Simultaneous Mobilization of Polychlorinated Biphenyl Compounds and Heavy Metals from a Field Contaminated Soil

By

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May 2006

A thesis submitted to McGill University in partial fulfillment of the requirements of the degree of Doctor of Philosophy

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Your file Votre référence
ISBN: 978-0-494-25137-9
Our file Notre référence
ISBN: 978-0-494-25137-9

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ABSTRACT

A major factor complicating the cleanup at many sites is co-contamination by both organic compounds and heavy metals. Whereas much research has focused on the removal of either organic compounds or metals, relatively few studies have investigated simultaneous removal of organic and inorganic pollutants from soil.

The studies reported in this thesis have evaluated a novel technique for the simultaneous mobilization of polychlorinated biphenyl (PCB) compounds and heavy metals (HMs) from a field contaminated soil. Soil extraction with washing aids {surfactants/cyclodextrin in combination with chelating reagent(s)} was optimized for mobilization efficiency, recovery/recycle of washing additives, and in parallel detoxification of mobilized contaminants. PCB extraction efficiencies were determined with a method that converted all the PCB congeners to dicyclohexyl by hydrogenation over palladium. Studies demonstrated that 10 minutes of ultrasonic mixing of field contaminated soil with a combination of surfactant (30 mL L^{-1}) or cyclodextrin (100 g L^{-1}) and a sparing quantity (2 mmoles) of EDTA, simultaneously mobilized appreciable quantities of PCBs and most analyte metals (Cd, Cu, Mn, Pb, Zn, Ni, Cr).

Relative to individual reagents, combinations of surfactant (Brij 98, Triton X-301, or Triton XQS-20) or cyclodextrin (RAMEB or HPCD) with EDTA did not influence PCB extraction efficiencies perceptibly. The presence of surfactant or cyclodextrin in admixture with EDTA did not appreciably change the efficiency of mobilization of most heavy metals (Al, Cd, Cr, Fe, Mn, Ni, and Zn) but did increase the recovery of Cu and Pb with nonionic surfactant and cyclodextrin. When coupled with PCB removal by hexane back-extraction and precipitation of the HMs {mediated by hydrolysis of zero-valent magnesium (Mg^o)}, aqueous washing suspension was regenerated and recycled twice to mobilize more contaminants from the soil. Three sonication-washes with the same charge of reagent mobilized appreciable quantities of PCBs (68 - 83%) and virtually all of the available Cd, Cu, Mn, and Pb and lesser amounts of the Zn (56%), Ni (59%), and Cr (50%) but only small quantities of Al (28%) and Fe (30%).

The release of EDTA from heavy metals complexes was efficient for most metals (99%) but was influenced by the nature of surfactant. EDTA recovery (62-65%) post three cycles of soil washing, hexane back-extraction, and Mg^o treatment was similar for all reagent combinations. Among surfactants and cyclodextrin, only anionic surfactants suffered losses to Mg^o treatment.

RESUME

Une entrave majeur au nettoyage de plusieurs sites Superfund est la présence simultanée de composés organiques et de métaux lourds. Alors que la plupart des recherches aient visé la décontamination d'un ou l'autre de ces contaminants, rares sont celles qui aient visé une décontamination simultanée de contaminants organiques et inorganiques des sols.

L'étude présentée dans la présente thèse évalua une nouvelle technique pour la mobilisation simultanée de diphényles polychlorés (DPC) et métaux lourds (MLs) de sols contaminés. Pour les sols contaminés, le mélange d'aides-lavage {agents de surface/cyclodextrines et chelateur(s)} fut optimisé par rapport à son éfficacité de mobilisationation, celle de recupération-recyclage de l'agent de mobilisation, et, en parallèle, avec la détoxification des contaminants mobilisés. L'éfficacité d'extraction des DPC fut déterminé par une méthode où tous les congénères de DPC furent convertis en dicyclohexyle par hydrogénation sur palladium. Le traitement de sols contaminés, en présence de 30 mL L^{-1} d'agent de surface ou de cyclodextrine (100 g L^{-1}) et de très peu (2 mmol) d'EDTA, avec 10 minutes d'ultrasons a permis de mobiliser une importante quantité de DPC et des différents métaux lourds analysés (Cd, Cu, Mn, Pb, Zn, Ni, Cr). Les surfactants testés (Brij 98, Triton X-301 ou Triton XQS-20) ou de cyclodextrines (RAMEB ou HPCD) ne furent pas plus éfficaces à extraire les DPC en combinaison avec l'EDTA qu'individuellement.

La présence d'agent de surface ou de cyclodextrine en mélange avec l'EDTA n'améliora pas la récupération de la plupart des métaux lourds analysés (Al, Cd, Cr, Fe, Mn, Ni, et Zn), mais la combinaison d'un agent de surface non-ionique et de cyclodextrine augmenta récupération de Cu et Pb. Lorsque couplé à la réextraction en hexane des DCPs et la précipitation des métaux lourds par l'entremise de l'hydrolyse avec magnesium zéro valent (Mg^0), la solution aqueuse nettoyante a pu être récupéré et recyclée deux fois, afin de mobiliser plus de contaminants dans le sol. Une suite de trois extractions avec ultrasons portant la même charge de réactifs ont permis d'extraire une importante quantité de DPCs (68 - 83%), pratiquement tout le Cd, Cu, Mn et Pb, ainsi

qu'une partie du Zn (56%), Ni (59%), et Cr (50%). Toutefois, la méthode fut moins efficace pour l'Al (28%) et le Fe (30%).

La recupération de l'EDTA complexé aux métaux lourds fût réalisée facilement pour la majorité des métaux (99%), mais fut influencé à un certain degré par l'agent de surface employé. Le taux de récupération de l'EDTA après trois cycles de lavage du sol, réextraction avec hexane et traitement au Mg zéro valent fut semblable pour toutes combinaisons de réactifs, soit de 62 à 65%. Parmi les agents de surface et la cyclodextrine, seulement les agents de surface non ioniques furent endommagés par le traitement au Mg^0.

CONTRIBUTION OF CO-AUTHORS

This research has been supervised by Dr. William D. Marshall in principal and Dr. Shiv O. Prasher as co-advisor. Dr. Marshall was responsible for defining the problem and provided direct advisory input as the work progressed. The author of this thesis was responsible for the design of experiments, experimental work, and manuscript preparation. The present work has been supported financially by the Natural Science and Engineering Research Council of Canada (NSERC). Dr. Marshall and Dr. Prasher are the co-authors for the materials that have been published and are co-authors for the manuscripts that have been submitted for publication or the manuscript under preparation.

Parts of these works have been published or submitted

Ehsan, S., S. O. Prasher, and W. D. Marshall. 2003. Estimates of total polychlorinated biphenyl (PCB) compounds in soils/sediments by hydrogenolysis to dicyclohexyl. ***J. Environ. Monit. 5:644-648.***

Ehsan, S., S. O. Prasher, and W. D. Marshall. 2005. A Washing Procedure to simultaneously Mobilize Mixed Contaminants from a Field-contaminated Soil. Part 1. Polychlorinated Biphenyl (PCB). ***Submitted for publication in J. Environ. Qual.***

Ehsan, S., S. O. Prasher, and W. D. Marshall. 2005. A Washing Procedure to simultaneously Mobilize Mixed Contaminants from a Field-contaminated Soil. Part 2. Heavy Metals. ***Submitted for publication in J. Environ. Qual.***

Ehsan, S., S. O. Prasher, and W. D. Marshall. 2006. Simultaneous removal of polychlorinated biphenyls and heavy metals from contaminated soil using cyclodextrins and EDTA. ***In progress.***

ACKNOWLEDGEMENT

I gratefully acknowledge Dr. William D. Marshall and Dr. Shiv O Prasher for giving me the opportunity to pursue my Ph.D studies in their research group. Their technical guidance, logistic support, monetary aid as well as emotional encouragement, throughout my studies is gratefully appreciated. I have been extremely fortunate that they were available when and wherever I needed them.

I am truly indebted for the invaluable scientific guidance, encouragement, and financial support provided by my supervisor Dr. W.D. Marshall. I also appreciate the counsel and advice he offered and the liberty I had to come and discuss any problems related to my studies. A valued recognition is given to him for mentoring this work and reading the thesis.

I would like to express my gratitude to my co-supervisor Dr. S. Prasher. Most of my research project was conducted in his laboratory. I would like to acknowledge the provision of his lab facilities in addition to the financial compensations that came in various shapes and forms.

I would like to acknowledge the assistance that was provided to me in completing my research work successfully by numerous people ranging from professors, technicians to my colleagues, friends, and family.

Appreciations are extended to Dr. V. A. Yaylayan for sharing his time and insight. I am also appreciative to his great scientific guidance and suggestions. Many thanks go to Dr. F. R. van de Voort and Dr. B. Lee for providing lab facilities and technical help. I would also like to thank Dr. W. Hendershot and Ms. Helen Lalande (Department of Natural Resource Sciences) for sharing laboratory facilities.

Thanks to my fellow graduate students, especially those from Dr. Marshall's and Dr. Prasher's labs for their help and co-operation during my studies. Last but not the least I would like to acknowledge the constant, incessant, and consistent support of my family. My deepest gratitude goes to my mother and father for their prayers and love. My deep gratitude also goes to my brothers, sisters, brothers and sisters in law, nieces, nephews, aunts, and uncles for their love, encouragement, and support.

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LIST OF ABBREVIATIONS AND SYMBOLS

The most commonly used symbols, abbreviations and nomenclatures are listed below. The specific symbols that are used in a particular section are described at their place of appearance in the text.

ASE	Accelerated-solvent extraction
APEG	Alkaline polyethylene glycolate
APEO	Alkylphenol ethoxylate
BCD	Base catalysed decomposition
BTEX	Benzene, toluene, ethyl benzene, xylene
HEDC	bis(2-hydroxyethyl)-dithiocarbamate
BPA	Bisphenol A
CEC	Cation exchange capacity
CMC	Critical micelle concentration
CDs	Cyclodextrins
DEDTC	Diethyldithiocarbamate
DTPA	Diethylenetriaminepentacaetic acid
DTD	Direct thermal desorption
EDTA	Ethylenediaminetetraacetate
HCB	Hexachlorobenzene
HLB	Hydrophile lipophile balance
HOC	Hydrophobic organic compounds
HPCD	Hydroxypropyl–β-CD
IUPAC	International Union of Pure and Applied Chemistry
LAS	Linear alkyl benzene sulfonate
MAE	Microwave assisted extraction
NIST	National institute of standards and technology
NPL	National priority list
NAPLs	Non-aqueous phase liquids
PAH	Poly aromatic hydrocarbons
PCB	Polychlorinated biphenyl
PCDD	Polychlorinated dibenzo-dioxins
PCDF	Polychlorinated dibenzo-furans
PCE	Perchloroethylene
PCP	Pentachlorophenol
PFE	Pressurized fluid extraction
RAMEB	Randomly methylated β cyclodextrin

LIST OF ABBREVIATIONS AND SYMBOLS cont'd

SVOCs	Semivolatile organic compounds
SOM	Soil organic matter
S/S	Stabilization/solidification
SFE	Supercritical fluid extraction
TCP	Tetrachlorophenol
TCE	Trichloroethylene
USE	Ultrasonic extraction
USEPA	United States Environmental Protection Agency
VOCs	Volatile organic compounds
ZV	Zero valent
ZnSe	Zinc selenide

Glossary of Terms

Aroclor	Commercial PCB formulation containing many different PCB congeners in a mineral-oil carrier
Congener	An individual PCB
Coplanar	A PCB having zero or one chlorine in an ortho position
Dechlorination	The process that replaces one or more chlorine atom from chlorinated compounds to make the substrate less toxic and/or virtually non-toxic
Ex-situ	Above ground (outside of ground)
In-situ	In the ground (within ground)
Internal Standard	Known amount of chemical added to a sample prior to measurement, to control for the sample quantity or instrument variability
Isomers	Chemicals having the same molecular formula, but different arrangements of their constituent atoms
Micelle	Self-aggregated surfactant molecules, having either hydrophobic ends out, or vice vresa
Remediation	The removal of contaminants from environmental media to achieve regulatory or risk-based goals
Solution	Homogeneous mixture of two or more substances
Surfactant	Molecules with polar and non-polar regions that self-aggregate into micelles

CHAPTER 1

INTRODUCTION

1.1 Rationale

Environmental contaminants often occur as mixtures of both organic and inorganic compounds. These contaminants can be grouped into distinct classes that can include synthetic or naturally occurring organic compounds volatile organic compounds; (VOCs), metals, semivolatile organic compounds (SVOCs), or radionuclides. Most of the National priority list (NPL) or superfund sites in the USA require remediation for more than one of these contaminant groups. Twenty-five percent of the sites contain two contaminant groups and 41% of the sites contain all three contaminant groups (U. S. EPA, 1997a). Among organic compounds, PCBs represent an important class of priority pollutant due to their persistence, toxicity, and tendency to bioaccumulate. For metals, the presence of lead, chromium, arsenic, zinc, cadmium, copper, and mercury in ground waters or soils pose an appreciable threat to not only to human health, but also to ecological systems. Heavy metals and hydrophobic polychlorinated biphenyls (PCBs) are two of the most frequently occurring soil and sediment contaminants. Both groups have been the focus of continuing research, partly because of their abundance, and partly because of the growing scientific and public awareness of environmental issues.

Heavy metals in soils are of concern when they are present at sufficient concentration to adversely affect human or environmental health. Excessive levels of metals can be accumulated from many sources, ranging from industrial activities such as mining, coal tar pits, landfill sites, waste waters, discharge accidents, and agriculture emissions involving pesticide and fertilizers applications. Whereas a primary source of heavy metals such as cobalt (Co), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn) results from mining activities, arsenic(As) and cadmium (Cd) contamination is caused principally by smelting of Cu, Pb, and Zn ores (Patterson, 1990). In addition, mining related wastes (waste rock and tailing) and smelter emissions represent potential sources of metals that can be redistributed to the surrounding environment by aerial and fluvial transport. Once the heavy metal accumulation exceeds the metal sorption capacity of the soil, metals are transported in runoff to rivers, leached into the groundwater threatening the subterranean ecosystem. Other industrial sources, such as foundries, oil refineries, metal molding, metal plating operations, paint and battery manufacture are also known to be appreciable sources of metal contaminations to soils (Di Palma, et al., 2003).

Heavy metal bioconcentration and extensive diffusion have stimulated research efforts to develop appropriate (efficient and cost effective) technologies for the treatment of metal-contaminated soils and sediments. There are numerous technologies for the remediation of heavy metal contaminated soils including chemical/physical methods, engineering solutions, and biological methods (Martin and Ruby, 2004). These methods are based on two main remediation strategies: stabilization/immobilization or extraction/mobilization. Stabilization/immobilization technologies include those processes that involve the use of chemical amendment(s) and/or plants to reduce the leachability and/or bioavailability of metals in contaminated soil. Removal technologies such as *ex situ* soil washing or *in situ* soil flushing include the use of chemical and/or physical processes for extracting the heavy metals into a liquid phase by desorption and solubilization.

In soil, heavy metals can exit as soluble ionic species, organically bound metal complexes or in exchangeable forms. However, heavy metals are generally rendered less mobile because of their association with different soil fractions and compartments such as carbonates, oxides, and organic matters (Huang et al., 1995; Tan, 1998). In soil/sediment, heavy metal retention is governed by several factors including pH, redox potential, soil type (*e.g.* particle size), cation exchange capacity (CEC), the content of natural organic matter, period of contact with the soil's natural constituents, and the presence of other inorganic contaminants. The effectiveness of any chemical for possible metal mobililization/displacement is a function of the factors mentioned above. A range of metal remediating reagents, including organic/inorganic acids (Elliot and Herzig, 1999), chelating agents (Sun et al., 2001), cyclodextrin (Brusseau et al., 1997), and surfactants (Mulligan et al., 1999) have been evaluated, with varying levels of success. Among all potential metal remediating reagents, chelating agents are the most effective extractants. Of the many commercially available chelating reagents, ethylenediaminetetraacetic acid (EDTA) has been the most extensively investigated and several studies have demonstrated its potential effectiveness for soil washing (Martínez and Motto, 2000; Lee and Marshall, 2002).

In the case of hydrophobic organic contaminants, certain synthetic substances are included in the class collectively known as chlorinated organic compounds. Members of this class of compounds continue to be used extensively by a number of industries. This class of pollutant is the subject of growing concerns due principally to their toxicity and low rate of degradation in the environment. Prominent among this class are polychlorinated biphenyl (PCB) compounds which have been recognized as a global environmental problem because of their presence in a large number of anthropogenic products/equipment/appliances and this has resulted in the wide dispersal of PCB in the environment. The primary source of PCB contamination is PCB-laden oil used in transformers and capacitors as dielectric fluids. Other sources stem from PCB uses as waxes, cutting oils, flame retardants, insulating paper for electric cables, dust-removing agents, hydraulic fluids, lubricants, certain paints, and plastics. In addition, PCBs can be released into the environment from hazardous waste sites and the illegal or improper dumping of PCB wastes. PCBs exist as mixtures of chlorinated biphenyl compounds - a maximum of 209 individual chlorinated congeners having varying degrees of chlorination. The primary concern with PCBs contamination stems from the fact that PCBs are known to cause cancer in laboratory animals, and are suspected of being human carcinogens. In addition to carcinogenicity, PCBs exhibit a variety of other detrimental health effects including skin disorders, liver damage, and reproductive and development disorders. Of the 209 PCB congeners, a dozen are most toxic because of certain features of their structure which make them similar to dioxins. Because of the strongly hydrophobic nature of PCBs and their low water solubility, they tend to sorb strongly to soil organic matter and can remain associated with this phase for many years (Erickson, 1997). Strong sorption of PCB to solid phase represents a significant limitation to the efficiency of water washing for the removal of PCBs from contaminated soil. Technologies, including incineration, thermal desorption, chemical dehaloganation, solidification, and vitrification that can be used to remediate PCB-contaminated soil are generally considered to be prohibitively costly as is excavation followed by disposal in a hazardous waste facility or incineration. Remediation treatments through biological transformations are limited by correct selection of active microbes and the possible formation of metabolites that can be more toxic than the parent compound. Technologies involving the mass transfer of contaminants from the solid to a liquid phase are relatively inexpensive alternative in soil remediation if a chemical transformation of contaminants into innocuous products is available. Hydrophobic PCBs can be desorbed from soil by using organic solvents or aqueous suspension of surfactants or cyclodextrin. In recent years, surfactants have been evaluated by several investigators for their ability to act as soil-washing agents for the remediation of organic contaminants and more recently, substituted cyclodextrins, cyclic oligomers of glucose, have been considered as alternative solubilization reagents for soil cleanup. Both surfactants and cyclodextrin are attractive for the solubilization of organic contaminants because of their efficiency, reduced acute toxicity and their favorable biodegradation rates. In addition, they are more environmentally benign than many organic solvents that can be used for soil cleanup. During *in-situ* soil flushing or ex-situ washing processes, both surfactant (Conte, et al., 2005) and cyclodextrin (McCray and Brusseau, 1999a) are considered to mobilize PCBs from soils by increasing their solubilities in water - solubilization results from the partitioning of contaminants into the hydrophobic core of surfactant micelles or hydrophobic cavity of the cyclodextrin.

The remediation of mixed contaminants represents one of the more common environmental problems these days because combination of organic compounds and metals are frequently found at many hazardous waste sites. In addition, industrialized urban areas are also often contaminated with both heavy metals and organics such as PAHs and PCBs (Weiss et al., 1994). The most popular remediation processes have been found to be successful only for the removal of specific groups of contaminants, either metals or organic compounds, and are not effective for the simultaneous removal of mixed pollutants. As a result, two or more remediation processes are used in combination to remove the mixed pollutant from the soils, increasing the expense of the remedial operation.

Soil washing is a treatment process that can be used for the removal of both heavy metals and PCBs from mixed contaminated soil. This process involves high energy contact between the contaminated soil and aqueous suspension of suitable remediating reagent(s). Soil washing can be a physical and/or chemical process that results in the separation, segregation and volume reduction of hazardous material and/or the chemical transformation of contaminants to innocuous, unregulated products (Semer and Reddy, 1996). The effectiveness of soil washing is dependent on the soil type, the chemical nature of the contaminants and the choice of mobilization aids. To date, there is no single reagent that can be applied to soil for the simultaneous and efficient removal of both organic compounds and heavy metals. For a limited number of reports that have evaluated a single extraction system consisting of surfactants, cyclodextrin or a combination of surfactant with ligands, a high degree of success has not been observed. Anionic surfactants have been reported to mobilize both PAH and Pb simultaneously from water (Dunn et al., 1989) or soil (Huang et al., 1997). Brusseau et al. (1997) demonstrated that carboxymethyl-β-cyclodextrin and hydroxpropyl-β-cyclodextrin were able to enhance the simultaneous desorption of phenantharene and Cd from soil. A study with a combination of a surfactant and ligand has been reported by Shin et al. (2004). They proposed that a ligand can form a hydrophobic complex with the heavy metal, which is then solubilized by the surfactant micelles along with the organics, thereby facilitating the simultaneous removal of both contaminants from soil. A specific ligand complexed with a specific metal - ligand I^- with surfactant was used for Cd desorption while Zn and Cu was found to be more effectively desorbed using SCN^- with surfactant. The shortcomings of above mentioned reagents or combination of reagents make it necessary to continue to develop increasingly efficient single extraction system for simultaneous extraction of a variety of heavy metals and common organic contaminants with an emphasis on detoxification of pollutants to mitigate economic and technical disadvantages.

1.2 Project Objectives

The need for appropriate methods for mixed contaminants is compelling when three objectives are considered: the more efficient simultaneous mobilization of mixed contaminants, the detoxification of contaminants into less hazardous products and the potential cost savings if reagents are recycled. The overall research objective was to develop an efficient remediation treatment for the simultaneous removal of heavy metals and PCBs from contaminated soil with recycling of mobilizing reagents and parallel detoxification of pollutants. The more specific research objectives, pertaining to soil remediation for mixed contaminants, were as follow:

1. To develop and optimize an analytical technique for the determination of total chlorinated biphenyls in soils,
2. To develop a single system for efficient extraction of both PCBs and heavy metals simultaneously,
3. To evaluate the PCB removal efficiency from a soil using a surfactant or cyclodextrin in admixture with a chelating reagent,
4. To evaluate the heavy metal removal efficiency from a soil using ethylenediaminetetraacetic acid (EDTA) or Bis(2-hydroxyethyl)-dithiacarbamate (HEDC) along with a surfactant or cyclodextrin,
5. To optimize the regeneration of both mobilizing reagents in terms of maximum contaminant removal and minimal reagent losses,
6. To evaluate the possibility of recycling mobilizing reagent for further removal of contaminants, and
7. To degrade/detoxify the mobilized contaminants into innocuous products.

1. 3 Scope of the Study

This study was conducted on soil from a land fill site that had been contaminated historically with high levels of heavy metals and PCBs. Whereas, Cr, Cd, Cu, Mn, Ni, Pb and Zn were selected as heavy metals in soils, levels of Al and Fe were also to be monitored as an index of the preservation of the original soil minerals. For PCB mobilization, cyclodextrins and surfactants were to be evaluated. Ten different commercial surfactants were to be evaluated including 3 anionic and 7 nonionic formulations. For metal extractions, EDTA and HEDC were chosen because of their high formation constants with the target metal ions. The laboratory experiments were to encompass the following steps:

1) Both ionic and nonionic surfactants were to be evaluated in combination with EDTA, or a mixture of EDTA and HEDC as washing agents to remediate soils contaminated with heavy metals.
2) Ultrasonication was to be evaluated for enhanced phase transfer of contaminants.
3) A bimetallic mixture consisting of zero-valent magnesium/palladium (Mg^o/Pd^o) followed by the addition of various calcium salts {$CaCl_2$ or $Ca(OH)_2$} was to be evaluated for efficient precipitation of metals.
4) Bimetallic mixture, Mg^o/Pd^o or Pd^o/Al_2O_3, was to be evaluated to determine the efficiency of hydrodechlorination of PCBs.

1.4 Organization of Thesis

This thesis is organized into seven chapters including the introduction and conclusions. The Introductory chapter describes the problem and lists the overall objectives. Chapter 2 reviews the previous research conducted on PCB and heavy metal soil contamination and the available remediation technologies using surfactant or cyclodextrins and EDTA. This literature review supports the overall research objective and reinforces the need to address the second objective. Chapter 3 describes the development and validation of a quantitative analytical method for the estimation of total PCBs in soil or natural water. The subsequent chapters evaluate and discuss the efficiency of a combination of surfactant and chelating agent as a washing reagent to simultaneously mobilize/extract both heavy metals and PCBs from a field-contaminated soil. Chapter 4 investigates both ionic and nonionic surfactants for their PCBs mobilization efficiency in the presence of EDTA. The PCBs recovery by back-extraction with hexane and recycle of surfactant suspension is also described. Chapter 5 evaluates EDTA alone or in combination with HEDC in the presence of either ionic or nonionic surfactant to mobilize target heavy metals from a contaminated soil. In this chapter, a sequential extraction method is used to investigate the binding avidity of heavy metals to the different soil fractions. Chapter 5 also evaluates the metal removal efficiencies from soil extracts with the view to recycle the complexing reagent. Chapter 6 evaluates the effectiveness of cyclodextrin in combination with EDTA for the simultaneous removal of PCBs and heavy metal from naturally contaminated soils. Chapter 7 provides an overall conclusion to the project and suggests some future research. The final section of this thesis includes the literature cited.

CHAPTER 2
LITERATURE REVIEW

This chapter provides a general background on polychlorinated biphenyl (PCB) compounds as organic and heavy metals as inorganic contaminants in order to understand the nature of mixed contamination in soils. After reviewing various conventional soil remediation techniques for PCBs, the potential of cyclodextrin and surfactants as remediating cum mobilizing agents will be discussed. A comprehensive assessment of the popular remediation technologies for heavy metals contaminated soil is also included. More specifically, the potential of EDTA for the removal of heavy metals from soil is examined in greater detail.

2.1 Polychlorinated Biphenyl Compounds

2.1.1 Structure and Nomenclature

Polychlorinated biphenyl (PCB) compounds are a group of 209 chemical congeners, consisting of a biphenyl ring system: (two benzene rings joined head to head) with one to ten possible chlorine substituents. PCB nomenclature is based on the location of chlorine substituents on the biphenyl ring. First synthesized some 100 years ago, PCBs have been available commercially on a worldwide basis since 1929 (Erickson, 1997). The synthesis of PCBs (pure congener or mixture) is carried out by chlorination of the biphenyl molecule with chlorine gas. There are no known PCBs that occur naturally. The empirical formula of PCBs is $C_{12}H_{10\text{-}x}Cl_x$, ($x$ = 1-10). The average degree of chlorination depends upon reaction conditions and can be manipulated to yield the desired chemical and physical properties of the resulting mixture (Erickson, 1997). When PCBs are grouped according to the degree of chlorination, the groups are called homologs. PCB homologs with the same number of chlorine substituents at different positions are referred as isomers. PCB congeners have been assigned unique identification numbers by several organizations. In general, two different numbering systems continue to be used for PCB congener identification; each arranges all congeners in order and assigns to them a number from 1 to 209. For convenience, the 209 congeners were numbered systematically by Ballschmiter and Zell (1980), and later revised by Ballschmiter et al., (1993). The second numbering system in common use is the International Union of Pure and

Applied Chemistry (IUPAC) system of nomenclature. The differences appeared for eleven congeners. The 209 PCB congeners are grouped according to the degree of chlorination of the molecule. The mono-, di-, tri-, tetra-, penta-, hexa-, hepta-, octa-, nona-, and decachlorobiphenyl congeners can exist in 3, 12, 24, 46, 42, 24, 12, 3, and 1 isomeric forms respectively. There are several registered trademarks in use for commercial PCB mixtures such as Aroclor, Therminol, Askarel, and Pydraul. The PCB naming convention in present day document uses the trademark Aroclor (Monsanto, Corp., USA) and the IUPAC numbering system.

2.1.2 Properties and Uses of PCBs

It has been estimated that total of 370,000 tons of PCBs were manufactured in the world from 1929 until the late 1970s, when their production was ceased in most western countries (Rahuman, 2000). PCBs occur as liquids or solids, are clear to light yellow in color, and have no odor or taste. Most PCBs are oily liquids in which the color darkens and the viscosity increases with increasing chlorine content. Chemical properties of PCBs include a high dielectric constant, high solubility in hydrocarbon solvents and virtual insolubility in water. They are nonvolatile and chemically inert. They do not undergo oxidation, reduction, addition, elimination, or electrophillic substitution reactions except under extreme conditions. These characteristics, combined with their chemical stability, have made PCBs valuable chemicals for various industrial applications. Seventy percent of the PCBs exploited in North America were used as dielectric fluids in electrical capacitors and transformers. Other commercial and industrial products that contained PCBs include hydraulic fluids, heat transfer fluids, lubricating and cutting oils, pesticides, paints, copy paper, carbon-less copy paper, sealants, adhesives, fluorescent light ballast, dyes/waxes and building materials (Erickson, 1997). The manufacture, uses, and disposal of these commercial PCB containing products resulted in widespread and persistent environmental contamination (Tanabe et al. 1993). Due to their toxicity and carcinogenic potential, concern over their presence in the environment has increased during past two decades. Consequently, restrictions both on manufacturing and use were introduced in Europe and North America in the early 1970s (TSCA, 1976).

2.1.3 Health Effects of PCBs

First detected in eagles and herring gulls in 1966, the presence of PCBs in various environmental compartments has been documented extensively. The potential for adverse effects on human health was first noted in Japan in 1968 when approximately 1600 people, who had consumed PCB-contaminated rice oil over a period of several months, developed skin disorders, including chloracne and respiratory problems (Kannan et al., 1998; Jorgensen, 2001). Global concerns were increased over the potential deleterious health effects of PCBs and were spurred on by human poisoning episodes that were similar to the incident of the PCB-contaminated rice bran oil in Japan (Rogan et al., 1988).

PCBs can enter the human body by inhalation, ingestion, or by direct dermal contact. The trace quantities present in most people are the result of ingestion through food. PCB compounds accumulate in fatty tissues from where they can be transmitted in breast milk and placenta. PCB residues in adipose tissue and milk samples from the general population in industrialized countries range from less than 1 to 5 ppm (fat basis). The toxic effects linked to PCBs include neurotoxicity, immunotoxicity, hepatotoxicity, reproductive toxicity, interference with growth and development, intellectual impairment and cancer (Jacobson and Jacobson, 1996; Eisler and Belisle, 1996). Much research efforts continue to be devoted to relating the structure of PCB molecules to their adverse biological activities (Wolff et al., 1997). Studies (American Council on Science and Health, 1997) have suggested that coplanar PCB congeners are carcinogenic. Coplanar PCBs mimic the action of dibenzodioxins in cells, binding to the Aryl (Ah) receptor. In vertebrates, PCB toxicity is linked to the induction of P_{450}-dependent monooxygenase system, which varies with the number and location of chlorine atoms on the PCB molecule. Non-coplanar PCBs have also been reported to influence the activity of neutrophils that are among first white blood cells responding to the site of infection or damage, thus affecting immune or inflammatory systems (NIEHS, 1999).

2.1.4 Remediation Treatments of PCBs

2.1.4.1 Incineration

Incineration dominates the market when PCB destruction protocols are required and remains the preferred disposal option for the destruction of PCBs under adequate operating conditions (Takeshi et al., 2003). Incineration involves higher temperature to combust the PCBs that may lead to the formation of more toxic compounds such as chlorinated dibenzo-dioxins and furans under inadequately controlled conditions (Wienecke et al., 1995). These products can be more acutely toxic than the PCBs themselves. In addition, the incineration processes can cause fugitive emissions from leaking valves, vented storage tanks, tank transfers and spills. According to a report (Galveston-Houston Association for Smog Prevention, 1996), in Canada, one PCB incineration facility was estimated to have released 75 pounds of PCBs into the environment during 1994. Investigations on the formation mechanisms of chloroaromatics in large-scale incinerators have demonstrated that there were two temperature ranges for PCDD/F formation. Within the low temperature range of about 300 °C, PCDD and PCDF were formed from precursor compounds by heterogeneously catalysed reactions on fly ash (Weber and Hagenmaier, 1999). The second formation window at high temperatures of about 700 °C was considered to be responsible for PCDD/F formation via the so-called *de novo* synthesis from carbon-like structures (Ghorishi Behrooz and Altwicker, 1996). The influence of combustion parameters on the formation of PCDD/F, PCBs as well as on PAH and other non-chlorinated aromatics (BTEX and methylated naphthalenes) at high temperatures in the post-combustion chamber were investigated by Heger and co workers (1999).

