equilibration was applied at 0.25 ml h^{-1}, otherwise a flow rate of 0.25 ml h^{-1} was used

Table 7.6 Increase in Extractions from a 24 to a 72-hour Washing Solution Retention for an Unsaturated Washing Cycle

Ca	Pb[c]	Zn[d]	Cu[d]	Fe	Al	Mg	Mn[c]	Ni[b]	Cr[b]	Cd[d]	Co[b]	S	P
(-0.7%)	28.6%*	6.8%	12.3%	(-40.2%)*	(-87.7%)***	(-27.1%)**	(-2.8%)	11.1%	(-11.0%)	10.6%	4.6%	(-26.6%)***	5.4%

[b] B-Level initial criterion, [c] C-Level initial criterion, [d] D-Level initial criterion

*** 99.9%, ** 99% or * 95% Significance Level

The longer equilibration time likely permitted the EDTA to more selectively complex Pb instead of Fe, Al and Mg, which were 1st, 2nd and 4th in abundance in the *M-soil.* The extraction of Ca, the 3rd most abundant element in the soil, was unaltered. Although the differences in the extractions of Zn, Cu, Ni, and Cd between the treatments were not significant, the 72-hour treatment showed a tendency to extract more of these chalcophiles (10% on average), as compared to the 24-hour treatment. It is hypothesised that the 72-hour treatment increased (*e.g.* Pb) or tended to increase the extraction of the chalcophiles (*e.g.* Zn, Cu, Ni & Cd) by favouring their transfer from the sulphides minerals to the EDTA. In exchange for the chalcophiles, Fe, Al and Mg would have decomplexed from EDTA and would have sorbed onto sulphides minerals, as the total decrease in extractions of Fe, Al and Mg (355 mmol) was similar to the decrease in extraction of S (*i.e.* 371 mmol).

7.6 Summary and Conclusions

The application of the EDTA washing solution to a dry soil instead of a moist soil decreased EDTA's extraction of Cu, Mn, Cd and Co. Increasing the oxidising conditions of the unsaturated extractions with convective airflow, with the ensuing crystallization of the drying soil solution, was inhibitory to EDTA removal of Mn and Co. The use of a citric acid washing cycle amongst EDTA washing cycles was disadvantageous as it decreased the extraction of Pb and the overall removal of trace metals, while adversely increasing the post-treatment leachability of these metals. Thereby, the first three modifications were rejected for their use in an unsaturated extraction procedure.

Increasing the soil-EDTA equilibration time was achieved by: (i) reducing the unsaturated flow rate by half, which left more residual EDTA within the soil after the soil washing; and (ii) waiting 72 hrs before applying the first rinse. By doing so, the extraction of Pb increased, while the extraction of the other chalcophiles showed a tendency to increase. As a result, the extractions of Fe, Al and Mg decreased, as did that of S.

From the results of the 72-hour equilibration experiment and of the previous column experiments, the extractions of Cr and Co either behaved like the extraction of Mg or Mn. It is hypothesised that Mg, Cr and Co were probably found within Mn nodule precipitates, which were likely abundant due to the Mn contamination. Chromium and Co might have also been associated with soluble Mg precipitates, but likely to a lesser extent.

The extraction of Pb was improved by increasing the EDTA equilibration time with the soil. The secure landfill soil was highly contaminated with Fe and a variety of trace metals, of which the amounts of Pb, Zn and Cu greatly exceeded the D-Level criterion (table 4.2). In contrast to Pb and Cu, the treated *M-soil*'s Cd level remained well above the C-Level criterion. The extremely low initial Cd content likely favoured a more selective and strongly bound co-precipitation, which would have made Cd more difficult to dissolve. In addition, Cd has a low EDTA formation constant (pK_f 6.5). Even if an increased equilibration time were to improve the extractions of Zn and Cd, it would likely be insufficient to decontaminate the *M-soil*, while maintaining the cumulative *EDTA:S* below a 15% wt target.

Preface to Chapter 8

Pilot-scale experiments, with increased equilibration times as per the finding of chapter 7, were done for both citric acid and $(NH_4)_2$EDTA. The experiments were carried out on the *J-soil*, whose only D-Level contaminant was Pb (*i.e.* 3.9%wt). To limit the decomposition of citric acid, the citric acid flash washing was done under saturated conditions in large columns; each sequential 1:8 *L:S* ratio wash addition was allowed to equilibrate for 48 hours. For the unsaturated-flow extraction with $(NH_4)_2$EDTA, the addition of the washing solutions in a very small *L:S* ratio (1:40) permitted to increase the equilibration time. The washing and rinsing solutions of the $(NH_4)_2$EDTA experiment were added atop small soil heaps with drip irrigation.

8

Pilot-Scale Experiments of a Citric Acid Saturated Flash Washing and $(NH_4)_2$EDTA Unsaturated-Flow Flash Washing

The previously examined secure landfill *M-soil* was contaminated with Fe and various trace metals. Following five washing cycles, which added an *EDTA:S* of 22.3% wt, the Zn and Cd levels were still well above the C-Level criterion. Even if the *M-soil* had been treated with a flash washing, with increased EDTA retention times, its Zn and Cd decontamination was unlikely. Therefore, the previously acquired knowledge was tested on the *J-soil* instead. The *J-soil* was contaminated with an extremely high levels of Pb (*i.e.* 3.9%). In contrast to the *M-soil*, Pb was the only potentially toxic trace metal in the *J-soil* present in excess of the D-Level criterion (table 3.2).

In order to better mimic an on-site treatment of excavated soil, the experiment was scaled-up from the previous small column experiments to large columns and small soil heaps. The scale-up would better represent the characteristic heterogeneities that are found within larger volumes of excavated soils, and might adversely affect the internal dispersion of the washing and rinsing solutions.

The objective of this experiment was to establish a pragmatic decontamination process, which would allow the *J-soil* to be used as fill for an industrial site (*i.e.* B-level criterion). As a requirement, an environmentally sustainable reclamation of the *J-soil* needed to ensure that the post-treatment leachable levels of Pb were below toxic levels. Investigation into the post-treatment leachability of Pb was conducted two years after the EDTA additions.

8.1 General Methodology

The pilot-scale flash washing consisted of successive washes with subsequent rinses..

The reclamation of the contaminated *J-soil*, obtained from an abandoned car battery manufacturing plant, was investigated at a pilot-scale level (1:10 000). In these experiments, the *J-soil* was sieved to 4 mm. The extraction and post-treatment leachability of Pb were examined for a citric acid flash washing experiment and an EDTA flash washing experiment. Both experiments were done in triplicate and used tap water as the diluting and rinsing liquid. The extraction solutions were analysed with a VARIAN *VISTA-MPX*, a radial ICP-OES. The results are presented as averages of the triplicates.

For the statistical analysis, the STATGRAPHICS®*PLUS 4.0* software was used to compute the t-tests. STATGRAPHICS®*PLUS* was also used to assess the equality of the variances between the two treatment populations, as well as the normality of each population's distribution.

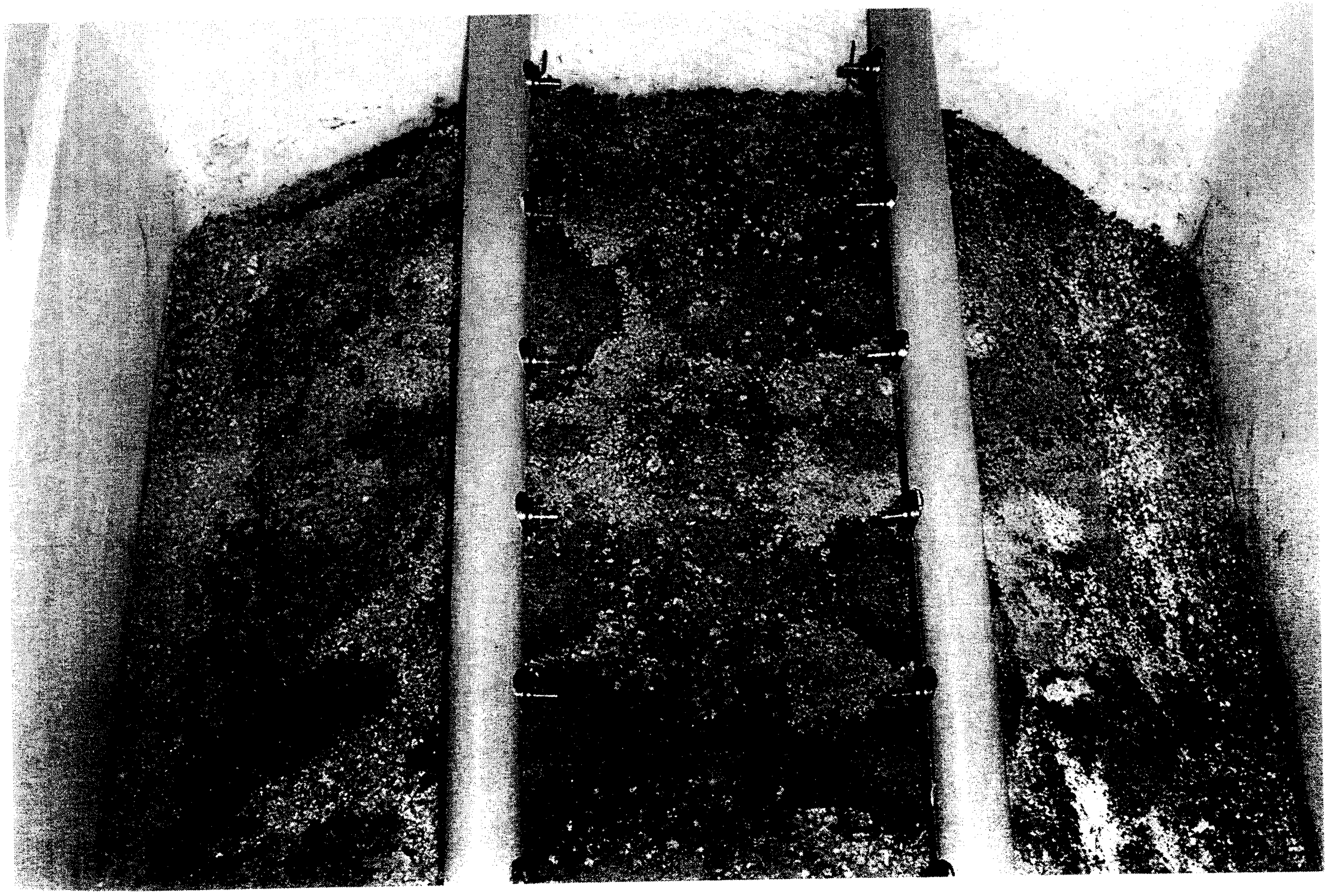
8.2 Citric Acid Saturated Flash Washing of 33 kg Soil Columns

Although citric acid is a weaker chelating agent than EDTA, its rapid biodegradation and resulting lower post-treatment leaching of toxic levels of trace metals warranted further investigation (chapter 6). In order to increase the extraction of Pb, the decomposition of citric acid was limited by conducting a flash washing experiment under saturated conditions. The flash washing consisted of 15 consecutive citric acid washes, for which each wash was equilibrated within the soil for 48 hours.

