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SOLVENT EXTRACTION OF SOILS CONTAMINATED WITH LEAD AND CADMIUM

By

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ABSTRACT

SOLVENT EXTRACTION OF SOILS CONTAMINATED WITH LEAD AND CADMIUM

By

Julie Lynn Board

This work evaluated the feasibility of using di(2-ethylhexyl) phosphoric acid (DEHPA) to solvent extract lead and cadmium from contaminated soil. Initial studies were conducted using a low organic, sandy soil contaminated with 80,000 mg/kg Pb. This soil was reduced to 270 mg/kg lead in the soil using a four stage extraction. Multi-metals removal capabilities were evaluated using the low organic soil spiked with lead and cadmium. Extraction efficiencies were 94% for Pb and 102% for Cd using a four stage extraction procedure.

A Metea soil was also spiked with 80,000 mg/kg Pb. A four stage extraction procedure resulted in 54% removal of lead. Three soil samples from a DNR remediation site known to contain Pb were extracted using the four stage extraction procedure. The greatest lead removal was 58% for the soil containing the lowest initial concentration of lead.

to my parents for their loving encouragement.

ACKNOWLEDGMENTS

Many thanks to Dr. Davis for being such an excellent advisor.

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CHAPTER I

INTRODUCTION

In response to Congressional mandates in CERCLA (Comprehensive Environmental Response, Compensation and Liability Act of 1980) and SARA (Superfund Amendments and Reauthorization Act of 1986), the EPA has placed approximately 1,200 uncontrolled hazardous waste sites on the National Priority List (NPL). Many of these sites contain high concentrations of metals and approximately one third list lead as a constituent of concern. If contaminated soil is to be left on site, a lead concentration of below 500-1000 mg/kg is mandated by the U.S. Environmental Protection Agency, Office of Emergency and Remedial Response.[1]

Traditional treatment of soils contaminated with metals has been stabilization/solidification with pozzolanic materials. If these soils also contain high levels of organics, then pozzolanic reactions that cause the cementatious materials to set-up can be inhibited. If the materials do not set-up, then the "stabilized" material will leach both the organics and the metals.[2] A treatment train consisting of incineration followed by stabilization destroys the organics but the metals pass through the incinerator. In some cases, such as with lead, the volatility of the metals will result in unacceptable emissions from the incinerator stack. The lead that is not volatilized is partitioned to the ash.

Due to problems in treating soils contaminated with both organics and metals, alternative methods of remediation need to be developed. One method that has been used to remove metals is a form of solvent extraction classified as liquid ion exchange. Liquid ion exchange has been used for many years to extract metals from complex ores in the nuclear industry and in copper mining.[3] It has been applied to the removal of metals from wastewater sludges, plating plant wastes, and uranium recovery from solutions.[4,5,6] Liquid ion exchange is also a popular separation technique for the analytical determination of metals. It is a particularly attractive metal removal technique due to the selectivity of solvents for a target metal ion. The B.E.S.T.™ and CF solvent extraction processes are examples of two solvent extraction technologies that have been commercially used for organic chemical removal from soils and sludges.[7,8] The Dapex process and a Dow Chemical process are examples of two commercial metal solvent extraction processes for removal of uranium from solutions.[6] No commercial solvent extraction processes have been demonstrated for removing metals from contaminated soils.

This thesis research focuses on using di(2-ethylhexyl) phosphoric acid (DEHPA) to solvent extract soil contaminated with approximately 80,000 mg/kg lead. DEHPA was also used to remove lead and cadmium from contaminated soil to test the capability of multi-metals removal. The efficiency of extraction was explored using a four stage extraction procedure. The effect of pH and DEHPA concentration on the extraction efficiency was also studied for process optimization. Research was performed first using a low organic (<0.2 %), sandy soil. A soil containing 7.7% clay and 0.5% organic was tested for comparison of extraction efficiency. A final

test of DEHPA lead removal capacity was performed on a contaminated soil provided by the Michigan Department of Natural Resources (DNR).

CHAPTER II

THEORY AND BACKGROUND

2.1 Theory and Background

The solvent extraction process investigated in this research is characterized as a liquid ion exchange reaction. In liquid ion exchange, the solvent trades a cation (commonly H^+) for a metal ion and forms an electrostatic bond. The generic reaction is as follows[9]:

$$M^{n+} + nHL \rightleftharpoons ML_n + nH^+ \qquad (1)$$

where

M = metal ion

H = hydrogen ion

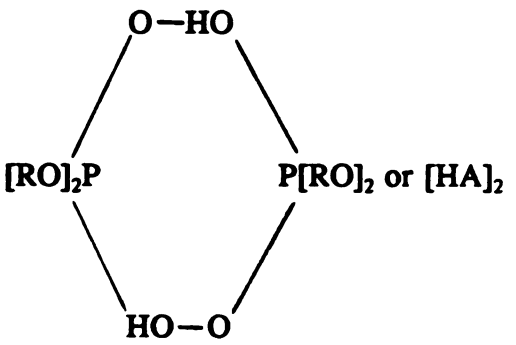
L = solvent ligand

Solvents are chosen based on selectivity for the desired metal, ability to form neutral chelate compounds that are soluble in an organic solvent (extracting solvents are typically diluted in a carrier solvent such as hexane, kerosene, etc.), insolubility in the aqueous phase (waste stream), and low cost.[6,10] Aqueous insolubility is

controlled by the chain length of the ligands. Solubility decreases as chain length increases.[6]

Blake, Baes, and Brown investigated a series of alkyl phosphoric compounds for the successful removal of uranium.[6] One solvent from this family, di(2-ethylhexyl) phosphoric acid (DEHPA), has been shown to extract Zn and Cu from a sulfate solution.[11] Cornwell and Westerhoff removed Fe, Zn, Cd, Mn, and Cu at greater than 95% efficiency from wastewater sludges using DEHPA.[4] They also stated that DEHPA is selective for Al^{3+} over heavy metals but will still extract other metals. DEHPA in toluene has been used to extract lead for analytical analysis with 90% efficiency.[9] Because of successful extraction of heavy metals, DEHPA was chosen for extraction studies with contaminated soils.

DEHPA exists as a dimer in most organic solvents.[9,12] The dimer has the structure:



where

A = $[RO]_2PO{\cdot}O^-$

R = CH_3-$[CH_2]_3$-$CH[C_2H_5]$-CH_2-

DEHPA may ionize as shown in the following reaction:

$$[HA]_2 \rightleftharpoons [HA_2]^- + H^+ \qquad (2)$$

The effectiveness of any solvent used for extraction of metals from soil is dependent on solvent selectivity, metal concentration, presence of other metals, length of time the metal resides in the soil, pH, temperature, mixing, and contact time.[13] Solvent selectivity is influenced by the basic principles for ion exchange. In general, ions of high valence are preferred over ions of low valence (i.e., $Fe^{3+} > Mg^{2+} > Na^+$). For ions of the same valence, ions of decreasing hydrated radius and increasing atomic number are selected first (i.e., $Ca^{2+} > Mg^{2+} > Be^{2+}$).[14] High concentrations of metals may necessitate the use of multiple extractions. One extraction may not remove enough of the metal because the solvent's exchange capacity is limited. The presence of other metals can greatly decrease extraction efficiency, rate, purity of the extracted metals and also necessitate multiple extractions. The length of time a metal resides in the soil affects extraction efficiency. The longer a metal resides in the soil, the more likely it is to be adsorbed into the soil matrix (non-exchangeable position) making it harder to extract. The pH during extraction is important because too low of a pH will drive reaction (2) backwards and no ion exchange will take place. Conversely, lead is more soluble in more acidic systems. Lead in a soluble form is easier to ion exchange. Thus, there is an optimum pH that balances the need to maximize lead solubility with the need to

maximize the exchange capacity of the solvent.

The solvent has to be sufficiently contacted (mixed) with the waste for ion exchange to occur, "mixing determines the amount of contact between two immiscible phases and affects the degree of mass transfer".[15] The solvent must be separated from the waste (insoluble in an aqueous solution or sludge/soil slurry) in a settling step. Solvent extraction can be performed in a batch mixer-settler as shown in Figure 2.1.1 or in a counter-current mixer-settler unit (Figure 2.1.2).[15,16] Pulsed columns which use the gravity difference between the solvent and waste to achieve both mixing and countercurrent flow have also been used.[17]

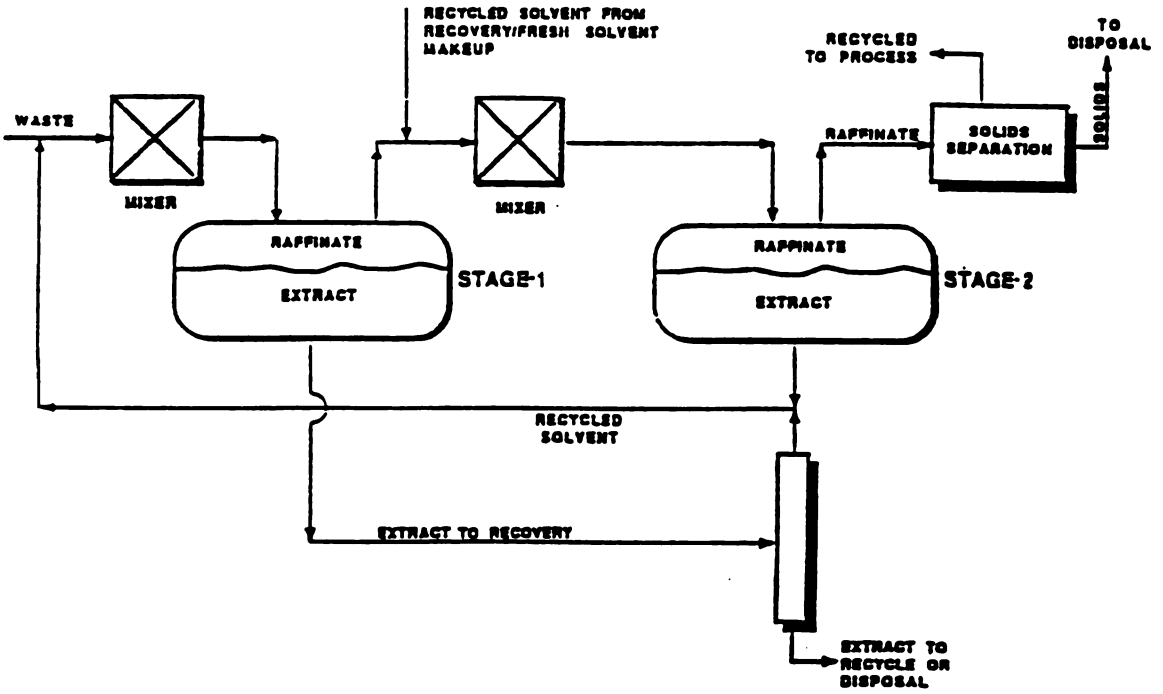


Figure 2.1.1. Batch mixer-settler diagram.[15]