2.1.4.2 Solvent Extraction

Solvent extraction is a well-established process for the separation of hazardous contaminants from soil and sediment that reduces the volume of hazardous waste that must be treated (U.S. EPA, 1997a). The venerable Soxhlet extraction with a mixture of organic solvents remains the predominant technique for extracting PCBs from environmental samples (Erickson et al., 1997). Other sophisticated extraction methods have also been proposed and applied in laboratory research including, microwave assisted extraction (MAE), supercritical fluid extraction (SFE), Ultrasonic extraction (USE), pressurized fluid extraction (PFE), sub-critical water extraction, and surfactant extraction. The overall extraction efficiency depends on the number of extraction cycles used (Meckes et al., 1996). Lopez-Avila and co-workers used MAE to extract Aroclors efficiently from sediments and soils (1995). The efficiencies of SFE or Soxhlet extraction of PCBs have been compared rigorously for industrial soil samples (Bowadt et al., 1995), spiked sand, and soil samples (Van de Velde et al., 1995). Other studies have compared USE and Soxhlet extraction of PCBs from soil (Kimbrough et al., 1994) and sediments. Chiu et al. (1997) reported the solvent extraction of PCBs and PCDD/Fs from lake and harbor sediments using microwave-assisted and Soxhlet extraction. Microwave-assisted extraction reduced the extraction time from 20 h to 20 min and solvent quantity was also reduced from 350 ml of toluene to only 20 ml of hexane/acetone.

An accelerated-solvent extraction (ASE) technique to determine PCBs in sediments of the Baltic Sea was evaluated by Bandh et al. (1998). The ASE method was characterized by equal or even improved precision relative to the Soxhlet extraction and was completed with less solvent consumption. Conventional organic solvent at elevated temperature (50-200 °C) and pressure (5-200 atm) were used in PFE to extract organic solid samples (Heemken et al., 1997). Quantitative extraction of PCBs from natural matrices using a microscale adaptation of pressurized fluid extraction (μPFE) was investigated and recoveries were measured for eight PCB congeners spiked into two soil types (Hageman et al., 1997; Szostek et al., 1999). The extraction process with hexane at 300 °C provided significantly increased recoveries for several representative PCBs congeners than that had been reported for a duplicate 16 h Soxhlet extraction with a mixture of acetone/hexane.

2.1.4.3 Thermal Desorption

Direct thermal desorption (TD) is one of the attractive alternatives to liquid extraction for removal of toxic pollutant(s) from soils, sediments or sludges. Thermal desorption heats the soil, volatilizing PCBs that are collected for further treatment. Efficient removal of PCBs from mineral oil dielectric fluids by using polyethylene glycol solvents as the primary extraction medium, followed by re-extraction of the polar liquids, using a volatile secondary solvent which facilitates the recovery of both the primary solvent for reuse and the PCBs for ultimate disposal has been demonstrated by Osborn et al. (1984). Thermal treatment has been demonstrated to remove PCBs efficiently from a contaminated soil without any unacceptable impacts on the soil medium and at a cost appreciably less than that of high temperature incineration (Wampler, 1998). Soils contaminated with PCBs (Krabill et al., 1996) and chlorinated solvents were treated successfully with removal efficiencies of 95.8 to 99.98% for trichloroethylene (TCE), 93.5 to 99.9% for perchloroethylene (PCE) and 90.1- 99.5% for PCBs. The results indicated the efficient removal for all soils contaminated with low- level PCBs (<50 ppm). Norris and co worker (1998) reported an effective remediation protocol for PCB contaminated soil using low temperature thermal desorption that was effected by applying a vacuum to the contaminated sample. Thermal desorption primarily has been used as a separation technology, but now it has been combined with other techniques to achieve simultaneous PCB separation and destruction. The important distinction between thermal desorption and incineration is that thermal desorption only volatilizes the PCBs to remove them from the soil, whereas incineration operates at much higher temperature to combust the PCBs and soil together. However, co-combustion can result in the formation of dibenzodioxins and dibenzofurans.

2.1.4.4 Stabilization/Solidification

Solidification is a treatment process that involves mixing of soil, sediment or sludge or contaminated extract with additives to convert contaminants into a less soluble, less mobile phase. PCB solidification treatments do not chemically fix the PCBs but it simply immobilizes the solid to which they are absorbed. Such technologies immobilize the PCB but do not concentrate or destroy them; the risks of leaching remain upon exposure to solvent or oils (U.S. EPA, 1997a). Therefore, further treatments must be employed. Sawyer and co-worker (1989) demonstrated an *in-situ* stabilization/solidification process using deep-soil-mixing equipment. The solidified material displayed satisfactory physical properties, with high, unconfined compressive strengths, moderately low permeabilities, and satisfactory integrity for the wet/dry samples. The microstructural results indicated a dense, low-porosity, homogeneous mass that indicated a potential for long-term durability.

2.1.4.5 Vitrification

Vitrification is an emerging remedial technology that uses electrical current to melt contaminated soils to form a rigid, glassy product on cooling (Erickson, 1997), thus immobilizing any contaminants that are not volatilized by the heat of the process. Melting processes (generally classified by heat sources such as electric or fuel-burning types) can lead to a volume reduction (Kinto, 1996). Process temperatures in the range of 1,000-2,000 ^{o}C can destroy PCBs but lead to secondary pollutants with a resulting need to treat off-gases for organic contaminants. The volume of contaminated waste is reduced 20-40% by the vitrification process since pore spaces in the soil are eliminated. The resulting vitrified material can be left in place and covered with clean fill or soil. Treatability tests are required before using this technology for PCBs contaminated soils because the process may not provide adequate immobilization in all cases. Since 1990s, the vitrification system has been authorized by U.S. EPA to treat PCBs in soil and sediment (U.S. EPA, 1997a).

2.1.4.6 Photolytic Dechlorination of PCBs

Solar energy can be used to degrade organic compounds of synthetic and natural origin. Short wavelengths (295 - 400 nm) are greatly attenuated by the atmosphere. Such radiation is capable of sustaining direct and indirect photolytic processes that can degrade pesticide or PCB polluted soil and surface waters. Since the desired wavelengths are attenuated more strongly than longer wavelengths in the visible region, the rate of photolysis of organochlorine compounds is highly dependent on latitude, season, and other meteorological conditions. Photolysis is a popular means of chemical degradation of PCBs (Rahuman et al., 2000). It involves dechlorination via homolytic fission of the C-Cl bond caused by free radicals generated by photo- or radiation- source. Photolytically induced chain dechlorination of PCBs solutions in a photoexcited state has been reported (Mincher 1995). The results demonstrated that the photodechlorination mechanism was a reductive dechlorination associated with the capture of solvated electrons by the PCBs. The more highly chlorinated the PCB substrate, generally the more reactive toward photodechlorination.

Chemical aided photolysis involves photolytic oxidation using titanium dioxide (TiO_2) as a catalyst. Chlorinated solvent, pesticides, and PCBs were degraded via photodegradation both in organic solution and in water (Lin and Baker, 1996) using simulated sunlight and a photosensitizer in the presence of TiO_2.

2.1.4.7 Biological Technologies

Biological techniques are frequently carried out with indigenous microorganisms in either aerobic or anaerobic environments. With advances in biotechnology, bioremediation has become one of the most rapidly developing fields of environmental restoration, utilising microorganisms to reduce the concentration and toxicity of various chemical pollutants including petroleum hydrocarbons, polycyclic aromatic hydrocarbons, polychlorinated biphenyl compounds, phthalate esters, nitroaromatic compounds, industrial solvents, pesticides and metals. A number of bioremediation strategies have been developed to treat contaminated waste sites. The term “bioremediation” has been used to describe the process of using microorganisms to degrade or remove the hazardous components of wastes from the environment (Glazer and Nikaido 1995). Biodegradation and its applications in bioremediation of organic pollutants have benefited from the biochemical and molecular studies of microbial processes (Bollag, 1992; Johri et al. 1996). Various authors have reviewed the subject of biodegradation of organic pollutants over the past decade (Kumar et al. 1996; Johri et al. 1999; Janssen et al. 2001). Biotransformation of organic contaminants in the natural environment has been studied extensively to understand microbial ecology, physiology and evolutionary potential in bioremediation (Mishra et al. 2001; Watanabe 2001). Microorganisms with the ability to degrade a wide variety of compounds including benzene, phenol, naphthalene, atrazine, nitroaromatics, biphenyls, polychlorinated biphenyls (PCBs) and chlorobenzoates, have been isolated and characterized (Faison, 2001). Although simple aromatic compounds are degradaded by a variety of pathways, their halogenated counterparts are more resistant to bacterial attack and often necessitate the evolution of novel pathways (Engasser et al. 1990).

Many of the environmentally important chemicals introduced for industrial uses are halogenated. Halogenation is frequently implicated as a reason for persistence. Among the halogenated compounds, the chlorinated compounds have been the most extensively studied (Cork and Krueger, 1992). Most of the information available on the biodegradation of chlorinated compounds is on oxidative degradation, since aerobic culture techniques are relatively simple, compared with anaerobic culture methods. Also, aerobic processes are considered the most efficient and most widely applicable (Adriaens and Vogel 1995). The reductive dechlorination of PCBs by anaerobic bacteria removes chlorines directly from the biphenyl ring (with replacement by hydrogen), resulting in a product mixture in which the average number of chlorine per biphenyl is decreased (Kawahara et al., 1997; Chuang, 1998).

An increased number of chlorine atoms on the aromatic ring is considered to greatly retard the rate of degradation. It has been reported that highly chlorinated congeners are degraded less readily than the less highly chlorinated congeners. The molecular shape and the position of chlorine substituents in the PCB also affect the rate of biodegradation (Alder et al., 1993).

2.1.4.8 Chemical Remediation

Conventional incineration and other combustion treatments have been recognized to be associated with the unexpected formation of more harmful compound such as polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofuran (PCDFs), whereas bioremediation require months and strongly depends on the ability of the microorganism to survive in system containing the chlorinated organic compounds. This has led to the addition of chemicals to conventional destruction techniques. Chemical destruction has been carried out by incineration, oxidation, and reduction with catalyst, superoxide, photolysis, and electrolytic reaction. Although, incineration and other oxidative methods are widely discussed methodologies, PCBs derive their environmental persistence from their resistance to oxidative degradation: the more highly chlorinated congeners, the greater the resistance to oxidation. Likewise, photolysis-involving substitution of chlorine is not very efficient for highly chlorinated congeners. Chemical dehalogenation is a chemical process used to remove chlorine from PCB molecule by hydrogen or reducing radical containing hydrogen. Removing halogen from PCBs by reductive treatment is an effective destruction treatment that offers appreciable advantages in both efficiency and cost over other technologies. A number of chemical reduction procedures such as alkaline polyethylene glycolate (APEG), base-catalyzed decomposition, and gas-phase reduction have been suggested including catalytic dehalogenation. Base catalysed decomposition (BCD) was developed by National Risk Management Research Laboratory of the U.S. EPA (1997b). The U.S. EPA developed the BCD technology to treat a variety of contaminants in different matrices, PCBs were treated in oil at 300-350 °C using base, a hydrogen donor, and a catalyst based on carbon. Kawahara and Michalakos (1997) investigated the use of sodium hydroxide and catalysts to improve the base-catalyzed decomposition of polychlorinated biphenyls (PCBs). The result demonstrated that reaction proceeded only in the presence of base, but the rate of PCB disappearance increased with increasing amount of hydrogen transfer agents and catalyst. Up to 99% dechlorination of 20 000 mg/kg Aroclor 1242 in paraffin oil was achieved within 1-4 h at 340-350 °C with the formation of biphenyl. A three-step mechanism was proposed for the formation of biphenyl: (1) hydrogen species were generated from the paraffin oil; (2) hydrogenation of aromatic catalysts (phenanthrene, anthracene, and alkyl naphthalenes) to form dihydroaromatics, or absorption of hydrogen by hexagonal forms of carbon (graphite or carbon black as present in scrap latex) or transition metals (zero-valent iron or stainless steel); and (3) transfer of the hydrogen species to the activated PCB molecule (Kawahara and Michalakos, 1997; Takada et al., 1997).

Glycolate dehalogenation involves APEG reagent, which consists of an alkali metal hydroxide and polyethylene glycol. The APEG dechlorinates the PCBs to form glycol ether and/or a hydroxylated product and an alkali metal salt (DeFilippis et al., 1997).

Over the last few years, interest in the reaction of reducing metal catalyst systems has continued to increase. More recently, among metals, zero valent metal catalysts have been evaluated for their ability to dechlorinate OC compounds under mild reaction conditions. As a focus of the present document, dechlorination with zero valent metal catalysts is discussed in detail.

2.1.4.8.1 Chemical Dechlorination with Zero-valent Metal Catalyst

The reduction of dilute aqueous solution of chlorinated solvents by zero-valent metals such as iron was first reported by Sweeny (1981). Each metal possesses a characteristic standard reduction potential, which determines its thermodynamic ability to spontaneously dechlorinate an organochlorine compound. The less positive the reduction potential is, the more complete is the chemical reduction (Matheson and Tratnyek, 1994). The standard reduction potential of common zero valent metals have been reported to be as follows:

$Cu^{2+} + 2e^- \rightarrow Cu^o$ $E^o = 0.337V$
$Cu^+ + e^- \rightarrow Cu^o$ $E^o = 0.521V$
$Fe^{2+} + 2e^- \rightarrow Fe^o$ $E^o = -0.440V$
$Fe^{3+} + e^- \rightarrow Fe^{2+}$ $E^o = 0.770V$
$Ni^{2+} + 2e^- \rightarrow Ni^o$ $E^o = -0.250V$
$Zn^{2+} + 2e^- \rightarrow Zn^o$ $E^o = -0.763V$
$Mg^{2+} + 2e^- \rightarrow Mg^o$ $E^o = -1.990V$

The mechanism for reduction of chlorinated solvents by zero valent iron metal has been suggested to be a direct electron transfer from the iron surface and not the result of reduction by either Fe^{2+} (which results from corrosion) or by catalyzed hydrogenation using the H_2 that is formed by iron metal reaction with water (Matheson and Tratnyek, 1994). Zero-valent metals act as both a reactant and surface substrate during the reduction of chlorinated organic compounds (R-Cl). Scott and Gillham (1996) described the general reaction as:

$$2Fe^o \longrightarrow 2Fe^{2+} + 4e^- \quad (1)$$
$$3H_2O \longrightarrow 3H^+ + 3OH^- \quad (2)$$
$$2H^+ + 2e \longrightarrow H_2 \quad (3)$$

$$\underline{\text{R-Cl} + \text{H}^{+} + 2e^{-} \longrightarrow \text{R-H} + \text{Cl}^{-}} \tag{4}$$

$$2\text{Fe}^{o} + 3\text{H}_2\text{O} + \text{R-Cl} \longrightarrow 2\,\text{Fe}^{2+} + 3\text{OH}^{-} + \text{H}_2 + \text{R-H} + \text{Cl}^{-} \tag{5}$$

For each mole of reduced chlorinated organic compound, two moles of Fe^{o} are oxidized to Fe^{2+}. A variety of zero valent (ZV) metals including Cu, Ni, Fe, Mg, or Zn and noble metal catalysts that have been employed for dechlorination, continue to be explored, depending upon the metal reactivity to the C-Cl bond and the aromatic nature of the substrate (Wang and Zhang, 1998; Shin and Kean, 1998; Wu and Marshall, 2000). Zero-valent iron promoted hydrodechlorination of PCBs at elevated temperature was investigated by Chuang et al. (1995). Most of the Aroclor 1221 was dechlorinated to biphenyl in 10 min at 400 °C. Yak et al. (1999) evaluated the method using zero-valent Fe as the dechlorination agent and subcritical water as the transporting medium and hydrogen source for the remediation of PCB contaminated soil and sediments.

More recently, the use of bimetallic mixtures ($\text{Pd}^{o}/\text{Fe}^{o}$, $\text{Ag}^{o}/\text{Fe}^{o}$, $\text{Pd}^{o}/\text{Mg}^{o}$) or supported noble metals (Pt^{o}, Pd^{o}, Rh^{o}, Ru^{o}) have provided dramatic improvements in rates and selectivities of hydrodechlorination reactions (Doyle et al., 1998; Wu and Marshall, 2000, Yuan and Marshall, 2002; Korte et al., 2002).

Noble metal catalysts on carbon, silica, or alumina support have been employed to promote hydrodechlorination reactions (Ordonez et al., 2003). Ono et al. (1996) reported that if a mixture of PCB, hexadecane, and Pd^{o}/C was bubbled with H_2 at 210 °C for 180 min, PCBs decomposition reached as much as 99.99% and reaction products included biphenyl, phenylcyclohexane, and dicyclohexane. Ukisu et al. (2000) reported that in the presence of C-supported noble metal catalyst (Pd^{o}/C, Pt^{o}/C Rh^{o}/C), PCBs could be dechlorinated efficiently to biphenyl and phenylcyclohexane using a NaOH solution in propan-2-ol at ambient temperature (27 °C). They suggested that the hydrogen species arising from the dehydrogenation of 2-propanol on Pt^{o} particles was likely to control the reduced state of Rh and facilitated the generation of active Rh sites. Activated Rh metal was speculated to be responsible for hydrogen transfer from 2-propanol to chlorotoulene at ambient temperature.

2.1.4.9 Chemical Soil Washing/Flushing

Soil washing is an *ex-situ* process capable of separating a wide variety of organic, inorganic, and radioactive contaminants into a concentrate of soil fines and sediment. Based on a combination of particle size separation, and agitation, soil washing involve use of organic solvent, surfactant suspension and/or cyclodextrins to rinse the contaminated soil and to transfer contaminants into the liquid phase (American Council on Science and Health, 1997). The second approach, soil flushing (*in-situ*), involves the use of water or another suitable solution to extract contaminants from soil matrix. The extraction fluid is passed through the soil via infiltration or injection techniques and then is recovered and treated to remove the contaminants. Surfactants have been demonstrated to enhance the solubility of PCBs and were used to separate PCBs from soil (Billingsley et al., 2002; Rojas-Avelizapa et al., 2000). Beck et al. (1997) evaluated soil washing using polyoxyetheylene (10) lauryl ether surfactant to mobilize PCBs and demonstrated that 75% of PCBs were removed from soil in relatively short period of time (2 days). Several studies involving surfactant/co-solvent mixtures have taken bench scale results into the field at the pilot scale level. In the USA, several full-scale site remediations have utilized surfactants for *in-situ* flushing. More recently, cyclodextrins have found application in soil remediation for organic pollutants. Cyclodextrins have been demonstrated to enhance the aqueous solubility of hydrophobic compounds (Szente and Szejtli, 1998).

2.1.4.9.1 Cyclodextrins

Cyclodextrin (CDs) or cycloamyloses are cyclic glucose oligosaccharides formed by the action of *Bacillus macerans* on starch. Depending upon the number of (1, 4)-linked glucose units in the ring, cyclodextrin are classified as α, β, or γ, corresponding to 6, 7 or 8 glucose units, respectively (Figure 2.1). The most important feature of these compounds is their toroid or donut- shaped structure that have one rim lined with primary -OH groups and the interior rim lined with secondary -OH groups. The -OH groups are directed outward, providing a hydrophilic exterior, while the interior is substantially hydrophobic, a result of the hydrocarbon portion of the glucose skeleton. The combination of these properties enables cyclodextrins to act as host in forming complexes with other guest molecules. Because of the inclusion capability of cyclodextrins or their derivatives, they have received considerable attention in various applied fields such as pharmaceutical (Milewski et al., 1998), textile manufacture (Szejtli, 2003), organic chemistry, foods and agriculture. They have been used extensively in chromatography (Jaus and Oehme, 2000; Forgacs and Demnerova, 1996; Wong and Garrison, 2000; Brown et al., 1996; Cserhati, and Forgacs 2000; Jia et al, 1998). In agriculture, they have been used to enhance aqueous solubility of herbicides/pesticide (Manolikar and Sawant, 2003; Morillo et al., 2001; Lou et al., 2003) and to improve residual activities of pesticides (Perez-Martinez et al., 2000).

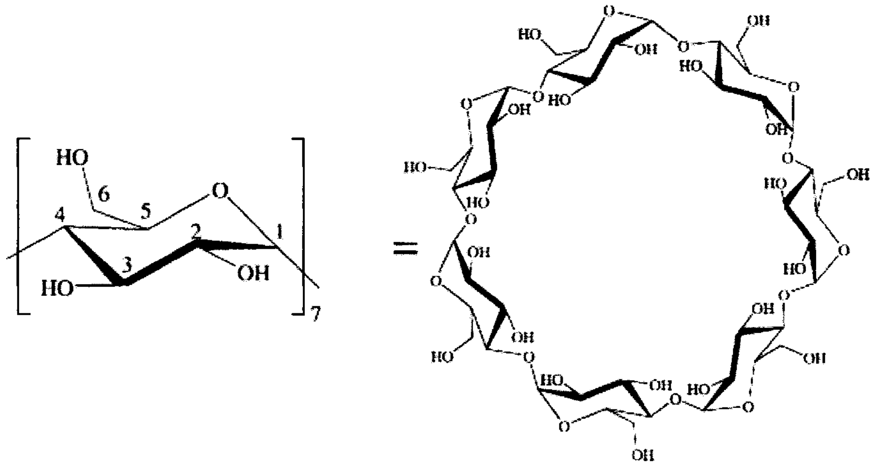

Figure 2.1 Illustration of β-CD with 7 glucose units. Substitution occur at the C-2, C-3, and C-6 hydroxyl functionalities in each unit.

Cyclodextrins have been shown to enhance the aqueous solubility of hydrophobic compounds (Szente and Szejtli, 1998). Due to the low-cost of production of certain of these CDs, cyclodextrins can be considered as alternative solublization reagents for environmental remediation especially for soil clean up. Ideally, most of the organic pollutants in the soil (PAH, PCB, PCP, dioxins and furans) can act as proper guests for complex formation with cyclodextrins. The degree of complex formation between host and guest is closely related to the steric fit of the guest inside the cyclodextrin cavity and to the hydrophobicity of the guest.

Importantly, cyclodextrins are nontoxic and environmentally benign. PAH compounds with 2 or 3 rings fit well into the β-CD cavity, whereas those with more rings (e.g. pyrene, benzo(*a*)pyrene, benzo(*e*)pyrene, perylene) prefer γ-CD as a host (Blyshak et al., 1988). CDs have been patented to extract bitumen from oil sand (Shibanai, et al., 1985). Nineteen chlorophenols including mono, di, tri, and penta-substituted derivatives were separated on β-CD bonded-phase column (Paleologou and Purdy, 1990). PCP was efficiently solubilized with methyl derivative of β-CD (Szeman, et al., 1992). Chlorinated benzene congeners, PCB congeners, tetrachlorodibenzo-p-dioxin isomer, and PAHs were successfully separated by cyclodextrin-modified miceller electrokinetic chromatography in which cyclodextrins were added to the miceller solution (Terabe, 1990).

Beta-Cyclodextrin Modification

Among the three cyclodextrin homologues (α, β, or γ), β-cyclodextrin is produced at commercial scales and is the least expensive. Thus far, β-CDs have been used more frequently than other CDs because of the appropriate cavity size with respect to a wide range of organic compounds. Unfortunately, the low water-solubility of β-CD and the decreased solubilities of its inclusion complexes limit its application as a solubility enhancement agent. Thus, chemically modified β-CD has been exploited extensively to enhance water solubility. For β-CDs, there can be from 0-21 degrees of substitution in each β-CD molecule (3 -OH group per glucose unit and the 7 glucose units in each molecule). The enhanced solubility that results from derivatization provides water-soluble inclusion complexes with a wide range of organic compounds. This makes them suitable for application in a variety of situations including in the pharmaceutical industry (time release drugs) and in the manufacture of household items (odor reducing spray). Certain derivatives such as methylated substrates are of practical importance (Szejtli, 1988). Methylated cyclodextrins deserve special attention due to their anomalous solubility properties. With increased methylation of up to two thirds of the hydroxyl groups, the solubility of B-CD (in cold water) increases but beyond two-thirds methylation it decreases again. Among methylated β-CDs, the congener bearing 14 methoxyl groups on the β-CD structure shows the highest aqueous solubility whereas the permethylated specie (21 methoxyls) has a lower solubility, which remains however, considerably greater than that of the unsubstituted β-CD. Little work has been carried out on the methylated α and γ CDs because they have good solubilities and there is little need for improvement through methylation. For many practical purposes, the heterogeneous, partially methylated β-CD seems to be applicable, but for specific applications such as pharmaceuticals, dimethyl {heptakis (2, 6-di-O-methyl)} and trimethyl [heptakis (2, 3, 6-tri-O-methyl)]β-CD are considered more practical.

Applications of Cyclodextrins to Soil Remediation

Most of the literature available on the interaction between CDs and hydrophobic organic pollutants, are directed mainly to the enhancement of pollutant bioavailability and degradation rates in various matrices such as waste waters, aquifers (Boving et al., 2000; McCray and Brusseau, 1999b), and liquid cultures of specialized bacteria (Bardi et al. 2000; Fava and Grassi 1996) along with contaminated soils (Fava et al., 1998, 2003; Sheremata and Hawari, 2000). Field PCB-contaminated soil was appreciably bioremediated in the presence of HP-β-CD and γ-CD that enhanced the process. Enhanced depletion rates of soil PCB were attained by the availability of HP-β-CD or γ-CD complexes in the aqueous phase of the soil slurry reactors. However, for fixed-phase reactors, similar depletion rates were observed only with HP-β-CD. In the further studies with randomly methylated-β-cyclodextrin (RAMEB), significantly enhanced PCBs biodegradation and dechlorination rates, along with a detectable initial depletion of soil ecotoxicity were observed in REMB treated soil reactors. The concentration of PCBs in soils decreased appreciably throughout the treatment under various conditions. The apparent solubility of Bisphenol A (BPA), an endocrine disrupter in hydroxypropyl-CDs was investigated as a means of evaluating the remediation of soil contamination and ground water pollution (Araki et al., 2001). Hydroxypropyl–β-CD was found to have a greater affinity for BPA as compared to hydroxypropyl-α or γ-CD.

In addition to the solubilizing power of an additive, its reactivity/binding affinity with other components of the matrix is an additional factor of importance. Ideally, an extracting agent should 1) interact very weakly with the soil/aquifer matrix as compared to target contaminants, 2) increase the mobility of the target contaminants, and 3) be generally nontoxic and biodegradable and cyclodextrins posse all these desirable characteristics. Brusseau's group (1994) investigated the influence of hydroxypropyl-β-CD (HP-β-CD) on the transport of low polarity organic compounds coupled with sorption/retardation interactions. The results of the studies showed that cyclodextrins did not interact with soils. There was no appreciable sorption, retardation, or pore exclusion of the cyclodextrins during transport. The retardation of compounds was also significantly reduced in the presence of cyclodextrins. In contrast, Fenyvesi et al. (2002) demonstrated that RAMEB has a tendency to interact with the clay content of soil.

Brusseau et al. (1997) investigated the ability of cyclodextrins to simultaneously complex heavy metals and low polarity organic compounds. The result of the experiment demonstrated that carboxymethyl-β-CD was capable of simultaneously increasing the apparent aqueous solubilities of the selected organic compounds (anthracene, trichlorobenzene, biphenyl, and DDT) and formed a complex with $Cd^{2+.}$ It was observed that cyclodextrin greatly enhanced the simultaneous desorption and elution of phenanthrene and cadmium from three different soils. The elution of phenanthrene that had been in contact with soil for 38 days exhibited greater tailing than the unaged phenanthrene when water was the flushing solution; indicating greater resistance to desorption and removal. Elution curves for aged and unaged contamination were identical for cyclodextrin solution. Aging appeared to have no impact on cadmium elution behavior for either solution. The success in simultaneous complexation of heavy metal and organic compounds has encouraged related areas of research. Carboxymethyl-β-CD and β-CD were investigated with the view to evaluating Fenton chemistry to degrade pollutants in a ternary pollutant-cyclodextrin-iron complex system (Lindsey et al., 2003). Various hydrophobic organic compounds (HOCs) such as pyrene, anthracene, and phenanthrene were degraded more rapidly with the addition of carboxymethyl-β-CD. Hydroxypropyl-β-CD was applied for enhanced solubilization and destruction of tetrachloroethylene with metallic iron (Bizzigotti et al., 1997).

The possibility of using cyclodextrins to remediate hydrophobic organic pollutants in subsurface non-aqueous phase liquids (NAPLs) has been investigated in a number of studies (Brusseau et al., 2000). These reports describe laboratory and field experiments that have demonstrated the application of unsubstituted CDs in environmental remediation strategies. In a laboratory study, it was observed that an increase in aqueous solubility of a range of nonpolar and low polarity organic compounds, including TCE and PCE, could be achieved using various substituted β-CDs.

In another study, the addition of 5% CD (HP-β-CD, sulfated-β-CD or methyl-β-CD) enabled the fairly efficient desorption of PCE or TCE; between 98 % and 73 % of the original material was removed with a single extraction (Shirin et al., 2003). McCray and Brusseau (1999a, 1999b) evaluated hydroxypropyl-β-CD for enhanced mobilization/removal of a multicomponent NAPL from an aquifer. Cyclodextrin solution (10% w/v) resulted in 45% reduction of global NAPL saturation after 8 pore volume flushing.

In the last decade a considerable amount of research has been devoted to cyclodextrin extraction of poly aromatic hydrocarbons (PAH) for soil clean up. In addition, CDs have been employed to develop methods for the prediction of PAH bioavailability. The application of cyclodextrin extraction for the prediction of bioavailability was first studied by Ried et al. (1998, 1999, 2000), who demonstrated that PAH extractability with hydroxypropyl-β-CD (HP-β-CD) was closely related to the degree of mineralization by microorganisms.

Cyclodextrins have also been reported to be able to increase HOC bioavailability (Volkering et al., 1998, Wang et al., 1998). Wang et al. (1998) claimed that HP-β-CD significantly increased the bioavailability of PAHs that were sorbed on a glass surface, thus significantly enhancing the biodegradation of these PAHs. Shixiang et al. (1998) has reported the solubilizing power of β-CD and carboxymethyl-β-CD to phenanthrene, 2-methylphenanthrene, fluorene, 1-ethylflourene, 1,2-benzofluorene and β-bromonaphthalene. The results indicated that both CDs significantly increased the apparent water solubilities of PAHs.

Soils contaminated from activities in the munitions and defense industries are a worldwide environmental problem. Cyclodextrins have also found some application in this area. Hawari et al. (1996) reported the enhanced recovery of the explosive hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) from soil. Hydroxypropyl-β-CD and methyl-β-CD were found to increase RDX recovery from the soil without hydrolyzing the target pollutant. It was suggested that cyclodextrins might act as complexing agents to active metabolites of RDX that were formed during chemical or microbial degradation. Hydroxypropyl-β-CD and heptakis (2,6-di-O-methyl)-β-CD were investigated for their ability to desorb 2,4,6-trinitrotoluene (TNT), 4-amino-2,6-dinitrotoulene (4-ADNT), and

2,4-diamino-4-nitrotoluene (2,4-DANT) from two artificially contaminated soils. All these studies demonstrate that cyclodextrins can be employed successfully in the remediation of contaminated soil.

2.1.4.9.2 Surfactants

The use of surfactants to enhance the removal of soil contaminants has received increasing attention in recent years (Chu and Chan, 2003; Mulligan et al., 1999a, 1999b, 2001). Surfactants are potential remediation agents as they promote the wetting, solubilization, and emulsification of organic compounds by altering the surface properties of liquids. The fundamental properties of a surfactant are its amphiphilic structure made up of hydrophilic head and hydrophobic carbon tail, monolayer orientation at interfaces, and adsorption at interfaces. Being amphiphilic, the surfactant tends to migrates to interface where both moieties exits in preferred phase (e.g. oil-water, air-water, water and solid-liquid). This arrangement creates a third layer at the interface, decreasing interfacial tension between the two phases. The balance of the head group and carbon tail determines which phase the surfactant molecule will dissolve into more readily. That is, if the head group is more heavily balanced, the surfactant will be water soluble. In this case it will pull oil into solution as droplet encased in the surfactant molecule. This accumulation, by acting as a bridge between air and liquid interface, can reduce the surface tension of water to approximately 25 ± 5 mNm^{-1} and thus promoting the mobilization of contaminants from unsaturated soils (Myers 1999). A surfactant's ability to lower surface tension is an important factor determining the efficacy of the surfactant. Previous studies have demonstrated that the point at which interfacial tension is minimized corresponds to the concentration where the most surfactant is found at interface. Generally, an efficient surfactant is able to lower the surface tension of water from 72 to 35 mN/m^{-1}.

In addition, the amphiphilic structure causes the molecules to aggregate into micelles at high concentration, which is a phenomenon unique to surfactants among amphiphilic molecules. Dynamic micelle aggregation permits the hydrophilic head to associate with water, while lipophilic tails to orient away from the bulk water phase. The micelle interior can be envisioned as pseudo-oil phase. Organic compounds preferentially partition into the interior of micelle, thereby increasing the solubility of organic compound in a surface solution relative to its water solubility. The critical micelle concentration (CMC) is the minimum concentration of surfactant required for the formation of micelles. Beyond the CMC, the concentration of monomer remains relatively constant. The micelle capacity to solubilize organic compounds makes these molecules suitable reagents for soil remediation of hydrophobic contaminants (Sabatini et al., 1999; Harwell et al., 2000).

Generally surfactants are classified mainly as either ionic or nonionic and can be further classified by the nature of the hydrophilic portion of the molecule. The head may carry a negative charge (anionic), a positive charge (cationic), both negative and positive (zwitterionic), or no charge (nonionic). The hydrophobic group establishes the degree of hydrophobic property of the surfactant, based on the length of the hydrocarbon chain. The most popular hydrophobic group used in surfactants is a hydrocarbon that has a total of 10 to 20 carbon atoms (Sabatini et al., 1999).

