Determination, mobilization and dechlorination of polychlorinated biphenyl (PCB) compounds in contaminated soils

By

Qixiang Wu

Department of Food Science and Agricultural Chemistry
Faculty of Agricultural and Environmental Sciences
McGill University, Montreal
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Abstract

Polychlorinated biphenyls (PCBs) are a group of 209 chemical congeners that are toxic and persistent organic contaminants that have been present in the environment for several decades. It has been estimated that some 11 million tons of PCBs have contaminated soil, sediments, vegetation and animals. About 300 million tons of PCBs, that remain in use in North America, represent a potential source of contamination that can further deteriorate the environment.

Due to their toxicity, physical and chemical stability and environmental persistence, PCBs have attracted a great deal of attention and have encouraged researchers to develop new techniques/approaches to detoxify PCBs and PCB contaminated matrices in a rapid, efficient and environmentally friendly manner. In 2000, the market for PCB treatment technologies is estimated to be \$300–\$600 million (Canadian) dollars.

This study investigated novel approaches/techniques for PCB dechlorination with zero-valent metals or bimetallic mixtures; optimised a method for PCB determination within contaminated soil/sediments and PCB washing/flushing from contaminated soil. Soil washing/flushing was combined with supercritical carbon dioxide ($scCO_2$) mobilization dechlorination *on-line* using zero-valent metals. Studies have demonstrated that PCB can be dechlorinated efficiently by heated columns of zero-valent metal or bimetallic mixtures. The limit of detection for PCBs within contaminated soil was estimated to be 0.15 mg/kg for a simple procedure that converted PCB residues to biphenyl. PCBs were flushed efficiently from polluted soils into surfactant suspension and then back-extracted into supercritical CO_2. Finally, they were dechlorinated virtually quantitatively in a continuous *on-line* process using heated columns of zero-valent bimetallic mixtures. The dechlorination yield for PCB extracts from contaminated soil or from PCB surfactant mixture was greater than 99.5%. The treated surfactant suspensions could be recycled to extract more PCBs from the contaminated soil. The techniques/approaches developed in this study would seem to have a broad application in PCB dechlorination/detoxification and in the remediation of historically contaminated soil/sediments.

Résumé

Les diphéniles polychlorés (DPC) sont un groupe de 209 molécules chimiques qui sont des contaminants organiques toxiques et persistants qui ont été présents dans l'environnement pendant plusieurs décennies. On estime qu'environ 11 millions de tonnes de DPC ont contaminés les sols, les sédiments, la végétation et les animaux. Environ 300 millions de tonnes de DPC sont toujours utilisés en Amérique du Nord, ce qui représente une source potentielle pour détériorer l'environnement. En raison de leur toxicité, leur stabilité physique et chimique, et leur persistance dans l'environnement, les DPC ont attirés l'attention de nombreux chercheurs à développer de nouvelles techniques/approches pour déchlorurer des matrices contaminées de DPC d'une façon efficace et rapide. En l'an 2000, on estime que le marché pour traiter les DPC est de \$300~\$600 millions (dollars canadiens). La présente étude démontre l'utilisation de nouvelles approches/techniques pour la déchloruration de DPC en utilisant des métaux de valence zéro ou des composés bimétalliques. L'optimisation d'une méthode pour déterminer les DPC de sols/sédiments contaminés fut développer de même que le 'lavage/purgage' de DPC de sols contaminés. Le 'lavage/purgage' de sols contaminés fut combiné avec l'extraction par fluide supercritique au dioxide de carbone (SC-CO_2) et les métaux de valence zéro. Ces études ont démontrées que les DPC peuvent être déchlorurés avec efficacité en chauffant des colonnes de métaux de valence zéro ou des composés bimétalliques. La limite de détection des DPC pour les sols contaminés fut estimée à 0.15 mg/kg pour la conversion de résidus de DPC au composé de diphénile. Les DPC de sols pollués furent purgés efficacement dans une suspension d'agent tensio-actif pour être par la suite extrait avec SC-CO_2. Finalement, les DPC furent déchlorurés quantitativement dans un procédé en continu utilisant des métaux bimétalliques de valence zéro. Le rendement de déchloruration fut de 99.5% et plus pour les extraits de DPC de sols contaminés ou les mélanges d'agent tensio-actif de DPC. Les suspensions d'agent tensio-actif furent recyclées de nouveau pour extraire de plus amples DPC de sols contaminés. Les techniques/approches développées dans cette étude ouvre de nombreuses perspectives d'applications pour la déchloruration/ détoxification de DPC et pour la remédiation de sols/sédiments contaminés.

Contribution of Co-authors

The present work has been *supported by* Strategic grants from the Natural Science and Engineering Research Council of Canada (NSERC). The research has been supervised by Dr. William D. Marshall from McGill University (Montreal, Canada). Dr. William D. Marshall is co-author for all the materials that have been published and will be co-author for the publications that have been submitted / accepted for publication.

Dr. Abdul Majid from the Institute for Chemical Process and Environmental Technology, National Research Council of Canada contributed to part of this work by supplying some PCB extract that had been isolated from contaminated soil using a patent technique and by providing supervisory assistance. He is a co-author for part of the project.

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Table of Contents

List of Figures

List of Tables

Table No. Page

Abbreviations and Glossary

Abbreviation	
AcA	Acetic Anhydride
ANOVA	Analysis of Variance
CAS	Chemical Abstract Service. CAS registry numbers are unique chemical identifiers
CB	Chlorobiphenyl
CEPA	Canadian Environmental Protection Agency
Cl	Chlorine
DME	Ethylene glycol dimethyl ether
ECD	Electron Capture Detector
FID	Flame Ionization Detector
GC	Gas Chromatograph, an analytical instrument
GC-MS	Gas Chromatograph Mass Spectrometry
HPLC	High performance liquid chromatograph
IBMK	Isobutyl methyl ketone
IUPAC	International Union of Pure and Applied Chemistry, IUPAC numbers are unique Chemical identifiers
kg	Kilogram (1000 g)
L	Litre
LOD	Limit of Detection
LOQ	Limit of Quantitation
mg	Milligram (0.001g)
mg/kg	Milligrams per kilogram
ml	Millilitre (0.001 litre)
MS	Mass Spectrometry
MW	Molecular weight
ng	Nanogram (0.000000001 g)
PCBs	Polychlorinated biphenyls

pg	Picogram (0.000000000001 g)
$scCO_2$	Supercritical carbon dioxide
µg	Microgram (0.000001 g)
µg/kg	Micrograms per kilogram (part per billion parts)
µl	Microlitre (0.000001 l)
US EPA	United States Environmental Protection Agency

Glossary of terms

Aroclor	Commercial PCB formulation containing many different PCB congeners in a mineral-oil carrier
CEPA	Canada Environmental Protection Agency
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)
Homolog	Group of PCBs having the same degree of chlorination
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 versa
Ortho	When referring to PCBs, ortho refers to the binding sites adjacent to the bridge between the two phenyl rings
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
Surrogate	Chemicals added to a sample prior to sample preparation to monitor for the loss of analyte during processing

Introduction

Rationale

Polychlorinated biphenyls (PCBs) are toxic, persistent organic contaminants that have been present in the environment for several decades (Erickson, 1997). According to studies (Rantanen *et al.*, 1975; Hester and Harrison, 1996), the global burden of PCBs is about 374,000 tons (31% of the cumulative world PCB production), of which 39 % is concentrated within the terrestrial and coastal environments. Although the total amount of PCBs produced annually has declined (on a worldwide basis) since the 1970s, the toxicological threat posed by these compounds has not decreased appreciably (U S Agency for toxic substance and disease registry, 1993). In fact, their persistence in the environment has been of growing concern due to their toxicity, low degradability, mutagenicity, and tendency to bioaccumulate (US EPA, 1996). Environmental cycling is suspected of being the current, major source of PCBs to soil outside of disposal and spill sites (U S Agency for toxic substance and disease registry, 1993). When PCBs are introduced into a soil medium they can become sorbed strongly and may remain there for many years. They are unlikely to be taken up by plants and therefore they are not readily mobilized from soil systems. The principal transportation route for PCBs through aquatic systems is from waste streams into receiving waters, with further downstream movement occurring by solution and readsorption onto particles as well as by the movement of sediments (Rantanen *et al.*, 1975). The widespread occurrence of PCBs in the environment and the apparent link to carcinogenesis has promoted an increasing world concern since the early 1970s, that has resulted in restrictions in using PCB in most countries.

According to information from Environmental Canada, approximately 40,000 tons of PCBs were imported into Canada prior to 1977, and there remains about 15,100 tons of PCBs still in use across the country. They were the first substances to be regulated and originally prohibited for certain applications under the Canada

Environmental Contaminants Act (1976). Several regulations have been developed in Canada for PCB compounds since 1988. Under these newer regulations, several standards, recommendations, guidelines and criteria for PCBs in the Canada environment have been established. The restriction for PCB application has increased the amount of PCB waste. By 1990, more than 150,000 tons of PCB wastes involving PCB contaminated soil, mineral oil, and other metallic components of electrical equipment had been stockpiled across Canada. Between 1989 and 1995, the federal government allocated $6 million for PCB destruction projects in Atlantic Canada, Quebec, and Ontario. With the implementation of PCB related regulations, more PCB waste will be produced and more financial resources will have to be allocated to the destruction and remediation of PCB contaminated media (Environment Canada, 1998).

Remediation of PCB matrices is a comprehensive process involving PCB extraction/ mobilization, PCB destruction and the restoration of cleaned materials. During the last two decades, more than 80 techniques have been developed for PCB destruction and decontamination (U S Agency for toxic substance and disease registry, 1993; US EPA 1996). However, the majority of these processes remain theoretical or they have been optimized only for small-scale destruction (US EPA, 1996). When used in the real-world, many methods still face challenges. The disadvantage of most methods for PCB remediation/destruction make it necessary to continue to develop increasingly efficient, rapid, and simple processes to destroy PCBs.

Objectives of theses studies

Due to the increasing concerns of PCB contamination and the potential deterioration of the environment, the strategy of these studies was focused on PCB dechlorination /detoxification and remediation of PCB contaminated soils. The major objectives were:

1) to apply the supercritical fluid technologies as an alternate method to conventional procedures for PCB mobilization from contaminated soils.

2) to explore novel techniques that use zero-valent metal/bimetallic particles as

accelerants that might rapidly and efficiently dechlorinate/detoxify PCBs and PCB contaminated materials.

3) to develop a quantitative analytical method that can accurately determine PCB concentrations within contaminated soils/sediments.

4) to investigate the feasibility of PCB extraction from contaminated soils using surfactant suspensions in combination with supercritical carbon dioxide (scCO_2).

5) to develop/optimize a process that combines PCB extraction with on-line dechlorination to make the PCB clean up procedure a continuous operation while recycling the surfactant back to the contaminated soil to mobilize more toxicant.

Organization of this thesis

This thesis is organized into 8 Sections. Section 1 provides a brief overview of the problem and lists the overall project objectives. Chapter 1 reviews background information on a range of topics that relate to PCB uses, environmental contamination and remediation/destruction processes. Chapter 2 describes the development and validation of a quantitative analytical method for the determination of PCB concentration in contaminated soils. Chapter 3 presents a novel approach/technique for PCB dechlorination under reducing conditions. Chapter 4 investigates PCB mobilization from contaminated soils with back-extraction from the soil extract. Chapter 5 evaluates the efficiency of PCB extraction from surfactant suspension and/or soil extracts with *on-line* dechlorination. Chapter 6 is the project summary and overall conclusions. The final section of this thesis contains the references.

Chapter 1

Literature review

1.1 Structure and nomenclature

Polychlorinated biphenyl (PCB) compounds are a group of 209 chemical congeners, each of which consists of 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, as illustrated in Figure 1.1. There are no known PCB that occur naturally. They were first synthesized some 100 years ago and have been available commercially available worldwide since 1929 (Erickson, 1997). All PCB mixtures were synthesized by chlorinating biphenyl with chlorine gas. The empirical formula of PCBs is $C_{12}H_{10-x}Cl_x$ ($x = 1$-10). The average degree of chlorination was controlled by the reaction conditions in order to yield the desired chemical and physical properties (Erickson, 1997; Rantanen *et al.*, 1975). When PCBs are grouped according to the degree of chlorination, the groups are called homologs. A given PCB homolog with different chlorine substituted at different positions are referred as to isomers. Individual PCB congeners are conventionally given a systematic name that identifies the position of chlorine substitution and the degree of chlorination.

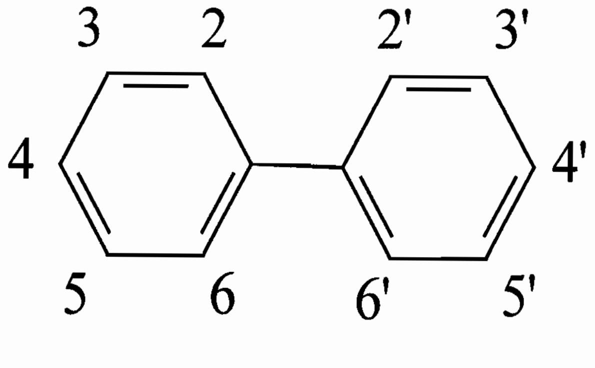

Figure 1.1 The General molecular structure of PCBs

Two different numbering systems continue to be used for PCB congener identification, each arranges all the congeners in order and assigns to them a number from 1 to 209. The first numbering system is the Ballschmiter system and was proposed by Ballschmiter and Zell in 1980 (Erickson, 1997). 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. This thesis uses the trademarks of Aroclor (Monsanto, Corp., USA) and the IUPAC numbering system.

1.2 The properties and use of PCBs

It was estimated that some 1.2 million tons of PCBs was manufactured in the world from 1929 until the late 1970s, when their production ceased in most western countries (Hester and Harrison, 1996). Polychlorinated biphenyls occur as liquids or solids, and they are clear to light yellow in color. PCBs have no odor or taste, and are insoluble in water, but are soluble in organic or hydrocarbon solvents, oils and fats (Table 1.1). PCBs are nonvolatile, chemically inert and do not undergo oxidation, reduction, addition, elimination or electrophillic substitution reactions except under extreme conditions. Most PCBs are oily liquids in which colour darkens and viscosity increases with increasing chlorine content. These characteristics, combined with their chemical stability, have made PCBs valuable for industrial applications such as in insulating liquids, capacitors and transformers and as additives in plastics, adhesives, paints, pesticides, carbonless copy paper, newsprint, fluoresence light ballasts, dyes and waxes (Table 1.2). PCBs do not degrade readily in the environment, and can bioaccumulate up the food chain with the possible adverse effects on wildlife and human health (Galveston-Houston Association for Smog Prevention, 1996). As increasing attention was turned to

Table 1.1 Characteristics of PCB mixtures

Aroclor	Density	Solubility in water at 25°C (μg/L)	Average number Cl/molecule	Approximate wt. Cl (%)
1221	1.18	15,000	1.15	21
1232	1.26	1,450	2	32-33
1016	1.37	420	3	40-42
1242	1.38	240	3	40-42
1248	1.44	52	4	48
1254	1.54	12	5	52-54
1260	1.62	3	6-6.3	60
1262	1.64		6.8	62
1268	1.81		8.7	68
1270	1.95		10	71

Source: from Erickson, 1997.

Table 1.2 Industrial uses of PCBs (1929-1975)

PCB use	Ton (millions)	Percentage of Total
World wide		
Capacitors	235	50.3
Transformers	123	26.7
Placticizers uses	42.8	9.2
Hydraulics and lubricants	30	6.4
Carbonless copy paper	16.8	3.6
Heat transfer fluids	7.5	1.6
Petroleum additives	0.4	0.1
Miscellaneous industrial uses	10.1	2.2
Total	467.4	100

Source: from US EPA Report, 1997.

PCBs, it became clearer that these compounds were causing a negative impact on many biological systems. When evidence of their toxicity began to be reported in the early 1970s, the use of PCBs became increasingly restricted and was being phased out (United Nations Environment Program, 1988; Galveston-Houston Association for Smog Prevention, 1996).

1.3 Environmental impact and health effects of PCBs

1.3.1 Pathways for PCB entry into the environment

The discharge of polychlorinated biphenyl compounds represents a serious threat to the environment and the biosphere (Galveston-Houston Association for Smog Prevention, 1996). PCBs have been discharged into the environment exclusively from anthropogenic activities. In the past, the release of PCB wastes into rivers, streams and open landfills was considered to be acceptable, and was thought to be hazard-free practices (American Council on Science and Health, 1997). Therefore, PCBs were able to enter into the environment from all of these activities, as well as from the incineration of waste, industrial discharges and sewage effluents (US EPA, 1997). There have also been accidental releases of PCBs and associated contaminants into the environment via the leaking of sealed PCB fluid compartments during use of transformers and capacitors, and as a result of improper disposal of PCB-containing equipment or chemical products (American Council on Science and Health, 1997).

1.3.2 PCBs in soil systems

PCBs are widespread contaminants in the environment primarily in soil systems (Erickson, 1997). According to studies (Rantanen *et al.*, 1975; Hester and Harrison, 1996), the global burden of PCBs is about 374,000 tons (31% of total world PCB production), of which 39 % burdened the terrestrial and coastal environment. Although the total amount of PCBs produced annually has declined (on a worldwide basis) since the 1970s, the toxicological threat posed by these compounds has not decreased appreciably (U.S. Agency for toxic substance and disease registry, 1993). In fact, their persistence in the environment has been of increasing concern due to their toxicity, low degradability, mutagenicity and tendency to bioaccumulate (US EPA, 1996). Environmental cycling is suspected of being the current, major source of PCBs in soil outside of disposal and spill sites (U.S. Agency for toxic substance and disease registry, 1993). Once introduced into a soil medium, PCBs can become sorbed strongly and can remain there for many years. They are unlikely to be taken up by plants, and therefore they are not readily mobilized from soil systems. In 1991, the cumulative burden at U.S. sites, that had been identified as having excessive PCB levels, was estimated at 382 million tons (US EPA 1994; 1996). PCB concentrations in soils at contaminated sites can be many-fold higher than background levels (Table 1.3).

1.3.3 PCBs in water systems

Open oceans contain about 228,140 tons of PCBs, of which 66,000 tons was held in North America basins (Rantanen *et al.*, 1975; Hester and Harrison, 1996). PCB concentrations are generally higher in waters near human activity and near shorelines. Currently, the major input of PCBs into surface waters is from environmental cycling (Hester and Harrison, 1996). Approximately 98% of the PCBs entering the ocean are currently deposited from the atmosphere. The principal transport route for PCBs through aquatic systems is from waste streams into receiving waters, with further downstream movement occurring by solubilization and readsorption onto particles as well as by the movement of sediments (Rantanen *et al.*, 1975). The release of PCBs from sediments to overlying waters can occur by slow desorption. Translocation can also occur through biological activity (US EPA, 1997). Desorption of PCBs from particulate is more likely to occur from lower chlorinated, more water-soluble PCB congeners. As a result, the marine environment becomes one of the terminal sinks for PCBs, and the concentration of PCBs in fish can be many-fold higher than that in the surrounding water due to the bioaccumulation (U.S. Agency for toxic substance and disease registry, 1993).

1.3.4 PCBs in the air

Traces of PCBs have been detected in the air far remote from their point of release (U.S. Agency for toxic substance and disease registry, 1993). Municipal waste combustion, hazardous waste incineration and medical waste incineration account for an appreciable portion of reported national PCB emissions to the air (US EPA,1996). Additional sources of PCB emissions included treatment, storage disposal facilities and landfills; hazardous waste sites; steel and iron reclamation facilities; accidental releases; and environmental sinks of past PCB contamination (US EPA, 1996). The most recent compilation of PCB concentrations in the air of the Great Lake area ranged from 30 to 400 picograms/m^3, and it is generally highest in the summer and lowest in the winter (The Royal Society of Chemistry, 1996). According to a report of World Health Organization (WHO, 1987), in Bangkok, Thailand, the average PCB concentration was 570-820 ng/m^3.

Table 1.3 The occurrence of PCBs in representative environments

Country	Location	Air(ng/M^3)	Water(ng/l)	Soil(μg/g)
Canada	Great Lakes	0.03-0.04	0.11-0.64	~0.2
	Montreal		0.18-0.55	
U.S./Canada	Arctic(81°N)	0.1-0.3		
U.S.	Great Lakes			0.03-0.2
	Lake Michigan		100-450	
Japan	Tokyo			
	Agricultural land	20		<1,000

Source: Hester, 1996; Pham,1999; Erickson, 1996.

These levels are 1000 times greater than those measured in urban air in the United Kingdom (WHO, 1987). About 25% of airborne PCBs was attributed to volatilization from capacitors and the remainder from volatilization of PCBs spilled on the surrounding soil.

1.3.5 Co-Planar PCBs and their health effect

Attention to the environmental presence of PCBs began in early 1960s when PCBs were reported in soil and water (Galveston-Houston Association for Smog Prevention, 1996). In 1968, an incident of widespread human poisoning in western Japan was attributed to the consumption of rice bran oil that had become contaminated with PCBs during processing (Busert *et al.*, 1978). Global concerns grew over the potential deleterious health effects of PCBs and were spurred on by human poisoning episodes that were similar to the incident of PCB-contaminated rice bran oil consumption in Taiwan (Rogan *et al.,* 1988).

PCBs are divided into 2 groups of isomers based on differences in structure:

i) Coplanar PCBs - these compounds have chlorinated substituents in both para positions, and any/all meta positions (Parkinson & Safe,1987). Meta or para chlorine substituents have, by their structures, low steric hinderance with neighbouring hydrogens, which allows free rotation about the phenyl-phenyl bond (Parkinson & Safe,1987).

ii) Mono-ortho chlorinated PCBs - all molecules have 1 or more chloro substitutions in the ortho positions only (Parkinson & Safe,1987). Ortho-substituents tends to create rigid bonds due to the large steric interference between the Cl and H atoms (Parkinson & Safe,1987).

PCB isomers react with different receptors. For example, co-planar molecules are more toxic than ortho isomers in the development of thymic atrophy, caused by a loss in cortical lymphocytes (Parkinson & Safe,1987). In comparison, ortho isomers have a higher affinity for estrogen receptors as compared to co-planar isomers; estrogenic hormonal activity was therefore increased (Korach *et al.*,1987).

Halogenated compounds tend to bind to estrogen receptors, resulting in abnormal estrogenic activity (Korach *et al.*,1987). Uterotropic activity has been studied in the rat using mixtures of either two isomer types of PCB, as well pure individual chlorobiphenyls (Korach *et al.*,1987). Only mixtures with 1 or more degree of ortho substitutions were active in estrogen-receptor binding, behaving as competitive inhibitors of estradiol (Korach *et al.*,1987). The ortho-chlorine substituents also forced conformational restrictions, which may have improved the estrogen receptor-binding activity through increased homology between estradiol and PCBs (Korach *et al.*,1987). Regions of homology include a hydrophobic area, the conformational inflexibility, and the phenolic ring between the biphenyl and the A-ring of estradiol (Korach *et al.*,1987).

However, while here may be a strong correlation between toxicity and structure, where ortho-para-meta- substituents can reliably predict or explain differences in toxicities, PCB carcinogenesis has little or nothing to do with PCB structure (Parkinson & Safe,1987). The latter depends primarily on the actions of cytochrome P-450 located primarily in the liver.

Within the liver endoplasmic reticulum, there is a mechanism used by most vertebrates to remove harmful lipophilic xenobiotics. Through biotransformation by at least 12 cytochrome P-450 isozymes, xenobiotics are nullified (Parkinson & Safe,1987). The cytochrome P-450 isoenzymes hydroxylate, epoxidate, dealkylate and oxygenate many compounds such as drugs, environmental pollutants and carcinogens, as well compounds found within the body such as fatty acids, sterols, steroid hormones and vitamins (Parkinson & Safe,1987). Cytochrome P-450 converts lipophilic compounds to metabolites that are more easily eliminated from the body, and thus works to defend the cells from PCB intoxication (Parkinson & Safe,1987). However, the PCB-metabolites that this cytochrome P-450 produces are often more toxic than the parent molecule itself (Parkinson & Safe,1987).

Some specific P-450 isozymes prefer to metabolize co-planar chlorophenyls, others prefer to act on non-coplanar PCBs (Parkinson & Safe,1987). Toxicity depends on the amount of conversion to reactive intermediates by monooxygenases, produced by cytochrome P-450. The greater the preference for metabolism, the more reactive intermediates that are produced, the more toxic the isomer. The co-planar molecules are the more toxic isomers, which induces cytochrome P-450 more powerfully than the ortho-substituents (Parkinson & Safe,1987). TPCBs, PCDFs, PCDDs, PCNs, PBBs, bromobenzenes, hexachlorobenzenes, DDT and others all induce cytochrome P450 isozymes (Parkinson & Safe,1987). Other xenobiotic metabolizing enzymes are also induced that may not be related to cytochrome P-450. For example, benzo(a)-pyrene hydroxylase is an enzyme that has similar functions to that of cytochrome P-450 (AHH activity). AHH activity results in the hydroxylization of benzo(a)-pyrene, a reactive intermediate of cytochrome P-450. PCBs can also be hydroxylated to stable molecules (eg. methlsulfonyl metabolites) and not just reactive intermediates (Schellman Sipes,1987). Accumulation of stable metabolites in bronchi caused "respiratory distress" in rodents (Schellman Sipes,1987).

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. As recorded in Table 1.4, the daily average intake of PCBs has been estimated to be as much as 60 μg per person. PCBs accumulate in fatty tissues, their half-life has been estimated to be 38 years (The Royal Society of Chemistry, 1996). 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). Plasma PCB residues in the general population have been found to range from 5 to 50 ng/g (Table 1.5). Studies (American Council on Science and Health, 1997) have suggested that certain mixtures of PCBs are carcinogenic. The potential health effects associated with exposure to PCBs include carcinomas, reproductive and development toxicities, impaired immune function, effects on the central nervous system and deleterious liver changes. Other non-cancerous, short-term effects of PCBs in humans include body-weight loss, headaches, dizziness, depression, nervousness and fatigue. Chronic exposure may also result in changes of enzyme activities (U.S. Agency for toxic substance and disease registry, 1993).

Table 1.4 Estimated dietary intake of PCBs in Canada

Food	Food intake (g/person/day)	Maximum residual level (μg/g)	PCB intake (μg/person/day)
Dairy	32.8	0.2	6.6
Meat	48	0.2	9.6
Poultry	3.6	0.5	1.8
Eggs	34	0.1	3.4
Fish	20	2	40
Total			61.4

Source: from report EPS 4/HA/1, Environment Canada.

Table 1.5 PCBs content in food and the human body

Area (mg/kg)	Year collected	Adipose (mg/kg)	Eggshell (mg/kg)	Cheese
Canada	1970s	0.91 ± 0.82		
(All regions)	1980s	0.94 ± 0.90		
Ottawa	1980-1981	2.0 ± 0.87		
Kingston	1971-1981	3.0 ± 3.6	550	250

Source: from Erickson, 1996.

1.4 PCB analysis and quantification

1.4.1 Qualitative analysis of PCB congeners

Qualitative analysis of PCB is to precisely identify each of the 209 PCB congeners, especially the identities of the coplanar PCBs because these compounds are more acutely toxic in terms of the environment impact. The analysis of PCBs in environmental and biological sample is a multi-step process (Ashok *et al.*, 1998) and includes steps of extraction, cleanup, removal of sulfur, column fractionation and gas chromatographic separation (Medes and Boer, 1997). The PCB congener separation in environmental matrices is based not only on the degree of chlorination but also on their structure and on the analytical protocal adopted. Most of the commercial mixtures and environmental samples exhibit a multitude of peaks. High-resolution isomer-specific analysis is now a feasible option for the identification and quantitation of individual PCBs present in commercial mixtures and in environmental samples (Mullin and Pochini, 1984). Identification of PCB congeners is made more difficult with the variation in composition of the environmental PCB mixtures among the sample types. Errors in the analysis of PCBs are further compounded by wide variations in the response of each congener for GC-ECD, the most common method of analysis. Environmental aging, varying degrees of volatility for each congener, and confounding factors due to of matrix also add to the uncertainty of PCB analysis. Until now, there is not a standard method for the qualitative analysis of PCB congeners. The optimal conditions are still being investigation, although the major congener mass spectral patterns are available (Figure 1.2).

Several attempts have been made in recent years to separate PCB mixtures. One of the two seminal works involved the synthesis of all 209 PCBs combined with their determination on a SE-54 column. Mullin and co-workers (1984) studied the retention times of 209 PCB congeners and response factors relative to the standard, octachloro- naphthalene, using a 50-m fused silica capillary column coated with SE-54 and equipped with a ^{63}Ni electron capture detector. They summarized a plot of relative retention times (RRT) vs. PCB isomer groups and illustrated the overall increase with increasing chlorine content of the congeners.

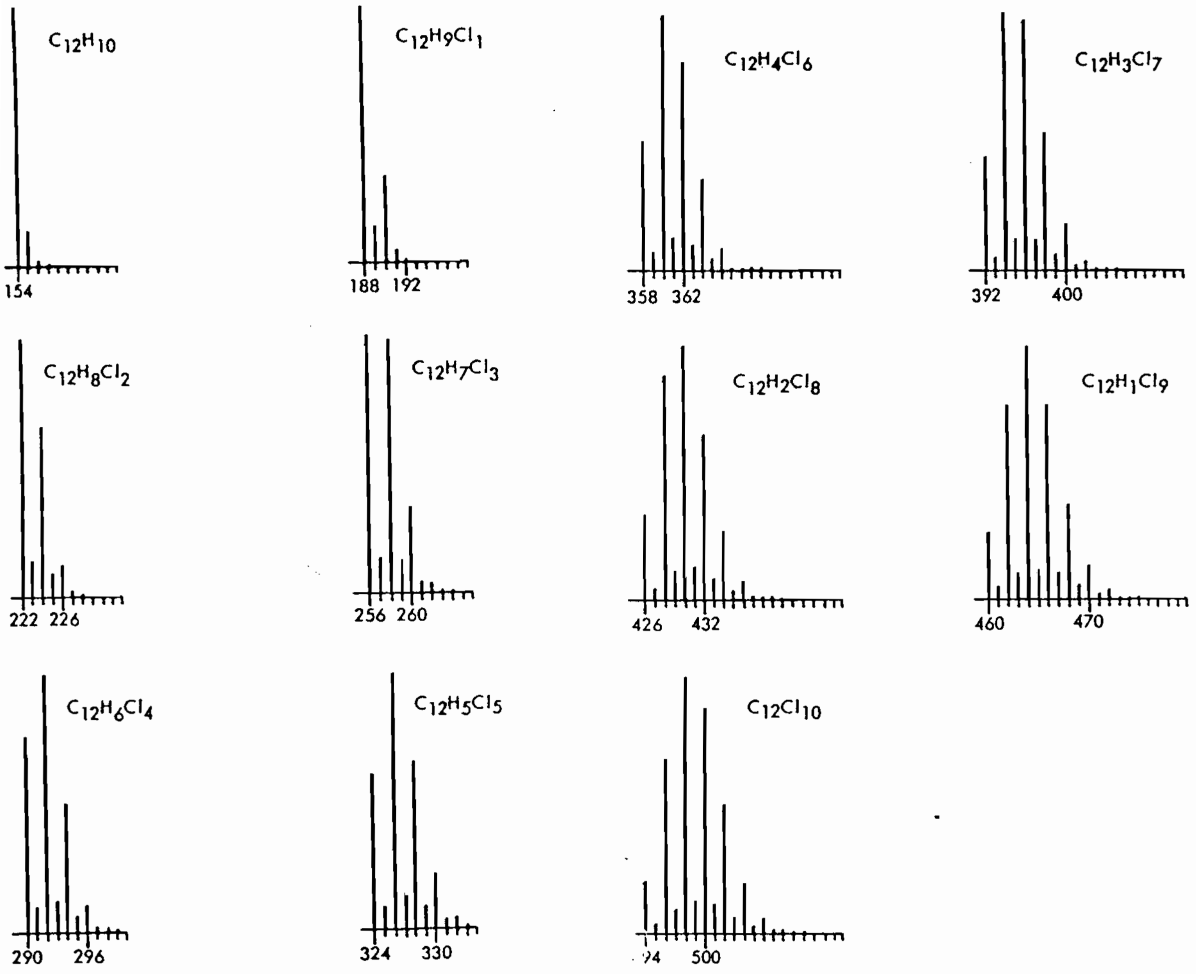

Figure 1.2 Molecular ion clusters of mass spectral patterns of PCB congeners (Source: from Erickson,1997)

Vetter *et al.* (1998) investigated all 209 PCB congeners using GC-electron ionization mass spectrometry equipped with a high temperature capillary column coated with Thermocap A phase. They separated and identified all of the 209 congeners and listed the unique retention times of different congeners. Recently, Bolgar *et al.* (1995) analyzed 209 PCB congeners by high resolution GC and low resolution MS and demonstrated the physical and spectral properties of all 209 PCB congeners.

When compared with the determination of individual PCB congener, the analysis of commercial mixtures is more difficult to identify because the multiple components of each mixture produce a characteristic chromatographic pattern that changes with exposure time in the field. Although by comparing the pattern for an unknown PCB mixture with patterns for standard Aroclor PCB mixtures, the unknown often can be identified. By contrast, the peak pattern for a chemically or biologically degraded Aroclor mixture can differ appreciably from that of the manufactured mixture. Problems also arise when a sample contains two or more Aroclor mixtures, or non-Aroclor mixtures of PCBs. Frame *et al.* (1998) studied 6 commercial Aroclors on 20 different high-resolution GC columns and demonstrated the variability in the numbers of congeners that each system could quantify. Their results indicated that the greater congener count in some GC-systems was due to difference in detector sensitivity and not to peak resolution. According to the bulletin 817C (Supelco report, 1996), ECD is more sensitive to PCB congeners, but mass spectrometric detection is more selective and enhances the chromatographic separation.

1.4.2 Quantitative analysis of total PCBs

The convential PCB quantitation methods include the calculation of the total integrated area of calibrated individual PCB congener/isomer peak by GC-ECD and/or GC-MS with the use of individual reference standards (Dowdall *et al.*, 1995). More frequently, some researchers use a set of PCB congeners with a complex calibration procedure to quantify the PCB content in routine analyses. The results of this method can deviate up to 100% from the true value for single CBs although the total amount could be determined correctly (Buthe and Denker, 1995).

For the determination of the correct amount of total PCBs, there are two principle approaches which are straightforward (Schuetz *et al.,* 1999). One is the complete hydrodechlorination of pure PCBs to biphenyl. Analysis of biphenyl may then be conducted by GC-FID and/or petentiometric detection of Cl^- post reaction. Doyle *et al.* (1998) demonstrated that dechlorination of PCBs to biphenyl can be effected within ten min under mild conditions in the presence of Mg and K_2PdCl_6 powders. For a given commercial Aroclor product, the chlorine and/or biphenyl content are fixed within the sample. When the chlorine atoms are displaced into solution, the liberated chloride ions can be determined by titration with silver nitrate. The disadvantage of this method is the requirement to determinine either the chloride ion or the biphenyl in the sample. Another approach for total PCB determination is perchlorination, in which all the PCB congeners are converted to decachlorobiphenyl. Although the conversion of PCBs to one species would be of great benefit, especially to the techniques employing chromatographic separations of complex matrices, perchlorination has been selected only infrequently due to its disadvantages involving harsh reaction condition, toxic reagents and a more demanding derivatization procedures (Schuetz *et al.,* 1999).

1.5 PCB regulations

The widespread occurrence of PCB in the environment and the apparent link to carcinogenesis has promoted an increasing concern throughout the world since 1970s, that has resulted in the increased restrictions on the use of PCB in most countries. In 1976, the U.S. congress imposed the Toxic Substance Control Act, which specifically regulates manufacture, processing, distribution in commerce and use of PCBs. The EPA subsequently promulgated a series of rules on the various aspects of the law, and many other PCB related federal, state, and local laws have been established (Erickson, 1997). Similar PCB related regulations were also imposed in South America, Australia, and most European countries (Erickson, 1997).

