

ABSTRACT

MUSELLA, JENNIFER SUZANNE. Impact of Plant Organic Matter on PAH Desorption from Petrogenic-Polluted Sediments. (Under the direction of Elizabeth Guthrie Nichols).

Polycyclic aromatic hydrocarbon (PAH) bioavailability does not correlate directly with total PAH sediment concentration because PAHs strongly sorb to organic matter. Many current toxicological models assume that PAHs present in the dissolved phase reflect actual PAH bioavailability to organisms. Plants can release significant amounts of plant organic matter (POM) to soils and sediments; however, the mechanisms by which POM may affect PAH bioavailability in sediments are unclear. The rhizosphere may increase PAH bioavailability by destabilizing soil organic matter (SOM) and enhancing PAH desorption, or the rhizosphere may alter SOM composition and provide new carbon matrices to sorb/sequester PAHs and reduce PAH desorption. Desorption studies were conducted to determine if vegetation decreased or increased the rate and mass amounts of desorbable PAHs. Replicate desorption studies were conducted using vegetated and non-vegetated bulk sediment and HF/HCl humin fractions; sediments were collected from a coastal refinery distillate waste pit (RP) and refinery-impacted sediments from a freshwater canal (IH). Desorption isotherms for four PAHs were determined by two methods, aqueous and TenaxTM bead extractions. PAHs were quantified by gas chromatography/mass spectrometry selected ion monitoring (GC/MS SIM). Results showed differences in PAH desorption based on the amount of time vegetation had been present in sediments. Vegetated sediments with 30+ years of vegetative growth (RP) desorbed more PAHs than non-vegetated sediments by TenaxTM extraction in both bulk and humin sediment fractions. Recently vegetated, IH freshwater sediments desorbed fewer PAHs than non-vegetated IH sediments by aqueous and TenaxTM extractions in

bulk and humin sediment fractions. These findings suggest that initial exposure of sediment to vegetation slows PAH desorption and that extensive exposure to vegetation enhances PAH desorption from both labile and refractory SOM.

**IMPACT OF PLANT ORGANIC MATTER ON PAH DESORPTION FROM
PETROGENIC-POLLUTED SEDIMENTS**

by

JENNIFER SUZANNE MUSELLA

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APPROVED BY:

Dr. Elizabeth G. Nichols, Committee Chair

Dr. Christopher S. Hofelt

Dr. Gregory W. Cope

BIOGRAPHY

Jennifer Musella was born in southern California in 1977. After a few years of soaking up the rays, she and her family moved to the east coast. As a US marine, her father's military career enabled her to travel extensively throughout her childhood. She spent several years in North Carolina, Virginia, and later moved to Western Europe where she lived for three years. She attended middle and began high school in Belgium where among other things she participated in soccer, dance team, and the environmental club. Upon moving back stateside she completed high school in northern Virginia and promptly left to attend Virginia Tech in Blacksburg, VA. She pursued a degree in environmental science with a concentration in plant resources while also becoming an avid outdoor enthusiast; hiking and camping every chance she got. Her bachelor's degree elevated her from a part-time tree hugger to an environmental crusader, ready to conquer the world. However, once reality set in she decided to hone her horticultural skills by working in a greenhouse. Upon reaching her potential there, she began working for a consulting firm in the hopes of getting more involved in remediation. While coordinating a meeting in Chicago, she serendipitously met her now advisor who offered her an excellent opportunity to earn a master's degree at North Carolina State University while conducting phytoremediation research. She currently resides in Raleigh, NC and aspires to restore sites in a town near you.

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Chapter 1 – LITERATURE REVIEW

1.1 Polycyclic Aromatic Hydrocarbons: Toxicity and Sources

Polycyclic aromatic hydrocarbons (PAHs) are an amalgamation of hydrogen and carbon atoms fused into two or more benzene rings (Coates, 2004). These ubiquitous, non-polar compounds exhibit low water solubility and a high affinity for soil organic matter. As ring numbers increase, PAHs become less soluble in water, increasingly resistant to biological degradation, and more persistent in the environment (Coates 2004, Latimer and Zheng 2003). PAH recalcitrance is problematic because the US Environmental Protection Agency (EPA) has identified sixteen PAHs as priority pollutants due to their toxicity to aquatic organisms and mammals (US EPA, 1986a). In addition, some PAHs are carcinogenic and mutagenic (Latimer and Zheng, 2003).

PAHs derive from petrogenic, pyrogenic, and/or biogenic sources. Petrogenic PAHs are petroleum derived and comprise PAH distributions with predominantly alkylated components (Page et al., 1999). Pyrogenic PAHs result from incomplete combustion of organic materials and primarily include 3-, 4- and 5- ring parent PAHs; biogenic PAHs are synthesized from diagenetic or other biological processes (Page et al., 1999). Whether PAHs derive from pyrogenic or petrogenic sources can be determined by comparing the ratios of parent PAHs to their alkylated homologue distributions. Weathering process may confound distribution patterns and complicate determination of petrogenic or pyrogenic sources of PAHs often found in sediments (Latimer and Zheng 2003, Page et al. 1999).

1.2 PAH Sorption to Sediments

Sorption is a general term that refers to surface retention; it can occur by both chemical and physical processes (Sparks, 2003). One primary sorbent for hydrophobic organic contaminants, such as PAHs, is soil organic matter (SOM); SOM is a complex heterogeneous material that may consist of decomposing animals and plants, humic substances, as well as soot, coke, coal, and charcoal. Different components of SOM, such as soot or humic materials, yield different sorption capacities for PAHs (Ghosh et al., 2003).

Ghosh et al. (2000) proposed three methods by which PAHs sorb to sediments including: 1) diffusion into various kinds of organic matter; 2) sorption near external particle surfaces; and 3) diffusion aided particle penetration. Other models have been presented to elucidate sorption mechanisms in natural organic matter. Pignatello and Xing (1996) proposed a dual-mode model that describes sorption processes as either surface adsorption to SOM or partitioning into sediment organic matter. A later study by LeBoeuf and Weber (1997) proposed the dual-reactive domain model (DRDM) to characterize sorption behavior of PAHs to sediments. Both models postulate that “rubbery” and “glassy” domains comprise SOM, an assumption that is widely accepted (e.g., Gunasekara and Xing 2003, LeBoeuf and Weber 1997, White and Pignatello 1999, van den Heuvel and van Noort 2003).

When organic contaminant concentrations are low, they generally partition into the fluid-like, “rubbery” domain producing linear isotherms. This “soft” or “rubbery” carbon has been described as diagenetically young with little cross-linking; “glassy” carbon is described as increasingly condensed and aromatic in nature and more heavily

cross-linked than rubbery carbon (LeBoeuf and Weber 1997, Huang and Weber 1997). Adsorption to condensed carbon decreases with increased contaminant concentration and generates non-linear isotherms (Pignatello and Xing 1996, Gunasekara and Xing 2003). In addition, glassy domains contain voids or sorption sites that possess heterogeneous energies where molecules can become immobilized (Pignatello and Xing 1996, LeBoeuf and Weber 1997, Huang and Weber 1997). Due to the glassy domain's rigidity, diffusion is more affected by sorbate molecular dimensions than the rubbery domain (Pignatello and Xing, 1996).

Differences between rubbery and glassy organic carbon cause PAHs to exhibit variable sorption and desorption behavior. Rubbery carbon's flexible nature enables rapid PAH diffusion into and out of such domains while diffusion rates into glassy carbon are slow and can differ by several orders of magnitude (LeBoeuf and Weber, 1997). Desorption from condensed carbon domains is equally slow. In fact, when a contaminant slowly diffuses into glassy organic matter, the process is not readily reversed. Desorption is rarely complete in condensed compartments (LeBoeuf and Weber, 1997).

1.3 Humic Substances

Humic substances (HS) account for over 80% of SOM and contain biopolymers, such as humin, humic acid (HA), and fulvic acid (FA) (Hayes and Malcolm, 2001). HA is SOM soluble in alkaline solutions but insoluble in acid. Humin is the portion of SOM that is insoluble in both acid and base, and FA is soluble at all pHs (Hayes and Malcolm 2001, Stevenson 1982, Jonker and Koelmans 2002). HA is diagenetically young and, as such, exhibits reversible and primarily linear sorption mechanisms (Xing and Pignatello

1997, Xia and Pignatello 2001) while humin is the high-molecular weight, refractory portion of humic materials. Research suggests that due to the increased degree of organic matter condensation and cross-linkage in humin, sorption kinetics are more nonlinear than those in HA (Gunasekara and Xing 2003, Shih and Wu 2002, Oren and Chefetz 2005). Johnson et al. (2001b) also observed increased isotherm nonlinearity and sorption capacity with geologic maturity of sorbents. Humin is speculated to be one of the most influential components with respect to sorption mechanisms (Clapp et al., 2001) due to its high sorption capacity (Oren and Chefetz, 2005). Humin is incorporated within the mineral matrix, and its sorption capacity is only fully realized when it is extracted from bulk sediment (Oren and Chefetz, 2005).

Aromaticity represents the ratio of aromatic to aliphatic carbon found in SOM fractions and can also facilitate humic materials identification (Tan 2003, Simpson et al. 2003 and references therein). Several researchers have focused on how the degree of aromaticity and aliphaticity of HS affects sorption and desorption of organic contaminants. In particular, some researchers propose that sorption and desorption of organic contaminants are highly dependent on organic matter aromaticity alone (Chin et al. 1997, Johnson et al. 2001b); others (Gunasekara and Xing 2003, Simpson et al. 2003, Salloum et al. 2002, Chefetz et al. 2000, Oren and Chefetz 2005) contend that aromatic and aliphatic components sorb considerable quantities of organic contaminants. Both aromatic and aliphatic C constituents can exist in rubbery or glassy domains of SOM. The age of organic matter may influence this association (Gunasekara and Xing, 2003). Cuypers et al. (2002) contend that aliphatic C is common to glassy or condensed domains of diagenetically young SOM while aromatic carbons are more prevalent in glassy

portions of diagenetically mature SOM. These findings suggest that both aromatic and aliphatic C moieties can enhance PAH sorption capacity and nonlinearity in SOM.

1.4 PAH Bioavailability and Desorption

Although PAHs are toxic, their sorption to SOM can reduce their bioavailability to organisms. Thus, PAH concentrations in sediment do not accurately reflect their potential toxicity to organisms. In fact, the “bioavailable fraction” is more accurately represented by PAHs that have desorbed into solution or pore water where they are more accessible for uptake by organisms (Alexander, 2000).

Desorption isotherm studies are a useful approach to determine bioavailability of organic contaminants. Some researchers employ two part systems that include an aqueous phase and a sediment phase (e.g., Gunasekara and Xing 2003, Lahlou and Ortega-Calvo 1999, Oren and Chefetz 2005, Yang et al. 2004, Pignatello 1990). Other studies have included a third phase such as TenaxTM beads to assist in desorption experiments (Rockne et al. 2002, Shor et al. 2003, Cornelissen et al. 1997a, Ghosh et al. 2000, Ghosh et al. 2003, Reeves et al. 2004, Cornelissen et al. 1999, van den Heuvel and van Noort 2003, Cornelissen et al. 1997b, Johnson et al. 2001a, Braida et al. 2004, Cornelissen et al. 1998a, Cornelissen et al. 1998b, Johnson et al. 2001b, Talley et al. 2002, Kukkonen et al. 2003, Weber and Kim 2005, Gomez-Lahoz and Ortega-Calvo 2005). TenaxTM is often used because it acts as an “infinite sink” and possesses an extremely high sorption capacity for PAHs; it also rapidly sorbs available organic solute from aqueous solutions (Cornelissen et al. 1997a, Braida et al. 2004).

1.4.1 Impact of PAH Aging on Desorption Kinetics

Several factors will influence rate and degree of PAH desorption, including type of organic matter inherent to geomedia and PAH “aging” (White et al. 1997, Johnson et al. 2001a). Cornelissen et al. (1997b) observed that desorption of organic contaminants occurred in three separate phases: a rapid, slow, and very slow phase. The first phase desorbs in a matter of hours; the slow and very slow phases may take weeks and months, respectively. Rapidly desorbing PAHs are thought to exist on external regions of sediment particles while slowly desorbing PAHs are attributed to retarded diffusion from within the organic matrix or through intraparticle pores (Cornelissen et al. 1997a, Pignatello and Xing 1996, Huang et al. 2003). In fact, van den Heuvel and van Noort (2003) postulated that slowly desorbing PAHs emanate from rubbery pores within condensed organic matter while the very slow desorbing PAHs derive from fixed sites within the glassy matrix.

PAH sequestration, or aging, is another phenomenon that may be responsible for different PAH uptake and release rates as well as decreased contaminant bioavailability (White et al. 1997, Johnson et al. 2001a); sequestration arises from extended periods of contact between SOM and PAHs. Continual exposure allows condensed organic domains to gradually relax which enhances molecular migration farther into micropores or remote areas of the soil matrix (Alexander 1995, LeBoeuf and Weber 1997). The process can take anywhere from several days to several years to occur and changes with different contaminants and SOM (Alexander 2000, LeBoeuf and Weber 1997). Sequestration greatly reduces the rate of PAH desorption from SOM and PAH bioavailability; sequestered PAHs are not readily accessible by plants, animals, or microorganisms

(Alexander 2000, Alexander 1995, LeBoeuf and Weber 1997). White et al. (1997) observed reduced bioavailability of phenanthrene to earthworms when several spiked soils were aged up to 155 days.

