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ABSTRACT

Title of Document: PAH TRANSPORT IN AMENDED SEDIMENT CAPS

Philip Thomas Gidley, Ph.D. 2012

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By isolating contaminated sediments, capping can effectively reduce exposure to contaminants and the potential for contaminant transport into the food chain. However, typical sand caps have little sorption capacity to retard the transport of hydrophobic contaminants such as PAHs that can be mobilized by groundwater flow. The overall objective of this research was to develop and improve engineering tools for more efficient cap designs by enhancing the scientific understanding of organic contaminant transport through sediment caps and the role of sorbent amendments in enhancing cap performance.

Laboratory column experiments were performed using contaminated sediments and capping materials obtained from a creosote contaminated EPA Superfund site. The study examined activated carbon and peat amendments to the cap as ways to enhance contaminant retardation and evaluated the effect of biological activity in the cap on PAH transport. A major contribution of this research was the measurement of very low concentrations of a range of PAHs in cap pore water using a recently developed solid phase microextraction analytical technique. Azoic laboratory column experiments demonstrated rapid breakthrough of lower molecular weight PAHs when groundwater seepage was simulated through a column packed with coarse sand capping material. After eight pore volumes of flow, most PAHs measured showed at least 50% of initial source pore water concentrations at the surface of 65 cm capping material. PAH concentration in the cap solids was low and comparable to background levels typically seen in urban depositional sediment, but the pore water concentrations were high. Thus, performance monitoring of sand caps need to include measurement of PAHs in cap porewater.

Column experiments with a peat amendment delayed PAH breakthrough. The most dramatic result was observed for caps amended with activated carbon at a dose of 2% by dry weight. PAH concentrations in the pore water of the activated carbon amended caps were 3-4 orders of magnitude lower (0.04±0.02 µg/L for pyrene) than concentrations in the pore water of the source sediments (26.2±5.6 µg/L for pyrene) even after several hundred pore volumes of flow. Enhancing the sorption capacity of caps with activated carbon amendment even at a lower dose of 0.2% demonstrated a significant impact on contaminant retardation suggesting consideration of active capping for field sites prone to groundwater upwelling or where thin caps are desired to minimize change in bathymetry and impacts to aquatic habitats. The major trends of PAH transport through sorbent amended caps were reasonably predicted using standard approaches used in groundwater transport modeling

Azoic caps were also compared with biologically amended caps. The biodegradation potential of PAHs in sand caps used for sediment remediation was high in the presence of oxygen and nutrients. An initial lag phase in the biological amended cap allowed the early breakthrough of some low molecular weight PAHs; however, over time PAH degradation occurred in the column reducing the concentrations through the cap. When pore water concentrations of 10 parent PAHs and 14 alkyl clusters were measured, the surface of the biological cap remained toxic (based on the US EPA's narcosis model). Results from this study indicate sorbent amended caps combined with biological activity may lead to long-term sustainable cap designs even in areas prone to groundwater upwelling.

PAH TRANSPORT IN AMENDED SEDIMENT CAPS

By

Philip Thomas Gidley

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Chapter 1: Introduction

1.1 *Background*

This section provides a brief overview of contaminated sediment remediation approaches with a focus on sediment capping, role of capping amendments, and characteristics of polycyclic aromatic hydrocarbon contamination in sediments.

1.2 Contaminated Sediments and Remediation

Aquatic sediments serve as ultimate repositories of legacy discharges of hydrophobic organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) that can result in long-term adverse impacts to the aquatic ecosystem and also potentially impact human health. There are three general approaches for managing sediments that pose risks to human and ecological health. The first is dredging, which, if effective, removes the source of the contaminant. The goal of dredging has been mass removal from an open aquatic system to a confined disposal facility, with the assumption that this could lead to long-term risk reduction. Dredging has been the most common remediation technique, is sometimes necessary anyway to maintain shipping lanes or sediment catch basins, and an entire industry has been built around this approach. As one may expect, dredging can temporarily increase the exposure of sediment contaminants to aquatic life through re-suspension. Residual sediments left after dredging often maintain high contaminant concentrations at the surface and prevent risk reduction. Measured risk reduction from dredging has only occurred in a few of numerous “megasites” with contaminated sediments (NRC 2007). A second and often additional approach is capping, which is the placement of clean material over the contaminated sediment, thereby minimizing sediment re-suspension and flux of pollutants to the surface water. The third approach is monitored natural attenuation (MNA), where natural biological or sorption processes, and natural deposition of clean sediments are allowed to reduce the risks posed by contaminated sediments over time. The U.S. Environmental Protection Agency (USEPA) reports 60 tier 1 contaminated sediment sites where at least 10,000 cubic yards of contaminated sediment must be dredged, or at least 5 acres must be capped or monitored for natural attenuation. About 33% of the 60 tier 1 sites involve capping, and about 20% of the tier 1 sites involve PAHs.

1.1.2 Polycyclic Aromatic Hydrocarbons

PAHs are a class of hazardous organic chemicals consisting of two or more fused aromatic rings. PAHs are known to be possible or probable human carcinogens (Menzie et al. 1992), and are known to have toxic effects in the environment (Paumen et al. 2008, Matson et al. 2009). PAHs occur in the environment from multiple sources, such as: the spill of petroleum products, oil seeps, forest fires, diesel exhaust, coal combustion and by-products such as coal tar and creosote. PAHs behave similarly to other nonpolar hydrophobic organic chemicals (HOCs), such as: polychlorinated biphenyls (PCBs), and some groups of pesticides. Therefore, physical-chemical concepts applied here for PAHs may be transferable to these other compounds. Past research on HOCs can also be applied to understand PAH behavior. Chemical properties of PAHs are provided in Table 5.S1. In addition to PAHs associated with sediment carbonaceous materials, this work has applications to dense non-aqueous phase liquid (NAPL) plumes in the subsurface that would be associated with creosote or former manufactured gas plants (MGPs) (Hatheway, 2002; Luthy et al. 1994). Both creosote and coal tar are composed primarily of PAHs, most of which are parent PAHs, however, alkyl PAHs are also present in these mixtures. Alkyl PAHs are particularly important because they are thought to contribute to toxicity to a greater extent than parent compounds (ASTM 2008).

1.1.3 Capping

The current state-of-practice in sediment cap design is provided by the USEPA and US Army Corps of Engineers capping guidance documents (Palermo et al. 1996, 1998). Design criteria have been presented by others (Mohan et al. 2000, Wright et al. 2000). Sediment caps have often been made of materials with low total organic carbon (TOC) (e.g. sand, gravel). By design, finer material should be placed first to provide filtration, followed by coarser material towards the cap-surface water interface. Coarser grained material is physically more stable. If placed in a high energy environment, the fine material may wash-out, leaving only the coarse grained material. Material is often chosen for convenience to save on the cost of material transport with less concern for the sorptive properties of that material. Early modeling and laboratory experiments focused on sediment caps subject to diffusive conditions (Thoma et al. 1993, Wang et al. 1991). Under diffusive conditions, sand caps have been shown to be effective in laboratory experiments (Eek et al. 2008). In the absence of advective forces, sand caps are effective by preventing the re-suspension of contaminated sediments and reducing the flux of contaminants to the food chain (Schaanning et al. 2006, Palermo et al. 1998). Under these conditions, capping with sand or gravel also serves to distance the benthic bioturbation zone from the contamination, and this reduces contaminant flux to the surface (Lampert et al. 2011). The current design documents define an effective cap thickness as the depth of cap that is not affected by sediment-cap mixing, consolidation-induced advection, or bioturbation at the surface.

The resuspension of contaminated sediment during the initial placement of a cap has been the suspected cause of increased concentrations of some PAH compounds in the vicinity of a cap (Hyötyläinen et al. 2002). However, this can be managed by placing the capping material in small layers or “lifts” (Lyons et al. 2006). “Natural capping” continually occurs in areas of deposition (Murphy et al. 2006). If there are no longer inputs of contaminant in the natural deposited material, deposition works to increase the thickness of the cap over time. In this way, engineered capping may be thought of as an accelerated burial process.

1.1.4 Consolidation-Induced Advection

In practice, consolidation (reduction in volume) of the sediment below a cap is rapid compared to the time scale of cap design life. Consolidation also changes the porosity and hydraulic conductivity of the sediments. Guidance documents state that the time scale of consolidation may be months, while the cap design life may span a range of 50 years or more. Modeling has shown consolidation to advance contaminant migration into the cap (Alshawabkeh et al. 2005) in what is called consolidation-induced advection. Experimental studies using material collected from the same site as the material used in this research, has shown that during consolidation, contamination would stay in place (Herrenkohl et al. 2001). Other experimental studies of different material found that consolidation-induce advection is still a concern (Kim et al. 2009) and that soft sediment with high nonaqueous phase liquid (NAPL) contents may be of particular concern (Ma et al. 2010).

Consolidation is expected to decrease the hydraulic conductivity of the sediment directly below the cap. In cases where the contamination is limited to the range of sediment consolidation, this could have beneficial results. Groundwater upwelling would be diverted from the contaminated zone and discharged around the periphery of the cap (Reible et al. 2006). If the sediment contamination extends into areas unaffected by consolidation, contaminants are still expected to reach the surface when pore water passes through this unconsolidated, contaminated material and to the surface by groundwater flow paths.

1.1.5 Gas Ebullition

Biological respiration processes in sediments can lead to biogas production (methane, carbon dioxide, and nitrogen). Researchers have found that a sand cap increased the rate of biogas production by increasing the anaerobic activity in the sediments at a field demonstration site (Wang et al. 2009). This could have serious effects on the performance of a sand cap as gas bubbles are suspected to be a medium for PAH transport (Yuan et al. 2007). Gas ebullition is not examined in this dissertation, but is an area for further research.

1.1.6 Groundwater Discharge

Burnett et al. (2003) defines submarine groundwater discharge (SGD) as “any and all flows of water on continental margins from the sea bed to the coastal ocean, regardless of fluid composition or driving force.” Advective pore water flows can be directed down into the sediments as well. Tidal currents are often highest in regions with shallow water, and energy from waves at the ocean surface can be carried to sediment pore water (Huettel and Webster, 2001). It has been suggested that SGD could contribute roughly 40% of the water supplied by rivers to the coastal ocean between Cape Fear and Savannah (Moore et al. 1996). Measurement of SGD is often based on geochemical tracers because the activities of tracers are elevated in groundwater relative to surface water. Sources and sinks of each tracer can be calculated or measured. Tracers and seepage meters often provide an estimate of total SGD, but are limited in their ability to distinguish between fresh-terrestrial discharge and recirculated sea water (McCoy et al. 2009). Table 5.S2. provides literature groundwater discharge rates for various locations around the continental US. SGD rates vary widely due to spatial and temporal variability as well as methods of measuring and interpreting SGD.

Groundwater discharge is receiving attention in the literature with regard to microbial pollution (Boehm et al. 2004), nutrients (Swarzenski et al. 2007) and mercury (Bone et al. 2007). Both SGD and tidal pumping can increase the migration of metals in sediment caps (Liu et al. 2001, Simpson et al. 2002). Improvements can certainly be made to the current cap design guidelines to predict behavior in various hydrodynamic environments. Lakes generally have less groundwater discharge than river and estuarine systems. Groundwater springs can form in localized areas, suspending material and creating conical depressions in the sediment bed (Mutch, 2011). Conversely, a sediment mound in a stream bed may also create a zone of low pressure and thus groundwater discharge (Huettel and Webster, 2001). Many contaminated sediments are in tidally influenced estuarine systems, which are especially subject to pore water advection. The capping guidelines state that caps can channel flow to clean uncapped sediment, however this does not mean that the pore water exiting the clean uncapped sediment has not passed through contaminated material. In addition, this diversion of groundwater flow paths can increase groundwater flow velocities (Figure 5.S1).

Groundwater discharge provides a source of temperature regulation for fish, providing cold water in the summer and warmer water in the winter (Power et al. 1998). The congregation of fish near groundwater seeps makes these areas especially important for risk assessment. Seeps can create localized areas of contamination in the sediments if the groundwater is coming from an upstream contaminant plume. It is possible that aquatic life near the benthic boundary layer could be exposed to high concentrations before the contaminant is diluted by the surface water. Pore water concentrations have been emphasized for predicting toxic effects of PAHs to benthic organisms (Hawthorne et al. 2007, Kreitinger et al. 2007).

For current cap designs, sediments and capping materials are assumed to be in equilibrium with the pore water. The assumption of local equilibrium is often made and seems reasonable considering some of the low flow rates often encountered in the field. However, under highly advective conditions, this assumption may not hold. Caps are currently monitored by taking cores of solid material and extracting that material in the lab. This may fail to detect toxicity due to high pore water concentrations, especially when the cap solids have low sorption capacity and are subject to intermittent flows. The toxicity could be caused by the flux of contaminants by the discharge of high dissolved concentrations in the pore water. If nonequilibrium conditions exist between the solid phase and the pore water, organic carbon-water partitioning coefficients in combination with concentrations on solid cap materials from cores, cannot be used to assess cap performance. Intermittent flows of SGD makes many direct pore water monitoring techniques challenging for example.

1.1.8 Cap Amendments

A variety of capping amendments are being explored to increase sequestration of metals and organics in sediment caps. Apatite and organoclay have the broadest range of effectiveness for metals (Viana et al. 2008, Knox et al. 2008), while activated carbon, coke (Murphy et al. 2006, Zimmerman et. al. 2004, Ghosh et al., 2011), peat (Rasmussen et al. 2002), and organoclays/zeolites (Jacobs and Fōrstner, 1999) are being explored for organics. With the use of new amendments, new materials will need to be characterized and their sorption behavior could change the complexity of the transport models required for adequate design of sediment caps.

Some sorbent materials may have different sorption kinetics than natural media, or exhibit isotherm nonlinearity due to the physical structure of the sorbent, or the physical arrangement (heterogeneity) of the amendment in the cap. This may necessitate the use of modeling approaches that are not currently discussed in capping design manuals. Assuming equilibrium conditions between the solid and pore water in SGD scenarios, a cap amended with activated carbon will greatly increase the time to contaminant breakthrough because of the increase in sorption capacity. This allows for the design of thinner caps (Cornelissen et al. 2011).

1.1.9 PAH Biodegradation

The influence of biological degradation of HOCs in a sediment cap is of interest for the long-term effectiveness of a cap, when source sediment depletion does not occur before amendment sorption capacity is reached. The placement of a cap prevents the deposition of new organic matter (nutrients) onto the sediment (Himmelheber et al. 2007) and reduces the oxygen levels there, both of which has a negative impact on potential biodegradation. Despite this, it has been demonstrated that bacteria can colonize capping material in column experiments (Himmelheber et al. 2008, 2009). Bodour et al. (2003) showed that a complex community of bacteria will degrade a single PAH (phenanthrene) in a column system. This bacterial community also changed temporally during the six month experiment (Bodour et al. 2003). It is conceivable that oxygen might be carried from the surface to serve as a terminal electron acceptor (TEA) for microbial respiration. Oxygen and nutrients have been found to have the greatest influence on the effectiveness of PAH degradation in sand caps (Hyun et al. 2006). With PAHs of MW greater than pyrene, degradation has been observed to be limited even in aerated conditions (Hyun et al. 2006). Within both sediment and cap layers, bioavailability will greatly influence degradation (Wammer and Peters, 2005). The bioavailability is largely dependent on the freely dissolved porewater concentration of the compound as PAHs strongly bound to the sediment will show less degradation. A review of PAH degradation pathways by bacteria, fungi, and algae is provided by Cerniglia (1992) and Haritash (2009). Caps may have oxygen introduced by benthic organisms, waves, tidal pumping (Simpson et al. 2002) or engineered introduction via air diffusers, electro-osmotic flow, or anodes (Sun et al. 2010).

Tang et al. (2005) observed the anaerobic degradation of phenanthrene in sediments from Eagle Harbor with the controlled release of nitrate and sulfate to serve as a TEA. Some have investigated the potential for groundwater to supply nitrate for nitrate reduction (Swarzenski et al. 2007, McNally et al. 1998). Groundwater typically has low nitrate levels (1 mg/L). The anaerobic degradation of some low molecular weight (MW) PAHs such as naphthalene and 2-methylnaphthalene can be significant if pore water levels of sulfate are maintained at 14-25mM (868-1550 mg/L), which could be supplied by advection from overlying marine water (Rothermich et al. 2002).

1.1.7 Eagle Harbor sediment cap

Sediment and capping material from Eagle Harbor was used in this research. For approximately 80 years, at least 400,000 gallons of creosote leaked into the ground and sediments at the Eagle Harbor wood treatment facility in Washington State (Krone et al. 1986, Stout et al. 2001, Brenner et al. 2002). In 1988, the site was placed on the national priority list as a Superfund site. In 1990, a groundwater extraction and treatment system was installed, and in 1994, a sand cap was placed there (Merritt et. al. 2010, Herrenkohl et. al. 2001, Lyons et. al. 2006). After the placement of the cap, biological indicators of pollution at Eagle Harbor were found to be improving (Myers et al. 2008). Evidence for the presence of PAH degrading bacteria have also been found at this site (Hedlund and Staley, 2006; Tang et al. 2005; Geiselbrecht et al. 1998) as it has been at other creosote sites (Mueller et al. 1989).

At Eagle Harbor, groundwater flow is suspected to be a pathway for PAH migration from the sediments to the cap surface in some locations (Merritt et al. 2010). These locations are influenced by tides and wave action. An estimate of the groundwater discharge rates over a 24 hour period (two tidal cycles) for two such locations are depicted in Figure 1.1 (Magar et al., 2007). The Peclet number (Pe) can be defined as d_{50} v/D_0 (the ratio of advective to dispersive (or diffusive) flux) where d_{50} is the median particle diameter of the capping material, v is the average pore velocity, and D_0 is the molecular diffusion coefficient in open water (phenanthrene).

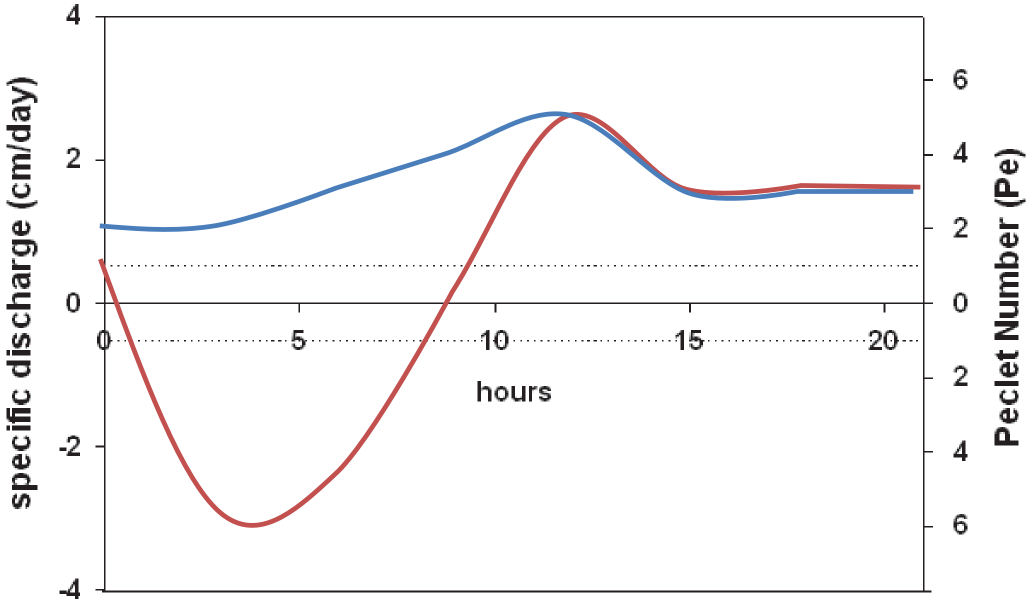

Figure 1.1 Specific groundwater discharge rates at two locations and corresponding Peclet number.

At Eagle Harbor (and at other sites) discharge will likely vary with time and location in the cap. A Peclet number greater than 1 indicates that advection dominates as a transport mechanism. Figure 1 shows advective conditions in a cap, even though daily average flow rates may indicate otherwise.

A schematic cross section is shown (Figure 1.2) to convey the conceptual layout of field sites. Based on sediment coring, it is hypothesized that compaction of the sediment at Eagle Harbor has resulted in the formation of an aquitard; however, groundwater is being expressed near the shore line/cap periphery (Merritt et al. 2010). These discharges may be a mixture of fresh groundwater and recently circulated (saline) surface water. Saline groundwater discharge can be formed from saltwater intrusion on a small scale near the shore, and on a larger spatial scale (Ghyben-Herzberg Relation). Figure 1.2 depicts these possibilities.

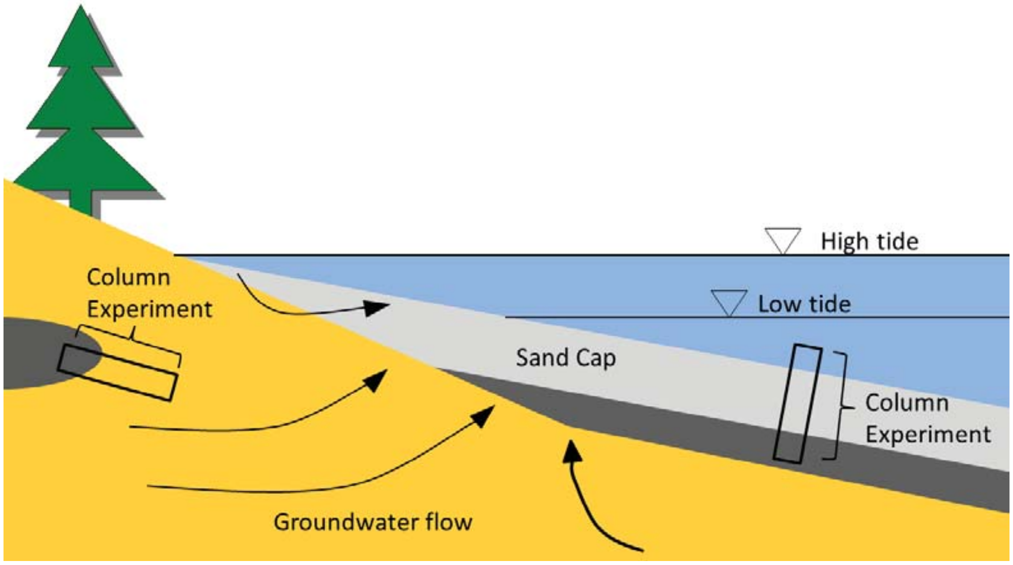

Figure 1.2 Schematic cross section of a hypothetical capping site with contaminated sediment/aquifer plume in dark grey with SGD (not to scale). Column experiments could provide insights applicable to the sediment, cap and surface water or plume and aquifer material.

1.2 Models to Describe Contaminant Transport

1.2.1 NAPL Dissolution

Contaminant mass will be lost from the sediments with time, but the assumption of constant source zone concentration is not necessarily a conservative one. There may be sediment pore water concentration depletion or increases due to NAPL dissolution dynamics. The current design guidelines reference a numerical model that examined a decreasing source zone concentration. However, when multiple components (PAHs) are released from a NAPL (creosote) exposed to advective flows, some PAHs can increase in pore water concentration while others decrease.

The temporal dissolution of PAHs from multi-component NAPLs has been modeled previously by Peters et al. 1999. Sediment that is coated with a thin layer of creosote can be modeled using Raoult's law and coupled mass balance equations for creosote, aqueous, and solid phases (Figure 3.) The solubility of PAH, *i*, is related to creosote composition through Raoult's law:

$$C_i^* = X_i^N Sw_i \qquad \text{eq. 1.}$$

where X_i^N is the mole fraction of i in the creosote phase, and Sw_i is the subcooled liquid solubility for i. Recent observations of an emplaced coal tar creosote source over 14 years showed that utilizing Raoult's law without solid crystal formation or mass transfer limitations adequately predicted the dissolution of most PAHs (Fraser et al. 2008).

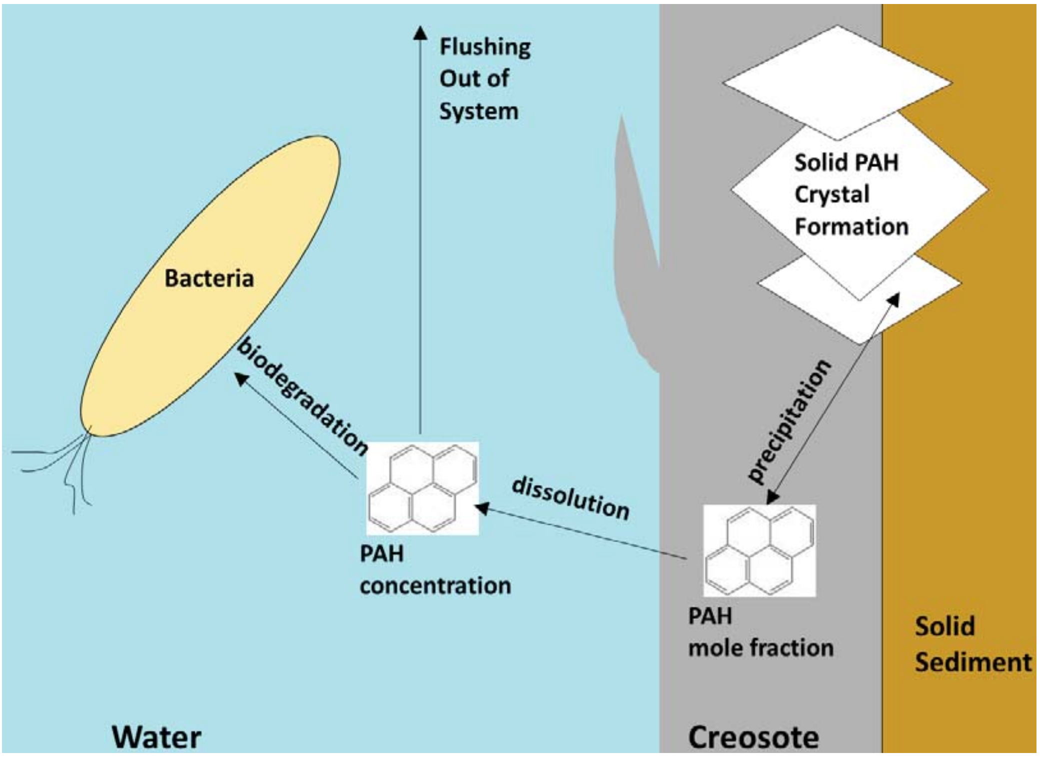

Figure 1.3 Possible mechanisms as described by Peters et al. 1999 in the sediment source.

The Peters et al. (1999) dissolution model uses a mass transfer rate that assumes homogeneous creosote/water surface area throughout the control volume. In reality, the creosote/water surface area will be smallest where the groundwater first contacts the creosote coated sediment and will increase as the dissolution front is reached (Imhoff et al. 1993). The Peters et al. 1999 model accounts for solid precipitation in the NAPL phase, which is not accounted for when simply applying equation 1, but does not account for the creosote/water mass transfer changes if a semi-solid film forms at this interface (Luthy et al. 1993, Ortiz et al. 1999). The model assumes that degradation occurs in the aqueous phase and not on the creosote or sediment surface. Errors in the Peters' model could be due to microbial utilization of sorbed phase PAHs (Xia and Wang, 2008).

1.2.2 Adsorption, Partitioning and Pore Filling

Linear distribution coefficients (K_d) can be used to describe equilibrium behavior of PAHs with sand and peat amended caps. In the case of amorphous organic carbon associated with a sand or peat amended cap, partitioning is theoretically linear all the way to the solubility limit (Kleineidam et al. 2002). Peat, along with other plant residue materials, have been characterized for the treatment of PAHs in wastewater, and these materials exhibit linear partitioning behavior (Chen et al. 2011). For linear sorption:

$$q_e = K_d C_e \qquad \text{eq. 2}$$

Where q_e and C_e are the solid and water concentrations at equilibrium. Extremely high partitioning of PAHs to AC has been measured (Jonker and Koelmans, 2002). PAH sorption to AC is known to exhibit nonlinear isotherm behavior. The most commonly used non-linear sorption model is:

$$q = K_f C_e^n \qquad \text{eq. 3}$$

where K_f is the Freundlich capacity coefficient and n is often called the Freundlich linearity index. The capacity coefficient (K_f) relates to the amount of a compound sorbed and the linearity index (n) relates to the relative magnitude and diversity of energies associated with a particular sorption process (Weber et al. 1992). For a system of a linear sorption material mixed with a non-linear sorption material we can assume a summation to estimate sorption capacity:

$$q = x_1 K_d C + x_2 K_f C^n \qquad \text{eq. 4}$$

Where x_1 is the mass fraction of capping material (with low but significant amorphous organic carbon content) and x_2 would be the mass fraction of the AC mixed into the cap (Weber et al. 1992).

Isotherm experiments are often performed with a mixture of PAHs. Langmuir isotherms have been suggested as a way of modeling the sorption capacity effects of PAHs to AC (Van Noort et al. 2004). However, it was pointed out that this failed to incorporate the pore filling mechanisms of AC and that an empirical Freundlich isotherm better captured the full sorption capacity behavior (Werner and Karapanagioti, 2005). Xia and Ball (1999) used a Polanyi-Manes modeling approach to examine the adsorption (including pore filling) and partitioning of PAHs to AC. At a low concentration, adsorption is the dominant mechanism, but at higher concentrations partitioning becomes important. This holds true for the range of concentrations examined in this study using the AC properties provided by Xia and Ball (1999) (Figure 1.4).

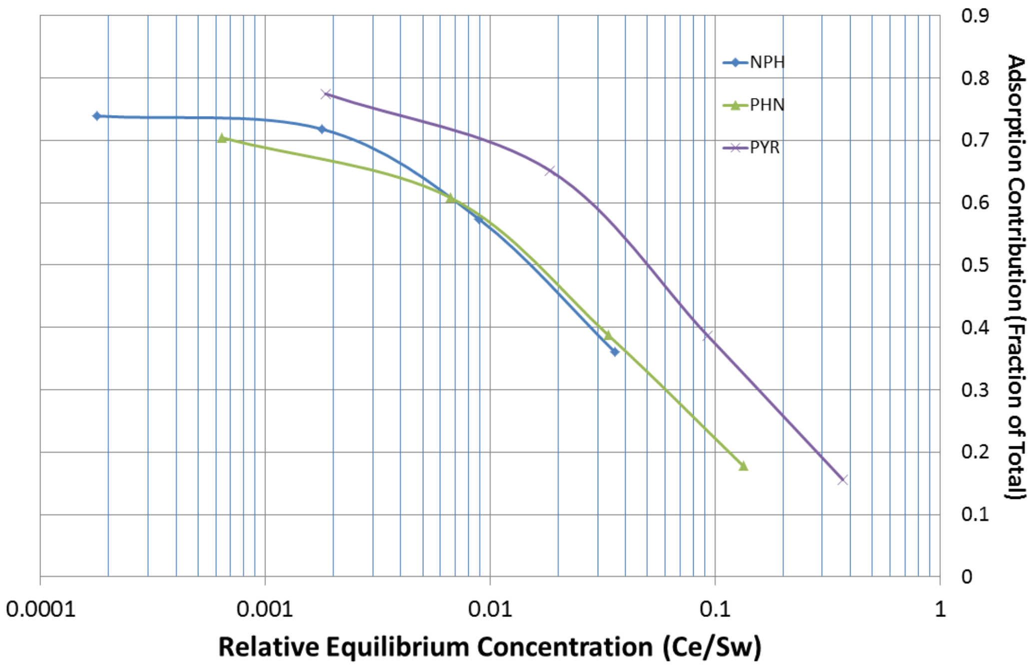

Figure 1.4 Adsorption vs. partitioning over a range of equilibrium concentrations normalized to the subcooled liquid solubility (Sw).

It appears that an empirical Freundlich isotherm is the best way to capture the full sorption behavior of PAHs to AC, however many of the isotherms in the literature may fail to account for any interaction among the PAHs in a complex NAPL such as creosote. Wang et al., 2006 showed that some sorption competition is evident between PAHs for sorption to wood chars at solute concentrations close to aqueous solubility. Even if all of the compounds in creosote (including unknown compounds) were included in a batch isotherm experiment, this process would still be different from the concentration gradients found in a flow-through system such as a sediment cap.

1.2.3 Advective Transport with Linear Equilibrium Partitioning

During advective conditions, contaminant migration in the effective layer thickness of a sediment cap is described using equations equivalent to the one dimensional advection-dispersion equation with retardation for steady state flow in saturated homogenous soil which has been summarized by Toride et al. 1999:

$$R\frac{\partial Cr}{\partial t} = D\frac{\partial^2 Cr}{\partial z^2} - v\frac{\partial Cr}{\partial z} - k_B Cr \qquad \text{eq. 5}$$

Where z is the distance into the cap, *Cr* is the volume averaged or resident concentration (gram/meter^3) of one particular PAH in the cap, *D* is the hydrodynamic dispersion coefficient (meter^2/day) obtained by tracer studies of capping material columns, *v* is the average pore water velocity (meter/day), k_B is a first-order biodegradation rate (day^{-1}), and *R* is a retardation factor given by:

$$R = 1 + \frac{\rho_b K_d}{n} \qquad \text{eq. 6}$$

where ρ_b is the cap solid bulk density (gram/meter^3), K_d is the solid-water distribution coefficient ((gram/gram)/(gram/m^3)), and *n* is porosity. The distribution coefficient depends on the properties of the capping material and assumes equilibrium partitioning in the cap:

$$K_d = (1 - foc - fac) * K_d sandcap + foc * K_{OC} + fac * K_{AC} \qquad \text{eq. 7}$$

where $K_d sandcap$ is the solid-water distribution coefficient for the non-amended cap, *f* is the fraction of added organic carbon (OC) or activated carbon (AC), K_{oc} and K_{AC} are the distribution coefficients for OC and AC (K_{AC} at a specific water concentration) respectively. This model can be used to simulate a constant source zone using the analytical solution developed by Ogata and Banks (1961). If a constant source zone cannot be assumed, the analytical CXTFIT code (implemented in STANMOD, from the US Salinity Laboratory) can incorporate a changing source term using a multiple pulse input, with linear sorption for AC at a single concentration. Go et al. (2009) present numerical models (finite difference method) similar to this to simulate phenanthrene transport in multiple layers (AC layer, sand layer, and benthic layer) over long time scales (up to 100 years). In addition to these models, non-ideal (nonequilibrium and non-linear sorption) transport equations were adapted for this research and are presented in Chapter 2.

1.3 Research motivation and objectives

1.3.1 Research motivation

Several recent studies have explored the use of strong sorbent amendments into sediments as a means of reducing bioavailability and transport of hydrophobic organic contaminants (Cornelissen et al. 2011; Beckingham and Ghosh 2011). Under certain site conditions, adding AC to a sand cap could have benefits over adding the AC directly to the sediments. First, if the AC is in the center of the cap (mid-height), it is protected from the sorption of competing organic matter that may reside in the sediments. AC may also be protected from depositing organic matter from the surface water. Again, depositional matter could contribute competing organic matter to sorption sites on the AC. Second, capping may be necessary anyway to maintain anaerobic conditions in sediments to prevent the mobilization of metal contaminants. Third, the cap may provide a desired benthic habitat different from the existing sediments. For example, the cap armor may be designed to support salmon spawning. Finally, there may be the need for protection of an AC amendment using an armored cap in high energy environments that would otherwise be unfit for AC amendment. Researchers have studied carbon amendments to sediments (Beckingham and Ghosh, 2011) and tested sediment amendment under various hydrodynamic conditions (Ghosh et al., 2011). There have been studies to look at carbon amendments to caps under diffusive conditions (Cornelissen et al., 2011). Modeling to predict the behavior of amended caps under advective flows has also been done (Murphy et al., 2006, Go et al., 2009). However, there is lack of experimental data on the migration of PAH compounds through sand and amended sand caps operated under advective conditions. Additionally, due to the challenge of measuring the low aqueous concentrations of PAHs, there is little understanding of how compound migration profiles develop over time in amended caps operated under slow groundwater flow conditions.