The head group of important commercial anionic surfactants can include sulfonate, sulfate, or a phosphate functional group. The most common type of anionic surfactants includes alkylbenzene sulfonates that are used in laundry and hand or dishwashing detergents, household cleaners, and personal cleaning products. They ionize in solution and have excellent cleaning properties. There are various kinds of anionic surfactants available such as linear alkyl benzene sulfonate (LAS), alcohol ethoxysulfates, alkylsulfates, and soap.

Non-ionic surfactants are uncharged and soluble through hydrogen bonding at oxygen or hydrolyzed groups. Typical nonionic surfactant contains polyhydoxyethylene as the soluble group. They are typically used in laundry and automatic dishwasher detergents and rinse aids. They do not ionize in solution and they are resistant to water hardness and clean well. Alkylphenol ethoxylate (APEO) surfactants have been used for more than 40 years in a variety of industrial processes and cleaning products (Tsujii, 1998).

Cationic surfactants contain a positive functional group, typically an amino or quaternary nitrogen group. Their use has been more as softener and coating agents, and they do not perform well in media with negative net surface charges.

Removal Mechanism of Surfactants

Surfactant enhanced soil remediation can result from two main detergency mechanisms; solubilization and mobilization. In the solubilization mechanism, the hydrophobic contaminant is dissolved in the hydrophobic core of micelles that are formed from the self-assembly of surfactant molecules in concentrations above the CMC, thereby effectively increasing the aqueous solubility of the contaminants. Solubility enhancement is the result of the contaminant hydrophobicity and surfactant concentration.

Mobilization refers to a phenomenon that occurs when the adhesion of the droplet to the surface is zero or negative thereby making it easier for the mechanical forces to completely detach the oil droplet from the solid surface. This reduction in interfacial tension between two phases (air-water, oil-water, and solid-water) virtually eliminates the capillary forces which cause hydrophobic contaminant to be trapped, thereby allowing the contaminant to wash out with the water (Edwards et al, 1991; Chu and Chan, 2003). Thus the mobilization mechanism depends on the tendency of surfactant to lower interfacial tension.

Several researchers (Abdul and Gibson, 1991, Edwards et al, 1994) have evaluated surfactants for their ability to act as soil-washing agents and as facilitators of subsurface remediation of hydrocarbon spills. The extent to which surfactants influence the distribution of hydrophobic organic compounds (HOCs) depends critically on the HOC's sorption to solid phases (Chiou et al, 1998). Surfactant washing can be ineffective for soils that contain more than 20-30% silt/clay (Riser-Roberts, 1998; Mulligan et al, 2001) or appreciable quantities of organic matter.

A surfactant that enhances soil remediation goes beyond the selection of a surfactant that will solubilize or mobilize the HOC efficiently. Surfactant itself must match soil conditions otherwise it may absorb onto certain soil minerals, a process that is considered to result from their high polarities and large molecular weights. There are three possible mechanisms whereby surfactants sorb to soil; ion exchange, adsorption, and surfactant partitioning to soil organic matter (SOM). For cationic surfactants, ionic bonding is the main mechanism because soils often contain negative charges on the surface. For nonionic surfactant, the adsorption usually occurs due to hydrogen bonding or the van der Waal forces. Surfactants may also partition into the SOM to an extent influenced by the properties of the surfactant and the SOM. The adsorption of anionic surfactants is similar to that for the nonionic surfactants, but the repulsive charge on the soil surface tends to weaken the adsorption. Although anionic surfactants are prone to less adsorption than nonionic surfactants, they are subjected to losses by precipitation. Because of significant losses of cationic surfactants, mainly anionic and nonionic surfactants are used for soil washing or soil flushing. It has been suggested (Abdul et al, 1990) that non-ionic surfactants are a better choices than anionic surfactants in washing performance to decrease the portion of HOCs sorbed to soil particles. The effectiveness of the surfactants in removing contaminant from soil is also dependent on the hydrophilic/hydrophobic structure [hydrophile lipophile balance (HLB)] of the surfactant molecule and the CMC.

Applications of Surfactants to Soil Remediation

Surfactants have been employed extensively to remove PCBs with soil washing and flushing processes. PCBs are considered to bind to the hydrophobic portion of the soil organic matter by nonspecific mechanisms. Several studies of desorption of HOCs such as PCBs, PAHs, hexachlorobenzene (HCB), and tetrachlorophenol (TCP), using surfactants have investigated their mechanisms of action (Jafvert et al., 1995; Park and Boyd, 1999; Chu and Chan, 2003).

Water solubility enhancements of naphthalene, acenaphthylene, anthracene, phenanthrene, and pyrene by micellar solution of individual surfactants were compared with mixed anionic-nonionic surfactants. Solubility enhancement efficiencies of surfactants above the CMC were observed to follow the order of TX100 > Brij 35 > TX305 > SDS. Polyaromatic hydrocarbons (PAHs) were solubilized synergistically in mixed anionic-nonionic surfactant solution at low surfactant concentration. The synergism for the mixed surfactants was attributed to a reduction in the CMC for the surfactant mixture and an increase in the partition coefficient between the mixed surfactant micelles and the aqueous phase (Lee et al, 2004; Zhu and Feng, 2003).

Effects of typical inorganic ions (NH_4^+, Na^+, and Mg^{2+}) present with organic pollutants, on water solubilities of polyaromatic hydrocarbons (PAHs) in the presence of single and mixed surfactants were also investigated. It was demonstrated that suitable quantity of inorganic cations enhance the solubilization capacities of anionic-nonionic mixed surfactants (Bettahar et al, 1999).

The addition of a water miscible organic solvent (often triethylamine, acetone or n-butyl alcohol) to the washing solution has also been reported to increase the mobilization of hydrophobic contaminants. The performance improvement of surfactant was described to be due to the formation of solvent-incorporated surfactant micelles, which increased both the size (i.e. capacity) and affinity of micelles for more effective contaminant extraction (Chu and Kwan, 2003).

Surfactant selection is critical to successful implementation of surfactant-enhanced subsurface remediation. It has been reported that surfactant solubilization of organic contaminants increased as the surfactant hydrophobicity increased (increasing alkyl chain length and with dialkylation for a given chain length) and as the surfactant hydrophilicity decreased (mono- vs. di-sulfonate). Surfactant sorption likewise was observed to increase with increasing surfactant hydrophobicity for monosulfonates and disulfonates (Desphande et al., 1999, 2000).

The potential of sulfate surfactants with degrees of ethoxylation ranging from 1 to 4 per mole was evaluated for use in subsurface remediation. Results demonstrated that no significant precipitation of surfactant occurred if the degree of ethoxylation was ≥ 2. Sorption assays demonstrated that these ethoxylated anionic surfactants were less prone to sorption on soil than nonethoxylated anionic and nonionic surfactants. Furthermore, enhanced solubilization of naphthalene was observed with increased degree of ethoxylation (Rouse et al., 1996). The feasibility of surfactants for simultaneous removal of metals and hydrophobic organic compounds from polluted soils has also been explored. Results showed that a decrease in pH from 8.3 to 1.0 had no significant effect on naphthalene and pyrene solubilization using surfactants (Benschoten et al., 1995). Mulligan et al. (1999b) also investigated the mechanism for metal removal from soil by biosurfactants. The removal occurred through extraction from the soil surface by the surfactant, followed by complexation with the metal. Surfactants have also shown a great ability to remove metals from soil with fewer toxic effects than acids or chelators.

Cationic, anionic, and nonionic surfactants have been used to remediate heavy metal from contaminated soils (Doong et al., 1998). They found that the addition of anionic and nonionic surfactants could enhance the extraction rates of Cd, Pb, and Zn, while the addition of a cationic surfactant decreased the extraction efficiency of heavy metals. However, at low pH cationic surfactants appeared to be more effective in extracting heavy metals than nonionic and anionic surfactants.

Surfactants have been used to aid the photolytic degradation of chlorinated compounds in soil. Photochemical dechlorination of 2-chlorophenol (2CP) dissolved in surfactant has been studied. The degradation and dechlorination were observed to increase in the presence of nonionic and anionic surfactants. A larger enhancement was observed at surfactant concentrations greater than the CMC and was attributed to partitioning of 2CP into the micelles. Furthermore, the study of 2CP photolysis in hexane, methanol, and dimethoxyethane suggested that the surfactant could serve as a hydrogen atom source in promoting 2CP degradation (Shi et al., 1997).

2.2 Heavy Metal Contamination

Discharge and disposal of wastes contaminated with heavy metals have resulted in the contamination of valuable land resources and ground water. Contaminated groundwater and soils can pose a significant threat to human health and ecological systems. Approximately, 75% of Superfund sites are contaminated with the heavy metals. Mostly, the metals commonly found at contaminated sites are in the following order of abundance Pb, Cr, As, Zn, Cd, Cu, and Hg (U.S. EPA, 1997b).

In soil, anthropogenic influxes of heavy metals undergo a variety of reactions such as sorption-desorption and precipitation-dissolution that determine the fate of metal in soil and groundwater. The mobility of metal is hindered by these reactions that cause metals to adsorb or precipitate, or chemistry that tends to keep metals associated with the solid phase and prevent them from dissolving. In terms of adsorption reactions, precipitation will have the most impact on a metal's fate and mobility whereas among other reactions, cation exchange will influences the fate of metals. Over all, the extent of these reactions is strongly influenced by soil type (e.g., texture), pH, and cation exchange capacity (CEC) of the soil (McBride, 1994).

Soil type or composition is a very important factor in heavy metal sorption-adsorption reactions where soil texture or soil particle size can influence the fixation of metals by soils. Clays are extremely important in fixation and adsorption reactions because of their high CEC and fine texture respectively (Wild, 1993).

Soil pH plays a very important role in the retention and mobility of metals in soil columns. The pH is an influencing factor for both sorption-desorption and precipitation-dissolution reactions. In addition, the CEC of soils generally increases with an increase in pH. Even with a soil that has a high affinity for a specific metal, the degree to which the metal is sorbed is a function of pH. Soil pH has been determined to be a major factor along with CEC for the sorbtion of lead by soils. The soil pH also influences the retention of zinc and copper (U.S. EPA, 1990).

The oxidation-reduction potential of a soil is critical in determining which species of an element is available for sorption, precipitation, or complexation. In general, the reduced forms of a metal are more soluble than the oxidized form. The redox potential of a soil system is usually altered through biological activity and a change in redox potential frequently is correlated with changes in pH. Reducing conditions may be associated with a low pH resulting in the formation of CO2 and organic acids formed by the microbial degradation of organic matter. Anaerobic conditions tend to enhance the mobility of metals in effluents (McBride, 1994).

Several technologies are available for the remediation of metal-contaminated sites. These technologies are contained within five categories of general approaches to remediation: (i) Isolation; (ii) immobilization; (iii) toxicity reduction; (vi) physical separation; and (v) extraction. Table 2.1 summarizes the key technologies within each category. All soil remediation technologies are based on either of the two basic approaches to achieve the same goal of making the heavy metal less available to biota. The first approach involves the stabilization of heavy metals within the soil matrix. This is accomplished by increasing the metals adsorption to soil particulates by increasing the pH and CEC. The second strategy to remediate soil for heavy metals involves the separation/removal of metals from the soil and this is done by reducing their adsorption to soil particles. Many of the metal remediation technologies work on this approach. As a detailed discussion of all of the soil remediation technologies is beyond the scope of this dissertation, only chemical solidification/stabilization, phytoremediation, and soil

Table 2.1 Summary of soil remediation technologies for heavy metals

Isolation	**Immobilization**	**Toxicity Reduction**	**Physical Separation**	**Extraction**
Capping	**Vitrification**	**Chemical Treatment**	**Screening**	**Soil Washing**
Subsurface Barriers	**Solidification/Stabilization**	**Biological Treatment**	**Magnetic Separation**	**Soil Flushing**
	Chemical Stabilization	Bioremediation		
	Phytostabilization	Phytoremediation		
			Froth Flotation	**Electrokinetic**
				Pyrometallurgical

washing/flushing will be reviewed because these methods are considered most frequently in the literature in terms of their feasibility for soil remediation of heavy metals.

2.2.1 Solidification/Stabilization

Stabilization/solidification (S/S) is one of the major methods in treating metals in soils and hazardous wastes (Lo et al., 2000; Poon and Lio, 1997). Solidification involves the formation of a solidified matrix that physically binds the contaminated material.Stabilization frequently utilizes chemical reagents to convert a metal into a less soluble and less mobile form. Over all, the process involves the addition of reagents to the soil matrix to immobilize the metal contaminant through a combination of chemical reaction, and encapsulation. Inorganic binders such as cement, blast furnace slag, or fly ash and organic binder such as bitumen are commonly used for binding the metals to the soil matrix. Cement based stabilization/solidification processes are particularly appropriate for treating heavy metal-contaminated wastes, sludges, and soils (Baker and Bishop, 1997; Awe et al., 2001). The dominant immobilization mechanism of metal precipitation of hydroxides, carbonates, and silicates is achieved by addition of alkaline reagents. The permeability and porosity of soils are often reduced, which restricts metal leaching to infiltering water.

The limitation of S/S technologies is that they can result in an appreciable increase in the soil volume and can dramatically alter the physical and chemical nature of the soil such as reducing the ability of soil to support vegetation without the addition of a clean soil cover, and can often limit the potential end uses for a site (FRTR, 2002). Furthermore, S/S technologies are not useful for certain metals, such as metals that exit as anions [e.g. Cr(VI), As(III, V)] or for metals with low-solubility hydroxides (Hg). This approach does not eliminate the threat of wind and water erosion of colloidal bound metals. Also, metal fixation may lead to future leaching problems caused by biological activities or soil acidification.

2.2.2 Phytoremediation

Phytoremediation involves the use of plants to aid in the extraction of toxic metals. Some plants have developed the ability to remove ions selectively from soil and to regulate their uptake of metals. Most metal uptake occurs in the root zone, usually via absorption. Potentially useful phytoremediation technologies for the removal of metal include two main approaches phytoextraction and phytostabilization (Martin and Ruby, 2004). Phytoextraction is an innovative and cost-effective technology for non-destructive remediation of heavy metal-contaminated soils. It involves the culture of hyperaccumulating plants that accumulate metals from the soil by absorption into their roots and shoots. A hyperaccumulator is defined as a plant that can incorporate up to 1.5% of its weight in heavy metals. The above ground shoots can be harvested for disposal to hazardous site or treatment for metal recovery. Phytoextraction with three plants {*Viola baoshanensis, Vertiveria zizanioides, and Rumex K-1* (*Rumex patientia R. timschmicus*)} and EDTA demonstrated that technique was the most efficient to enhance the phytoextraction of Pb and Zn from soil, but did not have significant effect on the levels of soil Cd. Lead phytoextraction efficiencies of *V. Baoshanensis, V. Zizanioides and Rumex K-1* were improved by 19-, 2-, and 13-fold respectively when compared with the control treatment (Zhuang et al., 2005). Phytoextraction technique utilizing a sterile strain of *Vetiver grass* (Vetiveria zizanoides) along with soil amendments was evaluated for their capacity to remove lead and other elements including Zn, Cu, and Fe from the soil of a 50-yr old active firing range at the Savannah River Site (SRS). The study indicated that the use of *Vetiver grass* coupled with the use of chelating soil amendments has considerable potential for use as a remedial strategy for lead-contaminated soils such as those associated with firing ranges (Wilde et al., 2005).

Phytostabilization involves the use of plants to limits the mobility and bioavailability of toxic metals within the soil. Phytostabilizers are characterized by a high tolerance to metals in the surrounding soil but a low accumulation of these metals within the plant. These plants stabilize metals by limiting their mobility and bioavailability. In addition, vegetation cover provides protection against erosion, reduces exposure to the contaminated soil, and reduces the infiltration of water (Vangronsveld and Cunningham, 1998). This technique is considered to be a containment technology that is most applicable as an interim measure (US EPA, 1997). A limitation of phytoremediation is that it can take many years for heavy metal concentrations within a soil to reach a regulatory level, while producing large amount of biomass, which will require safe disposal. Furthermore, plants roots can extract only the soluble or exchangeable fractions of metals ions.

2.2.3 Soil Washing/Flushing

Soil washing or flushing involves the use of aqueous solution to extract contaminants from the soil matrix (FRTR, 2001). This technique is designed to recover the contaminants by increasing their solubility and mobility in the extracting phase. The efficiency of metal removal during soil washing/flushing depends on the degree/duration of contact between the extraction fluid and the contaminated soil matrix, the solubility of the metal in the extraction fluid. Additionally for soil flushing, the tendency for the metal to sorb to the soil particulates as the metal-laden extraction fluid migrates to the water extraction points. Soil washing can be a physical and/or chemical process which results in the separation, segregation and volume reduction of hazardous material and/or the chemical transformation of contaminants into innocuous, unregulated products (Semer and Reddy, 1996). The effectiveness of soil washing is strictly dependent on the soil type, the identities of the contaminants it contains and the choice of extracting agents. A range of reagents including acids, chelating reagents, surfactants, and cyclodextrins have been evaluated for soil washing or flushing, with varying degrees of success (Dunn et al., 1989; Huang et al., 1997; Brusseau et al., 1997). Chelating agents are the most commonly investigated reagents; several researchers have demonstrated their potential effectiveness for enhancing the removal heavy metals from contaminated soil. The shortcoming of this technique is the cost associated with reagents.

2.2.3.1 Soil Washing/Flushing with Chelating Agents

Chelating agents are the most efficient extraction adjuvant that can be used to enhance the heavy metal extractions from contaminated soils. The advantages of chelating reagents in soil remediation are high metal extraction efficiencies, high thermodynamic stabilities of the product metal complexes, good solubilities of metal complexes, and low adsorption of chelating agents on the soil (Fischer et al., 1998). The chelating reagents enhance metal extraction from soil by furnishing strong formation energies that overcome the metal-soil particle sorption energies. Chelation occurs when an electron deficient metal ion associates with an electron rich ligand by forming a ring structure through one or more coordinate bonds. For chelation, the ligand must contain two or more separate donor sites that are capable of interacting with the same metal cation. Species that serve as electron donors are typically the more electronegative elements (nitrogen, phosphorus, oxygen, and sulphur) and often form part of a functional group that orients the donor site. Another condition for strong chelation is the relative geometric positions of these functional groups such that the metal ion can participate in the formation of one or more rings.

Conventionally, chelating agents are classified according to the number of donor sites and further sub-divided according to types of functional groups. There are several different types of chelating agents having different functional groups, with varying numbers of binding sites. Chelators with multidentate character are of special interest because of their higher avidity for metal cations through the formation of five or six member ring. Chelating reagents having four or six electron donor groups (tetra and hexadenate) are the most effective at extracting metal ions (Skoog et al., 2000). The capacity of a chelating agent to bind metals can be predicted from the formation constants for the metal-ligand complex. Larger formation constants are indicative of more stable chelates and suggest an increased ability to bind metals strongly, even under the influence of pH.

Aminopolycarboxylic acids were first recognized by Gerold Schwarzenbach (1945) for their ability to form remarkably stable chelates with metal ions. Aminopolycarboxylic acids are derived from amino acid glycine that contains one amino group and one caboxylate group within their molecular structure. With the nitrogen group, ring formation is characterized by a preference for soft sphere metal cations. The most commonly used aminopolycarboxylic acids are diethylenetriaminepentacaetic acid (DTPA) and ethythlenediamine tetraacetic acid (EDTA), which are widely used in industry, detergents, foods, and agriculture. Table 2.2 lists the formation constants of few representative aminopolycarboxylic acids.

From soil reclamation point of view, the ideal chelating agent would be: (i) soluble; (ii) toxicologically innocuous; (iii) strongly complexing over a wide range of pH; (vi) biodegradable; and (v) unreactive with soil. EDTA possessing these characteristics is one of the most widely used chelating agents in soil washing. Hereafter, the main focus is on EDTA for its intended use as chelating agent for soil washing.

Table 2.2 Formation Constants of Metal Complexes (pK_F)

Ligand	Al^{3+}	Cd^{2+}	Cr^{3+}	Cu^{2+}	Fe^{2+}	Mn^{2+}	Ni^{2+}	Pb^{2+}	Zn^{2+}
DTPA	-	19	-	20.5	16	15.5	20	18.9	18
EDTA	16.1	6.5	23.0	18.8	14.3	13.8	18.6	18.0	16.5
HEDTA[†]	3.0	2.9	2.3	3.0	2.8	3.1	3.2	2.8	3.0

[†] N-(2-Hydoxyethyl) ethylenediamine tetraacetic acid.

Source: NIST Standard Reference Database 46, Critically Selected Stability Constants of Metals Complexes, Version 6.

Metal Extractions with EDTA

Chelating agents are commonly used for leaching metal from soils since they form strong soluble complexes with these targets. Ethylenediaminetetraacetic acid is the most widely used synthetic chelating reagent in soil washing. The tetra acid has low water solubility (0.2 g per 100 mL) and therefore the disodium or diammonium salts are common replacements. In aqueous solutions, EDTA has no net charge but has four dissociable protons, two carboxyl groups and one with each amine group. The EDTA molecule is zwitterion, having two positive charges localized in one area and two negative charges in two other areas. Even though, EDTA is hexadentate and it forms water soluble stoichiometric 1:1 complexes with metal ions regardless of their charges (Skoog et al., 2000). The stabilities of metal•EDTA complexes in the presence of other metal ions can be predicted from their relative stability constants, the pH of solution, and the concentration of metal cations, EDTA and other electrolytes. Figure 2.1 provides a comparison of the stability constants for various metal•EDTA complexes as a function of pH. At low pH (<3), the tendency for these complexes to form can be assumed to follow the order: $Fe^{3+} > Cu^{2+} > Pb^{2+} > Al^{3+} > Zn^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$ (Kim and Ong, 1999; Stephen and Herbert, 1996).

EDTA has been explored extensively for soil treatment because of its ability to mobilize cations efficiently without affecting the soil's physical and chemical properties appreciably (Steele and Pichtel, 1998; Papassiopi et al., 1999; Garrabrant and Kosson, 2000, Kim and Ong, 2000). It is an effective, recoverable, and reusable chelating agent that has potential for large scale application. Wasay et al. (2001) evaluated natural and synthetic chelating reagents for their ability to remove heavy metals from artificially contaminated soils at various pHs. Aminocarboxylated acids (EDTA and DTPA) in comparison to citric acid proved to be more efficient at removing Pb from soil (even if present at a one tenth relative molar concentrations). Copper extraction from a sandy soil was evaluated by washing the soil with an aqueous solution of EDTA (Di Palma et al., 2005). The results of the study demonstrated that decreases in the pH of the washing solution resulted in increased Cu extraction. A virtually complete extraction Cu was achieved after 23 h of mixing with a liquid/solid (L/S) ratio of 5 whereas at L/S ratio of 12, 55 h of mixing were required.

A study of the effect of certain key factors on heavy metal removal efficiencies by chemical extraction revealed that strongly acidic soils cause the protonation of EDTA and decrease its ability to mobilize heavy metals. It was observed that EDTA was effective in extracting Pb and Cd whereas humic acids promoted the dissolution of Cu and Zn in extractants, but decreased Pb and Cd mobilization. Heavy metals were more difficult to extract from a high clay medium than from a high silt medium (Liu, et al., 2005).

Both soil washing (ex situ) and soil flushing (in situ) techniques using acid, EDTA or organic acid were evaluated by Tawinteung et al. (2005). Lead contaminated soils from battery recycling operation or from a Pb-smelting facility were investigated for decontamination (Kim et al., 2003). It was demonstrated that 85%, 84%, and 74% of the Pb burden was removed by EDTA (2:1 mol to Pb), 1M HNO_3, and 0.2M ammonium citrate, respectively, after flushing with 20 pore volumes of extractant. The flushing process using 1M HNO_3 increased soil acidity to extreme acid conditions (pH 2.0) resulting in adverse effects to physicochemical properties of the treated soil. Lead could be removed from contaminated soil using EDTA extraction however the efficiency was higher in the coarse texture soil fraction. As compared to NTA, EDTA was more efficient, demonstrating a molar chelant/Pb ratio above 1:1, and mobilizing 10 to 30%

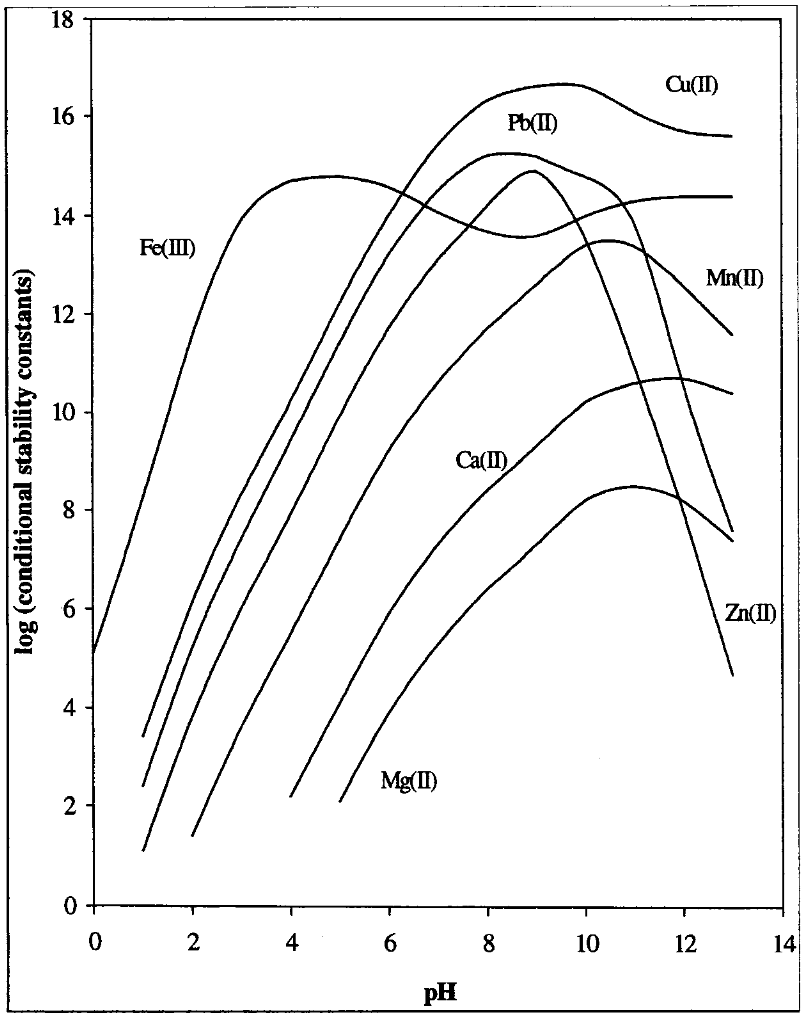

Figure 2. 2 A comparison of conditional stability constants for various metal–EDTA complexes as a function of pH adapted from Ringbom et al., 1979.

more of the Pb. A batch experiment demonstrated that PDA was effective in extracting 90% of the Cd from spiked soil and also reversibly released Cd under high pH conditions (Hong and Chen, 1996). According to Sun et al. (2001), EDTA showed similar extraction efficiencies for Zn, Cd, Cu, and Pb from four contaminated soils. Sequential fractionation experiment demonstrated the mobility of metals to follow the order Cu > Cd > Zn> Pb.

Chelating agents and acids were evaluated for removing Cu, Zn, and Pb from contaminated soils (Lee et al., 2004). The removal efficiencies of Cu, Zn, and Pb from soils for various chelating agents and acids followed the descending order EDTA > DTPA > citric acid > HCl. The effect of EDTA concentration on the removal efficiency of heavy metals was examined for a wide range of concentrations, 1×10^{-4}- 5×10^{-2} M. The removal efficiencies of heavy metals were high for soils containing weakly adsorbed target metals. Common chelating agents (citric acid, EDTA, HEDPA) have been observed to increase electroosmotic flow (EF) intensity in clayey soils. The intensity of EF depended on the character, concentration, and pH of complexing reagent solution, the character of soil and the voltage applied (Popov et al., 1999).

Recycling of EDTA

Despite the fact that EDTA presents many advantages for soil washing, EDTA is not frequently used in full scale soil washing projects due to the elevated cost and the necessity to remove metal complexes from spent fluids. The EDTA reagent is relatively expensive and given the tons of soil needing reclamation, soil washing with EDTA leads to an excessively costly remediation (Barona et al., 2001). Another nuisance associated with EDTA usage is that a large volume of metal-EDTA complexes is generated and must be treated before disposal due to environmental concerns that the chemical additives can be recalcitrant within soil. Hence the recovery of EDTA is important for cost effectiveness of this reagent and proper disposal.

Previous work has demonstrated that there are at least three possible techniques to recover and regenerate EDTA. In one of the recovery methods, the application of electrolysis in conjunction with a cation-exchange membrane was investigated for the regeneration of complexing reagent. This method involved electrochemical reduction of metal•EDTA complexes in which metals cations were reduced/deposited on the cathode surface while EDTA was released into solution and isolated from the anode using a cation exchange membrane (Juang and Wang, 2000; Arevalo et al., 2002). With current interest in remediation technologies, the electrolysis method has been extended by several researchers for the recycle of wastewater from soil washing. The results of their studies demonstrated that the recovery of metal and EDTA was virtually quantitative (99% and 91% respectively) by electrolysis (Turner et al., 1994). The electrochemical process was not without problems. These regeneration methods can be costly due to several potential operational problems such as membrane fouling/degradation and EDTA precipitation (Kim and Ong, 1999). The increase in hydroxide ion concentration results in high pH within the cathode compartment that caused degradation of the membrane and precipitation of EDTA on the membrane surface. Thus several operating problems must be addressed before the electro-membrane can become a practical treatment for the recovery of EDTA.

Another technique involves the removal of metal ions from solution by the addition of precipitating reagents such as NaOH, $Ca(OH)_2$, Na_2S, $FeSO_4$, $FeCl_3$, NaH_2PO_4, Na_2HPO_4 and diethyldithiocarbamate (DEDTC). On the basis of ease of operation and cost, chemical precipitation (hydroxide, carbonate, or sulfide reagents), is considered to be the most attractive scheme but the removal of metal from EDTA solution by such precipitation can be inefficient due to high stability of the metal-EDTA complexes. It has been shown that after soil washing, EDTA can be recovered and reused by the addition of Na_2S and $Ca(OH)_2$ (Hong et al., 1999, Zeng et al., 2005). Rudd et al. (1995) also proposed precipitating lead ions as lead hydroxide or as lead sulfide at high pH to recover the EDTA and to permit the EDTA wastewater to be discharged safely. Although sulfide precipitation was found to reduce the level of Pb, the effectiveness of recycled EDTA was not demonstrated. Metal•EDTA complexes have been separated by precipitating metal ions as sulfates or phosphates. The addition of an Fe salt with either sodium sulfate or phosphate at pH 6-9 was effective in treating Cu-EDTA complexes in metal finishing wastewaters. Ferric ion was able to displace Cu and Pb by forming a more stable Fe-EDTA complex. Further research demonstrated that the addition of NaOH or $Ca(OH)_2$ to a Fe-EDTA solution resulted in a virtually quantitative precipitation of ferric ions (Di Palma, 2003; Kim and Ong, 1999). In another study, post equilibration with EDTA to mobilize Cu, Mn, Pb, and Zn from a contaminated urban soil, the metal-laden aqueous extract was treated with sodium diethyldithiocarbamate (DEDTC) to precipitate the heavy metals from solution while liberating the chelating reagent. The aqueous supernatant fraction was then re-combined with the soil particulates to extract more pollutants. Result demonstrated that a sparing quantity of EDTA (10 mmol) was able to mobilize 32 - 54% of the 5 mmol of heavy metals from the soil with 3 cycles (Ting and Marshall, 2001).

An alternate means of regenerating the chelating reagent involved reacting metal•EDTA complexes with a bimetallic mixture, which can result in precipitation of metals as insoluble hydroxides while releasing the EDTA into solution. The precipitation of heavy metal is induced by corrosion and hydrolysis of zero-valent magnesium in the presence of palladium accelerator. It has been reported that when metal-laden soil extracts were treated with zero-valent magnesium (Mg^0) or bimetallic mixture (Pd^0/Mg^0 or Ag^0/Mg^0), an appreciable fraction of the mobilized metals (Pb, Cu and Zn) was cemented to the surfaces of the excess Mg whereas virtually all of mobilized Fe and Mn was removed from solution as insoluble hydroxides while liberating the EDTA (Lee and Marshall, 2002). This method could be economically prohibitive as well.

PREFACE TO CHAPTER 3

In Chapter 2, an overview of polychlorinated biphenyl (PCB) and heavy metal soil contamination, their remediation technologies and applications of surfactant, cylodextrins, and EDTA to soil washing was presented. The comprehensive literature view revealed the need for the development of efficient, economical, and environmentally sustainable technology for the remediation of mixed contaminated soil with the detoxification of contaminants.

The first stage of this study involved the reliable estimation of PCBs and heavy metals in soil and aqueous washes of soil. As congener specific PCBs are time consuming to analyze reliably, an approach to estimate total polychlorinated biphenyls compounds in soil matrix through hydrogenation to dicyclohexyl by reaction with noble metal catalyst was proposed.

In the following chapter, the ability of zero-valent magnesium (Mg^o) in the presence of Pd^o accelerator was compared with zero-valent magnesium (Mg^o) over alumina for the efficient dechlorination of PCBs solutions to dicyclohexyl. Finally, this procedure was evaluated with various PCBs contaminated soil/sediment samples in anticipation of its use it as detoxification technique for PCBs.