While numerous studies have utilized lab-contaminated materials to investigate desorption kinetics, (e.g., White and Pignatello 1999, Cornelissen et al. 1998b, Kukkonen et al. 2003, Weber and Kim 2005, Farrell et al. 1999, Yang et al. 2004), many others have employed field-contaminated geomeia (e.g., Rockne et al. 2002, Shor et al. 2003, Ghosh et al. 2000, Ghosh et al. 2003, Cornelissen et al. 1997b, Lei et al. 2004, Cornelissen et al. 1998a, Talley et al. 2002, Oen et al. 2006) to better represent biological availability and slow desorption phases of weathered materials (Rockne et al., 2002). For example, Rockne et al. (2002) examined the effects of plant detritus on sequestration and subsequent desorption of PAHs from field-contaminated estuarine sediments. Their data suggest that PAHs preferentially sequestered into SOM containing young plant detritus from sediments adjacent to emergent vegetation. Their results also imply that significantly higher fractions of PAHs desorbed from vegetated than non-vegetated sediments and that plant detritus enhanced PAH bioavailability. A later study (Shor et al., 2003) evaluated how soil-sediment organic matter properties and sediment's physical structure affected mass transport of individual PAHs in weathered estuarine sediments. Their results suggest that sediment characteristics such as porosity, organic matter concentration, and specific surface area were strongly tied to fast- and slow-domain diffusion. In particular, total sediment porosity and PAH hydrophobicity influenced PAH diffusion from the rapid-domain, while sediment specific surface area primarily impacted

diffusion from the slow-domain. Reportedly, greater specific surface area in fine sediment fractions (<63 μm) contributed to reduced PAH diffusion.

This thesis research used petrogenic-impacted sediments from an estuarine and fresh water site, respectively; sediments were fractionated into bulk sediment and humin fractions. Desorption isotherms were conducted using two methods, an aqueous phase dissolution method and Tenax™ beads, to determine desorbed PAHs. For both desorption methods, desorbed PAH concentrations were determined by GC/MS SIM.

Rockne et al. (2002) observed that emergent vegetation increased PAH desorption and bioavailability in sediments. *Phragmites australis* has naturally re-vegetated sediments at both field sites and is an invasive species tolerant of PAH contamination (Rock personal communication, 2003). Recently, significant reductions in PAH concentrations in refinery waste sediments were observed for sediments vegetated with *Phragmites australis* (Gregory et al., 2005).

Two hypotheses are addressed in this research. If vegetation enhances PAH bioavailability in sediments, then vegetated sediment should have statistically greater concentrations of desorbed PAHs from both bulk sediment and humin fractions of weathered petrogenic-polluted sediments relative to non-vegetated weathered, petrogenic-polluted sediment fractions. Secondly, if vegetation increases PAH desorption from sediments, then extended exposure of sediment to *Phragmites australis* should further increase statistically greater amounts or fractions of desorbed PAH relative to non-vegetated weathered, petrogenic-polluted sediments.

To test these hypotheses, the mass amounts of desorbed PAHs and fraction of desorbed PAHs of total PAH present were determined for vegetated sediment fractions

and compared to their respective non-vegetated sediment fractions using both desorption methods. Desorption isotherms were used to determine desorption kinetics between vegetated and non-vegetated sediments. Significance of differences between *Phragmites australis* sediment fractions and non-vegetated sediment fractions were determined by statistical comparison of total mass amount PAH desorbed and total fraction PAH desorbed.

Chapter 2-MATERIALS AND METHODS

2.1 Site Descriptions

Desorption experiments utilized sediments from a mixed-distillate refinery waste pit near a coastal estuary and a highly industrialized freshwater canal. The refinery waste pit is located on the northeastern US coast and naturally re-vegetated over a period of 40 years. Sediments were collected from the waste pit area where the vegetation gradient progresses from: (1) a region comprising bayberry shrubs (*Myrica* sp. L.), tree of heaven (*Ailanthus altissima*, Desf.), and a variety of grasses; (2) to an area dominated by *Phragmites australis* peppered with switchgrass (*Panicum* sp. L.) and goldenrod (*Solidago* sp. L.); (3) to a zone of sparse *P. australis* colonization; (4) to no vegetation (Gregory et al., 2005). The non-vegetated area is a result of high salinity due to saltwater intrusion by an adjacent estuary (Gregory et al., 2005). TPH contamination is 18% (Gregory et al., 2005). Sediments from the non-vegetated zone and *Phragmites* dominated area were used in desorption experiments.

The Indiana Harbor Canal (IH) sediments are located in a freshwater riparian ecosystem in a heavily industrialized section of Gary, Indiana. Total petroleum hydrocarbon (TPH) concentrations range from 2-43% along riverbanks, which are marked with a characteristic black residue (Sand Creek Consultants, Inc. 2002 and references therein). Extremely contaminated sediments are seemingly concentrated in the top six inches of the sediment profile (Sand Creek Consultants, Inc. 2002 and references therein). Diesel fuel is the predominant source of this historic contamination and pervades sediment, surface water, as well as pore, and ground water with a persistent petrogenic sheen (Sand Creek Consultants, Inc. 2002 and references therein). In 2002,

several varieties of hybrid poplars and willows were planted for a phytoremediation treatability study along the Indiana Harbor canal. Soon after trees were planted along the canal banks, *Phragmites* colonized sections of the study area.

2.2 Sediment Collection from Field Sites

Sediments were collected from the top 15 cm of the soil profile from previously described areas using a shovel or hand trowel. Samples were compiled from three and four areas within a 2 m diameter plot and mixed thoroughly in a steel bowl. Prior to sampling in vegetated zones, the sediment surface was rid of plants and litter. Composite samples were then collected by hand trowel or shovel in a steel bowl upon which sediments were shaken from root masses and manually rid of roots. Mixed samples were then placed into unused plastic bags, shipped on ice, and stored at 0 °C.

2.3 Fractionation of Sediments into Bulk Sediment and Humic Fractions

Visual root residuals were removed from sediments by sieving (2mm) before sediment fractionation and extraction for PAH analyses. Vegetated and non-vegetated sediments were chemically fractionated into two fractions, bulk sediment and humin. Humic fractions were extracted from both sediments using a previously described method (Guthrie et al., 1999). Essentially, bulk sediments were lipid extracted with DCM/Methanol (MeOH) (4:1, v/v, 25 mL) in 50 mL Teflon Oak Ridge centrifuge tubes and allowed to shake for 24 hours. Upon shaking, mixtures were centrifuged for 20 minutes at 2,500 rpm and solvent extracts were decanted. An additional 20 ml DCM was added to centrifuge tubes, which were then placed on the shaker table for 24 hours.

Tubes were removed, centrifuged for 20 minutes at 2,500 rpm, and solvent extracts were decanted. The remaining bulk sediment pellets were then treated with 0.1 M NaOH (20 mL) solution to extract fulvic and humic acids. Centrifuge tubes containing the 0.1 M NaOH solution were purged with N₂ gas, capped and shaken for an additional 24 hours. Mixtures were centrifuged for 20 minutes at 2,500 rpm, and solvent extracts were decanted. Bulk humin pellets were then lipid extracted as before, and allowed to air dry for 12 hours. Remaining bulk humin was then treated with a 10% hydrofluoric/hydrochloric (HF/HCl) acid solution (20 mL) to dissolve mineral constituents. Centrifuge tubes containing the HF/HCl solution were purged with N₂ gas, capped and allowed to sit for one week. Prior to decanting, HF/HCl treated humin was lipid extracted once more. Once the supernatant was removed, the HF/HCl humin was freeze-dried. Initial concentrations of PAHs in sediment fractions were determined by gas chromatography/mass spectrometry (GC/MS).

2.3.1 Desorption Experiment Methods

2.3.2 Aqueous Extraction

This technique was based on a modified version of a method previously employed by Cornelissen et al. (1997). PAH desorption was measured in triplicate for seven time points spanning a 120-day period. For each sample, approximately 5 g of air-dried contaminated sediments were added to 50 mL Teflon Oak Ridge centrifuge tubes. A mercuric chloride (HgCl₂) solution, which served as a biocide during desorption, was prepared at a concentration of 2 g/L by dissolving HgCl₂ in distilled H₂O. An aqueous slurry was created by adding 40 mL of HgCl₂ water to contaminated sediment in an Oak Ridge tube. Samples were capped, sealed with Teflon™ tape, and allowed to shake for

time periods ranging from 24 hours to 120 days. At each designated time point, samples were removed from the shaker table and centrifuged for 20 minutes at 2500 rpm. Upon spinning, the aqueous portion was decanted into a new 50 mL Teflon Oak Ridge centrifuge tube and allowed to sit for 24 hours to encourage settling of suspended sediments. The aqueous phase was replaced with fresh dosed water (40 mL) and samples were placed back on the shaker table until the next time point.

An aliquot of the decanted aqueous phase (35 mL) was removed with a 10 mL pipette and transferred to another 50 mL Teflon Oak Ridge centrifuge tube. Due to dichloromethane's (DCM) reduced polarity in comparison to water (DCM has a relative polarity of 0.309 where water is 1 (Abdullah et al., 2006 and references therein)), 5mL of DCM were added to each tube to sequester desorbed PAHs from the aqueous phase. The DCM layer was then removed via pipette and transferred to a 40 mL amber EPA vial. Any fraction of the aqueous phase remaining in the DCM was removed using anhydrous sodium sulfate (Na_2SO_4). Samples were then evaporated under a gentle stream of N_2 gas to approximately 1 mL. The concentrated sample was transferred to a gas chromatography/mass spectrometry (GC/MS) vial using a 500 μL syringe. Sample volumes were adjusted to 1 mL with DCM if they had been reduced beyond this amount. Concentrated samples were split between two GC/MS vials for archiving purposes and sample volumes were increased to 1 mL with additional DCM. Vials were sealed and stored at -2°C until GC/MS analysis.

2.3.3 TenaxTM Extraction

PAH desorption was measured in triplicate for seven time points spanning a 120-day period. Approximately 5 g of air-dried contaminated sediment along with 40 mL of

HgCl₂ dosed aqueous solution were added to a 60 mL amber glass jar with Teflon coated plastic lids. Approximately 0.15 g of Tenax-TA™ beads (20-35 mesh, Alltech Associates, Inc. College, PA) were placed into stainless steel baskets (small screen tissue basket and lid, 15mm dia. x 10mm high, Ted Pella, Inc., Reading, CA). Baskets were sealed with a lid and suspended in the jar above sediments by stainless steel wire platforms. Jars were capped, sealed with Teflon™ tape, positioned upright on the shaker table to prevent cages from sitting directly in sediment, and allowed to shake for time periods ranging from 24 hours to 120 days. At each time point, jars were removed from the shaker table and baskets were extracted and blotted with Kimwipes™ to capture excess water. Tenax™ beads were then removed from baskets, placed into 40 mL amber EPA vials, and extracted with approximately 10 mL of hexane for 30 minutes. Hexane extracts were decanted into a new 40 mL amber EPA vial and Tenax™ beads were extracted for a second 30-minute period using the same volume of hexane. Any water remaining in the hexane was removed using anhydrous sodium sulfate (Na₂SO₄). Samples were then evaporated to < 1 mL under a gentle stream of N₂ gas. Concentrated sample volumes were transferred to GC/MS vials using a 500 µL syringe. EPA vials used during concentration were rinsed with hexane to remove any remaining PAHs. The rinsate was then employed to raise concentrated sample volumes to 1 mL. Samples were split between two GC/MS vials for archiving purposes and volumes were diluted to 1 mL with additional hexane. The vials were sealed and maintained under refrigeration at -2 °C until analysis via GC/MS.

2.4 Gas Chromatography/Mass Spectrometry (GC/MS) analysis

Samples were analyzed using GC/MS select ion monitoring (SIM) to determine phenanthrene, pyrene, chrysene, and C3-phenanthrenes/anthracenes concentrations. Samples were spiked prior to analysis with 50 μ L of a PAH recovery internal standard (RIS) containing both deuterated phenanthrene-d₁₀ (500 ng/mL) and benzo[a]pyrene-d₁₂ (505 ng/mL). Sample extracts were analyzed using a modified method of EPA 8270 (US EPA, 1986b) similar to that employed by Luellen and Shea (2002). Samples were analyzed on an HP5890 Series II GC outfitted with electronic pressure control attached to an HP5970 or HP5972 MSD utilizing a Restek 30m x 0.25 mm Rtx-5 (film thickness 0.25 μ m) MS w/Integra-Guard column. The selected-ion-monitoring (SIM) mode was employed, which is more sensitive than the full-scan mode (Douglas et al., 2004) as it collects data at specific masses.

Chapter 3 - RESULTS

3.1 PAH Concentrations in Bulk and Humic Fractions of Sediments

Table 1 provides mean concentrations of individual PAHs (phenanthrene, pyrene, chrysene, and C3-phenanthrenes/anthracenes) for bulk sediment and humic fractions of vegetated and non-vegetated sediments collected from the Refinery Waste Pit (RP) and Indiana Harbor (IH) Canal sites. Concentrations of pyrene, chrysene, and C3-phenanthrenes/anthracenes are two orders magnitude greater in bulk sediments from Indiana Harbor than sediments from the Refinery Waste Pit. PAH concentrations in humic fractions for the two sites are similar and less than 1 mg PAH/kg humic fraction.

Concentrations of PAHs between vegetated (*Phragmites australis*) and non-vegetated sediment fractions (Table 1) were compared to determine if vegetation made a difference in PAH concentrations. Statistical significance was determined using a one-tailed student's t-test ($p < 0.05$) where the mean of a vegetated sediment fraction was compared to a non-vegetated sediment fraction. The number of samples used to determine the averaged PAH concentrations in sediment extracts is noted in Table 1.

Based on statistical analysis, *Phragmites* significantly reduced concentrations of pyrene, chrysene, and C3-phenanthrenes/anthracenes in RP bulk sediment versus non-vegetated RP bulk sediment; no significant change was observed for phenanthrene concentrations in vegetated versus non-vegetated RP bulk sediment. Results differed for RP humic. *Phragmites* significantly reduced concentrations of pyrene while no significant reduction of phenanthrene, chrysene or C3-phenanthrenes/anthracenes concentrations was observed in vegetated RP humic versus non-vegetated RP humic.

Table 1. Percent total organic carbon (%TOC), Percent Modern Carbon (PMC), and mean concentrations (mg PAH/kg sediment) of phenanthrene (PHEN), pyrene (PYR), chrysene (CHY), and C3-phenanthrenes/anthracenes (C3-PHEN) in bulk sediment and humin fractions.

