

# Optimizing Solvent Extraction of PCBs from Soil

by

Maureen O'Connell

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

**Master of Applied Science**

in

**Civil Engineering**

Waterloo, Ontario, Canada, 2009

© Maureen O'Connell 2009

## **AUTHOR'S DECLARATION**

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

## Abstract

Polychlorinated biphenyls (PCBs) are carcinogenic persistent contaminants. Although their manufacturing in North America ceased in the late 1970s, their high heat resistance made their use widespread over their production lifetime. As a result, PCB contamination has occurred globally and in particular has plague brownfield redevelopment in urban environments. The remediation of PCB contaminated soil or sediments has historically been dealt with through the expensive and unsustainable practice of excavation followed by off-site disposal or incineration. One potential technology that has shown some success with on-site remediation of PCB contamination is solvent extraction. Solvent extraction is technically simple; it involves excavating the contaminated soil, placing it in a vessel and adding solvent. The PCBs are extracted by the solvent and the treated soil is returned for use on site. Although successful at removing a large quantity of PCBs from some soils, this technology can be improved upon by extracting additional PCB mass and making the extraction more efficient and suitable for colder climates.

This thesis aimed to identify the factors controlling PCB extraction with solvents in order to optimize PCB extraction as it is applied on different soil types and in various climates. The research investigated the impact of elevated moisture contents ( $\leq 20\%$  by weight) on solvent extraction efficiency, the effects of low temperatures ( $<5^{\circ}\text{C}$ ) on solvent extraction, and developed a kinetic model to represent PCB solvent extraction. As past research has shown, weathered PCB in soil is more difficult to remove. Contaminated field samples from Southern Ontario, Canada were used for this work, rather than synthetically prepared samples.

The impact of elevated moisture contents and low temperature on extraction efficiency was determined through a series of screening experiments using polar and non-polar solvents at both  $20^{\circ}\text{C}$  and  $4^{\circ}\text{C}$ . It was hypothesized that improved extractions may be possible with combinations of polar and non-polar solvents. Based on the results of these screening experiments, a factorial experiment was designed using solvent combinations to further assess the role of moisture contents and low temperatures. The role of PCB mass distribution among grain sizes was also evaluated to see if optimization based on grain size separation is possible. Finally, experiments were performed to generate data suitable for the development of a kinetic model that incorporates key factors affecting solvent extraction.

Four suitable solvents for solvent extraction in Ontario were identified through a literature review and these were used for this work: isopropyl alcohol (polar), ethanol (polar), triethylamine (non-polar) and isooctane (non-polar). Triethylamine outperformed isooctane and performed best on its own rather than in combination with polar solvents. An interaction between soil moisture content and choice of polar solvent (isopropyl alcohol versus ethanol) was established: a given polar solvent achieves optimal PCB extraction at a specific moisture content range. Temperature was also identified as significantly influencing PCB extraction. Although it was determined that PCBs were distributed unevenly amongst grain sizes, a simple relationship between grain size and fractional organic carbon or organic content was not found.

A simple two-compartment kinetic model was developed which is suitable for predicting the PCB concentrations extracted up to 24 hours. The model incorporates both temperature and soil to solvent ratio in order to estimate PCB concentration extracted.

## **Acknowledgements**

I would like to thank Dr. Neil Thomson for providing me with this learning opportunity, for his determination to see this project through despite the many obstacles encountered, and for demanding I continue to improve my data interpretation and writing. Thank you to the Ontario Centers of Excellence for providing project funding and to Dr. Eric Reiner and Tony Chen from the Ontario Ministry of the Environment for taking the time to show me how they do PCB analysis and answering countless questions.

I would also like to thank the numerous co-op students who have helped me in the lab: Christina Bright, Harry Oh, David Thompson, Tanyakarn Treeratanaphitak, Daniel Princz and finally Victoria Chennette. I enjoyed working with all of you! I would like to thank Mark Sobon and Bruce Stickney for providing invaluable lab support.

Thank you to my family and friends for their support throughout this degree, especially Bill O'Connell and Jessica Pickel for proof reading draft thesis chapters. Finally, I would like to thank my husband Jonathan Musser for his patience, encouragement, friendship and love.

## **Dedication**

I would like to dedicate my thesis to my late grandmother Betty O'Connell.

# Table of Contents

List of Figures .....	x
List of Tables .....	xii
Chapter 1 Introduction.....	1
1.1 Research Objectives .....	4
1.2 Thesis Scope.....	4
Chapter 2 Background and Literature Review .....	5
2.1 Chemical Structure of PCBs.....	5
2.2 PCB Properties .....	5
2.3 Current Remedial Strategies.....	6
2.3.1 <i>In-Situ</i> .....	6
2.3.2 <i>Ex-Situ</i> .....	7
2.4 Solvent Extraction Systems.....	9
2.4.1 CF-Systems .....	9
2.4.2 B.E.S.T .....	10
2.4.3 Carver-Greenfield Process.....	11
2.4.4 Extraksol Process.....	12
2.4.5 Terra-Kleen .....	13
2.5 Factors Influencing Solvent Selection.....	13
2.5.1 Solvent Toxicity .....	13
2.5.2 Solvent Polarity .....	14
2.5.3 Solvent Viscosity.....	14
2.5.4 Solvent Freezing Point .....	15

2.5.5 Solvent Boiling Point .....	15
2.5.6 Solvent Cost .....	16
2.5.7 Solvent Selection .....	16
2.6 Properties Controlling PCB Sorption and Desorption.....	17
2.6.1 Soil Composition.....	17
2.6.2 Soil Grain Size.....	19
2.6.3 PCB Composition.....	19
2.6.4 Temperature.....	20
2.7 Modeling Sorption.....	22
2.8 Modeling Desorption.....	24
Chapter 3 Methods & Materials .....	34
3.1 Experimental Design .....	34
3.1.1 Single Solvent Screening Experiments.....	34
3.1.2 Solvent Combination Experiments.....	35
3.1.3 PCB Mass Distribution.....	35
3.1.4 Kinetic Experiments .....	36
3.2 PCB Sample Origin .....	36
3.3 PCB Analysis Procedures.....	37
3.3.1 Soil Extraction Methods .....	37
3.3.2 Analytical Soil Extraction .....	38
3.3.3 Sample Clean-Up.....	38
3.3.4 Gas Chromatograph Analysis.....	39
3.3.5 Comparisons with Accredited Laboratories .....	39
3.4 QA/QC.....	40



Chapter 4 Results and Discussion .....	49
4.1 Mass Balance Considerations .....	49
4.2 Moisture Content Effects on Solvent Extraction .....	50
4.2.1 Polar Solvents: At Room Temperature .....	50
4.2.2 Polar Solvents: At Lower Temperatures .....	51
4.2.3 Non-polar solvents: At Room Temperature .....	52
4.3 Solvent Combination Experiment .....	53
4.3.1 ANOVA Results for 2 <sup>4</sup> Factorial Experiment .....	54
4.4 PCB Mass Distribution .....	54
4.4.1 PCB Mass Distribution in Dixie0707 Soil .....	54
4.4.2 PCB Mass Distribution in Dixie0208 Soil .....	55
4.5 Effects of Moisture Content, Solvent Choice, Temperature and Grain Size on PCB Extraction .....	56
4.6 Kinetic Experiments .....	57
Chapter 5 Conclusions and Recommendations .....	78
5.1 Conclusions .....	78
5.2 Recommendations .....	79
Bibliography .....	80
Appendix A Ranking Potential Solvents .....	84

## List of Figures

Figure 2.1. Solvent viscosity versus temperature (Lide, 1998).....	32
Figure 2.2. Solvent viscosity versus percent solvent mass (Lide, 1998).....	32
Figure 2.3. Solvent freezing points versus percent solvent mass (Lide, 1998) .....	33
Figure 2.4. PCB mass extracted with ethyl acetate over time (Valentin, 2000).....	33
Figure 3.1. (a) Images of ethanol and isooctane reactors following 24hr extraction, (b) Image of reactors used to determine volume of solvent layers (isopropyl alcohol and isooctane at 20% moisture content).....	47
Figure 3.2. Grain Size Analysis of (a) Dixie0707 Soil and (b) Dixie0208 Soil .....	48
Figure 4.1. (a) PCB concentration removed using isopropyl alcohol at 20°C, (b) PCB concentration remaining in soil having undergone experimental extraction with isopropyl alcohol at 20°C, (c) PCB concentration extracted using isopropyl alcohol at 20°C - repeat, (d) PCB concentration extracted using isopropyl alcohol at 4°C, (e) PCB concentration remaining in soil having undergone experimental extraction with isopropyl alcohol at 4°C.....	67
Figure 4.2. PCB concentration removed using ethanol at 20°C (a) with DCB recovery corrections and (b) without DCB recovery corrections, PCB concentration in soil having undergone experimental extraction with ethanol at 20°C (c) with DCB recovery corrections and (d) without DCB recovery corrections, (e) PCB concentration removed from dry soil using Ethanol at 4°C, (f) PCB concentration remaining in dry soil after extraction with ethanol at 4°C .....	68
Figure 4.3. Percent mass extracted at 20°C with (a) isopropyl alcohol and (b) ethanol.....	69
Figure 4.4. Reactors following isopropyl alcohol extraction at (a) 20°C, (b) 20°C –repeat, (c) 4°C, (d) 4°C - 0% and 5% moisture content reactors only .....	69
Figure 4.5. Ethanol following extraction at (a) 20°C –decanted ethanol, (b) 4°C - reactors .....	70
Figure 4.6. Mean PCB mass removed at 4°C using (a) isopropyl alcohol and (b) ethanol .....	70
Figure 4.7. PCB concentration extracted at 20°C with (a) isooctane and (b) triethylamine, PCB concentration remaining in soil after extraction at 20°C with (c) isooctane and (d) triethylamine .....	71
Figure 4.8. Mean PCB mass removed at 20 °C using (a) isooctane and (b) triethylamine.....	71
Figure 4.9. Reactors after experimental extraction at 20°C with (a) isooctane and (b) triethylamine..	72
Figure 4.10. PCB concentration extracted with decanted solvent data at (a) 20°C and (b) 4°C. PCB concentration remaining in soil following extractions at (c) 20°C and (d) 4°C.....	73
Figure 4.11. Percent PCB mass extracted using sum of soil and solvent data at (a) 20°C and (b) 4°C	74

Figure 4.12. PCB concentration distribution by grain size for (a) Dixie0707, (b) Dixie0208, (c) Dixie0208 – without DCB recovery corrections, (d) Dixie0208 - repeat.....	75
Figure 4.13. Solvent following PCB extraction from grain size groupings with ASE200.....	76
Figure 4.14. PCB contaminated soil sorted by grain size (a) Dixie0208 and (b) Dixie0707 .....	76
Figure 4.15. (a) Percent organic content by weight for different grain sizes, (b) Percent fractional organic carbon by weight for different grain sizes .....	76
Figure 4.16. PCB Extraction over time using a (a) 1g:1mL soil to solvent ratio at 20°C, (b) 1g:0.75mL soil to solvent ratio at 20°C, and (c) 1g:1mL soil to solvent ratio at 4°C .....	77

## List of Tables

Table 2.1. Composition of PCB Isomer Groups from Erickson (Erickson, 1993).....	27
Table 2.2. Examples of PCB octanol-water partition coefficients (Hawker and Connell, 1988) .....	27
Table 2.3. Dielectric Constants (Lide, 1998).....	28
Table 2.4. Freezing and Boiling Points of Alcohols (Streitwieser et al., 1992) .....	29
Table 2.5. Freezing and Boiling Points of Non-Alcohols .....	29
Table 2.6. Pure Solvent and Azeotrope Boiling Points .....	30
Table 2.7. VWR Solvent Prices.....	31
Table 2.8. Glass Transition Temperatures.....	31
Table 3.1. Grain Sizes Assessed for PCB Mass Distribution .....	42
Table 3.2. Kinetic Experiment Design .....	42
Table 3.3. EPA Methods Considered for PCB Extraction for Quantification Purposes .....	43
Table 3.4. Comparisons between analytical soil extraction methods.....	44
Table 3.5. Gas Chromatograph Settings (Adapted from EPA Method 8082 Table 2).....	44
Table 3.6. PCB Concentrations in Soil Reported by Various Laboratories .....	45
Table 3.7. PCB Concentrations in Hexane Reported by Accredited Laboratories.....	45
Table 3.8. DCB Recovery for each experiment.....	46
Table 4.1. Comparison between PCB mass in controls and sum of PCB mass experimentally extracted and PCB mass remaining in soil following experimental extraction. ....	60
Table 4.2. Results from solvent extractions with polar solvents. ....	61
Table 4.3. Results from solvent extraction with non-polar solvents at 20°C.....	62
Table 4.4. ANOVA Table for decanted solvent data treated as 2 <sup>4</sup> Factorial Experiment. ....	63
Table 4.5. ANOVA Table for percent mass removed data treated as 2 <sup>4</sup> Factorial Experiment. ....	64
Table 4.6. Grain Size range where highest PCB mass resides. ....	65
Table 4.7 Kinetic Experiment Results.....	66
Table A.1. Ranking scheme for potential polar solvents.....	84
Table A.2. Ranking scheme for potential non-polar solvents .....	84

# Chapter 1

## Introduction

Polychlorinated biphenyls (PCBs) were developed in 1881 and were first industrially manufactured in 1929 (Hurst, 1987; Hutzinger et al., 1974). The earliest record of their conception was in a paper by Schmidt and Schultz (Waid, 1986). PCBs were introduced to replace mineral oil as a dielectric fluid because of the fire risk associated with mineral oil (Hurst, 1987). They were used in capacitors, transformers, industrial fluids for hydraulic systems and gas turbines, fire retardants, adhesives, textiles, printing ink, carbonless copy-paper, wood sealants, plasticizers, caulking, paint, petroleum additives and asphalt (Ackerman et al., 1983; Hurst, 1987; Hutzinger et al., 1974; Jakher et al., 2007; Strachan, 1988; Waid, 1986). The extensive use and numerous applications of PCBs resulted in their widespread distribution (Ackerman et al., 1983).

Monsanto, today a large agricultural company, was the only North American PCB manufacturer and was located in the United States. Monsanto manufactured over half of the world's PCBs (Strachan, 1988): approximately 57 million tonnes (Agarwal et al., 2007). It is estimated that 40,000 tonnes of Monsanto-produced PCBs were imported into Canada (Hurst, 1987; Strachan, 1988), and as of 1987 approximately 16,000 tonnes had entered the Canadian environment (Hurst, 1987). Approximately 83% of the total Canadian PCB imports as of 1974 were for the manufacture of transformers and capacitors (Strachan, 1988). The total quantity imported more than doubled between 1974 and 1977 (Strachan, 1988).

Monsanto's PCBs were manufactured under the trade name Aroclor. The Aroclor mixtures were labeled with a four digit number, the first two digits indicated its molecular structure type while the last two digits indicated the chlorine content by percent weight. The prefix 12 was used to classify PCBs, while 25 or 44 indicated blends of polychlorinated terphenyls (PCTs) with PCBs (Waid, 1986). As of 1970, Aroclor 1254 had been manufactured in the largest quantity, with approximately 22,700 tonnes having been produced (Waid, 1986). Globally, other major PCB manufacturers included: Clophen in Bayer, West Germany, Phenoclor in Caffaro, Italy, Kanechlor in Kanegafuchi, Japan, Pyralene in Prodelec, France, and Sovol in the former U.S.S.R (Waid, 1986).

As a result of international PCB manufacture and use, PCB contamination is now global with PCBs having been detected in open ocean water, as well as air and marine organisms (Waid, 1986). Certain congeners bioaccumulate more than others in wildlife and some congeners are successfully

metabolized. These two attributes result in PCBs in tissue or fat samples differing from Aroclor standards, and PCB signatures differing between species (Crine, 1988). PCBs have been found in fish and birds across Canada, including the Great Blue Heron in Vancouver, the Herring Gull in Lake Ontario, and the Atlantic Puffin in the Bay of Fundy (Crine, 1988).

PCB contamination is a concern in Ontario. The 1975 task force formed under the Environmental Contaminants Act found that gulls eggs from Lake Ontario had approximately three to four times higher PCB residues than the other Great Lakes (Strachan, 1988). Furthermore, the Ontario human population exceeded the national mean PCB concentration (0.91 µg/g) in adipose tissue by 18% (Strachan, 1988). It was estimated that 39% of the total quantity of PCBs in Canada was in Ontario (Hurst, 1987), and the highest concentration of PCBs were found in industrialized urban areas (Ackerman et al., 1983).

The investigation into the presence of PCBs in the environment accompanied the acknowledgement of the negative health effects they caused. Monsanto voluntarily restricted PCB sales in 1972 to the manufacture of electrical transformers and capacitors because of increased public awareness of their hazards (Ackerman et al., 1983). This followed an incident in 1968 in Yusho, Japan which received the attention of international governments and industry: PCBs in a heat exchanger had leaked, poisoning food supplies (Hurst, 1987; Waid, 1986). Victims suffered from such symptoms as chloracne, joint pain and swelling, gum and nail bed discoloration, and lethargy (Waid, 1986).

In addition to the acute symptoms, a wide range of chronic effects have been reported in part because PCBs bioaccumulate and biomagnify (Ackerman et al., 1983). PCBs can act as endocrine disrupting compounds (Lassere et al., 2008), and may have estrogenic or antiestrogenic effects (National Research Council, 2001). They are associated with lower birth weights and shorter pregnancies (Agarwal et al., 2007), compromise the immune system (National Research Council, 2001) and are commonly known to be carcinogenic. These as well as other negative health effects have created a strong need to restrict human exposure to PCBs by removing them from the environment.

Modifications to the Toxic Substances Control Act (TSCA) in the United States forced the U.S. Environmental Protection Agency (EPA) to control PCB disposal and manufacturing (Ackerman et al., 1983). PCB production at Monsanto ceased in 1977 before the ban date of July 2 1979 imposed by the TSCA (Ackerman et al., 1983).

Also in 1977, PCBs became regulated in Canada (Strachan, 1988). A task force was constructed in 1975 under the Environmental Contaminants Act. Their 1976 report proposed a regulation restricting PCB importations, manufacture, and use to PCBs containing two or less chlorine atoms or those with greater than two chlorine atoms for use as a dielectric fluid in transformers and power capacitors, and for use in heat transfer and used hydraulic equipment (Strachan, 1988). Chlorobiphenyl Regulations No. 1 resulted and was implemented under the Environmental Contaminants Act in 1978 (Hurst, 1987; Strachan, 1988). A revision in 1980 (Chlorobiphenyl Regulations No. 1 Amendment) forbid the use of PCBs in all new products and forbid its use for servicing existing electrical equipment (Hurst, 1987; Strachan, 1988). The Chlorobiphenyl Regulations No.2 and No.3 were introduced in 1985 (Hurst, 1987). PCBs are also regulated nationally under the Transportation of Dangerous Goods Act (TDGA).

“PCB Regulations SOR/2008-273” came into effect September 5, 2008 and replaced the Chlorobiphenyl Regulations (2008). This regulation is aimed at protecting both human health and the environment by providing more restrictions on the PCB use and storage. Some equipment containing PCBs must now be out of commission by the end of 2009.

In the province of Ontario, PCBs are currently regulated under Ontario Regulation 347: General-Waste Management, Ontario Regulation 362: Waste Management – PCB’s (Ontario Government, 1990b), and Ontario Regulation 352: Mobile PCB Destruction (Ontario Government, 1990a). The Ontario regulations define PCB waste as materials exceeding 50 ppm and require that Certificates of Approval or Director’s Instructions be obtained prior to any hauling, storage or remediation of PCB materials. PCB limits for what the Ontario Ministry of Environment describes as a full-depth generic site in the Soil, Ground Water and Sediment Standards are 25 ug/g for industrial/commercial land and 5 ug/g for residential land in (Ontario Ministry of the Environment, 2004).

Polychlorinated biphenyls are regulated internationally by the Stockholm Convention which was adopted in May 2001 (United Nations Environment Programme, 2008). Included in the requirements of the Convention is that all parties prohibit and/or take legal action against the production and import of persistent organic pollutants, including PCBs (United Nations Environment Programme).

PCBs are challenging organic pollutants when remediating a contaminated site. Although there are a few options for their remediation, none achieve complete PCB removal or destruction apart from the unsustainable practice of incinerating or landfilling the contaminated soil. Solvent extraction has

achieved extraction efficiencies as high as 99% (Meckes et al., 1997); however, successful extraction is dependent on a number of factors that have made this technology uncertain. There is a need to optimize PCB solvent extraction to improve contaminated site cleanup and to be able to predict PCB extraction efficiency.

## **1.1 Research Objectives**

The research objectives of this thesis are to:

- 1) Investigate the impact of elevated moisture content on solvent extraction efficiency
- 2) Investigate solvent extraction efficiency at low temperatures ( $<5^{\circ}\text{C}$ )
- 3) Develop a kinetic model to represent PCB solvent extraction

These research objectives were undertaken to improve PCB remediation options within the province of Ontario.

## **1.2 Thesis Scope**

The research objectives were met through laboratory studies conducted at the University of Waterloo using bench-scale reactors. Only contaminated soil from one location in Southern Ontario was used for all studies to allow for direct comparisons between experiments.

The thesis that follows provides background to PCB remediation options, factors influencing solvent extraction and PCB sorption and desorption (Chapter 2). Chapter 3 provides the methodology for the experiments conducted and the results are presented in Chapter 4. Finally conclusions and recommendations are provided in Chapter 5.



## Chapter 2

### Background and Literature Review

#### 2.1 Chemical Structure of PCBs

Prior to addressing remediation of polychlorinated biphenyl (PCB) contaminated soil, it is essential to have an understanding of what PCBs are. Polychlorinated biphenyls are chlorinated aromatic compounds of which there are 209 theoretically possible congeners (Dhol, 2005; Hurst, 1987; Hutzinger et al., 1974), and over 100 of these PCB congeners have been recognized in the natural environment (Strachan, 1988). All congeners consist strictly of carbon, hydrogen and chlorine (Hurst, 1987), and all have biphenyl as their fundamental structural unit (Waid, 1986). Specifically the chemical structure is  $C_{12}H_{(10-n)}Cl_n$  where  $n$  ranges from 1 to 10 results in ten PCB isomer groups (Table 2.1) (Crine, 1988; Dhol, 2005). The number of isomers in each group ranges from 1 to 46, with the most isomers being in pentachlorobiphenyl ( $C_{12}H_5Cl_5$ ).

#### 2.2 PCB Properties

PCBs are hydrophobic (Korte et al., 2002), nonpolar (Jakher et al., 2007) and generally stable (Strachan, 1988). It is this combination of properties that makes them persistent organic pollutants. PCBs are more dense than water (Hurst, 1987), and their densities increase with increasing chlorine content up to 1.8 g/mL (Crine, 1988).

Their water solubility decreases with increasing chlorine content (Hutzinger et al., 1974; Jakher et al., 2007), ranging from 0.007 ppm for octachlorobiphenyl to 6 ppm for monochlorobiphenyl (Waid, 1986). PCBs have a low volatility due to their low vapour pressures, which decrease with increasing chlorine content (Hurst, 1987; Waid, 1986). Vaporization rates are 0.00174 g/cm<sup>2</sup>/hr or less (Waid, 1986). In addition, PCBs have excellent heat resistance and nonflammability properties which contributed to their appeal (Waid, 1986).

PCB sorption increases with increasing chlorine content and increases linearly with increasing surface area of the adsorbents (Waid, 1986). PCB sorption onto soil or sediment can be estimated from octanol/water partition coefficients ( $K_{ow}$ ) for sorbents with sufficient organic material (Waid, 1986). Sediment-water distribution coefficients can also be estimated from  $K_{ow}$  values by

$$\log K_d = \log f_{oc} + \log K_{ow} - 0.21$$

where  $K_d$  is the distribution coefficient and  $f_{oc}$  is the fraction of organic carbon (by weight) (Lamoureux and Brownawell, 1999). Examples of  $K_{ow}$  values are given in Table 2.2. Hydrophobic organic contaminant partitioning to sediments is greater the larger the  $K_{ow}$  (Lamoureux and Brownawell, 1999).

## 2.3 Current Remedial Strategies

Both *in-situ* and *ex-situ* technologies are available for remediating PCB contaminated sites. The remediation options that are discussed are for soil and sediment.

