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Evaluation of Sorbing Amendments for In-situ Remediation of Contaminated Sediments

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Evaluation of Sorbing Amendments for In-situ Remediation of Contaminated Sediments

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Dedication

To my parents, Tasneem and Azhar Yaseen

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Evaluation of Sorbing Amendments for In-situ Remediation of Contaminated Sediments

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Contaminated effluents reaching surface water bodies have led to accumulation of contaminants in sediments. The significance of contaminated sediments has increased as we have cleaned up effluents, often representing the primary human and ecological health risk remaining in surface waters. Contaminants such as polychlorinated-biphenyls (PCBs) and certain metals are bioaccumulative and reach high doses as they travel to higher trophic levels. Monitored natural attenuation and ex-situ treatment are often ineffective and uneconomical, and placing clean inert material over sediments as a cap is sometimes insufficient to adequately reduce risk so sorptive amendments are increasingly being considered to reduce the availability and mobility of contaminants.

Laboratory sorption tests with different contaminants and sorbents were conducted to screen potential sorbent materials. Contaminants used in these screening studies included hydrophobic organic and selected inorganic contaminants common to sediments and sorbents included five types of clays and four types of carbon based sorbents.

These screening studies were used as a basis to evaluate an in-situ adsorptive remedy for a particular site, the Manistique Harbor and River Superfund site in Michigan. Sorption capacity of five polychlorinated biphenyls (PCBs) on granular activated carbon (GAC) and organophilic clay (OMC) and the influence of natural organic matter (NOM) were evaluated. Results show that NOM fouling reduces performance of the GAC by about half an order of magnitude while having minimal effect on OMC. Measured performance of the sorbents was used to evaluate in-situ treatment and capping remedial designs under conditions of weak (1cm/yr) and rapid (1cm/day) upwelling flow. Amended capping where the cap material is mixed throughout a thick cap layer provides the best performance, followed by capping in a thin layer followed by use of amendments as an in situ treatment.

A Polanyi based adsorption prediction model was developed to predict GAC performance degradation by NOM that requires only micropore volume of GAC and physico-chemical properties of adsorbate for prediction. It accurately predicts adsorption even for a different type of GAC and different source of NOM. The results suggest that NOM-associated reduction of GAC micropore volume is a good indicator of the performance degradation associated with NOM.

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List of Acronyms

AC	 activated carbon
B[a]A	 benzo[a]anthracene
B[a]P	 benzo[a]pyrene
DOC	 dissolved organic carbon
DOM	 dissolved organic matter
EPA	 Environmental Protection Agency
F400	 Filtrasorb-400
GAC	 granular organic carbon
GC-µECD	 gas chromatography with micro electron capture detector
HOC	 hydrophobic organic contaminant
HPLC	 high performance liquid chromatography
MHR	 Manistique Harbor and River
NAPL	 non-aqueous phase liquid
OMC	 organophilic clay
РАН	 polycyclic aromatic hydrocarbon
PCB	 polychlorinated biphenyl
PDM	 Polanyi-Dubinin-Manes
PDMS	 polydimethylsiloxane
SRL	 Suwannee River Low DOC
SRH	 Suwannee River High DOC
SUVA	 specific ultra-violet absorbance
TOC	 total organic carbon

Chapter 1: Introduction

1.1 OVERVIEW

Contaminated effluents from industrial, mining, agricultural and other operations have been released directly into water bodies or have eventually found their way to surface water bodies due to surface runoff. Since much of this contamination does not naturally exist in these ecosystems or represents persistent recalcitrant compounds, the natural processes in these environments are not able to degrade the chemicals effectively or quickly enough to prevent accumulation in the system. Several decades of such releases have led to accumulation of pollutants in sediments as well as organisms and biota. This leads to introduction of these contaminants into the food chain which poses human health hazards along with ecological impacts. Management of these sediments is difficult due to their areal extent, volume and cost and consequences of removal. This has encouraged the development of in-situ management approaches. In-situ management of contaminated sediments has significant advantages over more invasive means of sediment remediation. One particular promising approach is to use sorptive amendments. Sorptive treatment is the addition of reagents or amendments to contain or sequester contaminants to reduce their availability and mobility. This may involve application of the sorbent to the surface layer of a sediment or mixing of the amendment within a sediment cap, a clean substrate placed on top of the sediments. While both approaches are in-situ management approaches, the former is often termed in-situ sediment treatment while the latter is termed amended or active capping. For the purpose of this dissertation these will be collectively referred to as in-situ management techniques. These approaches have the advantage of being able to potentially meet remedial goals faster and

also exhibits greater public acceptance than simple containment solutions such as sand capping.

Carbon amendments including activated carbon, black carbon, charcoal, biochars, and coke are the most common sorbent materials used for treatment of sediments with hydrocarbon contamination. Activated carbon (AC) has the greatest capacity for organic sorption and small amounts can substantially reduce bioavailable contaminants in sediments by removing contaminants from the dissolved phase onto its surface via adsorption. When applied to contaminated sediments, AC can eliminate the flux of contaminants to the surface for long periods of time, well beyond the expected treatment design life in many cases. AC amendments are most suitable for hydrophobic organics such as polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dioxins and pesticides. Organophilic clay is another promising sorbent material that has the ability to treat hydrophobic organic contaminants. It exhibits lower sorption potential for dissolved organics but can retain substantial amounts of non-aqueous phase liquid (NAPL). Herein, we will focus on its sorbing characteristics in the presence of dissolved contaminants because it might be employed when NAPL is suspected or present only in small areas and the capability for dissolved sorption may still be desirable.

While the sorption of individual contaminants on these sorbent materials is relatively simple and well-understood, in a sediment environment there is exposure to potentially competitive compounds and substantial natural organic matter (NOM). Sediments exhibit higher concentrations and more complex NOM than surface waters and the contaminants of concern are typically highly hydrophobic PAHs and PCBs. There have been few studies evaluating the effect of NOM on sorbent performance and particularly lacking is the ability to predict the degradation in performance in the presence of NOM.

1.2 RESEARCH OBJECTIVES AND DISSERTATION OUTLINE

This research aims to explore the efficacy of sorptive amendments as an in-situ sediment remediation technique. Chapter 2 reviews relevant literature and chapters 3 to 6 address the following objectives:

- Assess sorptive treatment as a sediment remedial technique (Chapter 3)
- Screen different sorbent materials for sorption of organic and inorganic contaminants at actual contaminated sediment sites (Chapter 3)
- Determine comparative performance of activated carbon and organophilic clay, as the most promising commercially available sorptive amendment materials, for in-situ sediment management at a specific contaminated sediment site in Manistique Harbor in Michigan (Chapter 4)
- Evaluate the reduction in sorption capacity for both sorbents in the presence of NOM from the site (Chapter 4)
- Predict performance of selected remedial implementations of the sorbents at the site (Chapter 4)
- Demonstrate the applicability of Polanyi model to predict sorption of highly hydrophobic organic compounds such as PCBs onto GAC (Chapter 5)
- Examine competitive multi-contaminant sorption onto GAC from pore waters with two types of NOM (Chapter 5)
- Incorporate fouling effects of NOM into the Polanyi adsorption model to develop a predictive model of NOM-associated performance degradation of GAC (Chapter 5)

Conclusions and recommendations for future work are discussed in Chapter 6.

Chapter 2: Literature Review

2.1 CONTAMINATED SEDIMENT REMEDIATION

Contaminated effluents from industrial, mining, agricultural and other operations have led to accumulation of pollutants in sediments as well as organisms and biota. Remediation efforts to treat contaminated sediments were started in the 1960s (Renholds, 1998), well before comprehensive understanding of sediments acting as a sink for persistent pollutants such as PCBs and dioxins was developed. Conventional sediment remediation techniques include monitored natural attenuation, dredging, in situ stabilization techniques, and capping. In the past the primary treatment technique used for remediation at contaminated sediment sites was dredging, followed by treatment or disposal of the sediment. This has several disadvantages that include resuspension, residuals and higher cost. In-situ sorptive management of sediments is an attractive alternative and has been gaining more momentum in the last decade. Sorptive amendments are often more cost effective and can be implemented more quickly than removal options, and often exhibit fewer social impacts because of reduced risk to workers and neighboring communities. However, currently the technology has limited field applications and most in-situ techniques are still being researched on a laboratory scale so the long-term success of this technology is unknown.

2.2 IN-SITU REMEDIATION OF SEDIMENTS

In-situ sediment treatment refers to changes that can be made to stabilize contaminated sediments in a number of ways which usually involve applying an amendment to the surface of sediments with or without a diluent capping media, or injecting or mechanically mixing it within with the sediments. In-situ stabilization may include physical, chemical, and/or biological methods which are to be discussed herein.

In-situ techniques are designed to target freely dissolved contaminant concentrations thus limit the mobility and bioavailability of these compounds. In-situ sediment remediation has arisen as an alternative to existing monitored natural recovery (MNR) and enhanced monitored natural recovery (EMNR) techniques. In-situ management can prove to be an attractive solution in cases where MNR/EMNR may not be able to reach targeted criteria. In some cases in-situ management may be applied at sites to treat residual contamination after large scale dredging operations. It is important to fully understand the chemistry at the site because occurrence of undesirable chemical reactions is possible due to the application of such in-situ techniques (Ancheta, 1997).

It is also of importance to note that in-situ management provides options for achieving substantial benefits and remediation goals while minimizing the impacts of a more invasive remedial technique such as dredging or capping. In-situ remediation has fewer environmental, economic and social impacts. These exhibit less energy and emission intensity, fewer economic impacts due to cost effectiveness and faster completion times, and fewer social impacts because of reduced risk to workers and neighboring communities.

2.3 ADVANTAGES AND LIMITATIONS OF IN-SITU MANAGEMENT

In-situ management of sediments has the advantage of being low impact in comparison to invasive techniques such as dredging. It can lead to faster cleanup times compared to MNR and have similar advantages of being a low impact technique providing minimum disturbance to site conditions. Some in-situ technologies deliver treatment amendments in a low-impact manner and do not result in the same scale of impacts as dredging. Physical characteristics of the deeper sediments are usually left unaltered with such treatment technologies. In-situ management reduces the risk of exposure to workers as well as surrounding communities compared to dredging. Other benefits include reduced energy consumption and emissions. The benthic community may be minimally affected by the low intensity remedy, particularly in the case of an amendment incorporated directly into the sediments (e.g. versus capping with a thick layer of inert material).

Economic benefits also play a key role in the selection of in-situ management technologies as in-situ techniques are generally more cost-effective. In-situ management can also mean that the site operations can be completed in a relatively short time thus allowing affected local businesses to resume their own operations and services sooner.

The biggest limitation of in-situ management is that the long term effectiveness of these techniques has not been verified. In-situ management requires making changes to the physical, chemical and/or biological conditions of the site and the effects of doing so need to be fully understood before selection of a particular in-situ technology. Whether an amendment treats by sorbing on to its surface or by chemically reacting with the contaminants its ability to maintain this may become compromised with time. Amendments such as activated carbon may lose their ability to sorb due to fouling at the site. Allowance may need to be made for subsequent addition of more amendment material once initial amendments are exhausted. There are also concerns about the effectiveness of in-situ management in the natural environment. It is toward this latter concern that much of this dissertation is devoted.

Since in-situ management focuses mainly on surficial sediments the deeper sediments remain unaffected. This is usually not a big concern unless the deeper sediments act as a continuous source that may overwhelm the treatment amendment or unless erosive conditions will lead to exposure of the deeper sediments. Treatment efficacy is also governed by how well the contaminant comes into contact with the amendment. This requires suitable degrees of mixing or application to ensure relatively uniform vertical and spatial distribution of an amendment. Improper and non-uniform application of an amendment may lead to greater removal in areas with higher amendment dose and little or no removal/containment in areas with smaller doses.

2.4 Types of In-situ management methods

In-situ management of contaminated sediments can be achieved by biological, chemical or physical remedies. To better describe these types the following list has been developed (ITRC, 2014):

i. Biological

Biological in-situ management works on the principal that microorganisms can degrade organic contaminants. Biological techniques include the following types:

- Bioaugmentation addition of microbial cultures directly to the surface or into the sediments to initiate and/or enhance biological degradation of contaminants
- Biostimulation addition of chemicals to enhance biodegradation by indigenous microorganisms e.g. addition of oxidative chemicals to enhance aerobic biodegradation
- Inhibition addition of amendments that inhibit the microbial transformations of existing contaminants into more toxic forms (e.g. methylated mercury)
- ii. Chemical

Chemical treatment utilizes chemicals to neutralize, precipitate, or transform contaminants. This may include the following:

• Transformation – addition of chemical admixtures to transform existing contaminants to a less toxic or bioavailable form.

- Degradation addition of chemical admixtures that lead to degradation or decomposition of existing contaminant to less toxic or bioavailable forms.
- iii. Physical

Physical treatment techniques act to contain or immobilize the contaminants. Two common physical techniques include:

- Sequestration addition of materials (e.g., activated carbon, apatite, and organophilic clay) that physically adsorb or absorb contaminants reducing their bioavailability (e.g. HOCs) or ability to transform to more toxic components (e.g. mercury)
- Immobilization (solidification/stabilization) addition of cements or pozzolanic materials that harden after application and form a solidified sediment mass reducing mobility and bioavailability of contaminants

2.5 APPLICATION OF IN-SITU AMENDMENTS

The in-situ remedies discussed above may be applied in different ways. Broadly speaking, in-situ remedial actions may be applied to the sediments either by placing the amendment on the sediment surface or by mixing the amendment within the upper layers of sediment. To maximize the benefits of the amendment, it is normally desirable to mix the amendment through the biologically active zone of the sediments or in combination with isolating the contaminants below the biologically active zone. This can be accomplished by burial of sorbents (with a cap), mixing within the surficial sediments or by surface application and allowing bioturbation and the normal reworking activities of organisms to mix amendments into the sediments. Placement at the sediment surface is generally easier and less disruptive to the sediment but leaves the amendment exposed for

potential erosion and loss until natural processes (such as bioturbation) can mix the amendment over the desired layer.

i. Placement on surface

Placing an amendment on top of surficial sediments can be done in two ways. Amendments can be applied at the top or in the water column and allowed to settle to the bottom (if of sufficient density). Alternatively, amendments can be applied directly to the sediment by broadcasting directly onto the sediment surface.

Common issues with this application technique include ensuring uniform, desired dosage to the treatment area while reducing losses to surrounding areas. Low density amendments such as activated carbon may be carried away by currents during or after settling to the sediment surface. Placement with a more dense diluent material may lead to differential settling and non-uniformities in the resulting placement. Amendments with significant pore structure such as activated carbon must be pre-wetted to drive out air and increase the settling density. Larger particle sizes generally contribute to effective settling and retention at the sediment surface although this may also decrease the ability to mix the amendment at fine scales. Activated carbon and other light amendments may also be incorporated into higher density aggregates (e.g. Sedimite or AquaGate), to aid in settling. The aggregates may be degraded or disintegrate upon placement to aid mixing of the amendment and reworking by benthic organisms may move the amendment more uniformly through the biologically active layer.

SediMite[™] is not a type of treatment but a low-impact delivery system designed specifically for in-situ application of treatment materials to the sediment. The selected treatment amendment is combined with a weighting agent with an inert binding agent. This amendment is then sprayed on to the surface of the water column and the weighting agent allows it to sink. Bioturbation by the benthic community is relied on as a

mechanism for mixing the amendment within the top layer of the sediment (Sedimite, 2010).

SediMite[™] is a low impact technology best suited for in-situ application of amendments such as AC to contaminated sediments. AC delivered via SediMite[™] has been proposed for use to treat sediments contaminated with PCBs, mercury, methylmercury, dioxins, furans, PAHs, DDT and other hydrophobic chemicals.



Figure 2.1: Application of AC using SediMite[™] using an air blown dispersal device over a PCB contaminated wetland near James River, VA in 2009 (Ghosh et al., 2011)

AquaGate[™] is an AquaBlok[™] patented low impact delivery system used for application of powdered activated carbon (PAC), organophilic clay or other sorbent material. It has a purpose similar to SediMite but incorporates a granular core to aid settling. It relies on gravity mixing due to density of the material. It has been used for application at sites with PCBs, PAHs, and pesticides to date. For example, AquaGate+Organophilic clay particles adsorb oil and a wide range of hydrocarbons when applied to sediments. AquaGate[™] allows for in-situ treatment to be applied to greater depths and higher energy surface water systems and may be used for freshwater as well as marine environments (AquaBlok, 2013).

ii. Mixing in surficial sediments

Amendments for in-situ treatment are also applied by mixing into the top layer of sediment, effectively achieving at time of placement what benthic organisms may do over time. This can be done mechanically (e.g. by using augers) or by simple settling of higher density amendments through low density surficial sediments. Mixing in the amendments can have advantages such as more uniform application (if done correctly) and setting up of a diffusive flux that prevents breakthrough of contaminants for longer periods of time (Ghosh et al., 2011).

iii. Injecting in surficial sediments

Amendments can also be injected into the top layer of sediment. Limnofix is an in-situ sediment treatment technology developed and patented by Environment Canada and licensed to Golder Associates. It is used to inject amendments into the sediments through a series of tines and nozzles on an injection boom. It is most commonly employed for the delivery of oxidative amendments such as calcium nitrate for biodegradation of PAHs, BTEX and TPH. It may be used for both freshwater and marine sediments. A schematic of Limnofix technology can be seen in the figure below (Golder-Associates, 2003).



Figure 2.2: Schematic of Limnofix In-situ sediment treatment system (Golder-Associates, 2003)

2.6 EVOLUTION OF ACTIVATED CARBON AS AN ADSORPTIVE AMENDMENT

Extensive research has been done on the use of carbons as an amendment and it has widespread application as an adsorptive material in fields beyond sediment remediation as well (e.g. water and wastewater treatment). A study by Ghosh et al. (2003) documents that PAHs and PCBs more strongly sorb to the carbonaceous sediment fractions or black carbon than inorganic particles or natural organic matter. Black carbon is a condensed phase sediment carbon that is normally formed by high temperature combustion processes and has deposited and settled into the sediments. It exhibits a higher sorption capacity than natural amorphous vegetative matter but is present in many sediments. As a result, a majority of the hydrophobic chemicals present in sediments are associated with char, charcoal, soot and coal derived forms of carbon present in sediments (Ghosh et al., 2003). Several other studies reinforce the importance of soot or black carbon in the adsorption of PAHs (Accardi-Dey & Gschwend, 2002; Gustafsson & Gschwend, 1997) and discuss the effects of compound planarity on adsorption to black carbon (Cornelissen et al., 2004; Cornelissen et al., 2005). This adsorption to black carbon reduces bioavailability of PAHs and PCBs thus restricting the routes and magnitude of exposure (Ghosh et al., 2000; Ghosh et al., 2003). Other studies confirming that bioavailability of hydrophobic organic contaminants (HOCs) is reduced due to sorption onto carbonaceous particles also indicate the slower release of HOCs bound to carbonaceous fractions of sediments (Kraaij et al., 2001; Talley et al., 2002).

The effect of black carbon in sediments can be enhanced by introducing activated carbon (AC) into the sediment as a treatment. Activated is generally a stronger sorbent than black carbon and this is needed to out-compete the black carbon. Several studies performed sorption studies and determined partition coefficients for HOC sorption to AC (McDonough et al., 2008; Walters & Luthy, 1984). The strong sorption of HOCs onto AC makes the material an effective sediment treatment amendment if it can be introduced and retained in sediments. AC adsorbs and binds the freely available HOCs and thus reduces their mobility and bioavailability. Several studies have successfully demonstrated this use of AC as an effective adsorptive material for reducing HOC bioavailability (McLeod et al., 2007; Millward et al., 2005; Tomaszewski et al., 2007; Zimmerman et al, 2004). McLeod et al. (2007), Zimmerman et al. (2004) and Millward et al. (2005) all showed that adding AC in amounts equal to or greater than the natural organic matter in the sediment leads to 90% or greater reductions in PCBs, PAHs and DDTs in freely dissolved phase in the interstitial water and in body burdens of bioaccumulating benthic organisms.