This saturated experiment was carried out in 1 m high and 20 cm in diameter columns. To establish the initial water-leachable Pb levels, the *J-soil* columns were leached 15 times with tap water. After which, 0.5 M citric acid washes (1:8 *L:S* ratios) extracted the *J-soil* columns. The leaching and washing solutions were added through the bottom of the 32.7 kg columns. The recovered volumes were equal to the drainable pore volumes (*c.a.* 4 L), for both the water leaching and citric acid flash washing. Upon completion of the washes, the *J-soil* was left undisturbed in the columns for 1 year.

In order to measure the citric acid post-treatment leachability of Pb, the *J-soil* was removed from the columns and submitted to unsaturated rinses. Within 105 L polyethylene basins, measuring 50 x 50 cm, the *J-soil* was made into 32.7 kg soil heaps (picture 2). The basins had a sloping bottom leading to a 5 cm drain, through which the leachate was recovered. The irrigation was supplied by twelve NETAFIM drippers, with the specifications of delivering 2 L hr^{-1} at 207 kPa. However, the experimental flow rate design was roughly 50 ml hr^{-1} dripper^{-1}. The drippers were installed at 8 cm intervals along two longitudinal conduits, which were placed atop the soil heaps. The distance between the drippers from conduit to conduit was 12 cm.

PICTURE 2 Drip-Irrigated 32.7 kg *J-soil* Heaps



The results are presented in figure 8.1. The *J-soil's* initial water-leachable levels for Pb were extremely high, ranging from 7.86 mg L^{-1}, initially, down to 683 µg L^{-1}. These levels were roughly 800 and 70 times those of the allowable drinking water standards of 10 µg L^{-1} (MENV, 2001), and likely resulted from the remnants of the sulphuric acid that carried the Pb into the soil. The 15 washes added 18.1% wt of citric acid soil^{-1}, produced 190% wt more leachate than the *J-soil* it treated, but removed only 2.2% wt of the Pb.

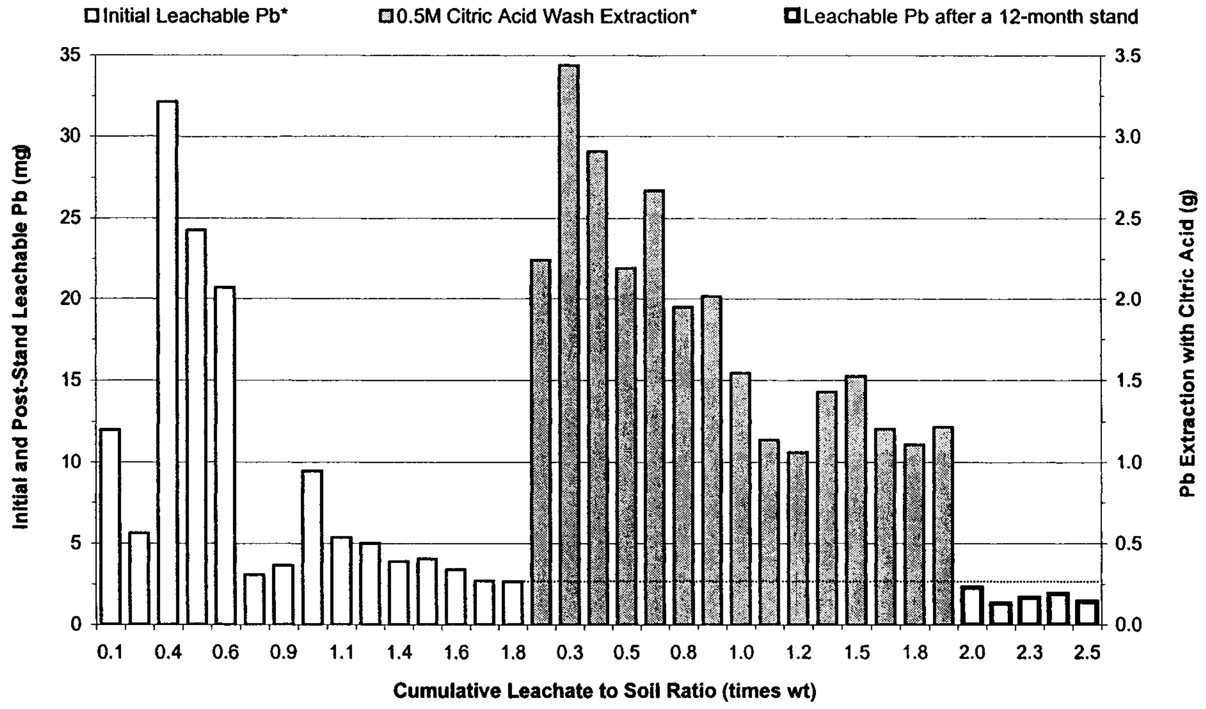
In the leachate collected after the12-month stand, the water-leachable levels of Pb were reduced below 590 µg L^{-1}. As compared to the initial water-leachable levels, this reduction was likely due to the removal the most easily dissolvable Pb by the flash washing, and to the biodegradation of the residual citric acid during the 12-month stand. The citric acid decomposition products may have coated the soil particles and helped stabilised the Pb. However, the reduced post-treatment leaching of Pb might not prevail in outdoor settings, where inputs of organic acids from decaying OM may adversely effect trace metal mobility; in section 7.4, the addition of an EDTA washing cycle following a citric acid washing cycle led to increased post-treatment leachability.

8.3 Diammonium EDTA Unsaturated-Flow Flash Washing of 33 kg Heaps

This experiment was carried out on the 32.7 kg *J-soil* heaps of the previous experiment, which underwent a saturated citric acid flash washing a year earlier. At the onset of the experiment, the moisture content of the heaps was approximately 21% wt. The washes and ensuing rinses were generally added in successive 1:40 *L:S* ratios, with 24-hour intervals between them. However, some sequences were made as multiple 1:40 *L:S* ratio additions and were regarded as juxtaposed 1:40 additions within a 24-hour sequence. For an un-juxtaposed wash addition, the 1:40 *L:S* ratio gave the EDTA a retention time in excess of 48 hours. Later on in the experiment, some rinses were added after a 7-day, 1-month or 12-month delay, instead of the general 24-hour interval.

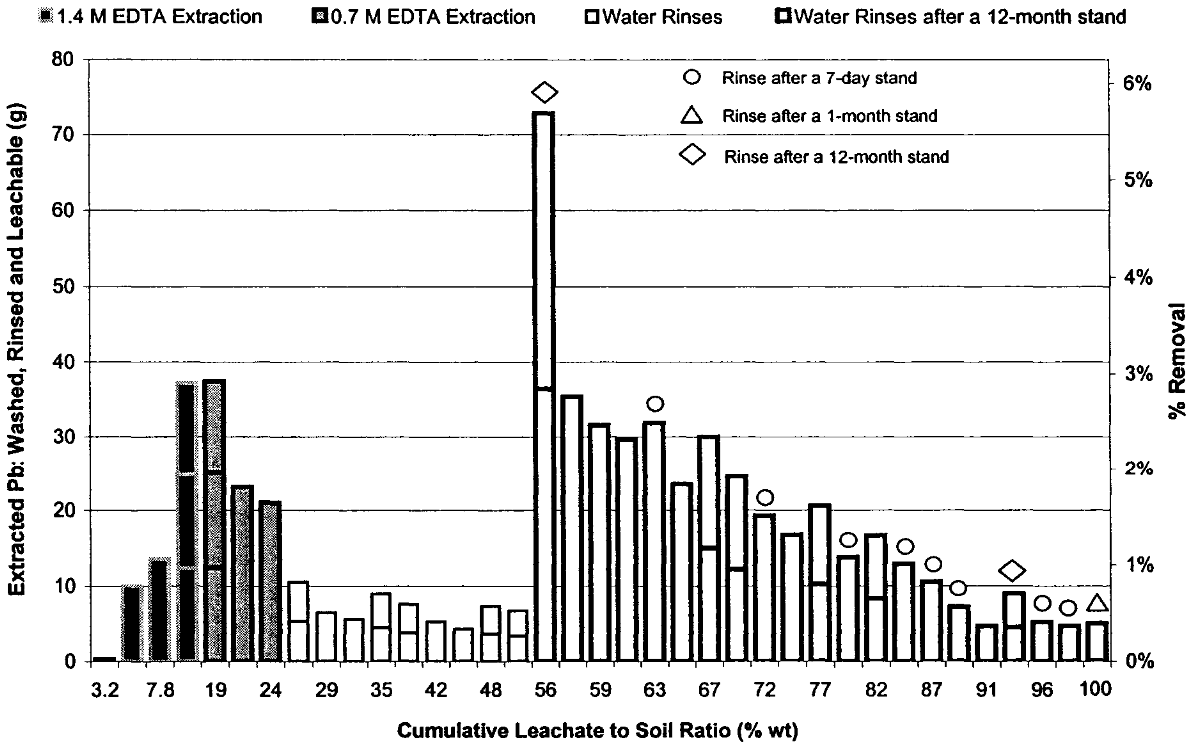
Varying factors such as viscosity of washing solutions of different concentrations, daily evaporation, moisture retaining capacity of the soil and unsaturated fluid dynamics did not permit the recovery of repetitive leachate volumes. The 1:40 *L:S* ratio additions gave an average leachate volume of 675 ml with a 25% variation. The amounts of extracted Pb are reported for each 675 ml±25% volume. When juxtaposed 1:40 additions were used, results are presented for each 675 ml±25% aliquot (fig. 8.2).

FIGURE 8.1 Water Leachable Pb and Extracted Pb from a Citric Acid Saturated Flash Washing of 33 kg Columns



* Credit is given to Dr Raman Bassi for carrying out this work (Bassi, 2000)

FIGURE 8.2 Extraction of Pb from 33 kg Soil Heaps from an Unsaturated-Flow EDTA Flash Washing



In order to reduce the cumulative leachate volume, a 1.4 M EDTA flash washing, consisting of seven aliquots, was used to rapidly load the soil with EDTA; this provided a soil solution with a very strong EDTA ionic strength to increase the extraction efficiency (chapter 4). The addition of the seven 1.4 M aliquots totalled a 1:7 *L:S* ratio. For the latter additions, evaporation losses of roughly 0.75 mm day^{-1} (150 ml day^{-1}) caused the precipitation of EDTA salts on the exposed surfaces of the heaps.

