A Thesis

entitled

Investigating the Performance of Active Materials Amended to Clay Minerals for

Sequestering Sediment Contaminants

By

Clint Andrew Messner

Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Master of Science Degree in Civil Engineering

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An Abstract of

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Contaminated sediment management represents one of the most challenging contaminated site issues facing freshwater and estuarine coastal environments due to the large volumes (several million cubic yards in the US annually), the wide range in contaminants and their concentrations, and the need to minimize exposure pathways. Removal technologies, when applied alone, can be limited by high costs, minimal access to some sites, possible ecological risks posed to aquatic species, and increasingly limited disposal options. In most cases, sediment remediation and restoration is best accomplished using a combination of both removal and in place technologies. This research focuses on sediment capping, an in place technology.

Traditionally caps have been mainly composed of granular materials, such as sand, because they are readily available and distinguishable from contaminated sediments. More recently, active capping materials have been selected since sediment contaminants may vary widely and may include heavy metals, persistent organic compounds (e.g., pesticides, PCBs), and nutrients. It is difficult to deliver active materials in sand since the components tend to separate. The main objective of this

ongoing research is to do a comparative study of the efficacy of active capping materials (e.g., activated carbon and chemisorptive media) when delivered alone or in combination using clay minerals as a binder.

Active capping materials are being synthesized by amending clay minerals (e.g. sodium bentonite and organoclay) with selected active materials (approx 5% by weight) including activated carbon and chemisorptive media. Shake tests were performed at 20°C in the dark for 7 days on a shaker table on sediments contaminated with heavy metals. Approximately 2mg/L of Hg, As, Se, and Pb were spiked into freshwater (laboratory grade water with 0.1%HNO3) and salt water (Instant Ocean® + laboratory grade water + 0.1%HNO3). Treatment efficacy was determined by calculating the sorption affinity (percent removal) and distribution coefficient (K_d) values of the various materials selected for testing alone and in combination with clay minerals. The chemisorptive media performed the best at removing all metals (~100%) except Pb (<30%) and performed almost as well when combined with sodium bentonite. The organoclay alone and in combination with powder activated carbon (PAC) was most effective at sequestering Pb (~40%). Similar experiments were repeated for each amendment to determine their ability to sequester the following polycyclic aromatic hydrocarbons (PAHs): phenanthrene and pyrene (~100 µg/L). Shake tests were performed at 20°C in the dark for 48 hours and the solution was then extracted with Methylene Chloride after centrifugation. PAC performed the best in both the fresh water and salt water environments. PAC had adsorbed a greater amount of phenanthrene and pyrene in the salt water environment.

It is imperative that sediment remediation approaches be adaptable and proficient at addressing a wide variety of sediment contaminants. This research will support the development of an active capping material which will target the sequestration or destruction of specific sediment contaminants including heavy metals, nutrients, and pesticides allowing broader application of the product.

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Chapter One

1   Literature Review

Contaminated sediment management represents one of the most challenging site issues facing freshwater and estuarine coastal environments due to the large volumes (several million cubic yards in the US annually), the wide range in contaminants and their concentrations, and the need to minimize exposure pathways of the contaminants. The EPA's Great Lakes program has identified polluted sediments as the largest major source of contaminants to the Great Lakes food chain. Significant progress over the past 15 years in sediment remediation has substantially reduced the discharge of toxic and persistent chemicals to the Great Lakes (See Figure 1-1 below).
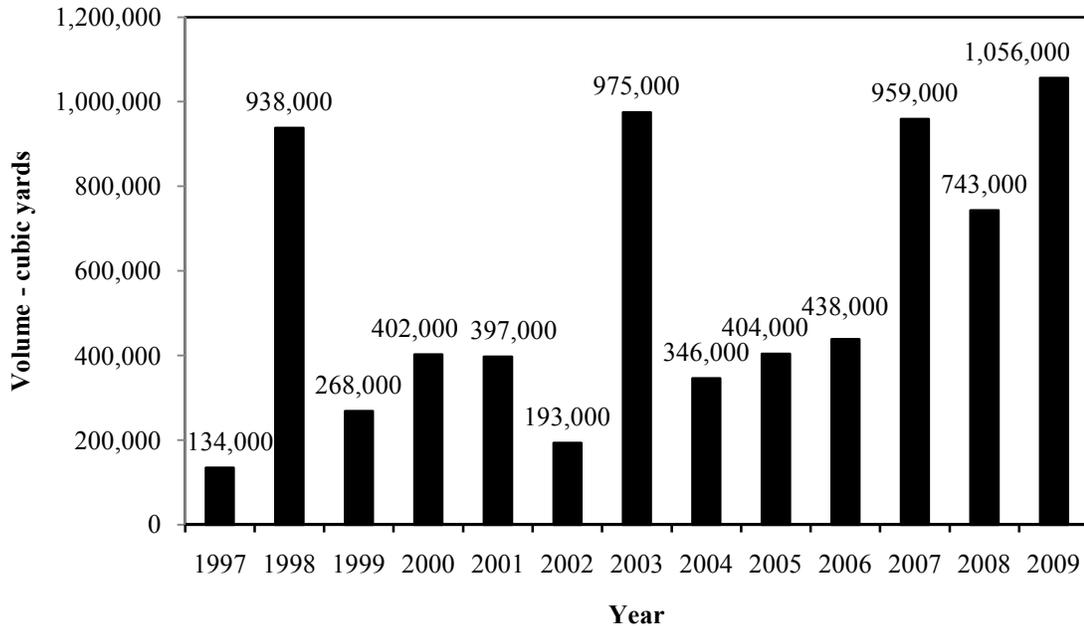
Figure 1-1: Annual Volume of Sediment Remediation in the U.S. Great Lakes Basin Since 1997 Courtesy of the Great Lakes Sediment Remediation Project Summary Support Quality Assurance Project Plan (GLNPO, June 2008)

However, high concentrations of contaminants in the bottom sediments of rivers and harbors have continued to pose a problem and have raised considerable concern about potential risks to aquatic organisms, wildlife, and humans. These contaminants come from a variety of sources, which are characterized by their degree of localization (point source or non-point source), their loading history (pulse source loading or continuous source loading), and the various contaminants emanating from them (Domenico & Schwartz, 1998). These sources are broken down into various types of categories according to the United States Congress Office of Technology Assessment 1984 and are as follows:

- Category I – Sources designed to discharge substances

- Category II – Sources designed to store, treat, and/or dispose of substances; discharge through unplanned release

- Category III – Source designed to retain substances during transport or transmission

- Category IV – Sources discharging substances as a consequence of other planned activities

- Category V – Sources providing conduit or inducing discharge through altered flow patterns

- Category VI – Naturally occurring sources whose discharge is created and/or exacerbated by human activity.

Examples of these sources include but are not limited to: combined sewer overflows (CSOs), storm drains, leaking underground storage tanks, leachate from a sanitary landfill, runoff from farming practices, or spills from industrial activities. Determining the loading history of these contaminants will have a significant impact on how a contaminant is treated. The loading history describes how the concentration of a contaminant or its rate of production varies as a function of time at the source (Domenico & Schwartz, 1998). Two main types of loading histories occur: pulse source loading and continuous source loading. Pulse source loadings include spills and the contaminants are produced at a fixed concentration for a relatively short period of time. Continuous source loadings occur when small quantities of contaminants are leached from a volumetrically large source over a period of time. Another type of continuous source can be from decades of light non-aqueous phase liquids (LNAPLs) (i.e. gasoline – benzene, toluene,

ethylbenzene, xylenes) or dense non-aqueous phase liquids (DNAPLs) (i.e. chlorinated hydrocarbons, TCE, chlorobenzene) dissolving at a slow rate.

A variety of contaminants can result from many different industrial, agricultural, and domestic activities. A majority of these contaminants occur as compounds; however, a list of priority pollutants is generally analyzed. The U.S. Environmental Protection Agency's list of priority pollutants contained 129 pollutants until 1981 when 3 pollutants were removed after determining their chemical properties did not justify their inclusion (US EPA, 2011). These contaminants are broken down into 6 major groups: radionuclides, trace elements, nutrients, other inorganic species, organic contaminants, and microbial contaminants. Contaminant characterization and biotoxicity analysis of sediments collected from more than 21,000 sampling locations in river reaches of 1,372 targeted watersheds across the U.S. indicate concentrations of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), pesticides, and/or heavy metals at levels which pose probable or potential risks to fish, wildlife, and humans (US EPA, 1997; US EPA, 1998).

Remediation of contaminated sediments is difficult if a site has more than one contaminant due to the chemical and physical properties and fate and transport mechanism differences between heavy metals and organic contaminants. Several options are available for contaminated sediment management including in place chemical or biological remediation (monitored natural recovery), contaminated sediment removal (dredging), and sediment stabilization via capping. Monitored natural recovery (MNR) techniques are viable where there is stable sediment and the short term risks of contamination in the water column are acceptable. However, MNR techniques are often

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rather expensive and could be an insufficient management technique alone due to insufficient sediment deposition or contaminant biodegradation (Murphy, Marquette, Reible, & Lowry, 2006). Dredging technologies, when applied alone, are often a viable option. However, dredging can be limited by high costs, minimal access to sites (i.e. landfills, confined disposal facilities, dumping sites), possible ecological risks posed to aquatic species by leaving residual contamination behind, and increasingly limited disposal options. For sites containing large volumes of sediment, in-situ capping (ISC) is often the most feasible as it manages contaminated sediment on-site without creating additional exposure pathways.

ISC is defined as the placement of a covering over contaminated sediment to provide three primary functions: physical isolation of the contaminated sediment from the benthic environment; stabilization of contaminated sediments, preventing re-suspension and transport to other sites; and reduction of the flux of dissolved contaminants into the water column (Palmero, Maynard, Miller, & Reible, 1998). The design of an in-situ sediment cap requires the proper engineering of hydraulic, chemical and geotechnical design principles. Each project is evaluated based on its site conditions which include the following (Mohan, Brown, & Barnes, 2000):

- physical site description (bathymetry, hydrology)
- site hydraulics (mean and extreme flow rates, velocities, currents and flood stages)
- nature and extent of contaminants of concern (type of chemicals, concentrations, spatial distribution)

- geophysical nature of native sediments (depth of native sediments, index properties, grain size distribution, organic content, consolidation, permeability, strength and bearing capacity)

- cap material properties (grain size distribution, organic content and permeability)

There are two main types of capping systems: traditional (passive) caps and active caps. Traditional (passive) capping involves the placement of clean granular sediment (generally sand) over the contaminated area sealing it off and minimizing contaminant release into the water column. This type of capping system is advantageous because it is readily available, is relatively easy to place and distinguishable from the underlying sediment. However, permanent stabilization of the contaminated sediment may not be suitable depending on the type of erosive forces (i.e. frequency, magnitude, and duration of high-flow conditions) acting upon it and the cap thickness.