The particle size and dose of activated carbon plays a key role in reduction of HOC bioavailability. Zimmerman et al. (2005) investigated the effects of AC dose and

particle size on aqueous PCB and PAH concentrations and their bioaccumulation. The study confirmed that increasing the dose of AC mixed with contaminated sediment substantially decreases aqueous PCB and PAH concentrations (see Figure 2.3). *Neanthes arenaceodentata* and *Leptocheirus plumulosus* showed 93 and 90% reduction in biouptake of PCBs, respectively, with 3.4% activated carbon. This dose response of PCB biouptake can be seen in Figure 2.4. A direct relationship was also seen with the particle size of AC (Figure 2.5), and the study confirmed that greater reduction in PCB concentrations can be achieved by decreasing the particle size and thus increasing the external surface area of the sorbent. This finding was in line with previous studies (Lebo et al., 2003; Lebo et al., 2000), which showed that the external surface area of the activated carbon can be more important than source of the carbon for contaminant uptake when equilibrium has not been reached. Lebo et al. studies had compared two size fractions of a synthetic activated carbon with same size fractions of coconut charcoal.



Figure 2.3: Aqueous polychlorinated biphenyl (PCB) (a) and polycyclic aromatic hydrocarbon (PAH) (b) concentrations for Hunters Point (San Francisco Bay, CA, USA) sediment contacted with varying doses of activated carbon for one month. The activated carbon is coarse (75–300 mm) type TOG. (Zimmerman et al., 2005)



Figure 2.4: Polychlorinated biphenyl (PCB) bioaccumulation by *N. arenaceodentata* and *L. plumulosus* during 56 day exposure tests. Sediment was contacted for one month with varying doses of 75 to 300 mm type TOG carbon before the bioaccumulation tests. (Zimmerman et al., 2005)



Figure 2.5: Aqueous polychlorinated biphenyl (PCB) concentrations for Hunters Point (San Francisco Bay, CA, USA) sediment contacted with varying sizes of TOG and F400 carbon for one month. (Zimmerman et al., 2005)

The studies mentioned above explore the effects of mixing AC directly into contaminated sediments. Field scale application of these mixing techniques have been successfully implemented at Hunters Point (Cho et al., 2009) and Grasse River (Beckingham & Ghosh, 2011). Others have explored the effectiveness of applying AC as a thin layer in-situ cap (Cornelissen et al., 2012; Cornelissen et al., 2011). The pilot studies by Cornelissen et al. looked at application of AC as a thin layer cap for in-situ management of PAH and polychlorinated dibenzodioxin and dibenzofuran (PCDD/F) contaminated sediments. The pilot study done in PAH contaminated sediments at Trondheim Harbor, Norway (Cornelissen et al., 2011) explored the application of thin layer caps of AC, AC+clay, AC+sand and sand only. AC + clay gave the strongest reductions in PAH pore water concentrations and PAH flux to the water column. These reductions in flux can be seen in Figure 2.6 below.


Figure 2.6: The in situ measured sediment-to-water flux for total PAH-11 (the 16 EPA-PAHs excluding naphthalene, acenaphthene, acenaphthylene, phenanthrene, and dibenz[a,h]anthracene), absolute fluxes (upper panel) and fluxes relative to the reference field ("REF"- lower panel), with standard deviations in duplicates or triplicates. Measurements generally lasted approximately three months, and were done 0–3, 4–7, and 9–12 months after field establishment. Some chambers for the period 0–3months were out for only 1–2months for practical reasons; however, fluxes were always normalized for exposure time (by dividing through the days of exposure) and therefore comparable. (Cornelissen et al., 2011)

The effects of AC treatment on pore water concentrations of total PAHs, Benzo[a]pyrene and pyrene for the AC+clay application can be seen in Figure 2.7. The reductions in pore water concentrations are clearly visible from the figure but the reduction observed is about 50% (with a high AC dose of 30 to 40%), which is much less than the 80% reduction observed at Hunter's Point (Cho et al., 2009) where a smaller amount of AC was mixed into the surficial sediments. This lower reduction has been attributed to slower mass transfer due to no initial mixing (Ghosh et al., 2011) indicating the importance of good mixing of the amendment in the sediment. The limited reduction in pore water concentration may also be due to the very thin capping layer (5 cm or less) which may lead to bioturbation-induced mixing with the underlying contaminated sediment. Bioturbation is the normal life-cycle mixing activities of benthic organisms.



Figure 2.7: Pore water PAH concentration profiles, determined by POM-17 passive samplers mounted on a rod and directly inserted into the sediment, and presented as (i) the ratio between CPW in the AC+clay field and CPW in the reference field, with standard deviations in duplicate or triplicate measurements (duplicates where POM-17 got lost during exposure), and (ii) absolute pore water concentrations. Ratios are shown to be able to present the different compounds in one figure and to correct for concentration variations with depth in the reference field. Negative depth: pore water concentration in the sediment; positive depth: concentration above the sediment surface. The AC was present in the 0 to 5 cm layer where concentrations were lowest compared to the reference. (Cornelissen et al., 2011)

Long-term efficacy of AC as an in-situ management has also been studied by evaluating the effects of aging AC (Oen et al., 2012). The study evaluates differences in sorption characteristics of fresh AC and AC aged by exposing to field sediment having different concentrations of NOM. AC amendments aged in the field for 12–32 months still managed to achieve significant pore water reductions in native HOC concentrations (30–95% reduction) and spiked HOC concentrations (10–90% reduction) in comparison to unamended sediment. AC–water distribution coefficients, KAC for field-aged AC were a factor of 10 lower than freshly added AC for spiked HOCs but the effect was less dramatic for native HOCs. The study demonstrates that AC can still be an effective adsorptive material after some years of field application but additional long term investigation is necessary to conclusively declare the long term efficacy of AC amendments in field (Oen et al., 2012).

2.7 ORGANOPHILIC CLAY AMENDMENTS

Organophilic clays (OMC) are clays (typically sodium bentonite) in which the sodium has been cation exchanged with organic quaternary amines. By using amines with long organic chains, the clay can be rendered organophilic rather than hydrophilic. Organophilic clays have a dramatically increased sorption capacity for nonpolar organic contaminants compared to natural clays (Smith et al., 1990). The clays can also be treated with chelating agents that increase their ability to absorb metals rather than HOCs.

Organophilic clays can have long chain and short chain molecular structures based on the structure of the organic amine being substituted in place of the clay's natural cation. Short chain organophilic clays are more suited for sorption of organic contaminants with lower hydrophobicity and long chain organophilic clays exhibit better sorption of more hydrophobic organic compounds (Dunlap, 2011).

The sorption of dissolved organics on organophilic clays appears to proceed via absorption rather than adsorption as with activated carbon. The organophilic clays also have a substantial affinity for organic phases, i.e. nonaqueous phase liquids (NAPLs), however far exceeding the capability of AC to absorb such phases. Thus organophilic clays are most effectively used for sites containing NAPL.

Studies have shown oganophilic clay sorption of dissolved HOCs to be less than GAC however they still have a reasonable ability to sorb dissolved organic comntaminants. For example, Knox, et al. (2008) measured sorption capacities for commercially available organophilic clays with various PAHs including phenanthrene (K_d =50-70 mL/g), pyrene(K_d =400–450 mL/g), and benzo(a)pyrene (K_d =3000-3500 mL/g). Even though organophilic clays are less sorptive than activated carbon for treatment of dissolved hydrophobic organic contaminants their ability to treat contaminants in NAPL form and to act as a barrier against NAPL advection makes it an attractive choice for an in-situ amendment (Lee et al., 2012). They may also be used where NAPL is suspected or present in small areas and thus the sorption of dissolved contaminants may still be of interest. Other studies looked at sorptive removal of lower molecular weight hydrophobic organics by organophilic clays in the presence of larger, relatively hydrophilic organic compounds such as tannic acid (Dentel, Bottero et al. 1995, Dentel, Jamrah et al. 1998).

2.8 COMPETITIVE EFFECTS OF NATURAL ORGANIC MATTER

The presence of natural organic matter (NOM) is an impediment for adsorption because it competes with the target contaminant or chemicals at active adsorption sites, particular for activated carbon. This competition effect may occur at the surface or by blocking of internal pores (Carter et al., 1992; Dentel et al., 1998; Hand et al., 1989). Natural organic matter consists of humic substances, hydrophilic acids, carbohydrates, carboxylic acids, amino acids and hydrocarbon. It is present in all surface and ground waters with total organic carbon (TOC) concentrations varying from 0.5 mg/L to 12 mg/L (Thurman, 1985). Dissolved organic carbon (DOC) concentration (TOC in water filtered through a 0.45 μ m filter) in sediment pore waters can be even greater (10-100 mg/L), hence their impact on in-situ sorbents may be substantial.

Reduced sorption effects due to the presence of NOM have been studied by many but in most cases the NOM is treated as a bulk adsorbate competing for adsorption sites. The effects of pore size distribution have been well characterized as described already but the effect of the variable size of NOM molecules still needs further examination. The mechanism of NOM adsorption onto AC is closely related with the surface and size characteristics of the adsorbent but little quantifiable data exists for the variation of these effects with varying NOM molecule sizes.

NOM varies not only in concentration but in molecular weight and size. Sizes of DOM have been recorded to range from 4 to 40 angstroms (Karanfil et al., 1999) while majority of GAC surface area is present in pores less than 20 angstroms in size (Fairey et al., 2006; Karanfil et al., 1999). The size of NOM molecules is important because it governs the mechanism by which it competes with target contaminants. If the NOM molecules are of comparable size to the contaminant molecules they will compete for the same sorption sites on the activated carbon surface. This reduces the number of active sites available for the adsorption of the contaminant which will lead to a reduced adsorptive capacity of the contaminants and lower partitioning coefficients (Carter et al., 1992). The severity of this direct competition for sites depends on the characteristics of NOM (Dentel et al., 1998; Najm et al., 1990), properties of sorbent (Ding et al., 2008; Fairey et al., 2006; Quinlivan et al., 2005), and initial concentrations of NOM and contaminants relative to each other (Najm et al., 1991; Wang, 2005).

If the NOM molecules are larger the dominant mechanism is pore blockage of the carbon which affects the kinetics of contaminant adsorption and also reduces adsorption capacity (Carter et al., 1992; Ding et al., 2008; Fairey et al., 2010; Matsui et al., 2003). This effect is more pronounced with pre-loading where the sorbent has been in contact with NOM loaded water before exposure to contaminants (Li et al., 2003; Najm et al., 1990). Other than pre-loading, pore blockage effect also depends on the pore size distribution (PSD) of the carbon (Ding et al., 2008). While PSD influences competitive adsorption it also has a role in non-competitive adsorption due to different adsorption capacities of different sized sorbents.

These competitive effects have been primarily observed in activated carbon where they combine to produce fouling. While most of these studies have been carried out in the sphere of water treatment, competitive effects due to the presence of NOM also have undesirable implications for sorptive treatment of sediments, particularly due to the higher concentrations of contaminants and NOM observed in sediment pore waters. Increasing use of activated carbon amendments for adsorptive treatment of sediments means greater focus needs to be brought on the fouling effects of activated carbon used in sediments. While these effects have been studied in great lengths for water treatment and even groundwater systems, they have yet to be quantified for sediments. Preliminary studies done by McDonough et al. (2008) and Fairey et al. (2010) have shown that the presence of NOM in the background causes fouling of activated carbon by both the mechanisms mentioned above. The degree and extent of these effects need to be quantified along with a more in depth analysis of the effects of fouling on sorption kinetics.

2.9 PERFORMANCE PREDICTION MODELS

Evaluation and design of sediment treatment techniques involving the use of AC as an adsorptive amendment requires modeling to predict the performance of AC in the

system. A few of these models will be discussed herein to provide an overview of the performance modeling tools available and what they have to offer.

The Equilibrium Column Model (ECM) is a fixed bed adsorption model that looks at multicomponent competitive adsorption by ignoring mass transfer resistances and uses IAST to predict effects of competitive adsorption (Hand et al., 1985; Crittenden et al., 1987). The ECM model requires Freundlich parameters for the components present in the system which again makes it unable to incorporate the effects of NOM. Its ability to accurately predict practical performance of AC is limited due to mass transfer limitations being ignored and it can only predict the lowest carbon usage rate and the highest possible effluent concentrations. In general equilibrium models can be used for sediments because the transport is slow whereas dynamic models are required for effluent treatment conditions because of the short contact time.

E. H. Smith and Weber (1988) developed a model to simulate and predict AC performance in fixed bed reactors. Their model was based on a modified homogeneous surface diffusion version of the Michigan Adsorption Design and Applications Model (MADAM) initially developed by Crittenden and Weber (1978). The model used equilibrium and kinetic coefficients obtained from bench-scale laboratory experiments for a particular landfill leachate site. They incorporated the effects of background DOM by employing coefficients determined experimentally and this made the model system specific to site conditions. Further investigations using carbons with variable particle sizes were proposed but MADAM has since been replaced by later developments to the Crittenden model.

A subsequent improved model of activated carbon performance prediction for the design of fixed bed reactors was developed by Crittenden et al.(1987). This Pore and Surface Diffusion Model (PSDM) incorporates kinetic and equilibrium parameters and

suggests correlations to determine mass transfer parameters based on single-solute isotherms. Due to the method being based on the use of single-solute isotherms its prediction capabilities are greatly hindered by large fluctuations of competing organic compounds in the influent. Its development is intrinsically based on calibration and verification for one particular treatment plant. Introduction of high concentrations of large hydrophobic compounds and large DOM would greatly affect its performance prediction capabilities.

This PSDM model is one of the models used in the Adsorption Design Software (AdDesignSTM) developed at Michigan Technological University by Crittenden, Hand et al for predicting the performance of fixed-bed granular activated carbon adsorbers. It uses Polanyi theory to correlate single component isotherm data using molar volume as a normalization factor which will be discussed in detail in later sections of this dissertation. Freundlich isotherm equation is used to describe adsorption equilibrium of individual compounds and Ideal Absorbed Solution Theory (IAST) describes competition between compounds. It incorporates the effects of AC fouling on adsorption equilibrium by using empirical equations for fouled Freundlich K values based on NOM adsorption studies done by Sontheimer, Crittenden, and Summers (1988), Hand et al. (1989), El-Behlil (1990) and Bhuvendralingam (1992). The software relies on an extensive database associated with the program but these empirical equations for fouled Freundlich K values are based on NOM adsorption of a limited number of surface and ground waters which generally have lower NOM concentrations than in surficial sediment pore waters. The model is developed for and verified using fixed-bed adsorption in water treatment plants and based on small moderately hydrophobic molecules.

Dynamic models are also needed to describe the dynamic response of sediment in which amendments are introduced. These dynamic models focus on inter-particle

transport limitations while equilibrium models assume these are negligible. Figure 2.8 shows a conceptual diagram for a model of HOC sorption onto AC developed by Werner, Ghosh, and Luthy (2006) which is used to demonstrate release of PCBs from sediment, sorption to AC and resulting aqueous concentrations in the presence of passive samplers or semi permeable membrane devices (SPMDs). Each domain shown in the figure (light and heavy sediment particles and AC) is represented by a geometric mean grain radius, solid density, and porosity. Linear partitioning is assumed between the surface of each particle type and the external aqueous PCB concentration. The movement of PCBs in or out of the different particles is described due to intraparticle diffusion with a concentration-independent apparent diffusion coefficient (Wu & Gschwend, 1988). For each time step, the amount of PCBs diffusing out of the sediment particles and into the AC are calculated from the PCB concentration gradients within the different particle types, and the amount exchanged with an SPMD (if present) and amount degraded is also calculated.



Figure 2.8: Five domains of the model: Light, low-density sediment particles; heavy, high-density sediment particles; AC particles; semipermeable membrane device (SPMD); and external aqueous phase. Each particle type is represented by a mean particle size (geometric mean); the surface of each particle type is in linear partitioning equilibrium with the external aqueous phase; and the movement of compounds in to and out of particles is described by apparent diffusivities. The contaminant uptake by SPMDs is described by first-order mass transfer kinetics. A first-order rate accounts for degradation in the external aqueous phase. (Werner et al., 2006)

Werner et al. (2006) model results were compared with experimental results from AC treatment of Hunters Point and Lake Hartwell sediments. The comparison of modeled and experimental aqueous and SPMD PCB concentrations showed that the model systematically under-predicts the aqueous and SPMD concentrations. Better understanding and incorporation of sorption kinetics and field conditions into the model need to be achieved for improved accuracy of predictions (Werner et al., 2006).

The Weber and Crittenden models discussed here focus on both equilibrium and kinetics of sorption because they are developed to predict performance of AC in fixed bed systems used in water treatment where the empty bed contact time is a key parameter of design. In case of sediments the kinetics may not be of great importance due to the long contact times and design lifetimes for the in-situ remedies (e.g. decades) hence the assumption of equilibrium may be valid. Also, the models discussed used equilibrium sorption parameters obtained experimentally for the system being studied in each case. This means that the sorption parameters obtained incorporate the effects of background NOM into the model but the model requires that data as inputs to be experimentally or previously determined. The use of experimentally determined isotherm parameters makes the model system specific and does not allow for effects of NOM to be intrinsically included in the model. For these reasons the use of the Polanyi model could prove to offer an alternative approach for AC performance prediction based on the assumption that equilibrium has been reached.

2.10 POLANYI-DUBININ-MANES MODEL

For performance prediction of activated carbon or any adsorbent it is important to be able to predict the adsorption capacities based on just the physical and chemical properties of adsorbents and contaminants/adsorbates. The Polanyi theory provides such a modeling tool for the prediction of adsorption for different adsorbent-adsorbate combinations. The Polanyi theory was initially developed for activated carbon adsorption of gases and was further developed by Dubinin and extended by Manes (1998) to describe adsorption from aqueous solutions. Due to the use of the developments made by all three authors it is sometimes referred to as Polanyi-Dubinin-Manes (PDM) model. The PDM theory assumes that a fixed adsorption space (micropore volume) is present and a molecule in this space will have an adsorption potential, ε , which is the energy required to move the molecule from the adsorption space to a point outside the attractive force field of the adsorbent. All points at an equal distance from the surface of the adsorbent will have an equal potential ε and the volume of an adsorbate will be a function of adsorption potential. A curve of liquid adsorbate volume against equilibrium adsorption will be temperature independent and depends on the structure of the carbon. This curve is called a 'characteristic curve' and it can eventually be used to predict adsorption isotherms for a different set of conditions (Manes, 1998).

Polanyi never suggested a theoretical equation for a characteristic curve but Dubinin later suggested that by plotting adsorbate volume against adsorption potential density (i.e. ratio of adsorption potential to adsorbate molar volume) different adsorbates would result in similar characteristic curves. Crittenden, Hand, et al. (1987) showed that this could be mathematically represented by the following equation:

$$logq_{v} = logQ_{v} + a \left(\frac{\varepsilon_{sw}}{V_{m}}\right)^{b}$$

Where qv is the adsorbed solute volume per unit mass of adsorbent (cm³/g), Qv is the adsorption volume capacity at saturation (cm³/g), Vm is the molar volume of solute (cm3/mol), a and b are fitting parameters, and ε sw is effective adsorption potential (kJ/mol). This is often referred to as the PDM equation and chi-squared tests are used to validate the results (Xu et al., 2008).