1.3.2 Research objectives

The primary objectives of this research are to develop and improve engineering tools for better sediment cap designs by enhancing the scientific understanding of these systems especially when amendments are introduced to promote retardation of contaminants.

This research addressed the following key scientific questions:

1. What is the effectiveness of azoic and biologically active cap systems for retaining PAH contaminants in the underlying sediments during conditions of advective transport associated with groundwater infiltration?
2. Are carbon amended caps effective in enhancing cap performance in the above scenario?
3. To what extent can contaminant binding to natural or engineered capping materials be predicted for effective design of amended caps?

1.3.3. Research contribution and outline of dissertation

The three research questions were addressed through laboratory experimental studies conducted with contaminated sediment and capping material obtained from a USEPA Superfund site coupled with PAH transport modeling. The research contributions are presented in this dissertation as a series of four distinct chapters and are briefly outlined here:

Chapter 1. Introduction: This chapter provides an introduction with a brief background of contaminated sediment remediation, discussion of challenges with capping, and PAH transport in sediment caps. Chapter 1 also provides a brief description of the research motivation, objectives, and contributions of this dissertation.

Chapter 2. Azoic Columns: This chapter was written as a stand alone paper that has been published in Environmental Science and Technology. This chapter describes the results of laboratory experimental investigations into the migration of PAHs in sand caps and sand caps amended with AC and peat that were operated in azoic conditions. The breakthrough of PAHs is modeled using standard transport modeling approaches. All three research objectives with the exception of the performance of biologically active caps are addressed in this chapter.
Laboratory work presented in this chapter was performed by the student with guidance from Seokjoon Kwon and Upal Ghosh. The Modeling work was performed by the student with guidance from Alexander Yakirevich and Upal Ghosh. The writing was performed primarily by the student with the help of the other authors. This material has been published in Environmental Science and Technology (2012, 46, 5032-5039).

Chapter 3. Biological Columns: This chapter is a working manuscript that will be submitted for publication. This chapter describes the results of laboratory experimental investigations into the migration of PAHs in sand caps innoculated with PAH degrading microorganisms. The breakthrough of PAHs is modeled using standard transport modeling approaches with first-order degradation.

Contributions of the student included laboratory work with guidance from Upal Ghosh and modeling work performed by the student with guidance from Alexander Yakirevich and Upal Ghosh. The writing was performed by the student with the help of the other authors.

Chapter 4. Research Summary: This chapter provides a summary of key research findings and explains how each of the three research questions posed in this dissertation has been addressed. Implications of this research to the field of sediment capping and recommendations for future work are also provided.

Chapter 5. Appendices: The appendices provide information about additional investigations mostly related to the azoic column experiments that were not incorporated in the submitted manuscript (chapter 2), which has been retained in its submitted form for this dissertation.

1.4 References

National Research Council. Sediment Dredging as Superfund Megasites: Assessing the Effectiveness; The National Academies Press: Washington, DC, 2007.

Menzie, C. A.; Potocki, B. B.; Santodonato, J. Exposure to Carcinogenic PAHs in the Environment. *Environ. Sci. Technol.* **1992**, 26, 1278-1284.

Paumen, M. L.; Stol, P.; Laak, T. L. T.; Kraak, M. H. S.; Gestel, C. A. M. V.; Admiraal, W. Chronic Exposure of the Oligochaete *Lumbriculus variegatus* to Polycyclic Aromatic Compounds (PACs): Bioavailability and Effects on Reproduction. *Env. Sci. Technol.* **2008**, 42, 3434-3440.

Matson, C. W.; Gillespie, A. M.; McCarthy, C.; McDonald, T. J.; Bickham, J. W.; Sullivan, R.; Donnelly, K. C., Wildlife toxicology: biomarkers of genotoxic exposures at a hazardous waste site. *Ecotoxicology* **2009**, 18, 886-898.

Hatheway, A. W., Geoenvironmental protocol for site and waste characterization of former manufactured gas plants; worldwide remediation challenge in semi-volatile organic wastes. *Eng. Geology* **2002**, 64, 317-338.

Luthy, R. G.; Dzombak, D. A.; Peters, C. A.; Roy, S. B.; Ramaswami, A.; Nakles, D. V.; Nott, B. R. Remediating Tar-Contaminated Soils at Manufactured Gas Plant Sites. *Env. Sci. Technol.* **1994**, 28, 266A-276A.

American Society for Testing and Materials. **2008**. Standard test method for determination of parent and alkyl polycyclic aromatics in sediment pore water using solid-phase microextraction and gas chromatography/mass spectrometry in selected ion monitoring mode. D 7363-07. In *Annual Book of ASTM Standards*, Vol. 11.02. West Conshohocken, PA.

Palermo, M. R. et al. Guidance for In-Situ Subaqueous Capping of Contaminated Sediments, in Assessment and Remediation of Contaminated Sediments (ARCS) Program; U.S. EPA: Chicago, IL, 1996.

Palermo, M. R.; Clausner, J. E.; Rollings, M. P.; Williams, G. L.; Myers, T. E.; Fredette, T. J.; Randall, R. E. *Guidance for subaqueous dredged material capping.*US Army Corps of Engineers: Vicksburg, MS, 1998.

Mohan, R. K.; Brown, M. P.; Barnes, C. R., Design criteria and theoretical basis for capping contaminated marine sediments. *Applied Ocean Research.* **2000**, 22, 85-93.

Wright, S. J.; Mohan, R. K.; Brown, M. P.; Kim, C. C., Filter Design Criteria for Sediment Caps in Rivers and Harbors. *J. Coastal Research* **2001**, 17, 353-362.

Thoma, G. J.; Reible, D. D.; Valsaraj, K. T.; Thibodeaux, L. J. Efficiency of Capping Contaminated Sediments in Situ. 2. Mathematics of Diffusion-Adsorption in the Capping Layer. *Env. Sci. Technol.* **1993**, 27, 2412-2419.

Wang, X. Q.; Thibodeaux, L. J.; Valsaraj, K. T.; Reible, D. D. Efficiency of Capping Contaminated Bed Sediments In Situ. 1. Laboratory-Scale Experiments on Diffusion-Adsorption in the Capping Layer. *Env. Sci. and Technol.* **1991**, 25, 1578-1584.

Eek, E.; Cornelissen, G.; Kibsgaard, A.; Breedveld, G. D. Diffusion of PAH and PCB from contaminated sediments with and without mineral capping; measurements and modelling. *Chemosphere.* **2008**, 71, 1629-1638.

Schaanning, M.; Breyholtz, B.; Skei, J. Experimental results on effects of capping on fluxes of persistent organic pollutants (POPs) from historically contaminated sediments. *Marine Chemistry.* **2006**, 102, 46-59.

Lampert, D. J.; Sarchet, W.V.; Reible, D. D. Assessing the Effectiveness of Thin-Layer Sand Caps for Contaminated Sediment Management through Passive Sampling. *Env. Sci. Technol.* **2011**, 45, 8437-8443.

Hyötyläinen, T.; Karels, A.; Oikari, A. Assessment of bioavailability and effects of chemicals due to remediation actions with caging mussels (*Anodonta anatina*) at a creosote-contaminated lake sediment site. *Water Research.* **2002**, 36, 4497-4504.

Lyons, T.; Ickes, J. A.; Magar, V. S.; Albro, C. S.; Cumming, L.; Bachman, B.; Fredette, T.; Myers, T.; Keegan, M.; Marcy, K.; Guza, O. Evaluation of Contaminant Resuspension Potential during Cap Placement at Two Dissimilar Sites. *J. Env. Eng.* **2006**, 132, 505-514.

Murphy, P.; Marquette, A.; Reible, D.; Lowry, G. V. Predicting the Performance of Activated Carbon-, Coke-, and Soil-Amended Thin Layer Sediment Caps. *J. Env. Eng.* **2006**, 132, 787-794.

Alshawabkeh, A. N.; Rahbar, N.; Sheahan, T., A model for contaminant mass flux in capped sediment under consolidation. *J. Contam. Hydrol.* **2005**, 78, 147-165.

Herrenkohl, M. J.; Lunz, J. D.; Sheets, R. G.; Wakeman, J. S. Environmental Impacts of PAH and Oil Release as a NAPL or as Contaminated Pore Water from the Construction of a 90 cm In Situ Isolation Cap. *Env. Sci. Technol.* **2001**, 35, 4927-4932.

Kim, Y. S.; Jafvert, C. T.; Yoon, S.; Hyun, S.; Johnson, B. Potential consolidation-induced NAPL migration from coal tar impacted river sediment under a remediation sand cap. *J. of Haz. Materials.* **2009**, 162, 1364-1370.

Ma, X.; Reible, D. D.; Harris, M. Assessment feasibility of in-situ capping and contaminant mobility in NAPL-contaminated sediments. *International J. Geotech. Eng*. **2010**, 4, 71-78.

Reible, D.; Lampert, D.; Constant, D.; Mutch, R. D., Jr.; Zhu, Y. Active Capping Demonstration in the Anacostia River, Washington, D.C. *Remediation*. **2006**, 39-53.

Wang, Q.; Kassem, I. I.; Sigler, V.; Gruden, C.; Short-Term Effects of Capping on Microbial Communities in Freshwater Sediments. *Water Env. Research*. **2009**, 81, 441-449.

Yuan, Q.; Valsaraj, K.T.; Reible, D.D.; Willson, C.S. A Laboratory Study of Sediment and Contaminant Release during Gas Ebullition. *J. Air & Waste Manage. Assoc*. **2007**, 57, 1103-111.

Burnett, W. C.; Bokuniewicz, H.; Huettel, M.; Moore, W. S.; Taniguchi, M. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry*. **2003**, 66, 3-33.

Huettel, M.; Webster, I. T. Porewater Flow in Permeable Sediments. In The Benthic Boundary Layer, Boudreau, B. P.; Jørgenson, B. B., Eds. Oxford University Press: New York, **2001**; pp 144-179.

Moore, W. S. Large groundwater inputs to coastal waters revealed by 226Ra enrichments. *Nature*. **1996**, 380, 612-614.

McCoy, C. A.; Corbett, D. R. Review of submarine groundwater discharge (SGD) in coastal zones of the Southeast and Gulf regions of the United States with management implications. *J. Env. Management.* **2009**, 90, 644-651.

Boehm, A. B.; Shellenbarger, G. G.; Paytan, A. Groundwater Discharge: Potential Association with Fecal Indicator Bacteria in the Surf Zone. *Env. Sci. Technol.* **2004**, 38, 3558-3566.

Swarzenski, P. W.; Simonds, F. W.; Paulson, A. J.; Kruse, S.; Reich, C. Geochemical and Geophysical Examination of Submarine Groundwater Discharge and Associated Nutrient Loading Estimates to Lynch Cove, Hood Canal, WA. *Env. Sci. Technol.* **2007**, 41, 7022-7029.

Bone, S. E.; Charette, M. A.; Lamborg, C. H.; Gonneea, M. E. Has Submarine Groundwater Discharge Been Overlooked as a Source of Mercury to Coastal Waters? *Env .Sci .Technol.* **2007**, 41, 3090-9095.

Liu, C.; Jay, J. A.; Ika, R.; Shine, J. P.; Ford, T. E. Capping Efficiency for Metal-Contaminated Marine Sediment under Conditions of Submarine Groundwater Discharge. *Env. Sci. Technol.* **2001**, 35, 2334-2340.

Simpson, S. L.; Pryor, I. D.; Mewburn, B. R.; Batley, G. E.; Jolley, D. Considerations for Capping Metal-Contaminated Sediments in Dynamic Estuarine Environments. *Env. Sci. Technol.* **2002**, 36, 3772-3778.

Mutch, Jr. R.D. P.Hg., P.E. In: A Case Study and Analysis of the Spatial Variability of Groundwater Discharge through Estuarine Sediments, Sixth International Conference on Remediation of Contaminated Sediments, New Orleans, LA, Feb. 7-10, **2011**; Foote, E. A.; Bullard, A. K., Eds. Battelle Memorial Institute: New Orleans, LA; A-26.

Power, G.; Brown, R. S.; Imhof, J. G. Groundwater and fish - insights from northern North America. *Hydrological Processes.* **1999**, 13, 401-422.

Hawthorne, S. B.; Azzolina, N. A.; Neuhauser, E. F.; Kreitinger, J. P. Predicting Bioavailability of Sediment Polycyclic Aromatic Hydrocarbons to Hyalella azteca using Equilibrium Partitioning Supercritical Fluid Extraction, and Pore Water Concentrations. *Environ. Sci. Technol.* **2007**, 41, 6297-6304.

Kreitinger, J. P.; Neuhauser, E. F.; Doherty, F. G.; Hawthorne, S. B. Greatly Reduced Bioavailability and Toxicity of Polycyclic Aromatic Hydrocarbons to Hyalella Azteca in Sediments from Manufactured-Gas Plant Sites. *Env. Tox. Chem.* **2007**, 26, 1146-1157.

Krone, C. A.; Burrows, D. G.; Brown, D. W.; Roblsch, P. A.; Friedman, A. J.; Malins, D. C. Nitrogen-Containing Aromatic Compounds in Sediments from a Polluted Harbor in Puget Sound. *Environ. Sci. Technol.* **1986**, 20, 1144-1150.

Stout, S. A.; Magar, V. S.; Uhler, R. M.; Ickes, J.; Brenner, R. Characterization of Naturally-occuring and Anthropogenic PAHs in Urban Sediments--Wycoff/Eagle Harbor Superfund Site. *Environmental Forensics.* **2001**, 2, 287-300.

Brenner, R. C.; Magar, V. S.; Ickes, J. A.; Abbott, J. E.; Stout, S. A.; Crecelius, E. A.; Bingler, L. S. Characterization and FATE of PAH-Contaminated Sediments at the Wyckoff/Eagle Harbor Superfund Site. *Environ. Sci. Technol.* **2002**, 36, 2605-2613.

Merritt, K.A.; Fimmen, R.; Sass, B.; Foote, E.; Mills, M. A.; Leather, J.; Magar, V. Characterization of contaminant migration potential in the vicinity of an in-place sand cap. *J. Soils Sediments.* **2010**, 10, 440-450.

Myers, M. S.; Anulacion, B. F.; French, B. L.; Reichert, W. L.; Laetz, C. A.; Buzitis, J.; Olson, O. P.; Sol, S.; Collier, T. K. Improved flatfish health following remediation of a PAH-contaminated site in Eagle Harbor, Washington. *Aquatic Toxicology.* **2008**, 88, 277-288.

Hedlund, B. P.; Staley, J. T. Isolation and characterization of Pseudoalteromonas strains with divergent polycyclic aromatic hydrocarbon catabolic properties. *Environ. Microbiology*. **2006**, 8, 178-182.

Tang, Y. J.; Carpenter, S.; Deming, J.; Krieger-Brockett, B. Controlled Release of Nitrate and Sulfate to Enhance Anaerobic Bioremediation of Phenanthrene in Marine Sediments. *Environ. Sci. Technol.* **2005**, 39, 3368-3373.

Geiselbrecht, A. D.; Hedlund, B. P.; Tichi, M. A.; Stanley, J. T. Isolation of Marine Polycyclic Aromatic Hydrocarbon (PAH)-Degrading Cycloclasticus Strains from the Gulf of Mexico and Comparison of Their PAH Degradation Ability with That of Puget Sound Cycloclasticus Strains. *Applied and Environ. Microbiology* **1998**, 64, 4703-4710.

Mueller, J. G.; Chapman, P. J.; Pritchard, P. H. Creosote-Contaminated Sites: Their potential for bioremediation. *Environ. Sci. Technol.* **1989**, 23, 1197-1201.

Magar, V.S, et al. Characterization of Contaminant Transport Potential Through in Place Sediment Caps. Society of Environ. Tox. & Chem. (SETAC) 28th Annual Meeting. **2007**. Milwaukee, Wisconsin.

Viana, P. Z.; Yin, K.; Rockne, K. J. Modeling Active Capping Efficacy. 1. Metal and Organometal Contaminated Sediment Remediation. *Environ. Sci. Technol.* **2008**, 42, 8922-8929.

Knox, A.S.; Paller, M.H.; Reible D.D; Ma, X.; Petrisor, I.G.,Sequestering Agents for Active Caps—Remediation of Metals and Organics. *Soil & Sed. Contam.* **2008**, 17, 516-532.

Zimmerman, J. R.; Ghosh, U.; Millward, R. N.; Bridges, T. S.; Luthy, R. G. Addition of Carbon Sorbants to Reduce PCB and PAH Bioavailability in Marine Sediments: Physicochemical Tests. *Environ. Sci. Technol.* **2004**, 38, 5458-5464.

Ghosh, U.; Luthy, R. G.; Cornelissen, G.; Werner, D.; Menzie, C. A. In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management. *Environ. Sci. Technol.* **2011**, 45, 1163-1168.

Rasmussen, G.; Fremmersvik, G.; Olsen, R. A. Treatment of creosote-contaminated groundwater in a peat/sand permeable barrier-a column study. *J. Haz. Materials B.* **2002**, 93, 285-306.

Jacobs, P. H.; Fōrstner, U. Concept of Subaqueous Capping of Contaminated Sediments with Active Barrier Systems (ABS) Using Natural and Modified Zeolites. *Wat. Res.* **1999**, 33, 2083-2087.

Cornelissen, G. et al. Remediation of Contaminated Marine Sediment Using Thin-Layer Capping with Activated Carbon-A Field Experiment in Trondheim Harbor, Norway. *Environ. Sci. Technol.* **2011**, 45, 6110-6116.

Beckingham, B.; Ghosh, U. Field-Scale Reduction of PCB Bioavailability with Activated Carbon Amendment to River Sediments. *Environ. Sci. Technol.* **2011**. 45, 10567-10574.

Himmelheber, D. W.; Pennell, K. D.; Hughes, J. B. Natural Attenuation Processes during In Situ Capping. *Environ. Sci. Technol.* **2007**, 41, 5306-5313.

Himmelheber, D. W.; Taillefert, M.; Pennell, K. D.; Hughes, J. B. Spacial and Temporal Evolution of Biogeochemical Processes Following In Situ Capping of Contaminated Sediments. *Environ. Sci. Technol.* **2008**, 42, 4113-4120.

Himmelheber, D. W.; Thomas, S. H.; Loffler, F. E.; Taillefert, M.; Hughes, J. B. Microbial Colonization of an In Situ Sediment Cap and Correlation to Stratified Redox Zones. *Environ. Sci. Technol.* **2009**, 43, 66-74.

Bodour, A. A.; Wang, J.-M.; Brusseau, M. L.; Maier, R. M. Temporal change in culturable phenanthrene degraders in response to long-term exposure to phenanthrene in a soil column system. *Environ. Microbiology.* **2003**, 5, 888-895.

Hyun, S.; Jafvert, C. T.; Lee, L. S.; Rao, P. S. C. Laboratory studies to characterize the efficacy of sand capping a coal tar-contaminated sediment. *Chemosphere.* **2006**, 63. 1621-1631.

Wammer, K. H.; Peters, C. A. Polycyclic Aromatic Hydrocarbon Biodegradation Rates: A Structure-Based Study. *Environ. Sci. Technol.* **2005**, 39, 2571-2578.

Cerniglia, C. E. Biodegradation of polycyclic aromatic hydrocarbons. *Biodegradation.* **1992**, 3, 351-368.

Haritash, A.K.; Kaushik, C.P. Biodegradation aspects of Polycyclic Aromatic Hydrocarbons (PAHs): a review. *J. Haz. Materials* **2009**, 169, 1-15.

Sun, M.; Yan, F.; Zhang, R.; Reible, D. D.; Lowry, G. V.; Gregory, K. B. Redox Control and Hydrogen Production in Sediment Caps Using Carbon Cloth Electrodes. *Environ. Sci. Technol.* **2010**, 44, 8209-8215.

McNally, D. L.; Mihelcic, J. R.; Lueking, D. R. Biodegradation of Three- and Four-Ring Polycyclic Aromatic Hydrocarbons under Aerobic and Denitrifying Conditions. *Environ. Sci. Technol.* **1998**, 32, 2633-2639.

Rothermich, M. M.; Hayes, L. A.; Lovley, D. R. Anaerobic, Sulfate-Dependent Degradation of Polycyclic Aromatic Hydrocarbons in Petroleum-Contaminated Harbor Sediment. *Env. Sci. Technol.* **2002**, 36, 4811-4817.

Peters, C. A.; Knightes, C. D.; Brown, D. G., Long-Term Compositional Dynamics of PAH-Containing NAPLs and Implications for Risk Assessment. *Environ. Sci. Technol.* **1999**, 33, 4499-4507.

Fraser, M.; Barker, J. F.; Butler, B.; Blaine, F.; Joseph, S.; Cooke, C. Natural attenuation of a plume from an emplaced coal tar creosote source over 14 years. *J. Cont. Hydrology*. **2008**, 100, 101-115.

Imhoff, P. T.; Jaffe, P. R.; Pinder, G. F. An experimental study of complete dissolution of a nonaqueous phase liquid in saturated porous media. *Water Res. Research.* **1993**, 30, 307-320.

Luthy, R. G.; Ramaswami, A.; Ghoshal, S.; Merkel, W. Interfacial Films in Coal Tar Nonaqueous-Phase Liquid-Water Systems. *Environ. Sci. Technol.* **1993**, 27, 2914-2918.

Ortiz, E.; Kraatz, M.; Luthy, R. G. Organic Phase Resistance to Dissolution of Polycyclic Aromatic Hydrocarbons. *Environ. Sci. Technol.* **1999**, 33, (235-242).

Xia, X.; Wang, R. Effect of Sediment Particle Size on Polycyclic Aromatic Hydrocarbon Biodegradation: Importance of the Sediment-Water Interface. *Environ. Tox. Chem.***2008**, 27, 119-125.

Kleineidam, S.; Schüth, C.; Grathwohl, P. Solubility-Normalized Combined Adsorption-Partitioning Sorption Isotherms for Organic Pollutants. *Environ. Sci. Technol.* **2002**, 36, 4689-4697.

Jonker, M. T. O.; Koelmans, A. A. Polyoxymethylene Solid Phase Extraction as a Partitioning Method for Hydrophobic Organic Chemicals in Sediment and Soot. *Environ. Sci. Technol.* **2001**, 35, 3742-3748.

Weber Jr.,W. J.; McGinley, P. M.; Katz, L. E. A Distributed Reactivity Model for Sorption by Soils and Sediments. 1. Conceptual Basis and Equilibrium Assessments. *Environ. Sci. Technol.* **1992**, 26, 1955-1962.

Van Noort, P. C. M.; Jonker, M. T. O.; Koelmans, A. A. Modeling Maximum Adsorption Capacities of Soot and Soot-like Materials for PAHs and PCBs. *Environ. Sci. Technol*. **2004**. 38, 3305-3309.

Werner, D.; Karapanagioti, H.K. Comment on “Modeling Maximum Adsorption Capacities of Soot and Soot-like Materials for PAHs and PCBs”. *Environ. Sci. Technol*. **2005**, 39, 381-382.

Xia, G.; Ball, W. P. Adsorption-Partitioning Uptake of Nine Low-Polarity Organic Chemicals on a Natural Sorbent. *Environ. Sci. Technol.* **1999**, 33, 262-269.

Wang, X; Sato, T.; Xing, B. Competitive Sorption of Pyrene on Wood Chars. *Environ. Sci. Technol.* **2006**. 40, 3267-3272.

Toride, N.; Leij, F. J.; van Genuchten, M. T. The CXTFIT Code for Estimating Transport Parameters from Laboratory or Field Tracer Experiments; U.S. Salinity Laboratory: Riverside, CA, **1999**.

Ogata, A.; Banks, R. B. A Solution of the Differential Equation of Longitudinal Dispersion in Porous Media. In Interior, U. S. D. O. T., Ed. United States Government Printing Office: **1961**.

Go, J.; Lampert, D. J.; Stegemann, J. A.; Reible, D. D., Predicting contaminant fate and transport in sediment caps: Mathematical modelling approaches. *Applied Geochemistry*. **2009**, 24, 1347-1353.

Chapter 2: Advection Dominated Transport of Polycyclic Aromatic Hydrocarbons in Amended Sediment Caps

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2.0 Abstract

Typical sand caps used for sediment remediation have little sorption capacity to retard the migration of hydrophobic contaminants such as PAHs that can be mobilized by significant groundwater flow. Laboratory column experiments were performed using contaminated sediments and capping materials from a creosote contaminated USEPA Superfund site. Azoic laboratory column experiments demonstrated rapid breakthrough of lower molecular weight PAHs when groundwater seepage was simulated through a column packed with coarse sand capping material. After eight pore volumes of flow, most PAHs measured showed at least 50% of initial source pore water concentrations at the surface of 65 cm capping material. PAH concentration in the cap solids was low and comparable to background levels typically seen in urban depositional sediment, but the pore water concentrations were high. Column experiments with a peat amendment delayed PAH breakthrough. The most dramatic result was observed for caps amended with activated carbon at a dose of 2% by dry weight. PAH concentrations in the pore water of the activated carbon amended caps were 3-4 orders of magnitude lower (0.04±0.02 μg/L for pyrene) than concentrations in the pore water of the source sediments (26.2±5.6 μg/L for pyrene) even after several hundred pore volumes of flow. Enhancing the sorption capacity of caps with activated carbon amendment even at a lower dose of 0.2% demonstrated a significant impact on contaminant retardation suggesting consideration of active capping for field sites prone to groundwater upwelling or where thin caps are desired to minimize change in bathymetry and impacts to aquatic habitats.

2.1 Introduction

Until recently, sediment caps have often been constructed of materials with low natural organic carbon with the intent being to maintain physical stability and contaminant isolation.[1] Therefore, preference has been on coarser grained (typically low organic matter) sediment that is physically more stable. Past modeling and laboratory experiments focused on sediment caps subject to diffusive conditions [2, 3] where caps appear to be effective,[4] by preventing the resuspension of contaminated sediments and greatly reducing the flux of contaminants to the food chain.[5] Under diffusive conditions, capping with sand or gravel also serves to distance the benthic bioturbation zone from the contamination, reducing contaminant flux to the surface.[5] Natural accretion of sediments continually occurs in depositional areas.[6] If the new sediments are clean, this can add to the thickness and effectiveness of the cap over time. Current state of practice in sediment cap design is provided by the USEPA[1] and the US Army Corps of Engineers.[5]

Many contaminated marine sediment sites currently under investigation are in shallow, near-shore areas that are impacted by additional transport processes such as groundwater flow, tidal pumping, wave setup, and resuspension via ship or storm activity.[7] If impacted sediments are to be managed in-situ, it is necessary to evaluate potential pathways by which contaminants might pose ecological or human health risks, and to manage those pathways appropriately to reduce the potential for adverse risks. Advection due to groundwater discharge and tidal pumping is not uncommon and has been reviewed elsewhere.[8, 9] Early in-situ column tracer tests showed the importance of organic carbon content in stream bed material to predict naphthalene (NPH) migration.[10]

Cap-induced sediment consolidation can decrease the hydraulic conductivity directly below the cap. In cases where the contamination is limited to the spatial range of sediment consolidation, this could have beneficial results by reducing advection through contaminated material.[11] Groundwater would be diverted from the contaminated zone and discharged around the periphery of the cap or from within the cap in preferential groundwater migration areas.[12] In the presence of groundwater advection, impermeable caps may not be practical and sediment caps may need to be permeable to allow groundwater migration through the cap. Under these conditions, the sediment cap may be designed as a reactive barrier by incorporating sorptive or other reactive materials into the cap. Peat has been explored for the removal of polycyclic aromatic hydrocarbons (PAHs) by reactive barriers.[13] Activated carbon (AC) amendment directly into sediment has been examined [14] and previously modeled as an amendment layer in caps.[6, 15] The main advantage with ACs are the high sorption capacity for a range of hydrophobic contaminants, and chemical stability of this form of carbon. Peat and other natural organic materials can biodegrade over time and lead to anoxic conditions in the sediment cap environment. Several recent studies have explored the use of AC as surficial sediment amendment to reduce contaminant bioavailability to benthic organisms and flux into the overlying water.[14] These studies have generally found remarkable effectiveness of AC in reducing pore water concentrations of hydrophobic chemicals in contaminated sediments.[14]

The main objectives of this research were to: 1) evaluate the advective migration of PAHs through field capping material under simulated groundwater flow conditions, 2) assess the effectiveness of peat and activated carbon amendments in reducing breakthrough of PAHs through the cap, and 3) test the ability of a mathematical model to predict the migration of PAHs in a cap with and without sorbent amendments. Physical models of sand and amended sand caps were constructed in the laboratory. Movement of groundwater through the cap was simulated and pore water PAH measurements were performed along the height of the cap.

2.2 Materials and Methods

2.2.1 Materials

The present study used sediments and capping material from the USEPA Superfund site at Wyckoff/Eagle Harbor, Washington. A sand cap was placed over creosote contaminated sediments at the site in 2000-2001.[11, 16, 17, 18, 19] Biological indicators of contamination at the site have been improving primarily from the elimination of direct exposure to contaminated sediments.[18] However, there is evidence that some groundwater discharge may still be expressed in the near shore areas along the periphery of the cap.[11] Sediment and clean capping material were collected from the Eagle Harbor site in June 2006 and stored at 4°C. The capping material ranged from medium sand to fine gravel with a median grain size of 2.75 mm (Supplemental Figure S1). PAH contaminated sediment was obtained from under the cap layer using multiple cores taken from 0-50 cm native sediment at two locations: a low concentration sandy sediment and a high concentration clayey sediment. To obtain a representative mixed sample of native sediment, that allowed flow without too much backpressure, the clayey and sandy sediments were mixed in the laboratory at a ratio of 1:4 clayey to sandy sediment (wet weight). The mixed sediment (hereafter called sediment) was further sieved through a #80 mesh to prevent excessive backpressure by the sediment layer of the column experiments. More details about the sampling sites are available in Sass et al., 2009.[20]

A fine coal based granular AC (TOG LF 80X325, 45-180 µm) was obtained from Calgon Corp. (Pittsburgh, PA). A similar TOG AC was used by other researchers who reported its physical properties.[21] Enriched Canadian *sphagnum* peat moss (peat) was obtained from "Miracle-Gro" Lawn Products, Inc. (Marysville, OH). *Sphagnum* peat is a geologically immature natural organic matter containing primarily cellulose, hemicelluloses, lignin, and humic acid forms of organic carbon.[22] The peat was sieved to 63-1000 µm and contained 30.9±1.6% organic carbon. Total organic carbon (TOC) was measured using hydrochloric acid pretreatment to remove inorganic carbon and combustion followed by nondispersive infrared detection of CO_2 in a Shimadzu TOC analyzer (Model TOC-5000A/SSM-5000A).

2.2.2 Columns

Experiments were conducted in 5 cm diameter glass columns with 6 equally spaced 1.5 cm diameter Teflon sampling ports (15 cm apart) as illustrated in Figure 1. Wet sediment was placed in the column from the top using a polyvinyl chloride (PVC) pipe to prevent pre-contamination of the glass side walls and wet capping material was dropped using a second PVC pipe through standing water (maintained with synthetic groundwater). The initial placement of the capping material was done with very little (~1cm) standing water, followed by larger depths (~8 cm) once the contaminated sediment had an initial covering. The flow of water was directed up through a 14 cm sediment layer, a 65 cm capping layer, and 32 cm of overlying water. The flow was maintained for specific discharge rates (q) of approximately 0.013 m/hr and average pore water velocities (v) of approximately 0.05 m/hr. These discharge rates are within, but on the high end, of the field groundwater discharge rates reported in the literature.[9, 23, 24] At Eagle Harbor, the specific discharge rates were measured at two locations. At 11.3 meters from shore the rates ranged from 0.001 to 0.002 m/hr, and at 17.4 meters from shore the rates were more steady, averaging 0.001 m/hr. The laboratory conditions were within laminar flow with a Reynolds number (Re) of 0.01, where Re = qd/ν, d is a "representative" length (taken to be 2.75 mm, Figure S1), and ν is the kinematic viscosity of water. The flow conditions are advection dominated, with a Peclet number (Pe) of 43, where Pe = vL/D, L is the column length, and D is the hydrodynamic dispersion coefficient ($L^2 T^{-1}$) (defined by tracer studies, Figure S2).

Compression of the sediment and capping layers was not observed in these experiments and thus, porosity was assumed to be constant. All columns were run with the influent water containing 0.01M calcium chloride ($CaCl_2$) to simulate the ionic strength of groundwater and 100 mg/L sodium azide (NaN_3) (to inhibit microbial activity). Glass wool separated the sampling ports from the sediment and capping material. Port 1 was positioned at mid-height in the sediment layer and sampled sediment pore water, ports 2-5 were positioned in the capping layer and port 6 was positioned at the overlying water. Approximately 1.5 mL water was purged from the ports prior to collecting 1.5 mL samples. The four column experiments that were run are as follows: no amendment to the capping material, capping material amended with 0.5% by weight peat (0.2% by TOC, and 4% by volume), 0.2% AC (0.2% by TOC, and 0.6% by volume), and 2% AC (2% by TOC, and 6% by volume). Columns were run for a period of 4 to 7 months with sampling intervals varying from days to weeks with the exception of the 0.2% AC column which was sampled less frequently. A 5% by weight peat amendment column was also constructed but was difficult to operate due to the high volume fraction of peat (40%) that resulted in clogging of the column. At the end of the non-amended column experiment, the column was frozen in dry ice and sectioned for ultrasonic extraction and measurement of 16 parent PAHs associated with the solid cap.

2.2.3 Batch equilibrium

For sediment equilibrium tests, one gram of sediment was placed into each of six 11.5 ml glass vials with a solution of 0.01 M $CaCl_2$ and 1000 mg/L NaN_3 in deionized water and secured with Teflon-lined caps. Vials were placed flat in a cylindrical container and on a roller for 16 days at 0.75 revolutions per minute (RPM). The equilibrated slurry was centrifuged at 4000 RPM for 6 minutes to produce 9 mL of aqueous supernatant from each sample vial that was transferred to new glass vials. Aqueous PAHs in all batch tests were analyzed using SPME. Colloids were removed from batch experiments using alum flocculation as described previously.[25]

For capping material equilibrium tests, 10 grams of capping material (dried at 105 °C for 4 hours) was placed in 40 ml vials, and then filled with a 1000 mg/L NaN_3 solution. Incremental amounts of PAH cocktails of known concentration in acetone solvent were added to 5 duplicate vials. The volume of acetone never exceeded 0.02% of the total solution volume. To one vial, no PAHs were added to measure any PAHs desorbing from the clean capping material. To other vials with no capping material, PAHs were spiked at a lower range of concentrations to account for sorption to glass side walls and the Teflon cap. The vials were placed on a roller for 22 days, after which time the water phase was measured for PAHs.