### 2.3.1 In-Situ

*In-situ* remediation of PCBs in soil is relatively uncommon compared with *ex-situ* remediation. Due to their hydrophobic and sorptive properties, PCB contamination tends to remain in the upper surficial zone in the region where the contamination occurred. The contaminated material is therefore easily excavated and remediated *ex-situ*. For *in-situ* treatment, it is difficult to effectively deliver reagents or catalysts (Calabrese et al., 2006). Capping is the only commonly used *in-situ* method for dealing with PCB contaminated sediment, however bioremediation and phytoremediation are also remediation options.

#### 2.3.1.1 Capping

*In-situ* capping is commonly used when dealing with PCB contaminated sediments. Capping refers to the placement of a layer of clean sand or other material above the contaminated sediment (Calabrese et al., 2006). This method is cost-effective when large areas of river bottoms must be remediated or when dredging is not feasible. At times both dredging and capping techniques are used, with capping used to cover residual left from dredging. Caps are susceptible to erosion caused by high water flow events (Calabrese et al., 2006), but can be used to help keep PCB contamination in place by using materials with organic amendments encouraging sorption to the cap and causing PCB retardation (Calabrese et al., 2006).

### 2.3.1.2 Bioremediation

Bioremediation is accomplished by the addition of carbon sources, nutrients, and/or oxygen to encourage indigenous microorganism growth to degrade the contaminant of concern (Agarwal et al., 2007). This can be done either *in-situ* or *ex-situ*. Dhol (2005) attempted to biostimulate Aroclor 1254 with an anaerobic nutrient media, however his results were inconclusive. In addition, aerobic biodegradation is best suited for some congeners while anaerobic biodegradation is more suitable for others (Agarwal et al., 2007). This divide creates a challenge when working with Aroclors that contain a spectrum of congeners. Intermediates may prove toxic to the microorganisms and the rate of destruction can be slow. Although there has been some success in remediating PCBs using bioremediation, PCB destruction is often incomplete.

### 2.3.1.3 Phytoremediation

With phytoremediation, plants are grown in soil or sediment and uptake the contaminant of concern. In the past, phytoremediation has not in general been considered for remediating PCBs; however research is being done to assess its applicability. Smith et al. (2007) found that high transpiring wetland plants may increase the degradation of the lower chlorinated PCBs produced in anaerobic environments. More research is needed before this becomes a viable PCB remediation technology.

### **2.3.2 Ex-Situ**

*Ex-situ* treatment is a more common method for dealing with PCB contamination in soil and is also applicable to sediments. *Ex-situ* treatment first requires that the contaminated soil is excavated or that the contaminated sediment is dredged. Treatment can then be achieved through disposal of contaminated soils or remediation.

While excavation of PCB contaminated soil on land is relatively simple, dredging of PCB contaminated sediment is more challenging. One of the largest drawbacks of dredging operations is that it can result in resuspension of contaminants. It is estimated that about 1% of the dredged sediment may be resuspended (Calabrese et al., 2006). There is also a fraction of sediments that are left at the sediment water interface as residual. Any residual can be eliminated by overdredging (Calabrese et al., 2006), however, this comes at an increased cost.

### 2.3.2.1 Disposal of PCB Contaminated Soils

Excavated or dredged PCB contaminated soils or sediments are often disposed of instead of being cleaned. This disposal is achieved through incineration or landfilling.

Incineration is the customary remediation method with highly contaminated materials (Meckes et al., 1997), even though incineration is expensive and the transportation of PCB materials to incineration facilities is dangerous (Dhol, 2005). The dominance of this technique is largely because the majority of the other remediation options are not successful at remediating PCBs to concentrations low enough to keep the soil on site. At present, PCB contaminated material in Ontario not meeting remediation targets must be transported to Swan Hills, Alberta for incineration. Not only is soil incineration an expensive alternative, it destroys what is increasingly becoming a valued commodity: soil.

Landfilling is the customary remediation method with slightly contaminated materials (Meckes et al., 1997). Many remediation technologies are used simply to reduce PCB concentrations to levels suitable for landfilling. Soil or sediment with a PCB concentration of less than 50 mg/kg in the province of Ontario and can be disposed of at a non-hazardous landfill site (Ontario Ministry of the Environment, 2000).

### 2.3.2.2 Remediation of PCB Contaminated Soils

Remediation of PCB contaminated soil or sediment is a more sustainable alternative to its disposal. Common *ex-situ* PCB remediation techniques include contact with palladized iron, chemical oxidation, and solvent extraction.

#### 2.3.2.2.1 Palladized Iron (Fe/Pd)

Dechlorination of PCBs has been achieved using palladium loaded zerovalent iron (Fe/Pd) by a number of researchers (Fang and Al-Abed, 2007; Korte et al., 2002). Korte et al. (2002) saw complete conversion of 2,3,2',5'-tetrachlorobiphenyl to biphenyl in the lab using 100-mesh Fisher iron filings palladized to 0.25% Pd. It is thought that PCBs are first adsorbed on the metal surface and then dechlorination occurs from the corrosion reaction of iron (Fang and Al-Abed, 2007), while palladium acts a catalyst. To be successful, the reaction requires the presence of water to supply sufficient hydrogen (Korte et al., 2002). The application of nanoscale iron particles is attractive due to its increased surface area and therefore increased reactivity. Nanoparticles are also small enough to be transported by groundwater transforming their application from *ex-situ* to *in-situ* (Zhang, 2003). As

the application of nanoparticles must receive approval under Section 9 of the Ontario Environmental Protection Act, it is currently difficult to get approval for application of this technology in Ontario.

#### 2.3.2.2.2 Chemical Oxidation

Recent research has explored using chemical oxidation to destroy PCBs. Earlier work focused on Fenton's reagent and more recent work on activated persulfate. Jakher et al. (2007) used hydrogen peroxide as a pretreatment step prior to solvent extraction in the laboratory. They found improved PCB removal after employing both techniques compared with solvent extraction on its own (Jakher et al., 2007). Waisner et al. (2008) successfully destroyed PCBs from contaminated soil using persulfate in bench-scale studies, but unfortunately were unable to reduce the PCB concentrations below the preliminary remediation goals. Laboratory studies by Cassidy and Hampton (2009) found PCB removal efficiency as high as 78% from contaminated river sediment using activated persulfate.

#### 2.3.2.2.3 Solvent Extraction

Solvent extraction is a relatively simple technology that uses solvents to extract PCBs from soil. Solvent extraction can be classified into three general types according to the type of solvent used. These include standard solvents, near-critical fluids/ liquefied gases, and critical solution temperature solvents (Meckes et al., 1992). Organic solvents can cause natural organic matter to swell and significantly increase the PCB desorption rate (Weber et al., 2001). Once the PCBs are transferred into the solvent, the solvent can be concentrated and the PCBs disposed of appropriately, or the PCBs can be transferred from the solvent into another medium for disposal, such as activated carbon. In either case, the solvent may be reused. If solvent extraction is successful at removing enough PCB mass, and the appropriate solvent is used, then the soil can ultimately be reused on site.

## 2.4 Solvent Extraction Systems

There have been a number of companies that have practiced variations of solvent extraction. Some examples are CF-Systems, B.E.S.T, Carver-Greenfield Process, Extraksol Process, and Terra-Kleen.

### 2.4.1 CF-Systems

CF-Systems of Arvada, Colorado uses liquefied propane to extract organic contaminants from soils, sludges, and sediments. The extractor is filled with screened solids (up to 45.5 kg) and liquid propane. The solids are mixed by a high-speed rotary mixer after which they are allowed to settle (Meckes et

al., 1997). The liquid propane is then removed and the vessel is refilled. After numerous extraction cycles, water is added to the vessel forcing residual propane to collect on the water surface. The residual propane liquid is removed by decanting after which the pressure in the extractor is reduced and any remaining propane returns to the gaseous state and separates (Meckes et al., 1997). The gas is reliquified for reuse. The solid-water slurry is sent to another vessel where water and solids are separated with vacuum filtration.

CF-Systems employed their mobile demonstration unit for treating solids with a mean PCB concentration of 260 mg/kg at a pilot-scale operation at Hazen Research Inc., Golden, Colorado. The trailer-mounted system housed extraction, solid-liquid separation, and solvent recovery operations. Three extraction cycles were used to achieve PCB removal efficiencies ranging from 91.4% to 99.4%. It was thought that additional extraction cycles would not significantly improve extraction efficiency. Final PCB concentrations were as low as 1.8 mg/kg following the three extraction cycles (Meckes et al., 1997).

#### **2.4.2 B.E.S.T**

Resource Conservation Company has a solvent extraction process entitled Basic Extractive Sludge Treatment (B.E.S.T). The process uses critical solution temperature solvents, whose solubility can be improved by changing the solvent temperature (Meckes et al., 1992). Meckes et al. (1993) reported on the results from a pilot-scale evaluation of the B.E.S.T. process on sediment samples collected from the Grand Calumet River in Gary, Indiana. Samples from two locations contained mean PCB concentrations of 10 mg/kg and 427 mg/kg. Over 99% of PCBs were removed after seven extractions (Meckes et al., 1993). The technology was also shown to be effective at removing polycyclic aromatic hydrocarbons from the soil samples.

Using B.E.S.T, organic contaminants are extracted from soils, sludges, or sediments using triethylamine or other organic solvents (Meckes et al., 1993). Through extraction, solvent recovery, solids drying, and water stripping, the process separates materials into oil, water, and solids. This is achieved in two vessels. Caustic soda is added to the contaminated solids such that the final pH is 10.5-11 (Anderson, 1995; Meckes et al., 1992). The vessel is purged with nitrogen prior to the addition of triethylamine to decrease the risk of combustion (Meckes et al., 1993). Triethylamine is first used at lower temperatures (<6°C) to dewater solids while also removing organic contaminants, then the vessel is heated externally to 77°C by steam, at a temperature where triethylamine is no

longer miscible with water, therefore ceasing to dewater (Anderson, 1995). The solvent is mechanically mixed with soil for 5 to 15 minutes with paddles (Anderson, 1995). Following mixing, solids are allowed to settle and fluids are decanted from the vessel where they go to a centrifuge to remove fines (Anderson, 1995; Meckes et al., 1993). Solids collected from the centrifuge are sent for additional extractions (Anderson, 1995; Meckes et al., 1993). These additional extractions occur at temperatures above 55°C to take advantage of the increasing organic contaminant solubility in triethylamine at elevated temperatures (Anderson, 1995).

Following all extraction, solids are dried by injecting steam into the jacket to raise the temperature of the solids to 77°C (Meckes et al., 1993). Mixing from the paddle improves heat transfer. Once the majority of the solvent is removed, steam is injected into the vessel and the resulting effluent is put through a condenser. Triethylamine is recovered from the process. Residual triethylamine in the Indiana solids from the pilot-scale evaluation varied between 28 mg/kg and 130 mg/kg (Meckes et al., 1993), and it was noted that extraction efficiency decreased with higher waste moisture content (Anderson, 1995)

### **2.4.3 Carver-Greenfield Process**

Carver-Greenfield Process is a solvent extraction and dehydration system operated by Biotherm LCC, formally known as Dehydro-Tech Corporation. The technology was developed by Charles Greenfield in the 1950s (Anderson, 1995). The first commercial plant was built to treat meat rendering wastes and over half of the plants built by the 1990s were designed for processing wastes of this type (Anderson, 1995). Commercial plants installed in the 1980s and early 1990s were designed to process a variety of wastes, mostly sludges, with different solid contents (2-20%) by removing oil-soluble organics (Anderson, 1995). In addition to operating in the United States, the process has an international market including Italy, Japan, and the former Soviet Union (Anderson, 1995).

Following screening or grinding, waste is mixed with a hydrocarbon solvent in a fluidizing tank, with a solvent to waste ratio of between 5:1 or 10:1 by weight (Anderson, 1995; Trowbridge and Holcombe, 1996). Isopar-L, the solvent commonly used (Trowbridge and Holcombe, 1996), extracts organic contaminants as well as keeps the waste in a slurry during water evaporation (Anderson, 1995).

A centrifuge is used to separate the oil from the solids (Meckes et al., 1992; Trowbridge and Holcombe, 1996). Material can be reslurried with clean solvent if additional extractions are required

(Anderson, 1995). A hot inert gas is used to vaporize remaining solvent and dried solids contain less than 1% solvent and less than 2 % water (Trowbridge and Holcombe, 1996). Recovered solvent is separated for reuse and vapours are condensed (Anderson, 1995; Trowbridge and Holcombe, 1996).

Trowbridge and Halcombe (1996) reported over 99.95% removal of Aroclor 1260 from a soil that underwent simultaneous soil drying and solvent extraction, followed by two solvent extractions using S-140 solvent. Removing water during solvent extraction is more effective for PCB removal than solvent extraction of a soil with a high moisture content (Trowbridge and Holcombe, 1996).

Wright and Rosta (1998) suggested a general dissatisfaction with the Carver-Greenfield product for use in dewatering wastewater effluent. There have not been any recent articles discussing this technology nor could accurate contact information for the Biotherm LCC company be located, suggesting that this company may no longer be operating under this name or at all.

#### **2.4.4 Extraksol Process**

CET Environmental Services, formally the Sanivan Group from Anjou, Quebec, developed the transportable Extraksol Process for solvent extraction (Anderson, 1995). The system uses proprietary solvents (Meckes et al., 1992) for batch extraction (Anderson, 1995). Washing begins when the mix tank /extraction vessel is filled with solids (Anderson, 1995). The tank is sealed and purged with an inert gas prior to the solvent addition and the tank is then rotated (Anderson, 1995; Meckes et al., 1992). Wastes with a moisture content above 30% may need dewatering prior to the washing process, as extraction efficiency decreased with higher waste moisture content (Anderson, 1995).

Following each extraction, rotation is stopped and solids settle (Anderson, 1995). The wash cycle is completed when solvent is decanted and sent for recovery (Anderson, 1995). Solvent is drained through a geotextile filter, which is unlikely to clog since Sanivan limits their application to solids with a maximum clay content of 30% (Anderson, 1995) or 40% (Meckes et al., 1992). Bench scale or pilot tests are used ahead of time to determine the appropriate solvent and number of washes (Anderson, 1995).

Once the solvent is removed, hot nitrogen gas and steam are added to heat the solids (Anderson, 1995; Meckes et al., 1992). The gas strips the solvent while the vessel is rotated and a vacuum removes the gas which is then sent to a condenser (Anderson, 1995). The contaminated solvent is then sent to the distillation unit (Anderson, 1995).



### **2.4.5 Terra-Kleen**

Terra-Kleen's solvent extraction process has evolved over the years. Previously, hot fluid was circulated through a jacket surrounding the extractor to increase temperatures in the extractor and solvent was continuously flushed through the extractor (Meckes et al., 1992). Today the extractor is filled with solvent and then drained. The technology has been improved so that the same vessel is used for drying the soil. Drying occurs with the addition of a hot inert gas used to vaporize any residual solvent. Vaporized and drained solvent is recovered and reused. The technology is now used by Sonic Environmental Solutions (Sonic Environmental Solutions Inc., 2007).

## **2.5 Factors Influencing Solvent Selection**

Solvent choice is a key factor in determining PCB extraction efficiency and rate. Section 2.4 demonstrated that numerous solvents have been used in field applications. A literature review was conducted to determine solvents previously studied or used for PCB or similar organic contaminant extraction. Jakher et al. (2007) listed many solvents that have been previously considered for extraction of organic contaminants. These included isopropyl alcohol, hexane, acetone, triethylamine, methanol, liquid propane, liquid CO<sub>2</sub>, dichloromethane, benzene, toluene, and mixtures of these. Others used or thought to be applicable were methyl isobutyl ketone (Valentin, 2000), dimethyl sulfoxide (Perkins, 2008), ethyl acetate (Valentin, 2000), 1-butanol, 2-butanol, 2-methyl-2-propanol, 1-propanol, ethanol and isooctane.

When evaluating potential solvents, solvent toxicity, polarity, viscosity, freezing points, boiling points, and cost need to be considered. The solvents that are reviewed in the following sections were ranked based on key properties in order to select four solvents for use in this research.

### **2.5.1 Solvent Toxicity**

It is important minimize risks to on-site operators and to ensure public safety so solvent toxicity is a key concern. A number of solvents were eliminated from the list provided above following consultation of the Ontario Ministry of the Environment's Soil, Ground Water and Sediment Standards for Use Under Part XV.1 of the Environmental Protection Act (Ontario Ministry of the Environment, 2004; Ontario Ministry of the Environment, 2007). Workplace Hazardous Materials Information System (WHMIS) classifications were also considered to evaluate solvent safety. On the basis of solvent toxicity, acetone, benzene, dichloromethane, hexane, methyl isobutyl ketone, and

toluene were deemed unsuitable for field extraction solvents. Liquefied CO<sub>2</sub> and propane were no longer considered due to their complicated and potentially dangerous handling. In general, hydrophilic solvents are considered more environmentally friendly (Jakher et al., 2007).

### **2.5.2 Solvent Polarity**

It was thought that non-polar solvents are best for extracting PCBs since PCBs are non-polar. Solvent selection for PCB extraction is complicated as Ontario soil is wet and hence a polar or hydrophilic solvent might be superior at reaching wetted pores. The PCB transfer rate into the solvent is not restricted to the solubility of the PCB in the solvent, but is also a function of the solvent penetration into the soil (Jakher et al., 2007).

Dielectric constants are a measure of attraction between two poles and were examined for the solvents under consideration (Table 2.3). It was suggested that the solvating abilities of an alcohol would increase as the chain length grew (Forsey, 2007). Dielectric constants (and hence polarity) of alcohols decrease as the chain length becomes longer therefore becoming more non-polar. At the same time, the extensively chlorinated PCB congeners are more hydrophobic and Jakher et al. (2007) suggested that as such it may be these more chlorinated PCB congeners that persist in weathered soil samples as opposed to the lesser-chlorinated PCB congeners. It is the lesser-chlorinated congeners that are more easily targeted by biodegradation, and are more soluble in water (Jakher et al., 2007). Looking solely at degree of polarity, the above arguments would suggest that the solvent with the smallest dielectric constant would be the best suited for extracting PCBs from soil. Jakher et al.'s findings support this theory as they concluded that isopropyl alcohol had a better extraction efficiency than methanol (2007). Isopropyl Alcohol was also selected by Dhol for PCB extraction in his thesis work (Dhol, 2005).

Unfortunately as the dielectric constant decreases, the solvents solubility in water decreases. This becomes problematic when trying to extract PCBs from soils with higher moisture content. In these cases, non-polar solvents are incapable of penetrating wet soils. In addition, dielectric constants may vary with temperature (Lou et al., 1997).

### **2.5.3 Solvent Viscosity**

Solvent extraction operators in colder climates claim to have witnessed noticeably increased solvent viscosity in colder weather, increasing the amount of time required to fill and drain extraction bins,

thus increasing the overall operation time. For this reason, viscosity data from CRC Handbook of Chemistry and Physics was examined (Figure 2.1) (Lide, 1998). Data were available for all of the solvents not removed due to toxicity concerns.

Triethylamine, ethyl acetate and isooctane consistently have the lowest viscosity and the smallest rate change as temperature decreases making them ideal solvent if only viscosity is considered (Figure 2.1). For the alcohols shown, their viscosities increase with increasing chain length.

The soil moisture content changes the viscosity of the solvent. For methanol, ethanol, 1-propanol, and 2-propanol, an increased water content increases the solvent viscosity, however the rate change is approximately the same (Lide, 1998) (Figure 2.2).

#### **2.5.4 Solvent Freezing Point**

Solvents used for solvent extraction must not freeze in Ontario winter temperatures and so freezing points for potential alcohol solvents were considered (Table 2.4). Based on this data alone, only 2-methyl-2-propanol was unsuitable for use in solvent extraction because it is solid at most of the relevant temperature range. The other alcohols are liquid at relevant temperatures.

The moisture content of the soil changes the freezing point of the solvent. Freezing point data at varying moisture contents for methanol, ethanol, 1-propanol, and 2-propanol are shown in Figure 2.3 (Lide, 1998). A moisture content of at least 50 % is necessary before the solvent/water mixture could potentially freeze in Ontario winters (Figure 2.3). Fifty percent moisture content is above the water saturation limit of a typical soil. Therefore the effect of soil moisture content on solvent freezing should not dictate solvent selection.

#### **2.5.5 Solvent Boiling Point**

Another important consideration is the boiling point of the solvent as distillation is frequently used as a solvent water separation technique, such as by CET Environmental Services in the Extraksol Process (Anderson, 1995). Solvents having boiling points very similar to that of water, such as 1-propanol or 2-butanol, are difficult to separate from water using this method. Since other separation techniques are available, potential solvents should not be eliminated based on their boiling point. Furthermore, solvents will only need to be separated from water if they are miscible with water. All the alcohols in Table 2.4 are completely soluble in water with the exception of 1-butanol and 2-butanol which have solubilities of 8.00 and 12.5 g/100 mL of water respectively (Streitwieser et al.,

1992). The non-alcohol solvents have suitable melting points with the exception of dimethyl sulfoxide (Table 2.5).

Azeotropes were present amongst the potential solvents considered, and were those solvents that when combined with water had different boiling points from that of pure solvent. Ethanol, 1-butanol, 2-butanol and ethyl acetate are all azeotropic mixtures with water (Lide, 1998) (Table 2.6). The change in boiling point is largest for the two butanols.

A combination of polar and non-polar solvents may be preferred over a single solvent as discussed in section 2.5.2. However, no azeotropes for binary combinations of the nine solvents were identified by examining “Azeotropic Data for Binary Mixtures” in the CRC Handbook of Chemistry and Physics (Lide, 1998).

### **2.5.6 Solvent Cost**

Solvent cost for the nine solvents passing the toxicity, polarity, viscosity, and freezing and boiling point screenings, was easily compared as most were available from the scientific chemical supplier VWR as BDH Reagent Grade Solvents in 19L steel cans (Table 2.7). Triethylamine, 2-butanol and isooctane were not available in the same volume and/or same grade which complicated the comparison as cost can be dependent on both these factors. Overall, methanol was found to be the cheapest, whereas isooctane the most expensive; however isooctane was only available in 2.5L volume from VWR perhaps contributing to its higher cost.

### **2.5.7 Solvent Selection**

Weights were applied to the solvent properties considered in order to rank the solvents (Appendix A). The polar and non-polar solvents were considered separately. Toxicity was given the highest weight for the polar solvents, followed by cost, while dielectric constant and recommendations were given equal weights. For the non-polar solvents, the largest weight was assigned to toxicity, followed by dielectric constant, and finally cost. The two highest ranking polar solvents were ethanol and isopropyl alcohol. The two highest ranking non-polar solvents were isooctane and triethylamine. These were therefore selected for use in laboratory experiments aimed at fulfilling the research objectives.

## **2.6 Properties Controlling PCB Sorption and Desorption**

Various properties control PCB absorption, adsorption and desorption to soil or sediments.

### **2.6.1 Soil Composition**

Soil composition plays an important role in PCB sorption. Natural organic materials in soils and sediments largely determine the sorption capacity of a soil and include humic substances, biopolymers from which they were derived, lipids, proteins and lignin, kerogen, and combustion-related black carbon or char materials (Huang et al., 2003). The organic matter in any given soil is a function of climate, vegetation, topography, and parent material (Stevenson, 1982).

Humic substances are a large and generally the most abundant portion of natural organic materials in soils and sediments (Weber et al., 2001). Carroll et al. (1994) described humic organic matter as a complex of swollen and condensed polymer-type phases bound to mineral surfaces. They can be classified into three groups: fulvic acid, humin, and humic acid (Huang et al., 2003; Stevenson, 1982). Humic substances are believed to be derived from biopolymers originating from lignin, a fundamental part of plant cell walls (Pignatello et al., 2006).

Biopolymers are a group of molecules produced by living organisms which consist of repeating structural units with large molecular mass. Included in this group are starch, proteins, peptides, deoxyribonucleic acid, and ribonucleic acid. The role of biopolymers in the sorption of hydrophobic organic chemicals (HOCs) such as PCBs is considered insignificant (Huang, Peng et al. 2003). Lipids also play a small and often insignificant role in the sorption of hydrophobic organic chemicals, despite their hydrophobicity, primarily because they comprise such a small fraction of soil/sediment organic matter (Huang et al., 2003).

