

MANAGEMENT OF PCB-CONTAMINATED SEDIMENTS THROUGH SEDIMENT  
CHARACTERIZATION AND EVALUATION OF ACTIVE CAPPING TECHNIQUES

A Thesis

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By

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## ABSTRACT

Polychlorinated biphenyls (PCBs) were heavily used for over fifty years in industrial applications, primarily inside capacitors and transformers. Over twenty years after their phase-out in the United States PCBs are still one of the most widespread contaminants in the environment. PCBs are stable compounds with low aqueous solubility and vapor pressure. These unique properties led to the extensive use of PCBs and are also responsible for their continued presence in the environment today.

Due to their hydrophobic nature PCBs tend to accumulate in soils and sediments, and also bioaccumulate in the fatty tissues of aquatic organisms. At higher levels of the food chain, biomagnification produces elevated PCB concentrations in tissue due to the transfer of PCBs from smaller organisms consumed by the larger organisms. Several locations across the United States have fish consumption advisories in place due to PCB contamination.

Currently used management techniques include monitored natural recovery, in-situ capping, and dredging and dewatering. All of these methods have major drawbacks preventing their wide-scale use. Monitored natural recovery is subject to a large degree of uncertainty and is also viewed negatively by the public. In-situ capping is prone to disruption and caps are difficult to install at a controlled thickness. Dredging and dewatering is the most commonly used process because it physically removes

contaminants from the site. However, it is also a very time consuming and costly process. An emerging technology in contaminated sediment management is active capping involving the use of a sorbent material instead of inert sand to control the release of contaminants from sediment. The application of the sorbent has been shown to be a problem, however a new product from CETCO (reactive core mat, RCM) has shown the potential to alleviate this problem.

This study examines sediment management technologies in two parts. First, sediments from three geographically diverse locations across the Great Lakes were characterized to examine trends in the distribution of PCBs throughout the sediment based on physical and chemical characteristics. The second part of the work evaluates the performance of CETCO's organoclay, activated carbon, and sand in sediment capping applications.

Sediment characterization involved measuring a variety of physical and chemical properties of bulk sediment from the Ashtabula River, the Lower Fox River, and the Grand Calumet River. Sediment fractions were isolated in order to evaluate variations in the carbon and nitrogen content, and the PCB content as a function of sediment grain size and specific gravity. Results from the characterization suggest that PCBs tend to accumulate in the large-sized, less-dense organic fraction in sediments with low levels of PCB contamination and low bulk sediment carbon concentration. The distribution of PCBs is more uniform in sediments with larger levels of contamination, and higher bulk carbon content.

Evaluation of the sorbents in ten day equilibrium batch tests showed for the two PCB congeners examined that activated carbon has a greater affinity for PCBs than organoclay. Both sorbents were found to have a greater affinity for the more highly chlorinated PCB congener, which is consistent with the literature. Consolidation tests used to simulate rapid dewatering revealed that the majority of PCBs released from the sediment are associated with suspended particles. The organoclay and activated carbon both proved to be more effective at reducing PCB release than sand; however, the organoclay was better able to control release for all PCB congeners examined, reducing the total amount of release by 94 percent. Loose organoclay and an organoclay filled RCM were found to be equally effective at removing PCBs during dewatering.

The results of this study suggest that sediment characterization at a given site may be beneficial when choosing an appropriate management strategy. CETCO's organoclay proved to be more effective during rapid dewatering than activated carbon, and the use of an RCM to retain the capping material was equally effective in removing PCBs from the pore water.

Dedicated to My Mother, Linda Schwallie

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## CHAPTER 1

### INTRODUCTION

#### **1.1 History & Background**

Polychlorinated biphenyls (PCBs) were first introduced to the world in 1929, and have since become one of the most widespread contaminants in the environment [1]. Over a fifty year period PCBs were used worldwide in a wide variety of commercial and industrial applications reflecting their unique and commercially desirable properties. Over 700,000 tons of PCBs were manufactured in the United States alone. In general, PCBs are extremely stable and hydrophobic compounds with low vapor pressures. Due to their insulating properties and solubility in oil, PCBs were commonly used in the dielectric fluids inside of capacitors and transformers, many of which are still in use today. Other uses of PCBs included; hydraulic fluids, lubricating oils, pesticides, paint, and carbonless copy paper. Unfortunately the inherent stability and widespread use of PCBs has resulted in their continued prevalence in the environment [2]

The detrimental impacts of PCBs have been known for many years. In 1936 PCBs were discovered to cause health problems in workers involved in their production, while their bioaccumulation in wildlife was first documented in 1966. Continued concern over the potential adverse health effects associated with PCBs led to their inclusion in the Toxic Substances Control Act of 1976 (TSCA). As a result of TSCA regulation and future amendments, the production and distribution of PCBs in the United

States was phased out by mid-1984 [2]. TSCA also regulates the disposal of existing PCB containing devices whereas PCB emissions are regulated by the Safe Drinking Water Act (starting in 1989) and since 1990 the Clean Air Act [2]. As of 2001, the production of PCBs was prohibited in nearly every country in the world, with the possible exceptions of the Russian Federation and North Korea [3].

## 1.2 PCB Chemistry & Properties

PCBs are composed of a biphenyl structure, comprised of two hexagonal rings of carbon atoms connected to one another via one carbon site on each ring. This basic biphenyl ( $C_{12}H_{10}$ ) structure has ten binding sites for hydrogen or chlorine atoms (See Figure 1). A polychlorinated biphenyl molecule contains one to ten chlorine atoms with various possible configurations, resulting in 209 unique PCB congeners [3].

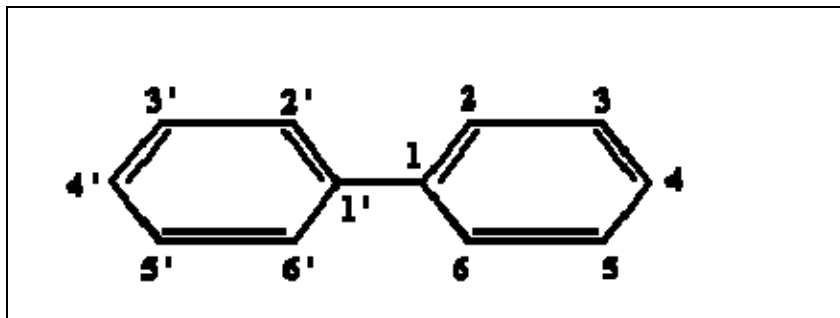


Figure 1.1: Structure of a PCB Molecule [4]

PCBs were produced commercially by combining biphenyl, anhydrous chlorine, and an iron catalyst. Following chlorination, this mixture was purified with an alkali or distillation method. The resulting mixture consisted of dozens of different individual PCB congeners [5]. In the United States PCB mixtures were sold under the trade name

Aroclor. Each Aroclor was designated by a four digit number generally starting with 12 followed by the weight percentage of chlorine in the mixture [3].

<b>PCB Isomer Group</b>	<b>Solubility (g/m<sup>3</sup>)</b>	<b>Vapor Pressure (Pa)</b>	<b>Log K<sub>ow</sub></b>
Biphenyl	9.3	4.9	4.3
MonoCB	4	1.1	4.7
DiCB	1.6	0.24	5.1
TriCB	0.65	0.054	5.5
TetraCB	0.26	0.012	5.9
PentaCB	0.099	0.0026	6.3
HexaCB	0.038	0.00058	6.7
HeptaCB	0.014	0.00013	7.1
OctaCB	0.0055	0.000028	7.5
NonaCB	0.002	0.0000063	7.9
DecaCB	0.00076	0.0000016	8.3

Table 1.1: Properties of PCB Homologs [2]

As shown in Table 1.1, many of the important physicochemical properties that dictate the environmental fate of PCBs vary as a function of the chlorine content. PCB solubility in water is fairly low, less than one gram per cubic meter for most congeners, and decreases with increasing chlorine content. The vapor pressures of most PCBs are also low, again decreasing with increasing chlorine content in general, leading to low atmospheric concentrations. On the other hand, the octanol-water partitioning coefficients (K<sub>OW</sub>) are large, showing that PCBs are more likely to partition into nonpolar phases, especially organic material, such as the tissue of people and animals, and natural organic material suspended in the water column as well as deposited in sediment beds [2]. Trends in the physiochemical properties affecting the environmental fate of PCBs are shown in Table 1.2.

<b>Property</b>	<b>Trend as Chlorine Content Increases</b>
Solubility	Decreases
Vapor Pressure	Decreases
Octanol-Water Partitioning Coefficient	Increases

Table 1.2: Trends in Physiochemical Properties

### **1.3 Environmental Fate**

Even though PCB production has been banned for decades, PCBs are still prevalent throughout the environment, especially in sediments [3]. This continued prevalence of PCBs in sediments is due primarily to two factors:

- The stability of PCBs inhibits biodegradation in the environment, and
- Low aqueous solubility and vapor pressures encourage partitioning into organic phases

Therefore much of the PCBs lost to the environment are still present in soils and sediments [3].

Within the water-sediment system PCBs are found in the aqueous pore water, sorbed to dissolved organic matter and colloidal matter, and sorbed to sediment grains. Thus, due to numerous exposure pathways, PCBs in sediments pose a risk worldwide. At the lowest level of the food chain, benthic invertebrates that contact PCB contaminated sediments bioaccumulate PCBs in their fatty tissue. Bioaccumulation of PCBs by benthic organisms can occur through direct contact with contaminated water, and sediment, or consumption of contaminated food. Other aquatic species such as small fish consume these invertebrates and also accumulate PCBs directly from the environment. PCB tissue concentrations increase at higher levels of the food chain due to the consumption of lower

organisms with PCB contaminated tissues, a process known as biomagnification. As a result, all organisms from insects, worms and snails to polar bears, birds and humans accumulate PCBs in their tissue [3].

Contaminated sediments are an issue worldwide. A recent EPA study rated over 70 percent of the 19,000 sites tested as possibly causing adverse effects, with an astounding 43 percent of the tested sites considered a probable risk for causing adverse effects to aquatic life or humans. In the Great Lakes Basin, there are 43 areas of concern (AOCs), all but one containing contaminated sediments. In many of these areas PCBs are a primary contaminant, leading to many fish consumption advisories and other limits on the use of these waters [6].

#### **1.4 Current Management Options for PCB Contaminated Sediments**

Current management options for the remediation of PCB contaminated sediments can be divided into three basic categories; monitored natural recovery, capping, and dredging. Monitored natural recovery relies on passive containment and degradation through natural processes to reduce contaminant release to the biosphere. Little is done to aid remediation, instead natural recovery of contaminated sediments often occurs through microbial degradation and/or sedimentation. Biological degradation of PCBs is often not effective due to their limited bioavailability, generally low pore water concentrations, and complex structure. Highly chlorinated PCBs are degraded by anaerobic processes, while less chlorinated PCBs are degraded by aerobic processes, resulting in incomplete dechlorination. Ortho substituted PCBs, however, are often resistant to degradation.

Natural recovery through sedimentation, thereby isolating the contaminants, can be an effective recovery option in certain situations. Unfortunately, in most cases there is too much uncertainty in the placement of new sediment to allow this to be an attractive option. For example, the colonization of the deposited sediment by benthic organisms and changes in flow patterns, e.g., storm events, could disturb the underlying sediment leading to further dispersion of the contaminants. Finally, natural recovery is often viewed negatively by the general public [3].

Capping processes physically separate the underlying contaminated sediment from the aquatic ecosystem. Traditional capping is similar to natural recovery through sedimentation, except that the thickness and composition of the cap can be controlled. Caps up to one meter thick can be used, depending on the type of material. It is also possible to install layered caps with heavier material or geomembranes acting as an initial barrier to prevent contaminant release. A layer of sand is installed on top of these layers to allow for the colonization and growth of benthic organisms. While capping allows for greater control than natural sedimentation, it is still susceptible to many of the same issues. The potential for disturbance of the cap and release of PCBs through groundwater flow are cause for concern and limit its use [3].

By default, dredging is the most commonly used management technique because it is the only technique that actually removes contaminants from the watershed. However, during the dredging process contaminated sediments can be resuspended and thus dispersed downstream of the contaminated area. Dredging is also a costly and time consuming process that requires additional treatment or disposal of the contaminated sediment. Once dredged, the contaminated sediments can be disposed of in a landfill or a

confined disposal facility (CDF). In a CDF the dredged sediment is temporarily or permanently deposited and dewatered. Water removed from the dredged sediment must be treated and then is typically returned to the watershed. After dewatering, treatment of contaminated sediments can include extraction through thermal desorption or a washing process, stabilization in a solid matrix, or destruction by a thermal process. While dredging and follow-up treatment or disposal is an effective method for the remediation of contaminated sediments the costs associated with the process are often prohibitive, and the process itself is intrusive and disrupts the watershed ecosystem [3].

### **1.5 PCBs in the Great Lakes Basin**

Of particular concern to the residents of Ohio is contamination in and near the Great Lakes. The Great Lakes basin is a unique resource, providing a home to a number of plant and animal species, while simultaneously providing millions of people from Canada and throughout the continental United States with their drinking water. Due to its natural beauty, and historic significance, the area has also developed into a popular destination for tourists and fisherman.

Beginning in the 1850s with the logging industry and through industrialization in the twentieth century, the Great Lakes basin was in a period of environmental decay [7]. The turning point for the Great Lakes was a June 22, 1969 fire on the Cuyahoga River in Cleveland, Ohio. While the river had caught fire on several previous occasions, this fire received national attention after being publicized in an article in Time Magazine [8]. While cleanup efforts over the last forty years have greatly improved the quality of the Great Lakes basin there are still a number of concerns that need to be addressed. For example, although contaminant levels in fish continue to drop they are still at a level that

requires fish consumption advisories in all five great lakes. This is evident in Lake Michigan, where PCB levels in Coho Salmon have decreased almost five-fold from about 2.3 ppm in 1980 to 0.5 ppm in 2000 [7]. The Great Lakes Binational Toxics Strategy, an agreement between the United States and Canada to reduce pollution inputs to the Great Lakes called for a ninety percent reduction in high-level PCB devices in the United States, greatly reducing the potential for further contamination, and the remediation of all priority sites with contaminated bottom sediments by 2006 [9]. From the signing of the protocol in 1997 to 2003 nearly 3.5 million cubic yards of sediment in the Great Lakes basin has been remediated, most of which was dredged and dewatered at a significant cost [10]. My proposed research examines ways to more effectively implement current management techniques at reduced cost.

## **1.6 Research Objectives**

A promising new option to manage contaminated sediments is to utilize an active sorbent layer in conjunction with current management techniques (e.g., in-situ capping). CETCO Corp has developed an innovative new product known as a reactive core mat (RCM). An RCM filled with an appropriate sorbent or reactive material is ideal for these remedial applications. An RCM is a recently developed type of geocomposite that consists of two layers of geotextile with an interior of high-loft core that can be filled with any type of material, for example activated carbon to sorb organics or apatite to remove metals. Currently an RCM filled with coke breeze (the particulate by-product of coke production) is being evaluated as part of a comparative study on the Anacostia River in Washington, D.C [11].

The Anacostia River is located in an industrial area near the Chesapeake Bay. The area under study is heavily contaminated with PCBs, PAHs, and heavy metals. In March and April of 2004, three active capping materials including; coke breeze, apatite, and AquaBlok (a material to control seepage and advective transport) were applied to the study area, along with a traditional sand cap. The apatite, sand, and AquaBlok were placed in the traditional manner, while the coke breeze was contained within an RCM. In four days an 8,000 square foot test area was covered with the RCM and a layer of sand, compared with five days for the other active caps. In addition, the RCM cap applies at a controlled rate of thickness nearly half that of other caps tested, allowing adequate access to shipping traffic. Currently, the site is being monitored to assess cap performance [11, 12].

A modified reactive cap may overcome some of the drawbacks that have prevented wide-scale use of traditional capping. A sediment cap consisting of a sorbent filled RCM sandwiched between two layers of sand is an ideal choice for a modified reactive cap. First, by choosing an appropriate sorbent or reactive material, release of PCBs from the sediment into the overlying water column can be controlled. The structure of the RCM also acts to both maintain physical separation of the contaminated sediment from the rest of ecosystem, and to ensure that the sorbent layer is not disrupted. Additionally, an RCM is easy to apply in most situations, for example, a coke filled RCM has been shown to readily sink during placement in initial testing [13].