For the peat equilibrium tests, approximately 0.1 gram of peat was placed in five 250 ml jars and filled with 1000 mg/L NaN_3 solution. Incremental amounts of PAH cocktails dissolved in acetone were spiked to these five jars and five additional jars that did not contain peat. Equilibration times were 3 weeks. Partitioning to the vial glass and vial cap was negligible in the presence of peat.

2.2.4 PAH analysis

The 16 EPA priority pollutant PAHs were measured in the solid phase after ultrasonic extraction (USEPA method 3550B) and silica gel cleanup (USEPA method 3630C). A gas chromatograph (GC, Agilent model 6890N) with a 0.25-µm bonded fused silica capillary column (DB-5MS, 60 m x 0.25 mm i.d.) coupled with a mass spectrometer (MS, Agilent model 5973 Network Mass Selective Detector) was used for analysis, based on USEPA method 8270C.

2.2.5 Pore water PAH measurement

Ten parent PAHs were measured in the aqueous phase by solid phase micro extraction (SPME) with GC-MS in selected ion monitoring mode.[26] Small sampling volume requirements for SPME analysis allowed monitoring of pore water PAHs through the length of the column without disrupting the flow within the column. Samples collected from the columns were not treated with alum flocculation based on initial assessment of minimal interference from colloids. The SPME analysis used commercially available fibers with 30 μm film thickness coating of PDMS [poly(dimethylsiloxane)] from Supelco (Bellefonte, PA). A four point calibration was run using deuterated PAH (d-PAH) internal standards: naphthalene-d8, acenaphthylene-d10, flourene-d10, phenanthrene-d10, fluoranthene-d10, pyrene-d10 and chrysene-d12. The fiber was cleaned under a helium stream at 320°C for 30 minutes prior to running samples and for 10 minutes between each sample. Further details on the SPME method can be found in USEPA Method 8272.

2.2.6 Hexane/acetone extractables

An initial ultrasonic extraction with acetone followed by a mixture of hexane/acetone (1:1) was used to extract the creosote from the sediment. The mass of the total extractable organics was determined gravimetrically by evaporating the solvent from the extract under a steady air stream (similar to EPA Method 9071A).

2.2.7 Contaminant transport modeling

Phenanthrene (PHN), pyrene (PYR), and chrysene (CHR) migration in the cap was modeled numerically using Hydrus 1D [27] applying either a chemical equilibrium model or a two-site chemical nonequilibrium transport model:[28]

$$\frac{\partial(n_e c)}{\partial t} + \rho\frac{\partial s}{\partial t} = \frac{\partial}{\partial z}\left(n_e D\frac{\partial c}{\partial z}\right) - \frac{\partial(qc)}{\partial z} \qquad \text{Eq.1}$$

$$s = s^e + s^k \qquad \text{Eq.2}$$

$$s^e = f_e K_f c^n \qquad \text{Eq.3}$$

$$\frac{\partial s^k}{\partial t} = \alpha\left[(1 - f_e)K_f c^n - s^k\right] \qquad \text{Eq.4}$$

Where c is the PAH concentration in pore water (ML^{-3}), t is time, n_e is the effective porosity (-) of the cap as determined from tracer tests, ρ is the bulk density(ML^{-3}) of the cap, s^e is the sorbed PAH concentration of sites where sorption is assumed to be instantaneous (MM^{-1}), K_f is the Freundlich coefficient ($MM^{-1}(ML^{-3})^{-n}$), n is the linearity index (-), s^k is the sorbed or immobile zone associated PAH concentration of kinetic sorption sites (MM^{-1}), α is a first order mass transfer coefficient describing the kinetics of the sorption process (T^{-1}), z is the vertical coordinate (L), $D = \tau D_m + \lambda(q/n_e)$, where D_m is the molecular diffusion coefficient (L^2T^{-1}), λ is the longitudinal dispersivity (L), q is the Darcy flux (LT^{-1}). Tortuosity (τ) was estimated to be 0.65 using the relation by Millington and Quirk.[29] Similar 1D equilibrium transport models have been used for the long-term prediction of contaminant migration in sediment caps.[6, 15]

The value for the instantaneously sorbed fraction (*f*e) in the equilibrium model was set at 1 and in the nonequilibrium model was assumed to be 0.5 for all capping materials.[30] For sand and peat amended caps, linear partitioning is a reasonable assumption,[30,31] n should be close to 1, and K_f approaches K_d (L^3M^{-1}). Linear partitioning for the peat and cap material was estimated using batch experiments. Freundlich parameters for an F400 AC [32] were used to model AC equilibrium sorption capacity. All equilibrium parameters are presented in Table 1. An empirical relationship (Eq. 5) [31] was used to estimate the first order mass transfer coefficient α.

$$\log \alpha = 0.301 - 0.668 \log K_d \quad (r^2 = 0.95) \qquad \text{Eq.5}$$

Initial conditions for the cap in the model were set equal to the measured pore water profiles, unless the initial measurement was below the limit of quantitation (LOQ), in which case, the initial conditions were set equal to the LOQ (Table S1).

2.3 Results and Discussion

2.3.1 Characterization and batch equilibrium

The initial PAH concentration in the cap material, prior to loading the column, was lower by four orders of magnitude (0.1 ± 0.01 µg/g; n=2) than the concentrations in the sediment (846 ± 90 µg/g; n=2; Table S2). The total PAH concentrations measured in 0-50 cm of native sediment in the present study is higher than those reported from the same site in the 0-7 cm surficial native sediment by Merritt et al. (2010)[11] but in the range of values reported by Krone et al. (1986)[33]. The capping material had low TOC (0.04±0.01% by wt.), a specific surface area of 2.54 m^2/g, and particle porosity by mercury porosimetry of 0.037. The porosity of the capping material determined from the bulk density and specific gravity was 0.38.

The 2-3 ring PAHs such as acenaphthene (ACE), PHN, anthracene, fluoranthene, and PYR were dominant in the sediment. The higher MW PAHs (greater than CHR) were found in continually decreasing concentrations. The TOC of the sediment was very low (0.40±0.01% by wt.) and decreased further to 0.09% after extraction with hexane/acetone, indicating that the extractable material (mostly PAHs and other components of creosote) accounted for most of the TOC in this sediment. Additionally, the creosote content of the sediment was measured gravimetrically to be 0.2% using the hexane/acetone extractables method. Using the two methods, we get two estimates of the creosote fraction between 0.2 – 0.3% of sediment. Some lighter MW PAHs may have been lost during evaporation of hexane/acetone in gravimetric method, therefore we used the higher estimate of 0.3% creosote to predict equilibrium partitioning. With the 16 PAH concentrations on the solid cap, a creosote content of 0.3 %, and an assumption of the uncharacterized creosote molecular weight of 300 g/mole[34, 35] , Raoult's law prediction of total aqueous PAH concentration was 2.7 mg/l compared to a measured value of 1.7 mg/L. This indicates that the PAH partitioning is close to the behavior of coal tar described by Peters et al., 1999.[34] Some of the observed differences are likely due to depletion of lower molecular weight PAHs such as NPH. Furthermore, initial pore water from the sediment layer of the column experiments show still lower concentration of 1.1 mg/l indicating possible nonequilibrium conditions or PAH depletion in the sediment layer of the column experiments.

In the sediment batch equilibrium experiments, the most abundant PAH in the aqueous phase was ACE followed by PHN and fluorene. The concentration of CHR and larger PAHs were low in the aqueous phase. The measured log K_d values for sediment, capping material, and peat amendment (based on batch experiments) are shown in Table 1. The log K_d values of the sediment are low (ranging from 2.0- 4.3), due to the low TOC and the creosote dissolution process in the sediment. For peat and capping material, the measured partitioning is close to the predicted K_{oc} values based on the frequently used correlations by Xia, 1998[36] and Karichoff et al., (1979)[37] (Figure S3).

Table 2.1 PAH partitioning in sieved Eagle Harbor sediment, Eagle Harbor capping material, and peat. Literature Freundlich coefficient, and linearity index for GAC. (Average±Standard Deviation (number of replicates)) *Walters and Luthy, 1984 [32]. K_d units are L/kg.

	Phenanthrene	**Pyrene**	**Chrysene**
Log Kd sediment	2.82±0.03 (6)	3.63±0.03 (6)	4.29±0.05 (6)
Log Kd capping material	0.59±0.07 (6)	1.38±0.08 (10)	2.01±0.06 (4)
Log Kd peat	3.85±0.11 (5)	4.82±0.12 (5)	5.59±0.13 (5)
Log Kf_{GAC}, n^*	7.22, 0.406	7.43, 0.386	7.48, 0.458

2.3.2 Columns without amendments

Column studies were conducted first without amendments to evaluate breakthrough of PAHs during advective conditions. Initially the high PAH concentrations were observed in the lower portion of the column, while after 8 pore volumes of flow (defined using effective porosity), concentrations appeared nearly flat along the entire length of the column indicating complete breakthrough of most PAHs (Figure 2.1A, S4A and S4B). Rapid breakthrough in sand caps has been previously observed by Hyun et al., (2006).[38] This research for the first time was able to measure low concentration of PAHs with MW up to CHR in cap pore water using a recently developed solid phase microextraction method.[26] Chrysene pore water concentrations

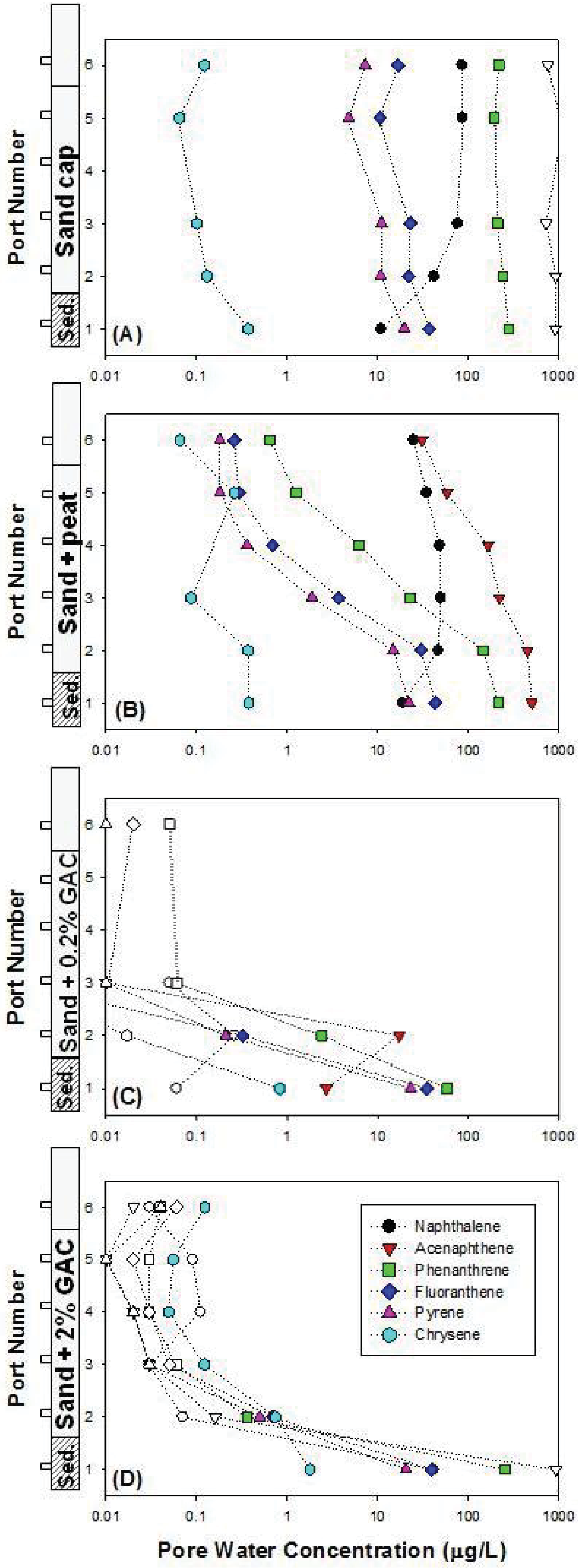

Figure 2.1 Spatial pore water PAH migration in sediment and coarse sand cap without amendment (A); and with amendments: 0.5% by weight peat (0.2% by TOC, and 4% by volume) (B); 0.2% AC (0.2% by TOC, and 0.6% by volume) (C); and 2% AC (2% by TOC, and 6% by volume)(D) after approximately eight pore volumes except for 0.2% AC which was at 27 pore volumes. Hollow symbols are either below the limit of quantification of above the known linear range of the calibration (Table S1).

decreased spatially along the length of the column from the sediment to the cap surface after 8 pore volumes. This is likely due to its low water solubility and higher partitioning to solids relative to the other PAHs measured. Initially NPH appears at higher concentrations in the cap pore water, 7.5 cm from the sediment (port 2), than in the sediment pore water (port 1) (Figure S4A). This is possibly due to the migration of NPH in pore water during column construction, when more soluble PAHs reside in sediment pore water and small amounts of water overlying the sediment. The expressed pore water during column construction transports PAHs nearly half way through the cap. Naphthalene is seen to be depleting in the sediment layer (port 1) at 8 pore volumes due to the higher aqueous solubility, and mobility, of this compound relative to other PAHs. Other low MW PAHs also appear to deplete during the length of the experiment because they are readily released from the creosote phase, while high MW PAHs such as PYR and CHR continue to increase in the sediment pore water throughout the length of the experiment.

Based on the low K_d values of the capping material (Table 1), PAH sorption to the cap is expected to be low. A near shore sediment core where groundwater discharge is occurring at the Eagle Harbor site (labeled TR1-10 in Merritt et. al., 2010 [11]) had a mean total of 16 parent PAH concentration of 3.2 mg/kg (range 1.1-9.3). The laboratory column exhibiting pore water breakthrough had a similar mean total PAH concentration in cap solids of 3.8 mg/kg (range 1.5-7.0). As shown in Figure 2.2, these measurements are also similar to PAH concentrations in many adjacent field cores measured by the enzyme-linked immuno-sorbant assay (ELISA) method.[11]

Thus,

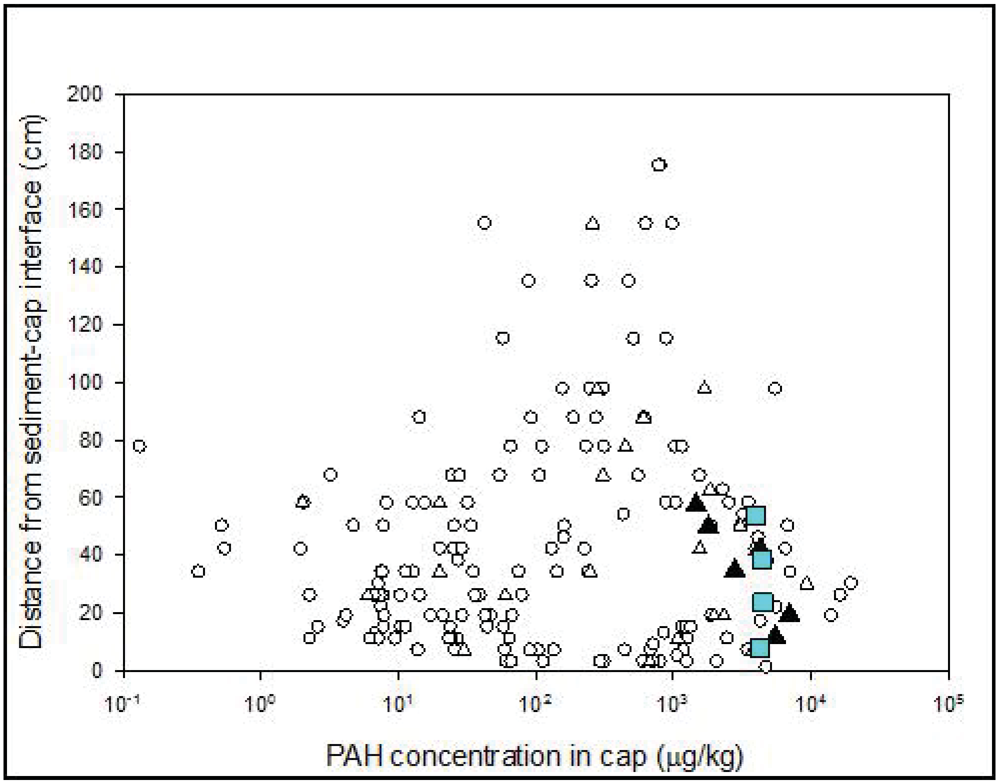

Figure 2.2 PAH concentration in cap solids measured independently in the field based on solids analysis of core samples of existing cap using two methods: ELISA method, shown as circles and extractions of 16 PAHs in sediment cores followed by GC-MS shown as hollow triangles, (both from Merritt et al., 2010 [11]). These field measurements are compared to PAHs measured in a laboratory physical simulation of a cap without amendments (large black triangles) and predictions (large blue squares) based on expected partitioning from the pore water concentrations of 10 PAHs using K_{oc} from Xia, (1998) [36]

PAH levels measured in the cap in the field are similar to PAH levels seen in the laboratory sand cap solids. These solid phase concentrations, in the range of 1-10 mg/kg, are also close to the background levels of PAHs often found at harbor sites.[39] The primary conclusion of this comparison is that PAH concentrations in cores from sediment caps are a poor indicator of dissolved contaminant breakthrough, especially in cases where there is little capacity in the cap material to sorb contaminants and where groundwater advection may be a vector for contaminant transport through a cap. It is apparent that measuring pore water concentrations is critical in determining breakthrough of PAHs in sand caps.

2.3.3 Columns with peat amendment

The peat was pre-wetted, mixed with the sand cap, and dropped through a column of water in a series of stages. Even with small settling increments, some separation of the cap and peat was observed. In a field application, there would be separation between the peat and sand cap if the materials were allowed to settle through the entire water column. Placement of a peat amendment with the sand cap in a field scenario would require careful engineering to minimize this segregation.

A column with 5% peat amendment (not presented in a figure) was equivalent to 40% peat by volume, created backpressure, and flow rates of 25 ml/hr could not be sustained. In a column with 0.5% peat amendment (4% amendment by volume), flow rates could be maintained and a delayed breakthrough of PAHs occurred relative to the column with no amendment (Figure 2.1B, S4C and 3). Slight turbidity was observed (3.3 Nephelometric Turbidity Units (NTUs)) initially in the column effluent, but reduced to 1.4 NTUs within a week, which corresponded to approximately 16 mg/L total dissolved organic carbon (DOC). The DOC-associated PAH fraction is small relative to the freely dissolved concentration for compounds of MW lower than PYR. For chrysene, the DOC associated fraction at 1.4 NTU turbidity will be approximately 72%.

The migration of PAHs in column pore water amended with peat was slower than that observed in columns with no amendment. Breakthrough of NPH was observed after 6 pore volumes and other low MW PAHs after 47 pore volumes. Pyrene and other high MW PAH concentrations in pore water from middle to upper heights in the capping layer and overlying water (ports 4-6) remained an order of magnitude less than pore water concentrations from the sediment layer (port 1).

2.3.4 Columns with AC amendment

It can be seen that AC greatly reduced the transport of PAHs through the cap (Figure 2.1C, 2.1D, S4D, and 3). In 0.2% AC amended columns, concentrations remained below the calibration range (Figure 1C) in the upper capping material. The source zone of the 2% AC column was a better comparison to the source zone of the columns with no amendment and peat amendment (Figure 2.1D). With 2% AC, the capping material (ports 3-5) were below the calibration range for over 360 pore volumes (data shown to 140 pore volumes in Figure 3). High MW PAHs (such as CHR) were within quantifiable levels in the lower part of the capping material initially (Figure 3). This initial transport is most likely due to pore water PAH displacement or contamination during column construction. Overall, amendment with AC resulted in 2-3 orders of magnitude reduction in pore water PAH concentration compared to the sand cap without amendments. The several orders of magnitude retardation of PAH transport achieved with AC amendment makes it possible to consider capping as a remedy for groundwater upwelling sites prone to contaminant migration where traditional capping with sand could be a concern. Slower groundwater advection at field sites would allow more time for sorption equilibrium with AC particles, thus enhancing effectiveness of the amended cap.

2.3.5 PAH transport modeling

The effective porosity of the cap was determined to be 0.28 (0.26 for peat amended) by fitting the results of a conservative tracer study as shown in Figure S2. Dispersivity was also fitted from the tracer study results. The model parameters and initial boundary conditions are provided in the supplemental information (Tables S3 – S6). The initial conditions were set based on measured values of pore water PAH concentrations at time zero and the assumption that local equilibrium existed between the pore water and solids at time zero. Phenanthrene, PYR, and CHR migration were modeled at port 5 and are compared with measured values in Figure 3.

For PHN, the input concentration to the cap remains around 100-400 μg/L for all three columns but the effluent concentrations vary greatly (Figure 3). Both the equilibrium and nonequilibrium model predictions are close to the observed profiles of PHN over 140 pore volumes of observation. The greater retardation of PHN in the peat amended column compared to the non-amendment column is well predicted by the two models. For the AC amended column, PHN concentrations remain at or

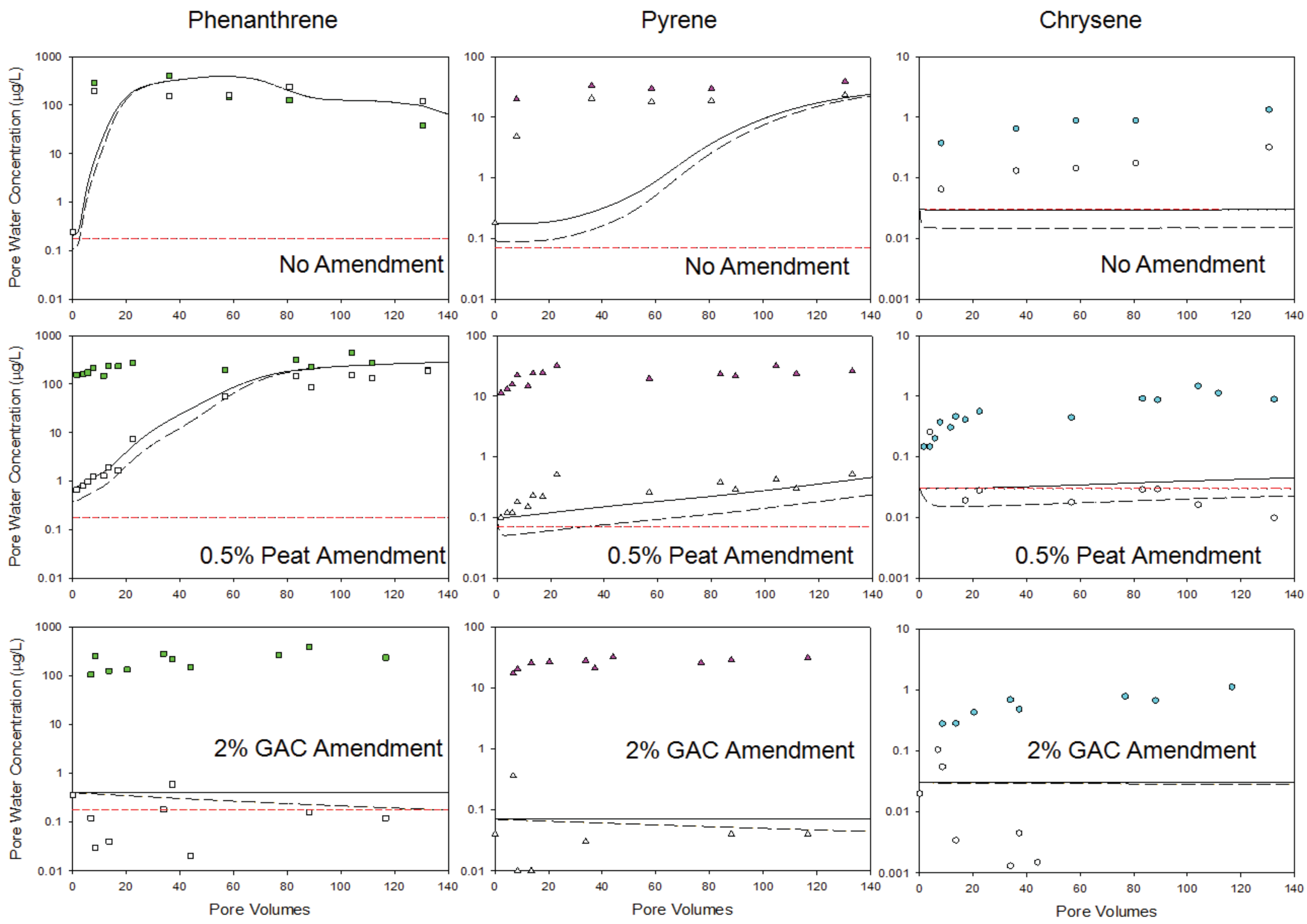

Figure 3. Temporal pore water concentrations of phenanthrene (squares), pyrene (triangles), and chysene (hexagons) at the sediment source (port 1-filled symbols) and cap surface (port 5-hollow symbols). Cap surface data was compared to single-solute equilibrium (solid lines) and nonequilibrium (dashed) model predictions. The limit of quantification is shown (red short-dashed).

below the calibration range both in the predictions and also in the experimental observations.

For PYR, the input concentrations remain close to 20-25 μg/L for all three columns and the effluent concentrations again vary greatly with complete breakthrough for the no amendment case, at two orders of magnitude below influent concentration for peat, and at three orders of magnitude below influent for the AC amendment column. These major trends with peat or AC amendment are predicted well by the equilibrium and nonequilibrium models and predicted concentration profiles of PYR over 140 pore volumes generally follow the observations. However, for the no amendment case, an earlier breakthrough is observed compared to the prediction likely due to the difficulty in predicting PAH sorption to sand with very low native TOC content (0.04%).

For CHR, the influent concentrations tend to approach 1 μg/L for all three columns and the effluent concentrations are typically close to or below the LOQ for the amended columns. For the no amendment column, the effluent concentration is higher, but about one order of magnitude below the influent concentrations. Pore water concentration of CHR in the cap is predicted to be one order of magnitude lower than observations in the non-amended column while for the two amended columns, the measured and predicted values are at or below the LOQ. When CHR concentrations are close to the LOQ, the model becomes very sensitive to the assumed initial conditions, which in this case were set at the LOQ.

The two site nonequilibrium model generally shows slower breakthrough than the equilibrium model because it allocates less than equilibrium sorption to the solid phase at time zero based on the initial measured pore water profiles (Table S5). For the nonequilibrium model, initial pore water profiles are assumed to be at 50% equilibrium with the solid phase. The initial pore water measurements were taken about a half an hour after column construction, but before starting the pump. Similar overall trends between the equilibrium and nonequilibrium models indicate that the local equilibrium assumption works reasonably well for sand and amended caps at the flow rates investigated.

For the AC amended caps, measured PAH concentrations and modeled PAH concentrations were mostly at or below the calibration range as shown in Figure 3. Over time, in the cap close to the sediment, the pore water concentrations decrease. Decreasing PYR concentrations can be observed well into the first 40 days of the experiment at port 2 close to the sediment (Figure S5).

It is not unreasonable to expect differences in the predicted values of PAH breakthrough using a model that uses independently measured or literature parameters. Note that the model parameters were not fitted to the PAH pore water data (as in Figure S5). Also, it is important to note that the PAH concentrations span 4-5 orders of magnitude and several of the measured and modeled concentrations (especially for CHR and for the column with GAC) fall below the LOQ. While the use of log-scale for concentration helps visualize the low concentration data better, it also accentuates the differences at the low concentration end where there is greater uncertainty, especially below the LOQ.

2.3.6 Field implications

At some field sites, regular sand caps may work better than these experiments would suggest because of lower discharge rates compared to the laboratory simulation, more organic carbon in the cap, dilution of pore water near the surface with overlying water, and the presence of biological activity-especially near the cap surface. Our experiments show that in the absence of organic carbon in the sand cap, and in the presence of significant groundwater advection, there can be breakthrough of dissolved PAHs in a short period of time. We also find that movement of PAHs through a cap is better monitored by measuring pore water concentrations than by measuring solid core samples that have low sorption capacity. These processes do not necessarily imply failure of a cap, which may have other functions, such as: the containment of contaminated sediment particles, prevention of erosion and off-site migration of contaminated sediment, and elimination of direct biological exposures to the capped sediment particles. Nonetheless, where dissolved chemical migration has the potential to pose unacceptable exposures to benthic and surface water biota, modeling chemical transport may be necessary to predict cap performance and to optimize performance by specifying the addition of cap amendments. Peat proved to be moderately effective in reducing PAH migration through the sand cap, while 2% and 0.2% AC was highly effective and virtually eliminated PAH migration for the duration of the experiment. This is the first report of laboratory performance of AC amended sand caps and paves the way for consideration of active capping in field sites. The addition of AC can also lead to much thinner caps in areas where change in bathymetry or loss of surface water aquatic habitat is of concern. Strong sorption within the cap combined with biological activity (e.g., microbial degradation of PAHs within the cap) can lead to long-term sustainable cap designs even for areas prone to groundwater upwelling.

2. 4 Acknowledgements

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2.5 References

(1) Palermo, M.R. et al. *Guidance for In-Situ Subaqueous Capping of Contaminated Sediments, in Assessment and Remediation of Contaminated Sediment (ARCS) Program*; U.S. EPA: Chicago, IL, **1996**.

(2) Thoma, G.J.; Reible, D.D.; Valsaraj, K.T.; Thibodeaux, L.J. Efficiency of Capping Contaminated Sediments in Situ. 2. Mathematics of Diffusion-Adsorption in the Capping Layer. *Environ. Sci. Technol*. **1993**, 27, 2412-2419.

(3) Wang, X.Q.; Thibodeaux, L.J.; Valsaraj, K.T.; Reible, D.D. Efficiency of Capping Contaminated Bed Sediments in Situ. 1. Laboratory-Scale Experiments on Diffusion-Adsorption in the Capping Layer. *Environ. Sci. Technol*. **1991**, 25, 1578-1584.

(4) Eek, E.; Cornelissen, G.; Kibsgaard, A.; Breedveld, G.D. Diffusion of PAH and PCB from contaminated sediments with and without mineral capping; measurement and modelling. *Chemosphere*. **2008**, 71, 1629-1638.

(5) Palermo, M. R.; Clausner, J. E.; Rollings, M. P.; Williams, G. L.; Myers, T. E.; Fredette, T. J.; Randall, R. E. *Guidance for subaqueous dredged material capping.*US Army Corps of Engineers: Vicksburg, MS, 1998.

(6) Murphy, P.; Marquette, A.; Reible D.; Lowry, G.V. Predicting the Performance of Activated Carbon-, Coke-, and Soil-Amended Thin Layer Sediment Caps. *J. of Environ. Eng*. **2006**, 132, 787-794.

(7) National Research Council. *Contaminated Sediment in Ports and Waterways;* National Academy Press: Washington, DC, **2003**.

(8) Burnett, W.C.; Bokuniewicz, H.; Huettel, M.; Moore, W.S.; Taniguchi, M. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry*. **2003**. 66, 3-33.

(9) McCoy, C.A.; Corbett, D.R. Review of submarine groundwater discharge (SGD) in coastal zones of the Southeast and Gulf regions of the United States with management implications. *Journal of Environ. Management*. **2009**. 90, 644-651

(10) Winters, S.L.; Lee, D.R. In Situ Retardation of Trace Organics in Groundwater Discharge to a Sandy Stream Bed. *Environ. Sci. Technol*. **1987**. 21, 1182-1186.

(11) Merritt, K.A.; Fimmen, R.; Sass, B.; Foote, E.; Mills, M.A; Leather, J.; Magar, V. Characterization of contaminant migration potential in the vicinity of an in-place sand cap. *J Soils Sediments*. **2010**, 10, 440-450.

(12) Reible, D.; Lampert, D.; Constant, D.; Mutch, R.D., Jr.; Zhu, Y. Active Capping Demonstration in the Anacostia River, Washington, D.C. *Remediation*. **2006,** 39-53.

(13) Rasmussen, G.; Fremmersvik, G.; Olsen, R.A. Treatment of creosote-contaminated groundwater in a peat/sand permeable barrier-a column study. *J. of Hazardous Materials B*, **2002**, 93, 285-306.

(14) Ghosh, U.; Luthy, R.G.; Cornelissen, G.; Werner, D.; Menzie, C.A. In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management. *Environ. Sci. Technol*. **2011**, 45, 1163-1168.

(15) Go, J.; Lampert, D.J.; Stegemann, J.A.; Reible, D.D. Predicting contaminant fate and transport in sediment caps: Mathematical modelling approaches. *Applied Geochemistry*. **2009**, 24, 1347-1353.

(16) Brenner, R.C.; Magar, V.S.; Ickes, J.A; Abbott, J.E.; Stout, S.A.; Crecelius, E.A.; Bingler, L.S. Characterization and FATE of PAH-Contaminated Sediments at the Wyckoff/Eagle Harbor Superfund Site. *Environ. Sci. Technol*. **2002**, 36, 2605-2613.

(17) Stout, S.A.; Magar, V.S.; Uhler, R.M.; Ickes, J.; Abbott, J.; Brenner, R. Characterization of Naturally-occurring and Anthropogenic PAHs in Urban Sediments--Wyckoff/Eagle Harbor Superfund Site. *Environmental Forensics*. **2001**, 2, 287-300.

(18) Myers, M.S.; Anulacion, B.F.; French, B.L.; Reichert, W.L.; Laetz, C.A.; Buzitis, J.; Olson, O.P.; Sol, S.; Collier, T.K. Improved flatfish health following remediation of a PAH-contaminated site in Eagle Harbor, Washington. *Aquatic Toxicology*. **2008**. 88. 277-288.

(19) Herrenkohl, M.J.; Lunz, J.D.; Sheets, R.G.; Wakeman, J.S. Environmental Impacts of PAH and Oil Release as a NAPL or as Contaminated Pore Water from the Construction of a 90-cm In Situ Isolation Cap. *Environ. Sci. Technol*. **2001**, 35, 4927-4932

(20) *Characterization of Contaminant Migration Potential Through In-Place Sediment Caps*. B.M. Sass, R.L. Fimmen, E.A. Foote, V.S. Magar, U. Ghosh. Final Project Report submitted to DoD. SERDP program. Project ER-1370, April **2009**. Available at www.serdp.org.

(21) McDonough, K.M., Fairey, J.L.; Lowry, G.V. Adsorption of polychlorinated biphenyls to activated carbon: Equilibrium isotherms and a preliminary assessment of the effect of dissolved organic matter and biofilm loadings. *Water Research*. **2008**. 42. 575-584.

(22) Johnson, M.D.; Huang, W.; Weber, W. J., Jr. A Distributed Reactivity Model for Sorption by Soils and Sediments. 13. Simulated Diagenesis of Natural Sediment Organic Matter and Its Impact on Sorption/Desorption Equilibria. *Environ. Sci. Technol*. **2001**. 35, 1680-1687.

(23) Liu, C.; Jay, J.A.; Ika, R.; Shine, J.P.; Ford, T.E. Capping Efficiency for Metal-Contaminated Marine Sediment under Conditions of Submarine Groundwater Discharge. *Environ. Sci. Technol*. **2001**, 35, 2334-2340.