In contrast to passive capping, active or reactive capping involves the use of fine grained soils (i.e. clay) combined with capping materials that are capable of actively demobilizing pollutants by sorption as contaminant flux through the cap occurs. For active cap materials to be effective they must have availability at low cost, active retention of contaminants, physical and chemical stability, and sufficient hydraulic conductivity (Jacobs & Forstner, 1999). A variety of materials exist that could be utilized in active caps for various purposes include: clays for permeability control, activated carbon and chemisorptive media for sequestration, organoclays for non-aqueous phase liquid (NAPL) control, clay and sequestration agent mixtures, phosphate additives for metals, oxygen and/or hydrogen release compounds, and biopolymers.

In order to evaluate the effectiveness of each material in an active sediment cap, it is necessary to understand the theory of movements of contaminants within solutes. Many processes influence the fate of contaminants in bottom sediments. Contaminants can be transported into the overlying water column by advective and diffusive mechanisms (Palmero, Maynard, Miller, & Reible, 1998). Advection is a process in which dissolved solutes are carried along by ground water flow. Since contaminants are advected and travel at the same rate as the ground water flow the rate of contaminant flow can be determined from Darcy's Law given by Equation 1-1 (Fetter, 2001):

$$v_x = -\frac{K}{n_e}\frac{dh}{dl}$$

Equation 1-1: Average Linear Velocity (v_x)

Where:

v_x = average linear velocity (distance/time)

K = hydraulic conductivity (distance/time)

n_e = effective porosity

dh/dl = hydraulic gradient

The second mass transport process that could occur is diffusion. Diffusion occurs when chemical activity is taking place as both ionic and molecular species dissolved in water move from areas of high concentration to areas of low concentration. The flux of a solute under steady-state conditions is described by Fick's first law which is given by Equation 1-2 (Fetter, 2001):

$$F = -D\, dC/dx$$

Equation 1-2: Mass Flux of Solute per Unit Area per Unit Time

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Where:

F = mass flux of solute per unit area per unit time

D = diffusion coefficient (area/time)

C = solute concentration (mass/volume)

dC/dx = concentration gradient (mass/volume/distance)

Generally speaking, the larger the molecule is, the lower the diffusion coefficient will be. Diffusion through a porous medium is slower when tortuosity is accounted for. Tortuosity is the ratio of the actual length of the flow path, L_e, to the length of the straight line distance between the ends of the flow path, L. Tortuosity is always greater than one. Using this ratio the resulting effective diffusion coefficient, D', given by Equation 1-3 can be calculated (Domenico & Schwartz, 1998).

$$D' = \frac{n}{\tau} D$$

Equation 1-3: Effective Diffusion Coefficient

Where:

n = porosity

τ = tortuosity

D = diffusion coefficient (area/time)

A variety of geological features in a sediment cap can tend to lead to both advective and diffusive processes occurring together (i.e. mechanical dispersion). These features include, but are not limited to, the pore size distribution, sorption, porosity, dispersivity, and bulk density and the permeability characteristics of the sediment cap. Generally, advection has little effect in determining the amount of mass transport through

a sediment cap and contaminant transport is diffusion dominated (Hull, Jersak, & Kasper, 1999).

Solutes can be broken up into two classes: conservative and reactive. Conservative solutes do not react with the medium they are flowing through while reactive solutes will adsorb to surfaces through a variety of ways. While it is difficult to pinpoint the type of adsorption forces or mechanisms occurring, general classifications can be broken into eight categories of physicochemical forces (Roy, Krapac, Chou, & Griffin, 1991): London-van der Waals, coulombic-electrostatic-chemical, hydrogen bonding, ligand exchange-anion penetration-coordination, chemisorption, orientation energy, induction, or hydrophobic effect. These adsorption forces are summarized in Table 1.1.

Table 1.1: Adsorption Forces and Mechanisms

Force	Description	Type of solute adsorbed
London-van der Waals	Weak attractive forces from momentary dipoles about atoms or molecules caused by small changes in electronic motions	Organic
Coulombic-electrostatic-chemical	Permanent charge - a charged surface has an isomorphous substitution in the crystal lattice pH-dependent charge - protonation of surface oxygen and OH groups and an oppositely charged species	Inorganic, Organic
Hydrogen bonding	The attractive interaction of a hydrogen bond with an electronegative atom	Inorganic, Organic
Ligand exchange-anion penetration-coordination	A chemical reaction in which one ligand in a chemical compound is replaced by another ligand	Inorganic
Chemisorption	A chemical bond which is usually covalent is formed between the molecule and surface atoms	Inorganic
Orientation Energy	Results in the attraction of a permanent dipole for another permanent dipole (weak)	Organic
Induction	Results from the attraction of an induced dipole brought about by either a permanent dipole or a charged site (weak)	Organic
Hydrophobic effect	The exact nature of this adsorption force is uncertain	Organic

It is possible that two or more of these mechanisms could compete against each other.

Reactions between solutes and the surfaces of solids play an important role in contaminated sediment management. Mass generally partitions between the solution and the solid when given time to equilibrate after mixing. Equation 1-4 results after this takes place (Domenico & Schwartz, 1998):

$$S = \frac{(C_i - C)(Solution\ Volume)}{SM}$$

Equation 1-4: Quantity of Mass Sorbed on the Surface

Where:

S = quantity of mass sorbed on the surface (mass/mass)

C = equilibrium concentration (mass/volume)

C_i = initial concentration (mass/volume)

SM = sediment mass (mass)

By performing experiments using varying values for either the sediment mass or the initial concentration, an isotherm (same temperature) curve can be formed. While isotherms have no real defined shape, sorption is modeled by fitting an experimental isotherm to theoretical equations. The two most common are the Freundlich isotherm (Domenico & Schwartz, 1998):

$$S = KC^n$$

Equation 1-5: Freundlich Isotherm

and the Langmuir isotherm:

$$S = \frac{Q^0 KC}{1 + KC}$$

Equation 1-6: Langmuir Isotherm

The extent of the sorption that takes place is given by the partitioning coefficient, K, while n is a constant that usually ranges between 0.7 and 1.2, and Q^0 is the maximum sorptive capacity for the surface. If the Freundlich or the Langmuir isotherm results in a linear relationship, the slope is equal to the distribution coefficient, K_d value. The

distribution coefficient can also be determined by using Equation 1-7 (American Society for Testing and Materials, 2008).

$$K_d = \frac{(A - B)V}{(M_s)B}$$

Equation 1-7: Distribution Coefficient, K_d (volume mass^{-1})

Where:

A = initial concentration of the solute, C_i (mass/volume)

B = final concentration of the solute after contact with the geomedia, C_f (mass/volume)

V = volume of solution used (volume)

M_s = mass of sorbent material (mass)

Higher K_d values indicate that a higher degree of sorption is taking place. Increasing the distribution coefficient in the sorbent layer will lengthen the amount of time it takes for the contaminant to break through that layer. The distribution coefficient will help determine how much the contaminated solute is being retarded as it passes through the active cap by calculating the retardation factor as given by Equation 1-8:

$$Retardation\ factor = 1 + (\rho_b/\theta)(K_d)$$

Equation 1-8: Retardation Factor

Where:

ρ_b = dry bulk mass density of the soil (mass/volume)

θ = volumetric moisture content of the soil (dimensionless)

K_d = distribution coefficient for the solute with the soil (volume/mass)

By incorporating this value into the calculation of the breakthrough time, the overall effectiveness of each amendment in an active sediment cap can be determined and evaluated.

It is necessary to carry out demonstrations of sequestering agents in active caps to evaluate their effectiveness versus traditional sand caps. Since the early 1980s, several countries have conducted pilot-scale and full-scale capping projects to evaluate the effectiveness of capping under a variety of site conditions (Mohan, Brown, & Barnes, 2000). Studies are taking place in the United States in a variety of locations such as the Anacostia River in Washington, D.C., the Ottawa River in Toledo, OH, and the Eagle River, Fort Richardson, Alaska).

While sediment remediation is best accomplished using a combination of technologies, in-situ sediment management strategies provide a viable alternative for contaminated areas where sediment removal technologies are cost prohibitive but remediation is necessary. The development of an active capping material will facilitate in situ sequestration or destruction of specific sediment contaminants including heavy metals, nutrients, and pesticides allowing broader application of each amendment or amendment combination.

Chapter Two

2 Introduction

Point source and non-point source contamination from various industrial,

domestic, and agricultural activities has had a considerable impact over the last few

decades. The runoff from this contamination has impacted sediments in approximately

96 watersheds nationwide, which comprises about 5 percent of all continental U.S.

watersheds (Hull, Jersak, & Kasper, 1999). Each watershed with contaminated sediments

is considered to be an area of concern (AOC). Forty three AOC's have been identified in

the Great Lakes with 26 located entirely within the United States, 12 located within

Canada, and five that are shared by both countries according to the United States

Environmental Protection Agency.

