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Evaluation of remediation agents for DDT- and PCB-contaminated wetlands

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EVALUATION OF REMEDIATION AGENTS FOR DDT- AND PCB-CONTAMINATED WETLANDS

BY

SCOTT CLOUTIER

B.S., University of New Hampshire, 2008

THESIS

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DEDICATION

I dedicate this thesis to my wife, Kari and my students at Innovation Academy Charter School. Kari, you made all of this possible, with your constant support; you have always believed in me. Students, never stop believing in yourselves and always dream big. You give me hope that change is possible and always make it easy to forget everything else going on in the world.

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This thesis has been examined and approved.

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ABSTRACT

EVALUATION OF REMEDIATION AGENTS FOR DDT- AND PCB-CONTAMINATED WETLANDS

by,

Scott A. Cloutier

University of New Hampshire, December, 2009

Wetland sediments that are contaminated with hydrophobic organic compounds, such as dichlorodiphenyltrichloroethane (DDT) and polychlorinated biphenyls (PCBs) can be remediated via in-situ methods. Four different amendment agents, activated carbon, zero valent iron, organoclay and seaweed were assessed. Activated carbon provided the greatest reduction in both PCB and DDx porewater concentrations: an average of 90% or greater reduction of the six congeners detected. Two amendment delivery technologies were evaluated in a microcosm experiment: a granular activated carbon slurry and Aquablok containing powdered activated carbon. The addition of activated carbon via both delivery techniques was found to significantly decrease PCB porewater concentrations (100% reduction).

CHAPTER 1

INTRODUCTION

1.1 Background

Wetlands often act as sinks for contaminants including persistent, bioaccumulative, and toxic (PBT) compounds [e.g., Dichloro-Diphenyl-Trichloroethane (DDT) and Polychlorinated Biphenyls (PCBs)], as well as inorganic constituents (e.g., copper and lead) and energetics from firing range operations. In addition, treatment wetlands designed to serve as polishing mechanisms for stormwater runoff are also increasingly being utilized and may require remediation if overloaded (US GAO, 2005). Federal and state agencies routinely mandate that the responsible parties, including private entities and the Department of Defense (DoD), conduct remedial actions to address contamination in wetlands. For example, the Army, Navy, and Air Force have millions of dollars of potential cleanup liabilities associated with contaminated wetlands (WR&TC, 2010).

Given the lack of a centralized DoD database of contaminated wetlands, in 2007 a DoD project team conducted a limited survey of Navy Remedial Project Managers (RPM's) and immediately identified over 7,000 acres of contaminated wetlands and a number of sites where substantial and costly wetland remediation plans are currently in place. These sites cover a total of 119 acres, with total costs for remediation, restoration, and monitoring estimated at $16.5 M. The

limited survey identified contaminated wetlands requiring cleanup at DoD installations throughout the country (RPM Report, 2007).

Wetlands provide critical ecosystem functions, yet are often very sensitive to disturbances related to environmental contamination. Remediation of contaminated wetlands traditionally has involved excavation of hydric soils and off-site transport of excavated materials for treatment and disposal (WR&TC, 2010). This type of remediation is both destructive and expensive. Wetland restoration efforts following excavation can be expensive and successful restoration is challenging at best. Alternative remedial approaches that would allow targeted in-situ remediation of wetlands would result in tremendous cost savings with the added benefit of minimizing impacts on ecosystem components (Perelo, 2010). Validated in-situ technologies for addressing and mitigating hydric soil contamination would be applicable to many wetland areas requiring active remedial responses, reserving excavation, dredging and other more extreme response actions for only the most highly contaminated areas where actionable risks are readily apparent (Perelo, 2010).

1.2 Objective and Scope

The overall objective of this research was to demonstrate in-situ wetland remediation technologies designed to sequester and/or degrade contaminants in wetlands without devastating the ecology of these systems. In addition, the research was meant to determine the most effective amendment agent to be used for field demonstration. Effectiveness was based upon pre and post

treatment contaminant concentrations (for amendments aimed at mass reduction) and reduction in porewater contaminant concentration. This included evaluation of several sequestration agents and delivery systems to determine which combination(s) provides the most cost-effective and environmentally protective solution(s). Monitoring was conducted following the field demonstration to evaluate treatment success. The specific objectives of this study were to:

- Determine amendment effectiveness (e.g. sequestration or dechlorination) through methods such as pore water analysis and bulk sediment concentrations.
- Compare equilibrium partitioning theorem calculations to estimate porewater concentrations vs. actual measured porewater concentrations utilizing passive samplers.
- Demonstrate reduced contaminant bioavailability through the means of pre- and post-treatment tissue contamination levels.
- Optimize the dose of amendment agents through a range of laboratory experiments.
- Determine ease of amendment use and mixing effectiveness through the use of a microcosm study.
- Recommend an amendment mix, based upon treatability study results, for use at the Aberdeen Proving Grounds (APG), Maryland wetland site using engineered *in-situ* remediation technologies to reduce the bioavailability of PCB and DDT contaminated hydric soils

1.3 Regulatory Drivers

Federal and state agencies routinely mandate that the DoD and other responsible parties conduct remedial actions to address contamination in wetlands. Wetland alteration concerns are not trivial: long-term harm to mature ecological communities may result from overly aggressive remedial strategies. Whenever remedial response actions in sensitive ecological systems are contemplated, it is important to balance the potential risks associated with chemical stressor exposure and the potential risks associated with wetland habitat alteration. This concern is explicitly recognized by USEPA (1999), which states that "even though an ecological risk assessment may demonstrate that adverse ecological effects have occurred or are expected to occur, it may not be in the best interest of the overall environment to actively remediate the site".

An EPA Science Advisory Board (USEPA, 1990) review of relative ecological risks indicates that environmental protection strategies should prioritize remedial options for the greatest overall risk reduction. USEPA (1990) recommends that the relative risks of remedial strategies be considered, particularly as they relate to natural ecosystem destruction. Habitat alteration may result in greater relative risk than environmental contamination. Suter (1993) identifies three categories for ecological (and public health) risk: (1) *de minimis* (i.e., risks that would not require remediation because they are considered trivial), (2) *de manifestis* (i.e., sites that would require remediation for ecological risk unless a compelling case can be made that remediation could conflict with

protection of human health, or sites where remediation is clearly required due to human health risk), and (3) intermediate (i.e., risks that fall between *de minimis* and *de manifestis*). Risks in the intermediate category are not always so compelling as to require immediate remediation, but require balancing of a number of factors, including costs, health risks, and the risks associated with remediation (e.g., habitat destruction). Based on the lack of human health risk from hydric soil exposure at many wetland sites, and the uncertainties associated with ecological risk analyses at these sites, it is likely that many DoD wetland sites fall into the intermediate category of Suter (1993). The use of innovative technologies, such as those used in this study, that result in *in-situ* remediation without destroying or functionally altering wetland ecosystems has the potential to result in remediation cost savings with minimal loss of ecological function. Therefore, these technologies could serve as viable alternatives for the management of wetland sites with intermediate risk level.

1.4 Site Description

Canal Creek on Aberdeen Proving Ground (APG), Maryland was identified as a potential demonstration site for field demonstration following laboratory results (Figure 1.1). Canal Creek is a non-tidal to tidal oligohaline creek located on the Edgewood peninsula at the APG and discharges to the Gunpowder River. The portion of the creek within the proposed study area is about 2 miles long with about 110 acres of associated tidal and non-tidal marsh. The site also includes areas that have been historically used as landfills. The study area boundaries

extend from the mouth of the creek in the south to a small wetland area north of Magnolia Road in the north, and from the western bank of the marsh in the west to Wise Road in the east.

The primary contaminants of concern at the site are PCBs, DDx (DDT, DDE and DDD), and metals. Historic data indicate that elevated concentrations of PCBs and to some extent DDx are present in surficial sediment samples collected in the channel and wetland areas above Hanlon Rd (Figures 1.2 and 1.3).

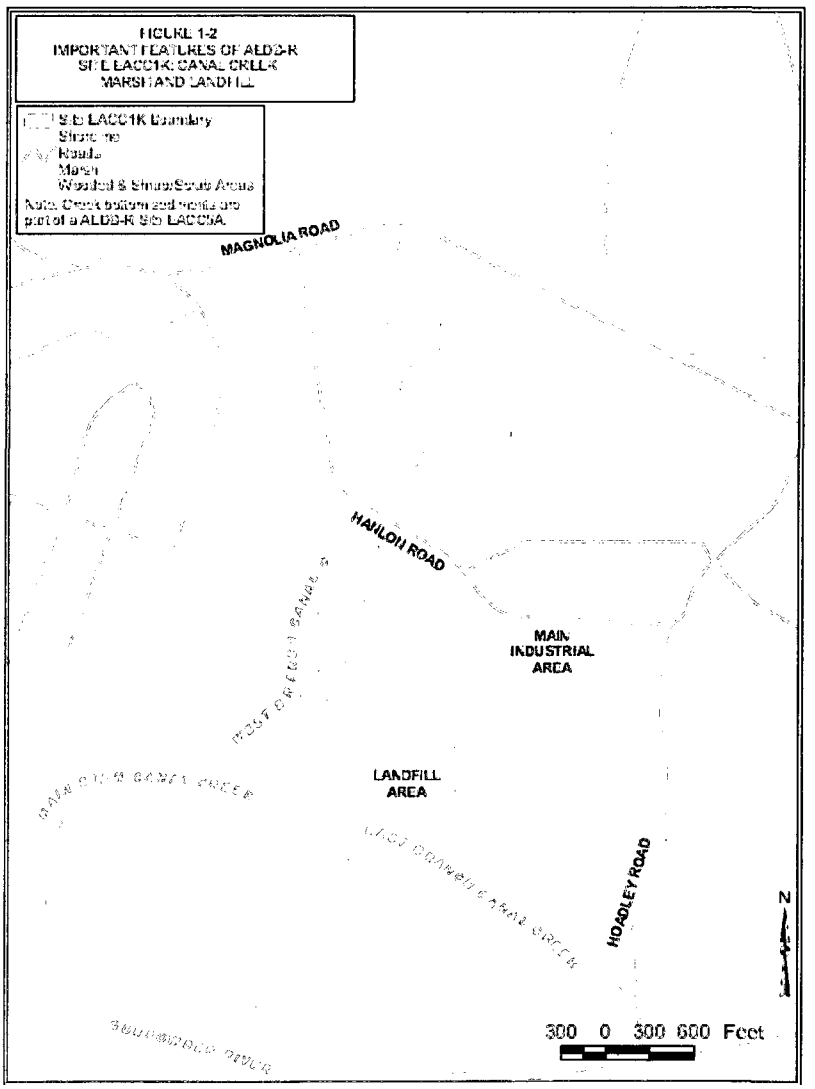

Figure 1.1 Proposed Canal Creek Study Area at Aberdeen Proving Ground, MD (Ciarlo et al., 2008)

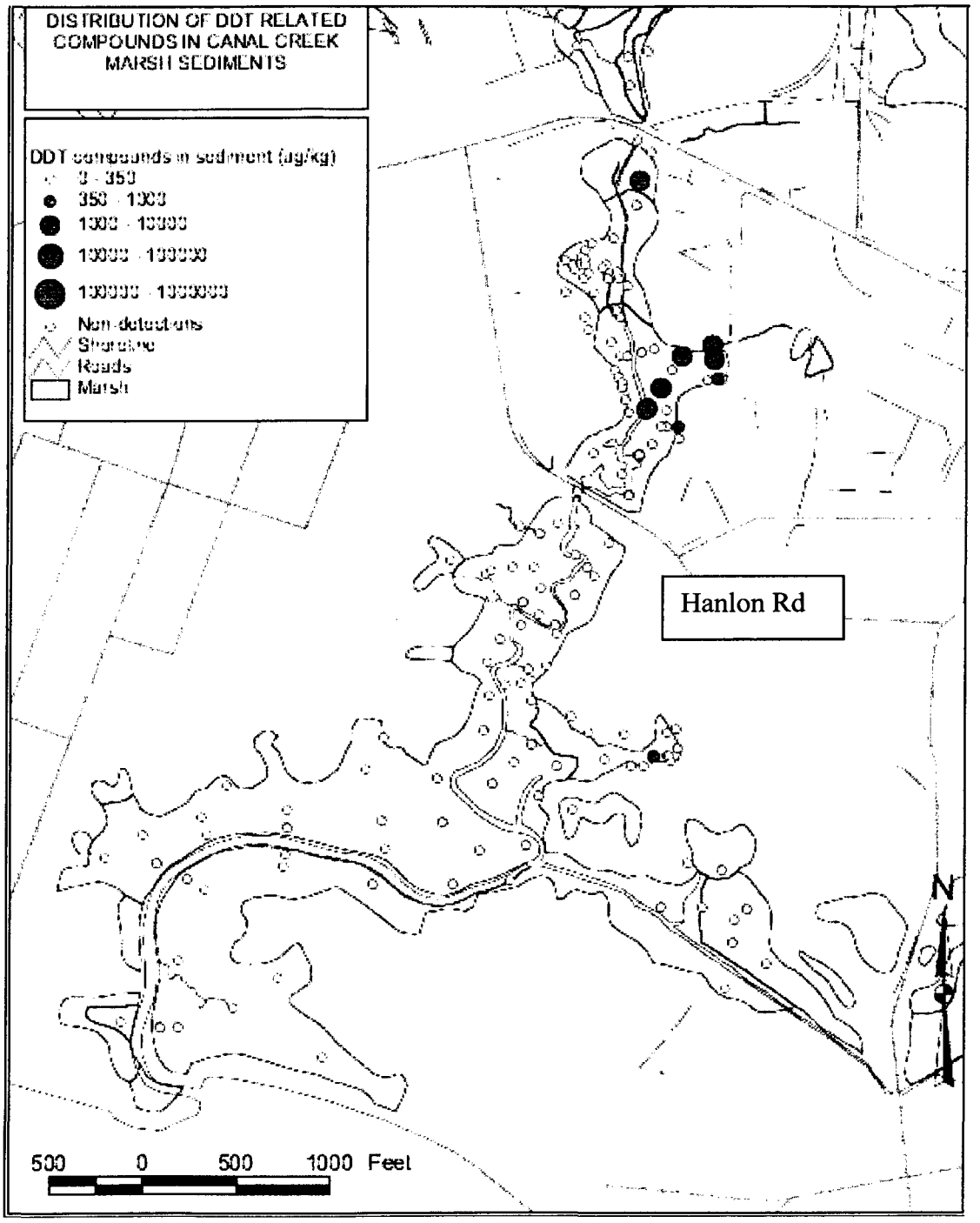

Figure 1.2 Historic PCB Concentrations in Canal Creek Marsh Sediments (Ciarlo et al., 2008)

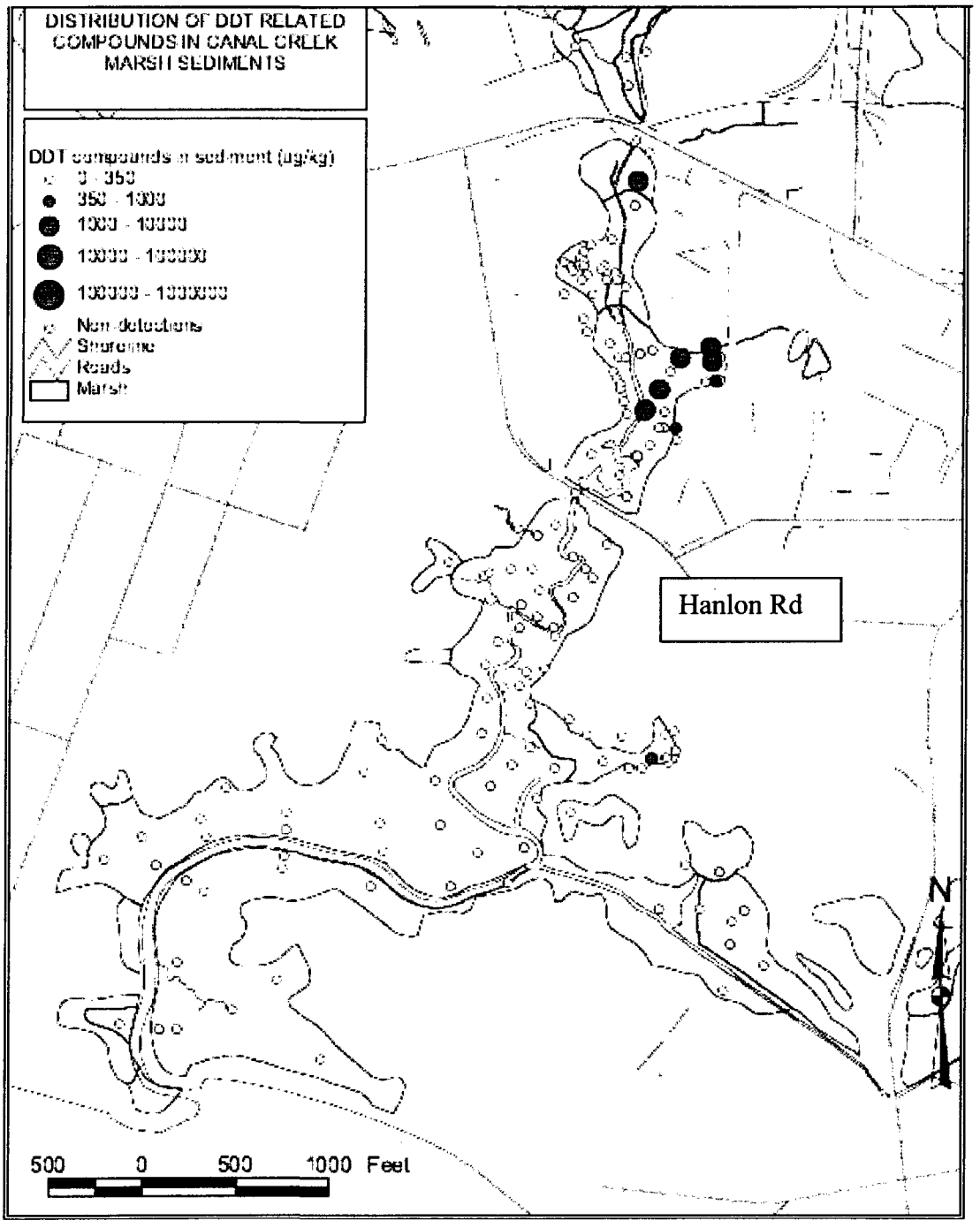

Figure 1.3 Historic DDx Concentrations in Canal Creek Marsh Sediments (Ciarlo et al., 2008)

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

A literature review based upon several books and journal articles is presented herein to better understand DDT and PCB properties and their behavior in the natural environment. The following sections are presented: DDT and PCB sources, chemistry, toxicity, environmental fate and transport, treatment techniques and finally detection methods are discussed for both compounds.

2.2 DDT Timeline and Sources

DDT was first synthesized in 1847 by Othmar Zeidler. However, Paul Meueller did not discover its insecticidal properties until 1939, a task for which he was awarded the Nobel Prize in Physiology and Medicine in 1948. Seven years later, in 1955, the World Health Organization (WHO) recommended the application of DDT to the interiors of households in the hopes of eradicating malaria. However, during this time, insects were demonstrating resistance to DDT and some of the associated negative health effects were being questioned. In fact, Rachel Carson published her book, Silent Spring, in 1962 questioning the use of pesticides like DDT and their negative impact on the environment. Ten years later, in 1972, the Environmental Protection Agency (EPA) banned DDT use in the United States. However, the World Health Organization (WHO) indicates DDT is still used overseas to combat malaria.

The main sources of DDT still found in the environment today are from its use as an insecticide and pesticide. DDT's first full-scale uses were as the main agent for the control of insect vectors of an impressive list of diseases, including malaria, Chagas' disease, plague, typhus, yellow fever, dengue/hemorrhagic fever, encephalitis, filariasis, African trypanosomiasis, onchocerciasis, and leishmaniasis (Mischke, 1985). In addition, DDT was found to be quite useful as a pesticide. The uses of DDT in California ranged from control of agricultural pests to control of cockroaches in residences to mosquito abatement in neighborhoods (Mischke, 1985). DDT proved useful for a number of years, however, insects quickly developed resistance leading to increases in dose amounts, further exacerbating the extent of DDT entering the environment.

2.3 DDT Chemistry

DDT is a highly hydrophobic organochlorine insecticide and is both an alkyl and aryl chloride. DDT stands for Dichlorodiphenyltrichloroethane, which is an incorrect name for the *2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane* structure (Figure 2.1).

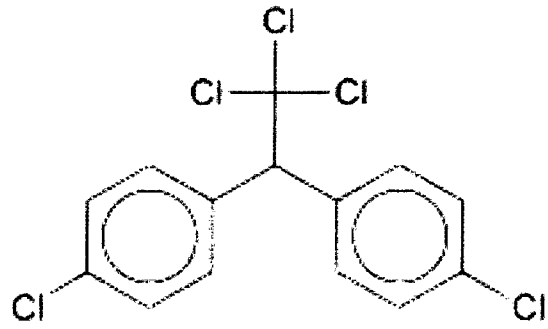

Figure 2.1 Chemical Structure of DDT Molecule

DDT is synthesized from tricholoroacetaldehyde and chlorobenzene by a modified Friedel-Crafts reaction (Figure 2.2).

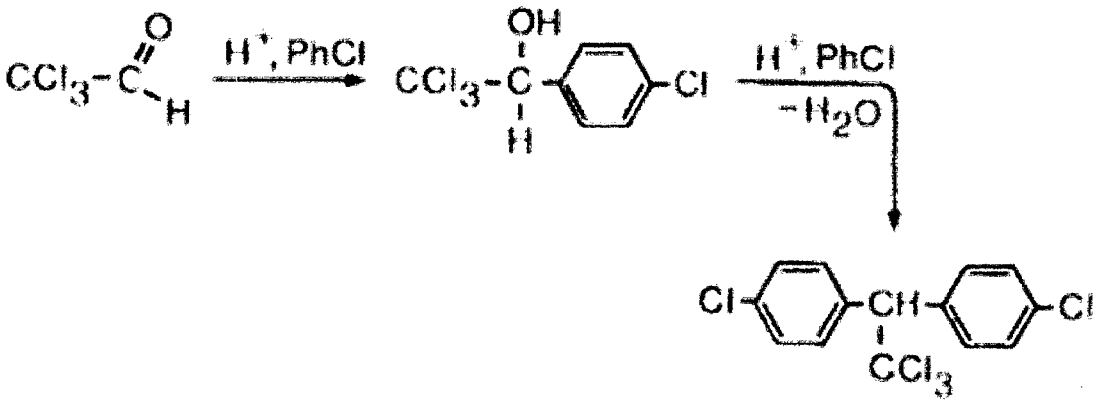

Figure 2.2 Modified Friedel-Crafts Synthesis of DDT

2.3.1 DDT Dechlorination

The dechlorination of DDT under anaerobic and aerobic conditions leads to the formation of DDD and DDE respectively (Kantachote et al., 2004). DDT undergoes dehydrochlorination both metabolically and in the environment under aerobic conditions to DDE, 1,1-dichloro-2,2-bis-(p-chlorophenyl)-ethene (Figure 2.3). The change in oxidation state of one of the carbon atoms involved in the reaction is compensated by the change in oxidation state of the adjacent carbon atom. Hydrodechlorination requires no net electron transfer from or to the compound, meaning it is not a redox reaction.