For the adsorption of organic contaminants from water the adsorption potential is given by (Manes, 1998):

$$\varepsilon_{sw} = RTln\left(\frac{C_s}{C}\right)$$

Where ε_{sw} is the effective adsorption potential in water, Cs and C are saturation and bulk concentrations respectively at temperature, T and R is the universal gas constant.

The Polanyi model is based on the following main assumptions (Manes, 1998):

- adsorption potential of a molecule is a function of its distance from the adsorbent surface
- adsorption potential is independent of temperature
- adsorption potential of a molecule is independent of its state of aggregation

Two supplementary assumptions of the theory suggest that (1) all adsorption space is accessible to adsorbate molecules, and (2) molar volume is the best normalizing factor, so characteristic curves for different adsorbates on a given adsorbent would result in a single curve (Manes, 1998). Using these assumptions it would be possible to predict the adsorption capacities of different contaminants by obtaining a characteristic curve of one of the compounds' adsorption on a specific activated carbon.

The PDM model has also been used to predict the adsorption of organic compounds on polymeric adsorbents (Long et al., 2008; Xu et al., 2008). The study by Xu et al. demonstrated the application of Polanyi potential theory to phthalate adsorption with two polymer resins and an activated carbon. Experimental results from sorption experiments for dimethyl phthalate (DMP) were successfully used to develop a Polanyi characteristic curve for each of the sorbents. Since the PDM model considers adsorption as a physical process the parameters obtained from the DMP Polanyi isotherms was used to predict diethyl phthalate (DEP) adsorption for the three sorbents. Predicted DEP adsorption performance agreed reasonably well with experimental adsorption results and proved potential applicability for performance predictions in the field (Xu et al., 2008).

Long et al. looked at naphthalene adsorption onto three different polymeric adsorbents and successfully demonstrated that a single correlation curve for naphthalene adsorption can be obtained for all three polymeric sorbents by normalizing with micropore volume. However the study only looked at naphthalene adsorption and other higher order organic compounds would need to be studied in order to establish the general applicability of this method in field predictions (Long et al., 2008). This study was supplemented with another study by the same group of authors which extended the findings to the adsorption of acenaphthene and fluorene. It looked at adjusting the normalizing factor to obtain a single characteristic curve for naphthalene, acenaphtene and fluorene thus demonstrating the potential to predict adsorption performance of one adsorbate from that of another adsorbate (Long et al., 2008). These studies present a basis for the development of the Polanyi model as a generalized performance prediction tool for porous adsorbents. While these studies illustrate the prediction capabilities of the Polanyi model they fail to address the competitive effects due to presence of competing organic contaminants or background NOM.

A study looking at the sorption of PAHs onto carbon nanotubes (Wang, 2005) evaluates the effects of three types of dissolved organic matter. Sorption of the individual DOMs led to comparable reductions in surface area as well as microporosity. This suggests that DOM was adsorbed by both surface adsorption and pore-blocking mechanisms. While this is the case for carbon nanotubes it may not be the case for granular or powdered activated carbon and further study of DOM sorption onto activated carbon is required. The DOM sorption reduced the sorption capacity of carbon nanotubes as was seen by the competitive adsorption experiments with PAHs. The study revealed that for the single characteristic curve achieved after normalizing could only be obtained for aromatic compounds having similar structure as established by others also (Crittenden

et al., 1999). It was also observed that the characteristic curves for similar structured aromatics were comparable for both virgin and DOM loaded sorbent (Wang, 2005).

Studies involving heavier PAHs and PCBs have looked at Polanyi adsorption onto anthracite based and biomass based AC (Amstaetter et al., 2012) and onto traffic soot and anthracite coal (Jantunen et al., 2010). Both these studies demonstrated that PCB adsorption with carbon based adsorbents can be defined using a PDM isotherm model. The PDM parameters did not differ significantly with changes in planarity of the PCBs (Jantunen et al., 2010) which can further support development of the PDM model as a performance prediction tool. Both these studies successfully demonstrated that the PDM model could be used to model PCB adsorption on carbon based adsorption. These results for experimentally obtained PDM adsorption isotherms for PCBs combined with the correct normalizing factors explored in other studies (Long, Li, Wu, et al., 2008; Wang, 2005; Xu et al., 2008) could be utilized to develop a PDM based AC performance prediction model.

Existing performance models are either unable to incorporate effects of NOM or require system specific NOM adsorption parameters. Due to its ability to collapse into a single characteristic curve for adsorption of different contaminants on a given adsorbent, the PDM model gives a promising alternative to provide a more generalized prediction method for AC performance. Detailed studies characterizing the competing effects of NOM need to be done and applied to the PDM model for prediction that is not site specific and is based only on physico-chemical properties of adsorbent and adsorbate.

2.11 SUMMARY

Contaminated effluents from industrial and mining operations flowing into surface water bodies have caused accumulation of harmful contaminants in sediments. Traditionally, the most common treatment technique used for remediation at contaminated sediment sites is dredging, followed by treatment or disposal of the sediment. Dredging is not only uneconomical due to excavation of large amounts of sediments, it also leads to resuspension into the water column and residual contamination. Due to these issues in-situ sorptive management of sediments is becoming a popular option for sediment remediation. Sorptive amendments are usually more economical and faster to implement. In-situ management also poses reduced risk to workers and neighboring communities because contaminated sediments are not removed physically.

However, sorptive in-situ management approaches for sediments currently have limited field applications and most in-situ techniques are still being investigated on a laboratory or pilot scale. Some of these studies for activated carbon and organophilic clays (OMC) have been discussed in this section. Along with the use of sorptive amendments for in-situ remediation in different pilot scale studies, this section also explores competitive effects in activated carbon adsorption due to natural organic matter (NOM) present at different sites. The various performance prediction models discussed look at both equilibrium and kinetics of sorption because they were developed for activated carbon in fixed bed reactors of water treatment systems where the empty bed contact time is a key parameter of design. Kinetics are not of the utmost importance in sediments due to long contact times and design lifetimes of in-situ remedies, thus the assumption of equilibrium for sediment systems is valid.

The models discussed use equilibrium sorption parameters obtained for the system being studied in each case as a means to incorporate the effects of background NOM into the model but that data is required as inputs and needs to be previously determined. This makes the models system specific and does not allow for effects of NOM to be intrinsically included in the model. For these reasons the use of the Polanyi

model could prove to offer an alternative approach for AC performance prediction based on the assumption that equilibrium has been reached. A Long et al., 2008 study shows that using micropore volume of adsorbent to normalize the PDM equation allows for a single correlation curve to be developed for different sorbents. Since NOM loading alters physical characteristics of activated carbon it may be possible to obtain a single correlation curve for fouled and unfouled activated carbon. This would provide a more generalized prediction method for activated carbon performance in the presence of NOM. However in order to achieve this detailed studies characterizing the competing effects of NOM need to be done and applied to the PDM model for prediction that is not site specific and is based only on physico-chemical properties of adsorbent and adsorbate.

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Chapter 3: Screening of Sorbing Amendments for Remediation of Contaminated Sediments

3.1 INTRODUCTION

The most common remediation technique utilized at contaminated sediment sites is dredging, usually accompanied with ex-situ treatment and/or disposal of the sediment. This can lead to resuspension of contaminated sediment, higher residuals and higher costs of treating the sediment off-site. In-situ management of sediments presents an alternative that is more cost effective and involves simpler operations (USEPA, 1994). This chapter discusses in-situ sediment remediation techniques with particular focus on sorptive amendments as an in-situ remedy.

Sorptive or sorbing amendments are materials that contain or sequester contaminants by adsorbing or absorbing the target chemical compound. These amendments reduce bioavailability and mobility by stabilizing sediments, isolating the contamination from the benthic community and by reducing flux to the water column. The objective of this study was to screen a variety of sorbents for their potential applicability to sediment remediation.

While anything from used tea bags to artificially generated nano-materials can be utilized as sorbing materials, this study focused on five types of clays and four types of carbon based sorbents for the sorption of some inorganic and organic contaminants. These sorbents and their respective properties are discussed below.

- i. Clays
 - CETCO Organoclay® PM-199 Commercially available organophilic clay (bentonite clay modified by cation exchange) obtained from CETCO
 - CETCO Organoclay® MRM Commercially available sulfur-impregnated macroporous organophilic clay obtained from CETCO

- Alumina pillared montmorillonite Montmorillonite clay synthesized with alumina "pillars" between clay layers
- Dimethyl Dioctadecyl Ammonium Modified Montmorillonite (DMDODA-MMT)
 laboratory produced organophilic clay not commercially available
- Kaolinite natural clay available abundantly
- ii. Carbon based sorbents
 - Calgon granular activated carbon (GAC) Granular activated carbon (TOG 20x50) commercially available from Calgon Carbon company
 - Iron-Palladium coated granular activated carbon GAC amended with nanoscale particles of bimetallic iron and palladium
 - Sulfur impregnated granular activated carbon (SIAC) Commercially available amended GAC
 - Rice husk char By-product of commercial harvesting of rice, used as low cost carbonaceous sorbent material

Rice husk char has a structure similar to green algae and has shown to be a low cost but effective sorbent for heavy metals, specifically having high adsorption capacities for chromium (Roy et al., 1993). Coal based granular activated carbon is a commonly used carbonaceous sorbent used in contaminated sediment treatment (Walters & Luthy, 1984; Werner et al., 2006) and the TOG 20x50 was chosen as it has been studied previously (McDonough et al., 2008) thus allowing a fair comparison. Iron-palladium and sulfur impregnated activated carbons are modifications to conventional GAC developed specifically to achieve greater adsorption of heavy metals compared to conventional GAC (Korpiel & Vidic, 1997; Choi et al., 2008) and are gaining more popularity. These four carbon based sorbents were chosen as a mix of emerging, low-cost and commonly used sorbents for comparison of adsorption capacities.

Natural clays are normally used for their ability to adsorb heavy metals due to their high cation exchange capacity but the same cannot be said for adsorption of hydrophobic organic compounds (HOCs). Kaolinite was chosen because it is common commercially available natural clay. Organophilic clays are clays in which the cation has been exchanged with organic quaternary amines and the long amine chains make them organophilic. The two commercially obtained organophilic clays Organoclay PM-199 and Organoclay MRM were used due to their high adsorption capacities for HOCs and heavy metals respectively (CETCO, 2014a; CETCO, 2014b). A laboratory generated organoclay Dimethyl Dioctadecyl Ammonium Modified Montmorillonite and an Alumina pillared montmorillonite, both synthesized at Purdue University, were also used for a comparative evaluation of these clay based sorbents. The PAH isotherm analysis was done with GAC and PM-199 only but all nine sorbents were screened for adsorption of heavy metals.

3.2 MATERIALS AND METHODS

3.2.1 Sites and Chemicals

Preliminary screening of sorbent materials was done with some common contaminants present in selected Great Lakes Areas of Concern exhibiting a range of contaminants and environments. These sites with their respective contaminants of concern (COC) are as follows:

- Deer Lake, MI Mercury contamination
- Torch Lake, MI Copper contamination
- Manistique Harbor and River, MI PCB contamination
- Grand Calumet River, IN PAH contamination

Inorganic contaminants tested included mercury, copper, chromium and arsenic, and organic contaminants of interest were polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). All chemicals were prepared for spiking in aqueous state.

Electrolyte solution for metals was prepared by adding 1 mM sodium bicarbonate (NaHCO₃) and 10 mM sodium nitrate (NaNO₃) to distilled-deionized water. For organic contaminants electrolyte solution was generated by mixing 10mM each of sodium chloride (NaCl), calcium dichloride (CaCl.2H₂O), and sodium azide (NaN₃) in distilled-deionized water. Site pore water was obtained by extrusion of pore water from one end of a sediment core (obtained from the sites mentioned above) by pumping water into the other end of the column.

3.2.2 Sorbents

This screening study focused on five types of clays and four types of carbon based sorbents which are listed in the introduction along with a discussion on their respective characteristics.

3.2.3 Analysis

3.2.3.1 Graphite Furnace Atomic Absorption

Heavy metals were analyzed by electrothermal atomic absorption spectroscopy with a Perkin Elmer AAnalyst Atomic Absorption Spectrophotometer. Standards were obtained as high purity 10,000 ppm stocks in 2% acid from Ultra Scientific. Copper, arsenic, and chromium were analyzed by direct injection of 20 μ L of the sample into the graphite tube. Ionization temperatures and hold times varied for the different analytes and were as recommended by the manufacturer. Also, 0.005 mg palladium and 0.003 mg magnesium nitrate (MgNO₃) were injected as a matrix modifier for these three metals.

New standard curves were run during each analysis and every 10 samples a check standard was run to ensure that variation was less than 10% from the standard curve. For mercury the Flow Injection Analysis System from Perkin Elmer was used for metal hydride injection into the graphite tube, alternatively, for lower Hg concentrations, cold vapor atomic fluorescence spectroscopy was used.

3.2.3.2 High Performance Liquid Chromatography

PAH analysis was performed using high performance liquid chromatography with a fluorescence detector (HPLC-FD). All analyses were performed in accordance with EPA Method 8310 using a Waters 2795 HPLC with a Waters 2475 multiwavelength fluorescence detector. A flow rate of 1.0 mL/min with a volumetric ratio of 3:7 water:acetonitrile was used for separation of the target analytes. All analyses utilized linear calibration curves with a minimum of five points. Check standards and blanks were used with every sample set to provide quality assurance.

3.2.4 Batch experiments

Batch tests were conducted with laboratory prepared distilled water (electrolyte solution described previously) and site pore water from the selected Great Lakes sites to measure sorption capacity of the sorbents of interest. Mercury batch tests with distilled water were done at varying concentrations to yield sorption isotherms. For the other inorganic contaminants that included arsenic, chromium and copper, partition coefficients were measured at only selected concentrations as a screening tool to evaluate relative sorption capacity of the various sorbents. In addition to distilled water batch tests, sorption tests for mercury and copper were done with extruded pore water from Deer Lake and Torch Lake respectively.

For batch tests on mercury the sorbents of interest were first measured into 50 mL Pyrex centrifuge tubes. In a large Pyrex jar, an electrolytic solution of distilled-deionized water with 1 mM NaHCO₃ and 10 mM NaNO₃ was spiked with stock solution of Mercury (II) in 2% nitric acid and mixed thoroughly by shaking. Using a volumetric pipette exactly 50 mL of the contaminated solution was added to the 50 mL Pyrex centrifuge tubes containing pre-weighed mass of sorbent, leaving little headspace. The samples were allowed to equilibrate in a tumbling box for 1 to 1.5 days. After removing from the tumbler the tubes were centrifuged at 3500 rpm for 15 minutes to remove the bulk of the sorbent and 30 mL of supernatant was extracted with a plastic syringe and filtered through a 13 mm Whatman GD/X syringe filter into a HDPE centrifuge tube. This was acidified with 2% HNO₃ and 0.2% KMnO₄ was added to the solution for storage. Mercury concentrations were then analyzed by atomic absorption as described in the Analysis section.

The method for batch tests on arsenic, copper and chromium was similar to mercury but 50 mL HDPE centrifuge tubes were used instead of Pyrex glass as losses to plastics are a greater concern with mercury. Additionally a Polypropylene (PP) syringe filter was used instead of the specialized mercury filter and for storage the samples were acidified with HNO₃ only. Arsenic, copper and chromium concentrations were then analyzed by atomic absorption as described previously.

A mass balance on each batch was used to calculate the concentration of contaminant sorbed to the sorbent by the following formula.

$$q = \frac{C_i - C_e}{M/V}$$

Where q is the contaminant concentration on the sorbent, C_i is the initial contaminant concentration in the water, C_e is contaminant concentration in the water at

equilibrium, M is the mass of the sorbent in the sample, and V is the volume of water in the batch. The initial water concentration was taken to be the average concentration of three blanks to account for losses of the contaminant. Partition coefficient, K_d was estimated using a linear regression for isotherm results and for single point batch experiments the following relationship was utilized:

$$K_d = \frac{Q}{C_E}$$

3.2.5 PAH Isotherm Experiments

Preliminary screening of PAH sorption with Organoclay PM-199, Organoclay MRM, Alumina pillared montmorillonite, DMDODA-MMT, GAC, Fe-Pd GAC, Sulfur impregnated GAC and Rice husk char was done in a previous study (Dunlap, 2011) and will not be presented here. GAC and PM-199 were chosen to be viable sorbent amendments for PAH sorption so isotherm experiments were carried out at a range of concentrations.

The PAH sorption study was carried out by using electrolyte solution and site pore water from Grand Calumet River. Grand Calumet pore water had a DOC concentration of 35 mg/L and a SUVA value of 0.9 L/mg-m. Electrolyte solution was generated by mixing 10mM each of sodium chloride, calcium dichloride, and sodium azide in deionized water. The site pore water in this case was centrifuged pore water obtained by centrifuging sediment from cores received from site and then passing it through a 0.45µm filter using vacuum filtration. Three PAHs were used for these tests and they included Pyrene, Benzo[a]anthracene (B[a]A) and Benzo[a]pyrene (B[a]P).

For spiking below the solubility limit, the initial concentration of PAHs was kept constant and the mass of the sorbents was varied to get a range of final concentrations for the isotherm. Batches were prepared in 250mL amber bottles with Teflon lined caps, sealed after spiking and placed on a tumbler to equilibrate for 21 days. This was done for both the granular activated carbon as well as the Organoclay PM-199. Blanks with different initial PAH concentrations were also prepared as controls.

Polydimethylsiloxane (PDMS) fibers obtained were used as passive samplers of pore water concentrations. The fibers were soaked in methanol (Mayer et al., 2000) to remove any surface contamination that may cause chemical interference. The fiber was used to get a measurement of the freely associated PAH concentration by inserting the fibers into each bottle for the duration of mixing. After 21 days the amber bottles were removed from the tumbler. The PDMS fiber was extracted and washed with de-ionized water and wiped clean with a Kimwipe to ensure that no sorbent was left clinging to the fiber's surface. The fiber was then immersed in 100µL of acetonitrile in a 2ml HPLC vial with a 200µL glass insert. Fibers were left immersed in solvent for at least 2 hours to ensure complete extraction. The solvent volume was then measured for PAH concentrations using the HPLC method described.

3.3 RESULTS AND DISCUSSION

3.3.1 Mercury

Sorption characteristics for mercury were measured for granular activated carbon (GAC), Organoclay PM-199, Iron-palladium coated GAC, Rice husk char, Kaolinite, DMDOMA-MMT and Alumina pillared MMT with laboratory prepared distilled water and for GAC, Sulfur impregnated GAC, Organoclay MRM and PM-199 with spiked pore water from Deer Lake. The linear regression plots for this preliminary screening of sorbents are shown in Figure 3.1 and Figure 3.2 and the partition coefficients obtained are summarized in Table 3.1 below.