The contaminated sediments within each AOC have the potential to detrimentally

impact the aquatic environment if not treated properly. Some common treatment and/or

disposal techniques include monitored natural recovery (MNR), removal of the

contaminated sediment (dredging), or in-situ sediment capping (ISC). MNR, which relies

on natural physical, chemical and biological processes, to reduce sediment

contamination is viable where short term risks posed by the contaminants are acceptable,

the sediments are stable, and the cost is desirable (Knox, Paller, Reible, Ma, & Petrisor,

2008). Dredging usually involves the removal of the contaminated sediment and disposal into a landfill or a confined disposal facility (CDF). However, it could also be removed and treated. Dredging is generally limited to small sites because of the expense. ISC is the placement of a covering over contaminated sediment to provide three primary functions (Palmero, Maynard, Miller, & Reible, 1998):

- Physical isolation of the contaminated sediment from the benthic environment

- Stabilization of contaminated sediments, preventing re-suspension and transport to other sites

- Reduction of the flux of dissolved contaminants into the water column

While traditional (passive) capping, which is the placement of a granular material on top of the contaminated sediment in an AOC to reduce contaminant flux into the water column, is commonly used, the focus of this research is to determine the effectiveness of various materials amended to clay minerals in active caps to sequester contaminants. Potential materials that are available to be utilized in active caps include: clays for permeability control, activated carbon and chemisorptive media for sequestration, organoclays for non-aqueous phase liquid (NAPL) control, clay and sequestration agent mixtures, phosphate additives for metals, oxygen and/or hydrogen release compounds, and biopolymers.   Active capping materials that were analyzed in this study include powder activated carbon and a chemisorptive media amended to either a sodium bentonite clay or organoclay. These materials were analyzed either as a single amendment or in combinations thereof.

Clay minerals commonly used in active sediment caps include sodium bentonite and organoclays. Sodium bentonite is untreated 200 mesh high purity Wyoming clay. It

is commonly used as a binder, but can serve as an adsorbent for non-polar pollutants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs). Advantages to sodium bentonite include its natural abundance, fast hydration process, and it is cost effective. Organoclay is sodium montmorillonite clay modified with a cationic quantenary amine salt, which makes it hydrophobic and selectively oleophilic. Organoclays are generally effective at removing dissolved hydrocarbons such as benzene, toluene, ethylbenzene, and xylene.

The powder activated carbon (PAC) amendment analyzed was a virgin, coal based material that is approximately less than 1.0 mm in size with an average diameter between 0.15 to 0.25 mm. PAC has a large surface to volume ratio creating countless bonding sites and giving it a high adsorption capacity. PAC primarily targets dissolved organics. The chemisorptive media analyzed in this study is sulfur enriched alumina media that will have a chemical reaction occur with the contaminants at the exposed surface. This material is efficient at removing inorganic materials such as heavy metals. It is especially efficient at removing mercury.

Additional variables that need to be considered in design of an active sediment cap include the advective (groundwater upwelling) and diffusive processes of the solute through the cap and the sorption and reaction processes that take place as contaminant flux occurs (Lampert & Reible, 2009). An analytical model for evaluation of these parameters was utilized to evaluate each of these amendments in this research and considered both steady state and transient conditions. It has been estimated that the time for typical sediment contaminants to migrate through strongly sorbing chemical isolation

layers may be hundreds or thousands of years (Murphy, Marquette, Reible, & Lowry, 2006).

The objective of this study was to evaluate these materials for incorporation into active caps for remediation of contaminated sediments. The evaluation of these materials was based on the ability of these materials to remove a broad range of inorganic and organic contaminants under fresh water and salt water conditions in a laboratory.

Chapter Three

3   Materials and Methods

Laboratory scale batch sorption tests were performed in fresh water and salt water environments to evaluate removal efficiencies of heavy metals and polycyclic aromatic hydrocarbons (PAHs) and the sorption affinity of various amendments and combinations thereof utilized in active caps. A list of these amendments and amendment mixtures are listed in Table 3.1.

Table 3.1: Amendments and Amendment Mixtures

#		Sorbent Material
1	A-C	Sodium Bentonite (Performance Minerals LLC)
2	A-C	Organoclay (Aquatechnologies of Wyoming Inc.)
3	A-C	Powder Activated Carbon (Calgon Corporation)
4	A-C	Chemisorptive (MAR Systems)
5	A-C	Bentonite/PAC (3:1 ratio)
6	A-C	Organoclay/PAC (9:1 ratio)
7	A-C	Bentonite/MAR (3:1 ratio)
8	A-C	Control (Spiked with no sorbent material)
NS	1	Bentonite w/solution not spiked
NS	2	Organoclay w/solution not spiked
NS	3	PAC w/solution not spiked
NS	4	Chemisorptive w/solution not spiked

The heavy metals and PAHs that were analyzed are listed in Table 3.2.

Table 3.2: Contaminants Analyzed

Type of Contaminant	Contaminant	Symbol
Heavy Metals	Arsenic	As
	Mercury	Hg
	Lead	Pb
	Selenium	Se
PAHs	Phenanthrene	$C_{14}H_{10}$
	Pyrene	$C_{16}H_{10}$

Treatment efficacy was determined by calculating the distribution coefficient of the various materials selected for testing alone and in combination with clay minerals.

3.1 Sorption of Heavy Metals

Sorption experiments for heavy metals were performed at room temperature (20°C) on an orbital shaker in the dark for a period of one week. The experiments were conducted in 50 mL plastic centrifuge tubes and contained suspensions consisting of 0.2 g of the amendments or amendment mixtures listed in Table 3.1 and 15 mL of a metal spike solution, which was prepared by USDA-ARS/The University of Toledo. This metal spike solution contained environmentally relevant concentrations of the heavy metals in their basic form listed in Table 3.2 (approximately 2 mg L^{-1} of each). These experiments were performed in triplicate. After shaking was completed, each sample was phase separated by centrifugation using the Eppendorf 5804R centrifuge operating at 3000 rpm for 20 minutes. Upon completion of phase separation, 10 mL of supernatant was decanted from the top of each sample and sent to the USDA laboratory for analysis using inductively coupled plasma optical emission spectrometry (ICP-OES).

The settings for the ICP-OES (Model IRIS Intrepid II; Thermo Electron Corp., Waltham, Mass.) were: flush and analysis pump rate: 130 rpm; RF power: 1150 W; nebulizer pressure: 32.1 PSI; auxillary gas: 1.0 L min^{-1}. The wavelengths (commonly referred to as lines) used for the elements were As 189.042 (178), Hg 184.950 (181), Pb 220.353 (152), and Se 196.090 (171). Calibration was done with a high standard composed of 0.1% nitric acid and approximately 2 mg L^{-1} of As, Hg, Pb, and Se. When samples were being analyzed for the salt water experiment, calibration was done with a high standard composed of 3.5% ocean water, 0.1% nitric acid, and approximately 2 mg L^{-1} of As, Hg, Pb, and Se. The blank had 0.1% nitric acid. Because the blank had no ocean water, the standard was run as an unknown and experimental results were compared to actual values to determine a correction factor. However, in this case, there was no difference between the experimental and actual values (Knox, Paller, Reible, Ma, & Petrisor, 2008).

3.1.1   Leaching of Metals from Sorbent Material

A similar experiment was performed for each amendment alone with laboratory grade water and 0.1% nitric acid to determine if the amendments were leaching metals. Samples were analyzed by ICP-OES. These values were used to provide corrected final concentrations in solution and have been accounted for in the results.

3.2 Sorption of Organic Contaminants

For the PAH experiments, solid standards of polycyclic aromatic hydrocarbons (PAHs) were purchased from a commercial supplier (Sigma-Aldrich Inc., MO). These

hard standards were used to prepare stock solutions of pyrene (1000 mg L^{-1} in methanol)

and phenanthrene (1000 mg L^{-1} in methanol). The PAHs were diluted in an electrolyte

solution (0.01M NaCl, 0.01M CaCL2.2H2O) to prepare a spiked solution with the

following constituents: 100 μg L^{-1} phenanthrene and 100 μg L^{-1} pyrene. Sodium azide

(0.05 M) was added to the spiked solution to inhibit bacterial degradation of the PAHs.

Sorption experiments were carried out in 50 mL glass centrifuge tubes with a

piece of aluminum foil attached to the inside of each tube cap to minimize sorption loss.

20 mg of 8 different amendments and combinations (see Table 3.1) were added to each

tube. An additional amendment of Ottawa Sand was analyzed in the PAH experiments to

serve as a control. Forty mL of PAH spiked solution was added to each of the tubes

(Knox, Paller, Reible, Ma, & Petrisor, 2008). These experiments were performed in

triplicate and were shaken at 30 rpm for 48 hours at 20°C. The samples were centrifuged

for 30 minutes at 1500 rpm after tumbling in the Eppendorf 5804R centrifuge.

Following centrifugation, 35 mL of liquid from each sample was decanted from the top

and transferred to a separate 50 mL tube. 5 mL of methylene chloride was added to each

of these centrifuge tubes so a liquid-liquid extraction of the contaminants could be

performed. The mixture was shaken overnight (~12 hours). 3 mL of methylene chloride

was transferred to a 15 mL glass centrifuge tube and analyzed by GC-MS by the

Department of Environmental Sciences at The University of Toledo.

Pyrene, phenanthrene and internal standard 2-fluorobiphenyl were identified and

quantified using a Hewlett Packard 6890 gas chromatograph coupled to a 5972A mass

selective detector. An HP-5 Trace Analysis (5% PHME Siloxane), 30 m x 0.25 mm x

0.25 um column was used for separation. The temperature program began at 100°C, held

for 1 minute and ramped at 10 °C/minute to 250 °C, and held for 2 minutes. The inlet was kept at 250 °C. Helium was used as the carrier gas and the injector was set for splitless injection of 1 μL. Quantitation using selective ion monitoring mode was used and is summarized in Table 3.3.

Table 3.3: Selective Ion Monitoring Mode Settings

Compound	Ions (SIM)	r/t [min]	LOD [μg/L]	Linearity [μg/L]
(1) 2-fluorobiphenyl[a] 2 mg/L	172[b] 171 146	6.8	n/a	n/a
(2) phenanthrene 0.5 mg/L	178[b] 176 76	11.7	25	25-1000 (r^2=0.997)
(3) pyrene 0.5 mg/L	202[b] 101 200	15.0	25	25-1000 (r^2=0.996)

[a] Internal standard
[b] Indicates quantitation ion

Five point calibration curves (r^2 >0.99) in solvent using internal standard ratios were run to encompass the range of concentrations observed in samples and used to quantify predominant ions. Instrument response variability was <5% RSD over the course of the study.