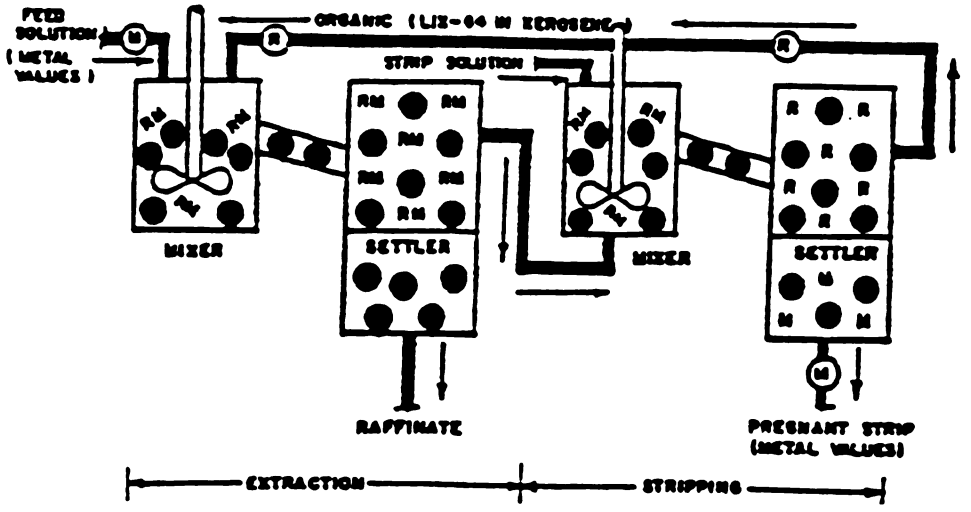


Figure 2.1.2. Counter-current mixer-settler diagram.[16]

Mixing is not the only reaction rate controlling mechanism. Impurities in the DEHPA such as large amounts of the mono-ester can slow kinetics.[12] Extraction has also been shown to be rate-limited by diffusion into soil particle pores. For metals that have resided in the soil for a long time, chemical limitations such as fixation or location of the metals in non-exchangeable positions are limiting factors.[18]

In solvent extraction of soils and sludges, it is highly probable that residuals of both the extracting solvent and the carrier solvent will be trapped in the treated soil or sludge. Solvents can adsorb to sludge and slurry particles or be lost to an aqueous-solid-organic emulsion referred to as crud. This reduces solvent efficiency and,

necessitates solvent removal through soil washing, thermal techniques, or preferably recovery of the solvent. Surfactants have been used with limited success to reduce crud formation, and flotation has been used to remove crud and reduce losses of solvent in the process.[17] The CF process has a propane recovery step to recover the solvent and the B.E.S.T.™ (Basic Extractive Sludge Treatment) process uses a biodegradable solvent (triethylamine).[8,7]

Two major economic costs of solvent extraction are the cost of soil excavation and the cost of the extracting solvent. Many of the solvents like DEHPA can be stripped of their metals with up to 99% efficiency and recycled for reuse. Recovery and reuse of solvents is necessary for an economical process.

2.2 Alternative Metals Removal Technologies

A number of other technologies have been used to remove lead from soils. These include soil washing, leaching, and chelation or combinations of these technologies. All these technologies are ex-situ processes like solvent extraction.

Soil washing mechanically scrubs soils to remove contaminants using a water-based process. The process dissolves and suspends contaminants in a wash solution for later removal from the solution, or concentrates them by particle size separation into a smaller volume of soil. Since most organic and inorganic contaminants tend to bind to clay and silt particles (either physically or chemically), separating the finer clay and silt particles from the coarser sand and gravel particles concentrates the contaminates into a smaller volume for further treatment. For this reason, soil washing is effective for soils containing large amounts of coarse sand and gravel but

not large amounts of clay and silt.[19] Along with clay and silt content (particle size), soil pH, contamination levels, and moisture content all have to be taken into account for soil washing.[20]

Since most metals are insoluble in water, soil washing can be enhanced with the addition of surfactants, acids, and chelating agents.[19] Schmidt compared soil washing with water, a surfactant, and EDTA (ethylenediamine tetraacetic acid) for several battery breaking wastes. The water and surfactant did not remove significant quantities of Pb in any of the particle size categories. EDTA was very effective but dependent on the type of lead compounds present and the type of EDTA used. Di-sodium EDTA was 100% effective for PbO_2, 0% for $PbSO_4$, and 2.7% for Pb metal. Tetra-sodium EDTA was 0% effective for PbO_2, 100% for $PbSO_4$, and 23.6% for Pb metal.[21] U.S. EPA Region V and PEI Associates evaluated EDTA and NTA (Nitrilotriacetic acid) for soil washing and found EDTA to be the more effective chelating agent with approximately 95% removal achieved with a 2 hour reaction time.[22] Chelating effectiveness is dependent on quantity and type of chelating agent used, pH, Pb form and location in the soil, and contact time.[20] Problems with liquid soil separation have been reported.[21] Recovery of the metal from the chelate has been demonstrated by Bhat and Gokhale. The metal can be recovered up to 99% through acidification or by precipitation with a hydroxide, sulfide, or oxalate. Recovery of EDTA using these methods is limited by its solubility and initial concentration in solution. Very dilute solutions are not recoverable.[23]

Recovered EDTA can be reused.[24] If the metal is recovered using acidification, the EDTA will form a solid precipitate. The precipitate can be recovered for reuse

by adding NaOH.[25] This is not true for all chelates. Chelating agents can form electrostatic, covalent, or a mixture of electrostatic and covalent bonds with metals to create a metal-ligand complex.[26] The more covalent the bond, the stronger the bond. A more covalent bond must be broken to recover the metal which in most cases destroys the chelate, rendering it useless.

An acid leaching process to remove lead has been developed by the Bureau of Mines. It uses acid leaching to convert lead sulfate and lead dioxide to lead carbonate, which is soluble in nitric acid. Lead is then precipitated as lead sulfate with sulfuric acid.[21] The TerraMet™ soil remediation system developed by COGNIS, Inc. leaches lead from contaminated soil, sludge, and sediment then recovers it. It uses a proprietary aqueous leachate that is tailored to the soil system and removes lead forms like metallic lead, soluble ions, and insoluble lead oxides and salts. Lead sulfate is not removed by this leachate. Lead is recovered from the leachate by liquid ion exchange, resin ion exchange, or reduction. A bench-scale test leached a 17,000 ppm lead-contaminated soil to less than 300 ppm residual lead.[27]

A lead recovery process using DEHPA has also been studied. Kaur and Vohra used a surfactant liquid membrane to recover lead (II) from wastewaters. The surfactant liquid membrane process consisted of a membrane phase of di(2-ethylhexyl) phosphoric acid (DEHPA), n-hexane, and span-80, an internal stripping solution of sulfuric acid, and an external phase of the wastewater. The wastewater was contacted with the membrane for removal of lead by complexing with the DEHPA. The lead was then removed from the DEHPA by the internal stripping solution. In bench-scale studies, an extraction efficiency of 87% was achieved with a 2% DEHPA

concentration. With a 10% DEHPA concentration, 100% removal of Pb(II) from the wastewater was achieved.[28]

2.3 Lead Partitioning in Soils

The efficiencies of the various extraction procedures discussed are all dependent or related to the location of the lead and heavy metals in the soil. Many factors affect the partitioning of metals from a solution (contaminated groundwater) to a solid phase (soil). These factors include dissolution and precipitation, sorption and exchange, complexation, and biological fixation.[29,30] Metals tend to reside on the finer soil particles and/or to be preferentially bound to clays and humic materials (organic matter).[31]

Lead in soils has been found in the exchangeable form, carbonate-bound, organic-bound, oxide-bound (Fe-Mn oxides co-precipitate and adsorb heavy metals), and in a "residual" fraction which is considered fixed in the soil. The location of the lead in the soil depends on the soil composition. If it has a high organic content, then there is a high probability that the lead will be bound to an organic ligand. The presence of other metals in the soil also affects the location of the lead because of the selectivity of metals for certain adsorption sites.[32,33] Lead has a strong metal-soil affinity and, particularly in aged soils, it is more likely to be found in the "residual" or unextractable form as insoluble precipitates or incorporated into soil minerals.[31,33]

The ease of extractability for these forms has been shown to follow the order of Exchangeable > Carbonates > Fe-Mn oxides > Organic/Sulfidic > "Residual".[32] The ease of extractability of organic matter depends on the relative binding strength

of the organic matter and the system pH.[33] Despite the fact that the "residual" fraction is the hardest to extract, "residual" lead has been extracted to a higher degree than other "residual" metals (Zn, Cu, Ni) in lab tests.[32]

The distribution of metals in soils that are artificially contaminated is different from the distribution found in soils contaminated from old industrial areas and waste disposal sites. In clay soils artificially contaminated with one or more metals, approximately 80-90% of the metals are located in the exchangeable, carbonate, and Fe-Mn oxide fractions. For clay soils from real waste sites, the metals are found more in the organic and "residual" fractions.[32]

2.4 Research Objectives

The objective of this research was to test the ability of DEHPA to extract lead and other selected heavy metals. This research was divided into the following areas:

1) Determination of optimum conditions for lead extraction.
2) Extraction efficiency of a two metal system.
3) Comparison of extraction efficiency for two different soil types.
4) Extraction of three samples of lead contaminated soils from a DNR remediation site.
5) Design of a simple process configuration and cost analysis.

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

Soil from a sandy glacial deposit in Ludington, Michigan containing 0.2% organic carbon was used for all initial and parameter optimization extraction studies. The soil characterization is listed in Table 3.1.1.

Table 3.1.1 Properties of glacial sand.[34]

mean grain diameter	0.3 mm
average porosity	0.37
bulk density	1.66 g/cm^3
organic content	0.2%
hydraulic conductivity	0.0036 cm/min

A comparative extraction study was also run on a Metea soil which was obtained from the south end of the Michigan State University campus near an old orchard

adjacent to the research farms and the Engineering Research Complex Building. It contained 34% fines and was characterized as shown in Table 3.1.2.

Table 3.1.2 Properties of Metea soil.[35]

organic content	0.5%
pH	6.6
lime index	71.0
sand	82.3%
silt	10.0%
clay	7.7%

* Soil analyzed by MSU Soil Testing Lab.

The di(2-ethylhexyl) phosphoric acid used for all studies was procured from the Sigma Chemical Company and used as received. A carrier solvent of n-hexane was used in all extractions except where noted. A 1-2 N NaOH and/or 50:50 water/HCl mixture was used to adjust the pH in all tests.

Soils were contaminated with lead sulfate. The lead sulfate was dissolved in hot 50:50 water/HCl. Soil was then added to the solution and the mixture was allowed to cool. The supernatant was drawn off if a large volume of liquid remained and the lead left in solution was measured using atomic absorption. The soil was then dried in a 100°C oven. The lead concentration spiked in the soil was determined by mass

balance. For a multi-metals contaminated soil, CdO was dissolved with the $PbSO_4$ using the same procedure.