Kerogen is the dominant fraction of organic matter from sedimentary rocks, deriving from plant and animals. Kerogen's three-dimensional structure and many parallel sheets forming its aromatic nuclei allow it to easily trap small hydrophobic organic solutes (Huang et al., 2003). It is insoluble both in nonpolar or weakly polar organic solvents (Pignatello et al., 2006) and inorganic solvents.

Black carbon is often called soot or char depending on the form it manifests (Huang et al., 2003). Black carbon does not contribute to the nonlinear and competitive sorption behaviour in bulk soils (Pignatello et al., 2006). Pignatello et al. (2006) demonstrated that humic acids and humic precursors

free of black carbon sorb non-polar compounds nonlinearly and with competition when two solutes are present.

Natural organic materials have been classified by some researchers as “soft carbon” or “hard carbon”. A good review is provided by Allen-King et al. (2002). According to Huang et al. (2003) sorption of HOCs into “soft carbon”, such as humic matter, occurs linearly whereas sorption on the “hard carbon”, such as kerogen, follows adsorption and absorption or partitioning. The ratio of soft carbon to hard carbon dictates whether sorption will occur linearly or nonlinearly (Huang et al., 2003). The mineral fractions have minor roles in the sorption of hydrophobic organic contaminants, other than having an effect on spatial distributions and arrangements of natural organic matter (Weber et al., 2001).

The distributed reactivity model separates the sorption areas into three types. The first is comprised of mineral sites. HOCs sorbed in this domain are done so by near-linear adsorption. The second type comprises unstructured and swollen organic matter, and sorption is similar to that of solute partitioning. The third type comprises a condensed yet unstructured fraction of natural organic matter. Weber et al. (2001) propose that the third type of sorption area is responsible for the variety of different adsorption processes due to different energy sites. They conclude that it is the third domain that largely dictates the slower HOC sorption and desorption rates and accounts for the nonlinear adsorption.

Carroll et al. (1994) observed both a rapidly desorbing labile component and a more slowly desorbing resistant component in sediment. They hypothesized that the labile and resistant fractions are due to the swollen (rubber-like) and condensed (glass-like) phases respectively of humic polymer in organic matter (Carroll et al., 1994). They measured desorption of PCBs from sediments under various conditions to explore the diffusion-controlling structure of the matrix.

The rubbery state is less condensed and has smaller cohesive forces than the glassy state. Sorption to the rubbery state occurs by dissolution, whereas sorption to the glassy state is from both dissolution and hole-filling (Xing and Pignatello, 1997). The glassy domain is composed of rigid and condensed organic matter and is responsible for slow desorption, nonlinear sorption, non-Fickian diffusion, and sorption/desorption hysteresis (Schaumann and LeBoeuf, 2005). Rubbery domains are responsible for the opposite: linear sorption and faster diffusion rates (Schaumann and LeBoeuf, 2005). Desorption from soils with low total organic carbon and higher contents of minerals with high internal surface

areas will be influenced more by the entrapment of sorbed molecules within organic components (Huang et al., 2003).

### **2.6.2 Soil Grain Size**

There is a lack of consensus as to whether grain size influences PCB sorption. Carroll et al. (1994) noted that PCB contamination in their samples was uniformly distributed between the different size fractions with the exception of the 293-990  $\mu\text{m}$  and  $<69 \mu\text{m}$  fractions. They concluded that particle size did not impact the fraction of PCBs in the resistant fraction, and that silt and clay did not appreciably affect the desorption of PCBs in their sample (Carroll et al., 1994). They also found that while bar-milling did change the grain size distribution, it had no effect of PCB desorption in their 7 day experiments.

Many solvent extraction companies screen their soils to avoid treating large grain sizes. CF-Systems screen soils to remove any materials greater than 0.64 cm (Meckes et al., 1997). Soil is pre-treated in the Carver-Greenfield Process with separation and/ or grinding to ensure particle sizes less than 6 mm (Anderson, 1995; Meckes et al., 1992). Sanivan Group's Extraksol process treats nonporous solids up to 0.6 m and porous solids up to 0.051 m (Anderson, 1995). The grain size limitations imposed by these companies may be imposed by the mechanics of the operation and not the PCB contamination.

Wu and Gschwend (1988) considered grain size in earlier modeling work. They created a numerical model capable of describing sorptive exchange in aqueous systems containing a range of particle sizes and temporally varying solution conditions. Contradictory to the findings of Carroll et al. (1994), their simulations showed that neglecting size distribution effects was a large source of prediction error (Wu and Gschwend, 1988).

### **2.6.3 PCB Composition**

In addition to soil composition and grain size, PCB composition plays a large role in PCB sorption. Carroll et al. (1994) noted that diffusion coefficients decreased with increasing congener molecular size and chlorine content in both the labile and resistant fractions (1994). They hypothesized that the PCBs from the labile compartment (the more rapidly desorbing PCBs), would be more bioavailable to anaerobes for reductive dechlorination producing ortho-substituted PCBs.

Lamoureux and Brownawell (1999) compared desorption from sediments containing compounds representing tetra-, penta-, hexa-, and heptachlorobiphenyl. They discovered that the least

hydrophobic congener underwent the quickest rate change from fast to slow desorption and consequently had the most sorption-resistant fraction. On the contrary, the most hydrophobic congeners do not show a significant change in desorption rate over the 480 hours that the experiments ran and had the smallest sorption-resistant fraction. Desorption of the majority of PCBs could be described by a two-compartment model, consisting of an initially higher desorption rate followed by a slower rate, however the highest molecular weight PCBs behaved differently (Lamoureux and Brownawell, 1999). Pignatello et al. (2006) noted that the most hydrophobic compound among the HOCs tested in their work also had the most nonlinear sorption.

## **2.6.4 Temperature**

Temperature plays a role in the sorption of PCBs. Xing and Pignatello (1997) observed that the linearity of sorption increased as the temperature increased however the effect of temperature on sorption remains nonlinear (Pignatello et al., 2006). Diffusion rates also increase with increasing temperature.

### **2.6.4.1 Glass Transition Temperature**

The glassy or rubbery state of soil or sediment influences PCB sorption. The transformation from glassy to rubbery state occurs at what is known as the glass transition temperature ( $T_g$ ). Thermal energy breaks noncovalent bonds allowing for this change of states (Pignatello et al., 2006).

A significant change in the heat capacity in a small temperature range typically reveals glass transition temperatures (Schaumann and LeBoeuf, 2005). Earlier work identified the difficulty in identifying single glass transition temperatures for whole soils and attributed this inability to heterogeneity of the soil organic matter. This heterogeneity explained why there could be a range of glass transition temperatures (Schaumann and LeBoeuf, 2005).

Pignatello et al. (2006) observed multiple transition temperatures in some macromolecules. The humic acid sorbent extract from topsoil collected in Chelsea, Michigan, had the first transition temperature between 3 and 6 °C and is in a range that may influence sorption at colder temperatures such as those encountered in Southern Ontario. They proposed that multiple transition temperatures could be caused by regions of varying physical or chemical properties. The lower temperature glass transition temperature is associated with side-chain mobility, whereas the higher temperature glass



transition temperature is associated with main chain mobility (Pignatello et al., 2006). This glass transition behavior was observed both in terrestrial and aquatic humic acids (Pignatello et al., 2006).

Schaumann and LeBoeuf (2005) suggest that the glass transition temperature may be impacted by thermal or sample history. Glassy character is increased by a reduction in the mobility of side chains caused by cross-linking. This change increases the glass transition temperature (Schaumann and LeBoeuf, 2005). Glassy polymers can be in non-equilibrium if they were formed by cooling quickly through the glass transition region. The glassy matrixes tend towards equilibrium by undergoing structural relaxation, thus changing the macromolecular structure over time. The rate of structural relaxation decreases with increasing glassy character. The rate is also a function of temperature, and increases with increasing temperature when approaching the glass transition temperature (Schaumann and LeBoeuf, 2005).

It may be that most glass transition temperatures in natural organic matter are above 20°C (Table 2.8) and that Ontario's decreasing temperatures in the fall and winter months would not cause a transition from rubbery to glassy state. However, the transition from glassy to rubbery state can also be achieved by saturating the polymer with high concentrations of a swelling solvent (Xing and Pignatello, 1997). This may be an important phenomenon during solvent extraction. The Fox-Flory equation describes the glass transition temperature of a polymer/water gel and is given by

(2-2)

$$\frac{1}{T_g} = \frac{C_w}{T_g^W} + \frac{1-C_w}{T_g^P}$$

where  $C_w$  is the dimensionless water content,  $T_g^W$  is the glass transition temperature of water (136-170K), and  $T_g^P$  is the glass transition temperature of dry polymer (Fox and Flory, 1954; Schaumann and LeBoeuf, 2005).

Also, temperature affects sorption behaviour even below the glass transition temperature. As temperature approaches the  $T_g$ , sorption tends to become more linear as a result of the solid becoming more rubbery. The solid-phase dissolution also becomes more important than hole filling as the temperature increases (Pignatello et al., 2006). Organosolv lignin showed nonlinear sorption below  $T_g$ , however no consensus exists in literature regarding this issue (Pignatello et al., 2006).

#### 2.6.4.2 Glass Transition Temperature & Moisture Content

Water can influence the glass transition temperature of a soil. It can reduce the overall glass transition temperature by acting as a plasticizer when the water content is increased (Schaumann and LeBoeuf, 2005). Other studies also exist that report antiplasticizing properties of water (Schaumann and LeBoeuf, 2005). Schaumann and LeBoeuf (2005) tested the hypothesis that water can act as a plasticizer and an antiplasticizer in the same sample, and that the differences in observed glass transition behaviours are due primarily to water. An air-dried peat sample was used for assessing glass transition behaviour by varying water content and thermal history (Schaumann and LeBoeuf, 2005). When the transition temperature was plotted versus the water content, Schaumann and LeBoeuf (2005) observed the maximum transition temperature occurred at a moisture content of 12% even though dried samples subject to hydration reached a maximum moisture content of  $24 \pm 1\%$ . The minimum transition temperature occurred in water-free samples suggesting water was acting as an antiplasticizer below a moisture content of 12% (Schaumann and LeBoeuf, 2005).

Schaumann and LeBoeuf (2005) observed the glass transition temperature of their initially air-dried sample decreased continually with increasing hydration time. They noted the transition temperature decreased at a slower rate than the rate of which the water content increased. The authors believe their findings suggest that changes in temperature and water content can induce slow structural relaxation processes in natural organic matter over periods of time as short as days. They identified three processes of structural relaxation (Schaumann and LeBoeuf, 2005):

- 1) Classical glass transition behaviour. This behavior occurs in thermally pretreated and very low water-content samples.
- 2) Decreased macromolecular mobility and decreased glass transition temperature caused by water acting as an antiplasticizer. In this study, this occurred in peat samples at water contents below 12%.
- 3) Slow swelling from water uptake caused by water acting as a plasticizer. In this study, this occurred in peat samples at water contents above 12%.

### 2.7 Modeling Sorption

Understandings of PCB sorption can aid in the understanding of PCB desorption. The simplest model describing the partitioning of hydrophobic organic contaminants between aqueous phase and soils or sediments is the linear partitioning model described by

(2-3)

$$q_e = K_D C_e$$

where  $q_e$  is the equilibrium solid-phase solute concentration in  $\mu\text{g/g}$ ,  $K_D$  is the partitioning coefficient in  $\text{mL/g}$ , and  $C_e$  is the equilibrium aqueous-phase solute concentration in  $\mu\text{g/mL}$  (Huang et al., 2003; Karickhoff, 1980). However the model assumes an excess of sites for hydrophobic organic contaminant molecules to sorb which is not always the case. The Langmuir model describes site-limited sorption by

(2-4)

$$q_e = \frac{Q^0 b C_e}{1 + b C_e}$$

where  $Q^0$  is the maximal sorption capacity in  $\text{ug/g}$ ,  $b$  is the solute-surface interaction energy-related parameter in  $\text{mL/ug}$ , and  $q_e$  and  $C_e$  are defined as in the linear partitioning model (Huang et al., 2003).

Although the model is simple, it is thought to be incorrect for hydrophobic organic contaminant sorption by soils or sediments (Huang et al., 2003). Instead, a model often used for describing sorption is the Freundlich model given by

(2-5)

$$q_e = K_F C_e^n$$

where  $K_F$  is the Freundlich model capacity factor or Freundlich constant in  $\text{mL/g}$ ,  $n$  is the dimensionless isotherm linearity parameter, and  $q_e$  and  $C_e$  are defined as in the linear partitioning model (Huang et al., 2003; Pignatello et al., 2006).

Xing and Pignatello (1998) used the Freundlich model to investigate the effect of natural aromatic acids on the adsorption of anthropogenic organic compounds in soil. Aromatic acids were selected based on their similarity of structure and size to many organic contaminants. They screened eleven different aromatic acids for their effect on sorption of 2,4-Dichlorophenol and discovered that sorption did not occur linearly ( $n \neq 1$ ) (Xing and Pignatello, 1998). Xing and Pignatello (1998) showed there is direct competition between aromatic acid and PCB congener 2,4-dichlorophenol for

sorption sites. They observed a decrease in the sorption distribution ratio with the presence of aromatic acids, although the decrease was not always statistically significant.

Pignatello et al. (2006) noted that the organic carbon adsorption coefficient decreased with increasing  $C_e$  and the rate depended on  $n$ . The values for  $n$  and  $C_e$  varied greatly for humic acids from different soils for the same hydrophobic organic contaminants. The Freundlich model continues to be used in more recent PCB research (Pignatello et al., 2006; Teuten et al., 2007).

## 2.8 Modeling Desorption

Karickhoff proposed the two-box release model for desorption of nonionic organic compounds from sediments (Karickhoff, 1980). The two-box release model encompasses both the labile and resistant fractions and is given by

(2-6)

$$\frac{M_t}{M_o} = x_1 e^{-k_1 t} + (1 - x_1) e^{-k_2 t}$$

where  $M_t$  is the amount of organic contaminant remaining at time  $t$  in  $\mu\text{g}$ ,  $M_o$  is the initial amount of organic contaminants in  $\mu\text{g}$ ,  $x_1$  is the labile fraction of organic contaminant,  $k_1$  is the first-order rate constant for the labile fraction in 1/hours,  $k_2$  is the first-order rate constant for the resistant fraction in 1/hours, and  $t$  is the desorption time in hours (Carroll et al., 1994; Karickhoff, 1980). The slow compartment represented a more condensed organic matter phase (Xing and Pignatello, 1997).

Another compartment model is the dual-mode model. It is a combination of both the linear partition model and the Langmuir model. It states that the total sorption to soil or sediment organic matter is the sum of sorption in both the dissolution and hole-filling domains, and agrees with the concept of both glassy and rubbery polymer states (Xing and Pignatello, 1997; Xing et al., 1996):

(2-7)

$$S = S(D) + S(H) = K_p C + \sum_{i=1}^n \frac{S_i^o b_i C}{1 + b_i C}$$

where  $S$  is the sorbed concentration in  $\mu\text{g/g}$ ,  $S(D)$  is the sorbed concentration in the dissolution domain in  $\mu\text{g/g}$ ,  $S(H)$  is the sorbed concentration in the hole-filling domain in  $\mu\text{g/g}$ ,  $K_p$  is the lumped sorption coefficient in  $\text{mL/g}$ ,  $C$  is the solute concentration in  $\text{ug/mL}$ ,  $b_i$  is the affinity constant in

mL/ug,  $S_i$  is the capacity constant in ug/g, and  $n$  is the number of unique holes. Xing and Pignatello (1997) generated data that supported the dual-mode model.

Similar to Karickhoff's model, Fang and Al-Abed (2007) presented another compartment model to describe desorption of hydrophobic organic compounds from soil and sediment:

(2-8)

$$\frac{C_t}{C_o} = F_{aq} e^{-k_{aq}t} + F_{fast} e^{-k_{fast}t} + F_{slow} e^{-k_{slow}t} + \dots$$

where  $C_o$  is the concentration of contaminant in the sediment at time zero in  $\mu\text{g/g}$ ,  $C_t$  is the concentration of contaminant in the sediment in  $\mu\text{g/g}$  at time  $t$  (hours),  $F_{aq}$  is the fraction of the contaminant present in the aqueous phase,  $F_{fast}$  is the fraction of the contaminant present in the fast desorbing sediment compartment,  $F_{slow}$  is the fraction of the contaminant present in the slow desorbing sediment compartment,  $k_{aq}$  is the rate constant of the extraction of PCBs in the aqueous phase in 1/hours,  $k_{fast}$  is the rate constant of fast desorption in 1/hours, and  $k_{slow}$  is the rate constant of slow desorption in 1/hours (can vary with time as sediments age).

Carroll et al.'s (1994) experiments suggested that kinetics and not thermodynamics were limiting PCB desorption from their samples. Valentin (2000) studied solvent extraction of PCB mass in soil using ethyl acetate, methyl iso-butyl ketone (MIBK) and hexane over time. One of her studies measured the amount of PCB mass removed in ethyl acetate using a 40:1 solvent volume to soil mass ratio. Like Weber et al. (2001) Valentin found that the removal rate was greatest initially and decreased until her last measurement at 1250 minutes (Figure 2.4). Her extraction data followed the fast compartment of the desorption models described by Karickhoff (1980) and Fang and Al-Abed (2007):

(2-9)

$$\frac{M_t}{M_o} = x_1 e^{-k_1 t}$$

where  $M_t$ ,  $M_o$ ,  $x_1$ ,  $k_1$ , and  $t$  are described as in the two-box release model. Karickhoff (1980) suggested that the chemicals in the labile phase are easily desorbed using solvents, however it is the resistant phase that will take much longer (days) to desorb (Karickhoff, 1980). He also noted that is the ratio of the two phases and the extraction time that will ultimately determine percent extracted.

Another model used to describe desorption is the radial intraparticle diffusion model which uses measurable sediment and HOC properties (Wu and Gschwend, 1988). Lamoureux and Brownawell (1999) attempted to fit desorption data to the model and found that although it accurately described desorption for high-molecular weight PCBs, it did not for low molecular weight PCBs. This conclusion confirmed research by Pignatello and Xing who found the model was unable to accurately describe slow sorption (Lamoureux and Brownawell, 1999). Lamoureux and Brownawell (1999) thought that the most likely explanation as to why the model did not accurately describe desorption of the less hydrophobic compounds was that there are micropores within the sediment matrix that are available to smaller compounds but not to larger compound, due to larger size and different shape. Lamoureux and Brownawell (1999) thought it more likely that the smaller, least hydrophobic PCBs be removed more quickly as they are more soluble, leaving behind a more hydrophobic and therefore resistant PCB pool. However, results contradicted their hypothesis and showed that the more hydrophobic fraction had the smallest desorption-resistant fraction.

**Table 2.1. Composition of PCB Isomer Groups from Erickson (Erickson, 1993)**

PCB Isomer Group	Empirical Formula	Percent Chlorine	Number of Isomers
Monochlorobiphenyl	C <sub>12</sub> H <sub>9</sub> Cl	9	3
Dichlorobiphenyl	C <sub>12</sub> H <sub>8</sub> Cl <sub>2</sub>	32	12
Trichlorobiphenyl	C <sub>12</sub> H <sub>7</sub> Cl <sub>3</sub>	41	24
Tetrachlorobiphenyl	C <sub>12</sub> H <sub>6</sub> Cl <sub>4</sub>	49	42
Pentachlorobiphenyl	C <sub>12</sub> H <sub>5</sub> Cl <sub>5</sub>	54	46
Hexachlorobiphenyl	C <sub>12</sub> H <sub>4</sub> Cl <sub>6</sub>	59	42
Heptachlorobiphenyl	C <sub>12</sub> H <sub>3</sub> Cl <sub>7</sub>	63	24
Octachlorobiphenyl	C <sub>12</sub> H <sub>2</sub> Cl <sub>8</sub>	66	12
Nonachlorobiphenyl	C <sub>12</sub> HCl <sub>9</sub>	69	3
Decachlorobiphenyl	C <sub>12</sub> Cl <sub>10</sub>	71	1

**Table 2.2. Examples of PCB octonol-water partition coefficients (Hawker and Connell, 1988)**

PCB Congener	Log K <sub>ow</sub>
2 - dichlorobiphenyl	4.46
2,2',5' - trichlorobiphenyl	5.24
2,2',4,5'-tetrachlorobiphenyl	5.85
2,2',5,5'-tetrachlorobiphenyl	5.84
2,2',4,5,5'-pentachlorobiphenyl	6.38
2,2',3,4,4',5'-hexachlorobiphenyl	6.83
2,2',3,4,4',5,5'-heptachlorobiphenyl	7.36
decachlorobiphenyl	8.18

**Table 2.3. Dielectric Constants (Lide, 1998)**

Solvent	Dielectric Constant @ 20.1 °C
Methanol	33.0
Ethanol	25.3
1-Propanol	20.8
2-Propanol	20.2
1-Butanol	17.8
2-Butanol	17.3
Ethyl Acetate	6.1
Triethylamine	2.4
Isooctane	1.9
Dimethyl sulfoxide	-
2-methyl-2-propano	-

- : unknown



**Table 2.4. Freezing and Boiling Points of Alcohols (Streitwieser et al., 1992)**

Solvent	Freezing Point (°C)	Boiling Point (°C)
Methanol	-97.8	65.0
Ethanol	-114.7	78.5
1-propanol	-126.5	97.4
2-propanol	-89.5	82.4
1-butanol	-89.5	117.3
2-butanol	-114.7	99.5
2-methyl-2-propanol	25.5	82.2

**Table 2.5. Freezing and Boiling Points of Non-Alcohols**

Solvent	Freezing Point (°C)	Boiling Point (°C)
Dimethyl sulfoxide <sup>a</sup>	19	189
Ethyl acetate <sup>b</sup>	-83.8	77.1
Isooctane <sup>a</sup>	-107.3	99.22
Propane <sup>a</sup>	-187.6	-42.1
Triethylamine <sup>a</sup>	-115	89

<sup>a</sup> (Lide, 1998)

<sup>b</sup> (Mackay, 2006)

**Table 2.6. Pure Solvent and Azeotrope Boiling Points**

Solvent	Boiling Point (°C)	Azeotropic Water-Solvent Mixture	
		Boiling Point (°C)	Mole Fraction
1-butanol	117.3 <sup>c</sup>	92.7 <sup>a</sup>	0.753 <sup>a</sup>
2-butanol	99.5 <sup>c</sup>	87 <sup>a</sup>	0.601 <sup>a</sup>
Ethanol	78.5 <sup>c</sup>	78.2 <sup>a</sup>	0.096 <sup>a</sup>
Ethyl acetate	77.1 <sup>b</sup>	70.4 <sup>a</sup>	0.312 <sup>a</sup>
Isooctane	99.22 <sup>a</sup>	-	-
Methanol	65.0 <sup>c</sup>	-	-
1-propanol	97.4 <sup>c</sup>	-	-
2-propanol	82.4 <sup>c</sup>	-	-
Triethylamine	89 <sup>a</sup>	-	-

<sup>a</sup> (Lide, 1998)

<sup>b</sup> (Mackay, 2006)

<sup>c</sup> (Streitwieser et al., 1992)