Refinery Waste Pit^a (30+ years vegetation)				
	Bulk Sediment		Humin	
	Non-vegetated	<i>Phragmites</i>	Non-vegetated	<i>Phragmites</i>
%TOC	21 ± 1.9	27 ± 0.37	10 ± 1.8	28 ± 0.98
¹⁴C PMC^b	2.0 ± 0.06	24 ± 0.16	2.1 ± 0.08	33 ± 0.20
PHEN	1.1 ± 0.41	1.0 ± 0.18 ^c	0.26 ± 0.099	0.18 ± 0.052
PYR	6.0 ± 0.96	1.5 ± 0.22	0.07 ± 0.01	0.05 ± 0.02
CHY	4.0 ± 0.41 ^c	1.4 ± 0.12	0.06 ± 0.01	0.06 ± 0.02
C3-PHEN	6.9 ± 0.23 ^c	2.3 ± 0.47	0.15 ± 0.040	0.12 ± 0.022 ^c

Indiana Harbor^d (3-4 years vegetation)				
	Bulk Sediment		Humin	
	Non-vegetated	<i>Phragmites</i>	Non-vegetated	<i>Phragmites</i>
%TOC	14 ± 0.96	14 ± 0.14	4.6 ± 0.31	3.7 ± 0.12
¹⁴C PMC^e	8.2 ± 0.075	21 ± 0.11	4.4 ± 0.073	8.2 ± 0.075
PHEN	8.2 ± 0.51	7.2 ± 0.58	0.09 ± 0.02 ^f	0.82 ± 0.31
PYR	457 ± 36.7	361 ± 23.6	0.13 ± 0.052	0.44 ± 0.13
CHY	229 ± 33.9	205 ± 15.7	0.09 ± 0.01 ^f	0.47 ± 0.087
C3-PHEN	346 ± 27.2	229 ± 19.07	0.20 ± 0.025 ^f	0.28 ± 0.11

^aValues are means (n=4) ± one standard deviation from Gregory et al., 2005 unless otherwise noted.

^bAnalyses conducted by NOAA/WHOI AMS facility. ^cValues are means (n=3) ± one standard deviation from Gregory et al., 2005. ^dValues are means (n=3) ± one standard deviation unless otherwise noted (personal communication with S. Thorne Gregory). ^eAnalyses conducted by LLNL AMS facility. ^fValues are means (n=2) ± one standard deviation (personal communication with S. Thorne Gregory).

Significant reductions in pyrene and C3-phenanthrenes/anthracenes concentrations in *Phragmites* IH bulk sediment relative to non-vegetated IH bulk sediment are evident in Table 1; whereas, no significant changes in phenanthrene or chrysene concentrations were observed between vegetated and non-vegetated IH bulk sediments. Significant reductions in concentrations of phenanthrene, pyrene, and chrysene were observed in *Phragmites* IH humin compared to non-vegetated IH humin.

However, no significant difference was observed for C3-phenanthrenes/anthracenes concentrations between vegetated and non-vegetated IH humin.

3.2 General Desorption Trends

Two methods were used to determine mass amounts of four desorbed PAHs from vegetated and non-vegetated sediment fractions. The first method determined mass amounts of desorbed PAHs by removing aliquots of water (35 mL) from sediment slurries (40 mL H₂O/ 5 g sediment) at specific time points; each aliquot was extracted with DCM and analyzed by GC/MS SIM to determine mass amounts of PAHs desorbed from sediment at that time. The second method used Tenax™ beads that were deployed in steel cages suspended in the aqueous fraction of sediment slurries (40 mL H₂O / 5 g sediment); cages were removed at the same time points, and Tenax™ beads were extracted with hexane for quantification by GC/MS SIM.

Mass amounts of desorbed PAHs and fraction PAH desorbed are reported for each method (aqueous versus Tenax™) and for each field site, the Refinery Waste Pit (RP) (Figures 3-1 - 3-4; Figures 3-9 – 3-12) and Indiana Harbor Canal (IH) (Figures 3-5 - 3-8; Figures 3-13 – 3-16), respectively. Overall, desorption patterns, such as greater desorption from *Phragmites* versus non-vegetated sediment fraction, were not always consistent between methods (aqueous versus Tenax™), PAHs, nor sites (RP versus IH). Mass amounts of PAH desorbed in aqueous experiments followed expected desorption patterns based on each PAH's water solubility except for C3-phenanthrenes/anthracenes and pyrene in bulk sediments of IH (Figure 3-5). Mass amounts of PAH desorbed using Tenax™ beads did not follow expected desorption based on PAH water solubility instead

more pyrene and chrysene desorbed from sediment fractions than phenanthrene (Figure 3-2, 3-4, 3-6, 3-8).

More consistent desorption patterns, particularly for IH sediment fractions, were observed when data was converted to fraction desorbed of total PAH present in sediment fractions (Figures 3-9 through 3-16). *Phragmites* sediment fractions desorbed more PAHs than non-vegetated fractions for RP sediments. Non-vegetated sediment fractions desorbed more than *Phragmites* sediment fractions for IH sediments.

3.2.1 Refinery Waste Pit Sediments

On a mass unit basis, more pyrene and chrysene (ng PAH/g sediment) desorbed from non-vegetated RP bulk sediment fractions than from RP *Phragmites* bulk sediment fractions; the opposite result was observed for phenanthrene and C3-phenanthrenes/anthracenes (Figure 3-1). On a mass unit basis, more phenanthrene and C3-phenanthrenes/anthracenes (ng PAH/g sediment) desorbed from *Phragmites* RP bulk sediment fractions than from non-vegetated RP sediment (Figure 3-1). Similar results were observed for Tenax™ bead desorption experiments (Figure 3-2).

Desorption behavior was more consistent among PAHs in aqueous desorption studies of RP humin fractions (Figure 3-3). On a mass unit basis, all four PAHs desorbed more from RP *Phragmites* humin than non-vegetated humin. Results were not the same for Tenax™ desorption experiments with RP humin. More pyrene, chrysene, and C3-phenanthrenes/anthracenes desorbed from non-vegetated RP humin while more phenanthrene desorbed from *Phragmites* RP humin (Figure 3-4). These results are similar to observed Tenax™ desorption patterns for RP bulk sediment fractions.

Overall, Tenax™ beads extracted greater mass amounts of all four PAHs than aqueous phase experiments for RP sediment fractions (Figures 3-2, 3-4). Table 2 provides desorption rate constants for RP sediment fractions for both desorption methods. For RP sediments, PAHs (except phenanthrene bulk sediment) had greater rate constants when desorbed with the Tenax™ method than by the aqueous desorption method; this was particularly true for RP humin fractions. Sorption isotherms for both methods do not appear to achieve steady state conditions over the 120-day period. This trend was evident for all PAHs except chrysene in *Phragmites* bulk sediment (Figure 3-2).

Table 2. Desorption rate constants (ng PAH/ day) for phenanthrene (PHEN), C3-phenanthrenes/anthracenes (C3-PHEN), pyrene (PYR), and chrysene (CHY).

	PHEN		C3-PHEN		PYR		CHY	
	H ₂ O	Tenax™						
Bulk Sediment								
Refinery Waste Pit								
Non-vegetated	0.14	0.21	0.12	0.41	0.11	0.48	0.051	0.48
<i>Phragmites</i>	0.23	0.22	0.23	0.27	0.088	0.28	0.039	0.12
Indiana Harbor								
Non-vegetated	0.22	1.4	0.43	12	0.49	69	0.23	13
<i>Phragmites</i>	0.12	0.77	0.17	2.4	0.25	9.7	0.039	4.7
Humin								
Refinery Waste Pit								
Non-vegetated	0.21	0.76	0.058	0.64	0.057	2.5	0.019	0.92
<i>Phragmites</i>	0.39	0.89	0.12	0.45	0.11	1.5	0.037	0.53
Indiana Harbor								
Non-vegetated	0.19	3.5	0.065	17	0.048	60	0.033	18
<i>Phragmites</i>	0.19	0.63	0.058	0.72	0.071	1.5	0.018	0.71

Desorption rates constants calculated with Origin™ 7 software by performing linear regression analyses on means of mass desorption data (n=3).

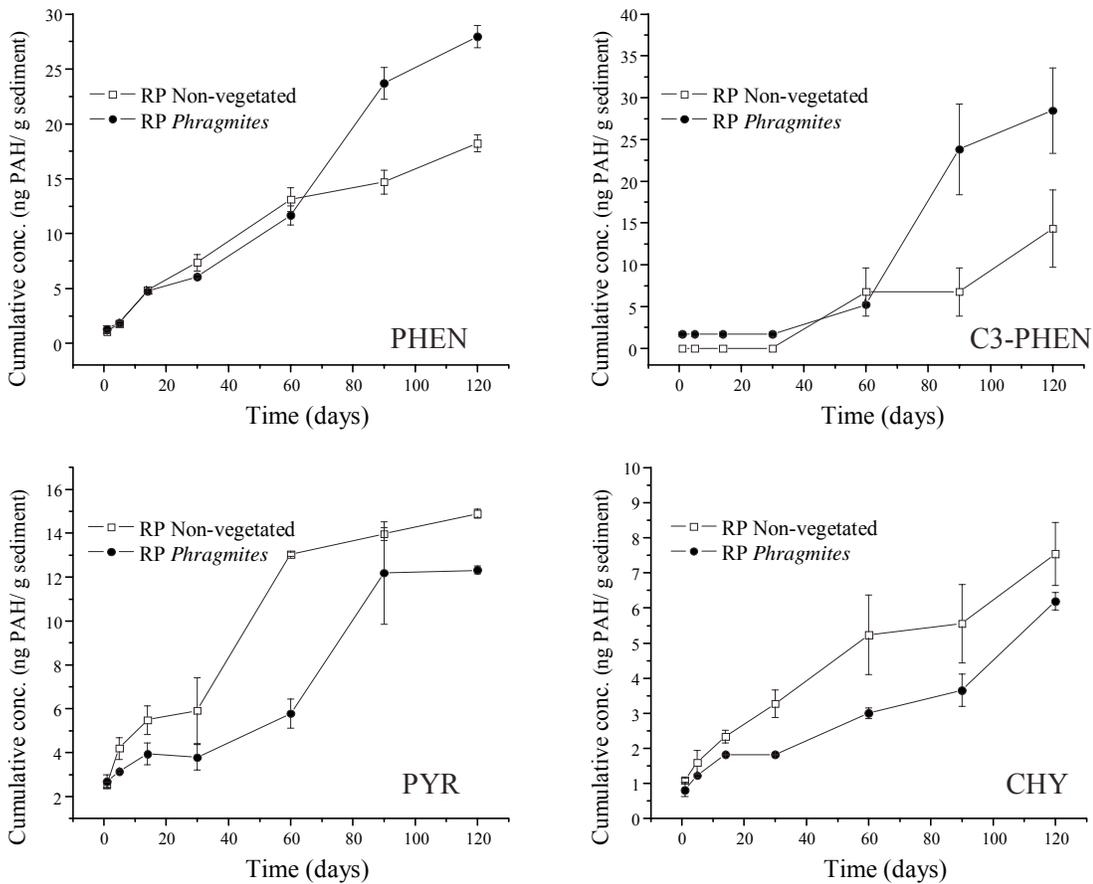


Figure 3-1. Mass amounts (ng/g) of desorbed PAHs for non-vegetated and *Phragmites* bulk sediments from the Refinery Waste Pit (RP) site. Desorption was quantified by removing aliquots of aqueous phase of sediment slurry, extracting aliquots with DCM, and quantifying PAHs in solvent extract by GC/MS SIM.

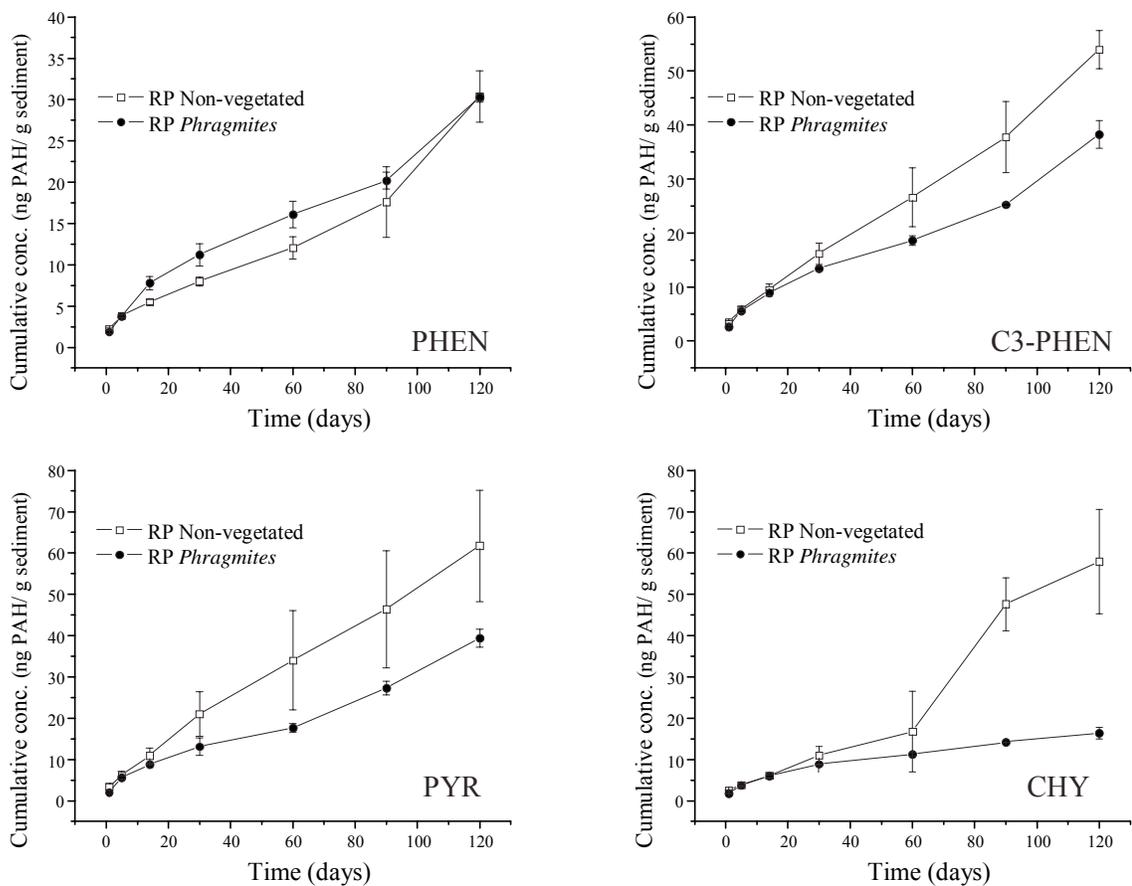


Figure 3-2. Mass amounts (ng/g) of desorbed PAHs for non-vegetated and *Phragmites* bulk sediments from the Refinery Waste Pit (RP) site. Desorption was quantified by placing Tenax™ beads in stainless steel cages in aqueous phase of sediment slurries. Tenax™ beads were removed at specific time points and extracted with hexane; PAHs in solvent extract were quantified by GC/MS SIM.