Chapter Four

4   Data Analysis

Using the data from the sorption studies of heavy metal contaminants, sorption

affinity (in terms of percent removal), and distribution coefficient (K_d) values were

calculated. A distribution coefficient is defined as the concentration of a solute sorbed to

a solid divided by its concentration in solution. The K_d value for each sample was

calculated using Equation 4-1 (American Society for Testing and Materials, 2008).

$$K_d = \frac{(A - B)V}{(M_s)B}$$

Equation 4-1: Distribution Coefficient, K_d (volume mass^{-1})
Where:

A = initial concentration of the solute, C_i (mass/volume)
B = final concentration of the solute after contact with the geomedia, C_f
(mass/volume)
V = volume of solution used (volume)
M_s = mass of sorbent material (mass)

Sorption affinity, defined as the relative degree of sorption that occurs by a

geomedia, was calculated to provide a means of comparing the amendments effectively.

This is calculated using Equation 4-2.

$$Sorption\ Affinity\ (\%\ Removal) = \left(1 - \frac{C_f}{C_i}\right) \times 100\%$$

Equation 4-2: Sorption Affinity

The initial concentrations of heavy metals in the spiked solute were adjusted by the heavy metal concentrations leaching from each amendment or amendment mixture to account for the overall sorption affinity of each material.

In the analysis of the PAHs, distribution coefficients were calculated using Equation 4-1. The calculated distribution coefficients were useful in a simplified model to estimate the breakthrough time for a contaminant to penetrate a 1-inch cap. Assumptions were made in this simplified model and are as follows: the underlying concentration of the contaminants remained constant and no degradation processes were operative. Using this data and simplified model, conclusions and recommendations for the most reliable active sediment cap are able to be provided.

Chapter Five

5 Results and Discussion

5.1 Removal of Metals

Sorption affinities were determined from batch sorption experiments for four
heavy metals commonly found in contaminated sediments (As, Hg, Pb, and Se). Tests
were carried out in both fresh water and salt water environments. Results of removal
efficiencies from batch sorption experiments can be found in Table 5.1 for fresh water
environments.

Table 5.1: Amendment Removal Efficiencies in Fresh Water

Amendment Removal Efficiencies in Fresh Water*				
Amendments/Combinations	**Metal Contaminants**			
	As	**Hg**	**Pb**	**Se**
Bentonite	X	XXXX	XX	X
Organoclay	X	XXX	XX	X
Powder Activated Carbon	XX	XXXX	X	XXX
Chemisorptive media	XXXX	XXXX	XX	XXXX
Bentonite/PAC (3:1 ratio)	XXX	XXXX	X	XX
Organoclay/PAC (9:1 ratio)	X	XXX	XX	X
Bentonite/Chemisorptive (3:1)	XXXX	XXXX	X	XXXX

*X -removal at 0-25%; XX - removal at 25-50%; XXX - removal at 50-
75%; XXXX - removal at 75-100%

The removal efficiencies presented in Table 5.2 are for salt water environments.

Table 5.2: Amendment Removal Efficiencies in Salt Water

Amendment Removal Efficiencies in Salt Water*				
Amendments/Combinations	**Metal Contaminants**			
	As	**Hg**	**Pb**	**Se**
Bentonite	X	XX	X	X
Organoclay	X	X	X	X
Powder Activated Carbon	X	XXXX	XXX	XXXX
Chemisorptive media	XXXX	XXXX	XXX	XXXX
Bentonite/PAC (3:1 ratio)	XX	XXXX	X	XXX
Organoclay/PAC (9:1 ratio)	X	XXXX	X	XX
Bentonite/Chemisorptive (3:1)	XXX	XXX	XX	XXX

*X -removal at 0-25%; XX - removal at 25-50%; XXX - removal at 50-75%; XXXX - removal at 75-100%

The heavy metals analyzed in these experiments may be adsorbed by ion exchange, chemisorption, and/or precipitated. The results shown here do not account for the type of sorption process that took place. In addition, trace amounts of metals that leached from the amendments were accounted for in the final results.

Results for single amendments showed that the chemisorptive media and powder activated carbon were the most effective sorbent materials for removal of mercury (Hg) and selenium (Se) in fresh water as well as salt water. Lead removal in a fresh water environment for all single amendments was poor (<40%). The chemisorptive media was the only single amendment that was effective at removing arsenic (As) both in fresh water and salt water environments.   Salt water significantly impaired the binding of mercury (Hg) and lead (Pb) to bentonite and organoclay.

Results for the combinations of amendments showed that the bentonite and chemisorptive media combination was most effective in a fresh water environment

having greater than 75% removal for all the heavy metals analyzed except for lead (Pb). Efficiency for this combination was reduced significantly in the salt water environment for arsenic (As), mercury (Hg), and selenium (Se) but increased for lead (Pb). Bentonite and powder activated carbon also worked well in combination. However, there was a significant reduction in arsenic (As), a slight reduction in lead (Pb), and a significantly greater removal efficiency of selenium (Se) in the salt water environment. The organoclay and powder activated carbon combination had less than 40% removal for arsenic (As), lead (Pb), and selenium (Se). This combination removed mercury (Hg) most effectively. Distribution coefficient values supporting these findings for both fresh water and salt water environments are provided in Table 5.3 and Table 5.4.

Table 5.3: Average K_d Values (Standard Deviations) for Metal Removal by Amendments Proposed for Sediment Capping in a Fresh Water Environment (in mL g^{-1})

Average K_d values for Metal Removal by Amendments (mL g^{-1}) (Standard Deviations)				
Amendments	Metal Contaminants			
	As	Hg	Pb	Se
Bentonite	4 (0)	8631 (6975)	42 (5)	5 (0)
Organoclay	6 (0)	87 (6)	46 (10)	11 (1)
Powder Activated Carbon	31 (1)	2880 (2312)	8 (1)	216 (5)
Chemisorptive media	6293 (1396)	3146 (660)	31 (2)	2398 (89)
Bentonite/PAC (3:1 ratio)	78 (6)	1613 (0)	17 (2)	41 (2)
Organoclay/PAC (9:1 ratio)	16 (8)	281 (257)	54 (34)	16 (6)
Bentonite/Chemisorptive (3:1)	439 (183)	1618 (0)	8 (4)	635 (352)

Table 5.4: Average K_d Values (Standard Deviations) for Metal Removal by Amendments Proposed for Sediment Capping in a Salt Water Environment (in mL g^{-1})

Average K_d values for Metal Removal by Amendments (mL g^{-1}) (Standard Deviations)				
Amendments	**Metal Contaminants**			
	As	**Hg**	**Pb**	**Se**
Bentonite	9 (7)	32 (8)	1 (6)	16 (9)
Organoclay	9 (5)	19 (3)	9 (5)	15 (2)
Powder Activated Carbon	25 (7)	1545 (0)	78 (11)	436 (122)
Chemisorptive media	1026 (420)	1211 (444)	149 (34)	259 (41)
Bentonite/PAC (3:1 ratio)	26 (7)	1613 (0)	11 (7)	128 (23)
Organoclay/PAC (9:1 ratio)	19 (13)	5303 (6263)	19 (11)	30 (21)
Bentonite/Chemisorptive (3:1)	111 (19)	96 (39)	30 (12)	81 (8)

Removal efficiencies for the batch sorption experiments performed in the fresh water and salt water environments are graphically summarized in Figure 5-1 to Figure 5-7.

Bentonite

	As	Hg	Pb	Se
Fresh Water	4.76%	97.12%	35.87%	6.36%
Salt Water	10.50%	29.63%	1.08%	17.42%
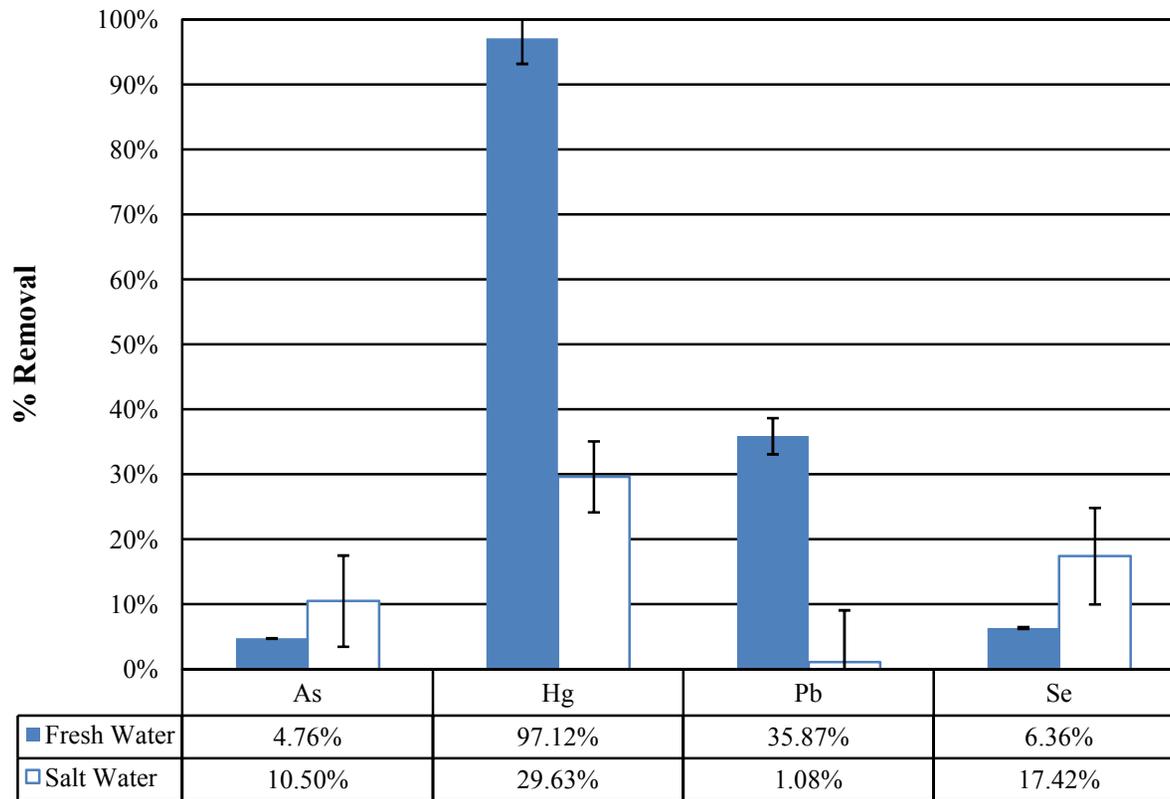
Figure 5-1: Removal Efficiencies of Heavy Metals (As, Hg, Pb, and Se) by Bentonite in Fresh Water and Salt Water Environments (initial heavy metals concentration was ~2 mg L^{-1})