PCBs were never manufactured in Canada (Environment Canada, 1997). According to Environment Canada, approximately 40,000 tons of PCB was imported into

Canada prior to 1977, and there remain about 15,100 tons of PCBs still in use across the country. PCBs are substances specified on the list of Toxic Substances in Schedule I to CEPA. They were the first substances to be regulated and originally prohibited for certain uses under the Canada Environmental Contaminants Act (1976). Four regulations have been developed in Canada for PCB compounds since 1988. They include the Federal Mobile PCB Treatment and Destruction Regulations; PCB Waste Export Regulations; Chlorobiphenyl Regulations; and Storage of PCB Material Regulation (Environment Canada, 1997). Under these regulations, several standards, recommendations, guidelines and criteria for PCBs in the Canadian environment have been established (Table 1.6). To date, there continues to be a great amount of PCB compounds in use across Canada (Table 1.7) and removal of PCBs from service has increased the quantities of PCB waste. By 1990, more than 150,000 tons of PCB waste involving PCB contaminated soil, mineral oil, and other metallic components of electrical equipment were stockpiled across Canada. Between 1989 and 1995, the federal government allocated $6 million for PCB destruction projects in Atlantic Canada, Quebec, and Ontario. With the implementation of PCB related regulations, more PCB waste will be produced and more investment will have to be allocated to the destruction of PCBs and the remediation of PCB contaminated media (Environment Canada, 1998).

1.6 Remediation and destruction of PCBs

Remediation of PCB contaminated matrices is a comprehensive process involving PCB extraction/mobilization, PCB destruction and the restoration of cleaned materials. During the last two decades, more than 80 techniques have been developed for PCB destruction and decontamination (U.S. Agency for toxic substance and disease registry, 1993; US EPA 1996). However, the majority of these processes remain theoretical or they have been optimized only for small-scale destructions (US EPA, 1996). When used in the real-world, many methods still face challenges. As summarized in Table 1.8, commercially available methods for PCB remediation and destruction can be divided into physical, chemical, biochemical, photolytic and more comprehensive combined methods. The disadvantage of most methods make it necessary to develop increasingly efficient, rapid and simple processes to destroy PCBs.

Table 1.6 Standards, recommendations, guidelines and criteria concerning PCBs in the Canada environment.

Environmental medium	Region	Concentration	Comments
Air	Ontario	35ng/m^3	Ambient air quality criteria
Drinking water	Ontario	3 µg/l	Recommended standard
	Quebec	0.1 µg/l	Recommended standard
Soil contaminated	Quebec	>5 mg/kg	Level considered
	Quebec	≤1 mg/kg	Target level for cleanup
Liquid waste Considered Hazardous	Canada	≥50 mg/kg	Regulated under the ECA*
	Quebec	≥0.3 mg/kg	Considered dangerous
waste			
			under Quebec's
Dangerous			
			Waste Regulation
Eggs	Canada	0.1mg/kg	Administrative guideline established by HC **
Poultry	Canada	0.5mg/kg	Administrative guideline established by HC
Beef	Canada	0.5mg/kg	Administrative guideline established by HC

Source: from Environment Canada,1987.

*: Environmental Contaminants Act.

**: Health Canada.

Table 1.7 Quantity of PCBs in use in Canada.

Province	Type of unit	Quantity of PCBs
(ton)		
British Columbia	transformers	1350
	capacitors	656
	non-electric	30.8
Alberta	transformers	324
	capacitors	46
	electromagetets	1.1
Saskatchewan	transformers	204
	capacitors	14.5
Manitoba	transformers	94.9
	capacitors	12.6
	electromagets	1.8
Ontario	transformers	6980
	capacitors	473.4
Quebec	transformer	2980
	capacitors	875
	electromagetets	12.4
New Brunswick	transformers	339
	capacitors	52.5
Nova Scotia	transformers	294
	capacitors	60
Prince Edward Island	transformers	1.5
	capacitors	0.2
Newfoundland	transformers	297.8
	capacitors	11.1
Nunavut	transformers	8.9
	capacitors	0.9
Total		15,100

Source: from Environmental Canada, Report EPS 3-Ec-83-1.

Table 1.8 The methods used for PCB remediation and destruction

Treatment Tech	**Type**	**Process**
Incineration	Destruction	Thermal
Thermal desorption	Separation	Thermal
Solidification/Stabilization	Isolation	Physical
Soil washing/flushing	Separation	Physical
Solvent extraction	Separation	Chemical
Reduction/oxidation	Destruction	Chemical
Bioremediation	Destruction	Biological
Soil vapour extraction	Separation	Physical
Landfilling	Isolation	Physical
Photoremediation	Destruction	Chemical
Supercritical extraction	Separation	Physical

Sources: from Erickson (1997) and Rantanen *et al.*(1975).

1.6.1 Physical dechlorination of PCBs

1.6.1.1 Incineration

Incineration remains the pre-eminant disposal option for the destruction of PCBs because of increased concerns about the potential impact of PCB disposal into the environment (Mullin *et al.*, 1984). This situation has not changed appreciably in the last two decades. PCBs can be destroyed by incineration under adequate operating conditions (Georges, 1987). When incinerated, PCBs are combusted at facilities that purportedly can achieve a 99.99% destruction removal equivalence (Mullin *et al.*, 1984; Yezzi *et al.*, 1984; Yu *et al.*, 1991; US EPA, 1996).

In North America, PCBs have been disposed of primarily by incineration (Galveston- Houston Association for Smog Prevention, 1996). However, the capacity of incinerators for PCB destruction is limited. With the thermal breakdown of PCBs occurring at high temperatures, both chlorinated furans and dioxins can be produced under inadequately controlled conditions (Hutzinger *et al.*, 1985; Georges, 1987). These products are more acutely toxic than the PCBs themselves. Furthermore, the incineration process 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.

1.6.1.2 Solvent extraction

This process uses an organic solvent to physically separate hazardous contaminants from soil and sediment, and to reduce the volume of hazardous waste that must be treated (US EPA, 1996). Several extraction methods have been proposed and applied in laboratory research including Soxhlet extraction, microwave assisted solvent extraction, sub-critical water extraction and surfactant suspension extraction. The overall extraction efficiency depends on the number of extraction cycles used (Meckes *et al.*, 1997). Solvent extraction of PCBs and PCDD/Fs from lake and harbor sediments using microwave-assisted and Soxhlet extraction was investigated by Chiu *et al.* (1997). Recovery and precision of both methods were comparable, but microwave-assisted extraction reduced the extraction time from 20 h to 20 min and solvent quantity was reduced from 350 ml of toluene to only 20 ml of hexane/acetone.

Bandh *et al.* (1998) evaluated an accelerated-solvent extraction (ASE) technique to determine PCBs in sediments of the Baltic Sea and compared the results with conventional Soxhlet extraction. The ASE method was characterized by equal or even improved precision relative to the Soxhlet extraction and was completed with less solvent consumption. Szostek *et al.* (1999) demonstrated the quantitative extraction of PCBs from environmental solids by using a microscale adaptation of pressurized fluid extraction (μPFE). Recoveries were measured for eight PCB congeners spiked into two soil types. The extraction process with hexane at 300°C provided significantly increased recoveries for several representative PCB congeners than had been reported for a duplicate 16 h Soxhlet extraction with a mixture of acetone/hexane.

1.6.1.3 Thermal desorption

Thermal desorption (TD) is a process that has been targeted to remediate hazardous waste from soils/sediments and sludges by removing sufficient PCBs, Hg and volatile organics to satisfy the criteria of waste disposal (Krabill *et al.*, 1996). Nardini *et al.* (1998) studied the thermal desorption of soils contaminated with numerous compounds involving low levels of PCBs and chlorinated solvents. The results indicated that all soils contaminated with low level PCBs (<50 ppm) were remediated to below the treatment standard of 1 ppm with removal efficiencies ranging from 90.11 to 99.47%. Soils contaminated with chlorinated solvents were treated successfully with removal efficiencies of 95.8 to 99.98% for trichloroethylene (TCE) and 93.5 to 99.98% for perchloroethylene (PCE). Norris *et al.* (1998) reported on an effective remediation of PCB contaminated soil using low temperature thermal desorption. Thermal treatment has been demonstrated to remove sufficient PCBs from a contaminated soil matrix to pass stringent residual contamination values, without any unacceptable impacts on the environment and at a cost per ton appreciably lower than that of high temperature incineration. The method, that used low temperature thermal desorption, could save 75% of the remediation cost (Brown *et al.*,1987). Osborn *et al.* (1984) investigated the extractive 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 from which the primary solvent can be recovered for reuse and the PCBs concentrated for ultimate disposal by incineration or chemical destruction.

1.6.1.4 Soil washing/flushing

There are two approaches for soil PCB removal. Soil washing (*ex-situ*) involves an organic solvent and/or surfactant suspension 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 infiltrating an aqueous solution into a zone of contaminated soil, followed by down gradient extraction of ground water, elutriate, above-ground treatment and re-injection of the cleaned aqueous fraction. Abdul *et al.* (1991) evaluated the extent of washing of PCBs from soil using an alcohol ethoxylate surfactant to mobilize contaminants and demonstrated that PCBs could be washed efficiently from sand using surfactant solutions. To date the majority of pilot-scale demonstrations of *in-situ* flushing have involved the use of surfactant and co-solvents. In the U.S., several full-scale site remediations have utilized *in-situ* flushing.

1.6.1.5 Stabilization/Solidification

Waste stabilization is a process that adds a binding agent to the waste to convert contaminants into a less soluble, less mobile phase. By contrast, waste solidification adds a binding agent to the waste to encapsulate the contaminants within a solid material. Both of these technologies reduce the mobility of PCB, but do not concentrate or destroy them (US EPA, 1996). Therefore, further treatments must be employed.

Sawyer *et al.* (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, indicating a potential for long-term durability.

1.6.1.6 Vitrification

Vitrification technologies use melting, induced by electrode heating of contaminated soil or sediment containing organic and inorganic contaminants, to form a rigid, glassy product when cooled (Erickson, 1997). Temperatures in the process are in the range of 1,000-2,000 °C. PCBs can be destroyed by the high temperatures during the process. In the 1990s, the vitrification system was authorized by U.S. EPA to treat PCBs in soil and sediment (U.S. Agency for toxic substance and disease registry, 1993; US EPA, 1996).

1.6.1.7 Photolytic dechlorination of PCBs

Photolysis is a popular means of both physical and chemical degradation of PCBs. This process uses free radicals, produced from sunlight or generated artificially, to remove the chlorine atoms from the biphenyl ring. Nishiwaki *et al.* (1981) concluded from their study that photo- or radiation-induced chain dechlorination of PCBs in alcohol proceeded by a homolytic fission of C-Cl bond in a photoexcited state to give substituted H^+ radicals and Cl^- (by decomposition of radical anion of PCB). Mincher (1995) studied the ability to degrade PCBs by exposure to gamma radiation from spent nuclear fuel in a number of solvents, including hydraulic oils. 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 PCB congeners were generally more reactive toward photodechlorination.

In the presence of TiO_2, chlorinated methanes, 2,4-dichlorophenoxyacetic acid (2,4-D), *p*-dichlorobenzene and PCBs were degraded through photodegradation both in organic solution and in water (Carey *et al.,* 1976; Menassa *et al.*, 1988; Rao *et al.,* 1993; Choi *et a*l., 1995). Lin *et al.* (1996), using simulated sunlight and a photosensitizer (diethylamine), studied the photodegradation of Aroclor 1254. The degradation rate of Aroclor 1254 congeners was $4.74 \pm 1.51 \times 10^{-9}$ mol/l/h. The half-lives of 5 major congeners of Aroclor 1254 (66, 101, 110, 118, and 138) ranged from 30.31 to 52.11 h. Chu and co-workers (1994) suggested that photoreduction, through photodechlorination, was the main decay pathway in which lesser chlorinated congeners and benzene were formed as intermediates. In addition, some minor pathways were observed including photochlorination, photoisomerization, and photohydrolysis, in which phenol was formed.

For most of the PCB destruction approaches, the cost is prohibitive and the processes are time consuming. An overall cost comparison of chemical and physical PCB destruction and disposal is povided in Figure 1.3.

1.6.2 Chemical dechlorination

Evidence of the environmental and public health impacts of incinerators and other combustion systems has created strong public opposition to incineration. This factor as well as increased infrastructural requirements, particularly those associated with the management of air emissions and other residues, has encouraged the development of alternative destruction technologies. Some of the more recently developed technologies offer appreciable advantages in both performance and costs over combustion using dedicated incinerators. Chemical degradation represents one of these technologies.

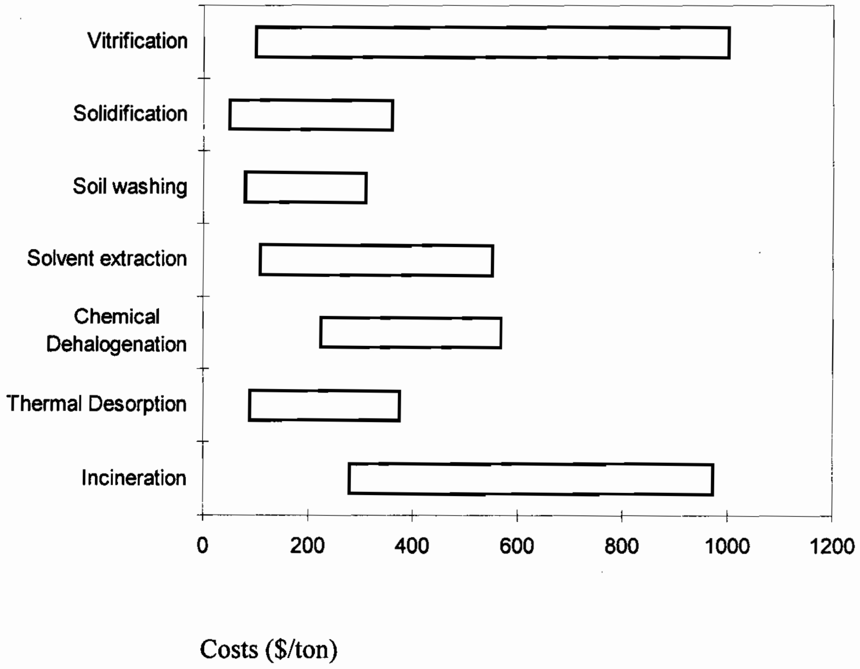

Figure 1.3. Estimated cost for different approaches of PCB dechlorination (Source: from US EPA, 1997).

Chemical dechlorination of PCBs uses chemical reactions to remove chlorine atoms from organic molecules (Oku *et al.*, 1978). One route to chemical dehalogenation is via base-catalyzed decomposition (BCD), which is an efficient and relatively inexpensive alternative for treating both PCB-contaminated equipment and PCB-contaminated soils and sediments (Amend and Lederman, 1992; Taniguchi *et al.*, 1998). Oku *et al.* (1978) reported that PCBs were dechlorinated completely by treatment with 1.1 equivalents of sodium naphthalenate (I) for 10 min at 0 °C, or with 0.5 equivalents of I for 5 h at 0 °C. Potassio- and lithionaphthalenates were also effective. These reactions proceeded via formation of aryl anions, followed by an SN_2-type arylation.

Takada *et al.* (1996) reported that the base catalyzed decomposition process for PCBs was based on the formation of hydrogen radicals through a liquid phase dehydrogenation reaction. Hydrogen radicals, generated from a suitable hydrogen donor, substitute H for Cl atoms and transforms the PCBs into non-toxic biphenyl. The dechlorination reaction by the BCD process was assumed to be a first-order reaction. They confirmed that the addition of sodium hydroxide had a beneficial influence on the reaction rate. Kawahara *et al.* (1997) investigated hydrogen transfer agents and catalysts to improve the base-catalyzed decomposition of PCBs. In the presence of base, the reaction increased with increased concentration of hydrogen transfer reagents and catalysts. Optimal reaction conditions proved to be 340-350 °C. According to a study (Takada *et al.*, 1997), optimal reaction temperature for PCB decomposition was >320°C for the base-catalyzed decomposition. The optimum concentration of KOH was determined to be 6 times the stoichiometric ratio. The most efficient combination for treatment was transformer oil and KOH. PCBs were dechlorinated completely and PCDD/F were also decomposed.

Another approach to the chemical dechlorination of PCBs is hydrogenative dechlorination in the presence of a metal catalyst(s). In saturated hydrocarbon solvents, Cl can be removed continuously and the catalysts and the solvents can be reused. Ono *et al.* (1996) reported that if a mixture of PCB, hexadecane, and Pd/C was bubbled with H_2 at 210 °C for 180 min, PCBs decomposition reached as much as 99.99%, the reaction products included biphenyl, phenylcyclohexane, and dicyclohexane. Ukisu *et al.* (1996) reported that in the presence of C-supported noble metal catalyst (Pd/C, Rh/C), PCBs could be dechlorinated efficiently to biphenyl and phenylcyclohexane using a propan-2-ol solution of NaOH at <82 °C. They postulated that the dechlorination reaction include H^+ transfer from propan-2-ol to the PCB substrate.

Polychlorinated biphenyls can also be degraded chemically by contacting a Lewis acid catalyst (a combination of $AlCl_3$ and $FeCl_3$), in a non aqueous medium in the presence of a cation (Wilwerding and Hoch, 1990). When present in oil, PCBs can be removed and dehalogenated by extraction of the oil with a cyclic ketone- or ester-based solvent containing an electrolyte. The PCBs can be dechlorinated by applying an electrical potential to the solvent in an electrolytic cell containing an anode (C or RuO_2-coated Ti) and (Hg) cathode. The solvent can be recycled during processing (Byker, 1984).

In short, most of chemical methods can achieve a very efficient dechlorination of PCBs. However, some chemical dehalogenation/dechlorination processes that use polyethylene glycol can cause the formation of dioxins and furans as byproducts (U.S. Agency for toxic substance and disease registry, 1993; US EPA, 1996).

1.6.3 Bioremediation

Bioremediation uses microorganisms to decompose or detoxify organic compounds, a process for destroying PCBs in both aerobic and anaerobic environments. The degradation of PCBs in soil or aquatic systems entails different mechanisms of chemical, biochemical or thermal destruction (Rantanen *et al.*, 1975). Substrates with a high degree of chlorination including 1248, 1254 and 1260 are resistant to biodegradation and are degraded only slowly in the environment.

Aerobic oxidative dehalogenation involves the oxidation of PCBs by aerobic microbes, especially by bacteria of the genus *Pseudomonas*. This involves the addition of oxygen to the biphenyl ring(s) (Boyle *et al.,* 1992). Although different bacterial species seem to produce benzoate through PCB metabolism, further breakdown of benzoate seems to differ among the different microbes. Nevertheless, the by-products are less toxic to animals and the environment (Bevinakatti and Ninnebar, 1992).

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 chlorines per biphenyl is reduced (Mousa *et al.*, 1998). Specifically, monochlorobiphenyl and ortho-substituted dichlorobipenyls are degraded in this way. Byproducts of this process are less toxic and can be degraded further by the aerobic microbes (Kawahara *et al.*, 1997).

Although several different dechlorination processes were observed for PCBs in sediment (Ye *et al.*,1992), there exists a similarity between degradation patterns (Alder *et al.*, 1993). Highly chlorinated congeners were degraded less readily than the less chlorinated congeners. The molecular shape and the position of chlorine atom substituents in the PCB also affected the rate of biodegradation. Unlike chemical dechlorination, PCBs with fewer chlorine atoms are more readily degraded in bioremediation than PCBs with a higher chlorine content.

The anaerobic biotransformation of PCBs is a relatively slow process. Rhee *et al.* (1993) investigated microorganisms in Hudson River sediment using the commercial mixture Aroclor 1242. They found that there was no change in congener composition at the given concentration of PCBs during 7 months of incubation. However, appreciable shifts in the degree of chlorination were observed in sediments.

Sokol *et al.* (1993) investigated the microbially meditated dechlorination kinetics of polychlorinated biphenyls (Aroclor 1248) spiked into sediments at 16 concentrations. The results demonstrated that a threshold concentration was observed at 35-45 ppm. No dechlorination was observed below the threshold level and the dechlorination rate increased with an increased PCB concentration in the sediment above the threshold concentration.

Many environmental factors can affect the degradation of PCBs. Natarajan *et al.* (1997) reported that the dechlorination rate at 30 °C was increased relative to the rate at either 12 or 37 °C by anaerobic microbial granules in a phosphate buffered medium under sediment-free conditions. The dechlorination rate was more rapid under strictly anaerobic conditions than under anoxic conditions. The dechlorination was enhanced appreciably by the addition of a carbon source. To date, however, no bioremediation system has been identified as being capable of biodegrading PCBs on a scale large enough to be used for site remediation (U.S. Agency for toxic substance and disease registry, 1993; US EPA, 1996).

1.7 Innovative techniques for remediation and dechlorination of PCBs

Over the last few years, increasing interest in the reactions of reducing metal systems has been sparked by concerns about environmental protection. An increasing number of research groups are working to assess the utility of these reactions in the treatment of contaminated materials. The most extensively studied reducing metal powders have been zero-valent copper, iron, magnesium, nickel and zinc (Seymour *et al.*, 1986; Ross *et al.*, 1987; Chuang *et al.*, 1995; Appleton, 1996; Roberts *et al.*, 1996; Shannon, 1996; Johnson *et al.*, 1998). Recent research has shown that dramatic improvements in rate and selectivity of dehalogenation can be obtained by employing bimetallic systems such as Ag^o/Fe^o, Pd^o/Fe^o, Pt^o/Fe^o and Ni^o/Fe^o (Boronina *et al.*, 1995; Grittini *et al.*, 1995; Bizzigotti *et al.*, 1997; Balko and Tratnyek, 1998; Doyle *et al.,* 1998). These bimetallic materials are considered to have extensive environmental and industrial applications.

1.7.1 Dechlorination of PCBs by zero-valent metal particles

Zero-valent copper (Cu°), iron (Fe°), magnesium (Mg°), nickel (Ni°), tin (Sn°) and zinc (Zn°) have been used to enhance the degradation of chlorinated organic compounds (Boronina *et al.*, 1996; Wafo *et al.*, 1996; Korte *et al.*, 1997; Su *et al.*, 1999). Hartmann *et al.* (1997) reported that halogen compounds were dehalogenated by contact with reducing agents such as hydrazine, hydrazine hydrate, hydroxylamine or their salts or alkali metal dithionites in solution in the presence of solid metal catalysts (e.g., Fe°, Cu°, Mo°, Ni°, Cr°, Mn°, Co°, Ti° or V°) at 0-100 °C.

Tatyana *et al.* (1995) investigated the dechlorination of organohalogen compounds in water systems by magnesium, tin and zinc. In the CCl_4/H_2O system, only a small amount of CCl_4 was destroyed yielding $CHCl_3$ with magnesium. However, CCl_4 destruction was increased to approximately 40% with tin in the tin/CCl_4/H_2O system. CCl_4 and $CHCl_3$ could be destroyed completely but CH_2Cl_2 and CH_4 remained when using Zn powder.

Reaction conditions have a pronounced effect on the rate of reductive dechlorination. Gotpagar *et al.* (1997) examined the effect of feed concentration, initial pH, zero-valent Fe loading and its particle size on the degradation of trichloroethylene (TCE). The degradation rate was first-order with respect to the organic molecule. The amount of trichloroethylene degraded at any given time was directly proportional to the quantity of dissolved Fe. The metal surface area apparently plays a crucial role in the process.

Cheng *et al.* (1998) studied the influence of an external electrical potential on the degradation rates of CCl_4 and CH_2Cl_2 by Fe° and Zn°, respectively. The results indicated that the application of an external electrical potential enhanced the degradation rate of CCl_4. CCl_4 was entirely depleted in 4 min and the half life for $CHCl_3$ was estimated to be about 30 h. Three hour was required to degrade CCl_4 completely and the half life for $CHCl_3$ was 100 h without an applied external potential.

Copper powder can enhance the dechlorination of PCBs, chlorinated dibenzofurans, dibezo-*p*-dioxins, and other aromatic compounds (Hagenmaler, 1987). Ross *et al.* (1987) studied the destruction efficiencies of Al alloy and Al_2O_3 surfaces toward PCBs and related systems, including decachlorobiphenyl and hexachlorobenzene. The dechlorination efficiencies that were observed exceeded 99.99%.

Romanova *et al.* (1992) studied the dechlorination of PCBs by treatment with a organosilicon hydride in the presence of a Ni catalyst. Homogeneous nickel and cobalt organophosphorus complexes, coupled with alkoxyborohydride reagents as a hydrogen source, can mediate chlorine displacement from PCB congeners through a reductive process. The efficiency of chlorine displacement is a function of chlorine position and the shape and steric bulk of the organophosphorus-metal complex (King *et al.*, 1997).

Chuang *et al.* (1995) investigated the zero-valent iron promoted dechlorination of PCBs at elevated temperatures. Above 300°C, dechlorination of Aroclor 1221 began to occur; at 400°C, most of the PCBs were dechlorinated to biphenyl within 10 min. Dechlorination and other reactions of PCBs took place at temperature of 500°C or higher. Almost all PCBs were destroyed by reactions other than hydrogenolytic dechlorination at 600°C. Yak *et al.* (1999) evaluated the method that using zero-valent Fe as the dechlorination agent and subcritical water extraction (SWE) as the transporting medium for remediation of PCB-contaminated soil and sediments. Results demonstrated that using 100-mesh Fe powder and SWE conditions of 250°C and 10 MPa on Aroclor 1260 for 1-8 h, the higher Cl^- substituted homologues were completely reduced to their lower-substituted counterparts. The lower-substituted congeners were subsequently dechlorinated nearly quantitatively.

In other advances, the metals used in dechlorinating organochlorine compounds (OCs) have been developed from micro-scale and electrolytic powders to nanoscale dusts. The nanoscale metal particles have specific surface area 1-2 orders of magnitude greater than commercially available micro-scale metal particles (Zhang *et al.*, 1998). Wang *et al.* (1997) demonstrated that nanoscale particles can rapidly and completely dechlorinate several chlorinated aliphatic compounds and a mixture of PCBs at relatively low metal to solution ratio (2-5 g/100 ml). Surface-area-normalized rate constant (K_{SA}) of nanoscale dusts were calculated to be 10-100 times greater than those of commercially available iron particles.

The success in dechlorinating OCs by zero-valent metallic powders has encouraged several related areas of research. Researchers (Zhao, 1994; Powell *et al.*, 1995; Agrawal and Tratnyek, 1996; Johnson *et al.*, 1996; Pratt *et al.*, 1997; Scherer *et al.*, 1997; Devlin *et al.*, 1998; Gillham *et al.*, 1998; Hung and Hoffmann, 1998) have found that doping of iron, zinc, and nickel with silver, palladium and gold can appreciably increase the rate of dechlorination of chlorinated compounds. Some researchers have even studied Pd/C/Fe ternary systems to remediate the haloorganics, and have reported promising results. The dechlorination technologies are considered to be based on metal corrosion (Fe, Zn and Ni). Palladium (Ag and Au) acts as a facilitor in the hydrodechlorination reaction.

Boronina *et al.* (1998) reported that using zinc dust doped with palladium, gold or silver resulted in 4-10 fold increase in the CCl_4 degradation rate and conversion into methane. The results indicated that bimetallic systems with Pd, Ag, Au as well as the cryo or mechanically activation of zinc, enhanced the metal surface reactivity and changed the priority of reaction pathways.

Zhang and co-workers (1998) demonstrated that using Pd alone and palladium doped Fe to dechlorinate tetrachloroethene (TCE), little degradation of TCE was observed in the presence of Pd particles alone. However, the dechlorination activity was enhanced appreciably with bimetallic particles of Pd/Fe. The dechlorination rate of TCE was faster using Pt/Fe than that when using Pd/Fe particles alone. Nickelized iron (Ni/Fe) exhibited higher activity than the nanoscale iron for dechlorination of trans-dichloroethene (DCE) but with lower activity than with Pd/Fe particles.

Grittini *et al.* (1995) reported that using Pd/Fe bimetallic mixture can completely and rapid dechlorinate a PCB solution at ambient temperature. Biphenyl was the reaction product during the dechlorination of Aroclor 1260 and 1254. PCB dechlorination achieved high efficiency with the acidic palladium-zinc catalytic system (Zhao, 1994). PCBs could also be dechlorinated in the presence of 10% Pd/C using ammonium formate as H^+ donor. Efficiencies of 94-100% dechlorination were achieved in neutral media at 60°C and ambient pressure (Metheson and Tratnyek, 1994).

1.7.2 Mechanism of dechlorination of PCBs by zero-valent metallic particles

The fundamental mechanisms of the degradation process have been of broad interest since the initial studies of zero-valent metal promoted dehalogenation were reported (Metheson and Tratnyek, 1994; Allen-King *et al.*, 1997; Zdemir and Tfekci, 1997; Arnold and Roberts, 1998; Eykholt and Davenport, 1998; Gotpagar *et al.,* 1998; Yoshihiro *et al.*, 1998). Recent studies have demonstrated that the dechlorination of both unsaturated and saturated chlorocarbons in water systems appear to take place by complex parallel sequential processes.

Metheson *et al.* (1994) postulated three possible pathways that might be contributing to the dechlorination of alkyl halides. The first pathway starts with an electron transfer from the Fe^0 surface to the adsorbed target materials. In the presence of a proton donor like water, the metal/halogenated system undergoes reductive dehalogenation:

$$M^\circ + RX + H^+ \rightarrow M^{2+} + RH + X^-$$

where M° represents the zero-valent metal, R is the alphatic molecule, and X is chlorine atom.

With certain metal powders, this dehalogenation process can undergo the second step:

$$2M^{2+} + RX + H^+ \rightarrow 2M^{3+} + RH + X^-$$

The third pathway involves hydrogen molecules produced as a product of corrosion with water.

$$M^\circ + RX + H_2O \rightarrow M^{2+} + RH + X^- + OH^-$$

Each metal possesses a characteristic standard reduction potential, which determines its ability to spontaneously dechlorinate an organochlorine compound. The less positive the reduction potential, the faster and more complete the chemical reduction (Metheson *et al.*, 1994). The standard reduction potentials of common zero-valent metals have been reported to be as follows (Kaplan *et al.*, 1996; Weber, 1996; Allen-King *et al.*, 1997; Zdemir and Tfekci, 1997; Arnold and Roberts, 1998; Gotpagar *et al.*, 1998; Yoshihiro *et al.*, 1998):

$$Cu^0 \rightarrow Cu^{2+} + 2e^- \quad E^0 = 0.337V$$

$$Cu^0 \rightarrow Cu^+ + e^- \quad E^0 = 0.521V$$

$$\mathrm{Fe^{o}} \rightarrow \mathrm{Fe^{2+}} + 2e^{-} \quad E^{o}= -0.440\mathrm{V}$$

$$\mathrm{Fe^{2+}} \rightarrow \mathrm{Fe^{3+}} + e^{-} \quad E^{o}= 0.770\mathrm{V}$$

$$\mathrm{Ni^{0}} \rightarrow \mathrm{Ni^{2+}} + 2e^{-} \quad E^{o}= -0.250\mathrm{V}$$

$$\mathrm{Zn^{0}} \rightarrow \mathrm{Zn^{2+}} + 2e^{-} \quad E^{o}= -0.763\mathrm{V}$$

Matheson *et al.* (1994) also concluded that the carbon tetrachloride degradation in water by iron was the result of direct electron transfer from the iron surface. The metal served both as an electron donor and as an adsorbent and catalyst (Cheng *et al.*, 1997). However, chlorocarbon degradation by metal particles in water has also been considered to be a heterogeneous, surface-mediated process (Wafo *et al.*, 1996).

The mechanisms discussed above are based on the metal corrosion process. However, catalytically promoted dechlorination might represent another important mechanism of dechlorination. Yumin *et al.* (1995) studied the mechanism of catalytically promoted PCB dechlorination. When titanocene dichloride ($CpTiCl_2$) reacted with sodium borohydride ($NaBH_4$), it produced titanocene borohydride ($CpTiBH_4$). In the presence of amine, $CpTiBH_4$ produced the unsaturated compounds, CpTiH, that was capable of promoting the dechlorination of PCBs. With the addition of pyridine, the catalytic rate was enhanced appreciably. Kawahara *et al.* (1997) proposed a three-step base-catalyzed mechanism of decomposition for PCBs. Initially, hydrogen species were generated from the paraffin oil then the hydrogenation of aromatic catalysts (phenanthrene, anthracene and alkyl naphthalenes) to form dihydroaromatics occurred. Alternatively, the absorption of hydrogen by hexagonal forms of carbon or transition metals occurred, and finally the hydrogen species was transfered to the activated PCB. The product biphenyl can be degraded further or possibly can form adducts or polymers (Tratnyek *et al.*, 1997). Yao (1997) reported that dechlorination occurred mostly on the more substituted ring. Antisymmetric congeners are more readily dechlorinated than relatively more stable symmetric isomers. Dechlorination occurred preferentially at the position to produce symmetric products. The *pi*-electronic densities of 4-Cl and 3-Cl affect their relative reactivities. Correlation analyses using K_{SA} revealed that dechlorination generally was more rapid at saturated carbon centers than unsaturated carbons and that high degrees of halogenation favoured rapid reduction (Johnson and Tratnyek, 1995; Johnson *et al.*, 1996).

A newly proposed dechlorination mechanism has involved the transient organometallic concept (Romanova *et al.*, 1992). During the dechlorination process, an initial electron transfer from the metal surface was followed immediately by direct attack of the chlorocarbon on the metal surface yielding a transient organometallic specie or radical-like specie, the C-Cl bond was then weakened and the chlorine was released.

In the bimetallic systems, dechlorination pathways are altered relative to mono-metal systems. Boronina *et al.* (1998) studied the dechlorination by zinc doped with Pd, Ag and Au. Ag and Au enhanced the dechlorination as well as Pd. Because Pd is a relative catalyst metal capable of facilitating bond cleavage of H-H, C-H and C-Cl bonds, it was concluded that the catalytic processes were of lesser importance, and that the doped metals serve only to facilitate the electron transfer. It was confirmed by Muftikian *et al.* (1996), who investigated the nature of the Pd/Fe surface by X-ray photoelectron spectroscopy, that the reactive Pd/Fe surface was formed by the stepwise reduction of Pd(IV) in solution to Pd(II) that replaced protons on the hydroxylated Fe-oxide surface and forms Pd(II)-O-Fe bonds. These bonds were unstable and collapsed spontaneously to yield reactive palladized iron. Enhanced reactivity of palladized iron was believed to be due to hydrogenation because Pd has the ability to intercalate hydrogen into its lattice (Grittini *et al.*, 1995). During dechlorination, the chlorinated organic compound is adsorbed to the Fe surface and reacts with the hydrogen intercalated by the Pd.