3.2 Solvent Extraction Procedure

Extractions were carried out using a bench scale beaker-mixer system with pH control as shown in Figure 3.2.1. DEHPA was diluted to the appropriate concentration using a carrier solvent of n-hexane. Fifty mL of the extracting solvent were mixed with 50 g of the metal spiked soil and 50 mL deionized water for an extraction. The soils were mixed for one hour, except where noted, and hexane was added as it evaporated to keep the volume constant. In initial extraction studies, Brent Wilson determined that a half hour extraction time was sufficient to extract a soil containing 80,000 mg/kg, but he chose a one hour extraction time as a conservative time.[36] For those soils spiked with less than 80,000 mg/kg, one half hour of mixing was used.

The mixing speed was set at 2.0 on the Cole-Parmer Stir-Pak Laboratory Stirrer (Model 4554) for all extractions. Phases were separated by settling and the solvent was removed and analyzed for lead concentration using atomic absorption spectrophotometry (AA). The aqueous phase was initially tested in early extractions but contained negligible amounts of lead and testing was discontinued. For those extractions where phase separation was poor, sonication of the sample was used to separate the fines and crud layer from the solvent phase. Initial work for Pb extraction using DEHPA was performed by Wilson.[36] Studies were initiated using his parameters and optimized as needed.[36]

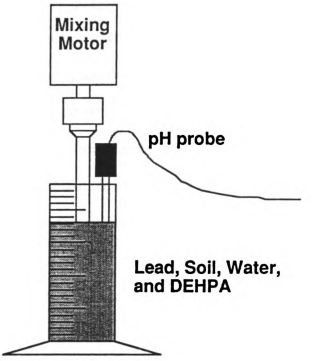


Figure 3.2.1 Bench scale beaker-mixer system for extractions.

3.3 Analytical Methods

A Perkin-Elmer Atomic Absorption Spectrophotometer (Model 1100) was used to analyze all extracting solutions for metals content. Standardization curves were made for the AA using metal reference standards from Fisher Scientific. For lead, the standard curve was made using standards of 3 ppm, 5 ppm, 10 ppm, and 20 ppm Pb. A linear line was fit using these standards for calibration of the AA. Standard curves for all the metals tested with the AA were fit in this manner. The samples tested for Pb, Cd, and Fe were flamed in an acetylene/air mixture. Those samples tested for Al were tested in a nitrous oxide flame with KCl added to the sample as an ion suppressant. This was necessary because other metal ions will be measured as Al.

Sample aliquots were each measured in triplicate.

For the measurement of metals in the extracting solvents, the solvents were diluted in 2-propanol for analysis. The standards used to calibrate the AA were also diluted in 2-propanol. The amount of lead removed from the soil was calculated based on the volume of solvent separated from the soil after extraction and the soil sample size (50 g for all extractions). Example calculations are in Appendix A.

To determine lead concentration in the soil before and after extraction, EPA Method 3050: Acid Digestion of Sediments, Sludges, and Soils was used.[37] The solution from the digestion was diluted in deionized water and also analyzed using the AA.

3.4 Experimental Design

The initial objectives of this project were to demonstrate that DEHPA could extract lead from soil, and to optimize and test the procedure. A low organic, glacial sand was chosen for initial work because adsorption effects due to organics would be low. The sand also settled better for cleaner separation of phases and, thus, minimized system losses. The soil was initially spiked with approximately 80,000 mg/kg Pb to mimic contamination levels found at battery reclamation sites on the NPL. Optimization of the extraction procedure was performed using this soil and the multi-metals removal capabilities of DEHPA were also tested in this soil.

Multi-metals removal capability of DEHPA was tested using a lower concentration of lead (approximately 7,000 mg/kg) so the solvent ion exchange capacity would not be overloaded and cause interference with the extraction of two

metals. A cadmium concentration of approximately 500 mg/kg was used. The idea was to see if DEHPA would select one metal over the other metal or extract both at the same time.

Tests were run substituting ethanol for n-hexane as the carrier solvent. Sigma Chemical uses ethanol to prepare DEHPA for thin layer chromatography.[38] Since ethanol is less hazardous than hexane and DEHPA is readily miscible in it, development of the extraction with ethanol as the carrier solvent was explored as an alternative to the hexane.

A Metea soil with a higher organic, silt, and clay content was tested using the same extraction conditions as the glacial sand to compare extraction in different soils.

A contaminated soil received from the DNR was extracted to determine DEHPA ability to remove lead in an industrially contaminated soil. This was the last experiment performed to test DEHPA metal extraction of soils.

3.4.1 Initial Extraction Efficiency Determination

For the initial extraction efficiency determination, the sandy glacial soil spiked with approximately 80,000 mg/kg was extracted four times (four stage) with fresh solvent (1 M DEHPA in n-hexane). The pH was held at 3.0 using 1 N NaOH. This pH and DEHPA concentration were selected based on preliminary work performed by Wilson.[36] The lead concentration left in the soil after extraction was determined using EPA Method 3050 and the lead concentration in the extracting solutions from each extracting stage was determined by AA. Three, replicate 50 g samples were extracted.

3.4.2 Optimization of pH and DEHPA Concentration

In a second set of experiments, the optimum pH for extraction was determined by extracting the sandy glacial soil (approximately 80,000 mg/kg Pb) at pH values of 2.00, 2.50, 3.00, 3.50, 4.00, and 5.00. The pH was adjusted using 1 N NaOH. One extraction was performed for each 50 g soil sample at each pH and the solvent was analyzed for lead. The pH experiment was performed in three separate series. In each series, a pH range of 2.0 to 4.0 or 5.0 was tested and then analyzed using the AA. Each pH point was tested in series three times. Each series was extracted on a different day and tested for lead concentration on a new calibration curve for the AA. This was done to randomize the experiments so that extraction performance due to pH could be duplicated by each individual series.

A series of tests varying the DEHPA concentration from 0.5 M to 1.5 M was performed to determine the effect of solvent concentration on extraction. The pH was held at 3.50 and one extraction was performed per soil sample. Each DEHPA concentration experiment was replicated three times and run in a set of three separate series similar to the pH experiment. Each series was from 0.5 M to 1.5 M, extracted on a different day and then analyzed on a new calibration curve for the AA.

3.4.3 Multi-Metals Extraction

Lead at 6,900 mg/kg and cadmium at 490 mg/kg were separately spiked into the sandy soil. A single stage extraction was performed on each metal spiked soil. A half hour extraction time was used. Three samples were run for each soil to determine the extraction efficiency of each metal separately. The two metals were

then spiked together at the same concentrations (6,900 mg/kg Pb and 490 mg/kg Cd) in the sandy soil. A four stage extraction on three samples was run to determine if extraction efficiency changed with multi-metals removal. The optimum extracting parameters (pH = 3.5, 1 M DEHPA) determined in earlier studies were used for this test.

3.4.4 Use of Ethanol as a Carrier Solvent

Ethanol was substituted for n-hexane in the extraction procedure. DEHPA is readily miscible in ethanol. A standard extraction was carried out on the sandy soil spiked with approximately 80,000 mg/kg lead. A second extraction was run without using water in the procedure and the liquid difference was balanced with excess ethanol. In both experiments the pH was 3.5 and the DEHPA concentration was 1 M.

3.4.5 Metea Soil

A Metea soil was spiked with approximately 80,000 mg/kg lead. A four stage extraction was performed using the optimum extraction parameters. Three soil samples were tested to determine extraction efficiency for comparison to the efficiency achieved in the sandy soil.

3.4.6 Soil from the Gratiot Metal Co. Site

Three soil samples were procured in April of 1994 from a DNR remediation site. The soils are from the Gratiot Metal Co. Site located in Ithaca, MI. It had formerly

been a battery and scrap-metal junk yard that opened in the 1930-40s and was closed in 1983 due to bankruptcy. It became a DNR clean-up site in 1987. The site contains a large number of contaminants including VOCs, polynuclear aromatic hydrocarbons (PNAs), and metals (Pb, Cd, Ba, Cr, Ni, Zn). The soil samples were obtained from an area expected to have high levels of Pb contamination. The DNR did not characterize the soil samples, but the soil around Ithaca is associated with glacial till deposits.

The initial pH of the soils was measured by taking a 5 g sample, mixing it with 15 mL water, and letting it sit for 15 minutes. The sample was then stirred and the pH measured. Three replicates from each DNR soil were measured. The soils were acid digested using EPA Method 3050 to determine the initial Pb concentration. A four stage extraction on one 50 g soil sample was performed for each of the three DNR soil samples.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Soil Spiking Results

The sandy soil was spiked with 122,000 mg/kg of lead. The estimated lead concentration left in the soil after the excess metal-dissolving acid was removed and the soil dried was 80,000 mg/kg. For the multi-metals soil spikes, the amount of acid that it took to dissolve the $PbSO_4$ and CdO was small enough to be evaporated out of the soil without removing excess acid. Therefore, the 6,900 mg/kg of Pb and 490 mg/kg of Cd that was dissolved in the acid solution was the amount left in the soil for both the metal spikes of Pb and Cd separately and together in the soil. The Metea soil was spiked with 80,000 mg/kg Pb. The excess acid was small enough to be evaporated off.

4.2 Extraction Efficiency Results

The results of the initial efficiency study using the sandy soil are shown in Table 4.2.1. The results of the extractions of the three soil samples were averaged by stage. Extracting four times resulted in an average of 98% removal. A mass balance is shown in Figure 4.2.1. The greatest amount of lead was removed in the first stage extraction (43%) and lesser amounts in the following stages. Using the EPA Method

3050, an average of 340 mg/kg lead remained in the soil after Ext. 2 and 190 mg/kg Pb was left in the soil after Ext.3. Sample calculations for determination of the amount of lead removed by extraction are in Appendix A.

There was approximately 2,000 mg/kg lead unaccounted for in the system. Losses occur due to soil fines being trapped in the solvent and solvent residual left on the sides of the extracting apparatus. The evaporation of hexane during the extractions adds to the experimental error as the exact amount of hexane lost can not be accurately replaced for each extraction stage due to the limitations of the bench-scale extraction apparatus. This will change the concentration of DEHPA during the extraction and, as will be shown in Section 4.4, this affects extraction efficiency. Small errors and losses propagate to large numbers due to dilutions made for AA analysis. Small matrix variability contributes to large standard deviations (S.D.). Round-off errors also occur due to AA analysis.

Table 4.2.1 Concentrations of lead extracted from the soil for an extraction mass balance.

Stage	Ext. 1 (mg/kg)	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)	S.D.	95%C.I. (mg/kg)	% Removal
1	31000	46000	26000	34000	10000	± 25000	43
2	27000	20000	33000	27000	6500	± 16000	34
3	12000	11000	13000	12000	1000	± 2500	15
4	3200	7700	2600	4500	2800	± 7000	6
Total	73000	85000	75000	78000	6400	± 16000	98

* The raw data for this table and all following tables is in Appendix C.

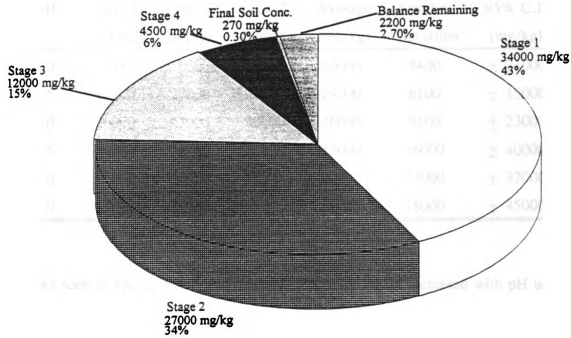


Figure 4.2.1 Mass balance of lead from four stage solvent extraction of soil using DEHPA.