**Table 2.7. VWR Solvent Prices**

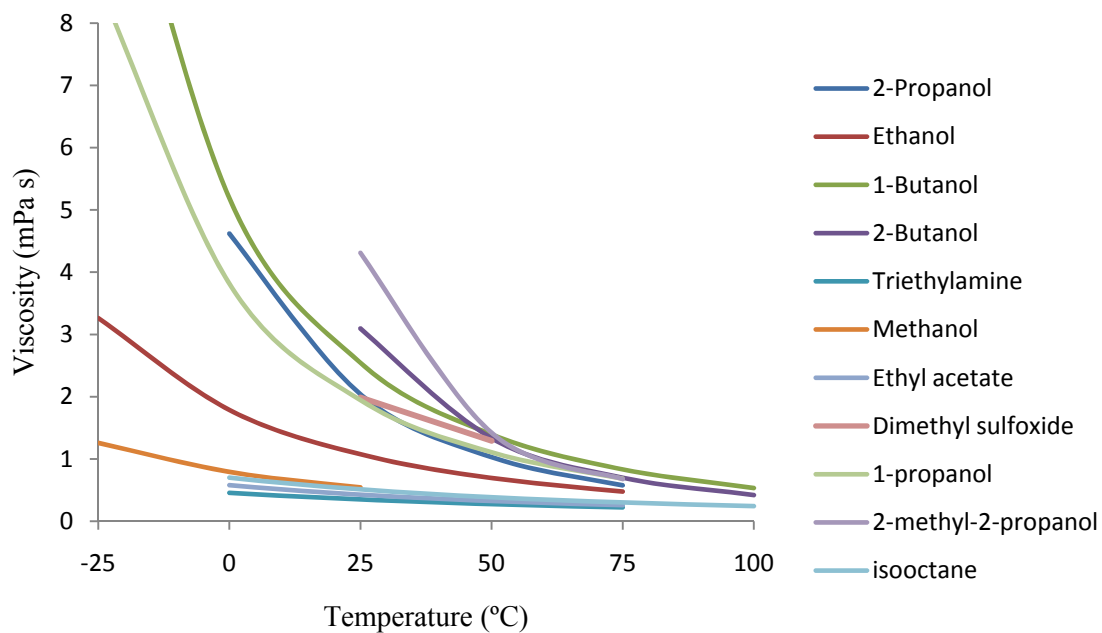
Solvent	Volume (L)	Unit Price (Canadian\$/L)
Methanol	19	3.81
2-Propanol, 99%	19	6.04
Ethanol, 95%	19	8.28
2-Butanol	208	10.35
Triethylamine	204	11.30
1-Propanol	19	13.19
1-Butanol	19	13.78
Ethyl Acetate	19	17.30
Isooctane	2.5	20.85

**Table 2.8. Glass Transition Temperatures**

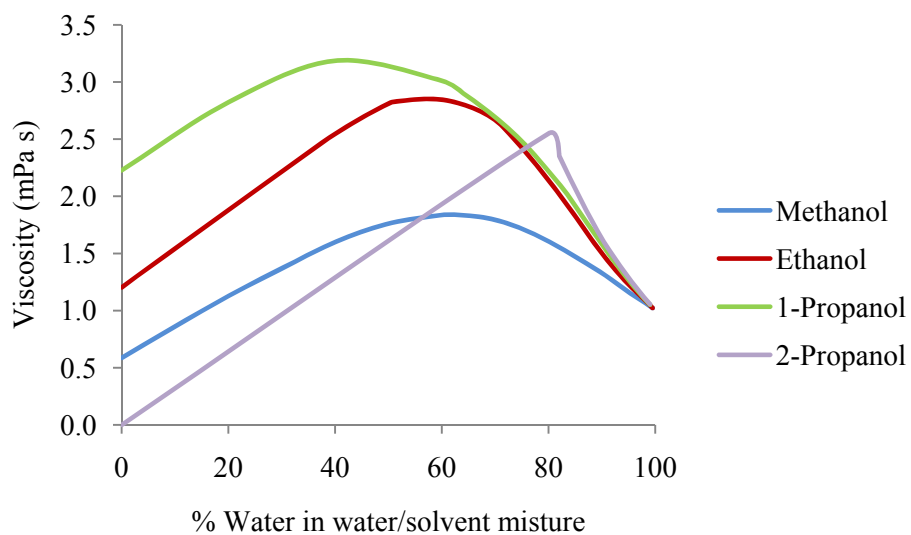
Fraction Organic Matter	Glass Transition Temp ( $T_g$ )
Lignins	68-83°C <sup>a</sup>
Coals	99-125°C, 307-359°C <sup>b</sup>

<sup>a</sup> (Kadla et al., 2002)

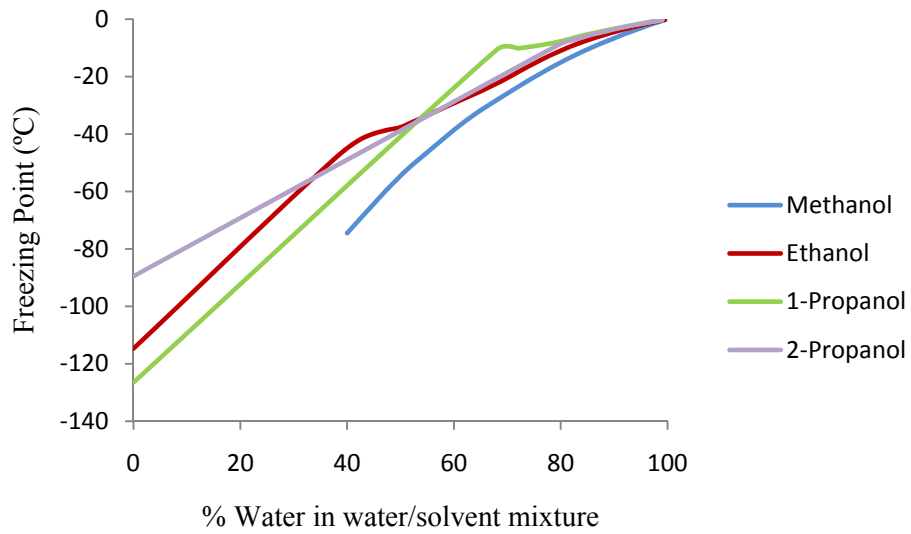
<sup>b</sup> (Lucht et al., 1987)



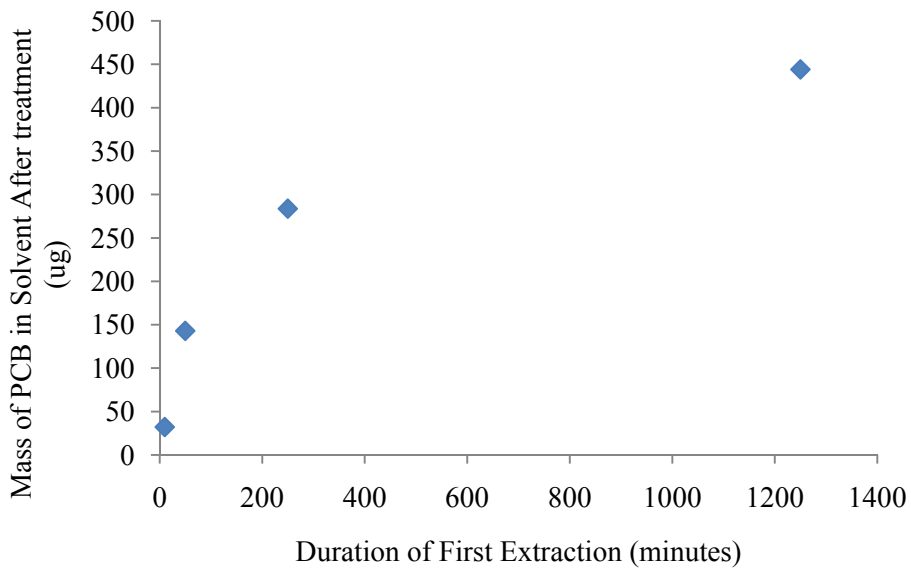
**Figure 2.1. Solvent viscosity versus temperature (Lide, 1998)**



**Figure 2.2. Solvent viscosity versus percent solvent mass (Lide, 1998)**



**Figure 2.3. Solvent freezing points versus percent solvent mass (Lide, 1998)**



**Figure 2.4. PCB mass extracted with ethyl acetate over time (Valentin, 2000)**

## **Chapter 3**

### **Methods & Materials**

#### **3.1 Experimental Design**

To meet the objectives of this research, the impact of elevated moisture contents and low temperature on extraction efficiency was determined through a series of screening experiments using polar and non-polar solvents at both 20°C and 4°C. It was hypothesized that improved extractions may be possible with combinations of polar and non-polar solvents. Based on the results of these screening experiments, a factorial experiment was designed using solvent combinations to further assess the role of moisture contents and low temperatures. The role of PCB mass distribution among grain sizes was also evaluated to see if optimization based on grain size separation is possible. Finally, experiments were performed to generate data suitable for the development of a kinetic model that incorporates key factors affecting solvent extraction.

##### **3.1.1 Single Solvent Screening Experiments**

Screening experiments were conducted to evaluate how extraction efficiency was dependent on the soil moisture content. Fifteen grams of PCB contaminated air dried soil was added to 40 mL EPA reactors and the moisture content was adjusted in each vial using Milli-Q water to either 0%, 5%, 10%, 15% or 20% w/w. After 24 hours, 15 mL of solvent was added to each reactor and the reactors were placed on a mixer (30 RPM) for 24 hours. This 1g soil:1mL solvent ratio was comparable to that used by Jakher et al. (2007). Following extraction, the reactors were centrifuged (1800 RPM, 5 min) and the solvent decanted. The decanted solvent and the soil were then analyzed for PCB concentration.

Isopropyl alcohol (polar), ethanol (polar), isooctane (non-polar) and triethylamine (non-polar) were utilized as solvents based on the review discussed in Chapter 2. To evaluate the impact of low temperatures on solvent extraction, extractions were also repeated at 4°C for the polar solvents (isopropyl alcohol and ethanol). The air dried soil had a residual moisture content (w/w) of 0.41 to 0.95% before the moisture content was adjusted (ASTM International, 2007). For simplicity this residual moisture content is neglected in the following discussion.

### **3.1.2 Solvent Combination Experiments**

A 2<sup>4</sup> factorial experiment (Johnson, 2000) was performed to evaluate combinations of both polar and non-polar solvents at both high and low moisture contents. The factors investigated were choice of polar solvent, choice of non-polar solvent, moisture content and temperature.

Reactors consisted of 40 mL EPA vials with 15 g of air-dried PCB contaminated soil, Milli-Q water added to the desired moisture content, 7.5 mL of polar and 7.5 mL of non-polar solvents. The reactors were mixed (30 RPM) for 24 hours before centrifugation (1800 RPM, 5 min) and decanting the solvent. The polar and non-polar solvents were the same as those used in the screening experiments.

The decanted solvent and soil were analyzed for PCB concentration. During the factorial experiments the solvents became separated in the reactors containing ethanol and isooctane at both the 5% and the 20% moisture content, as well as in the reactors containing isopropyl alcohol and isooctane at the 20% moisture content only (Figure 3.1 (a)). For these reactors, both layers of the decanted solvent were analyzed for PCB mass separately and then summed. The volume of each layer was estimated using digital images of the reactors and a ruler. It was assumed that the complete top layer was decanted following centrifugation and available for analysis and that only a portion of the bottom layer was lost during transfer. The controls next to the samples in Figure 3.1(b) contain 15 mL of solvent and were employed to determine a height per volume conversion.

### **3.1.3 PCB Mass Distribution**

Varying grain sizes were analyzed for PCB concentration. This analysis permitted an appraisal of PCB mass distribution throughout the grain sizes. The analysis also aimed to relate PCB mass distribution to organic content, determined using ASTM D2974-07a (ASTM International, 2007), and fractional organic carbon (Churcher and Dickhout, 1987) as literature has indicated that these are good tools for identifying where PCB mass resides (Allen-King et al., 2002). PCB concentration was reported per mass of air dried sample instead of mass of dry sample as not enough sample remained to determine the residual moisture content of each grain size grouping. The grain sizes examined are listed in Table 3.1. There was not enough Dixie0707 soil available to create the same grain size groupings as with the Dixie0208 soil.

### **3.1.4 Kinetic Experiments**

Experiments were conducted to observe extraction kinetics. The rate of PCB mass removal from soils using solvents is not well understood. The aim of these experiments was to collect significant data to develop a kinetic model for predicting solvent extraction rates during field applications. These experiments were performed using isopropyl alcohol, varying one parameter known to influence solvent extraction rate at a time. The initial experiment assessed PCB mass extracted after 1, 3, 6, 24 and 48 hours respectively. Most of the extraction occurred in the first hours, so subsequent experiments focused on collecting more early time data (0.5, 1, 3 and 3 hours). Thus PCB mass was extracted until 24 hours only. All reactors consisted of 40 mL EPA vials containing 15 g of air-dried PCB contaminated soil. Other design details for the experiments are shown in Table 3.2.

### **3.2 PCB Sample Origin**

Past research has demonstrated that weathered PCB contamination is more difficult to remove than synthetically prepared samples. Thus contaminated field samples from Southern Ontario, Canada were employed. Two soil samples of approximately 10 kg were collected from stock piles on site. Each was homogenized upon arrival at the lab. The first soil sample was collected in July 2007 and labeled Dixie0707. The second was gathered in February 2008 and labeled Dixie0208. The Dixie0707 soil was used for preliminary analysis while the Dixie0208 soil was utilized for the majority of the experimental work in this research.

Grain size analysis allowed the classification of Dixie0707 soil as a silty or clayey sand according to the British Soil Classification System and the Unified Soil Classification System (Craig, 2002) (Figure 3.2 (a)). Dixie0208 soil was classified as a very silty or very clayey sand by the British Soil Classification System or as a silty or clayey sand according to the Unified Soil Classification System (Craig, 2002) (Figure 3.2 (b)).

All experiments used grain sizes less than 2.00 mm to ensure homogeneity among smaller samples sizes unless otherwise specified. The specific gravity of the soil <2.00 mm was measured to be 2.68 g/cm<sup>3</sup>. Assuming a bulk density of 1950 kg/m<sup>3</sup> (that of a well graded sand) then water saturation is reached at a moisture content of 28.6% by weight.



### 3.3 PCB Analysis Procedures

#### 3.3.1 Soil Extraction Methods

Soxhlet extraction (EPA Method 3540C) is the most reliable method for PCB removal from solids. Unfortunately it is extremely time consuming requiring 16-34 hours per extraction (EPA, 1996a). There are other problems associated with this method, including the risk of fire from unattended samples. Soxhlet extraction was not selected as a result. Four other EPA methods were considered for PCB extraction for quantification prior to selecting a suitable method (Table 3.3) (EPA, 2007a). These methods were for semi volatile and nonvolatile organics.

Ultrasonic extraction (EPA Method 3550C) was appealing as it is employed by analytical labs such as Maxxam Analytics in Mississauga, Ontario (Gripton, 2007). However, inquiries made to the US EPA revealed problems with using this method for the soil type under consideration (Tisa, 2007). Other US EPA methods were also eliminated based on the recommended concentration range, such as EPA Methods 3541 and 3580 (Table 3.3).

Donnelly et al. (1996) evaluated PCB extraction using Soxhlet and the Dionex ASE ® 200 Accelerated Solvent Extractor (ASE200) (EPA Method 3545) and determined that both methods produced high and reproducible recoveries. The ASE200 also used less solvent (Donnelly et al., 1996). Furthermore, ASE200 holding times of 5 and 10 minutes produced the same outcome (Donnelly et al., 1996). Although the concentration span identified by EPA Method 3545 did not span the expected concentration of the samples (Table 3.3), the method appeared the most applicable due to its simplicity and speed.

The ability of the ASE200 to extract higher PCB concentrations than those specified in EPA Method 3545 was assessed by comparing soil extractions from the ASE200 and Soxhlet (Table 3.4). Using the ASE200, extractions were conducted on three sample sizes, including both larger and smaller sample sizes than the 15 g of soil typically used. Although PCB concentrations differed considerably depending on whether or not spike recovery (to be discussed in section 3.4) was applied (Table 3.4), neither data reported statistically significant higher PCB concentrations with the Soxhlet method than with the ASE200. As a result, EPA Method 3545 was deemed effective at extracting PCB mass from the soil used in this research.

### **3.3.2 Analytical Soil Extraction**

PCB mass was removed from soil samples using the ASE200 in accordance with EPA Method 3545A (EPA, 2000a). Contaminated soil was packed into 33 mL stainless steel cells with Ottawa sand to fill any remaining space in the cells. Glass fiber filters were positioned at both ends. HPLC grade hexane and acetone were flushed through the cells in a 1:1 ratio (v/v). PCB mass was transferred into the solvent from the soil under high temperatures and pressure, and collected into 60 mL EPA vials. The solvent extract was then reduced to approximately 1 mL with the Dionex SE500 Solvent Evaporator (SE500). The SE500 employed nitrogen gas at low pressure, approximately 5-20 kPa, a swirling motion, and upper and lower heated blocks set to 25°C.

### **3.3.3 Sample Clean-Up**

The majority of PCB samples underwent sample cleanup prior to being run on the gas chromatograph. Florisil cleanup was implemented with hopes that it would prolong the life of the gas chromatograph column and detector as well as provide more accurate PCB concentration measurements. The reduced solvent extract was passed through Florisil and sodium sulphate to remove chlorinated hydrocarbons and pesticide residues, and water respectively. The extract was diluted with HPLC grade hexane in the process. This procedure was comparable to the EPA Method 3620C (EPA, 2000b) column method and the approach employed by the Ontario Ministry of the Environment (MOE) labs for PCB sample preparation (Ontario Ministry of the Environment, 2006). A simple comparison was done at the beginning of the study to assess whether Florisil cleanup was required for the samples. No interference was visually observed in samples not having undergone Florisil cleanup, however, the cleanup was thought to prolong the life of the gas chromatograph electron capture detector. The MOE PCB lab in Toronto, Ontario uses Florisil cleanup for their PCB samples.

Similarly, sulphuric acid and permanganate cleanups were assessed at the beginning of the study in accordance with EPA Method 3665A (EPA, 1996b). As with the samples having undergone Florisil cleanup, no interferences were visually observed in the gas chromatographs not having undergone cleanup. Thus these additional sample clean-up steps were not used.

Copper was used to remove sulphur interference and is employed by the MOE lab (Ontario Ministry of the Environment, 2006). A known mass of copper was placed in the volumetric flasks used to collect the sample after it had passed through the Florisil and sodium sulphate.

### **3.3.4 Gas Chromatograph Analysis**

A Hewlett Packard G1530A gas chromatograph (GC) with an electron capture detector and Equity-1701 column from Sigma Aldrich Canada was used to quantify the PCB mass in samples. A 1-2  $\mu\text{L}$  aliquot of PCB sample in hexane was injected into the GC where the congeners eluted at different retention times depending on their mass. The types of Aroclors present in a sample were identified by studying the pattern of chromatograph peaks and comparing them to the pattern of peaks from Aroclor standards.

Although all common Aroclor standards were run on the GC with each sample set, only calibration curves for the Aroclor known to be in the soil sample were created following its identification. The Aroclor standards runs were prepared from more concentrated solutions or pure PCB obtained from Sigma Aldrich Canada (Catalogue numbers: 48589, 48318, 90129R, 48591, 48588, 48586, 442463, and 48585). Multiple calibration curves were created by plotting peak area versus concentration for many of the characteristic peaks as described by EPA Method 8000 and EPA Method 8082 (EPA, 1996c; EPA, 1996d). The reported sample concentration is the mean concentration determined from multiple peaks. Many samples were diluted so they fell within the calibration curve range prior to GC analysis. As the samples injected into the GC were in hexane, the PCB concentration determined from the calibration curves were in terms of mass per volume and were manipulated into concentrations in terms of PCB mass per mass of dry soil.

Details of the GC settings are provided in Table 3.5. It should be noted that a longer final holding time was used than was recommended by EPA Method 8082 due to preliminary analysis which found carryover between samples. A 1:10 split injection was used.

The data presented in Chapter 4 represent the mean concentration of three replicate reactors along with plus/minus one standard deviation between the triplicates. Two tailed t-tests evaluated the statistical difference between the means at the 10% level of significance. Statistical outliers were removed using Chauvenet's Criterion (Kennedy and Neville, 1976). The data collected in the factorial experiments underwent an analysis of variance (ANOVA).

### **3.3.5 Comparisons with Accredited Laboratories**

Homogenized Dixie0208 air-dried soil samples (<2.00 mm grain size) were submitted to Maxxam Analytics (Maxxam), ALS Laboratory Group (ALS) and the Ontario Ministry of the Environment

(MOE) for PCB concentration analysis as Aroclors (Table 3.6). The samples were submitted to establish an accepted PCB concentration in the soil.

PCBs in hexane from extracting PCB mass from soil samples with the ASE200 was also submitted to ALS and MOE to test for potential differences in the effectiveness of PCB extraction methods. Results from the submitted PCB extract in hexane were converted from  $\mu\text{g/L}$  to  $\mu\text{g/g}$  to allow for direct comparison with soil sample results (Table 3.7).

All three accredited laboratories reported different Aroclors for both the soil samples as well as the PCB extracts submitted (Table 3.6 and Table 3.7). In addition, the concentrations varied greatly between the various laboratories. Contaminated Dixie0707 soil submitted to Maxxam had been reported as Aroclor 1260, whereas the Dixie0208 soil was reported as Aroclor 1248. Although it is possible to have different types of PCB contamination on a given site, it was expected that the Dixie0707 and Dixie0208 soil samples would contain the same Aroclor type as the samples were taken from the same site. The PCB concentrations in the soil as determined from the submitted soil were  $925 \pm 100 \mu\text{g/g}$  (ALS),  $637 \pm 164 \mu\text{g/g}$  (MOE), and  $320 \pm 26 \mu\text{g/g}$  (Maxxam). The submitted solvent samples resulted in lower concentrations than the soil samples;  $745 \pm 70 \mu\text{g/g}$  (ALS) and  $555 \pm 59 \mu\text{g/g}$  (MOE).

The Dixie0208 soil was analyzed as both Aroclor 1248 and 1242 and compared with the reported concentrations from the accredited labs (Table 3.6). The internal and accredited laboratory analysis showed that the reported concentration depended on the Aroclor identified. Triplicates of sieved air-dried soil analyzed as Aroclor 1248 were most similar to the concentrations reported by MOE at  $606 \pm 28 \mu\text{g/g}$ , where as soil analyzed as Aroclor 1242 approximately one month later had concentrations most similar to those reported by ALS at  $1155 \pm 64 \mu\text{g/g}$ . It was decided that the Dixie0707 and Dixie0208 soil should be consistently analyzed only for Aroclor 1248 over the course of the study to allow for direct comparisons between experiments.

### **3.4 QA/QC**

Decanted solvent and soil samples were spiked with a known volume and concentration of decachlorobiphenyl (DCB) to check for recovery as recommended in EPA Methods 8000 and 8082 (EPA, 1996c; EPA, 1996d). Decachlorobiphenyl is the heaviest of the 209 congeners and has the longest retention time on the gas chromatograph, allowing it to be easily distinguished from the

common Aroclors and congeners. At times the DCB recovery was very poor and/or varied widely between samples (Table 3.8).

Experimental data was corrected for recovery prior to data analysis. The DCB recovery was not applied to the data from the experimental extraction done with isooctane at 20°C since the DCB calibration curve was poor and the recovery was in all cases over 1000%. Where DCB recovery changed the outcome, both uncorrected data and data corrected for DCB recovery are presented. In addition to spiking each sample with DCB, clean solvents were set up as controls as a check that no PCB mass was introduced through the solvents used or transferred from vial to vial over the course of the experiment.