This paper has been publication in *J. Environ. Monit.* 2003. Authors: Ehsan, S., S. O. Prasher, and W. D. Marshall.

CHAPTER 3

ESTIMATES OF TOTAL POLYCHLORINATED BIPHENYL (PCB) COMPOUNDS IN SOILS BY HYDROGENATION TO DICYCLOHEXYL

3.1 Introduction

Polychlorinated biphenyl (PCBs) compounds are ubiquitous environmental contaminants that represent an important class of priority pollutants characterized by their persistence, toxicity, and tendency to accumulate in fatty tissues. These compounds have received increased attention in recent years because of their widespread distribution and the increased public awareness of environmental issues. The release of PCBs is controlled by regulations that have been supported by extensive research into their fate, transport, and eventual disposition. As well, methods for the remediation of contaminated sites continue to be proposed and evaluated. These activities require a rapid/simple method to estimate the levels of these analytes in natural matrices. Unfortunately, among the regulated analytes, PCBs are one of the more difficult groups to analyze accurately because of the problems associated with the determination of 209 separate congeners. As substantial amounts of PCBs are associated with soils/sediments, the analysis of particulate media generally requires extraction/mobilization with organic solvents, clean up that can include the removal of sulphur and column fractionation, followed by separation with gas chromatography frequently with quantitation by electron capture (Vetter et al., 1998; Smedes and Boer, 1997) or mass spectrometric detection (Dowdall et al., 1995; Berset and Holzer, 1999). Mobilizations from particulate media have included super/subcritical fluid extraction (Hawthorne et al., 1998; Kimbrough et al., 1994) as well as conventional soxhlet, sonication (Abrha and Raghavan, 2001), solid-phase (Dmitrovic and Chan, 2002), or microwave-assisted (Harrison and Melnychuk, 1995) techniques that can be laborious, error prone and susceptible to inefficient recovery. Alternative approaches to PCB quantitation include immunoassay techniques and chemical class recovery techniques in which all 209 congener are converted to a common derivative (Chuang et al., 1998; Johnson and Emon, 1996; Schuetz et al., 1999). The chemical recovery has become more common because with immunoassay, the main difficulty is that one antibody does not respond equally to all congeners (Steinwandter and

Brune, 1983). The two principal approaches to chemical derivatization include perchlorination and reduction (dehydrochlorination) techniques. In perchlorination procedures, the various congeners are converted to decachlorobiphenyl resulting in a product that retains appreciable toxicity (Klucik, and Rivera, 2000). In addition to the use of noxious reagents and harsh reaction conditions, the disposal of hazardous products/reagents limits the appeal of this approach. The second approach, reductive dehalogenation, involves the quantitative conversion of the PCB congeners to an innocuous product. A broad array of techniques has been proposed to accelerate hydrodechlorination that include electrochemical (Hu et al., 2000), photochemical (Teo et al., 2001), ultrasonic (Wiegel and Wu, 2000), microbial (Yamamoto and Tagawa, 2001), radiolytic, catalytic (Wu and Marshall, 2000), and chemical methods (Yuan et al., 2002; Scherrer et al., 1998). In general, chemical methods remain the more widely exploited methods to accomplish the dechlorination of organochlorine (OC) compounds. Catalytic hydrodehalogenation with homogeneous or heterogeneous catalysis, have long been familiar to organic chemist, and more recently increasingly facile and efficient procedures have been described for the removal of organically bound chlorine from persistent organic pollutants (POPs).

A variety of metal catalysts has been evaluated for their ability to dechlorinate OC compounds under mild reaction conditions. Catalytic hydrodehalogenation of OC compounds mediated by metal [Na, Li or zero-valent (ZV) Ni, Fe, Mg, or Zn] are well known elimination reaction that have been utilized for more than a century (Wang and Zhang, 1997; Chuang et al., 1995; Zhang et al, 1998; Trost and Fleming, 1991). A variety of catalysts and diverse methods have been employed, depending upon the order of reactivity of both the halogen substituent(s) (I> Br > Cl >> F) and the susceptibility of the halo-substituent to dehalogenation (allylic ≈ benzylic > aliphatic > aromatic) which suggest that reduction of chlorinated aromatic compounds can be a difficult task (Doyle, et al., 1998). More recently, the use of ZV bimetallic mixtures (Pd^o/Fe^o, Ag^o/Fe^o, Pd^o/Mg^o) or supported noble metal (Pt^o, Pd^o, Rh^o, Ru^o) have provided dramatic improvements in rates and selectivities of hydrodechlorination reactions (Kabir and Marshall, 2001; Korte et al., 2002; Ordonez et al., 2002). Noble metal catalysts on carbon, silica and alumina support have been employed to promote hydrodechlorination reactions. Among the noble metals, palladium has been used most frequently for dechlorination.

Palladium either supported/unsupported or as a bimetallic mixture, has shown superior activity and selectivity to other metal catalysts, especially in the hydrodechlorination of polychlorinated compounds (Shin and Keane, 1998; Schuth and Reinhard, 1998; Rodriguez and Lafuente, 2002; Murena and Gioia, 2002; Sajiki et al., 2002; Ukisu et al., 2000).

Destruction of halogenated organic compounds by catalytic hydrogenation not only represents one of the more recent detoxification techniques for environmental remediation but also provides a basis for developing a method for characterizing PCB mixtures by conversion to a single derivative. The principle shortcoming of the strategy is that all congener-specific information is lost.

This report describes the hydrodehalogenation and hydrogenation of highly chlorinated PCB congener, PCB mixtures (Aroclors) and historically contaminated soil/sediment samples in the presence of $Pd^o/\gamma\text{-}Al_2O_3$ under mild temperatures. Palladium was chosen as the catalyst because of its broad reactivity in hydrodehalogenation reactions and γ-alumina was chosen as the support because relative to other supports, it is generally considered to minimize adsorption effects (Rodriguez and Lafuente, 2002).

3.2 Experimental

3.2.1 Reagents

Magnesium (98%, 20 mesh), $Pd^o/\gamma\text{-}Al_2O_3$ (reduced, 5% w/w, catalog # 11713) and potassium hexachloropalladate (K_2PdCl_6) were purchased from Alfa-Aesar, Ward Hill, MA, USA. Biphenyl, dicyclohexyl and phenylcyclohaxane, 2-bromonaphthalene, and ammonium formate were purchased from Sigma-Aldrich Chemical Co., Oakville, ON, Canada. Individual PCB (solid) congeners were kindly provided by Dr. L. Chan (CINE). Aroclor standards 1248, 1254, and 1260 ($1mg\ mL^{-1}$) were supplied by Supleco, Bellefont, PA, USA. Octan-2-ol, tetrahydrofuran (THF), propan-2-ol, methanol, hexane, and dichloromethane were obtained from Fisher Scientific, Ottawa, ON, Canada. All chemicals, solvents, and materials were of ACS Reagent grade or better and were used as received.

3.2.2 Reference Materials

Certified reference materials (CRM), BCR 481 and BCR 536, were purchased from the Community Bureau of References (BCR), Brussels, Belgium. Standard reference material SRM 1939a was purchased from the National Institute of Standard and Technology (NIST), Gaithersburg, MD, USA. Certified reference material CRM 915-050 was purchased from R. T. Corporation, Laramie, WY, USA.

3.2.3 Gas Chromatography –Mass Spectrometry

The Varian model 3400 gas chromatograph was equipped with a model 8200 auto-sampler and a model 2000D ion trap mass analyzer. Chromatographic separations were achieved on a DB5-MS column (30m x 0.25um i.d., 0.25um film thickness) that was eluted with helium at 1.0 mL min^{-1}. After an initial hold for 2 min at 70 °C, the temperature was ramped to 270 °C at 10 °C min^{-1} and held for a further 3 min before cool down. An on-column injection technique was performed and the injector and transfer line were maintained at 250 °C. Mass spectra were recorded in the full scan (50-550 amu, 1.5 scan/s) mode. Eluting components were identified tentatively by comparing retention times with those of authentic standards and corroborated by comparing experimental mass spectra with spectra catalogued in the National Institute of Standards and Technology (NIST) or the Saturn spectral libraries.

3.2.4 Soil Sample Pretreatment

Representative sub-samples of two agricultural soils and a field-contaminated soil from an industrial location were collected from appropriate sites. The agricultural soil has been under continued cultivation for more than 60 years. The PCB-contaminated soil sample was collected from an industrial landfill on the island of Montreal. The soil samples varied in pH, texture, and organic matter content. All soil samples were air dried, passed through 2 mm sieve (10 mesh) and mixed thoroughly. Samples were further air-dried and were passed through 50 mesh sieve and stored in sealed bottles at 4°C.

3.2.5 Pd^0/Mg^0 Bimetallic Mixture

Mg flakes (98 %, 20 mesh, 0.5g), potassium hexachloropalladate (K_2PdCl_6, 0.003 g), ammonium formate [$NH_4OC(O)H$, 0.4 g], and 2 mL of methanol - water (2 + 1, *v/v*) containing substrate were added to a 20 mL test tube. The reaction tubes were loosely capped (to permit the escape of H_2) and the dechlorination reaction were permitted to proceed for 1-2 h prior to extraction with two successive 0.5 mL portions of hexane-ethyl acetate (9 + 1, *v/v*). The organic extracts were combined and analyzed by GC/MS after the addition of 2-bromobiphenyl as an internal standard.

3.2.6 Pd^0/γ- Al_2O_3

In a typical experiment, 5.0% (w/w) $Pd^0/\gamma\text{-}Al_2O_3$ catalyst (25 mg) and a Teflon stirring bar were added to a glass vial (20 mL) and sealed with Teflon lined silicone septum and screw cap. During 5 min, the 20 mL capacity glass vial containing catalyst was flushed with a gentle stream of hydrogen, delivered from a cylinder via a 22-guage needle that pierced the septum, and exited via a second needle that was connected to a U-shaped glass tube containing water. Subsequently, PCB solution in methanol or hexane (1 mL) was added by syringe. The reaction temperature was maintained at 65 °C in a water bath. Post reaction, products were recovered by extraction with 1 mL of hexane in cases where PCB dilution was in methanol or the liquid hexane phase was collected as such after 1 hr of reaction.

For soil/sediment samples, 1g of sample was combined with 5.0% (w/w) $Pd^0/\gamma\text{-}Al_2O_3$ (0.025g) in a glass vial (20 mL) and sealed with Teflon-lined silicone septum and screw cap. During 5 min, the 20 mL capacity glass vial containing catalyst was flushed with a gentle stream of hydrogen as described above. Subsequently, methanol or hexane (1 mL) was added by syringe to initiate the stirred reaction. Post 1 h reaction at 65 °C, the mixture was diluted with water (2 mL) and products were recovered by extraction with hexane (1 mL). Extracts from reactions with either PCB standard or soil/sediment were analysed by GC/MS after the addition of 2-bromonaphthalene as an internal standard.

3.3 Results and Discussion

3.3.1 Neat PCB Mixtures

PCB conversion to biphenyl has been reported to be efficient (Engleman and Cheng, 1998) under mild conditions of temperature and pressure in the presence of palladium/magnesium (Pd^o/Mg^o) and a suitable reaction medium. As a prelude to extending the scope of this method to environmental matrices, hydrogenolysis of a range of individual PCB congeners including mono, di, tri, tetra, penta, and heptachlorobiphenyl were investigated. As summarized in Table 3.1 (data not shown for mono and dichlorobiphenyl), the efficiency of dechlorination was reduced by increasingly chlorinated biphenyl substrate. After 1.5 h of reaction, substrates containing one to three chlorine substituents were reduced quantitatively to biphenyl. By contrast, substrates with five to seven chlorines resulted in minor quantities of less highly chlorinated congeners (predominantly di- and tetrachlorobiphenyl) in addition to biphenyl. In our hands, the treatment of individual PCB congeners with the palladium-magnesium system was characterised by a decrease in dechlorination efficiency in the order: tri > penta > heptachlorobiphenyl. In subsequent experiments, the dechlorination of decachlorobiphenyl was also evaluated with similar reaction conditions. However, for this substrate, inefficient conversion to biphenyl was observed - only 6 mol % of product was recovered even after 12 h of reaction. After 3 h of reaction, 50 mol % of substrate had been converted to heptachlorobiphenyl, dichlorobiphenyl, and less than 10 mol % had been totally dechlorinated. Extended reaction times, various other support solvents, and ratios of bimetallic catalyst to substrate were evaluated but quantitative dechlorination was not achieved for highly chlorinated PCB congeners.

Subsequent experiments were directed to the palladium-alumina catalytic systems. Initial trials were conducted with decachlorobiphenyl ($C_{12}Cl_{10}$), to evaluate the extent of hydrogenolysis (hydrohalogenation plus hydrogenation) with commercial palladium (5% w/w) on a γ-Al_2O_3 support. First, $C_{12}Cl_{10}$ dechlorination was attempted with the minimum volume of solvent in an effort to maximize a single gas-solid reaction medium. Reaction with 0.1mL solvent at 65 ^oC for 0.5-1 h resulted in partial dechlorination as indicated by the detection of small quantities of several less highly chlorinated congeners (biphenyl substituted with 1-6 chlorine atoms). Incomplete

Table 3.1: Recoveries (mol % ± 1 RSD [†]) of biphenyl from the reaction in methanol, of various PCB congeners (100 μg) with Mg^0 (0.5 g) and K_2Cl_6Pd (0.003 g) during 1.5 or 3h

Product	Time (h)	Biphenyl recovery (mol %)
Trichlorobiphenyl	1.5	97 ± 2
Tetrachlorobiphenyl	1.5	96 ± 5
Pentachlorobiphenyl	1.5	91 ± 4
Heptachlorobiphenyl	1.5	53 ± 6
Decachlorobiphenyl	3.0	6.3 ± 7

[†] RSD = One relative standard deviation based on three replicate experiments.

dechlorination might have resulted from insufficient contact between substrate and the catalytic surface. In subsequent studies, various solvents were investigated as a support medium for the hydrogenolysis reactions (Table 3.2). The use of methanol was observed to dramatically improve the reactivity of the $Pd^{o}/\gamma\text{-}Al_2O_3$–catalyzed reaction. Within experimental error, decachlorobiphenyl was dechlorinated quantitatively, at ambient temperature, by one hour of reaction in methanol with 5.0% w/w ZV palladium on γ-alumina. Dicyclohexyl was obtained in high yield (95 ± 8 mol %) without apparent loss of material balance. Specifically, no chlorinated intermediates were detected in the hexane extract of the $Pd^{o}/\gamma\text{-}Al_2O_3$ catalyst. Dicyclohexyl was detected initially after 30 min of reaction (Figure 3.1) but non-chlorinated intermediates (biphenyl and phenyl cyclohexane) were also detected at this time.

Virtually quantitative conversion to dicyclohexyl was observed after one h, with a mean mass balance indicating 95 ± 8 mol % conversions in methanol. More highly chlorinated congeners were apparently dechlorinated more rapidly, leading to the transient accumulation of less highly chlorinated intermediates prior to complete dechlorination. The extent of conversion of $C_{12}Cl_{10}$ to dicyclohexyl was determined using 2-bromonapthalene as an internal standard.

Hydrodechlorination was considered to proceed principally in stepwise fashion. In subsequent hydrogenation reactions, biphenyl was converted to phenyl cyclohexane which, in turn, was hydrogenated further to dicyclohexyl. The efficiency of the subsequent hydrogenation (de-aromatization) reactions was influenced by the identity of the supporting solvent. With methanol, dicyclohexyl was formed with high selectivity (as compared to reactions in octan-2-ol or THF that contained both chlorinated and partially de-aromatized intermediates as well as final product (Table 3.2). In methanol, complete hydrogenolysis (hydrodechlorination plus ring hydrogenation) to dicyclohexyl was observed after 60 min of reaction at 65°C (Figure 3.2) and ambient pressure. Post 1 h of reaction in THF, in addition to unreacted substrate (~ 7 mol %), nonachlorobiphenyl (~2 mol %) and heptachlorobiphenyl (~2 mol %) represented the principal partially dechlorinated intermediates whereas dicyclohexyl (~72 mol %) was the major product.

Table: 3.2: Variation in the distribution of products (mol % ± 1 RSD [†]) after 0.5 h of hydrogenation (60°C) of decachlorobiphenyl (100 μg, ~0.2 μmol) in the presence of $Pd^0/\gamma\ Al_2O_3$ (25 mg) with various solvents

Product	Octan-2-ol	THF	Methanol
Dicyclohexyl	83 ± 6	70 ± 9	95 ± 8
Phenyl cyclohaxane	N. D. [‡]	3.5 ± 2	N. D.
Biphenyl	N. D.	5.1 ± 8	N. D.
Monochlorobiphenyl	0.5 ± 11	N. D.	N. D.
Dichlorobiphenyl	N. D.	N. D.	N. D.
Trichlorobiphenyl	N. D.	N. D.	N. D.
Tetrachlorobiphenyl	N. D.	0.3 ± 21	N. D.
Pentachlorobiphenyl	N. D.	0.2 ± 15	N. D.
Hexachlorobiphenyl	N. D.	0.7 ± 9	N. D.
Heptachlorobiphenyl	0.2 ± 13	2.5 ± 4	N. D.
Octachlorobiphenyl	N. D.	0.5 ± 7	N. D.
Nonachlorobiphenyl	0.9 ± 15	1.7 ± 9	N. D.
Decachlorobiphenyl	9.0 ± 5	7.2 ± 3	N. D.
Mass Balance	94 ± 6	92 ± 7	95 ± 8

[†] RSD = One relative standard deviation based on three replicate experiments.

[‡] N. D. = Not detected (less than 0.05 mol %).

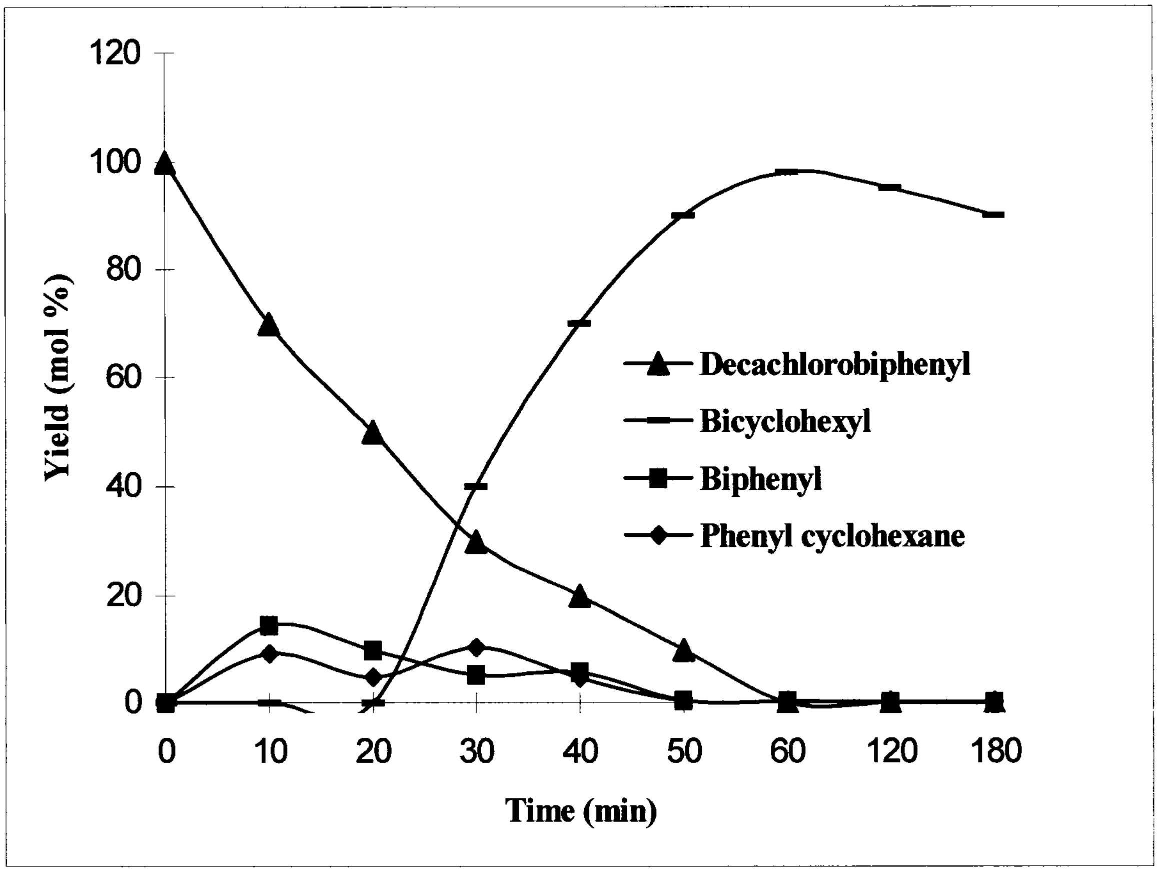

Figure 3.1 **The disappearance of decachlorobiphenyl (0.2 μmol) and the accumulation with time, of non-chlorinated products during hydrogenolysis at 65 °C over $Pd^0/\gamma\text{-}Al_2O_3$ (25 mg).**

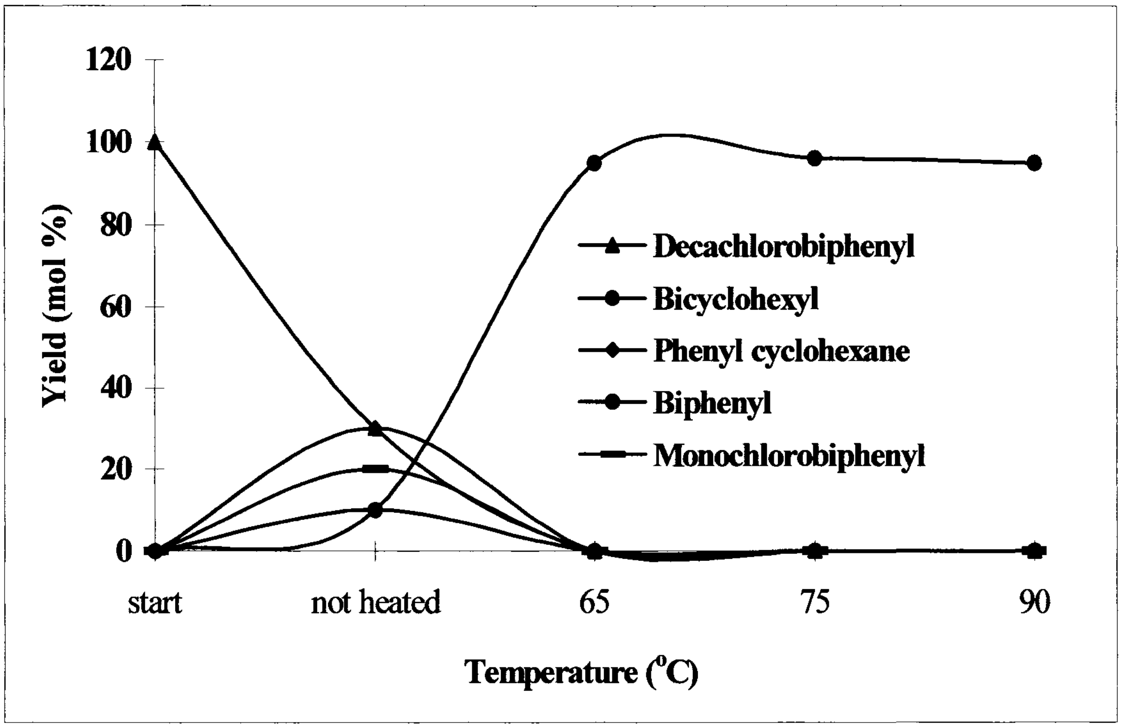

Figure 3.2 Variations in hydrogenolysis efficiency of $C_{12}Cl_{10}$ (0.2 μmol) over Pd^0/γ-Al_2O_3 (25 mg) after 1 h at various temperatures in methanol (1 mL).

Reaction in octan-2-ol shifted the reaction in favor of dicyclohexyl (~ 83 mol %) but more substrate, $C_{12}Cl_{10}$, remained (~8 mol %) and small quantities of nonachlorobiphenyl (~0.7 mol %), heptachlorobiphenyl (~0.2 mol %) were also detected. Other PCB congeners and PCB mixtures were subjected to dechlorination under similar conditions. As summarised in Figure 3.3, hydrodechlorination of low to high molecular weight polychlorinated biphenyl compounds over $Pd^o/\gamma\text{-}Al_2O_3$ were virtually quantitative.

In a further series of trials, biphenyl, phenyl cyclohexane, and dicyclohexyl served as substrate (Table 3.3). Post 0.5h reaction at 65 °C in the presence of $Pd^o/\gamma\text{-}Al_2O_3$ (25 mg), both biphenyl and phenyl cyclohexane were efficiently (93 ± 8 mol %) hydrogenated (de-aromatized) to dicyclohexyl yet no carbon-carbon bond scission was observed. Recoveries of product from hydrogenations of biphenyl or phenyl cyclohexane were not significantly different from recoveries of control dicyclohexyl (~93 mol %) that had been subjected to identical reaction conditions. Extended reaction (Table 3.4) however decreased the recovery of dicyclohexyl appreciably (4h, 77 ± 3 mol %), possibly the result of adsorption of product on the catalyst or by further reaction to form products that were co-eluted with the solvent during gas chromatography.

3.3.2 Soil/Sediments

The results using analytical PCB standards provided considerable encouragement for the application of this technique for particulate matrices. To test the efficiency of the dechlorination of PCB compounds within soil, five certified reference materials were used as well as spiked agricultural soils. Relevant physico-chemical characteristics of the soils and the sediment are summarised in Table 3.5. Concurrently, aliquots of each sample were extracted directly to determine the identities of the congeners that were present.

In contrast to neat PCB solutions, reaction of PCB-laden soil in the presence of ZV palladium on γ-alumina (0.025 g) in methanol resulted in total hydrodechlorination but only partial hydrogenation (de-aromatization) as indicated by the presence of biphenyl, phenyl cyclohexane, and dicyclohexyl. Interestingly, hexane was observed to favor more complete hydrogenolysis. Therefore, all reactions with soil matrix were conducted with hexane as supporting media.

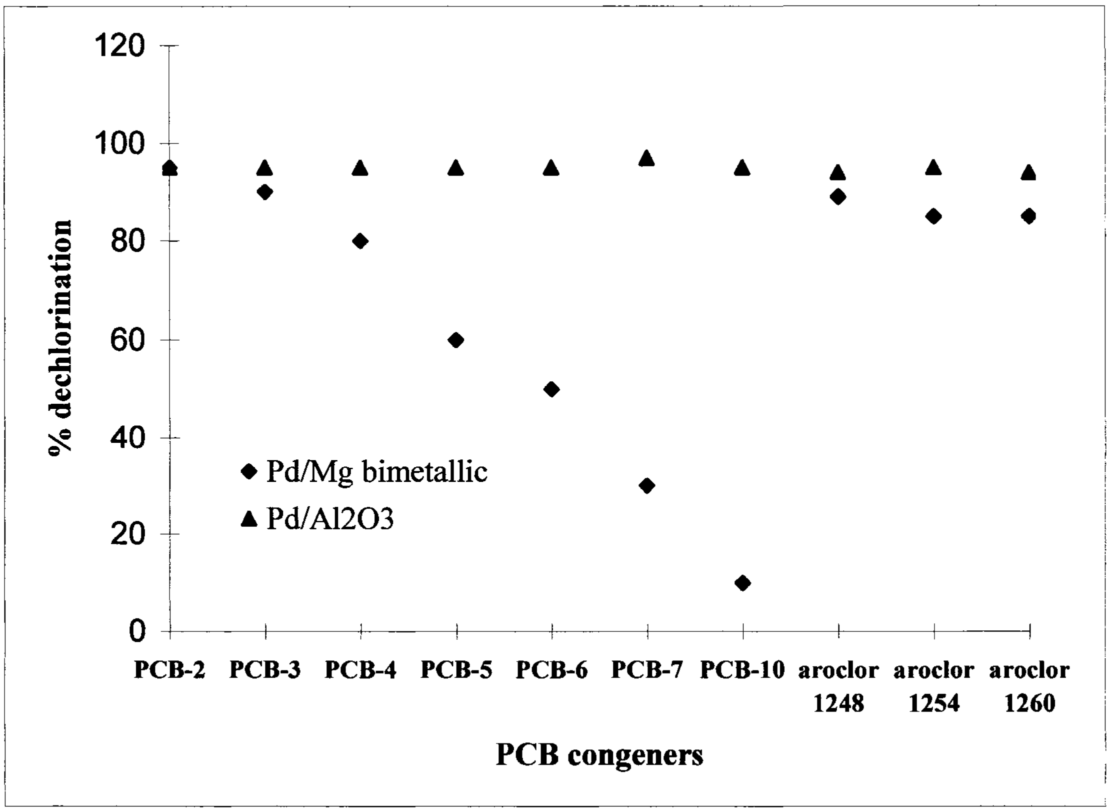

Figure 3.3 **Dechlorination efficiencies for chlorinated biphenyl compounds by reaction over Pd^0/Mg^0 bimetallic mixture or Pd^0 supported on alumina at 65 °C.**

Table 3.3 Variation in product recoveries (mol % ± 1 RSD [†]) after 0.5 h of hydrogenation (65 °C) of biphenyl, phenyl cyclohexane or dicyclohexyl (100 μg, ~0.65μmol) in the presence of $Pd^0/\gamma\ Al_2O_3$ (25 mg)

Product	Biphenyl		Phenylcyclohexane		Dicyclohexyl	
	With catalyst	Without catalyst	With catalyst	Without catalyst	With catalyst	Without catalyst
Biphenyl	N.D. [‡]	99 ± 3	-	-	-	-
Phenyl cyclohexane	N.D.	N.D.	N.D.	99 ± 7	-	-
Dicyclohexyl	91 ± 7	N. D.	95 ± 8	N.D.	92 ± 4	94 ± 8
Mass balance	91 ± 7	99 ± 3	95 ± 8	99 ± 7	92 ± 4	94 ± 8

[†] RSD = One relative standard deviation based on three replicate experiments.

[‡] N. D. = Not detected (less than 0.05 mol %).

Table 3.4 Variation in dicyclohexyl recovery (mol % ± RSD [†]) after 0.5, 2 or 4h of hydrogenation (65 °C) in the presence of 25 mg Pd/γ - Al_2O_3 (5%, w/w) in methanol (1 mL)

Hours of Reaction	Dicyclohexyl Recovery (mol %)
0.5	93 ± 2
2.0	89 ± 5
4.0	77 ± 3

[†] RSD = One relative standard deviation based on three replicate experiments.

Table 3.5 Physico-chemical properties of soil/sediment samples

Sample	Source	pH	PCB concentration (ppm)	Organic Matter (%)	Particle size (mesh)
SRM 1939a	River sediment		27.2	12	~ 325
BCR 481	Industrial soil		472	12.5	~170
BCR 536	Harbour sediment		0.34	15	~120
CRM 915	Industrial soil	7.5	1.4	7	~ 60
Soil 1	Agriculture soil	6.2	NA	5.8	~ 50
Soil 2	Agriculture soil	5.9	NA	2.8	~ 50
Soil 3	Landfill site	7.4	92.4	4.8	~ 50

Initial investigations of various contaminated soil/sediment samples demonstrated that the reaction was dependent on the concentration of contaminants. Among historically contaminated samples, catalytic conversion to dicyclohexyl reached ~99 mol % for the less highly PCB-laden BCR536 (0.344 mg Kg^{-1}) and CRM915 (1.44 mg Kg^{-1}) reference materials.

With similar reaction conditions, the soil sample (SRM 1939a, Soil3) that was burdened with medium PCB concentration (27.2 mg Kg^{-1}) was characterized by total hydrodechlorination but only partial hydrogenation as indicated by the presence of biphenyl, phenyl cyclohexyl as well as dicyclohexyl within the crude product mixture. Finally, the product mixture from reaction with the more highly contaminated sample (BCR 481) contained tetrachlorobiphenyl indicating only partial hydrodechlorination (Figure 3.3). There was no appreciable improvement in the combined efficiencies of reaction with extended reaction time (1.5 - 2 h) or/and higher temperature (70 - 80 °C).

In subsequent experiments, increased quantities of catalyst were evaluated to optimize hydrogenolysis reactions. The conversion of PCB mixture to dicyclohexyl within the soil matrix was increased when the quantity of catalyst was apparently insufficient for quantitative conversion within the soil/sediment if PCB burden was in excess of 30 mg Kg^{-1} (data not shown). This was true especially for historically PCB contaminated soil/sediment sample because for soil 2 that had been purposely spiked with heptachlorobiphenyl at 32.5 mg Kg^{-1}, 25 mg of $Pd^o/\gamma\text{-}Al_2O_3$ was sufficient to mediate virtually complete hydrogenolysis to dicyclohexyl (~ 95 ± 3 mol %).