Figure 2.3 Hydrodechlorination of DDT Molecule

Under anaerobic conditions, the transformation of DDT to DDD occurs through a process known as reductive dechlorination. This occurs when two electrons are transferred to DDT from an electron donor (Figure 2.4).

Figure 2.4 Reductive Dechlorination of DDT Molecule

2.4 DDT Toxicity

DDT's toxicity is not designed to specifically eliminate one pest; therefore it is broadly toxic to many species. DDT has been shown to bioaccumulate within the fatty tissues of fish and other aquatic species, leading predators to long-term exposure of high concentrations. DDT is hydrophobic and readily bonds with available carbon, thus making aquatic sediments an ideal environment for it to accumulate. After being introduced into the environment, DDT is modified by

biological or abiotic agents, but the products are not rapidly degraded; thus, the DDE and DDD formed from DDT remains in soils or waters for many years, and are eventually magnified in the food chain. Apex predators, such as bald eagles and peregrine falcons, consume these aquatic species and their reproductive cycle is highly affected. Upon examination, DDE, the major metabolite of DDT, was associated with altering the physiological process of eggshell formation that subsequently led to eggshell thinning and population declines of numerous avian species, particularly raptors and shorebirds (Lundholm, 1997). Furthermore, elevated DDT levels are still being found in the blood and tissues of marine mammals. Nino-Torres et al. (2009) found that 34 of 34 sampled California Sea Lions were found to have elevated levels of DDx in blubber samples.

The US National Toxicological Program has classified DDT as "moderately toxic". However, DDT is suspected of causing neurological damage and is thought to be a carcinogen in both humans and animals. In a 1969 study, a group of monkeys were dosed with DDT for over ten years and compared with a control group who were not exposed to DDT. Severe tremors and histological evidence of central nervous system and spinal cord abnormalities were observed in six out of six monkeys exposed to DDT. The present findings show clear evidence of hepatic and CNS toxicity following long-term DDT administration to cynomolgus and rhesus monkeys (Takayama et al., 1969). Subramanian et al. (1987) found a correlation between high levels of DDT and decreasing testosterone levels in *Phocoenoides dalli* (sea-lions). More recently, it was found there is a probable link between DDT and non-Hodgkins Lymphoma (Spinelli et

al, 2007).

2.5 DDT Environmental Fate and Transport

DDT is a persistent chemical in the environment that resists natural degradation and bioaccumulates through the food chain. In order to understand the environmental fate and transport of DDT, it is important to understand its octanol-water partition coefficient (K_{ow}) and aqueous solubility (S_w). The octanol-water partition coefficient is a ratio of concentrations of a compound in a mixture of two immiscible solvents at equilibrium (octanol and water). The partition coefficient is related to the differential solubility of the compound between two solvents and it represents a measure of how lipophilic (fat liking) a compound is. The larger the coefficient is, the more lipophilic and the more likely it is to bioaccumulate. The aqueous solubility (S_w) is the mass of a compound that will dissolve into one liter of water. The lower this number is, the more hydrophobic a compound will be.

Relative to DDT, the determination of log K_{ow} and S_w values can be difficult. S_w and log K_{ow} values can be determined directly using a variety of methods, though several different articles contain varying data. However, in the case of organic compounds that are sparingly soluble in water ($Sw \leq 10\text{-}5$ mol/L) and have log K_{ow} values $\geq 5–6$, such as DDT and DDE, direct experimental determination of S and K can be problematic (Pontolillo, Eganhouse, 2001). Based upon a statistical analysis of several articles, research and methods of

determining DDT properties, the Pontolillo and Eganhouse USGS study concluded that the mean log K_{ow} and S_w value for DDT is approximately 6.20 and 0.23 mg/L respectively.

Based upon the high K_{ow} and low S_w values, it is known that DDT is lipophilic and hydrophobic. Thus, in aquatic environments, DDT will tend to bond with organic compounds within sediments. However, when sediments are disturbed within the benthic zone, DDT can become available and be uptaken by organisms (i.e. exposure can be direct contact or ingestion), bioaccumulating through the food chain, typically at highest concentrations within apex predators such as raptors.

2.6 PCB Timeline and Sources

The first PCB-like chemical was discovered in 1865, as a byproduct of coal. In 1881, the first PCBs were synthesized and 46 years later, in 1929, the first PCBs were manufactured commercially by the Anniston Ordnance Company in Anniston, Alabama. Anniston Ordnance later changed its name to Swann Chemical Company and was purchased by Monsanto Industrial Chemical Company in 1933, the largest producer of PCBs in history. PCBs were known to be toxic and harmful for many years, however, the peak of PCB production was 85 million pounds in 1970 alone. Nonetheless, the toxic effects of PCBs were becoming evident and the EPA banned the United States manufacturing of PCBs in 1979. Between 1929 and 1977, approximately 1.25 billion pounds of PCBs were manufactured in the United States (Agarwal, 2007). Because of past

disposal practices and accidental releases that continue to the present day, 450 million pounds of PCBs have entered the environment over time (ATSDR 2000).

PCBs have been used as coolants and lubricants in transformers, capacitors and other electrical equipment because they don't burn easily and are good insulators (ATSDR, 2001). PCBs have also been used in old fluorescent lighting fixtures and electrical appliances, such as televisions and refrigerators. Relative to environmental contamination, PCBs differ from DDT, given that the main sources of PCB contamination in the environment are accidental spills, leakages or intentional dumping. Any accidents, fires, or spills involving transformers, fluorescent lights, and other old electrical devices have resulted in environmental contamination.

2.7 PCB Chemistry

PCBs are synthetic organic chemicals consisting of complex mixtures of individual chlorobiphenyls that contain 1 to 10 chlorine atoms (Figure 2.5). There are 209 variations of chlorine atom positions and arrangements, resulting in different PCBs known as congeners. Congeners are characterized as clear odorless crystals, while their mixtures are clear viscous liquids where the higher the chlorination the more viscous the mixture (Erickson, 1997). PCBs are commonly referred to in groups of congeners, known as Aroclors and are classified by a four-digit number. The first two digits represents the 12 carbons within the biphenyl molecule while the last two numbers indicate the chlorine content in percent by weight. Therefore, Arocolor 1242 is 42 percent chlorine by

weight.

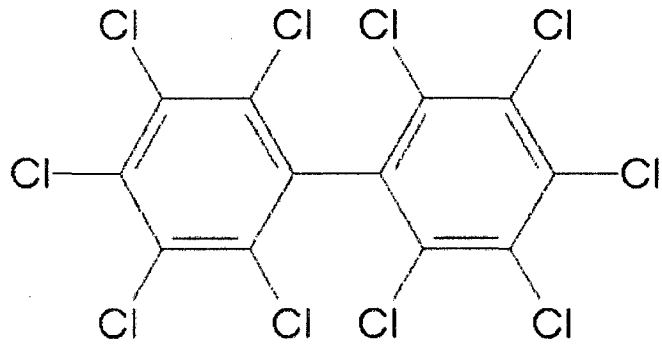

Figure 2.5 Chemical Structure of a Polychlorinated Biphenyl Molecule

2.8 PCB Toxicity

PCBs are toxic in both animals and humans. A number of studies have been done indicating the negative health effects of PCBs. The carcinogenicity of dioxins and PCBs have been demonstrated in animals and extrapolated to humans by evidence that it occurs through the same mechanisms in humans and animals (Erickson, 1997). Due to the continuous accumulation of organic contaminants (PCBs) repeated ingestion of contaminated food could result in an increase of the body burden and thus chronic toxicity. Many higher-chlorinated biphenyls, persistent and predominant in foods, are active as promoters in hepatocarcinogenesis (Ludewig, 2008).

PCBs are not only carcinogenic, they are considered to be endocrine disruptors as well. Exposure to endocrine-disrupting chemicals, such as polychlorinated biphenyls (PCB), may alter hormonal balance and therefore increase the risk of testicular germ cell tumors (TGCT) (McGlynn, 2009). In

addition, a study by Kilic et al. (2005) found that polychlorinated biphenyls had endocrine disruptive effects on the thyroid gland of female laboratory rats. Kilic (2005) suggests that these environmental contaminants may disrupt thyroid hormone homeostasis in exposed individuals and thus pose a threat to human health. Furthermore, studies have indicated a relation to bone mineral density changes and environmental PCB exposure. Environmental organochlorine exposures experienced by this population sample since the 1930s in Sweden may have been sufficient to result in sex-specific changes in bone mineral density (BMD) (Hodgson, 2008).

PCBs are extremely persistent in the environment and, therefore, studies have found elevated blood levels in animals and humans years after spills. Nino-Torres et al. (2009) found that 34 of 34 sampled California Sea Lions were found to have elevated levels of PCBs in blubber samples. In 1968, over 1800 persons in western Japan developed a strange skin disease, later named Yusho disease, which was found to have been caused by the ingestion of rice bran oil contaminated with PCBs, polychlorinated dibenzofurans (PCDFs), polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated quarterphenyls, and polychlorinated terphenyls (Kuratsune, 1996). 35 years later a study conducted by Todaka et al. (2009) found elevated blood levels of PCBs within humans still living within that same area.

2.9 PCB Environmental Fate and Transport

Although PCBs were banned over thirty years ago, their broad use and improper disposal have caused widespread environmental contamination. PCBs are contaminants of concern due to their large quantities, persistence and recalcitrance to degrade in the environment. PCBs act much like DDT in the environment; therefore, in order to understand the environmental fate and transport of PCBs, it is important to understand their octanol-water partition coefficients and aqueous solubility in mg/L. A 2005 study by Ballschmiter et al. found that the log K_{ow} values range from 4.83 to 8.18 for PCB congeners 1 through 209, respectively. Paasivirta and Sinkkonen (2009) found that log Sw values to range from -1.73 to -8.19 for PCB congeners 1 through 209, respectively.

A high octanol-water partition coefficient value indicates that PCBs are hydrophobic; they tend to bond to natural organic matter within sediments. The low water solubility values above also indicate PCBs will remain in sediments, rather than groundwater. Because of a low water solubility of PCBs, they migrate through soils at less than a few centimeters per year (Abdul, 1987). PCBs tend to remain within sediments, however, exposure to freely dissolved PCB porewater concentrations can result in bioaccumulation through the food chain.

2.10 Hydrophobic Organic Compound Remediation Techniques

Several methods of remediation, sequestration, and treatment relative to DDT and its metabolized forms DDE and DDD as well as PCBs have been

reviewed in journals, articles, and books. The following techniques are presented: seaweed addition, zero valent iron, photosensitized reduction using visible light, sodium (Na+) addition, electrokinetic remediation, Mg/Pd system, macrophytic sequestration, capping, activated carbon addition, and organoclay addition.

2.10.1 Dredging and Ex-situ Treatment

Sediments contaminated with DDx and PCBs are typically remediated via dredging and ex-situ methods. Currently, dredging followed by treatment and land filling are predominantly used, but they are disruptive (Agarwal, 2007). Dredging often has to be employed in shallow waters with limited equipment access and must be conducted slowly and deliberately with such controls as silt screens and water surface covers to limit resuspension and volatilization of sediments while aiming to remove limited amounts of sediments to conform to treatment and disposal constraints (Magar, 2001). Dredging and ex-situ methods of treatment can be invasive and expensive when compared to alternative in-situ methods. Therefore, the remaining remediation techniques below involve in-situ treatment methods.

2.10.2 Capping

Capping involves isolating a contaminated sediment bed through deployment of a clean layer or "cap" commonly consisting of sand, gravel and pebbles (Agarwal, 2007). Rather than physically altering or sequestering

contaminated sediments, capping ensures the entrapment of chemicals. Such passive caps made of unreactive material mainly rely on containment, rather than treatment, of the sediments to limit exposure and hence risk to the surrounding biota (SERDP 2004). There have been several studies utilizing capping as a method of contaminated sediments treatment.

A 1999 feasibility study by Palermo et al. (1999) evaluated variables related to capping including, but not limited to, cap thickness, equipment operations and placement of the cap and a monitoring plan for sediments on the Palos Verdes shelf off the coast of California. The Montrose/Palos Verdes Shelf (PV Shelf) site comprises a large area of DDT and PCB contaminated sediment located on the continental shelf and adjacent slope off the coast of the Palos Verdes peninsula near Los Angeles, California (Ellis, 2003). Approximately 11.7 million cubic yards (9 million cubic meters) of contaminated sediment, containing more than 110 tons (100,000 kg) of DDT and 11 tons (10,000 kg) of PCBs, are present over a 17 square-mile (44 square kilometers) area, although the extent of DDT-contaminated sediment is greater, extending northward into Santa Monica Bay and also to the southeast (Ellis, 2003).

The U.S. Army Engineer Waterways Experiment Station (WES) has performed an evaluation of in-situ capping options for sediment restoration of DDT and PCB contaminated sediments on the Palos Verdes (PV) shelf off the coast of Los Angeles, California, for Region 9 of the U.S. Environmental Protection Agency (Palermo, 1999). Two capping approaches were considered for selected areas of the shelf: (1) placement of a thin cap which would isolate

the contaminated material from shallow burrowing benthic organisms, providing a reduction in both the surficial sediment concentration and contaminant flux, and (2) placement of an isolation cap which would be of sufficient thickness to effectively isolate benthic organisms from the contaminated sediments, prevent bioaccumulation of contaminants, and effectively prevent contaminant flux for the long term (Palermo, 2009). The feasibility study found capping to be a potential solution for the Palos Verdes shelf and led to a pilot study by the United States Army Corps of Engineers.

The pilot study involved placement of approximately 103,000 m^3 of capping sediments using a split-hull hopper dredge. Three 18 hectare capping cells situated at water depths between 40 and 70 m were capped using both conventional placement methods and special spreading methods (Fredette, 2002). Generally speaking, the results of the pilot project suggest that a cap can successfully be constructed on the continental shelf portion of the site. EPA is continuing to monitor the pilot capping cells to assess changes in conditions since the capping was completed, including an assessment of decolonization by biota (Ellis, 2003).

Schaanning et al. (2006) researched the effects of capping contaminated sediments within Oslo Harbor, Norway. In many estuaries and fjords surrounded by large populations, harbours and a variety of potentially polluting anthropogenic activities, the top layer of marine sediments has developed into major reservoirs for a diverse mixture of contaminants (Schaanning et al., 2006). Harbour sediments were removed and covered with varying depths (10, 30 and 50 cm) of

caps. Three different cap materials were used; sandy till (S), untreated sandy till (R) and crushed stone material (M) (Schaanning et al., 2006). However, the type of cap material used had little effect on containing the pollutants. Covering the harbor sediments with a 10-50 cm cap of clean, sandy material practically eliminated the release of all major components contributing to the total flux of PAHs, PCBs, and DDTs (Schaanning et al., 2006).

Caps can consist of purely capping material and these are known as passive caps. However, caps constructed from capping materials, mixed with some form of amendment agent(s) (including ones described in later sections) are known as active caps. Capping is becoming a more relevant, highly researched and understood method of in-situ remediation in the scientific community. At the Fourth International Battelle Conference on Remediation of Contaminated Sediments (2005), several posters and presentation related to capping. About 30 platform or poster presentations dealt with in-situ capping as a technology, reflecting the rapid developments in this field, both in assessments and enhancements of 'classic' passive caps and the development and demonstration of active capping technologies (Forstner, 2007).

2.10.3 Macroalgae Addition

In order to decrease the bioavailability of PCBs and DDT and their metabolized forms, the addition of macroalgae or seaweed may be an effective technique. The addition of seaweed to sediments contaminated with organic

compounds can stimulate bioremediation and provide a source of organic carbon, a potential sequestration agent for any freely dissolved porewater contaminants. The addition of seaweed to DDT contaminated soils resulted in contaminant removals (Kantachote et al., 2004). Soils amended with between 0.5 and 3% (w/w) seaweed and untreated control soil showed DDT removal greater than 50% (Kantachote et al., 2004). The highest rate of DDT removal (80%) was found in soil amended with .5% (w/w) seaweed (Kantachote et al., 2004). Given the abilities of seaweed to sequester DDT and DDT's similarities to PCBs, it is possible that seaweed could serve as an effective amendment agent for this study.

2.10.4 Zero Valent Iron

The addition of zero valent iron (ZVI) can effectively remediate sediment and water solutions contaminated with hydrophobic organic compounds like PCBs and DDT. A 2005 study by Satapanajaru et al. (2005) found that DDT treatment with ZVI can promote rapid abiotic degradation via reductive dechlorination. It was found that ZVI successfully degraded DDT and DDD within solution and in soil slurries. The acidity of the water solution also had an effect on DDT reduction. DDT destruction rate increased with a decrease of pH from 9 to 3. (Satapanajaru et al., 2005).

In the early 1990s, the reducing capabilities of metallic substances, such as zero-valent iron (ZVI), began to be examined for their ability to treat a wide range of contaminants in hazardous waste/water (Zhang 2003). The most

common deployment of ZVI has been in the form of permeable reactive barriers (PRBs) designed to intercept plumes in the subsurface and subsequently remediate them (USEPA, 1998). This passive treatment system has been used to treat pollutants, including chlorinated hydrocarbons, nitro aromatics, polychlorinated biphenyls (PCBs), pesticides and even chromate (Watlington, 2005). The reducing capabilities of ZVI can dechlorinate chemicals such as trichloroethene (TCE) and polychlorinated biphenyls (PCBs) (Lien 2001).

Micro scale zerovalent iron (ZVI) fillings (um to mm particles) effectively dechlorinate many halogenated hydrocarbon compounds (Matheson 1994, Vogan 1999, Gillham 1994, Eykholt 1998). A 2004 study by Lowry and Johnson (2004) demonstrated that nanoscale ZVI dechlorinates PCBs to lower-chlorinated products under ambient conditions. The reductive dechlorination occurs by one or more of three mechanisms: direct electrolytic reduction at the metal surface, reduction by hydrogen produced in the corrosion process, and reduction by dissolved ferrous iron that is also produced by corrosion (Chang, 1995). The effectiveness of ZVI as a reductive dechlorination agent for PCBs and DDT is extremely relevant to this study.

2.10.5 Photosensitized Reduction using Visible Light

Dechlorination of PCBs and DDT and its metabolized forms is possible with the use of visible light. Lin and Chang (2006) stored DDT-contaminated sediments in the dark for 24 hours, exposed them to visible light and dechlorination was observed. In most cases, dechlorinated products were

observed, and a sequential dechlorination pathway was proposed (Lin, Chang, 2006). The value of this research is expected to enhance the contaminated natural environment recovery rate with the least human intervention by using sunlight, a natural photosensitizer, and existing humic substances as electron donors (Lin, Chang, 2006).

Matykiewiczova et al. (2007) conducted a laboratory study to observe the photochemical behavior of organic pollutants in snow at environmentally relevant concentrations. It was found that the main photodegradation pathway of two model snow contaminants, PCB-7 and PCB-153 (similar to 100 ng/kg), was found to be reductive dehalogenation. Therefore, there is evidence that sunlight can provide photodegradation of PCBs and possibly DDT as well. However, although the Aberdeen Proving Ground has been exposed to sunlight, most contamination is within sediments and porewater and will not be exposed. Given that the purpose of this study is to validate engineered in-situ methods of remediation, photosensitized reduction will not be considered.

2.10.6 Surfactant Enhanced Remediation

Surfactant electrokinetic remediation is a commonly used method to remove heavy metals from contaminated sediments. However, it is not commonly used as a method of remediating soils contaminated with organochlorine pesticides, mostly because they are not mobile under electrical field. The use of surfactants may increase the remediation efficiency by

increasing the solubility of organics (Karagunduz et al., 2007). DDT contaminated soils were prepared in lab, varying concentrations of surfactants were added and DDT/soil adsorbtion levels were measured. It was concluded that the amounts of surfactant added in the lab were not sufficient enough to mobilize DDT significantly. However, the addition of surfactants can increase the efficiencies of various remediation techniques.

Studies have also been performed on surfactant-based remediation of PCB contaminated sediments. A study conducted by Svab et al. (2008) demonstrated a soil washing method of decreasing PCB concentrations in a sandy soil. The pilot-scale demonstration study confirmed that it is technologically possible to remove the PCBs from real contaminated soil by flushing with a surfactant solution (Svab, 2008). It is thought that this method of remediation could be less expensive than comparable ex-situ methods. However, given that this method is mainly conducted via ex-situ means, it is not appropriate for this study.

2.10.7 Mg/Pd System

A magnesium and palladium (Mg/Pd) treatment is a possible remediation technique for soils contaminated with both PCBs and DDT. Guatam and Suresh (2006) created a DDT-contaminated soil slurry for a study using a Mg/Pd treatment method. Mg/Pd was able to dechlorinate >99% of extractable DDT (10mg/kg) and >90% of non-extractable DDT (50mg/kg) in a soil slurry (Gautam

and Suresh, 2006). As has been found in other studies, three soil properties (pH, clay content, and total organic matter content) affect the adsorption of pesticides onto soil. Another factor that affects the contact time between a chemical and soil is ageing (how long it is in contact with soil). The longer this period is, the longer the compound can strongly bond with soil components (Gautam, Suresh, 2006). Guatam et al. concluded, using a Mg/Pd treatment system, that DDT, DDD, and DDE can be completely dechlorinated without the accumulation of partially dechlorinated end products at much faster rates than microbiological systems.