(24) Mutch, Jr. R.D. P.Hg., P.E. A Case Study and Analysis of the Spatial Variability of Groundwater Discharge through Estuarine Sediments, *Sixth International Conference on Remediation of Contaminated Sediments*, New Orleans, LA, Feb. 7-10, **2011**; Foote, E. A.; Bullard, A. K., Eds. Battelle Memorial Institute: New Orleans, LA; A-26.

(25) Ghosh, U.; Weber, A.S.; Jensen, J.N.; Smith, J.R.. Relationship Between PCB Desorption Equilibrium, Kinetics, and Availability During Land Biotreatment. *Environ. Sci. Technol*. **2000**, 34, 2542-2548.

(26) Hawthorne, S.B.; Grabanski, C.B.; Miller, D.J.; Kreitinger, J.P. Solid-Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values. *Environ. Sci. Technol*. **2005**, 39, 2795-2803.

(27) Šimůnek, J.; van Genuchten, M.T. Modeling Nonequilibrium Flow and Transport Processes using HYDRUS. *Vadose Zone Journal*. **2008**, 7, 782-797.

(28) van Genuchten, M.T.; Wagenet, R.J. Two-Site/Two Region Models for Pesticide Transport and Degradation: Theoretical Development and Analytical Solutions. *Soil. Sci. Soc. of Am. J*. **1989**, 53, 1303-1310.

(29) Millington, R.J.; Quirk, J. P. Permeability of porous solids. *Trans. Faraday Soc.* **1961**, 57, 1200-1207.

(30) Sabbah, I.; Rebhun, M.; Gerstl, Z. An independent prediction of the effect of dissolved organic matter on the transport of polycyclic aromatic hydrocarbons. *J. of Cont. Hydrol*. **2004**, 75, 55-70.

(31) Brusseau, M.L.; Rao, P.S.C. The Influence of Sorbate-Organic Matter Interactions on Sorption Nonequilibrium. *Chemosphere*. **1989**, 18, 1691-1706.

(32) Walters, R.W.; Luthy, R.G. Equilibrium Adsorption of Polycyclic Aromatic Hydrocarbons from Water onto Activated Carbon. *Environ. Sci. Technol*. **1984**, 18, 395-403.

(33) Krone, C.A.; Burrows, D.G.; Brown, D.W.; Robisch, P.A.; Friedman, A.J.; Malins, D.C. Nitrogen Containing Aromatic Compounds in Sediments from a Polluted Harbor in Puget Sound. *Environ. Sci. Technol.* **1986**, 20, 1144-1150.

(34) Peters, C.A.; Knightes, C.D.; Brown, D.G. Long-Term Compositional Dynamics of PAH-Containing NAPLs and Implications for Risk Assessment. *Environ. Sci. Technol*. **1999**, 33, 4499-4507.

(35) Hong, L.; Ghosh, U.; Mahajan, T.; Zare, R.N.; Luthy, R.G. PAH Sorption Mechanism and Partitioning Behavior in Lampblack-Impacted Soils from Former Oil-Gas Plant Sites. *Environ. Sci. Technol*. **2003**, 37, 3625-3634.

(36) Xia, G. Sorption behavior of nonpolar organic chemicals on natural sorbents. PhD Thesis, The Johns Hopkins University, Baltimore, MD, 1998.

(37) Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Sorption of hydrophobic pollutants on natural sediments. *Water Research.* **1979**, 13, 241-248.

(38) Hyun, S.; Jafvert, C.T.; Lee, L.S.; Rao, P.S.C. Laboratory studies to characterize the efficacy of sand capping a coal tar-contaminated sediment. *Chemosphere*. **2006**, 63, 1621-1631.

(39) Stout, S.A., Graan T.P. Quantitative Source Apportionment of PAHs in Sediments of Little Menomonee River, Wisconson: Weathered Creosote versus Urban Background. *Environ. Sci. Technol*. 2010, 44, 2932-2939.

2.6 Supplemental Information:

PAH Transport in Amended Sediment Caps: an Advection-Dominated Column Study

Table 2.S1 Method detection limits (MDL), Limit of quantification (LOQ), and calibration range. (MDLs and LOQs were determined using 7 replicates of ½ the lowest calibration standard (for SPME). Other methods involving signal to noise ratios are used for the determination of instrument detection limits (Hawthorne et al. 2005).

Compound	**MDL μg/L**	**LOQ μg/L**	**Calibration Range μg/L**
Naphthalene	0.28	0.94	5.5-2210
Acenaphthylene	0.06	0.20	1.2-481
Acenaphthene	0.06	0.22	1.4-587
Fluorene	0.04	0.15	1.0-403
Phenanthrene	0.05	0.18	0.73-293
Anthracene	0.02	0.05	0.8-32
Fluoranthene	0.02	0.08	0.28-113
Pyrene	0.02	0.07	0.24-96
Benz(a)anthracene	0.02	0.07	0.11-4.27
Chrysene	0.01	0.03	0.04-1.6

Table 2.S2 Solid 16 PAH concentrations in the mixed and sieved sediment and capping material by ultrasonic extraction (based on EPA method 3550B).

PAH	**Mixed Sediment**	**Sieved Sediment**	**Initial Cap Material**
	(μg/g)	(μg/g)	(μg/g)
Naphthalene	16.2±9.1	4.8±1.3	0.002
Acenaphthylene	14.2±1.5	6.8±1.3	0.001
Acenaphthene	162.0±19.8	110.0±16.6	0.001
Fluorene	76.2±9.3	53.4±7.3	0.001
Phenanthrene	268.6±30.0	194.4±25.0	0.005
Anthracene	64.4±11.6	114.2±7.2	0.005
Fluoranthene	221.9±26.5	163.5±15.5	0.030
Pyrene	152.5±18.2	128.0±27.2	0.019
Benz(a)anthracene	30.7±3.4	22.0±2.5	0.009
Chrysene	23.0±3.2	27.7±6.1	0.010
Benzo(b)fluoranthene	10.1±0.9	6.9±2.5	0.005
Benzo(k)fluoranthene	8.4±1.0	5.7±1.3	0.004
Benzo(a)pyrene	8.3±1.0	5.5±1.1	0.004
Indeno(1,2,3-cd)pyrene	1.7±0.3	1.1±0.1	0.002
Dibenz(a,h)anthracene	1.3±1.2	0.5±0.04	0.0002
Benzo(g,h,i)perylene	2.9±2.4	1.2±0.1	0.001
Totals	**1062**	**846**	**0.098**

Table 2.S3 Model parameters

Cap Property	**Non-Amended Cap**	**Peat Amended Cap**	**GAC Amended Cap**
Effective Porosity	0.28	0.26	0.28
Dispersivity (cm)	1.65	1.08	1.65
Bulk Density (g/cm^3)	1.65	1.13	1.65
Cap Thickness (cm)	65	65	65
Sediment to P5 (cm)	52.5 cm, node 53	52.5 cm, node 53	52.5 cm, node 53
Sediment to P2 (cm)	7.5 cm, node 8	7.5 cm, node 8	7.5 cm, node 8
D_m (PHN,PYR,CHR) (cm^2/day)*	0.51, 0.484, 0.54	0.51, 0.484, 0.54	0.51, 0.484, 0.54

*Diffusivity in water, Hayduk and Laudie (1974) in Montgomery (1996)

Table S4. Time, Darcy flux, and concentrations for the sediment source term (Port 1) used in Hydrus 1D simulations.

No Amendment-Phenanthrene			**Peat Amendment-Phenanthrene**			**GAC Amendment-Phenanthrene**		
days	cm/day	ug/L	days	cm/day	ug/L	days	cm/day	ug/L
2	30	207.61	2	29.7	160	2	31	60
8	30	282.51	4	29.7	180	6	31	100
14	30	340	8	29.7	200	10	31	140
18	30	380	12	29.7	220	14	30	160
24	30	403.98	18	30.8	230	18	30	190
30	30	340	24	30.8	240	22	30	210
36	29	180	32	32.4	260	26	30	230
48	28.4	126.52	42	33.9	280	30	30	250
58	30	120	46	35.2	300	34	34	260
66	32	100	54	33	320	38	34	280
74	34	60	62	33.9	340	44	34	290
100	36	37.18	70	30.8	360	54	34	300
			78	30.7	380	60	32	290
			100	30.6	400	68	32	280
						76	32	260
						100	31	240
No Amendment-Pyrene			**Peat Amendment-Pyrene**			**GAC Amendment-Pyrene**		
days	cm/day	ug/L	days	cm/day	ug/L	days	cm/day	ug/L
2	30	39.03	2	29.7	14	2	31	8
4	30	30	4	29.7	18	4	31	16
6	30	19.84	6	29.7	21	6	31	19
8	30	20	8	29.7	22	8	31	21
10	30	22	10	29.7	23	10	31	23
12	30	24	12	30.8	24	12	30	24
14	30	26	14	30.8	24.5	16	30	25
16	30	28	16	30.8	25	20	30	26
18	30	30	18	30.8	25.5	24	30	27
20	30	32	20	30.8	25.5	32	32	28
24	30	33.33	22	32.4	26	36	34	29
28	30	32	26	32.4	26	44	34	30
32	29	31	30	32.4	26.5	54	32	30
36	29	29.68	34	33.9	26.5	70	32	31
40	28.4	29.5	42	33.9	27	100	32	31
44	28.4	29	50	35.2	27			
48	28	29.44	60	33	27			
52	28.4	30	70	30.8	27			
56	30	31	80	30.7	27			
60	31	33	100	30.6	27			
64	32	35						
68	33	37						
72	33.5	38						
76	34	38.5						
80	34.6	38.96						
100	35	40						
No Amendment-Chrysene			**Peat Amendment-Chrysene**			**GAC Amendment-Chrysene**		
days	cm/day	ug/L	days	cm/day	ug/L	days	cm/day	ug/L
2	30	5.98	2	29.7	0.15	2	31	0.2
4	30	3	4	29.7	0.25	4	31	0.25
16	30	0.38	6	29.7	0.3	8	31	0.3
26	30	0.65	8	29.7	0.35	12	30	0.35
30	30	0.8	10	29.7	0.4	16	30	0.4
40	29	0.88	12	30.8	0.45	20	30	0.45
50	28.4	0.89	14	30.8	0.5	24	30	0.5
60	30	1	16	30.8	0.55	28	30	0.55
70	33.2	1.2	20	30.8	0.6	32	32	0.6
80	34.6	1.34	26	32.4	0.7	36	34	0.65
100	35	1.4	32	33	0.8	40	34	0.7
			40	33.9	0.9	44	34	0.75
			48	35.2	1	50	34	0.8
			60	33	1.1	56	32	0.85
			70	30.8	1.15	60	32	0.9
			80	30.7	1.2	64	32	0.95
			100	30.6	1.2	68	32	1
						76	32	1.05
						100	32	1.1

Table 2.S5 Initial pore water PAH profiles in cap.

PAH	**node (cm from sediment)**	**porewater (ug/L) no amendment**	**porewater (ug/L) peat amendment**	**porewater (ug/L) GAC amendment**
PHN	0-7	207.6-60.3	138.6-60.6	27.1-1.4
	8-23	60.3-12.5	60.6-19.7	1.4-0.7
	24-38	12.5-0.3	19.7-2.1	0.7-0.7^{+}
	39-53	0.3-0.2	2.1-0.7‡	0.7^{+}-*0.4*
	54-68	0.2-0	0.7‡-0	*0.4*-0.04
PYR	0-7	39.0-2.6	12.9-5.8	0.8-1.0
	8-23	2.6-0.6	5.8-2.5	1.0-0.09
	24-38	0.6-0.2	2.5-0.4	0.09-*0.07*$^{+}$
	39-53	0.2-0.2	0.4-0.1‡	*0.07*$^{+}$-0.07*
	54-68	0.2-0	0.1‡-0	0.07*-0.01
CHR	0-7	6.0-0.4	0.29-0.56	0.2-0.3
	8-23	0.4-0.03	0.56-0.18	0.3-0.03
	24-38	0.03-0.03*	0.18-0.16	0.03-*0.03*$^{+}$
	39-53	0.03*-0.03*	0.16-0.03*	*0.03*$^{+}$-0.03*
	54-68	0.03*-0	0.03*-0	0.03*-0

$^{+}$estimate (port 4 sample was not taken with GAC column), *limit of quantification, ‡measurement taken at 0.77 days (1.5 pore volumes).

Table 2.S6 Nonequilibrium parameters used for forward simulations.

	Sand Cap (Figure 4A)		Peat Cap (Figure 4B)		GAC Cap (Figure 4C)	
	α (day^{-1})	f_e	α (day^{-1})	f_e	α (day^{-1})	f_e
PHN	19.37	0.5	6.95	0.5	0.0052^{+}	0.5
PYR	5.75	0.5	1.64	0.5	0.0025^{+}	0.5
CHR	2.18	0.5	0.52	0.5	0.00045^{+}	0.5

$^{+}$Using a K_{ac} of a high concentration for K_p to determine α.

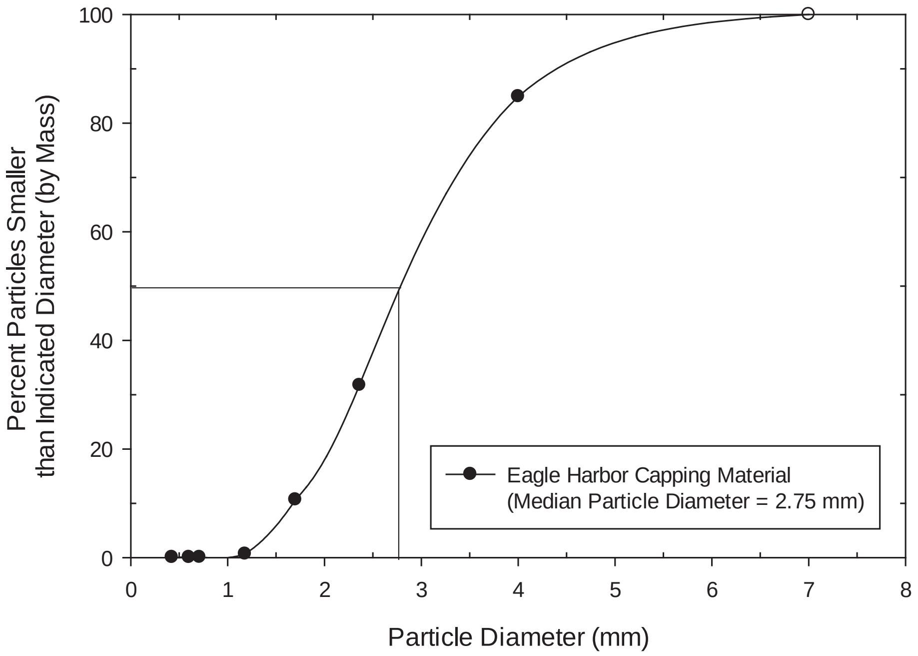

Figure 2.S1 Particle size distribution of capping material

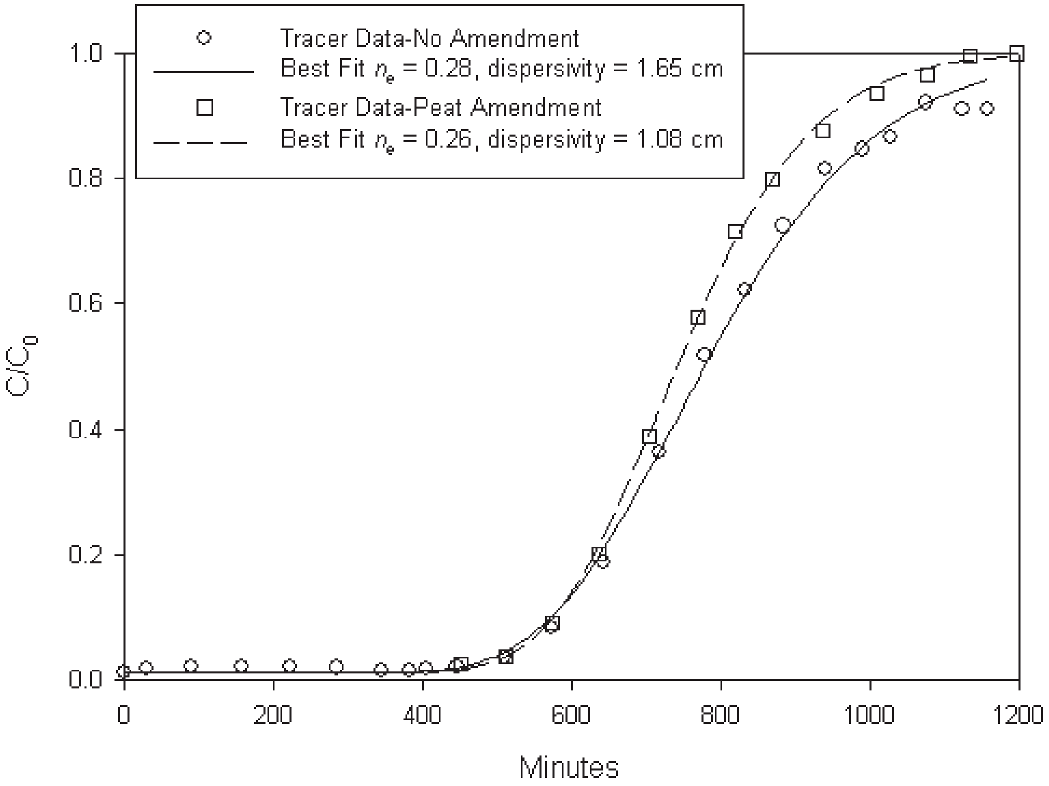

Figure 2.S2 Chloride tracer through 60 cm of capping material with no amendment and peat amendment (0.2% TOC amendment).

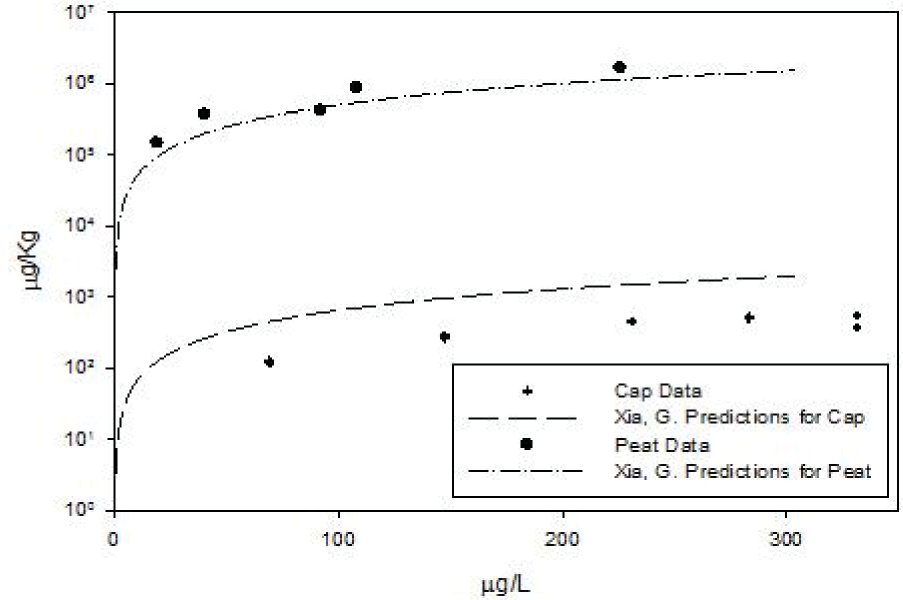

Figure 2.S3 Data for peat and cap partitioning (microgram per kilogram vs. microgram per liter) compared to predictions based on K_{ow}-K_{oc} regressions for PHN sorption to sediments (Xia, 1998). Each data point represents the average of two SPME measurements from a batch.

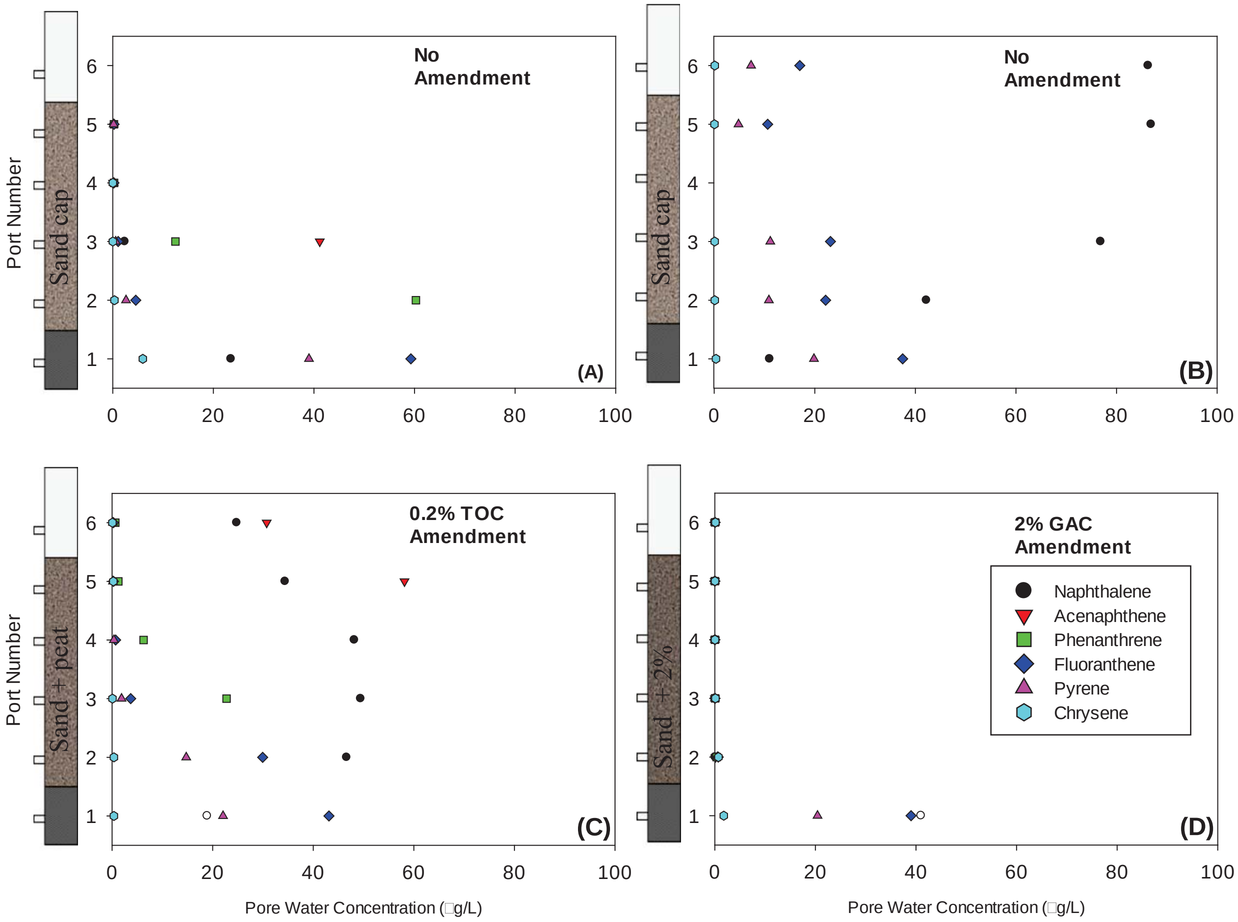

Figure 2.S4 Spatial PAH migration (port number vs. microgram per liter) in sediment and cap pore water initially without amendment (A); and after approximately eight pore volumes of flow without amendment (B), with 0.2% TOC (peat) amendment (C), and with 2% GAC amendment (D).

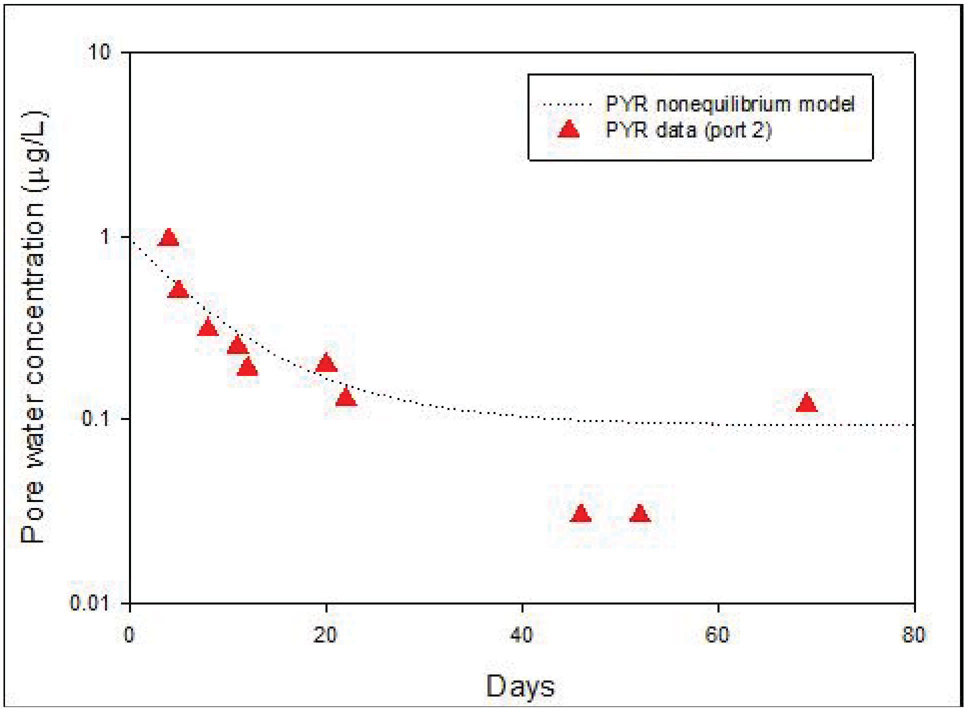

Figure 2.S5 Pyrene migration over time (at port 2) near the sediment (microgram per liter vs. days). Here, PYR was used as a tracer to determine a best fit f_e (0.4) given the α (0.0351 day^{-1}) calculated using the RateAC from Hale and Werner (2010). This was done using an average of the rates from a low and high concentration K_{ac}, and the relation: $\alpha = 22.7\ D_a/a^2$ developed by Wu and Gschwend (1988) (Schüth and Grathwohl, 1994)). This f_e was then used to run the forward problem. Port 2 shows initially higher concentrations than port 5, and thus a more dramatic decrease over time.

2.6.1 Supplemental References

Hale, S.E.; Werner, D. Modeling the Mass Transfer of Hydrophobic Organic Pollutants in Briefly and Continuously Mixed Sediment after Amendment with Activated Carbon. *Environ. Sci. Technol*. **2010,** 44, 3381-3387.

Hawthorne, S.B.; Grabanski, C.B.; Miller, D.J.; Kreitinger, J.P. Solid-Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values. *Environ. Sci. Technol*. **2005**, 39, 2795-2803.

Hayduk, W.; Laudie, H. Prediction of Diffusion Coefficients for Nonelectrolytes in Dilute Aqueous Solutions. *AIChE Journal*. **1974**, 20, 3, 611-615.

Montgomery, J.H. Groundwater Chemicals Desk Reference; CRC Press, Inc. Boca Raton, FL, 1996

Schüth, Ch.; Grathwohl, P. Nonequilibrium transport of PAHs: A comparison of column and batch experiments. *Transport and Reactive Processes in Aquifers*, ed. Dracos and Stauffer, Rotterdam: Balkema, **1994**.

Wu, S.; Gschwend, P.M. Numerical Modeling of Sorption Kinetics of Organic Compounds to Soil and Sediment Particles. *Water Resources Research*. **1988**, 24, 1373-1383.

Xia, G. Sorption behavior of nonpolar organic chemicals on natural sorbents. PhD Thesis, The Johns Hopkins University, Baltimore, MD, 1998.

Chapter 3: Biologically Active Capping Potential of PAH Contaminated Sediment

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3.1 Introduction

Biological activity in a sediment cap can reduce the concentration of hydrophobic pollutants in pore water and reduce the transport of these compounds through the cap as well as the accumulation of these compounds in the cap solids. Azoic systems showed that pore water concentrations remain high in a sand cap subjected to groundwater discharge (Gidley et al. 2012). Biologically active column experiments have been previously conducted to evaluate the degradation potential of PAHs in sand (Hyun et al. 2006) and peat amended sand (Rasmussen et al. 2002). Both authors emphasize the importance of oxygen for the degradation process. Hyun et al. (2006) found little degradation of pyrene (PYR), and hypothesized that PAHs of equal or higher molecular weight (MW) will degrade slowly even in the presence of oxygen. Biodegradation of PAHs in the field is controlled by the bioavailability of the compound, and is affected much less by the molecular weight or characteristics, such as: the number, length, or position of the substituents, and alternanant vs. nonalternant ring structures (Wammer and Peters, 2005). Previous studies have shown that complex communities of bacteria are able to colonize a sand cap in column systems (Himmelheber et al. 2009). Oxygen could potentially be available at a cap surface or delivered using engineered methods. Biological PAH degradation is not limited to heterotrophic bacteria, but may also involve fungi and autotrophic bacteria (Haritash A.K. et al. 2009).

Pore water measurements are of critical importance in assessing the effectiveness of a sediment cap subjected to advective groundwater flows (Gidley et al. 2012). The potential harmful effects of PAHs in the sediment environment are quantified by estimating or directly measuring freely dissolved pore water concentrations and converting these to toxic units (USEPA, 2003). The EPA narcosis model for benthic organisms is based on 34 pore water PAH concentrations. The model predicts toxicity if the sum of the toxic units is greater than 1. Ten parent compounds and 14 alkyl groups have been found to be responsible for 95% of the toxicity (Hawthorne et al. 2005, 2006). Coal tars are made up primarily of parent PAH compounds, however alkylated compounds are also present. For tar-impacted manufactured gas plant (MGP) sites, Hawthorne et al. (2006) showed that the priority pollutant PAHs comprised about 40% of the total PAHs. The total includes the major alkylated homologs (a total of 34 PAHs). Alkylated PAHs are important because they are generally more toxic than their corresponding parent compounds.

Hawthorne et al., 2005, studied sediments from former MGP sites with a range of solid phase concentrations (58 to 10,000 mg/kg), and found no significant effect on the sum of toxic units regardless of whether freely dissolved or total dissolved PAH pore water concentration was used (with DOC concentrations ranging from 3.7 to 27 mg/L). For pyrene and compounds of equal or lower MW, the freely dissolved and total dissolved concentrations were essentially the same. The PAHs of higher MW were found in low enough concentrations in the total dissolved phase that they did not contribute significantly to toxicity. The creosote laden sediments used in this study were had a similar distribution of PAHs and were assumed to behave similarly to the MGP impacted sediments studied by Hawthorne et al. 2005. The primary objective of this research was to evaluate the effectiveness of biologically active vs. azoic caps in preventing PAH transport from the underlying sediments to the surface during conditions of advection associated with groundwater infiltration. A secondary objective was to observe contaminant transport behavior in amended capping materials and compare this to simulations with a contaminant transport model.

3.2 Methods and Materials

3.2.1 Toxic Units

The toxic units for a single parent PAH or alkyl cluster was calculated as:

$$TU = (\text{Total Dissolved Pore Water Conc.}) \div (\text{Conc. for one TU}) \qquad \text{Eq. 1}$$

Where TU are the toxic units, and the concentration for one toxic unit is listed in supplemental Table S1 for 24 PAHs (ASTM D 7363-07). In the biological column, 10 parent PAHs were measured and 14 alkyl cluster PAHs were estimated at the cap influent (source zone (port 1), at four heights in the cap, and the overlying water layer using methods based on ASTM D 7363-07.

3.2.2 Batch Experiments

Biological batch degradation experiments provided active organisms that could be amended to the cap. Batch degradation experiments were started using sediment from both Eagle Harbor, Washington and the Anacostia river, Washington DC. Strains of PAH degrading bacteria have been isolated from Eagle Harbor sediment

(Hedlund and Staley, 2006; Geiselbrecht et al. 1998) and Anacostia river sediment (Himmelheber et al. 2009, Wang et al. 2009). Therefore, the microorganisms present in these experiments could represent a consortium of bacteria from both sites. Initially to 50 ml flasks, 5 grams of either Anacostia river sediment, or Eagle Harbor river sediment were added. The flasks were capped with a foam plug to allow for aerobic conditions, and to prevent low MW PAHs, such as naphthalene (NPH), from escaping. The batch degradation experiments were enriched using phenanthrene (PHN) and NPH as substrates. The flasks were placed on a shaker table that moved in a horizontal circular motion. A small portion (2ml) of the supernatant from the 50 ml batch slurries was then transferred to large 4L batch experiments. The 4L batches were mixed with a magnetic stir bar and killed control experiments using sodium azide (100 mg/L) were run in parallel to the living batch experiments. All batch degradation solutions contained $FeCl_3$, NH_4Cl, Na_2HPO_4, $CaCl_2$, $MgSO_4$, K_2HPO_4, and KH_2PO_4 nutrient biological oxygen demand (BOD) buffer solution (pH 7.1-7.6) (Wammer and Peters, 2005, Knightes and Peters, 2003). Exposure of PAHs to light is known to produce intermediates that are more susceptible to biodegradation than parent compounds (Lehto et al. 2000). The batch experiments were therefore covered in aluminum foil to minimize the impact of light.

Phenanthrene degradation was measured from grab samples treated by alum flocculation (Ghosh et al. 2000) followed by SPME-GCMS for analysis. The initial living 4L batch degradation experiment was reproduced by serially transferring from previous batches two times to produce a batch that was virtually free of original sediment particles. The final 4L batch degradation contained both NPH (2500 µg/L initially) and PHN (500 µg/L initially) with 100 ml transferred from the previous batch. The final concentrations of NPH and PHN in the batch, measured 24 hours prior to using it as a column amendment, were 25 and 4.2 µg/L respectively. These concentrations likely decreased further in the 24 hours before the batch was used as a cap amendment.

3.2.3 Column Inoculation

PAH degrading organisms from the final 4L degradation experiment was used as an amendment to the biological column capping material by mixing prior to column construction. The inoculum solution (500 ml) was mixed with 2092 g cap material (wt. weight) for 3 minutes with a clean metal bowl and spoon.

The influent solution to the column contained five BOD nutrient buffer pillows per 20 L and 30 g/L $CaCl_2$ (as in the azoic experiments). Biomass concentrations (W, mg/L) were measured by the following correlation to optical density at 660 nm (Koch, 1994) just prior to amending the column:

$$W = 364.74A_{660} + 6.7A_{660} \qquad \text{Eq. 2}$$

A "Genesys" 10 UV visible spectrophotometer was used to measure absorbance of the inoculum at 660 nm wavelength. This measurement was corroborated by a volatile suspended solids (VSS) measurement. VSS measurements made use of Whatman type GF/F (47 mm) glass microfiber disks. The filters were rinsed using a base, clamp and funnel vacuum system and baked in a muffle furnace at 450°C for 30 minutes and weighed. A measured 20 ml of sample was then filtered onto the disk. Volatile and nonvolatile solids were determined by baking the disks at 110°C to remove water and 475°C to remove volatiles followed by weighing after each baking step.

3.2.4 Column Experimental Set-up

The bio-amended cap solids were introduced to the column above a layer of contaminated sediment. Details of the column set-up construction technique have been described elsewhere (Gidley et al. 2012) with the exception of a glass beads zone, which was placed between the sediment and cap at port 1. The column was also opened at the top to the atmosphere with a foam plug (Figure S1). This column and previous columns were covered to minimize the effects of light. The temperature was at room temperature (20 °C).