Organoclay

	As	Hg	Pb	Se
■ Fresh Water	7.39%	53.54%	37.88%	12.80%
□ Salt Water	10.44%	20.31%	10.53%	16.50%
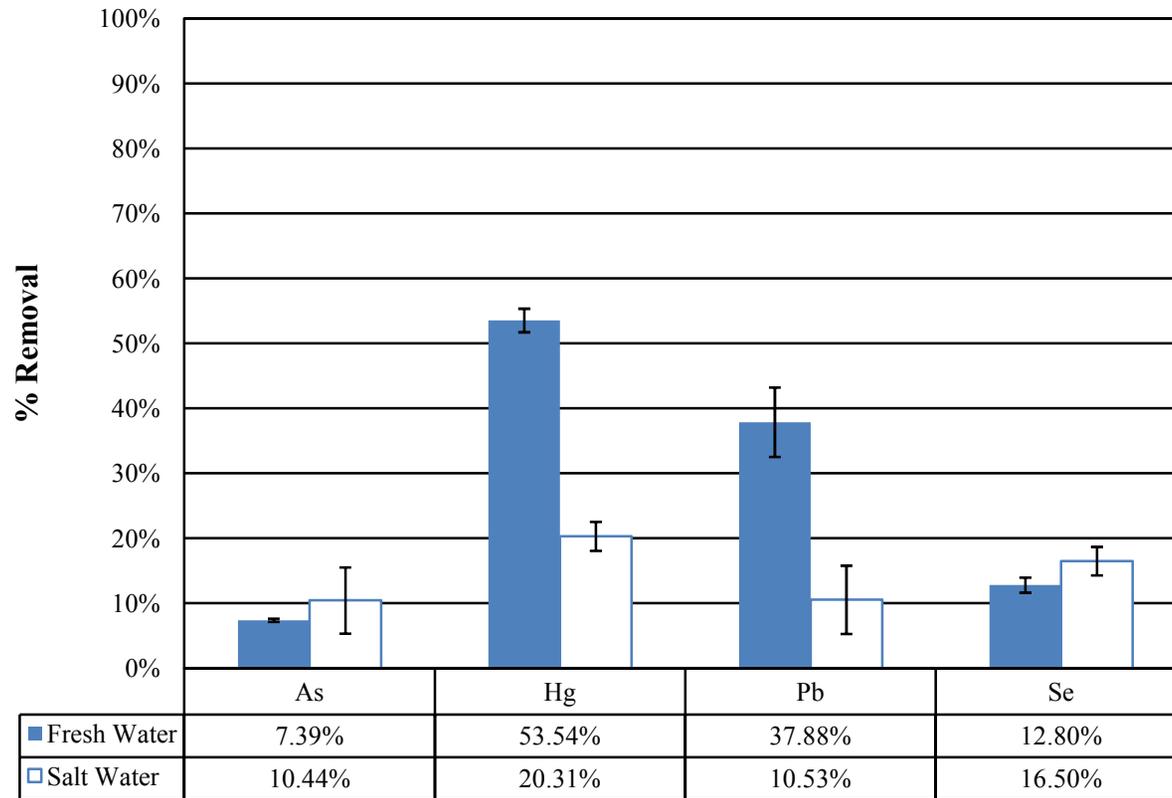
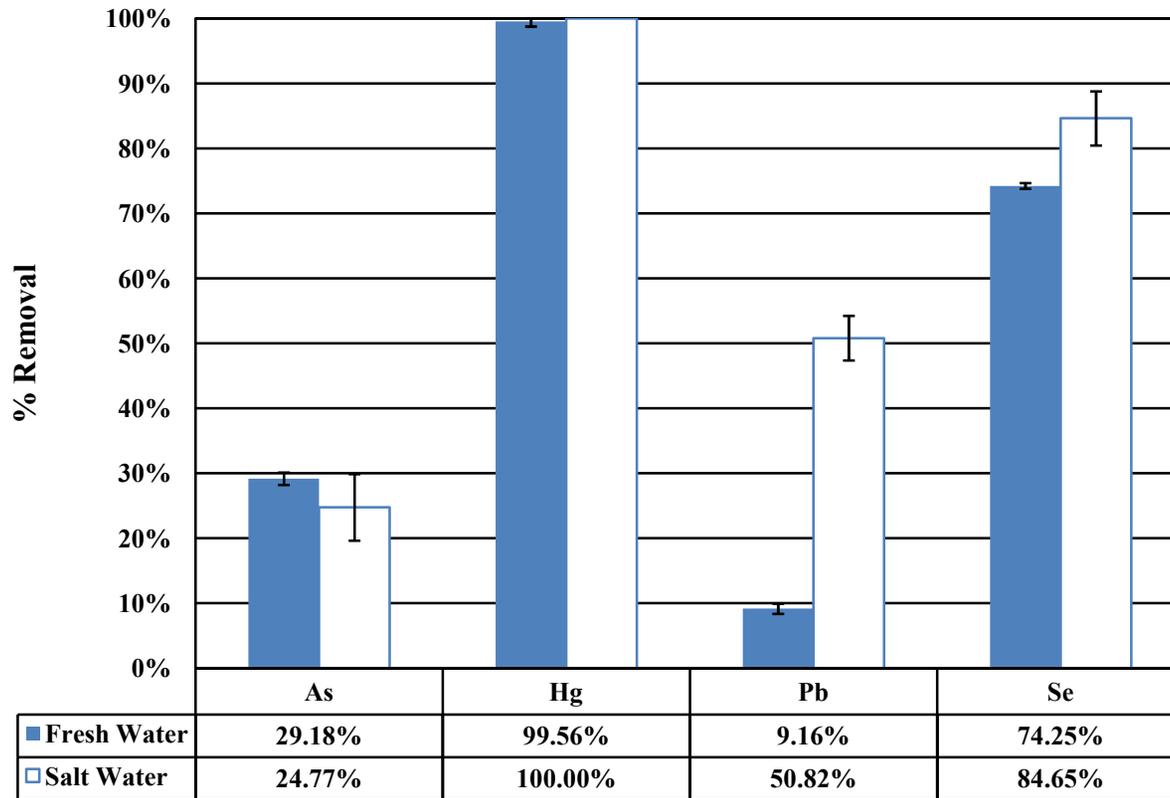**Figure 5-2: Removal Efficiencies of Heavy Metals (As, Hg, Pb, and Se) by Organoclay in Fresh Water and Salt Water Environments (initial heavy metals concentration was ~2 mg L^{-1})**

Powder Activated Carbon

	As	Hg	Pb	Se
■ Fresh Water	29.18%	99.56%	9.16%	74.25%
□ Salt Water	24.77%	100.00%	50.82%	84.65%

Figure 5-3: Removal Efficiencies of Heavy Metals (As, Hg, Pb, and Se) by Powder Activated Carbon in Fresh Water and Salt Water Environments (initial heavy metals concentration was ~2 mg L^{-1})

Chemisorptive

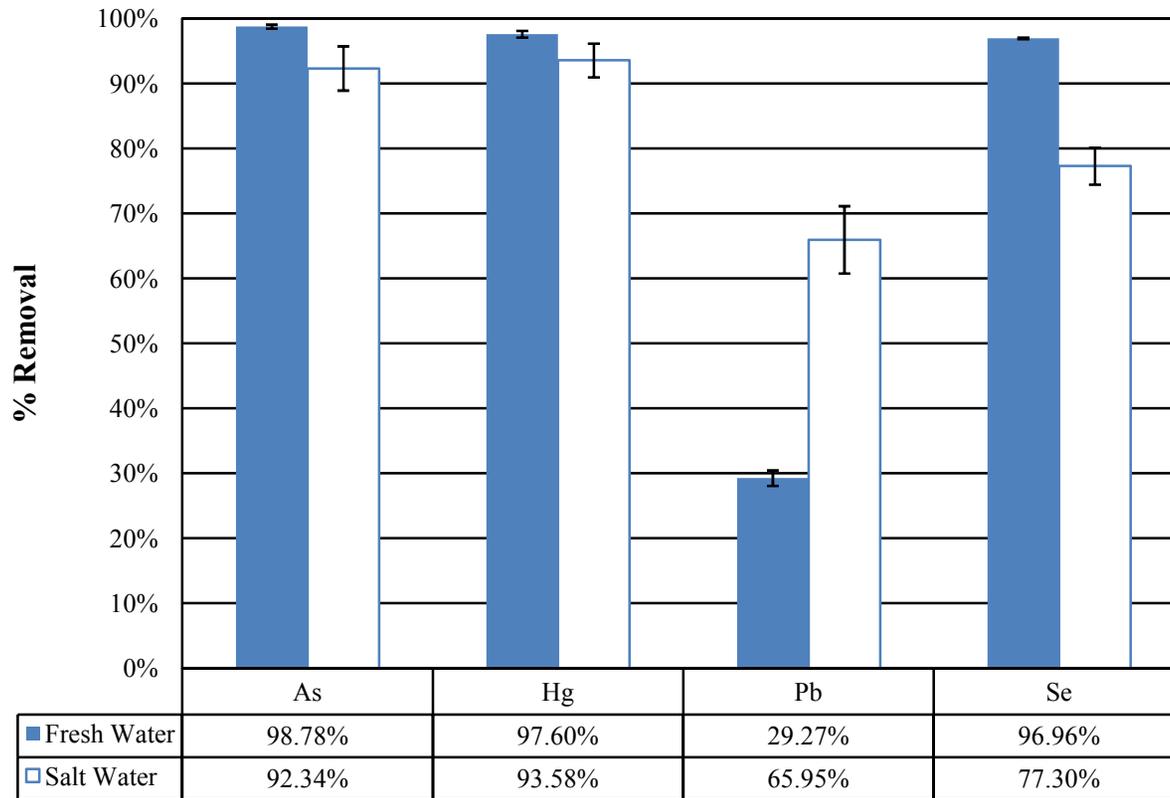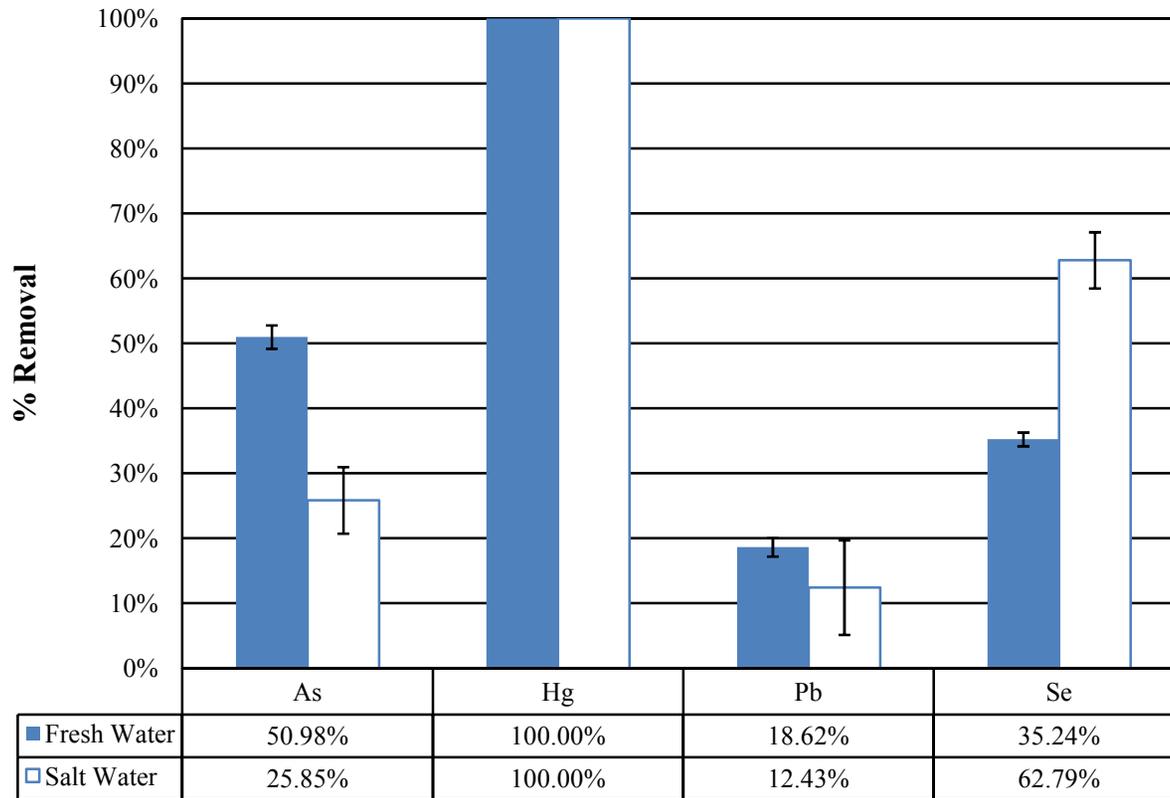|	As	Hg	Pb	Se
■ Fresh Water	98.78%	97.60%	29.27%	96.96%
□ Salt Water	92.34%	93.58%	65.95%	77.30%