An RCM layer is also a useful addition to a dredging and dewatering remedial approach. Due to its flexibility, an RCM layer can be applied over or under the sediment in almost any dewatering scheme. Sorbents inside the RCM will remove pollutants

including PCBs, and the structure of the RCM also acts as a coarse filter further reducing the need for secondary treatment. *My primary research objective is to examine whether sorbent-amended caps can effectively mitigate PCB release from contaminated sediments.* This work entails an investigation of solution-phase PCB sorption and bench-scale testing of rapid consolidation of PCB-contaminated sediment. I hypothesize that CETCO's organoclay will be more effective than activated carbon at removing PCBs from solution, and that an organoclay filled RCM will prove to effectively control the release of PCBs from sediment during dewatering. CETCO organoclay was specifically designed to have a large capacity for the sorption of organics, while the RCM can be expected to stabilize the cap and greatly reduce the potential for disruption, while not interfering with the upward flow of water released during consolidation.

*The secondary objective of this research is to evaluate the PCB content and distribution in sediments from across the Great Lakes Basin, and to correlate this data to physiochemical properties of the sediment.* The Great Lakes basin covers nearly 300,000 square miles, has over 10,000 miles of shoreline and spans two countries, eight states, and one province [7]. Over such a large area there are bound to be variations in both the characteristics of the sediment and the level of local contamination; however, I hypothesize that it is possible to correlate PCB content with identifiable sediment components. During the course of this research samples taken from three geographically diverse locations were assessed. These locations included; the Ashtabula River (Ashtabula, Ohio), the Grand Calumet River (Gary, Indiana), and the Lower Fox River (Green Bay, Wisconsin). The physical characteristics, chemical composition, level of contamination, and distribution of PCBs within size and density fractions of the bulk

sediment were all recorded to provide insight into expected variations and to aid in the development and application of contaminated sediment management strategies. I expected to see that the PCBs were more closely associated with the organic sediment fraction, with lower contaminant levels in the mineral fraction, composed of clays, silt and sand.

## CHAPTER 2

### CHARACTERIZATION OF PCB CONTAMINATED SEDIMENTS

#### **2.1 Introduction**

The United States Environmental Protection Agency estimates that approximately ten percent of the twelve billion cubic yards of sediment in the U.S. is contaminated with heavy metals and persistent organic pollutants, including PCBs [14]. Current management strategies cost on average 50 to 200 dollars per cubic yard of sediment [15]. Using existing technologies, remediation of the 1.2 billion cubic yards of contaminated sediments in the United States will take decades and billions of dollars to accomplish. As these contaminated sites sit waiting to be remediated, the problems tend to become worse as the sediment is readily dispersed over a larger area by storms or shipping traffic, and its contaminants are slowly released to the overlying water column [15].

Sediments are heterogeneous in composition and the different components exhibit different interactions with contaminants. Consequently, in the late 1990's the USEPA decided that variations in sediment composition were too numerous to permit the establishment of a set of national standards [16]. Geosorbents present in sediments such as organic matter and anthropogenic carbon have a greater affinity for hydrophobic organic contaminants such as PCBs, leading to two distinct pools of available contaminants. The first is a rapidly desorbing contaminant pool released quickly, within hours or days. The second is a slowly desorbing pool that desorbs over several years.

This slow desorption process is thought to result from diffusion limitations within the micropores of organic material and minerals within the sediment [17, 18]. Black carbon resulting from incomplete combustion of carbonaceous material is of particular importance in the sorption and release of hydrophobic organic contaminants [16]. Sorption of organic compounds by black carbon is extensive and non-linear. The presence of black carbon in sediment is thought to be the cause of slow desorption [19].

Characterization, at the particle-level, of the sediment at a specific site can provide information that could be exploited during the remedial process, potentially reducing the time and cost involved. Such characterizations, however, have only been done for a few locations. Ghosh et al. [16] found that 62 percent of the polycyclic aromatic hydrocarbons (PAHs) in Milwaukee Harbor sediment were associated with coal and wood derivatives that comprised only five percent of the sediment mass. It was also reported that only forty percent of the PAHs in this sediment were readily released. After three months 92 percent of the PAHs associated with the coal and wood particles were still strongly sorbed [16].

An additional study by Ghosh et al. [20] examined sediment samples taken from the Milwaukee Harbor as well as samples from Hunters Point, CA. and Harbor Point, NY. This study found that nearly sixty to seventy percent of the PCBs in the sediment were associated with a small quantity of low density carbonaceous particles. Within each size fraction examined the lower density material contained the majority of the PCBs and PAHs with one exception, the smallest size fraction (less than 63 micron), where the PCB contents are roughly equal, and PAHs are concentrated in the higher density fraction. At these locations five to seven percent of the sediment mass was found to contain sixty to

ninety percent of the PCBs and PAHs [20]. These results suggest most of the organic contaminants within sediments are sequestered by a fraction of the sediment, namely the low density fraction.

The intent of this work was to characterize contaminated sediments at select Great Lakes sites; the Ashtabula River in Ohio, the Lower Fox River in Wisconsin, and the Grand Calumet River in Indiana. Physical and chemical properties of bulk sediment samples were examined. Then the bulk sediment was separated into fractions based on size and density. The carbon and nitrogen content, and the PCB content in these fractions was measured and examined for any trends that could be exploited during remediation. Based on the results of this study, carbon content of the sediment and the level of contamination play key roles in the distribution of PCBs. Sediments with low carbon content and low PCB concentration tend to accumulate PCBs in the large, less-dense organic fraction. For sediments with high carbon content and high PCB concentration the distribution of PCBs is more even.

## **2.2 Materials and Methods**

Sediment was obtained from three regions around the Great Lakes basin; the Grand Calumet River (Gary, Indiana), the Ashtabula River (Ashtabula, Ohio), and the Fox River (Green Bay, Wisconsin).

The Grand Calumet River flows across northern Illinois and Indiana, emptying into the southern tip of Lake Michigan. Beginning in 1870 through around 1910, the area experienced heavy industrialization. Steel mills, foundries, a meat packing warehouse, and glue and cornstarch factories were all disposing of waste in the river. Additionally, it was not uncommon for local communities to discharge untreated sewage into the river

during this time [21]. In 1987 the Grand Calumet River was listed as an AOC due in large part to non-point source pollution coming from contaminated sediments. The USEPA estimates that the Grand Calumet River AOC contains five to ten million cubic yards of contaminated sediment, reaching up to twenty feet deep in some areas. Contaminated sediments are a source of PCBs, PAHs, heavy metals, phosphorus, nitrogen, volatile solids, oil and grease. Additional pollutants in the AOC include high levels of fecal coliform, biochemical oxygen demand (BOD), and suspended solids [22]. In 2003 over 800,000 cubic yards of sediment was hydraulically dredged from a five mile section of the Grand Calumet River and deposited in a corrective action management unit (CAMU) at the U.S. Steel facility in Gary, Indiana [10].

Grand Calumet River sediment samples were collected with the assistance of CETCO on August 9, 2005, from Unit 1 of CAMU at the U.S. Steel facility. Samples from the south end were collected from the surface, whereas sediment from the north end were collected at a depth of approximately 18 inches.

In the northeastern corner of Ohio, Fields Brook flows into the Ashtabula River which in turn empties into Lake Erie. In 1983 Fields Brook was placed on the USEPA's National Priorities List, while in 1985 the Ashtabula River basin was designated an AOC. Two metal scrap yards, a chemical plant, a plastics manufacturer, and a rail yard have been identified as potential sources of PCBs, heavy metals, and chlorinated organic compounds [23].

Ashtabula River sediment was collected with the assistance of OhioEPA on November 19, 2004 from a location just downstream from the entrance of Fields Brook. Four Teflon lined core tubes four inches in diameter were manually driven to a depth of

ten feet. Each tube contained approximately six feet of sediment and four feet of water. The bottom three feet of the sediment from each core was separated and homogenized under a nitrogen atmosphere prior to analysis [24].

The Lower Fox River empties into Green Bay, which is located on the northwest corner of Lake Michigan. Water quality problems in the area have been noted since the early 1900s. Industrial waste discharged from pulp and paper mills, as well as the discharge of untreated sewage is responsible for most of the contamination in the watershed. Paper mills operating near the Fox River produced a large quantity of NCR carbonless copy paper during the 1950s and 1960s. The production and recycling of this kind of paper was responsible for the release of large amounts of PCBs into the watershed. The area has been designated an AOC due to beneficial use impairments caused primarily by PCB contaminated sediments, and eutrophication due to elevated phosphorus levels. Heavy metals, dioxins, furans, and chlorinated pesticides are also present in the contaminated sediments in the region [25].

Due to the size of the Lower Fox River AOC, the area was divided into five separate operable units (OU) for cleanup. Three of these areas are being cleaned up using dredging and off-site disposal, while the remaining two sites are undergoing monitored natural recovery. This work focuses on OU 1, Little Lake Butte des Morts. Contaminated sediment from the Fox River was hydraulically dredged in 2004 and transported through a floating pipeline into large geotextile tubes placed on shore. Sediment was allowed to settle inside the tubes, while any supernatant water was removed, treated on-site, and discharged back into the river. After dewatering the sediment was transported by truck to a nearby disposal facility [25, 26]. Fox River

sediment was collected on June 6, 2005 by CETCO and USEPA officials from the Little Lake Butte des Morts (OU 1) cleanup site in Neenah, Wisconsin. Five gallon buckets of sediment were obtained from two regions in Sub-area A. Sub-area A region VIII (SA-08) is a highly vegetated fine grained sediment with a high percentage of organic material. Sub-area A region IV (SA-09) is composed of coarse grained sediment, with more sand and silt than SA-08 [27].

Physiochemical properties of the bulk sediment including the Unified Soil Classification, moisture content, and specific gravity were determined using standard ASTM methods. Grain size distribution was measured using a Malvern Mastersizer and a mineralogical analysis was performed using x-ray diffraction (Phillips Analytical). Pore water was extracted from the sediment using a centrifuge, and acidified by adding 100 microliters of trace metal grade nitric acid. Elemental composition of the pore water was determined with a Varian Vista AX CCD Simultaneous Inductively Coupled Plasma – Atomic Emission Spectrometer. All solvents were obtained from Fisher Scientific and were at least HPLC grade or better unless otherwise denoted. Throughout this document individual PCB congeners are referred to by using the Ballschmitter and Zell numbering system (BZ #) [28]

Sediment samples were wet sieved to isolate three size fractions, greater than 75 micron, between 75 micron and 25 micron, and less than 25 micron. The greater than 75 micron size fraction was further separated by density, based on difference in specific gravity, using a saturated calcium sulfate solution. Carbon and nitrogen content of each fraction, as well as the bulk sediment was measured with a Thermoquest NC 2100 carbon and nitrogen analyzer.

PCB content of each fraction was determined following EPA SW-846 protocol.

Table 2.1 provides a list of methods used for the analysis of PCB content in the sediment samples. Further details of the methods used are listed below.

Method #	Method Title
3541	Automated Soxhlet Extraction
3660B	Sulfur Cleanup
3620B	Florisil Cleanup
8082	PCBs by Gas Chromatography

Table 2.1: EPA SW-846 Methods Used in PCB Sample Analysis

Sediment samples were extracted with a Soxtec HT 1043 automated soxhlet extraction unit following Method 3541. In brief, two grams of sediment were placed in a cellulose extraction thimble and covered with a cotton plug. Extraction cups were filled with 50 milliliters of a 50:50 hexane:acetone solution and PTFE boiling chips. A Thermo Neslab RTE 7 water bath unit at 15°C was connected to the extraction unit. The extraction thimbles were immersed in the boiling solvent mixture for one hour, then raised above the extraction cup and rinsed for one hour. The condenser valves were then closed and the fan was turned on for approximately twenty minutes for evaporation. Extracts were then further reduced to one to two milliliters using nitrogen blowdown.

Following extraction, cleanup of the extracts was performed following Method 3660B for sulfur removal and Method 3620B for removing interferences. Copper shot (Sigma-Aldrich) for sulfur removal was cleaned using dilute nitric acid. This was

completed by placing the shot into a small beaker and covering it with de-ionized water. Concentrated nitric acid was added drop wise while swirling the beaker until the solution began to turn blue. The supernatant was drained, and the copper was rinsed with water until there was no longer a color change. This process was repeated twice, and finally the copper was rinsed with acetone and dried with nitrogen gas. For sulfur removal two grams of copper was added to a vial with one to two milliliters of extract and manually shaken for one minute. If the surface of the copper appears to be completely black, it was removed and more clean copper was added. The extract was then removed and placed in a clean vial.

Interfering organics, such as pesticides, were removed using six milliliter, one gram, Florisil cartridges (Restek Corp.) and a vacuum flask. Four milliliters of hexane was added to saturate the cartridge. The vacuum was turned on until only a thin layer of hexane remained above the cartridge. The extract was added to the top of the column as well as 500 microliters of hexane used to rinse the extract vial. The vacuum was used to draw the extract through the cartridge until only a thin layer remained. Three milliliters of clean hexane was added to the cartridge and drawn through with the vacuum within one minute. This fraction contains all of the PCBs, but most of the pesticides were removed. The hexane extract was reduced to one milliliter volume by nitrogen blowdown and analyzed using an HP 6890+ gas chromatograph equipped with an electron capture detector (GC-ECD) similar to EPA SW-846 Method 8082.

Quantification differed from the EPA method. Concentrations of selected individual PCB congeners were calculated as opposed to a total PCB concentration based on Aroclor patterns. Two microliters of each sample was injected into the GC-ECD by an

HP 7683 series autosampler. The GC operated with a split inlet at 200°C using helium at 14.89 PSI as a carrier gas through a 30 meter HP-5 column. The oven was initially at 50 °C, ramped to 200 °C at 30 °C per min, and again ramped to 320 °C at 10 °C per minute. The oven temperature was then held at 320 °C for five minutes. Three hexane blanks were injected before each run and between each sample. The inlet septa was changed daily. Calibration standards were created by diluting single PCB congener stock solutions with hexane. Six sample, linear, standard curves were created covering a concentration range of three orders of magnitude (8 ng/mL - 8µg/mL), inclusive of the concentration range studied. Decachlorobiphenyl (BZ # 209) was used as an internal standard to account for injection volume changes, and retention time shifts.

### **2.3 Results and Discussion**

The Ashtabula River sediment, classified as ML under the Unified Soil Classification System, was primarily composed of inorganic silts and fine sands. Mineralogical analysis indicated the sediment largely consisted of illite, with quartz and muscovite also present. The bulk sediment had a mean grain size of 37 microns with a specific gravity of 2.81, the highest of the samples examined, and an in-situ moisture content of 68.7 percent. Pore water extracted from the sediment contained large levels of calcium, magnesium, manganese, and sulfur. The principle inorganic components of the pore water for all samples studied are presented in Table 2.2 below.

Element	Ashtabula	Grand Calumet North	Grand Calumet South	Fox SA-08	Fox SA-09
Al	0.041	ND	ND	ND	ND
Ba	NA	0.52	1.3	0.13	0.09
Ca	610	216	86	142	117
Cr	ND	0.002	0.002	0.002	0.003
Cu	0.026	ND	ND	ND	ND
Fe	0.607	0.003	0.20	0.062	0.015
K	NA	42	30	10	7.8
Mg	NA	37	66	49	42
Mn	3.06	0.69	0.46	1.6	1.0
Mo	0.007	0.22	0.04	ND	ND
Na	NA	59	43	26	16
Ni	0.007	0.008	0.004	ND	ND
P	0.049	0.05	0.06	3.3	1.8
S	448	99	6.4	1.2	2.5
Si	NA	4.5	7.4	29	24
Sr	NA	2.5	1.7	2.0	0.67
Zn	ND	0.39	0.53	0.02	0.01

Table 2.2: Sediment Pore Water Elemental Composition (mg/L).

ND refers to not detected. NA refers to not analyzed.

Initial analysis of the PCB content of the bulk Ashtabula River sediment revealed 74 peaks, representing 104 different PCB congeners (see Appendix C for example chromatogram). Four primary PCB peaks representing seven congeners were selected for further analysis; 2,3-dichlorobiphenyl (BZ #5), 2,4'-dichlorobiphenyl (BZ #8), 2,4,4'-trichlorobiphenyl (BZ #28), 2,4',5-trichlorobiphenyl (BZ #31), 2,2',5,5'-tetrachlorobiphenyl, 2,3',4,4'-tetrachlorobiphenyl (BZ #66), and 2,2',3,5',6-pentachlorobiphenyl (BZ #95). These congeners were not only present in the largest concentrations in the bulk sediment samples, but were also principal components of the commercial Aroclor mixtures sold in the United States. Further analysis of the sediment revealed that the PCB concentrations in the sediment were highly variable. Table 2.3 below lists the concentration of these PCBs in the bulk sediment samples.