The biological columns contained an 11 cm contaminated sediment layer, a 4 cm glass bead separation layer, 65 cm of capping material, and 4.5 cm of overlying water. Port 1 was located 2.5 cm below the glass bead-cap interface at the glass bead layer. Port 2 is located 12 cm above the sediment-bead interface at the capping layer. Port 3 is located 15 cm above port 2 (at 27 cm) and so on.

Early on in the experiment, it was determined that samples from the column may be undergoing further degradation (particularly of PHN and PHN-d10) in the time between column sampling, and analysis by SPME-GCMS. To prevent this, samples collected after the first 3.8 days of column run time were frozen ("quenched") at -20º C for half an hour in a freezer after the addition of deuterated internal standards. The concentrations in the overlying water layer were taken by a glass pipet in the biological column. Alum flocculation was initially conducted (in the first 2.8 days) on a subset of the overlying water samples. Sample analysis with and without the alum flocculation step showed that interference from colloidal particles was not significant and this procedure was not necessary. Therefore, alum flocculation was not performed on port samples or overlying water samples for the remainder of the experiment. To evaluate changes in organic carbon content as a result of biological activity, the biologically active cap and azoic cap were frozen in dry ice and sectioned. These solid sections were sieved and analyzed for TOC and PAHs.

3.2.5 Biological Batch with Column Cap Material

In order to provide additional lines of evidence for the presence of PAH degrading microorganisms in the sand cap, a series of batch experiments were performed using material collected from the biological column after it had run for 106 days. Capping material (1.4-2 grams) was collected from each port using tweezers and added to 8 vials with 12.1-12.4 mLs water and spiked with PHN (4μL of 79 mg/L PHN dissolved in methanol). To 4 of the 8 vials, sodium azide (500 mg/L) was added to the water phase to stop microbial activity. To the other 4 vials, nutrient rich synthetic groundwater was added (same as influent water for biological column). After 4 days of rolling the vials in a container, the water phase was measured using SPME-GC/MS after alum flocculation.

3.2.6 Contaminant Transport Modeling

PAH migration in the columns was simulated using Hydrus 1D code (Šimůnek, 2009) using a two-site chemical nonequilibrium transport model with additional parameters to account for degradation in the water phase and solid phase based on previous work by van Genuchten and Wagenet, 1989:

$$\frac{\partial(n_e c)}{\partial t} + \rho\frac{\partial s}{\partial t} = \frac{\partial}{\partial z}\left(n_e D\frac{\partial c}{\partial z}\right) - \frac{\partial(qc)}{\partial z} - \mu_w n_e c - \mu_s \rho s \qquad \text{Eq.2}$$

$$s = s^e + s^k \qquad \text{Eq.3}$$

$$s^e = f_e K_f c^n \qquad \text{Eq.4}$$

$$\frac{\partial s^k}{\partial t} = \alpha\left[(1 - f_e)K_f c^n - s^k\right] - \mu_s s^k \qquad \text{Eq.5}$$

where c is the PAH concentration in pore water (ML^{-3}), t is time, n_e is the effective porosity (-) of the cap as determined from tracer tests, ρ is the bulk density(ML^{-3}) of the cap, s^e is the sorbed PAH concentration of sites where sorption is assumed to be instantaneous (MM^{-1}), K_f is the Freundlich coefficient ($MM^{-1}(ML^{-3})^{-n}$), n is the linearity index (-), s^k is the sorbed or immobile zone associated PAH concentration of kinetic sorption sites (MM^{-1}), α is a first order mass transfer coefficient describing the kinetics of the sorption process (T^{-1}), z is the vertical coordinate (L), $D = \tau D_m + \lambda(q/n_e)$, where D_m is the molecular diffusion coefficient (L^2T^{-1}), λ is the longitudinal dispersivity (L), q is the Darcy flux (LT^{-1}). Tortuosity (τ) was estimated to be 0.65 using the relation by Millington and Quirk (1961). Additional degradation terms, μ_s

(T^{-1}), a first-order degradation rate constant for the solid phase, and μ_w, a first-order degradation rate constant for the dissolved phase were introduced to account for biodegradation. Nonequilibrium parameters for kinetics (α) and the instantaneously sorbed fraction (*f*e) were set for this modeling as previously presented by Gidley et al. 2012 for non-amended caps. Sorption kinetics into a possible biofilm and degradation in a biofilm were not separate processes in this simulation.

Numerous first-order degradation rate constants for PAHs can be found in the literature. Often they are specific to the experimental conditions. As a starting place, the rates of Peters et al. (1999) were used as a measure of degradation rates in the dissolved phase (relative to other PAHs). Peters et al. obtained the majority of the degradation rates from a study by Park et al. 1990, who studied degradation in flasks of PAH spiked Kidman fine sandy loam (Calciaquell, Utah) maintained at 60% of water holding capacity and purged with air. Park et al. accounted for volatilization and sorption losses, but degradation losses were measured using concentrations on the solid phase. This indicates that the rates obtained by Park et al. include the bioavailablity limitations explained previously by Wammer and Peters, 2005, namely, the desorption from the solid phase before degradation in the dissolved phase. Peters et al. used these values to estimate aqueous phase degradation, and these values were used for initial simulations. If desorption was the limiting step in the Park et al. experiments, then it would seem reasonable to assume that degradation rates in the biological column pore water would be greater. In addition to this, many field capping sites subjected to advection would have less advection than in these columns, providing more time for degradation, given an adequate supply of oxygen and nutrients.

3.3 Results and Discussion

3.3.1 Batch Experiments

The presence of PAH degrading microorganisms in preliminary batch tests was confirmed by: visual turbidity changes, decrease in PHN concentration with time, staining and microscopy (Figure S2), biomass measurements using optical density, and biomass measurements by filtration for VSS. The visual turbidity changes became apparent when comparing the biologically active batches with the azoic batches. Biomass by optical density was 28.1±3.4 mg/L (3 reps) and VSS was measured to be 32.1±10.5 mg/L (6 reps) just prior to mixing the final batch solution with the capping material.

3.3.2 Column Experiments

Sediment and Cap Pore Water. It is possible that PAH degradation was occurring in the sediment layer and glass bead layer of the biological column even though these layers were not amended with microorganisms. The sediment layer for the biological experiments was prepared separately from many of the azoic columns, and it is also possible for characteristics to be different due to variation caused during sediment preparation and storage. During wet sieving it is possible for changes to occur in creosote composition, especially for low MW compounds. If degradation was occurring in the sediment layer, it would be occurring to the low MW compounds most rapidly as well.

Figure 1 shows the spatial pore water profiles of six PAHs after 8 bed volumes in the biological column relative to azoic columns. Source pore water concentrations were compared between azoic non-amended and biologically amended columns. Phenanthrene, along with lower MW PAHs, were depleting faster at the cap influent (port 1) relative to the previous azoic column experiments. This may be due to degradation in the sediment and glass bead zone. Amended organisms likely penetrated as far as the glass bead layer during column construction. Concentrations of PYR (and compounds of higher MW) are similar at port 1 for all of the column experiments (azoic and biological) and therefore these compounds were best for comparing azoic and biological systems for evidence of degradation in the cap pore water. Concentrations of high MW PAHs were clearly lower in the cap for the biological column than for the azoic columns as shown in Figure 1 and indicated possible loss from biodegradation in the cap.

The AC amended column reduces concentrations to a greater and more rapid extent than the biological amendment, though port 1 PAH concentrations were higher in the azoic columns than the biological column for low MW PAHs. In the cap, depletions in concentrations are seen in the biological column compared to the azoic non-amended column (Figure 3.1). The temporal PAH pore water concentrations at the source (port 1) and cap surface (port 5) are shown in Figure 3.2 for three PAHs. It is clear that the

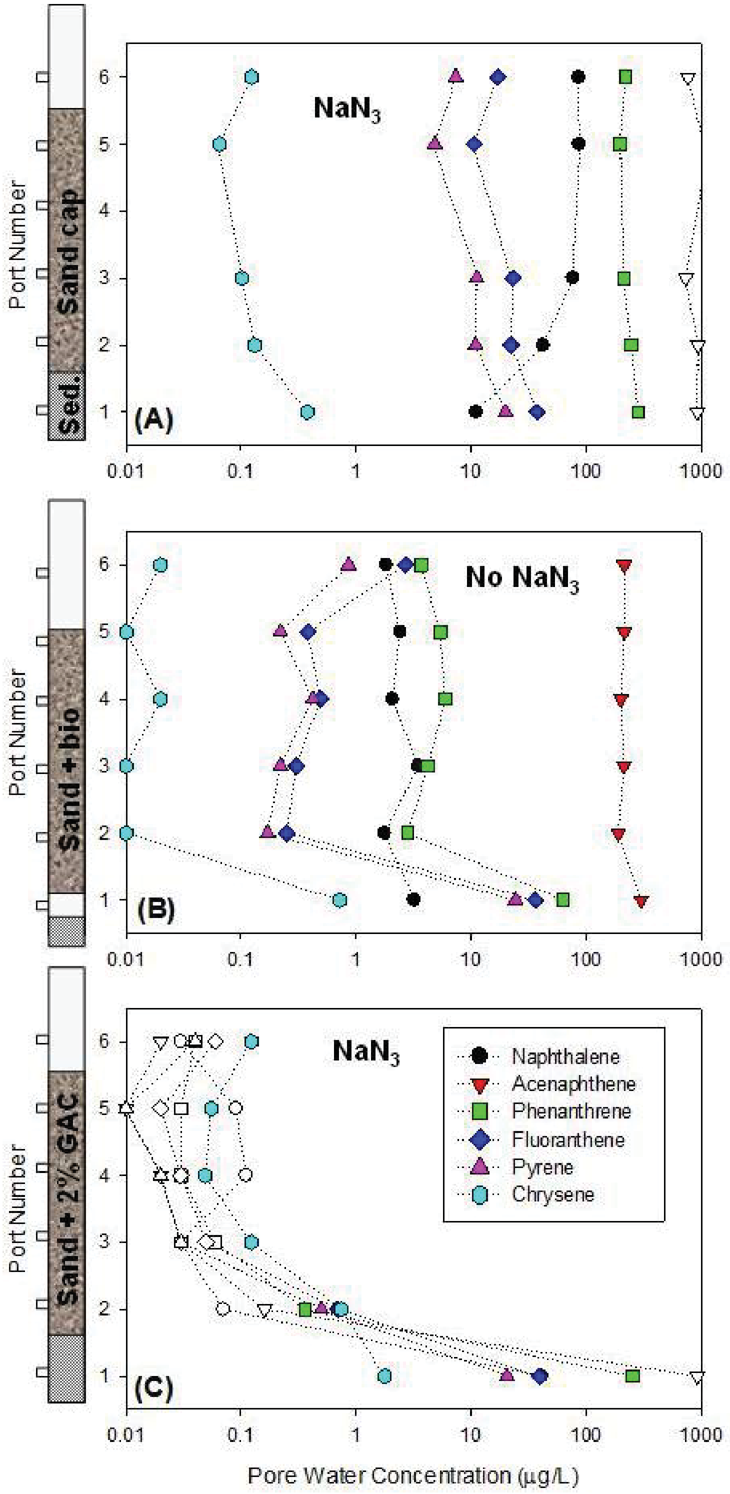

Figure 3.1 Spatial pore water PAH migration in sediment and coarse sand cap with no amendment (A), biological amendment (B) and GAC amendment (C) at 8 bed volumes. The biological column had a glass bead layer at port 1.

biological column reduced PAH concentration relative to the azoic column by two to three orders of magnitude at most times. Over time, depletions of all PAHs are seen in the lower cap (port 2) of the biological column relative to port 1 (data not shown). At approximately 63 pore volumes there was a leak in the tubing at the peristaltic pump. As a result, the flow was disrupted for one day and the column drained down to port 2. The resaturation process of the column after this point may have resulted in air bubbles, forcing preferential flow paths and a temporary increase in some PAHs--particularly pyrene (Figure 3.2). Pyrene concentrations decrease and then increase again during the biological column experiment. Bodour et al. found an oscillatory pattern in the temporal effluent PHN concentrations in a sand column that correlated well with effluent dissolved oxygen concentrations. A decrease in oxygen concentration below saturated levels was not observed in these column experiments and the pH remained neutral as well. Another explanation for this may involve the drying and rewetting of a possible biofilm, which has been shown to decrease the diffusivity of PAHs (Wicke et al. 2008).

*PAHs in the Sediment Source***.** Ultrasonic hexane/acetone extraction of the sediment material used in the biological column experiment, before (64.4 µg/g total PAHs) and after (10.8 µg/g total PAHs) it was run in the column, is presented in Figure 3.3. This is shown alongside sediment concentrations of an azoic column before (846 µg/g) and after (67.7 µg/g) it was run in a column. NPH was drastically depleted both initially and after being run in the biological column, relative to the azoic system, and relative to other PAHs. ACY does not show depletion in the sediment for the biological

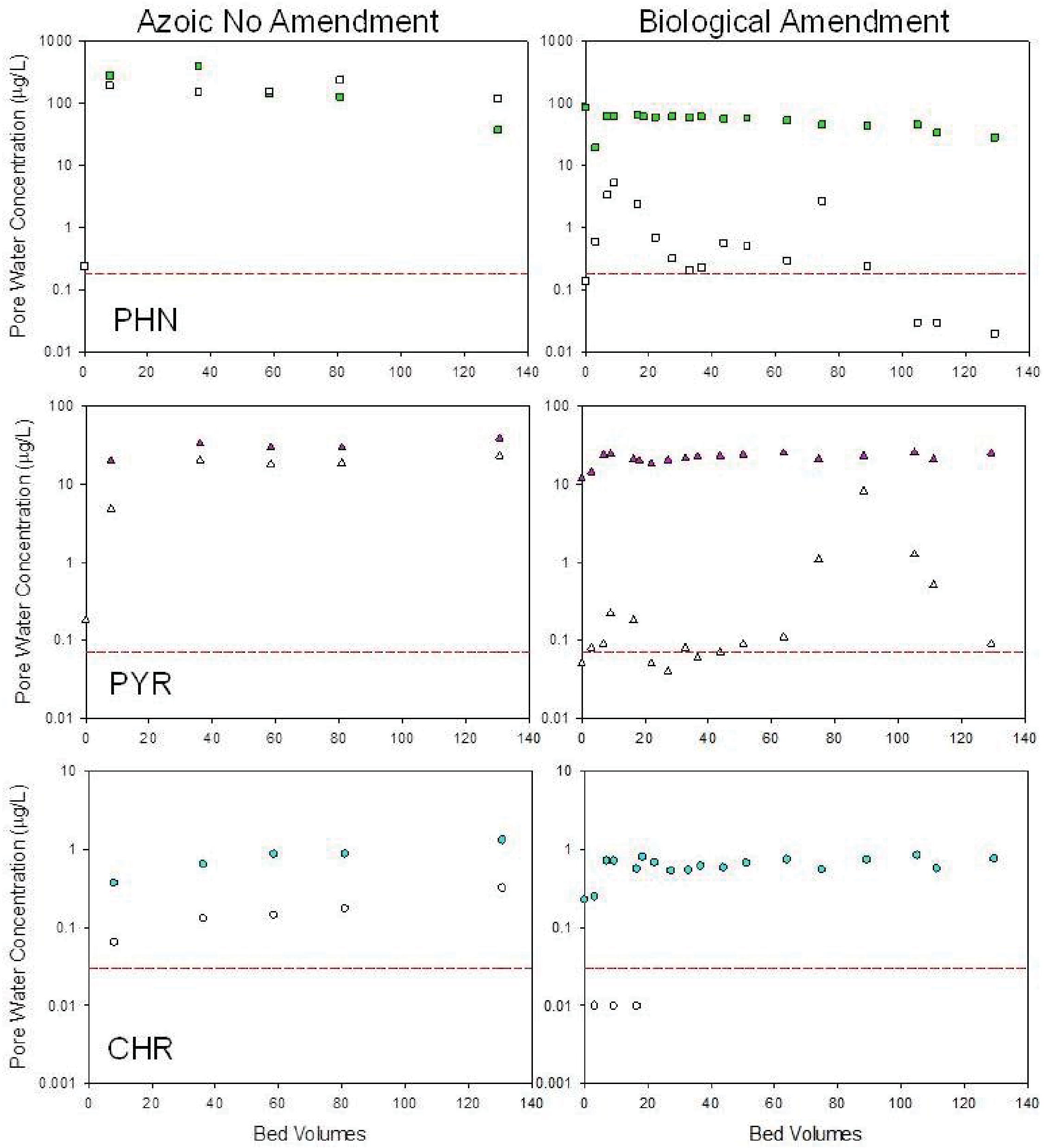

Figure 3.2 Trends at Port 1 (filled symbols) and Port 5, cap surface (hollow symbols) for the azoic column with no amendment and the biological column (3 mid-high MW PAHs shown).

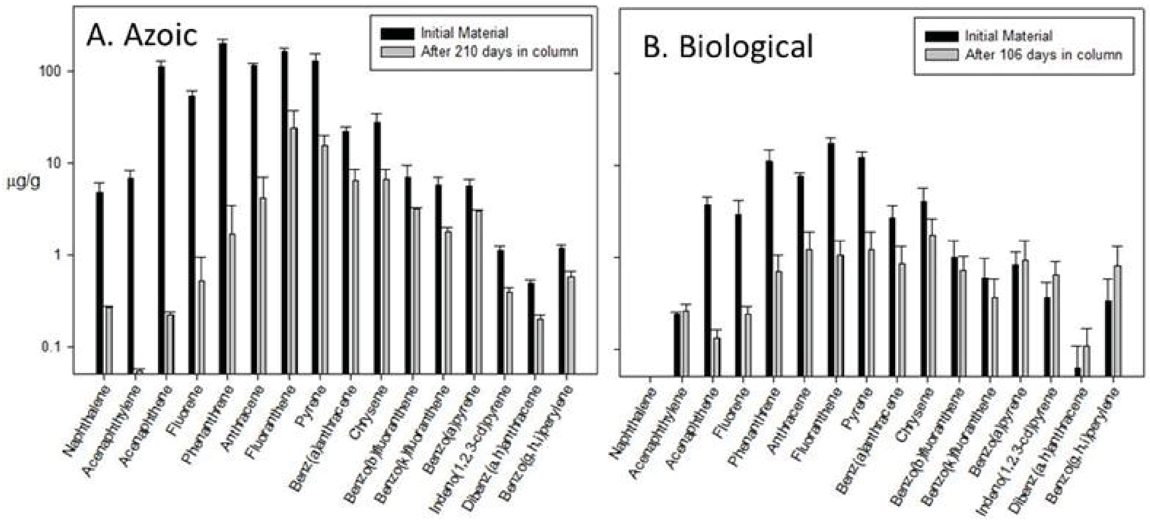

Figure 3.3 Solid phase PAH concentrations (µg/g) by sediment extractions from azoic (A.) and biological (B.) column experiment. Error bars show standard deviation. Data obtained for figure 7A.from the sediment layer of the peat amended column run for 300 bed volumes. Data obtained for figure 7B. from the sediment layer of the biologically amended column run for 150 bed volumes.

column, which may be experimental error due to the high volatility of this compound (losses in initial measurement). Otherwise, contaminant losses generally decrease with increasing MW. For benzo(a)pyrene, and compounds of higher MW, the concentration determined by ultrasonic extraction increases after the material was placed in the biological column experiment. These differences are not statistically significant for compounds of MW equal to or greater than chrysene (t-test, 95% confidence).

Relative to solid sediment concentrations, aqueous batch experiments of sediment used in the azoic columns and biological columns show similar concentrations for the initial material even though total solid concentrations were an order of magnitude different. Initial aqueous concentrations do not depend on solid sediment concentrations because creosote coats the sediment grains and Raoult's law partitioning controls the dissolution process. Batch equilibrium experiments (with NaN_3) of the sediment from an azoic column reveal depletions of all compounds (257 to 64 total 10 PAHs µg/L), as indicated by the water phase concentrations in Figure 3.4. Batch equilibrium experiments conducted with sediment in the biological column showed a greater depletion from 668 to 15 µg/L (total 12) in the aqueous phase after being run in the column for 106 days. These depletions are most likely due to reductions in mole fractions in the creosote, due to losses by dissolution from the sediment layer in the azoic column and also through biodegradation in the biological column. High MW PAHs (FLN through CHR) show greater depletion in batches of the sediment from the biological column than the azoic non-amended column. Batch equilibrium experiments with sediment from azoic columns (Figure 4A.) initially exhibited 14.5 toxic units and reduced to 8.4 toxic units at the end of the column run (approximately 300 bed volumes). Sediment in the biological column initially had total toxic units of 26.4, but reduced to 0.9 after being run in the column for 150 bed volumes (Figure 4B). Although starting aqueous concentrations were similar, PAH starting solids concentration was less in the biological column and seems to have flushed out more effectively to a low final toxicity.

*PAH Mass Balance***.** The mass of the total PAHs measured before and after the column experiments was totaled (Figure 3.5). Aqueous phase PAHs flushed out of the column were determined by the integration of water concentration over volume of water passing through the column. PAH mass from the solid sediment and cap phase PAHs were estimated by extractions before and after the experiment. Generally, the

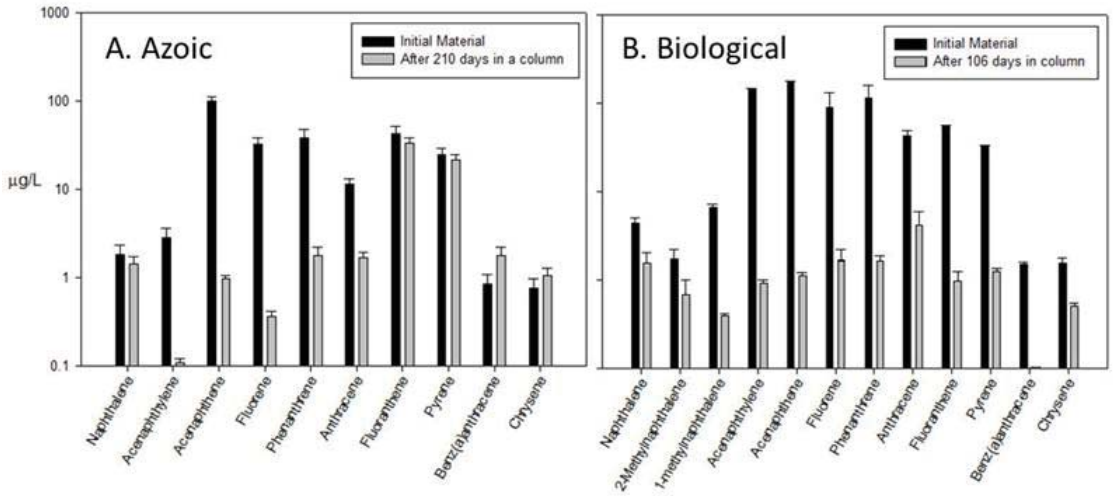

Figure 3.4 Water phase concentrations from aqueous batch equilibrium experiments using sediment used for azoic non-amended columns and biological column experiments. Error bars show standard deviation.

total PAH mass in the azoic columns was an order of magnitude higher than the biological column. In order to show changes within each experiment, the data were normalized to the total initial PAH concentrations in their respective column. Figure 3.5 shows a mass balance on four PAHs in the azoic non-amended and biological column. The data shows a large quantity of ACE (Figure 5, upper left) leaving both the azoic non-amended and biological columns in the effluent because of the high aqueous solubility and relatively low solid-water partitioning of this compound. The total ACE lost in the azoic system may appear greater than the total mass lost in the biological system because of the frequency of measurements taken in the two experiments. In the azoic experiment, fewer data points were used to estimate the shape of the plug (or peak) of ACE leaving the column, and mass release could have been misinterpreted. In the biological experiment, the column effluent concentration was monitored more frequently and the shape of the aqueous phase concentration integrated provides a better estimate of mass release. Also, much of the ACE lost in the biological column experiment occurred early during an initial lag phase in the degradation.

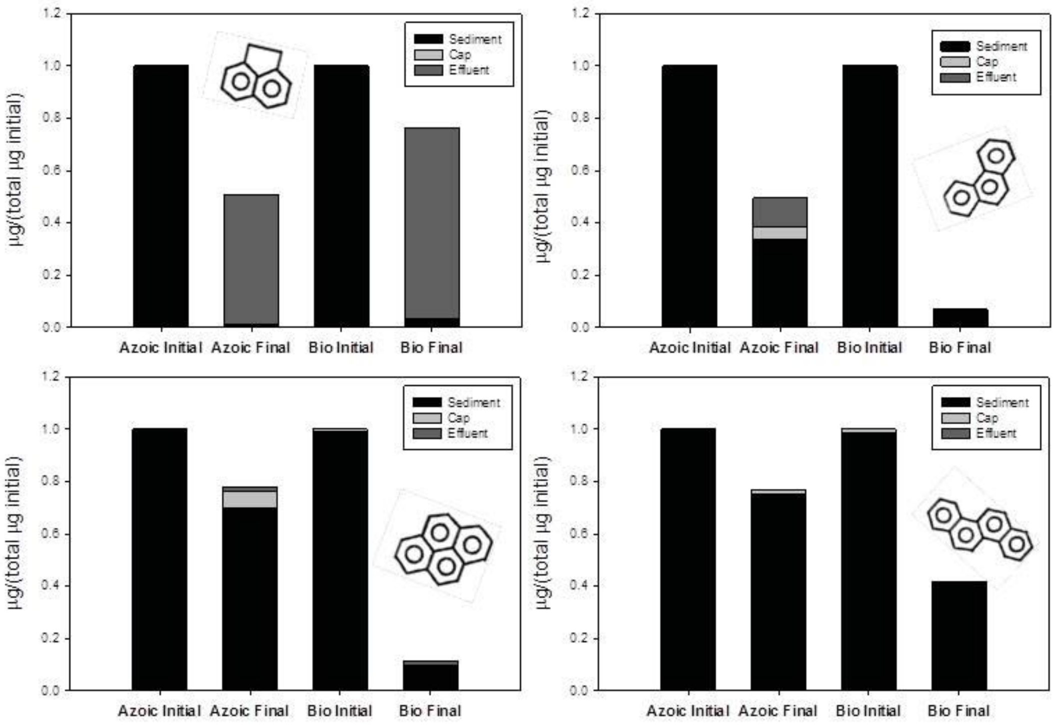

Figure 3.5 Mass balance in the azoic and non-amended biological columns before and after experiment. ACE upper left, PHN upper right, PYR lower left, CHR lower right.

A similar mass balance on a moderately high PAH, such as PYR (lower left, Figure 3.5) shows little mass loss in the effluent relative to the total PAH in either column. For PHN, PYR, and CHR, the mass of PAH unaccounted for is much higher in the biological column than in the azoic column. In addition, PYR (and other high MW PAHs) differs from ACE, in that much of the PAH remains in the azoic sediment layer. Losses in the biological layer appear to be due to biodegradation. It can also be seen that more PYR is trapped on the azoic capping material than for ACE. Compounds like PHN and CHR show similar trends observed for PYR in Figure 3.5. PAHs are lost from the source sediment in both azoic and biological columns, but the fate of most PAHs in the azoic columns is flushing and sorption to amendments (if present) while the fate is flushing and biodegradation in the biological columns.

Biological batch experiments with capping material. Results from the batch experiments with capping material that had been run in the biological column show significant reductions in the water phase concentrations of spiked PHN. The living batches relative to the killed batches (16.8±1.1 vs. 0.1±0.02 μg/L water phase PHN in batch), indicated that degradation and not simply sorption, was responsible for the concentration reductions in the biological column.

3.3.3 Analysis of Cap Pore Water Toxicity

Many of the most toxic alkylated PAHs remained in the sediment source pore water over time. C2,C3-naphthalenes, and C1 fluorenes show depletion near the sediment phase. However, the remainder of the alkylated PAH clusters increased or remained steady in concentration. When the toxic units for these alkylated compounds are calculated and plotted vs. pore volumes (Figure 3.6), it can be seen that the alkylated compounds alone contribute to a significant amount of toxicity (>1).

When all 24 PAH concentrations are added and plotted vs. pore volumes in the biological cap influent and effluent, there is depletion at the source zone and at the cap surface (Figure 3.7A and C). This trend is also seen for the summation of 10 parent compounds. The average ratio of surface to source concentrations for 24 and 10 total

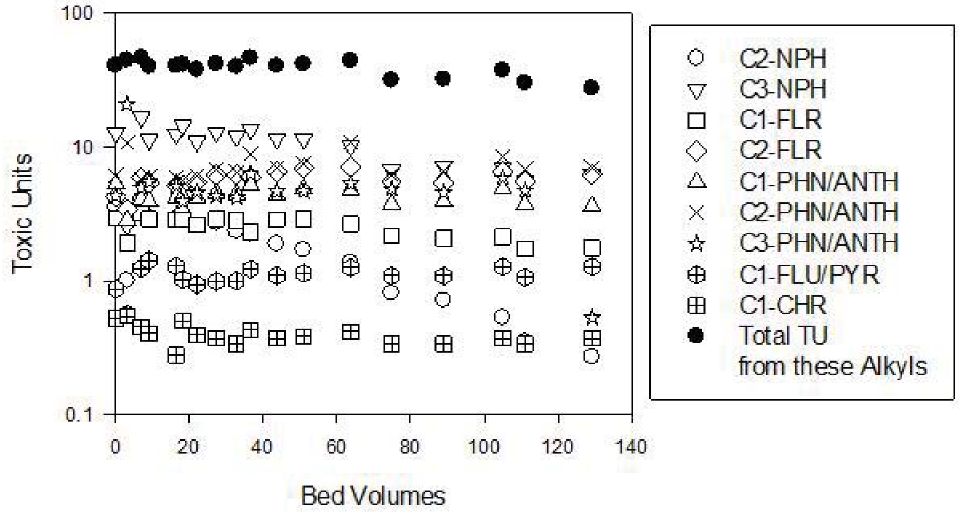

Figure 3.6 Toxic units from alkyl PAHs vs. bed volumes in the biological column at port 1 near the sediment source. These compounds are typically ignored, but contribute to a substantial portion of the toxicity.

PAHs are 0.11 and 0.13 respectively. When the toxic units are calculated, there is no longer a rapid decreasing trend in the sediment source zone (Figure 3.7B) as seen for the pore water concentrations. The decrease in total concentrations is due to the loss of low MW parent PAHs. The alkylated and high MW PAHs that contribute greatly to toxicity are not depleting over time, and thus toxicity remains fairly constant. The difference between the total 24 and 10 shows the importance of monitoring (or at least estimating) the toxicity contribution of alkylated compounds.

At the cap surface, toxicity reduces as the effectiveness of the biological amendment improves over time. The toxic units from just 10 PAH compounds show that the cap surface is no longer toxic, while the summation of toxic units from 24 reveal that the cap surface is still toxic (Figure 3.7D). The average ratio of surface to source total 24 toxic units and 10 toxic units are both 0.07, indicating that the true toxicity might be estimated by simply measuring 10 pore water PAH concentrations. Using a scaling factor, Hawthorne et al. 2006, found the toxicity of the 34 PAHs could be estimated with only measurements of parent PAHs at MGP sites.

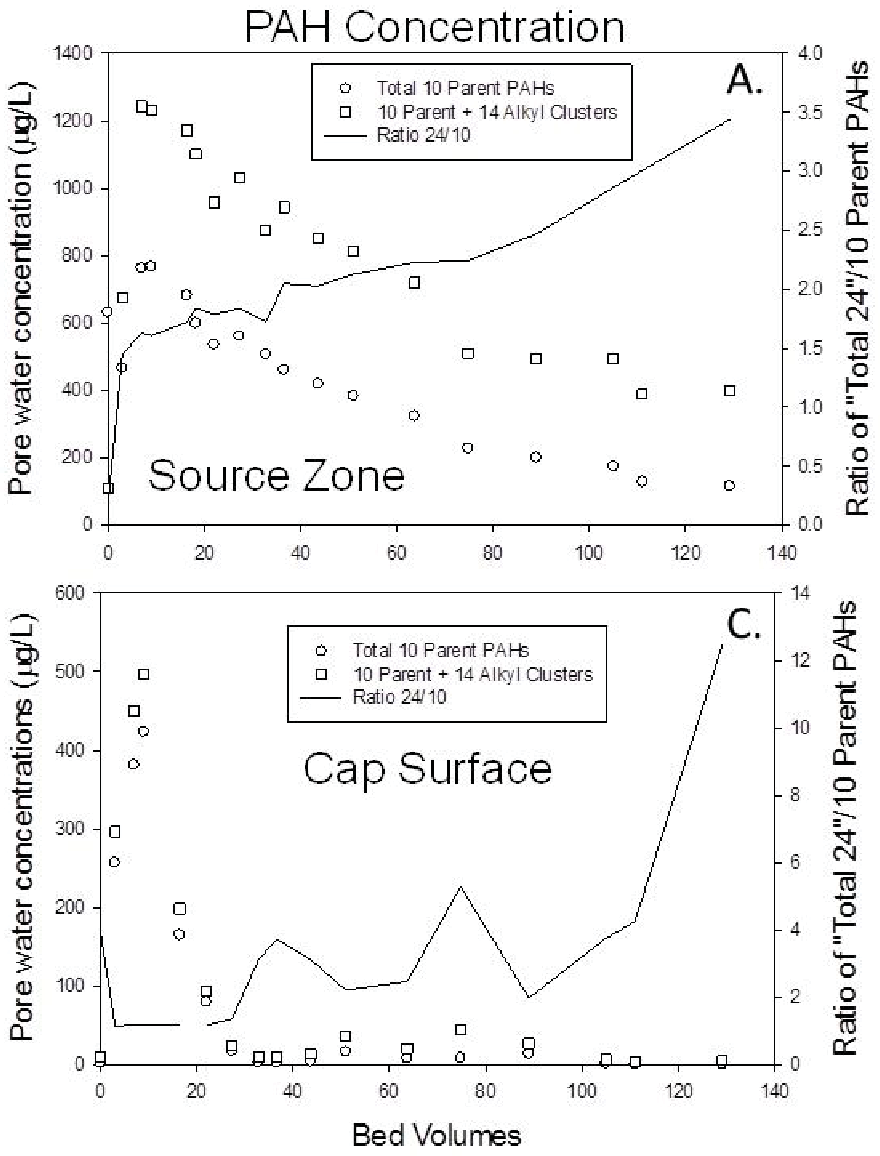

Figure 3.7A and 3.7C Observations of the biological column experiment. Total pore water PAH concentrations vs. bed volumes for 10 (circles) and 24 (squares) at the source zone (A.) and cap surface (C.