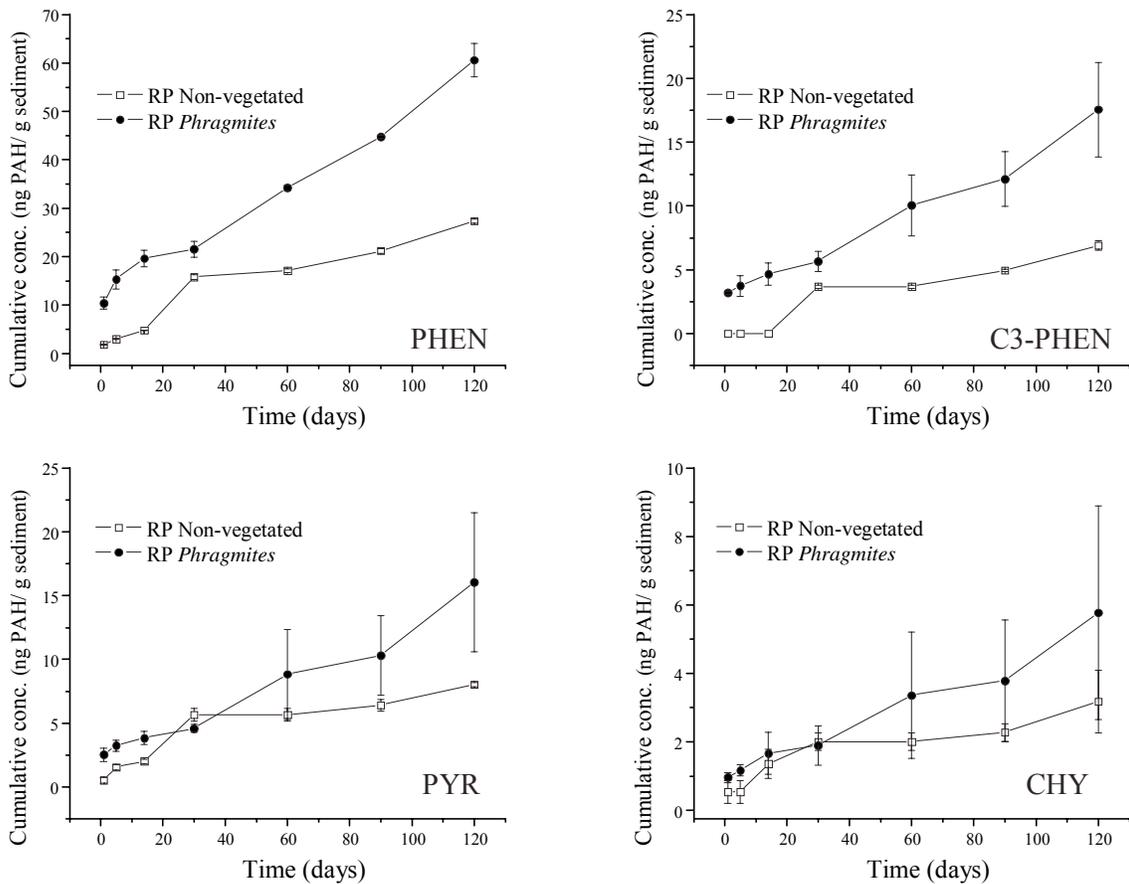


Figure 3-3. Mass amounts (ng/g) of desorbed PAHs for humin fractions of non-vegetated and *Phragmites* sediments from the Refinery Waste Pit (RP) site. Desorption was quantified by removing aliquots of aqueous phase of sediment slurry, extracting aliquots with DCM, and quantifying PAHs in solvent extract by GC/MS SIM.

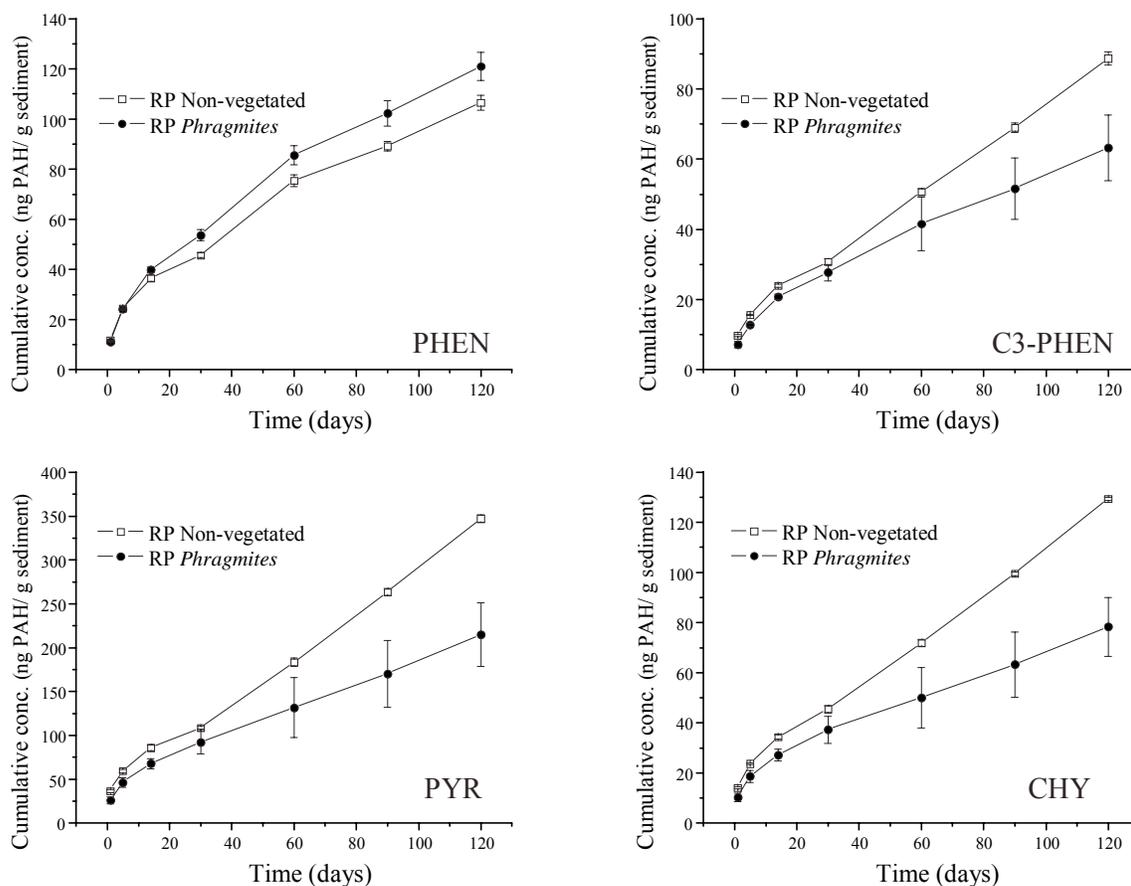


Figure 3-4. Mass amounts (ng/g) of desorbed PAHs for humin fractions of non-vegetated and *Phragmites* sediments from the Refinery Waste Pit (RP) site. Desorption was quantified by placing Tenax™ beads in stainless steel cages in aqueous phase of sediment slurries. Tenax™ beads were removed at specific time points and extracted with hexane; PAHs in solvent extract were quantified by GC/MS SIM.

3.2.2 Indiana Harbor Sediments

On a mass per unit basis, fewer PAHs desorbed from *Phragmites* IH bulk sediment than from non-vegetated IH bulk sediment in aqueous and Tenax™ desorption experiments (Figures 3-5, 3-6). The same trend was observed for humin fractions of IH sediment desorbed with Tenax™ (Figure 3-8). Exceptions to this trend were data for all four PAHs desorbed from humin in aqueous desorption experiments. Similar amounts of phenanthrene, chrysene, and C3-phenanthrenes/anthracenes desorbed from both *Phragmites* IH humin fractions and non-vegetated IH humin fractions; pyrene desorbed more readily from *Phragmites* IH humin fractions than from non-vegetated IH humin fractions (Figure 3-7).

Sorption isotherms for aqueous and Tenax™ bead extractions of non-vegetated IH sediment fractions did not appear to achieve steady state conditions in the 120-day experiment; sorption isotherms for aqueous and Tenax™ bead extractions of IH sediment fractions vegetated with *Phragmites* did appear to achieve steady state conditions. Overall, Tenax™ beads desorbed more PAHs from IH sediment fractions than aqueous desorption experiments as indicated by increased desorption rate constants (Table 2). Similar rate constants were observed for individual PAH desorption from non-vegetated IH bulk sediment and humin fractions using Tenax™ beads. Aqueous desorption rate constants were also similar between IH humin fractions (Table 2), but aqueous desorption rate constants were higher for non-vegetated IH bulk sediment than *Phragmites* bulk sediment. *Phragmites* bulk sediment had higher desorption rate constants than *Phragmites* humin for both Tenax™ and aqueous desorption methods.

3.3 Fraction Desorption Data

Because PAH concentrations differ between sediment samples at each site and between samples taken from different sites (Table 1), mass amount desorption data was converted to fraction-desorbed data to normalize PAH desorption data. This allows for better comparison between *Phragmites* and non-vegetated sediment fractions at each site and between RP and IH sediment fractions. As previously discussed, IH bulk sediments contained two orders magnitude more PAH than RP bulk sediments.

3.3.1 Refinery Waste Pit Sediments

On a fraction-desorbed basis, all four PAHs desorbed more from *Phragmites* RP bulk sediment than from non-vegetated RP bulk sediment in aqueous desorption experiments (Figures 3-9). Results were similar for TenaxTM desorption experiments; more pyrene, chrysene, and C3-phenanthrenes/anthracenes desorbed from *Phragmites* RP bulk sediment than from RP non-vegetated bulk sediment (Figure 3-10). More phenanthrene desorbed from RP non-vegetated bulk sediment than from *Phragmites* RP bulk sediment (Figure 3-10).

Results from aqueous desorption experiments using RP humin were similar to aqueous desorption experiments using RP bulk sediment as more PAHs desorbed from *Phragmites* RP humin than from RP non-vegetated humin fractions (Figure 3-11). Results differed for TenaxTM desorption experiments with humin. *Phragmites* RP humin desorbed more phenanthrene than non-vegetated RP humin, but more pyrene, chrysene, and C3-phenanthrenes/anthracenes desorbed from non-vegetated RP humin than *Phragmites* RP (Figure 3-12).

3.3.2 Indiana Harbor Sediments

On a fraction desorbed basis, more pyrene, C3-phenanthrenes/anthracenes, and chrysene desorbed from non-vegetated IH bulk sediment than from *Phragmites* IH bulk sediments in aqueous desorption experiments; however, the opposite was observed for phenanthrene. More phenanthrene desorbed from *Phragmites* IH bulk sediment than from non-vegetated IH bulk sediment (Figure 3-13). In Tenax™ desorption experiments, all four PAHs desorbed more from non-vegetated IH bulk sediment on a fraction-desorbed basis than *Phragmites* IH bulk sediment (Figures 3-14). Similar results were observed in humin fractions as more PAHs desorbed from non-vegetated IH humin fractions in aqueous and Tenax™ desorption experiments than from *Phragmites* IH humin fractions (Figures 3-15, 3-16).

3.3.3 Desorption Isotherms and Steady State Conditions

It is possible to determine whether PAHs in samples have reached steady state conditions by examining desorption isotherms. In particular, isotherms for aqueous extracts of vegetated RP bulk sediment illustrate that PAHs have yet to reach steady state conditions (Figure 3-9). Non-vegetated RP bulk sediment aqueous extract isotherms differed as pyrene and C3-phenanthrenes/anthracenes have reached steady state conditions, while phenanthrene and chrysene have not (Figure 3-9). Desorption isotherms for Tenax™ extractions of RP bulk sediment and humin were similar as all PAHs desorbing from vegetated and non-vegetated sediment fractions have not achieved steady state conditions (Figures 3-10 and 3-12, respectively). Isotherms for aqueous extracts of RP humin fractions were similar to aqueous extracts of RP bulk sediment fractions as PAHs have not reached steady state conditions in *Phragmites* RP humin

fractions. However, desorption isotherms for non-vegetated RP humin illustrate that phenanthrene, pyrene, and C3-phenanthrenes/anthracenes have reached steady state conditions while chrysene has not (Figure 3-11).

Indiana Harbor sediment fractions yielded contrasting results to those observed for RP sediments. Regardless of extraction method, PAHs in non-vegetated IH sediment fractions exhibited similar desorption isotherm patterns while PAH isotherms varied in *Phragmites* IH sediment fractions. In particular, PAH desorption isotherms have not reached steady state conditions in aqueous extracts of non-vegetated IH bulk sediment (Figure 3-13). Isotherms for phenanthrene, pyrene, and C3-phenanthrenes/anthracenes in *Phragmites* IH bulk sediment behaved similarly as steady state conditions were not attained; however chrysene did reach steady state conditions (Figure 3-13). Similar to aqueous extracts of non-vegetated IH bulk sediment, PAHs have yet to reach steady state conditions in TenaxTM extracts of non-vegetated IH bulk sediment (Figure 3-14). In contrast, pyrene, chrysene, and C3-phenanthrenes/anthracenes have reached steady state conditions in TenaxTM extracts of vegetated IH bulk sediment while phenanthrene has not (Figure 3-14). Isotherms for aqueous extracts of *Phragmites* IH humin illustrate that phenanthrene, pyrene, and chrysene have reached steady state conditions, however, C3-phenanthrenes/anthracenes has yet to do so (Figure 3-15). PAHs have not achieved steady state conditions in non-vegetated IH humin fractions extracted with TenaxTM but isotherms for TenaxTM extracted vegetated IH humin demonstrate that all PAHs have reached steady state (Figure 3-16). The fact that some PAHs in TenaxTM extracted sediment fractions have reached steady state conditions may seem ambiguous as TenaxTM can act as an “infinite sink” (Cornelissen et al. 1997a, Braida et al. 2004). This supposed

unlimited sorption capacity does not imply that PAHs will infinitely desorb from sediments but that TenaxTM beads are not likely to become saturated by desorbed solutes in the aqueous phase.