<b>PCB #</b>	<b>Ashtabula</b>	<b>Fox SA – 08</b>	<b>Fox SA – 09</b>	<b>Calumet North</b>	<b>Calumet South</b>
5/8	1000 ± 500	63	420	5100	2300
28/31	400 ± 300	920	1400	22000	7700
52	1000 ± 700	1300	160	8000	4500
66/95	500 ± 500	2400	100	9700	3500

Table 2.3: Concentrations of Selected PCB Congeners in the Bulk Sediment (µg/kg)

The Ashtabula River sediment was separated into three size fractions (less than 25 micron, 25 to 75 micron, and greater than 75 micron) for further analysis. The largest size fraction (greater than 75 micron) was further separated into two density fractions.

Carbon and nitrogen content, as well as PCB content were determined for each of the sediment fractions. The greater than 75 micron less dense fraction was found to contain the greatest percent carbon and percent nitrogen by dry weight. The carbon and nitrogen content of this fraction was significantly higher than the content of the bulk sediment indicating this fraction was primarily composed of organic matter. All of the other sediment fractions contained less than one sixth of the nitrogen and carbon present in the large, dense material, indicating these sediment fractions were composed primarily of inorganic material. Complete carbon and nitrogen distribution data is given in Table 2.4 and Table 2.5 below.

Nitrogen Content	Sediment Fraction				
	Bulk	< 25 µm	25 – 75 µm	> 75 µm Light	> 75 µm Dense
Ashtabula	0.14	0.17	0.12	1.02	0.00
Calumet North	0.37	0.39	0.36	0.85	0.50
Calumet South	0.33	0.34	0.39	0.83	0.31
Fox SA-08	0.66	0.45	0.45	1.03	0.79
Fox SA-09	0.56	0.43	0.70	0.83	0.80

Table 2.4: Sediment Fraction Nitrogen Content (Percent Dry Weight)

Carbon Content	Sediment Fraction				
	Bulk	< 25 µm	25 – 75 µm	> 75 µm Light	> 75 µm Dense
Ashtabula	3.24	1.98	1.69	28.35	1.44
Calumet North	32.48	32.21	31.92	58.77	40.19
Calumet South	27.3	26.76	31.52	56.7	23.96
Fox SA-08	18.48	8.37	11.56	48.27	27.42
Fox SA-09	10.12	6.77	12.17	35.11	14.46

Table 2.5: Sediment Fraction Carbon Content (Percent Dry Weight)

PCB analysis conducted on the Ashtabula River sediment fractions showed that the majority of PCBs were concentrated in the greater than 75 micron less dense fraction, which accounts for less than two percent of the total sediment mass. Sediment fractions below 75 micron in size contained trace levels of PCBs at or below the detection limits, but accounted for 86 percent of the total sediment mass. The large dense sediment fraction was also found to contain substantial levels of some PCB congeners. Concentrations of selected PCB congeners are presented in Table 2.6.

<b>PCB</b>	<b>Concentration (µg/kg)</b>			
	<b>&lt; 25 µm</b>	<b>25-75 µm</b>	<b>&gt;75 µm Dense</b>	<b>&gt; 75 µm Light</b>
5/8	10	10	10	16000
28/31	10	BDL	300	1000
52	BDL	BDL	900	4000
66/95	20	40	100	200
Mass	38%	48%	12.2%	1.8%

Table 2.6: Concentrations of PCB Congeners in Ashtabula Sediment Fractions

Characterization of the Ashtabula River sediment reveals that PCBs tend to concentrate in the large less dense organic fraction, which comprises only 1.8 percent of the sediment by mass. Additionally, particles less than 75 micron in size contain only trace levels of PCBs, but account for 86 percent of the total sediment mass. These results were consistent with the mineralogy of the sediment. The sediment was primarily composed of clays and inorganic minerals with a low affinity for PCBs. Coal and combustion byproducts were not present in significant quantities, and the carbon content of the bulk sediment was relatively low, primarily concentrated in the large less dense fraction. These findings are consistent with the work of Ghosh et al. [16, 20] that the less dense fraction of the sediment contained the majority of the PAHs and PCBs.

Fox River and Grand Calumet River samples were analyzed similarly to the Ashtabula River sediment with two primary differences. First, while the Ashtabula River sediments were obtained in-situ and kept under a nitrogen atmosphere, the Fox River and

Grand Calumet River samples were obtained ex-situ after they had been dredged and exposed to the atmosphere. Second, all four Ashtabula River sub-samples were combined and homogenized, while two sub-samples were taken and analyzed separately for the Fox and Grand Calumet Rivers.

Fox River sediment consists mainly of clay minerals similar to the Ashtabula River. Sediment from both locations contained large amounts of kaolinite, calcite, quartz, and dolomite. However, the most prevalent mineral in sediment from the SA-08 area was illite, while clinocllore was predominant at SA-09. The specific gravity of samples from both locations was nearly identical, 2.40 for SA-08 and 2.38 for SA-09. Water contents for both locations were extremely high. SA-08 had an average water content of 207 percent, compared with 313 percent at SA-09. These sediments were hydraulically dredged, adding water to the sediment before disposal. The dewatering process consists of two steps; settling, and consolidation. The settling process occurs quickly as the sediment particles settle out of suspension. Consolidation occurs over a longer time period forcing water out of the sediments due to pressure from overlying sediment. Water content of dredged sediment can be expected to be elevated initially after deposition in the geotextile tubes used at the Fox River site. Mean grain size was quite different between the two samples. The mean grain size of the SA-08 sediment (92 micron) was nearly twice that of the SA-09 sediment (48 micron), consistent with the sample locations. Grain size distributions for all of the sediment samples can be found in Appendix B.

Pore water samples extracted from the sediment primarily contained calcium, magnesium, sodium, potassium, silicon, and sulfur (see Table 2.2). Phosphorus

concentrations were also elevated, consistent with the site background. Trace levels of iron, strontium, and barium were also present.

Fox River sediment was separated into fractions in a manner similar to the Ashtabula River sediment. Bulk Fox River sediments were found to contain much higher levels of nitrogen and carbon than did the Ashtabula River samples. Nitrogen content in the Fox River sediment was approximately four times greater than the Ashtabula River sediment. While nitrogen content between the two Fox River sites was similar, carbon content in the SA-08 sediment was nearly twice that of the SA-09 sediment. The difference in carbon content was particularly noticeable for the large size fraction of the sediment. Visual inspection of the sediment fractions indicated that sediment from SA-08 was composed primarily of wood particles much larger than 75 micron, while the similar SA-09 fraction contained much smaller particles. Nitrogen and carbon content data for the Fox River sediment were presented in Tables 2.4 and 2.5. PCB analysis of the bulk sediment revealed different PCB distributions at each site. SA – 08 sediment contained larger amounts of the more highly chlorinated PCBs, and a greater total concentration of PCBs based on the selected congeners. Sediment from SA – 09 on the other hand, had higher concentrations of less chlorinated PCBs. The lower PCB concentrations in the SA – 09 sediment are consistent with the site characteristics (generally sandy and gravelly) [27]. The difference in PCB concentration also correlates with the difference in the carbon content at each site. PCB concentrations at the Fox River tended to be larger than those at the Ashtabula River, and more homogeneous from sample to sample.

PCB analysis of the Fox River fractions revealed that the same trend present in the Ashtabula River sediment was present in the SA – 09 sediment; the large light fraction contains the majority of the PCBs. In the SA – 08 sample, however, the large light sediment contains the smallest concentration of PCBs. The large dense fraction contains the largest concentration of PCBs for the SA – 08 sample. This may be due to the large carbon content of the sediment. While the large less dense fraction of the Fox River sediments still contains the most carbon, the differences are not nearly as striking as the Ashtabula River sediment fractions. The carbon content of the large less dense fraction of the Ashtabula sediment contained over 14 times more carbon than any of the other fractions, while the Fox River SA – 09 large less dense fraction contains 2.5 times as much carbon as any other fraction. For the SA – 08 sediment this difference in carbon concentration is less than 1.8, indicating that the fractions are more similar in composition than either the SA – 09 or Ashtabula River sediment. PCB content in each fraction is reported in Tables 2.7 and 2.8 below.

<b>SA – 08</b>	<b>Concentration (µg/kg)</b>			
<b>PCB</b>	<b>&lt; 25 µm</b>	<b>25-75 µm</b>	<b>&gt;75 µm Dense</b>	<b>&gt; 75 µm Light</b>
5/8	242	284	1000	409
28/31	3970	3400	2630	1120
52	121	87	528	1900
66/95	117	75	3140	134
Mass	19.9%	26.6%	2.7%	50.7%

Table 2.7: PCB Content in the Fox River SA – 08 Sediment Fractions

SA – 09	Concentration (µg/kg)			
PCB	< 25 µm	25-75 µm	>75 µm Dense	> 75 µm Light
5/8	140	260	150	240
28/31	26	77	130	650
52	19	19	18	72
66/95	150	29	15	18
Mass	49.4%	18.8%	29.9%	1.9%

Table 2.8: PCB Content in the Fox River SA – 09 Sediment Fractions

Two Grand Calumet River sediment samples were obtained from opposite ends of the CAMU. These samples are referred to as North and South to reflect the area of the CAMU where the samples were collected. Classification of the sediment under the Unified Soil Classification System was not possible due to the presence of oil coating the particles. The Grand Calumet River sediment composition was quite different than either the Ashtabula or Fox River samples. While those sediments were primarily composed of clay, the main components of the Grand Calumet sediment were metal oxides, consistent with the locations proximity to a steel mill. North sediment contained large amounts of wustite, magnesioferrite, hematite, and dolomite, while South sediment was primarily anorthite, cuprite, and graphite. Sediment samples from both locations also contained significant quantities of calcite and quartz. Moisture content of the sediment was determined to be 69.9 and 65.9 percent for the North and South samples respectively, while the mean grain size was also comparable at 32 micron and 42 micron (see

Appendix B). Specific gravities of both Grand Calumet samples were lower than the other sampling locations; 2.23 for the South, and 2.05 for the North.

The specific gravity of the sediment samples appear to be related to the carbon content and tended to decrease as the carbon content increased. Based on the data from these locations tripling the carbon content would correspond to a 0.2 reduction in specific gravity. The data was not well represented by a linear trend, likely due to the various forms of organic and inorganic carbon found in the sediment. A logarithmic trend (See Figure 2.1) provided a better fit to the data.

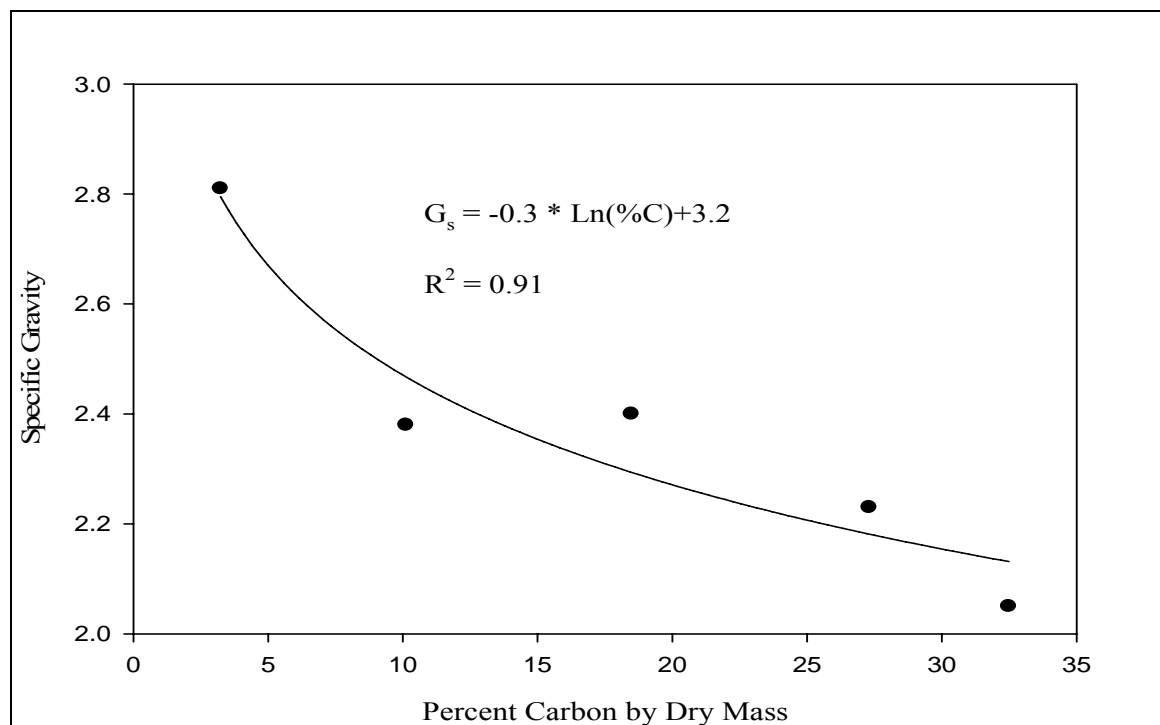


Figure 2.1: Specific Gravity Correlation to Percent Carbon

Mass balances were conducted on the carbon content of the sediment fractions by multiplying the carbon content of each fraction by the percent sediment mass, and summing the results of all four fractions. The mass balance carbon content of the Grand

Calumet and Fox River sediments were similar to the measured carbon content of the bulk sediments. The Ashtabula River sediment mass balance, however, differed from the measured bulk value by approximately thirty percent. The large difference in the case of the Ashtabula River sediment may reflect likely due to the fact the data is based on one sample. Carbon content measurements on the Grand Calumet and Fox River sediments were conducted in duplicate, with an average deviation of 1.4 percent carbon between the two analyses. Carbon content mass balance data is presented in Table 2.6.

Fraction	Ashtabula	Calumet North	Calumet South	Fox SA – 08	Fox SA – 09
Bulk	3.24	32.48	27.30	18.48	10.12
Mass Balance	2.25	37.16	28.09	19.95	10.62
Difference	0.99	-4.68	-0.79	-1.47	-0.50
Difference	30.6%	-14.4%	-2.9%	-7.9%	-5.0%

Table 2.9: Carbon Content Mass Balance (Percent Dry Weight)

Pore water from the Grand Calumet River sediment primarily contained calcium, potassium, magnesium, sodium, and sulfur. Smaller levels of barium, iron, manganese, molybdenum, nickel, phosphorus, silicon, strontium, and zinc were also present in the pore water (see Table 2.2 for complete pore water data). The Grand Calumet River sediment contained much higher levels of PCBs than either of the other locations. Across both sites the distribution of PCB congeners was similar, with PCB # 28/31 found at the highest concentration of the PCBs measured. Bulk sediment PCB concentrations

correlate well to carbon content, with higher carbon content indicating larger levels of contamination at the sites examined in this study.

Similar to the Fox River SA – 08 sediment, the large light fraction does not contain the majority of the PCBs for either Grand Calumet River sample. The medium size fraction contains the most PCBs in the case of the North sediment, while the small size fraction contains the most PCBs in the South sediment. This lack of a trend could again be due to the extremely high carbon contents of all of the sediment fractions. Sediment fractions from the south end of the CAMU all contain nearly 24 percent carbon, while the samples from the north end all contain nearly an astounding 32 percent carbon. Such large concentrations indicate that organic material and black carbon are prevalent throughout the sediment. This even distribution of carbon particles leads to a more uniform distribution of PCBs. Concentrations of selected PCB congeners are provided in Tables 2.9 and 2.10 below.