4.3 Optimization of pH

The results of the pH study are shown in Table 4.3.1. The pH results from each series were averaged and standard deviation (S.D.) and 95% confidence intervals (C.I.) calculated. These averages are displayed in Figure 4.3.1.

Table 4.3.1 Lead concentration extracted from the soil at various pH values.

pH	Ser. 1 (mg/kg)	Ser. 2 (mg/kg)	Ser. 3 (mg/kg)	Average (mg/kg)	Standard Deviation	95% C.I. (mg/kg)
2.0	7300	18000	24000	16000	8400	± 21000
2.5	17000	27000	28000	24000	6100	± 15000
3.0	26000	43000	40000	36000	9100	± 23000
3.5	24000	50000	54000	43000	16000	± 40000
4.0	47000	70000	68000	62000	13000	± 32000
5.0	47000	21000		34000	18000	± 45000

As seen in Figure 4.3.1., the amount of lead extracted increased with pH until the pH equaled 4.0. An average of 62,000 mg/kg lead was extracted at a pH of 4.0. Above and including the pH of 4.0, the solvent thickened up (perhaps polymerizing). Soil was more easily trapped in this phase and separating the solvent from the water and soil was more difficult. These factors contributed toward a decrease in the amount of lead removed from the soil by the solvent above the pH of 4.00. A pH of approximately 3.5 appears to be the optimum for extraction. The large standard deviation and 95% confidence intervals are due to the factors discussed in Section 4.2.

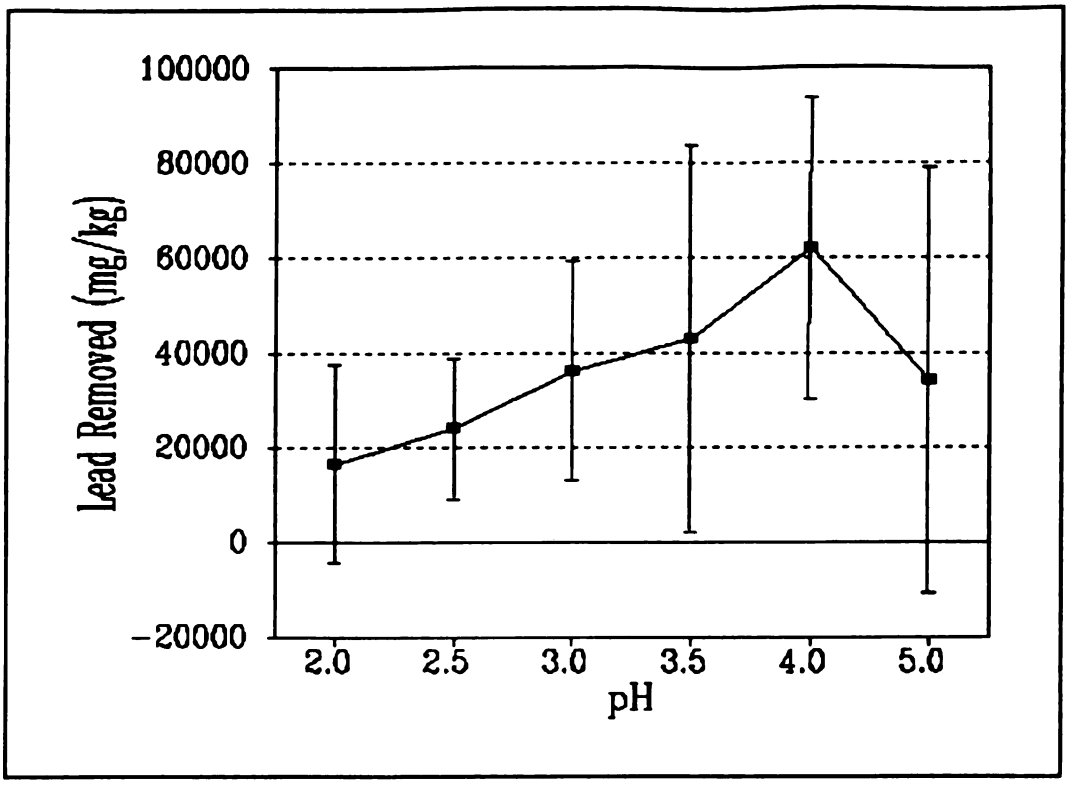


Figure 4.3.1 Effect of pH on DEHPA extraction efficiency of lead from soil.

4.4 Effect of DEHPA Concentration on Extraction

Using stoichiometry, it was calculated that a 0.77 M DEHPA concentration would extract a 50 g soil sample containing 80,000 mg/kg lead. (This calculation is in Appendix B.) This is assuming no interferences or losses. A concentration range of 0.5 to 1.5 M was chosen for testing based on this calculation. The results of the concentration study are shown in Table 4.4.1. The results from each series were averaged and standard deviation and 95% confidence intervals calculated. These averages are displayed in Figure 4.4.1.

Table 4.4.1 Lead concentration extracted from the soil at various DEHPA concentrations.

DEHPA Conc. (M)	Ser. 1 (mg/kg)	Ser. 2 (mg/kg)	Ser. 3 (mg/kg)	Average (mg/kg)	Standard Deviation	95% C.I. (mg/kg)
0.50	46000	42000	36000	41000	5000	± 12000
0.75	46000	52000	51000	50000	3200	± 8000
1.00	59000	66000	71000	65000	6000	± 15000
1.50	50000	61000	61000	57000	6300	± 16000

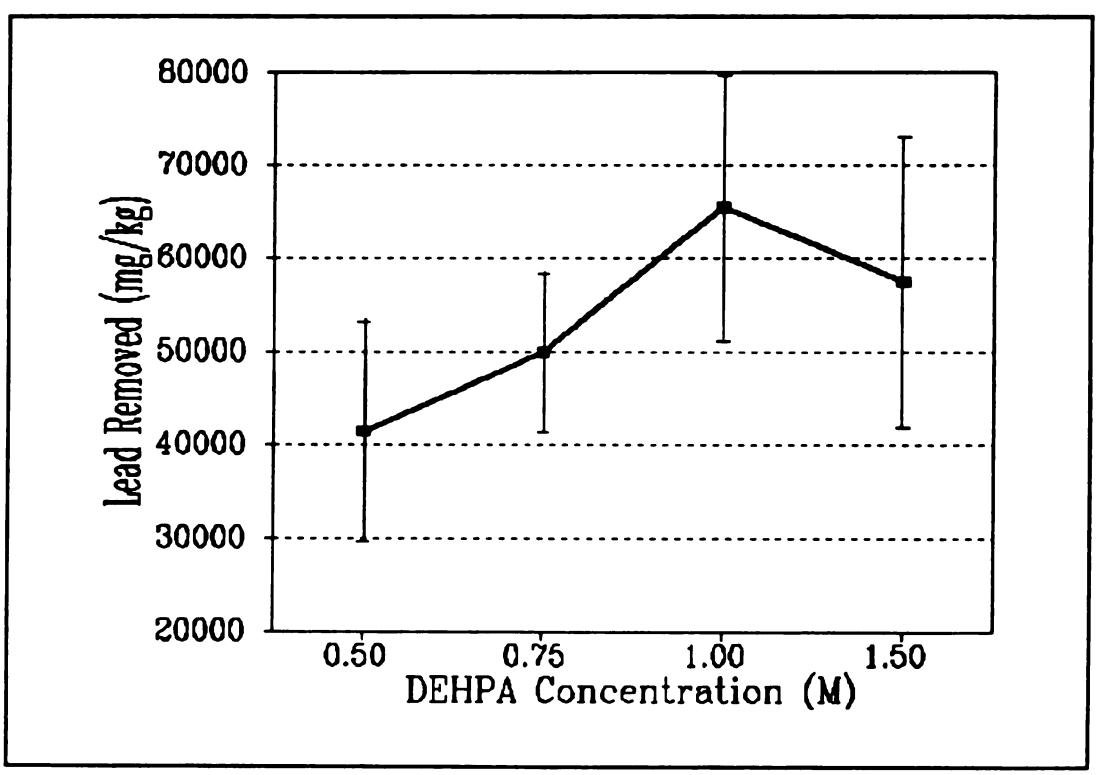


Figure 4.4.1 Effect of DEHPA concentration on extraction efficiency of lead.

Increasing the DEHPA concentration increased amount of lead extracted up to a concentration of 1 M. The concentration of lead extracted decreased at the 1.5 M DEHPA concentration. One soil sample was also tested using a DEHPA 2 M concentration. This resulted in 53,000 mg/kg Pb removal which was lower than both the 1 M and 1.5 M average extraction. The optimum concentration for extraction appears to be 1 M. The S.D. and 95% C.I. again were high.

4.5 Multi-Metals Removal

Initially, Pb and Cd were spiked separately in the sandy soil to determine extraction efficiency. A one stage extraction was performed on three soil samples for each metal. The results are shown in Table 4.5.1. The Pb and Cd spiked soil was extracted four times for each sample with three soil samples being tested. The extraction results are shown in Table 4.5.2 for Pb and Table 4.5.3 for Cd. The first stage extraction was compared between the Pb and Cd individually spiked soils and the soil spiked with Pb and Cd together.

Comparison of the first stage extractions for the metals spiked separately and together in the soil show that the results are similar. The Pb spiked soil had a lead removal of 72% and the Pb and Cd spiked soil had a lead removal of 72%. The Cd spiked soil had a cadmium removal of 68% and the Pb and Cd spiked soil had a cadmium removal of 80%. At the metal concentrations tested, concurrent removal of Pb and Cd does not appear to be a problem. With higher concentrations or different metals, one metal may preferentially extract before another metal.

Table 4.5.1 Single stage extraction of soil spiked separately with Pb and Cd.

Sample	Pb (mg/kg)	Cd (mg/kg)
I	5500	290
II	4600	340
III	5000	360
Average	5000	330
Standard Deviation	450	36
Average Removal	72%	68%
95% C.I.	± 1100	± 89

Table 4.5.2 Four stage extraction of Pb from soil containing Pb and Cd.

Pb Stage	Ext. 1 (mg/kg)	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)	S.D.	95% C.I. (mg/kg)	% Removal
1	4400	5400	5100	5000	510	± 1300	72
2	1100	1200	1600	1300	260	± 640	19
3	160	170	210	180	26	± 64	3
4	28	29	38	32	6	± 15	~0
Total	5700	6800	6900	6500	660	± 1600	94

Table 4.5.3 Four stage extraction of Cd from soil containing Pb and Cd.