1.8 Application of supercritical fluid on the remediation of PCBs

1.8.1 Supercritical fluid extraction

The supercritical phase was first described by Baron Cagniard de La Tour in 1822. He found that the gas-liquid boundary disappeared when the temperature of certain materials was increased by heating each of them in a closed glass container. Although Hannay and Hogarth (1879) demonstrated that a supercritical fluid has a strong solvating power for solids, it is only in the last two decades that numerous industrial and academic research and development laboratories have investigated the underlying fundamentals and process applications of supercritical fluid solvents. Supercritical fluid extraction (SFE) was introduced by Zosel in 1963. Since then, SFE technique has been developed rapidly (US EPA, 40 CFR 279) During the last ten years, the applications of supercritical fluids have seen emphasis in the following areas:

1. Environmental control and hazardous waste treatment
2. Chemistry and biochemistry
3. Removal of nicotine from tobacco
4. Cleaning of electronic parts
5. Extraction in the food and pharmaceutical industries

The most widely used SF solvent is carbon dioxide (CO_2) because it is not toxic, not flammable, not expensive and does not threaten the ozone layer. It can efficiently and economically improve recovery, increase reproducibility, decrease the use of halogenated solvents and provide solvent free extracts to the measurement instrument (Papilloud *et al.*, 1996; Bonshtain *et al.*, 1998). Its advantages include:

1) Supercritical CO_2 possesses a high thermal diffusivity and low kinematic viscosity that permits rapid mass transfer in tightly packed matrices. Compared to convential liquid extraction techniques, it can reduce the time required for the quantitative extraction and recovery of analytes from a wide variety of samples.
2) Its liquid-like density and high compressibility increase the solvating power. The solvent strength can readily be controlled/modified since the solubility depends on the pressure and temperature used for the extraction.
3) Its critical temperature and critical pressure are readily achieved with common laboratory equipment.
4) Supercritical CO_2 is the least expensive solvent with the exception of water.

1.8.2 Extraction and mobilization of PCBs with supercritical CO_2 fluid

Supercritical fluid technologies, as alternatives to conventional procedures, have been used to extract various herbicides from environmental matrices because of its desirable properties that include efficiency, selectivity and speed (Bunte *et al.*, 1996; Luque and Tena, 1996; Papilloud *et al.*, 1996; Reighard and Olesik, 1996; King *et al.*, 1997). These properties are being exploited for the direct extraction of acidic and polar contaminants from soils, sediments and contaminated aqueous matrices (Meredith and Burk, 1998). Studies with SFE have demonstrated that the dithiocarbamates, β-diketones and hydroxamic acids are effective chelating agents for a broad range of transition metal ions. Glennon *et al.* (1997) applied fluorinated mono hydroxamic acids and their N-substituted derivatives in the SFE of metal ions, in particular Fe(III), using unmodified supercritical CO_2. The extraction efficiency of Fe(III) from spiked filter paper can reach 97% with new ligands such as perfluorooctanohydroxamic acid under optimized conditions. The extraction efficiencies were determined to be a function of pressure and temperature.

Ashraf-Khorassani *et al.* (1997; 1999) demonstrated that nickel(II), copper(II) and chromium(III) could be extracted efficiently from aqueous media into SFE using fluorinated acetylacetonate chelates. The solubility of fluorinated acetylacetone chelates in SFE was at least an order of magnitude higher than that of non-fluorinated analogs.

Similarly, 2-methyl-5-hexyloxymethyl-8-quinolinol (HMO6Q) and 5-hexyloxymethyl-8-quinolinol (HO6Q) in supercritical CO_2 could extract gallium(III) from weakly acidic solution. The extractability of gallium(III) was dependent on the temperature and pressure of the supercritical CO_2 (Ohashi *et al.*, 1997).

Using both pure and methanol-modified supercritical CO_2, it was possible to extract both spiked mercury complexes and mercury ions from a variety of matrices including sludge, fly ash, soil, filter paper, and sand. The recovery of Hg(II) from soil, fly ash and sludge using sodium diethyldithiocarbamate (as the *in-situ* chelating agent) was <40% with pure CO_2 (400 atm) at 80°C, while recovery of

Hg(II) from the same matrices using lithium trifluoroethyldithiocarbamate was >90% under the same conditions (Boronina *et al.*, 1996). Wang *et al.* (1995) achieved quantitive extraction of Hg^{2+} from sand and cellulose-based filter papers using proton-ionizable crown ether (as an extract) in methanol (5%) modified supercritical CO_2 at 60 °C and 200 atm. Methanol-modified supercritical CO_2 containing the macrocyclic ligand also was capable of extracting Hg^{2+} from aqueous samples. Formation of extractable metal chelates with the ligand at the pH defined by the CO_2-H_2O system appeared to be an important factor in determining the extraction efficiencies of the metal ions.

Fiddler *et al.* (1999) extracted 16 common organochlorine pesticides (OCPs) from liquid whole eggs using supercritical CO_2. The OCPs included aldrin; α-, β-, δ- and γ-BHCs; DDD, DDE, and DDT; dieldrin; endosulfans I, II and sulfate; endrin; endrin aldehyde; heptachlor and heptachlor epoxide. Under condition of 10000 psi, 40 °C and $scCO_2$ flow rate of 3.0 l/min, the recoveries ranged from 81.8 to 108.3% at 0.05 ppm for an extraction time of 40 min.

Creutznacher (1997) used supercritical CO_2 as a solvent for extracting PCBs from contaminated soil samples. The results were compared with the Soxhlet-extraction in terms of extraction reliability and environmental exposure. Higher recoveries were found for more highly chlorinated PCBs with SFE. The consumption of organic solvents for 16 soil samples was 1600 ml for the Soxhlet-extraction and only 80 ml for the SFE. Researches have demonstrated that 11 phenolic and nitroaromatic compounds from a spiked river sediment can be extracted efficiently by methanol-CO_2 mixtures under supercritical conditions (Creutznacher *et al.*, 1994; Creutznacher, 1997)

1.9 Summary

In this study all effort would be made to try to develop a method that can determine PCB concentration rapidly, conveniently and quantitatively in contaminated soils/sediments; to develop a novel approach that can dechlorinate PCBs quantitatively and efficiently using supercritical carbon dioxide coupled with zero-valent metal/bimetallic metal mixture technologies; to establish a process that combine PCB extraction from polluted soils/sediments using surfactant suspensions with PCB mobilization by back-extraction; to develop a technique that combine PCB extraction from surfactant suspension with *on-line* dechlorination; and finally to optimize the PCB mobilization, dechlorination process to be operated efficiently, continuously and environmental friendly.

Chapter 2
Preface

In Chapter one, PCB properties, historical usage patterns, techniques for their mobilization from soil/sediment as well as possible treatments for PCB destruction were reviewed. The current problems of PCB contamination were discussed. Novel approaches/techniques that combined $scCO_2$ with zero-valent metal/bimetallic particles for PCB extraction/ mobilization and dechlorination were proposed.

As a prelude of PCB detoxification, Chapter two reports a novel method for the determination of total PCB content in contaminated soil/sediment. It is suggested that the contaminated sample be mixed with magnesium flakes, potassium hexachloropalladiate (K_2PdCl_6), propan-2-ol and water then permitted to react for a certain period of time. Under optimized conditions, all PCB congeners are anticipated to be converted to biphenyl and then recovered by extraction into hexane. Finally quantification by gas chromatography with flame ionization detection is used to estimate the total burden of PCB compounds that were present in the sample.

Approaches to the determination of polychlorinated biphenyl (PCB) concentrations in soils/sediments by dechlorination to biphenyl

2.1 Introduction

As a prelude to optimizing remediation techniques/procedures for soils and sediments burdened with polychlorinated biphenyl compounds (PCBs), a rapid technique to determine the levels of the target analytes in these matrices was required. Conventional methods have employed a variety of approaches for extraction/mobilisation followed by quantification of the analytes by high resolution gas chromatography (GC) frequently with electron capture or quadrupole mass spectrometric detection (Buethe and Denker, 1995; Frame, 1997; Smedes and Boer, 1997). Successful approaches to the mobilisation stage of the analysis have included extractions with supercritical carbon dioxide (Glazkov, 1999) and sub-critical water (Akgerman and Yeo, 1993) as well as the more conventional Soxhlet, sonication (Harrison and Melnychuk, 1995), solid-phase (Abdul, 1990; Akgerman and Yeo, 1993) or microwave-assisted extraction (Auerbach, 1997). Alternative approaches to the quantitation stage of the analysis have included immunoassay techniques (Huang *et al.*, 1997; Weerasooriya *et al.*, 2000) and conversion of the various PCB congeners to a common derivative prior to or during chromatography. Two approaches, complete chlorination (Beck *et al.*, 1997; Deshpande *et al.*, 1999; Kim and Lee, 2000) to decachloriobiphenyl or complete hydrodechlorination (Ang and Abdul, 1995; Sabatini *et al.*, 1998; Dierkes *et al.*, 2000; Haegel *et al.*, 2000; Kitiyanan *et al.*, 2000; Scamehorn and Harwell, 2000; Zhou and Rhue, 2000) to biphenyl have been pursued. Earlier dechlorination methods were directed to the potentiometric determination of chloride ion liberated by sodium dispersion (Ware *et al.*, 1988), the action of $LiAlH_4$ in an inert atmosphere (Sabatini *et al.*, 1998; Haegel *et al.*, 2000) or the action of Pt/Pd catalysts at elevated temperature (Kitiyanan *et al.*, 2000; Zhou, 2000). More recent procedures have employed facilely prepared iron/palladium (Fe^o/Pd^o) (Doyle *et al.*, 1998) or magnesium/palladium (Mg^o/Pd^o) bimetallic mixtures (Vane *et al.*, 2000) that function efficiently at room temperature in mixed aqueous organic medium. Alternate procedures have involved the use of ammonium format and Pd/C again in mixed medium (Anwer and Spatola, 1985; Barren *et al.*, 1993).

The generation of a single derivative to estimate the total PCB burden in natural matrices circumvents the influence of field weathering and variations in volatility that collectively cause appreciably alternations to the populations of specific PCB congeners with time. Subsequent quantification of aged field residues based on the "standard" commercial PCB mixtures can become increasingly uncertain. These difficulties can be confounded by the presence of chlorinated pesticides or other chlorinated organics in the extracts that must be removed prior to quantification.

Additionally, conversion to a single derivative provides increased detectability so that flame ionisation can suffice and the requirement for detection by electron capture and the attendant variations in congener-specific responses can be avoided. This Chapter extends the dechlorination procedure to soils and sediments. The principle disadvantage of the derivatisation approach remains the loss of all congener-specific information.

2.2 Material and methods

2.2.1 chemicals, solvents and standard reference materials

Magnesium granules (12~50 mesh, 99.8% purity) and potassium hexachloropalladate (K_2PdCl_6) were purchased from Alfa Aesar, Ward Hill, MA. Triton DF 16 and biphenyl were purchased from Sigma-Aldrich, Oakville, ON. Hexane, propan-2-ol (HPLC grade) and acid washed sea sand were purchased from Fisher Scientific, Ottawa, ON. Aroclor 1242 mixtures were kindly donated by Monsanto Company, Sauget, IL. Aroclor 1260 was purchased from Supelco, Bellefont, PA. Standard reference material, SRM 1939a, was purchased from National Institute of Standard and Technology, USA. CRM 481 and CRM 536 were purchased from European Commission LGC Lt. Teddington, UK. All chemicals, solvents and materials were used as received.

2.2.2 Soil samples and pretreatment

One agricultural soil and two field contaminated soil samples were collected from appropriate sites. The agricultural soil has been cultivated continuously for more than 70 years. The PCB-contaminated soil samples were collected from (i) a manufacturing facility where intermittent contamination had occurred from broken hydraulic lines during 1960s and 70s and (ii) a railway facility where PCB contamination had accumulated for more than 17 years. The soil samples varied in pH, texture, and organic matter (Table 2.1). After sample collection, all soils were air dried and were passed through a 2 mm sieve (10 mesh) and mixed thoroughly. One third of all the samples were further ground and passed through 50 mesh sieve, and then stored in refrigerator (-4 ^{0}C) for use.

2.2.3 Aroclor standard solution

Aroclor 1242 stock solution (1%, v/v) was prepared by diluting 1.0 ml pure Aroclor 1242 to 100 ml with hexane. Diluted working solutions of Aroclor 1242 (10 μg/ml) were prepared by further diluting 0.1 ml of 1% Aroclor 1242 solution with hexane or propan-2-ol. The 1% Aroclor aqueous emulsions were prepared by diluting 1 ml of Aroclor 1242 or 1248 or 1254 or 1260 stock solution plus 4.0 ml of Triton DF16 to 100 ml with distilled water. Biphenyl standard solution was prepared by diluting biphenyl standard (50.0 mg) to 100 ml with hexane.

2.2.4 Soxhlet extraction

EPA method 3540 was followed. Briefly, an accurately weighted aliquot of soil, 10 g, was mixed with 10 g anhydrous sodium sulfate, then added to an extraction thimble and extracted with 50 ml refluxing acetone-hexane (1+3, v/v) during 20 h. The extracts were subsequently concentrated to 40 ml under a gentle stream of nitrogen.

2.2.5 Sonication extraction

EPA method 3550 was followed. Briefly, a Polytron homogenizing unit (N.Y. 11590, Brinkmann Instruments, Mississauga, ON) was used with the output control knob set at

Table 2.1. Description of principle properties of soil/sediment samples

Samples	Certified PCB conc. (mg/kg)	pH 1:1 water/soil	Organic matter(%)	Particle size(mesh)	Note
Soil 1	N/A	7.1	2.1	10~50	Agricultural soil that had been under active cultivation during the last 70 years
Soil 2	N/A	7.38	4.8	~50	Soil from a railway facility contaminated with Aroclor 1242, 1248,1254 and 1260
Soil 3	N/A	7.75	3.6	~50	Soil from a manufacturing facility contaminated with Aroclor 1242,1254, oil, grease and heavy metals
SRM1939a	27.2 ± 3.0		N/A	~325	Contaminated freshwaterriver sediment
CRM 481	472.5 ± 29		12	~170	Industrial soil
CRM 536	0.34 ± 0.04		N/A	~120	Freshwater harbour sediment

11 and the mode switch was on pulse. A aliquot of soil (20.0 g) was mixed with 33.3 ml of acetone-hexane (1+3, v/v) and sonicated for 3 min. The procedure was repeated three times and a total volume of 100 ml was filtered and combined. The extracts were concentrated to 40 ml with a gentle nitrogen stream.

2.2.6 Extract clean-up

During Soxhlet or sonication extractions an appreciable quantity of the organic matter was co-extracted. The concern was that these organic materials might interfere the derivatization of PCBs. In an attempt to eliminate the effect of organic co-extractives, concentrated sulfuric acid was used to break down the compounds by dehydration or oxidation without affecting PCB compound. Sulfuric acid (4 ml, 17 M) was combined with 40 ml extract. After 30 min reaction, the decomposition products and excess acid were removed by washing the extract with distilled water.

2.2.7 Biphenyl conversion and determination

Magnesium flakes (2 g, 10-50 mesh), potassium hexachloropalladate (K_2PdCl_6), 10 mg, propan-2-ol, 2 ml, and test substrate were combined in a 50 ml flask. Distilled water, 2 ml, was added to initiate the reaction and the mixture was stirred for 1 min. The stirring procedure was repeated every 30 min. After 0.5-6 h of reaction, the mixture was extracted with 2 ml hexane (by vortex stirring for 1 min). After separation of the layers, one ml of the organic phase was withdrawn for biphenyl quantification. For sand or soil/sediment matrices, 1 g of sample was added to the reaction vial after the Mg particles (2 g) and 10 mg of K_2PdCl_6. The reaction procedure, as described above, was followed.
Quantification of biphenyl product was carried out using a Hewlett-Packard model 5890 (II) gas chromatography (GC) equipped with flame ionization detection (FID) and a model 5791 autoinjector. The 30 m (0.53 mm i.d.) DB-5 column was held at 50 ^{o}C for 1 min then ramped to 270 ^{o}C at 10 ^{o}C/min and held for 5 min. Analyte identity/purity was corroborated with a Hewlett-Packard model 5890(II) GC equipped with split/splitless injection and with a model 5971 mass-selective detector (MSD). An HP-1 column (30 m X 0.25 mm i.d.) was used and the MSD was operated in an electron impact (EI) mode.

Samples were resolved with a temperature program that started at 50 °C for 2 min followed by ramping to 280 °C at 10 °C /min then held for 5 min.

2.3 Results and discussion

2.3.1 Conversion of PCB compounds to biphenyl

Biphenyl formation from PCB mixtures has been reported to be efficient (greater than 98%, Engelmann and Cheng, 2000) under mild conditions in the presence of excess Mg^0 particles and potassium hexachloropalladate. As summarized in Table 2.2, conversion factors can be calculated based on the mean molecular weight for each commercial formulation.

Observed conversions to biphenyl of Aroclors 1242, 1248, 1254 and 1260 in propan-2-ol/water solution are summarized by the linear regressions of Figure 2.1 and for comparison, the FID response to biphenyl standard is also presented. As indicated in Figure 2.1, there was good agreement between the measured amount of biphenyl generated from the Aroclor standard mixtures and the amount predicted for quantitative conversion when the dechlorination was conducted in propan-2-ol/water solution. Within experimental error, the ratio of the slope of the regression equation for each Aroclor formulation relative to the regression line for biphenyl standard (Table 2.2) was similar to the corresponding ratio of their molecular weights (and accounted for approximately 95% conversion). Thus, over the limited range of concentrations (0.5-20 μg/ml) each formulation was converted efficiently but not quantitatively to biphenyl. To identify the parameters that influenced the efficiency of conversion of Aroclor mixtures, various matrices were also studied. Figure 2.2 summarizes the biphenyl conversion within (i.) a four percent (v/v) nonionic surfactant (Triton DF 16) emulsion; (ii.) a sand mixture; and (iii.) the propan-2-ol/water solution. Reaction products were extracted with 2 ml hexane after 2 h reaction.

There were no substantial differences in the contents of biphenyl generated from Aroclor 1242 that had been added, at 0.3-27 μg/g, to the different matrices. From the results of biphenyl formation from 1242, 1248, 1254 and 1260 in different media, several conversion models were established. As summarized in Table 2.3, all models were significant and could be used to estimate the concentration of PCBs in the different

Table 2.2 Conversion coefficients [a] for Aroclor formulations

Aroclor Mixture	Slope linear regression	Average M.W. for mixtures		Conversion coefficient (mass 12xx to mass $C_{12}H_{10}$)		Slope12xx/ $\text{Slope}_{\text{biphenyl}}$
1242	1289.3	258.2[b],	257.5[c]	0.5972,	0.5988	0.566
1248	1142.1	289.4[b],	291.9[c]	0.5328,	0.5283	0.501
1254	984.8	329.7[b],	326.4[c]	0.4677,	0.4724	0.432
1260	914.7	368.0[b],	366.0[c]	0.4190,	0.4213	0.401
biphenyl	2279.6	154.2		1.0	1.0	

[a]: Ratio was calculated by dividing the MW for biphenyl by the mean MW for the Aroclor formulation.

[b]: Data were adapted from Alford-Stevens *et al.* (1986).

[c]: Data were taken from Erickson (1997).

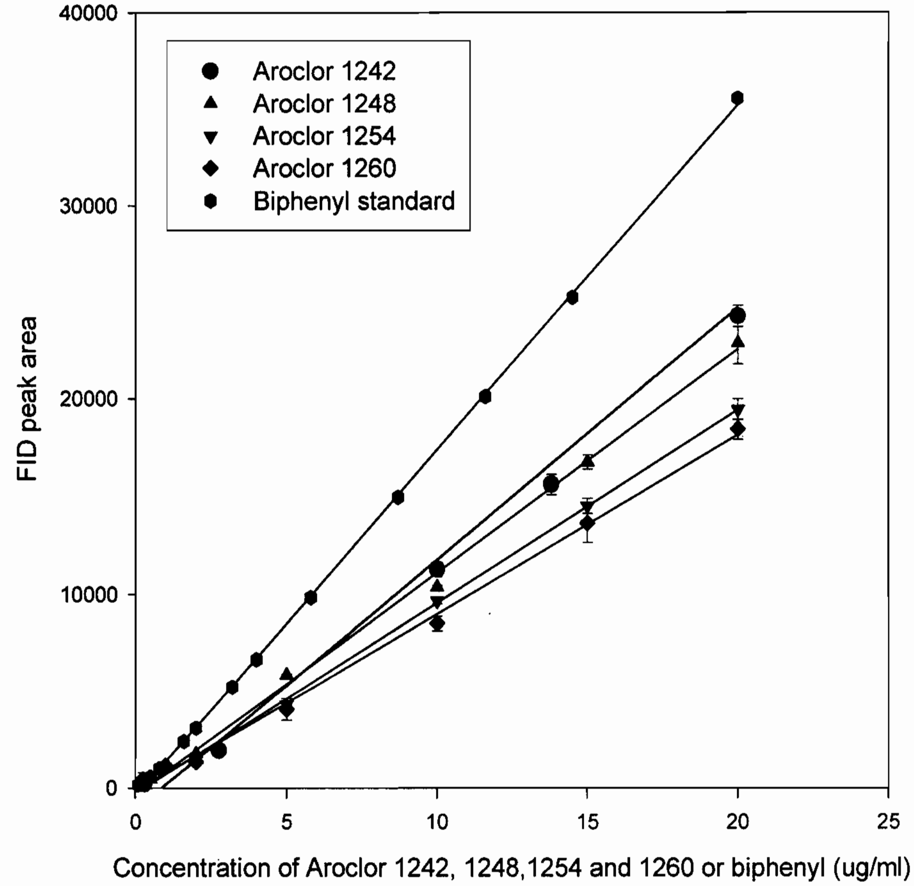

Figure 2.1 Linear regression of flame ionization peak area as a function of concentration (0.3-22 μg/g) of biphenyl, Aroclor 1242, Aroclor 1248, Aroclor 1254 and Aroclor 1260.

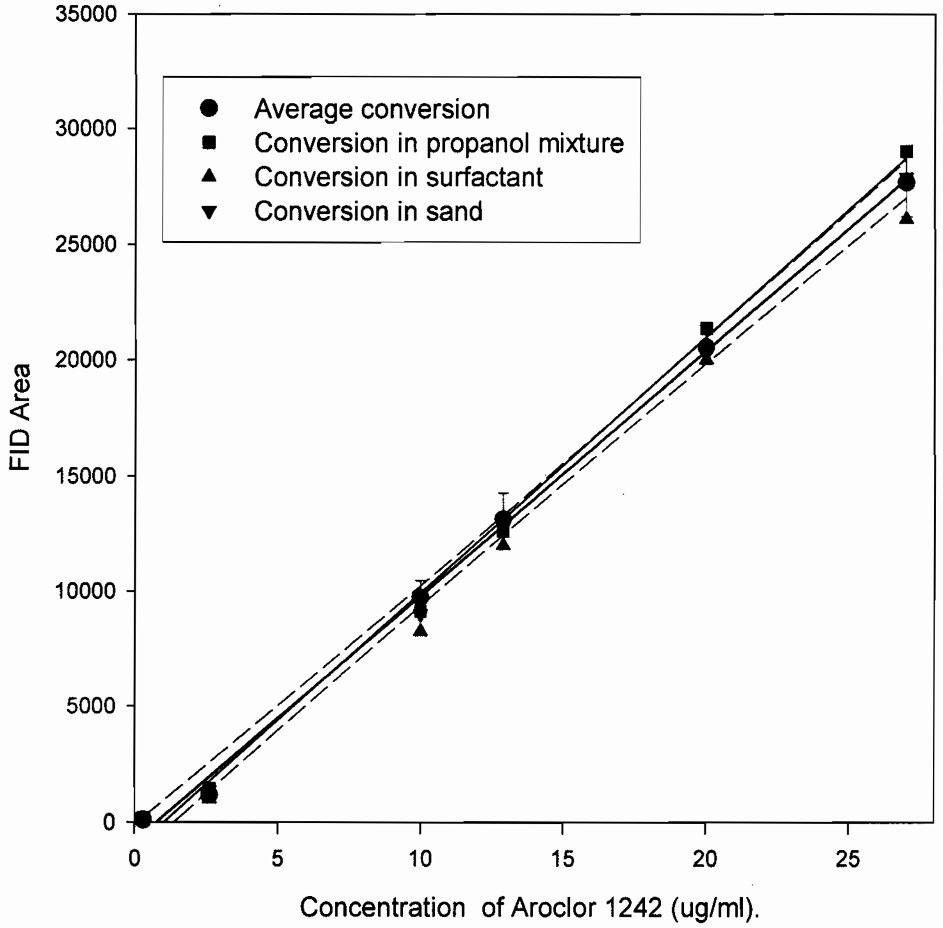

Figure 2.2 Means (plus 95% confidence interval) for biphenyl recovered from sand, surfactant emulsion or propan-2-ol/water solution for Aroclor 1242 formulation added to each matrix at 0.3-27 μg/g.

Table 2.3 Linear regression models for the conversion of Aroclor formulations to biphenyl in different matrices.

Aroclor	Matrices	Regression models[a]	Range (ppm)	Coefficient of determination (R^2)[b]
1242	Propanol mixture (3h reaction)	Y=1141*PCB-778.3	0.1-45	0.993
	Surfactant solution	Y=1106.1*PCB-1136	0.1-45	0.997
	Sand matrices	Y=1059.4*PCB-878.6	0.1-45	0.997
	Soil matrices (6h reaction)	Y=1230*PCB+563.7	0.1-140	0.993
	Average	Y=059.9*PCB-816.4	0.1-45	0.993
1248	Propanol mixture	Y=1142.1*PCB-336.9	0.1-20	0.996
	Soil matrices (6h reaction)	Y=1060*PCB+38.4	0.1-20	0.996
1254	Propanol mixture	Y=984.8*PCB-298.4	0.1-20	0.998
	Soil matrices (6h reaction)	Y=873.7*PCB+210.3	0.1-20	0.995
1260	Propanol mixture	Y=823.7*PCB-9.5	0.1-40	0.997
	Soil matrices (2h reaction)	Y=183.8*PCB+419.5	0.1-40	0.984
	Soil matrices (6 h reaction)	Y=770.1*PCB-845	0.1-40	0.996

[a] Y= flame ionization response.

[b] Significant at the 99% level of confidence ($p<0.0001$).

matrices. The Student T-test did not identify any statistically significant differences among models for different media. To monitor the conversion efficiency at higher concentrations, Aroclor 1242 and a 25 ml volume of hexane extractant were used. The reactions were performed with the same conditions of reagents as before [2g Mg^o, 10 mg K_2PdCl_6, 4 ml of 1+1 (v/v) propan-2-ol, water]. The results are summarized in Figure 2.2. Again, the efficiencies of conversion for Aroclor 1242 added at 69-6900 μg/ml to each of the three matrices were within the 95% confidence interval of the mean. Again, there were no significant differences among models for different media (Table 2.3). Neither the presence of the surfactant nor sand had any discernable effect on the conversion of PCB compounds to biphenyl at either higher or moderate concentrations.

2.3.2 Biphenyl conversion within soil matrices

To test the efficiency of the dechlorination of PCBs compounds within soil matrices, a spike of a cultivated soil (soil No.1) was used. Figure 2.3 summarizes the recoveries of biphenyl from Aroclor 1242 and 1260 standard spiked into the soil. For comparison, data obtained in propan-2-ol/water mixture are also presented. Surprisingly, the biphenyl concentrations generated within the soil were modestly greater (2.4-6.7%) than if the same quantity was added to the propan-2-ol/water mixture. However this increase, although consistent, remained within the 95% confidence interval associated with the linear regression model.

As indicated in Table 2.3, soils that had been spiked with Aroclor 1242 or 1248 or 1254 or 1260 standard, resulted in recoveries of biphenyl that were in good agreement with predicted values. It was observed that the Aroclor 1260 conversion model provided the closest agreement for the estimation of PCBs concentration for contaminated soil samples, especially close for certified reference materials. In consequence, all estimations of PCB concentration with soil samples were calculated based on the Aroclor 1260 model.

The method limit of detection in terms of direct PCB conversion to biphenyl within the soil was approximately 150 μg/kg using the model of three times baseline noise divided by the slope. The capacity to convert PCB mixtures to biphenyl within the soil was

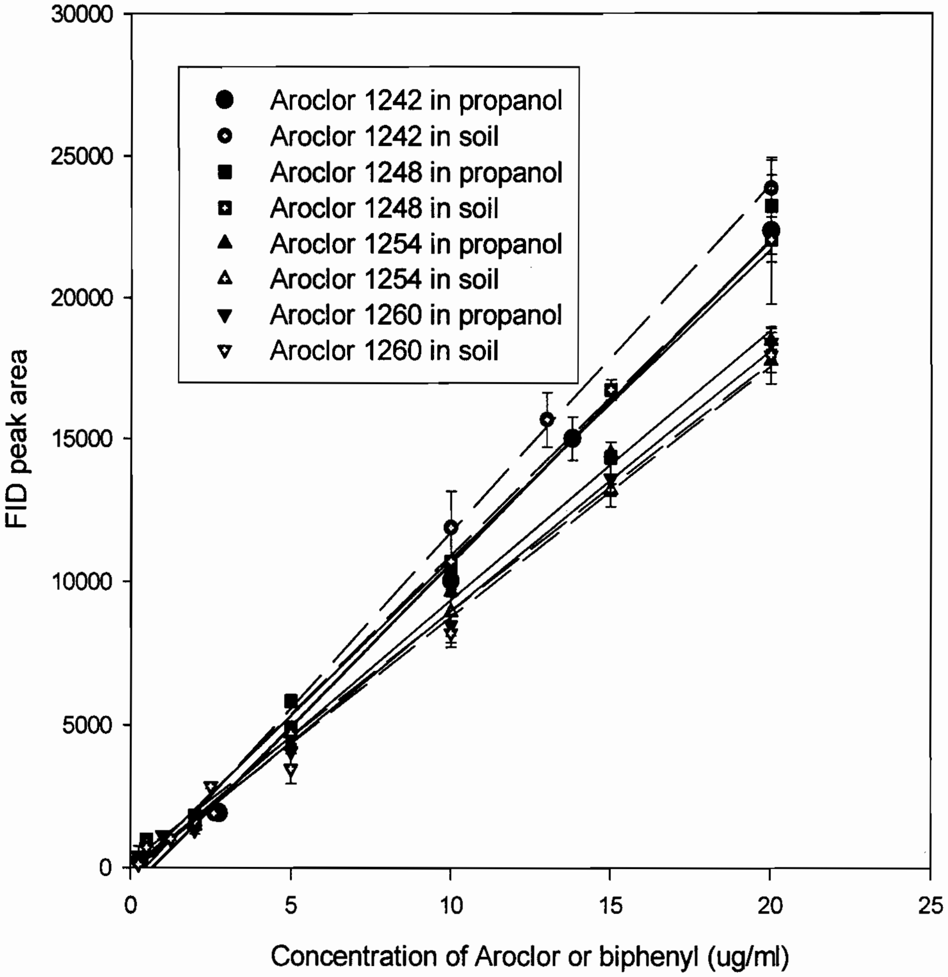

Figure 2.3. Variations in recoveries of biphenyl from Aroclor 1242, Aroclor 1248, Aroclor 1254 or Aroclor 1260 added to soil or propan-2-ol/water at 0.3-22 μg/g.

increased when the quantity of added magnesium was increased. One gram of Mg was insufficient for quantitative conversion within the soil if the PCB concentration was in excess of 5 mg/kg. This was true especially for more highly chlorinated substrates such as Aroclor 1260. All subsequent experiments were conducted with 2 g Mg added to the sample matrix. The quantity of K_2PdCl_6 used for the reaction mixture has less of an effect on the conversion efficiency of the PCBs. In preliminary studies, the yield of biphenyl from Aroclor 1242 was similar for increasing amounts of K_2PdCl_6 (10-40 mg) added to 2 g Mg in the presence of various quantities of 1242 substrate. Subsequent experiments were carried out with 10 mg K_2PdCl_6. The conversion of PCBs to biphenyl within soil, was also time dependent. There were substantial differences between the recoveries after 2 h and 6 h of reaction in the soil matrix. Although the calibration plots generated with 1260 substrate for both reaction times provided good fits with linear models (coefficients of determination, R^2=0.996, 0.983), 2 h of reaction was insufficient to quantitatively dechlorinate the substrates within the soil. By contrast, there was a good agreement with the theoretical biphenyl content of Aroclor 1260 for the longer reaction time. As measured by GC-FID (and peak purity corroborated by GC-MS), the conversion of PCBs to biphenyl within soil matrices was greater than 98% over the substrate concentration range of 1-52 μg/g.

The soil particle size influenced the dechlorination rate for PCBs. For samples of soil No.1 that had been spiked with Aroclor 1242 at 5 mg/kg, no differences in recoveries were observed from substrate that had been sieved to pass a 50-mesh screen vs. material that had been sieved to pass a 10-mesh screen. Analogous results were obtained for soils 2 and 3, the samples with a smaller particle size required a longer reaction time. In this study, 2 h of reaction were suitable for soils sieved to 10-mesh, 4 h for the samples of 50-mesh and 6 h for the samples of greater than 125-mesh.

2.3.3 Certified Reference Materials

The contaminated soils in this study were characterized by a relatively low content of organic matter that might have affected the recovery of biphenyl from PCBs. Other soil obtained between the PCBs concentration determined by dechlorination to biphenyl and

Table 2.4 Total soil PCB concentrations as determined using different procedures

Methods	Soil 1	Soil 2	Soil 3	RSM1939a	CRM 481	CRM 536
Direct conversion within the soil matrices	N.D.[a]	20.8 ± 1.2[b]	19.3 ± 0.9	32.7±1.5	437.4 ± 14.2	1.8 ± 0.2
Method of standard additions to the soil	N.D.	22.5 ± 1.4	21.3 ± 1.8	---	---	---
Conversion on the Soxhlet extract	N.D.	30.3 ± 6.6	36.2 ± 2	35.4 ± 1.8	478 ± 46.5	2.2 ± 0.2
Conversion on the sonication extract	N.D.	24.9 ± 1.1	28.1 ± 1	---	---	---

[a]: N.D. none detected- lessd than 0.1 mg/kg

[b]:one relative standard devation based on 3 replicate determination

properties were anticipated to have less of an effect on the conversion. Table 2.4 summarizes the results obtained for soil/sediment matrices. Acceptable agreements were the certified PCB content for two of the three reference materials. The PCB content of the third reference material (certified 0.34 μg/g) was appreciably overestimated by the biphenyl conversion procedure. Acceptable agreements were also observed between the estimated PCB concentrations for additions of standard back to contaminated soils and estimates based on direct conversion within the soil matrix.

To corroborate the hypothesis that organic matter could provide a source of biphenyl in soil samples, Soxhlet and sonication extractions were conducted with the three soils and the reference materials. For identical derivatization procedures performed directly on the three soils in the absence or presence of added PCB substrate, no contribution from the organic matter was observed. By contrast, both the sonication and the Soxhlet extracts from the soils 2 and 3 as well as the reference materials did reveal a contribution to the apparent biphenyl recovery from the background. These results indicated that soil samples, even with relatively low content of organic matter, can be converted in part to biphenyl under the mild reaction conditions. The biphenyl that results from soil organic compounds could cause an overestimation of PCB concentration in soil under the conversion conditions (CRM 536 in Table 2.4). Attempts were made to overcome the contribution from this source. Clean-up with concentrated H_2SO_4 was ineffective however. The use of this approach can result in increased variability of recoveries. (European Commission, BCR information, CRM 481 manual).

In summary, the direct derivatization within the sample matrix can be used to estimate the PCB concentration for soil/sediments and contaminated solutions. The concentrations of PCBs in two of the three reference materials (27.2 and 473 mg/kg) were determined successfully. The principle advantages of this procedure include convenience and simplicity but the principle disadvantage is that organic matter can also contribute to the apparent analyte recovery and must be accounted for in accurate estimates. The Aroclor 1260 model can be used to estimate the PCB concentration in contaminated soil/sediments samples.

Chapter 3

Preface

In Chapter two, a novel method for the determination of PCBs in contaminated soils was developed and validated. The reaction was very efficient in propan-2-ol/water, surfactant emulsion or sand mixture and virtually complete in soil provided that excess magnesium and the K_2PdCl_6 were added to the sample prior to the addition of water. High PCB loadings were readily determined in the field contaminated soils either by direct determination within the matrix or by standard additions.