The rate of PCB hydrodechlorination within the soil/sediment matrix can be influenced by several factors including the distribution and concentration of PCB congeners, the presence of electron acceptors, organic matter, and elevated levels of heavy metals. Bulk organic content frequently has been reported to have a major factor causing sorption of PCBs to sediments and soils. The hydrodechlorination efficiency of palladium on alumina apparently was independent of the factors above except for PCB content. Soil/sediment samples with a relatively higher organic content (CRMs and SRM) were hydrogenolysed with same efficiency as soils with a lower organic content (soil 1, 2 and soil 3). Furthermore, co-extractive from soil had no apparent effect on the efficiency

Table 3.6 Dicyclohexyl recoveries (mol % + 1 RSD[†]) in soil/sediments as determined by direct conversion

Sample	Theoretical dicyclohexyl yield (mol %)	Experimental dicyclohexyl yield (mol % ± RSD)	% Recovery
Soil 2	---	N.D. [‡]	---
Soil 2 (spiked)	13.5	12.8 ± 3	95
Soil 3	42.3	48.9 ± 2	115
SRM 1939a	16.7	15.4 ± 7	92
CRM 915	0.65	0.61 ± 2	94
BCR 536	0.174	0.186 ± 3	106
BCR 481	212	207 ± 3	97

[†] RSD = One relative standard deviation based on three replicate experiments.

[‡] N. D. = Not detected (less than 0.05 mol %).

of dechlorination. As summarized in Table 3.6, the results demonstrated that the technique provides a relatively rapid method for PCB quantitation by the conversion of chlorinated biphenyls to dicyclohexyl.

3.4 Conclusion

In summary, direct derivatisation within the sample matrix was complete in the presence of alumina supported ZV palladium under mild condition in 1 h. Hydrodehalogenation was considered to occur rapidly for the soil/sediment samples and apparently preceded hydrogenation. GC/MS monitoring of extract indicated >99% dechlorination for all soil/sediment reference materials (0.34 - 575 ppm) - no partially dechlorinated intermediates were detected. In the presence of sufficient $Pd^{0}/\gamma\text{-}Al_2O_3$ (0.050 g), dicyclohexyl was recovered (~ 95%) as a sole reaction product in all soil/sediment samples. The principal advantages of this technique include convenience and simplicity and the principal shortcomings are (*i.*) that losses of product dicyclohexyl can become appreciable with extended reaction and (*ii.*) polybrominated biphenyl compounds are anticipated to behave in analogous fashion under these reaction conditions so that they will also contribute to the total estimate.

PREFACE TO CHAPTER 4

In chapter 3, the hydogenelysis reaction of PCBs with palladium over alumina was investigated for efficient hydrodechlorination of PCB mixtures. The reaction conditions were optimized for quantitative analysis and subsequent detoxification of PCB contents within soil. Direct derivatization within the soil matrix provided a relatively rapid method for PCB quantitation by conversion of chlorinated biphenyls to dicyclohexyl under mild conditions.

Despite the progress, techniques for soil remediation burdened with mixed contaminants are still in their infancy. As new and improves processes are required to meet the challenge, a soil washing procedure for the simultaneous mobilization of PCBs and heavy metals from field contaminated soil with regeneration of mobilizing aids was proposed.

In the following chapter, both nonionic and anionic surfactants in combination with chelating agents are evaluated for their efficiency at removing PCBs and heavy metals. The experiments examine the PCBs extraction efficiency with surfactants in the presence/absence of EDTA. Post equilibration, the surfactant phase is washed with hexane to recover PCBs that are subsequently dechlorinated with Pd^0/Al_2O_3. Finally, the possibility of surfactant recycle is investigated. For three successive washes, the efficiency of PCB removal with fresh reagent is compared with the efficiency of PCB removal observed with recycled reagent. Observations related to PCB mobilization, surfactants regeneration, and recycle are discussed in this chapter.

This paper has been submitted for publication in *J. Environ. Qual.* 2005. Authors: Ehsan, S., S. O. Prasher, and W. D. Marshall.

CHAPTER 4

SIMULTANEOUS MOBILIZATION OF PCB AND HEAVY METALS FROM MIXED CONTAMINATED SOIL USING SURFACTANTS AND CHELATING AGENTS: POLYCHLORINATED BIPHENYL (PCB) COMPOUNDS

4.1 Introduction

Superfund sites are burdened with a range of contaminants inherited from past industrial or commercial activities. A number of these sites have mixed contaminants that can include volatile organic compounds (VOCs), metals or semivolatile organic compounds (SVOCs). Most of these sites are abandoned and are referred as brownfields. There are some 30,000 contaminated Brownfield sites in Canada (NRTEE, 2003) and 2940,000 such sites in the United States (U.S. EPA, 2004). Most sites require remediation for more than one of these contaminant groups (U. S. EPA, 2004). Whereas continued research has focused on the remediation of either organic contaminants or heavy metals, there have been fewer published studies (Dunn et al, 1989; Semer and Reddy, 1996; Bresseau et al, 1997; Huang et al, 1997; Tung et al, 2002; Baek and Yang, 2004; Shin et al, 2004; Iturbe et al, 2004) of the simultaneous removal of both organic and inorganic pollutants from soil. Soil washing is a treatment process that can be used for remediating both organic and inorganic chemical constituents from contaminated soils, sludges, and sediments (U.S. EPA, 1997c; FRTR, 2002). This process involves high energy contact between the contaminated soil and an aqueous washing solution. Soil washing can be a physical and/or chemical process resulting in the separation, segregation, and volume reduction of hazardous materials and/or the chemical transformation of contaminants to non-hazardous, unregulated substances.

There are several advantages to soil washing as a remediation technique. First, the actual process takes place in a closed system which permits control of the ambient environmental conditions. Secondly, the process can result in a significant volume reduction of the contaminated mass. Also, soil washing has extensive applications for varied waste groups and the hazardous waste can remain on site due to mobile technology. A well designed treatment can represent a permanent solution. The time to complete the cleanup is relatively short and the cost of soil washing is relatively small compared to other multicontaminant technologies and appreciably less than the cost of land filling. Finally, regulatory and public acceptance is generally high.

Surfactants are particularly attractive for such applications as they potentially have low toxicity and favorable biodegradability in the environment relative to organic-solvent based systems. Yet, guidance in selecting surfactants for *ex situ* soil washing remains somewhat fragmentary (Deshpande et al, 1999).

Soil washing also has disadvantages as a remediation procedure. When the soil washing treatment is only a physical process, there is little reduction in the toxicity of the contaminants. If chemical processes are involved, potentially hazardous chemicals that are used in the remediation process may then be difficult to remove from the treated soil. The effectiveness of soil washing is also limited by the following factors: (1) complex waste mixtures can make formulating the washing fluid difficult, (2) high humic content of the soil may require pretreatment, (3) the aqueous stream may require treatment post equilibration (4) Additional treatment steps may be required to address hazardous levels of washing solvent remaining in the treated soil and (5) high fine-grained clay content can compromise the efficiency of removal of the toxicants.

The success of soil washing with surfactants can be attributed to the capacity of these compounds, at concentrations above the critical micellar concentration (CMC), to appreciably enhance the aqueous solubility of lipophilic organic compounds. Surfactant-enhanced soil washing can result from three main detergency mechanisms that are active when a deposit is mobilized from the solid surface: solubilization, snap-off, and roll-up. In the solubilization mechanism, the hydrophobic contaminant is dissolved in the hydrophobic core of micelles that are formed from the self-assembly of surfactant molecules in concentrations above the CMC. The snap-off mechanism is operative when the mechanical agitation is stronger than the work of cohesion of the droplet, which leads to a break up of the droplet, leaving behind some oil residue. In the roll-up mechanism, the work of adhesion of the droplet to the surface is zero or negative that makes it easier for the mechanical forces to completely detach the oil droplet from the solid surface (Edwards et al, 1991; Chu and Chan, 2003). Several researchers (Abdul and Gibson, 1991, Edwards et al, 1994) have evaluated surfactants for their ability to act as soil-washing agents and as facilitators of subsurface remediation of hydrocarbon spills. The extent to which surfactants influence the distribution of hydrophobic organic compounds (HOCs) depends critically on the HOC's sorption to the solid phases (Chiou et al, 1998). Surfactant washing can be inefficient for soils that contain more than 20-30 % silt/clay (Riser-Roberts, 1998; Mulligan et al, 2001) or appreciable quantities of organic matter.

The magnitude of solubilization of HOCs by surfactant micelles is observed in the order of non-ionic, cationic, and anionic for similar non-polar chain lengths (Abu-Zreig, 1999). It has been suggested (Abdul et al, 1990) that non-ionic surfactants are better choices than anionic surfactants in washing performance to decrease the portion of HOCs sorbed to soil particles. It has also been suggested (Rosen, 1989) that surfactant effectiveness in washing out hydrophobic contaminants does not depend strongly on ionic characteristics of the surfactant, because the surfactants that increased contaminant removal from soil were characterized by identical properties such as low surface tension and soil dispersion, good detergency and solubilization. The effectiveness of the surfactants in removing contaminants from soil is also dependent on the hydrophilic/hydrophobic structure [hydrophile lipophile balance (HLB)] of the surfactant molecule and the CMC. Yet mixtures of two different surfactants often show a "synergistic" interaction (Lee et al, 2004; Zhu and Feng, 2003). This has been attributed to a reduction in the CMC for the surfactant mixture and an increase in the partition coefficient between the mixed surfactant micelles and the aqueous phase. The addition of a water miscible organic solvent (often triethylamine, acetone, or n-butylalcohol) to the washing solution has also been reported to increase the mobilization of hydrophobic contaminants (Bettahar et al, 1999; Chu and Kwan, 2003).

Proposals for the restoration of soils that have been polluted with polychlorinated biphenyl (PCB) compounds have included incineration, solidification/vitrification (Erickson, 1997), phytoremediation (Dzantor et al, 2000), bioremediation (Alder et al, 1993), and electrokinetic (Kim et al, 2000) approaches. These strategies, however, have been applied as treatments in the field only infrequently because of costs, environmental constraints and efficacy. Other more efficient methods for treating PCBs contaminated soils continue to be proposed, optimized, and evaluated (Abdul et al, 1992).

Soil remediation with a combination of techniques can improve the efficiency of exiting methods. The combination of ultrasonication with existing remediation techniques has been explored for contaminated soils (Feng et al, 2001; Hanna et al. 2004). Soil remediation using surfactant/chelant washing aided by ultrasound is a novel approach to improve contaminants extraction. A further processing stage that is able to decontaminate the soil extract can help to increase its remediation value (Sabatini et al, 1998) and often combinations of different techniques must be used during the processes (Haegel et al, 2000). An attractive combination has involved surfactant recovery and re-uses (Zhou and Rhue, 2000).

The objective of the current study was to combine a series of unit operations. Toxicant mobilization by soil washing with an aqueous mixture containing surfactant and a sparing quantity of EDTA was to be followed by back-extraction to remove PCB compounds, treatment with zero-valent magnesium (to precipitate heavy metals and liberate EDTA) and finally recycle of the cleaned extract. The precipitated heavy metal oxyhydroxides were to be recovered by filtration and the PCB laden organic back-extract was to be detoxified by hydrodechlorination. The recycle process was to be repeated at least twice. The current Chapter evaluates to mobilization of PCB compounds from a field contaminated soil. Chapter 5 considers the extraction efficiency of heavy metals that were extracted concurrently.

4.2 Materials and Methods

4.2.1 Chemicals

Test surfactants, nonionic (Tween 20, Tween 40, Tween 85, Tween 80, Brij 35, Brij 98 or Triton 405) or anionic formulations [Triton X-301, Triton XQS 20 or sodium dodecylsulfate (SDS)], were purchased from Sigma-Aldrich, Oakville, ON, Canada. Cobaltous nitrate [$Co(NO_3)_2 \cdot 6H_2O$], ammonium thiocynate (NH_4SCN), methylene blue, disodium ethylenediaminetetraacetate (EDTA), and potassium dihydrogenphosphate (anhydrous powder), were obtained from Fisher Chemical, Fair Lawn, NJ, USA. HPLC grade ethanol (C_2H_5OH), chloroform ($CHCl_3$), and hexane (C_6H_{14}), were obtained from Fisher Scientific, Ottawa, ON, Canada. All chemicals, solvents, and reagents were of ACS Reagent grade or better and were used as received.

4.2.2 Soil Sample Pretreatment

The soil was obtained from an industrial landfill site on the island of Montréal, Québec, Canada. The soil was classified as a sandy loam (USDA Texture triangle) and had been historically contaminated with Aroclors 1242, 1248, 1254, and 1260 along with Cd, Cr, Cu, Pb, Ni, Mn, and Zn. The soil was air dried, passed through 2 mm sieve (10 mesh), mixed thoroughly then further air dried and the fraction passing through a 500 μm sieve was stored in sealed plastic bag to await further testing.

The initial soil PCBs concentration (92.4 mg kg^{-1}) was estimated by gas chromatography-mass spectrometry (GC-MS) (Saturn 2000, Varian, Walnut Creek, CA, USA) following hydrodehalogenation with $Pd^{o}/\gamma\text{-}Al_2O_3$ (Ehsan et al, 2003).

4.2.3 Mixed Contaminant Extraction/Mobilization

In a typical trial, soil (3g) was equilibrated with 20 mL EDTA solution (0.1M) or EDTA solution containing 30 mL L^{-1} surfactant emulsion in 50 mL centrifuge tubes immersed in an ice bath. Equilibrations were achieved by sonicating the soil suspension for 10 min with an ultrasonic homogenizer (XL 2020 Sonic dismembrator, Misonix Inc. NY). An extended horn of 25 cm L x 1.2 cm W, tuned at 20 kHz frequency, delivered ultrasonic energy (240 W) in a pulsed mode with a fixed vibration amplitude setting of 6. The equilibration consisted of pulsed surges of power delivered for 3 s followed by a 2 s cooling phase. Post sonication, the suspension was centrifuged at 4000 rpm. A portion of the supernatant fraction was retained for determination of the total PCB or heavy metal content and the remainder was treated to remove solubilized contaminants.

4.2.4 PCB Removal from Soil Extracts

PCBs in the supernatant fraction were back-extracted three times with hexane (3 mL) to partition PCBs from the soil extract. The cumulative hexane fraction was centrifuged (4000 rpm, to remove aqueous surfactant) then diluted with 1 mL ethanol to disrupt the hexane-surfactant emulsion induced by agitation. PCBs that had been extracted with hexane were determined by GC-MS following hydrodechlorination in the presence of H_2 purged Pd^{o}/γ Al_2O_3 (Ehsan et al, 2003).

4.2.4 Heavy Metal Removal from Soil Extracts

Post PCB removal, the soil extracts were treated for metal removal following methods described in chapter 5.

4.2.5 Recycle of Mobilizing Reagents

Post PCB and heavy metal removal, the pH of the cleaned mobilizing reagent emulsion was adjusted to 6 and then re-equilibrated with the particulate fraction to mobilize more PCBs and metals. Soil particulates were equilibrated again by sonication with 20 mL of cleaned mobilizing reagent. The resulting aqueous supernatant fraction was treated for PCBs and heavy metal removal as described above. After 3 washing cycles, the soil particulate fraction was oven dried and analyzed for residual PCBs and heavy metal contents. A portion of the soil residue (0.2 g) was further equilibrated with deionized water (0.5 mL) for 1 h and the supernatant fraction was assayed for surfactant and EDTA contents as described below.

4.2.6 Surfactant Analysis

Surfactant concentrations were determined spectrophotometrically (DR 4000; Hatch Co., Loveland, CO, USA. single beam spectrophotometer). The standard Analysis Methods (APAH) 5540 C and 5540 D (APAH/AWWA/WEF, 1995) were followed (with minor modifications) to determine the concentration of anionic or nonionic surfactants respectively in both solid and supernatant fractions.

For nonionic surfactant, $Co(SCN)_2$ (3 mL, 0.2 M) was added to a small test tube {inner diameter 1.0 cm (O.D. 1.2 cm) x 10.0 cm} prior to the addition of nonionic micelle suspension {10, 30, 50, 80, or 100 μL aliquots of 30 mL L^{-1} concentration)} followed by 5 mL $CHCl_3$ to obtain calibration standards that were permitted to stand for 2h prior to 3 to 5 vigorous agitations with a Vortex mixer. After phase separation by centrifugation, the absorbance was recorded at 620 nm *vs*. a blank of $CHCl_3$.

For anionic surfactants, a mixture of methylene blue (0.1 mL, 0.25 mg L^{-1}) and phosphate buffer (0.4 mL, pH 7) was used as complexing reagent (George and White, 1999). $CHCl_3$ (6 mL) was added followed by surfactant solution and treated as described above. The absorbance at 655 nm was recorded vs. a blank of $CHCl_3$.

4.2.7 EDTA Analysis

EDTA concentrations were determined spectrophotometrically with a Hatch DR4000 single beam spectrophotometer following methods described in chapter 5.

4.3 Results and Discussion

4.3.1 PCB Mobilization

The sandy loam soil was obtained from a landfill site that had been contaminated historically with both heavy metals and persistent organic pollutants. The soil, sieved to pass a 35 mesh screen, was used for all experiments; relevant characteristics of the dried and sieved sample are presented in Table 4.1.

Ten surfactants that had been selected for this study included 6 nonionic and 4 anionic surfactants. Amphoteric and cationic surfactants were avoided because of their stronger tendencies to sorb to soil minerals (Mulligan et al, 2001). The 10 surfactants included at least one from each of the four common groups of commercial surfactants: (1) ethoxylated alcohols (nonionic), (2) ethoxylated alkylphenol (nonionic), (3) sulfate (anionic), and sulfonate (anionic) functional groups. The test surfactants, along with their relevant properties are summarized in Table 4.2.

Preliminary experiments consisted of identifying an optimal sonication time for efficient PCB mobilization from the test soil. Brij 98 and Triton XQS-20 were selected to define a suitable extraction time. The PCB content in the surfactant supernatant fraction, for equilibrations conducted for 3, 5, 10 or 30 min, (Table 4.3) were determined by conversion of the various PCB congeners to a common product, bicyclohexyl (Ehsan et al, 2003). For 30 min sonication with Brij 98, the quantity of mobilized PCBs (61%) was apparently no different from that for 10 min (60%) which in turn was slightly increased relative to 5 min (58%) or 3 min (58%) of sonication. Time trial with Triton XQS-20 followed the similar trend. The percent PCBs mobilized by 30 min of sonication (47%) were not appreciably different from that of 10 min (46%). Subsequent experiments were conducted with 10 min of sonication. Soil washings were performed with a surfactant

Table 4.1 Soil characteristics

Sample	Sand (%)	Clay (%)	Silt (%)	Organic C	pH	CEC (cmol kg^{-1})
Soil	78	12	10	7.4	7.38	9.8
Sieved Soil	52	16	33	12.5	7.50	9.5

Table 4.2 Chemical and physical characteristics of surfactants selected for the PCB extraction study

Trade name	Chemical structure	HLB [†]	Viscosity/cP [‡]
Anionic			
SDS	sodium dodecyl sulphate	51.4	0.2342
Triton X-301	sodium octylphenoxy polyethoxyethyl sulphate	N.A. [§]	0.3272
Triton XQS-20	phosphate ester, acid form	N.A.	0.2792
Nonionic			
Brij 35	POE [¶] (10) lauryl ether	16.9	0.9177
Brij 98	POE (20) oleyl ether	15.3	0.2433
Triton X-405	POE (40)-(aromatic ring)$_6$-(CH)$_8$	17.9	1.0410
Tween 20	POE (20) sorbitan monolaurate	16.7	0.2490
Tween 40	POE (20) sorbitan monopalmitate	15.6	0.2113
Tween 80	POE (20) sorbitan monoleate	15.0	0.2942
Tween 85	POE (20) sorbitan trioleate	11.0	0.1603

[†] HLB = Hydrophile lipophile balance.

[‡] Viscosity/ cP = Viscosity of surfactant solutions (30 mL L^{-1}) at 600 rpm and 20 °C.

[§] NA = Not available from manufacturer.

[¶] POE = Polyoxyethylene.

Table 4.3 Optimization of the sonication time with EDTA plus Brij 98 or EDTA plus Triton XQS-20

Cumulative sonication time (min)	PCB mobilization (% ± 1 RSD [†])	
	EDTA + Brij 98	EDTA + Triton XQS20
3	59 ± 4	45 ± 5
5	58 ± 3	46 ± 10
10	60 ± 6	46 ± 3
30	61 ± 3	47 ± 8

[†] RSD = One relative standard deviation based on three replicate trials.

concentration of 30 mL L^{-1} which had been reported to be comparable to 50 mL L^{-1} suspension and more efficient than washing PCBs from soil with a 10 mL L^{-1} suspension (Wu and Marshall, 2001). The observed extraction efficiencies are summarized in Table 4.4. At 30 mL L^{-1} concentration, a single soil-surfactant sonication mobilized appreciable quantities of PCB compounds, 63% with Brij 98, 60% with Triton X-301, 44% with Triton XQS-20, and 36% with the Tween 85 formulation.

Subsequent experiments were performed with selected nonionic (Brij 98, Tween 85) or anionic (Triton X-301, Triton XQS-20) surfactants. The selected surfactants were further assessed in terms of their tendency to sorbs to the soil, to foam during equilibration, or to separate from the aqueous carrier. Additionally, compatibility with disodium ethylenediaminetetraacetate (EDTA) and losses during the reagent regeneration sequence were assessed. After a single equilibration, it was observed that three of the surfactants (Brij 98, Triton X-301, or Triton XQS-20) did not induce visible changes in the soil but the Tween 85 formulation was observed to leave an oily residue on the soil particles that made soil drying difficult. Subsequent experiments were conducted with Brij 98, Triton X-301, or Triton XQS-20.

In further experiments, the extraction efficiency of surfactants in admixture with disodium ethylenediaminetetraacetate (EDTA) was evaluated for PCB mobilization from soil. Three surfactants were evaluated in the presence/absence of EDTA (Table 4.5). In a single equilibration/sonication with Brij 98 plus EDTA, the percent PCB mobilized (62%) was not different from the trial performed in the absence of EDTA (60%). Similar behavior was observed for Triton X-301 (58% *vs.* 60%) but extraction efficiency was improved somewhat relative to recoveries from the Triton XQS-20 formulation (43% *vs.* 41%). The results demonstrated that the complexation/solubilization of PCBs was not influenced by the presence of EDTA, in combination with any of the test surfactants. In a parallel series of trials, soil was shaken for 18 h with same combination of reagents (Table 4.5). The quantity of PCBs, mobilized with Brij 98 was decreased by 30% if the soil was equilibrated by reciprocal shaking for 18 h. Results for Triton X-301 (38%) and Triton XQS-20 (17%) also demonstrated that 18 h of continuous agitation did not mobilize as much PCB as the sonication process. It is considered that relative to

Table 4.4 PCB extraction efficiencies (percent) in the presence of selected surfactants

Surfactant	Bicyclohexyl yield (mg kg^{-1} ± 1 RSD [†])	PCBs Mobilized from Soil (%)
Brij 98	29 ± 7	63
Triton X-301	28 ± 10	60
Triton XQS-20	20 ± 5	44
Tween 85	17 ± 14	36
SDS	15 ± 5	33
Brij 35	15 ± 9	32
Tween 80	14 ± 12	30
Triton X-405	13 ± 15	28
Tween 40	13 ± 8	28
Tween 20	10 ± 9	23

[†] RSD = One relative standard deviation based on three replicate trials.

Table 4.5 Surfactant extraction efficiencies for PCB mobilization (percent ± 1 SD [†]) from the soil with shaking or sonication in the presence/absence of EDTA

Surfactant	Shaken for 18 h with EDTA	Sonication with EDTA	Sonication without EDTA
Brij 98	32 ± 4	62 ± 7	60 ± 7
Triton X-301	38 ± 7	58 ± 10	60 ± 11
Triton XQS-20	17 ± 5	43 ± 5	41 ± 9

[†] SD = One standard deviation based on three replicate trials.

reciprocal shaking, the increased power that was transferred to the soil suspension during sonication resulted in the increased PCBs mobilization. The attendant heating of the suspension was minimized by conducting the sonication in an ice bath. Subsequent recovery of the supernatant fraction was achieved by centrifugation.

Subsequent studies identified conditions that optimized the cleaning and recycle of the surfactant suspension. All surfactant recycling trials were carried out in the presence of EDTA post 10 min of sonication. The percentages of the PCB burden washed from the soil, together with the percentage of residual soil-bound PCB post 3 wash cycles are presented in Table 4.6. For these trials the mass balance was incomplete and accounted for some 90% of the original soil burden.

The first sonication proved to be the most efficient at mobilizing PCBs dislodging more than 60% of initial burden. However, the 2nd and 3rd equilibrations with recycled surfactant were less efficient dislodging a further 18% and 4% of remaining soil bound residue (Table 4.7). The quantity of extracted PCBs and efficiency of the washing process was observed to decrease with each successive cycle with recycled surfactant. Since all three surfactant formulations displayed a similar PCB mobilization efficiency with increases in the number of cycles, it is tempting to infer that this might be taken as evidence for a more tightly bound PCB fraction within this soil but there is simply not sufficient data to make such a claim.

The cumulative extraction efficiency for three successive washes with each of the test surfactants was also determined using fresh reagent for each cycle (Table 4.8). Only a minor difference for PCBs mobilization was observed between fresh (40.1 mg kg^{-1}) or recycled (38.2 mg kg^{-1}) surfactant. In toto, extraction with fresh reagent resulted in 87% PCB mobilization and 83% of PCBs were mobilized with recycled Brij 98 surfactant.

An aqueous suspension (30 mL L^{-1}) of Triton X-301 was equally efficient (60% *vs*. 58%) for the 1st soil equilibrium. However, the 2nd and 3rd washes with recovered Triton X-301 resulted in appreciably less PCB mobilization in comparison to the Brij formulation (Table 4.7) or to a fresh charge of the same reagent (Table 4.8).

The acidity of the Triton XQS-20 formulation required pH adjustment prior to combination with EDTA. The pH of the Triton XQS-20 formulation was increased to 6.5 prior to mixing with EDTA. Although, the initial soil equilibration with Triton XQS-20

Table 4.6 Cumulative bicyclohexyl yield (mg kg^{-1} ± 1 RSD [†]) from three successive soil washings with EDTA (20 mL) or surfactant (30 mL L^{-1}) plus EDTA

	Cumulative Recovery in Aqueous Fraction (mg kg^{-1})	Residual soil PCB pre/post extraction (mg kg^{-1})	Sum of PCBs in soil + aqueous extract (mg kg^{-1})
Original Soil		92.4 ± 12	92.4
EDTA (2 mmoles)	N.D.	76 ± 10	76
Brij 98 + EDTA	83 ± 9	9 ± 5	92
Triton X-301 + EDTA	72 ± 11	17 ± 9	89
Triton QXS-20 + EDTA	68 ± 5	22 ± 5	90

[†] RSD = One relative standard deviation based on three replicate trials.

Table 4.7 Mean cumulative mobilization of PCBs (mg kg^{-1} ± 1 RSD [†]) for three successive washes of the soil (3g) with the same charge of EDTA, surfactant (30 mL L^{-1}) combination

Surfactant	1st extraction (N = 15)	2nd extraction (N = 6)	3rd extraction (N = 4)	Sum (mg kg^{-1})	Cumulative PCBs Mobilized (%)
Brij 98	27.9 ± 2 (60.5 %)	8.3 ± 7 (18.0 %)	2.0 ± 9 (4.3 %)	38.2	82.8
Triton X-301	26.6 ± 3 (57.7%)	5.5 ± 10 (11.9 %)	0.8 ± 11 (1.7 %)	32.9	71.3
Triton XQS-20	23.9 ± 7 (51.8%)	6.3 ± 14 (13.7%)	1.4 ± 12 (3.0 %)	31.6	68.5

[†] RSD = One relative standard deviation

was reasonably efficient (51% soil PCB mobilization), the efficiencies of subsequent equilibrations were decreased appreciably relative to the same operations with fresh reagent (Table 4.8). The reduced mobilization efficiencies of anionic surfactants were the result, in part, of surfactant losses during the heavy metal precipitation sequence. It was necessary to decompose heavy metal (HM-EDTA) complexes in order to liberate the EDTA complexing reagent prior to the recycle sequence. Arbitrarily, the HM-EDTA complexes were disrupted by precipitating the HMs as insoluble oxy-hydroxides. Reaction of water with zero-valent magnesium (Mg^0) proved to be an efficient source of the precipitating reagent.

$$Mg^0 + 2H_2O === Mg^{2+} + H_2 + 2OH^-$$

Subsequently, the HM hydroxides were removed from the aqueous suspension by filtration.

4.3.2 Surfactant Fate post Washing and Mg^0 Treatment

Whereas, estimates of the nonionic surfactant content were based upon formation of tetrathiocyanatocobaltate (II) ion, anionic surfactant estimates relied on the formation of an ion pair with methylene blue (MBAS method). Because of the sensitivity of MBAS method, addition of chloroform was recommended before the addition of surfactant to assess any contamination due to reagents. The concentration of surfactant was monitored after each stage of the remediation protocol to determine the magnitude of any surfactant losses. The surfactant recoveries after each experimental stage calculated on the basis of starting concentration of surfactant (30 mL L^{-1}) are summarized in Table 4.9. As evidenced by the results, the type of surfactant appreciably influenced the recovery of surfactant particularly after Mg^0 treatment.

For Brij 98, a cumulative loss of 11% was observed after three successive washes of the soil. In contrast, the loss of ionic surfactant was appreciably greater. Cumulative losses of surfactant amounted to 42% for the Triton QSX-20 formulation and to 75% for the Triton X-301 formulation. The losses were most severe during treatments of aqueous phase with Mg^0/Pd^0 (to precipitate heavy metals). The loss of 37% of the Triton X-301 formulation occurred during the first treatment with bimetallic mixture and subsequent filtration and a loss of a further 25% had occurred after the second treatment/filtration

Table 4.8 Mean cumulative PCB mobilization (mg kg^{-1} ± 1 RSD [†]) for three successive washes of the soil (3g) with EDTA + surfactant (30 mL L^{-1}) using fresh reagents each time

Surfactant	1st extraction (N = 3)	2nd extraction (N = 3)	3rd extraction (N = 3)	Total	Cumulative PCBs Mobilized (%)
Brij 98	27.2 ± 5 (59.0 %)	9.1 ± 2 (19.7 %)	3.8 ± 6 (8.2 %)	40.1	86.9
Triton X-301	26.9 ± 8 (58.4%)	7.8 ± 9 (16.9 %)	2.8 ± 14 (6.0 %)	37.5	81.3
Triton XQS-20	23.5 ± 2 (51.0%)	8.5 ± 6 (18.4 %)	2.9 ± 5 (6.3 %)	34.9	75.7

[†] RSD = One relative standard deviation.

Table 4.9 Mean cumulative surfactant recovery (percent ± 1 SD [†]) post each experimental stage for three successive washes of the soil (3g) with the same charge of EDTA + surfactant (30 mL L^{-1})

Surfactant Recovery (% ± 1 SD [†])			
post	**EDTA + Brij 98**	**EDTA + Triton X301**	**EDTA + Triton QSX-20**
1^{ST} Equilibration	98 ± 1	96 ± 2	97 ± 7
Hexane Extraction	96 ± 2	90 ± 6	94 ± 5
Pd^0/Mg^0 treatment	97 ± 1	53 ± 1	73 ± 2
2^{ND} Equilibration	93 ± 4	48 ± 1	70 ± 4
2^{ND} Pd^0/Mg^0 treatment	92 ± 1	23 ± 0.02	61 ± 7
3^{RD} Equilibration	89 ± 2	25 ± 1	58 ± 4

[†] SD = One standard deviation based on three replicate trials.

sequence. These losses were not entirely unexpected. It had been reported that certain cations, especially Ca^{2+} can cause the precipitation of certain anionic surfactants (Jafvert and Heath, 1991). The addition of $Ca(OH)_2$ during metal removal was detrimental to the recovery of anionic surfactant. Surfactant losses during the heavy metal precipitation stage resulted in decreased PCBs mobilization efficiency observed with recycled surfactant.

4.4 Conclusions

In total, the results have demonstrated that some 83% of the total soil PCB burden can be extracted with three sequential washes with the same charge of non-ionic surfactant. This was made possible by cleaning the aqueous soil extract by back-extraction with hexane after each sonication/equilibration. If heavy metals were to be mobilized concurrently, then the heavy metal complexes had to be disrupted to liberate the complexing reagent (EDTA). The hexane back-extract could have been detoxified by catalytic hydrodechlorination over palladium sorbed to alumina. In this technique, the hexane is merged with a H_2/supercritical carbon dioxide mixture and transported to a heated reactor (Yuan et al, 2003). The reactor effluent containing product bicyclohexyl is judged to be toxicologically innocuous relative to the influent PCBs. The success of the overall process was critically dependant of efficiency of PCBs mobilization which, in this case, involved a high energy sonication that yielded fractions that were readily separated by centrifugation/filtration.

PREFACE TO CHAPTER 5

In Chapter 4, surfactants were investigated for their capacity to extract PCBs from the soil. Toxicant mobilization by soil washing with an aqueous mixture containing surfactant and EDTA was followed by hexane back-extraction to remove PCB compounds, treatment with zero-valent magnesium (to precipitate heavy metals and liberate EDTA) and finally the potential recycle of the cleaned extract was optimized. Relative to individual reagent, the presence of EDTA with surfactant did not influence the PCB extraction efficiencies perceptibly. When coupled with a hexane back-extraction process, surfactants could be recycled. Three successive soil washing cycles mobilized appreciable quantities of PCBs. Nonionic surfactant proved to be the most efficient for three successive extractions with a single charge, mobilizing almost the same quantity of PCBs that were mobilized in a companion extractions using fresh reagent for each cycle.