Cd Stage	Ext. 1 (mg/kg)	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)	S.D.	95 % C.I. (mg/kg)	% Removal
1	390	410	380	390	15	± 37	80
2	74	92	110	92	18	± 45	19
3	10	13	15	13	2	± 5	3
4	2	2	3	3	1	± 2	1
Total	480	520	510	500	21	± 52	102

For the four stage extraction, the average Pb removal was 94% and the average Cd removal was >100%. The standard deviation was fairly large but it is comparable to the other results that have been found in this research. An acid digestion of the soil (EPA Method 3050) resulted in an average of 29 mg/kg Pb (S.D. = 25) left in the soil and 5.0 mg/kg Cd (S.D. = 1.7). The Pb left in the soil is lower than expected because a mass balance on the system suggests that approximately 440 mg/kg Pb should be left. This deviation can be attributed to losses in the extraction system, analytical error, and experimental error in the EPA procedure 3050.

4.6 Ethanol as the Carrier Solvent

The n-hexane was replaced with ethanol in the standard extraction procedure and the sandy soil spiked with 80,000 mg/kg Pb was tested. The DEHPA was readily

miscible in the ethanol but ethanol was readily miscible in water. When the solvents, water, and soil were added together before the mixer was turned on, the ethanol mixed with the water leaving the DEHPA sitting on top of the water/ethanol phase. An extraction was then performed for 10 minutes and then stopped because no pH change was occurring. A pH drop occurs during successful extractions because lead is being ion exchanged with H^+ which makes the system more acidic. When the phases were allowed to separate, the DEHPA was under the water/ethanol solution resting on top of the soil. No attempt was made to separate phases for AA analysis.

One more extraction was performed with no water in the system. The liquid difference was made up with ethanol. This extraction was run for 20 minutes and the pH decreased slightly. Upon settling, a white precipitate settled on top of the soil. Again no attempt was made to analyze the phases for lead content. DEHPA does not remain miscible in the ethanol upon extraction as it does in n-hexane. It was determined that n-hexane was the better solvent to use in the extraction process.

4.7 Metea Soil

The Metea soil was tested as a comparison to the sandy glacial soil. Tests on the Metea soil were similar to the extraction efficiency tests with the glacial sand. The only difference was that pH at 3.5 was used during the extraction. The Metea soil was also spiked with approximately 80,000 mg/kg Pb. Results of the four stage extraction, on three separate soil samples are shown in Table 4.7.1.

Table 4.7.1 Four stage extraction of lead from a Metea soil.

Stage	Ext. 1 (mg/kg)	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)	S.D.	95% C.I. (mg/kg)	% Removal
1	210	4000	44	1400	2200	± 5500	1.8
2	8000	13000	3600	8200	4700	± 1200	10
3	14000	23000	8400	15000	7400	± 18000	19
4	17000	22000	15000	18000	3600	± 9000	23
Total	39000	62000	27000	43000	18000	± 45000	54

Phase separation was poor in these extractions. Fines were caught in the organic phase and solvents were caught in the soil phase. Losses in this manner contributed a large part to the large standard deviations and, perhaps, to the poor overall extraction efficiency. The average extraction efficiency was 54%.

Unlike earlier work in which the largest amount of lead was removed in the first stages, the largest amount of lead was removed in the later extraction stages. This lead to the conclusion that possibly another metal was interfering with the extraction. The extracting solvents were analyzed for iron because it is a common element in the soil matrix and because the extracting solutions that were separated for analysis were rust colored. The extracting solvents from Ext. 2 and Ext. 3 were analyzed for iron and results are presented in Table 4.7.2.

Table 4.7.2 Iron analysis of the Metea soil extracting solutions.

Stage	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)
1	5400	7700	6600
2	6600	2400	4500
3	2000	1700	1800
4	630	810	720
Total	15000	13000	14000

As can be seen from Table 4.7.2, there is iron present. The highest extraction of iron occurs in the first stage and decreases with subsequent extractions. This corresponds to the lead removal results, as more iron is removed from the system the lead extraction efficiency increases. DEHPA appears to preferentially extract iron over lead.

From these results, the unspiked metea soil was acid digested using EPA Method 3050 to determine the amount of iron in the soil. A concentration of 10,000 mg/kg Fe (S.D. = 180) was calculated to be in the soil. This is a little lower than the amount of iron that was extracted from the soil but within the range of experimental error. Aluminum was also tested in the digested solution to determine if it could be a possible interference. A concentration of 8,600 mg/kg Al (S.D. = 480) was calculated in the soil. It could also be interfering with lead extraction as DEHPA would probably preferentially extract Al before Pb.

Since preferential extraction of iron has been demonstrated, increasing the number

of extraction stages would be beneficial. Earlier stages will remove one metal (i.e., Fe) and later stages remove the remaining metals (i.e., Pb). This would increase the overall extraction efficiency.

4.8 Extraction Results from the Gratiot Metal Co. Site Soil

Three soil samples were received from the Gratiot Metal Co. Site. The samples were acid digested using EPA Method 3050 to determine the concentration of lead contamination. The digested solutions were also tested for copper, iron, and aluminum. Two portions from each DNR soil sample were digested and results are averaged and presented in Table 4.8.1. The soil pH is also in Table 4.8.1.

Table 4.8.1 AA analysis of acid digested DNR soils and initial pH of the soils.

Sample	DNR No.1 (mg/kg)	DNR No.2 (mg/kg)	DNR No.3 (mg/kg)
Pb	1600	4600	26000
Cu	6400	11000	56000
Fe	17000	31000	120000
Al	0	5500	7800
pH	8.2	8.1	7.7

The lead and other metals concentrations increased from DNR soil No. 1 to DNR soil No. 3. Iron concentrations in all three DNR soils were higher than in the Metea soil. Aluminum was present in two of the DNR soils. The soil pH was slightly

above neutral for all three samples.

A four stage extraction using the optimized extraction parameters was performed on each DNR soil. Only one replicate was tested for each DNR soil. Lead and iron were tested in the extracting solutions. The results are presented in Table 4.8.2 for lead and Table 4.8.3 for iron. All soils were acid digested after extraction to determine residual concentrations of the metals left in the soil. These are also included in Tables 4.8.2 and 4.8.3.

Lead extraction efficiency was highest at 58% for DNR No. 1 which contained the lowest initial concentration of lead. DNR No. 3 had the lowest extraction efficiency at 36%. This soil had the highest initial lead concentration. DNR soils No. 2 and No. 3 had better phase separation after extraction than DNR No. 1. These two soils appeared to be more sandy in nature than DNR No. 1.

Table 4.8.2 Lead extraction results of DNR soils No. 1, No. 2, and No. 3.

Pb Stage	DNR No. 1 (mg/kg)	DNR No. 2 (mg/kg)	DNR No. 3 (mg/kg)
1	240	690	820
2	380	420	3600
3	160	700	3000
4	120	370	2000
Total	900	2200	9400
% Removal	58%	47%	36%
Residual	1000	1700	14000

Table 4.8.3 Iron extraction results of DNR soils No. 1, No. 2, and No. 3.

Fe Stage	DNR No. 1 (mg/kg)	DNR No. 2 (mg/kg)	DNR No. 3 (mg/kg)
1	62	330	260
2	70	150	1200
3	34	250	2200
4	48	170	1600
Total	210	900	5300
% Removal	1%	3%	5%
Residual	11000	10000	64000

A significant amount of lead was left as residual in all three DNR samples. These removal results are much lower than those obtained in the sandy glacial soil but comparative to removals achieved in the Metea soil. Poorer phase separations left more solvent in the soil and crud in the extracting solvent. This contributed to decreased extraction efficiency. With these samples, the lead contamination has been in the soil up to 40 years. The lead appears to have become fixed in the soil matrix making it harder to extract. In the lab contaminated soils, lead was more likely to be in an exchangeable position or an easy to extract form.

Iron interference was not a problem with extractions in these soils despite high initial concentrations of iron. The iron extracted was minimal at 1%, 3%, and 5% for DNR soils No. 1, No. 2, and No. 3. The iron appears to be in fixed positions as opposed to the Metea soil in which high concentrations of iron were extracted. In the

Metea soil, it is hypothesized that the iron was mobilized due to the lead spiking procedure. The lead was added to the soil in an acid solution. The acid moved the iron from fixed positions to more exchangeable positions and hence, significant amounts of iron were extracted from the Metea soil.

Extraction efficiencies in the DNR soils might be improved by extracting more than four times and by also increasing the extraction time. Increasing extraction stages and longer extraction times would promote the lead from non-exchangeable to exchangeable positions through the influence of a concentration gradient. It would also enhance ion exchange within the soil. Acidifying the soil before extraction would also promote the lead to more exchangeable positions making it easier to extract.

CHAPTER V

PROCESS CONFIGURATION, RESIDUALS CLEAN-UP, AND ECONOMIC ANALYSIS FOR SOLVENT EXTRACTION

5.1 Process Configuration

The extraction process as designed uses a batch mixer-settler unit. A process flow diagram is in Figure 5.1.1.

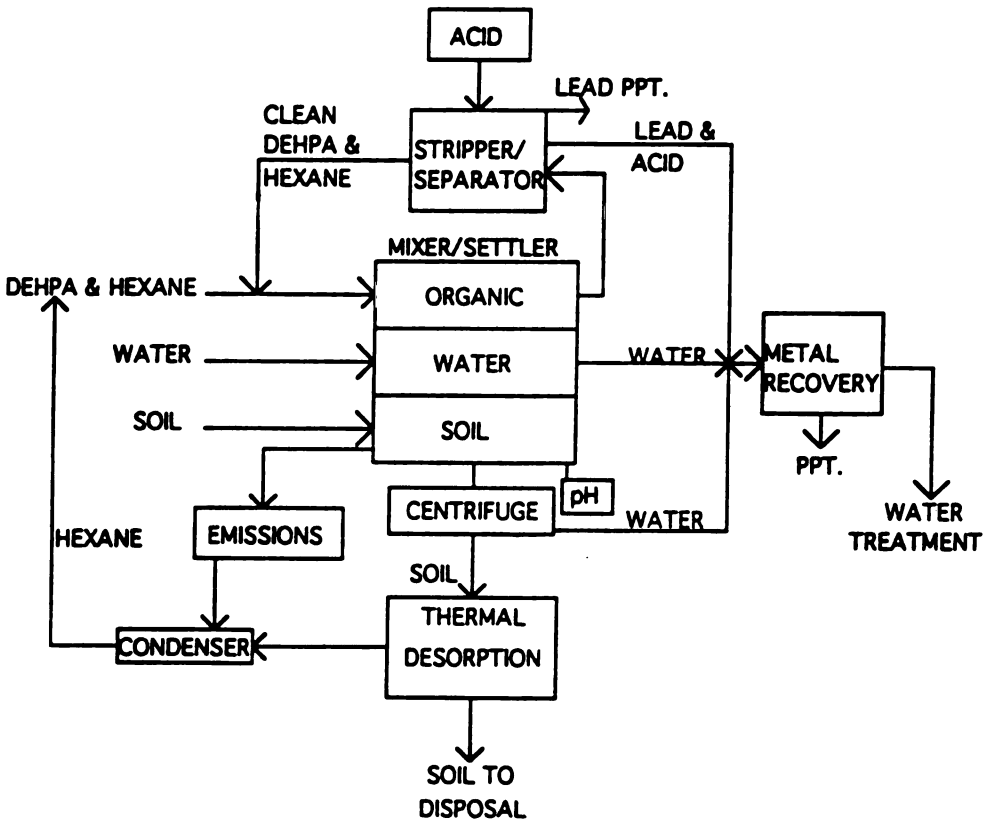


Figure 5.1.1. Extraction process flow diagram.