**Table 3.1. Grain Sizes Assessed for PCB Mass Distribution**

Soil ID	Grain Size (mm)	Sieve Number
Dixie0208	<0.425	Passing 40
	0.425 – 0.85	Retained on 40
	0.85 – 2.00	Retained on 20
	2.00 – 4.75	Retained on 10
	> 4.75	Retained on 4
Dixie0707	0.075 – 0.25	Retained on 200
	0.25 – 2.00	Retained on 60
	2.00 – 19.05	Retained on 10
	> 19.05	Retained on ½ inch

**Table 3.2. Kinetic Experiment Design**

Parameters	Experiment 1	Experiment 2	Experiment 3
Soil:Solvent ratio (g:mL)	1:1	1:0.75	1:1
Temperature (°C)	20	20	4
Grain size (mm)	<2.00	<2.00	<2.00
Moisture Content (%wt)	5	5	5

**Table 3.3. EPA Methods Considered for PCB Extraction for Quantification Purposes**

Method No.	Extraction Type	Concentration Range (µg/g)	Notes
3540C	Soxhlet Extraction	None listed	Lengthy extraction: 16-24 hrs (EPA, 1996a) The typical method used (Tisa, 2007)
3541	Automated Soxhlet Extraction	1-50	Shorter extraction time than Method 3540C (EPA, 1994)
3550C	Ultrasonic Extraction	Low concentration method: ≤20  Medium/high concentration method: >20	Not recommended for PCB extraction and considered less efficient than the other methods (EPA, 2007a) “May not be as rigorous” as the other methods (EPA, 2007b) Advised against its use for fine-grain sandy soils (Tisa, 2007) Many states are no longer allowing this method for extraction of PCBs in their QAPP programs (Tisa, 2007)
3580	Solvent Dilution	> 20 000	Advised against its use for fine-grain sandy soils (Tisa, 2007)
3545A	Pressurized Fluid Extraction (ASE) (Heat & Pressure)	0.001 – 1.400	It may be applicable to samples containing higher concentrations than specified range (EPA, 2000a)  For lower concentration, sandy soils, the method may work fine (Tisa, 2007)

**Table 3.4. Comparisons between analytical soil extraction methods**

Analytical Extraction Method	Sample Size (g)	PCB Concentration ( $\mu\text{g/g}$ )	
		Corrected for spike	No spike correction
Soxhlet	10	$577 \pm 27$	$827 \pm 29$
ASE200	30	$706 \pm 63$	$887 \pm 168$
	15	$2557 \pm 1748$	$803 \pm 77$
	7.5	$3012 \pm 1385$	$986 \pm 171$

$\pm$  Standard deviation

**Table 3.5. Gas Chromatograph Settings (Adapted from EPA Method 8082 Table 2)**

Parameter	Recommended Setting (EPA, 1996d)	Setting Used
Carrier Gas (Helium)	5-7 mL/min	4.4 mL/min
Makeup Gas (Nitrogen)	30 mL/min	30 mL/min
Injector Temperature	250°C	250°C
Detector Temperature	290°C	290°C
Initial Temperature	150°C, hold 0.5 min	150 °C, hold 0.5 min
Temperature Program	150°C to 270°C at 5°C/min	150°C to 270°C at 5°C/min
Final Temperature	270°C, hold 10 min	270°C, hold 15.5 to 25.5 min
Injection Volume	2 $\mu\text{L}$	1-2 $\mu\text{L}$



**Table 3.6. PCB Concentrations in Soil Reported by Various Laboratories**

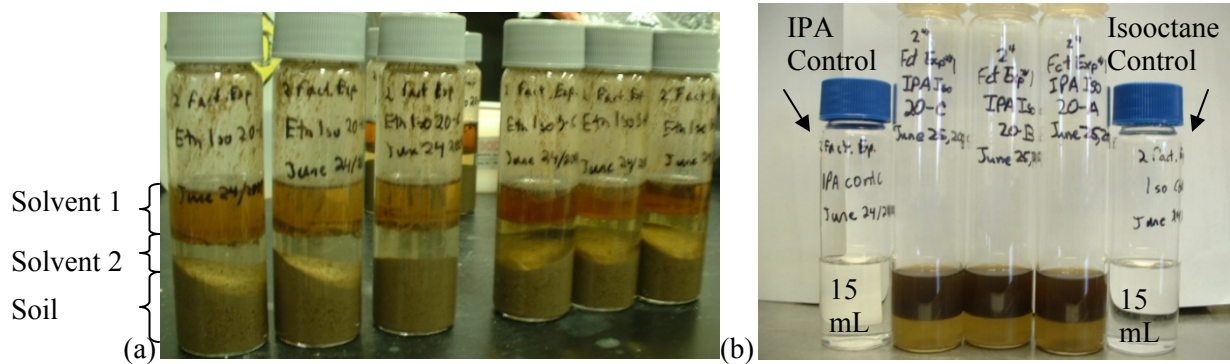
Laboratory	Aroclor	Replicate PCB Concentrations ( $\mu\text{g/g}$ )
ALS	1242	950, 815, 1010
MOE	1248, 1254, 1260	332, 830, 676, 658, 656, 672
Maxxam	1248	290, 340, 330
UW	1248	629, 575, 615
UW	1242	1150, 1094, 1222

**Table 3.7. PCB Concentrations in Hexane Reported by Accredited Laboratories**

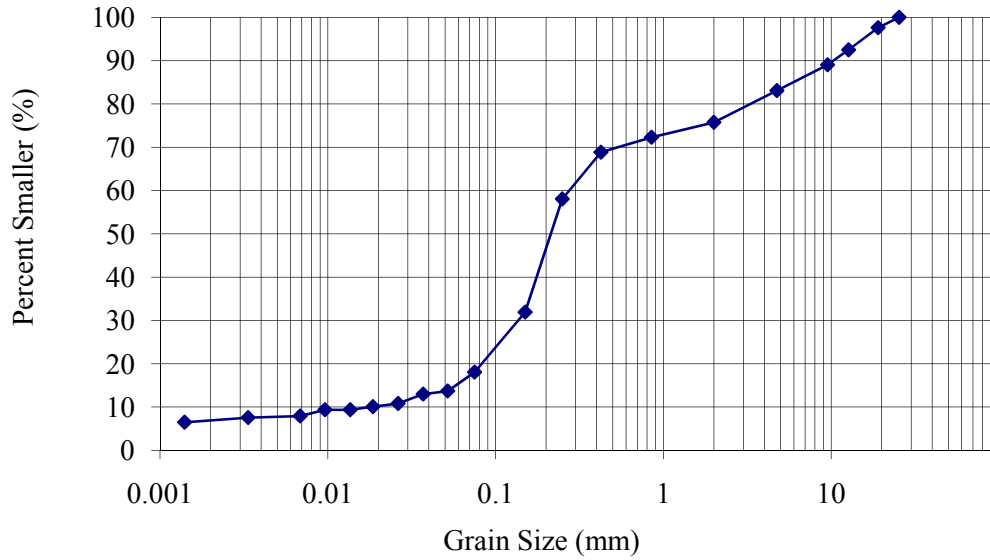
Laboratory	Aroclor	Triplicate PCB Concentrations ( $\mu\text{g/g}$ )
ALS	1242	822, 685, 728
MOE	1248, 1254, 1260	610, 562, 492

**Table 3.8. DCB Recovery for each experiment**

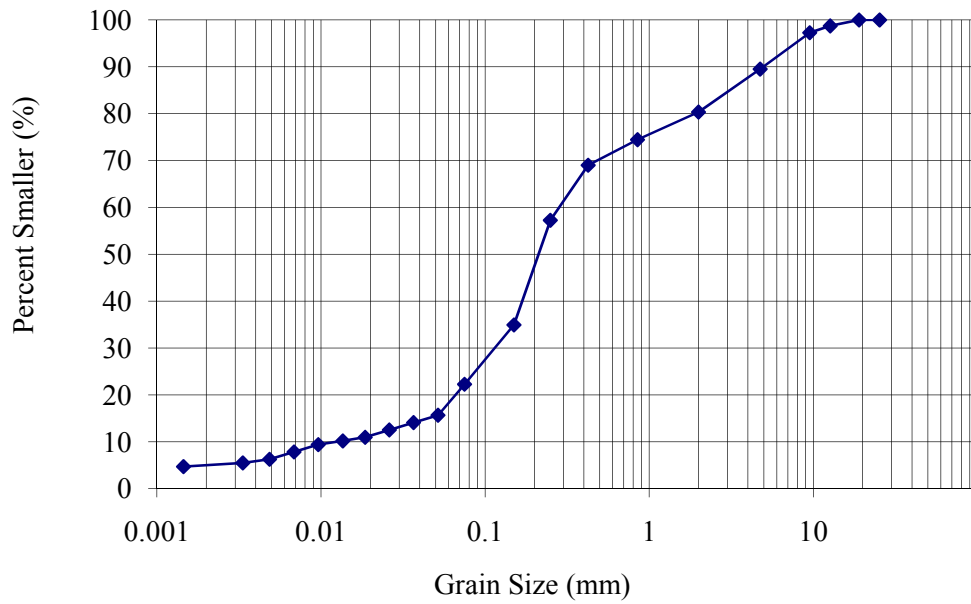
Solvent or Experiment	Temperature	Matrix	Min Recovery (%)	Max Recovery (%)
Isopropyl Alcohol	20°C	Decant	94	126
Isopropyl Alcohol	20°C	Soil	50	123
Isopropyl Alcohol	4°C	Decant	65	70
Isopropyl Alcohol	4°C	Soil	85	107
Ethanol	20°C	Decant	87	234
Ethanol	20°C	Soil	39	238
Ethanol	4°C	Decant	108	112
Ethanol	4°C	Soil	93	103
Isooctane	20°C	Decant	1989	2477
Isooctane	20°C	Soil	1080	2027
Triethylamine	20°C	Decant	98	120
Triethylamine	20°C	Soil	67	108
2 <sup>3</sup> Factorial	20°C	Decant	102	117
2 <sup>3</sup> Factorial	20°C	Soil	63	148
2 <sup>3</sup> Factorial	4°C	Decant	99	111
2 <sup>3</sup> Factorial	4°C	Soil	100	118
PCB Distribution– Dixie0208		Soil/ Rocks	29	137
PCB Distribution-Dixie0208 repeat		Soil/ Rocks	74	194
PCB Distribution– Dixie0707		Soil/ Rocks	68	160



**Figure 3.1. (a) Images of ethanol and isooctane reactors following 24hr extraction, (b) Image of reactors used to determine volume of solvent layers (isopropyl alcohol and isooctane at 20% moisture content)**



(a)



(b)

**Figure 3.2. Grain Size Analysis of (a) Dixie0707 Soil and (b) Dixie0208 Soil**

## Chapter 4

### Results and Discussion

Chapter 4 discusses mass balance considerations, presents the results from the screening and factorial experiments, and discusses the effects of moisture content, solvent choice, temperature, and grain size on PCB extraction. A kinetic model is presented based on the results from the kinetic experiments.

#### 4.1 Mass Balance Considerations

The initial mass of PCBs in the soil prior to the experimental extractions was assumed equal to the PCB mass in the controls, however the soil sample used was a natural weathered sample and was difficult to effectively homogenize as shown by the variability between replicates (Table 3.6 and Table 3.7). Therefore the initial concentrations in some of the test reactors may have been greater than in the controls. The data collected indicate that the sum of the mass of PCBs extracted by solvent and the mass of PCBs remaining in the soil following the experimental extraction was greater than the mass in the controls (Table 4.1). The inability to close the mass balance is likely due to a combination of factors.

The PCB concentration remaining in the soil may be overestimated as not all the solvent containing PCB mass is removed from the soil when it is decanted following an experimental extraction. For example, in the 20°C factorial experiment, 28 to 36% of the initial total weight of liquid remained in the soil after the solvent was decanted. This is typical for all the experiments. Subtracting the mass of PCBs in the solvent remaining in the soil from the mass of PCBs determined to be in the soil often leads to a negative value. Some of this solvent containing PCB mass is removed from the soil during preparation for extraction with the ASE200 but it is difficult to quantify.

It is possible that a more complete extraction may occur using the ASE200 following an experimental solvent extraction than without it (as was the case with the controls), contributing to the presence of more mass in the two phases (solvent and soil) following the experimental extraction than determined in the controls. The experimental extraction may act as a type of pre-treatment allowing for a more complete extraction when the soil is then put through a second extraction using the ASE200.

Different solvents may preferentially extract certain congeners. No preferential extraction was visually noted from examining the gas chromatographs but analyzing the samples in terms of Aroclors instead of congeners may be overestimating the total PCB concentration in the sample.

As there is more uncertainty associated with the PCB mass in the remaining soil, the decanted solvent data is considered more accurate. The soil data is presented for completeness.

## **4.2 Moisture Content Effects on Solvent Extraction**

### **4.2.1 Polar Solvents: At Room Temperature**

The decanted solvent data indicated that the best extraction with isopropyl alcohol at 20°C was achieved at 5% moisture content (Figure 4.1(a)). However, the least PCB mass remained in the soil at the 20% moisture content, indicating a different optimal moisture content (Figure 4.1 (b)). Since the decanted solvent and soil data were contradicting and the optimal moisture content identified with either data set was not statistically significant, the experimental extraction using isopropyl alcohol at 20°C was repeated. The second set of extractions confirmed the optimal extraction occurred at a moisture content around 5% (Table 4.2 and Figure 4.1(c)). A DCB spike was not added so these data were not corrected for DCB recovery.

The optimal extractions using ethanol at 20°C occurred at 5% or 15%, depending on whether or not the data were corrected for DCB recovery (Table 4.2). With the corrections applied, the optimal extraction occurred at 5% moisture consistent with isopropyl alcohol (Figure 4.2 (a)). When the data was not corrected for DCB recovery, the optimal extraction occurred at 15% moisture content (Figure 4.2(b)). The DCB corrected data showed that the lowest PCB concentration remained in the soil at 20% moisture content (Figure 4.2 (c)), and the lowest PCB concentration remained in the soil at the 0% moisture content when the uncorrected data were examined (Figure 4.2 (d)). The data presented for ethanol is inconclusive and the optimum depends on whether DCB correction is applied or not. Also, the soil data does not support the findings based on the decanted solvent data.

Isopropyl alcohol extracted 70 to 78% of the PCB mass at 20°C with the highest percent mass extracted at 20% moisture content and the lowest at 0% moisture content (Figure 4.3). However, none of PCB percent mass extracted were statistically different from one another for the range of moisture contents explored. Ethanol extracted 61 to 71% of the PCB mass at 20°C, and similarly to isopropyl alcohol, the highest extraction occurred at the 20% moisture content, however only the percent mass

extracted at the 0% and 20% moisture contents were statistically different from one another (Figure 4.3).

The 0% moisture content isopropyl alcohol reactors were cloudier than the others (Figure 4.4 (a)). This was again observed when the experiment was repeated with the same conditions, however the 5% moisture content reactors, were also much darker than the rest of the reactors the second time (Figure 4.4(b)). The darker and cloudier colour could be from the extraction of organic matter since organic matter is responsible for the dark colour in many soils (Stevenson, 1982). The 0% moisture content ethanol reactors were opaque and dark in colour (Figure 4.5 (a)).

#### **4.2.2 Polar Solvents: At Lower Temperatures**

The decanted solvent from the experimental extraction with isopropyl alcohol at 4°C showed the extraction efficiency increasing as the moisture content increased until the optimal extraction at moisture content of 15% (Figure 4.1(d)). The soil at 15% moisture content had more PCB mass remaining in it than at 20% moisture content, contradicting the decanted solvent data. The concentrations at 15% and 20% moisture content were statistically different (Table 4.2).

The optimal extraction using ethanol at 4°C occurred at 5% moisture content as indicated by the decanted solvent data (Figure 4.2(e)). In general, where the decanted solvent indicated higher PCB concentrations (Figure 4.2 (e)), lower PCB concentrations remained in the soil (Figure 4.2 (f)). This result was expected given the assumption that the initial PCB concentration in the soil samples was uniform.

The average percent of PCBs removed with isopropyl alcohol at 4°C ranged from 73 to 83 %, with the highest percentage removed at both the 15% and 20% moisture contents (Figure 4.6 (a)). The greatest percent extraction with ethanol at 4°C was 84% and occurred at a moisture content of 0% (Figure 4.6 (b)).

The trend observed at 4°C with isopropyl alcohol was different from that observed during the 20°C experiments where the optimal extraction occurred at lower moisture content. The optimal moisture content was consistent between both 4°C and 20°C for the decanted ethanol data using the DCB corrected data at 20°C (Table 4.2).

The reactors from the extraction at 4°C with isopropyl alcohol and with ethanol appeared similar to those at 20°C. The 5% moisture content isopropyl alcohol reactors were darker and cloudier than the

others at 4°C like the repeat extraction at 20°C (Figure 4.4 (b), (c) and (d)). The darkest and most opaque ethanol reactors at 4°C corresponded with 0% moisture content; however, the 5% moisture content reactors were not as dark as compared to the extractions performed at 20°C (Figure 4.5 (b)). The dark colour extracted at 5% moisture content with isopropyl alcohol and at 0% moisture content with ethanol was present regardless of temperature.

#### **4.2.3 Non-polar solvents: At Room Temperature**

It was hypothesized that increased water content would hinder the extraction with non-polar solvents giving optimum moisture content at 0%. The decanted isooctane indicated that the best extraction achieved with isooctane was at the lowest (0%) and highest (20%) moisture contents (Figure 4.7 (a)). Both these means were not statistically different from one another (Table 4.3). The residual PCB data from the isooctane soil extraction showed the lowest amount of PCBs remaining in the soil at the 0% moisture content (Figure 4.7(c)), suggesting that the highest extraction with isooctane did indeed occur at 0% moisture content. Neither the decanted isooctane data nor the isooctane soil data has been corrected for DCB recovery since the DCB calibration curve was not usable for this experiment.

The decanted triethylamine data indicated that the amount of PCBs extracted increased as moisture content increased and the best extraction was achieved at the highest (20%) moisture content (Table 4.3 and Figure 4.7 (b)). The soil data from the triethylamine extraction supports the decanted triethylamine results and indicates that the highest mass of PCBs remained in the soil with 0% moisture content and the lowest remained in the soil with 20% moisture content (Table 4.3 and Figure 4.7 (d)).

The percent of PCB mass extracted ranged from 66 to 84% with isooctane, with the highest extraction efficiency corresponding with the extraction at 0% moisture content (Figure 4.8 (a)), and from 81 to 90% with triethylamine (Figure 4.7 (d)).

The two non-polar solvents, both clear initially, changed appearance during these extractions. Unlike the polar solvents, isooctane became increasingly darker as the moisture content in the reactors increased (Figure 4.9 (a)). The decanted triethylamine was consistently very dark except for the 0% moisture content reactors, where the least mass of PCBs was extracted (Figure 4.9 (b)).



The decanted triethylamine data contradicted the hypothesis. The different optimal moisture contents between the two non-polar solvents studied suggests that the optimal moisture content is not dictated strictly by polarity, and so no general conclusions can be drawn about non-polar solvents.

### 4.3 Solvent Combination Experiment

The conditions for the optimal extractions were the same at both 4°C and 20°C. The decanted solvent data indicated the best PCB extraction was achieved at 20% moisture content using ethanol and triethylamine in combination (Figure 4.10(a) and (b)). At 4°C, the optimal extraction was not statistically different from that with isopropyl alcohol and triethylamine at 5% moisture content. The soil data contradicted the decanted solvent data, except for the ethanol and isooctane combinations (Figure 4.10(c) and (d)).

The extraction efficiencies were above 80% for all solvent and moisture combinations at 20°C and 4°C except for the ethanol and isooctane combination at 5% moisture content (Figure 4.11). The percent PCB mass extracted showed the best extraction at 4°C was achieved with the isooctane and ethanol combination at 20% moisture content, which differs from the result obtained by looking at the decanted solvent data only.

When isopropyl alcohol was used in combination with either non-polar solvent, more PCB mass was extracted at 5% than at 20% moisture content (statistically significant with triethylamine at 20°C, and statistically significant with isooctane at 4°C). The reverse was true when ethanol was used in combination with either non-polar solvent (statistically significant in all scenarios).

The optimal moisture content when ethanol was used in combination with a non-polar solvent was the opposite of what was observed when ethanol was used on its own (Figure 4.2 (e)), but the same as triethylamine on its own (Figure 4.7 (b)). It appears that triethylamine has the stronger influence when ethanol and triethylamine are used in combination.

At 4°C, the combinations which included triethylamine in general outperformed those using isooctane. This observation was statistically significant except among the mean concentrations extracted at 5% moisture content using isooctane and isopropyl together, and using triethylamine and ethanol together. At 20°C, triethylamine outperformed isooctane when it was used in combination with the same polar solvent at the same moisture content except with isopropyl alcohol at 5% moisture content, where the isooctane and isopropyl alcohol combination at 5% moisture content

significantly extracted more than triethylamine and isopropyl alcohol together at 5% moisture content.

#### **4.3.1 ANOVA Results for 2<sup>4</sup> Factorial Experiment**

When an ANOVA was performed on the 4°C and 20°C decanted solvent data treated as one 2<sup>4</sup> factorial experiment, the choice of polar solvent, the choice of non-polar solvent and temperature were identified as significant main effects. The significant interactions were between choice of polar solvent and choice of non-polar solvent, and between moisture content and choice of polar solvent (Table 4.4).

All the main effects were significant when the ANOVA was performed on the percent removed data (Table 4.5). Five interactions were significant: between choice of polar solvent and choice of non-polar solvent, between choice of polar solvent and temperature, between choice of polar solvent and moisture content, between choice of non-polar solvent and moisture content, and between choice of polar solvent, choice of non-polar solvent and moisture content.

Different ANOVA outcomes should not appear whether the analysis is conducted on data from the decanted solvent or the percent removed. The difference lies with the PCB mass that remained in the soil following the experimental extraction, as the concentrations in the soil did not support the decanted solvent data and may be less reliable as discussed in Section 4.1. Table 4.4 should be considered more correct due to the errors involved in calculating the PCB concentration in the soil.

### **4.4 PCB Mass Distribution**

PCB mass distribution was assessed amongst grain sizes. This was done with both Dixie0208 and Dixie0707 soil.

#### **4.4.1 PCB Mass Distribution in Dixie0707 Soil**

PCB mass was not evenly distributed amongst the grains sizes in the Dixie0707 soil and the highest mean PCB concentration was found in the 2 – 19.05 mm grain size range (Figure 4.12 (a)). The darkest extract from the ASE200 extraction corresponded with this grain size range (Figure 4.13), suggesting that PCBs were found where the most organics resided.

#### 4.4.2 PCB Mass Distribution in Dixie0208 Soil

Like the Dixie0707 soil, PCB mass was not evenly distributed amongst all the grain sizes in the Dixie0208 soil. The highest mean PCB concentration was found in the smallest grain sizes (<0.425 mm) when DCB recovery was applied, but in the 0.85 – 2.0 mm grain size range without DCB recovery corrections (Table 4.6 and Figure 4.12(b) and (c)). The experiment was repeated, accidentally excluding grain sizes less than 0.425 mm (Figure 4.14 (a)). Similar to the first effort (Figure 4.12(b)), the highest mean PCB concentration in the range studied resided in the 0.85 -2 mm grain size range (Table 4.6 and Figure 4.12(c)). Unfortunately no conclusions could be drawn as to whether the highest PCB concentration was in the less than 0.425 mm grain size or the 0.425 – 0.85 grain size range. The results between the two soil types could not be directly compared as the 0.85 to 2.00 mm grain size range only accounted for 21% of the 0.25mm to 2mm grain size range analyzed in the Dixie0707 soil.

Although PCB mass was unevenly distributed, the congeners present in the Dixie0208 soil were evenly distributed amongst the grain sizes. This was determined by assessing pattern consistency between sample chromatographs and it appeared that each grain size had the same signature.

It was thought that the uneven distribution of PCB mass amongst grain sizes may be related to soil organics in the grain size groupings and so each grain size range was analyzed for ash content and therefore organic content (Figure 4.15 (a)). The mean organic content ranged between 1.5 and 2.8% by weight for the different grain sizes. The highest organic content corresponded with the 2.00 to 4.75 mm grain size range, and therefore not where the highest concentration of PCBs was found (with or without DCB recovery corrections). Although this result was not expected, the highest concentration of organic content also had the largest standard deviation (0.49%) and was not statistically different from that of the 0.85 to 2.00 mm grain size range which contained the highest concentration of PCBs without DCB recovery corrections. It is however statistically significant from the <0.425 mm grain size range which contained the highest concentration of PCBs with DCB recovery corrections applied.

In a further attempt to relate PCB mass distribution to organic content, the same grain sizes were analyzed for percent fraction organic carbon (FOC) by weight. The results showed the amount of organic carbon decreased as the grain sizes increased (Figure 4.15 (b)). The grain size where the highest concentration of PCBs was found did not correspond with the grain size with the highest

percent of fractional organic carbon. The total fraction organic carbon for the Dixie0208 soil was estimated to be 1.6% by weight based on the fractional organic carbon results of the grain size groupings and the results from the grain size analysis. While the FOC content did not correspond with PCB mass, the organic content results did.

As a final check, the PCB mass extracted from the grain size groupings was summed after accounting for the fraction that each grain size represented in the initial sample. The total PCB mass in the complete soil sample was  $16.4 \pm 4.0$  mg, ( $10.1 \pm 1.3$  mg without DCB recovery), and the total PCB mass in the  $<2.00$  mm grain size, the grain size used in all the screening and factorial experiments, was  $14.2 \pm 3.7$  mg, ( $8.5 \pm 1.0$  mg without DCB recovery). This is not too dissimilar from the PCB masses in the controls from the previous experiments however they do represent a large range (Table 4.1).