In the following Chapter, EDTA, and HEDC alone or in combination with surfactants are evaluated to mobilize heavy metals from mixed contaminated soil. The ability of Mg^o/Pd^o bimetallic mixture to remove metals from soil extracts is optimized. Finally, the potential to recycle the recovered EDTA is considered. For three successive washes, metal removal efficiencies with fresh EDTA are compared with efficiencies observed with recycled reagent. Results related to metal extraction, EDTA regeneration and recycle are discussed in this chapter.

This paper has been submitted for publication in *J. Environ. Qual.* 2005. Authors: Ehsan, S., S. O. Prasher, and W. D. Marshall.

CHAPTER 5

SIMULTANEOUS MOBILIZATION OF PCB AND HEAVY METALS FROM MIXED CONTAMINATED SOIL USING SURFACTANTS AND CHELATING AGENTS: HEAVY METALS

5.1 Introduction

The presence of both persistent organic compounds and heavy metal ions at many contaminated sites complicate soil cleanup strategies. Most of the National Priority List (NPL) or Superfund sites in the USA are burdened with a range of contaminants that can include volatile organic compounds (VOCs), metals or semivolatile organic compounds (SVOCs). Most sites require remediation for more than one of these contaminant groups. Twenty-five percent of the sites contain two contaminant groups and 41% of the sites contain all three contaminant groups (U. S. EPA, 2004). Even though the possibility of the simultaneous removal of mixed contaminants has been discussed during the last two decades, relatively few reports are available that describe the simultaneous removal of oxy-anions/heavy metals and organic pollutants from natural waters or soils (Dunn et al., 1989; Semer and Reddy, 1996; Brusseau et al., 1997; Huang et al., 1997; Tung et al., 2002; Baek and Yang, 2004; Shin et al., 2004; Iturbe et al., 2004). The applications of these treatments to mixed contaminant sites have remained limited because of cost, environmental constraints, and/or efficacy. Yet the simultaneous remediation of mixed contaminants by soil washing becomes increasingly attractive if reagents are re-cycled and the extracts can be detoxified efficiently.

Surfactants

Surfactants are attractive for the mobilization/mass transfer of contaminants from soil (Wang and Mulligan, 2004; Conte et al., 2005; Kim et al., 2004; Chu and Chan, 2003) because of their decreased acute toxicity and their favorable rates for environmental degradation to innocuous products. Beside bioremediation, soil washing with surfactants has received increased attention as a valid and relatively less expensive treatment for soil remediation. Different classes of surfactants have been employed not only to enhance the removal of organic pollutants but also for the extraction of selected metals ions (Roundhill, 2001).

EDTA

Ethylenediaminetetraacetate (EDTA) continues to be explored extensively for soil treatment because of its ability to mobilize bound metal cations efficiently coupled with only a minor impact on the physical and chemical properties of the soil matrix. This reagent is considered to possess a low degree of biodegradability in soil (Peters, 1999; Hong et al., 1999) and a high level of complexing capacity with respect to heavy metals (Tejowulan and Hendershot, 1998; Martínez and Motto, 2000). Conversely, the low selectivity of EDTA causes increased consumption of this reagent due to the potential chelation of all the exchangeable cations present in soil, such as Ca^{2+}, Mg^{2+}, and Fe^{3+} (Kedziorek and Bourg, 2000). For limited EDTA concentrations in the extracting solution, the quantities of extracted cations displayed a complex behavior versus pH that varied with the cation identity and with the level of soil contamination (Ghestem and Bermond, 1998). A competition phenomenon between minor and major cations of the soil (iron and calcium) was revealed. However, when present in excess, EDTA remains a powerful extractant of trace metals: recoveries in excess of 60% have been observed frequently (Kim et al., 2003; Di Palma and Ferrantelli, 2005; Hong et al., 1999: Lo and Yang, 1999). Researchers (Brown and Elliott, 1992) have also studied the influence of electrolytes on EDTA extraction. The presence of sodium, lithium, or ammonium perchlorate increased Pb recovery compared to simple EDTA leaching, over the entire pH range from 5 to 9. Divalent electrolytes, calcium and magnesium perchlorate caused a similar improvement in Pb recovery at acidic pH but suppressed Pb mobilization in more alkaline media. In the presence of electrolytes, a stoichiometric amount of EDTA was sufficient for the extraction of all the non-detrital Pb at pH 4-6. This reagent also removed Pb efficiently from soil with a high clay and silt content (Peters and Shem, 1992) and from a calcarious soil (Papassiopi et al., 1999).

Remediation of metal-contaminated soils by chelation-extraction with the recovery and reuse of the complexing reagent represents an attractive objective. However, previous reports of the re-cycling of chelating reagent(s) often have been restricted mainly to the recovery of moderate-strength chelators (Chen and Hong 1995; Macauley and Hong, 1995) or the electrochemical reduction of metal•EDTA complexes

(Allen and Chen, 1993; Martin and Allen, 1996; Wong et al., 1997; Juang and Wang, 2000). During electrochemical reduction, metal cations were reduced/deposited onto the cathode surface while the complexing reagent was released into solution. Oxidation of EDTA species at the other electrode was minimized by surrounding the anode with a perm-selective membrane.

Authors (Tunay and Kabdasli, 1994; Skoufadis et al., 1994) have reported that the removal of metals from the EDTA solution by hydroxide precipitation was inefficient due to the high stability of the EDTA complexes. By contrast, precipitation as sulfides proved to be more efficient (Hong et al., 1999; Zeng et al., 2005). Hong et al. have re-evaluated the separation of metals from EDTA with Na_2S, resulting in >99%, 70-74%, and 93-98% recovery of extracted Pb, Zn, and Cu respectively. To aid in recovery, the Na_2S and $Ca(OH)_2$ precipitating agents were added at 5mM each. Whereas the $Ca(OH)_2$ provided Ca^{2+} ions to compete for EDTA ligand (by replacing the chelated contaminant metal and facilitating its release from the chelator), Na_2S was used as an anionic precipitant to provide HS^-/S^{2-} anions to compete with EDTA for the contaminating metal cations. Cu, Zn, and Pb were recovered efficiently with appropriate chelator-to-precipitant ratios. Improved extraction performance was achieved with higher EDTA concentration (50mM) and with more washing cycles. EDTA was reclaimed using a slight excess of Na_2S precipitant at moderately alkaline conditions (pH 10), so that the chelant could be reused over several cycles. Currently, hydroxide precipitation remains the most common approach on the basis of performance, ease of operation and cost. Although, sulfide precipitation has advantages that include increased efficiency and less pH dependency, it has found limited application because of the hazardous nature of the sludge produced, the cost, and operational difficulties. Other strategies to liberate EDTA from metal complexes have involved the use of ion exchange materials (Juang et al., 1999) or zero-valent bimetallic mixtures (Mg^0/Pd^0, Mg^0/Ag^0) (Ager and Marshall, 2001; Xie and Marshall, 2002; Lee and Marshall, 2003).

The objectives of the current study were to evaluate various surfactants in combination with chelating reagent(s) for the simultaneous mobilization of PCBs and heavy metals from soil and to optimize reaction conditions that permit the recycle of mobilization aids while generating innocuous extraction products.

5.2 Materials and Methods

5.2.1 Chemicals

Test surfactants, both nonionic (Tween 20, Tween 40, Tween 85, Tween 80, Brij 35, Brij 98, or Triton 405) and anionic formulations {Triton X-301, Triton XQS 20, or sodium dodecylsulfate (SDS)} were purchased from Sigma-Aldrich, Oakville, ON, Canada. Disodium ethylenedimainetetraacetate (EDTA), sodium acetate (NaOAc), magnesium chloride ($MgCl_2$), hydroxylamine hydrochloride ($NH_2OH \bullet HCl$), hydrogen peroxide (H_2O_2), ammonium acetate (NH_4OAc) and chromium nitrate $Cr(NO_3)_3 \cdot 9H_2O$ (anhydrous powder) were obtained from Fisher Chemical, Fair Lawn, NJ, USA. The ammonium or sodium salt of bis(2-hydroxyethyl)-dithiocarbamate (HEDC) was synthesized following the method of King and Friz (1985).

For metal analyses, distilled de-ionized water (18.3 MΩ) from a Milli-Q-purification system (Millipore Bedford MA, USA) was used throughout. Aqueous metal standard solutions of Al, Cr, Cu, Cd, Fe, Ni, Mn, Pb, and Zn [1,000 mg L^{-1}, traceable to the National Institute of Standards and Technology (NIST) primary standard] were purchased from SCP Chemical Co., St-Laurent, QC, Canada. Sulfuric acid (17 M), acetic acid and HNO_3 (700 g L^{-1}, trace metal grade) were purchased from Fisher Chemical, Fair Lawn, NJ, USA. All chemicals, solvents, and reagents were of ACS Reagent grade or better and were used as received. Standard reference material SRM 2711 was purchased from the National Institute of Standard and Technology (NIST), Gaithersburg, MD, USA.

5.2.2 Soil Pretreatment, Textural and Heavy Metal Characterization

The soil for this study was obtained from an industrial landfill site on the island of Montréal, Québec, Canada. The soil was classified as Sandy loam (USDA Texture triangle) and had been historically contaminated with Aroclors 1242, 1248, 1254, and 1260 along with Cd, Cr, Cu, Pb, Ni, Mn, and Zn. The soil was air dried, passed through 2 mm sieve (10 mesh), mixed thoroughly then further air dried, and the fraction passing through a 500 µm sieve was stored in a sealed plastic bag to await further testing.

The heavy metal burden of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in soil digest, prepared by conventional nitric acid block digestion, was determined both by inductively coupled plasma optical emission spectrometry (ICP-OES) (VISTA-MPX; Varian

Australia Pty Ltd., Australia) or flame atomic absorption spectroscopy (FAAS) (AAS903; GBC Scientific Equipment Pty Ltd., Australia).

5.2.3 Soil Fractionation

The general procedure described by Tessier et al. (1979) was followed. Dried, sieved soil (1g) was placed in a 100 mL polyethylene centrifuge tube followed by the required chemicals as per the procedure outlined below to isolate the different fractions.

(i.) Exchangeable fraction: $MgCl_2$ (1 M, 8 mL) was added to a fresh 1g aliquot of soil followed by shaking for 1h at room temperature. After equilibration, the liquid supernatant fraction was isolated by centrifugation (4000 rpm) for 15 min. A suitable aliquot of the supernatant fraction was analyzed for metal concentrations.

(ii.) Carbonate fraction: Aqueous sodium acetate (NaOAc, 8mL of 1M) was added to the residue from (i) and the pH was adjusted to 5.0 with acetic acid (HOAc). The suspension was agitated for 5h at room temperature.

(iii.) Iron/manganese oxy-hydroxides fraction: Hydroxylamine hydrochloride ($NH_2OH \bullet HCl$, 0.04 M, 20 mL) in 25% HOAc was added to the particulate fraction (generated from the soil above) and the suspension was heated to 96 °C for 6h with occasional agitation.

(iv.) Organic matter fraction: HNO_3 (0.02M, 3mL) and 30% H_2O_2 (5 mL, pH 2.0) were combined with the particulate fraction (generated above) and the mixture was heated to 85 °C for 2h with occasional agitation. H_2O_2 (300 g L^{-1}, 3mL) was added and the suspension was re-heated to 85 °C for 3h followed by addition of ammonium acetate (NH_4OAc, 3.2M, 5 mL) in HNO_3 (200 mL L^{-1}) upon cooling. Sample was diluted to 20 mL and agitated continuously for 30 min.

5.2.4 Mixed Contaminant Extraction/Mobilization

Soil (3g) was equilibrated with 20 mL EDTA (2 mmole), EDTA (1 mmole) + HEDC (2 mmoles) (1:1 *v/v*), EDTA + surfactant or with surfactant alone, in a 50 mL centrifuge tube. Equilibration was achieved by sonication of the soil suspension for 10 min with an ultrasonic homogenizer (XL 2020 Sonic dismembrator, Misonix Inc. NY, USA). An extended horn of 25 cm L x 1.2 cm diam, tuned at 20 kHz frequency, delivered ultrasonic energy (240 W) in a pulsed mode with fixed vibration amplitude setting of 6.

The extraction consisted of pulsed surges of power delivered for 3 s followed by a 2 s resting phase to the soil suspension contained in a plastic tube immersed in ice bath. Subsequently, samples were centrifuged at 4000 rpm (10 min) to recover the supernatant fraction. Aliquots of supernatants were saved for determining the PCB and heavy metal (HM) contents in this fraction.

5.2.5 PCB Removal from Soil Extract

PCBs were removed from supernatant fractions following methods described in Chapter 4.

5.2.6 Heavy Metal Removal from Soil Extract

Post PCB removal with hexane, the soil extracts were treated for metal removal. In a 50 mL test tube, magnesium flakes (Mg^0, 0.5 g) were combined with K_2PdCl_6 (5 mg) followed by the addition of the soil extract. The resulting suspension was stirred, heated to 70 °C, and permitted to react for 2 h. Post reaction, solid $Ca(OH)_2$ (40 mg) was added and final pH was adjusted to 12 with NaOH. The sample was centrifuged at 4000 rpm followed by filtration to remove precipitated metal oxy-hydroxides. Aliquots of extraction solution {before and after treatment with Mg^0 and $Ca(OH)_2$} were set aside for metal analyses.

5.2.7 Mobilizing Reagent Recycle

Post PCB and heavy metal removal, the pH of resultant cleaned mobilizing solution was adjusted to 6 and was recycled twice to mobilize more PCBs and metals from the soil particulate fraction. The soil particulate fraction was sonicated with 20 mL of cleaned mobilizing reagent. After centrifugation, the aqueous fraction was treated to remove PCBs and heavy metals as described above. After 3 washing cycles, the soil particulate fraction was oven dried and analyzed for residual PCB and heavy metal contents. A portion of the soil residue (0.2 g) was further equilibrated with deionized water (0.5 mL) for 1 h and the supernatant fraction was assayed for surfactant and EDTA contents as described below.

5.2.8 Surfactant Analysis

Surfactant concentrations were determined spectrophotometrically (DR 4000; Hatch Co., Loveland, CO, USA. single beam spectrophotometer) following methods described in Chapter 4.

5.2.9 EDTA Analysis

The combined concentration of free and complexed EDTA was determined spectrophotometrically (Flaska, 1964). Aqueous soil extract (1mL) was added to a glass tube (1 mm I.D. x 10 cm.) containing 0.1M $Cr(NO_3)_3{\cdot}9H_2O$ solution (1 mL). The pH of the solution was adjusted to 2-3 with HNO_3 (200 g L^{-1}) followed by digestion at 100 ^{o}C for 15 min. On cooling, the absorbance at 555 nm was recorded *vs.* a blank sample containing DDW that was treated analogously.

5.3 Result and Discussion

5.3.1 Soil Characterization

The sandy loam soil from a landfill site had been historically contaminated with both heavy metals and persistent organic pollutants. The soil, sieved to pass a 35 mesh screen, was used for all experiments. Initial experiments characterized the soil with respect to particle size, cation exchange capacity (CEC), and organic matter (Table 5.1); the relatively low levels of silt/clay, low organic matter content, and intermediate CEC suggested that the soil might be amenable to remediation by soil washing. The soil's textural properties were supplemented by determinations of the heavy metal composition of the soil and by a fractionation study to assess the ease of extraction of the analyte metals. Estimates of the heavy metal burden in soil digest, following conventional nitric acid block digestion, were determined by ICP-OES. The instrument response was optimized according to the manufacturer's specifications and line selection for the analyte metals was made from the spectral table, bearing in mind the sensitivity of the line and relative freedom from spectral interferences. Multiple emission lines for each

Table 5.1 Particle size characteristics of the soil

Sample	Sand (%)	Clay (%)	Silt (%)	Organic C	pH	CEC cmol kg^{-1}
Soil	78	12	10	7.4	7.38	9.8
Sieved Soil	52	16	33	12.5	7.50	9.5

element were selected to assess the spectral interferences and FACT (Fast automated correction technique) model was used to correct the possible interferences. Estimates of analyte levels in digest from a standard reference material (Montana soil, SRM 2711) were also determined with this technique and corroborated by FAAS (Table 5.2).

The soil was fractionated to determine the portions of each analyte metal (Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, or Zn) that could be dislodged from the soil with specific reagent protocols (Table 5.3). When performed successively on a soil sample, these protocols were considered to estimate the metal content associated with the exchangeable, carbonate, Mn/Zn oxy-hydroxide (reducible), organic, and residual fractions. The distribution of heavy metals as determined by sequential extraction does not necessarily reflect their association with discrete soil phases, but rather is operationally defined by the method of extraction.

As a means of characterizing the distribution within a soil, this approach is subject to limitations (Lo and Yang, 1998; Lo and Yang, 1999) that have been recognized widely. None the less, the procedure of Tessier et al. (1979) was followed in the current study. The soil was characterized with respect to heavy metal burdens in the exchangeable, carbonate, Fe/Mn oxy-hydroxide, and organic matter fractions. The residual fraction was determined as the difference between the total and the sum of the other four fractions.

It has been considered (Peters, 1999) that it is the sum of exchangeable, carbonate, and reducible fractions that approximates the portions of heavy metal that can be dislodged by complexometric washing procedures. This fraction of the total analyte metal burden was variable and ranged from a low of 7% for Fe to a high of 91% for Zn. These fractionation studies indicated that high proportion of the Zn (91%) and Pb (80%), intermediate proportions of the Cd (45%), Cu (44%), Mn (31%), Ni (34%). and Al (29%) but only minor proportions of Cr (7%) and Fe (8%) were susceptible to washing by complexometric extraction. Based on the sum of the metal burdens (other than Fe) in the soil (~ 4.2 mmoles/3g), a sparing quantity of EDTA (2 mmoles/3g soil) was chosen to perform the equilibration trials.

Table 5.2 Metal concentrations (mg kg^{-1} ± 1 RSD [†]) in Montana soil (SRM 2711) as determined by FAAS and ICP-OES

Element	FAAS	ICP –OES	Leach data
Cd	20.0 ± 4	21.0 ± 2	13 - 26
Mn	7027.7 ± 5	6476.8 ± 1	6200 - 9000
Cu	3123.2 ± 1	3198.4 ± 2	2400 - 3400
Fe	27392.4 ± 1	28866.5 ± 1	22000 - 32000
Pb	5160.9 ± 3	6008.7 ± 1	4300 - 7000
Zn	7173.5 ± 4	6227.7 ± 1	5900 - 6900

[†] RSD = One relative standard deviation based on three replicate trials.

Table 5.3 Metal fractionation of the soil in terms of the percentage (± 1 SD [†]) of the total burden (mmol kg^{-1} ± 1 RSD [‡]) that was associated with each successive leaching procedure

Analyte	Total soil Burden (mmol kg^{-1})	Exchangeable	Carbonate	Fe/Mn Oxide	Organic	Residual
Al	(1.09 ± 0.003) x 10^3	0.1 ± 0.005	8 ± 0.08	21 ± 0.6	2 ± 0.02	69± 3
Cd	0.50 ±0.0010	0.7 ± 0.01	36 ± 0.36	9 ± 0.3	7 ± 0.3	48 ± 2
Cr	8.4 ±0.2	0.2 ± 0.006	1 ± 0.07	6 ± 0.2	5 ± 0.2	87± 0.9
Cu	43.0 ±0.3	0.2 ± 0.006	18 ± 0.9	25 ± 2.0	14 ± 0.8	42 ± 4
Fe	(3.5 ±0.2) x 10^3	<0.1	0.3 ± 0.001	8 ± 0.2	<0.1	93 ± 0.5
Mn	26.5 ±1.3	1.4 ± 0.06	13 ± 0.9	18± 0.90	3 ± 0.1	66 ± 2
Ni	6.2 ± 0.2	4 ± 0.2	8 ± 0.3	21± 0.63	8 ± 0.2	59 ± 3
Pb	86.6 ± 0.4	0.1 ± 0.005	60 ± 0.2	19 ± 0.8	2± 0.1	18 ± 1
Zn	136.7 ± 2.7	0.2 ± 0.002	40 ± 2	50 ± 2	0.1± 0.006	9 ± 0.2

[†] SD = One standard deviation based on three replicate trials.

[‡] RSD = One relative standard deviation based on three replicate trials.

5.3.2 Heavy Metals Mobilization

In subsequent experiments, metal extraction efficiency was determined in the presence of 2 mmole EDTA alone or in combination with an anionic (Triton XQS-20 or Triton X-301) or a nonionic (Brij 98) surfactant. As summarized in Figure 5.1, soil (3g) was equilibrated by sonication for 3, 5, 10, or 30 min with 2 mmole EDTA (20 mL). For these trials, 10 min of sonication mobilized appreciably more heavy metal for all analyte elements than did the 5 or 3 min of equilibration. However, 30 min of sonication provided slightly more metal in the aqueous extract for certain analyte elements but equivalent amounts or less for others. It was anticipated that replicate trials would have resulted in mean mobilizations that would not have been significantly different between the 10 min and 30 min of sonication.

The 10 min of sonication was chosen for subsequent studies. A single equilibration of the soil with EDTA (20 mL, 2 mmole) alone or in combination with surfactant (30 mL L^{-1}) mobilized appreciable quantities (Table 5.4) of the Pb (61-73%) and the Zn (41-47%), intermediary quantities of Cu (41-49%), Cd (34-36%), and Mn (24-28%) but only minor amounts of Ni (15-19%), Al (6-8%), Cr (3-5%), and Fe (2-4%). With the exception of Cu and Pb, the presence of surfactant did not increase the extraction efficiency of EDTA appreciably. Statistically significant differences, when present, were relatively minor. None the less, Cu and Pb mobilization was increased by the EDTA-nonionic surfactant combination.

5.3.3 Mixed EDTA-HEDC Complexants

Analogous equilibrations (by sonication) were performed with a mixture of two chelating reagents {EDTA and NH_4HEDC, 1:2 (m/m)} in the presence/absence of surfactant to detect any possible interactions. For the combination of EDTA and HEDC, the pH was adjusted above 7 to minimize acid catalyzed hydrolysis of the dithiocarbamate ligand. In contrast to earlier observations (Lee and Marshall, 2002), the substitution of a stoichiometric equivalent of HEDC for one half of the EDTA was detrimental to the mobilization of most analyte metals (Table 5.5, column 3 *vs*. column 2) with one exception; Cr extraction was increased by the presence of HEDC. Possibly, Cr(VI) oxy-anion was reduced to form a cationic specie, Cr(III), that was solubilized by

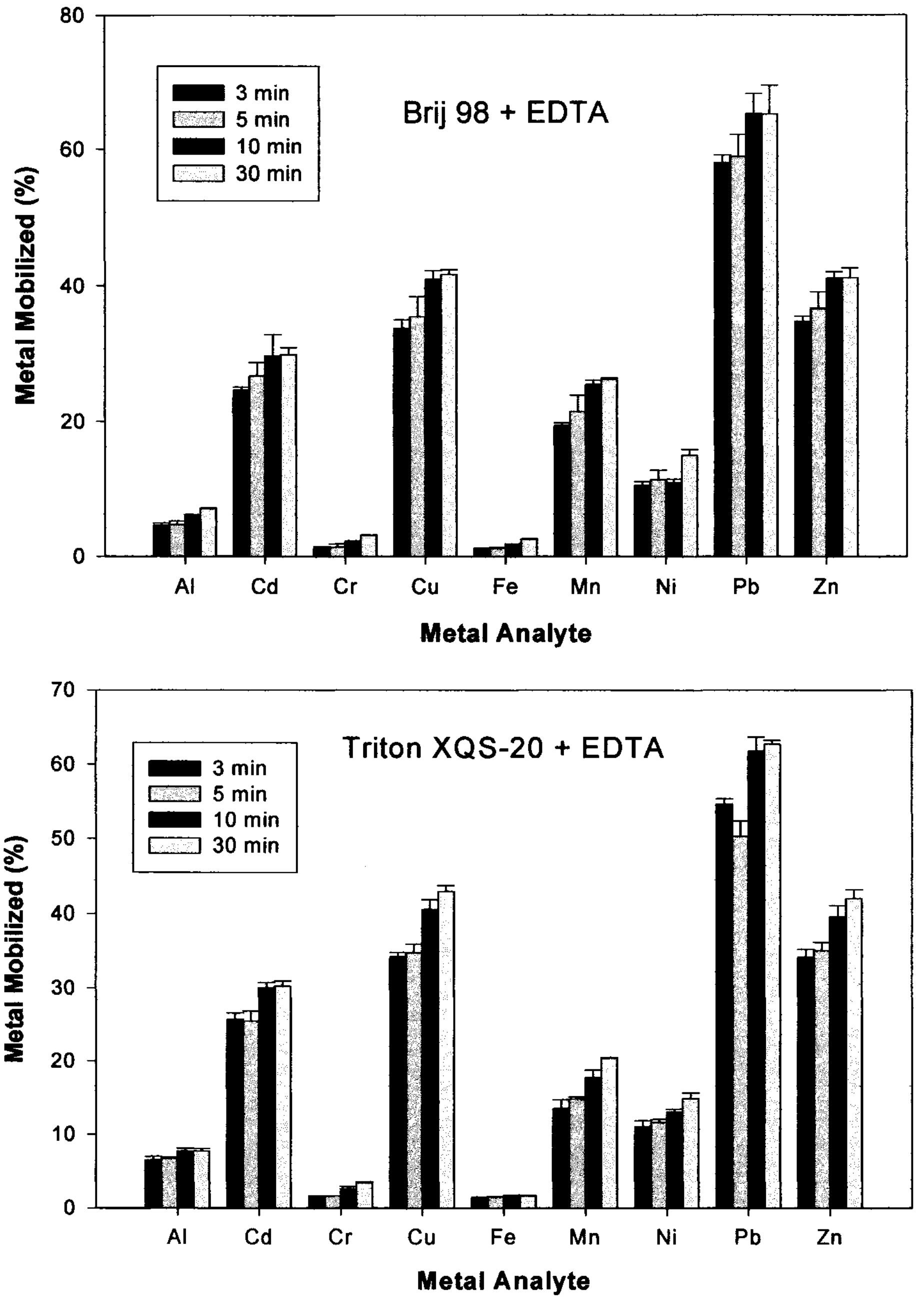

Figure 5.1 Optimization of the sonication time with EDTA + Brij 98 or EDTA + Triton XQS-20.

Table 5.4 Mean percent (± 1 SD [†]) of the soil metal burden mobilized by a single extraction of soil (3g) with 20 mL EDTA (2 mmoles) or EDTA (2 mmoles) + surfactant (30 g L^{-1})

Analyte	EDTA	EDTA + Brij	EDTA + TritonX-301	EDTA + Triton XQS-20
Al	6 ± 0.2 C [‡]	7 ± 0.6 B	8 ± 0.6 A	8 ± 0.2 A
Cd	35 ± 4 A	36 ± 1 A	34 ± 2 A	36 ± 3 A
Cr	3 ± 0.2 C	4 ± 0.3 B	5 ± 0.3 A	4 ± 0.04 B
Cu	42 ± 3 B	49 ± 1 A	41 ± 4 B	46 ± 5 A
Fe	2 ± 0.1 B	2 ± 0.2 B	3 ± 0.2 A	2 ± 0.04 B
Mn	28 ± 3 A	27 ± 0.5 A	28 ± 0.6 A	24 ± 0.5 B
Ni	15 ± 2 C	17 ± 0.5 B	16 ± 0.6 B, C	19 ± 1 A
Pb	66 ± 3 B	73 ± 0.7 A	61 ± 0.6 C	67 ± 6 B
Zn	42 ± 3 B	44 ± 4 A, B	47 ± 3 A	41 ± 4 B

[†] SD = One standard deviation based on three replicate trials.

[‡] For the same row, entries bearing the same letter are not significantly different ($P<0.05$) from each other.

complexation with EDTA. Decreased extraction efficiency of Cu in the presence of HEDC might be explained by the fact that Cu-HEDC complex precipitated and was retained with the soil as corroborated by mixing a simulated Cu standard of same molar strength with HEDC. The presence of surfactant together with mixed chelants did not restore the extraction efficiencies observed with EDTA alone. Again the presence of surfactant did not alter metal mobilization efficiency a great deal although small but statistically significant differences were observed in certain cases. The presence of nonionic surfactant (Brij 98) showed slightly enhanced mobilization for Cu (11%) relative to the EDTA-HEDC combination (6%). Only small quantities of Fe (1-2%) were mobilized in all cases.

5.3.4 EDTA Release

Other experiments involved maximizing the release of EDTA from the heavy metal (HM) complexes so as to permit the recycling of this reagent. Time of reaction and quantities of added bimetallic mixture and $Ca(OH)_2$ were varied to minimize the quantities of heavy metals remaining in the liquid phase (data not shown).

Filtrate, post the first equilibration, was treated with Mg^0 containing K_2PdCl_6 (50 mg) and precipitated as insoluble oxy-hydroxides when $Ca(OH)_2$ was added after 2 h reaction with Pd^0/Mg^0. The efficiencies of metal release from their HM•EDTA complexes are summarized in Table 5.6. For Al, Cu, Fe, and Zn, precipitation was virtually complete for all reagent combinations and very efficient for Mn and Pb for EDTA alone or in combination with non-ionic surfactant. However, Mn and Pb removal was less efficient for the EDTA - ionic surfactant combination. Similarly the removal of Cd, Cr, and Ni was decreased if they were present in ionic surfactant relative to either EDTA alone or EDTA-non-ionic surfactant. Maximum metal removal was usually achieved from the EDTA-non-ionic surfactant combination. Each of the EDTA surfactant combinations followed the same trend for metal removal post the 2nd and 3rd equilibrations with reclaimed EDTA (data not shown). Brij 98 and Triton XQS-20 proved to be more convenient for Mg treatment and filtration. Triton X-301 seemed to retain hexane during PCB back extraction that caused solution foaming during heating stage. The presence of the Triton X-301 formulation resulted in a more viscous suspension that

Table 5.5 Mean percent recovery of metal (± 1 SD [†]) in 20 mL EDTA (1 mmole) - HEDC (2 mmole) mixed extract or in a stoichiometrically equivalent quantity of EDTA solution (20 ml, 2 mmole)

Analyte Metal	EDTA	EDTA+ HEDC	EDTA + HEDC + Brij 98	EDTA + HEDC + Triton X 301	EDTA + HEDC + Triton XQS 20
Al	6 ± 0.2 A [‡]	3 ± 0.03 C	4 ± 0.2 B	2 ± 0.1 D	3 ± 0.3 C
Cd	35 ± 4 A	30 ± 3 A	30 ± 1 A	32 ± 1 A	32 ± 0.6 A
Cr	3 ± 0.2 C	1 ± 0.05 D	5 ± 0.7 A	4 ± 0.2 B	5 ± 0.6 A
Cu	42 ± 3 A	6 ± 0.2 C	11 ± 2 B	3 ± 0.2 C	4 ± 0.5 C
Fe	2 ± 0.1 A	1 ± 0.04 B	2 ± 0.4 A	1 ± 0.1 B	1 ± 0.1 B
Mn	28 ± 3 A	23 ± 0.7 B	23 ± 2 B	21 ± 0.2 B	22 ± 1 B
Ni	15 ± 2 A	5 ± 0.3 B, C	6 ± 0.4 B	3 ± 0.1 D	4 ± 0.1 C, D
Pb	66 ± 3 A	49 ± 2 B	47 ± 4 B	46 ± 0.1 B	45 ± 2 B
Zn	42 ± 3 A	21 ± 0.2 C	28 ± 1 B	27 ± 4 B	22 ± 1 C

[‡] SD = One standard deviation based on three replicate trials.

[‡] For the same row, entries bearing the same letter are not significantly different ($P<0.05$) from each other.

Table 5.6 Metal removal efficiencies (% ± 1 SD [†]) from soil supernatant fraction after reaction with Pd^0/Mg^0 for 2h followed by the addition of $Ca(OH)_2$

Analyte Metal	EDTA (2mmoles)	EDTA + Brij 98	EDTA + Triton X301	EDTA + Triton QSX-20
Al	99 ± 0.07	99 ± 0.05	99 ± 0.09	99 ± 0.04
Cd	73 ± 6	85 ± 5	54 ± 5	56 ± 6
Cr	44 ± 7	58 ± 7	43 ± 9	33 ± 3.9
Cu	100	100	99 ± 0.6	100
Fe	100	100	99 ± 2	100
Mn	98 ± 0.3	99 ± 0.2	85 ± 1	86 ± 3
Ni	58 ± 3	56 ± 6	4 ± 6	28 ± 11
Pb	96 ± 0.7	98 ± 0.1	77 ± 0.8	61 ± 1
Zn	100	100	97 ± 3	99 ± 0.6

[†] SD = One standard deviation based on three replicate trials.

was difficult to filter without suction.

5.3.5 Cumulative Heavy Metal Recoveries

Post metal removal, the pH of the aqueous phase was adjusted to 6 then recycled by recombination with the soil particulates to mobilize more heavy metals. The recycle procedure was repeated a second time. The cumulative quantities of metals extracted from the soil with 3 sonication wash cycles are summarized in Table 5.7. Relative to three washes using fresh EDTA each time (column 3), the use of recycled reagent was somewhat less efficient (column 2) for all analyte metals. In analogous fashion, the combination of fresh EDTA-surfactant mobilized more metal than the recycled reagents (column 5 *vs.* column 4, column 7 *vs.* column 6). However, the presence of anionic (Triton X-301 or XQS-20) or non-ionic (Brij 98) surfactant did not alter the efficiency of mobilization appreciably for either recycled reagents (column 2 *vs.* column 4 *vs.* column 6) or fresh reagents (column 3 *vs.* column 5 *vs.* column 7).