Figure 3.1: Mercury Sorption Isotherms in DI water for (a) Organoclay PM-199, (b) DMDODA-MMT, (c) Al-pillared MMT, (d) GAC and (e) Fe-Pd GAC

The units for Q, sorbent concentration and C aqueous concentration are mg/kg and mg/L which will yield partitioning coefficients based on slope of regression lines in the typical units of L/kg. As seen in Figure 3.1 above, except for Organoclay PM-199 the linear regression line fits all have r-square values of over 90%. The three clay sorbents Alumina Pillared MMT, Organoclay PM-199 and Dimethyl Dioctadecyl Ammonium Modified Montmorillonite (DMDODA-MMT) have increasing partition coefficients of

30 L/kg, 460 L/kg and 36,300 L/kg respectively in distilled water. Sorption of mercury onto a commercially available GAC and a laboratory synthesized Iron-Palladium impregnated activated carbon (Fe-Pd GAC) was also investigated which yielded partitioning coefficients of 143,00 L/kg and 76,600 L/kg respectively. So for both clay-based and carbonaceous sorbents the modified versions of natural clay and GAC, DMDODA- MMT and Fe-Pd GAC showed the highest sorption capacities for mercury in laboratory prepared distilled water. The improved sorption of mercury by organophilic clays vs unmodified clays had also been established by Phothitontimongkol et al., 2009.



Figure 3.2: Mercury Sorption Isotherms in Deer Lake pore water for (a) GAC, (b) SIAC, (c) Organoclay PM-199 and (d) Organoclay MRM

The mercury sorption isotherms shown in Figure 3.2 were done using mercury contaminated water from Deer Lake. By comparing the partition coefficient for the

commercially available GAC (8000 L/kg) with the sulfur impregnated GAC (209,700 L/kg) it is clear that the modified GAC would perform a lot better than its conventional form. A similar improvement in performance is observed for Organoclay MRM which has a sorption coefficient of 82,000 L/kg compared to the more commonly used organophilic clay Organoclay PM-199 having a sorption coefficient of 270 L/kg. Organoclay MRM is designed to offer improved adsorption for heavy metals (CETCO, 2014b) so this result is as expected based on the properties of this modified organophilic clay.

Sorbent Material	K _d (L/kg)	
	Lab Water	Deer Lake Pore water
GAC	14,300	8000
SIAC	_	209,700
PM-199	460	270
MRM	_	82,000
Fe-Pd GAC	76,600	-
Rice Husk Char	190 (single point)	-
Kaolinite	1490 (single point)	-
DMDODA-MMT	36,300	-
Al Pillared MMT	30	-

 Table 3.1:
 Mercury partition coefficients for the different adsorbents tested

Table 3.1 summarizes the sorption coefficients obtained from the linear regression isotherms obtained above. Additionally single point batch test results give sorption coefficients of 190 L/kg at a concentration of ~4000 μ g/L and 1,490 L/kg at a concentration of 54 μ g/L for rice husk char and kaolinite respectively. These two

materials were chosen as low cost alternatives and because they are more widely available. The laboratory prepared pillared clay yields a lower sorption coefficient of 30 L/kg compared to the natural clay, Kaolinite but the laboratory prepared DMDODA-MMT has a much higher sorption capacity at 36,300 L/kg.

Sulfur impregnated GAC and Organoclay MRM show greater mercury sorption compared to conventional GAC and Organoclay PM-199 because they are intended for heavy metal sorption as discussed previously. The observed difference in partition coefficients between lab prepared distilled water and site pore water is suspected to be due to significant association of the mercury with colloidal matter in the site pore waters. It should be emphasized that the sorption of mercury onto these materials is a strong function of the speciation of mercury. Mercury is often strongly associated with chlorides, organic matter and sulfides in increasing order and changes in concentration of these species may dramatically affect the mercury speciation and sorption. For example, organic-associated mercury may be as strongly sorbed by conventional organoclay as by the MRM, unlike the results observed for Deer Lake pore water.

3.3.2 Arsenic and Chromium

A single batch was run with the sorbent materials of interest to investigate the sorption of arsenic and chromium in distilled deionized water. The experiments for each sorbent were done at a specific concentration thus leading to single-point partition coefficients. The results of these experiments are meant as a screening for the variety of sorbents and are presented here in Table 3.2.
Metal	Sample	C (µg/L)	% Reduction	Sorbent Mass (mg)	Q (µg/mg)	Kd (L/kg)
	GAC	904	2%	99.7	0.010	11
	Al-Pil-MMT	584	37%	1000	0.017	29
	PM-199	814	12%	99.9	0.055	67
ic.	DMDODA-MMT	599	35%	999.1	0.016	27
.sen	Fe-Pd GAC	78	92%	60.3	0.700	8950
Ar	Kaolinite	783	15%	996.2	0.007	9
	Sand	775	16%	5070	0.002	2
	Rice Husk Char	884	4%	106.9	0.018	21
	Initial	972				
	GAC	470	40%	636.5	0.024	52
	Al-Pil-MMT	180	77%	2506	0.012	66
_	PM-199	639	18%	2504	0.003	4
um	DMDODA-MMT	560	28%	1320	0.008	15
omi	Fe-Pd GAC	486	38%	10.2	1.44	2970
Chro	Kaolinite	664	15%	2496	0.002	4
Ŭ	Sand	749	4%	503.4	0.003	4
	Rice Husk Char	558	28%	2566	0.004	8
	Initial	837				

 Table 3.2:
 Removal of Arsenic and Chromium in DI water in a single batch with different materials

Arsenic sorption batch tests show that the clay based sorbents Organoclay PM-199, Al-pillared MMT, DMDODA-MMT, and kaolinite yield single point partition coefficients of 67 L/kg, 29 L/kg, 27 L/kg and 9 L/kg respectively. The two lab prepared montmorillonite clays have a similar partition coefficient and Organoclay clay PM-199 performs better than the other clay based sorbents. This result was anticipated based on the organophilic properties of PM-199. Rice husk char, GAC and iron-palladium GAC have sorption coefficients of 21 L/kg, 11 L/kg and 8950 L/kg. The Fe-PD GAC which is a GAC amended with nanoscale particles of bimetallic iron and palladium performs substantially better than all the remaining sorbents because it is designed for improved dissolved heavy metal removal. Partition coefficient of arsenic with sand was also estimated for comparison purposes (2 L/kg). The cheaper natural sorbents kaolinite and rice husk char do not perform significantly better than sand and neither does GAC.

Chromium exhibits similar results to arsenic sorption with Fe-Pd GAC outperforming all the other sorbents by yielding a partition coefficient of 2970 L/kg. Organophilic clay PM-199 and natural clay kaolinite have the same sorption capacity as sand (4 L/kg) and rice husk char and DMDODA-MMT do not perform significantly better either. GAC and Al-pillared MMT perform slightly better than the other sorbents having partition coefficients of 52 L/kg and 66 L/kg respectively but these values are still substantially lower than Fe-Pd GAC. Based solely on comparative sorption results Fe-Pd GAC would be the clear choice for arsenic and chromium sorption but the cost and difficulty of preparing and maintaining large volumes of this material make it an unlikely choice for large scale sediment remediation operations. In general the other materials are relatively poor sorbents of these heavy metals.

3.3.3 Copper

For copper, the distilled water tests were prepared by mixing distilled-deionized water, copper from a standard solution (10,000 mg/L), 1mM NaHCO₃ and 10mM NaNO₃. The solution initial pH was adjusted to 7 ± 0.5 using diluted HNO₃ or NaOH. For copper sorption sulfur impregnated activated carbon (SIAC), GAC, Organoclay PM-199 and Organoclay MRM were focused on. During the course of the experiments it was found, that two of these four sorbents (GAC and PM-199) increased the solution pH, and Kaolinite lowered the pH. To ensure that copper sorption was really sorption and not precipitation due to pH changes a buffer which did not interact with Cu (PIPES buffer)

was used. PIPES buffer was added to the copper solution, the pH was monitored during the adsorption experiment and it was found that it did not change. Site pore water tests for copper were conducted with Torch Lake pore water spiked with copper. Sorbent mass was varied to get a range of equilibrium concentrations and linear regression was used to calculate the partition coefficients summarized in Table 3.3.

	Torch Lake	Pore water	Lab Water	
Sorbent	Avg. Kd (L/kg)	Std. dev.	Avg. Kd (L/kg)	Std. dev.
SIAC	200	115	100	120
MRM	180	83	140	45
GAC	5,490	2,340	11,200	6,230
PM-199	1,240	380	1100	360

 Table 3.3:
 Copper partition coefficients for selected materials

Organoclay MRM and SIAC yield similar sorption coefficients of 180 L/kg and 200 L/kg respectively for pore water tests and 140 L/kg and 100 L/kg respectively for laboratory distilled water. While both these sorbents are chosen for their heavy metal sorption potential MRM is specifically designed for mercury and arsenic treatment (CETCO, 2014a) and SIAC is generally used for mercury sorption (Korpeil et al., 1997). However, neither of these two sorbents performs exceptionally well for copper sorption. The more commonly used GAC and Organoclay PM-199 perform better than the two modified forms with partition coefficient of 5490 L/kg and 1240 L/kg respectively for porewater tests and 11,200 L/kg and 1,100 L/kg respectively for DI water. The reduction in sorption capacity in pore water compared to organi-free DI water is as expected for GAC because of fouling which will be further discussed in the following chapters.

However it is clear that this fouling effect is observed for copper adsorption with GAC. This effect is not seen in Organoclay PM-199 since the K_d values are not significantly different for pore water and DI water thus competitive adsorption is not a grave concern for sorption of copper with Organoclay PM-199.

3.3.4 PAHs

The preliminary screening of sorbent materials for PAHs was conducted by Dunlap (2011) in laboratory prepared electrolyte water and the results for the sorbents evaluated in that study are summarozed in the table below. The results clearly show that Organoclay PM-199 has the highest sorption capacity in the group of clays and GAC performs best among the carbon based sorbents.

Organic compound	PM- 199	DMDODA -MMT	Al- Pil- MMT	Kaolinite	Rice Husk Char	GA	С	Fe-Pd	GAC
-		log K _f	1/n	log K _f	1/n				
Benzene	80	49	5.6	1.4	69	6.11	0.39	4.53	0.40
Chlorobenzene	410	222	6.3	4.3	630	7.11	0.27	5.47	0.31
Naphthalene	3030	2070	28	5.0	33000	7.54	0.21	5.22	0.63

Table 3.4:Screening results for organic compounds (Dunlap, 2011)

The results discussed in this section are of further isotherm experiments done with granular activated carbon and Organoclay PM-199 which were chosen to be the more viable options according to the initial screening (Dunlap, 2011). The isotherms developed here used pore water from Grand Calumet River and looked at sorption of higher molecular weight PAHs; pyrene, benzo[a]anthracene and benzo[a]pyrene for a wider range of equilibrium concentrations.

Sorption isotherms for Calgon TOG 20x50 granular activated carbon followed the Freundlich model as shown by the following equation:

$$q_e = K_f C_w^{1/n}$$

Where q_e is the mass of the PCB sorbed to the GAC with units of mass of contaminant per mass of sorbent (µg/kg), C_w is the concentration of the PCBs dissolved in water with units of mass of contaminant per volume (µg/L), K_f is the Freundlich constant with units of mass contaminant times (volume)^{1/n} per mass sorbent times (mass contaminant)^{1/n} i.e. (µg/kg)(L/µg)^{1/n}, and 1/n is a dimensionless constant. Organoclay PM-199 sorption of PAHs follows a linear regression model. The isotherms obtained for sorption of pyrene, benzo[a]anthracene and benzo[a]pyrene are shown in Figure 3.4 below.



Figure 3.3: PAH adsorption isotherms in DI water and Grand Calumet pore water for (a) pyrene, (b) benzo[a]anthracene, and (c) benzo[a]pyrene

The isotherms for GAC and Organolcay PM-199 were plotted on the same graph for a better illustration of comparative sorption capacities. It should be noted that the linear PM-199 isotherms may not 'look' linear being plotted on a log-log scale.

For all three PAHs shown it can be clearly observed that the organophilic clay sorption is much less than GAC sorption capacities. Presence of NOM does not have significant effects on PM-199 sorption capacity so an isotherm in DI water was unnecessary and only PAH sorption in Grand Calumet pore water was evaluated. For higher concentrations of pyrene and benzo[a]anthracene the effects of competitive adsorption in the presence of NOM are more pronounced shown by higher sorption capacity in DI water compared to the pore water isotherm. For benzo[a]pyrene this effect is more pronounced due to its higher molecular weight and higher sorption to any NOM present.

	Lab DI wat	ter - GAC	Grand Cal Por	Grand Cal Pore water - PM199		
PAH	log K _f	1/m	log K _f	1/m	V	
	$(\mu g/kg)(L/\mu g)^{1/n}$	1/11	$(\mu g/kg)(L/\mu g)^{1/n}$	1/11	N d	
Pyrene	7.89 (±0.690)	1.63 (±0.915)	6.92 (±0.118)	0.504 (±0.138)	185,000 (±244,000)	
B[a]A	7.73 (±1.15)	0.806 (±0.422)	6.52 (±0.336)	0.410 (±0.135)	273,000 (±150,000)	
B[a]P	8.33 (±1.41)	0.915 (±0.423)	5.89 (±0.379)	0.407 (±0.171)	301,000 (±263,000)	

Table 3.4:Summary of sorption coefficients of PAH sorption with GAC and
Organoclay PM-199 (values in parentheses show 95% confidence limits)

Benzo[a]pyrene having the highest molecular weight has the highest sorption capacity with both GAC and PM-199. The Freundlich equation exponent obtained for pyrene is higher than 1 which is unexpected and not in line with other studies (Walters et al., 1984). However it should be noted that the uncertainty in this 1/n value is much higher as illustrated by the 95% confidence limit due to possible experimental inefficiencies. Due to the higher sorption capacities of GAC it would be the preferred sorption for adsorption of dissolved PAHs unless NAPL is present. The presence of other contaminants such as PCBs in the Grand Calumet pore water is also something to be considered when evaluating the sorption of PAHs onto GAC.

3.4. CONCLUSIONS

For the purpose of this study of a variety of clays and carbon based sorbents were evaluated for sorption of mercury, arsenic, chromium and copper and two of these sorbents were tested for PAH sorption. PCBs were also evaluated using selected sorbents but the PCB adsorption study is discussed with great detail in Chapter 4.

Results from the preliminary studies show that for mercury sorption the best suited materials are Sulfur Impregnated GAC and Organoclay MRM which are altered/enhanced forms of the conventional GAC and Organoclay PM-199, designed with heavy metal sorption in mind. While these modified sorbents might be best for some mercury contaminated sites, contaminated sediments are often contaminated with a range of contaminants, including organics. These materials are not as good at sorbing organics and are only modestly better for mercury so the GAC and Organoclay PM-199 might be best all-around sorbents.

The best sorption for arsenic and chromium is achieved by Iron-Palladium coated GAC which again is an altered form of conventional GAC designed specifically for inorganic/heavy metal removal. The performance of Fe-Pd GAC surpasses that of the other sorbents with the highest partition cofficients of 8950 and 2970 L/kg for arsenic and chromium respectively. However due to the cost and difficulty of use of Fe-Pd GAC, Organoclay PM-199 and Alumina Pillared GAC can be recommended as alternatives having sorption coefficients of approximately 65 L/kg. Conventional GAC is

demonstrated to be the superior choice of sorbent for a copper contaminated sediment site such as Torch Lake but it is subject to fouling in the presence of NOM thus affecting its long-term applicability. Organoclay PM-199 did not exhibit a similar reduction in sorption in the presence of NOM.

GAC and Organoclay PM-199 were tested for the sorption of organic contaminants after proving to be the preferred sorbents for hydrophobic organic compounds based on initial screening results (Dunlap, 2011). PAH sorption results obtained herein demonstrate the superiority of GAC as a sorbent compared to Organoclay PM-199 for dissolved organic compounds. Disregarding the effects of fouling for GAC it would be the preferred choice for removal of dissolved PAHs; however PM-199 performs much better in the presence of organic contamination in the form of Non-Aqueous Phase Liquid (Murphy et al., 1995). A detailed analysis of PCB sorption with GAC and PM-199 is presented in Chapter 4 along with the effects of NOM present in these porewaters.

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Chapter 4: Comparison of in-situ remedial approaches for PCB contaminated sediments at Manistique Harbor

4.1 INTRODUCTION

In-situ management of contaminated sediments has substantial advantages over dredging including less resuspension and surface residual concerns and avoidance of the cost and complexity of managing dredged sediments onshore. In-situ management is often accomplished via capping, either by conventional placement of sand or clean dredged material (Morton, 1992; O'Connor et al., 1983; Sumeri, 1989) or with amendments such as activated carbon or organophilic clay (Cho et al., 2009; Knox et al., 2006). Increasingly, in-situ management is also being accomplished via direct placement of the amendments into the sediments as an in-situ treatment (IST). In IST, amendments are either mechanically mixed into the surface layer (Beckingham & Ghosh, 2011; Cho et al., 2009) or placed as a layer on the surface where benthic organisms or other processes intermix the amendment over time (Cornelissen et al., 2012; Cornelissen et al., 2011).

In this chapter the relative performance of these in-situ management approaches are evaluated by consideration of a particular site, Manistique Harbor Superfund Site in Manistique, MI. Two types of sorptive amendments; GAC TOG 20x50 and Organoclay PM-199 are further examined based on the initial screening results of Chapter 3 for hydrophobic organic contaminants. The sorptive characteristics are used to evaluate three remedial scenarios; in-situ treatment, thin cap and thick amended cap and also compared to monitored natural attenuation (no remedy) and conventional sand capping. A numerical model is used to evaluate these remedial applications and illustrate the typical performance of the various approaches under realistic scenarios.

The Manistique Harbor Superfund site is located in Manistique, Michigan on the southern shore of Michigan's Upper Peninsula, 135 miles northeast of Green Bay Harbor,

Wisconsin and 220 miles north of Milwaukee, Wisconsin. The River and Harbor discharge into Lake Michigan. The site is contaminated with polychlorinated biphenyls (PCBs) from point and non-point sources from of industrial and paper milling operations (USEPA, 2012).

Remedial operations were initiated by the United States Environmental Protection Agency (USEPA) in 1995. Initially dredging operations were conducted until 2000 (USEPA, 2012). Additional remediation in the form of capping or in-situ treatment is currently being evaluated and the present work was a component of those efforts.

In this work, the performance of capping with conventional material, amended or active capping, and in-situ treatment via sediment amendments were evaluated. Potential amendments evaluated included granular activated carbon (GAC) and organophilic clays. Sorption studies were used to evaluate potential performance and performance degradation associated with site natural organic matter. The sorption studies were used to model expected field performance of the caps and in-situ treatment under various scenarios. The modeling results were used to compare the performance of various remedial scenarios including both amendments and different application scenarios.

4.2 MATERIALS AND METHODS

4.2.1 Chemicals

Five PCB congeners, representing a range of hydrophobicities, and planarities were chosen for evaluation of the performance of the amendments and the various remedial design scenarios. The sorption of these particular PCB congeners onto GAC were previously studied (McDonough et al., 2008) using artificial laboratory waters thus allowing a comparison to the site conditions evaluated here. IUPAC names of the chosen congeners are PCB 18 (2,2',5–trichlorobenzene), PCB 52 (2,2',5,5'– tetrachlorobenzene), PCB 77 (3,3',4,4'-tetrachlorobenzene), PCB 101 (2,2',4,5,5'pentachlorobenzene), and PCB 118 (2,3',4,4',5-pentachlorobenzene). PCB compounds were obtained from Ultra Scientific (North Kingstown, RI) in crystalline form. Acetone and hexane obtained from Fisher Scientific (Fairlawn, NJ) were used to make stock solutions and dilutions respectively by dissolving from crystalline form. Since PCBs exist as mixtures in the environment and not separate congeners competitive sorption between congeners might be important. However it has been suggested that if total solute concentration is less than 10⁻⁵ molar, competitive sorption will not be an issue (Coates & Elzerman 1986). The total solute concentration of PCB mixture was kept below 10⁻⁷ molar for each experiment.