<b>South</b>	<b>Concentration (µg/kg)</b>			
<b>PCB</b>	<b>&lt; 25 µm</b>	<b>25-75 µm</b>	<b>&gt;75 µm Dense</b>	<b>&gt; 75 µm Light</b>
5/8	3300	5500	2800	2200
28/31	1200	25000	14000	14000
52	6100	10200	3600	3100
66/95	5100	8000	4700	6300
Mass	16.8%	24.0%	57.6%	1.6%

Table 2.10: PCB Content in the Grand Calumet North Sediment Fractions

<b>South</b>	<b>Concentration (µg/kg)</b>			
<b>PCB</b>	<b>&lt; 25 µm</b>	<b>25-75 µm</b>	<b>&gt;75 µm Dense</b>	<b>&gt; 75 µm Light</b>
5/8	2200	1500	1100	1600
28/31	7200	4400	2900	4000
52	6100	1800	1400	1800
66/95	5100	2500	1500	2000
Mass	21.0%	15.7%	56.1%	7.2%

Table 2.11: PCB Content in the Grand Calumet South Sediment Fractions

The distribution of PCBs per unit mass of sediment was examined to evaluate the mass distribution of PCBs. Table 2.11 provides the mass of each PCB congener associated with each fraction assuming one kilogram of sediment. The large dense sediment fraction contains the greatest mass of PCB for most of the sediment samples examined. While the large less dense fraction contains larger concentrations, this fraction generally does not compose enough of the sediment to dominate the PCB distribution. Only the Ashtabula River sediment contains the largest mass of PCBs in the large light fraction.

PCB Congener #	8&5	28&31	52	66&95	Total
<b>Fox SA – 08</b>					
< 25 µm	50	790	20	20	880
25 - 75 µm	80	900	20	20	1020
>75 µm Less Dense	10	30	50	4	94
>75 µm Dense	510	1300	270	1600	3680
<b>Fox SA – 09</b>					
< 25 µm	70	10	9	70	159
25 - 75 µm	50	10	4	5	69
>75 µm Less Dense	5	10	1	2	17
>75 µm Dense	40	40	6	5	91
<b>Grand Calumet North</b>					
< 25 µm	560	2100	1000	860	4520
25 - 75 µm	1300	6000	2500	1900	11700
>75 µm Less Dense	30	230	50	100	410
>75 µm Dense	1600	8300	2100	2700	14700
<b>Grand Calumet South</b>					
< 25 µm	450	1500	720	720	3390
25 - 75 µm	240	700	280	400	1620
>75 µm Less Dense	120	300	130	140	690
>75 µm Dense	640	1600	810	830	3880

Table 2.12: Mass Distribution of Selected PCB Congeners (µg)

Table 2.12 Continued

<b>Ashtabula</b>					
< 25 $\mu\text{m}$	4	4	0	8	16
25 - 75 $\mu\text{m}$	5	0	0	19	24
>75 $\mu\text{m}$ Less Dense	280	20	70	4	374
>75 $\mu\text{m}$ Dense	1	40	110	10	161

## 2.4 Conclusions

Evaluation of the sediment characteristics revealed that carbon content has an influence over both specific gravity and bulk sediment PCB concentration. As the carbon content of the sediment increased, specific gravity decreased while sediment PCB content increased. After examining the sediment fractions, it appears that the large light fraction of the sediment does not always contain the majority of PCBs. This holds true for the Ashtabula River sediment where a large fraction of the organic matter is found in the large light fraction. However, for sediments similar to those from the Grand Calumet River where there is a significant amount of carbon in every fraction, the distribution of PCBs appears to be more uniform. The distribution of PCBs within the sediment may also be affected by the overall level of contamination. The Grand Calumet River sediments in particular were highly contaminated (exhibiting a noticeable organic compound odor) and contained nearly uniform PCBs distributions in all of the sediment fractions.

## CHAPTER 3

### EVALUATION OF SORBENTS FOR THE CONTROL OF PCB RELEASE FROM SEDIMENTS

#### **3.1 Introduction**

Treatment of contaminated sediments has traditionally involved either in-situ capping, or ex-situ treatment requiring dredging and dewatering. Ex-situ treatment of contaminated sediments through dredging and dewatering is the most commonly used management option due to the fact that it actually removes contaminants from the environment. However, dredging and dewatering of sediments is a costly and time consuming process. Dredging alone is estimated to cost 100 to 200 dollars per cubic yard and through 2003 the United States had spent 130 million dollars for the dredging of 1.6 million cubic yards of contaminated sediment from Great Lakes Areas of Concern (AOCs) [15]. While dredging and dewatering is an effective management option, the limited funding available has delayed the remediation of many contaminated sites, causing further problems. For example, PCBs and other contaminants are currently being discharged to Lake Michigan from several highly contaminated AOCs [15]. In-situ sediment capping is a more cost effective approach at 50 to 60 dollars per cubic yard [15]. However, maintaining the integrity of in-situ caps can be problematic due to the potential release of contaminants if the cap were to be disrupted by storm events, ships or

aquatic organisms. To avoid this, in-situ caps have been traditionally applied in layers up to three feet thick, a practice that prevents their implementation in many situations [15].

Recently, research has focused on the development of active capping methods involving the use of a reactive sorbent material to control the release of contaminants from sediments [11]. Traditional sand capping aims to separate contaminated sediments from benthic organisms and to prevent colloidal transport. It does little, however, to prevent the flow of contaminants associated with the pore water from being discharged into the overlying water column. Active capping, on the other hand, does remove contaminants from solution. Sorbent materials such as activated carbon, organically modified clay, and coke breeze (fine particles that are a by-product of coke production) have been examined for their effectiveness in controlling the release of organics from contaminated sediments [11, 12, 29, 30]. The controlled dispersal of these low density sorbents on the sediment bed is problematic. Incorporating these sorbent materials within engineered geotextiles such as the reactive core mat (RCM) produced by CETCO could greatly improve traditional sediment management strategies. The use of a reactive cap comprised of a sorbent filled RCM overlaid by sand in place of a traditional in-situ sand cap would allow for the controlled placement of a thinner sediment cap, with a lower risk of disruption. It is also possible that sorbent-amended geotextiles could be used to minimize contaminant loss during the dewatering of dredged sediments.

Previously, Zimmerman et al. [31] found that a cap incorporating TOG brand activated carbon effectively reduced the total PCB flux by 53 percent for one month, and by 89 percent during the following four months in a bench-scale study. Activated carbon

was found to be even more effective in reducing PCB release when mixed with the contaminated sediment [31]. CETCO's RCM is currently being evaluated in the Anacostia River in Washington, D.C. In April, 2004 a coke breeze filled RCM was applied to an 1100 square meter area of the river, with a fifteen centimeter sand layer applied over the RCM. Monitoring of the site showed that application of the RCM cap caused minimal re-suspension of contaminated sediment and that the seepage of pore water through the sediment was not reduced by the RCM cap. Eighteen months after the installation of the RCM cap, release of PCBs was still below the detection limit [32].

This section focused on evaluating three capping materials; traditional sand, activated carbon, and CETCO organoclay, for the control of PCB release from contaminated sediments. Batch tests were conducted to determine the effectiveness of each sorbent at removing individual PCB congeners from solution. Consolidation tests were conducted using contaminated sediment from the Grand Calumet River to simulate rapid dewatering. Sediment was first consolidated with no capping layer to determine the extent of PCB release during dewatering. Additional tests were conducted with fresh sediment and a layer of capping media to assess the potential for reducing PCB release from natural contaminated sediments. Examination of the sediment pore water revealed that most of the PCBs released were associated with colloidal and suspended particles. Activated carbon outperformed organoclay in the ten day equilibrium batch tests. However, the consolidation tests showed that organoclay is more effective at reducing PCB release from sediment during rapid dewatering.

### 3.2 Materials and Methods

Batch tests evaluating PCB sorption following the approach of Jonker and Koelmans [33] were performed in 250 mL amber glass vials (Fisher Scientific). Solid 2,4'-dichlorobiphenyl (BZ #8) and 2,3',4,4'-tetrachlorobiphenyl (BZ #66) were obtained as individual congeners from Ultra Scientific. Stock solutions were prepared by dissolving solid PCB in methanol. All solvents were obtained from Fisher Scientific and were of at least HPLC grade quality. The stock 2,4'-dichlorobiphenyl solution concentration was 250 mg/L, while the concentration of the stock 2,3',4,4'-tetrachlorobiphenyl solution was 100 mg/L. Prior to use in the batch tests the polyoxymethylene (POM) film (McMaster-Carr) was cut into roughly one quarter inch by four inch strips and cleaned by soaking in hexane for thirty minutes followed by soaking in methanol for thirty minutes, after Jonker & Koelmans [33]. The strips were then rinsed in de-ionized water and dried with a Kimwipe.

Three sorbents were tested in the individual batch tests; activated carbon, organoclay, and sand. TOG NDS brand activated carbon was obtained from Calgon Carbon Corp, while organoclay was extracted from a reactive core mat supplied by CETCO. Activated carbon and organoclay used in the batch tests passed a number 20 sieve, but were retained on a number 40 sieve. Percent carbon in the organoclay was estimated to be 31 percent. A 20 gram sample of organoclay was dried in an oven overnight at 105°C. The mass was recorded, and the sample was placed in a muffle furnace at 550°C for one hour. Thirty-one percent of the sample mass was lost after heating in the muffle furnace. Surface area of the organoclay and activated carbon was measured by nitrogen BET. However, the values obtained were lower than those

reported in the literature. The surface area of the activated carbon was measured at 220 m<sup>2</sup>/g, one-fourth of the 800 to 900 m<sup>2</sup>/g value reported by Hindarso et al. [34]. Similarly, the surface area of the organoclay was measured at 0.58 m<sup>2</sup>/g, while CETCO reports the value to be on the order of 800 to 1000 m<sup>2</sup>/g [35]. Fine grain Ottawa sand (Matheson Coleman & Bell) was used without further alteration.

Kaolinite and zeolite BET standards with known surface areas of 16.5 m<sup>2</sup>/g and 184 m<sup>2</sup>/g, respectively, were examined to evaluate the accuracy of the BET method. The surface area of 65 kaolinite measurements equaled  $11 \pm 3$  m<sup>2</sup>/g, whereas for kaolinite the average of 70 measurements provided a surface area of  $166 \pm 14$  m<sup>2</sup>/g. Based on these analyses it appears that while precise, the nitrogen BET method applied was not capable of measuring all of the internal surface area of the particles. Nevertheless, the error in the surface area measurements was only on the order of 5 to 20 m<sup>2</sup>/g. Based on this level of error, I conclude that the surface area measurements presented here were more representative of the sample than the values reported by the manufacturer.

Single POM strips were added to 250mL amber glass bottles filled with 245mL de-ionized water, 2.5mL calcium chloride stock solution and 2.5 mL sodium azide solution. Calcium chloride provided a 0.01M ionic strength, while 50 mg/L sodium azide was added to control bacterial growth. Initial tests were conducted without sorbent, while approximately 200mg of sorbent, or 400mg of sand were added to the subsequent tests. Each bottle was spiked with a methanol solution containing 3.5 mg/L of a single PCB congener. Spike solution volumes ranged from 20 to 800 microliters, to prevent co-solvent effects. The bottles were then placed on a table shaker for ten days.

Following the ten day equilibration period the POM strips were removed from the bottles for extraction. Each POM strip was folded in half and placed in a 25mL clear glass vial with 15mL hexane. The vials were then placed on a rotary shaker for 48 hours, following the procedure outlined by Cornelissen et al. [36]. The hexane extract was reduced to one milliliter volume by nitrogen blowdown. Selected samples were extracted a second time to evaluate the recovery of this method. All extracts were analyzed by GC-ECD as described in Chapter Two.

Sediment from the Grand Calumet River, a tributary of Lake Michigan, was used in the consolidation tests. Background on the Grand Calumet River AOC can be found in Chapter Two of this document. Sediment samples were collected in August 2005, from Unit 1 of CAMU at the U.S. Steel facility. Samples from the south end were collected from the surface, whereas sediment from the north end were collected at a depth of approximately 18 inches.

A custom built apparatus (see Figure 3.1) was used for the consolidation experiments. The system was single drained with a Validyne CD23 pore pressure gage attached to the bottom of the unit. Displacement was measured using a Kanetec dial gauge. The ten cm diameter stainless steel consolidation cylinder was filled with sediment to a height of five centimeters. A porous disk with a 100 micron nominal pore size was placed over the sediment to contain the sample. A twenty eight kilogram load was placed over the sediment to contain the sample. A twenty eight kilogram load was applied to the hanger for a period of twenty-four hours to rapidly dewater the sediment. Pore water samples were removed from the cylinder using a peristaltic pump. After measuring the PCB release from the sediment alone, the tests were repeated using fresh sediment covered with a sorbent layer. Sorbent was applied in a one centimeter

thick layer over a nylon mesh screen. Experiments were also conducted using the organoclay filled RCM. Each test was duplicated to account for the variability between the samples.

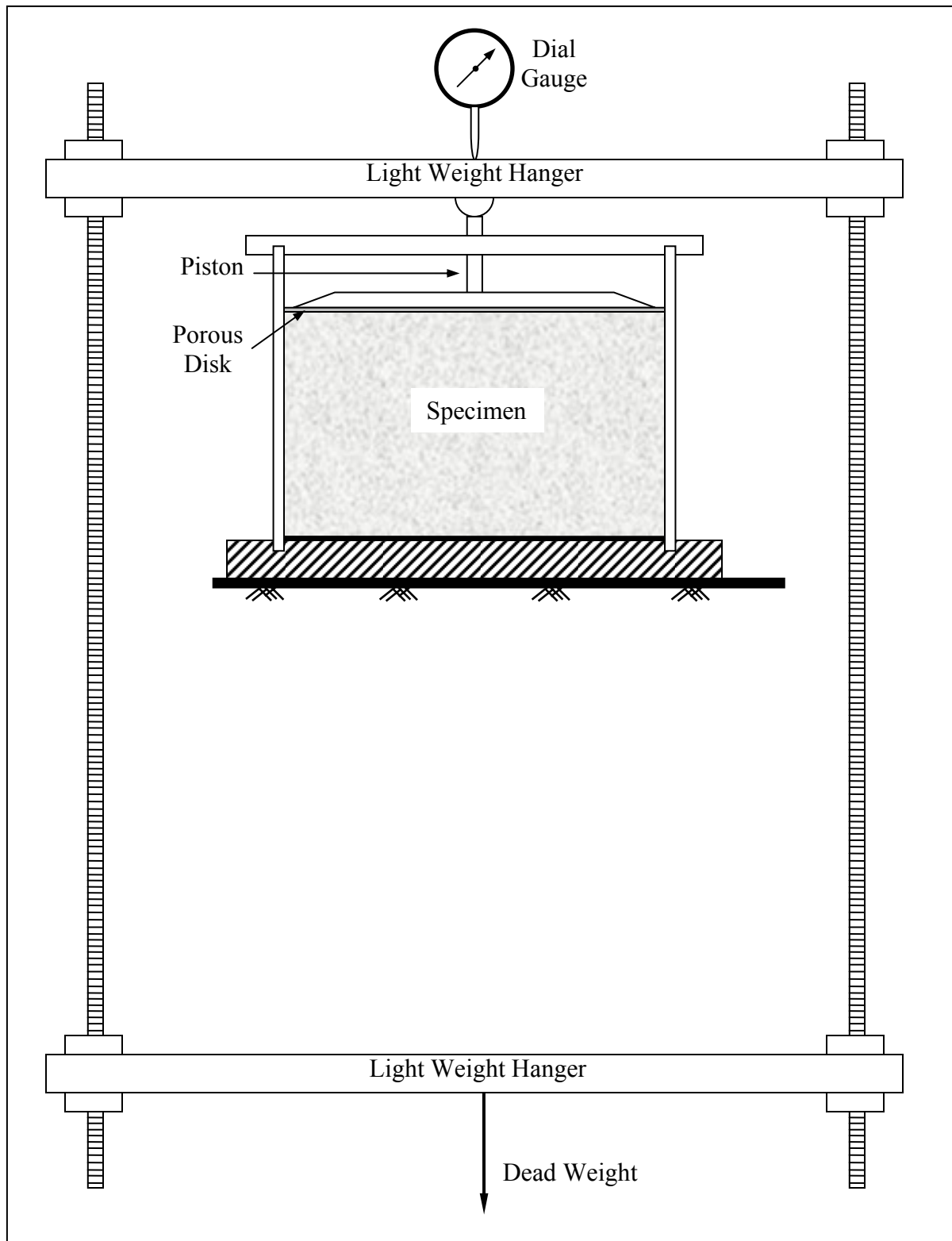


Figure 3.1: Schematic Diagram of the Consolidation Apparatus

Pore water collected during the tests was vacuum filtered through a 0.45 micron glass fiber filter. The filters were collected, dried, and extracted by automated soxhlet extraction following EPA SW-846 Method 3541. Filters were inserted into cellulose extraction thimbles and placed in the Soxtec HT 1043 extraction unit. Extraction cups were filled with 50mL of 50:50 hexane-acetone solution, and PTFE boiling chips. A Thermo Neslab RTE 7 water bath unit at 15°C was connected to the extraction unit. The extraction thimbles were lowered into the cups and boiled for one hour. The thimbles were then raised and rinsed for one hour. At the end of the rinse period, the condenser valves were closed, the extraction lever opened, and the fan turned on. After the solvent volume was significantly reduced (to approximately 10 mL) the extract was further reduced to one milliliter using nitrogen blowdown. Copper shot was used to remove sulfur, and Florisil cartridges were used to remove other interferences from all sediment and filter extracts using the procedures outlined in Chapter Two of this document. To determine the PCB content of the filtrate, each sample was extracted by continuous liquid-liquid extraction following a modified EPA SW-846 Method 3520C. Ten milliliters of hexane was added to 250mL amber glass bottles containing on average 50mL of pore water. The bottles were manually shaken for 5 minutes and allowed to sit until separate phases were distinguishable. The water and hexane phases were separated using a separatory funnel before the hexane extract was reduced to one milliliter using nitrogen blowdown. All extracts were analyzed by GC-ECD as described in Chapter Two of this document. Table 3.1 summarizes the EPA SW-846 method used for measuring the PCB content in each type of sample.