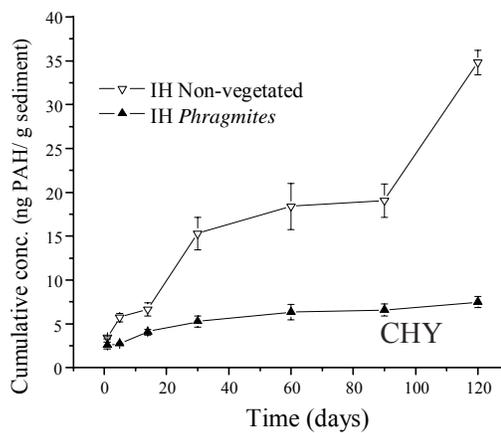
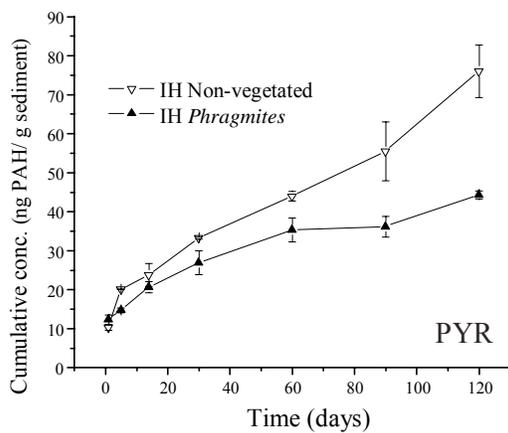
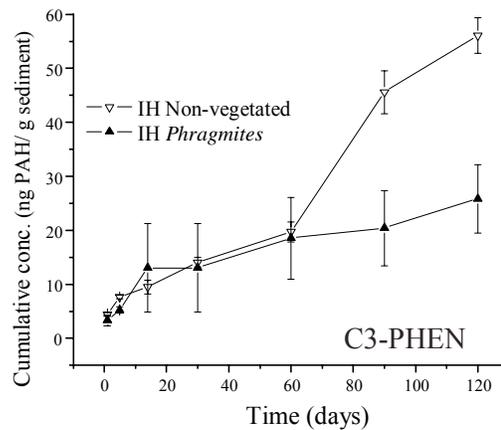
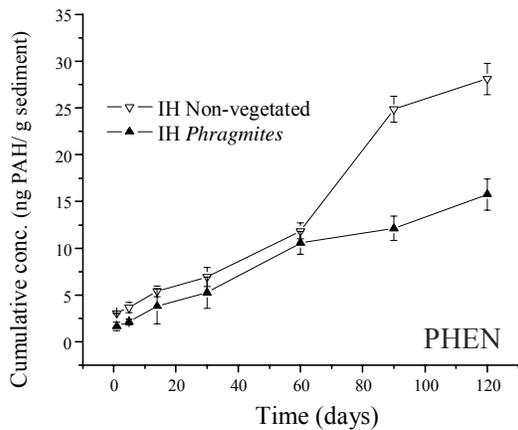


Figure 3-5. Mass amounts (ng/g) of desorbed PAHs for non-vegetated and *Phragmites* bulk sediments from the Indiana Harbor (IH) site. Desorption was quantified by removing aliquots of aqueous phase of sediment slurry, extracting aliquots with DCM, and quantifying PAHs in solvent extract by GC/MS SIM.

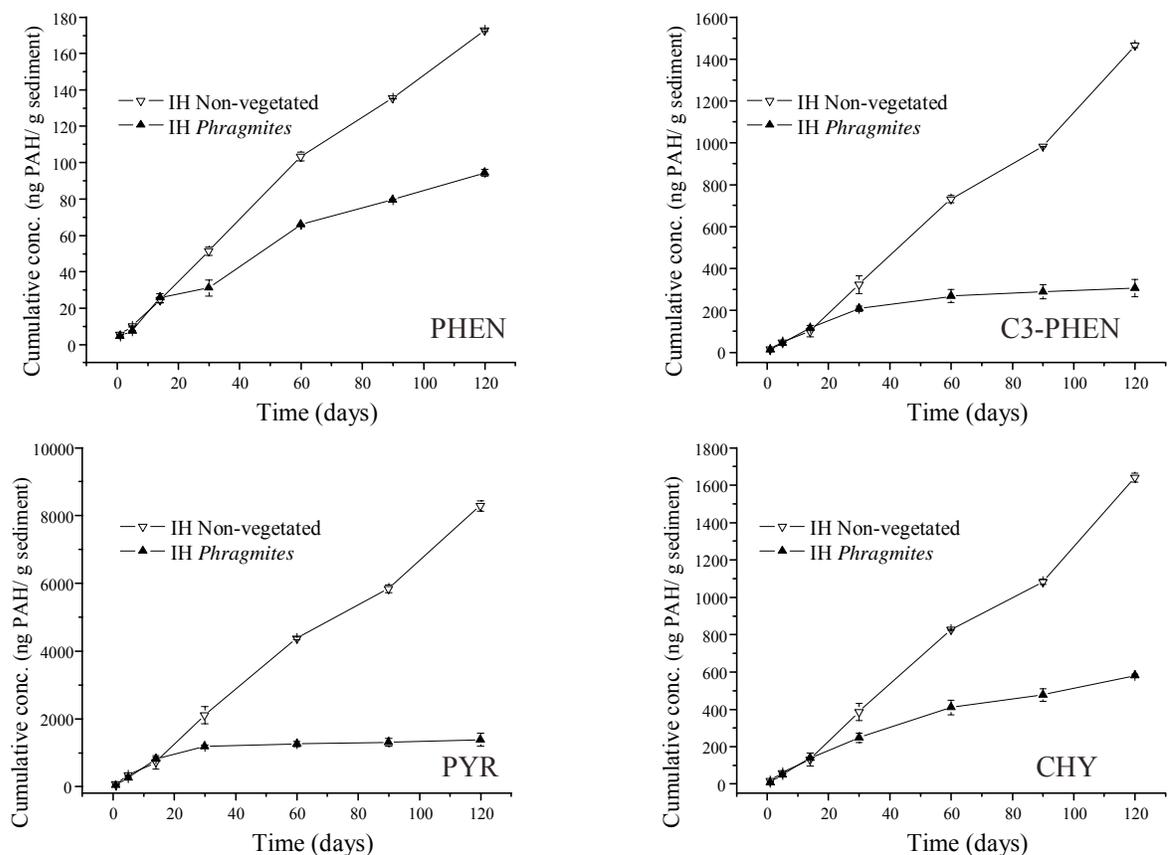


Figure 3-6. Mass amounts (ng/g) of desorbed PAHs for non-vegetated and *Phragmites* bulk sediments from the Indiana Harbor (IH) site. Desorption was quantified by placing Tenax™ beads in stainless steel cages in aqueous phase of sediment slurries. Tenax™ beads were removed at specific time points and, extracted with hexane; PAHs in solvent extract were quantified by GC/MS SIM.

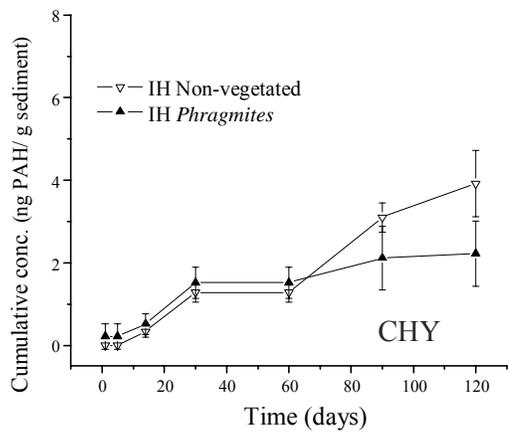
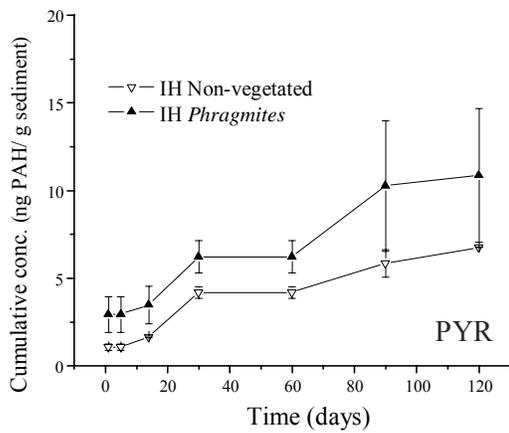
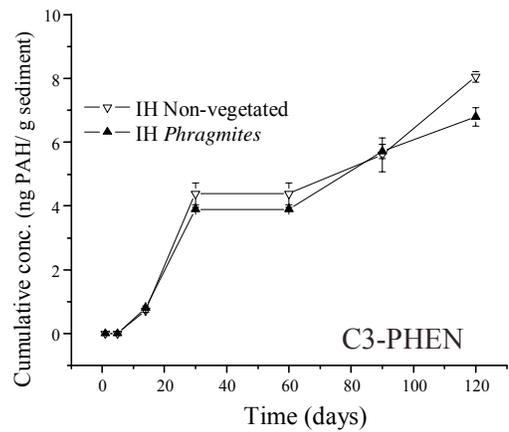
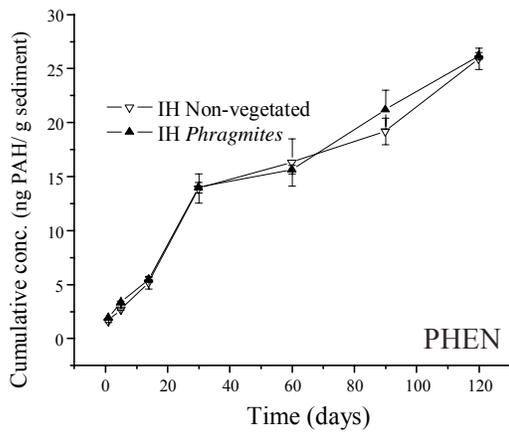


Figure 3-7. Mass amounts (ng/g) of desorbed PAHs for humin fractions of non-vegetated and *Phragmites* sediments from the Indiana Harbor (IH) site. Desorption was quantified by removing aliquots of aqueous phase of sediment slurry, extracting aliquots with DCM, and quantifying PAHs in solvent extract by GC/MS SIM.

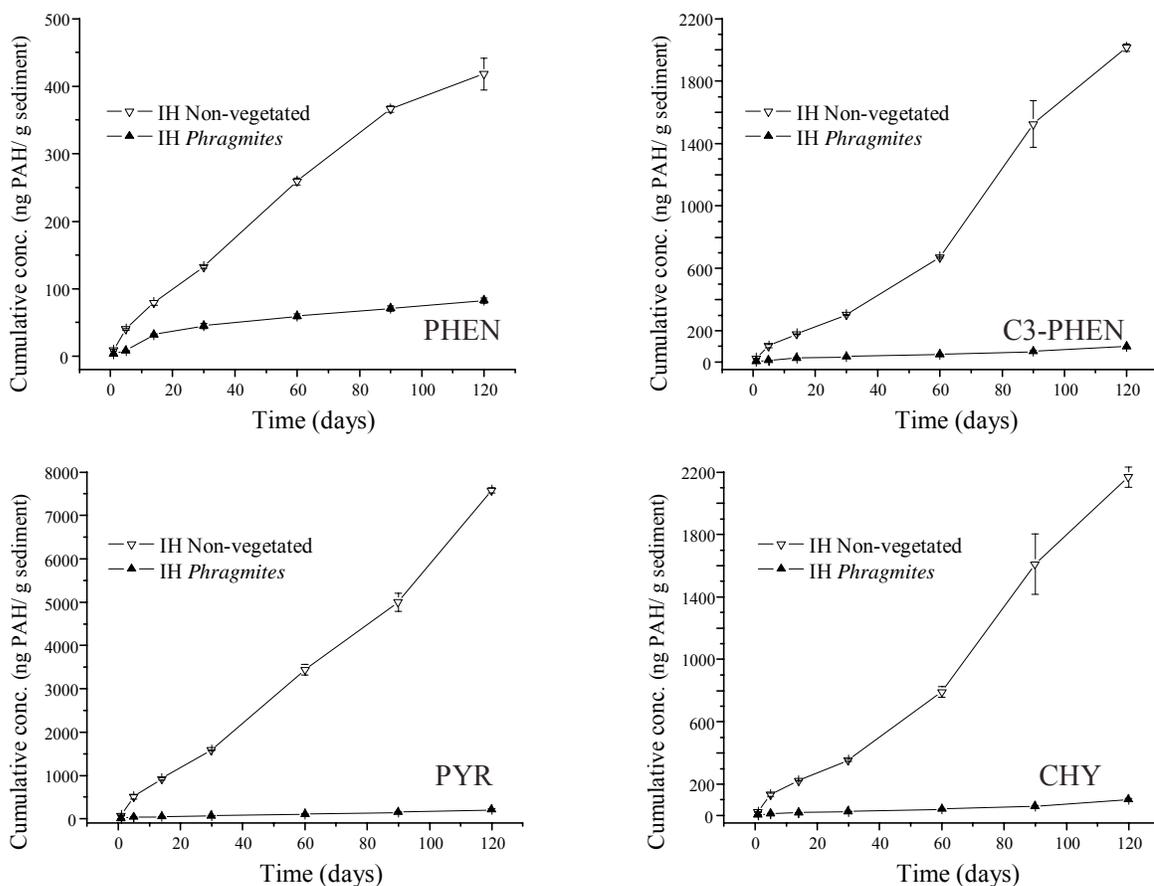


Figure 3-8. Mass amounts (ng/g) of desorbed PAHs for humin fractions of non-vegetated and *Phragmites* sediments from the Indiana Harbor (IH) site. Desorption was quantified by placing Tenax™ beads in stainless steel cages in aqueous phase of sediment slurries. Tenax™ beads were removed at specific time points and, extracted with hexane; PAHs in solvent extract were quantified by GC/MS SIM.