#### **4.5 Effects of Moisture Content, Solvent Choice, Temperature and Grain Size on PCB Extraction**

The solvent extractions conducted with polar solvents at 20°C are inconclusive due to the lack of a statistically significant difference and contradicting results whether DCB recovery was applied or not. The solvent extractions conducted with the polar solvents at 4°C are however more conclusive: Isopropyl alcohol achieved the best extraction at the highest moisture contents (15-20%) while ethanol had the best extractions at the lower moisture content (0-5%) (Table 4.2). The ANOVA on the solvent combination experiments confirmed there is interaction between moisture content (5% versus 20%) and choice of polar solvent (isopropyl alcohol versus ethanol). Ethanol and isopropyl alcohol consistently had opposing optimal moisture contents when in combination with a non-polar solvent at either 20°C or 4°C.

The unreliable DCB recovery values made numerical comparisons between the experiments untrustworthy so it was difficult to assess if either ethanol or isopropyl alcohol achieved better extractions. While the percent extracted showed that a better extraction was achieved with isopropyl alcohol at 20°C than with ethanol, and that similar percents were extracted with both solvents at 4°C, the values take into account the PCB concentration remaining in the soil which is unreliable as discussed in Section 4.1.

The solvent extractions at higher soil moisture contents (15-20%) were shown to be optimal when using triethylamine as the solvent (Table 4.3). Isooctane achieved optimal extractions at both the extreme moisture contents examined (0% and 20%). Triethylamine extracted a higher percentage of PCBs than isooctane and this observation was consistent with the solvent combination experiments at both 4°C and 20°C. The ANOVA analysis determined choice of non-polar solvent (triethylamine versus isooctane) to be significant.

Triethylamine performed best on its own rather than in combination with a polar solvent. The decanted data and the percent removed data supported this observation. The addition of a polar solvent was not required with elevated soil moisture contents when triethylamine was used, contrary to expectations. In addition, it was shown that elevated temperatures such as 55°C applied by B.E.S.T in their solvent extraction process is not required when using triethylamine to successfully extract PCB mass.

It was shown that moisture content does influence the PCB concentration extracted. As such, the moisture content in the field could be adjusted to achieve the optimal extraction given a particular solvent. Alternatively, a particular solvent could be selected based on the soil moisture content.

While the effect of temperature was shown to be significant, it did not influence the ideal moisture content for the solvent combination experiments. Although the optimal moisture contents for the extractions with single polar-solvents appeared influenced by temperature, there was insufficient statistically significant data to draw any conclusions.

Sorting PCB contaminated soil into grain sizes may be an efficient way to target PCB contamination as PCB mass was not evenly distributed amongst all grain sizes. The grain size with the highest PCB concentration appeared unrelated to the fraction of organic carbon as predicted, suggesting this was an insufficient tool for indicating where the highest PCB concentration resides. The large standard deviation associated with the organic carbon data made it difficult to accurately assess the relationship between PCB concentration and organic carbon.

## **4.6 Kinetic Experiments**

With all three kinetic experiments, the extracted PCB concentration had almost reached a plateau by the time of the first sampling event. This plateau differed between kinetic experiments partly as a

result of the experiments being conducted at different times. The extraction data from the kinetic experiments generally followed the two compartment model as described in Chapter 2 and given by:

(4-1)

$$C = x_1 C_{\max} (1 - e^{-k_1 t}) + (1 - x_1) C_{\max} (1 - e^{-k_2 t})$$

where  $C$  is the PCB concentration extracted in  $\mu\text{g/g}$ ,  $C_{\max}$  is the maximum extractable PCB concentration in  $\mu\text{g/g}$ ,  $t$  is the time in hours,  $x_1$  is the fraction of mass in the fast compartment,  $k_1$  is the extraction rate constant for the fast compartment and  $k_2$  is the extraction rate constant for the slow compartment. Examination of the kinetic data indicated that there was insufficient data to statistically capture the fast PCB extraction rate (Figure 4.16). In the first hour (the first or second sampling point), over 90% of the 24 hour extracted concentration was extracted under all three experimental conditions. As a result, the fast compartment extraction rate constant  $k_1$  and the product of  $x_1$  and  $C_{\max}$  were determined by considering the triplicate data at the first sampling time only (0.5 or 1 hr) and assuming the early time data could be approximated by only the first-term of equation (4-1).

The slow compartment rate parameter  $k_2$ ,  $C_{\max}$ , and subsequently  $x_1$  were determined by fitting equation (4-1) to the extracted PCB concentration data using the estimated  $k_1$  and restricting  $0 \leq x_1 \leq 1$ , and  $C_{\max} \geq (x_1 \times C_{\max})$ . The remaining parameters were fit by minimizing the squared error between observed and model estimates. The values for  $k_1$ ,  $k_2$ ,  $C_{\max}$  and  $x_1$  for each data set are given in Table 4.7. While the models appeared to fit the data well (Figure 4.16), there were large standard errors associated with some of the estimated parameters as would be expected given the lack of early time data. The extractions conducted at 20°C had larger  $k_1$  and  $C_{\max}$  values than the experiment at 4°C (Table 4.7). This result was expected as the earlier solvent combination experiments identified temperature as a significant effect, with more PCB mass extracted after 24 hours at 20°C than at 4°C. The extraction conducted with a 1g: 0.75 mL solvent ratio had a higher  $k_2$  than those conducted at the 1g: 1mL solvent ratio. Considering the limited early time data and experimental data sets, it was of interest to investigate potential relationships between the estimated model parameters and the experimental conditions (temperature or soil to solvent ratio).

It was observed that  $k_1$  and  $C_{\max}$  were functions of temperature and  $k_2$  was a function of soil to solvent ratio (g/mL). Linear relationships were assumed between  $k_1$  and temperature,  $C_{\max}$  and temperature, and  $k_2$  and soil to solvent ratio to develop the following relationships:

(4-2)

$$k_1 = 0.41T + 7.46$$

(4-3)

$$C_{\max} = 6.78T + 831.91$$

(4-4)

$$k_2 = 0.52R - 0.50$$

where  $T$  is temperature in °C, and  $R$  is the soil to solvent ratio in g/mL. No relationships between  $x_1$  and temperature or soil to solvent ratio were identified. Combining equations (4-1), (4-2), (4-3), and (4-4) the two-compartment model can be written as:

(4-5)

$$C = (6.78T + 831.91) * x_1 * (1 - e^{-(0.41T+7.46)t}) + (6.78T + 831.91) * (1 - x_1) * (1 - e^{-(0.52R-0.50)t})$$

Equation (4-5) is valid for temperatures from 4 to 20°C and for soil to solvent ratios from 1 to 1.3 g/mL. The two-compartment kinetic model was sufficient at predicting PCB extraction concentrations up until at least 24 hours. Due to the large standard error associated with some of the fitted parameters, the model should only be used as a preliminary tool for estimating PCB mass extraction. Following further model development, knowledge of the kinetics could be used to determine an appropriate solvent extraction time in order to meet remediation goals.

**Table 4.1. Comparison between PCB mass in controls and sum of PCB mass experimentally extracted and PCB mass remaining in soil following experimental extraction.**

Experimental Solvent	Temperature (°C)	PCB mass in controls (mg)	PCB mass in decanted solvent + PCB mass in soil (mg)
Isopropyl Alcohol (IPA)	20	10.22 ± 0.14	14.69 ± 0.62
	4	10.82 ± 0.04	19.23 ± 1.75
Ethanol (Eth)	20	3.45 ± 0.03	12.36 ± 3.88
	4	8.73 ± 0.02	15.81 ± 1.23
Isooctane (Iso)*	20	16.87 ± 0.76	35.43 ± 4.79
Triethylamine (Tri)	20	8.45 ± 0.45	12.76 ± 0.68
Eth or IPA with Iso or Tri	20	6.22 ± 0.73	11.11 ± 1.21
	4	6.69 ± 0.31	10.64 ± 1.29

\* No DCB correction applied.

± Standard deviation.



**Table 4.2. Results from solvent extractions with polar solvents.**

Temperature (°C)	Matrix	Moisture Content of Optimal Extraction (% wt)			
		With DCB Correction	Statistically Significant From	No DCB Corrections	Statistically Significant From
<u><i>Isopropyl Alcohol</i></u>					
20	Decant	5%	<i>None</i>	5%	<i>All but 10%</i>
20	Soil	20%	<i>0% and 5%</i>	20%	<i>5%</i>
<u><i>Ethanol</i></u>					
20	Decant	5%	<i>All but 0%</i>	15%	<i>All</i>
20	Soil	20%	<i>All but 15%</i>	0%	<i>10%</i>
<u><i>Isopropyl Alcohol</i></u>					
4	Decant	15%	<i>All but 20%</i>	15%	<i>All but 20%</i>
4	Soil	20%	<i>5% and 15%</i>	5%	<i>0% and 20%</i>
				10%	<i>None</i>
<u><i>Ethanol</i></u>					
4	Decant	5%	<i>All but 0%</i>	5%	<i>All but 0%</i>
4	Soil	0%	<i>All</i>	0%	<i>All</i>

**Table 4.3. Results from solvent extraction with non-polar solvents at 20°C.**

Matrix	Moisture Content of Optimal Extraction (% wt)			
	With DCB Correction	Statistically Significant From	No DCB Corrections	Statistically Significant From
<u>Triethylamine</u>				
Decant	20%	<i>All but 15%</i>	20%	<i>All</i>
Soil	20%	<i>All</i>	20%	<i>All</i>
<u>Isooctane</u>				
Decant			0%	<i>5%, 10%</i>
			20%	<i>All but 0%</i>
Soil			0%	<i>All</i>

**Table 4.4. ANOVA Table for decanted solvent data treated as 2<sup>4</sup> Factorial Experiment.**

	Sum of Squares	Degrees of Freedom	Mean Squared	F <sub>obs</sub>	
<i>Main Effects</i>					
Moisture Content (%)	1643	1	1643	1.9	
Polar Solvent	6380	1	6380	7.3	Significant
Non-Polar Solvent	149388	1	149388	170.9	Significant
Temperature	16678	1	16678	19.1	Significant
<i>Interactions</i>					
Non-Polar * Temp	1103	1	1103	1.3	
Polar * Temp	43	1	43	0.1	
Polar * Non-Polar	34573	1	34573	39.6	Significant
Polar * Non-Polar * Temp	821	1	821	0.9	
% * Temp	1340	1	1340	1.5	
% * Non-Polar	810	1	810	0.9	
% * Non-Polar * Temp	109	1	109	0.1	
% * Polar	49130	1	49130	56.2	Significant
% * Polar * Temp	165	1	165	0.2	
% * Polar * Non-Polar	2100	1	2100	2.4	
% * Polar * Non-Polar* Temp	474	1	474	0.5	
Error	27967	32	874		
Total	1.804E7	48			
Corrected Total	292727	47			

Factors with  $F > F_{1,32,0.05} = 4.2$  were considered significant

**Table 4.5. ANOVA Table for percent mass removed data treated as 2<sup>4</sup> Factorial Experiment.**

	Sum of Squares	Degrees of Freedom	Mean Squared	F <sub>obs</sub>	
<i>Main Effects</i>					
Moisture Content (%)	92	1	92	106.2	Significant
Polar Solvent	9	1	9	10.2	Significant
Non-Polar Solvent	15	1	15	17.6	Significant
Temperature	26	1	26	29.7	Significant
<i>Interactions</i>					
Non-Polar * Temp	2	1	2	2.1	
Polar * Temp	6	1	6	6.5	Significant
Polar * Non-Polar	36	1	36	41.3	Significant
Polar * Non-Polar * Temp	0	1	0	1.0	
% * Temp	0	1	0	0.0	
% * Non-Polar	87	1	87	100.1	Significant
% * Non-Polar * Temp	1	1	1	1.4	
% * Polar	30	1	30	35.0	Significant
% * Polar * Temp	3	1	3	3.9	
% * Polar * Non-Polar	109	1	109	126.5	Significant
% * Polar * Non-Polar* Temp	1	1	1	1.4	
Error	28	32	1		
Total	337496	48			
Corrected Total	444	47			

Factors with  $F > F_{1,32,0.05} = 4.2$  were considered significant

**Table 4.6. Grain Size range where highest PCB mass resides.**

Soil ID	Grain size range of highest PCB mass (mm)			
	With DCB Correction	Statistically Significant From	No DCB Corrections	Statistically Significant From
Dixie0707	2-19.05	<i>All</i>	2-19.05	<i>All</i>
Dixie0208	<0.425	>4.75	0.85-2.0	<i>All but 0.425-0.85</i>
Dixie0208-repeat*	0.85-2.0	<i>All but 2.0-4.75</i>	0.85-2.0	>4.75

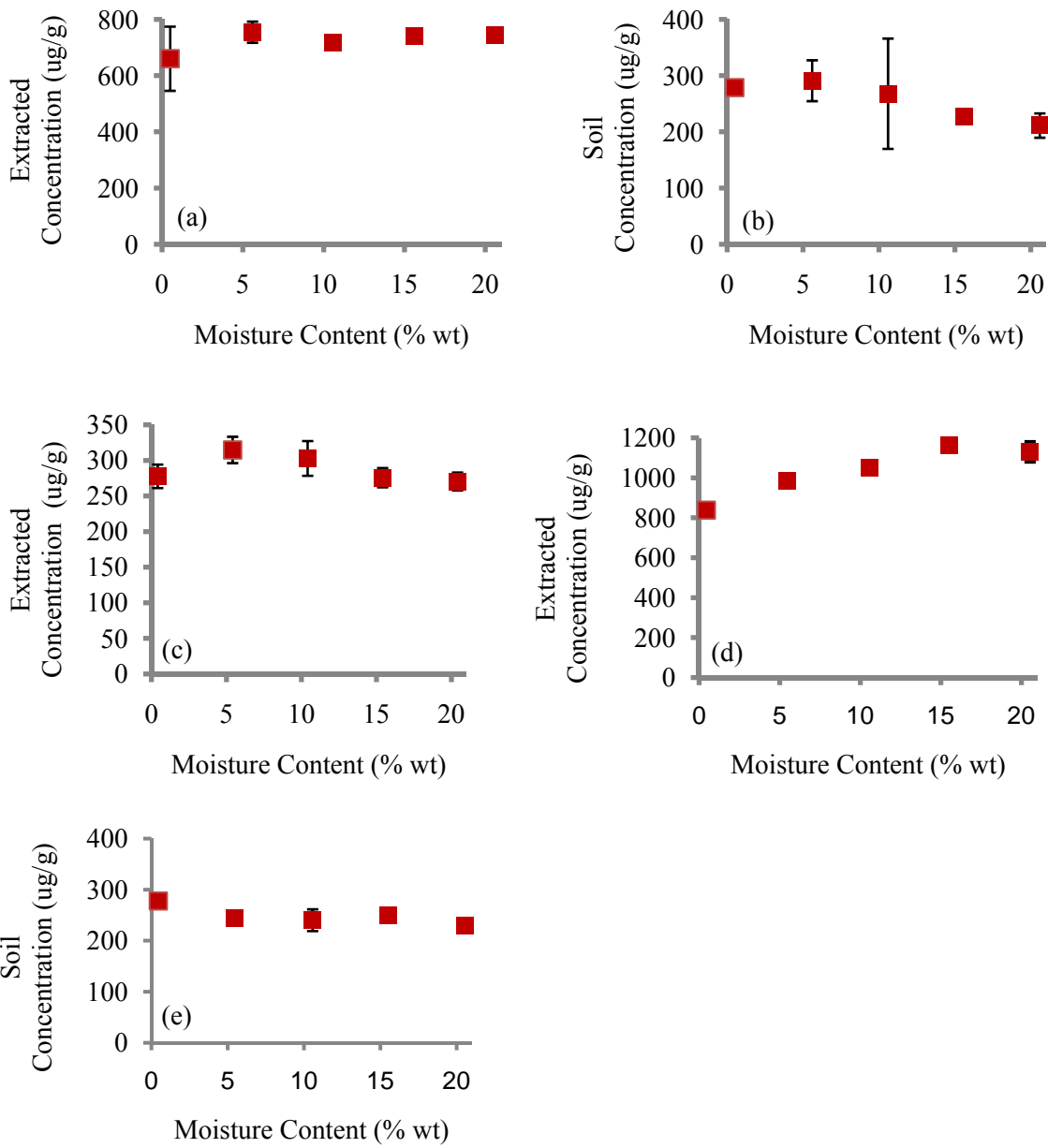
\* Excluded <0.425 mm grain sizes

**Table 4.7 Kinetic Experiment Results**

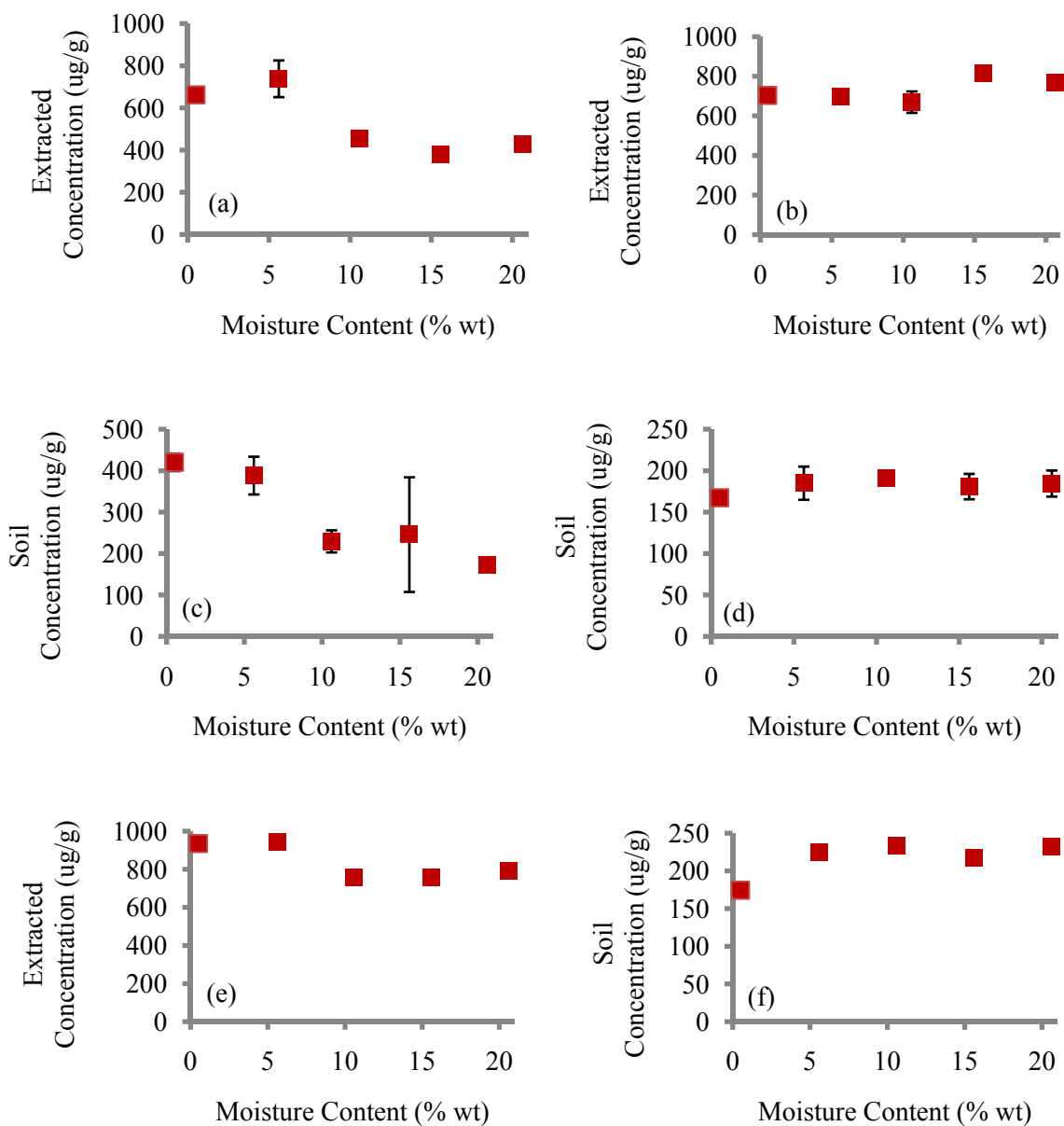
Two-Compartment Model Parameters	Experiment 1 20°C, 1g:1mL	Experiment 2 20°C, 1g:0.75 mL	Experiment 3 4°C, 1g:1mL
$k_1$ - Fast compartment extraction rate constant (1/hour)	15.56	15.59	9.08
$k_2$ - Slow compartment extraction rate constant (1/hour)	0.003	0.192	0.033
$C_{max}$ - Maximum extractable PCB concentration ( $\mu\text{g/g}$ )	967.6	967.6	859.0
$x_1$ - Fraction of mass in the fast compartment	0.69	0.91	0.88
$s_y^*$ - Standard deviation	41.0	30.7	16.1

$$* s_y = \sqrt{\frac{\sum_{i=1}^m (y_i - f_i)^2}{m - n}}$$

where  $y_i$  is the observed value,  $f_i$  is the predicted value,  $m$  is the number of data points, and  $n$  is the number of parameters fit (Baird, 1962; Bendat and Piersol, 1971).