In summary, three successive washes with the same charge of EDTA non-ionic surfactant mobilized appreciable quantities of certain metals from the soil (Pb, 84%; Cu, 64%; Zn, 52%; Cd, 41%), intermediate quantities of Mn (31%) and Ni (19%) but only small quantities of Al (6%), Cr (5%), or Fe (3%).

5.3.6 EDTA Fate post Soil Washing and Mg^0 Treatment

The fraction of EDTA remaining with the aqueous phase was monitored post each stage of the protocol (Table 5.8). After the first equilibration, some 11-12% had been lost to the solids phase presumably by adsorption of the chelating regent to the soil particle surfaces. Not surprisingly, the PCB back extraction with hexane did not cause detectable EDTA loss but a further small portion (1-2%) was lost during the Mg^0 treatment and subsequent filtration. Seemingly, losses were unaffected by the presence/absence of surfactant. EDTA release from 2nd and 3rd soil equilibration again resulted in a further 5-8% and 12-15% loss to the soil particulates fraction. A cumulative loss of 30% of the initial EDTA concentration to the soil particulates fraction was observed during three washing cycles, yet losses during the Mg^0 treatment or hexane back extraction were minimal.

Table 5.7 Mean cumulative metal recoveries (% ± 1 SD [†]) in the supernatant fraction after equilibration of soil (3g) with the same charge (recycle mode) of EDTA (2 mmoles) or with fresh reagent each time

	Cumulative % mobilized					
Analyte	**Recycled EDTA**	**Fresh EDTA**	**Recycled EDTA - Triton QSX-20**	**Fresh EDTA - Triton QSX-20**	**Recycled EDTA-Brij 98**	**Fresh EDTA-Brij 98**
Al	7 ± 0.3 C [‡]	16 ± 0.9 A	9 ± 0.2 B	16 ± 1 A	9 ± 0.8 B	16 ± 0.8 A
Cd	42 ± 4 A	49 ± 7 A	42 ± 3 A	49 ± 5 A	41 ± 0.8 A	49 ± 0.8 A
Cr	4 ± 0.3 C	10 ± 0.4 B	4 ± 0.04 C	11 ± 4 A	5 ± 0.4 C	11 ± 0.4 A
Cu	57 ± 4 C	71 ± 4 A,B	57 ± 4 C	72 ± 6 A,B	64 ± 4 B,C	78 ± 4 A
Fe	2 ± 0.1 C	10 ± 0.6 B	2 ± 0.1 C	12 ± 0.7 A	3 ± 0.3 C	12 ± 0.3 A
Mn	33 ± 3 B	38 ± 0.4 A	30 ± 2 B	36 ± 0.4 A	31 ± 2 B	37 ± 2 A
Ni	20 ± 2 D	33 ± 0.1 B	20 ± 0.8 D	31 ± 0.6 C	19 ± 1D	36 ± 1 A
Pb	78 ± 5 B	85 ± 4 A,B	77 ± 0.8 B	88 ± 2 A,B	84 ± 0.8 A,B	92 ± 0.8 A
Zn	51 ± 4 B	62 ± 4 A	47 ± 5 B	65 ± 3 A	52 ± 2 B	69 ± 2 A

[†] SD = one standard deviation based on three replicate trials.

[‡] For the same row, entries bearing the same letter are not significantly different ($P<0.05$) from each other.

Table 5.8 EDTA recovery (% ± 1 SD [†]) post each experimental stage for 3 sonication wash cycles of soil (3g) with EDTA (2mmole) or EDTA + surfactant (30 mL L^{-1})

	EDTA Recovery (%) ± 1 SD			
Post:	**EDTA**	**EDTA + Brij 98**	**EDTA + Triton X301**	**EDTA + Triton QSX-20**
1^{ST} Equilibration	89 ± 2	89 ± 1	89 ± 2	89 ± 0.6
Hexane Extraction	89 ± 2	89 ± 1	89 ± 3	89 ± 1
Pd^0/Mg^0 treatment	87 ± 0.1	87 ± 1	83 ± 2	86 ± 1
2^{ND} Equilibration	79 ± 3	82 ± 3	79 ± 5	80 ± 2
2^{ND} Pd^0/Mg^0 treatment	77 ± 4	78 ± 2	76 ± 5	78 ± 1
3^{RD} Equilibration	63 ± 1	65 ± 2	64 ± 2	66 ± 1

[†] SD = One standard deviation based on three replicate trials.

EDTA recovery (62-65%) from soil, hexane, or Mg^0 treatment post three wash cycles was consistent for all reagents combinations.

5.3.7 Heavy Metal Extractabilities

The relative extractabilities of the analyte metals showed good agreement with their labilities as revealed by metal fractionation results. As summarized in Table 5.9, the recycle technique mobilized virtually all of the Cd, Cu, Mn, and Pb (when the organic fraction is added to the sum of the exchangeable, carbonate and reducible fractions). Additionally, fresh reagents were also able to mobilize virtually all of the available Cr, Fe, Mn, and Ni. However, the mobilization of available Al and Zn remained incomplete. None the less, it seems that the strategy of repeated soil washing with a sparing quantity of EDTA can extract an appreciable portion of most of the heavy metals. When coupled with detoxification techniques (hydrodechlorination of PCBs or precipitation of heavy metals), the combined processes resulted in a soil particulate fraction that has been cleaned and a limited volume of aqueous extract that has been detoxified.

5.4 Conclusions

Soil washing with mixture of surfactants and EDTA can be an efficient remediation treatment for soil containing mixed contaminants. The optimum condition for heavy metal extraction from the contaminated soil depended on the geochemistry and metal fractionation, whereas the optimum condition for EDTA regeneration was influenced by the type of surfactant. The results have demonstrated that the strategy of repeated soil washing with a sparing quantity of EDTA can extract an appreciable portion of most of the heavy metals. The low dose EDTA was also favorable for retaining the original soil minerals. The integration of EDTA recovery/regeneration and metal precipitation by addition of $Ca(OH)_2$ in the presence of Mg^0 improved the economic viability of soil washing of contaminants sites. The overall process resulted in a soil particulate fraction that has been cleaned and a limited volume of aqueous extract that had been detoxified.

Table 5.9 Cumulative mobilization of heavy metal accomplished with three successive equilibrations of the soil particulate fraction with the same charge of reagents or with fresh reagent for each cycle

Analyte Metal	Σ(carb†+exch‡+red§) (%)	Cumulative % extracted			
		Recycled EDTA	**Fresh EDTA**	**Recycled EDTA-Brij 98**	**Fresh EDTA- Brij 98**
Al	29	7 ± 0.3	16 ± 0.9	9 ± 0.8	16 ± 0.8
Cd	45	42 ± 4	49 ± 7	41 ± 0.8	49 ± 0.8
Cr	8	4 ± 0.3	10 ± 0.4	5 ± 0.4	11 ± 0.4
Cu	44	57 ± 4	71 ± 4	64 ± 4	78 ± 4
Fe	7	2 ± 0.1	10 ± 0.6	3 ± 0.3	12 ± 0.3
Mn	31	33 ± 3	38 ± 0.4	31 ± 2	37 ± 2
Ni	34	20 ± 2	33 ± 0.1	19 ± 1	36 ± 1
Pb	80	78 ± 5	85 ± 4	84 ± 0.8	92 ± 0.8
Zn	91	51 ± 4	62 ± 4	52 ± 2	69 ± 2

† Carbonate fraction.

‡ Exchangeable fraction.

§ Reducible fraction.

PREFACE TO CHAPTER 6

In Chapter 5, the capacity of EDTA and HEDC alone or in the presence of surfactants was investigated to mobilize targeted metals (Al, Cr, Cd, Cu, Fe, Mn, Ni, Pb, and Zn) from a mixed contaminated soil. In addition, the capacity of Mg^0 in the presence of Pd^0 was investigated to remove metals that had been extracted from soil by chelation with EDTA. Finally, the potential to recycle the recovered EDTA was also evaluated. Three successive soil washing cycles mobilized virtually all of the available Cd, Cu, Mn, and Pb and lesser amounts of the Zn, Ni, and Cr. Whereas the presence of anionic surfactant did not affect the metal extraction efficiency with EDTA, the presence of nonionic surfactant enhanced the recovery of Cu and Pb. Metal removal with bimetallic mixture of magnesium and Pd was efficient for soil extracts containing nonionic surfactant but not as efficiently from those containing anionic surfactants. For Al, Cu, Fe, and Zn, precipitation was virtually complete for all reagent combinations and very efficient for Mn and Pb for EDTA alone or in combination with the non-ionic surfactant but was less efficient for the EDTA - ionic surfactant combination. The EDTA ligand, released from the metal•EDTA complex, could be recycled efficiently for at least two further cycles.

In the following Chapter, the potential of cyclodextrin derivatives in combination with chelating agents is investigated for the efficient removal of PCBs and heavy metals. Contaminants are mobilized from soil by sonication with cyclodextrin in the presence/absence of EDTA. The supernatant fraction is treated for the regeneration of cyclodextrin and EDTA. Cyclodextrins are recovered by hexane back extraction followed by EDTA recovery with Mg^0/Pd^0 in the presence of $Ca(OH)_2$. Finally, treated supernatant fraction is mixed with the soil for further mobilization of PCBs and metals. In three successive washes, PCBs and metal removal efficiency with fresh reagents is compared to the cyclic extraction.

CHAPTER 6

SIMULTANEOUS MOBILIZATION OF PCB AND HEAVY METALS FROM MIXED CONTAMINATED SOIL USING CYCLODEXTRINS AND CHELATING AGENTS

6.1 Introduction

The cleanup of soil contaminated with both heavy metals and organic compounds is a contemporary issue of remediation efforts considering the fact that most of the currently available technologies are directed to only the removal of a specific group of contaminants; either organic compounds or metals (U.S. EPA, 2004). Among organic compounds, polychlorinated biphenyls (PCBs) are frequently found at many hazardous waste sites, as are combination of PCBs and metals. From a remediation perspective, removing PCBs and metals together is difficult due to differences in their physical-chemical properties. PCBs are bound to soil by nonspecific hydrophobic mechanisms, whereas metal ions are bound to surface sites via specific chemical interactions and also weaker electrostatic forces. Consequently, it is usually difficult to define a remediation process that is equally efficient for both of these types of binding mechanism.

Excavation of contaminated soils was once the chosen solution that could also be applied to mixed contaminants. However, because of the high cost of excavation and final disposal at landfills, in addition to the lack of available landfill sites and environmental contamination due to leaking landfills, this remediation method is becoming less popular (U.S. EPA, 1988). Among the more popular remediation processes today, soil washing is a treatment process that can be used for both metals and organic compound if a suitable washing reagent or combination of reagents having strong affinity for both metals and PCBs can be identified. The most widely accepted soil washing technique for metal contaminated soil involves the use of chelating reagents such as ethylenediaminetetraacetic acid (Peters, 1999; Wasay et al., 2001). Whereas soil washing with surfactants remains a promising technology for enhancing the removal PCBs from soil (Abdul et al., 1992; Mulligan et al., 2001), cyclodextrins (CDs) have also been considered as alternative solubilization reagents for soil cleanup.

Cyclodextrin or cycloamyloses are cyclic glucose oligosaccharides classified as α, β, or γ, corresponding 6, 7 or 8 glucose units, respectively. The unique property of these lampshade-shaped molecules is that they have a hydrophilic exterior and substantially hydrophobic, apolar cavity. Low polarity organic compounds with a size and shape complementary to the cavity form water soluble, 1:1 inclusion complexes. Because of the inclusion complex forming ability of cyclodextrins or their derivatives, many of the persistent organic pollutants in the soil (PAH, PCB, PCP, dibenzodioxins or dibenzofurans) are suitable guests for complex formation with cyclodextrins. The ability of cyclodextrin to increase the apparent solubility of organic compounds is the basis for its potential use in soil remediation. Organic pollutants are extracted from contaminated soils without further contaminating or exhausting the soil (Reid et al, 1999; Doick et al., 2005). Cyclodextrin also can enhance the bioremediation of contaminated soils (Joszef and Eva, 1994). Because of its carbohydrate structure, cyclodextrin has some inherent advantages over surfactants for remediation. Importantly, cyclodextrins are nontoxic and environmentally benign. Cyclodextrin experience little or no sorption, retardation, or pore exclusion to soils (Brusseau et al., 1994). In addition, cyclodextrins are not subject to precipitation, phase separation, or foaming.

While natural cyclodextrins are themselves of interest as molecular hosts, much of their utility in superamolecular chemistry derives from their modification. Cyclodextrin can be carefully tailored to match particular guests and meet specific requirements in their host-guest interaction. Thus far, β-cyclodextrins have been used more frequently than other CDs because the cavity size is appropriate for range of organic compounds with the net effect that the formation of an inclusion complex results in increased aqueous solubility. Alkyl derivatized β-cyclodextrins have been successfully employed in the large-scale ex-situ bio-remediation of PCB contaminated soil (Fava et al., 1998). PCB-contaminated soil was significantly bioremediated and this process was enhanced by the addition of biodegradable hydroxyproply-β-CD (HP-β-CD) and γ-CD. Enhanced depletion rates of soil PCB were attained by the availability of HP-β-CD or γ-CD in the soil slurry-phase as well as in fixed phase reactors. In another study, randomly methylated-β-CD (RAMEB) markedly enhance the removal of PCBs from the soil (Fava et al., 2003). Modified β-cyclodextrin (Hydoxypropyl, sulfated, or methyl) have been exploited to enhance the aqueous solubility of trichloroethylene (TCE) and perchloroethylene (PCE). In the extraction process, it was observed that addition of methyl substituted cyclodextrin solution (5% w/v) resulted the fairly efficient desorption of PCE and TCE; 93% of the original soil-bound material (Shrin et al., 2003). The effectiveness of Heptakis-2,6-di-O-methyl-β-cyclodextrin (DM-β-CD) and HP-β-CD solution (1% w/w) in decontaminating a variety of soils containing 2,4,6-trinitrotoluene (TNT) as well as certain associated metabolites {4-amino-2,6-dinitrotoluene (4-ADNT), 2,4-diamino-4-nitrotoluene (2,4-DANT)} has been demonstrated by Sheremata and Hawari (2000). The ability of CD to form water-soluble inclusion complexes with a wide range of organic compounds makes them suitable for various other applications including pharmaceutical (time release drugs) and in the manufacture of household items (odor reducing spray).

Even though, the possibility for enhancing the simultaneous mobilization of organic compounds and metals using cyclodextrin was suggested a decade ago (Brusseau et al., 1994), only a relatively few reports discuss this topic (Wang and Brusseau, 1995; Brusseau et al., 1997; Vulava and Seaman, 2000). Based on published data, it would appear that cyclodextrins have not been used extensively for the extraction of metals.

In a previous investigation (Chapter 4 and 5), it was demonstrated that soil washing with an aqueous mixture containing surfactant and a sparing quantity of EDTA, mobilized both heavy metals and PCBs simultaneously. Soil washing was aided by high energy ultrasonication to enhance the extraction efficiencies of reagents and to reduce the processing time. Simultaneous toxicant mobilization followed by hexane back-extraction to remove PCB compounds, treatment with zero-valent magnesium (to precipitate heavy metals and liberate EDTA) and finally recycle of the cleaned extract increased the remediation value of soil washing process. The precipitated heavy metal oxy-hydroxides were recovered by filtration and the PCB content of the aqueous phase was removed by back-extraction with hexane. PCBs in the back-extract were detoxified by hydrodechlorination. The objective of the current study was to evaluate a combination of cyclodextrin and chelating reagent for the simultaneous mobilization of heavy metals and PCBs from a field contaminated soil. Unfortunately, the applications of cyclodextrins to soil washing have remained limited because of the costs of these reagents. These studies also evaluate the technical merits regarding its regeneration and recycle.

6.2 Materials and Methods

6.2.1 Chemicals

β-cyclodextrin and hydroxypropyl-β-cyclodextrin (HP-β-CD) were purchased from Sigma-Aldrich, Oakville, ON, Canada. In addition, a sample of hydroxypropyl-β-cyclodextrin (HP-β-CD) was also kindly provided by Dr. Jalal Hawari, Biotechnology Research Institute, Montreal, QC, Canada. Randomly methylated β-cyclodextrin (RAMEB), degree of substitution (DS):12.6 (CAVASOL W7 M) was generously donated by Dr. Mark Harrison, Wacker Specialities, Adrian, MI, USA. Disodium ethylenedimainetetraacetate (EDTA), and chromium nitrate Cr $(NO_3)_3 \cdot 9H_2O$ were obtained from Fisher Chemical, Fair Lawn, NJ, USA. HPLC grade ethanol (C_2H_5OH), and hexane (C_6H_{14}), were obtained from Fisher Scientific, Ottawa, ON, Canada.

For metal analyses, distilled de-ionized water (18.3 MΩ) from a Milli-Q-purification system (Millipore, Bedford, MA, USA) was used throughout. Aqueous metal standard solutions of Al, Cr, Cu, Cd, Fe, Ni, Mn, Pb, and Zn [1,000 mg L^{-1}, traceable to the National Institute of Standards and Technology (NIST) primary standard] were purchased from SCP Chemical Co., St- Laurent, QC, Canada. Nitric acid (700 g L^{-1}, trace metal grade) was purchased from Fisher Chemical, Fair Lawn, NJ, USA. All chemicals, solvents, and reagents were of ACS Reagent grade or better and were used as received.

The soil from an industrial landfill site had been historically contaminated with Aroclors 1242, 1248, 1254, and 1260 along with Cd, Cr, Cu, Pb, Ni, Mn, and Zn. Soil properties, mineralogy and pretreatment are described in detail in Chapter 5. The initial soil PCB concentration (92.4 mg kg^{-1}) was estimated by gas chromatography-mass spectrometry (GC-MS) (Saturn 2000, Varian, Walnut Creek, CA, USA) following hydrodehalogenation with $Pd^o/\gamma\text{-}Al_2O_3$ (Ehsan et al, 2003). The heavy metal burden of Al, Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn in soil digest, prepared by conventional nitric acid block digestion, was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (VISTA-MPX, Varian Australia Pty Ltd., Australia).

6.2.2 Mixed Contaminant Extraction/Mobilization

In a typical trial, soil (3g) was equilibrated with 20 mL EDTA solution (0.1M) or EDTA solution containing 100 g L^{-1} cyclodextrin in 50 mL centrifuge tubes immersed in an ice bath. Equilibrations were achieved by sonicating the soil suspension for 10 min with an ultrasonic homogenizer (XL 2020 Sonic dismembrator, Misonix Inc., NY, USA). An extended horn of 25 cm L x 1.2 cm W, tuned at 20 kHz frequency, delivered ultrasonic energy (240 W) in a pulsed mode with a fixed vibration amplitude setting of 6. The equilibration consisted of pulsed surges of power delivered for 3 s followed by a 2 s cooling phase. Post sonication, the suspension was centrifuged at 4000 rpm. A portion of the supernatant fraction was retained for determination of the total PCB or heavy metal content and the remainder was treated to remove solubilized contaminants.

6.2.3 PCB Removal from Soil Extracts

PCBs in the supernatant fraction were back-extracted three times with hexane (3 mL) to partition PCBs from the soil extract. The cumulative hexane fraction was centrifuged (4000 rpm, to remove aqueous cyclodextrin). PCBs in the hexane were determined by GC-MS following hydrodechlorination in the presence of H_2 purged $Pd^o/\gamma\ Al_2O_3$ (Ehsan et al, 2003).

6.2.4 Heavy Metal Removal from Soil Extract

Post PCB removal with hexane, the aqueous soil extracts were treated for metal removal. In a 50 mL test tube, magnesium flakes (Mg^o, 0.5g) were combined with K_2PdCl_6 (5 mg) followed by the addition of the soil extract. The resulting suspension was stirred, heated to 70 ^oC, and permitted to react for 2 h. Post reaction, solid $Ca(OH)_2$ (40 mg) was added and final pH was adjusted to 12 with NaOH. The sample was centrifuged at 4000 rpm followed by filtration to remove precipitated metal oxy-hydroxides. Aliquots of extract {before and after treatment with Mg^o and $Ca(OH)_2$} were set aside for metal analyses.

6.2.5 Recycle of Mobilizing Reagents

Post PCB and heavy metal removal, the pH of the cleaned mobilizing reagent emulsion was adjusted to 6 and then re-equilibrated with the soil particulate fraction to mobilize more toxicants. Soil particulates were equilibrated again by sonication with 20 mL of cleaned mobilizing reagent. The resulting aqueous supernatant fraction was treated for PCB and heavy metal removal as described above. After 3 washing cycles, the soil particulate fraction was oven dried and analysed for residual PCBs and heavy metal contents. A portion of the soil residue (0.2 g) was further equilibrated with deionized water (0.5 mL) for 1h and the supernatant fraction was assayed for cyclodextrin and EDTA contents as described below.

6.2.6 Cyclodextrin Analysis

Quantitative cyclodextrin analyses were performed using an ABB Bomem (Quebec City, QC, Canada) MB-150 dual range (NIR/mid-IR) FTIR spectrometer equipped with a deuterated triglycine sulfate (DTGC) detector and purged with dry air from a Balston dryer (Balston, Lexington, MA, USA). Single bounce attenuated total reflectance (SB-ATR) spectra were recorded with the use of ZnSe accessory (Harrick, Ossining, NY, USA). The spectral collection parameters for SB-ATR analysis were 32 co-added scans at resolution of 8 cm^{-1} and a gain of 1.0. In all cases, a background single beam spectrum was recorded prior to loading sample, followed by a series of aqueous standards of cyclodextrin. The quantity of cyclodextrin was calculated from the intensity of carbohydrate strong band at 1045 cm^{-1}.

6.2.7 EDTA Analysis

The combined concentration of free and complexed EDTA was determined spectrophotometrically (Flaska, 1964). Aqueous soil extract (1mL) was added to a glass tube (1 mm I.D. x 10 cm.) containing 0.1M $Cr(NO_3)_3 \cdot 9H_2O$ solution (1 mL). The pH of the solution was adjusted to 2-3 with HNO_3 (200 g L^{-1}) followed by digestion at 100 °C for 15 min. On cooling, the absorbance at 555 nm was recorded *vs.* a blank sample containing DDW that had been treated analogously.

6.3 Results and Discussion

6.3.1 PCBs Mobilization

The cyclodextrins, along with their relevant properties are summarized in Table 6.1. A previous study (Chapter 4 and 5) with surfactants had demonstrated that 10 min of sonication was sufficient for optimum processing without the loss of any contaminant mobilization efficiency, thus all soil washings for mobilization of mixed contaminants were performed with 10 min of ultrasonication. Initially, cyclodextrin extraction concentrations were optimized. Randomly methylated β-cyclodextrin (RAMEB) was selected to study the effect of increasing concentration on the mobilization of PCBs. It was observed that with increasing concentration of RAMEB, there were corresponding increases in the amount of PCBs extracted from soil. As summarized in Figure 6.1, increased concentrations of CD from 1%, 5%, 7%, 10% to 15% w/v resulted in increased recovery of PCBs from 6%, 17%, 36%, 40% to 48% respectively. Although a high concentration of cyclodextrin might not be cost effective from a soil remediation perspective, the10 % concentration was selected for further studies on the basis of increased recovery of PCBs with the anticipation that the chemical could be recycled. Subsequent soil washings with either RAMEB or HP-β-CD were performed with a cyclodextrin concentration of 10% (w/v).

The comparison of the 10% RAMEB soil washing experiments conducted in the presence/absence of EDTA revealed that the increase in PCB solubilization was approximately the same for both experiments (data not shown). Subsequently, RAMEB and HP-β-CD were evaluated for PCB extraction efficiency and their compatibility with reagent recycle in the presence of EDTA. The results of soil washing with RAMEB and HP-β-CD are presented in Table 6.2 along with extraction efficiencies as measured by the percent of PCBs mobilized from the soil. At 10% (w/v) cyclodextrin concentration, a single soil-equilibration with soil, an increased PCB mobilization was achieved with RAMEB (~41%) in comparison to HP-β-CD that mobilized only ~24% of the initial PCB burden under similar conditions. Subsequently, cyclodextrin release and recycle conditions were optimized. All recycle trials were carried out with 10 min of sonication in the presence of EDTA. PCB extraction efficiencies with reclaimed cyclodextrins in aqueous extracts for 3 wash cycles of soil are also summarized in Table 6.2.

Table 6.1 Chemical and physical characteristics of cyclodextrins selected for the PCB extraction study

Properties	RAMEB	HPCD
Molar mass (g mol^{-1})	1303	1460
Substituent group R	$-CH_3$	$-CH_2CH(OH)CH_3$
Degree of substitution	1.8	0.8
pH $_{H2O + EDTA}$	4.2	4.6
Viscosity/cP[a]	0.3799	0.3251

[†] Viscosity/ cP = Viscosity of cyclodextrin in 0.1 M EDTA (100 g L^{-1}) at 600 rpm and 20 °C.

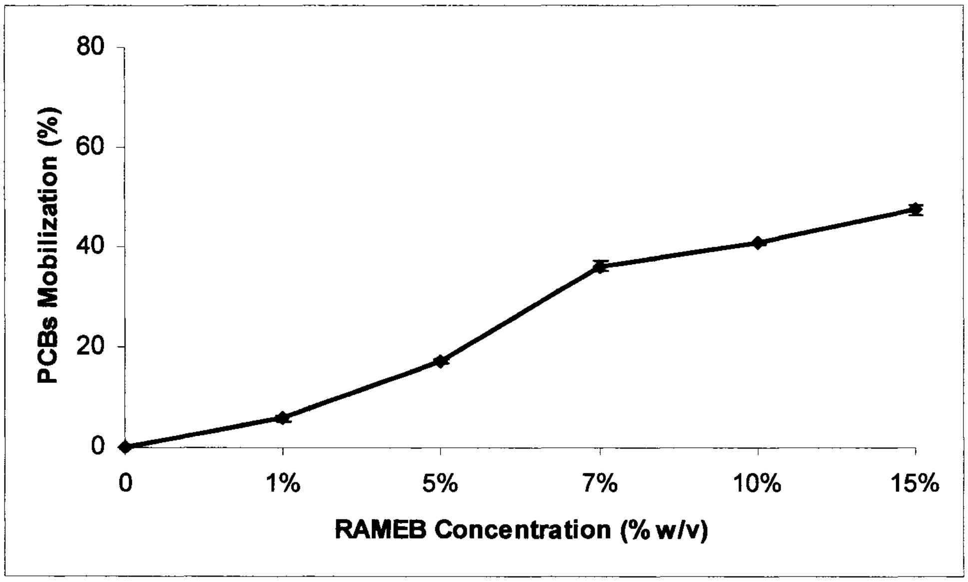

Figure 6.1 Effect of RAMEB concentration on PCBs mobilization efficiency (% ± 1 SD) from soil.

When RAMEB was used to facilitate the mobilization, the 2nd and 3rd soil washing with recycled cyclodextrin represented 35% of cumulative PCBs mobilization over 3 washing cycles. The quantity of extracted PCBs decreased with each washing cycle with recycled cyclodextrin. Extraction efficiencies for a series of companion trials that involved the use of fresh reagents each cycle are summarized in Table 6.3. No appreciable difference for PCBs mobilization was observed between fresh (36.0 μg g^{-1}) or recycled (35.1 μg g^{-1}) RAMEB. In toto, extraction with fresh reagent resulted in 78 % PCBs mobilization and 76 % PCBs were mobilized with the recycled cyclodextrin.

The soil sonication-washing with HP-β-CD was observed to be appreciably less effective at mobilizing PCBs from the soil. Three washes with regenerated HP-β-CD mobilized only 40% of total PCB burden from the soil. Whereas, the first equilibration resulted in the mobilization of 10.9 μg g-1, the second and third equilibrations added a further 5.6 μg g-1 and 2.1 μg g^{-1} respectively to the total mobilized (Table 6.2). The same equilibration/washing procedure but with fresh HP-β-CD/EDTA reagents for each cycle, only marginally increase (~2 %) the PCB extraction efficiency in comparison to efficiencies with reclaimed HP-CD (Table 6.2 *vs.* Table 6.3). The cumulative PCB extraction efficiency with fresh *versus* recycled reagents indicated that HP-β-CD could be regenerated efficiently and recycled. The reduced efficiency of HP-β-CD as compared to RAMEB, despite the fact that both are derivatives of β-cyclodextrin and have a similar cavity size, might be the result of the nature of substituent group. The hydroxypropyl group being larger in size as compared to methyl group may have caused some steric interference for the inclusion of PCB as suggested by Shirin et al. (2003).

6.3.2 Heavy Metals Mobilization

The soil that was studied in these experiments had been burdened with excesses of persistent organic pollutants and heavy metals. Sampled at a landfill site, soil was characterized in detail in terms of soil properties, metal fractionation, and the quantities of target metals (Chapter 5). Post equilibration, metal extraction efficiencies were determined in the presence of a sparing quantity of EDTA alone or in combination with RAMEB or HP-β-CD.

Table 6.2 Mean cumulative mobilization of PCBs (mg kg^{-1} ± 1 RSD †) for three successive washes of the soil (3g) with the same charge of EDTA + cyclodextrin (100 g L^{-1}) solution

Cyclodextrin	1st extraction (N = 8)	2nd extraction (N = 4)	3rd extraction (N = 3)	Sum (mg kg^{-1})	Cumulative PCBs Mobilized (%)
RAMEB	19.0 ± 10 (41.2 %)	12.3 ± 3 (26.7 %)	3.8 ± 5 (8.2 %)	35.1	76.1
HP-β-CD	10.9 ± 5 (23.6 %)	5.6 ± 4 (12.1 %)	2.1 ± 12 (4.6 %)	18.6	40.3

† RSD = One relative standard deviation based on N replicate trials.

Table 6.3 Mean cumulative PCB mobilization (mg kg^{-1} ± 1RSD [†]) for three successive washes of the soil (3g) with EDTA + cyclodextrin (100 g L^{-1}) using fresh reagents each time

Cyclodextrin	1st extraction (N = 5)	2nd extraction (N = 3)	3rd extraction (N = 3)	Sum (mg kg^{-1})	Cumulative PCBs Mobilized (%)
RAMEBCD	19.4 ± 2 (42.1 %)	11.8 ± 7 (25.6 %)	4.8 ± 4 (10.4 %)	36.0	78.0
HP-β-CD	10.9 ± 5 (23.6 %)	6.0 ± 3 (13.0 %)	2.5 ± 9 (5.4 %)	19.4	42.1

[†] RSD = relative standard deviation based on N replicate trials.

A single equilibration mobilized 29-31% of the Cd, 46-49% of the Cu, 27-29% of the Mn, 67-68% of the Pb and 38-41% of Zn with 0.1M EDTA in combination with RAMEB or HP-β-CD (Table 6.4). In comparison to metal extraction with only EDTA, the added presence of RAMEB (col 2 *vs*. col 3) or HPCD (col 2 *vs*. col 4) in the reagent mixture did not influence the mobilization of metals perceptibly. Similar to non-ionic surfactant (Brij 98), the presence of cyclodextrin did not influence the extraction efficiency of EDTA for most of the metals (col 3 *vs*. col 5 and col 4 *vs*. col 5).

Subsequent experiments involved the stripping of metals from metal•EDTA complexes to release EDTA that could be used to mobilize more heavy metals. The release of metals from their M•EDTA complexes is summarized in Figure 6.2. Most of the metals were stripped efficiently from their M•EDTA complexes and precipitated as insoluble hydroxides when $Ca(OH)_2$ had been added after 2h reaction with Pd^o/Mg^o. For EDTA alone or in combination with RAMEB or HP-CD, no appreciable difference was found for the precipitation of Al, Cu, Fe, Mn, Pb and Zn. Metal precipitation was virtually complete for Al (99%), Cu (100%), Fe (100%), and Zn (100%) and very efficient for Mn and Pb (>90%). Relative to EDTA alone, the presence of cyclodextrin depressed the stripping of Cd and Ni from their EDTA complexes but slightly improved the precipitation of Cr (58%). Metal stripping followed the same trend for metal precipitation post the second and third (data not shown) equilibrations with reclaimed EDTA. The fluid properties (Table 6.1) of 10% w/v RAMEB or HP-β-CD solutions were very favorable for Mg treatment and filtration in comparison with high-viscosity surfactant suspensions.

Post metal removal and pH adjustment to 5, the suspension was recycled for further washing of the soil particulate fraction. The recycle procedure was repeated a second time. The cumulative quantities of metals extracted from the soil with 3 sonication wash cycles are summarized in Table 6.5. Three successive equilibrations with EDTA alone or in combination with RAMEB or HP-β-CD mobilized 57-67% of the Cu, 50% of the Zn, 78-83% of the Pb and 33 % of the Mn from soil. For Al, Cr, Fe, and Ni, the metal extraction was not very efficient (9%, 4 %, 3 %, and 20% respectively). The presence of RAMEB slightly improved the extraction efficiency for certain metal. For

Table 6.4 Mean percent (± 1 SD [†]) of the soil metal burden mobilized with a single equilibration of the soil (3g) with 20 mL EDTA (2 mmoles) or EDTA + cyclodextrin (100 g L^{-1})

Analyte	EDTA	EDTA + RAMEBCD	EDTA + HP-CD	EDTA + Brij 98
Al	6 ± 0.2	7 ± 0.4	8 ± 0.2	7 ± 0.6
Cd	35 ± 4	31 ± 3	29 ± 4	36 ± 1
Cr	3 ± 0.2	3 ± 0.3	3 ± 0.4	4 ± 0.3
Cu	42 ± 3	49 ± 3	46 ± 2	49 ± 1
Fe	2 ± 0.1	2 ± 0.3	3 ± 0.2	2 ± 0.2
Mn	28 ± 3	29 ± 2	27 ± 0.8	27 ± 0.5
Ni	15 ± 2	15 ± 1	15 ± 0.4	17 ± 0.5
Pb	66 ± 3	67 ± 5	68 ± 4	73 ± 0.7
Zn	42 ± 3	41 ± 3	38 ± 1	44 ± 4

[†] SD = standard deviation based on five replicate trials.