Five 0.7 M EDTA aliquots followed the seven 1.4 M washes, thereby gradually diluting the ionic strength of the soil solution before the addition of the ensuing rinses; such a sequence of events would permit to more rapidly rid the *J-soil* of EDTA and toxic levels of leachable trace metals upon rinsing. Overall, the 11 washes produced a cumulative leachate to soil (Σ*L:S*) ratio of 24% wt. Once the Σ*L:S* ratio of the washes and ensuing rinses attained 53% wt, the soil was left to stand for 12 months. This gave the residual soil-retained EDTA a prolonged extraction time. Yet, the effective extraction time was less than 12 months: the heaps gradually dried out, thereby inhibiting chemical reactivity. The heaps were re-rinsed after this 12-month stand.

When interpreting figure 8.2, the following two factors need to be considered: (i) larger leachate volumes, which were divided into 675 ml ±25% aliquots, extracted more Pb, but in a more dilute solution; and (ii) longer extraction times caused supplemental dissolution of Pb and therefore increased the extraction efficiency. The wash extractions increased until the first 0.7 M EDTA wash, after which the extracted amounts of Pb declined until the 53% wt cumulative leachate. The 1st and 2nd 1.4 M EDTA aliquots were juxtaposed and composed the 1st wash sequence. Together, these 675 ml ±25% aliquots extracted almost no Pb. Hence, the quasi-totality of EDTA from the 2 x 1:40 aliquots were retained for at least 24 hrs (*i.e.* a 24-hour percolation time), which satisfied the recommendation to increase the post-wash residual EDTA (section 7.5). For the washes, the highest concentration of recovered Pb was 26.1 mg L^{-1}, obtained in the leachate of the first 0.7 M EDTA wash sequence. Due to the 24-hour percolation time for two 675 ml ±25% aliquots, this peak was therefore attributable to the last 1.4 M EDTA wash sequence.

Once 53% wt of cumulative leachate was reached, the soils heaps were left undisturbed for 12 months (*i.e.* 12-month stand). Following this unsaturated equilibration time of several months, a single 675 ml ±25% aliquot from the tap water rinse extracted much larger amounts of metals, as compared to any previous wash extraction. During the 1st rinse following the 12-month stand, the leachate reached a maximal Pb concentration of 66.4 mg L^{-1}, which was, on an aliquot basis, 3.2 times that of the maximum wash extraction and 16.1 times that of the previous water rinse. This was attributable to the prolonged equilibration time, given that the residual soil-retained EDTA was at its lowest level since the beginning of the experiment. Moreover, the amounts of residual EDTA retained in the soil after the 53% wt of cumulative leachate were much smaller than those in the soil at any other time under the washing solution additions.

Following the 12-month stand, the tap water rinses extracted significantly more Pb in their first 21% wt $\Sigma L{:}S$ ratio, as compared to the 53% wt $\Sigma L{:}S$ ratio prior to the 12-month stand ($t = -2.85$, $P = 0.0464^{*}$). This increased extraction was outstanding, since it was achieved although much of the added EDTA had been lost before the 12-month stand. Moreover, close to ⅔ of the total extracted Pb occurred after the 12-month stand.

For the *J-soil* to meet the C-Level criterion for industries, 97.4% of the Pb needed to be extracted. After reaching a $\Sigma L{:}S$ ratio of 1 by weight, 49.4% of the Pb had been extracted: slightly more than half of the Pb removal required to decontaminate the *J-soil*. The 1.4 and 0.7 M EDTA washes added an *EDTA:S* tallying 10.6% wt, of which the seven 1.4 M aliquots accounted for 7.8% wt.

Although the last rinse still contained 7 132 mg L^{-1} of Pb, increasing the extraction time became somewhat irrelevant, as seen by the small extraction increase that was obtained after a second 12-month stand (i.e. 94% wt $\Sigma L{:}S$ ratio). It is assumed that most of the residual EDTA had already complexed with Pb following the original 12-month stand. The last rinse (*i.e.* 100% wt $\Sigma L{:}S$ ratio) contained 1.5 times more Pb, on an aliquot basis, than the last rinse that preceded the 12-month stand (*i.e.* 53% wt $\Sigma L{:}S$ ratio). Continued rinsing of the soil would have produced large volumes of leachate without extracting the large amounts of Pb that were required to decontaminate the *J-soil*. Hence, re-adding fresh EDTA to the heaps and immediately giving them a prolonged extraction time was required. However, the experiment concluded by establishing a generic protocol for the unsaturated extraction procedure.

Greater amounts of post-wash residual EDTA within the soil coupled with long unsaturated equilibration times would be instrumental in increasing the extraction efficiency of EDTA. Hence, it is estimated that a more efficient and greater extraction of Pb would be obtained by: (i) adding a single 1.4 M EDTA wash, as a 1:20 *S:L* addition to well moistened *J-soil*, which would allow the bulk of the EDTA to be retained in the heaps; and (ii) immediately letting the post-wash residual EDTA equilibrate within the soil for several months. When provided with a very long extraction time, such a 2.2% wt *EDTA:S* addition could increase the extraction of Pb beyond the amounts that were extracted as a result of the 12-month stand.

8.4 Summary and Conclusions

Treating the *J-soil* with a citric acid flash washing demonstrated that citric acid is not strong enough to remediate soils highly contaminated with Pb. However, by biodegrading, citric acid reduced the post-treatment leachability of toxic levels of Pb by a small amount. Unfortunately, this reduction in Pb leachability was insufficient to detoxify the *J-soil* leachate. Furthermore, the apparent reduction in Pb mobility might not persist in natural settings, where percolated water containing dissolved OM would be more reactive than the tap water used in this experiment.

It was possible to use a concentrated 1.4 M EDTA unsaturated washing solution without hindering the extraction capability of the EDTA. The soil had been loaded with EDTA by sequentially adding, in 1:40 *L:S* ratios and with 24-hour intervals, seven 1.4 M and five 0.7 M aliquots. Following the flash washing, giving the residual EDTA in the soil an extraction time of several months greatly increased the extraction Pb from the soil heaps. However, by limiting the inputs of EDTA to environmentally sustainable amounts, it seems unlikely that the Pb level in the *J-soil* could have been reduced below the 1 000 mg kg^{-1} required by the C-Level criterion.

The persistence of EDTA in the heaps is of grave concern and not easily solved. Zeng *et al.* (2001) estimated that up to 23.5% of EDTA was retained by the soil, following six batch extractions with a recycling of the washing solution. By sorbing onto the soil particles and resisting decomposition, small amounts of the residual EDTA would continue to leach potentially toxic complexes over longer periods, as was observed in this experiment. Residual amounts of EDTA are likely to persist as complexes within the soil, even after several rinses or attempts to biodegrade the EDTA with acclimated bacteria (Hong *et al.*, 1999). Bacteria in soil treated with large amounts of EDTA would likely not survive. Re-inoculation of the soil would only be beneficial once the soil-retained EDTA is reduced to trace levels. Remediating soils contaminated with trace metals could tend to spread the contamination by increasing the mobility of the potentially toxic trace metals that remain in the soil, thereby making it an environmentally unsustainable endeavour.

By leaching toxic levels of Pb, the parent site of the *J-soil* undoubtedly poses health risks to the neighbouring community. With the knowledge of all the previous experimental results, it is believed that stabilising the Pb in the *J-site* by cementing it with an alkaline amendment could limit the leaching, at least temporarily. As a barrier against ingestion of contaminated soil, the *J-site* needs to be covered with 50 cm of clean fill of low organic matter and neutral pH. Yet in the end, the most viable remediation process for the severely Pb-contaminated *J-site* could end-up being excavation, stabilisation, cementation, and secure cell burial (*e.g.* STABLEX).

By relocating C-Level soils, with leachable Pb, to secure landfills, perhaps the leachable Pb would strongly sorb onto other soil particles present in the landfill and become immobile. Such leaching and sorption of trace metals within the landfill might have caused, in part, the contamination of the *M-soil*. Prior to treatment, none of the trace metal contaminants in the *M-soil* were leachable under water rinsing. Perhaps the PCBs contamination helped in stabilising the trace metal contaminants within the *M-soil*.

Preface to Chapter 9

In this chapter, the leachate from the $(NH_4)_2EDTA$ unsaturated pilot-scale experiment underwent different treatments. The goals were to limit chemical inputs, precipitate out the Pb and produce the least amount of solid waste by-product. Thus, chemicals inputs intended to selectively precipitate out the Pb from the severely contaminated leachate (*i.e.* 2.0% wt of Pb). Necessarily, the Pb had to be more concentrated in the solid waste, as compared to the initial soil for the process to be successful. Evaporation of the leachate was also examined, as a means to concentrate the Pb into a dehydrated waste product.

9 Treatment of Pb-laden Leachate from $(NH_4)_2$EDTA-treated Soil Heaps

Leachate treatment is an intrinsic part of the development of an environmentally sustainable soil washing process for soils with potentially toxic levels of trace metals. The leachate, from such a decontamination process, inevitably contains high levels of organically complexed trace metals. The challenge is to selectively precipitate out and concentrate the toxic metals. These precipitates (*i.e.* end-of-procedure by-products) can either be disposed of in cells at secure landfills, or potentially be purified for the recovery of the trace metals. The treatment of the leachate could perhaps regenerate the EDTA by freeing it from the more strongly complexed potentially toxic trace metals.

The effective use of Na_2S to precipitate toxic trace metals out of solutions has been reported (Bhattacharyya *et al.*, 1979; Skoufadis *et al.*, 1997). Using $Ca(OH)_2$ to raise leachate pH was reported to favour Na_2S precipitation of trace metals (Hong *et al.*, 1999; Zeng *et al.*, 2001); after which, the supernatants were re-acidified with HNO_3 for re-extraction of the contaminated soils. Herein, the environmental and economical benefits of EDTA leachate regeneration by Na_2S precipitation for recycling were estimated and compared to adding fresh EDTA for the re-extraction of the *J-soil*. The straightforward approach of leachate evaporation was also examined.

9.1 Characteristics of the *J-soil* leachate

The individual leachate volumes, obtained from the $(NH_4)_2$EDTA flash washing of the *J-soil* heaps, were mixed together in a reservoir; in total, 98.2 L were collected. The covered reservoir was equipped with venting holes, which allowed evaporation, concentration and supersaturation the recovered leachate; this caused the precipitation of CaEDTA salts. The final cumulative leachate mixture had a density of 1.05 g cm^{-3}. Table 9.1 lists the elemental composition of the leachate and tables 9.2 ranks the elements in mole quantities, as found within the 25 ml experimental aliquots.