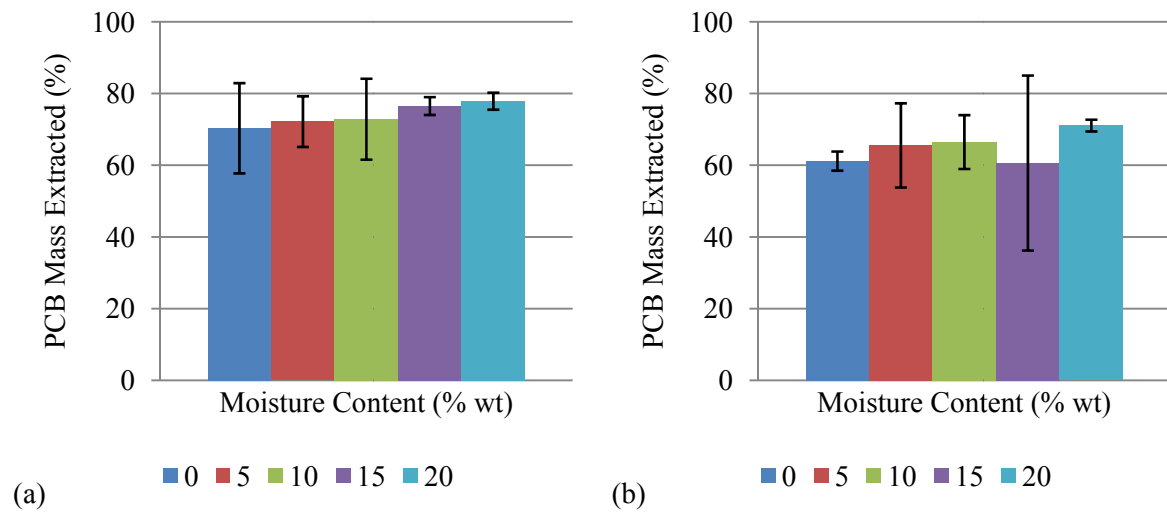


**Figure 4.1. (a) PCB concentration removed using isopropyl alcohol at 20°C, (b) PCB concentration remaining in soil having undergone experimental extraction with isopropyl alcohol at 20°C, (c) PCB concentration extracted using isopropyl alcohol at 20°C - repeat, (d) PCB concentration extracted using isopropyl alcohol at 4°C, (e) PCB concentration remaining in soil having undergone experimental extraction with isopropyl alcohol at 4°C**

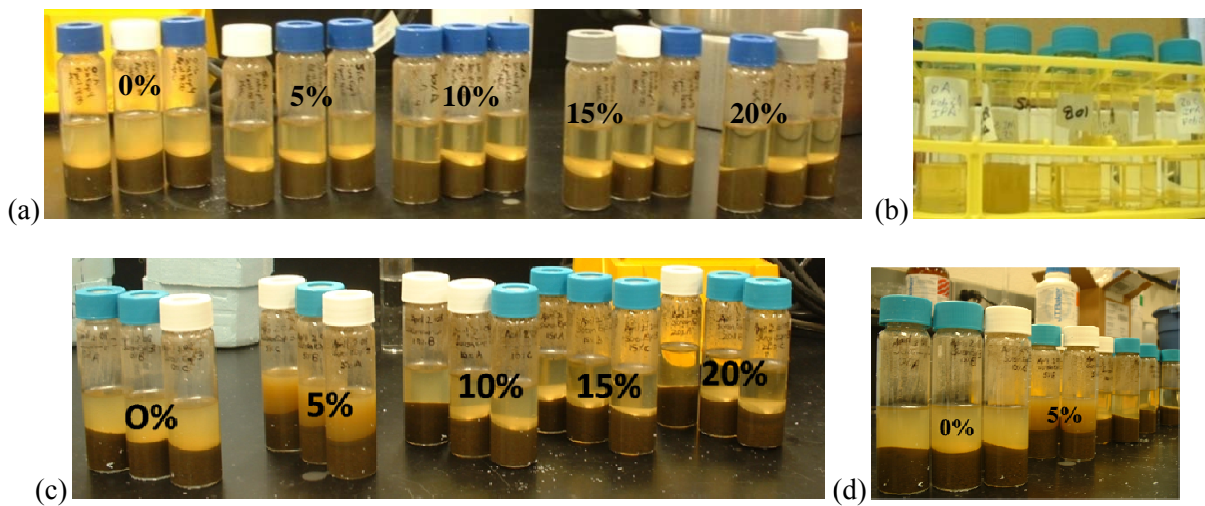


**Figure 4.2. PCB concentration removed using ethanol at 20°C (a) with DCB recovery corrections and (b) without DCB recovery corrections, PCB concentration in soil having undergone experimental extraction with ethanol at 20°C (c) with DCB recovery corrections and (d) without DCB recovery corrections, (e) PCB concentration removed from dry soil using Ethanol at 4°C, (f) PCB concentration remaining in dry soil after extraction with ethanol at 4°C**





**Figure 4.3. Percent mass extracted at 20°C with (a) isopropyl alcohol and (b) ethanol**



**Figure 4.4. Reactors following isopropyl alcohol extraction at (a) 20°C, (b) 20°C –repeat, (c) 4°C, (d) 4°C - 0% and 5% moisture content reactors only**

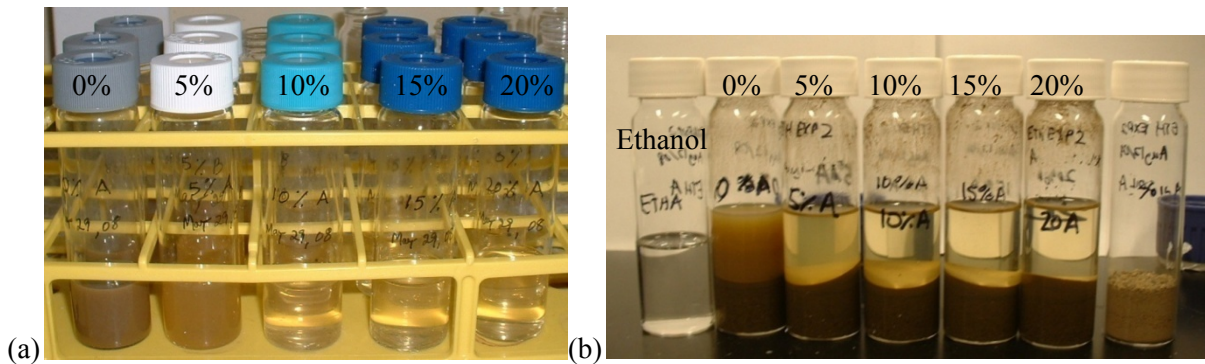


Figure 4.5. Ethanol following extraction at (a) 20°C –decanted ethanol, (b) 4°C - reactors

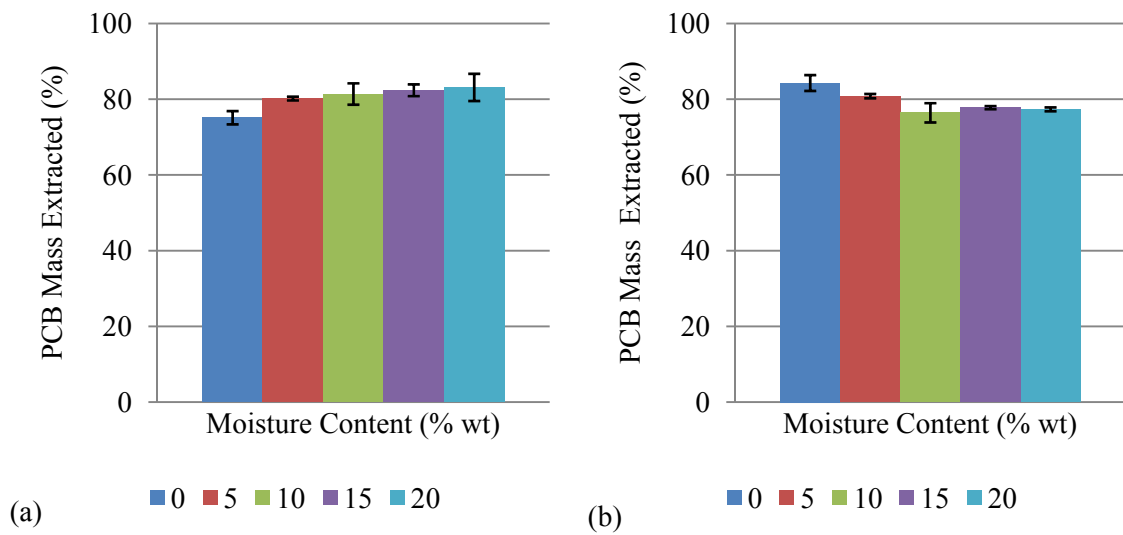
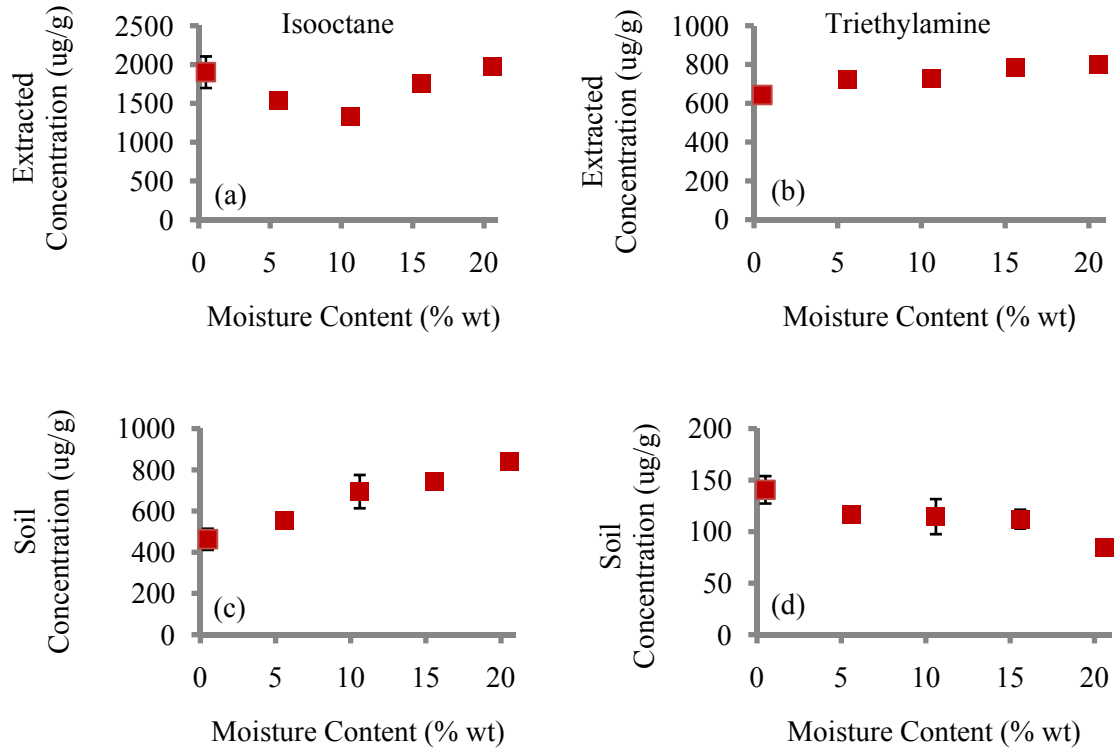
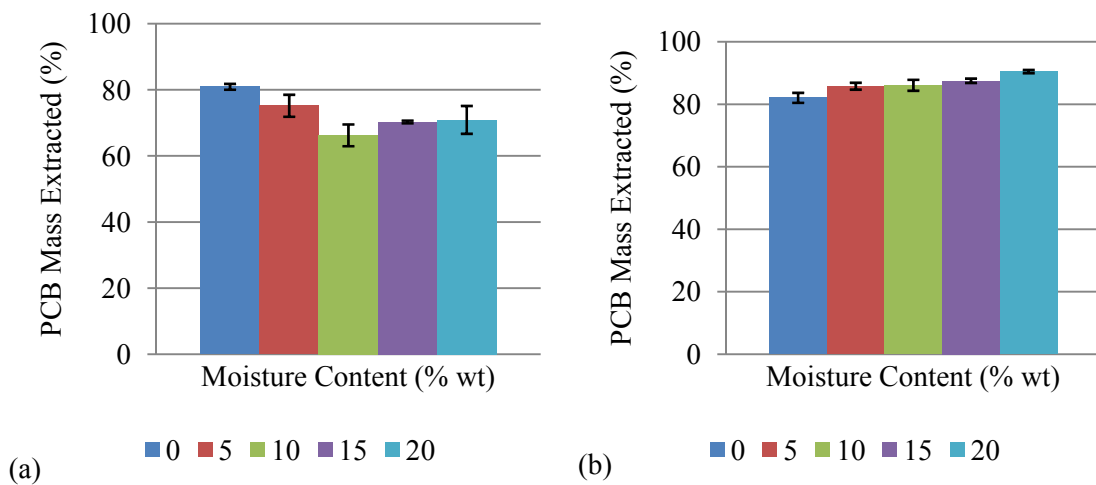


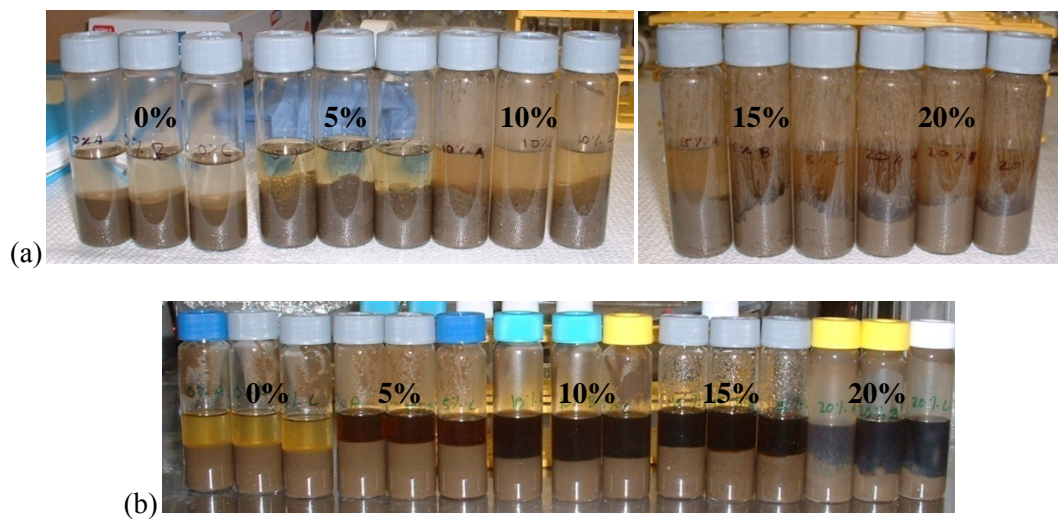
Figure 4.6. Mean PCB mass removed at 4°C using (a) isopropyl alcohol and (b) ethanol



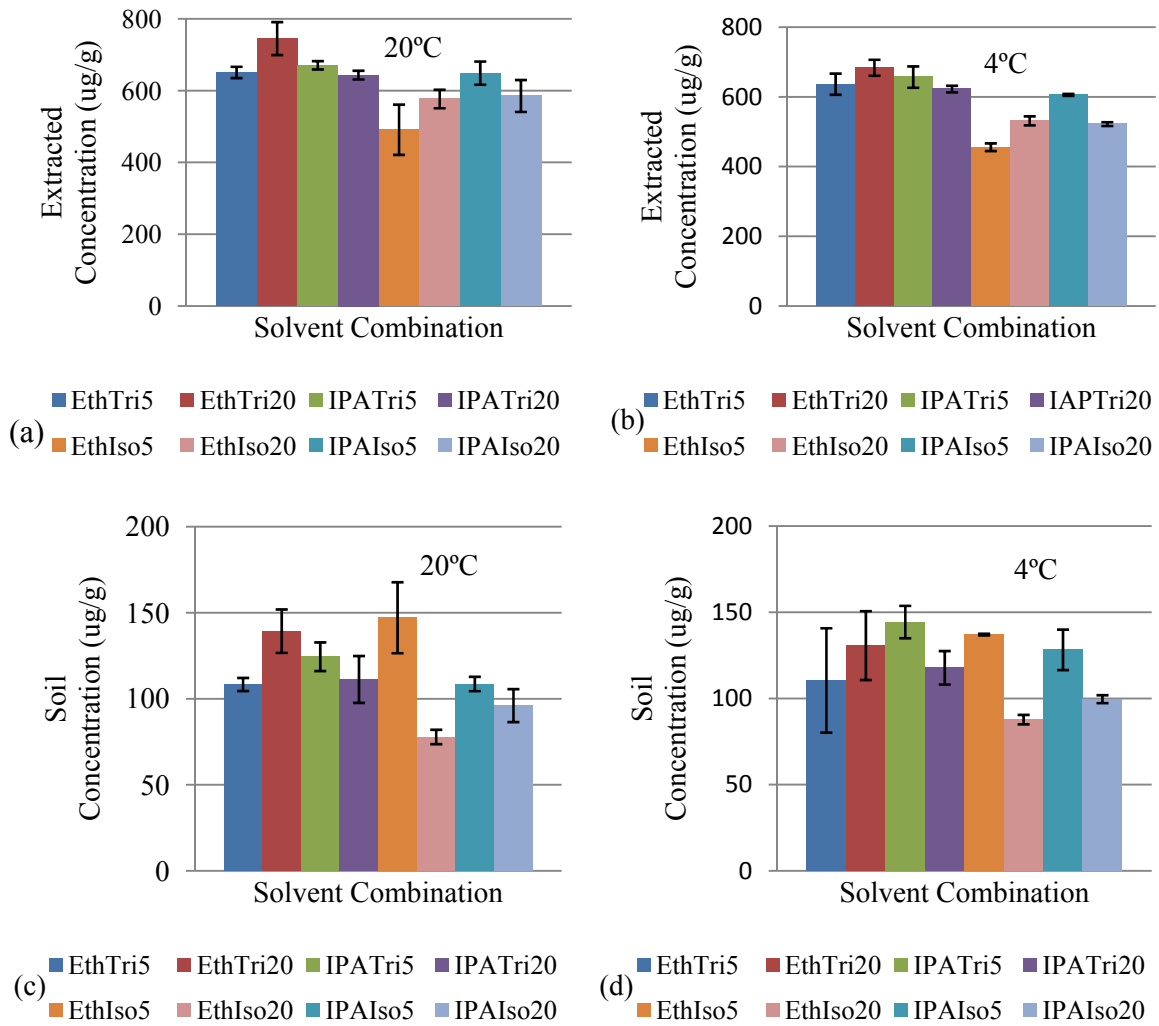
**Figure 4.7. PCB concentration extracted at 20°C with (a) isooctane and (b) triethylamine, PCB concentration remaining in soil after extraction at 20°C with (c) isooctane and (d) triethylamine**



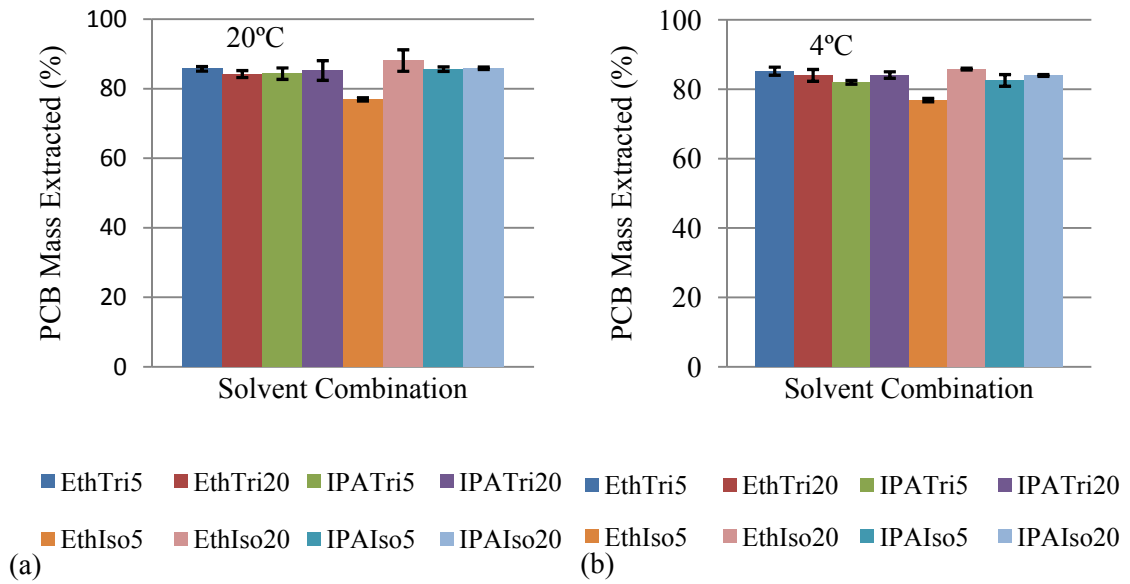
**Figure 4.8. Mean PCB mass removed at 20 °C using (a) isooctane and (b) triethylamine**



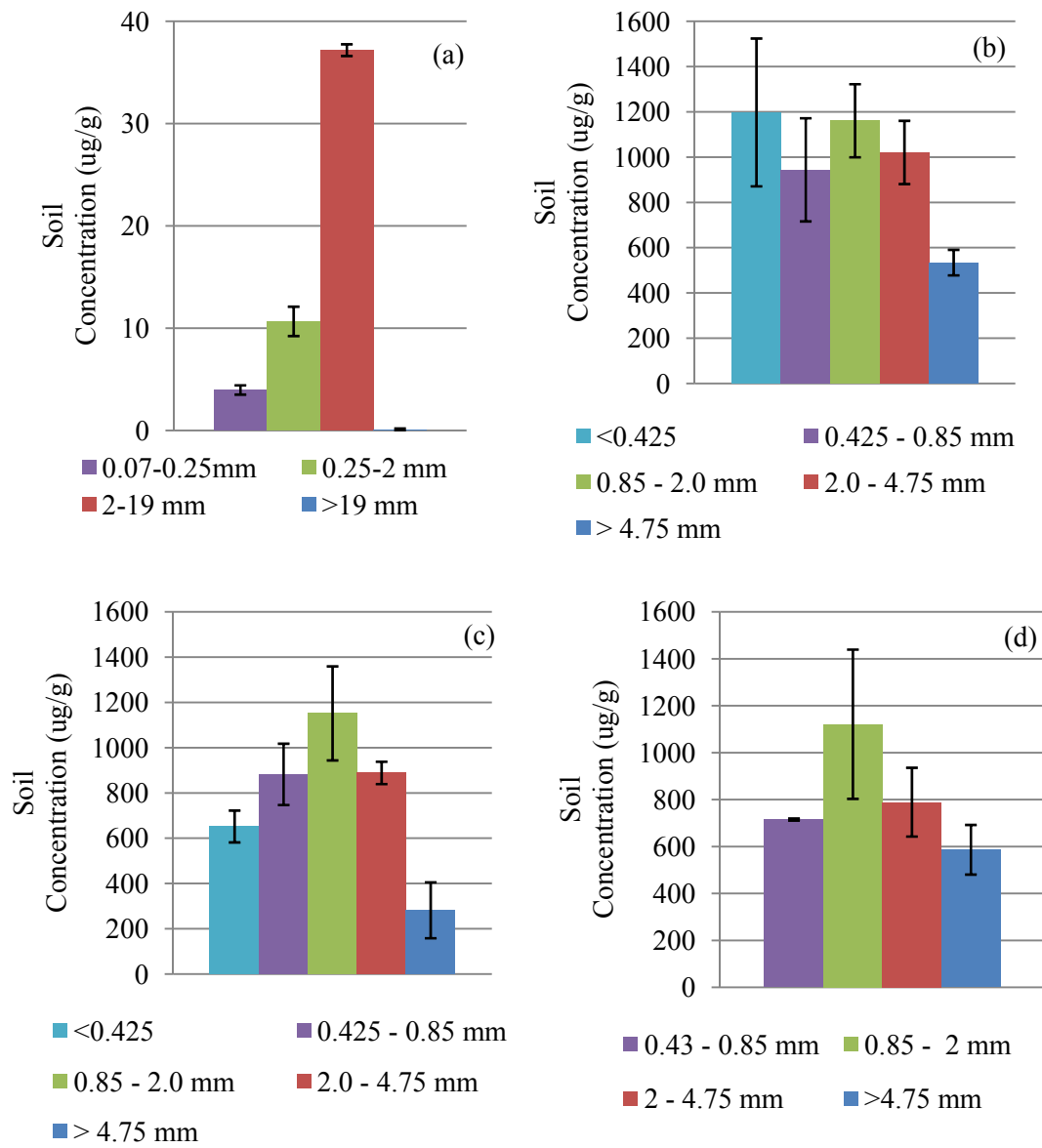
**Figure 4.9. Reactors after experimental extraction at 20°C with (a) isooctane and (b) triethylamine**



**Figure 4.10. PCB concentration extracted with decanted solvent data at (a) 20°C and (b) 4°C. PCB concentration remaining in soil following extractions at (c) 20°C and (d) 4°C.**



**Figure 4.11. Percent PCB mass extracted using sum of soil and solvent data at (a) 20°C and (b) 4°C**



**Figure 4.12. PCB concentration distribution by grain size for (a) Dixie0707, (b) Dixie0208, (c) Dixie0208 – without DCB recovery corrections, (d) Dixie0208 - repeat**

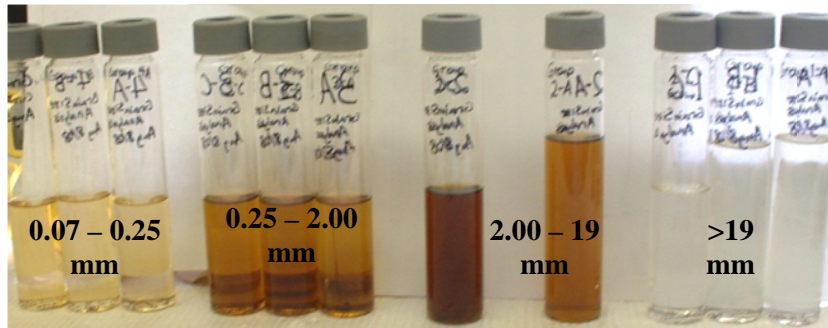


Figure 4.13. Solvent following PCB extraction from grain size groupings with ASE200

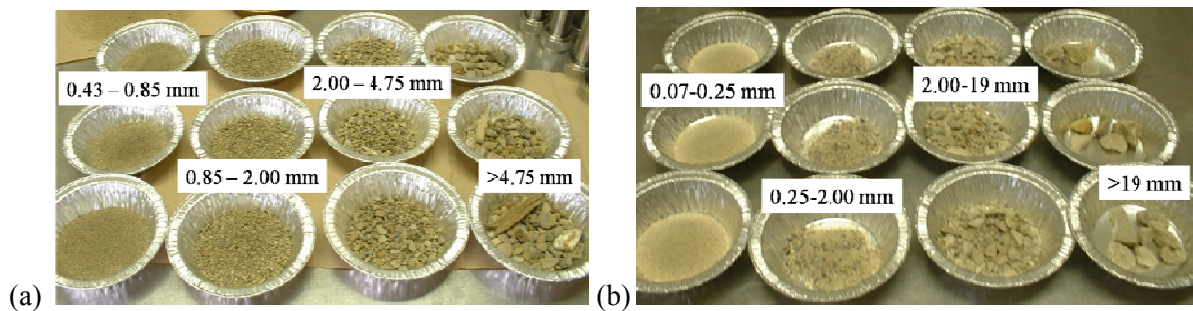


Figure 4.14. PCB contaminated soil sorted by grain size (a) Dixie0208 and (b) Dixie0707