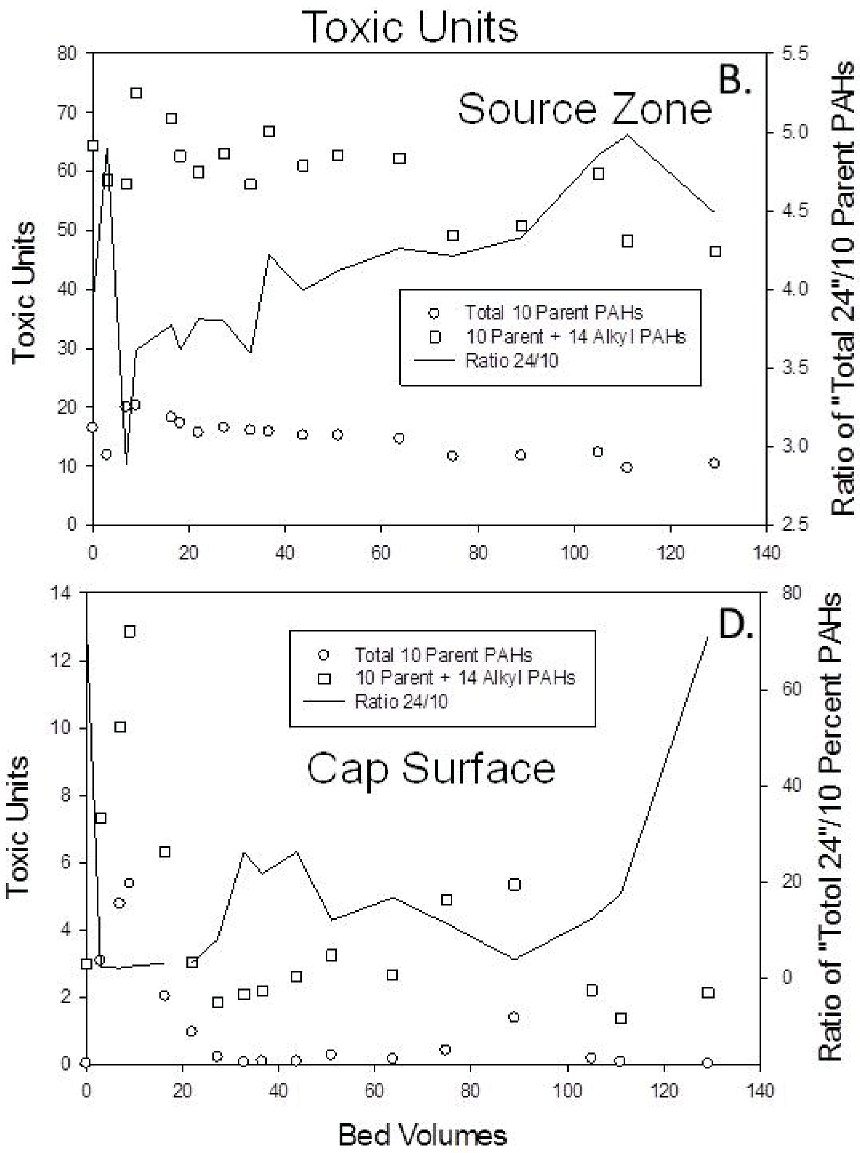

Figure 3.7B and 3.7D Observations of the biological column experiment. Total toxic units vs. bed volumes for 10 and 24 at the source zone (B.) and cap surface (D.) (note the change in scale for each graph.

The concentration in the overlying water was normalized to the source pore water concentration at each time in each column to compare the percent reduction in toxic units between each of the columns (Figure 3.8). Only 10 PAHs were monitored in the azoic columns. Both the biological column and the AC column resulted in similar

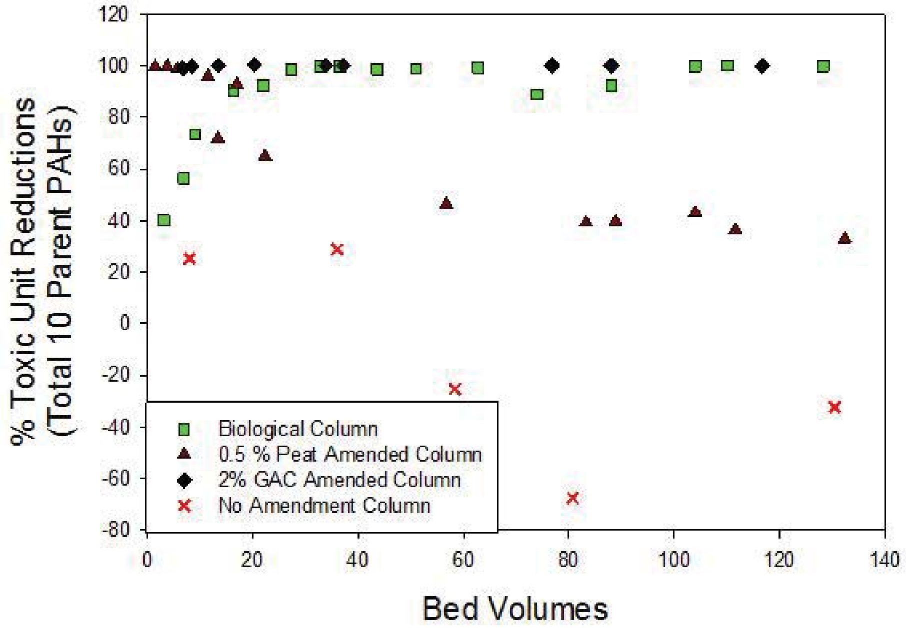

Figure 3.8 Percent reduction in total 10 PAH toxic units vs. bed volumes for azoic non-amended (red x), biological (green square), AC (black diamond), and peat amended (brown triangles) columns.

toxicity at the cap surface based on 10 PAHs, and both were much less than the azoic non-amended column. The AC amendment showed more rapid reductions than the biological cap, which may be desirable during cap placement in the field. Analysis of alkylated PAH clusters in AC amended caps may show that AC provides further reductions in toxicity compared to the biological amendment. Peat amendments show a decrease in overall performance over time due to gradual contaminant breakthrough. The azoic non-amended cap demonstrated negative reductions in total toxicity after 50 bed volumes, due to depletion or changing NAPL composition at the sediment source, while overlying water concentrations remained high.

3.3.4 Estimating First-Order Degradation Rates

The TOC of the various size fractions in the biologically active column can be compared to previous non-amended columns (Table S2). The overall TOC content of the biologically active material increased from 0.05% to 0.06% during the experiment in contrast to the azoic non-amended cap, which remained at 0.04%. The TOC contribution from the finest particles (< 0.425 mm) also increased in the biological experiments. The TOC increases were minimal and could be the result of biomass growth or heterogeneities in the biologically active cap.

Using Hydrus 1D, a model adapted from van Genuchten and Wagenet (1989) was used to simulate contaminant transport (equations 2-5) in the upper cap at Port 5. Initial conditions are provided in Table S3 and S4 and are otherwise similar to conditions described by Gidley et al. 2012 for the nonequilibrium case (Log K_{oc} = 3.98, α = 19.37, f_e = 0.5). Differences in TOC between the azoic non-amended and biological columns were first accounted for. This showed that the increased TOC in the biological column would not have been enough to decrease PHN concentrations to the levels observed (Figure 3.9). The PAH concentrations were low on the solid biologically active cap material, relative to the azoic column with no amendment (Figure 3.10). A first-order degradation rate parameter in the water phase was determined by trial and error to be 15 day^{-1} to best match the experimental data. This is much larger than the value of 0.0447 day^{-1} provided by Park et al. (1990). Peters et al. 1999 stated that the values could be vastly different depending on the availability of a terminal electron acceptor (in this case oxygen), nutrients, type of

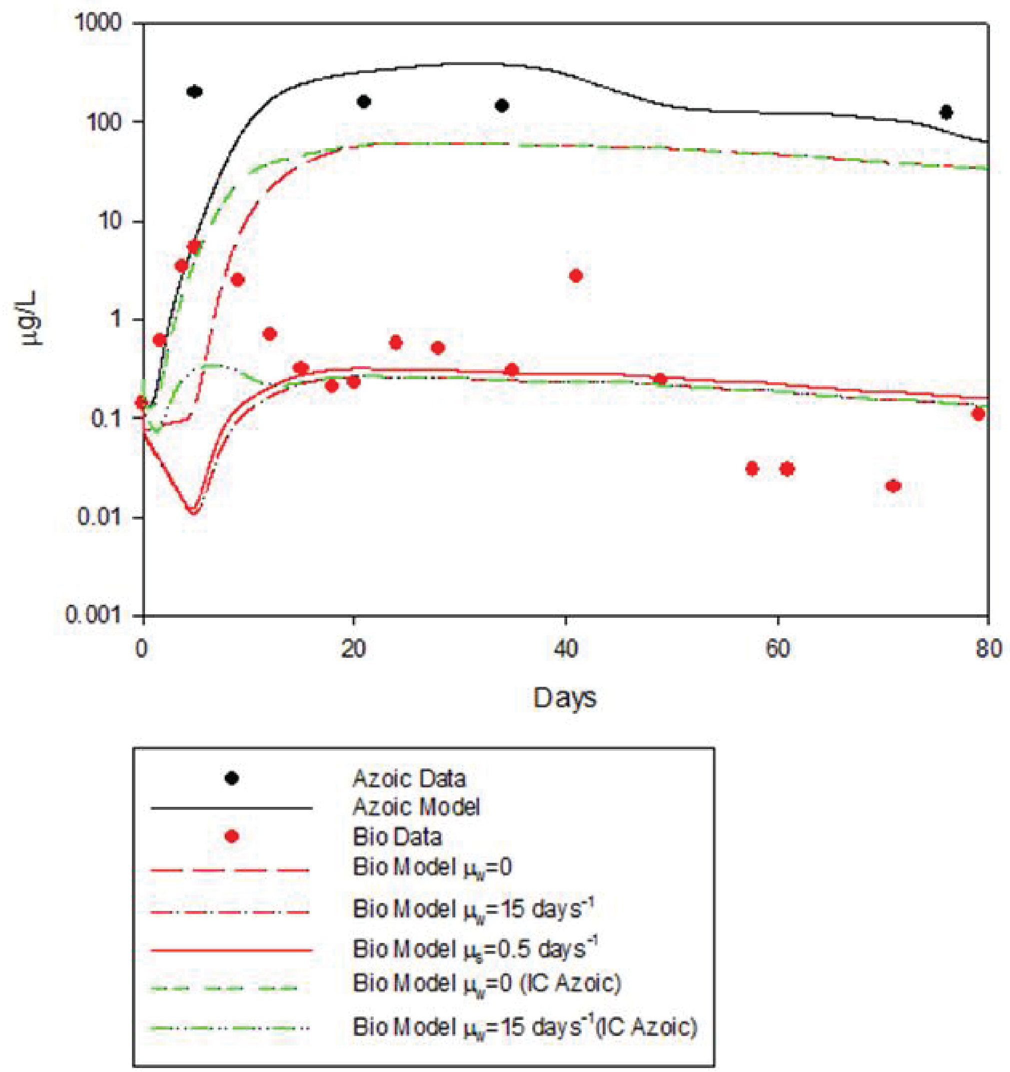

Figure 3.9 Phenanthrene migration in an azoic non-amended (black) and biological (red) cap. All models account for source concentrations specific to each column (Table S2 and S3). The first biological model (long dashed red) accounts for the slight increase in organic carbon (to 0.06%) in the biological column run. A first-order degradation coefficient (μ_w) of 15 days^{-1} in the water phase would be required to match the data (dash-dot red). If the degradation occurred on the sorbed solid phase, a degradation (μ_s) of only 0.5 days^{-1} would be required to match the data (solid red). The true initial concentrations (IC) in the biological column may be closer to that measured in the azoic non-amended column. The green lines investigate this possibility, for both zero degradation and a degradation rate of 15 days^{-1} in the water phase.

microorganisms, presence of supplemental substrates, temperature etc. A much smaller degradation term (0.5 days^{-1}) appears to be required if degradation were occurring on the solid phase (by comparison of the red dash dot μ_w = 15 days^{-1} and μ_s =0.5 days^{-1} simulations). Degradation of sorbed PAHs is likely, given the lower concentrations in the cap relative to the sediment (more conducive to microorganisms), the possible presence of a biofilm on the capping material surface, and the results presented in Figure 3.10, which show that solid phase concentration was less on the biologically amended cap.

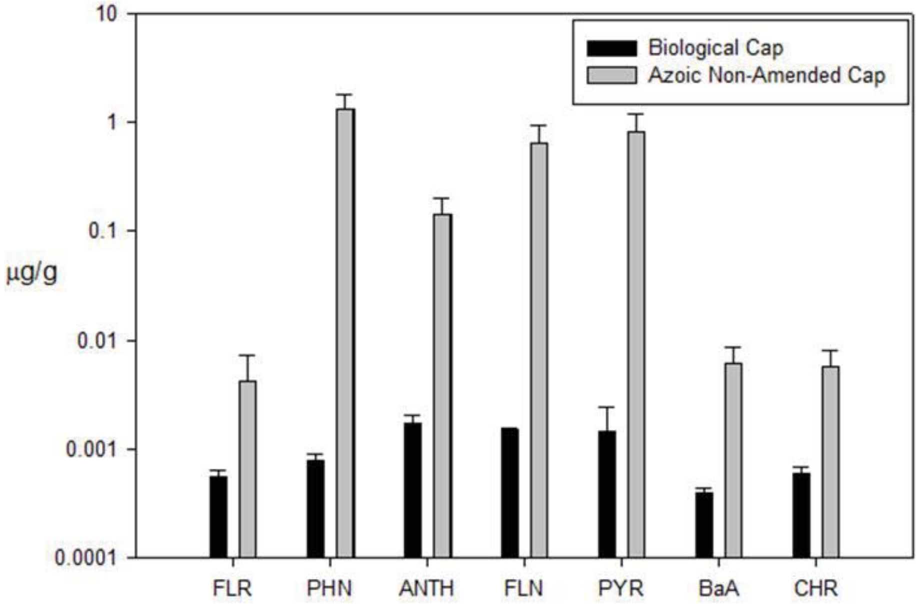

Figure 3.10 Solid concentrations in the top 30 cm of the biological and azoic non-amended columns (mean of three measurements with error bars as standard deviations).

The initial pore water concentrations of the biological cap material were much lower than the initial concentrations in the azoic non-amended cap material. It is possible that initial conditions of the biological column were similar to that in the azoic non-amended column, but that significant degradation occurred in the first half-hour before the initial measurements were taken relative to the azoic column. To explore this possibility, initial conditions (from Table S3) for the azoic non-amended column were used to model the biological column. The results are presented in green in Figure 3.9. It appears that there is an initial phase in the data where concentrations are increasing. This phase is modeled well using the initial conditions from the azoic column (green double dash). The concentrations begin to dip after about ten days till about 20 days. This parabolic shape was captured by the model that used initial conditions from the azoic column, but had a degradation coefficient in the water phase (green dash-dot). It is possible that the degradation rate increased over time (not modeled). A first-order degradation model assumes constant biomass. The biomass may have increased during the length of the experiment. If this were the case, the parabolic shape could be better captured with a lower initial degradation rate during the first 20 days. The remainder of the data could be matched with the high rate of 15 day^{-1} in the water phase. Instability in the data around 40 days is suspected to be due to a brief disruption in the column flow.

3.4 Conclusions and Implications

The findings demonstrate a great potential for degradation of 10 parent PAHs in a sediment cap amended with microorganisms compared to azoic control experiments. PAH concentrations and resultant toxicity at the cap surface continued to reduce until about 30 BV as organisms in the cap acclimated. This is possibly due to a lag phase in biodegradation which is not captured in a first order model. Degradation near the glass beads layer and lower cap may have also occurred at a different rate (likely more degradation) than at the cap surface where the model was applied. These special heterogeneities were not captured by the model. The initial observed migration of PAHs was then followed by sustained order of magnitude reductions in cap surface toxicity compared to the source zone. The findings also demonstrate that cap surface toxicity may occur from alkylated PAHs while it cannot be attributed to parent compounds alone. From model simulations, it appears that PAHs leaving the sediment source zone are initially in the bioavailable water phase and can then be degraded in the cap pore water or on the surface of cap materials where organisms may reside in a biofilm. In some field scenarios, oxygen may be present near the cap surface or engineered delivery of oxygen may be necessary in sediment caps to enhance PAH degradation. In the field, the oxygen and nutrients in the groundwater that has passed through the sediments would likely be far from optimal, however other terminal electron acceptors for microbial respiration might be present (sulfate or nitrate). Further research should be conducted with systems containing limited oxygen and nutrients. Temperature is known to affect biochemical reactions. In activated sludge treatment, for example, the reaction rate approximately doubles for each 10 °C increase in temperature (Reynolds and Richards, 1996). The microorganisms in the cap will likely behave similarly.

AC amendment decreased the concentration of PAHs reaching the cap surface much more effectively compared to biological degradation alone. While biological degradation can slow down the long-term breakthrough of PAHs through a cap, AC amendment can be a more effective means to control PAH migration, especially for consolidation-induced advection during cap placement. Other carbon amendments (such as peat) may lead to degradation and oxygen depletion, whereas AC is chemically stable and would be preferred at MGP or creosote contaminated sites, where PAHs should be the limiting substrate.

3.5 Acknowledgments:

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3.6 References

Gidley, P.T.; Kwon, S.; Yakirevich, A.; Magar, V.; Ghosh, U. Advection Dominated Transport of Polycyclic Aromatic Hydrocarbons in Amended Sediment Caps. *Environ. Sci. Technol*. **2012**, 46, 5032-5039

Hyun, S.; Jafvert, C. T.; Lee, L. S.; Rao, P. S. C. Laboratory studies to characterize the efficacy of sand capping a coal tar-contaminated sediment. *Chemosphere*. **2006**, 63. 1621-1631.

Rasmussen, G.; Fremmersvik, G.; Olsen, R. A. Treatment of creosote-contaminated groundwater in a peat/sand permeable barrier-a column study. *J. Haz. Materials B.* **2002**, 93, 285-306.

Wammer, K. H.; Peters, C. A. Polycyclic Aromatic Hydrocarbon Biodegradation Rates: A Structure-Based Study. *Environ. Sci. Technol.* **2005**, 39, 2571-2578

Himmelheber, D. W.; Thomas, S. H.; Loffler, F. E.; Taillefert, M.; Hughes, J. B. Microbial Colonization of an In Situ Sediment Cap and Correlation to Stratified Redox Zones. *Environ. Sci. Technol.* **2009**, 43, 66-74.

Haritash, A.K.; Kaushik, C.P. Biodegradation aspects of Polycyclic Aromatic Hydrocarbons (PAHs): a review. *J. Haz. Materials* **2009**, 169, 1-15

U.S. Environmental Protection Agency. **2003**. Procedures for the derivation of ESBs for the protection of benthic organisms: PAH mixtures. EPA/600/R-02/013. Office of Research and Development, Washington DC.

Hawthorne, S. B.; Grabanski, C. B.; Miller, D. J.; Kreitinger, J. P. Solid-Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values. *Environ. Sci. Technol.* **2005**, 39, 2795-2803.

Hawthorne, S. B.; Miller, D. J.; Kreitinger, J. P. Measurement of Total Polycyclic Aromatic Hydrocarbon Concentrations in Sediments and Toxic Units used for Estimating Risk to Benthic Invertebrates at Manufactured Gas Plant Sites. *Environ. Toxicol. Chem.* **2006,** 25, 287-296.

American Society for Testing and Materials. **2008**. Standard test method for determination of parent and alkyl polycyclic aromatics in sediment pore water using solid-phase microextraction and gas chromatography/mass spectrometry in selected ion monitoring mode. D 7363-07. In *Annual Book of ASTM Standards*, Vol. 11.02. West Conshohocken, PA.

Hedlund, B. P.; Staley, J. T., Isolation and characterization of *Pseudoalteromonas* strains with divergent polycyclic aromatic hydrocarbon catabolic properties. *Environ. Microbiology*. **2006**, 8, 178-182.

Geiselbrecht, A. D.; Hedlund, B. P.; Tichi, M. A.; Stanley, J. T. Isolation of Marine Polycyclic Aromatic Hydrocarbon (PAH)-Degrading Cycloclasticus Strains from the Gulf of Mexico and Comparison of Their PAH Degradation Ability with That of Puget Sound Cycloclasticus Strains. *Applied and Environ. Microbiology* **1998**, 64, 4703-4710.

Wang, Q.; Kassem, I. I.; Sigler, V.; Gruden, C. Short-Term Effect of Capping on Microbial Communities in Freshwater Sediments. *Water Environ. Research*. **2009**. 81. 441-449.

Knightes, C. D.; Peters, C. A. Aqueous Phase Biodegradation Kinetics of 10 PAH Compounds. *Environ. Engineering Sci.* **2003**, 20, 207-218.

Lehto, K.-M.; Lemmetyinen, H.; Puhakka, J. Biodegradation of Photoirradiated Polycyclic Aromatic Hydrocarbon Constituents of Creosote Oil. *Environ. Technol.* **2000**, 21, 901-907.

Ghosh, U.; Weber, A. S.; Jenson, J. N.; Smith, J. R. Relationship Between PCB Desorption Equilibrium, Kinetics, and Availability During Land Biotreatment. *Environ. Sci. Technol.* **2000**, 34, 2542-2548.

Koch, A. L. Growth Measurement. In Methods in General Molecular Bacteriology, Gerhardt, P., Ed. American Society of Microbiology: Washington D.C., **1994**, 248-277.

Šimůnek, J.; van Genuchten, M. T.; Šejna, M. **2008**. The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Version 4.0. HYDRUS Software Ser. 3. Dep. of Environmental Sciences, Univ. of California, Riverside.

van Genuchten, M.T.; Wagenet, R.J. Two-Site/Two Region Models for Pesticide Transport and Degradation: Theoretical Development and Analytical Solutions. *Soil Sci. Soc. Am. J.* **1989**, 53, 1303-1310.

Millington, R. J.; Quirk, J. Permeability of porous solids. *Trans. Faraday Soc.* **1961**, 57, 1200-1207.

Peters, C. A.; Knightes, C. D.; Brown, D. G., Long-Term Compositional Dynamics of PAH-Containing NAPLs and Implications for Risk Assessment. *Environ. Sci. Technol.* **1999**, 33, 4499-4507.

Park, K. S.; Sims, R. C.; Dupont, R.R.Transformation of PAHs in Soil Systems. *J. Environ. Eng.***1990**, 116, 632-640.

Bodour, A. A.; Wang, J.-M.; Brusseau, M. L.; Maier, R. M. Temporal change in culturable phenanthrene degraders in response to long-term exposure to phenanthrene in a soil column system. *Environ. Microbiol.* **2003**, 5, 888-895.

Wicke, D.; Böckelmann, U.; Reemtsma, T. Environmental Influences on the Partitioning and Diffusion of Hydrophobic Organic Contaminants in Microbial Biofilms. *Environ. Sci. Technol.* **2008**. 42, 1990-1996.

Reynolds, T.D.; Richards, P.A. *Unit Operations and Processes in Environmental Engineering;* PWS Publishing Company, Boston, MA, USA, 1996.

3.7 Supplemental Information

Table 3.S1 Toxic Units for 24 PAHs (ASTM D 7363-07)

PAHs (Parent and Alkyls)	**µg/L for One Toxic Unit**	**12 PAHs**	**10 PAHs**
naphthalene	193.47	x	x
2-methylnaphthalene	81.69	x	
1-methylnaphthalene	81.69	x	
C2 naphthalenes	30.24		
C3 naphthalenes	11.10		
C4 naphthalenes	4.05		
acenaphthylene	306.85	x	x
acenaphthene	55.85	x	x
fluorene	39.30	x	x
C1 fluorenes	13.99		
C2 fluorenes	5.30		
C3 fluorenes	1.92		
phenanthrene	19.13	x	x
anthracene	20.72	x	x
C1 phenanthrenes/anthracenes	7.44		
C2 phenanthrenes/anthracenes	3.20		
C3 phenanthrenes/anthracenes	1.26		
C4 phenanthrenes/anthracenes	0.56		
fluoranthene	7.11	x	x
pyrene	10.11	x	x
C1 fluoranthenes/pyrenes	4.89		
benz[a]anthracene	2.23	x	x
chrysene	2.04	x	x
C1 chrysenes	0.86		

Table 3.S2 TOC in the biological column

Size Fraction	F_{OC} Azoic	F_{OC} Bio
>2.36 mm	-	-
1.7-2.36mm	-	-
1.18-1.7mm	0.023	0.005
0.425-1.18mm	0.005	0.017
<0.425mm	0.001	0.079

Table 3.S3 Initial pore water PAH profiles in cap. Initial conditions of Hydrus 1D.

PAH	**node (cm from sediment)**	**pore water (ug/L)**	**pore water (ug/L) peat**	**pore water (ug/L) AC**	**pore water (ug/L) bio**
PHN	0-7	207.6-	138.6-60.6	27.1-1.4	86.8-0.4
	8-23	60.3-12.5	60.6-19.7	1.4-0.7	0.4-0.2
	24-38	12.5-0.3	19.7-2.1	0.7-0.7	0.2-0.2
	39-53	0.3-0.2	2.1-0	0.7-*0.4*$^{+}$	0.2-0.1
	54-68	0.2-0	0-0	*0.4*-0.04	*0.1-0*
PYR	0-7	39.0-2.6	12.9-5.8	0.8-1.0	11.8-0.2
	8-23	2.6-0.6	5.8-2.5	1.0-0.09	0.2-0.1
	24-38	0.6-0.2	2.5-0.4	0.09-*0.07*$^{+}$	0.1-0.1
	39-53	0.2-0.2	0.4-0	*0.07*-0.04	*0.1-0.1*
	54-68	0.2-0	0-0	0.04-0.01	0.1-0
CHR	0-7	6.0-0.4	0.29-0.56	0.2-0.3	0.54-0.02
	8-23	0.4-0.03	0.56-0.18	0.3-0.03	0.02-0
	24-38	0.03-0.02	0.18-0.16	0.03-*0.025*$^{+}$	0-0
	39-53	0.02-0	0.16-0	*0.025*-0.02	*0-0*
	54-68	0-0	0-0	0.02-0	0-0

*estimate (port 4 sample was not taken with GAC column)

Table 3.S4 Time, Darcy flux, and concentrations for the sediment source term (port 1) used in Hydrus 1D simulations in the biological column for phenanthrene.

days	**cm/day**	**µg/L**
1	30	86
3	34	20
5	34	53
8	34	58
14	34	64
24	34	60
38	34	56
44	34	50
52	34	46
58	34	40
66	34	36
100	34	32

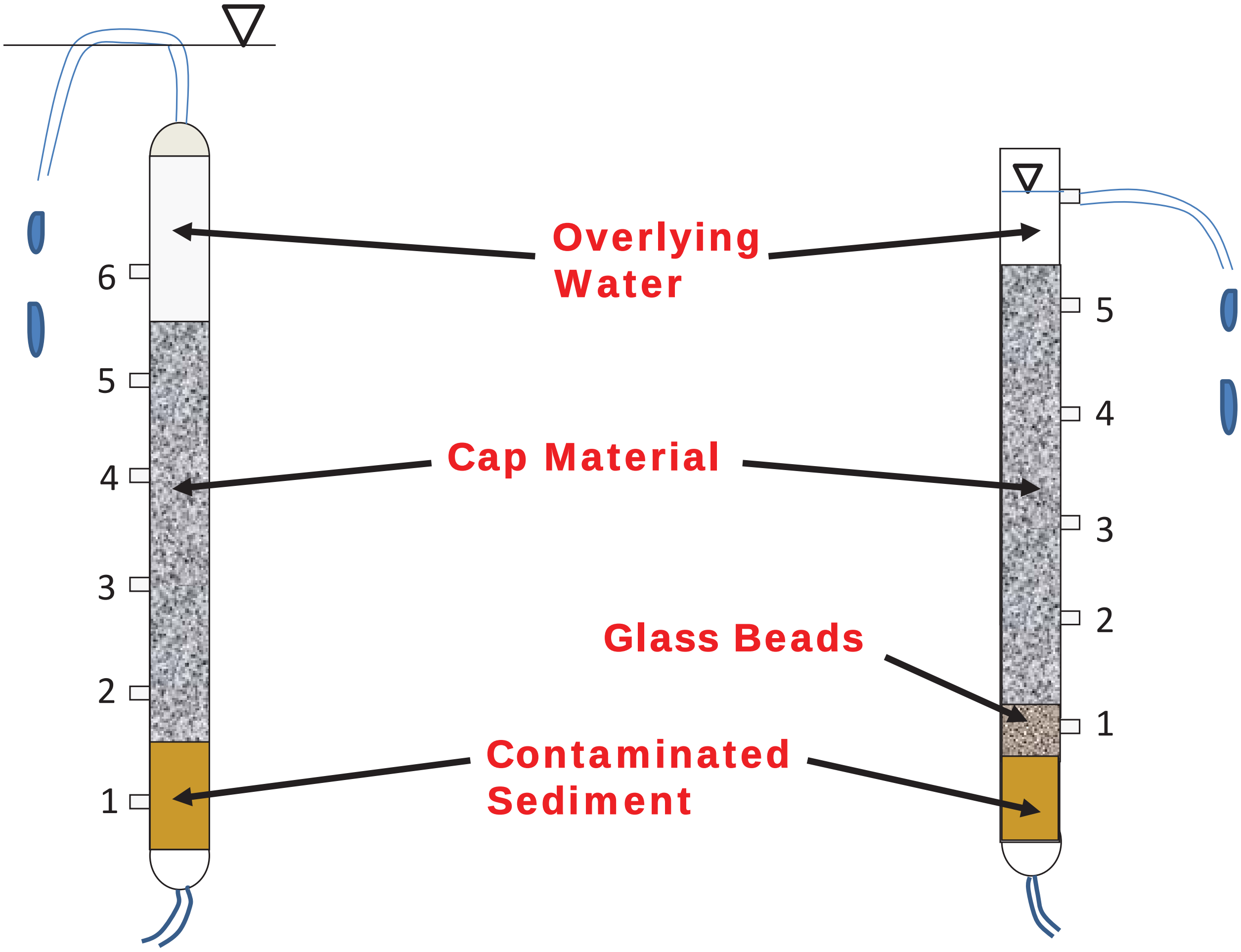


Figure 3.S1 Changes between the experimental set-up of the azoic non-amended columns (left) and the biological column (right)

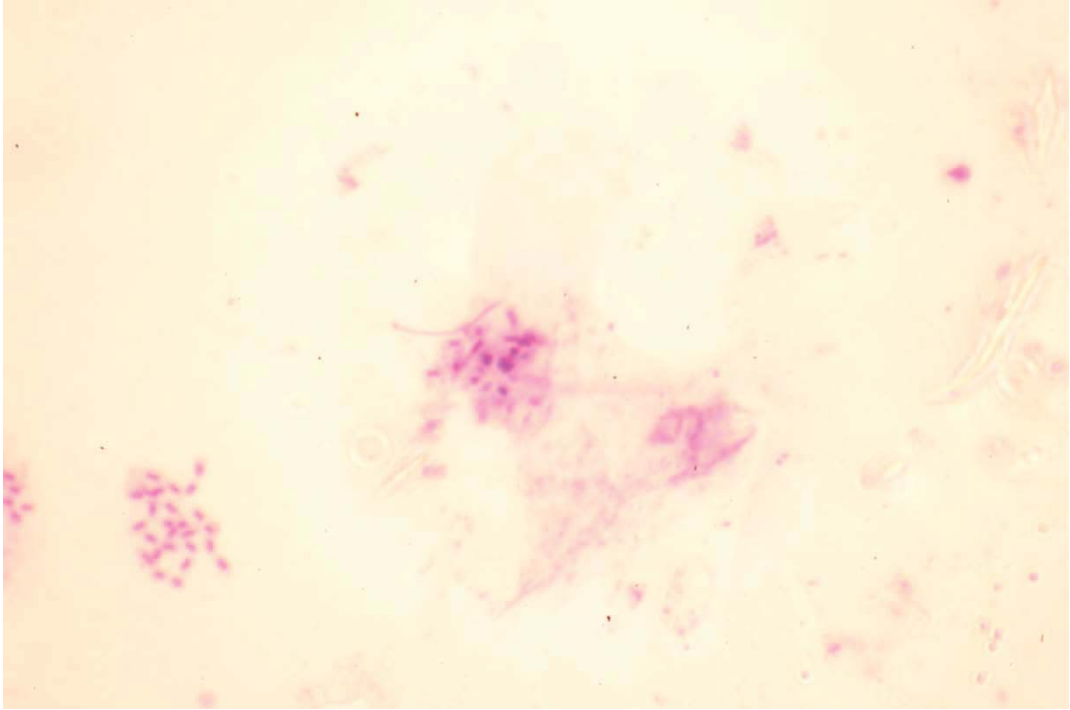


Figure 3.S2 Bacteria by microscopy at 100X with crystal violet dye.

Chapter 4: Research Summary

This chapter provides a summary of key research findings and explains how each of the three research questions posed in this dissertation has been addressed. Implications of this research to the field of sediment capping and recommendations for future work are also provided.

4.1 Azoic vs. Biological Caps (Research question #1)

Biologically active caps showed reductions in pore water concentrations, whereas azoic caps demonstrated little ability to retain pore water PAHs, especially for low MW PAHs. This indicates that biologically active caps could potentially have a significant impact on cap performance during conditions of groundwater infiltration. A biologically active cap would be effective in controlling exposure from sustained source zones. After an initial lag phase, biological column experiments showed two orders of magnitude reductions in cap surface pore water concentrations for most PAHs. Analysis of the biologically active capping material after the experiment revealed the accumulation of some biomass, but not PAHs. Oxygen and nutrients were required for this observed reduction in PAH concentration. In the field sediment cap environment, oxygen will likely be the greatest limiting factor to PAH degradation rates. Oxygen may be present near the cap surface due to natural exchanges with overlying water or delivered into the cap via engineered means.

4.2 Effectiveness of Carbon Amendments (Research question #2)

Carbon amendments can provide the retardation capabilities necessary for a cap under the hydrodynamic conditions studied. Activated carbon amendment even at a low dose of 0.2% by weight reduced pore water PAH concentrations to such an extent that most measurements of cap pore water for the duration of the study were below the limit of quantitation (LOQ) at the cap surface. Single solute models for pyrene assuming a constant source zone and conservative partitioning to 0.2% activated carbon show that the cap will last over 100 years. Peat amendment showed significant improvement over an azoic sand cap, however, degradation of the peat in the cap over time might lead to anoxic conditions and inhibit possible PAH degrading bacteria. When the sorption capacity of the carbon is reached, sufficient time should occur for microorganisms to colonize the cap in zones of optimal, oxygen and nutrient concentrations to continue to degrade PAHs in the cap.

4.3 Sediment Cap Modeling and Design (Research question #3)

4.3.1 Modeling the Source

PAH dissolution from the creosote source zone in these experiments was best modeled using Raoult’s law partitioning. However, not all sediments will be controlled by Raoult’s law partitioning and where partitioning to sediment organic matter is dominant, traditional organic matter partitioning models would be appropriate. Direct pore water measurements of the sediment (as was done in this research) was found to be critical in assessing source zone boundary conditions and validating model predictions.

4.3.2 Modeling the Amended Cap

Given an understanding of the source zone pore water concentrations, PAHs with molecular weight up to pyrene are well predicted by single solute transport models, in the presence of substantial amounts of organic carbon (>0.2%) in the cap. For the high MW PAHs, the concentrations remained close to the LOQ in caps with significant amounts of organic carbon. With the LOQ used as the source boundary condition, there is less discrepancy between model and data for high MW PAHs. Kinetic sorption parameters from the literature do not account for discrepancies that do exist, and therefore the local equilibrium assumption seems valid for these experimental conditions. The modeling shows that major trends of PAH transport through sorbent amended caps can be predicted using standard approaches used in groundwater transport modeling (such as Hydrus 1D). Modeling PAH migration in the presence of PAH degrading microorganisms showed a great potential for improved cap performance. However, this improvement will be far more unpredictable relative to carbon sorption mechanisms due to large uncertainties of biodegradation rates in the field.