<b>Method #</b>	<b>Method Title</b>	<b>Sample Type</b>
3541	Automated Soxhlet Extraction	Sediment, Filters
3520C	Continuous Liquid-Liquid Extraction	Aqueous
3660B	Sulfur Cleanup	Sediment, Filters
3620B	Florisil Cleanup	Sediment, Filters
8082	PCBs by Gas Chromatography	Sediment, Filters, Aqueous

Table 3.1: EPA SW-846 Methods Used in Sample PCB Analysis

### 3.3 Results and Discussion

Determining the partitioning characteristics of PCBs between solution and a solid phase is often complicated because of the low aqueous solubility of PCBs and the large affinity of PCBs for organic material. In addition, complete separation of the two phases is difficult. A recently developed method of measuring PCB sorption involves the use of the plastic polyoxymethylene (POM) as an additional phase. PCBs were found to strongly and reproducibly sorb to the POM phase. In addition, POM film has a very smooth non-porous surface making it easy to separate from the other components of the system. Anything on the surface of the film can be wiped away without affecting the partitioning behavior, and the POM itself is resistant to organic solvents so PCBs can easily be extracted [33].

Using Jonker and Koelmans [33] polyoxymethylene – solid phase extraction (POM-SPE) approach, the PCB content in the aqueous solution, as well as the PCB content of the sorbent medium can be calculated from the POM PCB content. An initial

isotherm must be constructed for the system with an aqueous phase and POM alone. The PCB-POM partitioning coefficient ( $K_p$ ) obtained from this isotherm can be assumed to remain constant in a system where the additional sorbent phase is added, when surface sites are in excess, no interactions occur between the two phases and the aqueous concentration range is the same. Using the mass balance below, the sorbent water partitioning coefficient can be derived [33]:

$$K_s = \frac{1}{M_s} \left[ \frac{K_p Q_{tot}}{C_p} - M_p K_p - V_w \right] \quad (3.1)$$

Where  $K_s$  represents the sorbent – PCB partitioning coefficient in L/kg,  $M_s$  is the mass of sorbent (kg),  $K_p$  is the predetermined POM – PCB partitioning coefficient (L/kg),  $Q_{tot}$  is the total mass of PCB in the system in ( $\mu\text{g}$ ),  $C_p$  is the concentration of PCB sorbed to the POM ( $\mu\text{g/kg}$ ),  $M_p$  is the mass of POM (kg), and  $V_w$  is the volume of water (L). Equation 3.1 was calculated using the PCB mass balance in the system, and assumes linear partitioning over the entire concentration range. Jonker and Koelmans [33] found that for the majority of PCB congeners sorption was linear over the entire range of concentrations examined. However, for some PCBs sorption at very low concentrations exhibited non-linear behavior and only the linear range of concentrations was examined. Both PCB congeners used in this study exhibited linear partitioning over the concentration range studied.

Initial batch tests were conducted with a two-compartment system consisting of POM and solution spiked with a single PCB congener. The POM – PCB partitioning coefficients ( $K_p$ ) obtained in these experiments were assumed to be valid for the additional three phase experiments because; the aqueous concentration range examined

was the same, there was an excess of surface sites on both the POM and the sorbent medium, and there were no POM-sorbent interactions. Initial batch tests to determine  $K_p$  were conducted using a no-sorbent system. However, these results were inconclusive due to a limited recovery of PCBs from the POM during extraction. Instead,  $K_p$  values were calculated based on batch tests set up with POM, sand, and solution. The PCB concentration of all three phases was measured to perform a mass balance. The sand was found to be inert, able to sorb negligible amounts of PCB from solution. Log  $K_p$  values were determined to be 3.15 and 4.01 for PCB 8 and PCB 66 respectively. The PCB 66 value is similar to those reported by Jonker and Koelmans for tetra-chlorobiphenyls [33]. They did not report values for di-chlorobiphenyls, however, based upon trends in their data the PCB 8 value appears reasonable.

Similar experiments were conducted with organoclay or activated carbon in place of the sand, and isotherms were constructed to examine the interactions between the sorbents and PCBs in solution. Activated carbon proved to be better than the organoclay at removing PCBs from solution in both instances (See Figures 3.1 – 3.4). In the case of the lower molecular weight PCB 8, the activated carbon had an affinity nearly three times that of the organoclay.

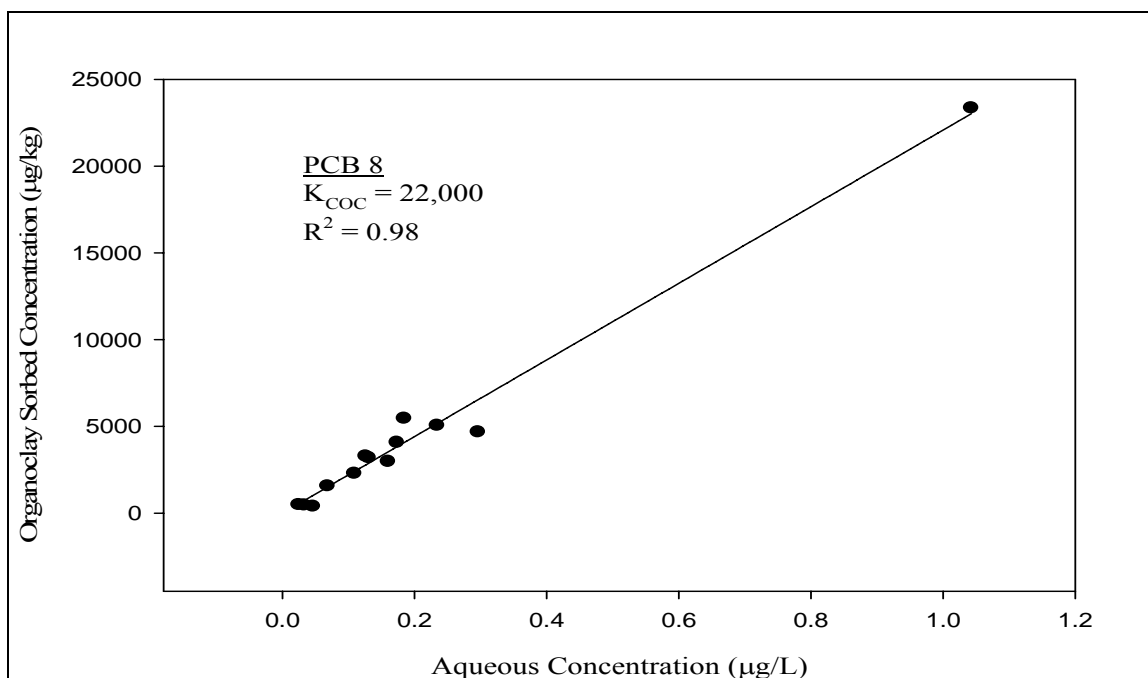


Figure 3.2: Organoclay – PCB 8 Partitioning Isotherm

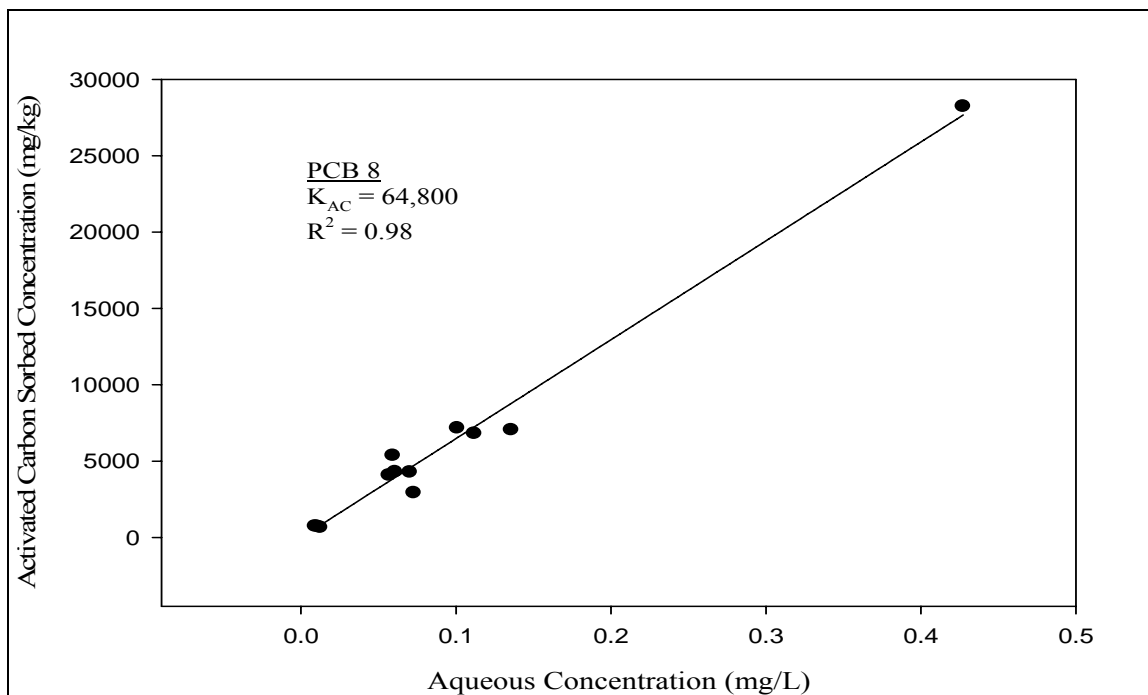


Figure 3.3: Activated Carbon – PCB 8 Isotherm

While activated carbon still had a greater affinity for the higher molecular weight PCB 66 than organoclay, there was less of a difference. Activated carbon had an affinity for PCB 66 that was only twice that of the organoclay albeit there is more scatter in the activated carbon isotherm than the other isotherm. Based on the limited data presented here, it would appear that as the level of chlorination increases the degree of difference between the two sorbents may be expected to decrease. Organoclay may be a better sorbent for the PCBs with greater than four chlorines, but examination of larger molecular weight PCBs is required before any definitive conclusions can be reached. In this case, PCB uptake also appears to be well correlated to the carbon content of the sorbents. Activated carbon is composed of 100 percent carbon; while the carbon content of the organoclay was estimated at 31 percent based a volatile solids analysis. The activated carbon contains approximately three times as much carbon as the organoclay, and its affinity for the lower molecular weight PCB 8 is nearly three times as great. With the high molecular weight PCB 66, where hydrophobic expulsion is more significant, the higher carbon content of the activated carbon leads to more sorption, but the difference is not as pronounced. These isotherms also only consider the ten day equilibrium condition. Further information is needed on such parameters as kinetics, capacity, and PCB release.

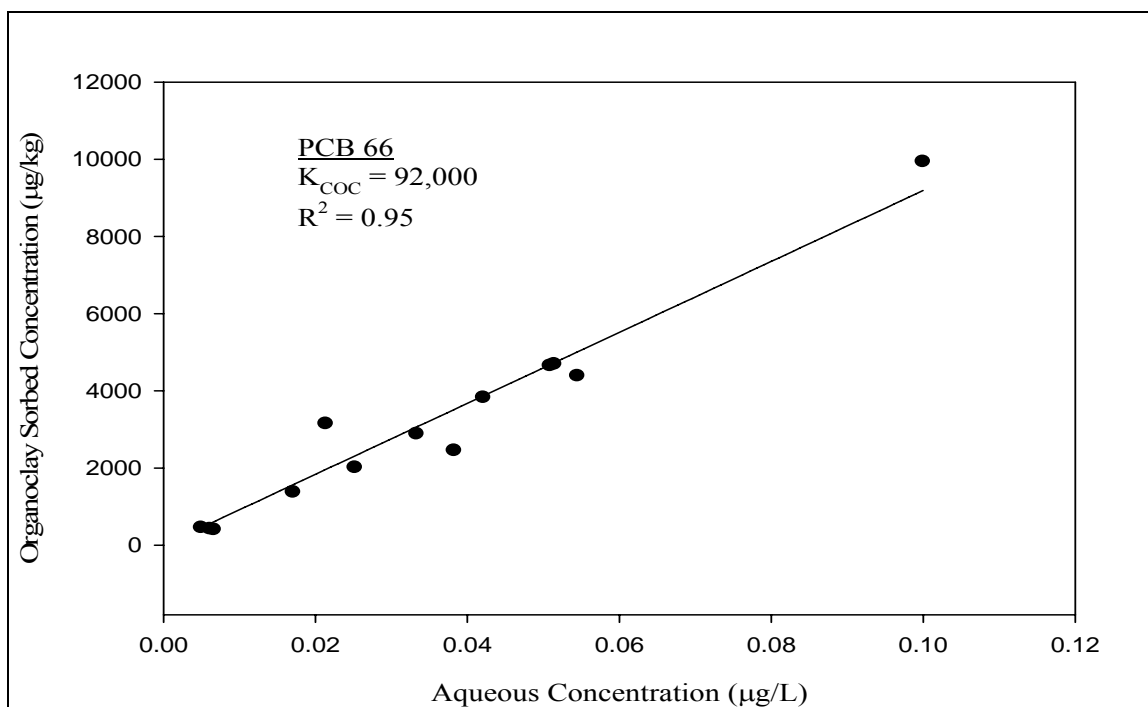


Figure 3.4: Organoclay – PCB 66 Partitioning Isotherm

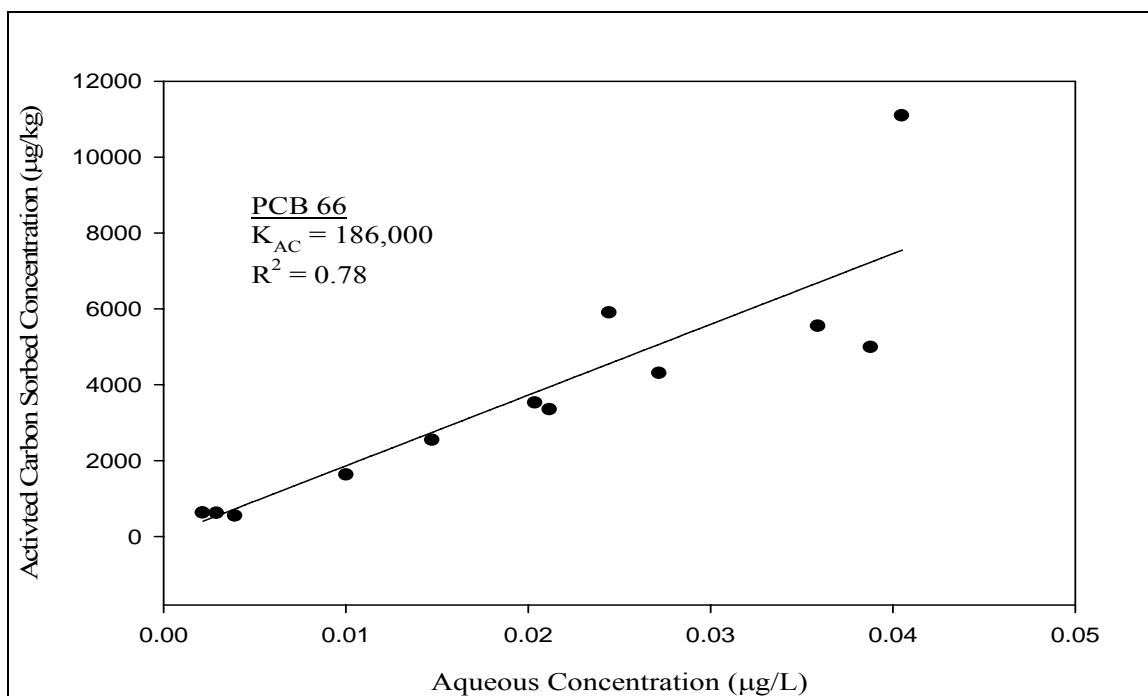


Figure 3.5: Activated Carbon – PCB 66 Partitioning Isotherm

Further evaluation of the sorbents compared to traditional sand capping was completed using consolidation tests. Consolidation tests were used to simulate rapid dewatering of the sediment. A single load was applied to the sediment for a twenty-four period forcing the pore water and small particles out of the sediment. Figure 3.6 provides a graphic representation of the consolidation process. As shown in the figure, aqueous PCBs and PCBs associated with suspended particles are removed during the dewatering process.