An Mg/Pd system was used by Hadnagy et al. (2007) to demonstrate rapid dechlorination of PCBs, PCNs, and dioxins by palladium-coated magnesium. A significant amount of PCBs were extracted from the filtered Mg/Pd material suggesting that PCBs first adsorb to the surface of the bimetal and then dechlorination occurs; lesser chlorinated congeners and biphenyl were also found adsorbed to the Mg/Pd material (Hadnagy, 2007). Systems where palladium catalysts are deposited onto magnesium particles are proving useful for both treatment and analysis. The treatment has the advantage of converting the complex chromatographic pattern that arises from the multiple congeners and degradation products of PCB and DDT into peaks corresponding to their representative hydrocarbon skeletons (Engelmann, 2003). It has been demonstrated that Mg/Pd systems are effective in dechlorinating organic compounds, however, there would be technical challenges applying this method to a wetland environment (i.e. extreme reactivity and explosivity).

2.10.8 Phytoremediation / Macrophytic Sequestration

Phytoremediation is the use of plants to remove pollutants from the environment or to render them harmless. The plants can remove a wide range of organochlorine pollutants (OCPs) from soil and water without much damage to the contaminated areas. One of the most important factors affecting plant uptake of organic pollutants is their lilophilic nature. Some organic residues can bind in plant tissues in non-available forms (Chu et al., 2006). Pollutants may be translocated and accumulate in plant tissues or they may be volatilized, degraded or transformed (Chu et al., 2006). Chu et al. studied the ability of common reed (*Phragmites australis)* and rice (*Oryza sativa)* to remove DDT and PCBs from a culture solution. *P. australis* was effective in removing DDT and PCBs from the culture solution (Chu et al., 2006). *O. sativa* also removed DDT and PCBs from the hydroponic medium (Chu et al., 2006).

In another study, Cruz-Uribe et al. focused on removal of TNT in water solution with three marine macroalgae, the temperate green alga *Acrosiphonia coalita*, the temperate red alga *Porphyra yezoensis*, and the tropical red alga *Porteria hornemannii.* While most macroalgae grow just above the sediment, some are capable of growing in the sediment itself (Cruz-Uribe et al., 2006). TNT contaminated solutions were prepared and a liquid algae biomass was added. At a biomass density of 1.2 g l^{-1} and initial TNT concentrations of 10 mg l-1 or less, TNT removal from seawater was 100% within 72h for *P. hornemannii* and *P. yezoensis* (Cruz-Uribe et al., 2006). Only trace amounts of TNT were

found within the biomass (Cruz-Uribe et al., 2006). Cruz-Uribe et al. concluded that all species of macroalgae tested reduced TNT.

The ability of different species of plants to uptake organochlorine pesticides such as PCBs and DDT has the potential to provide levels of sequestration, especially in wetland environments. Because of its limited mobility and its potential to sorb organic substances, macrophytes have the potential to function as an in-situ biomonitor of contaminants (Miglioranza et al., 2003). Miglioranza et al. studied the levels of OCPs sequestered in bulrush roots and the validity of using *S. Californicus*, a species of wetland plant, as a concentrator of bioavailable OCPs in a lake ecosystem in Argentina. *S. Californicus* accumulated significant amounts of OCPs in-situ (Miglioranza et al., 2003). Studies do suggest that some aquatic plants can accumulate, degrade or transform DDT and PCBs in the aquatic environment, however, phytoremediation and macrophytic sequestration is not feasible in a wetland setting. Introducing a plant species into the Aberdeen Proving Ground ecosystem could prove detrimental or invasive to local species. In addition, the ability to control growth and plant placement would be difficult given the nature of the shifting waters of the tidal wetland.

2.10.9 Activated Carbon Addition

The addition of activated carbon to contaminated sediments is a proven technique to decrease contaminant bioavailability. Previous laboratory studies

have shown reductions in PCB bioavailability for sediments amended with activated carbon (Cho et al, 2007). In one month after AC treatment, 34% less PCB uptake into SPMDs and 24% less PCB bioaccumulation in *M. Nasuta* (clams) deployed in the field was found upon exposure to AC-amended sediment in comparison to untreated sediment (Cho et al, 2007). Seven months after the AC treatment occurred, the differences further increased up to 62% less in SPMD uptake and 53% less in clam bioaccumulation, which implies the long-term effectiveness of AC (Cho et al, 2007).

A later study by Cho et al. (2009) was performed on a tidal mud flat at South Basin, adjacent to the former Hunters Point Naval Shipyard. The major goals of the field study were to (1) assess scale up of the AC mixing technology using two available, large-scale devices, (2) validate the effectiveness of the AC amendment at the field scale, and (3) identify possible adverse effects of the remediation technology (Cho et al., 2009). Activated carbon was added to a nominal depth of 30 cm during a single mixing event, with dose levels of 2.0-3.2 wt%. Field-deployed semi permeable membrane devices and polyethylene devices showed about 50% reduction in PCB uptake in AC-treated sediment and similar reduction in estimated pore-water PCB concentration (Cho et al., 2009). As indicated by Cho et al., this reduction was evident even after 13-month post-treatment with then 7 months of continuous exposure, indicating AC treatment efficacy was retained for an extended period.

Studies have also been done on the effects of activated carbon amendments on the bioaccumulation of PCBs within benthic organisms. Sun

and Ghosh (2008) performed a study to determine the effect of activated carbon on partitioning, desorption, and biouptake of native polychlorinated biphenyls in four freshwater sediments. The results showed that PCB aqueous equilibrium concentrations, rapid desorption fractions, and biouptake by the oligochaete were reduced after activated carbon amendment (Sun and Ghosh, 2008).

In addition to the 2008 study, Sun et al. (2009) developed a model for PCB mass transfer and bioaccumulation in a freshwater oligochaete before and after the amendment of sediment with activated carbon. The model was also tested for its ability to predict changes in PCB bioaccumulation in the three sediments after amendment with activated carbon to reduce PCB bioavailability. For most PCB congeners, the modeled results and measured values (from the 2008 study) agree within a factor of 2 for all three sediments before and after treatment with activated carbon (Sun et al., 2009).

Activated carbon additions have not only been studied with PCBs but DDT as well. A 2007 study by Tomaszewski et al. observed activated carbon amendment as a treatment for residual DDT in sediment from a superfund site in San Francisco Bay in Richmond, California. High DDT concentrations (up to 52 mg/kg) were found in Young Bay Mud sampled across the channel (Tomaszewski et al., 2007). The results indicate that activated carbon is a successful for of treatment for DDT. Four different activated carbons were tested and, after one month of treatment with 3.2 weight % carbon, DDT aqueous equilibrium concentrations were reduced up to 83% and SPMD uptake was reduced up to 91 % (Tomaszewski et al., 2007).

A later study by Tomaszewski et al. (2008) confirmed the initial study. Tomaszewski et al. observed mussel uptake, passive sampler uptake and measured the reduction of DDT available in the water column after the addition of activated carbon to contaminated sediment. The study utilized contaminated sediment from the same superfund site, Lauritzen Channel, Richmond, California (16.5 mg total DDT/kg). Mussels (Mytilus edulis) suspended above activated carbon-treated sediment accumulated significantly less total DDT in soft tissue, 91% and 84% for virgin and reactivated carbon, respectively, as compared to untreated sediment. Mussel tissue concentrations correlated to concentrations in semipermeable membrane devices (SPMDs) and polyethylene devices (PEDs) suspended over the same sediments (Tomaszewski et al., 2008).

2.10.10 Organoclay Addition

Organoclays have been shown to be effective at adsorption of PCBs and PAHs, and may be an effective sequestration agent for delivering to wetland soils. Sharma et al. (In Press) found the effectiveness of commercially available organoclays were comparable in effectiveness to activated carbon. In some cases, organoclays were found to be superior to activated carbon, depending on the specific compound being investigated and the presence of high-DOC porewater.

Studies have also found success with organoclay and herbicides. A comparative study of the use of organoclay-based formulations as an amendment to reduce the leaching of the herbicide 4-chloro-2-

methylphenoxyacetic acid (MCPA) was conducted by Cabrera et al. (2008). The aim of this work was to study the effects of organoclay-based formulations of MCPA and olive oil waste amendment on MCPA leaching in a sandy loam soil (Cabrera et al., 2008). The study amended sediments with organoclay-based residues at the rate of 10 % (w/w). The increase in soil organic matter of the soil upon amendment with the organic residue also resulted in greater adsorption and reduced leaching of MCPA in the soil (Cabrera et al., 2008).

2.11 Detection Methods

2.11.1 Passive Samplers

The use of passive sampling is gaining considerable interest in monitoring programs because it has the potential to confront the enormous challenges of achieving representativeness in environmental systems subject to high spatial and/or temporal variability in a reliable, robust, cost-effective manner (Rubio and Perez-Bendito, 2009). Passive samplers were originally used to measure pollutants in air, however, their use in water and sediments is becoming more common. Several studies have used passive samplers to detect environmental contaminants such as PAHs, DDx and PCBs. Future use of passive samplers is dependent upon successful research and technology developments to improve viability.

Passive sampling is based on the free flow of analyte molecules from the sampled medium by effect of a difference in chemical potential of the analyte

between the two media (Rubio and Perez-Bendito, 2009). For example, some percentage of DDx within contaminated sediment has a potential, described as a partitioning coefficient, to sorb to a passive sampler. Most passive samplers consist of a barrier and a receiving phase (Rubio and Perez-Bendito, 2009). Typically, an inner core (barrier) is surrounded by a membrane (receiving phase) usually made of a material that attracts chemical compounds. The receiving phase can be a solvent, polymer resin, chemical reagent, or porous sorbent (Rubio and Perez-Bendito, 2009).

Passive samplers are designed to operate in either conditions of equilibrium or of kinetic domain. Passive sampling based on equilibrium extraction only reflects the analyte concentrations at the time the samplers are retrieved (Rubio and Perez-Bendito, 2009). A kinetic based extraction, based on linear uptake rates, reflects the concentration of the target analytes over the duration of the sampling exercise. In order to use passive samplers in conditions of either equilibrium or kinetic domain, it is important to understand the characteristics of the contaminants of interest as the equilibrium time for individual constituents varies from chemical to chemical. Most passive samplers are being used for periods of 2 weeks to about 3 months; however, whether a passive sampler behaves as an equilibrium or nonequilibrium sampler is also dependent on the partitioning properties of the chemicals involved (Rubio and Perez-Bendito, 2009). A large array of passive samplers exist, however, this study utilized passive samplers known as solid phase microextraction fibers

(SPMEs) and polyoxymethylene strips (POM). This decision was based upon the literature review below.

2.11.2 Solid-Phase Microextraction Fibers (SPMEs)

An analytical process typically consists of several discrete steps: sampling, sample preparation, separation, quantification and data analysis (Pawliszyn et al., 1997). Sampling and sample preparation often tends to be time consuming, given that conventional methods involve the extraction of target analytes (i.e. DDT) from a media (i.e. water, sediments) into organic solvents. Solid phase microextraction was created to decrease the preparation time involved in sample analysis. SPMEs extract a small percentage of target analytes, thus, they require a small amount of extraction solvent. Exhaustive removal of analytes to the extracting phase does not occur, rather an equilibrium is reached between the sample matrix and the extracting phase (Pawliszyn et al., 1997).

Solid phase microextraction fibers (SPMEs) are a relatively new and growing technology used for environmental analysis. In SPME, coated fibers are used to isolate and concentrate analytes into a range of coating materials (Pawliszyn et al., 1997). The most typical coating materials are made of polydimethylsiloxane (PDMS) and polyacrylate. A coated fiber is placed into a sample media (i.e. water, sediment, air) and the target analyte is absorbed into the coating. Once the fiber has been equilibrated for the desired amount of time, it is necessary to extract the target analyte from the fiber for analysis. This can

be done in two ways: through the use of an extracting solvent or through direct injection of the fiber (thermal desorption) into analytical equipment. This study utilized the solvent extraction method.

After equilibrating a fiber with a desired water phase (e.g. porewater), the analysis proceeds by first desorbing the contaminant mass from the fiber into a phase suitable for analysis (Reible, 2008). For PCB analyses by gas chromatography, hexane is a suitable solvent (Reible, 2008). The solvent can then be analyzed for target contaminants by injecting a small amount into a GC/MS.

2.11.3 Polyoxymethylene (POM)

Polyoxymethylene (POM), also commonly referred to as polyacetal, is becoming a more commonly used material for passive sampling and porewater contaminant concentration analysis. Hawthorne et al., (2009) performed a study to determine the POM/water portioning coefficient (K_{POM}) values for all 62 PCB congeners that are present at greater than trace concentrations in commercial Aroclors. Sheets of POM, 76 um thick, were cut into 4x6 cm strips and were cleaned by sequential extraction in hexane followed by methanol. POM strips were allowed to dry and were placed in 40 mL vials containing 15g of spiked sediment and 30 mL of water containing 50 mg/mL of sodium azide. Vials were then constantly mixed on a rotating box at 6 rotations per minute and were selected for analysis at predetermined time intervals. KPOM values were

determined for all 62 congeners and it was also found that 30 days is sufficient time for the POM to come to equilibrium within the vials.

Although this method is performed ex-situ, Hawthorne et al. (2009) mention the application of their method to various field sediments. Methods developed on well-characterized and spiked sediments sometimes fail to perform adequately when a range of field sediments are tested, since interferences from non-target organics, and sediment characteristics (especially colloidal content) can both adversely affect the performance of methods based on non-depletive sorbents (Hawthorne et al., 2009). However, Hawthorne et al. tested their method with 19 freshwater sediments having a range in total PCB concentrations (62 congeners) from 800 to 1000 ng/g and found no significant interference. This method can prove useful when sediments can be placed in vials in a laboratory setting for thirty days, however, it is also important to understand the application of in-situ methods with POM and corresponding equilibrium times.

Cornelissen et al. (2010) conducted a study comparing the equilibria of passive sampling techniques (POM) and active water sampling. POM (55-um) was placed in-situ at a site where the Frierfjord in Norway flows into the outer Grenlansfjords. POM was sampled after 179, 270 and 363 days and was found to be maximally 20-30% short of equilibrium. However, POM does have distinct advantages as a passive sampler. Cornelissen found the passive sampling method (POM) only deviated less than an order of magnitude from porewater concentrations obtained with conventional active sampling through pumping/filtration over glass fiber filters and polyurethane foam. The

conventional active method is tedious, time consuming and costly. POM provides an alternative to this. Furthermore, Hawthorne et al. (2009) indicated that POM is fairly inexpensive, is superior in its physical strength (showed no abrasion after 84 days of mixing) and is easy to prepare and recover.

CHAPTER 3

MATERIALS AND METHODS

3.1 Overview

Laboratory procedures involved three stages: amendment selection, amendment dose consideration and a microcosm study. First, amendment selection involved laboratory batch experiments with amendment agents that were selected based upon literature review. Second, amendment dose consideration was based upon experimental results from the amendment selection phase and was used to identify the best amendment and the ideal dose. Finally, a microcosm study was performed with an estuarine water feed to recruit benthic organisms. In addition, *macoma nasuta* and *nereis virens* were added to each microcosm. This allowed for the mixing of sediments and amendment agents in a simulated natural setting. The three stages, including materials and methods are described below.

3.2 Materials

3.2.1 Aberdeen Proving Ground Field Sediments

Sediment samples were obtained from Aberdeen Proving Ground, Maryland by AECOM, chilled and shipped to the University of New Hampshire.

Samples were collected and shipped on two separate dates, December 2008 and December 2009. December 2008 samples were analyzed for total both PCB and DDx total concentrations, porewater concentrations and total organic carbon content. The sediments collected in December of 2009 were analyzed for congener-specific PCB concentrations, congener-specific porewater concentrations, total organic carbon content and black carbon content. Shipped samples were received and stored at 4°C.

3.2.2 Activated Carbon

Activated carbon (WPH®) was obtained from Calgon Carbon Corporation in Pittsburgh, Pennsylvania. WPH® is a virgin, high performance powdered activated carbon ideally suited for removing herbicides and pesticides plus many other organic chemical compounds. The specifications for the WPH® activated carbon are shown below in table 3.1.

Table 3.1 Calgon WPH® Activated Carbon Specifications

Iodine Number	800 mg/g (min)
Moisture as packed by weight	8% (max)
Screen size by weight, U.S. Sieve Series	
Through 100 mesh	99% (min)
Through 200 mesh	95% (min)
Through 300 mesh	90% (min)

3.2.3 Organoclay

Organoclay (PM-200®) was obtained from CETCO Remediation Technologies in Lovell, Wyoming. PM-200® is a granular media that is highly effective in absorbing organic compounds. Typical properties of the PM-200® organoclay is provided below in table 3.2.

Table 3.2 CETCO PM-200® Organoclay Specifications

Bulk Density Range	44-56 lbs/ft^3
Hydraulic Conductivity	1 x 10^{-3} cm/sec minimum
Oil Adsorption Capacity	0.5 lb of oil per lb of Organoclay minimum
Quaternary Amine Content	25-33% quartenary amine loading
No. 10 Sieve Size (Retained)	1% Maximum
No. 100 Sieve Size (Retained)	3% Maximum

3.2.4 Zero Valent Iron

Zero valent iron powder (H200 Plus™) was obtained from Hepure Technologies in Wilmington, Delaware. H200 Plus™ typically contains 95.5% iron, representing a combination of iron grades in order to provide superior reactivity. Typical H200 Plus™ ZVI powder characteristics are provided in table 3.3.

Table 3.3 H200 Plus™ Zero Valent Iron Characteristics

Chemical Analysis	
Carbon	1.75 - 4.50%
Silicon	1.0 – 2.50%
Sulfur	0.01 – 0.15%
Oxygen	2.5% Max
Particle Size Distribution	
+60 Mesh (>250 microns)	1.0% Max
-100/+325 Mesh (45-150 microns)	59-84%
-325 Mesh (<45 microns)	15-40%
Apparent Density	2.8 – 3.2 g/cm^3

3.2.5 Macroalgae

Macroalgae was obtained from Keep It Simple Incorporated in Redmond, Washington. The macroalgae is a soluble seaweed derived from *Ascophyllum Nodosum Seaweed*.

3.2.6 Polyoxymethylene (POM) Strips

Polyoxymethylene was obtained in a 12 linear foot roll (76 um thick) from CS Hyde, Lake Villa, Illinois.

3.2.7 Solid Phase Microextraction (SPME) Fibers

Solid phase microextraction fiber (outer and inner diameters of 300 um; 200 um, respectively) was obtained from Fiberguide Industries, Sterling, New Jersey.

3.2.8 *Macoma nasuta* and *Nereis virens*

Macoma nasuta and *nereis virens* were obtained from Aquatic Research Organisms in Hampton, New Hampshire.

3.3 Methods

This study was performed using a staged approach. Major stages of the design included: 1) evaluation of amendment effectiveness, 2) amendment dose consideration, and 3) bioaccumulation/microcosm study. First, the effectiveness of amendments selected, based on literature review, were tested in laboratory batch experiments to evaluate if the reagents successfully sequester or dechlorinate PCBs and/or DDx in Canal Creek APG wetland hydric soils. Effectiveness was measured based on decrease in contaminant concentrations in pore water. Next, the most effective amendment, activated carbon, was further evaluated to determine the optimum dose necessary to achieve maximum decrease in contaminant pore water concentrations. Finally, a microcosm experiment was performed with hydric soils amended with activated carbon to demonstrate decrease in hydrophobic organic contaminant porewater concentrations. The three study stages are described in detail below.

3.3.1 Three Stages

Sediment Amendment Screening: Evaluation of Amendment Effectiveness

In order to select the most appropriate agents for analysis in a laboratory setting, a thorough literature review was conducted. The amendment agents

chosen, based upon the literature review, were activated carbon, organoclay, macroalgae and zero-valent iron. The addition of these amendments either increase sorptive phase content of wetland hydric soils or result in reductive dechlorination. Increased sorptive content of particulate matter in hydric soils will result in increased sequestration of DDx and PCBs, resulting in lower pore water concentrations.

Sediment samples were obtained (December 2008) from Aberdeen Proving Ground, Maryland by AECOM and shipped to the University of New Hampshire. Samples that had the highest PCB and DDx concentrations (sample APG-SED-2C for PCBs and APG-SED-4C for DDx, see Table 3.1) were selected for laboratory batch experiments and to evaluate porewater contaminant concentrations. Two sets of experiments were performed; one with PCB and one with DDT contaminated sediments. The sample for PCB analysis (SED-2C) contained Total Organic Carbon (TOC) of 15.9% and total PCB concentration of 5.70 mg/kg. The sediment sample for DDx (SED-4C) contained 14.2% TOC and total DDx concentration of 6.92 mg/kg.

Both hydric soil samples were homogenized prior to taking subsamples to prepare batches. The samples were split into 4 sets of 50 gram subsamples, referred to as batch reactors, and were either amended with activated carbon, organoclay, macroalgae, ZVI or were used as controls (i.e., unamended hydric soils). Table 3.4 shows the experimental design for the sediment amendment screening stage including the number of batches and dosage levels for each treatment. Samples amended with activated carbon, organoclay and macroalgae

were amended at levels of 3% and 6% (w/w) while the samples amended with zero valent iron were amended at levels of 5% and 10% (w/w). All experiments were allowed to equilibrate for eight weeks, were performed in duplicates and two controls were maintained for the entire experiment.

Table 3.4 Sediment Amendment Screening Stage Experimental Design

Amendment	Dose, % (w/w)	Number of Batches
NA (unamended control batch)	0	2
Activated Carbon	3	2
	6	2
Organoclay	3	2
	6	2
Macroalgae	3	2
	6	2
ZVI	5	2
	10	2
Total Number of Batches:		**18**

After eight weeks, porewater samples were obtained from both non-amended and amended sediments APG-SED-2C for and APG-SED-4C following the standard method for porewater separation (ASTM D7363 – 07). Briefly, sediment samples are centrifuged and flocculated with alum and sodium hydroxide to remove colloids. Porewater is decanted and SPME fibers are added to the porewater and allowed to equilibrate for 48 hours. SPME fibers are then removed from the porewater and extracted in hexane. Vials with fibers and hexane were sent to Dr. Kannan Kurunthachalam, Laboratory of Organic Analytical Chemistry, Albany, New York for analysis using high resolution gas

chromatography / high resolution mass spectrometry. The results of this analysis are shown below in the Results and Discussion section.

Amendment Dose Consideration Stage

The amendment dose consideration stage involved the determination of the most appropriate amendment dose. Experimental results from the sediment amendment screening were evaluated to understand dose-response relationship. Observation of amendment effectiveness, through reductions in porewater concentrations, determined activated carbon to be the most effective amendment agent. Furthermore, little difference was observed between an activated carbon dose of 3% and 6%, leading to a recommended dose of 3%. The new dose percentage was determined as lower amendment concentrations were still very effective at reducing contaminant bioavailability, and a lower dose would not only be more cost-effective but may result in minimizing adverse ecological impacts.