4.4 Implications of research findings

4.4.1 Initial Cap Placement

For sand caps with little sorption capacity, the initial contamination can have a significant contribution to early breakthrough. Pore water displacement is expected to occur due to initial mixing between the sediment and the cap and due to sediment consolidation. Low-impact placement methods exist to minimize mixing and native sediment disturbances. Establishing initial conditions in a cap should be done by measuring pore water concentrations in addition to measuring solid core samples a few months after cap placement.

4.4.2. Assessment of cap performance in the field

PAH concentrations in cores from sediment caps are a poor indicator of dissolved contaminant breakthrough, especially in cases where there is little capacity in the cap material to sorb contaminants and where groundwater advection may be a vector for contaminant transport through a cap. It is critical that scientifically appropriate performance criteria are chosen to monitor the performance of a capping remedy. For example, if PAH concentration in the cap solids is the criteria, an unamended sand cap that allows PAH laden groundwater to flow through and contaminate the overlying surface water may look superior to a carbon amended cap that adsorbs the migrating PAHs, and retains the contaminants in the cap. It is apparent that measuring pore water concentrations is critical in determining breakthrough of PAHs in sand caps.

4.4.3. Sorbent amendments in caps.

Results from this research indicate that enhancement of sorption within a sand cap is necessary to prevent migration of contaminants in situations where groundwater advection is anticipated. Experimental results indicate that even at a low amendment rate of 0.2% activated carbon, an effective reduction in PAH migration is observed. It is possible that mass transfer limitations within carbon particles and fouling of the carbon with other organic molecules may degrade long-term performance to some extent. However, with the large reductions in PAH transport evident from the laboratory experiments and modeling simulations with activated carbon amended sand caps, it appears promising to include these amendments in sand caps to enhance performance where groundwater advection is of concern. Future cap designs should incorporate active cap amendment options. Recent initiatives by the USEPA and the Army Corps of Engineers at the Lower Duwamish Waterway restoration effort is starting to consider incorporation of sorbent amendments into cap designs.

4.4.4. Biological degradation in a cap.

Biodegradation activity within a cap was shown to greatly enhance the effectiveness of a sediment cap. Other researchers have shown that PAH biodegradation occurs in AC amended soil and that bacterial community structure is not changed (Meynet et al., 2012). Results from this study indicate that more effort should be taken in the design stage to incorporate engineering actions that can enhance oxygen availability and biodegradation within sand caps or amended caps for PAH remediation.

However, care must be taken to assess the influence redox changes could have on possible mobilization of metal contaminants.

4.5 Future Work

Based on this research, the following recommendations are made for future work that can enhance our understanding and help refine capping technologies further.

1) Future work should seek to better understand the impact of dissolved organic carbon from various sources on PAH partitioning and transport through sand caps.

2) A better understanding of the competition effects of the many PAHs (and other forms of DOC) for sorption sites in a range of amendments would be helpful for selection of sorbents and better cap designs.

3) Future research on safe, cost effective delivery of oxygen to caps will further improve this option for PAH remediation.

4) Unsaturated flow in the biological column resulted in increased concentrations of some PAHs. Sediment caps placed in the intertidal zone may be subjected to similar unsaturated conditions during low tide. Further research may look into understanding contaminant migration in sediment caps placed in the variably saturated zone.

5) Additional laboratory-scale research is needed to develop efficient methods to deploy amendments to caps without having the sand and amendment segregate during placement underwater due to density differences. Delivery of amendments through specially manufactured pellets could be a viable option but needs to be tested. The sorbents could be delivered to achieve a uniform distribution within the cap or as a distinct layer within the cap. Engineering feasibility and effectiveness of either approach needs to be tested in the field.

6) The next step in the technology transition process should involve pilot-scale testing of amended sand caps placed over contaminated sediments at a site where groundwater flow has been documented. A long-term monitoring plan should evaluate migration of pore water contaminants through the cap over time for a variety of amended caps.

4.6 References

Meynet, P.; Hale, S.E; Davenport, R.J.; Cornelissen, G.; Breedveld, G.D; Werner, D. Effect of Activated Carbon Amendment on Bacterial Community Structure and Functions in a PAH Impacted Urban Soil. *Environ. Sci. Technol*. **2012**, 46, 5057-5066.

Chapter 5: Appendices

5.1 Introduction

This chapter provides information about additional investigations mostly related to the azoic column experiments that were not incorporated in the submitted manuscript, which has been retained in its submitted form in this dissertation. These additional results were not incorporated into chapter 2 due to size limitation or due to the fact that these additional experiments were performed later in time. These additional topics include: details of sorption isotherms; sorption kinetics on cap solids; spatial data in relation to detection limits; comparing partitioning data to the Raoult's law model; discussion on the influence of particle, colloid, and dissolved organic matter on the transport of PAHs, and finally; alternative modeling techniques for use in activated carbon (AC) amended caps.

5.2 Methods and Materials

Many of the methods used to collect the data discussed in this supplement have been presented in chapter 2. These methods include: column experimental set-up, batch equilibrium tests, PAH analysis, pore water PAH measurement and hexane/acetone extractables. Contaminant transport modeling is discussed briefly in the background section and also in chapter 2. Additional materials and methods not described in chapter 2 are discussed here.

5.3.1 Materials

Two size fractions of the capping material are shown in Figure 5.1. The small size fractions of the capping material contained some shell fragments in addition to mineral particles. The > 2.36 mm particle fraction was composed primarily of mineral grains.

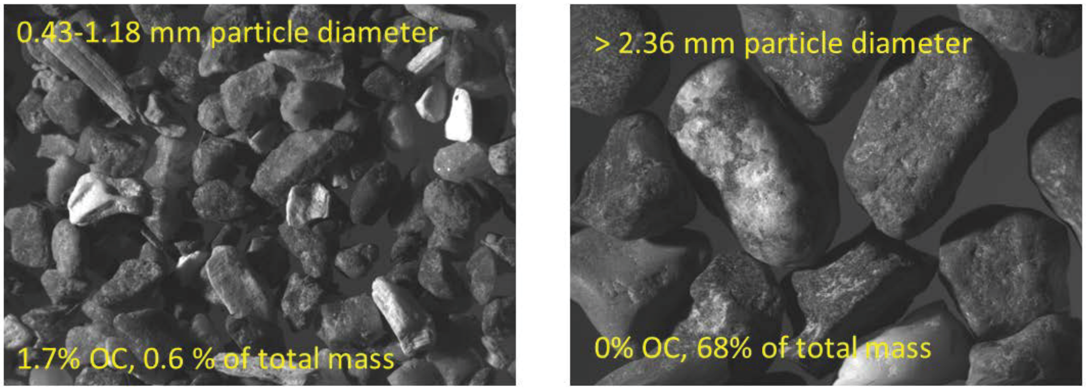


Figure 5.1 Two size fractions of the Eagle Harbor cap material (20X).

The capping material, along with the dried sediment, peat and AC amendment materials are shown in Figure 5.2 for comparison. A penny is included in the figure for scale. It can be seen that the capping material is quite large in comparison to the amended peat and AC particles. The AC used was in the size range of 45-180 µm and considered to be fine granular.

Figure 5.2 Dried sediment, cap, and amendment materials used in the study.

5.2.2 Column freezing and sectional analysis

At the end of each column experiment, the columns were frozen with dry ice, the glass was shattered to expose the frozen sediment and capping materials, and it was sectioned into approximately ten three inch sections. Two to three of these sections were in the sediment layer and eight were taken from the capping layer.

Just before freezing, the column was turned on its side. Overlying water, along with some pore water from the cap, drained from the column. Once the columns were frozen solid (after about 2 hours), the columns were removed from the ice, they were allowed to thaw for about a half hour and the glass was broken away from the frozen sediment and capping material. The solid sediment and cap often broke into sections while removing the glass, but it was possible to keep track of the arrangement of these sections. After further thawing, the softened core was sectioned into 3-inch sections using a clean knife or saw. The sections were placed in glass jars and stored in the refrigerator at 4°C until further analysis.

In an effort to better confirm the visual observation that no AC particles were migrating out of the cap, the sections from the capping layer of the 2% AC amended column were analyzed for solid carbon content. The TOC of the native cap material is so low (0.04%) that it has relatively no impact on the carbon content relative to the AC added.

Two approaches were used in the analysis of the cap sections. First, it was assumed that all of the AC would remain with the smallest dried size fraction of the sieved material. The carbon was measured in the smallest fraction (< 245µm) with the mass fraction of that sieve size and the carbon content of the AC accounted for. Some of the AC particles also remained attached to the large size fractions in the cap (Figure 5.3). The percent of the total AC attached to the large size fractions was small, as determined from the analysis of prepared mixtures of 2% AC amended cap material. This analysis and recovery of the prepared 2% AC amended cap provides some confidence that only small amounts of AC is lost during sieving of the dry capping material.

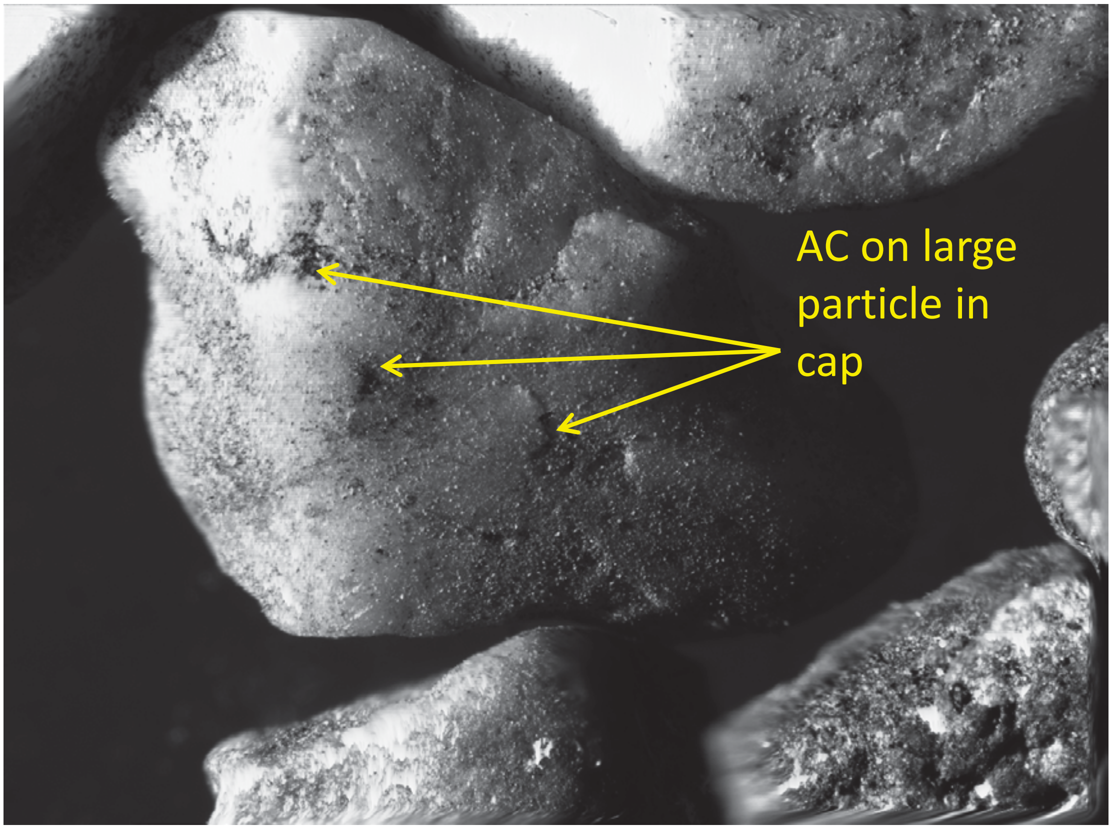


Figure 5.3 AC particles attached to large size fraction (1.7-2.36mm) of dried amended cap material.

The second method used for the analysis of AC content involved measuring the carbon of each individual size fraction of the capping material. The carbon content of the AC was again accounted for, and a weighted average of seven size fractions was obtained.

5.3 Results and Discussion

5.3.1 Long-Term Models

Hydrus 1D Simulations were run to show spatial migration (Figure 5.4) with a cap thickness of 65 cm (as in the columns) with amendments. It can be seen that AC amended caps (modeled over years) are predicted to work far better than organic carbon (peat) amended caps (modeled over days) for pyrene migration.

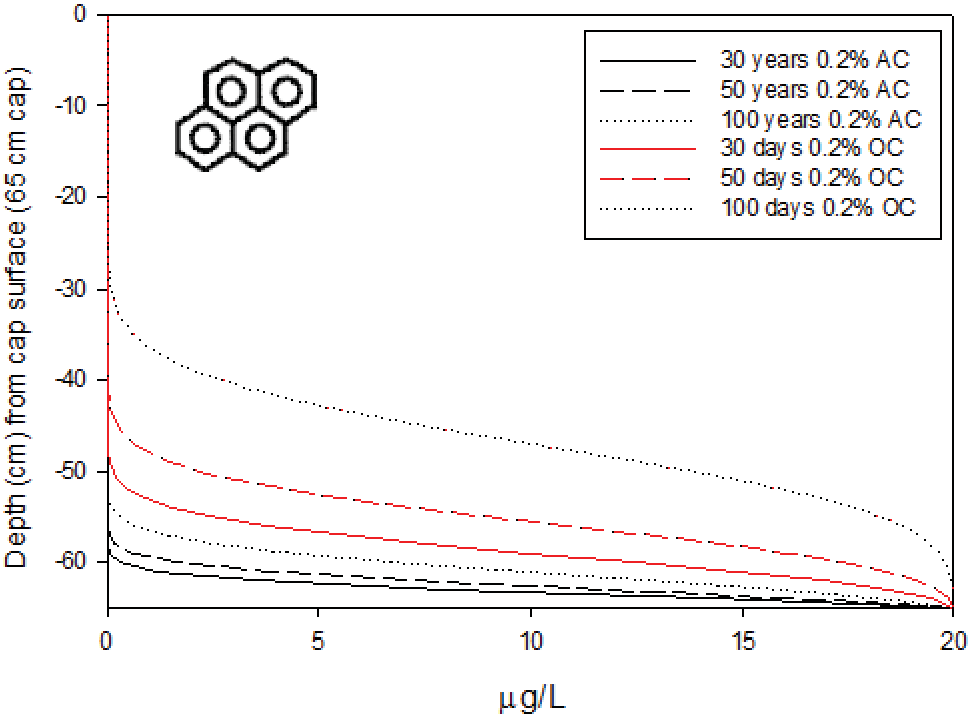


Figure 5.4 Nonequilibrium models (adapted from van Genuchten and Wagenet, 1989 run using Hydrus 1D) of pyrene migration in the column experiments with 30 cm/day Darcy velocity with a constant source concentration (20 µg/L). A conservative estimate of partitioning of pyrene to AC is assumed to be linear from a high concentration level (48µg/L). Organic carbon (OC) is from peat amendment. Nonequilibrium parameters are half those shown in Table S6 (for sand and peat) and for AC the values used in Figure S5 were applied here (discussed later in section 5.3.9). 20 µg/L pyrene is a typical concentration released from the sediment source in the column experiments.

5.3.2 Isotherms

Transport models with linear equilibrium partitioning are considered a good approach for sand and peat amended caps, because the materials have linear isotherms. These values were compared to the regression by Xia (in Allen-King et al. 2002), which is similar to the regression by Karickhoff et al. (1979) (chapter 2, Figure S3). Less sorption by the cap than predicted by these studies, indicates the possibility of some inaccessible OC in the cap material. When peat or AC are mixed into the sand, the combined sorption capacity can be determined by equation 4 (chapter 1). Figure 5.5 shows the isotherms of the sand, peat, AC, and sand amended with peat and AC. It can be seen on the scale shown that combining peat and sand isotherms makes a more noticeable difference, than does peat alone, but that combining GAC and sand isotherms appears the same as the isotherm for GAC alone. These results indicate that for 0.2% TOC amendment, sorption on sand is still significant, whereas for 0.2% AC amendment, sorption on sand appears negligible (note the log scale).

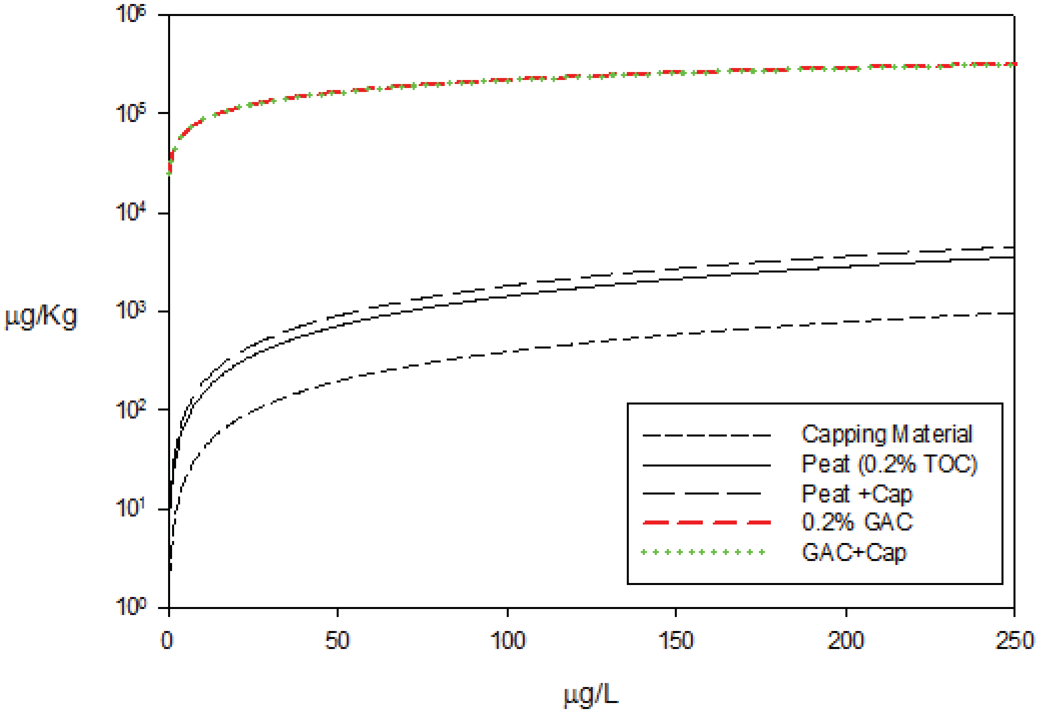


Figure 5.5 Phenanthrene isotherms for materials used in the column experiments separately and as mixtures.

5.3.3 Kinetics

Batch sorption kinetics data of the capping material after 2 and 22 days of contact was compared to interpretations of batch kinetic data from Ran et al. (2005) for PHN sorption to Borden sand (Figure 5.6). Interpretations were back calculated by trial and error given the Freundlich parameters from Ran et al. and the known mass of PAH in the batch experiment. Borden sand is a low TOC aquifer material that should behave similarly to the capping material used in the present study. In order to make these interpretations, a total mass of PHN had to be selected in the system initially in the water phase. The total mass of PHN and CHR in the batch experiments with the capping material was 6 and 0.1 μg respectively. The data presented in Figure 5.6 show that a fraction of instantaneous sorption of 0.4 seems reasonable. A possible fast fraction is sorbing within the first 2 days followed by a slow rate of sorption extending out past 25 days. The 1st order rate (α) for the non-instantaneous fraction was calculated to be 1.6 days^{-1} based on the Ran et al. (2005) interpretations for 6 μg total PHN. Previous researchers have found that kinetic information obtained from batch experiments for lindane and nitrobenzene on aquifer materials could be used to predict column systems (Weber and Miller, 1988, part 1; Miller and Weber, 1988, part 2). Miller and Weber applied this to systems with linear isotherms and recognized that the column flow rate could alter the rate coefficients. This kinetics data can later be compared to the modeling discussion in section 5.3.9.

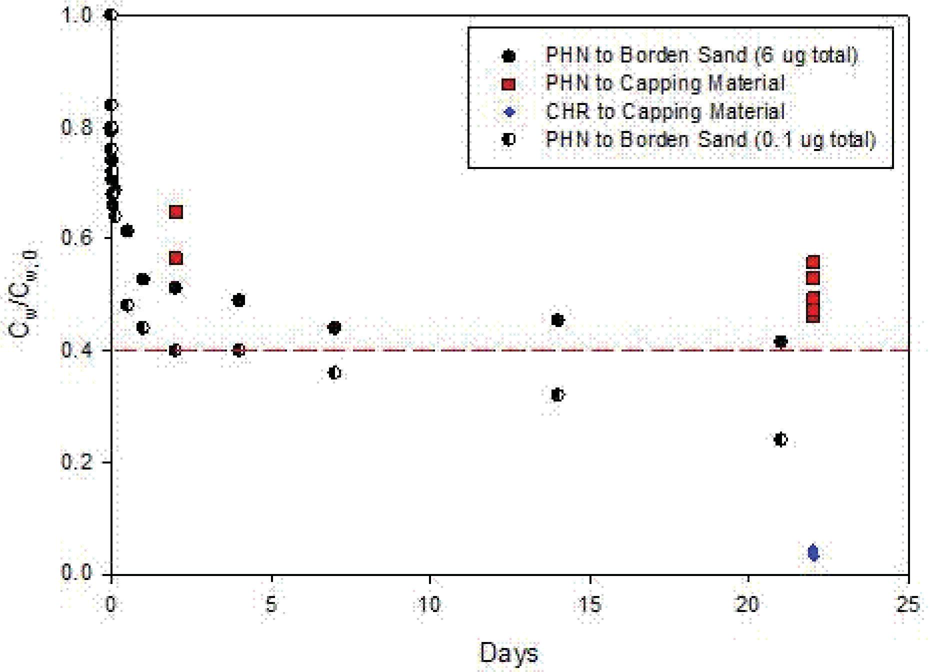


Figure 5.6 Batch sorption kinetics of capping material compared to estimates from Borden sand data (Ran et al. 2005). Y-axis is the concentration in the water phase normalized to the initial water concentration.

5.3.4 Colloids and dissolved organic matter

In the presence of 5 mg/L colloids in a creosote contaminated aquifer, PAHs with $K_{ow} > 10^{5.7}$ partitioned to colloids significantly while less hydrophobic PAHs did not (Villholth, 1999). This cut off occurs around the molecular weight (MW) of pyrene. Therefore, PAHs with a MW greater than pyrene may be most affected by colloid transport.

Rapid breakthrough was expected in the sand cap based on the low organic carbon content. However, it should be recognized that modeled breakthrough of this system was slower than the experimental results of the non-amended column (pyrene and chrysene in non-amended). Colloids can interfere with the SPME measurement (Hawthorne et al. 2005, Hong et al. 2003). Supernatant water from the capping material (prior to loading in the columns) contained 9 mg/L total organic carbon (suspended + dissolved) and after filtering (with a 0.45 micron filter) contained 8.6 mg/L organic carbon (by liquid TOC analysis).

Slight turbidity was observed (3.3 NTUs) initially in the peat column effluent, but reduced to 1.4 NTUs within a week. This 1.4 NTUs corresponded to approximately 16 mg/L total suspended organic carbon and dissolved organic carbon (DOC) (after filtering through a 0.45 micron filter). NTUs measures light scattering particles in water. Therefore, there is no good correlation between NTUs and DOM as they are measuring two different things. Large organic molecules are sometimes filtered out from the DOM measurements (M. Robin Collins, Ph.D. P.E. personal communication). Examining DOM before and after filtration show that PAH carrying colloids, and DOM larger than 0.45 microns, were not present in the peat amended column. Rather, the DOC in the peat amended column effluent is probably due to humic and fulvic acid, which is known to be derived from peat (Sabbah et al, 2004, Johnson et al, 2001). SPME, using d-PAH internal standards, measures total dissolved PAHs (freely dissolved and DOC associated) (Hawthorne et al. 2005, Pöerschmann et al. 1997, Pöerschmann et al. 1998). For many of the PAHs measured, the DOC associated fraction is small relative to the freely dissolved concentration, especially for compounds of MW lower than PYR. For the PAHs: NPH, ACE, PHN, PYR, and CHR, the percent associated with 16 mg/L DOC rather than being freely dissolved, is 4, 11, 30, 56 and 72% respectively (based on K_{DOC} values derived from the relation presented by Sabbah et al. 2004).

5.3.5 AC particle migration

If particles are mobilized, they could carry sorbed PAHs off site. This section explores the possibility of particle mobilization in a cap due to groundwater discharge. During the startup of the AC amended columns, there was a dark color observed in the overlying water initially due to suspended fine-sized AC particles. This dark color was no longer present after about twelve hours of flow and there was no visual observation of AC particle mobilization after this point. Table 5.1 shows the results of AC particle analysis, where fraction of AC (f_{ac}) was determined assuming all carbon was from AC. The "AC mixture" was a 2% AC by wt mixed in sand. The "2% AC left over" was excess material that had been used to construct the AC column experiment on that day. The column sections, in inches from cap surface, as well as a composite sample where all sieve sizes were analyzed after the experiment was run, are shown in Table 5.1 Inaccuracy in these measurements may have occurred during the sectioning of the column, and small amounts of AC may have been lost during dry sieving. During column sectioning, the column was laid on its side in dry ice. Before the column froze, pore water drains from the top of the column and some AC particles may have been lost with the draining water. Thus, the AC measurement in the cap confirmed the presence of some AC at the end of the experiment, but is not conclusive of any fraction lost during column operation.

Table 5.1 Fraction of AC remaining in the 2% AC amended cap material.

Sample	**Measured**	f_{ac}
2% AC mixture	<245µm	0.021
2% AC left over	“”	0.021
3-6” from surface	“”	0.006
6-9” “”	“”	0.005
9-12” “”	“”	0.003
12-15” “”	“”	0.004
18-21” “”	“”	0.005
21-24” “”	“”	0.011
2% AC mixture	All sizes	0.019
3-6”, 9-12”, 12-15”	All sizes	0.005

Table 5.2 TOC in the Cap

Size Fraction	F_{OC}
>2.36 mm	**-**
1.7-2.36mm	**-**
1.18-1.7mm	**0.023**
0.425-1.18mm	**0.005**
<0.425mm	**0.001**

Most of the TOC of the non-amended column cap layer was in the medium size fraction, therefore the mobilization of native organic carbon during column sectioning caused by particle migration was not a concern (Table 5.2) during the sectioning of this column. If much of the TOC (and thus PAHs) resided in the fine fraction of particles (<0.425 mm) there may have been reason to suspect that solid PAH concentrations were lost from the sectioning and extraction analysis of the non-amended cap. Table 5.2 can be compared to the biologically active column (chapter 3, Table 3.S2).

AC migration from the columns during the experiment was unlikely, but has not been disproven. Migration of OC during column sectioning was unlikely because most of the OC resided in mid-sized particles. However, migration of AC particles during column sectioning was likely. Some further losses may have occurred during sample handling/sieving.

In a field scenario, any loss of AC amendment could be minimized by:

1. Using a larger sized AC particle
2. Blending a fine grained sand into the coarse grained cap material.

5.3.6 Pyrene migration at all observation ports

The spatial migration of pyrene was examined closely for a number of bed volumes (Figures 5.7-5.9). Here, three figures are presented: the non-amended column, a 0.2% TOC (peat) amended column, and a 2% AC amended column. Detection limits are also reported on these graphs. Detection limits have been determined as theoretically described by Miller and Miller (2000). Seven replicates of a low concentration standard were injected using the SPME method. The standard deviation of these seven replicates were multiplied by 2.998 to obtain a method detection limit (MDL). Below this level it cannot be stated (statistically, 99% confidence) whether or not the PAH is present. The standard deviation was multiplied by 10 to obtain a limit of quantitation (LOQ). Between the MDL and the LOQ it can be stated (statistically) that the PAH is present, but the quantity is still unknown. Above the LOQ, the concentration measured can be stated with statistical confidence. Placing the data in the context of the detection limits puts constraints on attempts to model low concentration data. In the non-amended column, the initial profile of pyrene shows the presence of this PAH initially from all measured ports in the column. Rapid migration of pyrene was observed after eight pore volumes (here labeled bed volumes (BV)), to concentrations well over quantifiable levels (Figure 5.7).

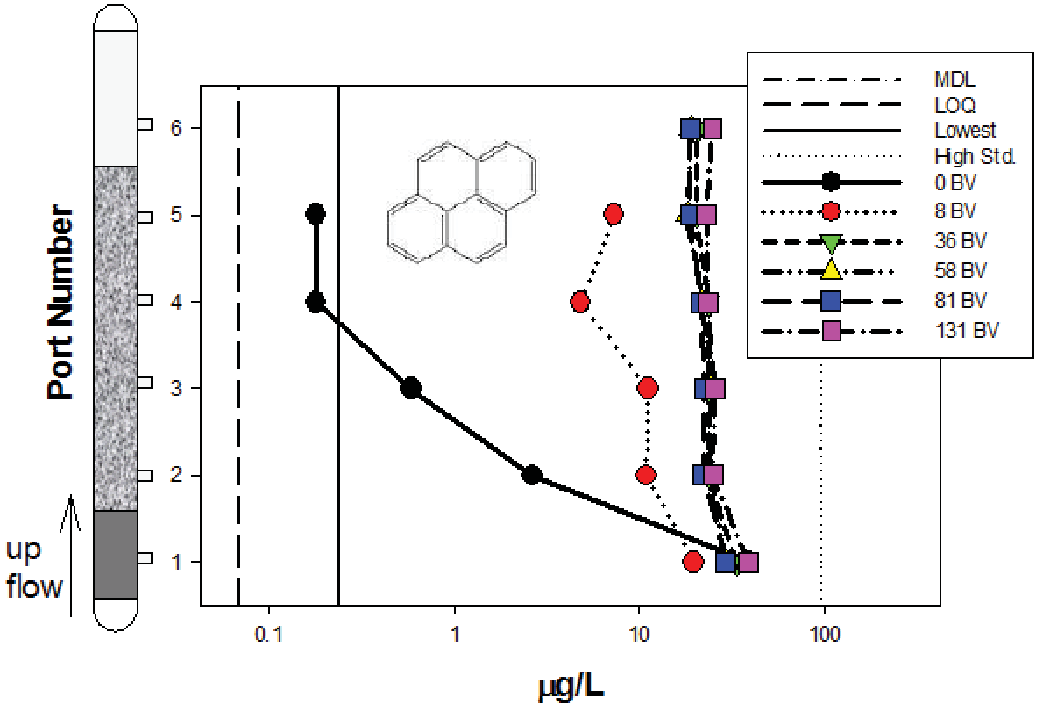


Figure 5.7 Pyrene breakthrough for many bed volumes (BV). Initial pore water concentrations in ports 4 and 5 were below the calibration range.

Adding a small amount of peat to the column experiment had a great impact on the retardation of pyrene (Figure 5.8). The hydrodynamic properties of the column did not appear to change much with the addition of peat (Figure S2 in chapter 2), but the additional organic carbon had a great impact on PAH migration. Initially, the pyrene profile is much like the column with no amendment, with pyrene concentrations in the upper portions of the cap that were lower than the LOQ. As the peat amended column was run for a similar duration as the non-amended cap, the migration of pyrene slowly increased at a rate that was much slower than the non-amended cap. This column may be showing behavior in some field caps that contain more organic carbon than the Eagle Harbor cap material.

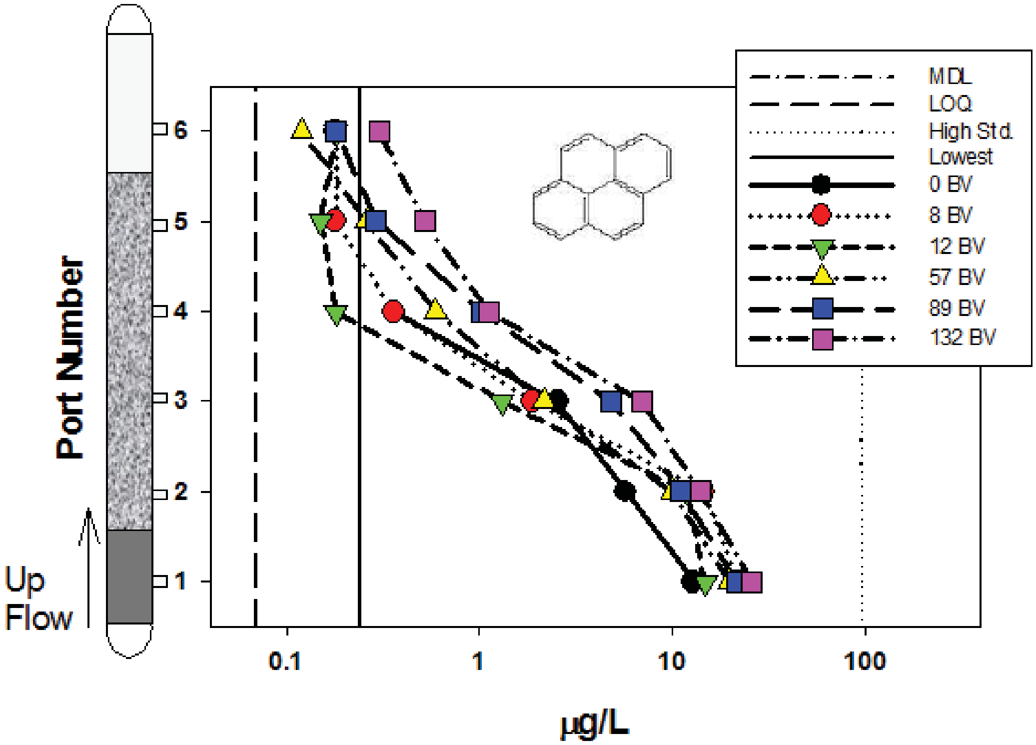


Figure 5.8 Delayed migration of pyrene in a 0.2% TOC amended cap by peat addition.

In a cap amended with 2% AC there is no contaminant breakthrough (Figure 5.9). The concentration of pyrene above port 3 remained below the method detection limit for much of the experiment. At ports 2 and 3 in the capping layer some interpretations can be made about the data, but the concentrations are still near the limit of quantitation. Therefore, any interpretations of PAH profiles, in the AC amended column is difficult, beyond the fact that concentrations are very low. For example, observation of the data without regard for the detection limits might lead to over speculation about kinetic limitations to AC sorption.