Figure 5-4: Removal Efficiencies of Heavy Metals (As, Hg, Pb, and Se) by Chemisorptive Media in Fresh Water and Salt Water Environments (initial heavy metals concentration was ~2 mg L^{-1})

Bentonite/PAC

	As	Hg	Pb	Se
Fresh Water	50.98%	100.00%	18.62%	35.24%
Salt Water	25.85%	100.00%	12.43%	62.79%

Figure 5-5: Removal Efficiencies of Heavy Metals (As, Hg, Pb, and Se) by a Bentonite/PAC (3:1 ratio) Combination in Fresh Water and Salt Water Environments (initial heavy metals concentration was ~2 mg L^{-1})

Organoclay/PAC

	As	Hg	Pb	Se
■ Fresh Water	17.35%	72.03%	38.86%	17.06%
□ Salt Water	19.61%	96.49%	19.30%	27.09%

Figure 5-6: Removal Efficiencies of Heavy Metals (As, Hg, Pb, and Se) by an Organoclay/PAC (9:1 ratio) Combination in Fresh Water and Salt Water Environments (initial heavy metals concentration was ~2 mg L^{-1})
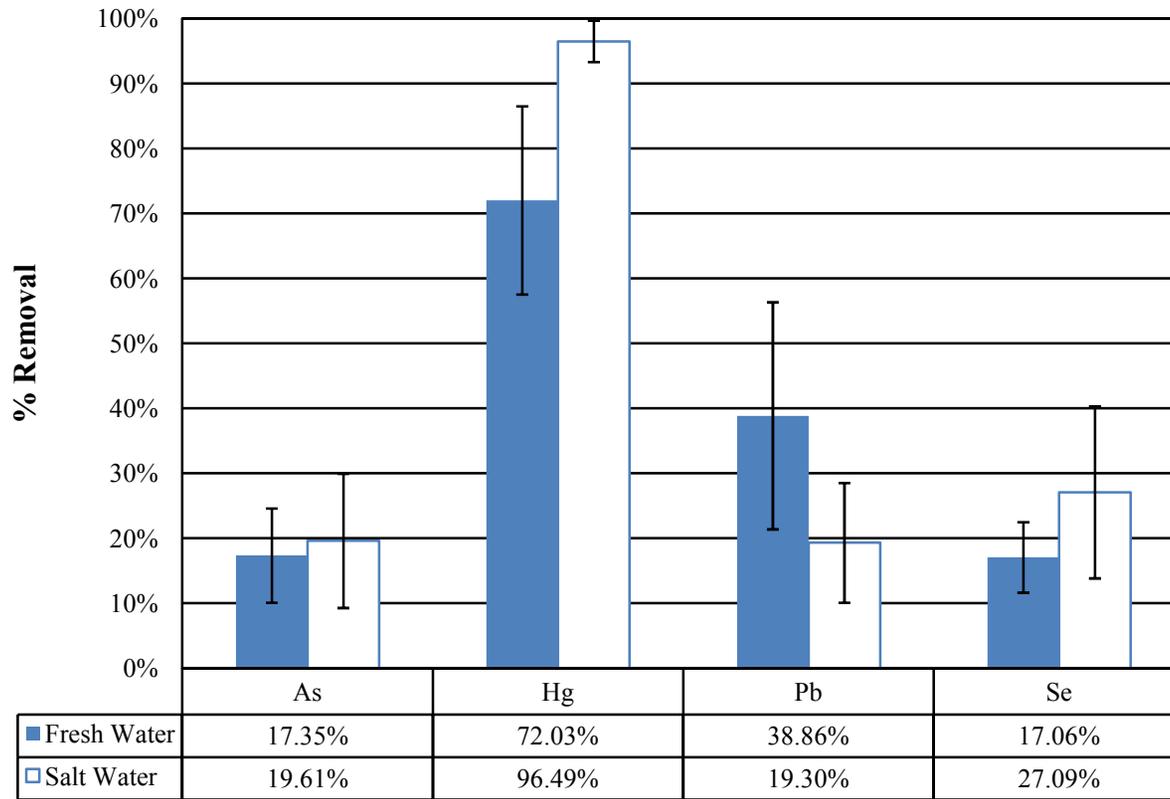
Bentonite/Chemisorptive

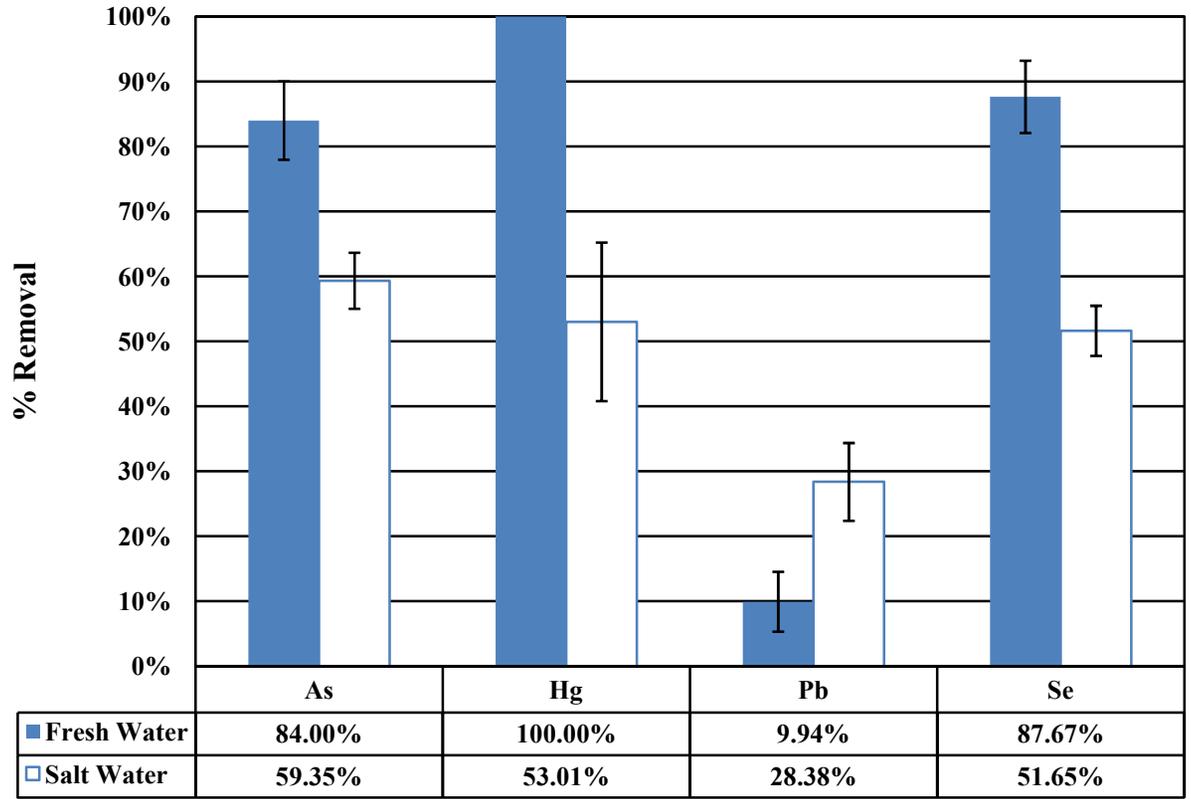|	As	Hg	Pb	Se
■ Fresh Water	84.00%	100.00%	9.94%	87.67%
□ Salt Water	59.35%	53.01%	28.38%	51.65%

Figure 5-7: Removal Efficiencies of Heavy Metals (As, Hg, Pb, and Se) by a Bentonite/Chemisorptive Media (3:1 ratio) Combination in Fresh Water and Salt Water Environments (initial heavy metals concentration was ~2 mg L^{-1})

5.2 Sorption of Organic Contaminants by Sequestering Agents

Following batch sorption experiments of phenanthrene and pyrene, analysis was done to calculate the average distribution coefficient values (K_d) in both fresh water and salt water environments. Freshwater K_d values can be viewed in Table 5.5.