4.2.2 Sorbents

As established in Chapter 3, granular activated carbon (GAC) and organophilic clay (OMC) are suitable sorbents for hydrophobic organic contaminants. TOG 20x50 was chosen as the GAC in order to have a fair comparison to existing PCB adsorption studies (i.e. McDonough et al., 2008). This GAC was used as a dissolved constituent sorbent and was obtained from Calgon Carbon (Pittsburgh, PA), ground to a powder using a mortar and pestle and passed through a 200 mesh sieve. The sieved GAC was boiled in deionized water for 30 minutes, dried in an oven at 105°C and stored in a desiccator (McDonough et al., 2008).

Organoclay PM-199 (CETCO, Hoffman Estates, IL) was chosen as an alternate granular sorbent which has great potential as a permeable adsorptive barrier for in-situ sediment remediation (CETCO, 2014). This organophilic clay (OMC) is considered to be most effective to absorb NAPL while activated carbon is more susceptible to fouling in the presence of pure phase organic contaminants and is expected to perform better for dissolved contaminants. Physical properties of GAC and OMC are shown in Table 4.1.

Sorbent	Apparent Density g/cm ³	Total Pore Volume (cm ³ /g)	Surface Area (m ² /g)	Organic Carbon Content
GAC TOG 20x50	0.5 ¹	0.435	1035	-
OMC PM-199	0.75	- 2	- ²	21-23%

1. Calgon Personal Communication

2. OMC absorbs in organic matter ~30 % by mass, pore volume and surface area are not relevant

 Table 4.1:
 Table of properties for GAC and OMC

4.2.3 Isotherm Experiments

Sorption studies were carried out by using a laboratory prepared electrolyte solution (organic free water) and site pore water as two different media in order to evaluate the effects of fouling by natural organic matter. The lab electrolyte solution was generated by mixing 10mM each of sodium chloride, calcium dichloride, and sodium azide (Fisher Scientific, Fairlawn, NJ) in deionized water. The site water was pore water obtained by centrifuging sediment from cores received from site and then passing it through a 0.45µm filter using vacuum filtration to remove any particulate matter suspended by processing. The Manistique pore water contained approximately 14 mg/L of dissolved organic carbon (DOC) and had a specific ultra-violet absorbance (SUVA) of 0.35 L/mg-m. A SUVA low value indicates that low concentrations of humic acids are present in this porewater.

For spiking below the solubility limit, the initial concentration of PCBs was kept constant and the mass of the sorbents was varied to get a range of final concentrations to provide data for isotherm measurements. Two batches containing a constant mass of sorbent were spiked 2 times and 5 times above solubility. Final concentrations at equilibrium were well below congener solubilities. Batches were prepared in 250mL amber bottles with aluminum lined caps, sealed after spiking and placed on a tumbler for 28 days which is sufficient time for equilibrium to be reached (Jonker & Koelmans, 2002). This was done for both the granular activated carbon as well as the OMC. Blanks with different initial PCB concentrations were also prepared as controls.

4.2.4 Extraction Procedures

Polydimethylsiloxane (PDMS) fibers obtained from Polymicro Technologies (Phoenix, AZ) were used as passive samplers of pore water concentrations. The fibers were soaked in methanol (Mayer et al., 2000) to remove any surface contamination that may cause chemical interference. The fiber was used to get a measurement of the freely associated PCB concentration by inserting the fibers into each bottle for the duration of mixing (28 days). The maximum contaminant mass sorbed onto the PDMS at equilibrium was not a significant influence on the water-sorbent equilibrium.

After 28 days the amber bottles were removed from the tumbler. The PDMS fiber was extracted and washed with de-ionized water and wiped clean with a Kimwipe to ensure that no sorbent was left clinging to the fiber's surface. The fiber was then immersed in 140 μ L (enough to completely submerge the fibers) of hexane in a 2ml HPLC vial with a 200 μ L glass insert. Fibers were left immersed in solvent for at least 2 hours to ensure complete extraction.

4.2.5 GC-µECD Analysis

The solvent containing the dissolved PCBs were analyzed using EPA Method 8082 on an Agilent 6890 Series Gas Chromatograph with a 30cm HP-5 column and a micro-electron capture detector (µECD). Hydrogen gas at a pressure of 8.0psi was allowed to flow through the column with the oven held at a temperature of 100°C for 2 minutes, increased at a rate of 15°C/min to 160°C and then increased to 270°C at a rate of 5°C/min and held for 15 minutes. The inlet was operated in splitless mode with a pressure of 8.0psi. The detector was kept at a temperature of 300°C with 60mL/min makeup flow of Nitrogen gas.

4.2.6 CAPSIM

The numerical sediment-cap model CAPSIM was employed to evaluate cap and in-situ remedial scenarios using the measured sorption isotherms of the various cap materials. CAPSIM is a finite difference model using Crank –Nicholson solution scheme and is designed to simulate surficial sediment processes such as bioturbation, benthic boundary layer exchange as well as deep bed advection, diffusion, sorption and reaction processes in a multi-layered media (Reible & Lampert, 2014). It was designed for application to contaminant migration in surficial sediments and cap layers and can be applied over timescales of years to decades. Although field validation data over those time frames are not yet available, the model components have been separately evaluated through field and laboratory evaluation in much the same way that the components of a groundwater model are developed and tested.

Sorption was modeled with non-linear (GAC) and linear (OMC), sediment and conventional cap material) models. Remedial scenarios were evaluated considering two groundwater upwelling flow rates of 1cm/yr and 1cm/day to evaluate behavior under diffusion dominated and advection dominated conditions, respectively. 1 cm/yr is a

typical upwelling velocity near the center of a lake or bay while 1 cm/day is a common groundwater/surface water exchange rate along a river bank (Reible et al., 2006). PCB 18, PCB 52 and PCB 101 were selected to illustrate the behavior of a tri-chloro, tetrachloro and penta-chloro PCB respectively. All models assumed a bioturbation depth of 10cm (Reible, 2008; Reible, 2014) and a bottom boundary condition of constant flux. The tetra-chloro biphenyl predicted closely the total PCB performance (by summing all congeners) and the results for that congener will be emphasized herein. Table 4.2 shows a summary of the key parameters used as model inputs including the densities (Mackay, 2006), K_{ow} values (Hawker & Connell, 1988) and diffusivites in water (Hayduk & Laudie, 1974) for the three congeners. Log K_{oc} was determined using the equation developed by (Baker et al., 1997).

РСВ	Model Congener	Molecular Weight	Density (g/cm ³)	log K _{ow}	log K _{oc}	H ₂ O Diffusivity (cm ² /s)	Pore water Concentration (ng/L)*
Tri-PCB	18	257.5	1.149	5.24	4.83	5.47x10 ⁻⁶	10.0
Tetra-PCB	52	292.0	1.202	5.84	5.37	5.22x10 ⁻⁶	6.6
Penta-PCB	101	326.4	1.280	6.38	5.86	5.07x10 ⁻⁶	4.1

* Pore water concentration for trichlorobiphenyl estimated, others measured Common Bioturbation Parameters:

Bioturbation depth	10 Cm
Particle biodiffusion coefficient	$1.0 \text{ cm}^2/\text{yr}$
Pore water biodiffusion coefficient	$100 \text{ cm}^2/\text{yr}$
Bottom boundary condition	Constant Flux

Table 4.2:Key Model Input Parameters

While diffusive processes vary from site to site and according to the layer, diffusion coefficient for transport in each layer is modeled as a sum of molecular diffusion and hydrodynamic dispersion. For the topmost layer bioturbation is incorporated into the effective diffusion coefficient and it includes particle biodiffusion as well as pore water biodiffusion (Reible et al., 2014). Deposition has not been modeled because it is unrealistic to assume constant deposition rates can be sustained over long periods of time (Reible et al., 2014).

4.3 RESULTS AND DISCUSSION

4.3.1 Activated Carbon Isotherms

The sorption isotherms for the granular activated carbon (GAC) followed the Freundlich model as shown by the following equation:

$$q_e = K_f C_w^{1/n}$$

Where q_e is the mass of the PCB sorbed to the GAC with units of mass of contaminant per mass of sorbent ($\mu g/kg$), C_w is the concentration of the PCBs dissolved in water with units of mass of contaminant per volume ($\mu g/L$), K_f is the Freundlich constant with units of mass contaminant times (volume)^{1/n} per mass sorbent times (mass contaminant)^{1/n} i.e. ($\mu g/kg$)($L/\mu g$)^{1/n}, and 1/n is a dimensionless constant which is usually less than one.

The following linearization has been applied to obtain the log plots for each PCB congener as shown in Figure 4.1.

$$\log(q_e) = \log(K_f) + (1/n) \cdot \log(C_w)$$



Figure 4.1: log-log equilibrium isotherms of Granular Activated Carbon sorption for (a) PCB18, (b) PCB 52, (c) PCB 77, (d) PCB 101 and (e) PCB 118 in NOM-free water (Blue) and site water containing 14 mg/L NOM

			Site V	Vater	DI Water		
РСВ	Cl Atoms	Planarity	log K	1/n	log K		
			$(\mu g/kg)(L/\mu g)^{1/n}$	1/11	$(\mu g/kg)(L/\mu g)^{1/n}$	1/11	
18	3	Non Planar	6.95 (±0.141)	0.556 (±0.115)	7.32 (±0.213)	0.514 (±0.133)	

52	4	Non Planar	6.23 (±0.186)	0.306 (±0.077)	6.91 (±0.216)	0.416 (±0.089)
77	4	Non-Ortho Planar	6.45 (±0.477)	0.298 (±0.145)	7.82 (±0.902)	0.666 (±0.304)
101	5	Non Planar	6.20 (±0.260)	0.399 (±.0.125)	6.89 (±0.343)	0.478 (±0.130)
118	5	Mono-Ortho Planar	6.29 (±0.241)	0.374 (±0.099)	7.27 (±0.557)	0.542 (±0.186)

Table 4.3:Summary of Freundlich parameters of the five PCB congeners for GAC
sorption (values in parentheses show 95% confidence limits)

A summary of the Freundlich parameters along with the number of chlorine atoms and planarity for the five congeners is shown in Table 4.3. In all cases the PDMS fiber adsorbed less than 1.5% of the system mass which is not enough to appreciably alter equilibrium concentrations. For each PCB congener the sorption capacity is higher with organic free water than the site pore water which confirms the effects of natural organic matter fouling of activated carbon. Other researchers have shown that planar PCBs are more strongly sorbing than non-planar PCBs (McDonough et al., 2008; Jonker & Koelmans, 2002) consistent with the observations here.

4.3.2 Organophilic Clay Isotherms

CETCO Organoclay PM-199 was used as the organophilic clay (OMC) for the purpose of this study. Sorption of PCBs on OMC follows a linear model described as follows:

$$q_e = K_d C_w$$

Where q_e is the mass of the PCB sorbed to the OMC with units of mass of contaminant per mass of sorbent ($\mu g/kg$), C_w is the concentration of the PCBs dissolved in water with units of mass of contaminant per volume ($\mu g/L$), and K_d is a linear constant with units of volume per mass of sorbent (L/kg). The linear sorption model is consistent

with a mechanism of non-specific organic absorption into the organic fraction of the OMC.



The results for the linear isotherms are illustrated in Figure 4.2 for both the site pore water and the organic free water/electrolyte solution.

Figure 4.2: Equilibrium Isotherms of OMC PM-199 sorption for (a) PCB18, (b) PCB 52, (c) PCB 77, (d) PCB 101 and (e) PCB 118.

A summary of the linear partition coefficients obtained from the isotherms for the five congeners can be seen in Table 4.4. As was the case of GAC isotherms, the PDMS fiber adsorbed less than 1.5% of the system mass. The effects of fouling were minimal for OMC and partition coefficients were essentially identical for both aqueous media. This is consistent with an absorption partitioning phenomena where the potential effects of NOM on GAC such as closing off fine pore spaces and the associated surface area is not relevant. In general, the sorption capacity increases with increasing hydrophobicity.

		Site Water	DI Water	
РСВ	Cl Atoms	K _d	K _d	
		(L/kg)	(L/kg)	
18	3	209,000 (±12,600)	156,000 (±19,100)	
52	4	402,000 (±30,000)	300,000 (±41,000)	
77	4	4,660,000 (±1,010,000)	5140,000 (±471,000)	
101	5	1,210,000 (±132,000)	1,120,000 (±157,000)	
118	5	1,050,000 (±186,000)	1,360,000 (±161,000)	

Table 4.4:Summary of linear partition coefficients of the five PCB congeners for
Organoclay sorption (values in parentheses show 95% confidence limits)

4.3.3 Competitive Adsorption due to NOM

Competitive effects of NOM present in the system cause fouling of GAC which is evidenced by the results showing site pore water is 10 to 33% less sorbing than organic free water. OMC was not as strongly sorbing as GAC but is linear, i.e. independent of sorbate concentration and not degraded by competitive sorption or fouling with NOM. GAC is an adsorbent and the presence of NOM can exclude fine pores and all of the associated surface area. In addition, other contaminants can compete for the finite surface area available, suggesting that the sorbing constituents can strongly influence sorption onto GAC. For OMC, however, absorption is largely associated with hydrophobic interactions between the organic matter in the OMC and the contaminants. The sorption is proportional to the total volume of organic matter but there is little competition between solutes. This might suggest that at high concentrations or with significant NOM present the OMC could be similar to sorption onto GAC. In the lower concentrations typically of interest, however, the GAC remains a much stronger sorbent. Figure 4.3 illustrates these effects for the two sorbents.



Figure 4.3: Comparison of competitive effects of NOM for activated carbon (AC) and organophilic clay (OMC) sorption for PCB52

4.3.4 Comparison of Sorption with Existing Literature

The results of the GAC equilibrium isotherms were also compared with McDonough et al. (2008). The study evaluated GAC sorption in electrolyte water and in artificial pore water containing organic matter. Three PCB congeners from that study are the same as those of the current study. PCB 77 sorption results of McDonough et al. (2008) and of this study are shown in Figure 4.4.



Figure 4.4: Comparison of GAC isotherms for PCB 77 with 95% confidence limits from McDonough et al. (2008) study

The green dashed line represents the upper confidence interval for McDonough et al. data and the orange dashed line represents the lower confidence interval. The deionized water (organic free water) isotherms obtained, shown in blue, lie within the 95% confidence limits provided by the 2008 study for the congeners being compared i.e. PCB 18, PCB 52 and PCB 77 and the comparison plot for PCB 77 can be seen in Figure 4.4. Pore water isotherm represented by solid red line is also shown.

4.3.5 CAPSIM Modeling

CAPSIM, a numerical sediment-cap model developed by Reible et al. (2014) was used to predict transport through different in-situ applications of the two sorbents discussed. Three different sets of remedial scenarios were simulated; existing condition of sediment without adsorptive amendment, GAC and OMC in-situ amendments and caps with conventional cap material (sand), and with GAC and OMC cap amendments placed in a mixed thick layer or in a pure thin layer. The amount of sorbents used for simulation purposes were equivalent to a commercial reactive core mat i.e. 0.4 lb/ft² (CETCO, 2013a) of activated carbon and 0.8 lb/ft² of organophilic clay (CETCO, 2013b).

All model scenarios predicted concentration (pore water concentration) and vertical flux of particular PCBs as a function of depth at different times, and predictions of the pore water concentration and flux versus time at a depth of 5 cm into the sediment (or cap) over time. The depth of 5 cm into the sediment (or cap) was chosen as the midpoint of the bioturbation layer and therefore an indicator of the average exposure concentration and flux to benthic organisms. Flux at the sediment-water interface was also simulated by incorporating molecular diffusion, hydrodynamic dispersion and bioturbation (see Table 4.2).

4.3.5.1 Existing Condition Modeling

Modeling was done for the existing condition of sediments considering no remedial action as a reference for the remedial scenarios. The results of this model scenario show that PCB 52 reaches a near surface steady state flux of 440 μ g/m²/yr and 157 μ g/m²/yr for upwelling flow rates of 1 cm/day and 1 cm/yr respectively. Under existing conditions it will take PCB 52 more than 100 years to achieve significant depletion of the surface layer with either upwelling flow rate. PCB 18 takes less time to

show such depletion and PCB 101 takes longer because of their respective sorption characteristics and mobility.

Another simulation was carried out by using a passive cap of a 30cm sand layer over the top of the sediments. This cap proved to increase the time required for contaminants to migrate into the surface water although the improvement was less dramatic for the high upwelling rate scenario in the non-sorbing cap. The maximum flux (steady state flux) at the surface in the low upwelling rate scenario was less than 1% of the unremediated baseline case (compared at t = 500 years), illustrating the effectiveness of even a non-sorbing cap with diffusion dominates over much of the chemical isolation layer. In the high upwelling rate scenario the steady state flux into the overlying water was still 11% of the unremediated baseline case.

4.3.5.2 Organophilic Clay Modeling

The OMC sorption parameters for pore water summarized in Table 4.4 were used for the three congeners to obtain results for three simulations; in-situ application of OMC, 1cm mat of OMC, and 30 cm OMC amended sand cap. In each case the amount of OMC applied was 0.8 lb/ft², the equivalent loading of OMC in a CETCO Reactive Core Mat.

For the first set of simulations 0.8 lb/ft² of OMC was mixed with the 10cm layer of overlying sediment. The results were essentially identical to that observed in the base case. This is because the OMC is only marginally more sorbing than the existing sediment (based upon measured pore water concentrations and sorption isotherm information). For in-situ treatment to be effective, the sorbent must be much stronger than the surrounding sediment. This can be explained by considering the following linear sorption model described by the quation:

Sorbed loading of contaminant = $f_{sorbent}K_{sorbent}C_{pw} + f_{sediment}K_{sediment}C_{pw}$

Where $f_{sorbent}$ and $f_{sediment}$ are fraction of sorbent or sediment in system respectively, $K_{sorbent}$ and $K_{sediment}$ are partition coefficients with the contaminant for sorbent and sediment respectively, and C_{pw} is the equilibrium porewater concentration of the contaminant. This means that:

$$C_{pw} = \frac{Sorbed \ loading \ of \ contaminant}{f_{sorbent}K_{sorbent} + f_{sediment}K_{sediment}}$$

In order to be cost effective the fraction of sorbent used is usually a small percentage whereas the fraction of sediment is $1-f_{sorbent}$ or close to unity. Therefore if the sorbent does not have a high enough partition coefficient it would not be effective in sorbing the contaminant. Thus the addition of OMC at 0.8 lb/ft² has minimal effect on pore water concentration and flux. A much higher fraction of OMC would be needed to significantly reduce pore water concentrations or flux. OMC usage in this manner would likely only be justified if NAPL were present and the OMC could eliminate or reduce NAPL release (Knox et al., 2008).

For the next set of simulations a 1cm mat of OMC covered with a 10cm layer of sand was modeled as an active cap over the underlying sediment. As seen in Figure 4.5 and Figure 4.6, the 1cm mat leads to longer breakthrough times compared to the 30 cm sand only cap although steady state fluxes (after several hundred years) are higher due to the thinner cap thickness in this simulation. The presence of the sorbent in the cap significantly delays transport through the cap but provides only a transient effect. Once the sorbent has sorbed to capacity, the subsequent fluxes will exhibit behavior as though it were a nonsorbing medium. When compared with the first case of mixing with sediments, the 1cm mat is much more effective than the amendment mixing with sediment.