A four stage extraction will be performed in one unit. Soil, water, and organic will be mixed, settled, and the organic decanted to the stripper for recycle of the solvents. Clean hexane and DEHPA will be added for the second stage extraction and the process repeated until four extractions have been completed. At the end of each stage, the organic will be decanted and sent to the stripper. The aqueous phase is to be pumped to a metals recovery step to remove any dissolved metal before the water is sent to a public wastewater treatment plant or recycled through the process. The soil is processed through a centrifuge to reduce water content, and then to a low temperature thermal desorption to remove hexane, before it is returned to site.

This process can be modified to a continuous flow by separating the mixer and settler into two units. The mixer will be feed continuously and reaction time optimized depending on the lead concentration. The mixed soil, water, and solvents will then be sent to settlers and the effluents sent to the various treatment options after separating.

5.2 Clean-up of Extraction Residuals

As shown in the proposed process diagram, the organic phase (n-hexane plus DEHPA) can be stripped of lead and reused. The ion exchange process can be reversed using HCl or H_2SO_4 and replacing the Pb with H^+. Wilson recovered greater than 99% of the lead from the organic phase using HCl.[36] The Pb is then removed from the acid by neutralization/precipitation. The precipitate is disposed of by solidification/stabilization and land disposed in a RCRA (Resource Conservation and Recovery Act) Type C facility.

After extraction, some residual organics will be left in the soil. The hexane can be recovered using low temperature thermal desorption operating between 68°C to 100°C. The hexane gas can then be condensed and reused. Any residual DEHPA is not expected to decompose at 100°C. It can remain in the soil to be returned to the site. It is hypothesized that aerobic degradation will degrade DEHPA to CO_2, biomass, and H_3PO_4 over a period of time.[39] The expected degradation mechanism is diagrammed in Figure 5.2.1.

5.3 Economic Analysis

Costs were estimated using the B.E.S.T.™ commercial solvent extraction technology as a base line.[7] Costs for equipment not in the B.E.S.T.™ system such as thermal desorption, metal precipitation, and a condenser were added to the base line.[40,41,42] Equipment life was 10 years, treatment costs were calculated for 186 tons/day of soil, with an 80% online factor to account for maintenance, delays, etc. The itemized cost schedule in Table 5.3.1 includes equipment, labor, supplies, consumables, effluent/residuals handling and disposal, analytical costs, maintenance, repair, and replacement. Site preparation, permitting and regulatory costs, and facility start-up are not included and will vary from site to site. The total treatment costs of the solvent extraction system is about $277/ton of soil. Increasing the number of extraction stages will increase costs.

This estimate of $277/ton is based on the assumption that the DEHPA will be recycled and reused. Because of the high cost of DEHPA, it is recommended that a soil containing very high concentrations of lead (greater than 80,000 mg/kg Pb) be

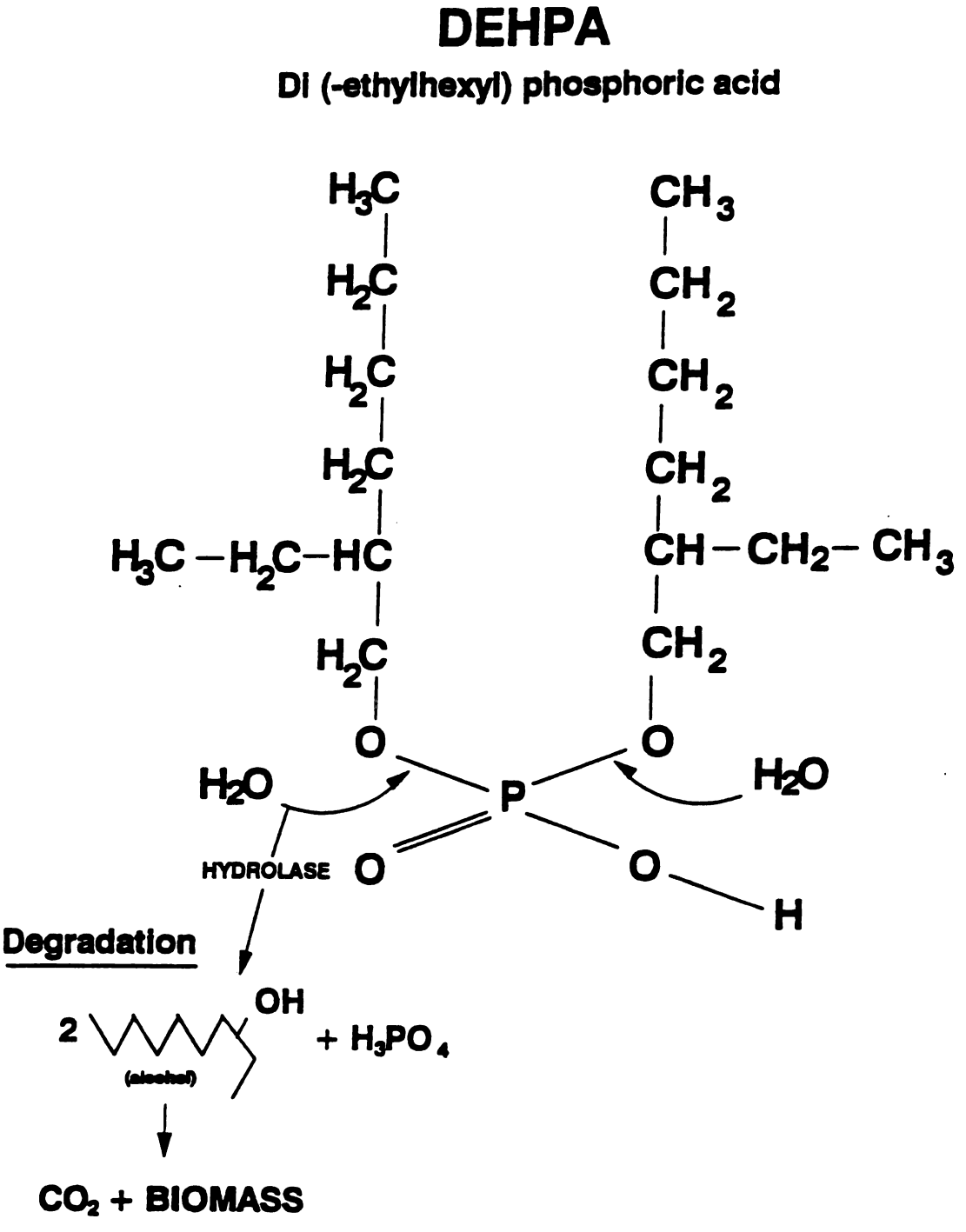


Figure 5.2.1 Biological degradation of DEHPA.[39]

acid washed to approximately 20,000 mg/kg of lead. Even at this concentration, the cost in DEHPA to remove 20,000 mg/kg Pb from a ton of soil would be $363.00 with no recycle. Although this is still very expensive, the cost may be reduced by increasing the number of times DEHPA is recycled.

Table 5.3.1 Solvent extraction treatment costs for 186 tons/day of soil.

Item	Cost ($/ton)
Equipment[7,41,42]	10.16
Labor[7,40]	129.86
Supplies[7,41]	15.74
Consumables[7,40,41,42]	49.66
Effluent/Residuals Handling & Disposal[40,41]	50.44
Analytical Costs[8,40]	20.44
Maintenance, Repair, & Replacement[7,41,42]	0.51
Total Treatment Costs	276.81

* The cost of DEHPA from the manufacturer Albright and Wilson Americas is $2.77/lb if greater than 20,000 lbs is ordered.(August 19, 1993)

CHAPTER VI

CONCLUSIONS

6.1 Conclusions

DEHPA has been shown to extract 80,000 mg/kg lead from an artificially contaminated sandy soil with up to 98% efficiency using a four stage extraction. The optimum pH appears to be approximately 3.5 and the optimum DEHPA concentration for extraction is 1 M in the Pb concentration range tested. Substituting ethanol for hexane in the extraction process is not feasible because ethanol is also miscible in water and mixes with the water instead of DEHPA. When no water is present, the ethanol does not hold the DEHPA in solution once the extraction starts. The extraction is inhibited by the phase separation.

Lead and cadmium removal was successful using a four stage extraction procedure on sandy soil spiked with 6,900 mg/kg Pb and 490 mg/kg Cd. At these concentrations, neither metal interfered with the extraction of the other. At much higher concentrations and more or different metals, preferential extraction might take place. More extraction stages or alternative process steps would become necessary to remove all the metals.

The four stage extraction procedure was not as successful on the Metea soil as on the sandy soil. Iron interfered with the extraction and phase separation was poor due

to the fine grain size of the soil. This, obviously, implies that the feasibility of DEHPA extraction must be evaluated on a case by case basis.

A four stage extraction of the soils from an actual site resulted in a much lower extraction efficiency than in the sandy soils. It appears that the soil's physical and chemical composition interfered with extractions. Poorer phase separations caused losses of solvent to the soil and resulted in crud and soil material in the extracting phase. The length of time the lead had resided in the soil may have played an important part. The lead may now be in non-exchangeable positions making it harder to extract. Increased extraction stages and increased extraction times will need to be studied to determine if they will improve extraction efficiency.

Clean-up of extraction residuals involves acid stripping the solvents of the extracted lead for reuse in subsequent extractions. Removal of solvents from the soil after extraction is necessary before disposal. It is proposed that hexane be removed using low temperature thermal desorption. Any residual DEHPA will be left in the soil and is expected to biologically degrade. The total treatment costs for the system proposed is approximately $ 277/ton.

6.2 Recommendations for Future Work

The following are some recommendations for future work to characterize the solvent extraction process more thoroughly and to discover DEHPA limitations:

1) Study increasing the extraction stages and extraction times to increase extraction efficiency in the harder to treat soils from the DNR.

2) Study extraction efficiency in soils with aged contaminates.

3) Test DEHPA extraction of different lead compounds: oxides, carbonates, chlorides, etc.

4) Develop a stripping procedure and determine number of times DEHPA can be stripped and reused.

5) Determine amount of DEHPA losses to soil and it's biodegradability.

6) Study solvent extraction effectiveness in high organic, clay, and calcareous soils.

7) Determine if concurrent removal of organics (PCBs, etc.) and metals is possible.