Using this newly developed method, a novel remediation approach for soils contaminated with PCB compounds is designed and evaluated. However, before carrying out the remediation technique, an approach that is capable of dechlorinating commercial PCB mixtures using heated columns of zero-valent metal or bimetallic mixture in a continuous process is described, optimized and then incorporated into the process. In Chapter 3, supercritical carbon dioxide ($scCO_2$) is combined with zero-valent metal(s), tested and then optimized for dechlorinations. An efficient PCB dechlorination scheme results.

Reductive dechlorination of polychlorinated biphenyl compounds in supercritical carbon dioxide

3.1 Introduction

A popular strategy to effect abiotic dehalogenations has been to mediate the reduction in aqueous media in the presence of a sacrificial metal in its elemental form. Zero-valent iron (Gilham and O'Hannesin, 1994; Matheson and Tratyek, 1994; Helland *et al.*, 1995; Warren *et al.*, 1995; Orth and Gillham, 1996; Johnson *et al.*, 1996; Wang and Zhang, 1997; Sayles *et al.*, 1997) and iron-palladium (Muftikian *et al.*, 1995; Grittini *et al.*, 1995; Muftikian *et al.*, 1996) bimetallic mixtures have become especially popular for this purpose. In anoxic aqueous media, free metal ions, chloride ion and hydrogen gas were produced by reaction at the surface of metal particles and protons were consumed. The process kinetics were dependent on solution pH, surface area of the metal particle, substrate concentration, buffer selection and solvent composition (Johnson *et al.*, 1996). Dechlorination approximately followed first-order kinetics and rate coefficients tended to increase with time, an observation that was postulated to have resulted from an increase in reactive metal surface area due to cathodic depolarization and pitting of the iron surface (Helland *et al.*, 1995). Dechlorination occurred under oxic conditions as well, although the rates were appreciably slower. A rapid pH increase was synchronous with dissolved oxygen consumption and the pH remained constant after the oxygen had been depleted. This was attributed to the proton and oxygen consuming aerobic corrosion of the Fe^0 surface (Helland *et al.*, 1995).

Normalization of the apparent rate constants for the dechlorination of different halogenated substrates to the iron surface area yielded a specific rate constant (k_{SA}) that varied by only one order of magnitude for individual halocarbons (Wang and Zhang, 1997). Surface area normalised rate constants for nanoscale Fe^0 particles (1-100 nm diameter) were 10-100 times higher than for commercial particles (Wang and Zhang, 1997). Correlation analysis also revealed that dechlorination is generally more rapid at saturated carbon centres than at unsaturated carbons and that high degrees of halogenation favoured rapid reduction (Johnson, 1996).

Based on the low concentration of chlorinated degradation products in the solution phase it was suggested that most of the substrate remained sorbed to the iron surface until complete dechlorination had been achieved (Orth and Gillham, 1996). Prolonged exposure of the Fe^o or Pd^o/Fe^o surface to a saturated solution of aqueous organochlorine compounds resulted in the growth of a hydroxylated iron oxide film that deactivates the Pd^o/Fe^o surface. The thick hydroxylated iron oxide film could be removed and the original activity of the Fe^o (Pd^o/Fe^o) surface restored by washing the surface with a dilute acid (Matheson and Tratnyek, 1994; Muftikian *et al.*, 1995; Muftikian *et al.*, 1996; Balko and Tratnyek, 1998).

A mechanistic model for the zero-valent metal (Fe^o) mediated dechlorination has suggested a surface mediated process (Weber, 1996) and indicated that rates of decomposition were limited by the sparing solubilities of substrates in the aqueous phase (Sayles *et al.*, 1997). When iron was used to mediate anoxic dechlorination, the slow adsorption of the target compounds to the iron surface and the desorption of hydrocarbon products became the rate-limiting steps that retarded the overall process appreciably (Hardy and Gillham, 1996). It is often considered that water is a necessary component component of metal-mediated corrosion reactions with chlorinated alicyclics. However, there are several literature reports (Archer, 1978; Archer, 1982; Smentkowski *et al.*, 1989; Smentkowski *et al.*, 1990) emphasising that zero-valent iron or aluminum can react dfirectly with these substrates to yield chlorocarbon radicals, metal chlorides and/or chloride ion.

Somewhat less is known about reactions of halogenated aromatics with zero-valent metals. Copper metal has been reported to dechlorinate polychlorodibenzo dioxin (PCDD) and furan (PCDF) derivatives (Hagenmater *et al.*, 1987). Similarly, Fe^o can mediate the dechlorination of chlorinated benzenes (Morlando, 1997), DDT and derivatives (Sayles *et al.*, 1997) and chlorinated phenols (Grittini *et al.*, 1996). Although polychlorinated biphenyl compounds (PCBs) are generally considered to be unreactive to Fe^o at ambient temperature, they have been dechlorinated efficiently with bimetallic iron mixrures. A methanol-water solution of a commercial mixture of PCBs when contacted, for a short time, with palladized iron at ambient temperature, the only reaction products were biphenyl and chloride ions (Grittini *et al.*, 1995). Success has also been achieved using Fe^o at elevated temperatures. At 400 °C in the presence of solvent, PCB mixtures underwent hydrogenolytic dechlorination in the presence of Fe^o powder that led to the complete loss of chlorinated congeners (Chuang *et al.*, 1995) and the recovery of a maximum of biphenyl. Nanoscale Fe^o particles have also been demonstrated to mediate PCB dechlorinations efficiently (Wang and Zhang, 1997). More recently, sub-critical water at 250 °C and 10 MPa pressure has been used to mediate PCB dechlorinations by Fe^o (Yak *et al.*, 1999).

As a remediation strategy, extractions are limited in that the target toxicant(s) can only be transferred/concentrated from one medium to another but are not detoxified per *se*. A more efficient strategy would be to couple the extraction with an *on-line* modification of the toxiforic groups. The objectives of this Chapter were to develop and optimize the operation of a continuous reactor to dechlorinate PCBs. It was anticipated that supercritical carbon dioxide ($scCO_2$) could be used advantageously to mobilize PCBs from particulate media and to transport them through the reactor. Supercritical fluids including $scCO_2$ possesses several advantages that can be exploited in dechlorinations including appreciable substrate solubility (Anitesscu and Tevlarides, 1999) and enhanced rates of solute partitioning and diffusion relative to the liquid phase. On the other hand, CO_2 has been reported to cause the gradual deactivation of Pd supported catalyst (Munakata *et al.*, 1988). PCBs have been purged efficiently from soils with $scCO_2$ (Bjorklund *et al.*, 1999; Pilorz *et al.*, 1999). It remains among the least expensive of solvents. It is non-polar yet is readily separated from non-polar solutes, non-explosive, virtually non-toxic, non-flammable, relatively non-reactive, and waste emissions do not directly increase the burden to greenhouse gases.

3.2 Materials and Method

3.2.1 Chemicals

Copper (electrolytic grade, 40-100 mesh, nominally 99.5% purity), iron (40 mesh, nominally 99.5% purity), nickel (50-100 mesh, nominally 99.5% purity), zinc particles (100 mesh, nominally 99.9% purity) and sodium dispersion, 40% (w/v) in oil, were purchased from Alfa Aesar, Ward Hill, MA and used as received. Acetic anhydride (AcA), ethylene glycol dimethyl ether (1,2-DME), hexane, acid washed sea sand and silver nitrate were purchased from Fisher Scientific, Ottawa, ON and were used as received. Aroclor 1242 and Aroclor 1248 mixtures were kindly donated by Monsanto Company, Sauget, IL.

3.2.2 Ag^o/$Metal^o$ Bimetallic mixtures

The general preparations described by Zhang *et al.* were followed. Ag^o/Fe^o and Pd^o/Fe^o were prepared from 40-mesh iron that had been washed copiously with 6M HCl and rinsed with distilled water. Sufficient aqueous $AgNO_3$ or K_2PdCl_6 to result in a 2% (w/w) surface coverage of the iron, was added to the aqueous iron suspension that was gently mixed on a rotary evaporator for 12 h. Ag/Ni^o was prepared in similar fashion by reaction of aqueous $AgNO_3$ [sufficient to provide a 2% (w/w) surface coverage] with aqueous suspension of pre-washed 50-100 mesh nickel granules during 12 h.

3.2.3 Mixed particle size Pd^o /Fe^o

Mixed particle size Pd^o /Fe^o was prepared by mixing freshly precipitated micron-scale iron particles with 40-mesh iron granules (Zhang *et al.*, 1998). Aqueous 1.6 M $NaBH_4$ was added dropwise to 1.0 M $FeCl_3 \cdot 6H_2O$ with constant stirring. The precipitated product was mixed with an equal quantity of freshly washed 40-mesh Fe^o particles and the mixture was treated with sufficient aqueous K_2PdCl_6 to result in a 2% surface deposit of Pd^o.

3.2.4 Reactor

The dechlorination assembly (Figure 4.1) consisted of standard HPLC fittings and column assemblies that were rated to 6,000 psi. A diaphragm compressor (Newport Scientific, Jessup, MD) delivered liquid carbon dioxide from the eductor tube of the K-type cylinder of CO_2 [bone dry grade ex MEGS, Montreal QC] to a large heated (1.4L) reservoir (temperature and pressure equilibration vessel, TPEV) that served as both a pressure dampener and as a source of supercritical carbon dioxide (scCO2) for the system. The supercritical solvent (~0.8 or 1.5 l/ min of decompressed gas) was

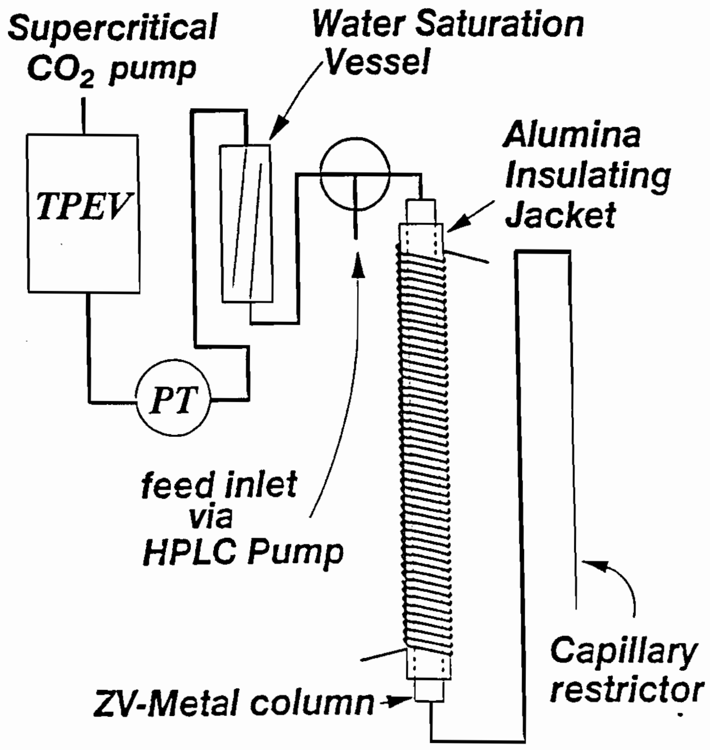

Figure 3.1 Dechlorination reactor assembly consisting of a temperature and pressure equilibration vessel (TPEV), a pressure transducer (PT), a saturation vessel (SV), a mixing tee to merge the supercritical carbon dioxide with feedstock solution, one or more zero valent metal columns and a capillary restrictor all connected in series.

transferred to a five ml saturation vessel (SV, Keystone Scientific, Bellefonte, PA) mounted vertically, a pressure transducer (PT) connected to a digital readout meter, a mixing tee and a reactor unit. Polychlorinated biphenyl (PCB) substrate, dissolved in a suitable solvent, was delivered at 0.1 ml/min to the mixing tee (1/16''i.d.), merged with the $scCO_2$ stream (~4 ml/ min) and fed to one or two stainless steel (ss) HPLC column assemblies [10 mm inner diameter (i.d.) x 25 cm] that were filled with test zero-valent metal (or metal mixture) encased in an insulating alumina jacket (fashioned from thin walled alumina 12 mm o.d. 10 mm i.d. tube, Alfa Aesar, that had been cut lengthways to provide two semi-cylinders) and mounted in series. The ss column-alumina jacketed assemblies were encased separately with 80-turn coils of high resistance heating wire that were energized form variable transformers. Pressure within the assembly was maintained at the desired pressure with a flexible polyamide coated silica capillary restrictor (~25 cm x 0.05 mm, Chromatographic Specialties, Brockville, ON).

3.2.5 Reactor operation

After a short delay to purge residues of air from the system (during which time only $scCO_2$ was fed to the reactor), feedstock 0.1 ml/min of 2-20% (v/v), was added continuously via the HPLC pump to the $scCO_2$ stream and transported to the reactor. Measurements at the exit of the capillary restrictor indicated a flow rate corresponding to 800 - 850 ml/ min of decompressed gas. The exit tip of the capillary restrictor was immersed in hexane (25 ml) to trap products from the reactor eluate. Each experiment was continued until six successive traps had been collected, each corresponding to 10 min of cumulative trapping of reactor eluate. The course of the dechlorination was monitored by gas chromatography (GC) or occasionally by GC-MS to monitor the spectrum and identities of products and by titration to measure levels of residual organically bound chlorine in the eluate.

3.2.6 Organically bound chlorine

The general procedure of Ware *et al.* (1988) was followed. Residual organically bound chlorine in the hexane trapping solution was determined by titration with standardised $AgNO_3$ (~0.01M). Sodium dispersion, 2 ml, was added to a vigorously stirred 10 ml aliquot of hexane trapping solution that had been further diluted 5-fold with fresh hexane. Methanol, 1ml, was added dropwise; the reaction was continued for 5 min then quenched by the addition of propan-2-ol (15 ml) followed by 90 ml water. The aqueous phase, after separation from the organic phase, was diluted to 100 ml in a volumetric flask. A 20 ml aliquot of the reaction mixture was acidified to pH 6-7 with nitric acid (7M), supplemented with 5 drops of potassium chromate indicator solution then titrated with $AgNO_3$. Blank determinations for chloride in reactor eluate consisted of an identical procedure in the absence of added sodium dispersion.

3.2.7 Biphenyl formation from PCB mixtures.

Aroclor mixtures were converted quantitatively to biphenyl by reaction with a solid mixture of Mg^0 and K_2PdCl_6 following the procedure of Doyle *et al.*(1998) (Chapter 2).

3.2.8 Gas Chromatography determination

Gas Chromatography was performed on a Varian Model 3700 GC fitted with a 25 m megabore DB5 column and a flame ionization detector. Helium, delivered at 3.0 ml/min, served as the carrier gas and after an initial temperature hold at 50 ^oC during 5 min, the column temperature was ramped to 250 ^oC during 30 min then held at the upper temperature for a further 5 min. GC-MS were performed on a Saturn-3400 system. The DB-5 capillary column (30 m x 0.2 mm), eluted with helium at 1.0 ml/min, was temperature programmed from 40-300 ^oC during 45 min then held at the final temperature for a further 5 min. Eluting components were identified tentatively by comparison of experimental mass spectra with spectra catalogued in the data base and corroborated by co-chromatography and spectral matching with authentic standards.

3.3 Results and discussion

3.3.1 The efficiency of PCB dechlorination

The dechlorination efficiency (yield) was defined as one minus the ratio of the quantity of organically-bound chlorine in the reactor eluate divided by the chlorine content in an equivalent quantity of feedstock. The extent of dechlorination was influenced appreciably by the identity of the zero-valent (ZV) metal, by the temperature and pressure within the reactor column(s) and especially by the composition of the feedstock. As summarised in Table 3.1, the replacement of water-ethylene glycol dimethyl ether (1,2-dimethoxyethane, DME) mixture with acetic anhydride (AcA) was beneficial to both the dechlorination yield and the repeatability among the six samples collected sequentially during 1 h of operation. Moreover, the dechlorination efficiency seemed to depend on the content of acetic anhydride in the transporting solvent. Whereas 5% and 10% (v/v) of acetic anhydride (AcA) in the DME feedstock provided mean dechlorination efficiencies of 63 ± 10 and 74 ± 9% respectively, an increase in the AcA content to greater than 40% (v/v) resulted in the virtually complete (~99%) dechlorination of feedstock containing 10% PCBs (Figure 3.2). The error bars of this Figure reflect one relative standard deviation (RSD) associated with three replicate determinations, by titration, of residual organically bound chlorine in the eluate trap (mean RSD for the ten separate samples was ±1.3%). Figure 3.2 also summarises the influence of operating pressure on the mean dechlorination efficiency. An increase of 1500 psi in operating pressure increased the mean dechlorination yield by approximately twenty percent. Increased operating pressure result in increased densities of the $scCO_2$ and a greater solvating power of the fluid for the substrate PCBs. Because the components of the reactor were standard HPLC fittings that were rated to 6000 psi at ambient temperature, it was decided arbitrarily to limit the operating pressure of the reactor to 4500 psi or less for reason of safety. The presence of water was not necessary for the dechlorination reaction (Table 3.1). The requirement for at least some water in the reductive dechlorination at metal surfaces had been suggested by the reported lack of any measurable reaction at ambient temperature of neat chlorinated liquid substrate in contact with reducing metal surfaces. It was anticipated that, in the presence of $scCO_2$, the pH of the entrained aqueous phase would be decreased sufficiently (2.8-2.95, Toews *et al.*, 1995) to minimize the build-up of an oxide (hydroxide)/carbonate layer on the ZV metal surfaces. In consequence, we had added the saturator vessel (SV, Figure 3.1) to the $scCO_2$ inlet line. However, when water was removed from the transporting solvent and the SV was removed from the inlet train no diffferences in the dechlorination efficiencies were detected. If AcA alone or diluted with ethylene glycol diethyl ether was fed a single reactor column containing ZV iron (Fe^0) (400 ^{o}C, 4500 psi) no starting material was

Table 3.1 variations in the mean[a] percent dechlorination (± 1 SD) for 2 successive columns (i.) containing various zero-valent metals and (ii.) with different solvent compositions to transfer a 20% (v/v) Aroclor 1242 to the reactor.

ZV-Metal	Feed stock composition (v/v) in the prese of 20% (v/v) Aroclor 1242	Mean dechlorination r (%) for two columns
Cu	5%H_2O, 75%DME	36.0 ± 11.3
Cu	10%DME, 70% Acetic anhydride	86.0 ± 7.6
Fe	5%H_2O, 75%DME	36.3 ± 30.4
Fe	10%DME, 70% Acetic anhydride	94.5 ± 4.4
Ni	5%H_2O, 75%DME	67.8 ± 8.1
Ni	10%DME, 70% Acetic anhydride	91.7 ± 6.1
Zn[b]	5%H_2O, 75%DME	67.0 ± 11.4
Zn[b]	10%DME, 70% Acetic anhydride	89.8 ± 7.5

[a]: Determined at 400 °C using 2 columns.

[b]: Determined at 200 °C using 2 columns.

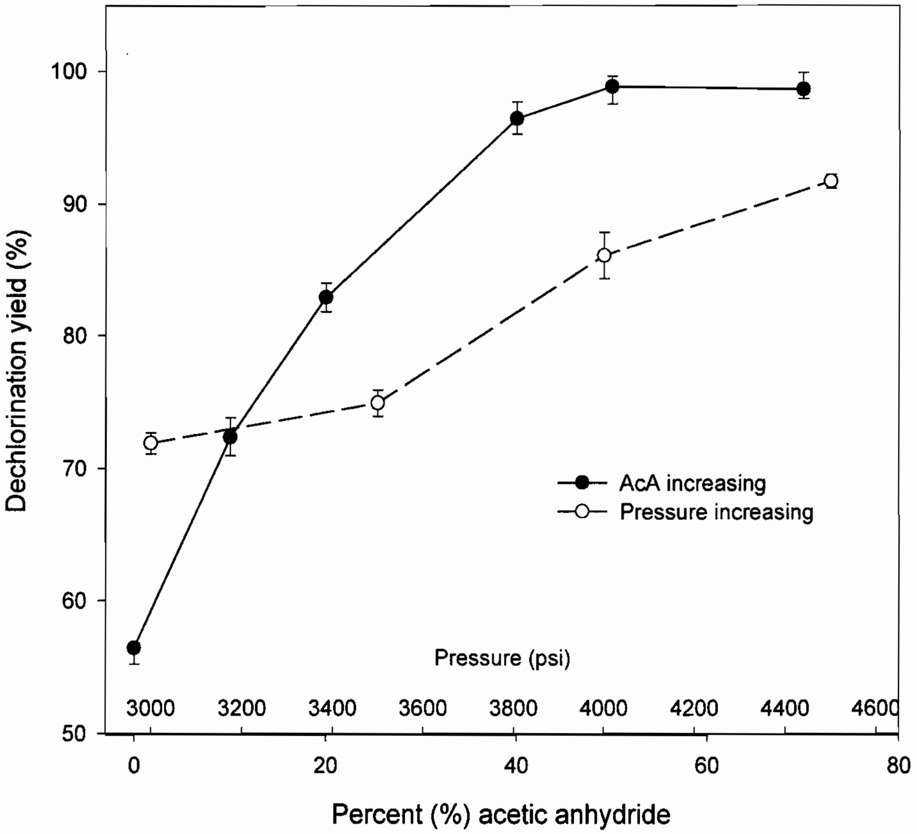

Figure 3.2 Variations in the dechlorination efficiency for 10% (v/v) solutions of Aroclor 1242 in 1,2-dimethoxyethane with (a.) increasing percent of acetic anhydride in the solvent mixture delivered to two Ag^0/Fe^0 columns at 400 °C and 4500 psi or (b.) with increasing pressure for the same feedstock delivered to two Ag^0/Fe^0 columns at 400 °C.

detected in the trapped column eluate. Fourier transform infrared (FTIR) spectroscopy indicated that in addition to residual dissolved carbon dioxide, the product mixture was composed predominantly of methyl ketone(s). A possible source for these compounds would involve the capture of alkyl radicals by a methylated carbon monoxide radical species. $ScCO_2$ is known to form short chain (C_1-C_5) alkyl radicals by catalytic reduction at iron surfaces (Hardy and Gillham, 1996).

3.3.2 The effect of temperature on dechlorination efficiency

The dechlorination process was also temperature dependent. As summarized in Table 3.2, an increase in the operating temperature (as measeured by the outer skin temperature of the reactor columns) improved both the extent of dechlorination and the repeatability between cumulative 10-minute traps that had been collected sequentially during 1 h. For zero-valent zinc, the metal granules were observed to soften appreciably at reactor skin temperatures above 200 °C, so that dechlorination trials were limited to this temperature. Trials were also conducted with Aroclor 1248 (Table 3.2). Yields between the Aroclor 1248 and 1242 are not directly comparable because of differences in density (20 °C) [(1.44 *vs*. 1.38 respectively), (Ware, 1988)] and differences in the spectrum of congener for these mixtures (Doyle, 1998). Additionally, for incomplete dechlorinations, identical rates of reaction would have resulted in lower dechlorination yields for Aroclor 1248 because of the greater chlorine concentrations in the substrate.

The effect of increased operating temperature can be seen more clearly in Figure 3.3 which compares Fe^0 meditated dechlorination efficiencies for sequential traps at different operating temperatures. There was a gradual decrease in dechlorination yield with increasing trap number. The gradual decrease in efficiency was characteristic of all four ZV-metals and the three bimetallic mixtres that were studied. The negative slopes of the spline curves were greater at lower than at higher operating temperatures for different zero-valent (ZV) metal substrates. Other zero-valent metals (Cu^0, Ni^0, and Zn^0, Figures 3.3, 3.4) behaved similarly but the dechlorination was not as extensive.

Table 3.2 Influence of temperature, for two reactor columns connected in series, on the mean percent dechlorination (± 1 RSD) of feedstock containing 20% (v/v) Aroclor 1242 (or Aroclor 1248), 70% (v/v) acetic anhydride and 10% (v/v) dimethoxyethane.

	Temperature					
ZV-Metals	200 °C		300 °C		400 °C	
	1242	1248	1242	1248	1242	1248
Cu	69.1 ± 9		73.1 ±23		86 ± 8	
Fe	86.0 ± 8	69±15	87.6 ±10	71.8 ±1	94.5 ± 4	92 ± 6
Ni	55 ±12	68.9±15	61.9 ± 14	67 ± 2	92.5 ± 6	89 ±2
Zn	68.9 ±15					
Ag/Fe	63.3 ±17		73.3 ± 10		97.5 ± 3	
Pd/Fe	60.2 ±23	56.1 ±26	74.9 ±16		96.4 ± 3	93 ± 5

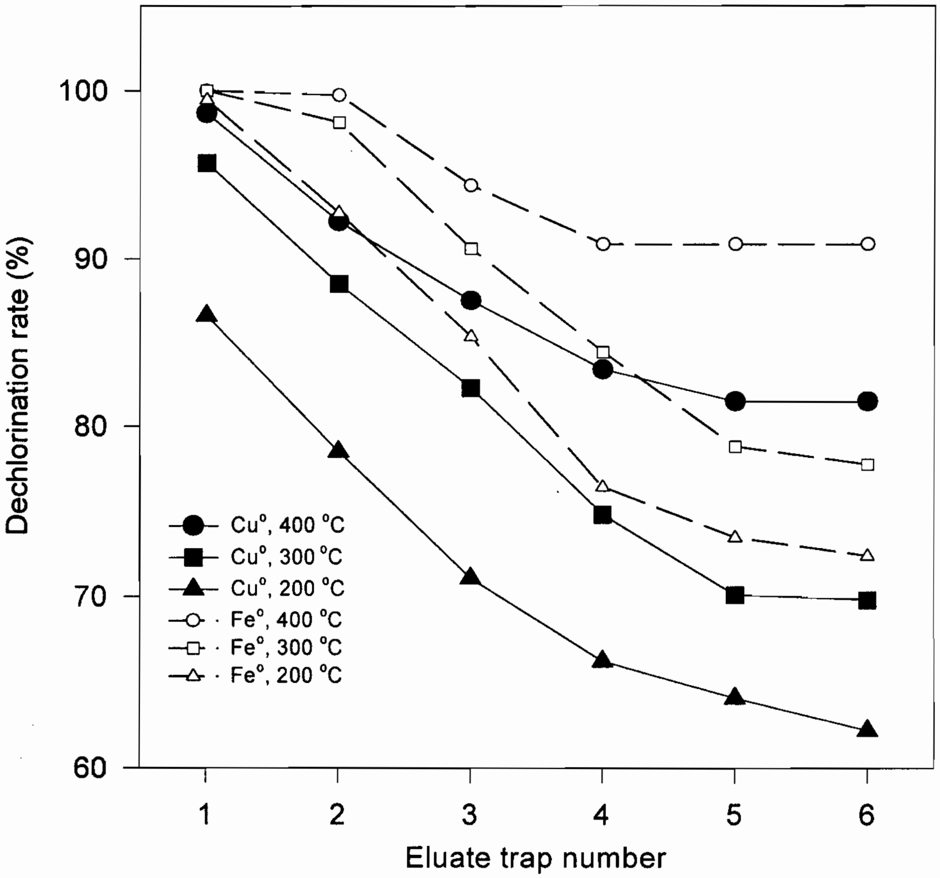

Figure 3.3 Efficiencies for Cu^0 meditated (filled symbols) or Fe^0 meditated (hollow symbols) dechlorinations of 20% (v/v) Aroclor 1242 solution delivered at 0.1 ml/min to two reactor columns maintained at 400 °C and 4500 psi (mean dechlorination in six successive traps, 86± 8% and 95± 4% respectively), or at 300 °C (mean dechlorination in the six traps, 73 ± 23% and 88 ± 10% respectively) or at 200 °C (mean dechlorination in the six traps, 69 ± 9% and 84 ± 12% respectively).

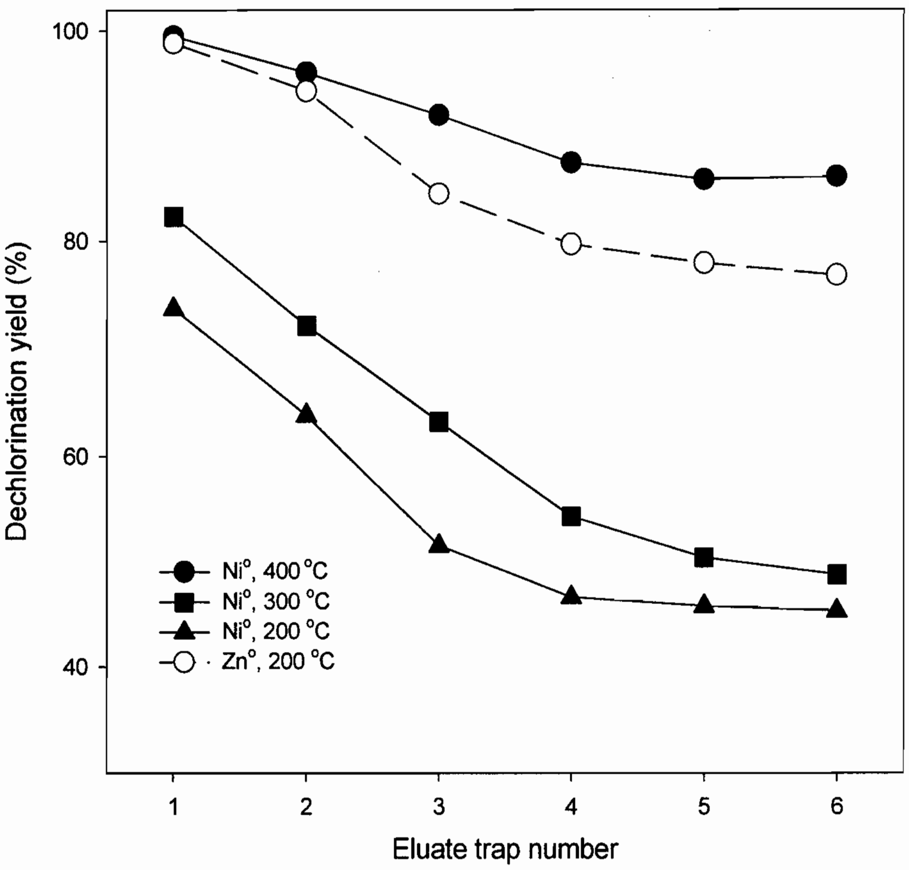

Figure 3.4 Efficiencies for Ni^0 meditated (filled symbols) or Zn^0 meditated (hollow symbols) dechlorinations of 20% (v/v) Aroclor 1242 solution delivered at 0.1 ml/min to two reactor columns maintained at 400 °C and 4500 psi (mean dechlorination in six successive traps, 91± 6%), or at 300 °C (mean dechlorination in the six traps, 67 ± 6%) or at 200 °C (mean dechlorination in the six traps, 54 ± 11% and 85 ± 11% respectively).

3.3.3 The dechlorination efficiency of bimetallic mixtures

In addition, three bimetallic mixtures of ZV-metal [(Ag^o/Fe^o, Figure 3.5), (Ag^o/Ni^o, Figure 3.6), and (Pd^o/Fe^o, Figure 3.7)] were assessed for dechlorinating efficiency in this system. All three mixtures further improved both the dechlorination yield and the repeatability of the reaction over 1 h (Table 3.3). For these trials, the reactor temperature was maintained at 400 °C and the substrate composition was varied using two ZV-metal columns. Although efficient, the reactions were not quantitative. For a single reactor column (Table 3.4), there was no apparent differences between the use of acetic anhydride or methylisobutyl ketone (IBMK) in the transporting solvent although the use of 2-heptanone depressed dechlorination by approximately 10 percent. Surprisingly, the inclusion of 1,2 DME (10%, v/v) in the solvent increased the yield by 9 and 14 percent over neat acetic anhydride for the Ag^o/Fe^o and the Ag^o/Ni^o mixtures respectively. The dechlorinating activities of silver-coated iron and nickel were also more durable as seen in Table 3.3. Although the efficiency of dechlorination appeared to decrease monotonically for the Ag^o/Ni^o bimetallic mixture, it appeared to level off for the Ag^o/Fe^o support-term trials.

Two Ag^o/Fe^o reactor columns in sequence, that resulted in a 9% decrease in organically–bound chlorine, provided a chromatogram that was reduced approximately 94% in total peak areas in the PCB eluting region indicating that the majority of products were eluted more rapidly. When only biphenyl dissolved in DME comprised the feedstock for the Ag^o/Fe^o column (operated under optimized dechlorination conditions), a maximum of only

84% could be recovered in the hexane traps indicating further reaction. There were no products that were more retained than biphenyl on the GC column. With Ag^o/Fe^o bimetallic mixture and 99.5% dechlorination of the 1242 substrate only two chlorinated products (*o*-chlorobiphenyl and 2, 4 dichlorobiphenyl and/or 2, 6 dichlorobiphenyl, (which collectively accounted for appreciably less than 1% of the starting material) were detected by GC-MS (Figure 3.8). Similarly, for substrate that had been 99.8% dechlorinated, only *o*-chlorobiphenyl was detected among the chlorinated products. Other non-chlorinated products that were identified tentatively include methylbiphenyl(s), dimethylbiphenyl(s), toluene and short chain esters of 1,2-benzenedicarboxylic acids. The

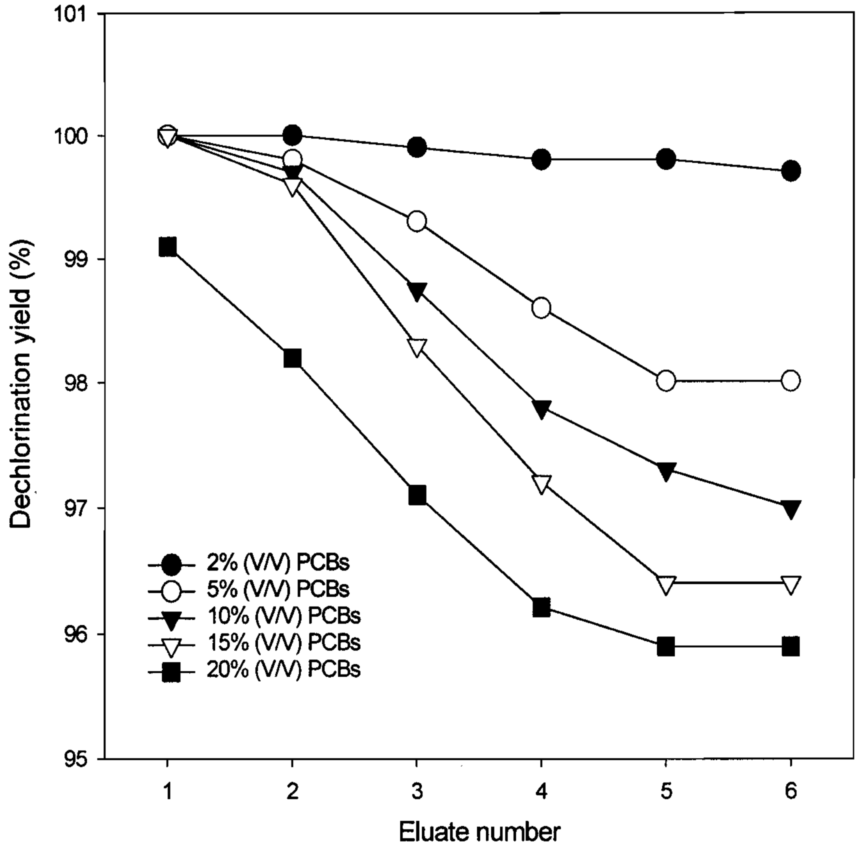

Figure 3.5 Dechlorination efficiencies for 2%, 5%, 10%, 15% or 20% (v/v) Aroclor 1242 feedstock delivered to two columns mounted in series of Ag^0/Fe^0 (mean dechlorination for six successive traps, 99.8 ± 0.1%, 98.7 ± 0.9%, 98.3 ± 1.2%, 98.0 ± 1.6% and 97.0 ± 2.6% respectively) at 400 °C and 4500 psi.