Table 9.1 Levels in the Cumulative Leachate from the EDTA Unsaturated Flash Washing of the *J-soil* (μg ml^{-1})

Al	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Na	Ni	Pb	Zn	P	S
2.76	7478	0.42	0.27	0.52	4.53	741.3	34.4	429.9	37.8	66.5	3.79	20306	63.1	1.14	789.1

Table 9.2 Amounts in 25 ml of Cumulative Leachate from the EDTA Unsaturated Flash Washing of the *J-soil* (μmol)

Ca	Pb	S	Mg	Fe	Na	Zn	K	Mn	Al	Cu	Ni	P	Cr	Co	Cd
4664	2450	615	442	332	72	24	22	17	3	1.78	1.62	0.93	0.25	0.11	0.09

9.2 Treatment of the Cumulative Leachate by Thermal Dehydration

Dehydration is an inexpensive approach that was evaluated for its ability to condense the post-treatment by-products. Unfortunately, dehydration is unrefined as it concentrates all metal and metalloid elements into a toxic solid waste product, devoid of water and volatile components. The resulting waste could be disposed of in cells of a secure landfill, or perhaps recycled for its trace metal contents.

Prior to dehydration, the evaporation losses saturated the cumulative leachate and triggered roughly 49.8% of the extracted Ca to precipitate out as CaEDTA. These pre-treatment precipitates amounted to 2.3% wt soil^{-1}; it is unsure if they could have been dissolved to re-extract the soil.

The dehydration of the leachate yielded a solid waste that amounted to 12.7% wt soil^{-1}, which was mainly composed of EDTA (73.3%), followed by Pb, which made up about 13.6% wt soil^{-1} (table 9.3). The dehydrated waste insufficiently concentrated the Pb by a factor of 3.76, relative to the initial *J-soil* content. Moreover, the solid wasted stemmed from a soil for which only half of the required removal of Pb was achieved (*i.e.* 49.4%). Hence, the dehydration procedure produced too much waste, thus was not environmentally sustainable. It is hypothesised that 6% wt of the dehydrated waste came from citric acid degradation products, that were left over from the previous *J-soil* pilot-scale treatment.

Table 9.3 Composition of the Waste from the Dehydrated Cumulative Leachate Mixture and Waste to Soil Ratios

	Amounts in the Pre-Treatment Precipitates and the Dehydrated Waste (wt wt^{-1})				
	EDTA	Pb	Ca	Fe	Mg
Pre-Treatment Precipitation of CaEDTA	84.3%	1.05%	6.90%	0.13%	0.03%
Dehydration of the Leachate	73.3%	13.6%	5.0%	0.50%	0.29%
EDTA : *J-soil (EDTA : S)*			10.6% wt		
Pre-treatment precipitated CaEDTA salts : *J-soil*			2.3% wt		
Dehydrated waste : *J-soil*			12.7% wt		
Initial Pb content in the *J-soil*			3.91% wt		
Final Pb content in the *J-soil*			1.97% wt		
Concentration factor of the dehydrated Pb waste to the initial *J-soil*			3.76 times		

9.3 Chemical Treatment of the Cumulative Leachate with Na_2S

The generic term Na_2S was used to abbreviate $Na_2S{\cdot}9H_2O$.

The molecular weight of $EDTA^{-4}$ is 288 g and is heavier than Pb (*i.e.* 207 g), the heaviest of the examined metals. If EDTA was to bind solely with Pb in a solution and that the EDTA-Pb complexes were precipitated out, EDTA would make up 58% wt of the solid waste. Therefore, to further concentrate the waste product, the Pb in solution must be precipitated out as a much lighter salt. This requires that the Pb be de-complexed from the heavy EDTA molecule and precipitated as PbS or $Pb(OH)_2$. Although the main objective was to concentrate the Pb into a solid waste, the feasibility of recycling a treated leachate to extract the soil anew was also considered.

9.3.1 Methodology

Experiments tested the effectiveness of different additions of Na_2S and combined additions of Na_2S and $Ca(OH)_2$ to precipitate out the EDTA-complexed Pb. In addition, the results include the precipitation responses of Ca, Fe and Mg, the three most abundant non-toxic metals within the leachate. The mixtures were equilibrated for 24 hrs, the resulting suspensions were centrifuged and the supernatant fractions were recovered for analysis.

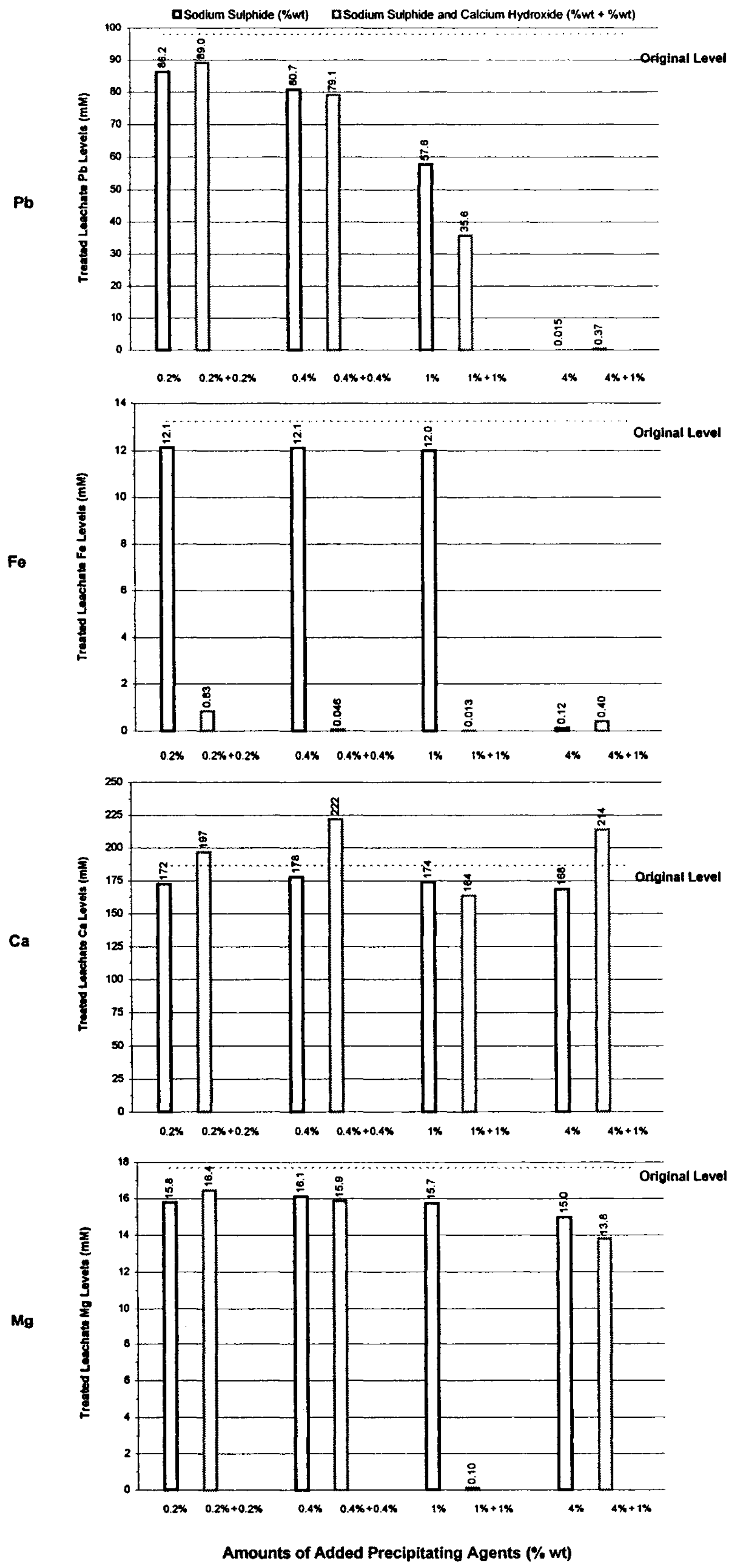
The experiments were carried out in quadruplicate. The solutions were analysed with a VARIAN *VISTA-MPX*, a radial ICP-OES. The results are presented as averages. The confidence intervals of the four-sample populations and the normality of each population's distribution were confirmed with the STATGRAPHICS®*PLUS 4.0* software.

9.3.2 Use of Na_2S and $Ca(OH)_2$ in Equal Proportions

The leachate levels of Fe and of the weaker EDTA-complexed Ca and Mg were best left unreduced, since their precipitation would unduly increase the amount of solid waste. However, the precipitation of Fe could be beneficial for regenerating and recycling the leachate, as it would liberate EDTA from the strongly complexed Fe^{3+}. The amount of EDTA-complexed Fe^{2+} was assumed to be negligible.

Figure 9.1 compares the molarities of the Pb, Fe, Ca and Mg in the supernatants that resulted from the additions of Na_2S alone to those that resulted from the combined

FIGURE 9.1 Preliminary Na_2S and $Ca(OH)_2$ Leachate Precipitation of the Four Most Abundant Metals



additions of Na_2S and $Ca(OH)_2$. For the lower two combinations of Na_2S and $Ca(OH)_2$, the latter helped in precipitating the EDTA complexed with Fe, but not with Pb. In the combined 1% wt addition, $Ca(OH)_2$ helped precipitate Fe and Pb, but the Pb in solution was still too high.

The addition of 1% wt of $Ca(OH)_2$ with 4% wt of Na_2S reduced the precipitation of Pb and Fe, as compared to the addition of 4% wt Na_2S alone. However, the combined addition increased Mg and Ca precipitation, thereby unfavourably increasing the amount of solid waste; the amount of precipitated Ca was roughly equivalent to 80% of the Ca that was added in the 1% wt addition of $Ca(OH)_2$.

By helping decomplexe Fe from EDTA, the use of $Ca(OH)_2$ might have been beneficial for EDTA regeneration, with the exception of the 4 and 1% wt Na_2S combinations (table 9.4). Alone, the 4% wt Na_2S addition was the most efficient of all. The latter precipitated out the quasi-totality of Pb and Fe, thereby theoretically regenerating 3.63% wt of the EDTA (*i.e.* 2.8 mmol). The last two columns of table 9.4 present the hypothetical reduction of chemical inputs (*i.e.* Na_2S & EDTA combined) that might be afforded by regenerating and recycling the leachate. For example, the 4% wt addition of Na_2S would have led to an additional chemical input of at least 0.37% wt.