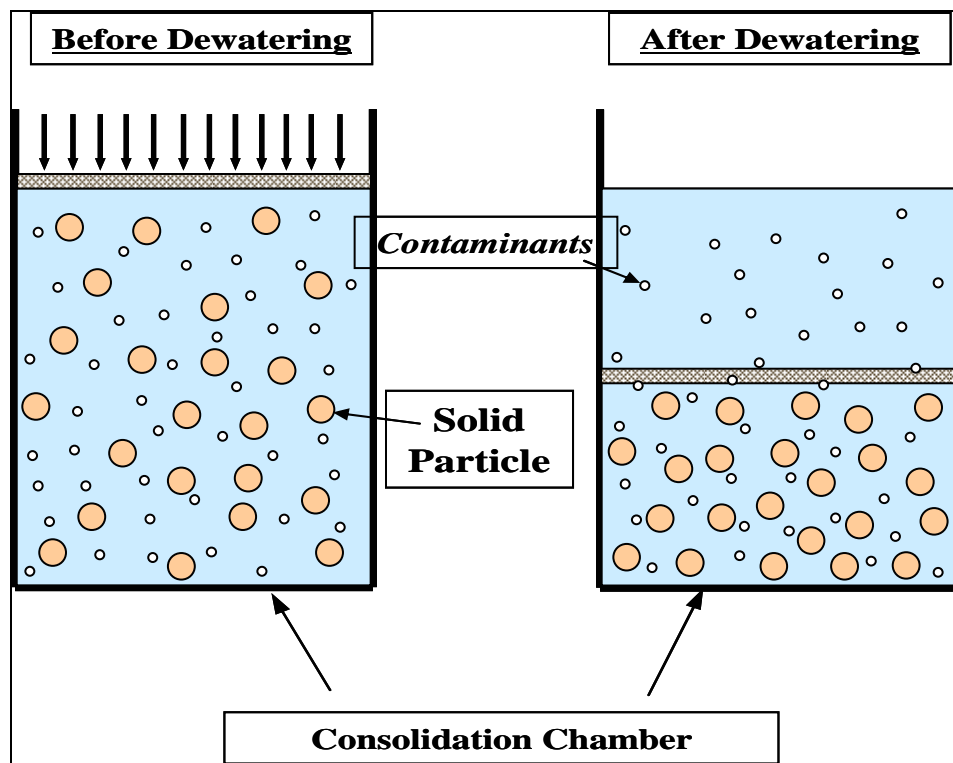


Figure 3.6: Graphic Representation of the Consolidation Process

Sediment from the south end of the Grand Calumet River was chosen for the consolidation test based on its high PCB content and relatively low sulfur content. Sediment was first consolidated without a cap to determine an initial value. Subsequent

tests employed fresh sediment samples overlain with the capping materials. The no-cap consolidation tests were conducted in triplicate, while all other consolidation tests were conducted in duplicate.

Initial sediment moisture content averaged 69 percent with a standard deviation of 16 percent based on 22 samples. After dewatering, the sediment moisture content was reduced to 43 percent on average with a 13 percent standard variation. The final moisture content of the samples appeared independent of the type of cap used; however, the variations between the samples were quite large. Variation in the rate of consolidation of each sample run was also evident (See Figure 3.7).

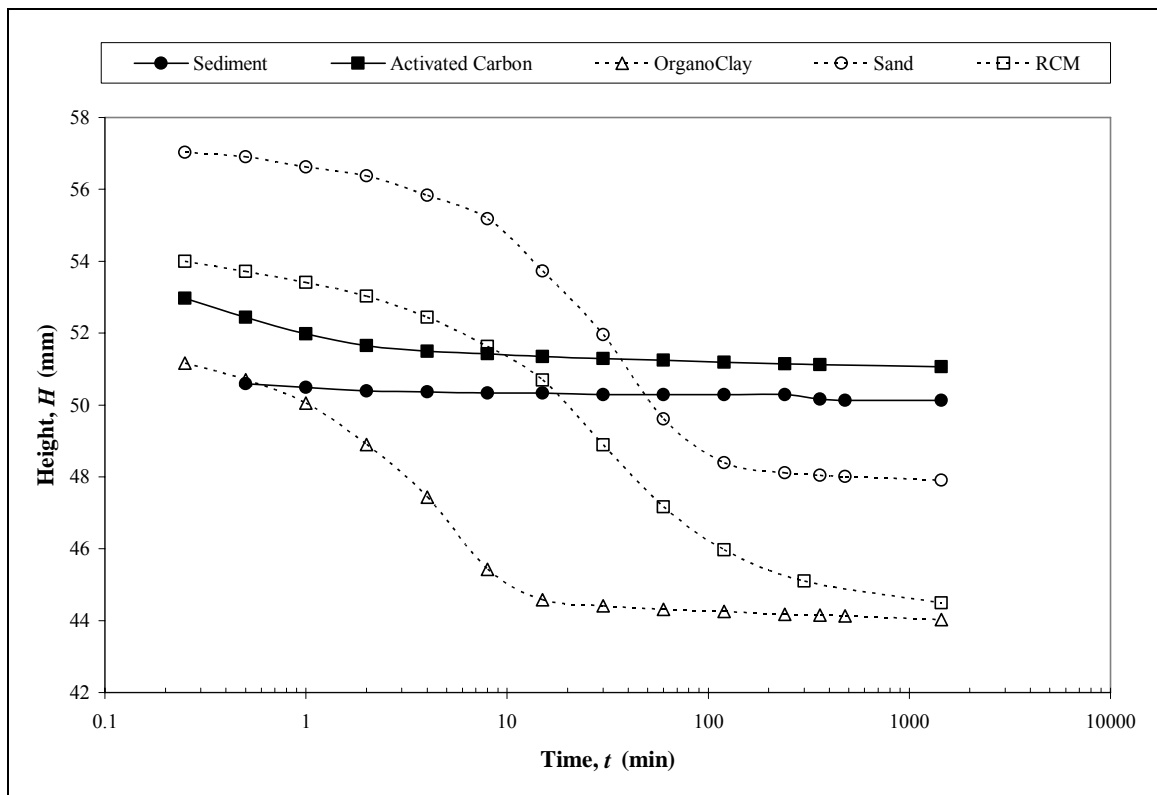


Figure 3.7: Comparison of Rate of Consolidation with Different Caps

Differences in the initial sediment height and water content are potentially responsible for some of the variation between samples. However, the different hydraulic conductivity values of the capping materials likely played a larger role. The no cap (sediment alone) and activated carbon samples appeared to experience minimal consolidation, due to side friction caused by particles around the edge of the porous disk.

Measurement of the PCB release from the sediment during consolidation considered two separate PCB fractions; those in the aqueous phase, and those associated with particles released during dewatering (particle phase). Pore water extracts were vacuum filtered through a 0.45 micron glass fiber filter to separate the particle phase from the aqueous phase. The PCB concentrations in both phases were measured independently. Figure 3.7 shows the pore water extracted from the sediment with no cap present on the left, and a vial of de-ionized water on the right. There is quite a large difference in turbidity between the two samples.

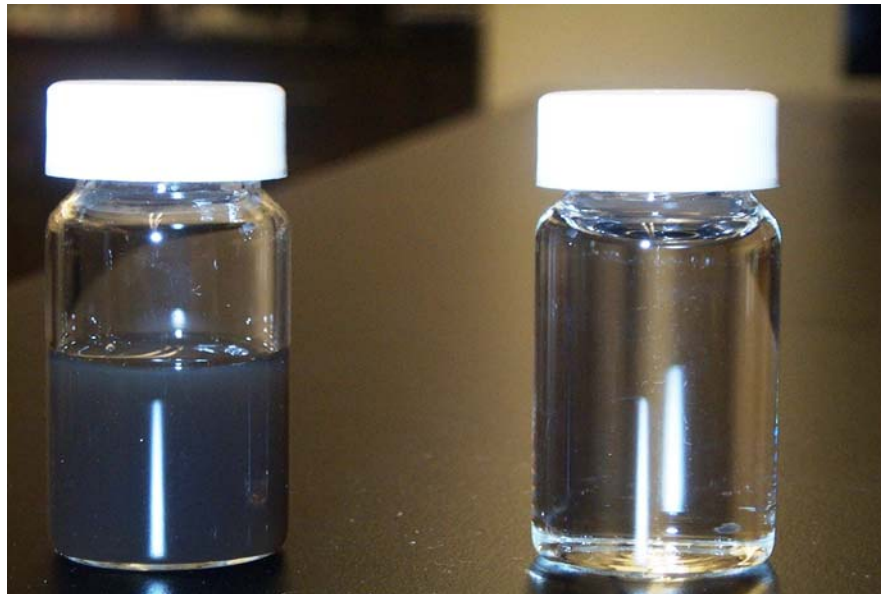


Figure 3.7: Water Released During Consolidation with No Cap

Initial tests on the sediment with no cap present revealed the highest levels of PCB release for nearly every congener. The consolidation tests with no cap were also the only samples with PCBs detected in the particle phase, presumably because the caps themselves act as a filter to prevent the release of larger particles. In all cases where a cap was present, visual inspection of the filters revealed minimal amounts of solid were retained. On the other hand, the filters from the no cap samples were coated with a black film (not shown). PCB concentrations in the particle phase of the pore water are presented in Table 3.2. The concentrations were calculated from the mass of PCB extracted from the particle phase divided by the total volume of pore water. ND is used in the table to note “Not Detected”, meaning that the concentrations were below 500 ng/L.

Capping Material	PCB 5/8	PCB 28/31	PCB 52	PCB 66/95	Total
None	3 ± 2	2 ± 1	3 ± 1	8 ± 7	15 ± 7
Activated Carbon	ND	ND	ND	ND	ND
Organoclay	ND	ND	ND	ND	ND
RCM	ND	ND	ND	ND	ND
Sand	ND	ND	ND	ND	ND

Table 3.2: PCB Concentrations in the Particle Phase of the Water (µg/L)

Total PCB pore water concentrations were calculated to present total PCB release during sediment dewatering. Total concentration refers to the sum of the mass of PCB in the aqueous phase and the particle phase divided by the pore water volume. These values are presented in Table 3.3.

<b>Capping Material</b>	<b>PCB 5/8</b>	<b>PCB 28/31</b>	<b>PCB 52</b>	<b>PCB 66/95</b>	<b>Total Release</b>	<b>Percent Reduction</b>
None	3 ± 2	2 ± 1	5 ± 1	8 ± 7	17	NA
Activated Carbon	1	0	1	1	3	80%
Organoclay	0	0	0	0.	1	90%
RCM	1	0	0	0	1	90%
Sand	3	1	2	1	7	60%

Table 3.3: Total PCB Water Concentrations after Consolidation (µg/L)

For the congeners measured, the use of a sand cap is able to reduce the amount of PCB by approximately 60 percent. This can be mostly attributed to the limited release of particle bound PCBs. Sand is a relatively inert material and it is not expected to remove significant amounts of PCBs from solution. However, the use of sorbent in an active cap can be expected to sorb PCBs from solution and prevent release of particle bound PCBs into solution. Use of an activated carbon or organoclay cap was able to reduce the release of each PCB congener by an order of magnitude. Organoclay proved to be the better of the two sorbents during rapid dewatering, with pore water PCB concentrations

less than half of the activated carbon values. Overall, the organoclay provided a 90 percent reduction in PCB concentrations compared to 80 percent for the activated carbon, although the variations in the measurements prevent the difference from being statistically significant. Organoclay and organoclay filled RCM caps of the same thickness were equally effective in reducing total PCB release but the PCB distribution was quite different. PCB 5/8 concentrations from the RCM experiments were nearly double those in the organoclay cap experiments, however, the RCM was much more effective at removing all of the other PCB congeners examined. These results indicate that retaining the sorbent within an RCM does not impact its ability to remove PCBs from solution.

### **3.4 Conclusions**

Based on the ten-day equilibrium batch experiments it appears that activated carbon has a greater affinity for PCBs than organoclay. This is especially true for less chlorinated congeners such as dichlorobiphenyls. However, this difference becomes less apparent as the molecular weight of the PCB increases. With the limited data available it is impossible to reach a definite conclusion. Further testing is needed to determine if organoclay would be a better sorbent for more chlorinated PCBs (Pentachlorobiphenyls and above).

Both sorbents proved to be more effective than no treatment or traditional sand capping during rapid dewatering. For the group of congeners studied, organoclay was more effective than activated carbon at reducing the amount of PCB released from solution. This type of situation, where contact time was limited, is likely to be more representative of conditions encountered during actual use. However, more data is

needed on the capacity for PCB sorption and release kinetics before any further conclusions can be reached.

## CHAPTER FOUR

### CONCLUSIONS AND FUTURE RECOMMENDATIONS

Sediment samples from three locations were characterized to better understand the effect of physical and chemical characteristics on the distribution of PCBs. Sediment classification, mineralogy, grain size, specific gravity, and pore water composition were evaluated. Carbon and nitrogen content and PCB analysis were then conducted on sub-fractions of the sediment.

It appears that carbon content and level of contamination play a critical role in determining the distribution of PCBs throughout the sediment. Sediments with ten to fifteen percent carbon, and low levels of PCBs, similar to the Ashtabula River and Fox River SA – 09, tend to concentrate PCBs in the large less dense fraction of the sediment, consistent with the findings of Ghosh et al. [16, 20].

On the other hand, for sediments similar to the Grand Calumet River samples where the carbon content is high throughout the sediment and PCB contamination is more extensive there is no correlation between sediment fraction and PCB content. While the large less dense fraction of the Grand Calumet sediments still contained more carbon than the other fractions, the difference was not as dramatic as in the other sediments. Additionally, the PCB content of the Grand Calumet samples was much higher than the other two sites examined. Based on these two pieces of information, it can be concluded that this sediment has a more even distribution of PCB binding sites than sediment from the other locations. Specific gravity was also found to be correlated to carbon content with the higher the carbon content, the lower the specific gravity.

The second part of this study examined two sorbents for the control of PCB release from sediments. Batch tests were conducted to examine the uptake of PCBs from solution at equilibrium. Bench-scale consolidation tests were also conducted to simulate rapid dewatering. These experiments allow the comparison of sorbents to a no treatment scenario and traditional sand capping, as well as the fact that they are applicable to both an in-situ capping approach and an ex-situ dredging and dewatering approach.

Equilibrium batch tests indicated that activated carbon was the more effective of the sorbents at removing PCBs from solution, similar to those conducted by Jonker and Koelmans [33]. Isotherms were constructed to examine the sorption behavior at different PCB concentrations. PCB 8 was sorbed three times as strongly to the activated carbon, while PCB 66 was sorbed twice as strongly to the activated carbon. Partitioning coefficients were much higher with the tetrachlorobiphenyl PCB 66, than with dichlorobiphenyl PCB 8, similar to what is reported in the literature [33]. While activated carbon has a greater affinity for the PCBs examined, the difference between the two sorbents decreased with the increase in chlorination. If this trend continues, organoclay may be more effective at removing highly chlorinated PCBs from solution than the activated carbon.