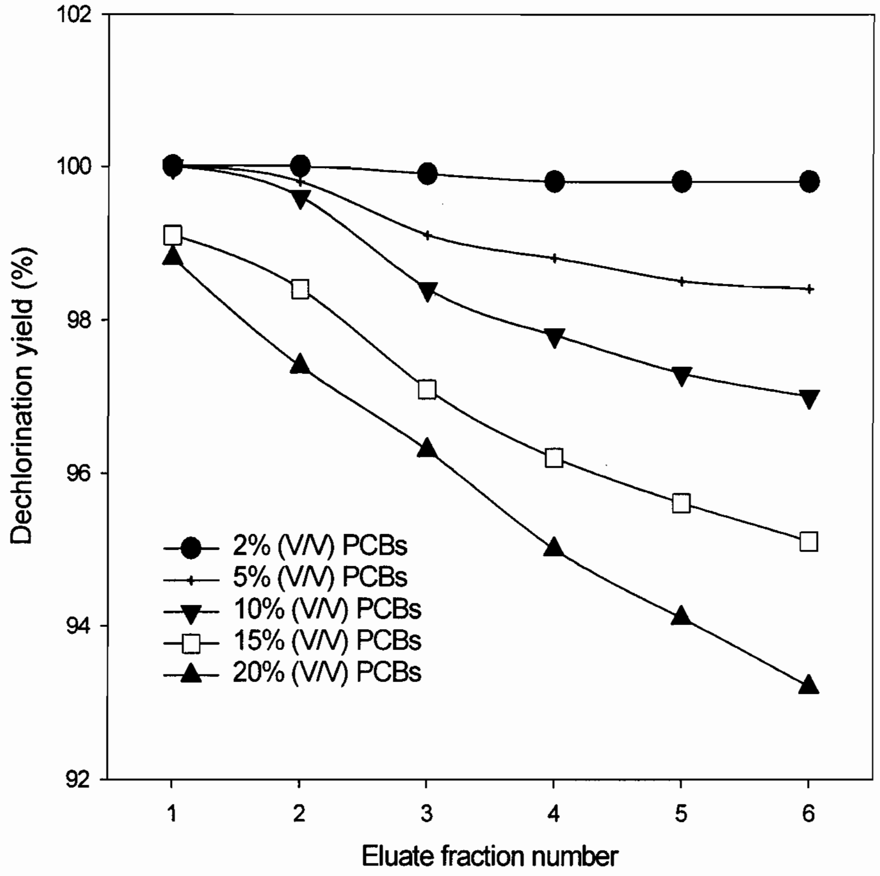

Figure 3.6 Dechlorination efficiencies for 2%, 5%, 10%, 15% or 20% (v/v) Aroclor 1242 feedstock delivered to two columns mounted in series of Ag^0/Ni^0 (mean dechlorination for six successive traps, 99.9 ± 0.1%, 99.0 ± 0.8%, 97.8 ± 1.1%, 83.9 ± 8.9% and 95.8 ± 2.1% respectively) at 400 °C and 4500 psi.

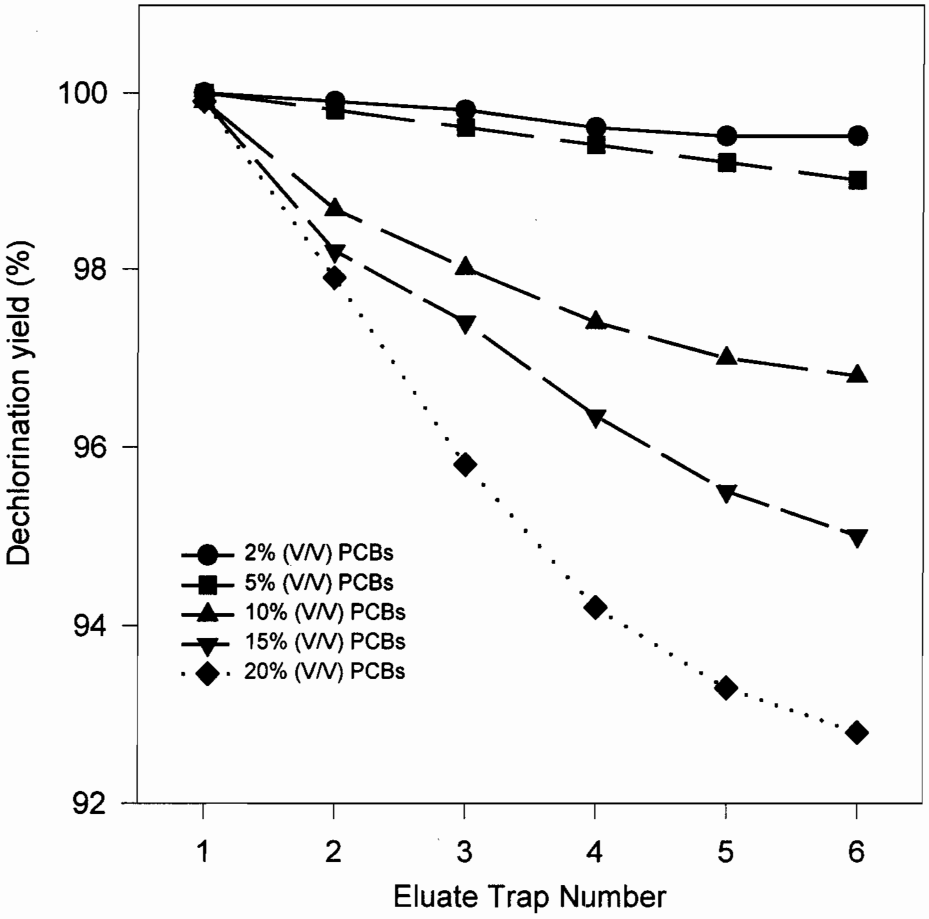

Figure 3.7 Dechlorination efficiencies for 2%, 5%, 10%, 15% or 20% (v/v) Aroclor 1242 feedstock delivered to two columns mounted in series of Pd^o/Fe^o (mean dechlorination for six successive traps, 99.9 ± 0.2%, 99.0 ± 0.8%, 97.8 ± 2.1%, 97.0 ± 2.4% and 96.1 ± 3.1% respectively) at 400 °C and 4500 psi.

Table 3.3 Variations in the mean[a] percent dechlorination (± 1 RSD) for 2 successive columns maintained at 400 °C and 4500 psi (i.) containing different zero-valent bimetallic mixtures and (ii.) with varying acetic anhydride-dimethoxyethane mixtures to transfer Aroclor 1242 (or Aroclor 1248) to the reactor.

Bimetall mixture	PCB conten % (v/v)	Feedstock composition (v/v) the presence of 20% (v/v) Aroclor 1242 (or 1248)	Mean % Dechlorination
Ag/Fe	2	20% AcA, 78% DME	99.8 ± 0.1
	5	20%AcA, 75% DME	98.7 ± 0.9
	10	50% AcA, 40%DME	98.3 ± 1
	15	50% AcA, 35%DME	98.0 ± 2
	20	70% AcA, 10%DME	97.0 ± 3
	20	80% AcA	88.9 ± 5
Ag/Ni	2	20% AcA, 78% DME	99.9 ± 0.1
	5	20% AcA, 75% DME	99 ± 0.8
	10	50% AcA, 40% DME	97.8 ± 1
	15	50% AcA, 35%DME	83.9 ± 9
	20	70% AcA,10%DME	95.8 ± 2
	20	80% AcA	81.1 ± 4
Pd/Fe	2	20% AcA, 78% DME	99.9 ± 0.2
	5	20% AcA, 75% DME	99 ± 0.8
	10	50% AcA, 40% DME	97.8 ± 2
	15	70% AcA, 15%DME	97.0 ± 2
	20	70% AcA,10%DME	96.1 ± 3
	20	80% AcA	84.3 ± 5
	5 (Aroclor 1248)	70% AcA, 25% DME	97.9 ± 1
	10 (Aroclor 1248	70% AcA, 20% DME	95.6 ± 2
	15 (Aroclor 1248	70% AcA, 15%DME	93.8 ± 5
	20 (Aroclor 1248	70% AcA, 10% DME	92.9 ± 5

[a]: Mean ± 1 relative standard deviation (RSD) of six successive traps of reactor eluate.

Table 3.4 Variations in mean dechlorination efficiencies (± 1 RSD) for one column of silver (or palladium, 2% w/w) iron bimetallic mixture maintained at 400 °C and 4500 psi for 15 or 20% (v/v) Aroclor 1242 and different transporting solvent mixtures.

Bimetallic mixtures	Feedstock composition (v/v)[a]	Mean % dechlorination[b]
Ag/Fe	15% PCBs, 70% MIBK, 5% DME	92.1 ± 2
Ag/Fe	20% PCBs, 80% MIBK	83.6 ± 6
Ag/Fe	15% PCBs, 40% AcA.,45% DME	96.7 ± 7
Ag/Fe	20% PCBs, 50%AcA.,30% DME	88.5 ± 5
Ag/Fe	15% PCBs, 60% 2-heptanone, 25% DME	93.3 ± 4
Ag/Fe	20% PCBs, 70% 2-heptanone,10% DME	79.5 ± 6
Ag/Ni	20% PCBs, 50%AcA.,30% DME	83.9 ± 9
Ag/Ni	20% PCBs, 70%AcA.,10% DME	95.8 ± 2
Pd/Fe	20% PCBs, 50% MIBK, 30% DME	85.9 ± 10
Pd/Fe	20% Aroclor 1248, 70% MIBK, 10% DME	82.0 ± 7
Pd/Fe	20% PCBs, 70% 2-heptanone,10% DME	77.8 ± 9
Pd/Fe	20% Aroclor 1248, 70% 2-heptanone,10% DME	77.0 ± 8

[a] : DME= 1,2 dimethoxyethane, IBMK= methyiosbutyl ketone.

[b]: Mean in six 10-min cumulative traps that were collected sequentially during 1 h.

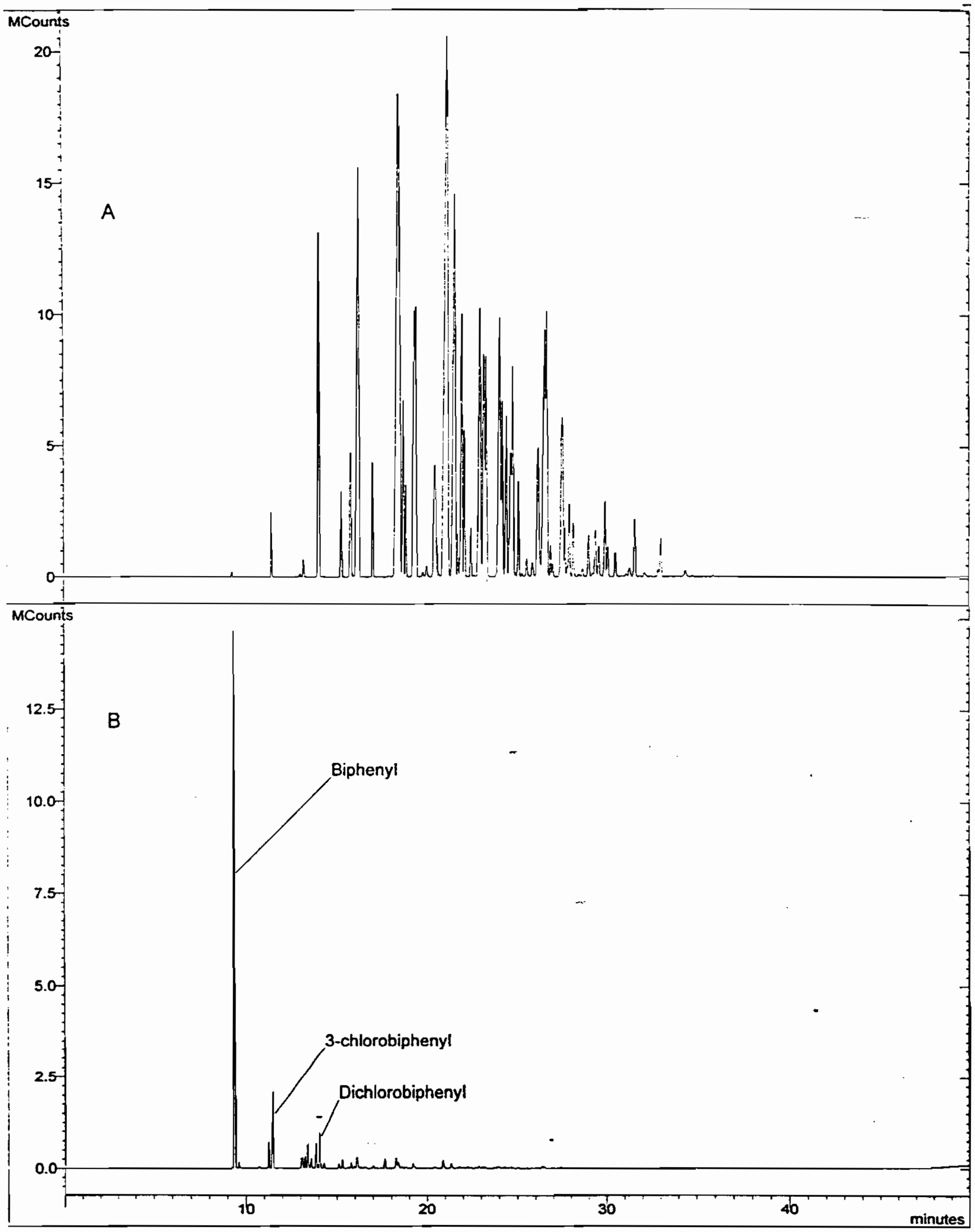

Figure 3.8 GC/MS chromatograms of Aroclor 1242. (A) starting material diluted to 20 mg/L. (B) spectrum of products that resulted from two Ag°/Fe° reactor columns connected in series (conducted at 400 °C and 4500 psi).

latter products (that were observed for 2% loadings of Aroclor 1242 in the mobile phase) are thought to arise via carboxylation and reductive catenation of the CO_2.

Having optimized the reaction conditions for virtually complete PCB dechlorination (based on the loss of organically-bound chlorine) a series of further trials were undertaken to corroborate the efficiency of the process. Initially, the temperature of the single Pd^o/Fe^o column was lowered to 300 °C and 20% (v/v) PCB feedstock in hexane was delivered to the reactor column at 0.1 ml/min. The mean recovery of organically-bound chlorine in successive traps of hexane was virtually quantitative at this temperature (Aroclor 1242, 99.0 ± 4.7%; Aroclor 1248, 103.9 ± 6.6%). Further experiments monitored the eluate for products that could be converted to biphenyl. Aliquots of eluate were reacted with Mg^o and K_2PdCl_6 to produce biphenyl. With 20% (v/v) 1242 in acetic anhydride (70% v/v) dimethoxyethane (10% v/v) as feed stock, the recovery of biphenyl was virtually quantitative, 99.1 ± 8.7% at 300 °C but was reduced to 84.0 ± 12.9% at 400 °C. For these trials, the reactor column was packed freshly prior to each trial. Despite equilibration with mobile phase in the absence of substrate, the contents of the first trap were converted to biphenyl less efficiently. Mean recoveries were based on traps two to six. These results indicated that at the higher operating temperature a portion of the biphenyl derivatives were further degraded on column. To demonstrate an active role for the zero-valent metal(s) in the dechlorinations, companion experiments wre also conducted using silica (sea sand) to fill the reactor column. With the optimized reaction conditions (400 °C, 4500 psi and 800 ml/min of decompressed flow), the mean recovery of substrate(s) in the six trapping solution that could be converted to biphenyl was virtually quantitative (104 ± 11%). Finally the chloride ion accumulated on the Pd^o/Fe^o column during 1 h of continued operation (optimizal operating conditions) as determined by titration of the wash water accounted for 99.6% of the total chlorine in the feedstock.

In further trials, acetone/hexane extract from a spiked sandy soil that had been extracted using a patented SESR (Solvent Extraction Soil Remediation Technology) were dechlorinated with a single Ag^o/Fe^o column maintained at 4500 psi and 400 °C. No chlorine containing materials were detected by GC-MS in the reactor eluate when acetone hexane extract supplemented with 30% (v/v) AcA, that had contained approximately 600 μg/ml PCBs, was fed continuously at 0.1 ml/min to the reactor. Of equal importance, soil co-extractives in the PCB solution did not affect either the course of the efficiency or the reaction perceptibly.

3.3.4 Conclusion

Based on the dechlorination results, it was presumed that the following chemical reactions participated in the dechlorination process:

(1) In the presence of zero-valent metal(s), propan-2-ol (or methanol) is converted to acetone (or formaldehyde) and two hydrogen atoms are released. In a redox reaction, the chlorine atom is reduced to chloride while the sacrificial zero-valent metal is oxidized to ferrous/ferric ion.

$$CH_3CH(OH)CH_3 \rightarrow CH_3C(O)CH_3 + 2H^{\bullet}$$

$$Fe^{o} \rightarrow Fe^{2+} + 2e^{-}$$

$$2C_{12}H_9Cl + 2H^{\bullet} + 2e^{-} \rightarrow 2C_{12}H_{10} + 2Cl^{-}$$

(2) In the presence of zero-valent metal, acetic anhydride reacts with solvent to produce ketone-like products and during this process a hydrogen atom is released. Under the influence of the zero-valent accelerator, the chlorine of PCB is substituted by a hydrogen atom and becomes reduced to chloride:

$$(CH_3CO)_2O + CH_3OCH_3 \rightarrow RC(O)CH_3 + H^{\bullet}$$

$$C_{12}H_9Cl + H^{\bullet} \rightarrow C_{12}H_{10} + Cl^{-}$$

(3) With the solvent reaction produced H^+, the catalyst (Pd or Ag) promoted PCB dechlorination could undergo multiple and/or single substitution process:

$$C_{12}H_{(10-n)}Cl_n + nH^{\bullet} \rightarrow C_{12}H_{(10-n)} + nCl^{-}$$

$$(C_{12}H_9Cl)_n + nH^{+} \rightarrow (C_{12}H_{10})_n + nCl^{-}$$

Successive dechlorinations are considered to be sequential rather than conserted. In summary, it has been demonstrated that zero-valent metal meditated reactions of Aroclor mixtures at elevated temperature in $scCO_2$ provides an efficient technique for PCB detoxification by dechlorination. The quantities of Aroclor 1242 or 1248 substrate that were dechlorinated efficiently (but not quantitatively) are considered to far exceed the burdens in concentrated extracts that could be isolated from polluted environmental matrices.

Chapter 4

Preface

In Chapter 3, an approach that can dechlorinate PCB mixtures (Aroclor 1242 and 1248) efficiently with heated columns of zero-valent metal or bimetallic mixture in a continuous process has been developed. The quantities of Aroclor 1242 or 1248 substrate that were dechlorinated efficiently (but not quantitatively) are considered to far exceed the burdens in the most concentrated extracts that c*an* be isolated from polluted environmental matrices.

The following Chapter evaluates an approach/technique for the remediation of PCB contaminated soil. A wide range of surfactants are screened for suitability to extract PCB from contaminated soils *in combination* with $scCO_2$. Soils that had been historically contaminated with Aroclor 1242, 1248, 1254 and 1260 were be evaluated with *ex-situ* soil washing and *in-situ* soil flushing processes. Then the combined PCB-laden aqueous suspensions were to be back-extracted with $scCO_2$ and the eluate was anticipated to be dechlorinated as it traversed a short, heated column of silver-iron bimetallic mixture.

Approaches to the remediation of a polychlorinated biphenyl (PCB) contaminated soil

4.1 Introduction

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.*, 1999) approaches. These strategies, however, have been applied as treatments in the field only infrequently because of costs, environmental constraints and efficacy (Kovalick and Kingscott, 1996). Other more efficient methods for treating PCB contaminated soils continue to be proposed, optimized and evaluated (Abdul and Gibson, 1991).

In recent years, the use of surfactants has received increased attention as a means of enhancing the removal of organic contaminants from contaminated soils (Abdul *et al.*, 1990; Burchfield *et al.*, 1994; Huang *et al.*, 1997), especially for those situation when conventional "remove and treat" protocols have proven to be prohibitively costly (Weerasooriya *et al.*, 2000; Kim and Lee, 2000). Surfactants are attractive for the mobilisation/mass transfer of organic contaminants because of their reduced acute toxicity and their favourable rates of environmental degradation to innocuous products. Aqueous surfactant suspensions have been considered as more environmentally friendly than competing organic-solvent based extraction systems (Deshpande *et al.*, 1999; Beck *et al.*, 1997).

Surfactant enhanced soil remediations include both soil washing (*ex-situ*) and soil flushing (*in-situ*) (Scamehorn and Harwell, 2000). These processes become economically feasible only if they are of low cost. 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 processing

(Haegel *et al.*, 2000). Attractive combinations have involved surfactant recovery and re-use (Zhou and Rhue, 2000).

Other approaches to the removal of hydrophobic contaminants with volatile organic solvents or surfactants have been proposed and tested (Kim and Lee, 2000; Kitiyanan *et al.*, 2000). These separation methods have included: air-stripping or vacuum-stripping within packed columns, hollow fiber membrane contactors (Kitiyanan *et al.*, 2000), liquid-liquid extraction within a hollow fiber membrane contactor (Ang and Abdul, 1995) and pervaporation of surfactant solution (Vane *et al.*, 2000). Although their high removal efficiencies have encouraged researchers to evaluate these processes in the field, often they have not been sufficiently efficient, they have been environmental damaging or they have been viewed as being too expensive. More information of the effects of surfactants on the extraction operation and novel separation techniques remain to be identified/ optimized. Promising in this respect are the reports by Hawthorne and co-workers (1998) who mobilized PCBs from field-contaminated soil with pressurized sub-critical water and the report of Wai and co-workers (1999) who observed the virtually quantitative dechlorination of PCBs during extraction with sub-critical water in the presence of zero-valent iron.

Supercritical carbon dioxide ($scCO_2$) based separations possess several advantages over conventional extractions with organic solvents including cost, a lack of appreciable toxicity of the solvent, increased diffusivities and penetration rates through particulate media, high extraction efficiencies for relative non-polar analytes, and environmental friendliness (Bjorklund, 1999). For particulate matrices, extractions with $scCO_2$ are inherently batch processes in which the extractor is charged with soil, pressurized, extracted with $scCO_2$ then depressurized and the soil is replaced with fresh substrate before the cycle can be repeated. Conventionally, pressure within the extractor is maintained with a capillary restrictor (~50 μm i.d.) that is easily fouled with particles. Two stages of processing were chosen to minimize the fouling. PCBs were to be mobilized from the soil into an aqueous surfactant emulsion and then stripped from the water medium with $scCO_2$. It seemed probable that a surfactant could be identified that would promote the mobilization from soil but would be relatively insoluble in the $scCO_2$ and it was anticipated that the cleaned surfactant suspension could be recycled back to the soil to mobilize more toxicant. It also seemed to be inefficient to simply transfer the toxicants from one medium to another (soil to $scCO_2$) so that an *on-line* detoxification stage was envisaed for the process. The effluent from the $scCO_2$ extractor would be dechlorinated by passage through a short column of zero-valent bimetallic mixture at elevated temperature under conditions that had been demonstrated to dechlorinate a continuous stream of these substrate virtually quantitatively (Chapter 3, Wu and Marshall, 2001). This chapter focuses on the use of surfactants to mobilize PCBs from the PCB-surfactant suspension. Once in $scCO_2$, the dechlorination over Pd^o/Fe^o was also evaluated.

4.2 Materials and methods

4.2.1 Chemicals, solvents and surfactants

Magnesium granules (12~50 mesh, 99.8 % purity), potassium hexachloropalladate (K_2PdCl_6), cobaltous nitrate [$Co(NO_3)_2 \cdot 6H_2O$], and ammonium thiocyanate (NH_4SCN) were purchased from Alfa Aesar, Ward Hill, MA USA. Hexane, ethylene glycol dimethyl ether, isobutylmethyl ketone (IBMK, 99+%), methanol, methylene chloride (CH_2Cl_2), propan-2-ol (all HPLC grade), and glass wool were purchased from Fisher Scientific, Ottawa, ON. Biphenyl, surfactants, antifoam A, and antifoam B were purchased from Sigma-Aldrich, Oakvill, ON. All chemicals (ACS Reagent grade or better), solvents and surfactants were used as received.

The surfactants selected for study included anionic (Aereasol OT, sodium dodecyl sulfate) and nonionic chemicals (Brij 30, Brij 56, Brij 78, Brij 97, Brij 98, Triton X-100, Triton X-405, Triton X-705, Triton CF54, Triton DF16, Tween 20, Tween 40, Tween 60, Tween 80, Tween 85).

4.2.2 Soil samples and pre-treatment

The soil had been contaminated by polychlorinated biphenyl compounds for more than 30 years. The pH of the contaminated soil was 7.4 and organic matter content was 4.8%. The properties of this soil have been described elsewhere (Chapter 2, Wu and Marshall, 2000). The total PCB content was determined to be 30.3 ± 6.6 μg/g and involved Aroclors 1242, 1248, 1254 and 1260. Post sampling, the soil was air dried, mixed thoroughly, passed through a 2 mm sieve (10 mesh), and stored at 4 °C to await further treatment.

4.2.3 PCBs extraction/mobilization

In preliminary trials, 17 surfactants were screened to mobilize PCBs from an aqueous PCB-surfactant mixture into supercritical CO_2 ($scCO_2$). The aqueous suspension (25 ml) consisting of surfactant (3%,v/v), Aroclor 1242 (1%, v/v) and distilled water was supplemented with 5 ml IBMK, and the resulting suspension (30 ml) was well mixed and placed in a cylindrical supercritical fluid (SCF) extraction vessel [320 mm X 15 mm inner diameter (i.d.)]. The vessel was wrapped with a heating tape (Swagelok, Montreal) and heated to the operating temperature (30-80 °C) of the experiment. $ScCO_2$, provided by an $scCO_2$ pump (Newport Scientific Inc., Jessup, MD USA) was then added to the base of the extraction vessel and permitted to percolate up through the surfactant suspension and to accumulate within the headspace above the suspension. The fluid in the headspace was replaced continuously with fresh solvent from below and pressure within the system was maintained with a short section of flexible silica tubing (~25 cm x 50 µm i.d.) that terminated with the stainless steel transfer line and acted as a capillary restrictor. Extractor eluate was trapped in 25 ml hexane contained in a 50 ml test tube. Once suitable surfactants had been identified, $scCO_2$ extractions (second stage) were performed on PCB-surfactant mixtures at various temperatures.

The third stage consisted of evaluations of the optimized surfactant-extraction time-extraction temperature combinations to mobilize PCBs from the contaminated soil. Both sonication (soil washing) and soil flushing within soil packed column were evaluated. The sonication washing treatment was performed by placing the air dried soil sample (10g) into a fritted glass funnel (30 cm X 40 cm, Fisher Scientific), together with surfactant and the suspension was sonicated [Polytron homogenizing unit (N.Y. 11590, Brinkmann Instruments, Mississauga, ON) for 10 min prior to filtration under a gentle vacuum. Separate soil washes were performed with 1, 3, 5% (v/v) aqueous surfactant suspension and each extract was analyzed for PCB and surfactant content. Each sonication-vacuum filtration procedure was repeated 15 times with the same soil sample but with fresh surfactant suspension each time.

An empty HPLC column [30 cm X 1 cm (i.d.) Swagelok, Montreal, QC] was used to perform the soil column flushing experiments. Soil (30g) was packed into the column and terminated with a coarse filter at both column ends. The column was mounted horizontally and flushed for 20 h (1.0 ml/min) with 1, 3 or 5% (v/v) surfactant suspension delivered from an HPLC pump (model 100A, Altex Scientific, Berkley, CA). The effluent was analyzed at hourly intervals for PCB and surfactant content.

Finally, the cumulative soil extracts were back-extracted with $scCO_2$ under the optimized mobilization conditions to recover the PCBs from the surfactant suspension. PCBs that had been extracted into $scCO_2$, were dechlorinated with zero-valent bimetallic mixture (Ag^o/Fe^o) and the cleaned surfactant suspension in the retentate was then re-used for the soil PCB extraction.

4.2.4 PCB analysis

The total content of PCBs in soil was determined by gas chromatography equipped with flame ionization detection (GC-FID) or a Hewlett-Packard model 5890 (series II) gas chromatography equipped with a model 5971 mass selective detector (GC-MS). Both methods were described previously (Wu and Marshall, 2000; 2001). In brief, the PCB concentration in soil extracts was determined by conversion of PCB residues to biphenyl. Magnesium flakes (1 g, 12-50 mesh), potassium hexachloro-palladate (K_2PdCl_6), 2 mg, propan-2-ol (2 ml), and 2 ml soil extract were combined in a 50 ml flask. The mixture was vortex stirred for 1 min, and repeated at approximately 2 h intervals. After 10 h reaction, the biphenyl was extracted into hexane (1 ml) and quantified as described previously (Chapter 2). The estimation of PCB content was based on the calibrations using Aroclor 1260.

4.2.5 Surfactant analysis

The Standard Analysis Method, APHA (Dreebberg *et al.*, 1992), was followed to determine the surfactant concentration in both soil and in the micelle suspension post treatment. Because anionic surfactants proved to be unsuitable, analysis was performed only for nonionic surfactants. A standard calibration curve was generated for each nonionic surfactant. Micellar-suspension (1 ml) was diluted (0-10 fold) to obtain a suitable working concentration. Diluted surfactant suspension (2 ml) contained in a 100 ml flask, was evaporated to dryness on a water bath. The residues were triturated with methylene chloride (10 ml) and the resulting extract was added to a 125-ml separatory funnel containing 5 ml cobaltous thiocyanate solution. After 60s vigorous shaking and phase separation, the lower aqueous layer was transferred, via a funnel containing a plug of glass wool, to a 5 ml spectrophotometer cell. The absorbance, at 620 nm, was determined *vs.* a blank of CH_2Cl_2.

4.3 Results and discussion

4.3.1 Surfactant screening

Seventeen surfactants were screened in this study. Each of the surfactants, along with its relevant properties is listed in Table 4.1. The factors that influenced selection for further study included an ability to increase the mobilization of Aroclor 1242 into $scCO_2$, a lack of appreciable foaming during the extraction process and efficient recovery of surfactant in the aqueous retentate. Surfactant suspension that could be extracted with $scCO_2$ during 30 min, without the addition of antifoaming reagent and/or co-solvent(s) and with only minimal losses to the mobile phase were to be selected. Aqueous mixtures of PCB-surfactant suspension (1% or 3%, v/v) could be extracted with $scCO_2$ if IBMK [17% (v/v)] was added to the suspension coupled, in exceptional cases, with supplementing the $scCO_2$ mobile phase with IBMK (0.4 or 0.2 ml/min added prior to its entry into the extraction vessel).

4.3.2 PCB mobilization from aqueous surfactant suspension

To optimize the extraction conditions, suspensions of 1% (v/v) Aroclor 1242 with each of four selected surfactants [Brij 97, Triton CF54, Triton DF16 or Tween 85, (3%, v/v)] and 5 ml IBMK were extracted with $scCO_2$ (4500 psi and 30–80 °C) for either 30 or 60 min. For suspensions of PCB and Brij 97 that had been extracted for 30 min, mobilization efficiencies increased with increased operating temperature (Figure 4.1). However, the content of Brij 97 in the retentate also decreased substantially with increased operating temperature. As summarized in Table 4.2, the quantity of mobilized PCBs was only 15% for 30 min of extraction at 30 °C, however the content of Brij 97 in the retentate remained

Table 4.1 Chemical and physical characteristics of surfactants selected for the PCB extraction study*.

Trade name	Chemical structure	HLB[a]	Viscosity (cp)	Molecular weight
Anionic				
SDS	Sodium dodecyl sulfate		1.12	288
Aerosol OT	Dioctyl sulfosuccinate		0.95	445
Nonionic				
Brij 35	POE(10) lauryl ether	16.9	1.21	1198
Brij 56	POE(10) cetyl ether	12.9		683
Brij 78	POE(20) stearyl ether	15.3		1152
Brij 97	POE(10) lauryl ether	12.4	1.28	
Brij 98	POE(20) oleyl ether	15.3	1.38	1150
Triton X-100	POE(10) isooctylphenyl ether	13.5		624
Triton X-114	POE(8) isooctylphenyl ether	12.4		
Triton X-405	POE(40)-(aromatic ring)6-(CH)8	17.9		1966
Triton CF54	Alkylaryl Polyether	13.6		
Triton DF16	POE linear alcohol			
Tween 20	POE(20) sorbitan monolaurate	16.9	1.19	1266
Tween 40	POE(20) sorbitan monopalmitate	15.6	1.18	
Tween 60	POE(20) sorbitan monostearate	14.9		1312
Tween 80	POE(20) sorbitan monoleate	15	1.19	1310
Tween 85	POE(20) sorbitan monolaurate	11		1840

*: Source from Kim and Lee (2000); Zhou and Rhue (1985).

[a]: HLB: Hydrophilic-Lipophilic Balance.

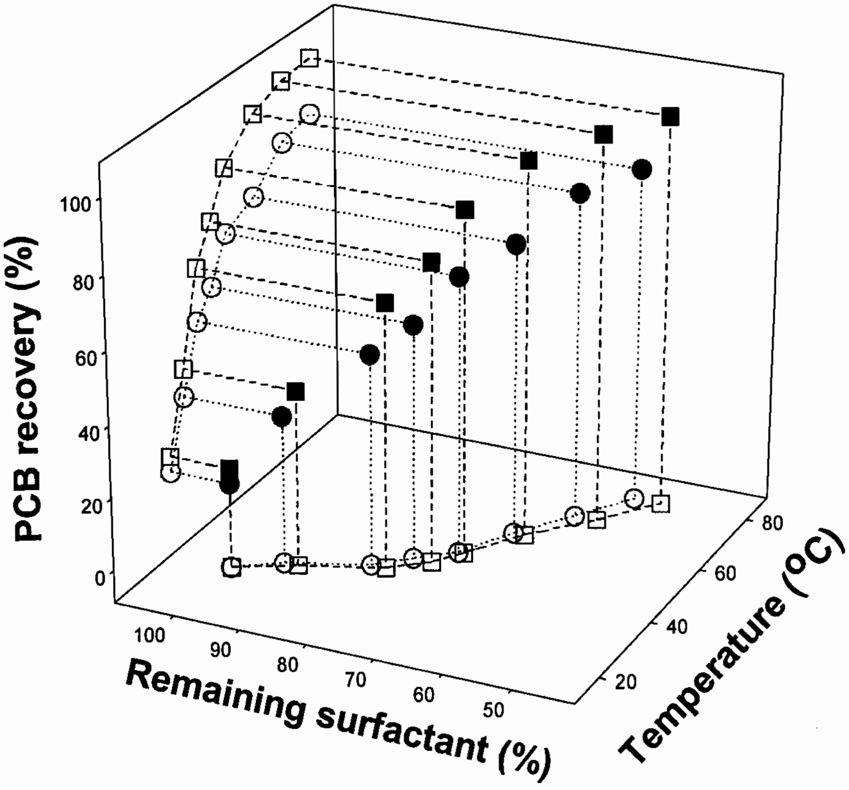

Figure 4.1 PCB mobilization efficiency (%) as a function of operating temperature and surfactant remaining with the aqueous phase (%) for 30 min (●) or 60 min (■) of $scCO_2$ extraction, at 4500 psi, from suspensions containing Brij97 surfactant.