Table 9.4 Precipitated Pb and Fe from Combined Additions of Na_2S and $Ca(OH)_2$ and the Effects on EDTA Regeneration

Inputs of Precipitating Agents			Precipitation of Strongly EDTA-complexed Cations				Regenerated	Theoretical effect of recycling the leachate on the chemical input requirements *cf.* Regenerated EDTA to Precipitating Agents	
Na_2S	$Ca(OH)_2$	Total	Pb		Fe		EDTA		
% wt[L]	% wt[L]	% wt[L]	% removal	% wt[L]	% removal	% wt[L]	% wt[L]	Δ (% wt)	Ratio (%)
0.2%	-	0.2%	12.0%	0.24%	8.7%	0.01%	0.42%	0.22%	2.11
0.2%	0.2%	0.4%	9.1%	0.19%	93.7%	0.07%	0.70%	0.30%	1.74
0.4%	-	0.4%	17.6%	0.36%	8.7%	0.01%	0.60%	0.20%	1.50
0.4%	0.4%	0.8%	19.3%	0.39%	99.7%	0.07%	1.05%	0.25%	1.31
1%	-	1%	41.2%	0.84%	9.7%	0.01%	1.36%	0.36%	1.36
1%	1%	2%	63.7%	1.29%	99.9%	0.07%	2.47%	0.47%	1.23
4%	-	4%	100%	2.03%	99.1%	0.07%	3.63%	(-0.37%)	0.91
4%	1%[f]	4%	99.6%	2.02%	97.0%	0.07%	3.61%	(-1.39%)	0.90

[L] With respect to the leachate

[f] The solubility of $(CaOH)_2$ hindered its use beyond 1%

The regeneration data are speculative, as they present best case scenarios of regenerated EDTA solutions, as having the full extraction potential of fresh EDTA additions. Unfortunately, this would not be the case. These theoretical best case scenarios should not distract the reader from the main objective, which was to de-complex the Pb from the EDTA and to concentrate it into a solid waste. Optimised combinations of Na_2S and $Ca(OH)_2$ were investigated in the next section.

9.3.3 Use of Na_2S and Small Amounts of $Ca(OH)_2$

A second series of experiments added 2 to 5% wt of Na_2S, alone and in combination with a small 0.2% wt addition of $Ca(OH)_2$ (fig. 9.2). Overall, the precipitated amounts of Pb and Fe increased with greater additions of Na_2S. However, the optimised addition would depend on whether or not the leachate treatment also intended to regenerate the EDTA. Since, the efficiency of the regeneration and recycling procedure remains unproven, the upcoming discussion is divided into two parts. Part I deals with the concentration of Pb into a solid waste and resulting toxicity of the leachate. Whereas Part II looks at the feasibility of regenerating and recycling EDTA. Thus, the conclusions for each part could differ, as do their end-objectives.

Part I: Leachate Treatment for Disposal

Table 9.5 list the Pb levels in the leachate after the Na_2S treatments, alone and in combination with $Ca(OH)_2$. The use of $Ca(OH)_2$ only increased the precipitation of Pb when it was added with 3% wt of Na_2S ($t=4.79$, $P=0.0087^{**}$). Alas, even with a 5% wt addition of Na_2S, the treated leachate contained 1.74 mg L^{-1} of Pb, which is well in excess of the 0.6 mg L^{-1} established for the electroplating industry discharge standards (EPA, 2000). Thus, discharging the leachate treated with 5% wt of Na_2S into the municipal sewers would have required dilution and special permits for its Pb and EDTA contaminants. The local governing bodies would have to determine the appropriate discharge standards for such exceptional one-event disposals.

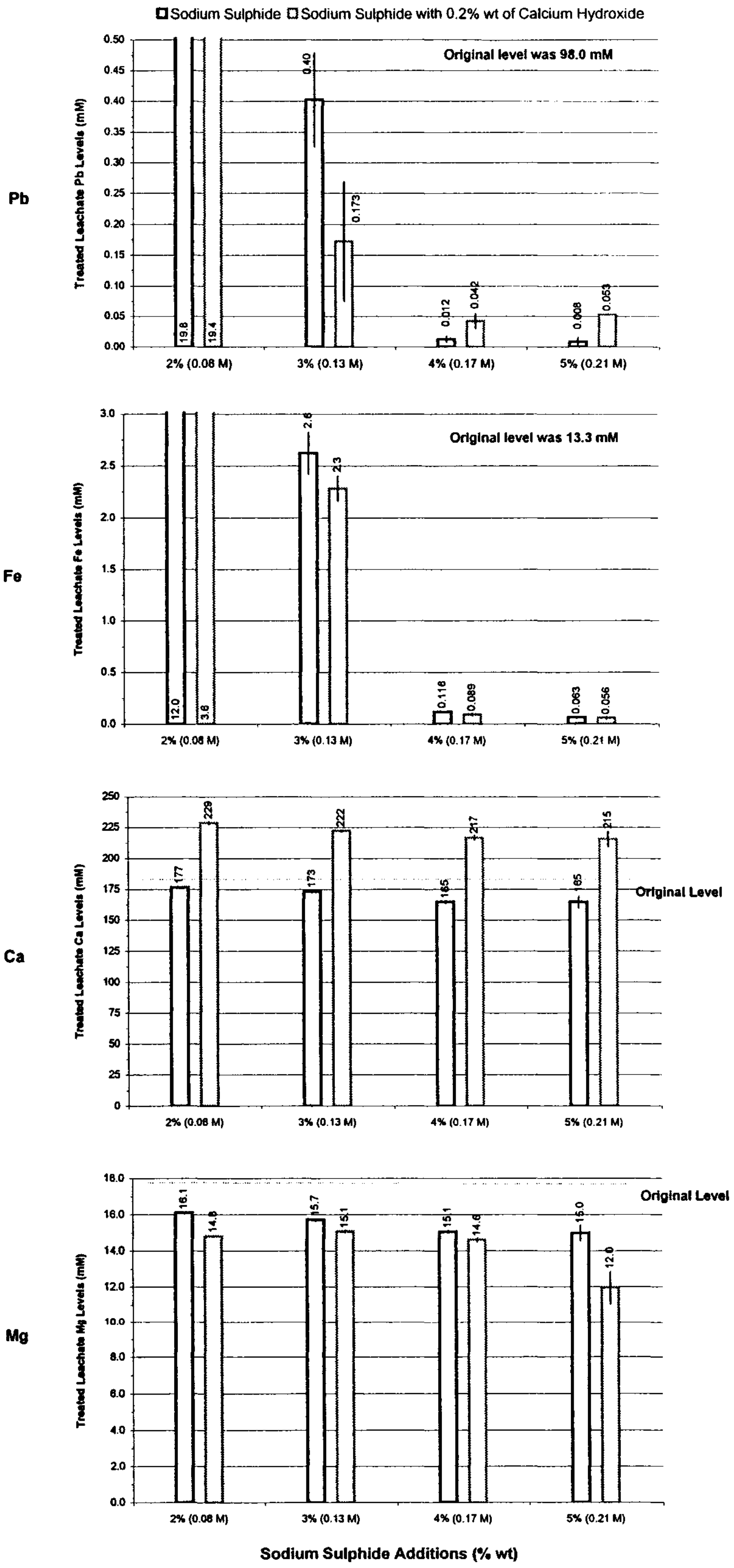
Table 9.5 Levels of Pb in the Na_2S-Treated Leachate for Different Precipitating Agent Inputs

Inputs (%wt^L)	Na_2S	2%	2%	3%	3%	4%	4%	5%	5%
	$Ca(OH)_2$	-	0.2%	-	0.2%	-	0.2%	-	0.2%
Pb Levels	(mg L^{-1})	4102	4020	83.3	35.7	2.57	8.79	1.73	11.0

[L] The % wt is with respect to the leachate

In order to limit the dilution that would be required for municipal sewage, the lowest possible concentration of Pb would need to be achieved. However, this must not be done at the expense of adding large and environmentally unsustainable amounts of Na_2S. Hence, the use of 4% wt of Na_2S alone was the most appropriate amount, as increasing the addition to 5% wt did not provide a large enough decrease in the Pb level.

FIGURE 9.2 Sodium Sulphide Precipitation of the Four Most Abundant Metals with 99% Confidence Intervals



In regards to the initial Pb content of the *J-soil*, the 4%wt addition of Na_2S concentrated the Pb by a factor of 8.93 (table 9.6). Thus, the quantity of dry waste was 60.8% less than that obtained in the dehydration experiment (section 9.2). Within this 2.6 times reduced quantity of dry waste, the content in EDTA (%wt) was also reduced by roughly 3.4 times, as compared to the dehydrated waste.

Table 9.6 Composition of the Concentrated Solid Waste from the 4%wt Na_2S-treated Leachate

Amounts in the Solid Wastes (% wt)							
EDTA	Pb	Ca	Fe	Zn	Mg	Na	S
20.7%	56.7%	2.5%	2.1%	0.18%	0.18%	7.0%	10.8%

EDTA : *J-soil (EDTA : S)*	10.6% wt
Precipitated dry waste : *J-soil*	4.64% wt
Concentration factor of the post-precipitation Pb waste to the initial *J-soil*	8.93 times

The 4.64%wtsoil^{-1} of dry waste, obtained from this 49%-decontaminated *J-soil*, would at least double for a near complete Pb removal from the *J-soil*. Still, Na_2S precipitation could provide environmental and economical benefits by concentrating the Pb into a reduced amount of solid waste. This would reduce secure-cell disposal requirements or the extent of refining that is required for the recovery of the toxic metals. The use of $MgSO_4$ (Epsom salt), $(NH_4)_2HPO_4$ (P fertiliser) and NaF were also tested as precipitating agents, alone and in combinations (data not presented), but to no avail.

Part II: Leachate Treatment for Recycling

The maximum increase in Pb precipitation, afforded by adding $Ca(OH)_2$, was 0.005%wt, as obtained for the 3 and 0.2%wt combination of Na_2S and $Ca(OH)_2$ (table 9.7). This added amount of $Ca(OH)_2$ was 40 times greater than the potentially recovered amount of EDTA. Thus, it is concluded that the use of $Ca(OH)_2$ is unfavourable for EDTA regeneration.

For re-extraction, optimised amounts of Na_2S must limit inputs, while providing a well-regenerated EDTA solution. The 3%wt addition of Na_2S theoretically regenerated 99.6% of the EDTA, equivalent to 3.53%wt of the leachate. Although the latter precipitated only 99.6% of the Pb, it was still the best addition for recycling, as it theoretically decreased the net process inputs by 0.53%wt. Further increasing the addition of Na_2S by 1% (*i.e.* to 4%wt) regenerated only 0.1% more EDTA, moreover it theoretically increased the net process inputs by 0.37%wt.