Figure 4.5: 1 cm OMC mat with 1cm/yr upwelling flow for PCB 52 (Max time = 1000 yrs)



Figure 4.6: 1 cm OMC mat with 1cm/day upwelling flow for PCB 52 (Max time = 1000yrs)

The third case explores the OMC applied as an amended sand cap modeled in Figure 4.7 and Figure 4.8. 0.8 lb/ft² OMC was mixed with sand to form a 30cm layer placed over the sediment. The combination of the thicker cap layer and the OMC sorbent provided excellent performance with low pore water concentrations and fluxes observed in the bioturbation layer after times approaching 1000 years in the slow upwelling case. Concentration and fluxes began to increase after a few decades in the high upwelling case. The comparison of breakthrough times in Figure 4.5 and Figure 4.7 shows that the uniform mixing of the sorbent leads to better performance than a thin layer placed as a mat. This effect is more pronounced for the slow upwelling case but the high upwelling case yields almost identical breakthrough times for mixed layer and mat case. Although not as effective as GAC, the easier placement of OMC (due to its greater density) may make this option a viable remedy and certainly effective at reducing exposure to benthic and surface water organisms.



Figure 4.7: OMC mixed in 30cm sand with 1cm/yr upwelling flow for PCB 52 (Max time = 1,000 yrs)



Figure 4.8: OMC mixed in 30cm sand with 1cm/day upwelling flow for PCB 52 (Max time = 200 yrs)

4.3.5.3 Activated Carbon Modeling

The Freundlich parameters listed in Table 4.3 were used to model the effects of using GAC as a sorbent material for PCB 18, PCB 52 and PCB 101. The three cases modeled include GAC mixed with 10cm of overlying sediment (in-situ treatment), GAC in a reactive core mat (1 cm thick) with a 10 cm sand cover, and GAC mixed with sand to form a 30cm amended cap. For all three cases the amount of GAC used was 0.4lb/ft², the typical loading of GAC in a reactive core mat.

As an in-situ treatment in the top 10 cm of sediment, the presence of the GAC reduces the pore water concentration which has been shown to be directly proportional to the bioaccumulation of contaminants in benthic (Lu et al., 2011). Initial concentration was recalculated for the sediment layer considering the mixing of 0.4 lb/ft² GAC which led to an 80% reduction in the initial concentration and flux for both the upwelling flow rates. The following mass balance equation was applied in order to calculate this immediate reduction in concentration upon sorbent mixing and solved for C_w. It was assumed that sorption onto organic carbon fraction of the sediments is linear whereas GAC sorption is nonlinear.

Total Mass in system = Mass sorbed by Organic Carbon + Mass sorbed by GAC

$$M = f_{oc} K_{oc} C_w \rho_b V_s + K_f C_w^{1/n} \rho_{ac} V_{ac}$$

 $C_{doc}K_{doc} \emptyset VC + f_{oc}K_{oc}C\rho_{b}V = f_{oc}K_{oc}C_{w}\rho_{b}V_{s} + K_{f}C_{w}^{1/n}M_{ac} + C_{doc}K_{doc}\emptyset VC_{w}$

Where C_{doc} , C and C_w are DOC, bulk and pore water concentrations respectively, K_{doc} and K_{oc} are dissolved organic carbon and sediment organic carbon partition coefficients, V, V_{ac} and V_s are volumes of water, activated carbon and sediment, f_{oc} is the fraction organic carbon of sediment, K_f and 1/n are Freundlich parameters, M denotes the mass of the entire system and M_{ac} is the mass of activated carbon applied, ρ_b and ρ_{ac} are bulk densities of sediment and activated carbon, and ϕ is the porosity of sediment.

For tetra-chlorobiphenyl, mixing 0.4 lb/ft² of GAC into the top 10 cm of sediment reduces pore water concentration approximately 80%. For the model trichlorobiphenyl and pentachlorobiophenyl the reductions are 95% and 29%, respectively. The reductions are sensitive to the sorption of the PCB onto the existing sediment and the proportion of PCBs carried by dissolved organic carb on (14 mg/L in the Manistique sediment). The smaller reduction associated with the higher molecular weight PCB is associated with the strong sorption of that congener onto the sediment and the NOM (i.e. the GAC is not as dominant as with less hydrophobic compounds). Flux reductions are proportional to the pore water concentration reductions since release from the surface is solely by the water pathway. Model results for this scenario are shown in Figure 4.5 and Figure 4.6 for the two upwelling flow rates.



Figure 4.9: GAC mixed in 10cm overlying sediment with 1cm/yr upwelling flow for PCB 52 (Max time = 1,000yrs)



Figure 4.10: GAC mixed in 10cm overlying sediment with 1cm/day upwelling flow for PCB 52 (Max time = 1,000 yrs)

For another simulation scenario a 1cm mat of GAC covered with a layer of sand was modeled as an active cap over the underlying sediment. This provides a remedy with the sorptive capacity of a cap plus the effect of a sand capping layer. The 1cm mat leads to long breakthrough times in the field of more than 1000 years for both the flow rates. The results have not been included due to redundancy of the figures showing no concentration for the maximum simulation time of 1000 years. The presence of the mat effectively makes the capping remedy permanent and effectively eliminates fluxes and concentration of PCBs in the surface layers of the cap. The cap will be effective as long as it is kept in place and/or maintained to its original design.

For the third simulation scenario 0.4lb/ft² of GAC was mixed in a 30cm layer of sand to form an amended cap. The uniform mixing of the GAC will in general perform better than GAC placed in a thin layer but according to the modeling results either

approach effectively eliminates concentration and flux for at least 1000 years. The thick uniformly mixed amendment layer is expected to perform better than the thin mat for both sorbent materials and this effect is more clearly seen from the OMC modeling results. Due to the strong sorption of GAC this effect is not as obvious for the design period but the same can be expected for GAC. The basic reason is that a thin layer will set up higher concentration gradients that encourage greater diffusive transport which leads to poor use of the amendment. Thin layers can also lead to breakthrough before equilibrium sorption is achieved.



Figure 4.11: Flux near surface for PCB 52 at 1cm/day upwelling flow rate for a design period of 100 years (Note: y-axis has been limited to 120 μg/m².yr for better comparison)

Figure 4.11 illustrates the effects of all the treatment scenarios for PCB 52 with an upwelling flow rate of 1 cm/day and a design period of 100 years. For the existing condition the steady state flux in this case is reaching 440 μ g/m².yr so it has not been shown on the graph to maintain clarity of the other curves. It can be observed that reduction is not substantial for in-situ application of OMC compared to the 30 cm passive cap. The 30 cm sand layer with no adsorptive amendment increases the time for PCBs to migrate to surface but only for the first few years. The GAC mat eliminates any concentration and flux to the surface for at least 1000 years as discussed previously but it there are issues with uniform placement of the thin mat due to the low density of GAC. The OMC mat leads to longer breakthrough times compared to the passive sand cap but is not able to inhibit flux to the surface for a long duration. GAC amended cap eliminates any concentration and flux to the surface for at least 1000 years and is expected to perform better than the thin mat. The amended cap provided the best performance for OMC with low pore water concentrations and fluxes observed at the surface in slow upwelling case (up to 1000 years) and in the high upwelling case concentration and fluxes began to increase after a few decades as seen in Figure 4.11.


Figure 4.12: Flux near surface for PCB 52 at 1cm/year upwelling flow rate for a design period of 100 years (Note: y-axis has been limited to 50 μg/m².yr for better comparison)

Figure 4.12 shows the flux at the surface for PCB 52 at the low upwelling rate of 1 cm/yr. The existing condition steady state flux for this figure was 157 μ g/m²/yr and cannot be seen due to the y-axis being limited in order to see the remediated results more clearly. Similar to the 1 cm/day case, in-situ application of OMC provides nominally improved flux at the surface compared to no remediation. In-situ application of AC performs a lot better with a rapid decrease in flux at the surface and eventually reaching a low steady state flux. All other amendment scenarios, include the passive cap, effectively

eliminate flux to the surface for the design period of 100 years for the 1 cm/yr upwelling flow.

4.3 CONCLUSIONS

Based solely on sorption of dissolved PCBs and in the absence of NAPL, GAC is a better amendment or in-situ treatment than OMC. However, high concentrations of NOM or the presence of NAPL are conditions which would suggest better performance of OMC. Under the evaluated conditions the breakthrough times for GAC are much higher (several orders in most cases) than the OMC modeling results. The difference between GAC and OMC is particularly significant with an in-situ treatment since the performance of an in-situ treatment depends largely upon the difference in sorptive capacity of the amendment (GAC or OMC) and the sorptive capacity of the sediment itself. At least under conditions of low to moderate levels of NOM and no NAPL, the GAC is orders of magnitude more sorbing than the sediment and OMC.

By comparing performance predictions for in-situ application of GAC and OMC it is clear that GAC would lead to longer breakthrough times because it is the stronger sorbent. Even a conventional non-sorbing sand cap is much more effective than an insitu treatment in a low upwelling situation although in high upwelling, rapid breakthrough would be observed unless a sorbent is incorporated into the cap. However, a cap will have more dramatic impacts on water depth and surficial substrate character than an in-situ treatment and may not be preferred. A mixed amendment throughout a thick cap is also more effective than placing the sorbent in a thin layer which is more clearly illustrated by OMC predictions. GAC eliminates flux to the surface for both amended thick layer and thin cap scenarios because of its higher sorption capacity but the amended layer is expected to perform better than the thin cap over a longer period of time as shown by OMC.

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Chapter 5: Polanyi based Model for AC Adsorption Prediction

5.1 INTRODUCTION

Activated carbon adsorption is environmentally important because in many systems it is the preferred method of contaminant removal or remediation. As discussed in the previous chapter, it has proved to be the preferred sorbent for many contaminated sediment systems as well, especially in sediments with hydrophobic organic contaminants such as PAHs and PCBs. Since adsorption is a surface process, activated carbons perform as ideal adsorbents due to their high surface areas and porosities. Other than surface area and porosity activated carbon is a superior adsorbent due to its strong attraction to organic adsorbates and weak attraction of water molecules (Manes, 1998).

However as established in the previous chapter, AC performance is highly susceptible to competitive adsorption in the presence of NOM. It was observed that fouling of AC in NOM containing Manistique Harbor pore water reduces sorption capacity by approximately half an order of magnitude when compared to sorption in NOM-free water. This reduction in capacity of AC directly defines its performance at a contaminated sediment site. In order to more accurately predict the sorption strength and efficiency of sorptive amendments in the field, accurate prediction of their sorption characteristics in the presence of NOM is critical. The Polanyi-Dubinin-Manes (PDM) model presents a useful tool to achieve that.

For years the Polanyi theory has been recognized as the most efficient model for dealing with adsorption on energetically heterogeneous surfaces (Brunauer, 1943), such as carbon surfaces, due to its ability to handle a variety of systems. The PDM model which is an extension of the initial Polanyi theory to describe AC adsorption in aqueous solutions is described below. Some developments to the PDM model are suggested that could allow incorporation of fouling effects into the model in order to predict AC

performance in the presence of NOM, and experiments to support this effort are included herein.

5.2 POLANYI-DUBININ MANES ADSORPTION MODEL

The Polanyi theory postulates an adsorption space (micropore volume) which acts as an attractive force field. A molecule within that space has an adsorption potential, ε , which is defined as the energy required to move that molecule from within the adsorption space of the carbon to a point outside the field of attraction. So every molecule within this space would have a different adsorption potential based on its proximity to carbon atoms. Adsorption potential would be higher inside a narrow pore due to closeness to more solid carbon atoms. All points at an equal distance from the surface of the adsorbent will have an equal potential ε and the volume of an adsorbate will be a function of adsorption potential.

The Polanyi theory was initially developed for activated carbon adsorption of gases and it suggests that the difference between ambient pressure of a gas (away from the adsorption space) and local pressure in the adsorption space is given by the Boltzmann equation:

$$\varepsilon = \int V dP$$

which is valid for non-ideal gases and vapors. When the ideal gas assumption applies this equation takes on the following form:

$$\varepsilon_{local} = RTln(\frac{p_{local}}{p_{ambient}})$$

 $\varepsilon = RTln(\frac{p_s}{p})$

or in other terms:

Where p_s is the saturation pressure of the gas and p is the bulk pressure at temperature, T and R is the universal gas constant.

The basic Polanyi model was further developed by Dubinin and extended by Greenbank and Manes (1981) to describe adsorption from aqueous solutions. For the adsorption of organic contaminants from water the adsorption potential is given by (Manes, 1998):

$$\varepsilon_{sw} = RTln\left(\frac{C_s}{C}\right)$$

Where ε_{sw} is the effective adsorption potential in water, C_s and C are saturation and bulk concentrations respectively at temperature, T and R is the universal gas constant.

Since the model for activated carbon adsorption of organic liquid mixtures from aqueous solutions in its current form came into being due to the work done by Polanyi, Dubinin and Manes it is now referred to as the Polanyi-Dubinin-Manes (PDM) model. According to the PDM model a curve of liquid adsorbate volume against equilibrium adsorption will be temperature independent and depends on the structure of the carbon. This curve is called a 'characteristic curve' and it can eventually be used to predict adsorption isotherms for a different set of conditions (Manes, 1998).

Polanyi never suggested a theoretical equation for a characteristic curve but Dubinin later suggested that by plotting adsorbate volume against adsorption potential density (i.e. ratio of adsorption potential to adsorbate molar volume) different adsorbates would result in similar characteristic curves. Crittenden, Hand, Arora, and Lykins (1987) showed that this could be mathematically represented by the following equation:

$$logq_{v} = logQ_{v} + a \left(\frac{\varepsilon_{SW}}{V_{S}}\right)^{l}$$

Where q_v is the adsorbed solute volume per unit mass of adsorbent (cm³/g), Q_v is the adsorption volume capacity at saturation (cm³/g), V_s is the molar volume of solute (cm³/mol), a and b are fitting parameters that are related to the nature of the activated

carbon (Crittenden et al., 1999), and ε_{sw} is effective adsorption potential (kJ/mol). This is often referred to as the PDM equation.

The Polanyi model is based on the following main assumptions (Manes, 1998):

- adsorption potential is a function of a molecule's distance from the surface
- adsorption potential is independent of temperature
- adsorption potential is independent of a molecule's state of aggression

Two additional assumptions state that:

- all adsorption space is accessible to adsorbate molecules
- molar volume is the best normalizing factor

Based on these assumptions, characteristic curves for individual adsorbates on a specific activated carbon would be the same except for a constant scale factor in the adsorption potential abscissa. By finding out that scale factor the different characteristic curves for each adsorbate would result in a single curve called a 'correlation curve' (Manes, 1998). In principle, given the characteristic curve for only one adsorbate on a specific activated carbon the scale factor for a second adsorbate on that carbon could be obtained by a single adsorption point at any temperature. This could then be used to predict the entire sorption isotherm for the second adsorbate over the capacity range of the characteristic curve and over a range of temperatures. This is what makes this model such a useful tool in predicting activated carbon adsorption.

The applicability of the PDM model for hydrophobic organic compounds such as PAHs and PCBs has been demonstrated by others (Amstaetter et al., 2012; Jantunen, Koelmans, & Jonker, 2010; Long et al., 2008a) and the sorption of dissolved organic matter (DOM) has also been evaluated (Wang, 2005). Some of these studies also explore different normalization factors to obtain useful correlation curves and molar volume of adsorbate is a commonly used normalizing factor. However, using molar volume as a

normalizing factor seems to work well only for a certain class of organic compounds such as aromatic compounds having similar structure (Crittenden et al., 1999; Wang et al., 2005). Long et al., 2008 looked at naphthalene adsorption onto three different polymeric adsorbents and successfully demonstrated that a single correlation curve for naphthalene adsorption can be obtained for all three polymeric sorbents by normalizing with micropore volume. Treating virgin and NOM-loaded GAC as two different sorbents due to the physical changes in the carbon structure, it may be possible to develop a single correlation curve for fouled and virgin GAC for specific sediment pore water. The primary effect of NOM is blockage of fine pores thus reducing available micropore volume and surface area. This suggests that micropore volume may be an appropriate normalizing factor and that measurement of the micropore volume changes as a result of exposure to NOM may provide a good indication of the changes in sorption capacity. Based on these concepts it may be possible to use experimentally obtained PDM adsorption isotherms for PCBs combined with the correct normalizing factors to develop a PDM based AC performance prediction model that incorporates the effects of fouling.

5.3 MATERIALS AND METHODS

5.3.1 Chemicals

Of the five PCB congeners studied in Chapter 4, three were selected for the purpose of this study. The sorption of these particular PCB congeners onto one TOG 20x50 carbon was previously studied for use as in-situ adsorptive treatment at Manistique Harbor and is discussed in Chapter 4. PCB 18 (2,2',5–trichlorobenzene), PCB 52 (2,2',5,5'–tetrachlorobenzene) and PCB 77 (3,3',4,4'–tetrachlorobenzene) were used for this study. PCB compounds were obtained from Ultra Scientific (North Kingstown, RI) in crystalline form. Acetone and hexane obtained from Fisher Scientific (Fairlawn, NJ)

were used to make stock solutions and dilutions respectively by dissolving from crystalline form.

Two types of NOM waters were used for the experiments. Manistique Harbor and River (MHR) site water was centrifuged pore water obtained by centrifuging sediment from cores received from site and then passing it through a 0.45μ m filter. As a second NOM containing water Suwannee River NOM obtained from International Humic Substances Society was dissolved in distilled deionized water. pH was adjusted to 7±0.1 in order to achieve complete dissolution followed by filtration through 0.45µm filter. Suwannee River waters were prepared at a low (SRL) and high (SRH) DOC concentration of 14 mg/L and 25 mg/L respectively.

5.3.2 Sorbents

Two types of granular activated carbons; TOG 20x50 and Filtrasorb-400 (F400) were obtained from Calgon Carbon (Pittsburgh, PA), ground to a powder using a mortar and pestle and passed through a 200 mesh sieve. The sieved GAC was boiled in deionized water for 30 minutes, dried in an oven at 105°C and stored in a desiccator. This technique has been utilized by other researchers to achieve equilibrium faster (McDonough et al., 2008). TOG 20x50 was chosen as it has been studied previously for PCBs and is often used at sediment sites (McDonough et al., 2008; Zimmerman et al., 2005). Filtrasorb-400 is a more common activated carbon studied extensively for adsorption of organic contaminants (Walters et al., 1984) and also applied at contaminated sediment sites (Zimmerman et al., 2005).

Sorbent	Carbon Source	Apparent Density (g/cm ³)	Percent Elemental Carbon ¹	Total Pore Volume (cm ³ /g)	Surface Area (m ² /g)
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TOG 20x50	Coal	0.50	87%	0.435	1035
Filtrasorb 400	Coal	0.54	89%	0.655	1101

1. Zimmerman et al., 2005

Table 5.1: Table of properties for GAC and OMC

To obtain fouled GAC for carbon characterization both carbons were preloaded with Suwannee River NOM waters at a high and low DOC concentration and Manistique Harbor pore water. Ratio of mass of DOC to mass of GAC was kept at 88% for the 14 mg/L pore waters and 188% for SRH (30 mg/L). This was done to ensure the loading of GAC for 14 mg/L pore waters was the same as the isotherm experiments done previously. The fouled carbon was removed by filtration after 28 days equilibration time, dried at 105°C and used for surface area and micropore analyses based on nitrogen gas adsorption isotherms at 77 K. The DOC concentration values were measured with a TOC analyzer before and after loading of GAC to estimate the DOC loading achieved which was greater than 10% in all cases. Specific ultraviolet absorbance (SUVA) was also measured before and after loading. These two analyses are described with greater detail in the Analysis section below.