Table 4.2. Remaining surfactant concentrations in the extracts after soil PCB extraction/flushing treatments

Surfactants	Brij 97			Triton CF54			Triton DF16			Tween 85		
Concentration	1%	3%	5%	1%	3%	5%	1%	3%	5%	1%	3%	5%
Sonication treatment No.												
1	68.6± 6.9	76.1± 7.1	79.4± 4.3	62.1± 6.3	74.6± 5.6	80.1± 4.7	63.4± 5.4	70.6± 5.1	78.6± 4.8	60.3± 3.6		
2	80.2± 4.2	89.3± 3.9	92.8± 4.0	83.8± 4.8	87.5± 3.9	94.8± 3.2	78.6± 4.1	86± 3.8	95.2± 3.1	72.5± 4.2		
3	90.1± 2.1	93.5± 2.7	98.5 ± 1.9	91.8± 3.0	98.2± 2.5	99.1± 2.2	89.8± 3.0	98± 2.3	99.5± 2.2	80.9± 2.7		
4	95.6± 1.6	98.0± 1.7	100± 2.0	97.9± 2.3	99± 1.7	100± 1.3	98.9± 2.1	100± 1.5	100± 1.4	89.3± 4.8		
5	99.0± 2.0	100± 1.1	100± 1.8	100± 1.2	100± 1.3	100± 1.0	100± 2.0	100± 1.4	100± 1.2	95.5± 4.6		
Column flushing (min)												
10	32.4± 13.9	38.6± 10.1	43.2± 8.9	37.8± 9.9	42.4± 5.8	45.7± 6.5	39.4± 8.6	40.5± 6.7	47.1± 6.6	43.5± 6.7	47.6± 6.4	48.2± 7.1
20	47.2± 9.8	53.2± 8.9	60.4± 5.5	49.7± 6.5	53.9± 4.5	57.8± 4.1	47.5± 5.8	52.8± 5.4	60.2± 4.5	50.9± 6.8	58.5± 4.5	66.5± 6.1
30	66.3± 7.4	69.7± 5.5	76.8± 3.5	64.9± 4.4	68.9± 2.3	71.9± 3.3	68.1± 4.6	65.7± 3.7	73.2± 4.5	71.4± 4.5	73.6± 3.3	77.7± 4.6
40	75.7± 5.7	80.7± 4.6	89.8± 3.5	79.9± 2.9	83.2± 3.9	87.4± 2.8	78.8± 3.8	85.6± 3.6	88.9± 3.1	83.5± 4.6	88.8± 4.7	90.9± 3.6
50	82.6± 5.4	89.6± 3.6	95.6± 2.7	88.5± 2.4	93.6± 2.9	96.5± 3.7	89.2± 3.5	92.6± 3.2	97.4± 3.4	92.2± 3.8	96.8± 3.9	98.1± 2.4
60	95.8± 4.5	99.8±2.3	99.8± 1.0	98.9± 2.5	98.4± 2.5	99.2± 2.6	97.9± 3.4	99.4± 2.4	98.8± 3.5	100± 2.3	99.6± 2.4	99.2± 1.3
70	98.9± 2.6	99.9± 1.6	99.9± 1.0	100± 1.6	100± 0.5	100± 1.0	100± 1.5	100± 1.7	100± 2.1	100± 1.4	100± 2.0	100± 1.7

virtually unchanged (99.9%) for extraction at this temperature. The PCB mobilization increased to 80% when the extraction was conducted at 80 °C, however the remaining content of Brij 97 was reduced to 58%. Linear regression (Table 4.3) of three factors (PCB recovery, extraction temperature, and surfactant content that remained with the aqueous retentate) indicated that the quantity of PCB and the quantity of Brij 97 surfactant that was mobilized were both related linearly to the operating temperature. Increased operating temperatures enhanced PCB extraction efficiencies but reduced the content of surfactant that remained with the aqueous suspension.

The PCB mobilization efficiency reached 99% if the extraction was continued for 60 min at 60 °C (Table 4.2, Figure 4.1). The quantity of Brij 97 that remained in the treated suspension did not changed substantially when 30 min mobilization (58% retention) was increased to 60 min (54% retention) for extraction at 80 °C. The three-factor linear regression model (Table 4.3) again indicated that the PCB extraction efficiency was related linearly to extraction temperature and increased substantially with increases in this parameter. For the Brij 97 surfactant, the optimized PCB mobilization conditions included supplemental IBMK (0.4 ml/min) that was merged with the $scCO_2$ stream prior to entry into the extraction vessel.

Extraction with 3% (v/v) Triton CF54 were characterized by analogous but not identical results. During the extraction, foaming was readily controlled and 45% of the PCBs were mobilized from the suspension during 30 min of extraction at 30 °C (Table 4.2). Approximately 92% of the surfactant was recovered in the retentate under these conditions. The PCB extraction efficiencies increased with the increased extraction temperature (Figure 4.2), while the remailng content of Triton CF54 in the retentate was decreased appreciably. The PCB mobilization was increased to 92% when the extraction was performed at 80 °C, however, the remaining Triton CF54 in the retentate was decreased to 30% of its initial value. The optimized linear regression model (Table 4.3) indicated that the PCB extraction efficiency was positively related to the operating temperature, but that the content of surfactant in the retentate was negatively related to the temperature.

Table 4.3 Linear regression models for three factors consisting of PCB mobilization efficiency, percent of initial surfactant remaining in the retentate and processing temperature for 30 or 60 min of extraction.

Surfactant	30 min of extraction [a,b]	R^2	60 min of extraction [a,b]	R^2
Brij 97	% PCBs mobilized = 3.5(S)+0.7(T) -6.4	0.998	% PCBs mobilized = 1.4(S)+2.9(T) -68.8	0.996
Triton CF54	% PCBs mobilized = 0.9(S)+2.1(T) +79.0	0.999	% PCBs mobilized = -1.2(S)+0.9(T) +14.0	0.996
Triton DF16	% PCBs mobilized = 0.4(S)+0.6(T) +67.5	0.996	% PCBs mobilized = 0.3(S)+0.7(T)+82.0	0.994
Tween 85	% PCBs mobilized = -2.9(S)+4.9(T) +143.3	0.982	% PCBs mobilized = 12.4(S)-13(T)+130.8	0.989

[a] : S = percent of initial surfactant content remaining in the treated solutions.

[b] : T = extraction temperature.

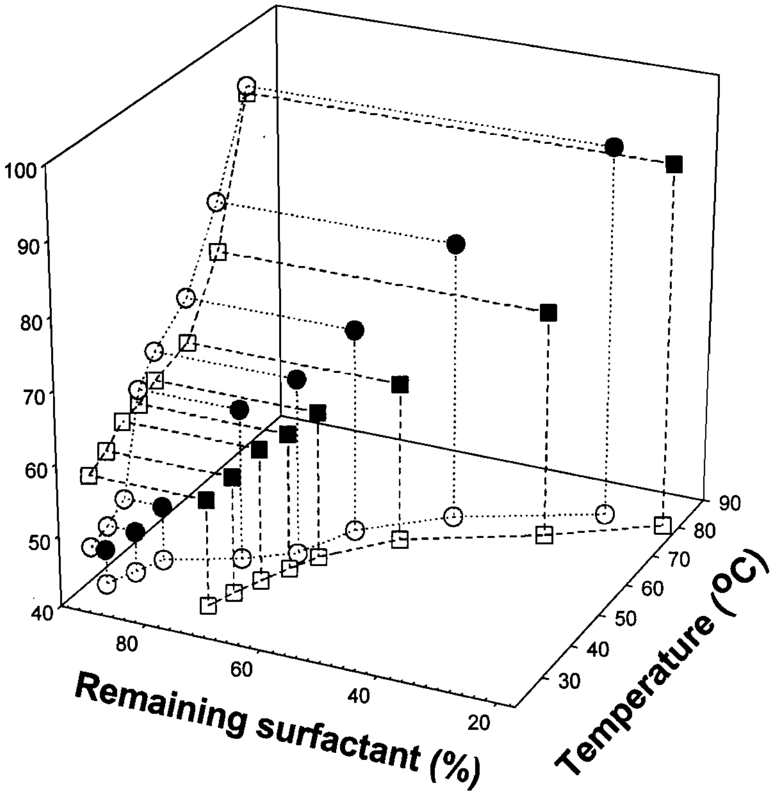

Figure 4.2 PCB mobilization efficiency (%) as a function of operating temperature and surfactant remaining with the aqueous phase (%) for 30 min (●) or 60 min (■) of $scCO_2$ extraction, at 4500 psi, from suspensions containing Triton CF54 surfactant.

The mobilization of Aroclor 1242 was 91% at 80 °C after 60 min, but the content of Triton CF54 that remained with the retentate was only 20% (Table 4.3). When the mobilization was performed at 30 °C, the PCB recovery was 55% and the remaining surfactant content was 74% of its initial value. Unlike the PCB-Brij 97 suspension, approximately 55% of the PCBs was extracted from the PCB-Triton CF54 mixture and 65% of this surfactant was retained by the aqueous suspension post treatment at 50 °C. The linear regression model (Table 4.3) again indicated that operating temperature was positively related to PCB mobilization efficiency but negatively related to the content of remaining surfactant. For mobilizations from Triton CF54 suspensions, it was necessary to supplement the $scCO_2$ mobile phase with 0.2 ml/min IBMK.

PCB mobilization from an aqueous suspensions of Aroclor 1242 and Triton DF16 (3%, v/v) were more efficient, however the quantity of surfactant remaining was relatively lower (Figure 4.3, Table 4.3). The PCB extraction efficiency reached 100% for extraction at 60 °C (or higher) during 30 min, however, the content of remaining surfactant was only 20% (or less). Most of PCB (80%) was mobilized during 30 min at 30 °C and 52% the DF16 surfactant remained in the extraction vessel.

It was possible to mobilize the 1242 mixture very efficiently at various temperatures if the extraction was continued for 60 min. The quantity of mobilized PCB was 91.6% for extraction at 30 °C and 100% at 50 °C (Figure 4.3). However, most of surfactant was co-extracted at the same time. Post processing, the remaining content of Triton DF16 was 40% at 30 °C and only 20% at 50 °C. The linear regression model (Table 4.3) again indicated that extraction temperature was positively related to the PCB mobilization efficiency but negatively related to the remaining content of DF16 surfactant. Increased extraction temperatures did not reduce the remaining quantity of surfactant substantially. It was not necessary to supplement the $scCO_2$ mobile phase with IBMK during extractions of PCB-DF16 suspensions. The addition of IBMK (5 ml) directly to 25 ml of the aqueous suspension was sufficient.

Extraction efficiencies of the aqueous suspensions containing Tween 85 (3%, v/v) depended on the temperature of the extractions. For lower extraction temperatures, PCB recoveries from Tween 85 mixture were relatively higher than from PCB-Brij 97 mixture but lower than from PCB-Triton suspension. The amount of PCB mobilized during 30

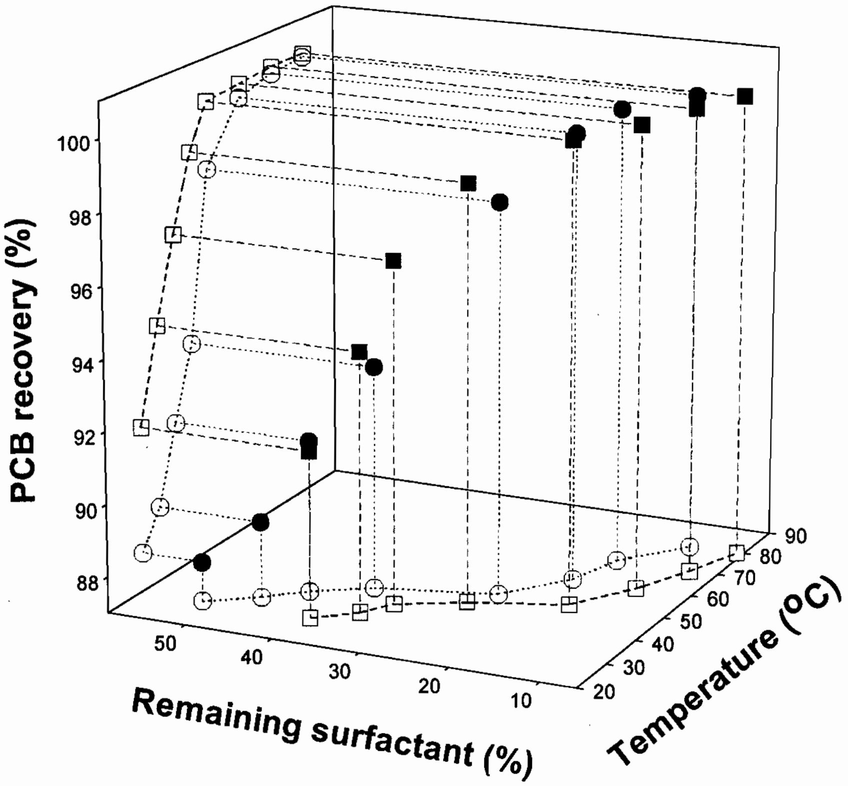

Figure 4.3 PCB mobilization efficiency (%) as a function of operating temperature and surfactant remaining with the aqueous phase (%) for 30 min (●) or 60 min (■) of $scCO_2$ extraction, at 4500 psi, from suspensions containing Triton DF16 surfactant.

min from Tween 85 mixture was 34% at 30 °C and the remaining content of surfactant was 80%. The PCB extracted at 80 °C was 96% and the remaining surfactant content was 34%. Extraction efficiencies again increased with increased operating temperature (Figure 4.4, Table 4.3).

PCB extraction efficiencies were increased substantially for 60 min mobilizations and reached 60% at 30 °C whereas the remaining surfactant content was 72%. If the extraction was performed at 50 °C or above, PCB extractions became quantitative but the content of remaining surfactant was decreased, 50% at 50 °C but only 30% at 80 °C. The experimental results demonstrated that extractions could be effected smoothly if 5 ml IBMK was added to the PCB-Tween 85 mixture (25 ml) prior to extraction.

In summary, optimal surfactant performance was in the order: Tween 85>Triton DF16> Triton CF54> Brij 97.

4.3.3 PCB extraction/mobilization from soil

Since surfactant, at concentrations less than their critical micelle concentrations (CMC), have been reported to promote the sorption of PCBs to soil particles during extraction (Kim and Lee, 2000), the same surfactant at 1, 3 or 5% (v/v) were evaluated for PCB mobilization from the contaminated soil. Both *ex-situ* sonication-washing and *in-situ* flushing of a packed soil column were evaluated. To optimize the sonication treatment with the soil-surfactant suspensions, Brij 97 was selected to define a suitable sonication time. PCB mobilization efficiencies from 10g soil, increased moderately with increased sonication times (Figure 4.5). Although 15-min of sonication mobilized more PCB than the 10-min treatment that, in turn, was more efficient than the 5-min treatment, appreciable foam formation was observed with the later washes. Therefore, 10 min of sonication was employed in subsequent trials. A single "exponential rise to a maximum" term provided an expression that modelled the experimental data accurately. The cumulative percent PCBs mobilized was modelled as the sum of a constant plus an exponential term that took the form $A(1-e^{\lambda x})$ where A is a coefficient, λ is a "time" constant and x represents the number of successive sonication-washings. The optimised models indicated that "t_{50}", the number of sonication-washings required to mobilise one-half of the extractable fraction of total PCB soil burden, was 4.08 and 2.20 for 5-min and

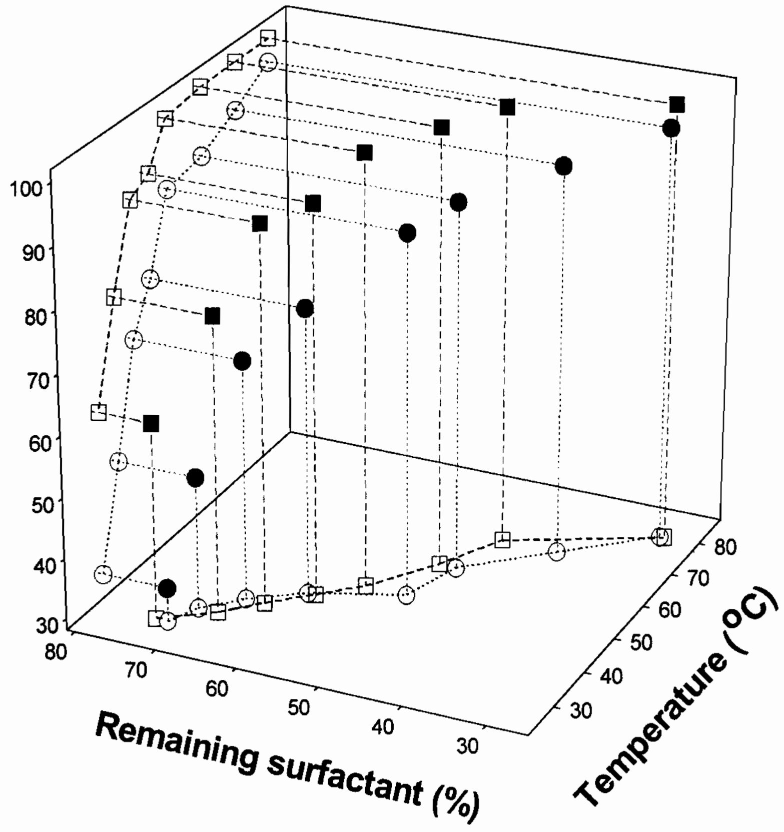

Figure 4.4 PCB mobilization efficiency (%) as a function of operating temperature and surfactant remaining with the aqueous phase (%) for 30 min (●) or 60 min (■) of $scCO_2$ extraction, at 4500 psi, from suspensions containing Tween 85 surfactant.

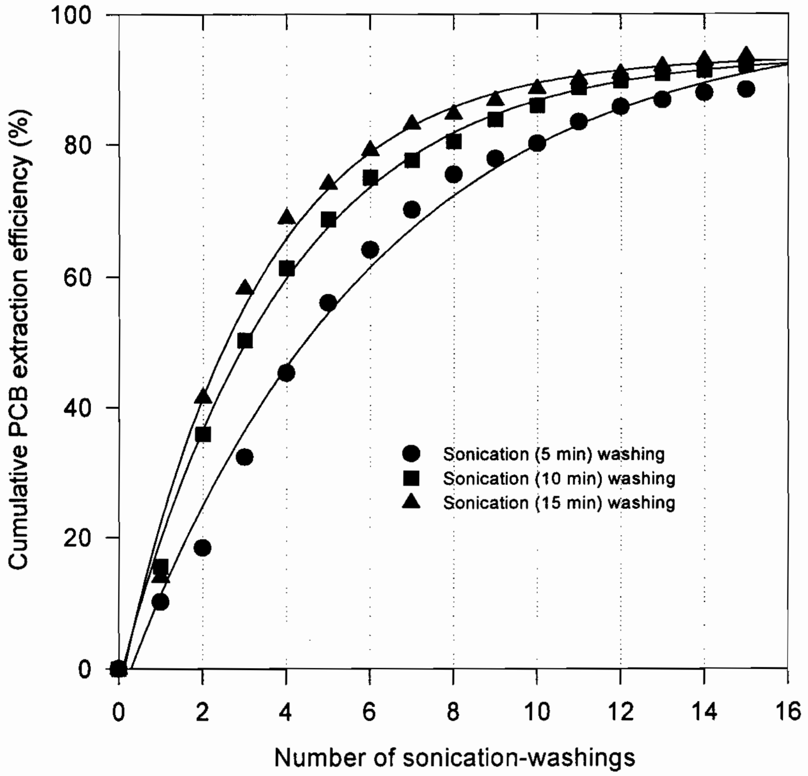

Figure 4.5 Cumulative extraction efficiency from soil (10g) in consecutive 10 ml washes with Brij 97 aqueous suspension (3% v/v) following sonication for 5 min, 10 min or 15 min. The best fit curves were generated with a model consisting of a single exponential increase to a maximum.

10-min treatments respectively. The inclusion of additional exponential terms in the model did not increase the goodness of fit to the experimental data. Thus, there was no evidence for the existence of separate fractions of soil-PCBs that could be differentiated based on their rates of mobilization. This contrasts an earlier report (Bjorklund *et al.*, 1999) that described the $scCO_2$ fractionation of soil-PCBs from "rapidly desorbing, moderately, slowly and very slowly desorbing" sites. If present, the differences in the fractions were masked by including the IBMK within the aqueous slurry.

As illustrated in Figure 4.6, 87%, 92%, or 95% of the PCBs were extracted from the soil (10g) with 15 consecutive sonication-washing treatments using 1%, 3% or 5% (v/v) Brij 97 suspension respectively. An increased concentration of surfactant in the aqueous suspension enhanced PCB extraction (Bjorklund *et al.*, 1999), however, recoveries from 3 or 5% suspension were not significantly different from each other. A single exponential increase to a maximum modelled the experimental data accurately for all three concentrations and indicated "t_{50}" values of 6.93, 2.98 and 2.89 sonication-washes for the 1%, 3% and 5% surfactant solutions respectively. The standard error of estimate (a parameter of goodness of fit) were satisfyingly low (1.94, 1.59 and 3.57 respectively). The mean PCB content remaining in the soil post sonication–washing (± 1 relative standard deviation, RSD) was 2.4 ± 0.6, 1.6 ± 0.3 and 1.5 ± 0.4 μg/g (dry weight basis) for the 1, 3 and 5% (v/v) surfactant suspensions respectively (Table 4.4). The loss of Brij 97 surfactant from the soil suspension was appreciable for the early washes (Table 4.5) but losses became negligible in the later fractions indicating that sorption to soil particles was the principle route of loss. Once the soil had become saturated with surfactant, further losses were negligible. The net percent loss (by difference) to the soil (Table 4.6) was 3.6 ± 3.3, 8.4 ± 4.5 or 10.4 ± 5.6 for the 5%, 3% or 1% Brij 97 treatments respectively. The results of packed column soil flushing trials (Figure 4.6), hollow symbols) were rather similar to the observations in the soil washing experiments. Most of PCBs (>95%) had been extracted/mobilized after 20 h (1200 ml) of continued flushing with 5% (v/v) Brij 97 suspension. Decreasing the concentration of surfactant in the carrier reduced the extraction efficiency. For 1% Brij 97 suspension, 85% of the PCB soil burden had been mobilized after 20h of flushing (Figure 4.6) and differences in extraction

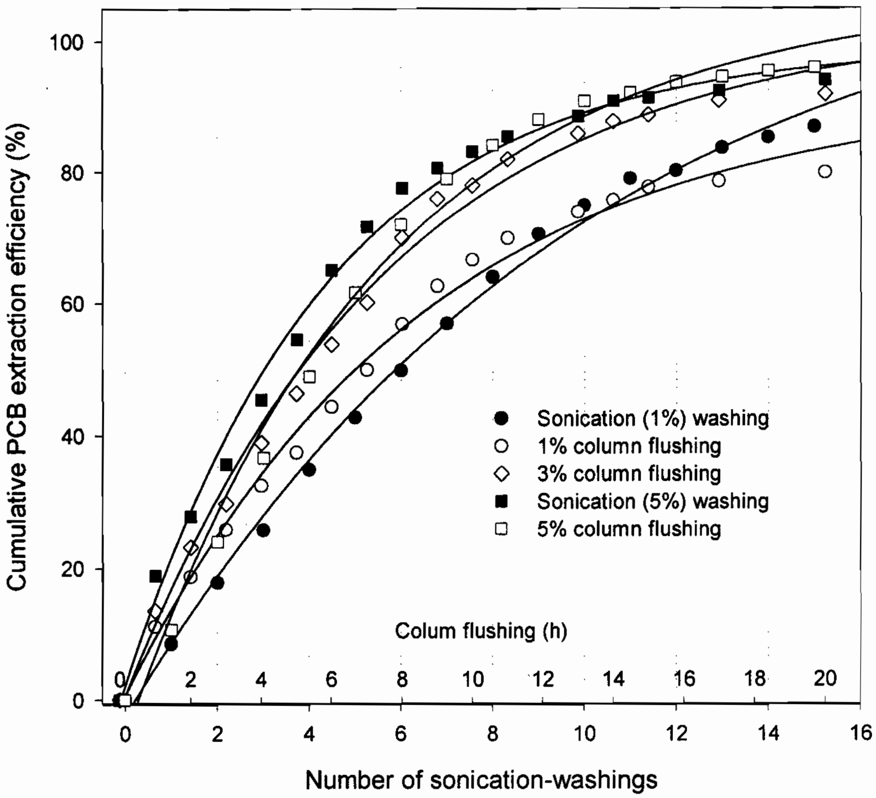

Figure 4.6 Cumulative PCB extraction efficiencies for mobilizations from 10g soil by sonication (10 min)-washing with 1% or 5% or by continuous flushing from 30g soil with 1%, 3% or 5% aqueous suspension of Brij 97 surfactant.

Table 4.4 Residual PCB concentrations (ug/g, dry weight ± 1 RSD based on 3 separate determinations) in soil post 15 consective sonication-washing or continuous flushing during 20h.

	Brij 97			Triton CF54			Triton DF16			Tween 85		
	1%	3%	5%	1%	3%	5%	1%	3%	5%	1%	3%	5%
Sonication-washing	2.4 ± 0.6	1.6 ± 0.3	1.5 ± 0.4	1.0 ± 0.2	0.3 ± 0.1	0.2 ± 0.1	1.5 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	4.8 ± 05	-----	-----
Column flushings	2.7 ± 0.4	2.1 ± 0.5	1.5 ± 0.3	1.2 ± 0.3	0.8 ± 0.2	0.4 ± 0.2	2.8 ± 0.1	0.9 ± 0.2	2.1 ± 0.2	2.0 ± 0.3	1.8 ± 0.3	2.9 ± 0.4

Table 4.5 Surfactant content (%) remaining in the extract post soil sonication-washing (10g) or continuous column flushing (30g)

Surfactants	Brij 97			Triton CF54			Triton DF16			Tween 85		
Concen.	1%	3%	5%	1%	3%	5%	1%	3%	5%	1%	3%	5%
Sonication treatment No.												
1	68.6± 6.9	76.1± 7.1	79.4± 4.3	62.1± 6.3	74.6± 5.6	80.1± 4.7	63.4± 5.4	70.6± 5.1	78.6±4.8	60.3± 3.6		
2	80.2± 4.2	89.3± 3.9	92.8± 4.0	83.8± 4.8	87.5± 3.9	94.8± 3.2	78.6± 4.1	86± 3.8	95.2± 3.1	72.5± 4.2		
3	90.1± 2.1	93.5± 2.7	98.5± 1.9	91.8± 3.0	98.2± 2.5	99.1± 2.2	89.8± 3.0	98± 2.3	99.5± 2.2	80.9± 2.7		
4	95.6± 1.6	98.0± 1.7	100± 2.0	97.9± 2.3	99± 1.7	100± 1.3	98.9± 2.1	100± 1.5	100± 1.4	89.3± 4.8		
5	99.0± 2.0	100± 1.1	100± 1.8	100± 1.2	100± 1.3	100± 1.0	100± 2.0	100± 1.4	100± 1.2	95.5± 4.6		
Column flushing (min)												
10	32.4± 13.9	38.6± 10.1	43.2± 8.9	37.8± 9.9	42.4± 5.8	45.7± 6.5	39.4± 8.6	40.5± 6.7	47.1± 6.6	43.5± 6.7	47.6± 6.4	48.2± 7.1
20	47.2± 9.8	53.2± 8.9	60.4± 5.5	49.7± 6.5	53.9± 4.5	57.8± 4.1	47.5± 5.8	52.8± 5.4	60.2± 4.5	50.9± 6.8	58.5± 4.5	66.5± 6.1
30	66.3± 7.4	69.7± 5.5	76.8± 3.5	64.9± 4.4	68.9± 2.3	71.9±3.3	68.1± 4.6	65.7± 3.7	73.2± 4.5	71.4± 4.5	73.6± 3.3	77.7± 4.6
40	75.7± 5.7	80.7± 4.6	89.8± 3.5	79.9± 2.9	83.2± 3.9	87.4± 2.8	78.8± 3.8	85.6± 3.6	88.9± 3.1	83.5± 4.6	88.8± 4.7	90.9± 3.6
50	82.6± 5.4	89.6± 3.6	95.6± 2.7	88.5± 2.4	93.6 ± 2.9	96.5± 3.7	89.2± 3.5	92.6± 3.2	97.4± 3.4	92.2± 3.8	96.8± 3.9	98.1± 2.4
60	95.8± 4.5	99.8± 2.3	99.8± 1.0	98.9± 2.5	98.4± 2.5	99.2± 2.6	97.9± 3.4	99.4± 2.4	98.8± 3.5	100± 2.3	99.6± 2.4	99.2± 1.3
70	98.9± 2.6	99.9± 1.6	99.9± 1.0	100± 1.6	100± 0.5	100± 1.0	100± 1.5	100± 1.7	100± 2.1	100± 1.4	100± 2.0	100± 1.7

Table 4.6 Surfactant content remaining with the aqueous phase post soil flushng soilsonication washing or remediation of the eluate by back-extraction with $scCO_2$

Surfactants	Brij 97			Triton CF54			Triton DF16			Tween 85		
Concentrations	1%	3%	5%	1%	3%	5%	1%	3%	5%	1%	3%	5%
Surfactant content (%) in eluate post soil sonication-washing	89.6 ± 6	91.6 ± 5	96.4 ± 3	90.1 ± 4	95.6 ±4	98.1 ± 3	91.4 ± 5	96.6 ± 3	98.6 ±4	80.1 ± 7	-----	-----
Surfactant content (%) in eluate post soil colum flushing	90.6 ± 4	93.4 ± 4	97.6 ± 4	89.3 ± 4	94.9 ± 4	98.8 ± 3	92.3 ± 3	95.7 ± 3	97.7± 3	85.6 ± 7	90.8 ± 6	92.3 ± 5
Surfactant content (%) in aqueous retentate post $scCO_2$ extraction	70.2 ± 4	76.3 ± 6	78.8 ± 5	60.9 ± 5	66.6 ± 5	75.3 ± 5	20.3 ± 6	23.6 ± 5	31.6 ± 5	45.3 ± 6	48.6 ± 5	58.8 ± 3

efficiencies between the 3% and 5% Brij 97 suspensions were not significant. The mean PCB contents in the soil post flushing (± 1 RSD) were 2.7 ± 0.4, 2.1 ± 0.5 and 1.5 ± 0.3 μg/g for the 1, 3 and 5% aqueous suspension respectively (Table 4.4). The residual quantities of surfactant sorbed to the soil post flushing were similar to the quantities observed for the sonication-washing experiments. Quantities of surfactant in the extract post processing did not differ greatly (Table 4.6) from the quantities present in the suspension prior to processing.

The PCB extractions from soil by sonication-washing with Triton CF54 were reasonably efficient. As illustrated in Figure 4.7, the quantities of mobilized PCB were 80.1%, 91.1% and 93.5% for aqueous suspensions of 1%, 3% and 5% respectively. The single exponential rise to a maximum also accurately modelled the experimental observations with the CF54 surfactant. Values for t_{50} of 5.74, 5.73 and 2.94 sonication-washing and 3.95, 2.85 and 2.92 h of flushing were predicted for the 1, 3 and 5% suspensions. The quantities of PCBs in the soil post treatment with 1%, 3% or 5% Triton CF54 were 1.0 ± 0.2, 0.3 ± 0.1 and 0.2 ± 0.1 μg/g respectively (Table 4.4). Results for soil column flushing with this surfactant were comparable to extractions by sonication-washing (Figure 4.7, hollow symbols). The PCB extraction was enhanced when the concentration of CF54 was increased from 1% to 3% (v/v) but a further increase from 3% to 5% did not significantly increase the mobilization further. The amount of PCB that remained in the treated soil was 1.2 ± 0.3, 0.2 ± 0.2 or 0.4 ± 0.2 μg/g for flushing with 1%, 3% or 5% Triton CF54 suspension (Table 4.4).

PCB sonication-washing treatments with Triton DF16 proved to be the most efficient among the four surfactants (Figure 4.8). The efficiency of PCB purging from the soil was 89%, 95% and 97% for 1%, 3% and 5% suspension respectively. Analyses of variance (ANOVA) indicated that differences in efficiency among the treatments were not significant. The PCB contents remaining with the soil post washing were 1.5 ± 0.2, 0.2 ± 0.1 and 0.2 ± 0.1μg/g for the 1%, 3% or 5% DF16 suspensions. Soil flushing treatments with Triton DF16 provided analogous results (Figure 4.8, hollow symbols). The quantities of mobilized PCBs were 89%, 95% or 97% with suspensions of 1%, 3% or 5% respectively. The residual PCB contents in the treated soil were 2.8 ± 0.4, 0.9 ± 0.2 and 2.1 ± 0.3 μg/g after flushing with 1%, 3% and 5% DF16 suspension respectively.

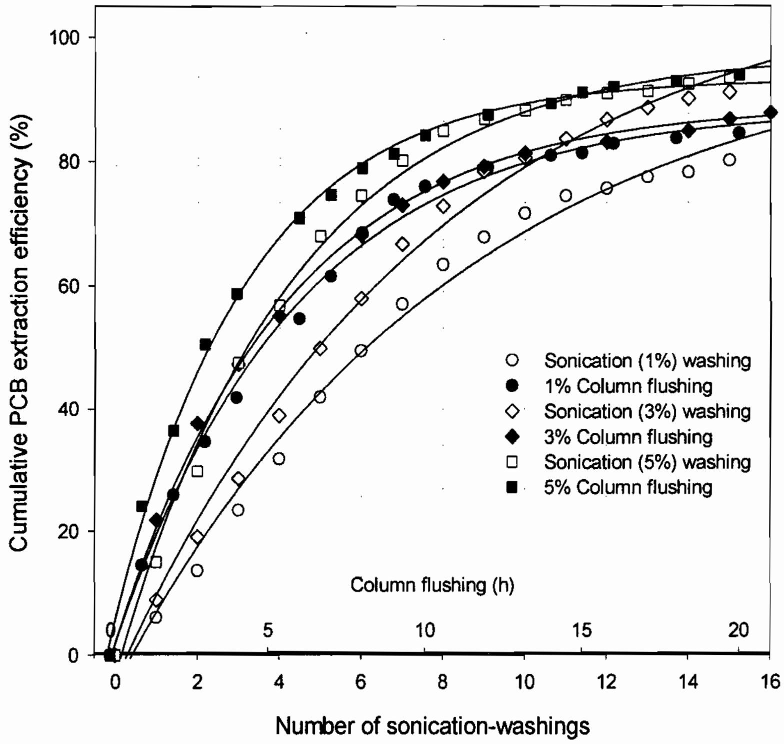

Figure 4.7 Cumulative PCB extraction efficiencies for mobilizations from 10g soil by sonication (10 min)-washing with 1%, 3% or 5% or by continuous flushing from 30g soil with 1%, 3% or 5% aqueous suspension of Triton CF54 surfactant.