Table 9.7 Precipitated Pb and Fe from Na_2S Additions with/without 0.2% of $Ca(OH)_2$ and the Effects on EDTA Regeneration

Inputs of Precipitating Agents			Precipitation of Strongly EDTA-complexed Cations				Regenerated	Theoretical effect of recycling the leachate on the chemical input requirements *cf.* Regenerated EDTA to Precipitating Agents	
Na_2S	$Ca(OH)_2$	Total	Pb		Fe		EDTA		
% wt^L	% wt^L	% wt^L	% removal	% wt^L	% removal	% wt^L	% wt^L	Δ (% wt)	Ratio (%)
2%	-	2%	79.8%	1.62%	10.0%	0.01%	2.59%	0.59%	1.30
2%	0.2%	2.2%	80.2%	1.63%	72.7%	0.05%	2.88%	0.68%	1.31
3%	-	3%	99.6%	2.02%	80.3%	0.06%	3.53%	0.53%	1.18
3%	0.2%	3.2%	99.8%	2.03%	82.8%	0.06%	3.55%	0.35%	1.11
4%	-	4%	99.987%	2.03%	99.1%	0.07%	3.63%	(-0.37%)	0.91
4%	0.2%	4.2%	100%	2.03%	99.3%	0.07%	3.63%	(-0.57%)	0.86
5%	-	5%	100%	2.03%	99.5%	0.07%	3.63%	(-1.37%)	0.73
5%	0.2%	5.2%	99.9%	2.03%	99.6%	0.07%	3.63%	(-1.57%)	0.70

^{L} With respect to the leachate

When reapplying a washing solution regenerated with $Ca(OH)_2$, Na_2S and HNO_3, Zeng *et al.* (2001) obtained 87.8 and 43.5% extraction efficiencies for the 1st and 2nd reapplications, as compared to their initial fresh-EDTA extraction of Pb. Lee and Marshall (2002) obtained 85.4 and 78.3% extraction efficiencies for their 1st and 2nd reapplications of a Mg^0-regenerated EDTA washing solution. The extraction efficiencies of both experiments continued to decline for successive reapplications. It is unclear to what extent the regenerated EDTA contributed to the extraction of Pb, since residual Pb-EDTA complexes could have been released in large amounts subsequent to the initial addition, as seen in section 4.6. On the other hand, to what extent the increased dissolution resistance of the remaining metals or a degradation of regenerated EDTA was responsible for successively reducing the extractions of the potentially toxic trace metals is also unclear.

Hypothetically, if the extraction potential of the regenerated EDTA could be greater than 82.3% of that of a fresh EDTA solution, the addition of 3%wt of Na_2S could reduce the required amounts of EDTA by an equivalent 3%wt. Again, assuming an equal Na_2S addition and EDTA reduction by weight, adding Na_2S, costing \$1.90 kg^{-1} (UNIVAR, Montréal), would provide a 42% savings as compared to adding fresh $(NH_4)_2EDTA$. However, our assumptions of a regenerated leachate having 82.3% efficiency, as compared to a fresh wash, and of a Na_2S addition that fully transpose into an EDTA savings are unlikely. In reality, regeneration could likely increase the overall chemical inputs and provide little to no savings. In the end, maybe the only attractive aspect of regenerating and recycling an EDTA washing solution would be the ability to reduce the amount of cumulative leachate.

Since citric acid biodegrades, a leached citric acid washing solution does not permit effective recycling. After 5 days, roughly 58 and 38% of Ca and Co precipitated out from the first 10 ml of leachate, collected from the citric acid flash washing of the *M-soil* (section 6.2). Furthermore, recycling a spent citric washing solution caused the Pb to re-sorb onto soil particles (Bassi, 2000).

9.4 Summary and Conclusions

By simply dehydrating the leachate, the mid-process solid waste output was too large (*i.e.* 12.7% wt soil^{-1}) to make it environmentally or economically viable. The use of $Ca(OH)_2$ to compliment Na_2S in order to concentrate the Pb, complexed with EDTA in solution, into a solid waste was counterproductive, as it unduly increased the amount of solid waste. Of all the experiments, the 4% wt addition of Na_2S alone provided the most environmentally sustainable precipitation of Pb and treatment of the leachate; it produced 4.64% wt soil^{-1} of dehydrated waste, for a 49%-remediated soil. A fully decontaminated *J-soil* would inevitably produce more than twice the quantity of post-treatment waste.

Adding Na_2S could provide a relatively economical and environmentally sustainable procedure to precipitate out the Pb into a concentrated solid waste. This precipitation of the Pb could also serve to regenerate the spent EDTA. However, the reduction in EDTA requirements would need to be further investigated as it is anticipated to be slight. The efficiency of a Na_2S-regenerated washing solution would need to be established by successively applying it to untreated soils (*i.e.* fresh soils). In addition, the reapplication of regenerated EDTA solutions to treated soils could be compared to the re-extraction of previously treated soils with fresh EDTA. Such studies could ascertain the benefits of recycling regenerated EDTA, for its ability to reduce both chemical input costs and cumulative leachate volumes.

10 General Summary and Conclusions

This research was undertaken with the understanding, as elaborated in the literature review chapter, that there is a concern regarding the threats posed by trace metal contaminated soils. Much energy has been spent, by many researchers, on examining ways of reclaiming such soils. However, no existing laboratory procedure is suitable for site-scale remediation. Based on the previous work, an economical, pragmatic and environmentally sustainable, remediation process was sought through innovative approaches to the traditional laboratory studies, which have usually been conducted as small batch extractions. To assess the feasibility of the proposed remediation process, many facets were considered, such as the on-site apparatus mobilisation, application of process procedures, contaminant concentration, contaminated by-product disposal and post-treatment safety of the remediated soil.

This research examined the decontamination of two severely contaminated soils, the *M-soil* and the *J-soil*. The *M-soil*, a loamy sand, was contaminated with Fem and an array of trace metals, which were initially immobile under deionised water leaching, or did not initially leach toxic levels of trace metals. In contrast, the *J-soil* , a sandy loam, initially leached toxic levels of Pb. In order to assess the scalability of the proposed remediation process, different tests were performed either on 25 g of soil in 60 ml soil columns or on 32.7 kg soil heaps.

This chapter is divided into three parts. Firstly, the summary addresses the results that were obtained in this research. Secondly, the contributions to knowledge are listed in point form. Each finding is novel in its extension of the understanding of the challenges that face attempts to remediate trace metal contaminated soils, and in the new means that are advanced to address these challenges. Thirdly, recommendations for carrying out, likely needed, future experiments are given.

10.1 Summary

A heavy metal is a metal that has a density greater than 5 g cm^{-3} Herein, the term toxic heavy metal refers to potentially toxic levels of trace metals within contaminated soils. Unless specified otherwise, the conclusions were drawn from the treatment of the M-soil and the generic term EDTA was used specifically to abbreviate $(NH_4)_2$EDTA. A saturated extraction describes of the physical state of a submerged soil. An unsaturated-flow extraction was abbreviated by unsaturated extraction. A washing cycle is synonymous with a cyclic washing, and was made of a one-step EDTA wash and subsequent deionised water rinses. A flash washing consisted of successive sequential additions of EDTA washes, which were followed by a series of water rinses. The 1.37 M EDTA washing solution and its derivatives were abbreviated, such 1.4 M, 0.7 M etc. *The mmol quantities of added EDTA represent the amounts added to 25 g of soil, and should not be confused with the molarity of the washing solutions in which they were found. A liquid to soil ratio is abbreviated by L:S ratio.*

Chapter 4 *Exploratory saturated extraction and saturated washing cycle*

Diammonium EDTA is highly soluble (>45% wt) and is more than five times cheaper than Na_2EDTA. Under shaken saturated conditions, $(NH_4)_2$EDTA was observed to be more effective in extracting Cu and Zn from the *J-soil*, as effective for Pb, but slightly less effective in removing Cd, as compared to Na_2EDTA. No difference in Cd, Cu, Pb or Zn extractions occurred by extending the duration of the unshaken saturated treatment beyond 12 hours up until 24 hours, or by shaking the *J-soil* as a slurry.

The treatment of a soil with an EDTA wash leaves behind considerable amounts of residual EDTA. Upon rinsing the treated soil with deionised water, the residual EDTA caused considerable water-rinse extractions of heavy metals. The 1st rinse that followed each washing solution addition extracted heavy metal in smaller by comparable amounts to those of the wash extractions; the extracted quantities diminished with each successive rinse.

The saturated extraction efficiencies of Al, Ca, Cr, Cu, Fe, Ni and P were unaffected by the molarities of the washing solutions (*i.e.* from 0.07 M to 1.4 M), when added in a small 2:5 *L:S* ratio. However, the 0.07 M washing solution limited EDTA's extraction potential towards Mn and Co, and the 1.4 M washing solution limited EDTA's extraction potential towards Mg. For the other heavy metals, the reduction in extraction efficiencies, which occurred as washing solutions increased in molarities, was attributable to the increasing difficulty in dissolving the residual amounts of these depleted metals. Concentrating the saturated washing solution and applying it and the ensuing rinses in smaller *L:S* ratios increased the dissolutions of the trace metals, with the exception of Cd, Co and Mn. Furthermore, for equivalent amounts of added EDTA, increasing the molarity of the washing solution and adding it in a smaller 1:5 *L:S* ratio was more beneficial than adding it in a 2:5 *L:S* ratio.

The highly concentrated 1.4 M treatment caused the dissolution of mineral forms of Fe and Al; this unproportionally increased their mobilisation, as compared to the 0.7 M treatment. In contrast, the smallest jumps in the extracted amounts, when doubling the molarity of the EDTA washing solution to 1.4 M, occurred for Pb, Cd and S. Commonly, their resistance to dissolve probably indicated the prior depletion of the soluble sulphate minerals, which likely contained Pb and Cd.

Chapter 5 *Unsaturated washing cycle with high molarities in a low 1:5 L:S ratio*

Small soil columns were submitted to an EDTA unsaturated washing cycle procedure. The oxidising conditions of the unsaturated experiment were likely responsible for the increases in extractions of Cd, Cr, Cu, Ni and Zn, as compared to the reducing conditions of the saturated experiment. The unsaturated treatment extracted as much Pb, but less Mn and Co, as compared to the saturated treatment. In general, each successive washing cycle extracted fewer elements than its predecessor, with the exception of Fe and Al. Readily solubilised Ca represented more than 40% of the total amount of extracted metals, thus it bound with much of the EDTA.