Microcosm Study

The sediment amendment screening and dose consideration involved the addition of amendment agents, well mixed by hand, to hydric soil representing a best case scenario. However, field conditions will most likely not represent an ideal well-mixed scenario but less efficient mixing circumstances that will primarily rely on natural processes to aid the incorporation of amendments into hydric soils and thus the stabilization of contaminants. In addition, there is a chance that mixing may not occur in the absence of benthic organisms. To

replicate these scenarios, a microcosm study was performed at the Jackson Estuarine Laboratory in Durham, New Hampshire (figure 3.1).

Figure 3.1 Microcosm Setup, Jackson Estuarine Laboratory, Durham, NH.

Contaminated sediments from the Aberdeen Proving Ground (APG) were used to create the microcosms. In order to represent natural mixing, a continuous estuarine feed water was supplied from the Great Bay Estuary surrounding the Jackson Estuarine Laboratory, allowing for the recruitment of benthic organisms. In addition, *macoma nasuta* and *nereis virens* (figure 3.2 and 3.3) were added to the microcosms to aide in the mixing process.

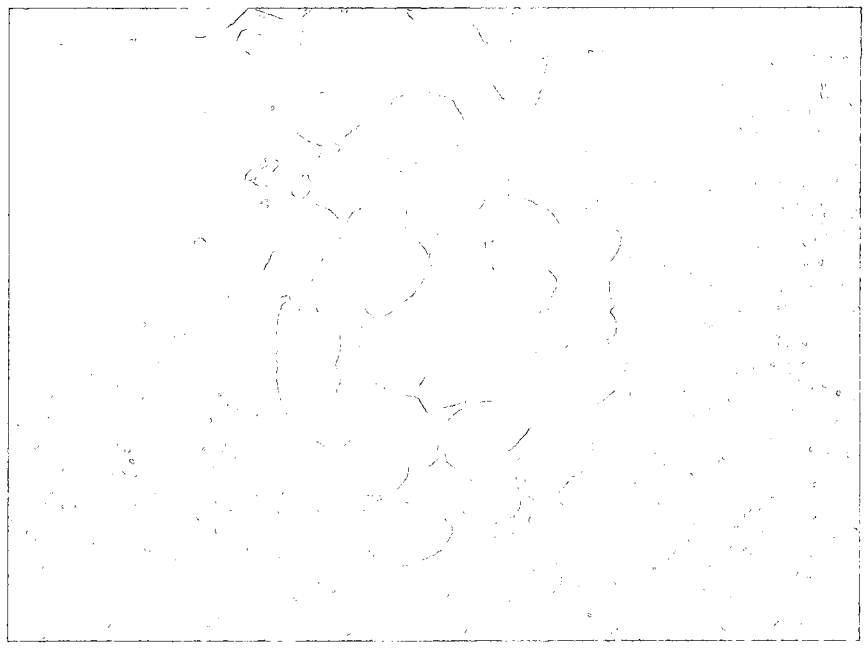

Figure 3.2 *Macoma Nasuta* Utilized in Microcosm.

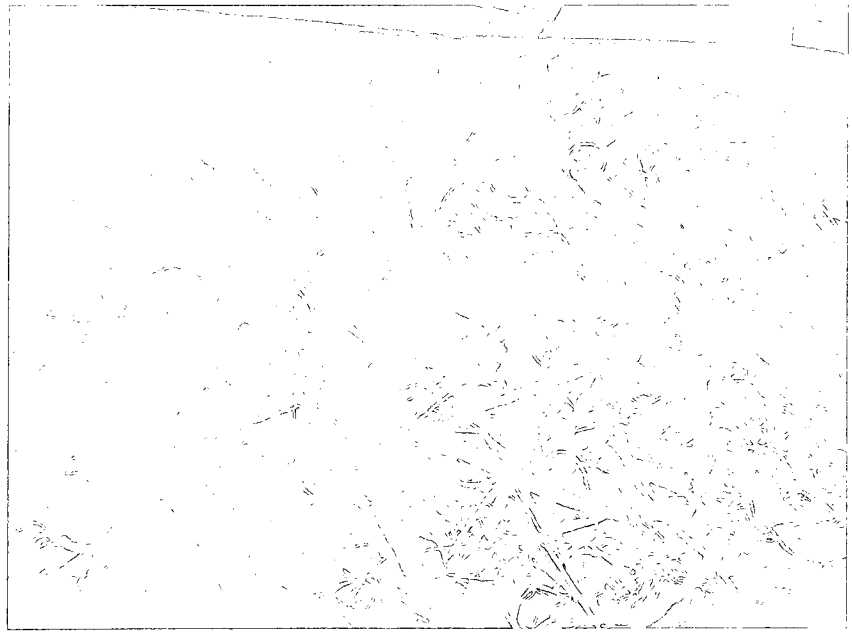

Figure 3.3 *Nereis Virens* Utilized in Microcosm.

Approximately twenty-five gallons of hydric Aberdeen Proving Ground sediments were homogenized and equally split between five microcosms. In order to represent natural mixing five microcosms were created; two for activated carbon using (2) proposed field application methods, Aquablok (figure 3.4), a slurry and a control. The amended microcosms were both created in duplicate. The microcosms that were amended were five-gallon aquariums, while the control microcosm was a ten-gallon aquarium. Figure 3.5 is the microcosm layout after the first amendment. The control microcosm is the large tank in the foreground of the picture, while the Aquablok microcosms are in the middle and the activated slurry microcosms are in the rear. After the addition of the amendements, the microcosms were allowed to equilibrate for twenty-four hours.

Figure 3.4 Aquablok Pre-application to Microcosm.

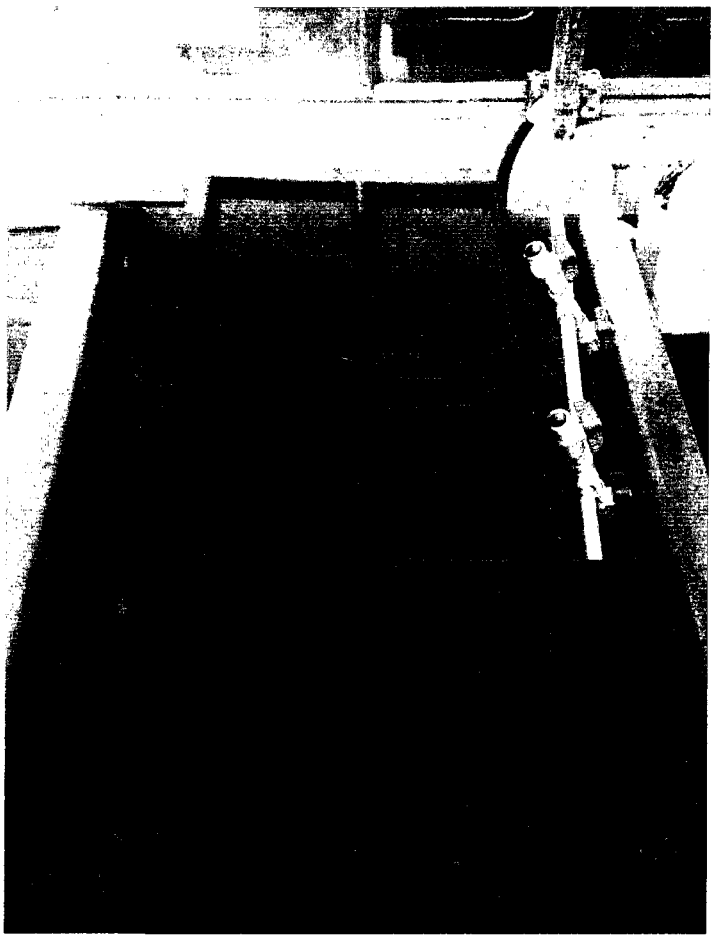

Figure 3.5 Microcosm Layout Post-application.

After twenty-four hours six POM strips, ten *macoma nasuta* and twelve *nereis virens* were added to each of the five microcosms (figure 3.6 and 3.7), numbers determined both by cost and typical organism densities. The microcosms were allowed to equilibrate for thirty days and the POM, clams and worms were then harvested from each microcosm. Survival rates for *macoma nasuta* were approximately forty percent on average, or four out of ten, and one hundred percent for *nereis virens*.

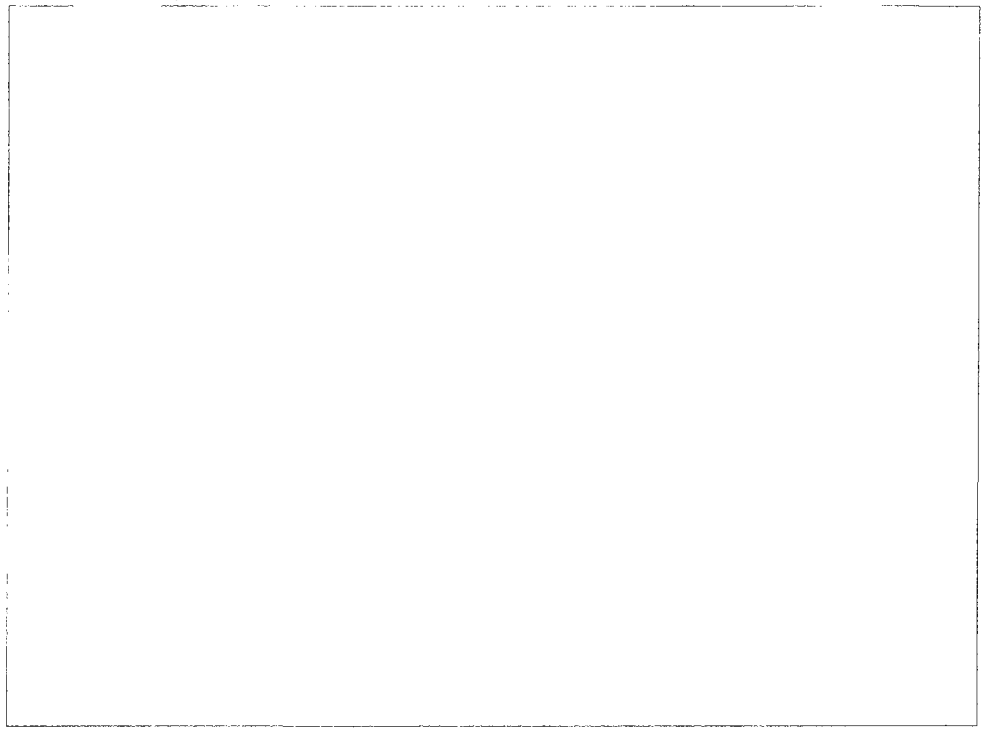

Figure 3.6 *Macoma nasuta* in Microcosm.

Figure 3.7 *Nereis virens* in Microcosm.

Harvesting of the clams and worms resulted in the unavoidable consequence of the disturbance and mixing of the microcosm sediments and amendments. Although this was unexpected, it allowed for a simulated long-term amendment and sediment mixing scenario, therefore, POM, *macoma nasuta* and *nereis virens* were again added to the microcosms. The microcosm were allowed to equilibrate for another thirty days and the POM and organisms were harvested. Survival rates for the second microcosm experiment was also forty percent for *macoma nasuta* and one hundred percent for *nereis virens*. The organisms were processed and prepared for PCB analysis as described in section 3.3.2.

3.3.2 Sampling Plan

In order to determine amendment effectiveness, pore water analysis and bioaccumulation testing were performed for both the sediment amendment screening batch experiment and the microcosm experiment. They are detailed below.

Sample Cleanup

A cleanup step was necessary, for the *nereis virens* and *macoma nasuta* extractions samples and the sediment extraction samples, due to the presence of organic compounds that cause interference during analysis. Therefore, a silica gel cleanup based on EPA 3630C was utilized. Silica gel cartridges were

washed with 10ml of hexane and then were loaded with 2mL of concentrated sediment extracts. The cartridge was then loaded with 130mL of hexane, which was collected and concentrated to 1mL. Samples were then diluted to 10mL and transferred to GC vials for analysis.

Sediment Amendment Screening Batch Experiment Porewater Analysis

The method that was used for the sediment batch experiment pore water analysis was Solid Phase Microextraction (SPME) analysis. This method has been performed with PCBs (Yang Z.Y. et al 2008, You, J. et al 2007) and DDx (Wennrich L et al. 2001, Rodrigues, M.V.N. et al. 2004). Briefly, solid Phase Microextraction fibers were allowed to equilibrate for 48 hours in centrifuged porewater (ASTM Method ASTM D7363 – 07). SPME fibers then were removed from the porewater and extracted in hexane. Vials with fibers and hexane were sent to Dr. Kannan Kurunthachalam, Laboratory of Organic Analytical Chemistry, Albany, New York for analysis using high resolution gas chromatography / high resolution mass spectrometry.

Microcosm Porewater Analysis

The method that was used for the microcosm pore water analysis was Polyoxymethylene (POM) analysis. This method has been performed with PCBs (Hawthorne et al., 2009; Cornelissen et al, 2010). Briefly, polyoxymethylene strips were placed in microcosm sediments and were allowed to equilibrate for thirty days. POM strips then were removed, dried by hand and extracted in a

20mL 1:1 acetone hexane mix. Samples were then blown down to 5 ml and brought back up to 20 mL with hexane. Sample extracts were then analyzed as described in the Microcosm PCBs-GC Method section below.

Microcosm Organism Preparation for Analysis

Macoma nasuta and *nereis virens* were removed from the microcosms and weighed out (15-20g wet weight) into 40 mL vials and were frozen for later processing. Samples were later removed, thawed, cut into small pieces and placed on a Labconco freezone six freeze drier system for forty-eight hours. Vacuum was maintained at $33x10^{-3}$ mbar and the collector temperature was kept at -49 °C. Samples were then prepared and extracted using Dionex Accelerated Solvent Extraction with a 1:1 acetone hexane mix. Sample extracts were then cleaned according to EPA 3630C (silica gel cleanup for PCBs) and were analyzed as described in the Microcosm PCBs-GC Method section below.

Sediment Amendment Screening Batch Experiment PCBs-GCMS Method

The oven was programmed from 140 °C (1.5 min) at 20 °C/min to 190 °C (0 min hold); then at 1 °C/min to 216 °C (0 min hold); and then at 20 °C to 300 °C (5 min). Splitless injection (2 uL) was done at T_{inj} = 270 °C; $T_{transerline}$ at 270 °C. Helium was used as carrier gas at a flow rate of 1 mL/min. The GC used was a Finnigan Trace GC Ultra. The column used was a Restek Rxi-5 MS 30 m (length) x 0.25 mm (ID) x 0.25 um (film). The MS used was a Thermo MAT-95XT high res mass spectrometer. The ion source temperature was 270 °C. This method was performed at the Laboratory of Organic Analytical Chemistry, Albany, New York.

Microcosm PCBs-GCMS Method

The oven was programmed from 40 °C (2.0 min) at 12 °C/min to 184 °C (0 min hold); then at 4 °C/min to 280 °C (0 min hold); and then at 280 °C to 300 °C at 8 °C/min (4.5 min hold). Splitless injection (2 uL) was done at T_{inj} = 300 °C. Helium was used as carrier gas at a flow rate of 1 mL/min. The GC used was a Varian CP-3800 gas chromatograph. The column used was a Varian Factor Four Capillary column: VF-5ms 30m (length) x 0.25 mm (ID) x 0.25 um (film). The MS used was a Saturn 2000 mass spectrometer. The ion source temperature was 300 °C.

Sediment Amendment Screening Batch Experiment Pesticides-GCMS Method

The oven was programmed from 80 °C (2 min) at 10 °C/min to 150 °C (2 min hold); then at 3 °C min to 200 °C (0 min hold); and then at 6 °C to 270 °C (5 min). The MS used was a Thermo MAT-95XT high res mass spectrometer. The ion source temperature was 270 °C.

Bioaccumulation Testing

Bioaccumulation testing was provided by Ghosh et al. and was reported in the sedimite treatability study report on the Aberdeen Proving Ground sediments. Briefly, a subsample of sediment was shipped to UMBC from our lab at the University of New Hampshire and bioaccumulation testing was performed as described below (Ghosh et al., 2009).

Sediment Treatment with Activated Carbon (Ghosh et al., 2009)

Prior to processing, the sediment was stored in a refrigerator at 4 degree Celsius temperature. Twelve beakers of 500 ml volume were filled with 150 ml of homogenized sediment slurry and 300 ml of filtered stream water obtained from a natural stream in the UMBC campus. The beakers were allowed to aerate for 1 week to reduce ammonia content in the overlying water to less than 1.5 mg/L to minimize any toxic effect on the test organisms. The following treatments were performed:

1) Control: 4 beakers for control (no amendment),
2) Activated carbon-low: 4 beakers with a low dose of activated carbon (0.5 x TOC as carbon)
3) Activated carbon-high: 4 beakers with a high dose of activated carbon (1.0 x TOC as carbon)

The activated carbon treatment pellets were applied on the sediment surface and allowed to soften overnight before being manually mixed into the sediment as described in the treatability study plan. The beakers after mixing the treatments were allowed to settle for one day before starting the bioaccumulation test.

14 day Bioaccumulation Study of PCBs and DDx (Ghosh et al., 2009)

PCB uptake in the freshwater oligochaete L. variegatus was measured to assess the change in PCB bioavailability to benthic organisms after amending

with activated carbon. The bioaccumulation test method used was based on the method described in USEPA (2000). Fresh L. variegatus were obtained from Aquatic Research Organisms, Hampton, New Hampshire. The worms were maintained in the laboratory using standard culturing procedures outlined in the USEPA (2000). Essentially the culturing method involves maintaining the worms in plastic containers with pureed unbleached paper towel and stream or site water with daily renewal of the overlying water. The water in the culture chamber is aerated using an aquarium air pump and an air stone.

At the initiation of the bioaccumulation test, 0.5g wet worms were weighed and added to each test beaker described above. The worms were exposed to the test sediment for 14 days and maintained at 23 ± 1 °C in an aquarium maintained with a 16 hour light:8 hour dark photoperiod. The aquarium contained water to a depth of 3" (partially immersing the exposure beakers) to maintain a constant temperature for all the beakers. A thermometer placed in the aquarium water was used to monitor temperature of the test. Average values of water quality parameters in overlying water at test initiation were: temperature 23 °C, DO 5.5 mg/L, pH 6.8, general hardness 280 mg/L as $CaCO^3$, alkalinity 160 mg/L as $CaCO^3$.

At the termination of the experiment, worms were removed from the sediments and allowed to depurate for 6 hours in clean beakers containing stream water. The worm wet tissue mass was measured after removing the excess water and frozen until further analysis.

PCB and DDx analysis (Ghosh et al., 2009)

The organisms were ground with anhydrous sodium sulfate and extracted by sonication using three volumes of 40 ml each of hexane-acetone mixture (1:1) according to EPA SW846 method 3550B. Total extracted solvent were split into two for DDT and PCB analysis. Sample cleanup was performed based on EPA SW846 methods 3660B (activated copper cleanup), 3665A (sulfuric acid cleanup), 3620B (activate florosil cleanup for DDT) and 3630C (silica gel cleanup for PCB). DDT & PCB analysis were performed using an Agilent 6890 gas chromatograph with a micro electron capture detector. One of the PCB congeners (#153) coeluted with a contaminant peak in the tissue extracts and was removed from the analysis from all samples. This congener contributed less than 0.2% of total PCB in the sediment extraction. The results of this analysis are provided below in the Results and Discussion section.

Total Organic Carbon (TOC) Analysis

In order to determine the total organic carbon of Aberdeen Proving Ground Sediments, a loss-on-ignition method (LOI) was used. The LOI method for the determination of organic matter involves the heated destruction of all organic matter in the soil or sediment. A known weight of sample was placed in a ceramic crucible (or similar vessel) that was then heated to between 350 °C and 440 °C overnight (Blume et al., 1990; Nelson and Sommers, 1996; ASTM, 2000). The sample was then cooled and weighed. Total organic carbon content was calculated as the difference between the initial and final sample weights

divided by the initial sample weight times 100%.

Black Carbon Analysis

A modified method adapted from Gustafsson et al. (1997) was used to determine the black carbon totals in Aberdeen Proving Groundfield sediments. The method is described below.

Removal of OC: Samples were dried in covered containers at 60 °C and ground to <500 μm individual particle size. About 50 mg of each sample was weighed into pretared porcelain crucibles with a silica glaze surface (Coors Ceramics, Golden, CO). Crucibles, covered with precombusted aluminum foil, were placed inside a muffle furnace and were oxidized at 375 °C for 24 h in the presence of excess oxygen (air).

Removal of IC: The cooled samples were subsampled and weighed into pretared weigh boats using an electrical microbalance. After wetting each sample with 25 μL of water, 25 μL of 1 M HCl was added into each crucible. Then, the samples were allowed to sit for 1 h at room temperature covered with clean Al foil. When the capsules had cooled, another 50 μL of 1 M HCl was added, followed by 30 min of cooling. The Al tray with samples was then placed in an oven and dried at 60 °C. The last three steps were repeated until effervescence upon acid addition ceased, indicating complete removal of carbonates.

Finally, a thermo gravometric analysis (TGA) machine (SQ 600, TA Instrument, Texas, USA) was used to analyze for sediment black carbon content. As highlighted by Gustafsson et al. (1997), SC was oxidized at 450-500 °C, therefore, any compound that was oxidized within the range of 450-500 °C was assumed to be black carbon. Black carbon content was calculated as the difference between the initial and final sample weights divided by the initial sample weight times 100%.

3.3.3 Calibration of Analytical Equipment and Quality Assurance

Gas chromatographic analysis was used to quantify PCB and DDT porewater concentrations. All porewater concentration samples were analyzed with a high resolution mass spectrometer (Thermo MAT-95XT) and a gas chromatograph (Finnigan Trace GC Ultra). All microcosm porewater samples and *macoma nasuta* and *nereis virens* extracts were analyzed with a Varian CP-3800 gas chromatograph with a Saturn 2000 mass spectrometer. The instruments are maintained according to manufacturer's instructions and are calibrated accordingly.

An external calibration curve was used for all samples to ensure a high level of analysis efficiency. To provide quality assurance, all samples were amended in duplicate and controls were maintained in the experimental design. Finally, method blanks were used to ensure there was no carryover between samples or contamination from reagents, air, instruments, sample preparation or glassware.