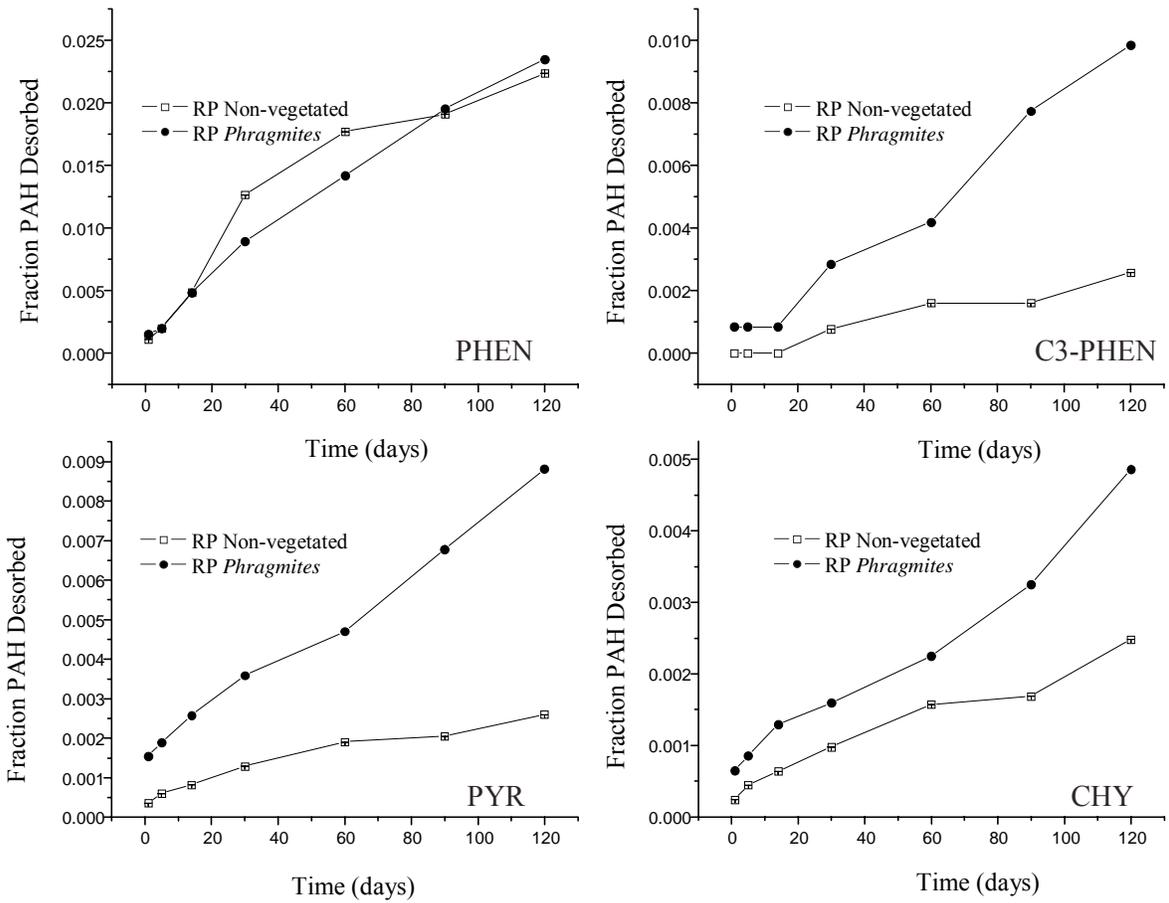


Figure 3-9. Fraction of PAHs desorbed from aqueous slurries of non-vegetated and *Phragmites* bulk sediments from the Refinery Waste Pit (RP) site. PAH fraction was quantified by comparing mass amounts of PAHs desorbed to total PAHs present in solvent extracted sediments (Table 1).

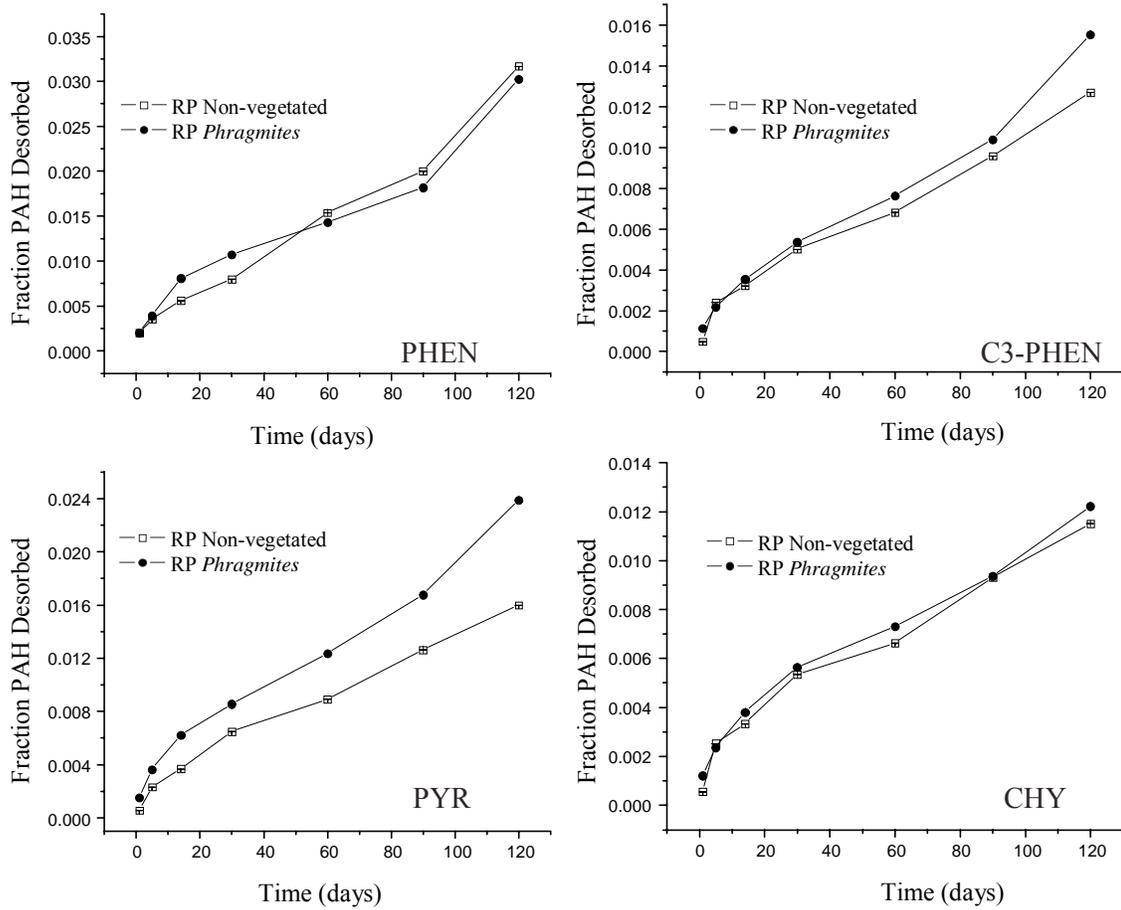


Figure 3-10. Fraction of PAHs desorbed from TenaxTM bead extracts of non-vegetated and *Phragmites* bulk sediments from the Refinery Waste Pit (RP) site. PAH fraction was quantified by comparing mass amounts of PAHs desorbed to total PAHs present in solvent extracted sediments (Table 1).

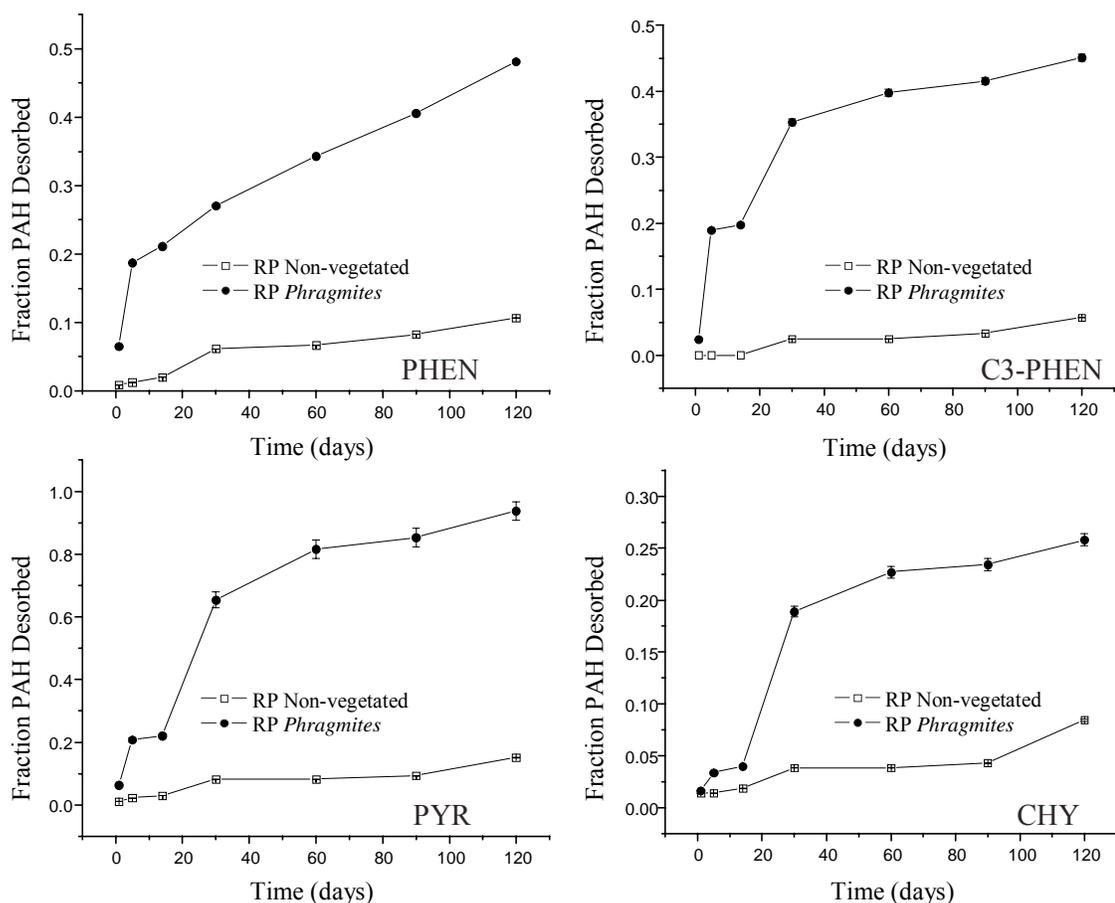


Figure 3-11. Fraction of PAHs desorbed from aqueous slurries of non-vegetated and *Phragmites* humin fractions from the Refinery Waste Pit (RP) site. PAH fraction was quantified by comparing mass amounts of PAHs desorbed to total PAHs present in solvent extracted sediments (Table 1).

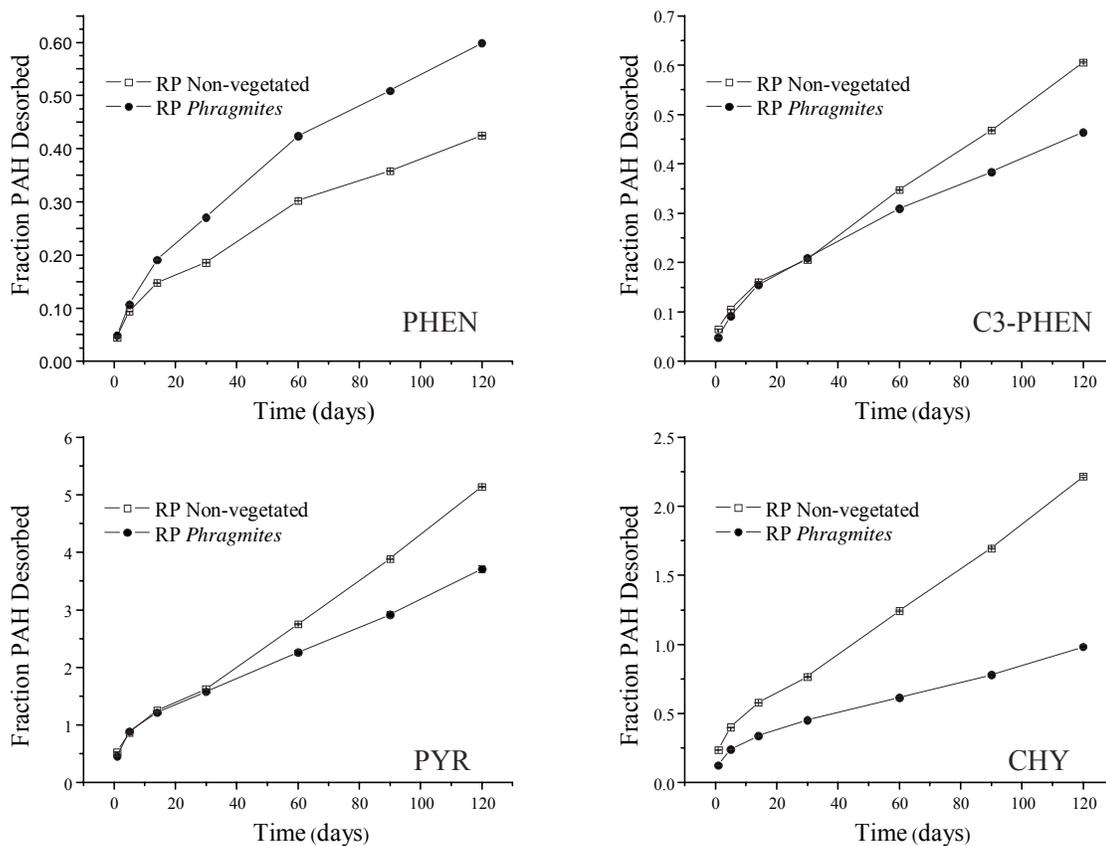


Figure 3-12. Fraction of PAHs desorbed from TenaxTM bead extracts of non-vegetated and *Phragmites* humin fractions from the Refinery Waste Pit (RP) site. PAH fraction was quantified by comparing mass amounts of PAHs desorbed to total PAHs present in solvent extracted sediments (Table 1).