5.3.3 Isotherm Experiments

Isotherm experiments were carried out by using MHR pore water and SRL and SRH NOM waters. For spiking below the solubility limit, the initial concentration of PCBs was kept constant and the mass of the sorbents was varied to get a range of final concentrations for the isotherm. Batches were prepared in 250 mL amber bottles with aluminum lined caps, sealed after spiking and placed on a tumbler for 28 days which is sufficient time for equilibrium to be reached (Jonker & Koelmans, 2002). This was done for both the granular activated carbons. The isotherms obtained were used to develop

Polanyi isotherms for each PCB congener and eventually incorporated into a PDM model based on micropore volume as a normalization factor. No-sorbent blanks were used for each isotherm to account for losses of the PCBs.

5.3.4 Extraction Procedures

Polydimethylsiloxane (PDMS) fibers obtained from Polymicro Technologies (Phoenix, AZ) were used as passive samplers of pore water concentrations. The fibers were soaked in methanol (Mayer et al., 2000) to remove any surface contamination that may cause chemical interference. The fiber was used to get a measurement of the freely associated PCB concentration by inserting the fibers into each bottle for the duration of mixing (28 days).

After 28 days the amber bottles were removed from the tumbler. The PDMS fiber was extracted and washed with de-ionized water and wiped clean with a Kimwipe to ensure that no sorbent was left clinging to the fiber's surface. The fiber was then immersed in 140 μ L (enough to completely submerge the fibers) of hexane in a 2 mL HPLC vial with a 200 μ L glass insert. Fibers were left immersed in solvent for at least 2 hours to ensure complete extraction.

5.3.5 Analysis

5.3.5.1 GC-µECD Analysis

The solvent containing the dissolved PCBs were analyzed using EPA Method 8082 on an Agilent 6890 Series Gas Chromatograph with a 30 cm HP-5 column and a micro-electron capture detector (μ ECD). Hydrogen gas at a pressure of 8.0 psi was allowed to flow through the column with the oven held at a temperature of 100°C for 2 minutes, increased at a rate of 15°C/min to 160°C and then increased to 270°C at a rate of 5°C/min and held for 15 minutes. The inlet was operated in splitless mode with a

pressure of 8.0 psi. The detector was kept at a temperature of 300°C with 60 mL/min makeup flow of Nitrogen gas. A new calibration curve was developed before every analysis and check standards were analyzed after every 10 samples to ensure variation from calibration was within $\pm 10\%$.

5.3.5.2 GAC Characterization

The surface area and micropore volume of the virgin and NOM-loaded activated carbons were determined using nitrogen gas adsorption isotherms at 77 K carried out on an Autosorb iQ Gas Sorption Analyzer (Quantachrome Instruments). Samples were degassed at 423 K for 18 hours prior to analysis. Physisorption results were analyzed using Quantachrome ASiQwin software to determine total surface area based on the BET equation, total pore volume at a relative pressure of 0.95, and micropore volume based on the t-method of de Boer (Gregg & Sing, 1991). Density functional theory (DFT) was used to determine the specific surface area distribution as a function of pore size (Olivier et al., 1995).

5.3.5.3 DOC and SUVA Analysis

To get a more specific parameterization of the organic matter present in the NOM waters dissolved organic carbon (DOC) and specific ultraviolet absorbance (SUVA) measurements were carried out. DOC concentration represents all the dissolved organic components present in solution and SUVA is used as an indicator of the humic content of that organic matter. This correlation between absorbance at 254 nm and humic acid content of water has been studied by (Chin et al., 1994). DOC measurements were made using Standard Method 5310B on a Shimadzu TOC-VCSH Total Organic Carbon Analyzer. SUVA analysis was done by measuring UV absorbance at a wavelength of 254 nm using Beckman Coulter DU-730 Life Science UV/VIS Spectrophotometer with a

quartz cell length of 10 mm. The following equation was used to calculate SUVA as prescribed in EPA Method 415.3:

$$SUVA\left(\frac{L}{mg},M\right) = \frac{UVA(cm^{-1})}{DOC(mg/L)} \times 100 \ (cm/M)$$

UVA Calculation: UVA = A/d

Where;

UVA = Calculated UV absorbance of the sample in absorbance units (cm⁻¹)

A = Measured UV absorbance at 254 nm of the sample

d = Quartz cell path length in cm

5.4 RESULTS AND DISCUSSION

5.4.1 GAC Characterization

Both TOG 20x50 and Filtrasorb-400 activated carbons were analyzed for pore size distribution, surface area, micropore volume and total volume. Nitrogen gas adsorption isotherms at 77 K were used to determine BET total specific surface area, total pore volume at a relative pressure of 0.95, and micropore volume based on the t-method of de Boer (Gregg & Sing, 1982) were obtained. While the Brunaur-Emmett-Teller (BET) isotherm is the most common approach to represent total specific surface area, Density functional theory (DFT) also provides a suitable analysis technique for microporous sorbent materials and was used to determine the specific surface area distribution as a function of pore size (Olivier et al., 1995). Pore size distributions were separated into three categories corresponding to surface area contained within pores greater than 0.5 nm, 1 nm, and 1.5 nm. The results of these physical characterizations are discussed herein.

GAC	Surface Area (m²/g)					Pore Volume (cm ³ /g)		
GAC	BET	DFT	> 0.5 nm	>1 nm	> 1.5 nm	Micropore	Total pore	
TOG	1035	1129	1129	165	16	0.385	0.435	
F400	1101	1011	1011	286	34	0.372	0.655	

 Table 5.2:
 Physical characteristics of virgin TOG and F400

By the International Union of Pure and Applied Chemistry (IUPAC) classification of pore size distribution, microporous materials have pore diameters less than 2 nm. Based on this classification both the TOG and F400 activated carbons studied fall into the microporous category. The total specific surface areas for both materials are not significantly different from each other based on the varying numbers obtained from BET and DFT theory. For both sorbents a substantial fraction of surface area was contained in pores less than 1 nm which is in agreement with other studies (Dastgheib et al., 2004; Fairey et al., 2006). The difference between the two activated carbons lies in the fraction of surface area present in pore sizes is greater than 1 nm. F400 has more surface area for pores greater than 1 nm compared to the TOG activated carbon.



Figure 5.1: Physical characteristics of virgin and DOC-loaded activated carbons

The virgin and DOC-loaded activated carbons were analyzed as described earlier to obtain the physical characteristics shown in Figure 5.1. When equilibrated with waters containing NOM, the surface area and pore volumes of the carbons decrease due to mechanisms such as pore blocking as well as direct adsorption onto the surface. This is apparent from the decrease in values for both TOG and F400 carbons when they were equilibrated with NOM water. The decrease in both surface area and micropore volume indicates that DOC adsorption is taking place by both surface adsorption and poreblocking mechanisms as was indicated for a study with carbon nanotubes (Wang, 2005). For all three NOM waters (MHR, SRL, SRH) the surface area and pore volume reductions for TOG are more moderate compared to reduction in F400. Especially for SR waters the reduction in F400 pore volumes is more extreme which may be experimental or just the nature of interaction of F400 with Suwannee NOM. This may be explained by the F400 having a bigger fraction of surface area present in pores greater than 1 nm in size, thus allowing DOM in that size range to be more easily adsorbed within the pores.

5.4.2 DOC and SUVA Results

The DOC and SUVA for all waters used in the isotherm experiments was measured before equilibrating with the two types of activated carbons using the methods described. Results of these tests are summarized below.

Pore water	DOC (mg/L)	SUVA (L/mg-m)
Manistique Harbor (MHR)	13.8	0.35
Suwannee River Low (SRL)	13.9	7.32
Suwannee River High (SRH)	25.3	5.97

Table 5.3: DOC concentrations and SUVA values of NOM waters

Even though the SRL water was prepared to keep the same DOC concentration as Manistique pore water it can be seen by the higher SUVA values that the humic acids are much higher for the Suwannee NOM waters. A low SUVA value indicates lower aromaticity and lower amount of humic acids (Weishaar et al., 2003). This might indicate that a major contributor of DOC in Manistique pore water is fulvic acid content and not humic acids. Fulvic acids are lower in molecular weight and also lead to lighter colors in solution compared to humic acids (Piccolo & Stevenson, 1982). Aquatic humic acids are 2–3 times larger than aquatic fulvic acids (Wagoner et al., 1997). This was also observed visually during the experiments as Suwannee River pore waters containing more humic acids were of darker color compared to almost colorless Manistique pore water.

5.4.3 PDM Characteristic Curves for PCBs

Polanyi-Dubinin-Manes characteristic curves for PCB 18, 52 and 77 were developed to evaluate applicability of this model to PCBs. This was done by using the PDM equation in Origin's non-linear curve fitting function against the isotherm data obtained. The resulting characteristic curves of TOG activated carbon are shown below for all three PCB congeners in both lab DI water and Manistique pore water. PCB 18 provided the best fit for the data. PDM characteristic curves are essentially adsorption isotherms and can be seen in Figure 5.2 below.



Figure 5.2: Characteristic Curves of (a) PCB 18, (b) PCB 52 and (c) PCB 77 in Lab DI water (blue) and Manistique Pore water (red) for TOG

The PDM characteristic curves show that Polanyi model provides a good fit for the experimental isotherms. For each of the PCB congeners Manistique pore water shows lower sorption compared to its corresponding isotherm in DI water. This substantiates that the presence of natural organic matter reduces the sorption capacity of activated carbon. The PDM parameters for all three congeners are summarized in Table 5.4. The parameters listed are the PDM parameters as defined by the equation discussed previously and included here:

$$logq_{v} = logQ_{v} + a \left(\frac{\varepsilon_{sw}}{V_{m}}\right)^{b}$$

Molar volumes used were obtained from Mackay et al. (1992) and PCB solubilities were taken from Dunnivant et al. (1992) and these values can be found in Appendix B.

Congener	Water/Medium	$Q_{\rm v}$	а	b	\mathbb{R}^2
PCB 18	Lab/DI water	0.0644	-84.1	1.824	0.975
	MHR Pore water	0.0201	-328.6	2.385	0.991
PCB 52	Lab/DI water	0.0026	-28.1	1.132	0.784
	MHR Pore water	0.0006	-59.2	1.470	0.818
PCB 77	Lab/DI water	0.0035	-78.8	1.246	0.923
	MHR Pore water	0.0004	-3779.2	2.867	0.949

Table 5.4: Summary of PDM parameters from characteristic curves for TOG

These results demonstrate that PCB adsorption with activated carbon can be effectively described by the PDM adsorption model as assessed previously for other types of carbon based sorbents (Amstaetter et al., 2012; Jantunen et al., 2010). For each PCB congener it is observed that the adsorption volume capacity (Q_v) decreases for the pore water results in comparison to the organic free electrolyte solution which suggests that the combined micropore and mesopore volume of the AC has decreased (Dobruskin, 1996, 2001), thus reinforcing that there is reduction in adsorption capacity in the presence of NOM.

5.4.4 Development of Correlation Curves

Based on existing studies discussed in detail in Chapter 2, adsorption of a contaminant on different types of sorbents can be defined by a single correlation curve by normalizing the equilibrium volume adsorbed, q_v with micropore volume of the respective adsorbents (Long et al., 2008b). It has already been established that the presence of NOM leads to decreased sorption capacity and as seen by the results summarized in Table 5.2 these changes are reflected by the changes in surface area and micropore volume of the activated carbon.

Since a fouled AC has distinctly different micropore volume it may be assumed to be a different sorbent. Micropore volume as a normalizing factor for q_v has proved to work for obtaining a single correlation curve for different sorbent materials (Long et al., 2008b), the same normalization may be applicable to fouled and un-fouled AC. So the characteristic curves obtained from the sorption results obtained of TOG isotherm experiments with organic free lab water and Manistique pore water were normalized with the measured micropore volumes for virgin and NOM-loaded TOG. These results are plotted in the graph below.



Figure 5.3: PCB 18 q_v/V_{micro} vs. ε_{sw}/V_s plot for TOG activated carbon

From this plot it seems that at lower equilibrium concentrations i.e. higher ε_{sw}/V_s values the points for lab water and pore water almost lie on the same curve. The nonlinear curve fitting function in Origin 9.1 (2013) was used to develop correlation curves having equations of the following form:

$$\log \frac{q_{v}}{V_{micro}} = \log Q_{v} + a \left(\frac{\varepsilon_{sw}}{V_{s}}\right)^{b}$$

Where q_v is the adsorbed solute volume per unit mass of adsorbent (cm³/g), Q_v is the adsorption volume capacity at saturation (cm³/g), V_s is the molar volume of solute (cm³/mol), a and b are fitting parameters, ε_{sw} is effective adsorption potential (kJ/mol), and V_{micro} is micropore volume of fouled or un-fouled carbon.

This was done for each of the PCB congeners and their respective correlation curve equations obtained from Origin's non-linear curve fitting function were used as a basis for predicting adsorption isotherms discussed in the following sections. The correlation curves and model equations for the three PCB congeners are shown in Figure 5.4 below.



Figure 5.4: PDM correlation curves for (a) PCB 18, (b) PCB 52 and (a) PCB 77 based on MHR pore water and DI water experimental isotherms for TOG

The correlation curves obtained show the correlations based on micropore volume normalization that will be used to predict adsorption for other NOM waters. In all three correlation curves the correlations are more accurate for lower equilibrium concentrations of PCB i.e. higher ε_{sw}/V_s values. However the prediction capability of these PDM correlation curves still warrants further examination. TOG isotherms in Manistique pore water and DI water were used to develop the correlation curves because of the detailed preliminary assessments carried out in Chapter 4. Also because TOG isotherms were obtained for MHR, SRL and SRH waters as opposed to F400 isotherm experiments for MHR only.



Figure 5.5: Comparison of correlation curves for TOG

If we plot all three correlation curves on one graph it can be seen from Figure 5.5 that while the curves separate at higher concentrations (lower x-axis values), at lower concentrations the three lines collapse on to each other. This means that the correlation curve obtained from one PCB congener could be used to predict sorption for other PCB congeners only at lower equilibrium PCB concentrations but not at higher equilibrium concentrations. This would necessitate the requirement to develop correlation curves for

each PCB congener separately, especially to obtain isotherms at higher equilibrium concentrations. It also suggests that at lower concentrations pore blocking is the dominant mechanism of capacity reduction in activated carbon and direct competition for surface area is not governing because all adsorption sites have not yet been occupied.

In order to see how well the prediction compares to the original isotherm data obtained experimentally, the TOG based model equations developed as shown in Figure 5.4 were used to plot the predicted isotherms for lab water and Manistique pore water against the experimental data previously obtained in lab. These results are shown in Figure 5.6 and 5.7 for all three PCB congeners. The error bars for experimental data points represent 95% confidence limits.



Figure 5.6: Experimental data with predicted isotherms in organic free water for TOG



Figure 5.7: Experimental data with predicted isotherms in MHR pore water with TOG

As seen in Figure 5.6 and Figure 5.7, for all three PCB congeners the predicted isotherm does a good job at predicting back to the original experimental data. For both DI water and Manistique pore water the predicted lines align reasonably well with the experimental data points obtained in the lab. Chi-squared tests to check goodness of fit for PDM predictions have been used by others (Xu et al., 2008) and were carried out here to check the goodness of fit for our predictions. PCB 18, PCB 52 and PCB 77 had chi-squared values of 0.115, 0.070 and 0.077 for DI water isotherms and 0.083, 0.018, and 0.561 for MHR isotherms respectively. These chi-squared values are well below their critical values from chi-squared distribution thus verifying that the predicted isotherms fit the experimental data well. A detailed summary of chi-squared goodness of fit tests is

included in Appendix B. These results give validity to the premise that a prediction has merit to predicting isotherms for virgin as well as fouled GAC. However this may be limited to lower equilibrium concentrations as seen in the discussion of Figure 5.5 and would be best suited for systems where pore blocking is the dominant mechanism of activated carbon fouling.

5.4.5 Prediction of Existing Literature Data

To check the prediction potential of the model the PDM correlations obtained were used to predict PCB adsorption isotherms for McDonough et al. (2008) and compared with the measured adsorption isotherms presented in the McDonough et al., 2008. Since this study used the same type of activated carbon (TOG 20x50) and included micropore volumes for the carbon the data could be used easily by the model developed. The study reported a Freundlich log K_f value of 8.23 (ng/kg)(L/ng)^{1/n} and a Freundlich 1/n of 0.70 for their virgin TOG isotherm. It also reported 95% confidence limits of the isotherm parameters. Since actual data from the study was not available dotted lines representing upper and lower confidence limits for PCB 18 adsorption are plotted in Figure 5.4 below. Using their reported 0.327 cm³/g fouled micropore volume and the Prediction model equations shown in Figure 5.4 the predicted isotherm was plotted in blue.



Figure 5.8: TOG-MHR based predicted PCB 18 isotherm with 95% confidence limits from McDonough et al. (2008) study

The isotherms are compared here because exact data points for McDonough et al. data were not available. The comparison of McDonough et al. isotherm and the model prediction shows good agreement of the model with the experimental isotherm for the range of measured adsorption, as seen for PCB 18 in Figure 5.5. This shows that the model equation based on fouled and unfouled TOG isotherms from one experiment may be used to reasonably predict adsorption isotherms for another study.

5.4.6 Effects of Type of GAC

The PDM correlation curves were developed on the basis of experimental data for TOG 20x50 type activated carbon. In order for the prediction model to be useful its applicability for a different type of activated carbon was tested. Isotherm experiments for PCB adsorption in Manistique Harbor pore water were carried out using F400 type carbon. The model equations developed based on TOG (shown in Figure 5.4) were used to predict the adsorption of PCBs with fouled F400 AC using measured micropore volumes for fouled F400 (shown in Figure 5.1) and experimental isotherm data obtained from lab experiments for F400 in MHR water were used to compare. F400 was chosen because it is one of the most common types of activated carbon that is commercially available today. Figure 5.9 shows a comparison plot of the prediction against the experimental data. The solid lines in Figure 5.9 represent the predictions for the three PCB congeners and the experimental data is shown as data points in corresponding colors.



Figure 5.9: Experimental data and TOG-MHR based predicted PCB isotherms for Manistique pore water and F400 carbon

It can be seen that the predicted isotherm for F400 adsorption of PCB 18 and PCB 52 fits the experimental data obtained from the laboratory tests pretty well. The PCB 77 prediction diverges from the actual data points more than the other two PCBs but still provides a reasonable estimate. As shown in Table 5.1, F400 has higher specific surface area in pores >1 nm compared to TOG. The availability of more >1 nm allows for greater sorption of PCB 77 which has the largest molecular volume out of the three PCBs. This might be the reason that the PCB 77 experimental adsorption data points are slightly higher than the predicted isotherm. However this difference is not significant and

the predicted and experimental results seem to be in good agreement of each other over the whole range of equilibrium concentrations measured in the laboratory, especially for PCB 18 and PCB 52 adsorption on F400 carbon in MHR pore water. Chi-squared tests were carried out to check the goodness of fit for our predictions. PCB 18, PCB 52 and PCB 77 had chi-squared values of 0.054, 0.018 and 0.561 respectively which are well below their critical values from chi-squared distribution. A detailed summary of this goodness of fit test is included in Appendix B. However this confirms that the prediction developed using TOG carbon can be suitably used to predict adsorption for F400 carbon in MHR pore water.