3.3.4 Decontamination Procedures

To ensure no contamination of personnel or equipment, the appropriate safety precautions were taken. Personal safety equipment was used including gloves, lab coats, closed toed shoes, long pants and goggles. Laboratory equipment was properly washed and stored in designated cabinets and contaminated protective gear was properly disposed.

3.3.5 Sample Documentation

Sediment samples were taken from wetlands of Canal Creek at the Aberdeen Proving Grounds (APG), Maryland and labeled by sampling location. Samples were received at the laboratory with a chain-of-custody form and the sample IDs identified on the form was carried through all experiments.

3.3.6 Data Analyses

As previously indicated, DDx and PCBs are the main contaminants of interest. Analytical methods included the detection of DDT, DDE, DDD, and congener-specific PCBs for the first sediments collected in December of 2008. The second sediments collected in December 2009 were analyzed for total sediment PCB concentrations and also congener-specific PCBs. All data was analyzed using traditional statistical analysis, such as t-tests, ANOVA, standard deviation and statistical significance.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This study consisted of multiple stages of research and analysis. Sediments were collected from Aberdeen proving ground on two separate events (December 2008 and December 2009) that traditionally consisted of high PCB and DDx concentrations. Sediments collected in December 2008 were analyzed for both PCB and DDx total concentrations, porewater concentrations and total organic carbon content. The sediments collected in December of 2009 were analyzed for congener-specific PCB concentrations, congener-specific porewater concentrations, total organic carbon content and black carbon content.

Total hydrophobic organic contaminant (HOC) sediment concentrations are important and relevant for determining risk factors associated with contamination. However, it is crucial to determine the levels of freely dissolved organic contaminant concentrations in porewater, as this is what determines uptake amounts. Therefore, this study utilized passive samplers (SPME and POM) to assess the reduction of HOC porewater concentrations provided by amendments with remediation agents. Amendments of activated carbon,

seaweed, organoclay and zero valent iron were applied to the most contaminated sediments (collected in December 2008), in order to determine the most effective amendment agent, and reductions in porewater concentrations were observed through the use of solid-phase microextraction (SPME) fibers. The optimal dose was then determined and utilized in a microcosm study, simulating field conditions. In addition, another small batch of these sediments were combined and sent to Upal Ghosh at the University of Maryland, Baltimore County (UMBC) for a bioaccumulation study using lumbricus variegatus.

For the microcosm study, all remaining sediments were homogenized and split equally into five microcosms, in hopes of simulating actual field conditions, which were supplied with a continuous estuarine feedwater. Microcosms were amended with two activated carbon amendment delivery techniques (activated carbon slurry and Aquablok). Reductions in PCB porewater concentrations were analyzed with the use of polyoxymethylene (POM) strips and through biouptake in the organisms *macoma nasuta* and *nereis virens*. Finally, the comparisons of two different methods of POM analysis and amendment delivery techniques were considered. The results of all stages of this study are presented below.

4.2 Sediment Characterization

Sediments samples were obtained in December 2008, from Aberdeen Proving Ground, Maryland by AECOM, and shipped to the University of New Hampshire. Analysis with the 2008 samples involved a batch reactor amendment study, also referred to as the sediment amendment screening.

Samples were analyzed for total PCB and DDx concentrations and the results are shown below in table 4.1. Sediments have total PCB concentrations ranging from 0 to 5700 ppb, a clear indicator of the difference in sediment physical characteristics. Those samples with the highest PCBs and DDx concentrations (sample APG-SED-2C for PCBs and APG-SED-4C for DDx) were selected for use in the batch reactor amendment assessment study (sediment amendment screening). Sediment samples SED-2C and SED-4C had average total organic carbon concentrations of 15%, while black carbon content was not determined.

Table 4.1 PCB and DDx concentrations detected in surficial sediments of Canal Creek (December 2008 sampling event).

Sample ID	Total PCBs, µg/kg	Total DDx, µg/kg
APG-SED-1A	4700	410
APG-SED-1B	2700	316
APG-SED-1C	740	0
APG-SED-2A	1100	233
APG-SED-2B	4900	0
APG-SED-2C	5700	0
APG-SED-3A	2500	178
APG-SED-3B	1180	87
APG-SED-4A	0	1150
APG-SED-4B	0	6000
APG-SED-4C	0	6920
APG-SED-4D	0	408

The total sediment PCB and DDx concentrations in table 4.1 are important, however, they also indicate a large range of contaminant concentrations from sediments at the same site. This is mostly due to differences in sediment heterogeneity and the partitioning of HOCs to the sediment solid phase (mainly total organic carbon and black carbon). HOCs tend to bond more readily with total organic carbon and black carbon and partition to porewater. Therefore, the total sediment concentrations were utilized to determine the estimated porewater concentrations, using the Equilibrium Partitioning Theorem (table 4.2). However, for the first sediments (collected in December 2008) black carbon content was not determined, therefore, the calculations provided below do not account for black carbon.

Calculations of theoretical partitioning of PCBs and DDT are based on the Equilibrium Partitioning Theorem (DiToro et al., 1991) provided below (Eq 4-1).

$$C_{porewater} = C_{sediment} / f_{oc} * K_{oc} \qquad \text{Eq. 4-1}$$

$C_{porewater}$ = concentration of the individual PAH, pesticide or PCB in porewater

$C_{sediment}$ = concentration of DDx (sed. 4C) or PCB (sed. 2C) in sediment ()

f_{oc} = fraction organic carbon (f_{oc} = % total organic carbon (TOC) / 100)

K_{oc} = carbon/water partitioning coefficient log ($\log K_{oc} = 0.00028 + 0.983 * \log K_{ow}$)

As shown in table 4.2, the theoretical porewater concentrations are calculated for 15% TOC and selected PCB congeners. A TOC of 15% is considered to be high, however, wetland samples are known to have high total

organic content and heterogeneity. In addition, the method used to determine TOC was only able to be performed on one occasion, as all remaining sediments were mixed and shipped off site for a bioaccumulation study.

Table 4.2 Porewater Concentrations Calculated via Equilibrium Partioning Theory vs. Measured Results (December 2008 sampling event)

Contaminant	C sediment (ug/kg)	Average Log Kow*	log Koc	% TOC	foc	Calculated Cporewater (ug/L)	Measured Cresults (ug/L)
PCB	5700	6.06	5.85	15	0.15	5.40E-02	1.17E-04

As shown in table 4.2, the calculated total porewater concentration is orders of magnitude larger than the measured value. We suspect this is because partitioning to black carbon was not considered. Furthermore, only total PCB sediment concentrations were reported for the sediments, while the K_{oc} is the average of congener specific values. Therefore, the second set of sediment samples, collected in December 2009, from Aberdeen Proving Ground, Maryland were analyzed for total PCB sediment concentrations, PCB porewater concentrations using POM, total organic carbon and black carbon content (see corresponding tables in Appendix A.1 and A.2, respectively). Below, table 4.3 indicates total PCB sediments concentrations, measured PCB porewater concentrations, total organic carbon (TOC) content and black carbon (BC) content for these sediments. PCB sediment concentrations range from the minimum detection limit (<4.28E-04 ug/L) ug/kg to 3940 ug/kg, while PCB porewater concentrations (for congener-specific data, see Appendix table A.3) range from the minimum detection limit (<4.28E-04 ug/L) to .045 ug/L. PCB

surrogate standard recoveries were >80%. TOC content ranges from 2.12% to 4.78%, while BC content ranges from .09% to .91%.

Table 4.3 Sediment Characterization of Aberdeen Proving Ground Sediments (December 2009 sampling event).

Sample	f_{OC}	f_{BC}	Total PCBs (ug/kg)	Measured Porewater Concentration (ug/L)
a1	2.48%	0.12%	107	1.56E-01
a2	2.70%	0.33%	165	<4.28E-04
a3	3.42%	0.14%	1663	2.50E-01
a4	2.92%	0.35%	891	1.08E-02
a5	4.68%	0.19%	101	2.47E-02
a6	2.64%	0.15%	488	2.21E-02
a7	3.44%	0.36%	1101	9.22E-02
a8	2.12%	0.33%	1638	4.46E-01
a9	4.41%	0.19%	1278	3.63E-02
a10	3.28%	0.41%	146	4.83E-02
a11	3.58%	0.22%	243	4.55E-02
a12	3.71%	0.22%	328	5.39E-03
c1	2.51%	0.41%	1266	1.30E-01
c2	3.09%	0.38%	68	<4.28E-04
c3	3.30%	0.90%	<4.28E-04	<4.28E-04
c4	2.35%	0.11%	<4.28E-04	1.77E-03
c5	2.58%	0.91%	<4.28E-04	3.76E-01
c6	2.55%	0.67%	1094	1.30E-01
c7	4.40%	0.18%	<4.28E-04	2.46E-02
c8	3.22%	0.56%	1884	2.47E-01
p1	4.43%	0.33%	3940	3.28E-01
p2	4.78%	0.42%	2753	4.34E-01
p3	2.40%	0.12%	298	1.51E-02
p4	3.99%	0.09%	1379	6.01E-03

In order to determine the relationship between total PCB sediment concentrations, total organic carbon content, black carbon content and porewater concentrations, equilibrium partioning calculations were utilized. Theoretical porewater concentrations for Koc only were determined using the Di Toro et al.

(1991) equilibrium partioning thereom (equation 4.1) and those that consider Koc and Kbc utilized equation 4.2 from Gschwend et al. (2002). Equation 4.2 was rearranged to solve for Cw (porewater concentration). The results of these calculations are shown below in table 4.4. Congeners were selected for the sediment samples that contained four common congener concentrations (PCB 28, 47, 66 and 95). The calculation results for all congeners are provided in Appendix table A.3.

$$K_d = f_{oc}K_{oc} + f_{bc}K_{bc}C_w^{n-1} \qquad \text{Eq. 4-2}$$

K_d = Sediment solid phase to water partioning coefficient
f_{oc} = fraction organic carbon (f_{oc} = % total organic carbon (TOC) / 100)
K_{oc} = carbon/water partitioning coefficient log
f_{bc} = fraction black carbon (f_{oc} = % total organic carbon (TOC) / 100)
K_{bc} = black carbon/water partitioning coefficient log
C_w^{n-1} = Porewater concentration (n=0.7 for PCBs) (ug/L)

Table 4.4 Porewater Concentrations Calculated via Equilibrium Partioning Theory vs. Measured Results (December 2009 sampling event).

Sample		PCB 28 (ppb) Log Kbc* = 5.5		PCB 47 (ppb) Log Kbc* = 5.8		PCB 66 (ppb) Log Kbc* = 6.7		PCB 95 (ppb) Log Kbc* = 6.1	
		Calculated	Measured	Calculated	Measured	Calculated	Measured	Calculated	Measured
p1	Koc only	1.40E-02	7.12E-03	7.32E-02	1.73E-02	3.59E-03	1.59E-03	3.62E-02	1.27E-02
	Koc & Kbc	1.24E-04	7.12E-03	4.89E-03	1.73E-02	4.11E-03	1.59E-03	5.73E-04	1.27E-02
p2	Koc only	9.13E-03	5.79E-04	5.64E-02	8.29E-03	3.39E-03	3.63E-04	3.41E-02	2.91E-03
	Koc & Kbc	2.98E-04	5.79E-04	1.27E-02	8.29E-03	9.58E-03	3.63E-04	1.38E-03	2.91E-03
a7	Koc only	0.00E+00	0.00E+00	3.13E-02	7.63E-03	2.96E-03	7.98E-05	2.98E-02	6.38E-04
	Koc & Kbc	0.00E+00	0.00E+00	4.46E-03	7.63E-03	4.87E-03	7.98E-05	6.24E-04	6.38E-04
c8	Koc only	1.24E-02	3.34E-04	5.89E-02	9.98E-03	4.94E-03	8.09E-05	4.97E-02	6.47E-04
	Koc & Kbc	5.61E-04	3.34E-04	1.80E-02	9.98E-03	2.07E-02	8.09E-05	2.60E-03	6.47E-04

***Log Kbc values obtained from Lohmann et al. (2005)**

As shown in table 4.4, calculated porewater concentrations that only consider Koc values overestimate porewater concentrations, while calculations that consider both Koc and Kbc more closely resemble measured concentrations. We suspect this is due to variation in other forms of organic carbon and sediment heterogeneity. Figure 4.1 shows the relationship of the calculated vs. measured porewater concentrations. The forty-five degree trendline is the expected outcome for the calculated vs. measured porewater concentrations while the other trendline represents the trend for all data points. Figure 4.1 clearly indicates that, for this study on average, the equilibrium partioning theory overestimated (even when considering black carbon) calculated porewater concentrations. Therefore, while the use of the equilibrium partioning theory provides estimated porewater concentrations, direct measurement provides a better understanding of actual porewater concentrations.

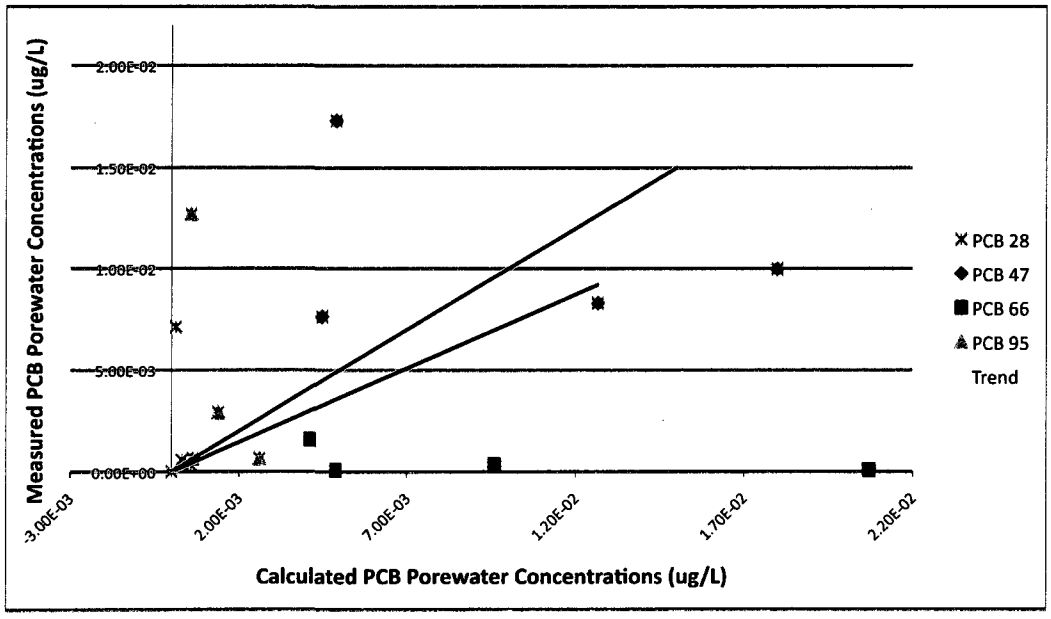

Figure 4.1 Calculated vs. Measured Porewater Concentrations

A study by Arp et al. (2008) conducted a detailed review of several hundreds of data for PAHs, PCBs, PCDD/Fs, and chlorinated benzenes, covering a large variety of sediments, locations, and experimental methods. Data from Arp et al. suggests that traditional methods of estimating porewater concentrations based upon octanol-water partitioning generally overestimate native porewater concentrations, while approaches accounting for multiple carbon fractions, including black carbon, appear sediment specific.

The calculation and determination of hydrophobic organic contaminants in sediments based upon partioning to and from the sediment solid phase is important, however, it is this partitioning of PCBs and DDx to porewater that determines bioavailability. Moreover, Arp et al. (2008) specifically mention that the only way to accurately obtain porewater concentrations is to measure them directly, and not infer them from sediment concentrations.

4.3 Sediment Amendment Screening and Dose Consideration

The direct measurement of PCB porewater concentrations accounts for freely dissolved contaminants and avoids the need for calculations and estimates based upon sediment physical characteristics. Therefore, solid-phase microextraction (SPME) fibers were used to determine both the unamended and amended PCB and DDx porewater concentrations within the first sampling event (December 2008) sediments. Sediment amendment screening involved the observation of reduction of porewater PCBs and DDT concentrations in

Aberdeen Proving Ground Sediment. Changes in contaminant porewater concentrations were observed in sediment batch reactor experiments, through the use of SPME fibers, utilizing various amendment agents. The purpose of this was to screen the effectiveness of a variety of different types of amendments reported in literature. Amendments of activated carbon (AC), organoclay (OC), macroalgae (seaweed - SW) and zero valent iron (ZVI) were added to sediment. The corresponding data, figures and tables for the sediment amendment screening and dose consideration are discussed below.

Amendment Effectiveness in PCB Contaminated Sediment

Figure 4.2 shows percent reduction in porewater concentrations of five PCB congeners while table 4.5 includes the raw data. Organoclay was added at 3% (OC-3) and 6 % (OC-6), seaweed was added at 3% (SW-3) and 6% (SW-6), ZVI was added at 5% (ZVI-5) and 10% (ZVI-10) and activated carbon was added at 3% (AC-3) and 6% (AC-6). These data indicate that seaweed had marginal effectiveness at 3% (SW-3) and resulted in increases in PCB concentrations at 6% (SW-6), organoclays had mixed results – decreasing some porewater congener concentrations and apparently increasing others. ZVI resulted in increases in PCB bioavailability, and activated carbon significantly reduced PCB porewater concentrations.

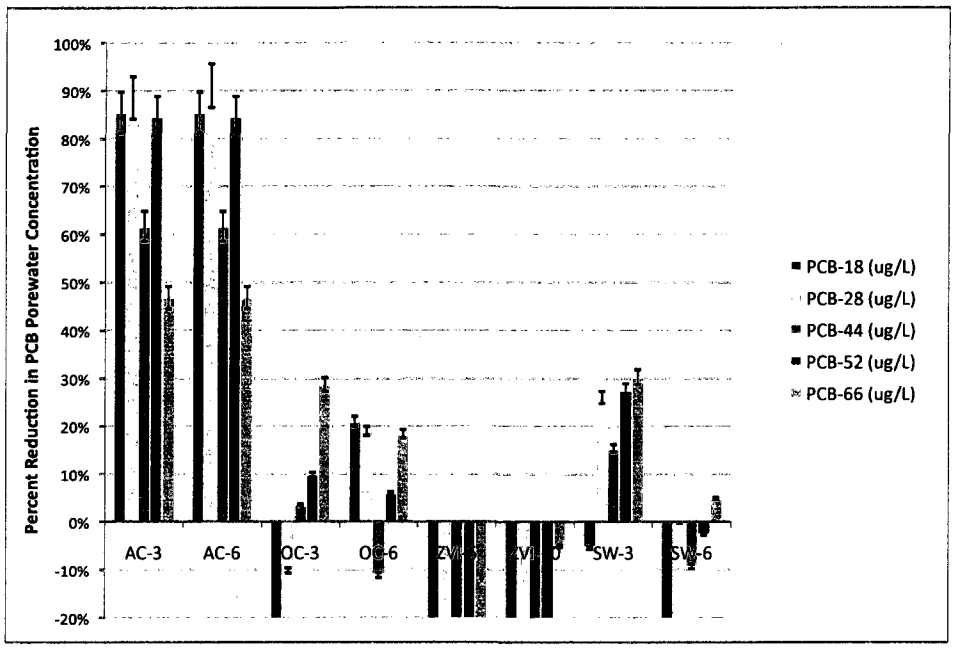

Figure 4.2 Percent Reductions in PCB Porewater Concentrations with Amendment Addition

Table 4.5 PCBs concentrations in porewater (ug/L)

Sample	pcb-18	pcb-28	pcb-44	pcb-52	pcb-66
Control (avg)	1.05E-03	5.61E-05	3.23E-05	7.71E-05	1.02E-05
oc3a	1.84E-03	6.57E-05	3.68E-05	7.41E-05	5.72E-06
oc3b	1.35E-03	5.78E-05	2.55E-05	6.49E-05	8.76E-06
oc6a	9.36E-04	5.07E-05	3.80E-05	7.36E-05	7.01E-06
oc6b	7.24E-04	4.01E-05	3.38E-05	7.12E-05	9.58E-06
zv1-10b	2.39E-03	9.49E-05	6.44E-05	1.39E-04	1.21E-05
zv1-10b	1.31E-03	5.27E-05	3.24E-05	6.56E-05	9.27E-06
zv1-5a	2.12E-03	7.91E-05	5.10E-05	1.17E-04	1.26E-05
zv1-5b	5.39E-03	2.25E-04	1.16E-04	2.38E-04	2.74E-05
ac6a	1.52E-04	3.78E-06	1.24E-05	1.18E-05	5.40E-06
ac6b	1.52E-04	6.18E-06	1.24E-05	1.18E-05	5.40E-06
ac3a	1.52E-04	4.47E-06	1.24E-05	1.18E-05	5.40E-06
ac3b	1.52E-04	8.37E-06	1.24E-05	1.18E-05	5.40E-06
sw3a	1.07E-03	3.41E-05	2.47E-05	4.56E-05	6.42E-06
sw3b	1.14E-03	4.87E-05	3.00E-05	6.60E-05	7.74E-06
sw6a	1.69E-03	6.18E-05	4.00E-05	8.89E-05	1.03E-05
sw6b	1.35E-03	5.06E-05	3.06E-05	6.94E-05	9.07E-06

Assuming a normal distribution and a confidence interval of 90%, the data in table 4.6 shows whether the PCB porewater change was statistically significant. Organoclay shows a statistically significant decrease in PCB concentrations for only congener 18 at a dose of 3% (w/w). Zero valent iron results in statistically significant increases in porewater concentrations for every congener at 5% (w/w) amendment and an increase of congener 18 at 10% (w/w). Seaweed does not provide a statistically significant increase or decrease in PCB concentrations. Therefore, seaweed and organoclay do not provide enough of a reduction in PCB concentration while zero-valent iron significantly increases the concentrations of PCBs. Activated carbon resulted in statistically significant PCB concentration decreases, with the exception of congener 44, further indicating its potential as the most effective amendment agent.

Table 4.6 Statistical Significance for PCBs

Sample	pcb-18	pcb-28	pcb-44	pcb-52	pcb-66
Control (avg)	0.35	1.16	0.26	0.65	0.19
Std Dev	0.079	0.411	0.138	0.272	0.033
OC-3	YES	NO	NO	NO	NO
OC-6	NO	NO	NO	NO	NO
ZVI-5	YES	YES	YES	YES	YES
ZVI-10	YES	NO	NO	NO	NO
AC-3	YES	YES	NO	YES	YES
AC-6	YES	YES	NO	YES	YES
SW-3	NO	NO	NO	NO	NO
SW-6	NO	NO	NO	NO	NO

Figure 4.3 indicates the effectiveness of activated carbon added at 0% (control), 3% and 6%. Because there is little difference observed between 3% and 6% and both levels are statistically significant (as shown in table 4.6), 3% activated carbon is the most cost-effective approach for amendment addition.