APPENDICES

APPENDIX A

APPENDIX A

Calculations for Pb Removed Using a Four Stage Extraction

Soil Sample Size = 50 g Pb Concentration in Soil = 80,000 mg/kg

Stage 1
Volume of organic decanted = 30 mL
Organic dilution for AA = 1:5000
AA sample reading = 8.50 mg/L Pb

Calculation for Pb extracted:

$$8.50 \text{ mg/L} \times 5{,}000 = 42{,}500 \text{ mg/L} \times 0.03\text{L} = \frac{1.275 \text{ mg}}{50 \text{ g soil}} \times \frac{1{,}000 \text{ g}}{\text{kg}} = 25{,}500 \text{ mg/kg Pb}$$

Stage 2
Volume of organic decanted = 48.5 mL
Organic dilution for AA = 1:5000
AA sample reading = 6.89 mg/L Pb

Calculation for Pb extracted:

$$6.89 \text{ mg/L} \times 5{,}000 = 34{,}450 \text{ mg/L} \times 0.0485\text{L} = \frac{1.671 \text{ mg}}{50 \text{ g soil}} \times \frac{1{,}000 \text{ g}}{\text{kg}} = 33{,}420 \text{ mg/kg Pb}$$

Stage 3
Volume of organic decanted = 44.3 mL
Organic dilution for AA = 1:2000
AA sample reading = 7.26 mg/L Pb

Calculation for Pb extracted:

$$7.26 \text{ mg/L} \times 2{,}000 = 14{,}520 \text{ mg/L} \times 0.0443\text{L} = \frac{643 \text{ mg}}{50 \text{ g soil}} \times \frac{1{,}000 \text{ g}}{\text{kg}} = 12{,}860 \text{ mg/kg Pb}$$

Stage 4
Volume of organic decanted = 54.7 mL
Organic dilution for AA = 1:2000
AA sample reading = 1.17 mg/L Pb

Calculation for Pb extracted:

$$1.17 \text{ mg/L} \times 2{,}000 = 2{,}340 \text{ mg/L} \times 0.0547\text{L} = \frac{128 \text{ mg}}{50 \text{ g soil}} \times \frac{1{,}000 \text{ g}}{\text{kg}} = 2{,}560 \text{ mg/kg Pb}$$

Total = Stage 1 + Stage 2 + Stage 3 + Stage 4 = 74,340 mg/kg Pb

% Removal = (74,340/80,000) x 100 = 93 %

* The numbers used for this example are from Ext. 3 in Table 4.2.1.

APPENDIX B

APPENDIX B

DEHPA Concentration Needed to Extract 80,000 mg/kg Pb

Soil Sample Size = 50 g

Reaction:

$Pb^{2+} + 2 - (DEHPA) \leftrightarrow 2H^{+} + Pb - (DEHPA)_2$

Grams of DEHPA needed to extract a 50 g soil sample:

$$(80{,}000 \frac{mg}{kg}\ Pb)\left(\frac{g\ Pb}{1000\ mg\ Pb}\right)(0.05\ kg\ soil)\left(\frac{mol\ Pb}{207.2\ g}\right)$$

$$\left(\frac{2\ mol\ DEHPA}{1\ mol\ Pb}\right)\left(\frac{322.4\ g\ DEHPA}{mol}\right) = 12.45\ g\ DEHPA$$

If use 50 mL of DEHPA + hexane for an extraction, the concentration of DEHPA is:

$$\left(\frac{12.45\ g\ DEHPA}{0.050L}\right)\left(\frac{mol\ DEHPA}{322.4\ g}\right) = 0.77\ M\ DEHPA$$

APPENDIX C

APPENDIX C

Raw Data

This appendix contains the calculated results tables from the text. Following each text table are tables containing the raw data for the calculated results.

Table 1. Text Table 4.2.1 (p 24) - Concentrations of lead extracted from the soil for an extraction mass balance.

Stage	Ext. 1 (mg/kg)	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)	S.D.	95%C.I. (mg/kg)	% Removal
1	31040	46120	25500	34220	10671	± 26492	42.8
2	26660	20440	33420	26840	6492	± 16117	33.6
3	12000	11020	12860	11960	921	± 2286	15.0
4	3200	7680	2560	4480	2790	± 6926	5.6
Total	72900	85260	74340	77500	6759	± 16780	97.0

Table 2. Raw data for Table 4.2.1, Ext.1 in Section 4.2.

Ext.1	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)*
Stage 1	31	1:5000	10.01
Stage 2	33	1:5000	8.08
Stage 3	33	1:2000	9.09
Stage 4	40	1:2000	2.00
Aque. Phase**	60	1:100	0.44

* The AA Number is an average value from 2 or more dilutions of the organic sample with 3 readings taken for each dilution sample. This will be true for all AA Numbers in the Raw Data.

** The aqueous phase was only tested in Ext. 1, Ext. 2, and Ext.3 of Section 4.2.

Table 3. Raw data for Table 4.2.1, Ext.2 in Section 4.2.

Ext.2	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	40	1:5000	11.53
Stage 2	22	1:5000	9.29
Stage 3	30	1:2000	9.19
Stage 4	52	1:2000	3.7
Aque. Phase	40	1:100	0

Table 4. Raw data for Table 4.2.1, Ext.3 in Section 4.2.

Ext.3	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	30	1:5000	8.50
Stage 2	48.5	1:5000	6.89
Stage 3	44.3	1:2000	7.26
Stage 4	54.7	1:2000	1.17
Aque. Phase	44.5	1:100	0.43

Table 5. Raw data for acid digestion of Ext.2 and Ext.3 in Section 4.2

Ext.2*	Aqueous Volume (mL)	Soil Wt. (g)	AA Reading (mg/L)
A.D.1	100.5	1.0879	4.33
A.D.2	100	1.0810	3.14
Ext.3*	Aqueous Volume (mL)	Soil Wt. (g)	AA Reading (mg/L)
A.D.1	100	1.0820	2.12
A.D.2	100.5	1.0785	1.92

* A.D.1 and A.D.2 were averaged for the calculated result in the text.

Table 6. Text Table 4.3.1 (p 26) - Lead concentration extracted from the soil at various pH values.

pH	Ser. 1 (mg/kg)	Ser. 2 (mg/kg)	Ser. 3 (mg/kg)	Average (mg/kg)	Standard Deviation	95% C.I. (mg/kg)
2.0	7298	18317	23808	16474	8408	± 20874
2.5	17110	26624	28162	23965	5986	± 14861
3.0	25500	42685	40327	36171	9316	± 23128
3.5	24034	50198	54468	42900	16477	± 40906
4.0	47082	70288	68198	61856	12837	± 31869
5.0	46768	21193		33980	18084	± 44896

Table 7. Raw data for Table 4.3.1, Ser.1 in Section 4.3.

pH	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
2.00	41	1:5000	1.78
2.50	29.5	1:5000	5.80
3.00	30	1:5000	8.50
3.50	24.6	1:5000	9.77
4.00*	39	1:5000	13.28
4.00*	36	1:5000	11.77
5.00	39.5	1:5000	11.84

* The calculated value from these two numbers was averaged for the value in Table 4.3.1.

Table 8. Raw data for Table 4.3.1, Ser.2 in Section 4.3.

pH	Aqueous Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
2.0	38.4	1:5000	4.77
2.50	32	1:5000	8.32
3.00	33.4	1:5000	12.78
3.50	38	1:5000	13.21
4.00	46	1:5000	15.28
5.00	17.5	1:5000	12.11

Table 9. Raw data for Table 4.3.1, Ser.3 in Section 4.3.

pH	Aqueous Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
2.0	46.5	1:5000	5.12
2.50	37.3	1:5000	7.55
3.00	36.2	1:5000	11.14
3.50	34	1:5000	16.02
4.00	43.3	1:5000	15.75

Table 10. Text Table 4.4.1 (p 28) - Lead concentration extracted from the soil at various DEHPA concentrations.

DEHPA Conc. (M)	Ser. 1 (mg/kg)	Ser. 2 (mg/kg)	Ser. 3 (mg/kg)	Average (mg/kg)	Standard Deviation	95% C.I. (mg/kg)
0.50	45750	42011	36344	41368	4736	± 11758
0.75	45936	52260	51342	49846	3417	± 8483
1.00	59214	66468	70560	65414	5746	± 14265
1.50	50140	61305	60680	57395	6273	± 15573

Table 11. Raw data for Table 4.4.1, Ser.1 in Section 4.4.

DEHPA Conc. (M)	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
0.5	37.5	1:5000	12.2
0.75	35.2	1:5000	13.05
1.0	41.7	1:5000	14.2
1.5	46	1:5000	10.90
2.0*	45.3	1:5000	11.7

* The 2.0 M concentration was only tested in this series. The results are in the text of Section 4.4.

Table 12. Raw data for Table 4.4.1, Ser.2 in Section 4.4.

DEHPA Conc. (M)	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
0.5	43	1:5000	9.77
0.75	40.2	1:5000	13.0
1.0	34.8	1:5000	19.1
1.5	33.5	1:5000	18.3

Table 13. Raw data for Table 4.4.1, Ser.3 in Section 4.4.

DEHPA Conc. (M)	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
0.5	41.3	1:5000	8.8
0.75	39.8	1:5000	12.9
1.0	42	1:5000	16.8
1.5	37	1:5000	16.4

Table 14. Text Table 4.5.1 (p 30) - Single stage extraction of soil spiked separately with Pb and Cd.

Sample	Pb (mg/kg)	Cd (mg/kg)
I	5480	288
II	4555	342
III	4974	364
Average	5003	331
Standard Deviation	463	39
Average Removal	72%	68%
95% C.I.	± 1149	± 97

Table 15. Raw data for Table 4.5.1, Pb and Cd in Section 4.5.

Pb Samples	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
I	50	1:1000	5.48
II	46.1	1:1000	4.94
III	46.4	1:1000	5.36
Cd Samples	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
I	35.5	1:100	4.06
II	40.5	1:100	4.22
III	46.7	1:100	3.90

Table 16. Text Table 4.5.2 (p 30) - Four stage extraction of Pb from soil containing Pb and Cd.

Pb Stage	Ext. 1 (mg/kg)	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)	S.D.	95% C.I. (mg/kg)	% Removal
1	4444	5456	5125	5008	516	± 1281	72
2	1053	1210	1581	1281	271	± 673	18
3	164	170	208	181	24	± 60	3
4	28	29	38	32	6	± 15	1
Total	5689	6865	6952	6502	705	± 1750	94

Table 17. Raw data for Table 4.5.2, Ext.1 in Section 4.5.

Ext.1	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	48.3	1:1000	4.6
Stage 2	54.3	1:100	9.7
Stage 3	51.6	1:50	3.17
Stage 4	53.5	1:10	2.65

Table 18. Raw data for Table 4.5.2, Ext.2 in Section 4.5.

Ext.2	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	46	1:1000	5.93
Stage 2	55.2	1:100	10.96
Stage 3	52.7	1:50	3.22
Stage 4	54.3	1:10	2.65

Table 19. Raw data for Table 4.5.2, Ext.3 in Section 4.5.

Ext.3	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	41	1:1000	6.25
Stage 2	55.1	1:100	14.35
Stage 3	51.5	1:50	4.04
Stage 4	53	1:10	3.55

Table 20. Text Table 4.5.3 (p 31) - Four stage extraction of Cd from soil containing Pb and Cd.

Cd Stage	Ext. 1 (mg/kg)	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)	S.D.	95 % C.I. (mg/kg)	% Removal
1	388	414	385	396	16	± 40	80
2	74	92	106	91	16	± 40	18
3	10	13	15	13	2	± 5	3
4	2	2	3	3	1	± 2	1
Total	474	521	509	502	26	± 64	102

Table 21. Raw data for Table 4.5.3, Ext.1 in Section 4.5.