The consolidation experiments have more applicability to natural systems than the batch tests, due to the limited contact time PCBs have with the sorbent in natural systems, as well as the fact that they were conducted with highly contaminated natural sediments containing other contaminants such as PAHs that have the potential to compete with the PCBs for binding sites. These consolidation experiments provided a great deal of information on the release of PCBs during rapid dewatering.

A large fraction of the PCBs released are associated with suspended particles. A traditional sand cap which exhibits no interactions with the PCBs was able to reduce release by 59 percent simply by acting as a filter to remove these suspended particles from solution. An organoclay-filled RCM was also found to control PCB release just as effectively as a loose organoclay cap. Both an organoclay cap and an organoclay filled RCM cap were found to reduce the PCB release by 90 percent. In contrast to the equilibrium batch tests, the organoclay performed better than the activated carbon (80 percent reduction in release) in the consolidation tests. This suggests the organoclay is more efficient than activated carbon in removing contaminants from pore water expelled during rapid dewatering.

The results of the sediment characterization study show that there is a correlation between sediment characteristics and PCB distribution in some instances. However, these results are not consistent across all of the sites examined. Future work focusing on different sites would be able to help expand on the results of this work, and test the conclusions reached across a wider variety of sediment samples. It would also be useful to spike some of the less contaminated sediments to examine the concentration dependence of the PCB distribution at a single site. Spiking sediments with low PCB concentrations like the Ashtabula River would also allow comparison to the Grand Calumet River sediment and other sites without a concentration effect.

Batch test data suggests that the organoclay may be better able to remove highly chlorinated PCBs from solution than the activated carbon. Examination of a larger number of PCB congeners is needed to reach a definite conclusion. It would be useful to develop trends across the entire range of PCB homolog groups. Additional study is also

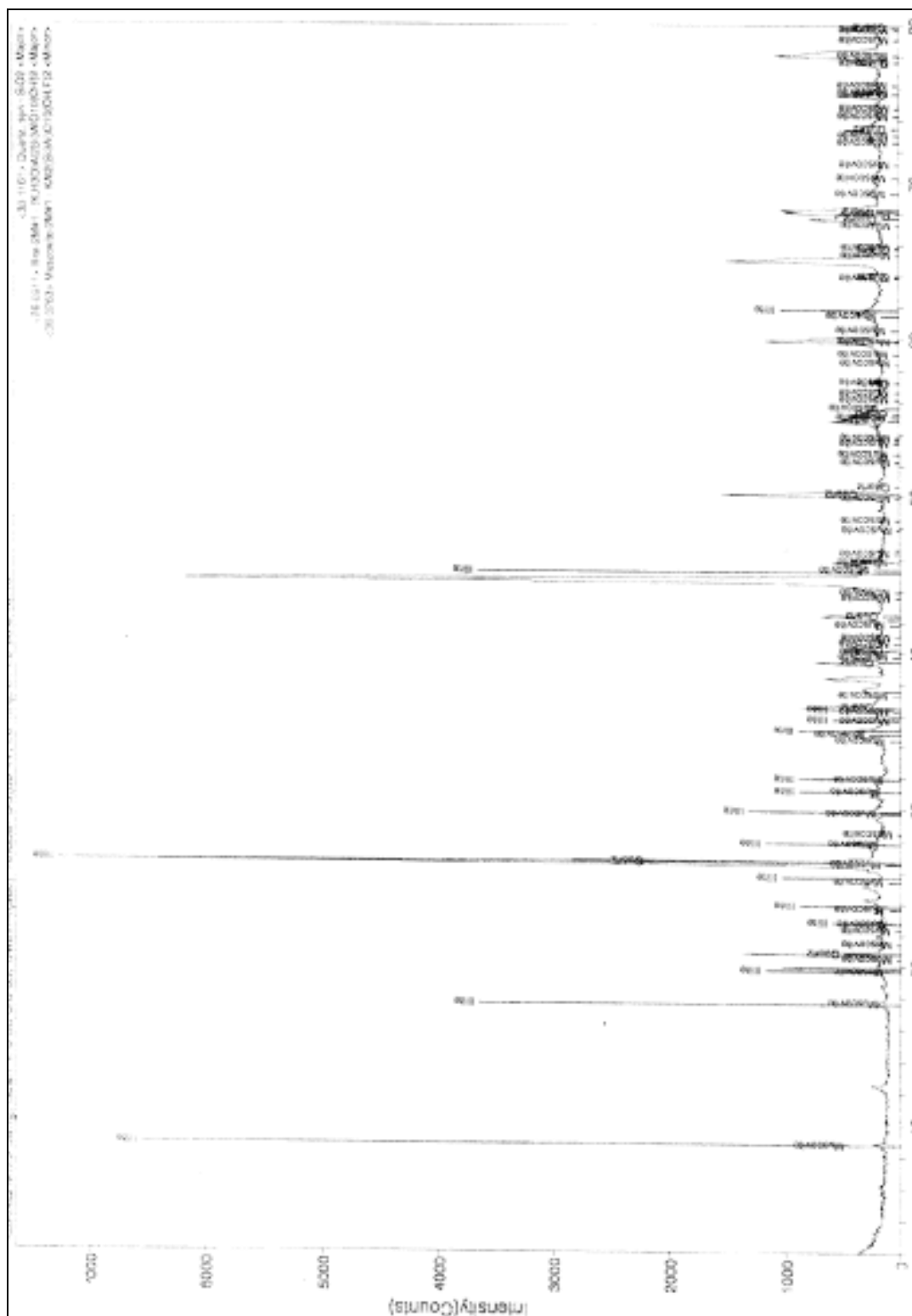
needed into the PCB sorption capacity and the kinetics of uptake and release for each of these sorbents.

Consolidation tests provide opposite conclusions to those reached in the batch test study. Examination of the consolidation of larger sediment volumes under natural conditions would provide a better understanding of the effectiveness of these capping materials in natural systems.

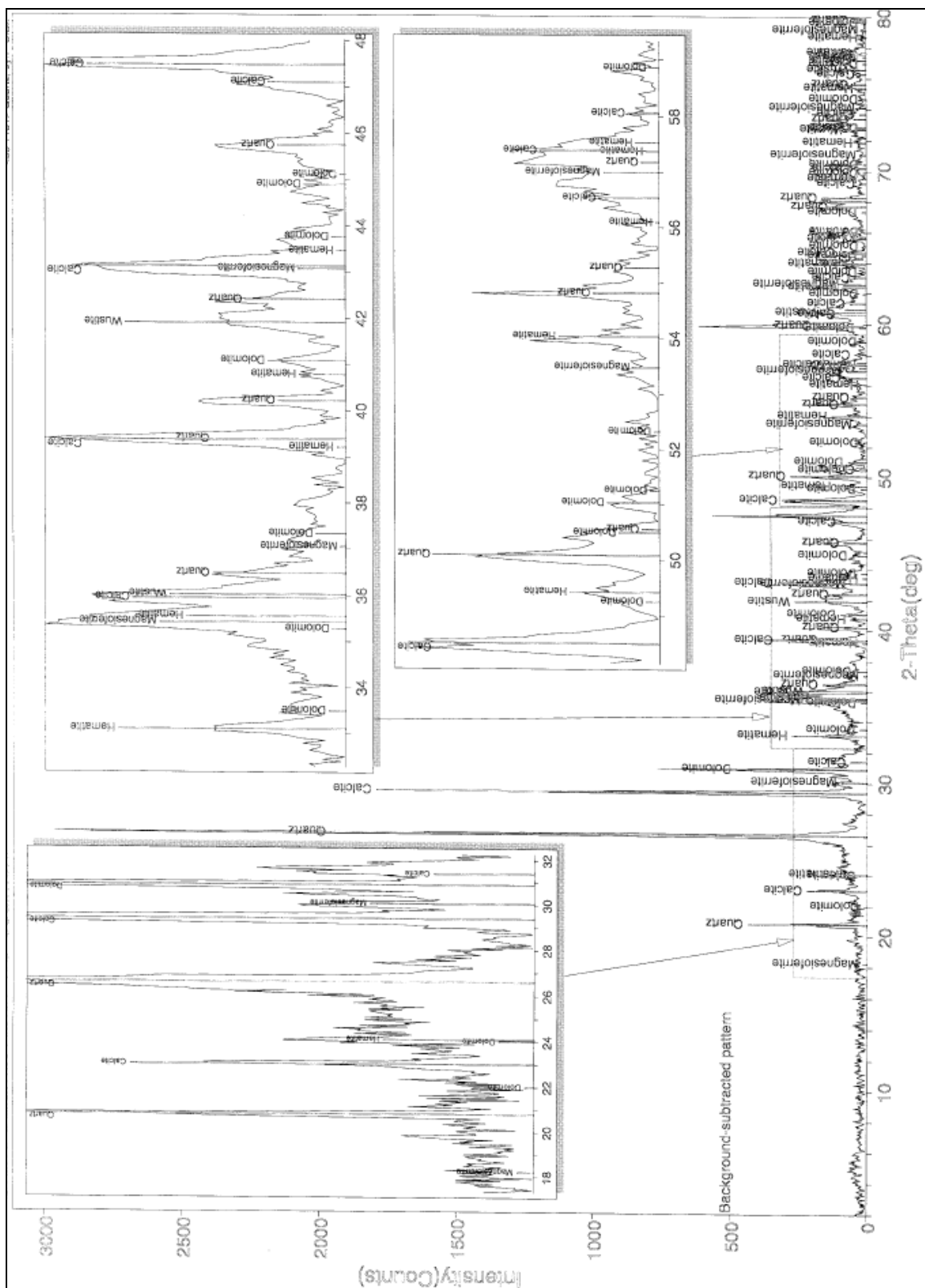
These results provide some insight into the distribution of PCBs within sediments, and also to the applicability of sorbents for use in the remediation of contaminated sediments. However, the heterogeneity between the characteristics of different sediments is overwhelming. Characteristics are so different from site to site and even with samples from the site that reaching any definite conclusions is impossible at this time. Characterization of a larger number of sites would greatly enhance the ability to reach conclusions, and aid in the process of deciding on a management technique for a given site.

**APPENDIX A**  
**MINEROLOGICAL ANALYSIS**

# Ashtabula River Sediment Mineralogical Analysis



# Grand Calumet River North Mineralogical Analysis



# Grand Calumet River South Mineralogical Analysis

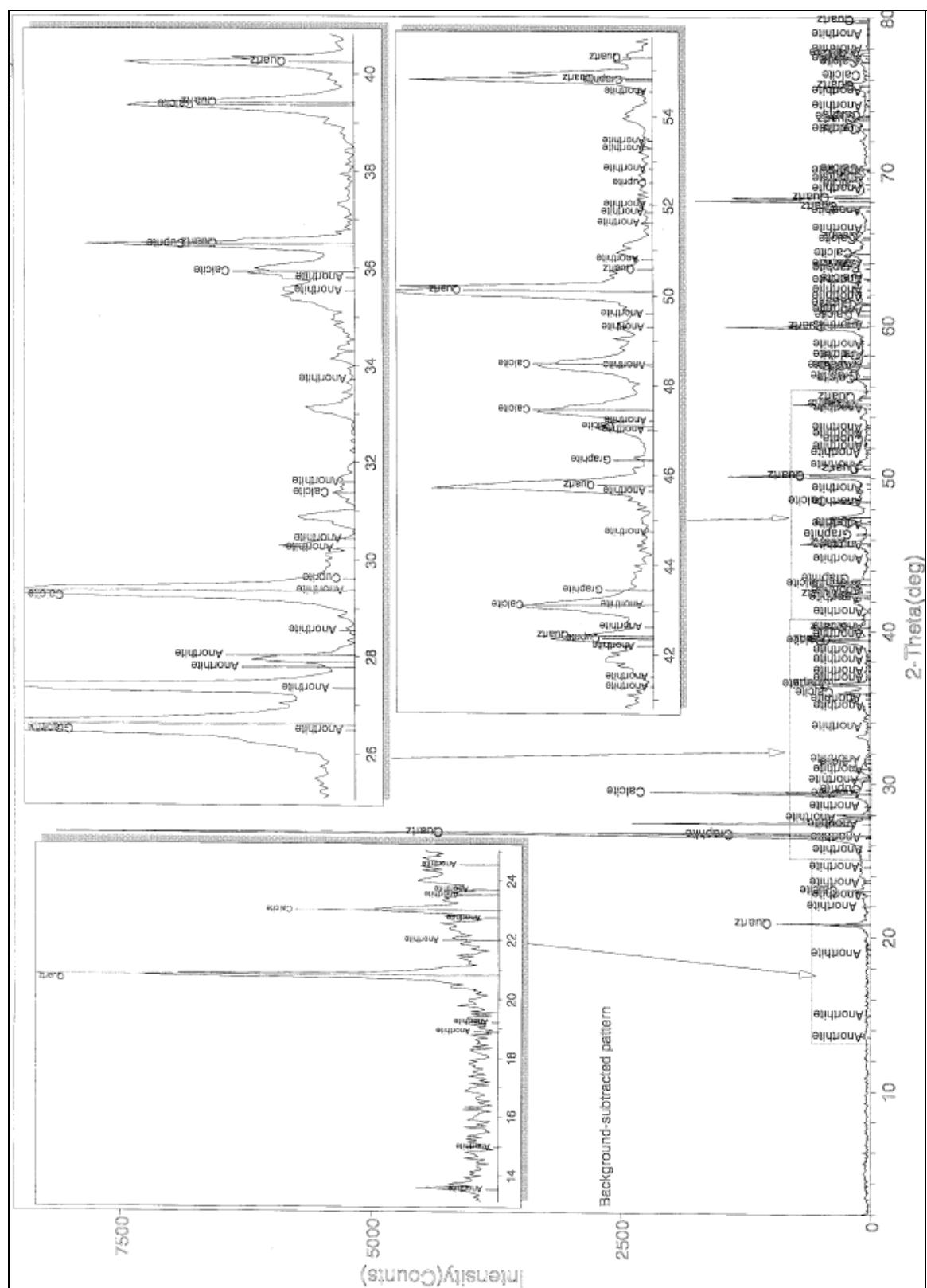
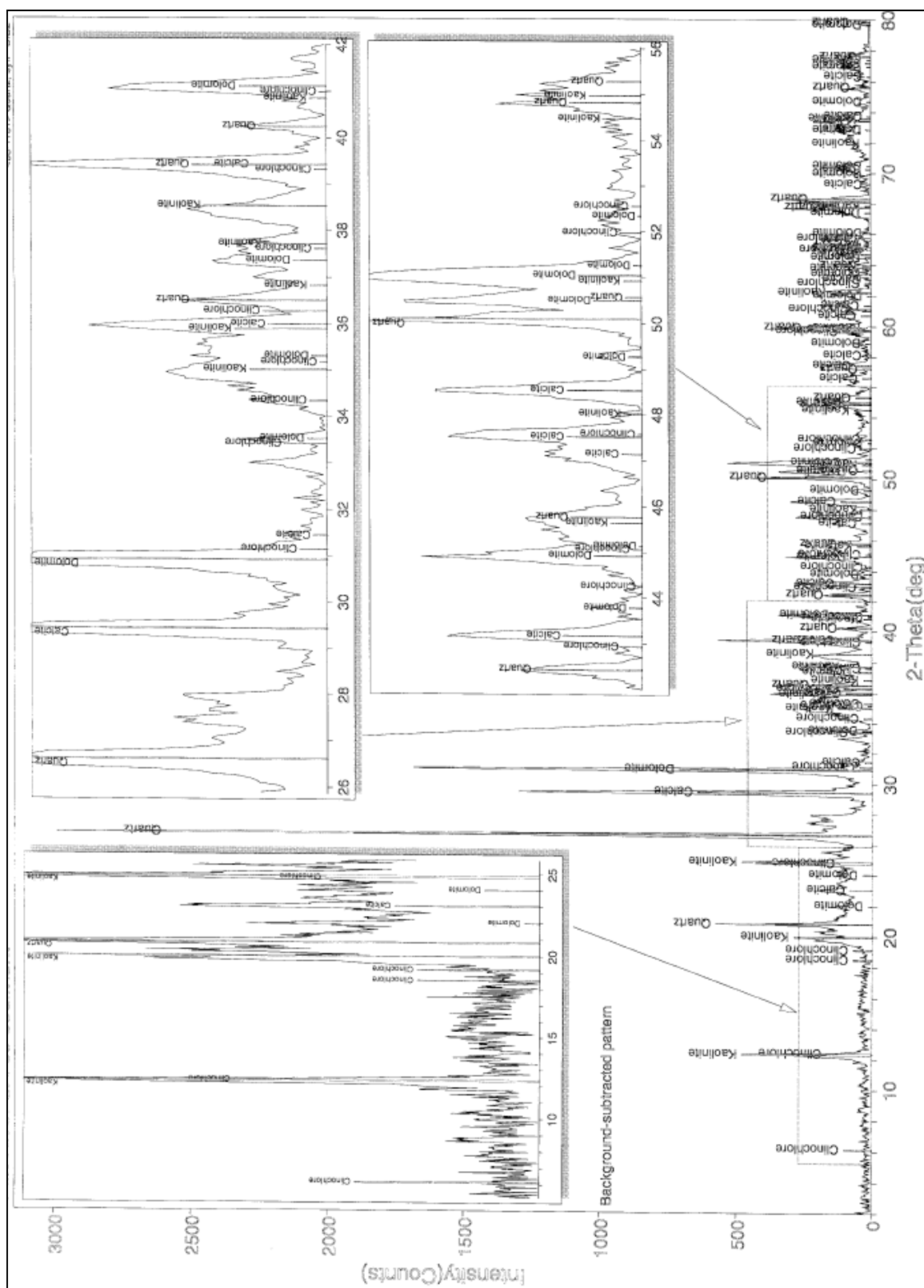