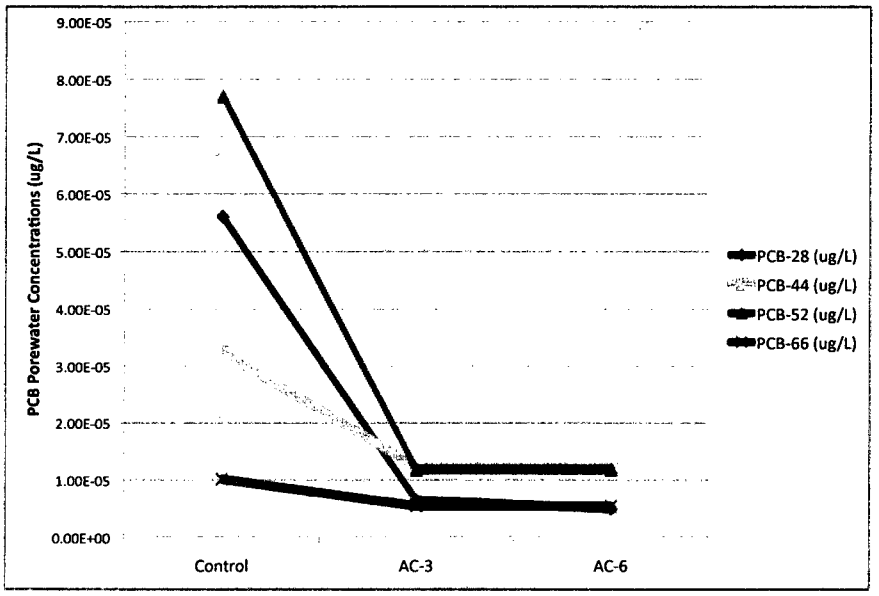

Figure 4.3 Activated Carbon Effectiveness for PCBs

Amendment Effectiveness in DDx Contaminated Sediment

Figure 4.4 shows % reduction in porewater concentrations of DDT and its reduced forms while table 4.7 indicates the raw data for average porewater concentrations of DDx. Concentrations listed as <1.53E-05 ug/L were below the detections limits, therefore, for the purpose of concentration reduction calculations, they were assumed to be equal to 1.53E-05 ug/L. Organoclay was added at 3% (OC-3) and 6 % (OC-6), seaweed was added at 3% (SW-3) and 6% (SW-6), ZVI was added at 5% (ZVI-5) and 10% (ZVI-10) and activated carbon was added at 3% (AC-3) and 6% (AC-6). These data show that seaweed had marginal effectiveness at 3% (SW-3) and resulted in increases in DDx concentrations at 6% (SW-6), organoclays had marginal effectiveness for reducing these porewater concentrations, ZVI resulted in increases in DDx

concentrations, and activated carbon significantly reduced DDx porewater concentrations.

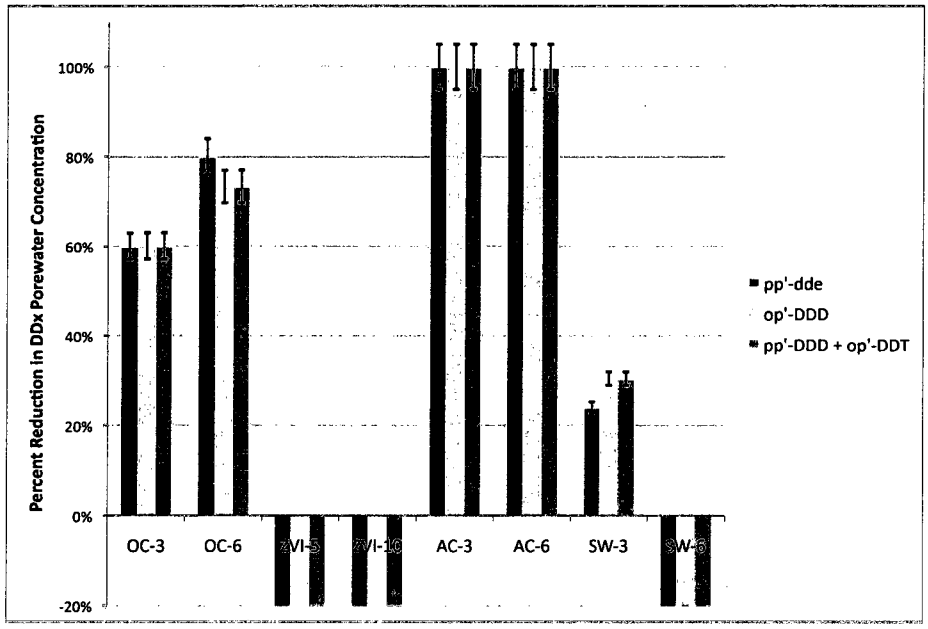

Figure 4.4 Percent Reductions in DDx Porewater Concentrations with Amendment Addition

Table 4.7 DDx average concentrations in porewater (ug/L)

Sample	op'-dde	pp'-dde	op'-DDD	pp'-DDD + op'-DDT	pp'-DDT
Control (avg)	1.67E-05	1.40E-04	5.00E-04	6.14E-04	< 1.52 E-05
zvi5	< 1.52 E-05	2.10E-04	9.19E-04	1.13E-03	< 1.52 E-05
zvi10	< 1.52 E-05	2.54E-04	1.08E-03	1.33E-03	< 1.52 E-05
ac3a	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05
ac3b	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05
ac6a	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05
ac6b	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05	< 1.52 E-05
oc3a	< 1.52 E-05	3.74E-05	9.23E-05	1.13E-04	< 1.52 E-05
oc3b	< 1.52 E-05	7.49E-05	3.07E-04	3.77E-04	< 1.52 E-05
oc6a	< 1.52 E-05	2.81E-05	1.34E-04	1.64E-04	< 1.52 E-05
sw3a	< 1.52 E-05	1.07E-04	3.48E-04	4.28E-04	< 1.52 E-05
sw6b	< 1.52 E-05	1.87E-04	6.07E-04	7.46E-04	< 1.52 E-05

Assuming a normal distribution and a confidence interval of 90%, the data in table 4.8 shows the statistical significance of the DDx amendment agents. Zero-valent iron results in statistically significant increases of DDx concentration while organoclay, seaweed and activated carbon result in statistically significant decreases. However, given the raw data in table 4.7 and the information in figure 4.4, it is clear that activated carbon is an extremely effective remediation agent.

Table 4.8 Statistical Significance for DDx Porewater Changes

Sample	pp'-ddt	op'-DDD	pp'-DDD +op'-DDT
control (avg)	0.46	1.65	2.02
std dev	0.05	0.11	0.14
ZVI-5	YES	YES	YES
ZVI-10	YES	YES	YES
AC-3	YES	YES	YES
AC-6	YES	YES	YES
OC-3	YES	YES	YES
OC-6	YES	YES	YES
SW-3	YES	YES	YES
SW-6	YES	YES	YES

Figure 4.5 shows the effectiveness of activated carbon added at 0% (control), 3% and 6%. Because there is little difference observed between 3% and 6% and both levels are statistically significant (as shown in table 4.8), 3% activated carbon is the most cost-effective approach for amendment addition.

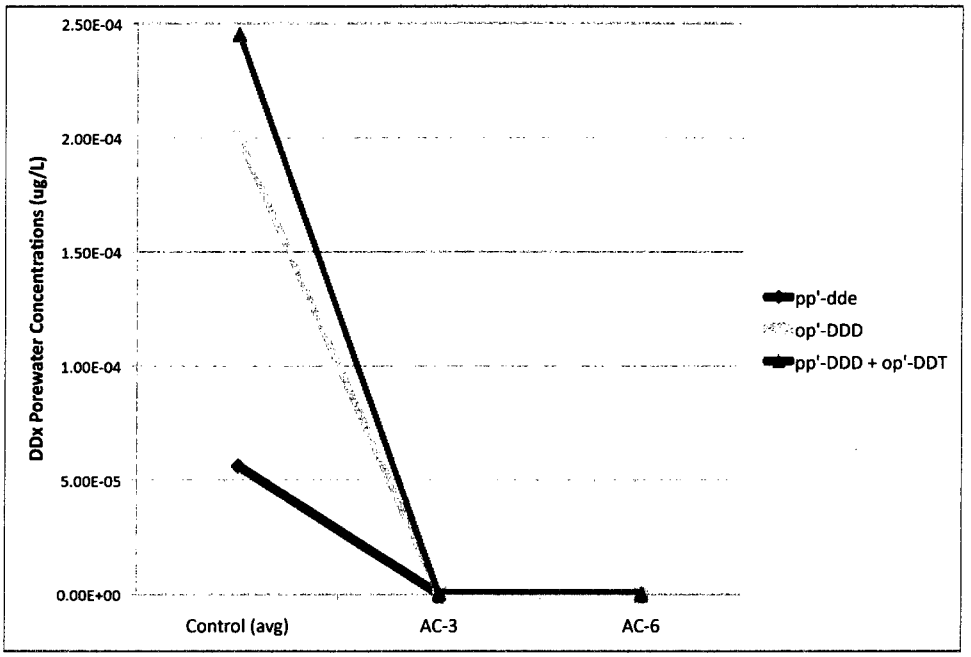

Figure 4.5 Activated Carbon Effectiveness for DDx

Observation of amendment effectiveness, through reductions in porewater concentrations, determined activated carbon to be the most effective amendment agent. Furthermore, little difference was observed between an activated carbon dose of 3% and 6% (w/w). In conclusion, the results of the sediment amendment screening indicated activated carbon as the most effective remediation agent for hydrophobic organic contaminants and the dose consideration stage shows the most effective dose to be 3% (w/w).

4.4 Bioaccumulation Study (Ghosh et al., 2009)

Bioaccumulation testing was provided by Ghosh et al. and was reported in the activated carbon treatability study report on the Aberdeen Proving Ground sediments. Briefly, a subsample of sediment was shipped to UMBC from our lab

at the University of New Hampshire and bioaccumulation testing was performed and the results are described below (Ghosh et al., 2009).

Water quality parameters (DO, pH, temperature, hardness, and conductivity) remained within acceptable range during the 14-day bioaccumulation study. Worms applied to control and treated sediments exhibited normal burrowing and feeding behavior during the study. The recovery of worm tissue at the end of the exposure period was acceptable for all exposure beakers and was greater than 70%. PCB concentration measured in recovered worm tissue from control and exposure beakers are shown in Figure 4.6 by homolog groups. For the untreated sediment, PCB homolog distribution in worm tissue showed the tetra, penta, and hexachlorobiphenyls are the most abundant homologs in worms exposed to untreated sediment. Treatment at the low dose of activated carbon (2.85% w/w as carbon) reduced total PCB bioaccumulation in worms by 81%. At the higher dose of activated carbon (5.70% w/w as carbon), PCB bioaccumulation by the worms was reduced further to 95%.

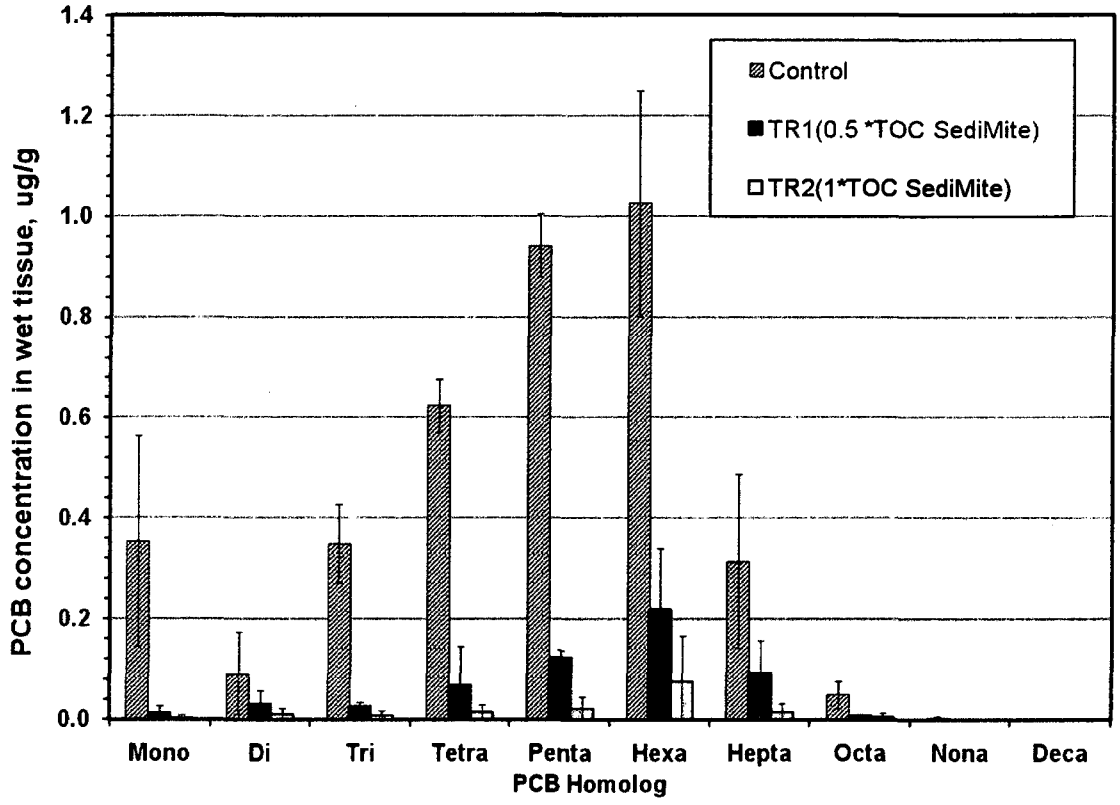

Figure 4.6 Concentration of PCB homologs in wet tissue of *L. variegatus* for untreated sediment and sediment treated with different amounts of activated carbon (Ghosh et al., 2009).

DDx concentration measured in recovered worm tissue from control and exposure beakers are shown in Figure 4.7. After 14 days contact, total DDx bioaccumulation was significantly reduced compared to control. Treatment at the low dose of activated carbon (2.85% w/w as carbon) reduced total DDx bioaccumulation in worms by 87%. At the higher dose of activated carbon (5.70% w/w as carbon), DDx bioaccumulation by the worms was reduced further to 92%. The percent reductions in bioaccumulation close to 90% observed in

this study are similar to reductions reported previously after amending activated carbon to PCB contaminated sediment (Sun and Ghosh 2007).

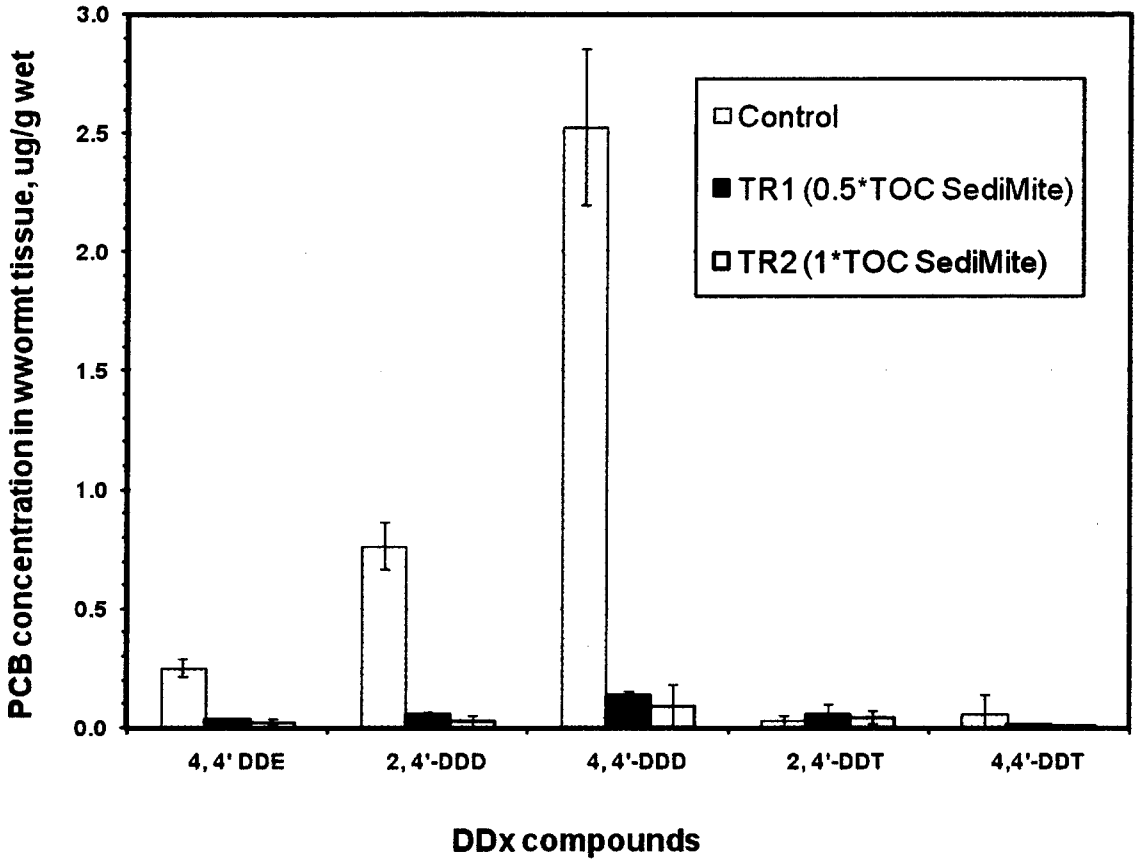

Figure 4.7 Concentration of PCB homologs in wet tissue of *L. variegatus* for untreated sediment and sediment treated with different amounts of activated carbon (Ghosh et al., 2009).

Ghosh et al. (2009) found that a dose of activated carbon approximately equal to 1xTOC indicated greater than 90% reduction in PCB and DDx bioaccumulation after amendment. Based on information collected here, the

addition of activated carbon matching the native organic carbon of sediment appears to provide an optimal dosing of the sorbent (Ghosh et al., 2009).

4.5 Microcosm Study

Sediment amendment screening and dose consideration involved the addition and consideration of amendment agents, well mixed by hand, to hydric soil representing a best case scenario. However, field conditions will most likely not represent an ideal well-mixed scenario but less efficient mixing circumstances that will primarily rely on natural processes to aid the incorporation of amendments into hydric soils and thus the stabilization of contaminants. In addition, there is a chance that mixing may not occur in the absence of benthic organisms. To replicate these scenarios, a microcosm study was performed at the Jackson Estuarine Laboratory in Durham, New Hampshire (Figure 4.8).

Figure 4.8 Microcosm Setup, Jackson Estuarine Laboratory, Durham, NH.

Contaminated sediments from the Aberdeen Proving Ground (APG) were used to create the microcosms. Approximately twenty-five gallons of sediment was homogenized and equally split between five microcosms. In order to represent natural mixing, a continuous estuarine feed water was supplied from the Great Bay Estuary surrounding the Jackson Estuarine Laboratory, allowing for the recruitment of benthic organisms. In addition, *macoma nasuta* and *nereis virens* were added to the microcosms to aide in the mixing process (Figure 4.9 and 4.10). Activated carbon was added in the form of an activated carbon slurry and as Aquablok. Microcosm PCB porewater concentrations were determined by two methods: polyoxymethylene (POM) analysis and organism uptake through *macoma nasuta* and *nereis virens* tissue concentrations. The results of these methods are shown below.

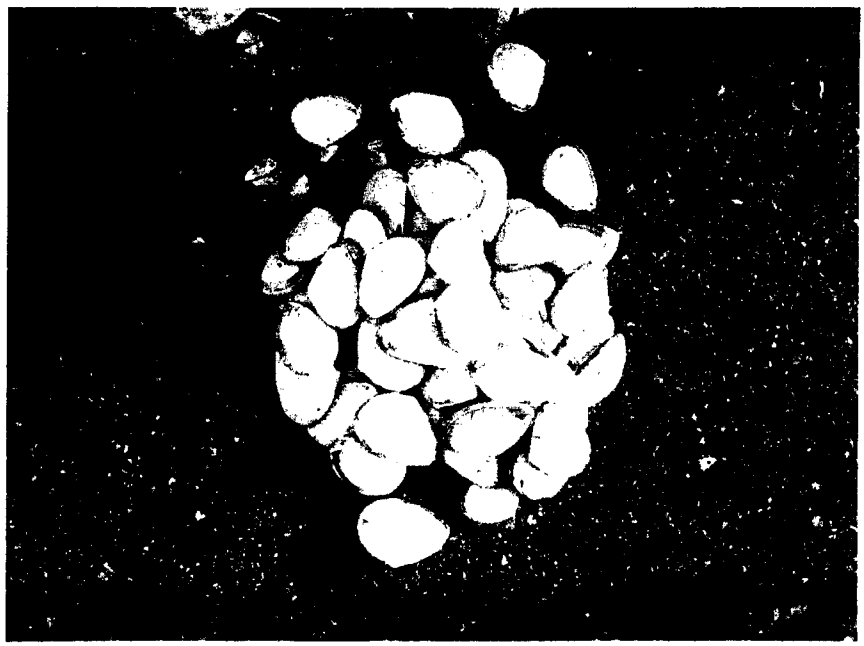

Figure 4.9 *Macoma nasuta* Utilized in Microcosm.

Figure 4.10 *Nereis virens* Utilized in Microcosm.

Microcosm Polyoxymethylene (POM) Analysis

In order to represent natural mixing five microcosms were created; two for activated carbon using (2) proposed field application methods (Aquablok and a slurry) and a control. POM, *macoma nasuta* and *nereis virens* were collected thirty days after they were first placed into the microcosms (hereafter referred to as the first sampling event). A second batch of POM, *nereis virens* and *macoma nasuta* were introduced at the thirty day point and allowed to equilibrate for thirty days after the first sampling event. These were sampled at the sixty day point (hereafter referred to as the second sampling event).