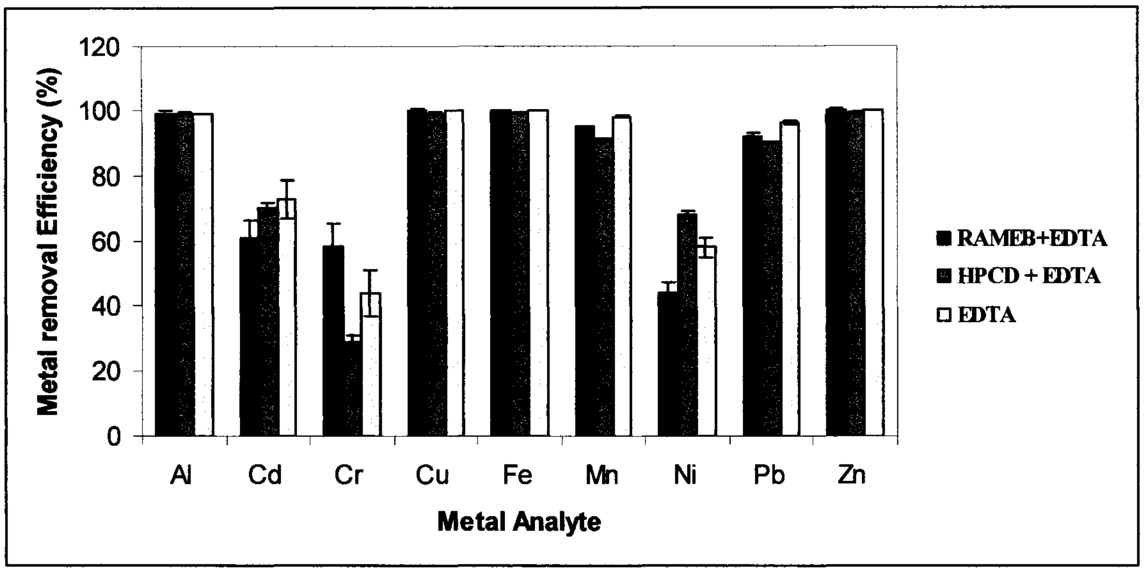

Figure 6.2 Metal removal efficiency (% ± 1 SD) from soil extracts after reaction with Pd^0/Mg^0 for 2h followed by the addition of Ca(OH)$_2$.

example, 64-67% of Cu and 82-83% of Pb were removed by the EDTA and RAMEB combination over 3 successive washings cycles as compared to 57% and 78% for EDTA alone. The cumulative extraction efficiency of target metals for three sequential washes with fresh reagents is also summarized in Table 6.5. In comparison to recycled EDTA, three successive equilibrations with fresh reagent were characterized by an appreciable increase for the mobilization of all metals (column 2 *vs*. col 3, col 4 *vs*. col 5 and col 6 *vs*. col 7). Again, the presence of either RAMEB or HP-CD with EDTA did not contribute to these differences. Cumulative metal extraction with fresh reagents were characterized by a mean increase of 7-9% for Cd, 13-15% for Cu, 13-16% for Ni, 7-12% for Pb, and 11-17% for Zn from the soil when compared with recycled reagents. Even though, fresh EDTA was characterized by increased extraction efficiency, the recovered EDTA demonstrated the potential for economic viability of EDTA based remediation. The recycling technique mobilized virtually all of Cd, Cu, Mn, and Pb (col 2 *vs*. col 5 or col 7). None the less, appreciable quantities of selected metals were mobilized from the soil (Pb, 78-83%; Cu, 57-67%; Cd, 42-49%; Zn, 51-67%) but only small quantities of Al (9%) or Fe (3%) were mobilized as predicted by fractionation study.

6.3.3 EDTA Fate Post Soil Washing and Mg Treatment

Analyses for EDTA in the aqueous phase that were performed at each stage of the process are presented in Figure 6.3. The initial quantity of EDTA added to the soil was used to calculate EDTA recovery. The first soil wash resulted in a 10% decrease in concentration possibly due to adsorption of the chelating regent to the solids phase. As expected, the PCB back-extraction with hexane did not cause any detectable EDTA loss and only a small portion (a further 2-3%) was lost during the Mg^o treatment and subsequent filtration. The recovery of EDTA post 2nd and 3rd soil equilibration again resulted in a further 9% and 8% loss to the soil particulates fraction. A cumulative loss of 32 % was observed during three washing cycles, of which only 4-5% was the result of two Mg^o treatments and two hexane back extraction. EDTA recovery (68%) from soil, hexane, or Mg^o treatment post three wash cycles was independent of the presence and kind of cyclodextrin in the solution.

Table 6.5 Mean cumulative metal recoveries (% ± 1 SD[ϕ]) in the supernatant fraction after equilibration of soil (3g) with the same charge (recycle mode) of EDTA (2 mmoles) or with fresh reagent each time

Analyte	Σ(carb[†]+exch[‡]+red[§]) (%)	Cumulative % extracted					
		Recycled EDTA+Brij98	Fresh EDTA+Brij98	Recycled RAMEB +EDTA	Fresh RAMEB + EDTA	Recycled HPCD+EDTA	Fresh HPCD+EDTA
Al	29	9 ± 0.8	16 ± 0.8	9 ± 0.8	17 ± 2	9 ± 0.3	18 ± 3
Cd	45	41 ± 0.8	49 ± 0.8	39 ± 0.8	48 ± 3	34 ± 5	46 ± 1
Cr	8	5 ± 0.4	11 ± 0.4	4 ± 0.2	12 ± 0.3	4 ± 0.01	12 ± 0.6
Cu	44	64 ± 4	78 ± 4	67 ± 5	80 ± 7	64 ± 2	79 ± 5
Fe	7	3 ± 0.3	12 ± 0.3	3 ± 0.3	8 ± 0.4	4 ± 0.1	9 ± 0.7
Mn	31	31 ± 2	37 ± 2	33 ± 0.9	39 ± 2	31 ± 1	37 ± 0.8
Ni	34	19 ± 1	36 ± 1	20 ± 1	35 ± 2	19 ± 2	35 ± 2
Pb	80	84 ± 0.8	92 ± 0.8	82 ± 0.8	94 ± 1	83 ± 1	92 ± 2
Zn	91	52 ± 2	69 ± 2	50 ± 2	67 ± 5	49 ± 3	66 ± 4

[ϕ] SD = One standard deviation based on three replicate trials.

[†] Carbonate fraction

[‡] Exchangeable fraction

[§] Reducible fraction

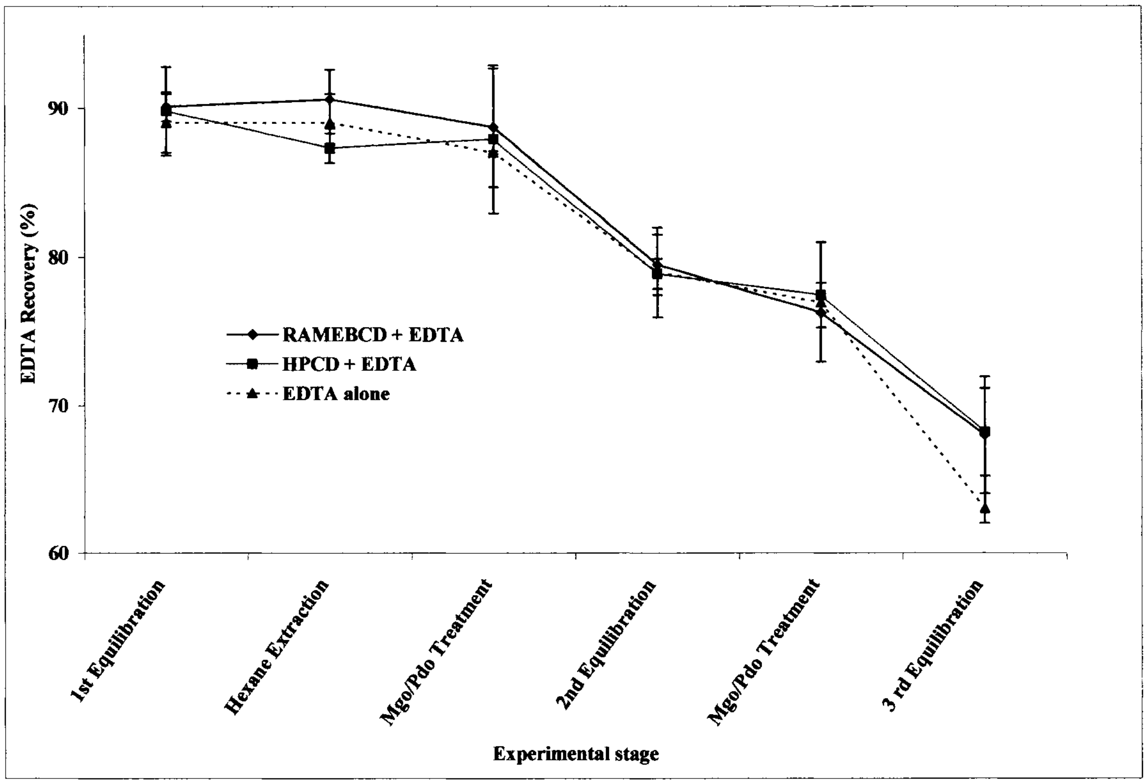

Figure 6.3 Mean EDTA recovery (% ± 1SD) post each experimental stage for three successive washes of soil (3g) with same charge of EDTA (2 mmole) or EDTA + cyclodextrin (100 g L^{-1}).

6.3.4 Cyclodextrin Fate during Soil Washing and Mg Treatment

The concentrations of RAMEB and HP-β-CD were monitored after each experimental stage to estimate the cyclodextrins adsorption to soil or losses to Mg^0 treatment. The reagents recovery post treatment was calculated on the basis of starting concentration of cyclodextrins (10 w/v %). As illustrated in Figure 6.4, only 3% RAMEB was lost to the soil particulate fraction after the 1st equilibration and a 5% decrease in the starting concentration of HP-β-CD was observed. This decrease in cyclodextrin content was not the result of biodegradation but was due to adsorption process in soil as samples were reanalyzed after 4 weeks. The quantities of RAMEB (97%) and HP-β-CD (95%) did not change perceptibly when the suspension was back extracted with hexane but a further loss of 1-2% loss was observed when suspensions were treated with Mg^0. Similar recoveries were observed for the recycle stages. In total, 4% of RAMEB and 5% HP-β-CD were sorbed to the particulate fraction during 3 soil washings and further 5% and 4% were lost during two Mg^0 treatments. Cyclodextrin stability during recycling stages resulted in equally efficient PCB mobilization with recycled cyclodextrin to that with the fresh reagent. The quantity of cyclodextrin remaining in the suspension (90-91 %) after the third soil wash indicated the potential of cyclodextrin recycle for economic viability during soil remediation.

6.4 Conclusion

Soil washing with mixture of cyclodextrins and EDTA can be an efficient remediation treatment for soil containing mixed contaminants. Results have demonstrated that RAMEB significantly increased the solubilization of PCB and some 76% of the total soil PCB burden can be extracted with three sequential washes with the same charge. Due to its less polar character and its impact on interfacial tension, RAMEB proved to be better than HP-β-CD. On the other hand, metal extraction efficiency of EDTA was not influenced by the cyclodextrins and extracted appreciable portions of most of the heavy metals. The recycling of reagents by cleaning the aqueous soil extract by back-extraction with hexane after each sonication/equilibration followed by heavy metal precipitation to liberate the EDTA, resulted in a soil particulate fraction that has been cleaned and a limited volume of aqueous extract that has been detoxified. The optimum conditions for

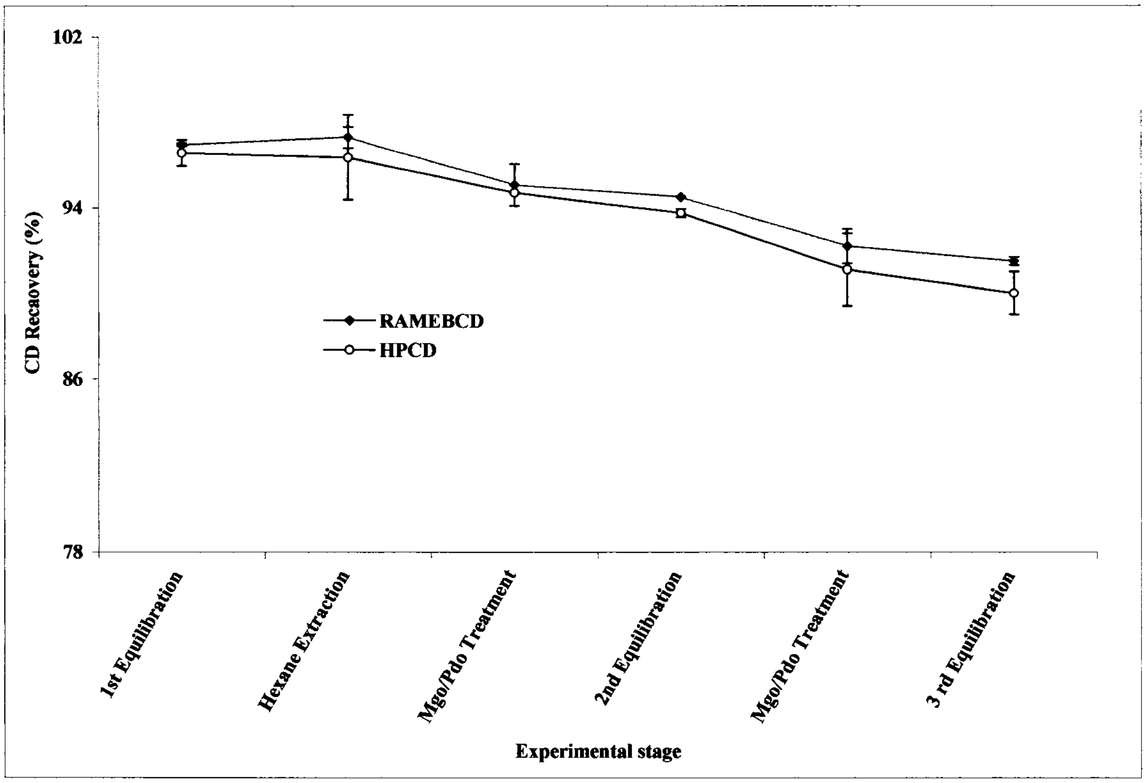

Figure 6.4 Mean Cyclodextrin recovery (% ± 1 SD) post each experimental stage for three successive washes of soil (3 g) with the same charge of EDTA (2 mmole) or EDTA + cyclodextrin (100 g L^{-1}).

EDTA and cyclodextrins regeneration were not influenced by the quantity of cyclodextrins or by the identity of the cyclodextrin. The success of the overall process was critically dependant on the efficiency of PCBs mobilization which, in this case, involved a high energy sonication that yielded fractions that were readily separated by centrifugation/filtration.

PREFACE TO CHAPTER 7

These studies have investigated the surfactant or cyclodextrin in combination with chelating reagent to mobilize PCBs and heavy metals simultaneously from a field contaminated soil while liberating the mobilizing aides for further use. In parallel, contaminants were detoxified. These studies have demonstrated that the combination of surfactant suspension or cycldextrin with EDTA mobilized appreciable quantities of both PCBs and heavy metals. It was also demonstrated that when a bimetallic mixture of Mg^o with Pd^o was reacted with soil extracts, metal removal was very efficient. It was further demonstrated that alumina supported Pd^o was very efficient for the hydrodechlorination of PCBs. Finally, the strategy of repeated soil washing with regenerated reagents mobilized appreciable quantities of both contaminants.

In the following Chapter, firstly a concise summary addresses the findings in the chronological order of this research. Secondly, a brief conclusion lists the contributions to knowledge. Thirdly, some suggestions for further studies are presented.

CHAPTER 7

SUMMARY AND CONCLUSION

7.1 Summary

A general background for the understanding of mixed contaminants as well as major sources of this contamination was provided in Chapter one. A brief introduction to the available remediation reagents suitable for the treatment of heavy metal or PCB contaminated soil was included. This research was undertaken based upon the judgment that the need for appropriate methods for mixed contaminants remained compelling. There is a requirement for more efficient mobilization of mixed contaminants, their detoxification into innocuous/less toxic products and an assessment of the cost savings associated with recycling the reagents. A novel approach/technique of combining a surfactants or cyclodextrin with a chelating agent for the simultaneous mobilization/extraction of PCBs and heavy metal was proposed along with the possible regeneration of reagents for recycling purpose.

Chapter two embodied a review of PCB dechlorination techniques, surfactant, and cyclodextrin potential for the mobilization of organic contaminants, and application of chelating reagent for the extraction of heavy metals. An overview of soil washing relevant to PCBs and heavy metals removal was presented to assess the present soil remediation technique and to identify the most promising areas for further work.

In Chapter three, a new method for the dechlorination of highly chlorinated PCB congeners and Arochlor mixtures was extended to soil/sediment samples. The contaminated soil was suspended in hexane in the presence of $Pd^o/\gamma\text{-}Al_2O_3$ in a hydrogen atmosphere and then permitted to react for one hour at 65 ^oC. The reaction product dicyclohexyl, recovered in the hexane, was quantified by gas chromatography mass spectrometry. The reaction was very efficient for soil/sediment in hexane suspension and virtually complete - no chlorinated intermediates were detected in the hexane extract of the $Pd^0/\gamma\text{-}Al_2O_3$ catalyst. More highly chlorinated congeners were apparently dechlorinated more rapidly, leading to the transient accumulation of less highly chlorinated intermediates prior to complete dechlorination. Hexane was observed to favor more complete hydrogenation when compared with methanol as reaction medium.

Hydrodehalogenation was considered to occur rapidly for the soil/sediment samples and apparently preceded hydrogenation. Soil samples that were burdened with higher PCB loadings required excess catalyst (0.05 g) otherwise reaction in the presence of palladium on γ-alumina (0.025 g) resulted in total hydrodechlorination but only partial hydrogenation (de-aromatization) as indicated by the presence of biphenyl, phenyl cyclohexane as well as dicyclohexyl within the crude product mixture. Derivatization directly within the sample matrix was used to estimate the total PCB content in soil/sediment by hydrogenation (hydrodechlorination and de-aromatization) of chlorinated biphenyl compounds. The proposed method was validated with the analysis of four certified reference materials and one spiked sample. The concentrations of PCBs in each of the CRMs were determined successfully and dicyclohexyl yields were in satisfactory agreement (~99 %) with the theoretical values. The principal advantages of this technique include convenience and simplicity and the principal shortcoming is that losses of dicyclohexyl product can become appreciable with extended reaction.

The feasibility of a washing process with nonionic/anionic surfactant in combination with ethylenediaminetetraacetate (EDTA) for the simultaneous mobilization of heavy metals and PCBs from a field contaminated soil was evaluated in Chapter four and Chapter five. The results related to PCB mobilization such as surfactant selection, surfactant regeneration and successive soil washing with reclaimed surfactant were discussed in Chapter four. Test soil that had been heavily contaminated with PCB and heavy metals was obtained from a landfill site. Before treatment, the soil was characterized for particle size, pH, percent organic matter, cation exchange capacity, PCB burden, and heavy metal content. A preliminary screen selected two anionic (Triton X-301 and Triton XQS-20) and one nonionic (Brij 98) surfactant (from among 10 commercial formulations) based upon PCB mobilization efficiency, interaction with soil, and losses to contaminant removal treatments. Studies demonstrated that 10 minutes of ultrasonic mixing of field contaminated soil with a combination of 30 mL L^{-1} surfactant suspension and a sparing quantity (2 mmoles) of EDTA mobilized appreciable quantities of PCBs. Relative to individual reagents, combinations of surfactant (Brij 98, Triton X-301, or Triton XQS-20) with EDTA did not influence the PCB extraction efficiencies perceptibly. The method of equilibration with the soil appreciably influenced the efficiency of PCB mobilization. Relative to the quantity of PCBs mobilized by sonication with Brij 98, the PCB recovery was decreased 30% if the soil was equilibrated by reciprocal shaking for 18 hours. Subsequently, unit processes including PCB removal by hexane back-extraction and precipitation of the HMs, generated aqueous washing suspension that was recycled twice to mobilize more contaminants. Three sonication-washes with the same charge of reagent mobilized appreciable quantities of PCBs (68 - 83%) and appreciable quantities of metals. Of the three surfactants, the Brij 98 formulation proved to be the most efficient for three successive extractions with a single charge, mobilizing 83% of the PCB burden whereas companion extractions that used fresh reagent each time, mobilized 87% of the soil PCB content. On the other hand, the quantity of PCB mobilized with recovered anionic surfactant (Triton X301, 71%; Triton XQS-20, 68%) decreased in subsequent washings relative to same number of washing with fresh surfactant. This decrease was the result of anionic surfactant losses during EDTA regeneration process with zero-valent magnesium.

Chapter five described the heavy metal extraction efficiencies of EDTA and HEDC in the presence of surfactants. The soil textural properties were supplemented by a soil fractionation study. These fraction studies indicated that high proportion of Zn (91%) and Pb (80%), intermediate proportion of Cd (45%), Cu (44%), Mn (31%), Ni (34%), and Al (29%) but only minor quantities of Cr (7%) and Fe (8%) were susceptible to complexometric extraction. A sparing quantity of EDTA in the combination with nonionic or anionic surfactant mobilized most of analyte metals (Cd, Cu, Mn, Pb, Zn, Ni, and Cr) from a mixed contaminated soil. Post PCB removal, the aqueous washing suspension was regenerated by precipitation of the HMs (induced by corrosion and hydrolysis of Mg^0) to provide a cleaned soil and innocuous extract. Finally, the washing suspension was recycled twice to mobilize more contaminants from the soil particulate fraction. Three equilibration with reclaimed EDTA in admixture with surfactant mobilized virtually all of the available Cd, Cu, Mn, and Pb (~ 99%) and lesser amounts of the Zn (56%), Ni (59%), and Cr (50%) but only small quantities of soil minerals (Al, 28% and Fe,30%). Anionic surfactant did not appreciably change the efficiency of mobilization of most heavy metals (Al, Cd, Cr, Fe Mn, Ni, and Zn) but nonionic surfactant did increase recovery of Cu and Pb by 7 % relative to sonication with EDTA alone. Analogous experiment with a mixture of two chelating reagents [EDTA and HEDC (1:2 m/m)] proved to be detrimental to the mobilization of all analyte metals. The presence of surfactant together with mixed chelants did not restore the extraction efficiencies observed with EDTA alone.

The demetallization of metal•EDTA complexes in soil extracts was efficient for most analytes (~99%) but was influenced by the identity of the surfactant. Whereas, metal precipitation efficiency for Cd, Ni, and Pb was decreased in the presence of anionic surfactant, nonionic surfactant enhanced the EDTA release. EDTA recovery (>60%), post three cycles of soil washing, hexane back-extraction and Mg^0 treatment was similar for all reagent combinations. In toto, these studies demonstrate that PCB compounds and heavy metals can be co-extracted efficiently from soil with a single charge of washing suspension containing EDTA and a non ionic surfactant.

The feasibility of the remediating mixed contaminated soil using cyclodextrin in combination with EDTA was investigated in Chapter six. Two derivatives of β-cyclodextrin were evaluated for PCBs removal efficiency alone or in admixture with EDTA. Studies demonstrated that 10 minutes of ultrasonic mixing of field contaminated soil with a combination of 100 g L^{-1} cyclodextrin solution and a sparing quantity (2 mmoles) of EDTA, simultaneously mobilized appreciable quantities of PCBs and much of the analyte metals (Cd, Cu, Mn, Pb, Zn, Ni, Cr). Relative to individual reagents, combinations of cyclodextrin (RAMEB or HP-β-CD) with EDTA did not alter the PCB extraction efficiencies. Similar to surfactants, cyclodextrins did not appreciably change the efficiency of mobilization of most heavy metals (Al, Cd, Cr, Fe Mn, Ni, and Zn) but did slightly increase the recovery of Cu and Pb. Three sonication-washes with the same charge of reagent mobilized appreciable quantities of PCBs (40 - 76%) and quantitatively extracted the labile fraction [Σ(carbonate + exchangeable + reducable)] of the Cd, Cu, Mn, and Pb. RAMEB proved to be the more efficient than HPCD for PCB extraction. Three successive extractions with a single charge of cyclodextrin mobilized almost same quantity of PCBs (RAMEB, 76%; HP-β-CD, 40%) as the companion extractions that used fresh reagent each time (RAMEB, 78%; HP-β-CD, 42%).

7.2 Conclusions

These studies have identified novel approaches of using surfactant or cyclodextrin in combination with EDTA for the simultaneous desorption of mixed contaminants from soil. They have combined techniques for the regeneration of mobilizing aids with the recycling of reagents and dechlorination of polychlorinated biphenyl (PCB) compounds. This project is one of the very first applications of such single extraction system for the efficient mobilization of both PCBs and heavy metals from field contaminated soil. Based on the results from several experiments, this research dissertation can be concluded as having made the following major contributions to knowledge:

1. A novel washing procedure to simultaneously mobilize mixed contaminant from historically contaminated soil was demonstrated. PCBs and heavy metals were co-extracted efficiently from soil with a single washing suspension containing EDTA and surfactant or EDTA and cyclodextrin.
2. The possibility of recycling the surfactants or cyclodextrin by back-extraction with hexane to remove hydrophobic organic contaminants was optimized. The results have demonstrated that recovery of surfactant from soil extracts was efficient for PCBs removal but was influenced adversely by the treatment to remove metals.
3. A technique to demetallize metal•EDTA complexes efficiently in aqueous soil washing suspensions (containing surfactants or cyclodextrin) using zero-valent metal/bimetallic mixture (Mg^o/Pd^o) and $Ca(OH)_2$ was optimized. Release of EDTA was efficient for most metals but was influenced by the nature of the surfactant.
4. A complete process of mobilizing mixed contaminants with recycling of the mobilizing aid and the detoxification of contaminants has been demonstrated. Relative to three washes using fresh reagent, the use of recycled reagent was somewhat less efficient for both PCBs and metals but still resulted in clean soil and the generation of a limited volume of aqueous extract that was readily detoxified.

5. The possible application of soil remediation using soil washing aided by high energy sonication was demonstrated. Ultrasonication improved the soil remediation process by increasing both the rate of equilibration and the recovery of contaminants.
6. A reliable and quantitative analytical method was developed to determine the total PCB concentration in soil by hydrodechlorination of PCBs into dicyclohexyl. The procedure was validated by performing analyses on several certified reference materials.

7.3 Recommendations for Future Research

Future studies for the simultaneous removal of organic and inorganic contaminants from soil should include the following:

1. The continuation of current laboratory-based investigations with other field-contaminated soils and different types of contaminants such as PAHs, organochlorine, and BTEX compounds as well as radionuclides to provide potential types of mixed contaminants which can be removed by a mixture of surfactant/cyclodextrin and EDTA.
2. Further investigations need to identify other surfactants formulations that are more efficient at mobilizing PCBs and are more resistant to metal removal treatments. Since biosurfactants are environmentally friendly, they should be tested instead of commercial surfactants in combining with EDTA to use as washing agents for metal and organic removal from soils.
3. Cyclodextrins as alternate remediation agents are more favorable because their chemical nature offers the potential for the extraction of hydrophobic contaminants and impart less toxicity to the soil. Future studies need to identify other cyclodextrin derivatives for enhanced mobilization of PCBs from soil. Research could also be focused on the developing more efficient and cost effective derivatives of cyclodextrin.

4. Further investigations need to identify other iminodiacetate complexing reagents (EDTA analogs) that in combination with surfactants or cyclodextrin are capable of mobilizing metals from soil more efficiently and can be efficiently recycled.
5. The application of soil washing aided by ultra-sonication using a single extraction system as remedial technology in *ex- situ* soil washing or *in-situ* soil flushing.
6. Further optimization of bimetallic treatment for efficient demetallizing of metal•EDTA complexes should be carried out. The bimetallic accelerator Pd^o/Mg^o used in this study should be investigated for possible recycling to reduce the cost and to prevent any secondary contamination.

APPENDIX

There remains a lack of an efficient technique to remediate soils that have been burdened with mixed contaminants. Ideally, the process would be efficient, economical and would have a minimal environmental impact. Superfund amendments (U.S. EPA, 1988) have spurred interest in technologies that detoxify the contaminants or drastically reduce their availability to biota. Newer technologies have emphasized detoxification of contaminants along with the recovery of reagents because a major obstacle in implementation of soil remediation techniques remains the high cost of the techniques.

There are numerous treatment technologies for the removal of either heavy metals or hydrophobic organic contaminants. These techniques transfer toxicants from one medium to another and concentrate them efficiently. From an environmental point of view, the transfer of contaminants from one medium to another is not a detoxification process per se; it does not make them less available to contacting organisms. Eventually, the cost of such technologies become too high whether measured in dollars spent for treating the soil or for the safe disposal of contaminants.

This short supplementary section attempts to estimate the cost of the chemical inputs required to treat 1Kg of soil contaminated with both PCB and heavy metals.

Cost to Wash the Mixed Contaminated Soil

The main reagents that were used to wash the soil in these studies were either surfactant or cyclodextrin and EDTA. The chemicals needed to recover mobilizing reagents were associated with EDTA recovery and included zero-valent magnesium (Mg^0), the accelerator K_2PdCl_6 (5% w/w), and $Ca(OH)_2$ to raise the process pH to 12. The quantity of Mg^0 available for metal precipitation was estimated from the pH of the mixture post reaction that was observed to be approximately 12. Thus, final $[OH^-]$ was 1×10^{-2} M and 0.005 mole of Mg^0 must have been hydrolyzed to generate this quantity of hydroxide in one liter. For three soil wash cycles, mobilizing aids were added prior to the first wash and were recycled twice after regeneration.

Table A.1 provides an estimate of the costs of chemicals (based on the Alfa Aesar or the Aldrich 2005 Chemical Catalogue prices) consumed by three soil washes with a

Table A.1 Cost comparison of three soil washes with fresh Brij 98 to that with recycled Brij 98 at pH 12

Chemical	\$ Cost[†]/g	Quantity of reagent required for washing soil (g Kg^{-1} of Soil)	3 soil washing with fresh reagent	3 soil washing with recycled reagent
$Ca(OH)_2$	\$0.041	13.33	\$0.55[§]	\$1.10
Mg granules	\$0.098	0.80	\$ 0.06[§]	\$0.12
K_2PdCl_6	\$22.80	0.04	\$0.09[§]	\$1.80
Brij 98	\$0.10	200	\$60.00	\$19.99
EDTA	\$0.071	0.25	\$0.05	\$0.02
Total	-	-	\$60.75	\$23.03
Value of recovered surfactant	-	-	\$54.00	\$18.2[§]
Actual cost	-	-	\$6.75	\$4.83

[†] Cost based on Alfa Aesar or Aldrich Chemical Catalogue prices, 2005-2006.
[‡] Cost of two EDTA recovery treatments.
[§] Cost of reagents spent on soil washing to recover Brij 98 (91%) and EDTA (65%) post three soil washes.

single charge of mobilizing aids and compare it with the cost of three soil washes using the same concentrations of fresh reagents for each wash using the Brij 98/EDTA combination as an example. The actual quantities of reagents (surfactants/cyclodextrin/Mg^o/Pd^o) consumed have not been evaluated to treat larger soil samples. The estimates below are based on a scale up of the quantities of reagents consumed on a laboratory scale (3g). The estimates of costs for hexane and Pd^o/Al_2O_3 that were used for surfactant recovery and PCBs detoxification are not included in the table because their amounts are not proportional to sample volume.

It is evident from the Table A.1 that recycling treatment can partially offset the cost associated with the application of these remediation reagents. The interesting aspect of the integration of reagent recovery/regeneration during soil washing is not only the saving in the use of Brij98 and EDTA but also the reduction of liquid waste that would require safe disposal of the processing wastes. The ability to recycle these reagents will also reduce their loading into the environment which can cause adverse secondary problems. Although the experiments were conducted over three cycles, the recycled reagents can continue to be recycled for several more cycles. Obviously, some of the Brij 98 and EDTA will be lost during the recycling process and will need to be replaced to maintain the extraction efficiency. The cost of Pd is anticipated to be the major limitation in using this technique, however, other ways of Mg hydrolysis can be explored.

Over all, it can be concluded that this technique is appealing because it not only serves to remediate the mixed contaminated soil but at the same time detoxify the contaminants. The cost saving offered by recycling and detoxification processes make it substantially relative to conventional remediation strategies, such as excavation and disposal and the added expense of recycling reagents is not appreciable.

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