Applying two washing cycles with 0.7 M washes, instead of a single washing cycle with a near saturated 1.4 M wash, extracted more Zn, Cu, Mn, Cd and Co. In addition, the two distinct wash additions, extracted more Fe, Mg and S. As compared to the 1.4 M single-cycle extraction, the 0.7 M two-cycle extraction benefited from increased equilibration time, compounded strength of fresh and residual EDTA and doubled cumulative liquid volumes additions. Five 0.7 M unsaturated EDTA washing cycles, amounting to a 22.3% *EDTA:S,* were unable to reduce the *M-soil*'s levels of Zn or Cd below the C-Level criterion for industries. Even though dividing the EDTA additions into multiple washings might extract more of the targeted metals, it should be optimised to limit the production of leachate.

Chapter 6 *Unsaturated flash washing with 0.5 M washes in a low 1:5 L:S ratio*

Rather than following each wash by several rinses, as was the case for the cyclic washing, a flash washing was applied to the small soil columns. The three consecutive washing solutions additions intended to increase the extraction efficiency, and reduce the leachate volume and post-treatment leaching of toxic levels of trace metals. In addition to an EDTA flash washing, a parallel citric acid flash washing was performed to assess the impact of its biodegradability on the post-treatment leaching of toxic levels of trace metals.

Compared to the cyclic washing procedure, the flash washing addition of EDTA did not increase the extraction of potentially toxic trace metals, but reduced the cumulative leachate volume by more than half. On the other hand, the citric acid flash washing greatly increased the extraction of Pb, Zn and Ni, as compared to the citric acid cyclic washing procedure. On a molar basis, the EDTA cyclic and flash washings extracted multivalent cations in excess to the added quantity of EDTA. Reducing the concentration of the EDTA washing solution from 0.7 M to 0.5 M lowered the ionic strength of the soil solution and limited the extraction capability of the EDTA solution. Although six 0.5 M washing cycles used 9.5% more EDTA, as compared to four 0.7 M washing cycles, the latter extracted more Cr and as much of the other trace metals.

On a molar basis, the extraction of trace metals with EDTA was much higher than with citric acid. However, calculated on a weight basis, the difference is much less between the two, since the molecular weight of citric acid is 41.1% lighter than that of EDTA. One advantage of the citric acid treatment is the short-lived post-treatment leaching of toxic levels of trace metals, which quickly met the *MDDSEI* standards under tap water rinses. In contrast, the prolonged EDTA post-treatment leachability of Pb would not have permitted the disposal of untreated leachate into municipal sewers.

Chapter 7 *Improvement trials for the unsaturated washing procedure*

The application of EDTA to a dry soil, instead of a moist soil, impeded EDTA's unsaturated extraction of Cu, Mn, Cd and Co. Using convective air exchange to increase the oxidising conditions in the soil during an EDTA unsaturated washing cycle, until the soil solution crystallized upon the drying of the soil, was inhibitory to the extraction of Mn and Co. The use of a citric acid unsaturated washing cycle in a sequence of three unsaturated EDTA washing cycles decreased Pb extraction and increased the post-treatment leaching of toxic levels of trace metals, as compared to three unsaturated EDTA washing cycles without the insertion of a citric acid washing cycle.

More EDTA was retained in the soil during a wash sequence, when the unsaturated flow rate was cut in half. The greater amount of residual EDTA within the soil was given a 72-hour equilibration time, instead of the 24 hours previously used. After the 72-hour equilibration time, the columns received their first rinse. As a result, the extractions of Pb, Fe, Mg and S increased, as compared to the 24-hour washing cycle with the full flow rate wash. However, it was unclear if the improvements afforded by the increased post-wash residual EDTA and the 72-hour equilibration time would be sufficient to permit an environmentally sustainable decontamination of the *M-soil*; the Zn and Cd contents could still perhaps remain above the C-Level criterion, even for large EDTA inputs.

Chapter 8 *Pilot-scale saturated and unsaturated flash washing*

Treating the *J-soil* with a citric acid saturated flash washing extracted merely 2.2% wt of the Pb. Thus, citric acid is likely not a sufficiently strong chelating agent to remediate soils highly contaminated with Pb, even when used in large amounts. Letting the residual citric acid biodegrade reduced the leachability of toxic Pb by a small amount as compared to the initial soil. Unfortunately, the Pb leachability was still above the drinking water standards.

In combination with increasing the soil's post-wash residual EDTA content, increasing the unsaturated equilibration time to several months appreciably increased the extraction of Pb from small soil heaps. However, the reduction of the *J-soil*'s Pb level below the required 1 000 mg kg^{-1} is uncertain, even for large EDTA inputs. Furthermore, the residual amounts of EDTA in the soil seem to indicate that EDTA could persist and continue to leach Pb, even if the remaining levels of trace metals were to satisfy the C-Level criterion.

Chapter 9 *Leachate treatment*

Simply evaporating the leachate produced too much solid waste to be environmentally sustainable. Other experiments were performed to precipitate the Pb from the leachate, with the objective of concentrating it into a solid waste product. The 4% wt addition of Na_2S was the most environmentally sustainable approach for precipitating out the Pb, with a quasi-total precipitation of the Pb (*i.e.* 99.99%). The 4% wt addition of Na_2S produced a 4.6% wt soil^{-1} mid-decontamination amount of dry waste. When considering recycling the washing solution, a 3% wt addition of Na_2S was found to be the most promising for providing environmental and economical benefits by reducing the amount of chemical entrants and the leachate volume to a minimum. However, further work would be required to validate the merit of regenerating spent washing solutions. The use of $Ca(OH)_2$ for precipitating Pb from the leachate or regenerating the spent EDTA was counterproductive.

10.2 Contributions to Knowledge

These contributions to knowledge, fulfill in part or as a whole, the main objective of this research, which was to develop an economical, pragmatic and environmentally sustainable decontamination process for soils contaminated with trace metal. The contributions to knowledge extended the understanding of the challenges, as seen by our endeavour to remediate soils severely contaminated with trace metals (*i.e.* D-Level criterion). With the development of the process, novel means and procedures improved the extraction of targeted potentially toxic trace metals and increased the real-life feasibility of reclaiming soils contaminated with trace metals. The contributions to knowledge from this study, limited to the soils used in this study, are as follows:

1. Establishing VERSENE as an effective $(NH_4)_2EDTA$ chelating agent of high solubility; it affords a 68.8% cost savings on a molar basis as compared to Na_2EDTA;
2. For saturated extractions at the flask-scale level, an unshaken 12-hour equilibration extracts as much Cd, Cu, Pb and Zn as compared to 12-hour shaken and 24-hour unshaken equilibrations;
3. An EDTA wash leaves in the soil considerable amounts of residual EDTA, which can be water-rinsed to extract heavy metals in amounts comparable to the amounts extracted by the washing solution. This persistence of the post-treatment leachability of toxic levels of metals from EDTA treated soil will inhibit the use of EDTA for soil remediation;

4. Adding the washing solution to a moist soil increases the extraction of Cu, Mn, Cd and Co as compared to its addition to a dry soil;
5. An unsaturated treatment extracts more Cd, Cr, Cu, Ni and Zn, as much Pb, but less Mn as compared to a saturated treatment;
6. For equal amounts of added EDTA, adding the washing solution in a higher molarity and in a lower *L:S* ratio extracts more Cr, Cu, Ni, Pb and Zn; a near saturated EDTA washing solution of 1.4 M would provide the greatest extraction efficiency;
7. Adjusting the flow rate of the unsaturated washing solution to limit the immediate leaching of EDTA increases the soil-retained EDTA and ensuing rinse-extractions of Pb. Giving the unsaturated post-washing soil-retained EDTA a prolonged extraction time of several months affords a large increase in the extraction of Pb;
8. There was a reduction in post-treatment leaching of toxic levels of trace metals from soils treated with citric acid, for which the citric acid had a chance to biodegrade prior to rinsing with water. However, this might not persist in outdoor conditions with acidic influxes to percolating water; and
9. Alone a Na_2S addition is most efficient in concentrating the Pb, complexed in solution with EDTA, into a solid waste and in reducing the toxicity of the leachate. The use of $Ca(OH)_2$ in combination with Na_2S to precipitate Pb from the leachate produces larger amounts of solid waste and is counterproductive.

10.3 Recommendations for Future Research

Remediating soils severely contaminated with trace metals requires a harsh chemical treatment to desorb the potentially toxic trace metals, which are specifically sorbed to mineral or organic particles, and to dissolve their metals precipitates and metal oxides co-precipitates. A high a molarity EDTA treatment likely eradicates the microbial populations and leaves behind large quantities of soil-retained EDTA, which contribute to leach toxic levels of trace metals. Therefore, EDTA-treated soils could be inoculated with acclimated bacteria in order to degrade the soil-retained EDTA, which could eliminate the end of process leachability of toxic levels of trace metals. Measuring the amounts of soil-retained EDTA throughout the washing cycle could help estimate its long-term leachability. Measuring pH and redox potential could provide information towards understanding the governing chemical reactions within trace metal contaminated soils, treated with an EDTA unsaturated-flow process.

Hypothetically, Na_2S could be used to regenerate the EDTA and provide a net cost savings in chemical inputs through recycling, which would also reduce the cumulative leachate volume to a minimum. Therefore the extraction efficiency of Na_2S-recycled leachate [without $Ca(OH)_2$ or HNO_3] should be established by successively adding it to fresh soils. Such an experiment would also require measurement of the EDTA content present in the soil and regenerated washing solution. Even though, Na_2S is more expensive than non-toxic scavenger ions like Fe^{3+}, it is more efficient for treating trace metal contaminated liquids, as it provides a much more concentrated waste. Furthermore, treating a leachate with Fe oxides would not permit the recycle of EDTA. Nevertheless, the requirements and efficiencies of both processes should be compared in parallel experiments.

The extraction of potentially toxic trace metals from contaminated soils can merely be partial, with the conservative expectation of meeting the C-Level criterion. In the end, the residual amounts of non-biodegradable EDTA that remain in the soil long after a treatment is done, would contribute to an ongoing leachability of the remaining EDTA-complexed trace metal(s). It is estimated that the post-treatment leaching of toxic levels of trace metals, resulting from an EDTA wash, would inhibit the utilisation of such non-biodegradable chelating agents. However, long-term leaching experiments, which would involve larger volumes of rinsing solution and inoculation of the soil with EDTA acclimated micro-organism, could better assess the leaching persistence of the toxic metal-EDTA complexes. It may be possible to rinse treated soils with chemicals that would favour the removal of EDTA (*e.g.* PO_4^{3-}).

Tap water rinses of soils treated with citric acid, which had time to biodegrade, reduced the post-treatment mobility of the potentially toxic trace metals. However, the mobility of the remaining resorbed trace metals, stemming from the decomposed citric acid, needs to be established under more representative conditions. Leaching such a treated soil with a more reactive rinse solution (*e.g.* with small levels of fulvic acids) would better represent percolation of rain water through the OM-containing topsoil.