The results of the microcosm porewater analysis are shown in table 4.9. As indicated, samples AQ-1 and AQ-2 are the first sampling event Aquablok microcosms. Samples AS-1 and AS-2 are the first sampling event activated

carbon slurry microcosms and sample C is the control microcosm for the first sampling event. Samples 2AQ-1, 2AQ-2, 2AS-1, 2AS-2 and 2C all represent the second sampling event microcosm concentrations. The control microcosm (C) at the end of the first sampling event had markedly lower total PCB concentrations than the control microcosm (2C) at the end of the second sampling event. We suspect this is mainly due to heterogeneity in the sediments. Activated carbon, when both applied in the form of an activated carbon slurry and as Aquablok, provided significant reductions in PCB porewater concentrations. AS-1, AS-2, AQ-1 and AQ-2 porewater concentrations were reduced to undetectable limits, reported as less than the minimum detection limit (<4.28E-04 ug/L), proving that activated carbon is an extremely effective amendment agent for PCBs. The measurements indicate a >86% reduction of porewater concentrations.

Table 4.9 Total PCB Porewater Concentrations for Individual Microcosms After First and Second Sampling Events

First Sampling Event	Concentration (ug/L)	Standard Deviation
C	2.91E-03	3.69E-04
AS-1	2.47E-02	3.31E-03
AS-2	2.47E-02	3.35E-03
AQ-1	2.04E-02	2.84E-03
AQ-2	8.57E-03	1.45E-03
Second Sampling Event	**Concentration (ug/L)**	**Standard Deviation**
2C	1.27E-02	1.58E-03
2AS-1	< 4.28E-04	0
2AS-2	< 4.28E-04	0
2AQ-1	< 4.28E-04	0
2AQ-2	< 4.28E-04	0

As shown below in table 4.10, the first sampling event concentrations are the PCB isomer porewater concentrations thirty days after the initial application

of an activated carbon slurry and Aquablok. The values shown in table 4.10 that are expressed as less than (<) are those that were below detection limits. Therefore, detectable porewater isomer concentrations ranged from 0.12 to 5.03 ng/L and the total first sampling event PCB porewater concentrations that were detected are 1.48E-02 ug/L. The second amendment microcosm concentrations consist of the PCB isomer porewater concentrations determined via POM that was placed in the microcosm sediments (second control, activated carbon slurry and Aquablok duplicates) immediately following the harvesting of the first POM, *macoma nasuta* and *nereis virens*. The total PCB concentrations of the second sampling event are the total PCB concentrations of the remaining microcosms that tested below detection limits. Therefore, the total second sampling event PCB porewater concentrations must be less than 4.28E-04 ug/L.

Table 4.10 Porewater PCB Concentrations for Amended Microcosms After First and Second Sampling Event

Isomer	First Sampling Event (ug/L)	Second Sampling Event (ug/L)
Mono	<1.01E-04	< 1.01E-04
Di	<1.01E-04	< 1.01E-04
Tri	2.12E-03	< 1.30E-04
Tetra	5.03E-03	< 5.28E-05
Penta	3.56E-03	< 2.06E-05
Hexa	2.93E-03	< 1.27E-05
Septa	8.13E-04	< 5.93E-06
Octa	1.18E-04	< 1.36E-06
Nona	3.15E-05	< 1.31E-06
Deca	< 8.18E-07	< 8.18E-07
Total PCBs	1.48E-02	< 4.28E-04

As a result of the harvest, sediments and amendments were well mixed simulating a long-term natural mixing scenario. Therefore, significant reductions in PCB porewater concentrations were observed, a result expected based upon literature review, previous sediment batch experiments and the bioaccumulation study, indicating activated carbon as an effective amendment agent. Furthermore, every isomer, ranging from low to highly-chlorinated congeners was effectively sequestered to non-detectable levels (>94% reduction).

Significant reductions were observed in PCB porewater concentrations and table 4.11 confirms these concentrations, for the two application methods, after the first and second microcosm amendment measured via POM. Figure 4.11 compares the total PCB porewater concentrations for both amendment application techniques (activated carbon slurry and Aquablok) after each amendment.

Table 4.11 Total PCB Porewater Concentrations for Specific Amendments

Amendment	First Sampling Event		Second Sampling Event	
	ug/L	Std Dev	ug/L	Std Dev
Control	2.91E-03	1.89E-05	1.27E-02	1.69E-03
AC Slurry	2.47E-02	3.21E-03	< 4.28E-04	0.00E+00
Aquablok	1.45E-02	2.29E-03	< 4.28E-04	0.00E+00

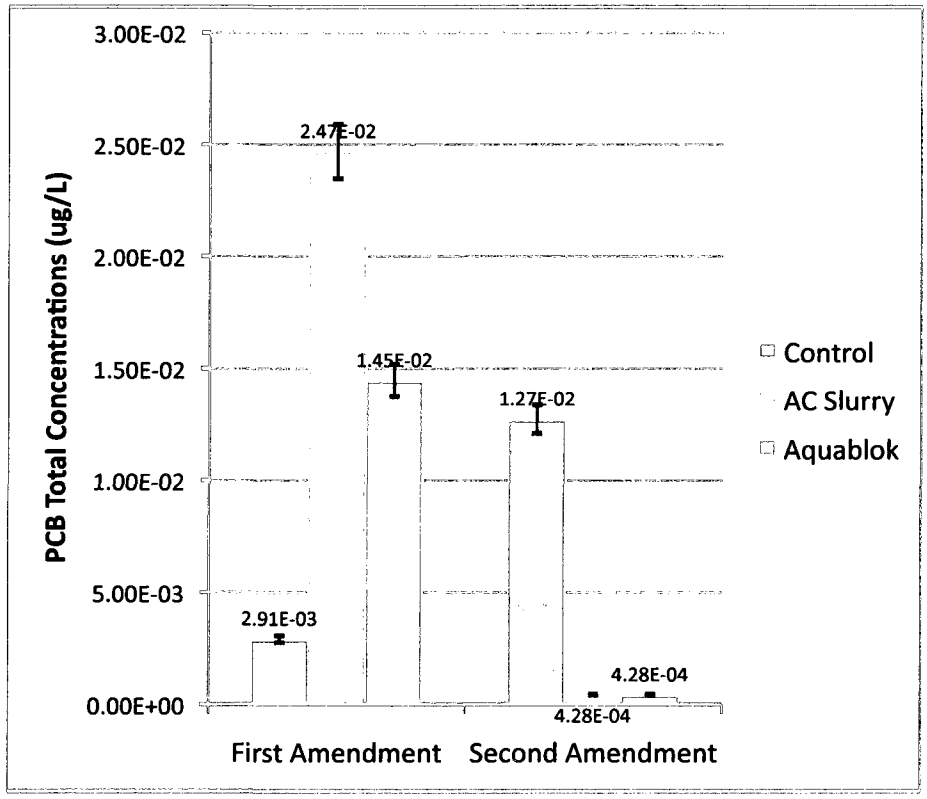

Figure 4.11 PCB Total Porewater Concentrations Post Amendments Measured via POM.

The control concentration after the second sampling event (2C) was, on average, 1.27E-02 ug/L (standard deviation of 1.69E-03 ug/L). We suspect this is mostly due to heterogeneity in the sediments. The second sampling event resulted in PCB porewater concentrations below the minimum detection limit of the GMCS (< 4.28E-04), further proof that activated carbon is an effective in-situ remediation agent for sediments contaminated with organic compounds.

Microcosm *Macoma Nasuta* and *Nereis Virens* Analysis

Macoma nasuta and *nereis virens* were removed from the microcosms during the first and second sampling events and were prepared for PCB tissue concentration analysis. Average surrogate recovery rates for *macoma nasuta* and *nereis virens* are 21% (standard deviation of 35%) and 61% (standard deviation of 25%), respectively. The results of this analysis are shown below in table 4.12.

Table 4.12 PCB *Macoma nasuta* and *Nereis virens* Average Tissue Isomer Concentrations

Isomer	Macoma Nasuta First Sampling Event Concentration	Macoma Nasuta Second Sampling Event Concentration	Nereis Virens First Sampling Event Concentration	Nereis Virens Second Sampling Event Concentration
Mono	< 1.73E-03	< 1.73E-03	< 1.73E-03	< 1.73E-03
Di	< 2.19E-03	< 2.19E-03	< 2.19E-03	< 2.19E-03
Tri	< 5.84E-03	< 5.84E-03	< 5.84E-03	< 5.84E-03
Tetra	< 8.16E-03	< 8.16E-03	< 8.16E-03	< 8.16E-03
Penta	< 1.03E-02	< 1.03E-02	< 1.03E-02	< 1.03E-02
Hexa	< 1.80E-02	< 1.80E-02	< 1.80E-02	< 1.80E-02
Septa	< 1.16E-02	< 1.16E-02	< 1.16E-02	< 1.16E-02
Octa	< 1.01E-02	< 1.01E-02	5.35E-02	< 1.01E-02
Nona	< 6.03E-03	< 6.03E-03	< 6.03E-03	< 6.03E-03
Deca	< 1.24E-02	< 1.24E-02	< 1.24E-02	< 1.24E-02
Total PCBs	< 8.62E-02	< 8.62E-02	5.35E-02	< 8.62E-02

As indicated in table 4.12, the first sampling event tissue concentrations are the *macoma nasuta* and *nereis virens* tissue concentrations found in organisms removed from the microcosm sediments thirty days after the

application of an activated carbon slurry and Aquablok. For the first sampling event, tissue concentrations were below detection (< values), therefore, *macoma nasuta* and *nereis virens* tissue concentrations were <8.62E-02 and 5.35E-02 ug/g, respectively. The second sampling event PCB tissue concentrations (table 4.12) are the PCB isomer contaminant concentrations found in *macoma nasuta* and *nereis virens* that were removed from the microcosm sediments thirty days after the collection of the first POM, *macoma nasuta* and *nereis virens*. There were no detectable tissue concentrations for either *macoma nasuta* or *nereis virens* after the second collection (<8.62E-02).

The low surrogate recovery rate for *macoma nasuta* (21%) is concerning. Many of the individual *macoma nasuta* samples (AS-1, AS-2. AQ-2, C, 2AS-2, 2AQ-1 and 2AQ-2) had no detections and a 0% (standard deviation of 0%) recovery rate of the surrogate standard. However, the samples that had detections (2AS-1, AQ-1 and 2C) had an average surrogate recovery of 73% (standard deviation of 7%). These data, with a surrogate recovery rate of 73%, alone indicate that there were no *macoma nasuta* tissue PCB concentration detections in either the first sampling event Aquablok microcosm (AQ-1) or the second sampling event control (2C) and activated slurry microcosm (2AS-1). On the other hand, the *nereis virens* samples had surrogate recoveries within all samples. Furthermore, the surrogate recovery rate for the *nereis virens* (61%) is somewhat acceptable and suggests reduction in PCB tissue concentrations within the activated slurry microcosm, as seen below in table 4.13.

Table 4.13 PCB *Macoma nasuta* and *Nereis virens* PCB Tissue Concentration by Individual Microcosm

Sample	Macoma Nasuta (ug/g)	Nereis Virens (ug/g)
AS-1	< 8.62E-02	6.31E-01
2AS-1	< 8.62E-02	< 8.62E-02
AS-2	< 8.62E-02	< 8.62E-02
2AS-2	< 8.62E-02	< 8.62E-02
AQ-1	< 8.62E-02	< 8.62E-02
2AQ-1	< 8.62E-02	< 8.62E-02
AQ-2	< 8.62E-02	< 8.62E-02
2AQ-2	< 8.62E-02	< 8.62E-02
C	< 8.62E-02	< 8.62E-02
2C	< 8.62E-02	< 8.62E-02

Table 4.13 indicates the *macoma nasuta* and *nereis virens* tissue concentrations for each individual microcosm. These concentrations exclude the surrogate standard, therefore, all of the samples except for AS-1 have no detectable PCB tissue concentrations (<8.62E-02 ug/g). It is suspected that the detectable concentration for AS-1 is due to an abnormally large *nereis virens* (the only one of all the microcosms) that may have ingested *macoma nasuta* or large amounts of recruited benthic organisms. The ingestion of other organisms could have led to bioaccumulation within that particular worm, and concentrations well above detectable limits. Furthermore, the average surrogate recovery rate for the AS-1 microcosm alone was 65%.

Table 4.14 Total Organism Tissue Concentrations for Specific Amendments

Microcosm Total PCB Porewater Concentrations for Specific Amendments (ppm)			
Macoma Nasuta Tissue Concentration (ug/g)			Surrogate Recovery
Amendment	First Amendment	Second Amendment	
Control	< 8.62E-02	< 6.82E-02	21%
AC Slurry	< 8.62E-02	< 8.62E-02	
Aquablok	< 8.62E-02	< 8.62E-02	
Nereis Virens Tissue Concentration (ug/g)			Surrogate Recovery
Amendment	First Amendment	Second Amendment	
Control	< 6.82E-02	< 6.82E-02	65%
AC Slurry	6.31E-01	< 6.82E-02	
Aquablok	< 6.82E-02	< 6.82E-02	

Table 4.14 indicates the total tissue concentrations for specific amendments. There is indication of a possible reduction in *nereis virens* tissue concentrations from the application of the activated carbon slurry. In addition, the samples from microcosm AS-1 have an average surrogate recovery rate of 65%, perhaps providing somewhat accurate proof that the AS-1 *nereis virens* tissue concentrations were reduced to undetectable limits.

As a result of the first POM, *macoma nasuta* and *nereis virens* collection, sediments and amendments were well mixed simulating a long-term natural mixing scenario. As stated above, significant reductions in PCB porewater concentrations were observed in the second sampling event. In addition, there were no detections of PCB tissue concentrations in *macoma nasuta* or *nereis virens*, however, organism tissue concentrations were not detected in the control microcosms meaning it is possible that the organisms did not ingest or absorb

detectable PCB concentrations. It is also possible that the solvent extraction method was not effective at properly removing all contaminants from the organism tissue, as average surrogate recovery percentages for *macoma nasuta* and *nereis virens* are 22% and 61%, respectively. However, all *nereis virens* samples had surrogate sample detections, indicating that the extraction method worked somewhat efficiently for them. Moreover, all *nereis virens* samples were collected and extracted in triplicate because of their high survival rate (100%). *Macoma nasuta*, on the other hand, had low survival rates (40% or less) and were only extracted as single samples.

The lack of detection of PCBs in the *nereis virens* and *macoma nasuta* is concerning, however, studies have been done using these organisms that have made some observations that provide some possible insight. Organism size is of concern when conducting a bioaccumulation study. In fact, many studies have selected the oligiochaete lumbriculus variegatus, rather than *nereis virens*, because of their physical characteristics. Van Der Heijden and Jonker (2008) conducted a study using lumbriculus variegatus as a test organism in sediments contaminated with PAHs. Lumbriculus variegatus was selected as a test organism, because (i) it is a commony used test organism in ecological studies, (ii) it has a limited PAH biotransformation capability, (iii) the worms are resistant to multiple stress factors (e.g. anoxia, temperature shifts, high contamination levels), and (iv) their size and surface/volume ratio enable relatively fast equilibrium with environmental media (Van Der Heijden and Jonker, 2008). *Nereis virens* and *macoma nasuta* are very large (surface/volume ratio is much

lower than that of the lumbriculus variegatus) compared to lumbriculus variegatus, and it could be possible that the *nereis virens* and *macoma nasuta*, therefore, the kinetics of PCB porewater contamination are affected (longer periods of time for bioaccumulation). In addition, even though the organisms were cut up into small pieces prior to extraction, they may have needed to be further reduced in size. Larger pieces can make it challenging to extract the PCBs within the inner organism tissues. Rather than smaller organisms, *nereis virens* and *macoma nasuta* were mostly selected for the microcosm study because they are easy to recover and are commonly found in the sediments adjacent to the Jackson Estuarine Laboratory, Durham, New Hampshire (the source of fresh feedwater for the microcosms).

Van Der Heijden and Jonker (2008) also mention that lumbriculus variegatus will not metabolize organic contaminants. There has been some concern with *nereis virens* metabolizing the lower chlorinated congeners. In fact, a study conducted by Friedman et al. (2009) compared PCB uptake in *nereis virens* to uptake in polyethylene passive samplers. It was found that the *nereis virens* may have been metabolizing lower chlorinated congeners. These lower chlorinated congeners represent a large percentage of the PCB porewater contamination found in the microcosm sediments, therefore, it is possible that some PCB concentrations were metabolized by the organisms.

Overall, the organism extraction method worked moderately well for *nereis virens* and did not work properly for those individual *macoma nasuta* samples with low surrogate recovery rates (AS-1, AS-2, AQ-2, C, 2AS-2, 2AQ-1 and 2AQ-

2). It is possible that the silica gel cleanup steps for PCBs removed detectable concentrations from the solvent. However, the silica gel cleanup for PCBs is a proven method and it did work well for the *nereis virens* and bulk sediments. Therefore, based upon overall recoveries for *macoma nasuta* (22%), and the lack of replicate samples, it is likely that PCB concentrations were not properly extracted from the organism tissue.

Comparison of POM Methods

The equilibration time of passive samplers is extremely important when trying to detect low concentrations of PCBs in porewater. Hawthorne et al. (2009) developed an effective method for utilizing POM to detect low-level PCB concentrations in porewater. As a conclusion to our study, site sediments from Aberdeen Proving Ground, Maryland were tested utilizing the Hawthorne et al. (2009) POM method. Sediments, on average (see table A.1 and A.2 in Appendix A), had a total organic carbon content of 3.18% (standard deviation of 0.75%) and a black carbon content of .34% (standard deviation of .23%). These TOC values are much lower than the samples collected in December 2008 (15% TOC). We suspect this is because of sediment heterogeneity, however, were unable to verify this as all avalaible sediments had been shipped off site for a bioaccumulation study. For the Hawthorne et al. (2009) method, sheets of POM (76 um thick) were cut into 4x6 cm strips and were cleaned by sequential extraction in hexane followed by methanol. POM strips were allowed to dry and were placed in 40 mL vials containing 15g of site sediment and 30 mL of water

containing 50 mg/mL of sodium azide. Vials were then constantly mixed on a rotating wheel and were removed for analysis after 30 days.

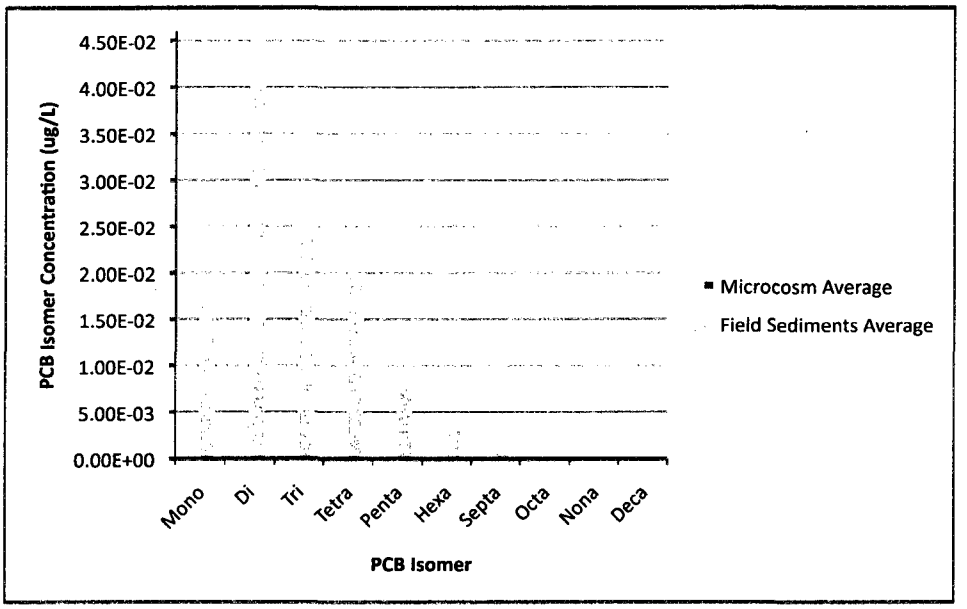

Figure 4.12 Hawthorne et al. POM Method with Site Sediments vs. In-situ Microcosm POM

The Hawthorne et al. method was then compared against the in-situ microcosm method (figure 4.12). The concentrations from the Hawthorne et al. method are significantly greater than those in the microcosm POM. It is quite clear, based upon literature values and figure 4.12, that the equilibration time for the microcosm POM was not reached, as the strips were removed after thirty days along with the *macoma nasuta* and *nereis virens*. As mentioned in the literature review, Cornelissen et al. (2010) conducted a study and allowed POM to equilibrate in-situ for 179, 270 and 363 days and POM was found to be maximally 20-30% less than equilibrium.

Considering the Cornelissen et al study and the fact that the microcosm POM was removed after 30 days, a comparison is drawn between the field sediment concentration (determined by the Hawthorne et al method.) and a longer period of equilibrium time for the microcosm POM. Assuming linear adsorption kinetics, the POM microcosm porewater concentrations are extrapolated to represent the maximum amount of equilibrium time in the Cornelissen study (363 days) and are represented in figure 4.13. The microcosm concentrations only include the total PCB porewater concentrations that were untreated, the first sampling event control (C) and the second sampling event control (2C). The reason for only including the untreated sediments is that extrapolated adsorption kinetics do not account for the natural mixing of amendments and sediments, within the amendmed microcoms, which would provide a reduction in PCB porewater bioavalability over the same period of time. After a period of 363 days, microcosm porewater concentrations for the tetra isomer could have been as high as 5.12E-03 ug/L (about 26% of its field sediment counterpart). This analysis suggests that, even when correction for kinetics, the porewater PCB concentrations in microcosm sediment is less than expected in the field based on the average of twenty-four field samples.