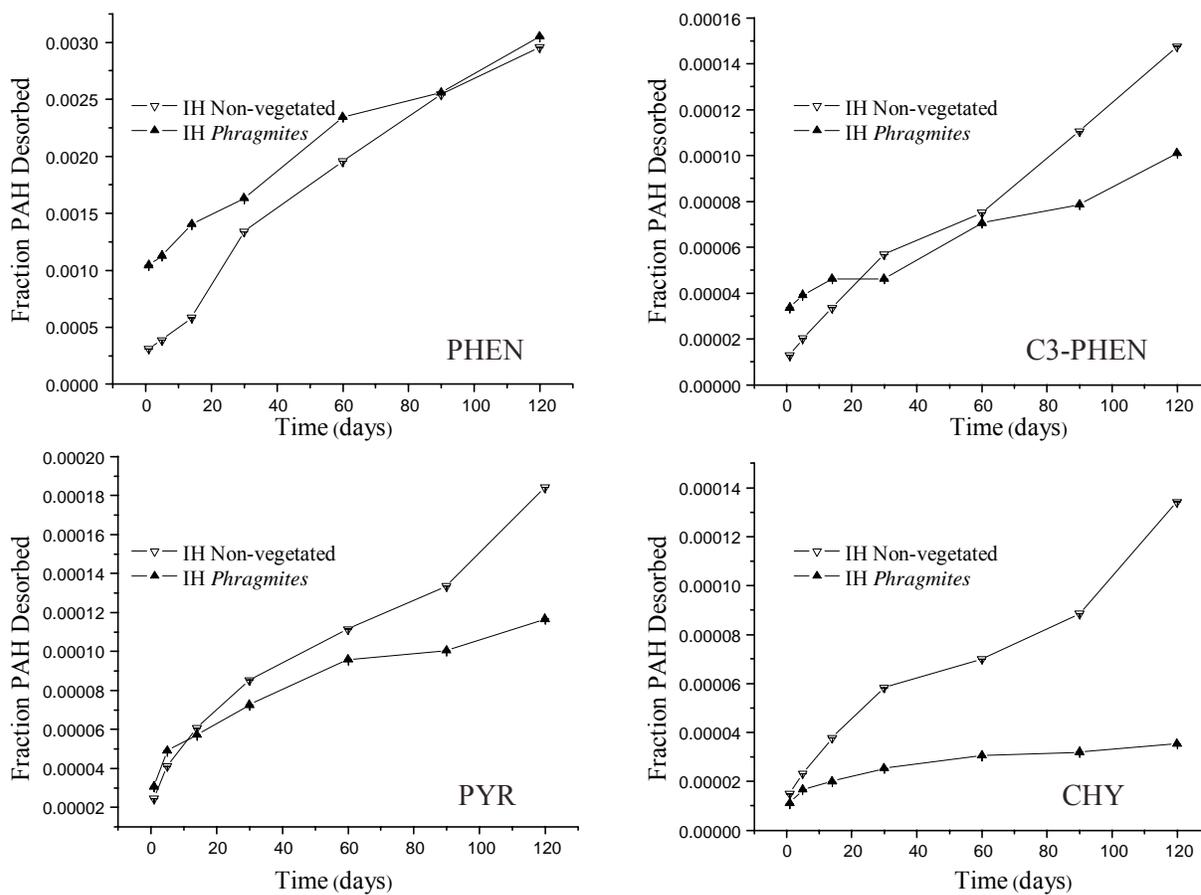


Figure 3-13. Fraction of PAHs desorbed from aqueous slurries of non-vegetated and *Phragmites* bulk sediments from the Indiana Harbor (IH) site. PAH fraction was quantified by comparing mass amounts of PAHs desorbed to total PAHs present in solvent extracted sediments (Table 1).

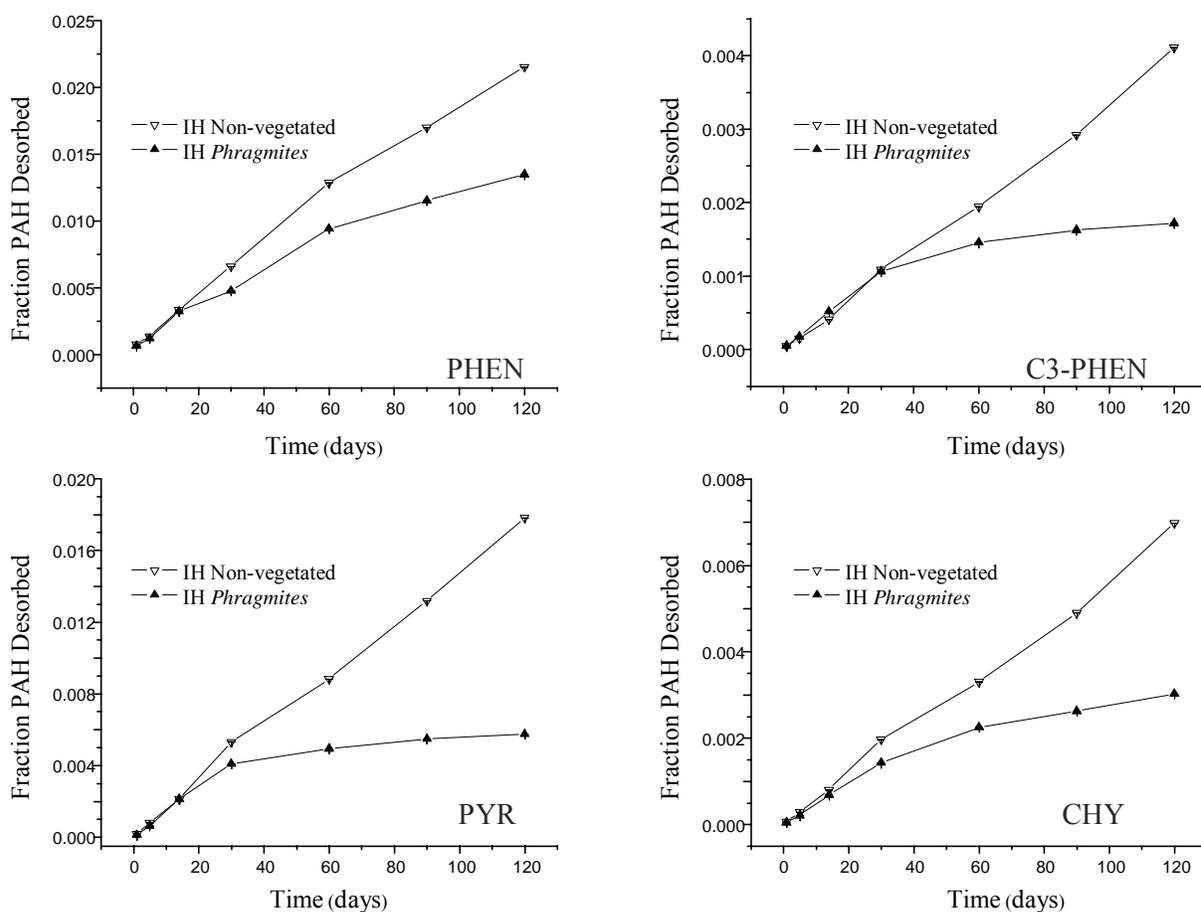


Figure 3-14. Fraction of PAHs desorbed from TenaxTM bead extracts of non-vegetated and *Phragmites* bulk sediments from the Indiana Harbor (IH) site. PAH fraction was quantified by comparing mass amounts of PAHs desorbed to total PAHs present in solvent extracted sediments (Table 1).

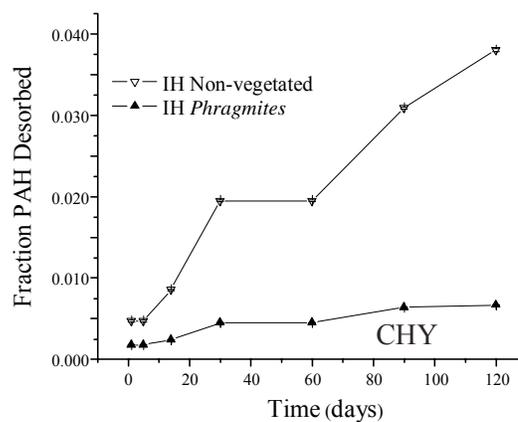
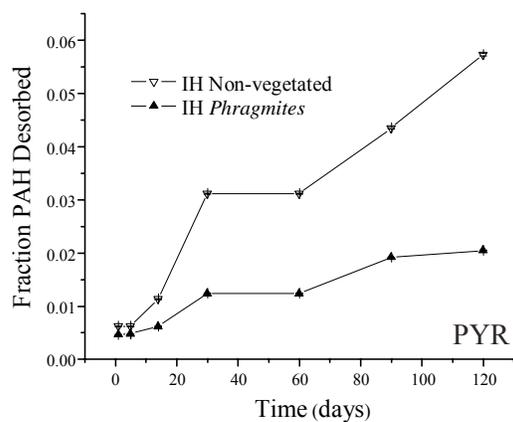
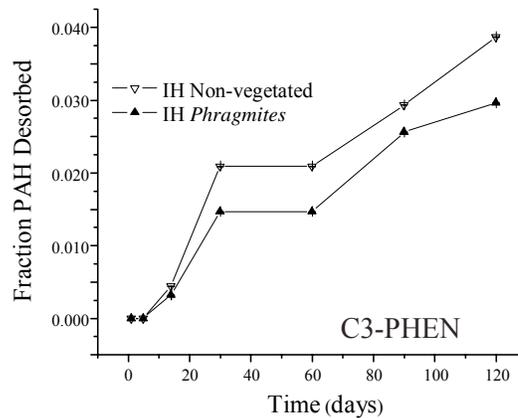
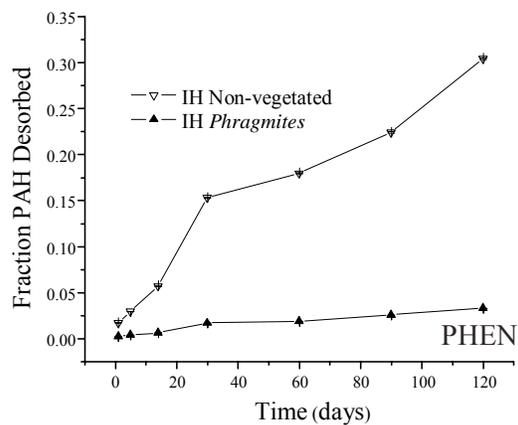


Figure 3-15. Fraction of PAHs desorbed from aqueous slurries of non-vegetated and *Phragmites* humin fractions from the Indiana Harbor (IH) site. PAH fraction was quantified by comparing mass amounts of PAHs desorbed to total PAHs present in solvent extracted sediments (Table 1).

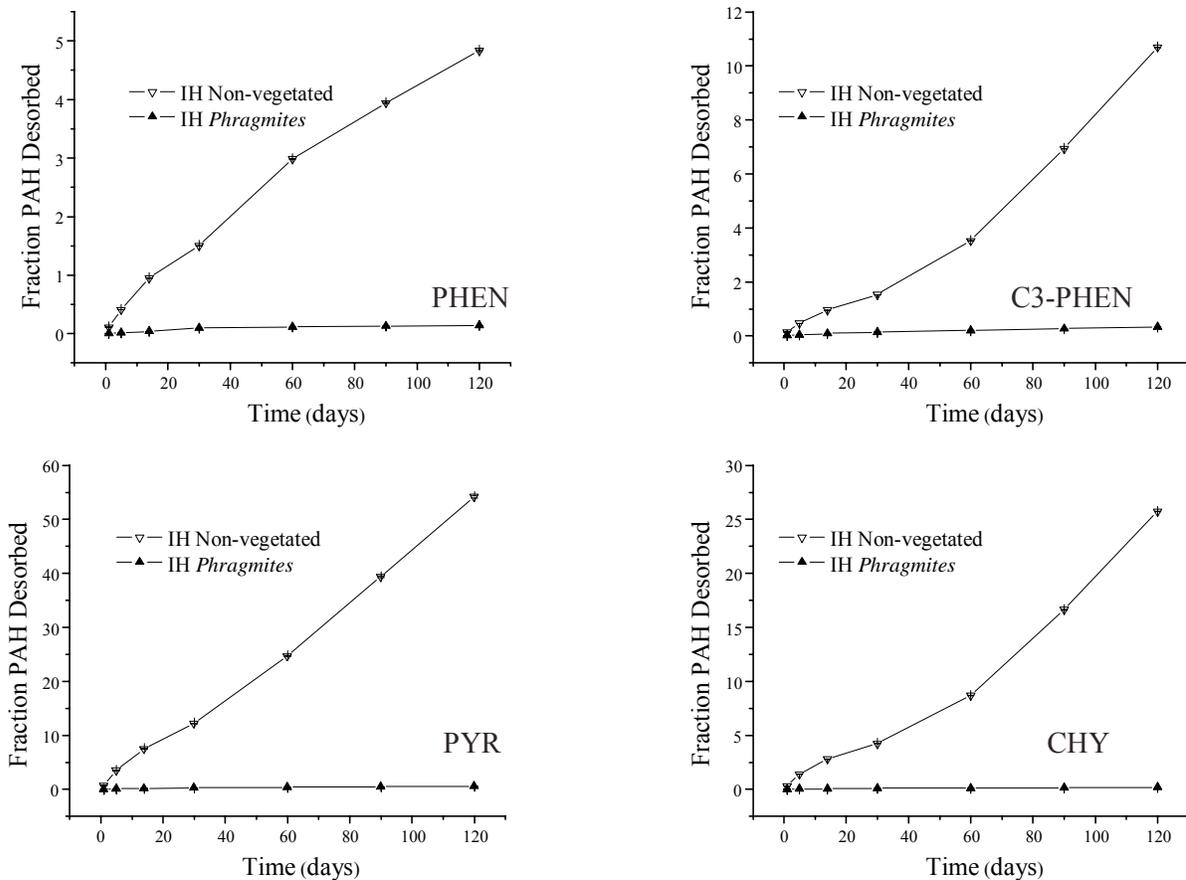


Figure 3-16. Fraction of PAHs desorbed from TenaxTM bead extracts of non-vegetated and *Phragmites* humin fractions from the Indiana Harbor (IH) site. PAH fraction was quantified by comparing mass amounts of PAHs desorbed to total PAHs present in solvent extracted sediments (Table 1).