The biodegradability of the citric acid does not allow the regeneration and recycling of spent washing solutions. In addition, it is unclear if the precipitation of Ca out of the leachate, upon citric acid decomposition, would affect the concentration of the contaminants into a solid waste; since, some trace metals did co-precipitate within the large amount of crystallised Ca salts. This could be troublesome as for the *J-soil*, which contains 10.7% wt of Ca. Other than Na_2S precipitation, new means to concentrate the toxic metals within a citric acid leachate into a solid waste might need to be devised.

The results from this study have demonstrated to the author that, apart from ingesting the soil, As and trace metal contaminated soils really pose a risk to human health, when As, Cd, Cr(VI), Hg, and Pb are being released into soil solution in excess to the drinking water standards. These elements could then end up in drinking water resources or enter the food chain through plant uptake. Such sites should be covered to limit the infiltration of water, and on-site cementation with lime or soda ash should be investigated for short-term and long-term effects on the stabilisation of the leachable As, Cd, Cr(VI), Hg and Pb. However, excavation, stabilisation, cementation and burial in secure landfill cells could remain the most appropriate solution under such circumstances.

When the leachable amount of As, Cd, Cr(VI), Hg, Pb and other trace metals meet the drinking water standards, the contaminated sites may be covered with 50 cm of clean fill of low organic matter and neutral pH. After which, they could even serve as green spaces (EPA, 1999). This reclamation method could even be applied when Cu, Ni and Zn are being leached in excess of the irrigation water standards, since their phototoxic levels are well under the anthropotoxic levels.

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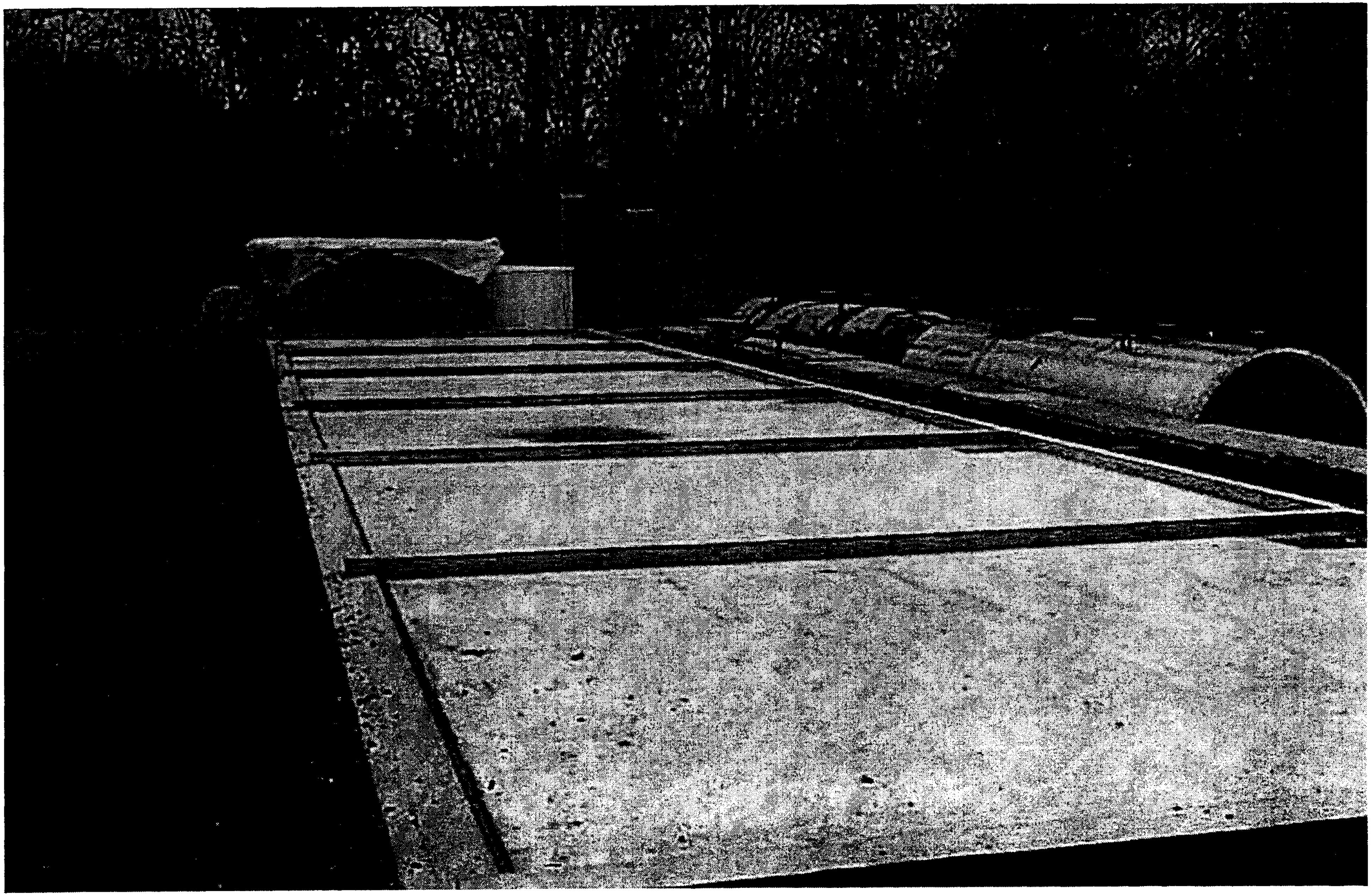
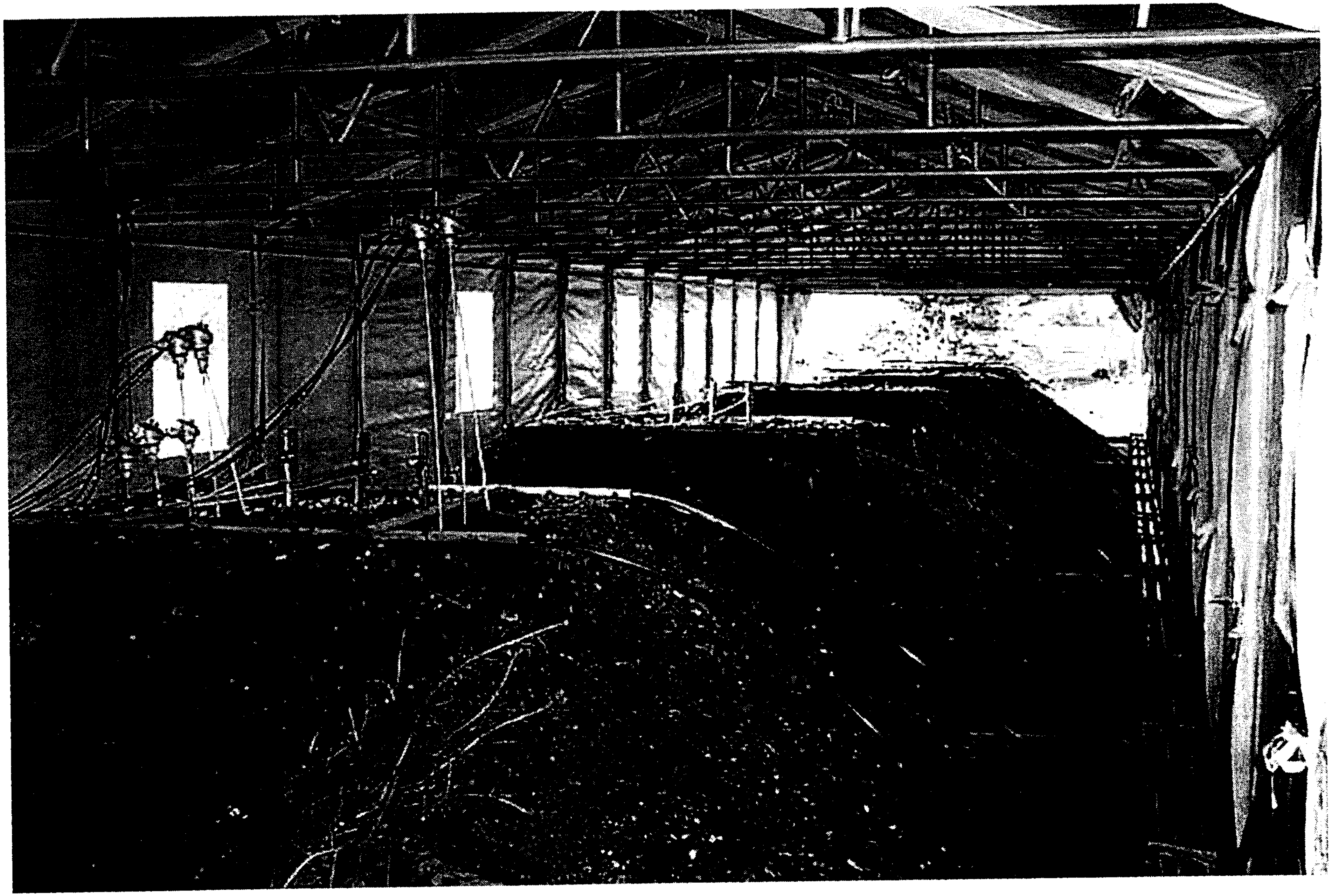
APPENDIX 1 Decontamination Platform for Six 75-ton Heaps



APPENDIX 2 Experimental Set-up of 75-ton Heaps



Appendix 3

Cost Analysis for Treating 5 000 tons of D-Level Contaminated Soil (1% wt Pb)

Related Expenditures	Excavation for Secure Landfill Burial	Unsaturated-Flow	Saturated mixing
Time	one month	15 months	15 months
Estimated Breakeven Costs			
landfill costs (Stablex Canada inc.)	$750,000	-	-
refilling of the site with fresh soil	$75,000	-	-
infrastructure	-	$5,000	$25,000
geomembrane	-	$14,000	$3,500
drip irrigation tape	-	$500	-
plumbing / reservoirs	-	$15,000	$200,000
mechanical mixer	-	-	$15,000
wringer / dryer	-	-	$10,000
soil manipulation	-	$60,000	$300,000
operation	-	$20,000	$60,000
$(NH_4)_2$EDTA	-	$205,000	$205,000
Na_2S	-	$95,000	$95,000
post-treatment cementation	-	$50,000	$50,000
disposal of waste by-products	-	$75,000	$75,000
Total Cost	$825,000	$539,500	$1,038,500
Cost per ton	$165	$108	$208
Submissioned Costs			
(Safety Factor)	(1.25)	(2)	(2.5)
Total Cost	$990,000	$1,079,000	$2,596,250
Cost per ton	$206	$216	$519