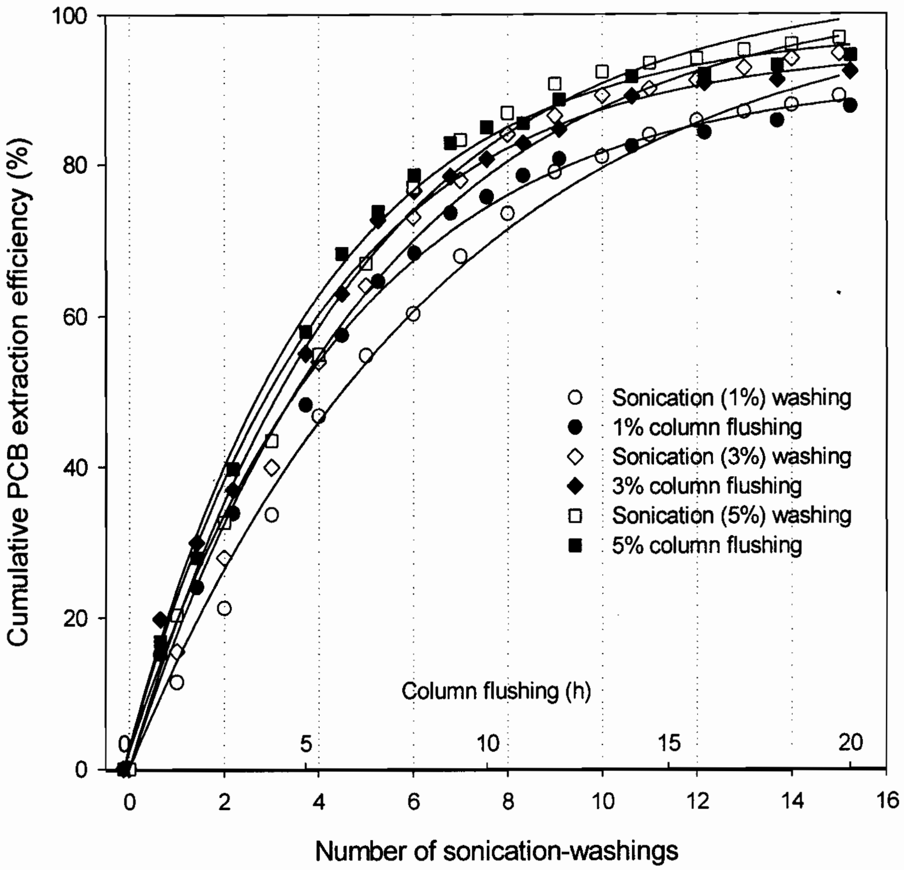

Figure 4.8 Cumulative PCB extraction efficiencies for mobilizations from 10g soil by sonication (10 min)-washing with 1%, 3% or 5% or by continuous flushing from 30g soil with 1%, 3% or 5% aqueous suspension of Triton DF16 surfactant.

Unlike the other surfactants, Tween 85 proved to be less suitable for soil sonication-washings (Figure 4.9). The Tween 85 suspension dispersed soil particles very strongly so that, once sonicated, it became difficult to filter materials from the treated slurry. This behavior was evident even after the initial treatment with the 1% (v/v) suspension. The more treatments that were performed, the more difficult it became to filter the suspension and increased concentration of this surfactant only exacerbated the problem. In consequence, sonication-washing with the 3% and the 5% Tween 85 suspension were not completed. Extracted PCBs amounted to 81% for 1% suspension (Table 4.6) and the residual PCB content was 4.8 ± 0.5 μg/g (Table 4.4). This residual PCB content was higher than for similar treatments with the other surfactants.

The concentration of aqueous Tween 85 solutions had less of an effect on the packed soil flushing treatments (Figure 4.9), although the appreciable soil particle dispersion required higher pressure to force mobile phase through the column. The quantity of PCB extracted from the soil was 85%, 89% and 90% for the flushing trials with 1%, 3% or 5% suspension. The residual PCB contents were 2.8 ± 0.4, 1.8 ± 0.3 and 2.9 ± 0.4 μg/g for suspensions containing 1%, 3% or 5% surfactant. The fraction of surfactant that remained with the soil was also relatively greater than with similar concentrations of other surfactants for both the flushing and washing treatments (Table 4.6).

For the soil cleaning trials, the mean standard error of estimate (a measure of the goodness of fit of the mathematical model to the data) for the 22-trials (2.0 range 1.19-3.57) did not vary appreciably as the quantity of surfactant in the suspension (2.53 for 1% *vs.* 2.55 for 3% *vs.* 2.39 for the 5% sonication and 1.91 for 1% *vs.* 1.8 for 3% *vs.* 1.80 for 5% flushing). The corresponding t_{50} estimates ranged from 6.96-1.92 sonication-washings and from 6.45-2.85 h for the flushing trials. They decreased with increasing surfactant concnetration in the suspension. Despite differences in the quantity of soil treated (10 g for sonication-washing *vs.* 30 g for soil flushing) comparable mobilization efficiencies were achieved with the sonication-washing and column flushing.

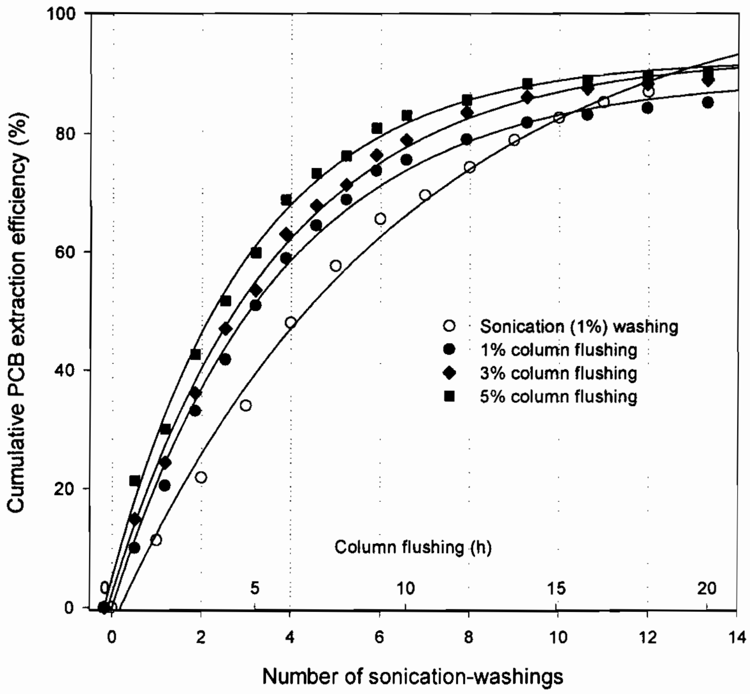

Figure 4.9 Cumulative PCB extraction efficiencies for mobilizations from 10g soil by sonication (10 min)-washing with 1% or by continuous flushing from 30g soil with 1%, 3% or 5% aqueous suspension of Tween 85 surfactant.

4.3.4 PCB separation from soil extract and surfactant regeneration

PCBs were mobilized from the contaminated soil suspensions by back-extraction with $scCO_2$ during 30 min at 50 °C. The results indicated that >99% of PCBs (data not shown) were mobilized from the soil extracts and 23-78% of surfactant (Table 4.6) remained in the aqueous suspension post treatment. The cleaned surfactant suspension could then have been reused to mobilize more PCB from the contaminated soil. Based on the PCB extraction efficiencies, the suitability of surfactants for either soil sonication-washing or column flushing treatments were in the order: Triton DF16 >Triton CF54 >Brij 97 > Tween 85 whereas increased surfactant losses were observed in the order: Tween 85 < Brij 97 < Triton CF54 < Triton DF16.

4.3.5 PCB dechlorination

Once PCBs had been mobilized into $scCO_2$, they were dechlorinated (*on-line*) to biphenyl by passing the effluent through a reactor column of zero-valent silver iron (Ag^0/Fe^0) bimetallic mixture under anoxic condition (Wu and Marshall, 2000). Analysis by GC-MS did not detect any chlorinated products that were eluted from the analytical capillary column within the chromatographic window for PCB compounds. There was no evidence that organic matter or surfactant that had been mobilized from the aqueous surfactant-soil suspension affected the dechlorination efficiency. Dechlorination proved to be both rapid and apparently quantitative.

In total, the results have demonstrated that PCBs can be removed from the soil by extraction with dilute suspensions (1-5% v/v) of aqueous surfactant. The four commercial non-ionic formulations were approximately equally efficient when used with procedures designed to minic either *ex-situ* washing or *in-situ* soil flushing. The removal efficiency from the soil was predicted accurately with a simple exponential expression that included the number of successive treatments and a "time constant" (λ) that was characteristic of the washing process. The number of successive washings required to extract 50% of the PCBs (t_{50}) varied as the concentration of surfactant in the emulsion for both washing and flushing experiments. Equilibration with Triton CF 54 was typical; 5.74 and 2.94 washes were predicated to be required for the t_{50} with 1% and 5% surfactant emulsions, respectively. The mathematical model also accurately predicated the course of the flushing process with the soil column. In this case, the PCB concentration was predicated to be reduced two-fold after 3.95 (237 ml) or 2.92 h (~175 ml) of flushing. Comparable values for sonication-washing and for flushing were observed with similar concentrations of the other surfactants. Despite differences in the quantity of soil treated (10 g for sonication-washing vs. 30 g for soil flushing) comparable mobilization efficiencies were achieved with both procedures.

There were no apparent differences in the avidity with which separate fractions of the total PCB burden interacted with the soil. Although three of the surfactant formulations did not change the physical properties of the soil, one formulation was observed to disperse the soil agglomerates appreciably and required increased pressure to force the aqueous phase through the soil. Nonetheless, large volumes of surfactant suspension were required to mobilize the PCBs efficiently. The challenge remains to improve the efficiency of this stage of the overall process. The PCBs in the cumulative aqueous extracts were back-extracted efficiently (>99%) into $scCO_2$-IBMK. Losses of surfactant to the mobile phase during this stage were appreciable but the dechlorination was quantitative.

Chapter 5
Preface

In Chapter 4, PCBs were extracted from contaminated soil with selected surfactants and mobilized from the PCB containing suspension by back-extraction with $scCO_2$. The results indicated that >99% of PCB were mobilized from the soil extracts and 23-78% of surfactant remained in the aqueous suspension post treatment. The cleaned surfactant suspension could then have been reused to mobilize more PCB from the contaminated soil. The challenge remains to improve the efficiency of this stage of the overall process.

In the current Chapter, models for PCB mobilization from surfactant suspensions with $scCO_2$ is evaluated and the feasibility to both clean the surfactant suspension and to regenerate zero-valent metal/bimetallic particles is re-investigated. It was anticipated that PCB mobilization efficiencies with time could be predicted accurately using mathematical models for PCB mobilization at various PCB burdens, and the combination of PCB mobilization with dechlorination on-line could be established and could be applied to the PCB detoxification process.

Mobilizations of polychlorinated biphenyl (PCB) compounds from surfactant suspension/soil extract with dechlorination on line

5.1 Introduction

Previous studies (Chapter 4; Wu and Marshall, 2001) had demonstrated that polychlorinated biphenyl (PCB) compounds could be mobilized efficiently from contaminated soil(s) into a surfactant suspension and then removed from the aqueous phase by back-extraction with supercritical carbon dioxide (scCO_2). It was also possible to detoxify the PCB-laden eluate from the scCO_2 extractor with an *on-line* dechlorination process that converted the substrates to biphenyl and chloride. The dechlorination reactor consisted of a column zero-valent bimetallic mixture of palladium and iron (Pd^o/Fe^o) that was heated to 450 °C. The mobilization efficiency from either the contaminated soil or the resulting aqueous surfactant suspension was influenced by the solubility of PCBs in the scCO_2 (Yu *et al.,* 1995), the concentration of PCB in the aqueous phase (Akgerman *et al.,* 1993; Glazkov *et al.,* 1999), the operating pressure and temperature (Aranda *et al.*, 1997; Miller *et al.*, 1997) and the solvent modifier that was added to the scCO_2 (Auerbach *et al.*, 1996; Anitescu *et al.*, 1999). For optimized reaction conditions, the dechlorination proved to be very efficient, however the time required for efficient scrubbing was anticipated to depend on the loading of PCBs within the soil/aqueous surfactant emulsion. An objective of the studies had been to recycle the surfactant suspension back to mobilize more PCBs from contaminated soil. However, a portion of the surfactant was lost during the initial soil washing and a further portion was lost during the back-extraction stage (Chapter 4). Whereas losses during the initial washing seemed to depend on the quantity of soil treated, losses from the aqueous surfactant suspension depended on the duration and operating conditions of the back-extraction stage. To identify the optimized mobilization conditions that could be coupled with *on-line* dechlorination, it was necessary to examine PCB mobilization efficiencies from a range of PCB concentrations in surfactant suspensions that might be encountered in soil washing procedures. The objectives of the this Chapter were: i) to model the mobilization process of PCBs from various PCB-surfactant mixtures; ii) to optimize operating conditions for the combined PCB mobilization-reductive dechlorination and iii) to extend the PCB mobilization *on-line* dechlorination to a continuous process so as to enable the cleaned surfactant suspensions to be returned to fresh substrate soil to mobilize-detoxify more target PCBs.

5.2 Materials and methods

5.2.1 Chemicals, solvents and surfactants

Magnesium granules (12-50 mesh, 99.8 % purity), potassium hexachloropalladate (K_2PdCl_6), cobaltous nitrate [$Co(NO_3)_2 \cdot 6H_2O$], ammonium thiocyanate (NH_4SCN) and sodium dispersion [40% (*w/v*) in oil] were purchased from Alfa Aesar, Ward Hill, MA USA. Hexane, ethylene glycol dimethyl ether, isomethylbutyl ketone (IBMK, 99+%), methanol, methylene chloride (CH_2Cl_2), propan-2-ol (all HPLC grade), and glass wool were purchased from Fisher Scientific, Ottawa, ON. Biphenyl, Brij 97 and Triton CF54 were purchased from Sigma-Aldrich, Oakville, ON. Aroclor 1242 and Aroclor 1248 mixtures were kindly donated by Monsanto Company, Sauget, IL. All chemicals (ACS Reagent grade or better), solvents and surfactants were used as received.

5.2.2 PCBs mobilization from surfactant suspension or soil extract

The aqueous suspension (90 ml), consisting of surfactant [Brij 97 or Triton CF54 (3%, v/v)], Aroclor 1248 (0.1-1.0%, *v/v*) and distilled water, was supplemented with 10 ml IBMK. The resulting suspension was well mixed and placed in a cylindrical supercritical fluid (SCF) extraction vessel [300 mm X 23 mm inner diameter (i.d.)] that had been fitted with 2 inlet and 2 outlet ports that enabled the addition or removal of sample to/from the vessel during pressurised operation. The vessel was wrapped with a heating tape (Swagelok, Montreal, QC) and heated to maintain the operating temperature at 50 °C. $ScCO_2$, provided from a diaphragm compressor (Newport Scientific Inc., Jessup, MD USA) was added to the base of the extraction vessel and permitted to percolate up through the surfactant suspension and to accumulate within the headspace above the suspension. Fluid in the headspace was replaced continuously with fresh solvent from below and pressure within the system was maintained with a short section of flexible silica tubing (~25 cm x 50 μm i.d.) that terminated the stainless steel transfer line and acted as a capillary restrictor. Extractor eluate was trapped in 25 ml hexane or propan-2-ol contained in a 50 ml test tube. Measurements at the exit of the capillary restrictor indicated a flow rate corresponding to 1500 ml/min of decompressed gas. The extraction was continued for up to 15 h. The cumulative PCB mobilization efficiency was measured after 5 min and subsequently at 10 min intervals. All trials were replicated three times.

5.2.3 On-line PCB dechlorination

5.2.3.1 Dechlorination reactor

The dechlorination assembly consisted of standard HPLC fittings and column (25 x 1 cm i.d., containing 45 g Pd^o/Fe^o bimetallic mixture) assemblies that were rated to 6,000 psi. The outlet stream from the extractor was connected with a stainless steel transfer line (0.625 mm o.d.) to one or two stainless steel HPLC columns [10 mm i.d. X 25 cm] that were jacketed with an alumina tube (12 mm i.d., Alfa Aesar, that had been cut lengthways to provide two semi-cylinders) and mounted in series. The column-alumina jacketed assemblies were heated separately with 80-turn coils of high resistance heating wire that were energized with variable transformers. Pressure within the assembly was maintained at 4500 psi with a flexible polyamide coated silica capillary restrictor (~25 cm x 0.05 mm, Chromatographic Specialties, Brockville, ON). For diluted PCB substrate, a mixture of Aroclor 1248 (10%, v/v) dissolved in acetic anhydride and DME (8+1) was delivered at 0.1 ml/min to the mixing tee (1/16''i.d.), merged with the $scCO_2$ stream (~4 ml/min) and fed to a single ss (Figure 3.1) reactor column.

5.2.3.2 Dechlorination operation

Two approaches were evaluated to interface the extractor effluent with the dechlorination reactor. The outlet stream from the extractor was merged, via a mixing tee (1/16" i.d.), with a solution [acetic anhydride and DME (9+1)] delivered at 0.2 ml/min by an HPLC pump (Beckman, 100A). The alternate approach involved interposing a second extraction vessel (300 mm X 25 mm i.d.) that contained 20 ml acetic anhydride plus DME, (4+ 1).

After mixing with the solvent in the second vessel, the effluent was transferred to the dechlorination reactor. After a short delay to purge residues of air from the system (during which time only $scCO_2$ was fed to the reactor) Aroclor 1248 [10% (v/v)] feedstock, delivered from the HPLC pump, was merged, at 0.1 ml/min, with the $scCO_2$ stream and transported to the reactor. Measurements at the exit of the capillary restrictor indicated a flow rate of 800-1000 ml/min of decompressed gas. The exit tip of the capillary restrictor was immersed in hexane (25 ml) to trap products from the reactor eluate. Each experiment was continued until six successive traps had been collected, each corresponding to 10 min of cumulative trapping of eluate. The course of the dechlorination was monitored by gas chromatography (GC-FID) and by GC-MS to monitor the identities of products and by titration to measure levels of residual organically bound chlorine in the eluate.

5.2.4 PCB analyses

If the initial PCB concentration in the surfactant mixture was less than 1% (v/v), conversion to biphenyl was used. Aroclor 1248 mixture was converted quantitatively to biphenyl by reaction with Mg^0 and K_2PdCl_6 following the procedures reported previously (Wu and Marshall, 2001). For higher initial Aroclor 1248 concentrations in surfactant suspension (>1%, v/v), the titration method was followed (Wu and Marshall, 2001). In brief, residual PCBs in hexane trapping solution was determined by titration with standardised $AgNO_3$ (~0.01M) post conversion of organically bound chlorine to chloride. Sodium dispersion, 2 ml, was added to a 10 ml aliquot of vigorously stirred hexane trapping solution that had been further diluted 5-fold with fresh hexane. Methanol, 1 ml, was added dropwise. The reaction was continued for 5 min then quenched by the addition of propan-2-ol (15 ml) followed by 90 ml water. Post phase separation, a 20 ml aliquot was acidified to pH 6-7 with nitric acid (7M), supplemented with 5 drops of potassium chromate indicator solution then titrated with $AgNO_3$. Blank determinations for chloride in reactor eluate consisted of an identical procedure in the absence of added sodium dispersion.

5.2.5 Surfactant analysis

The Standard Analysis Methods, APHA (Dreebberg *et al.*, 1992), was followed to determine the residual surfactant concentration post $scCO_2$ mobilization. A standard calibration curve was generated for each surfactant. Micellar-suspension (1 ml) was diluted five-fold to obtain a suitable working concentration. Diluted surfactant suspension (2 ml) contained in a 100 ml flask, was evaporated to dryness then triturated with methylene chloride (10 ml) and the resulting extract was added to a 125-ml separatory funnel containing 5 ml cobaltous thiocyanate solution. After 1 min of vigorous shaking and phase separation, the lower aqueous layer was transferred, via a funnel containing a plug of glass wool, to a 5 ml spectrophotometer cell. The absorbance, at 620 nm, was determined *vs*. a blank of CH_2Cl_2.

5.2.6 Gas Chromatography Mass Spectrometry

The total content of PCBs was determined by gas chromatography equipped with flame ionization detection (GC-FID) or a Hewlett-Packard model 5890 (II) gas chromatography equipped with a model 5971 mass selective detector (GC-MS). Both methods were described in previously reports (Wu and Marshall, 2000; 2001).

5.3 Results and discussion

5.3.1 The efficiency of PCB mobilization into supercritical CO_2

To study the rate of PCB mobilization from surfactant suspension into $scCO_2$, of mixtures containing various concentrations of Aroclor 1248 (0.1-1.0%, v/v) in Brij 97 (3%, *v/v*) or Triton CF54 were extracted at 50 °C and 4500 psi. As illustrated in Figure 5.1 (dashed lines), the quantity of PCB mobilized with time from PCB-Brij 97 suspension were dependent on the duration of extraction and on the initial PCB content. To the extent that the rate of PCB mobilization from surfactant suspension can be approximated as a time constant (λ) multiplied by the PCB concentration (Y) in the suspension at time t

$$dY/dt = \lambda Y \qquad (1)$$

This rate expression can be re-written as an exponential decay function:

$$Y = CY_0e^{-\lambda t} \qquad (2)$$

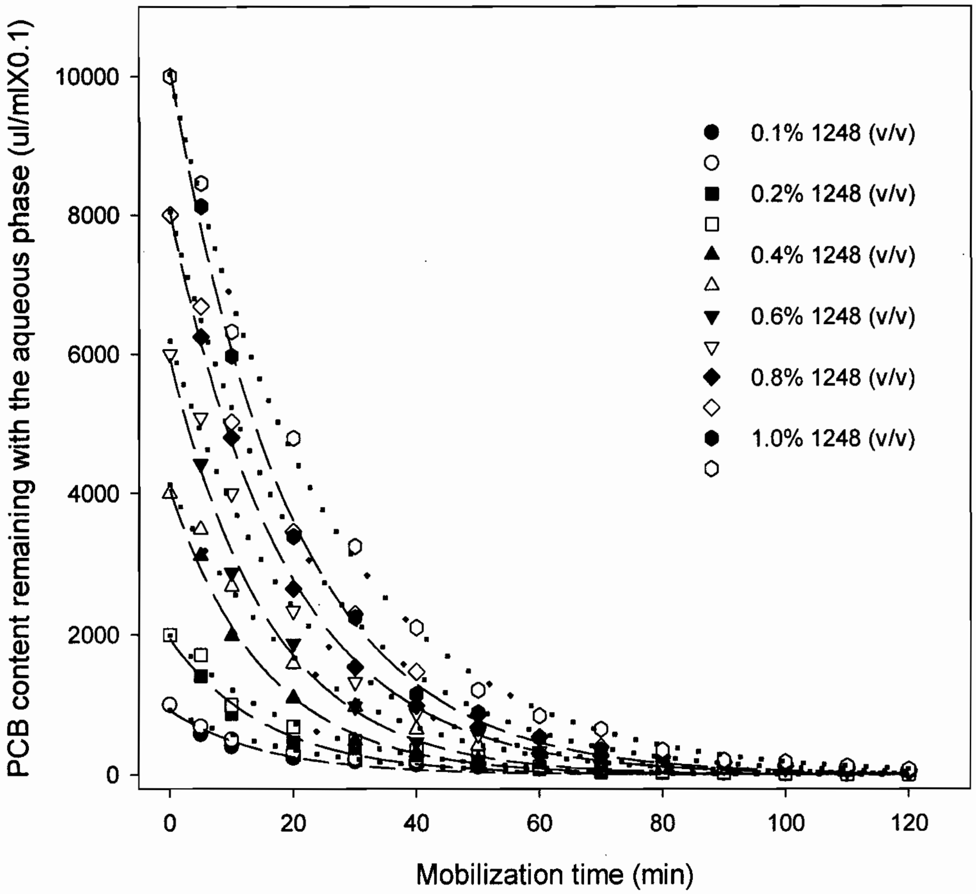

Figure 5.1 Mobilizations, with time, of Aroclor-1248 (0.1-1.0 %, v/v) from (1+9) IBMK-aqueous Brij 97 (3%, v/v) suspension.

where C is a constant of proportionality, Y_0 is the PCB content at time zero and λ is a time constant characteristic of the extraction processes. Expression (2) was observed to provide an accurate estimate (Figure 5.1 and Figure 5.2, dashed curves) of the experimental data for each of the loadings of PCBs in the Brij 97 and Triton CF54 surfactant suspensions respectively. The optimized regression models for mobilizations from Brij 97 are provided in Table 5.1 and from Triton CF54 in Table 5.2. The parameter of the goodness of fit of the model to the data (R^2) for surfactant suspensions (0.989 ± 2%, Table 5.1; 0.983±2%, Table 5.2 respectively) were satisfyingly close to 1. When the extraction process was interfaced with *on-line* dechlorination, the rate of PCB mobilization was decreased (Figure 5.1 and 5.2, dotted lines). The dechlorination reactor (discussed below) contributed appreciably to the back-pressure within the system so that for the same $scCO_2$ head pressure (4500 psi), the flow rate of decompressed gas at the exit of the capillary restrictor, 1500 ml/min, was reduced to 900-1000 ml/min by interposing the heated dechlorination column within the reaction train. When corrected for the differences in flow rates, the curves at each loading in the absence/presence of the dechlorination reactor became virtually identical.

An interesting feature of the exponential decay model is that the time required to mobilize one half of the initial burden ($t_{1/2}$) is predicted to be independent of the initial PCB loading. For the range of loadings studied (0.1-1.0% v/v), the $t_{1/2}$ values were independent (within experimental error) of quantity of PCB formulation that had been added to the suspension. The mean $t_{1/2}$ for the six loadings in Brij 97 was 11.6 min ±11% (Table 5.1) and 10.3 min ±11% (Table 5.2) for the Triton CF54 for mobilizations alone and 15.4 min ± 8% and 16.8 min ±14% for mobilizations combined with dechlorination.

An alternate way to express the course of these mobilizations that is anticipated to be independent of the flow rate of $scCO_2$, is in terms of the number of exchanges of headspace fluid required to reduce the PCB burden in the aqueous suspension to one half of its initial value. For a flow rate of 8.8 ml/min of compressed fluid in the absence of the reactor and 6.0 ml/min when it was connected *on-line*, the mean number of exchange volumes per half life were calculated to be 9.0 ± 8% and 10.0 ± 11% respectively for the Brij surfactant (Table 5.1). Similarly, the number of exchange volumes observed for the

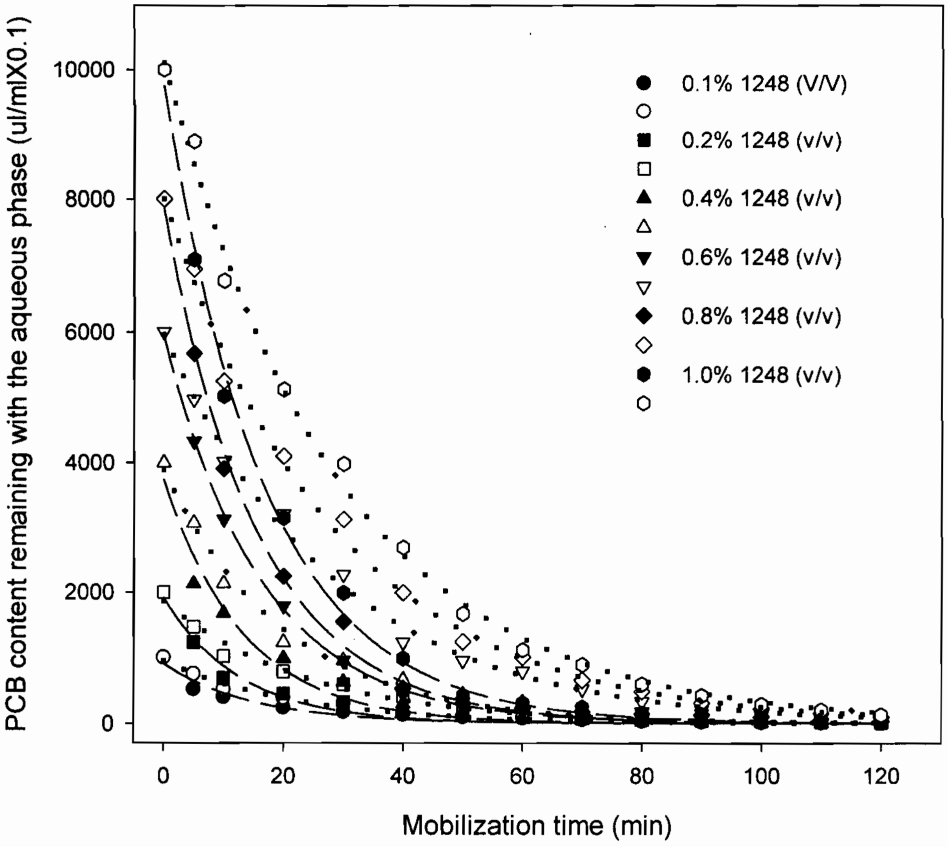

Figure 5.2 Mobilizations, with time, of Aroclor-1248 (0.1-1.0 %, v/v) from (1+9) IBMK-aqueous Triton CF54 (3%, v/v) suspension.

Table 5.1 Best-fit exponential decay models for extractions of Aroclor-1248 from Brij 97 (3% v/v) emulsion into $scCO_2$ (performed at 50 °C and 4500 psi).

Aroclor-1248 concentration	Optimised decay model for mobilisation	R^2	Fitted Y_0	$t_{1/2}$ min	# headspace exchanges	Optimised model for mobilisation + dechlorination	R^2	Fitted Y_0	$t_{1/2}$ min	# headspace exchanges
0.1	$Y= 832.3e^{-0.0646t}$	0.961	0.0857	10. 6	8.7	$Y=924.7e^{-0.0471t}$	0.979	0.0716	14.8	9.1
0.2	$Y=1938e^{-0.0641t}$	0.983	0.1996	10.8	8.3	$Y=1993e^{-0.0493t}$	0.984	0.1747	14.1	9.3
0.4	$Y=4060e^{-0.0650t}$	0.995	0.4182	10.7	9	$Y=4128e-^{0.0450t}$	0.996	0.3809	15.4	9.2
0.6	$Y=5945e^{-0.0624t}$	0.996	0.6123	11.1	8.6	$Y=6194e^{-0.0476t}$	0.997	0.587	14.6	9.5
0.8	$Y=8045e^{-0.0531t}$	0.999	0.8287	13.1	9.4	$Y=8053e^{-0.0431t}$	0.999	0.7932	16.1	11.3
1	$Y=10120e^{-0.0515t}$	0.998	1.042	13.5	10.3	$Y=10030e^{-0.0395t}$	0.997	0.9993	17.6	11.6
Mean±1RSD		0.989±2%		11.6±11	9.0±8%		0.992±0.8%		15.4 ± 8%	10.0±11%
Brij 97 content (3% v/v)	$Y= 81.6e^{-0.0516t} +$ 20.1	0.988		13.5						

Table 5.2 Best-fit exponential decay models for extractions of Aroclor-1248 from Triton CF54 (3% v/v) emulsion into $scCO_2$ (performed at 50 °C and 4500 psi).

Aroclor-1248 concentration	Optimised decay model for mobilisation	R^2	Fitted Y_0	$t_{1/2}$ min	# headspace exchanges	Optimised model for mobilisation + dechlorination	R^2	Fitted Y_0	$t_{1/2}$ min	# headspace exchanges
0.1	$Y=903.8e^{-0.0681t}$	0.95	0.1009	10. 2	9.3	$Y=897.1e^{-0.0437t}$	0.969	0.0739	15.9	8.8
0.2	$Y=1917e^{-0.0794t}$	0.976	0.202	8.8	8.4	$Y=1887e^{-0.0485t}$	0.983	0. 1752	14.3	7.6
0.4	$Y=3742e^{-0.0760t}$	0.979	0.4041	9.1	8.3	$Y=3270e^{-0.0492t}$	0.986	0.3779	14.1	7.8
0.6	$Y=5942e^{-0.0633t}$	0.998	0.6062	11	11.1	$Y=5931e^{-0.0366t}$	0.997	0.5805	19	9.4
0.8	$Y=7866e^{-0.0633t}$	0.997	0.8083	11	11.5	$Y=8053e^{-0.0355t}$	0.996	0. 7832	19.6	9.4
1	$Y=9756e^{-0.0589t}$	0.997	1.0104	11.8	10.5	$Y=10030e^{-0.0389t}$	0.998	0. 9860	17.9	10.1
Mean ± 1RSD		0.983±2%		10.3±11%	9.9±14%		0.991±1%		16.8±14%	8.8±11%
Triton content (3%,v/v)	$Y=78.9e^{-0.0559t}+16.7$	0.976		12.4						

Triton surfactant was 9.9 ± 14% and 8.8±11% respectively (Table 5.2). These results indicate that observed differences in $t_{1/2}$ were the result of changes in the flow rate of mobile phase rather than a change in the efficiency of the process. It is anticipated that the rate of mobilization could be accelerated by further increasing the flow-rate of mobile phase and/or by reducing the volume of headspace above the sample.

5.3.2 Surfactant retention

One of the objectives of the study was to retain as much surfactant as possible within the aqueous retentate (surfactant phase) during the mobilization processes. However, as illustrated in Figure 5.3, the content of Brij 97 or Triton CF54 remaining with the aqueous phase also decreased with increased extraction time. From the decreasing profile with time, it seemed that the decrease of surfactant content in the aqueous suspension was closely related to the mobilization efficiencies of PCBs. Although the Triton CF54 content decreased slightly more rapidly during the early stages of the mobilization process, both surfactants had reached similar concentrations post 40 min of mobilization (Figure 5.3). It was concluded that differences, if present, were within the range of surfactant replicate determinations. The optimized regression models for the content of remaining surfactant provided accurate estimates of the analytical data (R^2, 0.988 and 0.976 (Tables 5.1 and 5.2 respectively) yet they approached a limiting value corresponding to 20.1% for the Brij 97 and 16.7% of the initial content for the Triton CF54 surfactant suspension.

To study the "residual" fraction in more detail, a 15% (v/v) Triton CF54 suspension (90 ml) was extracted for 2 h with $scCO_2$, the mobile phase was interrupted and the sample was amended with IBMK (10 ml) and 1% (v/v) Aroclor-1248. The extraction was then continued for a further 4 h. A total of nineteen 0.5 ml aliquots of aqueous sample were removed at 20-min intervals throughout the 6 h trial. The results are presented in Figure 5.4. Both phases of the trial were adequately modelled as an exponential decay function (R^2, 0.9927, 0.9982) but the rate of CF54 surfactant mobilization was decreased appreciably during the initial 2 h by the absence of IBMK ($t_{1/2}$, 71.1 min). A residual fraction corresponding to 13.2% of the surfactant loading was predicted by the model.

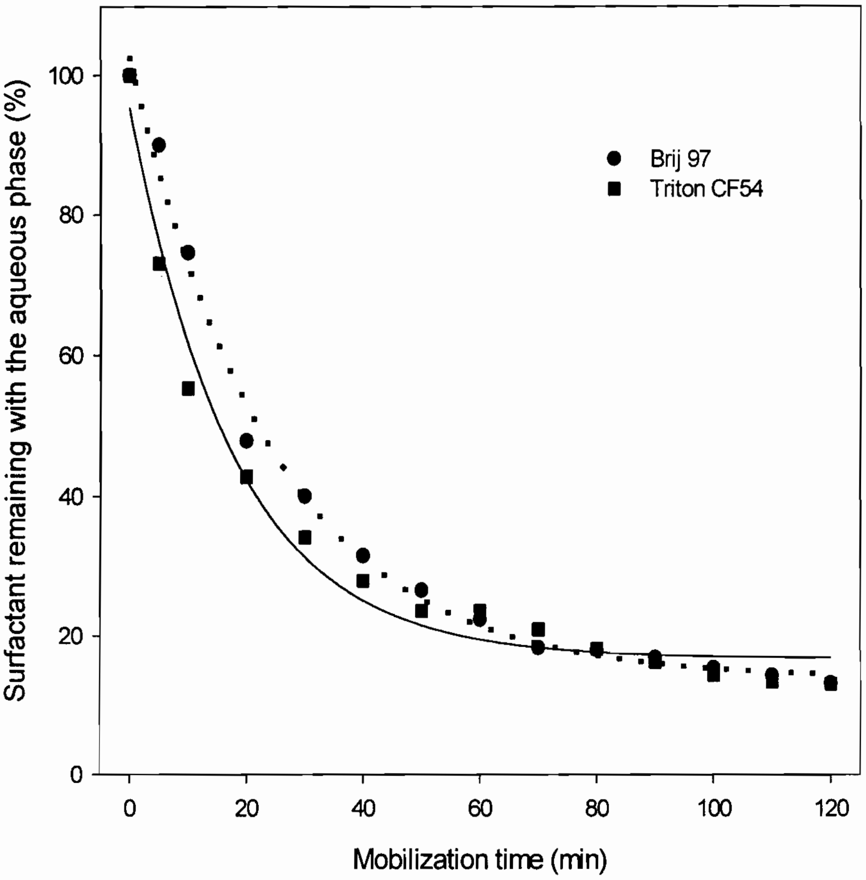

Figure 5.3 Percent surfactant remaining in the aqueous retentate fraction, with time, post extraction with scCO2 at 50 °C and 4500 psi.