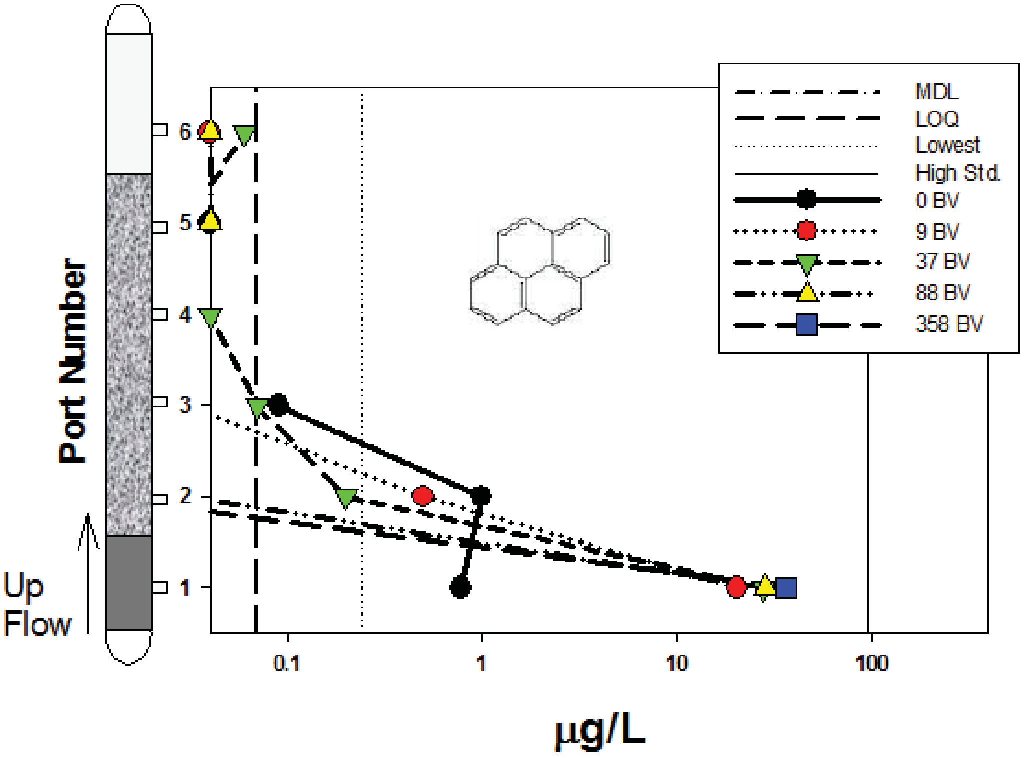


Figure 5.9 Spatial concentration profile of pyrene for a number of bed volumes in a 2% AC amended cap.

5.3.7 PAH Dissolution from Sediment

The creosote content of the sieved sediment was measured to be 0.002 g/g by the hexane/acetone extractables method. Some low MW PAHs may have been lost during this analysis, so the true creosote content is expected to be higher. The TOC of the sediment was 0.004 g/g and after ultrasonic extraction it was found to be 0.0009 g/g. If we assume that all of this extracted material was PAHs from the creosote, this would indicate a creosote content of 0.003 g/g. It is safe to assume that the creosote content of the initially prepared sieved sediment was between 0.002 and 0.003 g/g.

The higher value of 0.003 g/g may be more accurate due to volatile losses during the hexane/acetone extractables method. The 16 EPA priority pollutant PAHs were measured in this solid sediment material (Table S2). This material was also used in batch equilibrium experiments where the water phase was measured using SPME. The PAH mole fractions can be determined using the solid concentrations, the total creosote content (0.003), the molecular weights, and the assumed molecular wt. of the uncharacterized fraction of 300 g/mole (Peters et. al. 1999). The water concentrations can be calculated knowing the mole fraction and subcooled liquid solubilities of each compound. Table 5.3 compares the measured and predicted water concentrations for several PAHs.

Table 5.3 Concentrations from aqueous phase of batch equilibrium, and predicted from solid extractions (assuming creosote content of 0.003g/g)

PAH	µg/L measured (Aqueous conc. on 12-06-06)	µg/L predicted based on Raoult's law
Acenaphthylene	40.5±6	72±11
Phenanthrene	292±35	364±38
Pyrene	30±2	64±12
Chrysene	1.4±0.2	2.1±0.4

Mean±Standard Deviation

The water concentrations of each PAH from aqueous batch equilibrium measurements are less than estimates from the solid phase measurements. Non-amended, peat amended, and 2% GAC amended columns all used this sediment. The pore water concentrations of the sediment phase from these columns were all very similar, though less than the aqueous phase concentrations from the batch equilibrium experiments. This suggests potential mass transfer limitation to the water phase.

A comparison of three PAHs (ACE, PHN, and CHR) reveal that there are dissolution dynamics in the sediments (Figure 5.10). From observations of the aqueous batch equilibrium experiments, low and middle MW PAHs are depleting in the columns while high MWs (CHR) are increasing. These trends can also be seen in the pore water data observed directly from the column experiments. After four months in the column flow through system, ACE was no longer the most dominant PAH in the water phase. After 7 months, CHR concentrations are higher than ACE in the water phase.

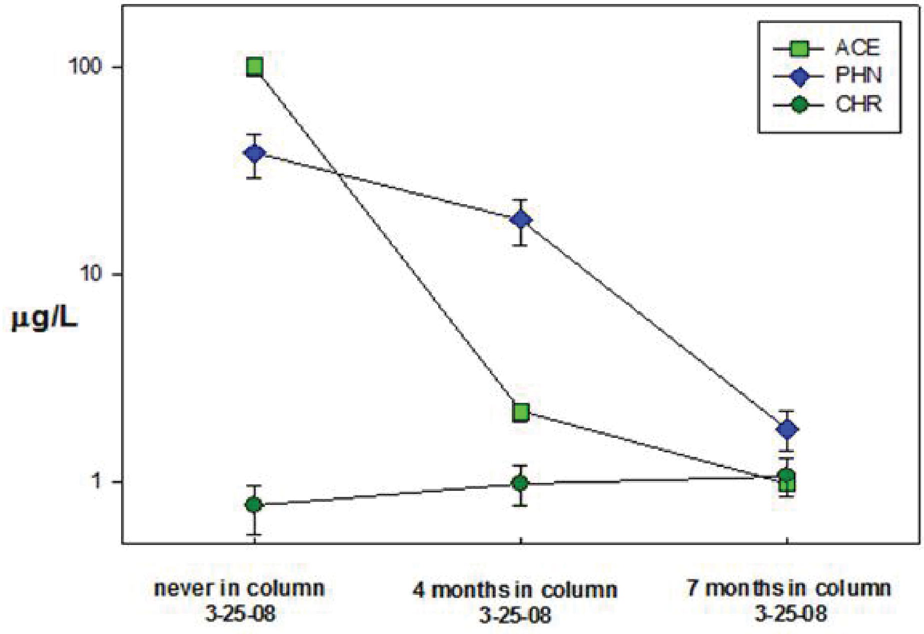


Figure 5.10 ACE, PHN, and CHR water concentrations from batch experiments using sieved material.

Analyzing the solid material in the sediment phase for PAHs (in µg/g) shows depletion after running the material in a column (Figure 3.3 chapter 3). In the sediment, with the exception of NPH, compounds of MW less than fluoranthene show an increasing trend of depletion relative to decreasing MW. For compounds of MW greater than fluoranthene, the depletion is less in magnitude and more consistent. Depletions are least for the highest MW compounds, and their mole fractions are increasing. The mass depletion of compounds with MW greater than benzo(g,h,i)perylene may not be changing at all, but their mole fractions are increasing due to the depletion of the low MW compounds.

5.3.8 Raoult's law dissolution model for sediment

Assuming equilibrium partitioning using Raoult's law, and initial conditions based on best available initial measurements (creosote content, solid and pore water PAH measurements, uncharacterized fraction of 300 g/mole Peters et al. 1999), very little depletion in aqueous concentrations were found to occur in the column simulations over a short duration of 140 bed volumes in the cap (80 days) (Figure 5.11). This temporal equilibrium model (with no mass transfer limitation) was constructed for an approximate sediment void volume of 0.05 liters with times steps of 0.01 bed volumes (Darcy velocity = 30 cm/day). The results show concentrations of most PAHs in the water phase remaining level on a log scale. Only NPH, ACY, ACE, and FLR appear to be decreasing over an 80 day period.

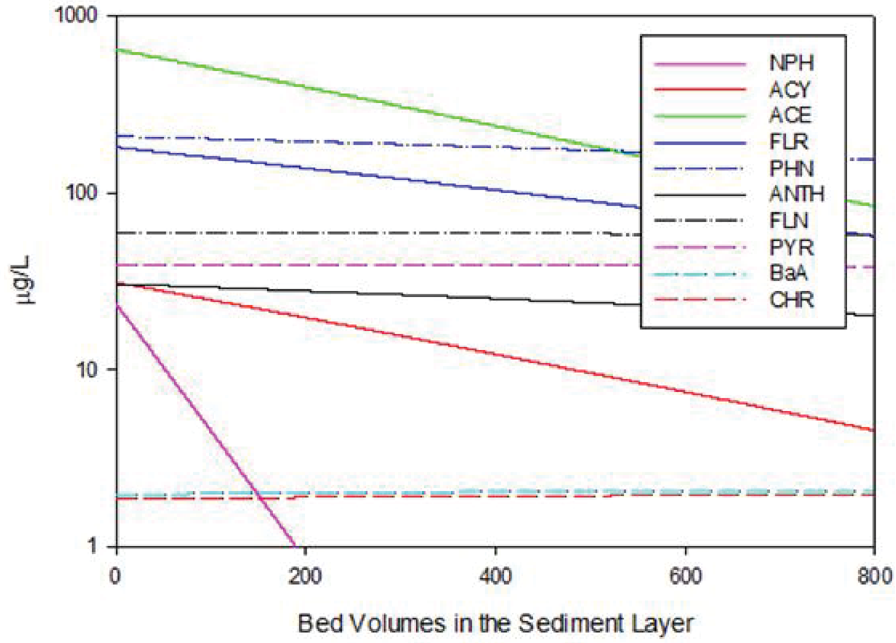


Figure 5.11 Equilibrium model of temporal PAH concentrations in the sediment using Raoult's law with no mass transfer limitations (bed volumes in the sediment layer, 875.6 BV ~ 80 days).

The data were compared to a Raoult's law model with initial conditions based on creosote content and solid PAH measurements. As in Figure 5.11, the model assumed equilibrium partitioning and mass depletion, but with initial conditions determined from initial solid concentration only (creosote content of 0.003g/g). It appears that the concentrations of PHN, PYR and CHR reach the model predictions after the experimental period of 140 BV of flow through the cap layer (Figure 5.12). The experiments were killed with 100 mg/L sodium azide in the influent solution, so biodegradation is not suspected.

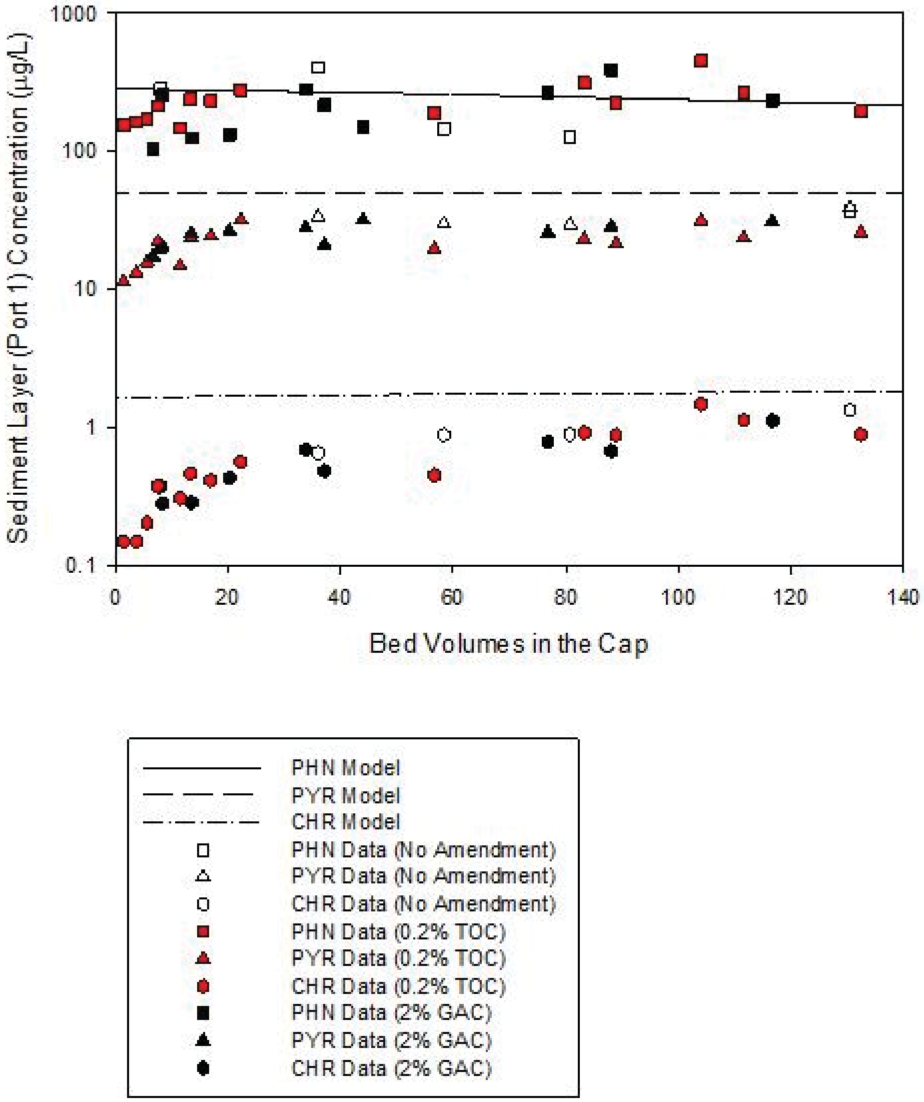


Figure 5.12 Port 1 (sediment layer) data trends for 3 PAHs compared to Raoult's law equilibrium model with PAH mass depletion.

5.3.9 Additional transport modeling of GAC amended cap

The modeling of the GAC cap, as presented in chapter 2, is an extension of the method used for the non-amended and peat amended cap. The methods use an empirical relation from Brusseau and Rao, 1989, who never discussed scenarios with partitioning coefficients as high as PAHs to AC. Thus, the value of alpha (α) obtained from these interpretations may not represent the true kinetics of sorption for the AC amended cap system. This interpretation was done (for a high concentration) as an initial presentation of the models for comparison to the non-amended and peat amended cases.

In the AC amended cap presented here, the AC is dispersed in a mixture of sandy gravel and PAH/AC contact will be less frequent than a column packed with 100% AC. On the other hand, PAH/AC collision is highly likely at some point along a 65 cm cap, and a fraction of instantaneous sorption that best fits the column data from the effluent could be high.

In regards to AC diffusion rate of pollutant uptake, Hale and Werner (2010) provide a relation for estimating a concentration dependent "rate_{AC}" which was used for this discussion to estimate α using the relation, $\alpha = 22.7\, D_a/a^2$ from Wu and Gschwend (1988) (Schüth and Grathwohl, 1994). "D_a" is the apparent diffusion coefficient (L^2/T) (Schüth and Grathwohl, 1994) of AC (Werner et al. 2006). The term "D_a/a^2" is a diffusion rate constant and has been determined by fitting the model to data using aquifer materials (setting $f_e = 0.4$) by Schüth and Grathwohl. A batch system can be used to estimate α without concern for the "shrinking gradient effect" if the linearity index is more than 0.8 (Braida et al. 2001). In the case of AC, the linearity index is less than 0.8. Rügner et al. (1999) provide a relation for estimating D_a, given the Freundlich parameters, bulk density, porosity, aqueous diffusivity coefficient and a "tortuosity factor". A calculation of "tortuosity factor" for AC amended caps could not be interpreted from Rügner et al. The diffusion rate constant "D_a/a^2" was assumed to equal $D_{AC}/R^2_{AC} = \text{rate}_{AC}$, from Hale and Werner. Schüth and Grathwohl recognized the dependence of α on flow velocity. The flow velocity dependence of both f_e and α have been investigated for simazine sorption on sandy soil by Kookana et al. (1993) who emphasize how batch systems differ from flow through systems. Hale and Werner were not examining flow through systems, so deriving kinetics from their research invokes pore diffusion in the absence of advection. In this research, the fraction of instantaneous sorption (f_e) was first presented as 0.5 to be a comparison to methods used for non-amended and peat amended systems, and then left as a fitting parameter using the kinetics from Hale and Werner (using pyrene data from all ports as a tracer).

The "rate_{AC}" involves only the diffusion kinetic rate of uptake into the AC particles. These column experiments may have other rate limiting mechanisms occurring, such as: the frequency of PAH/GAC particle collision; solid media film diffusion; AC particles trapped in less mobile zones; or desorption kinetics from creosote blobs and sediment particles, which mixed into the lower portions of the cap during column construction. The α determined from equation 5 (chapter 2) is derived from multiple types of systems gathered from the literature (described in Brusseau and Rao, *Chemosphere*, 1989) and is therefore a lumped transport kinetic parameter. The α determined from Hale and Werner's "rate_{AC}" isolates the pore diffusion aspects of GAC (without advection), but the fitted f_e is a lumped kinetic parameter, which then captures the other processes described. Mathematically, the non-ideal equation for solute transport in porous media is the same for chemical and physical nonequilibrium. In the physical system, sorption reaction kinetics and pore diffusion kinetics blend as well.

Obtaining a $rate_{AC}$ from Hale and Werner and converting this to α, gives larger values than deriving them from Brusseau and Rao, 1989 (0.035 vs. 0.0025 days^{-1} for pyrene). Using an f_e of 0.5, the concentrations decrease to a greater extent over the 80 day (140 bed volume) time period when using the larger value. Apparently, diffusion into the AC particles is not the bottleneck to sorption kinetics in the system. Still, if we observe PAH concentrations in the cap close to the sediment (port 2) there is depletion of PAH pore water concentration over time. Using the α derived from the $rate_{AC}$ from Hale and Werner is a better match of the data observed at port 2 than the rates from Brusseau and Rao. Using pyrene as a tracer, f_e was determined (became a fitting parameter) given the α for pyrene determined from Hale and Werner's $rate_{AC}$ relation (Figure S5). A value of 0.4 for the fraction of instantaneous sorption (f_e) fits the data, seems reasonable from batch kinetic studies (section 5.3.3), and is close to the value of 0.5 used by Sabbah et al. 2004. It should also be noted that some of the data used to derive this value were at the limit of quantitation.

Experimental isotherms were obtained for the peat and capping material used in this study. Comparisons to literature values reveal that the peat behaves similarly to an amorphous organic carbon, and that the capping material behaves like some low organic carbon aquifer materials. Literature values for activated carbon sorption isotherms were used to model column data. Data on the kinetics of the sorption of PAHs to the Eagle Harbor cap reveal that a fraction of instantaneous sorption of approximately 0.4-0.5 seems reasonable. The migration of colloids and GAC particles was not suspected to be the cause of PAH transport in these column experiments. DOM may enhance the transport of some high MW PAHs, but this is captured by the type of SPME method used. Raoult's law is able to describe many of the dissolution mechanisms occurring in the sediment layer (and subsequently the trends in water concentrations). Nonequilibrium conditions appear to be occurring in the AC amended caps, however, measurements are very low in concentration. Therefore, little attempt was made to over interpret this data. AC pore diffusion does not appear to be the bottleneck in the sorption process for pyrene and PAHs of lower MW.

5.4 References

Ogata, A.; Banks, R. B. A Solution of the Differential Equation of Longitudinal Dispersion in Porous Media. In Interior, U. S. D. O. T., Ed. United States Government Printing Office: **1961**.

Go, J.; Lampert, D. J.; Stegemann, J. A.; Reible, D. D. Predicting contaminant fate and transport in sediment caps: Mathematical modelling approaches. *Applied Geochemistry*. **2009**, 24, 1347-1353.

Allen-King, R. M.; Grathwohl, P.; Ball, W. P. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. *Advances in Water Resources*. **2002**, 25, 985-1016.
Karickhoff, S.W.; Brown, D.S.; Scott, T.A. Sorption of hydrophobic pollutants on natural sediments. *Water Research*. **1979**, 13, 241-248.

Ran, Y.; Xing, B.; Rao, P. S. C.; Sheng, G.; Fu, J. Sorption Kinetics of Organic Contaminants by Sandy Aquifer and Its Kerogen Isolate. *Environ. Sci. Technol.* **2005**, 39, 1649-1657.

Weber Jr., W. J.; Miller, C. T. Modeling the Sorption of Hydrophobic Contaminants by Aquifer Materials - I. *Wat. Res.* **1988**, 22, 457-464.

Miller, C. T.; Walter J. Weber, J. Modeling the Sorption of Hydrophobic Contaminants by Aquifer Materials - II. *Wat. Res.* **1988**, 22, 465-474.

Villholth, K. G. Colloid Characterization and Colloid Phase Partitioning of Polycyclic Aromatic Hydrocarbons in Two Creosote-Contaminated Aquifers in Denmark. *Environ. Sci. Technol.* **1999**, 33, 691-699.

Hawthorne, S.B.; Grabanski, C.B.; Miller, D.J.; Kreitinger, J.P. Solid-Phase Microextraction Measurement of Parent and Alkyl Polycyclic Aromatic Hydrocarbons in Milliliter Sediment Pore Water Samples and Determination of K_{DOC} Values. *Environ. Sci. Technol*. **2005**, 39, 2795-2803.

Hong, L.; Ghosh, U.; Mahajan, T.; Zare, R.N.; Luthy, R.G. PAH Sorption Mechanism and Partitioning Behavior in Lampblack-Impacted Soils from Former Oil-Gas Plant Sites. *Environ. Sci. Technol*. **2003**, 37, 3625-3634.

Sabbah, I.; Rebhun, M.; Gerstl, Z. An independent prediction of the effect of dissolved organic matter on the transport of polycyclic aromatic hydrocarbons. *J. of Cont. Hydrol*. **2004**, 75, 55-70.

Johnson, M.D.; Huang, W.; Weber, W. J., Jr. A Distributed Reactivity Model for Sorption by Soils and Sediments. 13. Simulated Diagenesis of Natural Sediment Organic Matter and Its Impact on Sorption/Desorption Equilibria. *Environ. Sci. Technol*. **2001**. 35, 1680-1687.

Pörschmann, J.; Zhang, Z.; Kopinke, F.-D.; Pawliszyn, J. Solid Phase Microextraction for Determining the Distribution of Chemicals in Aqueous Matrices. *Analytical Chemistry* **1997**, 69, 597-600.

Pörschmann, J.; Kopinke, F.-D.; Pawliszyn, J. Solid-phase microextraction for determining the binding state of organic pollutants in contaminated water rich in humic organic matter. *Journal of Chromatography* . **1998**, 816, 159-167.

Miller, J. N.; Miller, J. C. Statistics and Chemometrics for Analytical Chemistry. 4th ed.; Prentice Hall: Essex, England, **2000**; p 120-123.

Peters, C. A.; Knightes, C. D.; Brown, D. G., Long-Term Compositional Dynamics of PAH-Containing NAPLs and Implications for Risk Assessment. *Environ. Sci. Technol.* **1999**, 33, 4499-4507.

Brusseau, M.L.; Rao, P.S.C. The Influence of Sorbate-Organic Matter Interactions on Sorption Nonequilibrium. *Chemosphere*. **1989**, 18, 1691-1706.

Hale, S.E.; Werner, D. Modeling the Mass Transfer of Hydrophobic Organic Pollutants in Briefly and Continuously Mixed Sediment after Amendment with Activated Carbon. *Environ. Sci. Technol*. **2010,** 44, 3381-3387.

Wu, S.; Gschwend, P.M. Numerical Modeling of Sorption Kinetics of Organic Compounds to Soil and Sediment Particles. *Water Resources Research*. **1988**, 24, 1373-1383.

Schüth, Ch.; Grathwohl, P. Nonequilibrium transport of PAHs: A comparison of column and batch experiments. *Transport and Reactive Processes in Aquifers*, ed. Dracos and Stauffer, Rotterdam: Balkema, **1994**.

Werner, D.; Ghosh, U.; Luthy, R. G. Modeling Polychlorinated Biphenyl Mass Transfer after Amendment of Contaminated Sediment with Activated Carbon. *Environ. Sci. Technol.* **2006**, 40, 4211-4218.

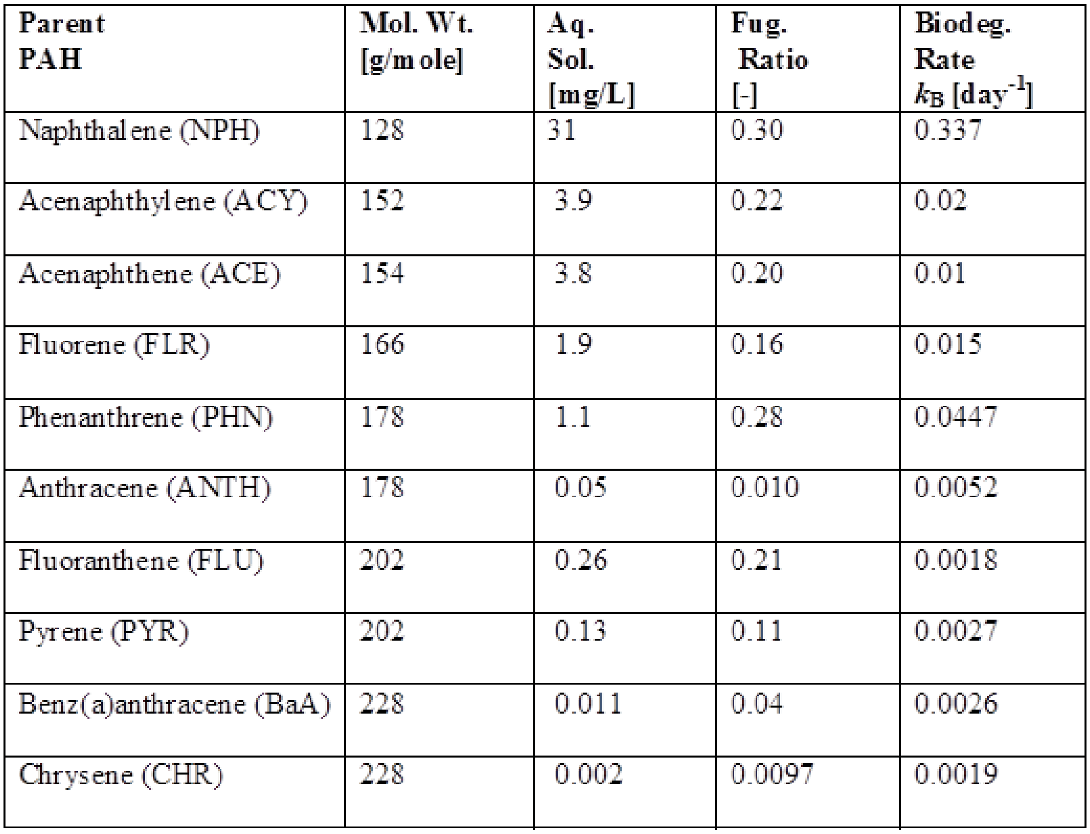
Braida, W. J.; White, J. C.; Ferrandino, F. J.; Pignatello, J. J. Effect of Solute Concentration on Sorption of Polyaromatic Hydrocarbons in Soil: Uptake Rates. *Environ. Sci. Technol.* **2001**, 35, 2765-2772.

Rügner, H.; Kleineidam, S.; Grathwohl, P. Long Term Sorption Kinetics of Phenanthrene in Aquifer Materials. *Environ. Sci. Technol.* **1999**, 33, 1645-1651.

Kookana, R. S.; Schuller, R. D.; Aylmore, L. A. G. Simulation of simazine transport through soil columns using time-dependent sorption data measured under flow conditions. *J. Cont. Hydrology* **1993**, 14, 93-115.

5.5 Supplemental Information

Table 5.S1 Properties of Parent PAHs (Peters et al. 1999)



Parent PAH	Mol. Wt. [g/mole]	Aq. Sol. [mg/L]	Fug. Ratio [-]	Biodeg. Rate k_B [day^{-1}]
Naphthalene (NPH)	128	31	0.30	0.337
Acenaphthylene (ACY)	152	3.9	0.22	0.02
Acenaphthene (ACE)	154	3.8	0.20	0.01
Fluorene (FLR)	166	1.9	0.16	0.015
Phenanthrene (PHN)	178	1.1	0.28	0.0447
Anthracene (ANTH)	178	0.05	0.010	0.0052
Fluoranthene (FLU)	202	0.26	0.21	0.0018
Pyrene (PYR)	202	0.13	0.11	0.0027
Benz(a)anthracene (BaA)	228	0.011	0.04	0.0026
Chrysene (CHR)	228	0.002	0.0097	0.0019

Table 5.S2 Submarine groundwater discharge rates

Location	**Reference**	**Method**	**Mid SGD**	**Max SGD**
Chesapeake Bay, Virginia	Harvey, 1990*	Mass Balance	0.8 cm/day	1 cm/day
Onslow Bay, North Carolina	McCoy et al., 2007^{+}	Radon	2.2 cm/day	4.4 cm/day
Biscayne Bay, Florida	Top et al., 2001^{+}	^{3}H, ^{4}He	8.7 cm/day	10.5 cm/day
Florida Keys	Simmons, 1992*	Seepage Meters	408 cm/day	504 cm/day
Northeast Gulf of Mexico	Lambert et al., 2003^{+}	Radon	28 cm/day	50 cm/day
Mississippi Delta	Krest et al., 1999^{+}	$^{226, 228}$Ra	1 cm/day	1 cm/day
Northwest Beaches, U.S.A.	Isaacs et al., 1949*	Potassium permanginate fluorescein dye	720 cm/day	720 cm/day
Eagle Harbor, Washington	Courtesy Battelle and Environ	Seepage Meters	0.813 cm/day	3.58 cm/day
Column Experiments, UMBC	Gidley et al., 2012	Direct Collection in Graduated Cylinder	30 cm/day	35 cm/day

* from Liu et al. 2001; $^{+}$ from McCoy et al. 2009

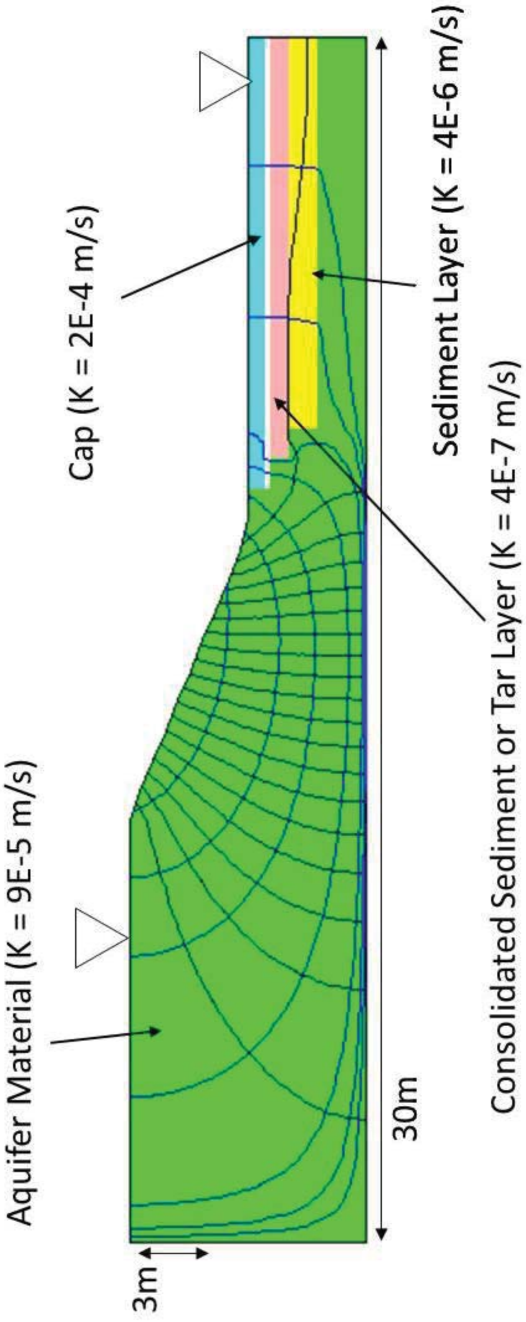


Figure 5.S1. Possible groundwater flow paths based on estimates of hydraulic conductivity (not to scale). K values provided by Battelle Memorial Institute for Eagle Harbor. Graphics by Paul Hsieh's interactive groundwater model.

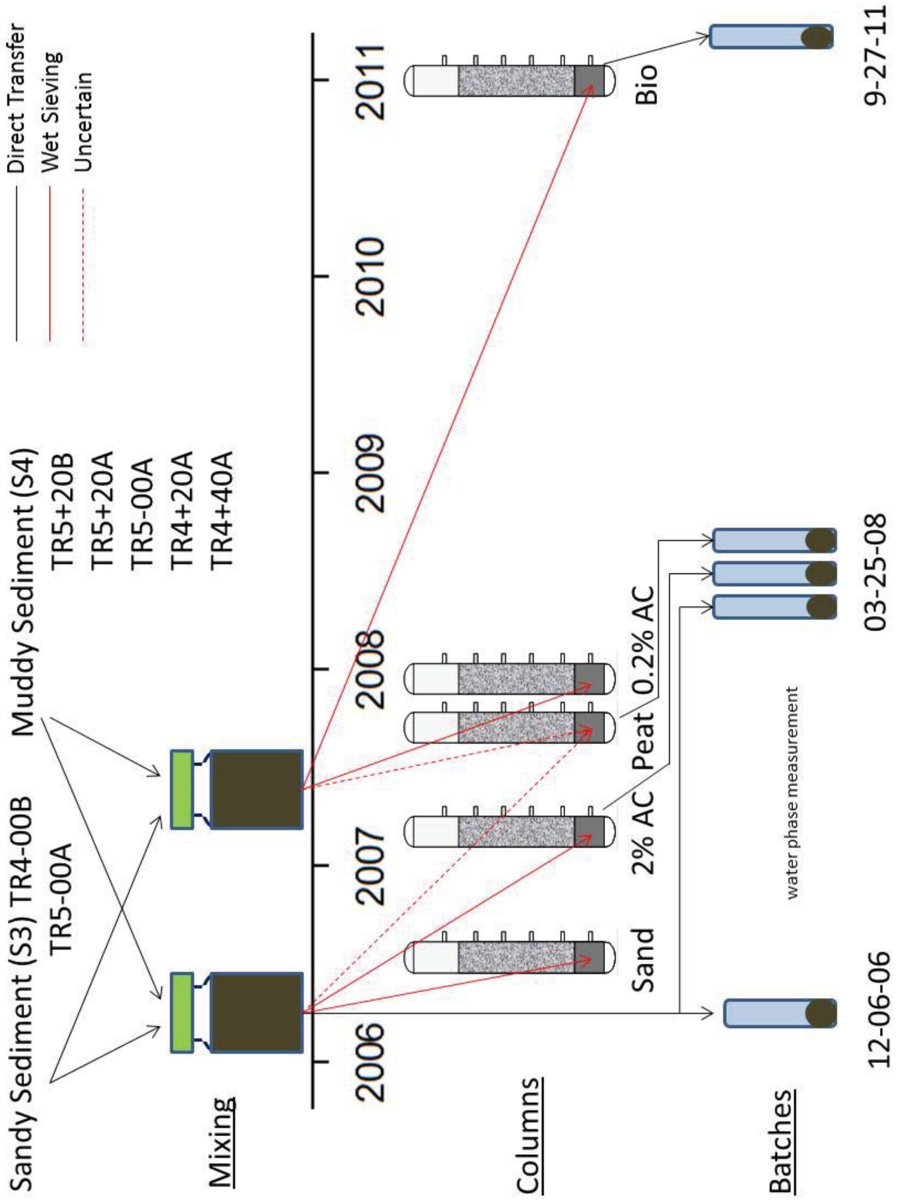


Figure 5.S2. Time line for material mixing, column construction, and batch equilibrium