Table 5.5: Average Distribution Coefficient (K_d) Values (Standard Deviations) for Organic Contaminant Sequestration by Amendments in a Fresh Water Environment (in L g^{-1})

| Average Kd values (L g^{-1}) (Standard Deviations)		
Amendment	**PAH Contaminants**	
	Phenanthrene	**Pyrene**
Bentonite	4 (1)	9 (4)
Organoclay	8 (2)	12 (4)
Powder Activated Carbon	64 (8)	39 (10)
Chemisorptive	7 (2)	15 (3)
Bentonite/PAC	39 (10)	23 (2)
Organoclay/PAC	19 (10)	45 (16)
Bentonite/Chemisorptive	3 (2)	6 (4)
Sand	3 (0)	11 (1)

Fresh Water distribution coefficients were relatively low for all amendments and amendment combinations with a range of 3 - 64 L g^{-1} for phenanthrene and 6 - 39 L g^{-1} for pyrene. This was expected for the chemisorptive media as it is primarily used for metal removal. Organoclay, which generally has a high sorption capacity for non-polar organic solutes, performed relatively poorly compared to OCB-750 and PM-199 studied in previous research (Knox, Paller, Reible, Ma, & Petrisor, 2008). Powder activated carbon proved to have the most effective sorption capacity of these two contaminants when it was used as a single amendment. A reduction in the sorption capacity of phenanthrene occurred when in combination with bentonite and organoclay. The same is

true for pyrene when powder activated carbon is in combination with bentonite.

However, there was an increase in the sorption capacity of pyrene when powder activated

carbon was in combination with organoclay. Distribution coefficients for each

amendment when exposed to a salt water environment were about the same except for the

powder activated carbon and the combinations including powder activated carbon. There

was a significant increase in sorptive capacity when powder activated carbon was used as

a single amendment. A noticeable increase was also observed when powder activated

carbon was in combination with either sodium bentonite or organoclay. These K_d values

are provided in Table 5.6.

Table 5.6: Average Distribution Coefficient (K_d) Values (Standard Deviations) for Organic Contaminant Sequestration by Amendments in a Salt Water Environment (in L g^{-1})

| Average Kd values (L g^{-1}) (Standard Deviations)		
Amendment	PAH Contaminants	
	Phenanthrene	Pyrene
Bentonite	2 (1)	10 (6)
Organoclay	9 (4)	39 (14)
Powder Activated Carbon	570 (287)	2371 (971)
Chemisorptive	6 (3)	34 (13)
Bentonite/PAC	124 (36)	1709 (431)
Organoclay/PAC	115 (59)	856 (537)
Bentonite/Chemisorptive	5 (1)	32 (6)
Sand	3 (0)	15 (3)

These findings for the batch sorption experiments of PAHs performed in fresh

water and salt water environments are graphically summarized in Figure 5-8 to Figure