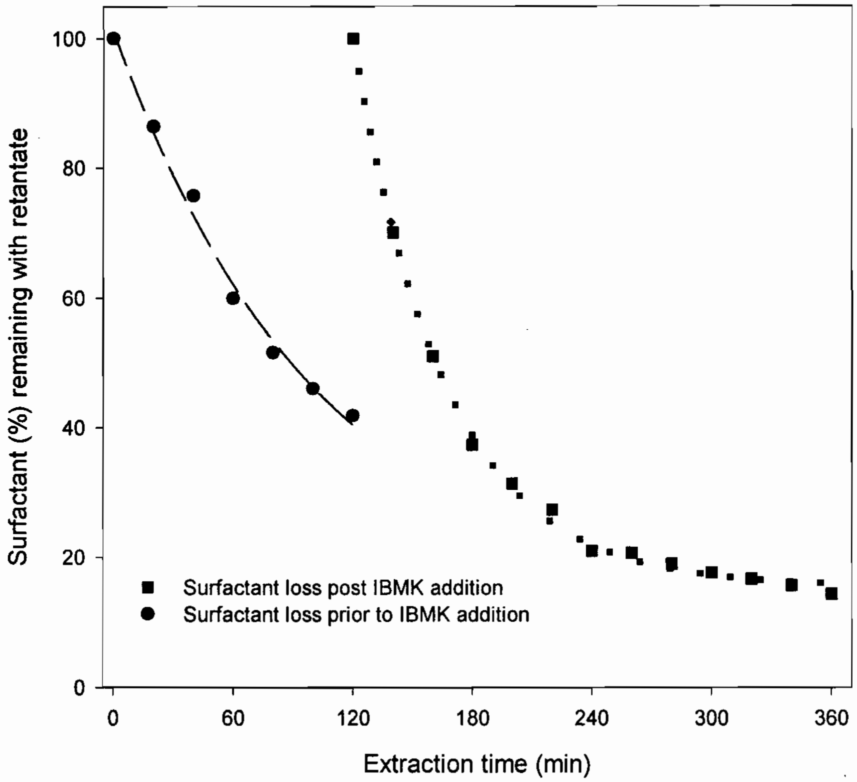

Figure 5.4 Mobilization, with time, of Triton CF54 surfactant in the absence / present of Aroclor 1248 (1%, v/v)-IBMK (10%, v/v).

Post addition of IBMK, the rate of surfactant mobilization was increased ($t_{1/2}$, 27.9 min) but models for both phases of the trial predicted a residual fraction (13.2 and 15.5% pre and post-addition of IBMK respectively). It seems likely that post cleaning of the aqueous retentate with IBMK-$scCO_2$, this fraction could be fortified with more surfactant and returned to the contaminated soil to mobilize more pollutant(s).

5.3.3 On-line PCB dechlorination

Efforts were turned to interfacing the extractor outlet stream to a heated reactor column(s) of zero-valent bimetallic mixture (Pd^0/Fe^0) so as to effect dechlorination(s) of the effluent *on-line*. Two configurations were evaluated. Because IBMK was a component of the effluent, it was anticipated that a direct coupling might be efficient (Wu and Marshall, 2000; 2001). Effluent from the reactor was trapped in hexane during 3 h of continued mobilization-dechlorination. As recorded in Table 5.3, the dechlorination yields for various PCB concentrations (0.1–1.0%, v/v) ranged from 99.7–72.4% for Brij 97 suspensions and 99.8-73.8% for Triton CF54 suspensions when the outlet stream of mobilized PCBs was interfaced directly to two zero-valent columns (connected in series) that were heated to 400 °C. In an attempt to increase dechlorination efficiency, a second means of coupling was also evaluated. A vessel containing 20 ml mixed solvent (acetic anhydride, DME, IBMK, 8+1+1 v/v/v) was interposed between the extraction vessel and the reactor. With this modification, the dechlorination efficiency was improved appreciably (Table 5.3). The dechlorination yields ranged from 100–90.5% and 100-93.6 % for PCB effluent from suspensions [that had contained 0.1–1.0 % (v/v) Aroclor 1248] in Brij 97 and Triton CF54 suspensions respectively. There were no significant differences between dechlorination efficiencies from Brij 97 and Triton CF54 suspensions.

The exponential model was evaluated for extended mobilization times. Table 5.4 summarizes the predicted and measured PCB and surfactant contents remaining with the aqueous phase post approximately 14 half-lives of extraction. The time predicted to reduce PCB residues in the aqueous retentate fraction to non-hazardous levels (≤0.1 μg ml) ranged between 194-297 min. Post extraction, the measured PCB levels exceeded this level in all cases indicating that for extended extraction times the decay model

Table 5.3 The dechlorination yields of PCB mixtures moilized from suspension of Aroclor 1248 (0.1~1%, v/v), water and Brij 97 (3%, v/v) or Triton CF54 (3%, v/v) using 2 Pd°/Fe° reactor columns connected in series. Dechlorinations were performed in $scCO_2$ at 400 °C and 4500 psi.

	Brij 97 suspension		Triton CF54 suspension	
Aroclor 1248 loading (%,v/v)	Dechlorination (%) via direct interface	Dechlorination (%) with solvent reservoir	Dechlorination (%) via direct interface	Dechlorination (%) with solvent reservoir
0.1	99.7 ± 0.2[a]	100	99.8 ± 0.2	100
0.2	92.2 ± 2	99.9 ± 0.1	93.3± 2	99.9 ± 0.1
0.4	89.6 ± 6	98.7 ± 0.3	90.5 ± 4	99.9 ± 0.1
0.6	87.4 ± 5	95.9 ± 3	86.6 ± 5	97.5 ± 2
0.8	76.5 ± 5	92.8 ± 3	74.5 ± 5	95.6 ± 3
1.0	72.4 ± 5	90.5 ± 3	73.8 ± 6	93.6 ± 4

[a] :Mean ± 1 SD for three replicate determination.

Table 5.4 Residues of Aroclor 1248 and surfactant content remaining with the aqueous phase post processing (mobilization with *on line* dechlorination) predicted to be sufficient to reduce PCB burdens to non-hazardous levels (0.1 μg/ml).

	Measured PCB residues (μg/ml) in the aqueous phase		Percent of initial surfactant remaining with the aqueous phase	
Aroclor 1248 loading (%, v/\	Brij 97	Triton CF54	Brij 97	Triton CF54
0.1	0.5 ± 0.3 [a]	0.2 ± 0.2	4.4 ± 1	5.5 ± 1
0.2	1.1 ± 0.3	0.5 ± 0.2	14.3 ± 3	15 ± 4
0.4	2.9 ± 0.5	1.2 ± 0.2	13.3 ± 3	15.3 ± 4
0.6	3.6 ± 0.6	2.1 ± 0.3	18 ± 4	16.3 ± 3
0.8	3.9 ± 0.6	2.9 ± 0.4	17.3 ± 4	16 ± 3
1.0	3.8 ± 0.8	3.1 ± 0.4	17 ± 4	16.3 ± 4

[a] :Mean ± 1 SD for three replicate determination.

appreciably over-estimated the extraction efficiency. If non-hazardous PCB levels are actually required in the aqueous washing suspension, then 3-5 more half lives of extraction are predicted to be required to decrease the content to non-hazardous levels. However, after ~14 half lives of extraction, the surfactant content remaining in the retentate fraction was 16.0 ± 6% and 15.8 ± 0.6% of the quantity added initially and was in reasonable agreement with predicted surfactant levels of 20.1 and 16.7%.

The main products of dechlorination, as identified by GC-MS, were biphenyl and methylated benzenes (xylenes to pentamethylbenzene). In addition, 1,3-dimethyl-5-methylethy-benzene, 1-(2-butenyl)-2,3-dimethyl-benzene, methylated phenols, (xylenols, trimethyl-phenol), trimethyl-cyclohexene, dimethyl-cyclopentane, and trimethyl-cyclopentene were present (Figure 5.5). Presumably the benzene and phenol originated from the biphenyl but the source of the methyl groups remains to be identified. Possible sources include the solvent IBMK or DME but the source might have been the CO_2 as well. Methylated benzenes and methylated phenols had been observed previously for Ag^o/Fe^o mediated dechlorinations of pentachlorophenol in $scCO_2$ (Kabir and Marshall, 2001).

5.3.4 Extended dechlorination and zero-valent Pd^o/Fe^o column(s) regeneration

To mimic continuous processing, dechlorinations were also applied to soil extracts (containing 6 μg/ml PCB) that were extracted from a PCB contaminated soil using Brij 97 (3%, v/v) and Triton CF54 (3%, v/v) suspensions (Wu and Marshall, 2001). PCB laden surfactant extract, 90 ml, plus 10 ml IBMK was transferred to the pressurized extraction vessel with an HPLC pump. The process of PCB mobilization-dechlorination was conducted (4500 psi, 400 °C) during 30 min. The $scCO_2$ stream was interrupted, the retentate fraction was drained from the extraction vessel and replaced with fresh soil extract plus IBMK (90 + 10 ml) and the mobilization-dechlorination cycle was repeated. The cycles, operated under optimized mobilization-dechlorination conditions, were continued during 5 h by replacing the cleaned aqueous suspension each 30 min. The dechlorination yield remained virtually quantitative over the course of the extended trial and the PCB content that remained with the aqueous retentate was less than 0.1 μg/ml for 30 min of processing. Thus, neither the organic matter that was mobilized from the soil

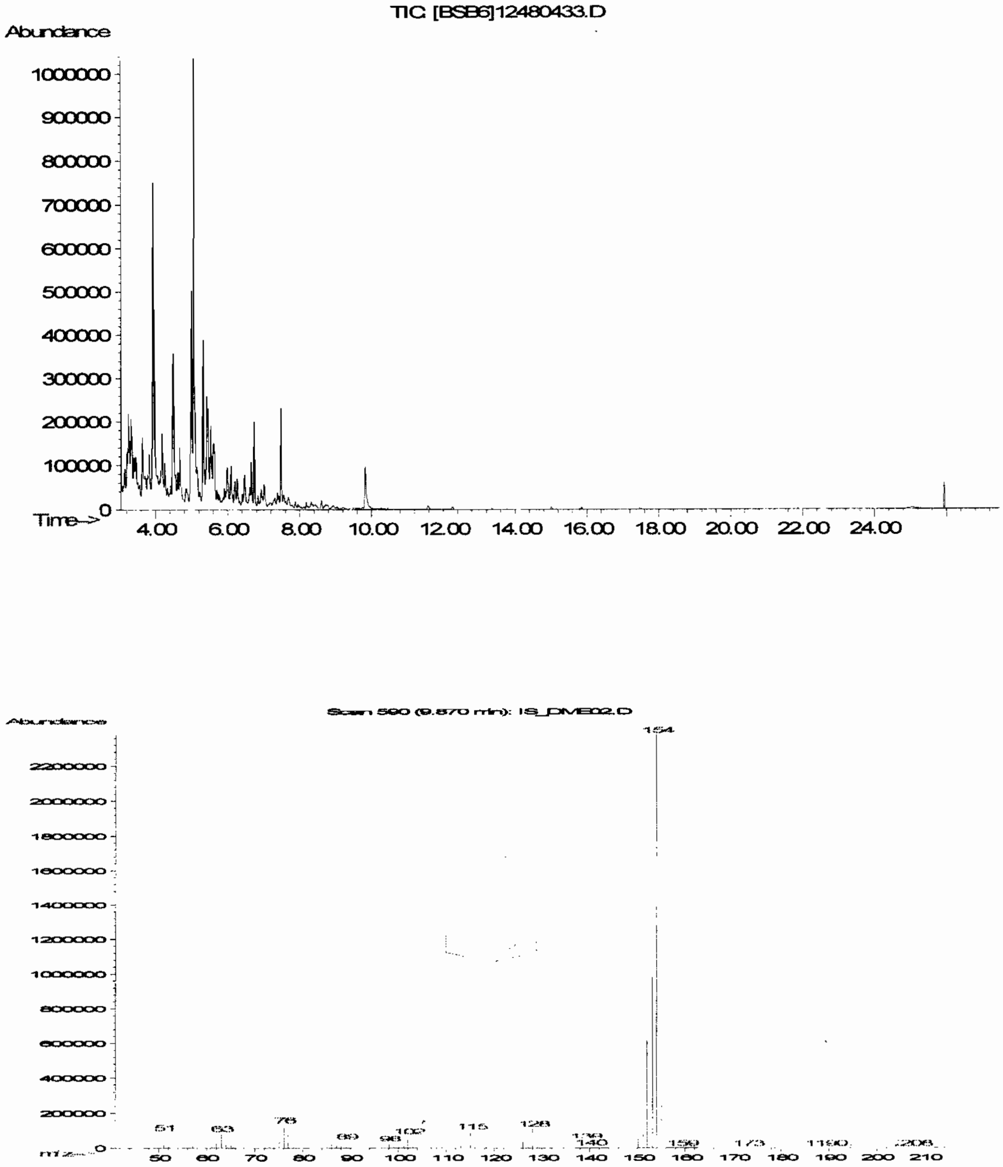

Figure 5.5 GC-MS chromatograms of dechlorination yield of soil extracts. (A) The principle products of dechlorination (1: 4-methyl-2-pentanone; 2: *o*-cresol; 3: 1, 6-dimethylcyclohexene; 4: *m*-xylenol; 5: mesitylene; 6: 4-methylphenol; 7: 2, 6,-dimethylphenol; 8: biphenyl). (B) Mass spectrum of biphenyl, retention time 9.87 min. The dechlorination was performed at 400 °C and 4500 psi with two zero-valent columns of Pd^0/Fe^0 connected in series.

nor the surfactant had any perceptible impact on the dechlorination efficiency. The products that resulted from the dechlorination with soil extract were comparable to those that resulted from the surfactant suspensions.

5.3.5 Regeneration of reactor activity

To accelerate the reduction in dechlorination efficiency with time, that had been observed earlier for PCP dechlorinations (Kabir and Marshall, 2001), the reactor was purposely overloaded by continuously adding excess substrate. PCB substrate [containing Aroclor 1242 or 1248 (10%, *v/v*), acetic anhydride (80%) and DME (10 %)] was merged (at 0.1 ml/min) with $scCO_2$ and delivered continuously to a new column (containing 45 g Pd^o/Fe^o) for 5 h. Repeatabilities for three replicate trials conducted during 5 h were adequate (Table 5.5). The dechlorination efficiency that was observed in successive traps during 15 h of extraction-dechlorination (■ symbol for Aroclor 1242, ▲, ▼,◆ symbols for Aroclor 1248) is illustrated in Figure 5.6. The dechlorination yields decreased with time. The dechlorination efficiency was reduced to 48-59% after 3 h of continued operation and to 34-55% after 5 h of operation. Presumably, catalytic sites on the surface of the Pd^o/Fe^o particles were inactivated by the extended process of dechlorination.

In an attempt to regenerate the Pd^o/Fe^o particle dechlorinating activity three methods were evaluated. The methods included 3 h of *on-line* flushing with $scCO_2$ (■, ▲ Figure 5.6) at elevated temperature (400 °C), flushing *on-line* with 30 ml water-methanol mixture (7+3, ▼, Figure 5.6) at ambient temperature and washing of the column packing *off-line* (◆, Figure 5.6) with 30 ml water. The dechlorination yields indicated that the all three re-activation methods were at least partially effective. The method using 3 h $scCO_2$ flushing *on-line* proved to be the most efficient regeneration method, followed by the *on-line* water-methanol flushing procedure. There was no apparent advantage to removing the packing and re-packing the reactor column with cleaned material.

In summary, the PCBs from surfactant suspension or polluted soil extract were mobilized virtually quantitatively and dechlorinated *on-line*. The combination of PCB mobilization into $scCO_2$ with *on-line* dechlorination was an efficient process for longer processing times, that can be applied to the PCB-containing surfactant slurry. The processing time required to achieve any desired level of cleaning can be predicted accurately. Differences

Table 5.5 Decreases in dechlorination yields with extended processing.

Time	Aroclor 1242 Flushing with $scCO_2$ for 3 h at 5 h interval	Aroclor 1248 Flushing with $scCO_2$ for 3 h at 5 h interval	Aroclor 1248 Flushing with 30 ml water-EOH (7+3) at 5 h interval	Aroclor 1248 Washing with 30 ml water at 5 h interval
30	91.9 ± 2[a]	68.0 ± 5	64.4 ± 2	55.8 ± 6
60	84.8 ± 9	68.0 ± 5	62.3 ± 2	55.4 ± 6
90	84.4 ± 9	62.5 ± 1	61.2 ± 1	54.1 ± 5
120	83.4 ± 9	62.5 ± 1	60.8 ± 2	52 ± 7
150	81.1 ± 10	61.4 ± 1	57.6 ± 2	51.1 ± 5
180	78.5 ± 9	58.8 ± 5	56.8 ± 3	48.2 ± 5
210	75.2 ± 4	57.1 ± 5	53.3 ± 1	39.6 ± 12
240	74.9 ± 4	56 ± 5	51.8 ± 1	39 ± 11
270	72.9 ± 4	56.6 ± 5	48.2 ± 5	35.2 ± 13
300	71.4 ± 4	54.7 ± 5	48.6 ± 3	34.6 ± 12

[a] :Mean ± 1 SD based on three replicate determination.

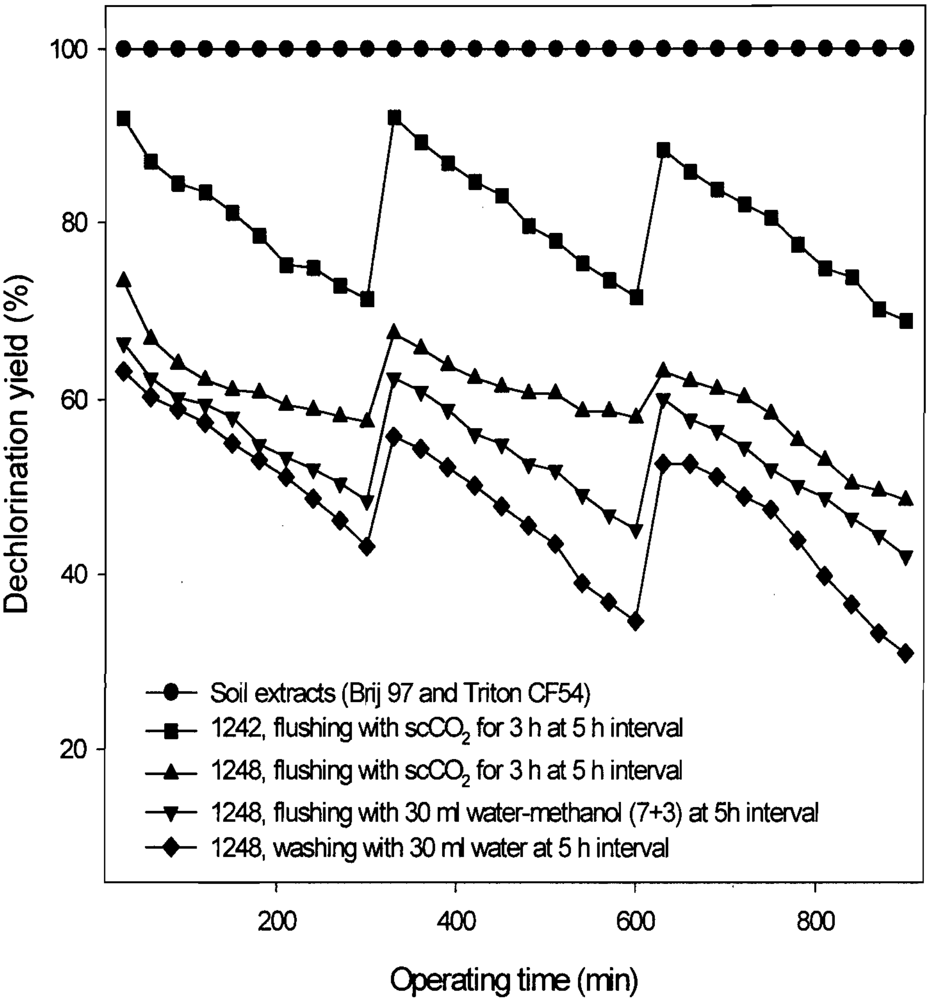

Figure 5.6 Changes, with time, in dechlorination efficiencies of Aroclor 1242 soil extract (●), Aroclor 1242 solution [10% (v/v) ■] or 10% (v/v) Aroclor 1248 (▲,▼,◆) observed in cumulative 30-min traps pre- and post reactivation. At 5 h intervals, the reactor column was washed on line for 3 h at 400 °C with $scCO_2$ (▲),or at ambient temperature with 30 ml water-methanol (7+3) (▼) or the packing was washed with water (30 ml, ◆).

in behaviour between the two surfactants were not evident. The advantage of this approach is that the PCBs can be detoxified rapidly and efficiently and the cleaned surfactant suspension can be returned to the contaminated soil to extract more PCB (contaminants). The disadvantage of the method is that an appreciable portion of the commercial surfactant formulation was mobilized into the $scCO_2$ during processing. The challenge remains to identify $scCO_2$ insoluble surfactant formulations that mobilize the PCBs more rapidly from the aqueous phase.

Chapter 6
Preface

These studies have investigated/optimized a method for PCB determination within contaminated soil/sediments; established novel approaches/techniques for PCB dechlorination with zero-valent metals or bimetallic mixtures; optimized a method for PCB washing/flushing from contaminated soil. Soil washing/flushing was combined with supercritical carbon dioxide ($scCO_2$) mobilization - dechlorination *on-line* using zero-valent metals. The studies have demonstrated that PCB can be dechlorinated efficiently by heated columns of zero-valent metal or bimetallic mixtures. PCBs *can be* flushed efficiently from polluted soils into surfactant suspension and then back-extracted into supercritical CO_2. Finally, the toxicants were dechlorinated virtually quantitatively in a continuous *on-line* process using heated columns of zero-valent bimetallic mixtures. A general conclusion and summary is generated in Chapter six.

Summary and conclusion

6.1 Summary

PCB properties, historical usage patterns, impact on the environment and techniques for their destruction as well as possible treatment for the remediation of contaminated matrices were reviewed in Chapter one. Novel approaches/techniques combining $scCO_2$ with zero-valent metal/bimetallic particles for PCB extraction/mobilization and dechlorination were proposed.

In Chapter two, a new method for the dechlorination of PCB commercial mixtures (Aroclor formulations) to biphenyl was extended to soils. The contaminated sample was mixed with magnesium flakes, potassium hexachloropalladiate (K_2PdCl_6), propan-2-ol and water then permitted to react for up to six hours. Biphenyl, recovered by extraction into hexane, was quantified by gas chromatography with flame ionization detection. The reaction was very efficient in propan-2-ol/water, surfactant emulsion or sand mixture and virtually complete in soil provided that excess magnesium and the K_2PdCl_6 were added to the sample prior to the addition of water. High PCB loadings were readily determined in the field contaminated soils either by direct determination within the matrix or by standard additions. However, analyte concentrations were appreciably over-estimated in Soxhlet or sonication extracts of a certified reference material that contained sub-ppm levels (0.34 mg/kg) of analyte. The over-estimation was considered to result from the conversion, in part, of natural organic matter to biphenyl. The direct derivatization within the sample matrix can be used to estimate the PCB concentration for soil/sediments and contaminated solution suspensions. The concentrations of PCBs in two of the three reference materials (27.2 and 472.5 mg/kg) were determined successfully. The principle advantages of this procedure included convenience and simplicity but the principle disadvantage was that organic matter can also contribute to the apparent analyte recovery and had to be accounted for in accurate determinations. The method of standard additions provided reliable estimate level at sub ppm concentrations. The Aroclor 1260 model can be used to estimate the PCB concentration in contaminated soil/sediments samples.

An approach that can dechlorinate PCB mixtures (Aroclor 1242 and 1248) efficiently with heated columns of zero-valent metal or bimetallic mixture in a continuous process has been developed (Chapter 3). Supercritical carbon dioxide ($scCO_2$) transferred the substrates through the reactor and cumulative ten minute fractions of eluate were trapped in hexane during 1 h of continued operation. The extent of dechlorination were influenced appreciably by the identity of the zero-valent metal ($Fe^0 > Ni^0 > Zn^0 > Cu^0$), by the temperature (400>>300 > 200 °C) and pressure (≤ 4,500 psi) within the reactor column(s) and especially by the composition of the feedstock. Although water was both unnecessary and detrimental to the dechlorination yields, the inclusion of methyl ketone(s) in the feedstock solution improved the extent of dechlorination appreciably. Two columns (25 x 1 cm) of Ag^0/Fe^0 or Ag^0/Ni^0 bimetallic mixture resulted in a virtually quantitative dechlorination of substrate Aroclor 1242 (~28 mg/min). Moreover, during 1 h of continued operation, dechlorinations were very repeatable. In preliminary treatments of 30% (v/v) acetone-hexane extract (~600 µg/ml PCBs) of a spiked sandy loam soil, no chlorinated organics could be detected in the PCB eluting region by GC-MS. It has been demonstrated that zero-valent metal meditated reactions of Aroclor, mixtures at elevated temperature in $scCO_2$, provided an efficient technique for PCB detoxification by dechlorination. The quantities of 1242 or 1248 substrate that were dechlorinated efficiently (but not quantitatively) are considered to far exceed the burdens in concentrated extracts that could be isolated from polluted environmental matrices.

An approach/technique for the remediation of PCB contaminated soil was evaluated in Chapter four. A soil that had been historically contaminated with Aroclor 1242, 1248, 1254 and 1260 was decontaminated by two surfactant-meditated cleaning procedures that had been chosen to mimic *ex-situ* soil washing and *in-situ* soil flushing processes. A preliminary screening selected four surfactants (from among 17 commercial formulations) for their ability to mobilize PCBs from the soil while suffering minimal losses to the supercritical carbon dioxide mobile phase. The mobilization was enhanced with minimal foam formation by the presence of 17% (v/v) IBMK in the surfactant suspension. Each of the four surfactants, at 1, 3 or 5% (v/v) concentration, was evaluated by fifteen successive 10-min sonication-filtrations and continuous soil column flushing during 20 h. Filtrates from each sonication-filtration step and samples taken at hourly intervals from column eluate were analyzed for PCB and surfactant content. Both extraction procedures mobilized PCBs efficiently when extended for longer periods and were modelled accurately as the sum of a constant and single-term exponential increase to a maximum. The predicted number of replicate stages required to mobilize 50% of the toxicants varied from 7 to 3 cycles for sonication-washings of the soil or from 6.8 to 2.8 h for column flushing and decreased as the concentration of surfactant in the aqueous phase was increased. The combined PCB-laden aqueous suspensions could then be back-extracted with $scCO_2$ and the eluate could be dechlorinated quantitatively as it traversed a short, heated, column of silver-iron bimetallic mixture.

In Chapter 4, PCBs were mobilized from contaminated soil suspension by back-extraction with $scCO_2$ during 30 min at 50 °C. The results indicated that >99% of PCB were mobilized from the soil extracts and 23-78% of surfactant remained in the aqueous suspension post treatment. The cleaned surfactant suspension could then have been reused to mobilize more PCB from the contaminated soil. Based on the PCB extraction efficiencies, the suitability of surfactants for either soil sonication-washing or column flushing treatments were in the order: Triton DF16 >Triton CF54 >Brij 97 > Tween 85 whereas increased surfactant losses were in the order: Tween 85 < Brij 97< Triton CF54< Triton DF16.

There were no apparent differences in the avidity with which separate fractions of the total PCB burden interacted with the soil. Although three of the surfactant formulations did not change the physical properties of the soil, one formulation was observed to disperse the soil aggregates appreciably and required increased pressure to force the aqueous phase through the soil. Nonetheless, large volumes of surfactant suspension were required to mobilize the PCBs efficiently. The challenge remains to improve the efficiency of this stage of the overall process. The PCBs in the cumulative aqueous extracts were back-extracted efficiently (>99%) into $scCO_2$-IBMK. Losses of surfactant during this stage were appreciable but the dechlorination was quantitative.

A set of models for PCB mobilization from surfactant suspensions with $scCO_2$ has been established and the feasibility to both clean surfactant suspension and to regenerate zero-valent metals/bimetallic particles was re-investigated in Chapter 5. Mobilization efficiencies as a function of time of extraction were predicted accurately using the models for PCB mobilization for a given PCB burden. The mobilization time ranged from 102 to 179 min when mobilizing PCB (1000-10,000 μl/ml) from Brij 97 suspension to "non-hazardous" concentration (≤ 0.1 μg/ml).

The dechlorination yields for various PCB concentrations (0.1–1.0%, v/v) ranged from 99.7–72.4% in Brij 97 suspensions and 99.8-73.8% in Triton CF54 suspensions when the outlet stream of mobilized PCBs was directed to two heated zero-valent columns connected in series. In an alternate interfacing scheme, the outlet stream of mobilized PCB from the extraction vessel was channeled to a second extraction vessel containing 20 ml mixed solvent (acetic anhydride, DME, IBMK, 8+1+1) prior to entry into the reactor columns. The dechlorination efficiency for this interface increased appreciably when compared with the direct coupling. The dechlorination yields ranged from 100 – 90.5% and 100-93.6% respectively for Aroclor 1248 concentrations between 0.1 and 1.0% (v/v) in Brij 97 and Triton CF54 suspensions. The surfactants remaining with the aqueous phase was 14.3 ± 0.2 % for Brij 97 suspension and 15.7 ± 0.2% for Triton CF54 suspension with a 3% (v/v) initial concentration post mobilization/dechlorination processing. Preliminary analyses of HPLC and FTIR of the properties of the residual surfactant in the aqueous retentate did not detect any changes other than the decrease in surfactant concentration. These observations suggested that the treated surfactant suspensions could be recycled to extract more PCBs (pollutants) from the contaminated soil.

During 5 h of continued dechlorination of influent from surfactant suspension that contained 10 % (v/v) Aroclor 1242 or 1248, the dechlorination efficiency decreased gradually with time. Three approaches were evaluated to regenerate the reactivity of Pd^0/Fe^0 reactor column including (*i.*) 3 h *on-line* flushing with $scCO_2$ at elevated temperature (400 °C), (*ii.*) *on-line* flushing with 30 ml water-methanol mixture (7+3) at ambient temperature and (*iii.*) washing of the particles with 30 ml water. The recovery of dechlorinating capacity by the three approaches indicated that 3 h $scCO_2$ flushing *on-line* was the most efficient. The average dechlorination yield was 81.7 ± 3% for Aroclor 1242 and 61.4 ± 5% for Aroclor 1248. The *off-line* water wash was characterized by the lowest regeneration capacity. The average dechlorination yield was 56.5 ± 2% for Aroclor 1248 at 5 h continuous operation. The regeneration power produced by *on-line* water-methanol flushing treatment was intermediary between other two treatments and the dechlorination yield was 45 ± 9% for Aroclor 1248 after 5 h of continued operation.

It has been demonstrated that the PCB-surfactant suspension or soil extract can be freed of PCB residues by back-extraction with $scCO_2$. The $scCO_2$ stream can then be dechlorinated quantitatively. The combination of PCB mobilization-*on-line* dechlorination with $scCO_2$ is an efficient process that can be applied to the PCB-containing slurry. The optimal processing time can be predicted accurately. The advantage of this approach is that the PCB in the surfactant suspension can be detoxified in a rapid and efficient manner and the remaining surfactant suspension can be reused to extract more PCB contaminants. The disadvantage is that an appreciable fraction of the surfactant is also lost during the back-extraction stage.

6.2 Conclusions

These studies have identified novel approaches for the detoxification by dechlorination of polychlorinated biphenyl (PCB) compounds and have optimized techniques for the remediation of PCB contaminated soils.

1. A rapid, quantitative analytical method to determine the total PCB concentrations in contaminated soil/sediment by conversion of PCB residues to biphenyl has been developed and validated.
2. A novel technique to efficiently detoxify PCBs and PCB contaminated materials by dechlorination with zero-valent metal/bimetallic particles in $scCO_2$ has been investigated systematically. The results have demonstrated potential applications in industry for PCB detoxification and for environmental remediation.

3. A continuous process that combines PCB mobilization from historically contaminated soil into surfactant suspension followed by back-extraction of the PCBs in supercritical carbon dioxide with *on-line* dechlorination was demonstrated to a be practical approach that enabled the polluted soil to be decontaminated in an economical and environmental friendly way.
4. A set of models for PCB mobilization into surfactant suspensions was established. These models can be used to predict rates of PCB transfer from the soil into surfactant suspension as well as the rates of the subsequent cleaning stages with $scCO_2$.

6.3 Contribution to the original research

1. A novel method for total PCB determination by conversion to biphenyl within contaminated soils was developed and validated. This technique has been demonstrated to be rapid and easily conducted. This technique can be applied in polluted soils and sediments.
2. This study has elaborated a successful process that can be used to remediate/restore soils that has been contaminated with excesses of polychlorinated biphenyl (PCB) compounds. A rapid technique has been developed to detoxify PCB compounds to biphenyl in a continuous process that can dechlorinate some 28 mg of PCB mixture per minute using a short heated column of zero-valent bimetallic mixture of iron doped with either silver or palladium. This loading of chlorinated substrate(s) far exceeds the quantities that might be extracted from a highly polluted matrix such as soil or sediment.
3. Extraction with supercritical carbon dioxide combining PCB back-extraction from aqueous surfactant suspension(s) with optimized on-line dechlorination using zero-valent bimetallic mixture is a novel contribution. The commercial surfactants were screened and promising candidates were selected based on their ability to promote the extraction from surfactant suspension(s). This approach can be used not only on PCB extraction from polluted soils, PCB mobilization and on-line dechlorination, but also can be applied to other matrices that have been contaminated with halogenated compounds.
4. Mathematical modeling of the process of supercritical carbon dioxide extraction combined with PCB back-extraction from aqueous surfactant suspension(s) and with on-line dechlorination using zero-valent bimetallic mixture is a novel contribution. The

models established for PCB mobilization both from contaminated soils/sedimens and from surfactant suspension(s) have a great potential application in the environmental industry.

6.4 Suggestion for further studies

1. The mechanisms of PCB dechlorination using zero-valent metal/bimetallic particles in $scCO_2$ need to be investigate in greater detail. Preliminary studies have indicated that the solvent compositions in the substrate have an appreciable effect on the dechlorination efficiency. Different products of dechlorination were observed during the processes when using various solvent substrate. Although the substrate of [PCB (2-20%, v/v), solvent (10-70%, v/v, acetic anhydride, ethanol, methanol or 2-methyl-propanon), DME (10%, v/v)] demonstrated higher dechlorination efficiency, the solvent function and the source of H^+ still remains to be identified.
2. The by-products of the dechlorination should be monitered carefully under the experimental conditions. Specifically, chlorinated dibenzo-furan and chlorinated dibenzo-*p*-dioxin should be determined post the processing.
3. The technique of interfacing the PCB-laden $scCO_2$ stream with the dechlorination reactor requires further investigation and optimization. The dechlorination efficiency of extractor effluent was increased appreciably when channeled to a vessel containing suitable solvent or co-solvent(s). The technique of dechlorination with zero-valent bimetallic particles might be extend to other organic contaminants in soil using optimized processing conditions.
4. Further investigations need to be carried out to identify other surfactant formulations that are capable of transferring PCBs from soil into suspension more efficiently but that remain insoluble in the $scCO_2$-IBMK mobile phase.

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