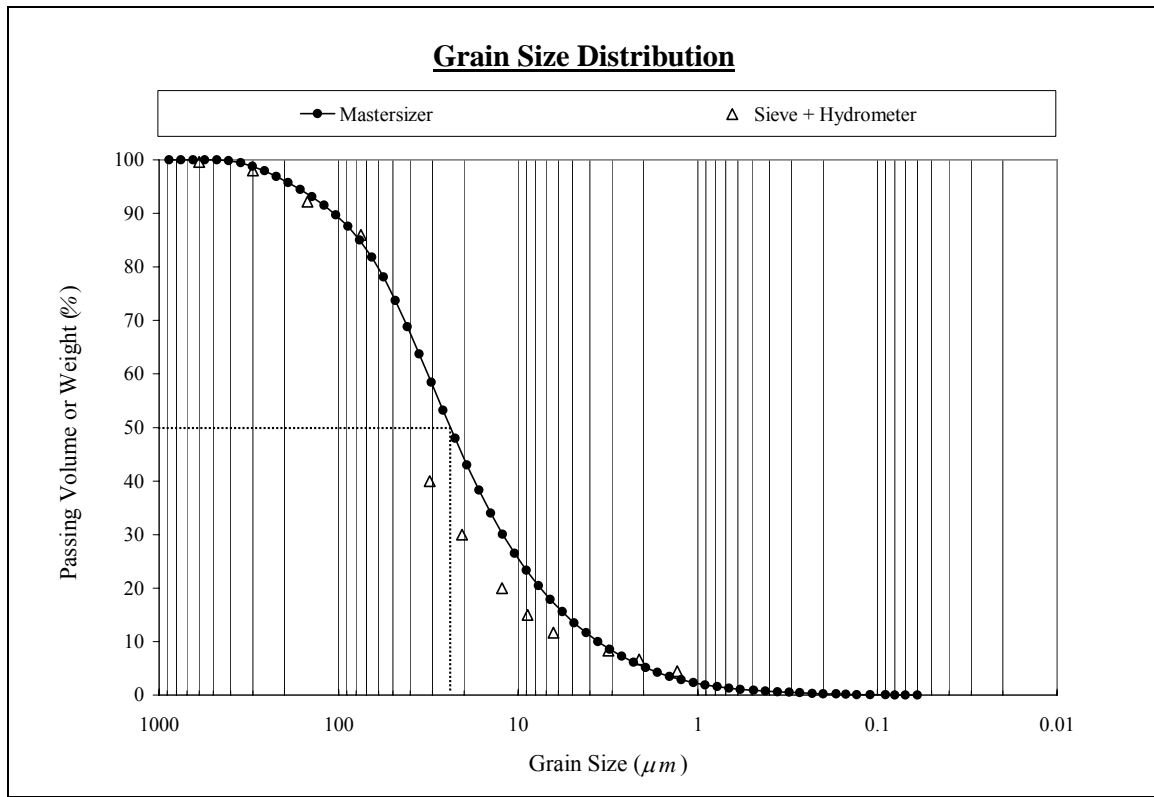
Figure 1 displays X-ray diffraction (XRD) patterns. The main plot shows Intensity (Counts) on the y-axis (ranging from 0 to 4500) versus 2-Theta (deg) on the x-axis (ranging from 10 to 60). The top curve represents the background-subtracted pattern, and the bottom curve represents the reference pattern. The background-subtracted pattern shows peaks for Kaolinite, Illite, Dolomite, Quartz, and Calcite. The reference pattern shows peaks for Kaolinite, Illite, Dolomite, Quartz, and Calcite. An inset shows a zoomed-in view of the 26-42 degree range.

# Fox River SA – 09 Mineralogical Analysis

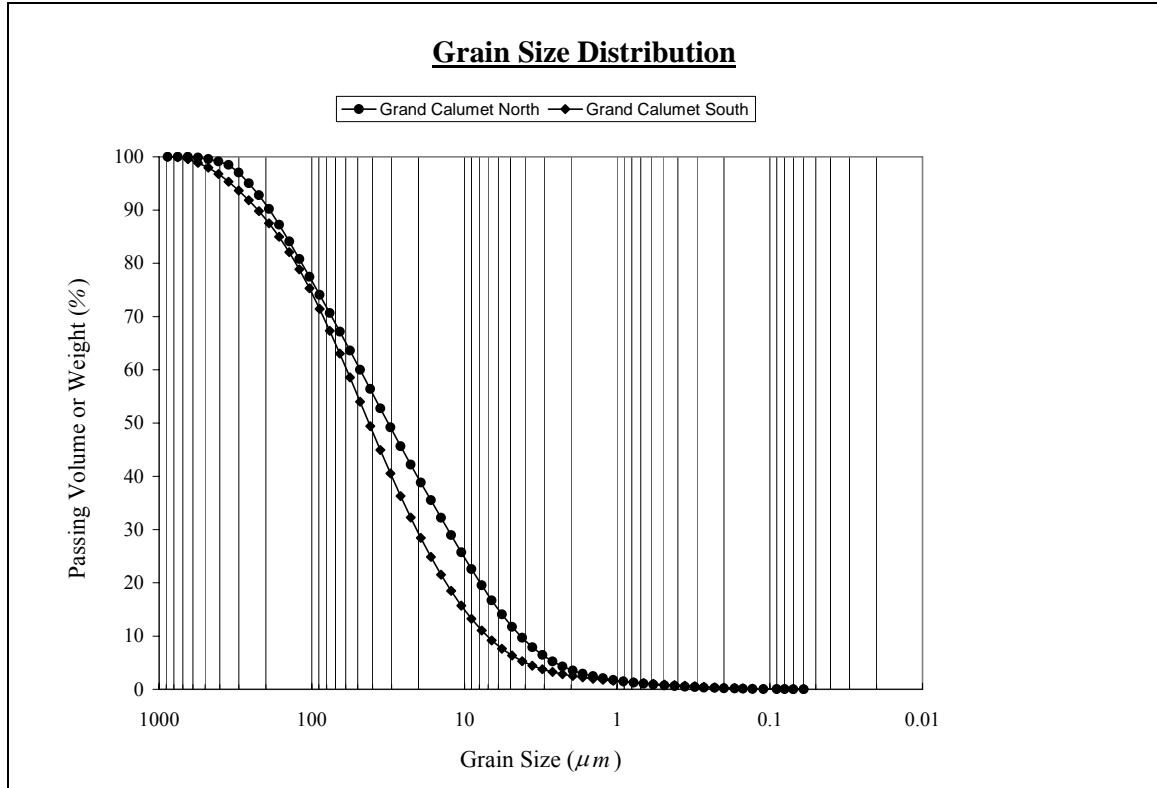


**APPENDIX B**  
**GRAIN SIZE DISTRIBUTIONS**

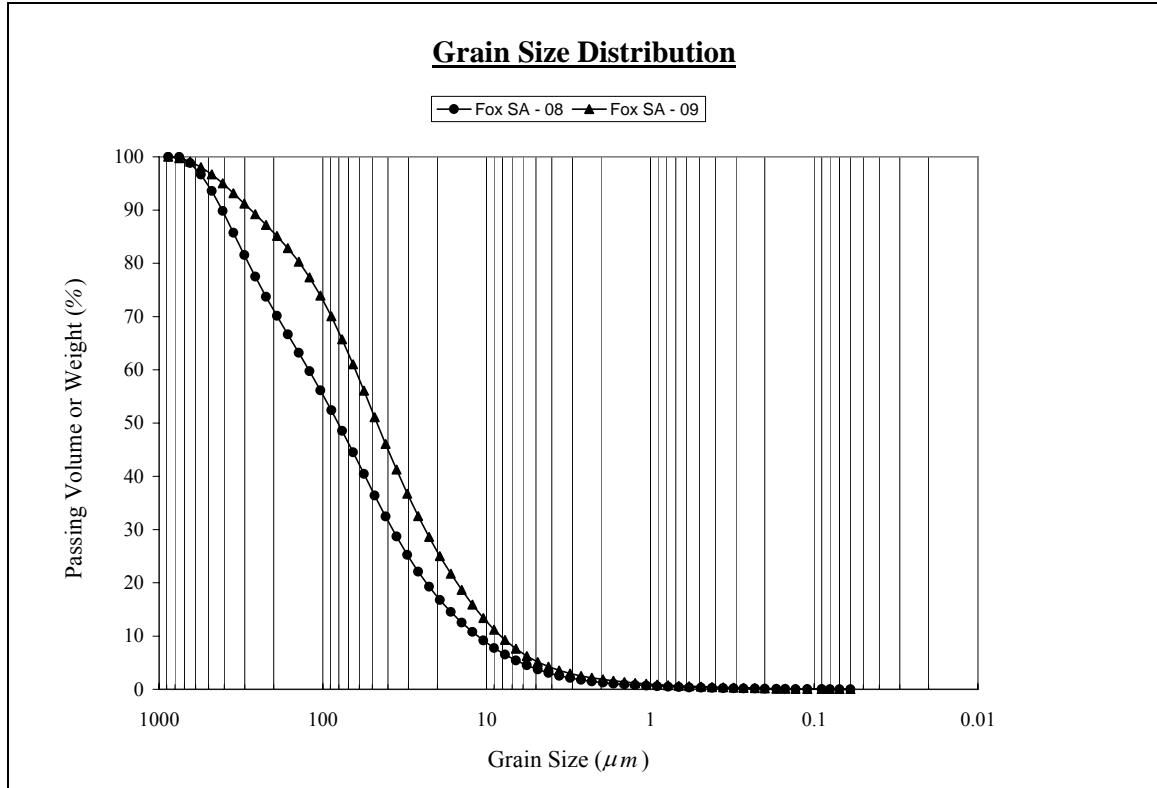
## Ashtabula River Grain Size Distribution



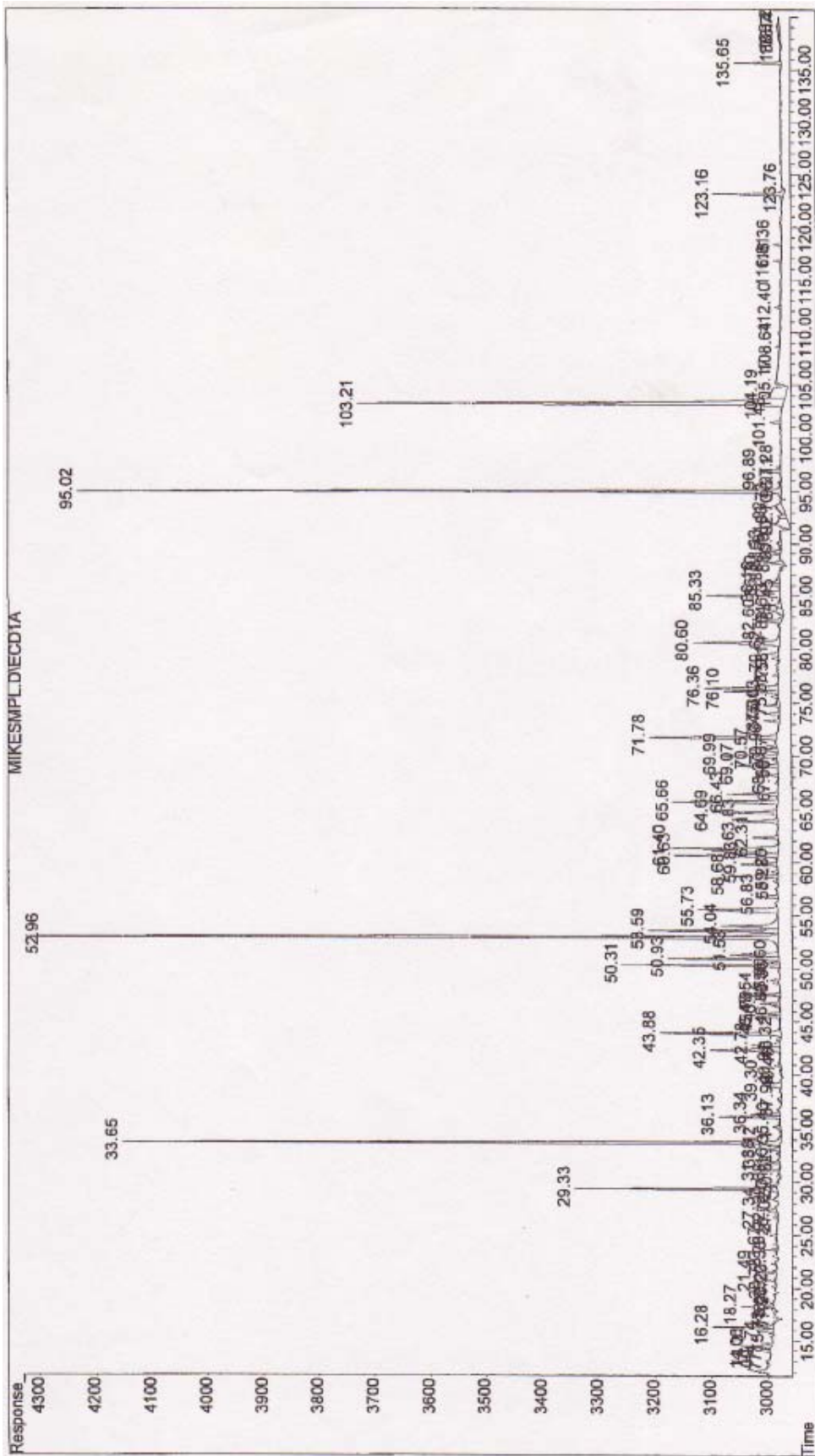
## Grand Calumet River Grain Size Distribution



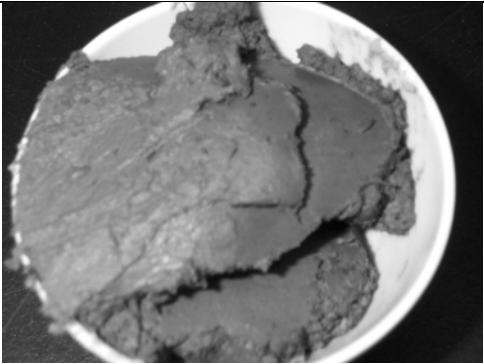

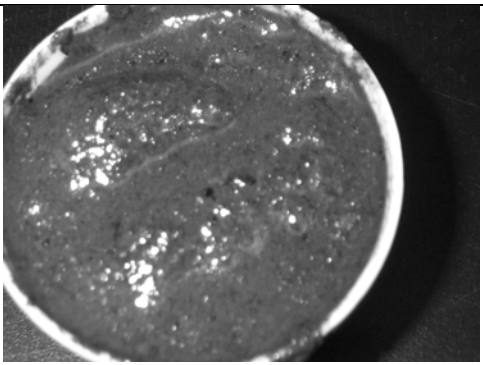

## Fox River Grain Size Distribution



**APPENDIX C**  
**ASHTABULA RIVER CHROMATOGRAM**



**APPENDIX D**  
**SEDIMENT PICTURES**

Ashtabula River Sediment	Grand Calumet River Sediment
	
Fox River SA – 08 Sediment	Fox River SA – 09 Sediment
	

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