5.4.7 Effects of Type and Concentration of DOC

Another thing to consider for the potential applicability of this model is its prediction accuracy for pore waters with higher DOC concentrations. The two types of NOM used are Manistique Harbor and River NOM and Suwannee River NOM. As seen in Table 5.3 the Suwannee River pore waters have much higher SUVA values so not only is a difference in DOC concentrations is being evaluated here but also a difference in humic acid content of the two NOM sources. In order to examine model effectiveness for higher DOC concentrations Suwannee NOM waters with two different DOC concentrations of 14 mg/L (SRL) and 25 mg/L (SRH) were used in isotherm experiments with TOG carbon. Model prediction for adsorption based on model equations (shown in Figure 5.4) developed from original TOH-MHR adsorption data along with experimental results obtained from lab experiments for both Suwannee NOM waters are illustrated in Figure 5.10 and Figure 5.11 below.



Figure 5.10: Experimental data and TOG-MHR based predicted PCB isotherms for Suwannee River NOM (SRL) and TOG carbon

When looking at the predicted isotherms against the adsorption data of their respective PCB in Figure 5.10, it can be seen that the prediction works extremely well of PCB 52 and PCB 77 adsorption in the low DOC Suwannee water which had the same DOC of 14 mg/L as Manistique pore water. The PCB 18 isotherm seems to deviate from the experimental data at higher concentrations but chi-squared goodness of fit tests suggest that the predictions for TOG adsorption in SRL water provide good fits to the experimental data. PCB 18, 52 and 77 predictions had low chi-squared values of 0.215, 0.045 and 0.015 respectively which were well below their respective critical values.

The prediction developed from MHR adsorption data performs well for Suwannee NOM water as well. Even though the DOC concentration for both these waters was the same the SUVA value of SRL water was almost 7 L/mg-m higher which is almost 2000% higher. This higher SUVA value means that the Suwannee water has higher amounts of humic acids and thus bigger sized NOM compared to Manistique pore water. Even with such a stark difference in humic acids the prediction developed based on the low humic acid water works quite well for the water with much more humic acid.



Figure 5.11: Experimental data and TOG-MHR based predicted PCB isotherms for Suwannee River NOM (SRH) and TOG carbon

-4

4.5

4.0

-5

-3

log Ce (µg/L)

-2

-1

Figure 5.11 shows the MHR based prediction against experimental data points for SRH isotherms which have a DOC concentration of 25 mg/L. Even though the two waters have different DOC concentrations the model seems to predict the experimental results with accuracy. Chi-squared values in this case were 0.181, 0.009 and 0.015 for PCB 18, PCB 52 and PCB 77 respectively, again confirming that the predicted isotherm is a good fit with the observed data. The Manistique NOM based prediction works well for TOG Suwannee adsorption isotherms at both DOC concentrations of 14 mg/L and 25 mg/L. These results suggest that DOC concentration does not directly affect the prediction capability of the model. SRL and MHR waters both had exactly the same DOC concentration and the model seems to soundly predict adsorption in both NOM waters with greatly varying humic acid content and the prediction also gives good results for a higher Suwannee DOC concentration.

5.4.8 Extension to PAHs

The PDM model uses molar volume of adsorbate as a normalizing factor and suggests that all adsorption space of a sorbent is available to all adsorbates i.e. there is no molecular sieving effect. Based on this assumption the model developed using PCBs could be extended to predict PAH adsorption in a similar way. Based on the correlations already obtained from PCB adsorption (shown in Figure 5.4) a predicted isotherm for pyrene was compared with the virgin F400 isotherm for pyrene developed by Walters and Luthy (1984). This was achieved by using solubility and molar volume of pyrene and the micropore volume of virgin F400 in the correlation equations shown in Figure 5.4. The study reported a Freundlich K_f of 389 (mg/g)(L/mg)^{1/n} and a Freundlich 1/n value of 0.386 for their virgin F400 pyrene isotherm. The results of their isotherm are plotted in
red along with a pyrene adsorption model prediction based on the previous PCB 18 PDM correlation in red.



Figure 5.12: TOG-MHR based predicted Pyrene isotherm vs. Experimental isotherm from Walters & Luthy, 1984

While the predicted isotherms are not extremely accurate at all equilibrium water concentrations the maximum divergence from experimental results for the PCB 18 based prediction is not more than half an order of magnitude. PCB 52 and PCB 77 based correlations were also considered but the results are not included here because they give a less accurate prediction of pyrene adsorption. PCB 18 is closest in hydrophobicity to pyrene therefore it is not surprising that the PCB 18 based correlation provides the best

prediction of pyrene adsorption. Just looking at the PCB 18 based prediction we can say that this merits the potential use of the model for prediction of other hydrophobic organic compounds (HOCs) when an estimate of adsorption potential of a contaminant is required. However the current results suggest that the hydrophobicity of the HOC to be predicted would need to be similar to the HOC used to develop the PDM correlation in order to get more accurate predictions. Further investigation would be needed in order to use the prediction across a wide range of HOCs and this would require research into alternate normalizing factors such as adsorbate molecule size (Long et al., 2008) or linear solvation energy relationships (Crittenden et al., 1999) in place of the molar volume, V_s term in the original PDM equation.

The results discussed in the previous sections give a glimpse of the potential of this PDM based adsorption prediction model. The biggest advantage of using such a model is that adsorption isotherms would not need to be developed for each contaminated sediment site with hydrophobic organic contaminants in order to obtain the reduction in sorption capacity due to the presence of NOM. Adsorption of HOCs in the presence of NOM could be predicted solely based on micropore volume of fouled carbon and physico-chemical characteristics of the contaminant.

5.5 CONCLUSIONS

A PDM based model was developed for adsorption prediction of polychlorinated biphenyls on activated carbon based on bench-scale laboratory experiments. Sorption parameters of three individual PCB congeners obtained from isotherm experiments were used to develop PDM characteristic curves and successfully demonstrate the applicability of the PDM model to hydrophobic organic adsorption on fouled and un-fouled activated carbon. Using AC micropore volume as a normalization factor for q_v a single correlation curve was obtained for fouled and un-fouled PCB adsorption for each congener on TOG carbon, essentially treating them as two different sorbents. Results showed that this modification to the basic PDM model allows accurate prediction of an existing literature isotherm from a McDonough et al. study. The McDonough et al. experimental isotherms agreed well with the model prediction that was based on MHR isotherms for all three PCB congeners.

The McDonough et al. data used the same type of carbon i.e. the TOG used to develop the PDM correlation. However the same model correlation was used to predict PCB adsorption on to F400 carbon in MHR water. The predicted results again show that the model performs well for adsorption prediction of a different type of GAC when compared to results obtained from laboratory experiments with F400 carbon.

Experimental data for TOG carbon in two different Suwannee NOM waters having ~14 mg/L and ~25 mg/L DOC concentrations was also obtained from laboratory experiments. Again the predicted isotherms agree with the experimental data points obtained from the laboratory study for both DOC concentrations of Suwannee NOM. This suggests that DOC concentration does not have an effect on the ability of the model to predict adsorption in different NOM waters. Suwannee NOM waters also had much higher amounts of humic acids compared to the Manistique porewater which was used to develop the correlations however this didn't affect the accuracy of prediction either.

Based on the same MHR-TOG correlations for PCBs, a predicted pyrene adsorption isotherm was generated and compared to existing pyrene adsorption isotherms from a Walters et al., 1984 study in order to assess the applicability of the model to HOCs other than PCBs. This extension of the model to predict PAH adsorption did not result in extremely accurate results but can be of use when estimates of sorption potential of AC are needed. Even though the Polanyi theory suggests that molar volume is an appropriate normalizing factor, HOCs with different molecular weights and different organic groups have different steric effects which may need to be incorporated by exploring alternate normalizing factors.

The use of micropore volume of activated carbon as a normalizing factor for the q_v in PDM model presents an appealing alternative for predicting adsorption potential of activated carbon at a site when limited sorption information is available. As previously established, the adsorption capacity of activated carbon decreases in the presence of NOM. This decrease in capacity can be estimated using this model with knowledge of just micropore volume of fouled carbon and physico-chemical characteristics of the contaminant. With increasing use of activated carbon as an in-situ adsorptive treatment at HOC contaminated sediment sites such a simple tool could prove to be useful with further development.

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Chapter 6: Conclusions and Recommendations

6.1 RESEARCH OBJECTIVES

The purpose of this research was to evaluate different sorptive amendments for insitu management of contaminated sediments. This was achieved by focusing on the following main objectives:

- Assessing the current state of in-situ management techniques applied at contaminated sediment sites and concentrating on the use of sorptive amendments as an in-situ remedy
- Screening different sorbent materials for sorption of organic and inorganic contaminants at actual sediment sites
- Comparing performance of activated carbon and organophilic clay as sorptive amendment materials for in-situ remediation at Manistique Harbor in Michigan
- Evaluating the reduction in sorption capacity for both sorbents in the presence of NOM
- Predicting field performance of selected in-situ remedial applications of the two sorbents at the site
- Demonstrating the applicability of the Polanyi model to hydrophobic organic compounds such as PCBs and
- Incorporating fouling effects of NOM into the Polanyi adsorption model to develop a predictive tool for NOM-associated reduction in GAC adsorption

These objectives were achieved by conducting extensive laboratory experiments and modeling simulations geared towards examining and accurately predicting expected field performance of selected sorptive amendments for in-situ sediment remediation.

6.2 RESEARCH CONCLUSIONS

6.2.1 Screening of Sorptive Amendments

Laboratory experiments in the form of equilibrium isotherm tests were carried out to determine sorption characteristics of five types of clays (PM-199, MRM, Al-Pillared MMT, DMDODA-MMT, and kaolinite) and four types of carbon based sorbents (GAC, Fe-Pd GAC, SIAC, rice husk char). The contaminants of concern included mercury, arsenic, chromium, copper and PAHs. All batch tests were carried out in lab prepared distilled-deionized water to get sorption capacities of virgin sorbents. Additionally mercury, copper and PAHs were tested in NOM waters from actual sediment sites from Great Lakes Areas of Concern. The pore waters used for these experiments were obtained from sediment cores received from Deer Lake, Torch Lake, Manistique Harbor and River in Michigan and Grand Calumet River in Indiana.

Results show that mercury sorption is strongest with sulfur impregnated activated carbon (209,700 L/kg) and Organoclay-MRM (82,000 L/kg) which are enhanced forms of conventional granular activated carbon and organophilic clay. Since SIAC and MRM are not cheaply available, for large scale applications the use of conventional GAC and OMC would still be the preferred options. Iron-palladium coated activated carbon proved to be the superior sorbent choice for arsenic and chromium with partition coefficients of 8950 L/kg and 2965 L/kg respectively. Conventional granular activated carbon acts as a good sorbent for copper contamination with a sorption coefficient of about 11,000 L/kg but is subject to fouling in the presence of NOM.

Sorption of polyaromatic hydrocarbons (PAHs) was evaluated using pyrene, benzo[a]anthracene and benzo[a]pyrene as representative PAHs. Granular activated carbon (TOG 20x50) and Organoclay PM-199 were the chosen sorbents for PAH sorption. Isotherm experiments show that GAC achieves higher sorption capacities compared with OMC. GAC is not only more strongly sorbing for dissolved hydrophobic organic compounds but is commercially available usually at a lower price compared to other commercial sorbents. OMC is also commercially available and has exceptional performance in the presence of non-aqueous phase liquid contamination (Knox et al., 2006; Lee et al., 2012) while also having moderate sorption capabilities for dissolved contaminants.

6.2.2 In-situ Adsorptive Remedy Design for Manistique Harbor

Equilibrium isotherm experiments and design simulations were used to compare amended capping and in-situ treatments using granular activated carbon (GAC) and organophilic clay (OMC). Isotherm measurements with pore water from Manistique Harbor, MI were used to determine sorption capacity of five polychlorinated biphenyl (PCB) congeners on GAC and OMC and evaluate the influence of natural organic matter (NOM) on both. Results of the sorption show that fouling reduces performance of the GAC by about half an order of magnitude while having minimal effect on organophilic clay.

The measured performance of the sorbents was used to evaluate capping and insitu treatment remedial designs with an analytical model under conditions of weak upwelling (1 cm/yr) and rapid upwelling (1 cm/day) flow rates. Remedial designs considered GAC (0.4 lb/ft²) and OMC (0.8 lb/ft²) as an in-situ treatment, in a thin (1 cm) reactive core mat and mixed throughout a 30 cm capping sand layer. Designs were compared on the basis of the reduction in PCB flux at the cap-water interface. A sensitivity analysis showed the relevance of key parameters and their influence on in-situ treatment and capping performance. Performance for amended capping (mixed layer) was better than thin layer capping, followed by in-situ mixing in sediments. In all cases GAC acted as a far superior sorbent compared to OMC, which was supported by the sorption properties for both sorbents. However the usefulness of OMC in the presence of NAPL hot spots cannot be ignored. Although the analysis was focused on Manistique Harbor, the relative performance of the various remedies is expected to be observed at many contaminated sediment sites.

6.2.3 Polanyi based Adsorption Prediction Model

The Polanyi-Dubinin-Manes (PDM) model was used to describe adsorption isotherms of three PCB congeners in order to demonstrate the applicability of the PDM model to adsorption of hydrophobic organic contaminants. PDM characteristic curves or Polanyi isotherms for adsorption of each PCB congener with fouled and un-fouled TOG activated carbon were developed. By normalizing the PCB loading on the activated carbon in organic free water and Manistique pore water characteristic curves with measured micropore volumes of un-fouled and fouled TOG carbon respectively, a single correlation curve was obtained. A non-linear curve fitting function was used to acquire mathematical equations to describe the correlation curves.

Using these model correlations, accurate prediction of existing literature isotherm data for a PCB adsorption study done by McDonough et al. was achieved. Model predictions for PCB adsorption on to a different type of activated carbon (Filtrasorb 400) also work well and this was verified by data obtained from isotherm experiments done with F400. Further laboratory experiments to evaluate the effectiveness of the model under higher DOC concentrations and higher humic acids were conducted. Higher DOC concentration does not seem to have a direct effect on the adsorption prediction potential of the model since reasonably valid prediction of experimental data was obtained when Suwannee River NOM was used as the medium of isotherm experiments at two different DOC concentrations.

The PCB based model was extended to predict pyrene adsorption and compared to existing pyrene isotherms from a Luthy et al. study to assess the applicability of the model to hydrophobic organic contaminants other than PCBs. The model prediction of PAH adsorption gave results that were accurate within less than half an order of magnitude so it may be of use when estimated sorption potential of activated carbon at PAH contaminated sites is needed. However assessing normalizing factors other than the traditional molar volume of adsorbate may be required to achieve more accurate predictions for other HOCs.

The use of this model presents an alternative for predicting adsorption potential of activated carbon at a site when limited sorption information is available. The decrease in activated carbon adsorption capacity in the presence of NOM can be estimated using this model with only the information of micropore volume of fouled carbon and physico-chemical characteristics of the contaminant of concern. The simplicity of the model could prove to be a useful basis for getting adsorption capacity estimates for hydrophobic organic contaminants at sediment sites.

6.3 RECOMMENDATIONS FOR FUTURE WORK

In-situ remediation of sediments is set to gain more wide-scale acceptance with several pilot scale applications done at a variety of contaminated sediment sites. This research aims to support those efforts but since in-situ management of contaminated sediments is still a relatively new remediation technique some outstanding issues that need to be addressed in the future are discussed here.

- Field scale evaluation of application techniques While strength of sorption
 is helpful in determining the choice of sorptive amendment to be used, other
 factors such as ease of application when considering a certain type of remedy
 need to be studied at a field scale. For example, due to its low density
 activated carbon is harder to spread uniformly on top of sediments and this
 would be an important consideration at site.
- Further investigation of NOM effects on inorganic contaminants An in-situ
 remedial design similar to the one developed in this research for PCBs should
 be evaluated for inorganic contaminants. Effects of NOM on the sorbents
 selected for inorganic contaminants in the beginning of this study should be
 investigated with greater detail and incorporated into potential remedy
 designs.
- Further investigation of dominant mechanism of fouling the current study suggests that the model is valid in systems where the dominant mechanism of fouling of activated carbon due to the presence of NOM is pore blocking. This needs to be verified by further experimentation exploring the mechanisms of capacity reduction in the presence of NOM.
- *Exploring model validity at higher equilibrium concentrations* –model correlations provide accurate predictions for the range of equilibrium concentrations tested in that lab. However these predictions may not be accurate for concentrations much higher than this which needs to be explored in order to recognize the limitations of the model.
- Long term monitoring of in-situ amendments all in-situ applications of sorptive amendments in the field were either done at a pilot scale or have been done within the recent past. This allows for very little data collection on a 138

long term basis. Long term monitoring of the application of in-situ amendments at contaminated sediment sites is required in order to verify the long term effectiveness of designed remedies.

• *Empirical approaches to estimate micropore volume reduction* – Since the PDM based model developed uses micropore volume of fouled AC combined with physico-chemical characteristics of the contaminants of concern it would be useful to consider empirical approaches to estimate reduction in micropore volume for a variety of carbons at different DOC concentrations. This would allow estimates for adsorption potential to be derived without having to carry out assessments of fouled AC characteristics.

Appendix A – CAPSIM Modeling Results

The following legend will be used for all figures in this appendix:

Legend for Profiles						
-0 years						
- 10% of max time						
-20% of max time						
= 30% of max time						
- 40% of max time						
= 50% of max time						
= 60% of max time						
/0% of max time						
80% of max time						
= 90% of max time						
100% of max time						



Figure A.1: Existing condition with 1cm/day upwelling flow for PCB52



Figure A.2: Existing condition with 1cm/yr upwelling flow for PCB52



Figure A.3: 30cm sand layer simulation with 1cm/day upwelling flow for PCB52



Figure A.4: 30cm sand layer simulation with 1cm/yr upwelling flow for PCB52



Figure A.5: AC mixed in 10cm overlying sediment with 1cm/day upwelling flow for PCB52



Figure A.6: AC mixed in 10cm overlying sediment with 1cm/yr upwelling flow for PCB52



Figure A.7: OC mixed in 10cm overlying sediment with 1cm/day upwelling flow for PCB52



Figure A.8: OC mixed in 10cm overlying sediment with 1cm/yr upwelling flow for PCB52



Figure A.9: 1 cm mat of AC with 1cm/day upwelling flow for PCB52



Figure A.10: 1 cm mat of AC with 1cm/yr upwelling flow for PCB52



Figure A.11: 1 cm mat of OC with 1cm/day upwelling flow for PCB52



Figure A.12: 1 cm mat of OC with 1cm/yr upwelling flow for PCB52



Figure A.13: 30cm AC amended layer with 1cm/day upwelling flow for PCB52



Figure A.14: 30cm AC amended layer with 1cm/yr upwelling flow for PCB52



Figure A.15: 30cm OC amended layer with 1cm/day upwelling flow for PCB52



Figure A.16: 30cm OC amended layer with 1cm/yr upwelling flow for PCB52

РСВ	Density @ 20°C	Molar Volume	Solubility @ 25°C	
	(cm ³ /g)	(cm³/mol)	(mg/L)	
18	1.1485	247.3	0.51	
52	1.2024	268.2	0.11	
77	1.2024	268.2	0.016	

Molar volumes used were obtained from Mackay et al. (1992) and PCB solubilities were taken from Dunnivant et al. (1992)

Table B.1: Solubilities, densities and molar volumes

РСВ	Parameter	TOG-DI	TOG-MHR	F400-MHR	TOG-SRL	TOG-SRH
18	critical value	19.7	16.9	19.7	22.4	22.4
	χ^2	0.115	0.083	0.054	0.181	0.215
52	critical value	19.7	18.3	18.3	16.9	15.5
	χ^2	0.070	0.095	0.018	0.045	0.009
77	critical value	19.7	11.1	18.3	18.3	16.9
	χ^2	0.077	0.050	0.561	0.015	0.015

Table B.2: Summary of chi-squared goodness of fit tests

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