5-11.
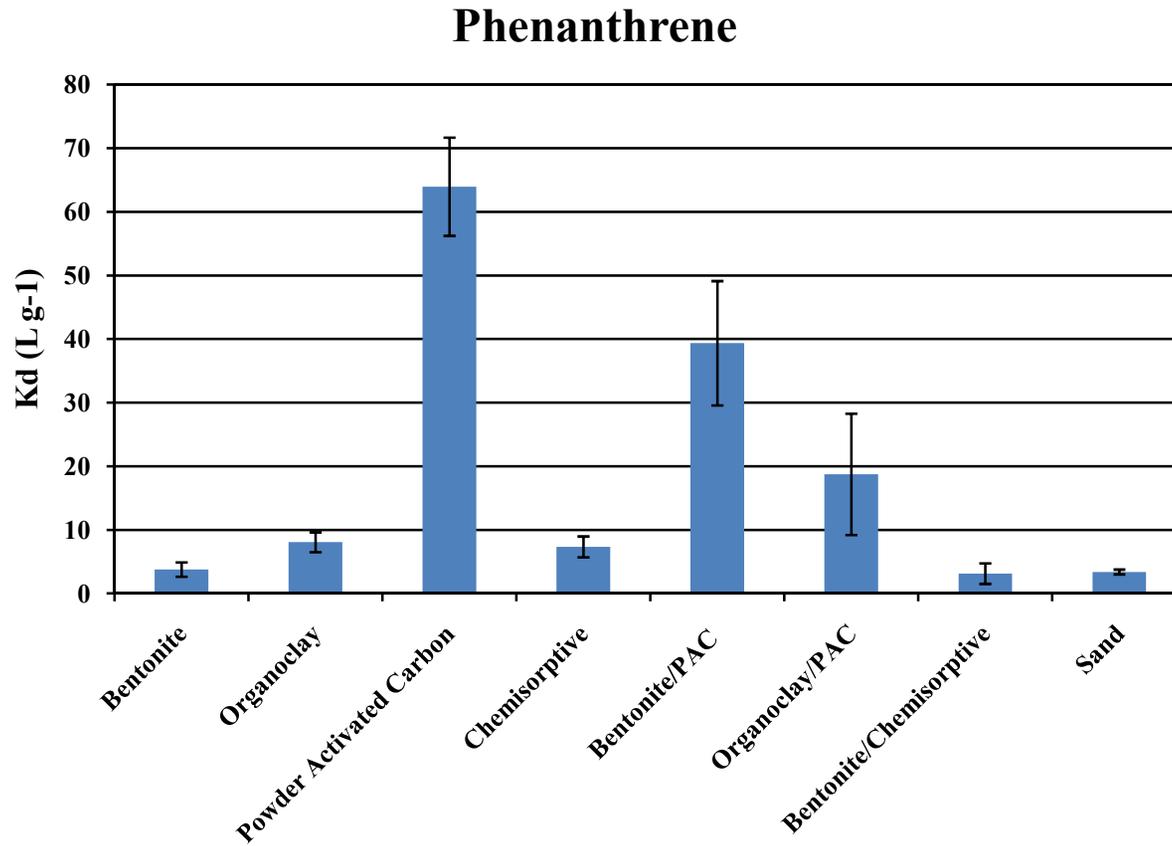
Phenanthrene

Figure 5-8: Distribution Coefficient (K_d) Values of Phenanthrene by Amendments and Combinations Thereof in Fresh Water (initial phenanthrene concentration was ~100 µg/L)
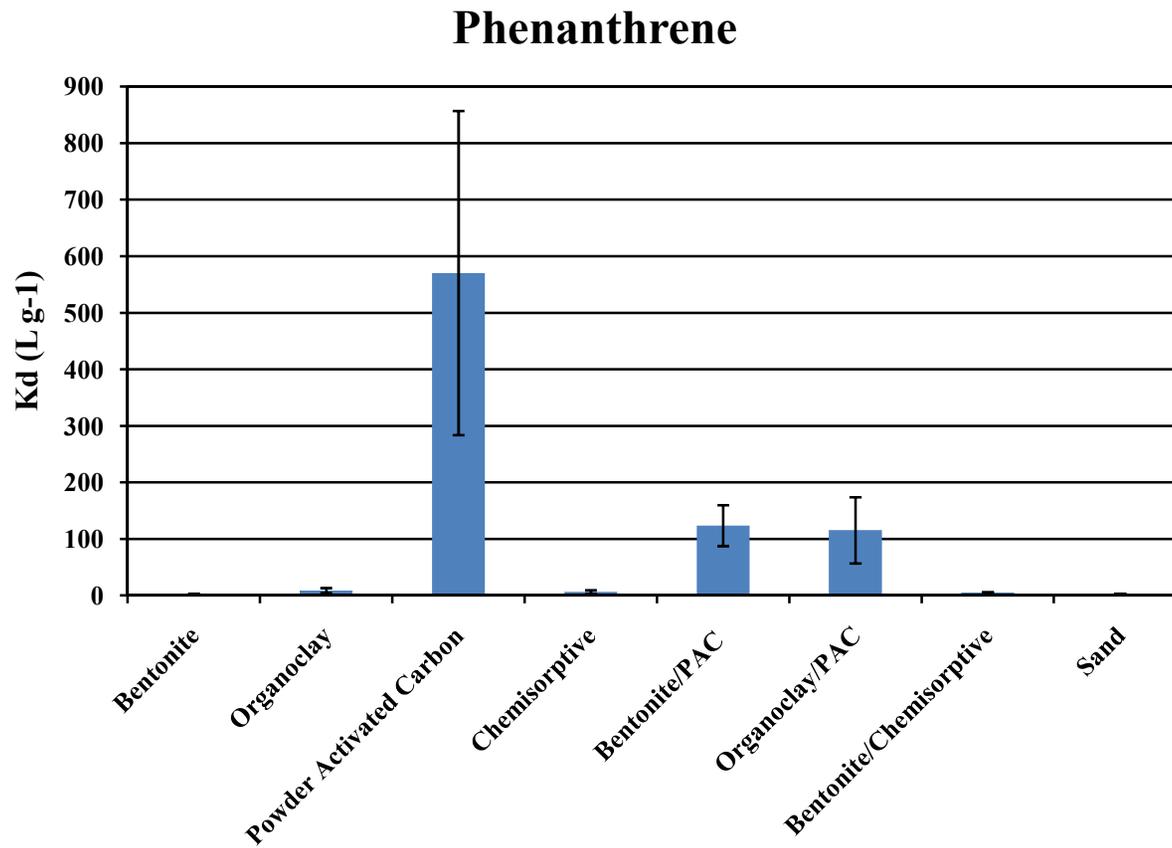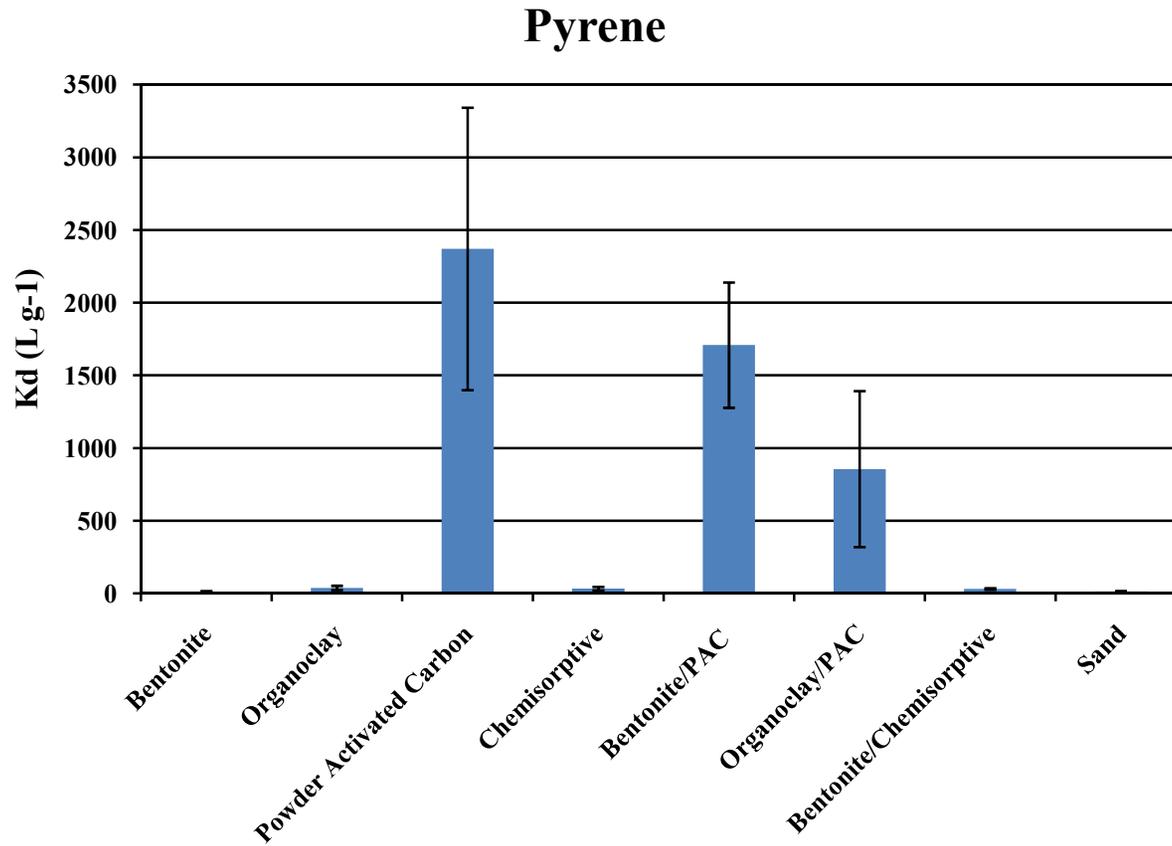
Figure 5-9: Distribution Coefficient (K_d) Values of Phenanthrene by Amendments and Combinations Thereof in Salt Water (initial phenanthrene concentration was ~100 µg/L)
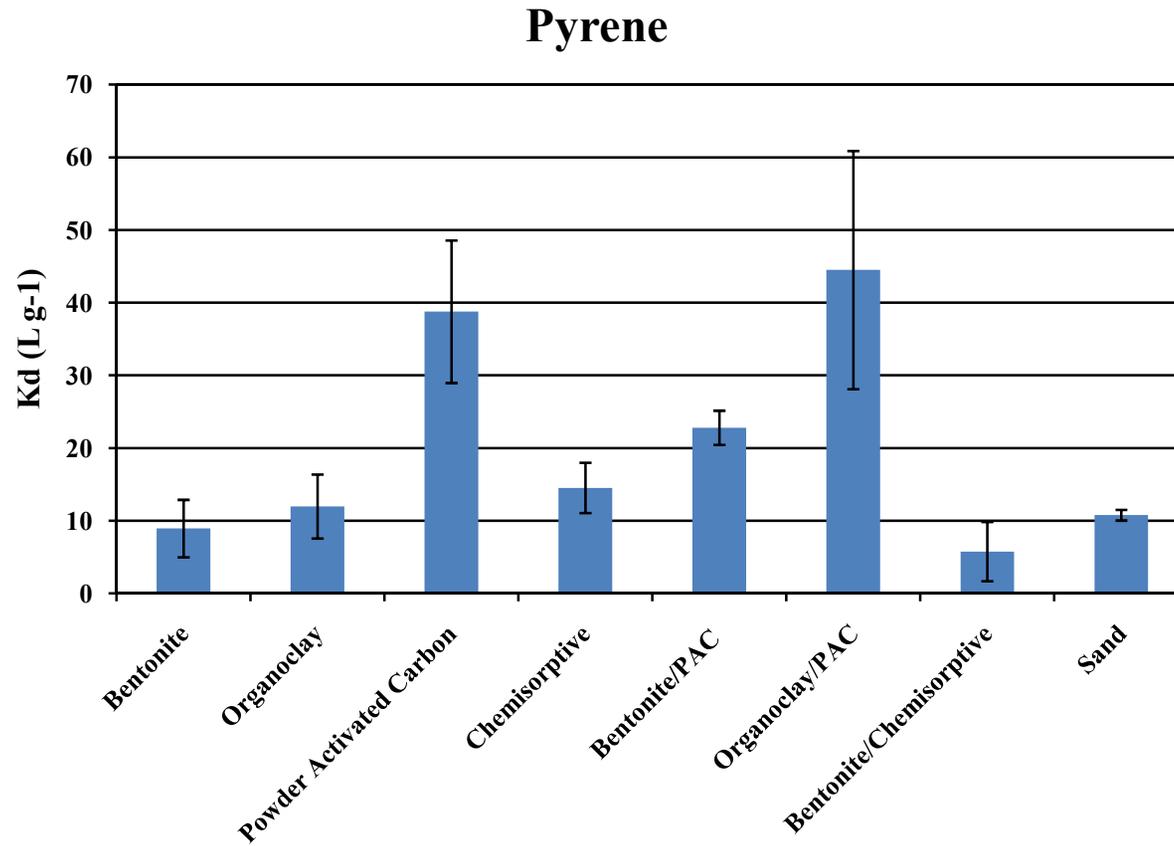
Figure 5-10: Distribution Coefficient (K_d) Values of Pyrene by Amendments and Combinations Thereof in Fresh Water (initial pyrene concentration was ~100 µg/L)

Figure 5-11: Distribution Coefficient (K_d) Values of Pyrene by Amendments and Combinations Thereof in Salt Water (initial pyrene concentration was ~100 µg/L)

Chapter Six

6   Conclusions

This research was conducted to analyze the sorption performance of active materials amended to clay minerals for the sequestration of contaminants within sediments. Separate batch sorption experiments were completed for both heavy metals and PAHs in fresh water and salt water environments. The results indicate that the amendments and combinations thereof would enhance the performance of an active sediment cap. The chemisorptive media proved to be the most effective amendment at removing heavy metals in both the fresh water and salt water environment. The powder activated carbon proved to be the most effective amendment for removal of PAHs in the fresh water environment and salt water environment. The combinations utilized in this research showed that there was no significant enhancement in the removal of contaminants. Future experiments will provide data to determine if these amendments react differently when heavy metals and PAHs exist on the same site. It should be noted a different type of organoclay may be utilized due to the current organoclay's poor performance with PAHs.   This research showed that in-situ sediment management strategies provide a viable alternative for contaminated areas where sediment removal technologies are cost prohibitive yet remediation is necessary.

Chapter Seven

7 Future Work

After analyzing the results obtained from this research, it is imperative that further

research be completed in the future to better predict the performance of an active

sediment cap with the amendments and amendment mixtures that were analyzed. To

better understand the effectiveness of these amendments and amendment mixtures

located at sites with multiple contaminants combined, contaminant studies with PAHs

and heavy metals should be performed. In addition, the concentrations of the

contaminants should be varied by either varying the concentration of the contaminants in

solution or the sorbent mass while temperature remains constant. This will provide the

capability of constructing either the Langmuir or Freundlich isotherms, which will better

estimate the distribution coefficient of each material. A greater number of experiments

would verify a more exact distribution coefficient as well and could pinpoint flaws in the

procedure that was used. This would determine how to modify the procedures and adjust

soil to solute ratios accordingly. While analyzing these amendments and amendment

mixtures is vital to determining the effectiveness of an active cap, the sorption affinity of

the polymer and the aggregate within the active cap should also be tested to determine

what kind of additional advantages or disadvantages occur. An active cap with the

addition of these amendments and amendment mixtures would reduce the hydraulic conductivity significantly. Therefore, hydraulic conductivity experiments of sediment caps with these amendments in place should be performed.

A variety of site conditions exist at locations where in situ sediment capping technology is being used. In some locations, the cap is being placed in very deep water. Regulators are skeptical if the amendments are staying bound to the particles during delivery as they settle through the water column. Settling tests should be performed for these materials to verify that the amendments are not dispersing away from the particles which would produce an ineffective cap. Finally, questions regarding potential for minimization of Methyl mercury (MeHg) formation and release should be addressed as it is a contaminant which is most easily bioaccumulated in organisms that live in sediments. Carrying out this research will provide great insight to the benefits of the addition of amendments to active sediment caps.

7.1 Cap Effectiveness

The results from this study can be used in conjunction with site specific information to evaluate cap effectiveness by calculating the time required for each contaminant to pass through the active layer containing each amendment or combination thereof. The time is calculated in years using a model developed by David Lampert and Dr. Danny Reible from the University of Texas (Lampert & Reible, 2009). This model is the most utilized in industry for active sediment capping and contains the following input properties: contaminant properties at the site, sediment and bioturbation layer properties at the site, active layer properties of the amendments being utilized, and conventional cap

properties. Evaluation is able to be completed for contaminants migrating through active sediment caps by both advective and diffusive processes in either a fresh water or salt water environment. Materials that have a high sorptive capacity can lead to longer breakthrough times with the potential to be longer than the expected lifetime of the contaminant. If this is the case, significant contaminant flux will not occur.

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