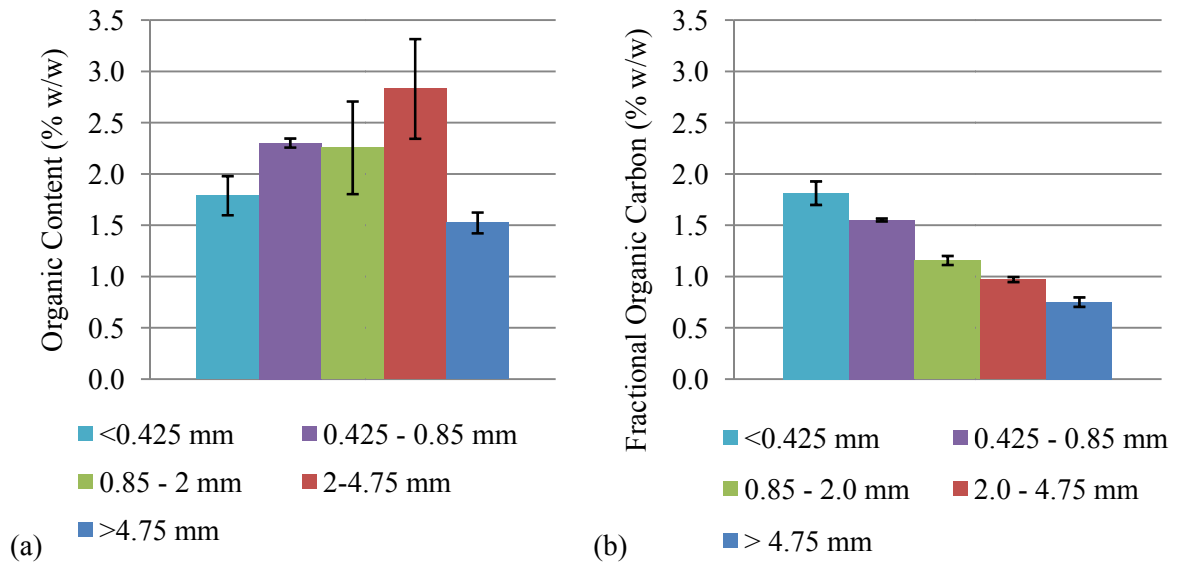
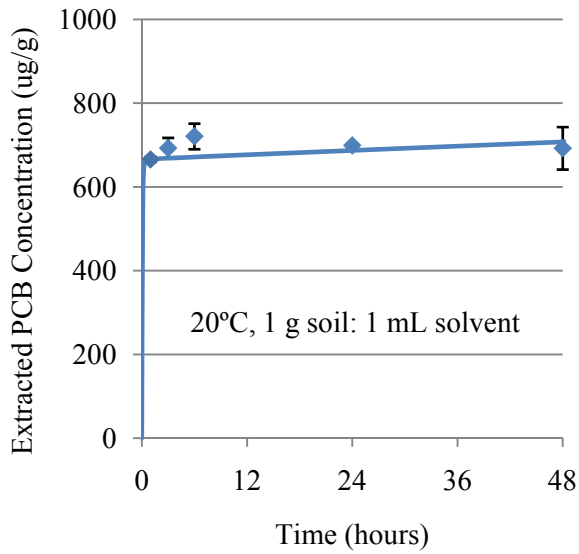


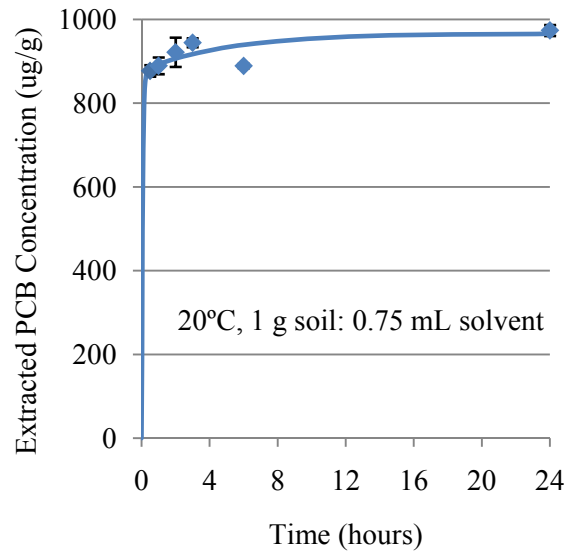
Figure 4.15. (a) Percent organic content by weight for different grain sizes, (b) Percent fractional organic carbon by weight for different grain sizes





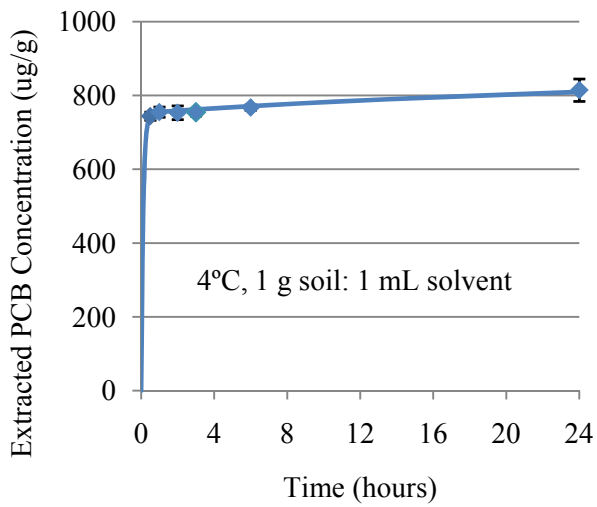
— Two Compartment Model

(a)



— Two Compartment Model

(b)



— Two Compartment Model

(c)

**Figure 4.16. PCB extraction over time using a (a) 1g:1mL soil to solvent ratio at 20°C, (b) 1g:0.75mL soil to solvent ratio at 20°C, and (c) 1g:1mL soil to solvent ratio at 4°C**

## Chapter 5

### Conclusions and Recommendations

#### 5.1 Conclusions

Isopropyl alcohol, ethanol, triethylamine and isooctane were identified as promising solvents for PCB extraction based on a literature review. The bench-scale experiments identified an interaction between moisture content (5% versus 20%) and choice of polar solvent (isopropyl alcohol versus ethanol) which influences solvent extraction efficiency. The solvent extractions conducted at 4°C showed that isopropyl alcohol performed better at higher moisture contents (15-20%) rather than at the lower ones, and ethanol performed better at the lower moisture content (0-5%) as opposed to the higher ones. There was a lack of statistically significant data to draw conclusions about the polar solvents at 20°C. The impact of elevated moisture content on solvent extraction efficiency could not be quantified due to unreliable DCB spike recovery values.

The choice of non-polar solvent (triethylamine versus isooctane) was identified as significant. Triethylamine achieved higher PCB extractions than the non-polar solvent isooctane. Triethylamine was capable of achieving high PCB extraction efficiencies at both low and high moisture contents; however, the best solvent extractions occurred at higher soil moisture contents (15-20%).

Combinations of solvents were also tested, but triethylamine alone performed best rather than in combination with a polar solvent. While a polar solvent could be selected for a given soil moisture content and temperature to achieve optimal extraction, it seems simplest that triethylamine be used and that water is added to elevate the moisture content if it is not already high.

Temperature was determined to be significant in the mass of PCBs extracted. However no significant interactions were determined between soil moisture content and temperature.

PCB mass was not evenly distributed amongst all grain sizes, and sorting PCB contaminated soil into grain sizes may be an efficient way to target PCB contamination. It may allow for the exclusion of less contaminated or uncontaminated soil that may otherwise be targeted, and reduce operation time and expenses. More work is needed to establish a simple relationship between soil organic carbon and PCB concentration.

The two-box release model proposed by Karickhoff (1980) fit PCB solvent extraction data for three data sets for up to at least 24 hours of extraction. The two-compartment kinetic model was written in terms of temperature and soil to solvent ratio to reflect the dependence of some of the model parameters on these factors. This equation is valid for the Dixie0208 soil at temperatures ranging from 4°C to 20°C, and a soil to solvent ratio from 1 to 1.3 g/mL. The model can be used to estimate ideal solvent extraction conditions to meet remediation goals. The research conducted has improved the understanding of solvent extraction so that PCB solvent extraction can be optimized in various climates and under different conditions.

## **5.2 Recommendations**

In future studies, it is recommended that PCBs be analyzed as congeners as opposed to Aroclors. This change will eliminate the uncertainty caused by analyzing weathered samples that differ from Aroclor standards and provide a more accurate picture of PCB extraction efficiency. Additional attempts should be made to determine where the PCB mass is being lost during the analysis procedure in order to improve DCB spike recovery and to improve PCB recovery consistency between samples. This would likely eliminate contradicting results depending on whether or not DCB recovery is applied. Further investigations are needed to determine the cause of the mass balance errors discussed in section 4.1. Focus should be directed to how the soil is being handled and analyzed for remaining PCBs.

It is recommended that triethylamine be used in the field as it outperformed isooctane and is optimal at higher moisture contents. Water should be added to the soil to raise the moisture content to 15-20% by weight to achieve optimal extraction. Further studies should be made into the effect of temperature on solvent extraction using triethylamine.

A number of experiments had large variability between replicates and could be repeated. These include the extractions using polar solvents at 20°C. Repeating the organic carbon analysis on larger sample sizes should reduce the variability between replicates and refine the relationship between PCB mass and organic carbon amongst grain sizes. Finally, these studies should be repeated on other contaminated soils to assess applicability to other sites and soil types.

Additional studies should be conducted to further develop the kinetic model and other factors known to influence extraction should be considered. Data should be collected at earlier times (>0.5 hours) in order to refine the fast extraction rate.

## Bibliography

2008. Canadian Environmental Protection Act, SOR/2008-273, pp. 2078-2140.
- Ackerman, D.G. et al., 1983. Destruction and Disposal of PCBs by Thermal and Non-Thermal Methods. Pollution Technology Review, 97. Noyes Data Corporation, New Jersey.
- Agarwal, S., Al-Abed, S.R. and Dionysiou, D.D., 2007. In Situ Technologies for Reclamation of PCB-Contaminated Sediments: Current Challenges and Research Thrust Areas. Journal of Environmental Engineering, 133(12): 1075-1078.
- Allen-King, R.M., Grathwohl, P. and Ball, W.P., 2002. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. Advances in Water Resources, 25: 985-1016.
- Anderson, W.C. (Editor), 1995. Solvent/ Chemical Extraction. Innovative Site Remediation Technology, 3. WASTECH.
- ASTM International, 2007. D 2974 - 07a: Standard Test Methods for Moisture, Ash, and Organic Matter of Peat and Other Organic Soils, West Conshohocken.
- Baird, D.C., 1962. Chapter 6: Experiment Evaluation, Experimentation: An Introduction to Measurement Theory and Experiment Design. Prentice-Hall, Inc., Englewood Cliffs, New Jersey.
- Bendat, J.S. and Piersol, A.G., 1971. Chapter 4: Review of Statistical Principles, Random Data: Analysis and Measurement Procedures. Wiley-Interscience, New York.
- Calabrese, E.J., Kostecki, P.T. and Dragan, J. (Editors), 2006. Successes and Challenges. Contaminated Soils, Sediments and Water, 10. Springer, New York.
- Carroll, K.M., Harkness, M.R., Bracco, A.A. and Balcarcel, R.R., 1994. Application of a Permeant/Polymer Diffusional Model to the Desorption of Polychlorinated Biphenyls from Hudson River Sediments. Environmental Science and Technology, 28(2): 253-258.
- Cassidy, D. and Hampton, D., 2009. The Effect of Persulfate Oxidation of PCBs in River Sediments on Sulfate-Reducing Bacteria (SRB), Fifth International Conference on Remediation of Contaminated Sediments. Battelle, Jacksonville, Florida.
- Churcher, P.L. and Dickhout, R.D., 1987. Analysis of Ancient Sediments for Total Organic Carbon - Some New Ideas. Journal of Geochemical Exploration, 29: 235-246.
- Craig, R.F., 2002. Soil Mechanics. Spon Press, New York.
- Crine, J.-P. (Editor), 1988. Hazards, Decontamination, and Replacement of PCB: A Comprehensive Guide. Environmental Science Research, 37. Plenum Press, New York.
- Dhol, A.S., 2005. An Investigation of a Photochemical Approach for the Remediation of PCB-Contaminated Soils, University of Calgary, Calgary, 260 pp.
- Donnelly, J.R. et al., 1996. Modular Methodology for Determination of Polychlorinated Biphenyls in Soil as Aroclors and Individual Congeners. Journal of AOAC International, 79(4): 953-961.
- EPA, 1994. Method 3541: Automated Soxhlet Extraction.
- EPA, 1996a. Method 3540C: Soxhlet Extraction.
- EPA, 1996b. Method 3665A: Sulfuric Acid/ Permanganate Cleanup.
- EPA, 1996c. Method 8000B: Determinative Chromatographic Separations.
- EPA, 1996d. Method 8082: Polychlorinated Biphenyls (PCBs) by Gas Chromatography.
- EPA, 2000a. Method 3545A: Pressurized Fluid Extraction (PFE).
- EPA, 2000b. Method 3620C: Florisil Cleaup.
- EPA, 2007a. Method 3500C: Organic Extraction and Sample Preparation.
- EPA, 2007b. Method 3550C: Ultrasonic Extraction.
- Erickson, M.D., 1993. Remediation of PCB Spills. Lewis Publishers, U.S.A.

- Fang, Y. and Al-Abed, S.R., 2007. Partitioning, Desorption, and Dechlorination of a PCB Congener in Sediment Slurry Supernatants. *Environmental Science and Technology*, 41(17): 6253-6258.
- Forsey, S., 2007. Organic Chemistry Lecturer, Chemistry Department, University of Waterloo, Waterloo, pp. Conversation.
- Fox, T.G. and Flory, P.J., 1954. The Glass Temperature and Related Properties of Polystyrene. Influence of Molecular Weight. *Journal of Polymer Science*, 14: 315-319.
- Gripton, C., 2007. Maxxam Analytics, pp. Phone Call.
- Hawker, D.W. and Connell, D.W., 1988. Octonol-Water Partition Coefficients of Polychlorinated Biphenyl Congeners. *Environmental Science and Technology*, 22(4): 382-387.
- Huang, W., Peng, P.a., Yu, Z. and Fu, J., 2003. Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Applied Geochemistry*, 18: 955-972.
- Hurst, R.W. (Editor), 1987. Practical Solutions to PCB Problems. Industry and PCBs, 1. The Canadian Electricity Forum Inc., Pickering.
- Hutzinger, O., Safe, S. and Zitko, V., 1974. The Chemistry of PCB's. CRC Press, Cleveland.
- Jakher, A., Achari, G. and Langford, C.H., 2007. An Investigation Into Solvent Extraction of PCBs From Weathered Soils. *Environmental Technology*, 28(1): 49-57.
- Johnson, R.A., 2000. Chapter 13: Factorial Experimentation, Miller & Freund's Probability and Statistics for Engineers. Prentice Hall, Upper Saddle River, NJ.
- Kadla, J.F., Kubo, S., Gilbert, R.D. and Venditti, R.A., 2002. Lignin-based Carbon Fibers. In: T.Q. Hu (Editor), Chemical Modification, Properties, and Usage of Lignin. Kluwer Academic/Plenum Publishers, New York, pp. 121-139.
- Karickhoff, S.W., 1980. Sorption Kinetics of Hydrophobic Pollutants in Natural Sediments. In: R.A. Baker (Editor), Contaminants and Sediments. Ann Arbor Science, Michigan, pp. 193-205.
- Kennedy, J.B. and Neville, A.M., 1976. Chapter 11: Rejection of Outliers, Basic Statistical Methods for Engineers & Scientists. Harper & Row, Publishers, New York.
- Korte, N.E. et al., 2002. The effect of solvent concentration on the use of palladized-iron for the step-wise dechlorination of polychlorinated biphenyls in soil extracts. *Waste Management*, 22: 343-349.
- Lamoureux, E.M. and Brownawell, B.J., 1999. Chemical and Biological Availability of Sediment-Sorbed Hydrophobic Organic Contaminants. *Environmental Toxicology and Chemistry*, 18(8): 1733-1741.
- Lassere, J.-P. et al., 2008. Effects of the endocrine disrupting compounds atrazine and PCB 153 on the protein expression of MCF-7 human breast cancer cells. *Toxicology Letters*, 180: S122.
- Lide, D.R. (Editor), 1998. CRC Handbook of Chemistry and Physics (1998-1999). CRC Press.
- Lou, J., Paravastu, A.K., Laibinis, P.E. and Hatton, T.A., 1997. Effect of Temperature on the Dielectric Relaxation in Solvent Mixtures at Microwave Frequencies. *Journal of Physical Chemistry A*, 101(51): 9892-9899.
- Lucht, L.M., Larson, J.M. and Peppas, N.A., 1987. Macromolecular Structure of Coals. 9. Molecular Structure and Glass Transition Temperature. *Energy & Fuels*, 1(1): 56-58.
- Mackay, D., 2006. Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals. CRC Press, 919 pp.
- Meckes, M.C., Renard, E., Rawe, J. and Wahl, G., 1992. Solvent Extraction Processes: A Survey of Systems in the SITE Program. *Journal of Air Waste Management Association*, 42(8): 1118-1121.

- Meckes, M.C., Tillman, J., Drees, L. and Saylor, E., 1997. Removal of PCBs from a Contaminated Soil Using CF-Systems Solvent Extraction Process. *Journal of Air Waste Management Association*, 47: 1119-1124.
- Meckes, M.C., Wagner, T.J., Tillman, J. and Krietemeyer, S., 1993. SITE Demonstration of the Basic Extractive Sludge Treatment Process. *Journal of Air Waste Management Association*, 43(9).
- National Research Council, 2001. A risk-management strategy for PCB-contaminated sediments. National Academy Press.
- Ontario Government, 1990a. R.R.O. 1990, Regulation 352 - Mobile PCB Destruction Facilities.
- Ontario Government, 1990b. R.R.O. 1990, Regulation 362 - Waste Management - PCB's.
- Ontario Ministry of the Environment, 2000. Protocol for Sampling and Testing at PCB Storage Sites in Ontario. In: S.D. Branch (Editor). Queen's Printer for Ontario.
- Ontario Ministry of the Environment, 2004. Soil, Ground Water and Sediment Standards for Use Under Part XV.1 of the *Environmental Protection Act*. Queen's Printer for Ontario.
- Ontario Ministry of the Environment, 2006. The Determination of Polychlorinated Biphenyls (PCBs), Organochlorines (OCs) and Chlorobenzenes (CBs) in Soil and Sediments by Gas Liquid Chromatography-Electron Capture Detection (GLC-ECD). In: Q.M.U. Laboratory Services Branch (Editor).
- Ontario Ministry of the Environment, 2007. Soil, Ground Water and Sediment Standards for Use Under Part XV.1 of the *Environmental Protection Act*.
- Perkins, C., 2008. Conversation, Waterloo.
- Pignatello, J.J. et al., 2006. Nonlinear and Competitive Sorption of Apolar Compounds in Black Carbon-Free Natural Organic Materials. *Journal of Environmental Quality*, 35: 1049-1059.
- Schaumann, G.E. and LeBoeuf, E.J., 2005. Glass Transitions in Peat: Their Relevance and the Impact of Water. *Environmental Science and Technology*, 39(3): 800-806.
- Smith, K.E., Schwab, A.P. and Banks, M.K., 2007. Phytoremediation of Polychlorinated Biphenyl (PCB) - Contaminated Sediment: A Greenhouse Feasibility Study. *Journal of Environmental Quality*, 36: 239-244.
- Sonic Environmental Solutions Inc., 2007. Sonic POP Treatment Facilities.
- Stevenson, F.J., 1982. *Humus Chemistry: Genesis, Composition, Reactions*. John Wiley & Sons, Toronto.
- Strachan, W.M.J., 1988. Polychlorinated Biphenyls (PCBs) - Fate and Effects in the Canadian Environment. In: C.a. Protection (Editor). Environment Canada.
- Streitwieser, A., Heathcock, C.H. and Kosower, E.M., 1992. *Introduction to Organic Chemistry*. Maxwell MacMillan Canada, Toronto.
- Teuten, E.L., Rowland, S.J., Galloway, T.S. and Thompson, R.C., 2007. Potential for Plastics to Transport Hydrophobic Contaminants. *Environmental Science and Technology*, 41(22): 7759-7764.
- Tisa, K.N., 2007. Re: PCB analysis, Boston, pp. Email.
- Trowbridge, T.D. and Holcombe, T.C., 1996. The Carver-Greenfield Process: Dehydration / Solvent Extraction Technology for Waste Treatment. *Environmental Progress*, 15(3): 213-220.
- United Nations Environment Programme, Stockholm Convention on Persistent Organic Pollutants.
- United Nations Environment Programme, 2008. Stockholm Convention on persistent organic pollutants (POPs). Secretariat of the Stockhold.
- Valentin, M.M., 2000. Laboratory Study of Solvent Extraction of Polychlorinated Biphenyls in Soil, McGill University, Montreal.
- Waid, J.S. (Editor), 1986. *PCBs and the Environment*, 1. CRC Press.

- Waisner, S., Medina, V.F., Morrow, A.B. and Nestler, C.C., 2008. Evaluation of Chemical Treatments for a Mixed Contaminant Soil. *Journal of Environmental Engineering*, 134(9): 743-749.
- Weber, W.J., LeBoeuf, E.J., Young, T.M. and Huang, W., 2001. Contaminant Interactions with Geosorbent Organic Matter: Insights Drawn from Polymer Sciences. *Water Resources Research*, 35(4): 853-868.
- Wright, A.G. and Rosta, P.R., 1998. Dewatering System Is High and Dry. *ENR*, 240(13): 10-11.
- Wu, S.-c. and Gschwend, P.M., 1988. Numerical Modeling of Sorption Kinetics of Organic Compounds to Soil and Sediment Particles. *Water Resources Research*, 24(8): 1373-1383.
- Xing, B. and Pignatello, J.J., 1997. Dual-Mode Sorption of Low-Polarity Compounds in Glassy Poly(Vinyl Chloride) and Soil Organic Matter. *Environmental Science and Technology*, 31(3): 792-799.
- Xing, B. and Pignatello, J.J., 1998. Competitive Sorption between 1,3-Dichlorobenzene or 2,4-Dichlorophenol and Natural Aromatic Acids in Soil Organic Matter. *Environmental Science and Technology*, 32(5): 614-619.
- Xing, B., Pignatello, J.J. and Gigliotti, B., 1996. Competitive Sorption between Atrazine and Other Organic Compounds in Soils and Model Sorbents. *Environmental Science and Technology*, 30(8): 2432-2440.
- Zhang, W.-x., 2003. Nanoscale iron particles for environmental remediation: An overview. *Journal of Nanoparticle Research*, 5: 323-332.

## Appendix A

### Ranking Potential Solvents

**Table A.1. Ranking scheme for potential polar solvents**

<i>Weight</i>	<i>0.2</i>	<i>0.05</i>	<i>0.3</i>	<i>0.05</i>	<i>0.4</i>	
Polar Solvent	Influence of temperature on Viscosity	Polarity *	Cost	Recommendations	Toxicity	Score
Methanol	5	5	5	4	0	2.95
Ethanol	4	2.6	2.8	0	3	2.96
1-propanol	3	1.1	0.3	0	5	2.74
Isopropyl alcohol	2	0.9	3.9	5	4	3.46
1-butanol	1	0.2	0	0	2	1.11
2-butanol	0	0	1.7	0	1	0.8

\* based on dielectric constants

**Table A.2. Ranking scheme for potential non-polar solvents**

<i>Weight</i>	<i>0.15</i>	<i>0.3</i>	<i>0.15</i>	<i>0.4</i>	
Non-Polar Solvent	Influence of temperature on Viscosity	Polarity *	Cost	Toxicity	Score
Isooctane	0	2	5	1.5	1.20
Triethylamine	2	1.8	2.8	0	1.13
Ethyl acetate	1	0	0.3	2	1.06

\* based on dielectric constants