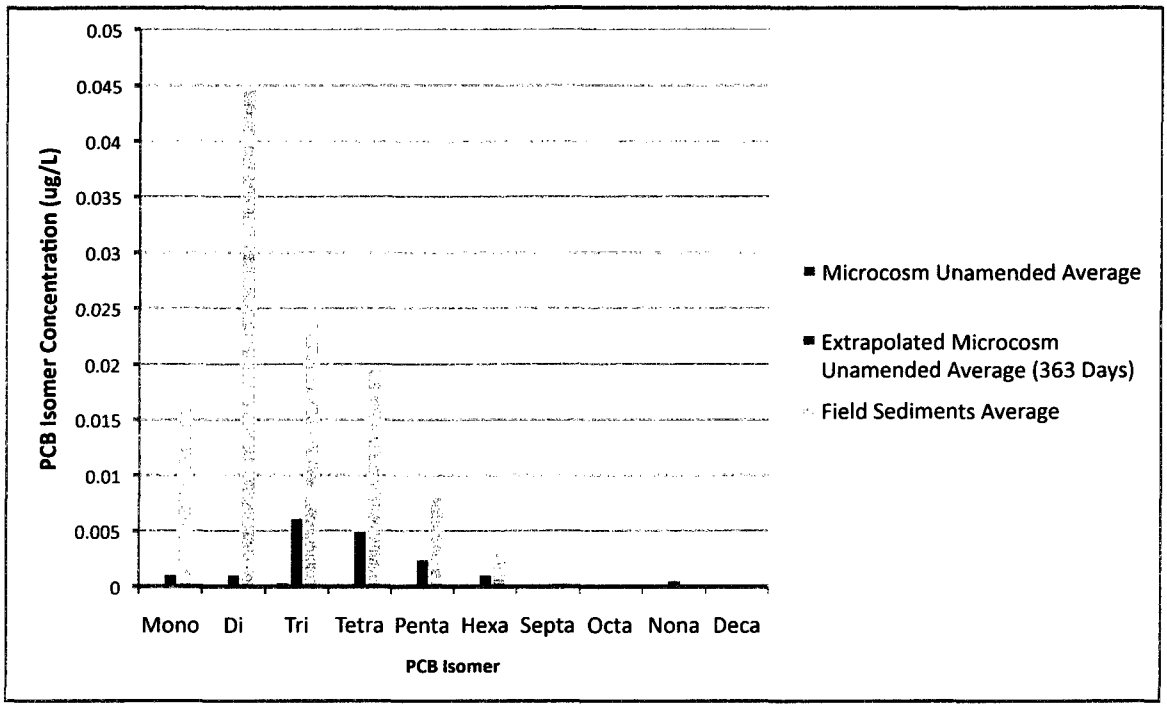

Figure 4.13 Estimated Microcosm Porewater Concentrations for Extended POM Equilibrium Times

POM vs. SPME

The sediments amendment screening utilized solid-phase microextraction (SPME) fibers while the microcosm study and the Hawthorne et al. method with the Aberdeen Proving Ground sediments utilized POM to detect porewater organic contaminant (PCB and DDx) concentrations. The use of SPME vs. POM as passive samplers is a debated topic in the environmental remediation community. There are a few characteristics to consider when choosing either POM or SPME as a passive sampling technique. The first is the partioning coefficients (K_{POM} and K_{SPME}) for each. Studies by Reible (2008) and Hawthorne et al. (2009) have extensively researched and produced similar numbers for

partitioning coefficients. SPME fibers come to equilibrium extremely fast when compared to POM, however, POM has a great deal of mass when compared to an SPME fiber. For example, a POM strip as used in the Hawthorne et al. method (4cm x 6cm strip – 76um thick) is the equivalent of 46.4 one centimeter SPME fibers (300/200).

The second thing to consider in the POM vs. SPME debate is ease of handling. SPME fibers are extremely delicate and are quite difficult to find once placed within a sediment sample. Even in a porewater sample within a vial, the fibers are challenging to see with the naked eye and to recover. SPME fibers that are to be used in-situ require some sort of chamber or device in which they can be stored and recovered. Inherently, this leads to the issue of ensuring that the SPME fiber comes into contact with porewater. The POM strips, on the other hand, are extremely durable and are easy to recover within sediments or in porewater samples. POM placed in-situ also can be easily recovered and is sure to come into contact with sediment porewaters over a greater surface area. Lastly, cost of the passive sampler being selected should be considered in the POM vs. SPME debate. When comparing one 4cm x 6cm strip of POM to 46.4 one centimer strips of SPME (300/200) fiber, or 46.4 cm, POM and SPME fibers are comparable in price. Overall, when choosing between passive samplers, it is important to make decisions based upon adsorption kinetics, overall mass, handling, ease of use and cost.

Amendment Delivery Techniques

Two activated carbon amendment delivery techniques were utilized for this study, an activated carbon slurry and Aquablok. Both amendments showed equal reductions in PCB porewater concentrations. However, when choosing between varying amendment delivery methods, it is also important to understand the handling and mixing characteristics of each. In this study, the activated carbon slurry immediately rested on the sediment surface; it was peppered with activated carbon. This is because the activated carbon used in the slurry was granular and quickly settled. The Aquablok, which delivered powdered activated carbon, also easily went to the sediment surface but the water column quickly turned black with dilute activated carbon. However, a layer of activated carbon quickly formed on the surface that was quite noticeable the first time the microcosm organisms and POM was harvested. It is noted that, while cost and availability of amendment delivery methods are important, ease of use, handling and mixing characteristics must be understood as well.

CHAPTER 5

SUMMARY AND CONCLUSIONS

Sediments were sampled during two separate events (December 2008 and December 2009) and it was found that the sediments varied in contaminant concentrations and physical characteristics. Total organic carbon content and black carbon content were used with the Equilibrium Partitioning Theory to calculate porewater concentrations; these were compared with porewater concentrations directly measured through the use of passive samplers.

For the first sediments sampled (December 2008), SPME fibers were utlilized to measure porewater concentrations. Sediments amended with zero valent iron (ZVI) resulted in significant increase of PCBs and DDx porewater concentrations while those amended with organoclay (OC) resulted in marginal reductions of PCBs and DDx. Amendment of sediments with activated carbon resulted in significant PCB and DDx porewater concentration reductions at levels ranging from 40 to greater than 90%. Bioaccumulation study results also indicated significant decreases in bioavailable PCBs and DDx with activated carbon addition. Furthermore, the microcosm amendment studies also showed significant reductions of PCB porewater concentrations for both methods of application (activated carbon slurry and Aquablok).

The second set of sediments sampled (December 2009) received amendments of activated carbon via two delivery techniques (activated carbon

slurry and Aquablok), which significantly reduced porewater concentrations in a microcosm experiment. Activated carbon in the form of a slurry and Aquablok reduced PCB porewater concentrations from 2.47E-02 ug/L and 1.45E-02 ug/L, respectively, to less than the detection limits of the GCMS (< 4.28E-04 ug/L). Furthermore, the use of polyoxymethylene (POM) as passive samplers proved beneficial for determining PCB porewater concentrations in both microcosms and a method with Canal Creek sediments in completely mixed vials, although the long equilibration time of in-situ deployment limited the sensitivity of the POM for the microcosms.

The physical properties of the sediments played a major role in the observed results. The bioaccumulation studies were conducted with a homogenous blend of two different sediment samples (Canal Creek field samples APG-SED-2C and APG-SED-4C), while the pore water testing used only sediment sample set APG-SED-2C for PCB amendment analysis, likely resulting in different congeners being present. The microcosm study was also a blend of many different site sediments. In addition, TOC levels in bioaccumulation tests were 5.7% while SED-2C used for porewater testing had TOC levels of nearly 16%. Those sediments along with other sediments from Canal Creek were all mixed together and used for the microcosm experiments, providing yet another set of sediments with varying physical characteristics.

The bioaccumulation study, the sediment amendment screening activated carbon study and the microcosm study are all in agreement that amendments with activated carbon provide promising results. We recommend that activated

carbon dose levels be no higher than the average TOC of surficial sediments at the site. We base this recommendation on the bioaccumulation test results, which showed reductions in bioaccumulation when activated carbon dose was increased to 5.7% (equal to the TOC of the sediment sample). Lower amendment concentrations were still very effective at reducing contaminant bioavailability, and a lower dose would not only be more cost-effective but may result in minimizing adverse ecological impacts. A greater activated carbon dose could require a thicker cap, and the ecological impact of this will vary depending on the type of delivery (e.g. in a slurry vs. in a clay matrix such as Aquablok).

Porewater concentrations were measured using both SPME fibers and POM strips. It is important to consider the many variables at play when utilizing passive samplers. Overall, when choosing between passive samplers, it is important to make decisions based upon adsorption kinetics, overall mass, handling, ease of use and cost.

Finally, when choosing between varying amendment delivery methods, it is important to understand the handling and mixing characteristics of each. In this study, the activated carbon slurry immediately rested on the sediment surface. This is because the activated carbon used in the slurry was granular and quickly settled. The Aquablok also easily went to the sediment surface but the water column quickly turned black with dilute activated carbon. However, a layer of activated carbon quickly formed on the sediment surface that was quite noticeable the first time the microcosm organisms and POM was harvested.

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APPENDICES

APPENDIX A

Table A.1 Field Sediments Total Organic Carbon Content (%)

Sample ID	Pre Muffle Weight (g)	Post Muffle Weight (g)	TOC (%)
APG-C1-CC-HS	25.026	24.397	2.51%
APG-C2-CC-HS	24.156	23.409	3.09%
APG-C3-CC-HS	25.96	25.103	3.30%
APG-C4-CC-HS	25.585	24.983	2.35%
APG-C5-CC-HS	25.918	25.25	2.58%
APG-C6-CC-HS	24.778	24.145	2.55%
APG-C7-CC-HS	16.152	15.442	4.40%
APG-C8-CC-HS	18.049	17.468	3.22%
APG-P1-CC-HS	16.946	16.196	4.43%
APG-P2-CC-HS	17.933	17.075	4.78%
APG-P3-CC-HS	17.244	16.831	2.40%
APG-P4-CC-HS	15.413	14.798	3.99%
APG-A1-CC-HS	24.026	23.429	2.48%
APG-A2-CC-HS	24.968	24.293	2.70%
APG-A3-CC-HS	25.821	24.937	3.42%
APG-A4-CC-HS	25.403	24.662	2.92%
APG-A5-CC-HS	25.111	23.936	4.68%
APG-A6-CC-HS	23.914	23.282	2.64%
APG-A7-CC-HS	16.842	16.263	3.44%
APG-A8-CC-HS	17.612	17.238	2.12%
APG-A9-CC-HS	15.529	14.844	4.41%
APG-A10-CC-HS	15.757	15.24	3.28%
APG-A11-CC-HS	14.866	14.334	3.58%
APG-A12-CC-HS	15.996	15.402	3.71%
APG-C1C2-CC-HS	24.984	24.171	3.25%
APG-C3C4-CC-HS	24.945	24.162	3.14%
APG-C5C6-CC-HS	28.591	28.001	2.06%
APG-C7C8-CC-HS	24.322	23.811	2.10%
APG-A1A3-CC-HS	25.636	24.634	3.91%
APG-A2A5-CC-HS	24.952	24.211	2.97%
APG-A4A8-CC-HS	18.936	18.438	2.63%
APG-A6A7-CC-HS	15.843	15.266	3.64%
APG-P1P2-CC-HS	18.959	18.422	2.83%
APG-P3P4-CC-HS	28.181	27.332	3.01%
APG-EB-CC-AQ	27.274	26.486	2.89%
Average	21.7608	21.0826	3.18%
Std Dev	4.53	4.46	0.75%

Used LOI method (Blume et al., 1990; Nelson and Sommers, 1996; ASTM, 2000)

Briefly, The loss-on-ignition (LOI) method for the determination of organic matter involves the heated destruction of all organic matter in the soil or sediment. A known weight of sample is placed in a ceramic crucible (or similar vessel) which is then heated to between 350 C and 440 C overnight.

Table A.2 Field Sediments Black Carbon Content (%)

Sample ID	Black Carbon (%)	Percent of TOC
APG-C1-CC-HS	0.41%	16.2%
APG-C2-CC-HS	0.38%	12.3%
APG-C3-CC-HS	0.90%	27.3%
APG-C4-CC-HS	0.11%	4.8%
APG-C5-CC-HS	0.91%	35.1%
APG-C6-CC-HS	0.67%	26.1%
APG-C7-CC-HS	0.18%	4.0%
APG-C8-CC-HS	0.56%	17.45%
APG-P1-CC-HS	0.33%	7.52%
APG-P2-CC-HS	0.42%	8.82%
APG-P3-CC-HS	0.12%	5.06%
APG-P4-CC-HS	0.09%	2.26%
APG-A1-CC-HS	0.12%	4.77%
APG-A2-CC-HS	0.33%	12.21%
APG-A3-CC-HS	0.14%	4.03%
APG-A4-CC-HS	0.35%	12.10%
APG-A5-CC-HS	0.19%	4.10%
APG-A6-CC-HS	0.15%	5.49%
APG-A7-CC-HS	0.36%	10.36%
APG-A8-CC-HS	0.33%	15.60%
APG-A9-CC-HS	0.19%	4.20%
APG-A10-CC-HS	0.41%	12.35%
APG-A11-CC-HS	0.22%	6.08%
APG-A12-CC-HS	0.22%	5.85%
Average	0.34%	11.01%

Table A.3. Overall Sediments Calculated vs. Measured Porewater Concentrations

Sediment Sample	Contaminant	C sediment (ug/kg)	log Kow*	log Koc	% TOC	foc	log Kbc**	% BC	fbc	Kd	Calculated Cporewater (ug/L) Koc Only	Calculated Cporewater (ug/L)Koc and Kbc	Measured Cresults (ug/L)
p1	PCB 28	62	5.7	5.0	4.43	0.044	5.5	0.33	0.003	4.30	1.40E-02	1.24E-04	7.12E-03
	PCB 47	408	5.8	5.1	4.43	0.044	5.8	0.33	0.003	4.20	7.32E-02	4.89E-03	1.73E-02
	PCB 66	50	6.2	5.5	4.43	0.044	6.7	0.33	0.003	5.00	3.59E-03	4.11E-03	1.59E-03
	PCB 95	403	6.1	5.4	4.43	0.044	6.1	0.33	0.003	4.70	3.62E-02	5.73E-04	1.27E-02
p2	PCB 28	44	5.7	5.0	4.78	0.048	5.5	0.42	0.004	4.30	9.13E-03	2.98E-04	5.79E-04
	PCB 47	339	5.8	5.1	4.78	0.048	5.8	0.42	0.004	4.20	5.64E-02	1.27E-02	8.29E-03
	PCB 66	51	6.2	5.5	4.78	0.048	6.7	0.42	0.004	5.00	3.39E-03	9.58E-03	3.63E-04
	PCB 95	410	6.1	5.4	4.78	0.048	6.1	0.42	0.004	4.70	3.41E-02	1.38E-03	2.91E-03
p3	PCB 28	0	5.7	5.0	4.43	0.044	5.5	0.33	0.003	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	4.43	0.044	5.8	0.33	0.003	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	21	6.2	5.5	4.43	0.044	6.7	0.33	0.003	5.00	1.52E-03	4.11E-03	8.54E-05
	PCB 95	171	6.1	5.4	4.43	0.044	6.1	0.33	0.003	4.70	1.53E-02	5.73E-04	6.84E-04

p4	PCB 28	0	5.7	5.0	3.99	0.040	5.5	0.09	0.001	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	3.99	0.040	5.8	0.09	0.001	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	3.99	0.040	6.7	0.09	0.001	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	3.99	0.040	6.1	0.09	0.001	4.70	0.00E+00	0.00E+00	0.00E+00
a1	PCB 28	0	5.7	5.0	2.48	0.025	5.5	0.12	0.001	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	2.48	0.025	5.8	0.12	0.001	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	2.48	0.025	6.7	0.12	0.001	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.48	0.025	6.1	0.12	0.001	4.70	0.00E+00	0.00E+00	0.00E+00
a2	PCB 28	0	5.7	5.0	2.70	0.027	5.5	0.33	0.003	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	2.70	0.027	5.8	0.33	0.003	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	2.70	0.027	6.7	0.33	0.003	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.70	0.027	6.1	0.33	0.003	4.70	0.00E+00	0.00E+00	0.00E+00
a3	PCB 28	41	5.7	5.0	3.24	0.032	5.5	0.14	0.001	4.30	1.28E-02	5.54E-06	6.96E-04
	PCB 47	235	5.8	5.1	3.24	0.032	5.8	0.14	0.001	4.20	5.77E-02	1.78E-04	1.83E-02
	PCB 66	0	6.2	5.5	3.24	0.032	6.7	0.14	0.001	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	3.24	0.032	6.1	0.14	0.001	4.70	0.00E+00	0.00E+00	0.00E+00
a4	PCB 28	0	5.7	5.0	2.92	0.029	5.5	0.35	0.004	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	2.92	0.029	5.8	0.35	0.004	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	2.92	0.029	6.7	0.35	0.004	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.92	0.029	6.1	0.35	0.004	4.70	0.00E+00	0.00E+00	0.00E+00
a5	PCB 28	0	5.7	5.0	4.68	0.047	5.5	0.19	0.002	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	4.68	0.047	5.8	0.19	0.002	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	4.68	0.047	6.7	0.19	0.002	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	4.68	0.047	6.1	0.19	0.002	4.70	0.00E+00	0.00E+00	0.00E+00
a6	PCB 28	0	5.7	5.0	2.64	0.026	5.5	0.15	0.002	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	2.64	0.026	5.8	0.15	0.002	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	2.64	0.026	6.7	0.15	0.002	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.64	0.026	6.1	0.15	0.002	4.70	0.00E+00	0.00E+00	0.00E+00
a7	PCB 28	0	5.7	5.0	3.44	0.034	5.5	0.36	0.004	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	136	5.8	5.1	3.44	0.034	5.8	0.36	0.004	4.20	3.13E-02	4.46E-03	7.63E-03
	PCB 66	32	6.2	5.5	3.44	0.034	6.7	0.36	0.004	5.00	2.96E-03	4.87E-03	7.98E-05
	PCB 95	258	6.1	5.4	3.44	0.034	6.1	0.36	0.004	4.70	2.98E-02	6.24E-04	6.38E-04
a8	PCB 28	24	5.7	5.0	2.12	0.021	5.5	0.33	0.003	4.30	1.12E-02	7.78E-05	2.02E-03
	PCB 47	147	5.8	5.1	2.12	0.021	5.8	0.33	0.003	4.20	5.51E-02	2.13E-03	1.16E-02
	PCB 66	0	6.2	5.5	2.12	0.021	6.7	0.33	0.003	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.12	0.021	6.1	0.33	0.003	4.70	0.00E+00	0.00E+00	0.00E+00
a9	PCB 28	0	5.7	5.0	4.41	0.044	5.5	0.19	0.002	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	4.41	0.044	5.8	0.19	0.002	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	51	6.2	5.5	4.41	0.044	6.7	0.19	0.002	5.00	3.65E-03	6.51E-04	7.44E-05
	PCB 95	408	6.1	5.4	4.41	0.044	6.1	0.19	0.002	4.70	3.68E-02	9.07E-05	5.96E-04
a10	PCB 28	0	5.7	5.0	3.28	0.033	5.5	0.41	0.004	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	3.28	0.033	5.8	0.41	0.004	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	3.28	0.033	6.7	0.41	0.004	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	3.28	0.033	6.1	0.41	0.004	4.70	0.00E+00	0.00E+00	0.00E+00
a11	PCB 28	0	5.7	5.0	3.58	0.036	5.5	0.22	0.002	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	129	5.8	5.1	3.58	0.036	5.8	0.22	0.002	4.20	2.85E-02	9.10E-04	3.52E-03
	PCB 66	0	6.2	5.5	3.58	0.036	6.7	0.22	0.002	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	3.58	0.036	6.1	0.22	0.002	4.70	0.00E+00	0.00E+00	0.00E+00
a12	PCB 28	0	5.7	5.0	3.71	0.037	5.5	0.22	0.002	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	3.71	0.037	5.8	0.22	0.002	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	3.71	0.037	6.7	0.22	0.002	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	3.71	0.037	6.1	0.22	0.002	4.70	0.00E+00	0.00E+00	0.00E+00
c1	PCB 28	0	5.7	5.0	2.51	0.025	5.5	0.41	0.004	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	2.51	0.025	5.8	0.41	0.004	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	2.51	0.025	6.7	0.41	0.004	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.51	0.025	6.1	0.41	0.004	4.70	0.00E+00	0.00E+00	0.00E+00
c2	PCB 28	0	5.7	5.0	3.09	0.031	5.5	0.38	0.004	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	3.09	0.031	5.8	0.38	0.004	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	3.09	0.031	6.7	0.38	0.004	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	3.09	0.031	6.1	0.38	0.004	4.70	0.00E+00	0.00E+00	0.00E+00
c3	PCB 28	0	5.7	5.0	3.30	0.033	5.5	0.90	0.009	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	3.30	0.033	5.8	0.90	0.009	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	3.30	0.033	6.7	0.90	0.009	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	3.30	0.033	6.1	0.90	0.009	4.70	0.00E+00	0.00E+00	0.00E+00
c4	PCB 28	0	5.7	5.0	2.35	0.024	5.5	0.11	0.001	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	2.35	0.024	5.8	0.11	0.001	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	2.35	0.024	6.7	0.11	0.001	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.35	0.024	6.1	0.11	0.001	4.70	0.00E+00	0.00E+00	0.00E+00
c5	PCB 28	0	5.7	5.0	2.58	0.026	5.5	0.91	0.009	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	2.58	0.026	5.8	0.91	0.009	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	2.58	0.026	6.7	0.91	0.009	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.58	0.026	6.1	0.91	0.009	4.70	0.00E+00	0.00E+00	0.00E+00
c6	PCB 28	0	5.7	5.0	2.55	0.026	5.5	0.67	0.007	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	141	5.8	5.1	2.55	0.026	5.8	0.67	0.007	4.20	4.38E-02	2.60E-02	4.68E-03
	PCB 66	0	6.2	5.5	2.55	0.026	6.7	0.67	0.007	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	2.55	0.026	6.1	0.67	0.007	4.70	0.00E+00	0.00E+00	0.00E+00
c7	PCB 28	0	5.7	5.0	4.40	0.044	5.5	0.18	0.002	4.30	0.00E+00	0.00E+00	0.00E+00
	PCB 47	0	5.8	5.1	4.40	0.044	5.8	0.18	0.002	4.20	0.00E+00	0.00E+00	0.00E+00
	PCB 66	0	6.2	5.5	4.40	0.044	6.7	0.18	0.002	5.00	0.00E+00	0.00E+00	0.00E+00
	PCB 95	0	6.1	5.4	4.40	0.044	6.1	0.18	0.002	4.70	0.00E+00	0.00E+00	0.00E+00
c8	PCB 28	40	5.7	5.0	3.22	0.032	5.5	0.56	0.006	4.30	1.24E-02	5.61E-04	3.34E-04
	PCB 47	239	5.8	5.1	3.22	0.032	5.8	0.56	0.006	4.20	5.89E-02	1.80E-02	9.98E-03
	PCB 66	50	6.2	5.5	3.22	0.032	6.7	0.56	0.006	5.00	4.94E-03	2.07E-02	8.09E-05
	PCB 95	402	6.1	5.4	3.22	0.032	6.1	0.56	0.006	4.70	4.97E-02	2.60E-03	6.47E-04

*PCB values based on Chou and Griffin (1986). **Log Kbc values obtained from Lohmann et al. (2005)