Ext.1	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	48.3	1:100	4.02
Stage 2	54.3	1:100	0.68
Stage 3	51.6	1:10	1.0
Stage 4	53.5	1:10	0.2

Table 22. Raw data for Table 4.5.3, Ext.2 in Section 4.5.

Ext.2	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	46	1:100	4.5
Stage 2	55.2	1:100	0.83
Stage 3	52.7	1:25	0.51
Stage 4	54.3	1:10	0.2

Table 23. Raw data for Table 4.5.3, Ext.3 in Section 4.5.

Ext.3	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	41	1:100	4.7
Stage 2	55.1	1:100	0.96
Stage 3	51.5	1:25	0.6
Stage 4	53	1:10	0.25

Table 24. Raw data for acid digestion of the soil samples extracted in Table 4.5.2 and Table 4.5.3.(p 31)

Pb*	Aqueous Volume (mL)	Soil Wt. (g)	AA Reading (mg/L)
A.D.1	100	1.0349	0.6
A.D.2	100	1.0561	0.6
A.D.3	100	1.0113	0.23
A.D.4	100	1.0301	0
A.D.5	100	1.0307	0.07
A.D.6	100	1.0244	0
A.D.7	100	1.0028	0.07
A.D.8	100	1.0157	0.53
Cd*	Aqueous Volume (mL)	Soil Wt. (g)	AA Reading (mg/L)
A.D.1	100	1.0349	0.08
A.D.2	100	1.0561	0.06
A.D.3	100	1.0113	0.04
A.D.4	100	1.0301	0.07
A.D.5	100	1.0307	0.04
A.D.6	100	1.0244	0.04
A.D.7	100	1.0028	0.03
A.D.8	100	1.0157	0.03

* Values calculated from A.D.1 - A.D.8 were averaged for the results in the text.

Table 25. Text Table 4.7.1 (p 33) - Four stage extraction of lead from a Metea soil.

Stage	Ext. 1 (mg/kg)	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)	S.D.	95% C.I. (mg/kg)	% Removal
1	211	4038	44	1431	2260	± 5609	1.8
2	7984	13356	3590	8310	4891	± 12143	10
3	14073	23240	8448	15254	7466	± 18536	19
4	17137	22272	14872	18094	3792	± 9413	23
Total	39405	62905	26954	43088	18256	± 45323	54

Table 26. Raw data for Table 4.7.1, Ext.1 in Section 4.7.

Ext.1	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	33	1:100	3.2
Stage 2	41.8	1:5000	1.91
Stage 3	42.8	1:2000	8.22
Stage 4	50.7	1:1000	16.9

Table 27. Raw data for Table 4.7.1, Ext.2 in Section 4.7.

Ext.2	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	30	1:1000	6.73
Stage 2	53	1:2000	6.3
Stage 3	70	1:2000	8.3
Stage 4	64	1:2000	8.7

Table 28. Raw data for Table 4.7.1, Ext.3 in Section 4.7.

Ext.3	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	43.5	1:100	0.5
Stage 2	26.4	1:2000	3.4
Stage 3	48	1:2000	4.4
Stage 4	67.6	1:2000	5.5

Table 29. Text Table 4.7.2 (p 34) - Iron analysis of the Metea soil extracting solutions.

Stage	Ext. 2 (mg/kg)	Ext. 3 (mg/kg)	Average (mg/kg)
1	5400	7673	6536
2	6572	2376	4474
3	1960	1690	1825
4	631	811	721
Total	14563	12550	13556

Table 30. Raw data for Table 4.7.2, Ext.2 in Section 4.7.

Fe Ext.2	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	30	1:2000	4.5
Stage 2	53	1:2000	3.1
Stage 3	70	1:2000	0.7
Stage 4	64	1:100	4.93

Table 31. Raw data for Table 4.7.2, Ext.3 in Section 4.7.

Fe Ext.3	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	43.5	1:1000	8.82
Stage 2	26.4	1:2000	2.25
Stage 3	48	1:2000	0.88
Stage 4	67.6	1:2000	0.3

Table 32. Raw data for acid digestion of Metea soil, Fe and Al analysis.(p 34)

Fe*	Aqueous Volume (mL)	Soil Wt. (g)	AA Sample Dilution	AA Reading (mg/L)
A.D.1	100	1.2333	10	12.9
A.D.2	100	1.2351	10	12.8
A.D.3	100	1.2355	10	12.5
Al*				
A.D.1	100	1.2333	10	11.0
A.D.2	100	1.2351	10	9.9
A.D.3	100	1.2355	10	10.8

* A.D.1 - A.D.3 were averaged for the calculated results in the text.

Table 33. Text Table 4.8.1 (p 35) - AA analysis of acid digested DNR soils.

Metal	DNR #1 (mg/kg)	DNR #2 (mg/kg)	DNR #3 (mg/kg)
Pb	1554	4611	25860
Cu	6358	11380	56204
Fe	17430	30736	116129
Al	0	5476	7764
pH	8.2	8.1	7.7

Table 34. Raw data for Table 4.8.1, Pb analysis in Section 4.8.

DNR No.1*	Aqueous Volume (mL)	Soil Wt. (g)	AA Sample Dilution	AA Reading (mg/L)
A.D.1	100	1.4452	0	20.4
A.D.2	100	1.2260	0	20.8
DNR No.2*				
A.D.1	100	1.3020	10	8.1
A.D.2	100	1.3326	10	4.0
DNR No.3*				
A.D.1	100	1.2624	100	2.4
A.D.2	100	1.3146	100	4.3

* A.D.1 and A.D.2 were averaged for calculated results in the text.

Table 35. Raw data for Table 4.8.1, Cu analysis in Section 4.8.

DNR No.1*	Aqueous Volume (mL)	Soil Wt. (g)	AA Sample Dilution	AA Reading (mg/L)
A.D.1	100	1.4452	50	1.2
A.D.2	100	1.2260	50	2.1
DNR No.2*				
A.D.1	100	1.3020	50	2.8
A.D.2	100	1.3326	50	3.2
DNR No.3*				
A.D.1	100	1.2624	100	6.7
A.D.2	100	1.3146	100	7.8

* A.D.1 and A.D.2 were averaged for calculated results in the text.

Table 36. Raw data for Table 4.8.1, Fe analysis in Section 4.8.

DNR No.1*	Aqueous Volume (mL)	Soil Wt. (g)	AA Sample Dilution	AA Reading (mg/L)
A.D.1	100	1.4452	50	4.3
A.D.2	100	1.2260	50	4.9
DNR No.2*				
A.D.1	100	1.3020	50	7.8
A.D.2	100	1.3326	50	8.4
DNR No.3*				
A.D.1	100	1.2624	100	15.3
A.D.2	100	1.3146	100	14.6

* A.D.1 and A.D.2 were averaged for the calculated results in the text.

Table 37. Raw data for Table 4.8.1, Al analysis in Section 4.8.

DNR No.1*	Aqueous Volume (mL)	Soil Wt. (g)	AA Sample Dilution	AA Reading (mg/L)
A.D.1	100	1.4452	0	0
A.D.2	100	1.2260	0	0
DNR No.2*				
A.D.1	100	1.3020	50	1.5
A.D.2	100	1.3326	50	1.4
DNR No.3*				
A.D.1	100	1.2624	100	1.0
A.D.2	100	1.3146	100	1.0

* A.D.1 and A.D.2 were averaged.

Table 38. Raw data for pH in Table 4.8.1 in Section 4.8.

pH	DNR No.1	DNR No.2	DNR No.3
pH.1	8.05	8.06	7.67
pH.2	8.17	8.07	7.71
pH.3	8.23	8.10	7.75

Table 39. Text Table 4.8.2 (p 36) - Lead extraction results of DNR soils No. 1, No. 2, and No. 3.

Pb Stage	DNR No. 1 (mg/kg)	DNR No. 2 (mg/kg)	DNR No. 3 (mg/kg)
1	243	693	818
2	381	416	3632
3	161	705	2980
4	121	370	1990
Total	906	2184	9420
% Removal	58%	47%	36%
Residual	1003	1666	13742

Table 40. Raw data for Table 4.8.2, DNR No.1 in Section 4.8.

DNR No.1	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	26	50	9.3
Stage 2	63.5	50	6.0
Stage 3	57.5	50	2.8
Stage 4	48.5	50	2.5

Table 41. Raw data for Table 4.8.2, DNR No.2 in Section 4.8.

DNR No.2	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	60	50	11.6
Stage 2	47.3	50	8.8
Stage 3	66.2	50	10.6
Stage 4	46	50	8.1

Table 42. Raw data for Table 4.8.2, DNR No.3 in Section 4.8.

DNR No.3	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	18.5	250	8.8
Stage 2	83.5	250	8.7
Stage 3	53.7	250	11.1
Stage 4	50	250	8.0

Table 43. Raw data for Pb residual in Table 4.8.2 in Section 4.8.

DNR No.1*	Aqueous Volume (mL)	Soil Wt. (g)	AA Sample Dilution	AA Reading (mg/L)
A.D.1	100	1.2629	0	12.7
A.D.2	100	1.4907	0	14.9
DNR No.2*				
A.D.1	100	1.4911	10	3.5
A.D.2	100	1.2904	10	1.7
DNR No.3*				
A.D.1	100	1.3360	25	8.6
A.D.2	100	1.5802	25	7.2

* A.D.1 and A.D.2 were averaged for the calculated result in the text.

Table 44. Text Table 4.8.3 (p 37) - Iron extraction results of DNR soils No. 1, No. 2, and No. 3.

Fe Stage	DNR No. 1 (mg/kg)	DNR No. 2 (mg/kg)	DNR No. 3 (mg/kg)
1	62	330	264
2	70	147	1211
3	34	251	2202
4	48	166	1625
Total	214	894	5302
% Removal	1%	3%	5%
Residual	11265	10542	63973

Table 45. Raw data for Table 4.8.3, DNR No.1 in Section 4.8.

DNR No.1	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	26	50	2.4
Stage 2	63.5	50	1.1
Stage 3	57.5	50	0.6
Stage 4	48.5	50	1.0

Table 46. Raw data for Table 4.8.3, DNR No.2 in Section 4.8.

DNR No.2	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	60	50	5.5
Stage 2	47.3	50	3.1
Stage 3	66.2	50	3.8
Stage 4	46	50	3.6

Table 47. Raw data for Table 4.8.3, DNR No.3 in Section 4.8.

DNR No.3	Organic Volume (mL)	AA Sample Dilution	AA Reading (mg/L)
Stage 1	18.5	250	2.8
Stage 2	83.5	250	2.9
Stage 3	53.7	250	8.2
Stage 4	50	250	6.5

Table 48. Raw data for Fe residual in Table 4.8.3 in Section 4.8.

DNR No.1*	Aqueous Volume (mL)	Soil Wt. (g)	AA Sample Dilution	AA Reading (mg/L)
A.D.1	100	1.2629	10	16.0
A.D.2	100	1.4907	10	14.7
DNR No.2*				
A.D.1	100	1.4911	10	14.8
A.D.2	100	1.2904	10	14.4
DNR No.3*				
A.D.1	100	1.3360	25	36.5
A.D.2	100	1.5802	25	37.7

* A.D.1 and A.D.2 were averaged for the calculated result in the text.

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