Chapter 4 – DISCUSSION

Over the last decade, investigations have yielded mixed results as to whether plants may or may not reduce PAH concentrations in soils and sediments. Plants release organic matter to sediments, but the impact of plant organic matter on PAH bioavailability (attenuation versus PAH sequestration) is unclear. One primary measure of bioavailability is the rate and amount of contaminant that desorbs from sediment to water where uptake by organisms would most rapidly occur. I proposed two hypotheses to investigate how vegetation may affect PAH bioavailability. First, if vegetation enhances PAH bioavailability from sediments, then vegetated sediment should have statistically greater concentrations of desorbed PAHs from weathered petrogenic-polluted sediments relative to non-vegetated weathered, petrogenic-polluted sediments. Secondly, if vegetation increases PAH desorption in sediments, then extended exposure of sediment to *Phragmites australis* should further increase statistically greater amounts or fractions of desorbed PAH relative to non-vegetated weathered, petrogenic-polluted sediments.

Two methods, an aqueous and TenaxTM extraction method, were used to assess bioavailability of four PAHs from vegetated and non-vegetated petrogenic-polluted sediment fractions. Greater PAH desorption was observed for TenaxTM beads than for aqueous extractions in RP and IH sediment fractions. On a fraction-desorbed basis, more phenanthrene, pyrene, chrysene, and C3-phenanthrenes/anthracenes desorbed from TenaxTM extracted vegetated and non-vegetated RP bulk sediment and humin fractions (Figures 3-10 and 3-12, respectively) compared to aqueous extractions of these sediment fractions (Figures 3-9 and 3-11, respectively). IH TenaxTM desorption isotherms for all four PAHs (Figures 3-

14 and 3-16, respectively) were more similar to each other than aqueous desorption isotherms (Figures 3-13 and 3-15, respectively).

While aqueous extractions may more accurately mimic bioavailability of PAHs under field conditions, there are several advantages to utilizing TenaxTM beads in laboratory scale experiments. For example, due to their ability to serve as an infinite desorption sink (Braidia et al., 2004), TenaxTM beads prevent saturation of the aqueous phase by rapidly adsorbing available PAHs (Cornelissen et al. 1997a, Cornelissen et al. 1999). Quick adsorption of available PAHs augments the contaminant concentration gradient between the sediment and aqueous phase; aiding in continuous PAH desorption from sediment as well as rapid assessment of PAH biodegradability (Cornelissen et al., 1998a). Another advantage over aqueous extraction is that the rate at which TenaxTM removes contaminants from the aqueous phase exceeds that of slowly desorbing contaminants, thus reducing re-adsorption potential to soils/sediments (Cornelissen et al. 1997a). In addition, aqueous extraction data may be more subjective than TenaxTM extraction data as aqueous aliquots can contain suspended sediments, possibly introducing variability or artificially increasing quantitation results. TenaxTM bead extractions enhance desorbing fractions of PAHs compared to aqueous extractions and also provide a rapid and cost-effective method for measuring bioavailability as well as biodegradation potential of field-contaminated sediments.

These characteristics make TenaxTM bead experiments attractive for desorption studies (Rockne et al. 2002, Shor et al. 2003, Cornelissen et al. 1997a, Ghosh et al. 2000, Ghosh et al. 2003, Reeves et al. 2004, Cornelissen et al. 1999, van den Heuvel and van Noort 2003, Cornelissen et al. 1997b, Johnson et al. 2001a, Braidia et al. 2004, Cornelissen et al. 1998a, Cornelissen et al. 1998b, Johnson et al. 2001b, Talley et al. 2002, Kukkonen et al.

2003, Weber and Kim 2005, Gomez-Lahoz and Ortega-Calvo 2005), but TenaxTM beads have rarely been employed to examine vegetative effects on PAHs. Recently, TenaxTM was utilized to investigate the influence of emergent vegetation (predominantly *Spartina alterniflora*) on PAH sequestration and release from contaminated estuarine sediments (Rockne et al., 2002). Findings indicated that PAH desorption from vegetated sediments was significantly higher than from non-vegetated sediments and that PAHs preferentially sequestered into SOM enriched with young *Spartina alterniflora* detritus and not into soot carbon as predicted. Rockne et al.'s (2002) results are similar to desorption results observed for RP sediments but not for IH sediments. One explanation for similarity between RP and Rockne's desorption results is that both sediments are estuarine sediments with vegetation that had been present for extended periods of time. Thus similarities between sediment organic matter composition may exist and explain similar desorption behavior.

PAH desorption behavior is highly correlated with sediment organic matter (SOM), a substrate whose diversity is partially affected by degree of diagenetic maturation. It may contain a variety of different sorbents including humic and fulvic acids, humin, black carbon, and kerogen. The latter two are rigid and aromatic carbonaceous materials, possessing few polar functional groups (Cornelissen et al., 2005 and references therein). Cornelissen et al. (2005) proposed that these condensed materials can be described as glassy domains within SOM and are likely responsible for slow desorption of PAHs.

Huang and Weber (1997) used sorbents such as peat, humic acid, shale, and kerogen to study phenanthrene sorption and desorption equilibria. Their findings indicated that diagenetically mature kerogen and shale samples possessed significantly higher sorption capacities and sorption-desorption hysteresis than diagenetically immature materials, such as

peat. They proposed that sorption-desorption hysteresis was primarily caused by contaminant sequestration in rigid organic domains; a phenomenon likely exacerbated by aging. Johnson et al. (2001a) also indicated that sorption-desorption hysteresis was more significant in geologically mature, rigid, “kerogen-like” sorbents compared to younger, less recalcitrant organic matter (Johnson et al. 2001a and references therein). A later study used an array of natural sorbents to examine SOM affects on contaminant desorption (Johnson and Weber, 2001). Results indicated that sorbents dominated by humic-like organic matter supported rapid PAH desorption while organic matter with kerogen characteristics exhibited slower and less complete desorption.

During diagenesis, biopolymers such as lipids, proteins, carbohydrates, and cellulose metamorphose from extremely amorphous and oxidized compounds to increasingly condensed humic substances, which eventually evolve into extremely condensed and reduced kerogens (Huang and Weber 1997 and references therein, LeBoeuf and Weber 1997 and references therein). As diagenesis proceeds, SOM becomes increasingly aromatic while O/C and H/C atomic ratios decrease (Huang and Weber, 1997). Reductions in O/C ratios result in decreased polarity of the SOM matrix. Because diagenetically young SOM is less rigid and relatively more polar than condensed carbonaceous materials, PAHs likely desorb more readily from such regions than from increasingly hydrophobic and rigid regions (Johnson et al., 2001b). A study by Oren and Chefetz (2005) observed that PAH sorption was greater in organic portions of river sediments that were relatively less polar than other sediments. Gunasekara and Xing (2003) also observed an inverse relationship between organic contaminant sorption capacity and polarity of organic matter (Gunasekara and Xing 2003 and references therein).

The influence of diagenetically young SOM on PAH desorption is apparent in this study. On a fraction-desorbed basis greater PAH desorption was observed for *Phragmites* RP bulk sediment and RP humin as well as TenaxTM extracted RP bulk sediment versus non-vegetated sediment counterparts. Previous research (Gregory et al., 2005) demonstrated higher total organic carbon (TOC) as well as considerably higher percent modern carbon (¹⁴C PMC) (Table 1) inputs to vegetated RP sediment fractions; the greater ¹⁴C PMC reflects carbon deposition from *Phragmites* as petrogenic carbon contains little to no ¹⁴C.

Gregory et al. (2005) also conducted cross-polarization magic angle spinning (CPMAS) ¹³C nuclear magnetic resonance (¹³C NMR) analysis of RP sediment fractions. Figure 4-1 shows distinct shifts in *Phragmites* humin at 33 and 72 ppm. Chemical shifts between 0 and 50 ppm are indicative of aliphatic carbon compounds. Research has shown that sorption to rubbery, amorphous carbon and aliphatic carbon is analogous (Salloum et al., 2002) and that modern organic carbon may readily absorb available PAHs (Chen et al., 2003). Methylenic carbon may exhibit amorphous or crystalline domains (31 and 33 ppm, respectively) (Salloum et al., 2002) that both sorb PAHs, but the latter does not adsorb PAHs as readily as the amorphous form (Hu et al., 2000). As such, recalcitrant PAH bioavailability is quite possibly fostered by partitioning from the relatively condensed sediment matrix into modern aliphatic carbon fractions where desorption may be somewhat enhanced. Thus, aliphatic carbon in *Phragmites* humin may act as a solvent to extract PAHs from other condensed domains and account for increased fraction of PAHs desorbing from vegetated versus non-vegetated RP sediment fractions.

Increased PAH desorption from vegetated compared to non-vegetated RP sediment fractions may also result from increased polarity in vegetated sediment fractions. Plant roots

exude readily degradable organic compounds (Joner et al. 2002, and references therein) that serve as a primary source of SOM and enhance microbial population activity (Aprill and Sims 1990 and references therein, Joner et al. 2001, Joner et al. 2002 and references therein). It has been suggested that these compounds not only increase microbial action thus augmenting PAH degradation by direct and indirect metabolism (co-metabolism) (Joner et al., 2001), but they may also influence degradation by enhancing PAH solubility and bioavailability (Qui et al., 1997). Improved PAH solubility and resulting bioavailability likely arises from increased polarity. In Figure 4-1, *Phragmites* humin has distinct chemical shifts at 72 ppm. Chemical shifts between 50-112 ppm are indicative of polar compounds such as alcohols, amines, carbohydrates, ethers, methoxyl and acetal carbon compounds. Thus, *Phragmites* humin for RP sediments contains more polar groups in the region than non-vegetated humin; this increased polarity may facilitate more rapid PAH desorption as observed in my desorption studies.

Desorption behavior in IH sediment fractions was markedly different than that observed in RP sediments. In particular, PAHs desorbed more readily on a fraction basis from non-vegetated compared to vegetated IH sediment fractions with the exception of aqueous extracts of IH humin. Previous research (Gregory et al., 2006) indicated that ^{14}C PMC inputs are elevated in vegetated compared to non-vegetated IH sediment fractions, however this trend is not consistent in TOC values (Table 1). Little difference exists between TOC in vegetated and non-vegetated IH sediment fractions; TOC is in fact, higher in non-vegetated than in vegetated IH sediment fractions. The observed increase in TOC in vegetated versus non-vegetated RP sediment fractions but not in IH sediment fractions may reflect differences in vegetative maturity. While RP *Phragmites* has been established for

over 30 years, IH *Phragmites* has only been present for approximately 4 years and has yet to alter the sediment organic matrix to the same degree. The presence of modern carbon in refractory portions of *Phragmites* IH humin quantitatively shows that plant carbon is present. CPMAS ^{13}C NMR analysis of IH humin fractions does not show great differences in carbon composition between *Phragmites* and non-vegetated humin (Figure 4-2). The only distinct difference is aliphatic carbon (30.4 ppm) for *Phragmites* humin; aliphatic carbon has been shown to sorb PAHs as strongly as aromatic carbon (Salloum et al., 2002). The particular shift at 30.4 ppm is indicative of amorphous aliphatic C, which according to Hu et al. (2000) is the primary sorbent for non-polar contaminants such as PAHs in humic substances. As such, amorphous aliphatic C would sorb PAHs and increase PAH desorption hysteresis more so than more crystalline aliphatic C as well as aromatic C. The presence of amorphous aliphatic carbon in *Phragmites* IH sediment may explain why PAH desorption from *Phragmites* IH sediment and humin is less than PAH desorption observed for non-vegetated IH sediment fractions. Amorphous aliphatic carbon would make *Phragmites* sediment more non-polar than non-vegetated sediment; as a result, PAH desorption rates are slower.

Overall, results show that petrogenic-contaminated sediments with extensive exposure to *Phragmites* exhibit greater PAH desorption than non-vegetated sediments. Greater PAH desorption in these sediments relative to non-vegetated sediments can be linked to the presence of more polar carbon compounds in *Phragmites* sediments and the presence of significant amounts of biogenic plant carbon (^{14}C PMC). Sediment with less exposure to *Phragmites* desorbed less PAHs than non-vegetated sediments; this behavior can be linked to increased amorphous aliphatic carbon in vegetated sediments. Although the two vegetated sites are at different locales, results suggest a process by which plant organic matter initially

retards PAH bioavailability by making SOM more non-polar due to the presence of aliphatic carbon (Figure 4-3). Over time, plant organic matter reverses SOM condensation in petrogenic-contaminated sediments and increases PAH bioavailability by making SOM more polar in both labile and refractory portions of the sediment matrix. Such long-term changes enhance PAH release but, as concentration data suggest, desorbed PAHs are attenuated, most likely, by the resident *Phragmites* affiliated microbial community that has had time to develop and flourish (Figure 4-4).

While *Phragmites australis* exhibits success in attenuating PAHs in petrogenic-polluted sediments, it is imperative to regard it as a model plant as *Phragmites* is non-native and has a highly invasive nature. As such this study is not necessarily advocating its use as a remediation tool but rather that vegetation with similar attributes are employed. If *Phragmites* is used, its colonization should be closely monitored and controlled.

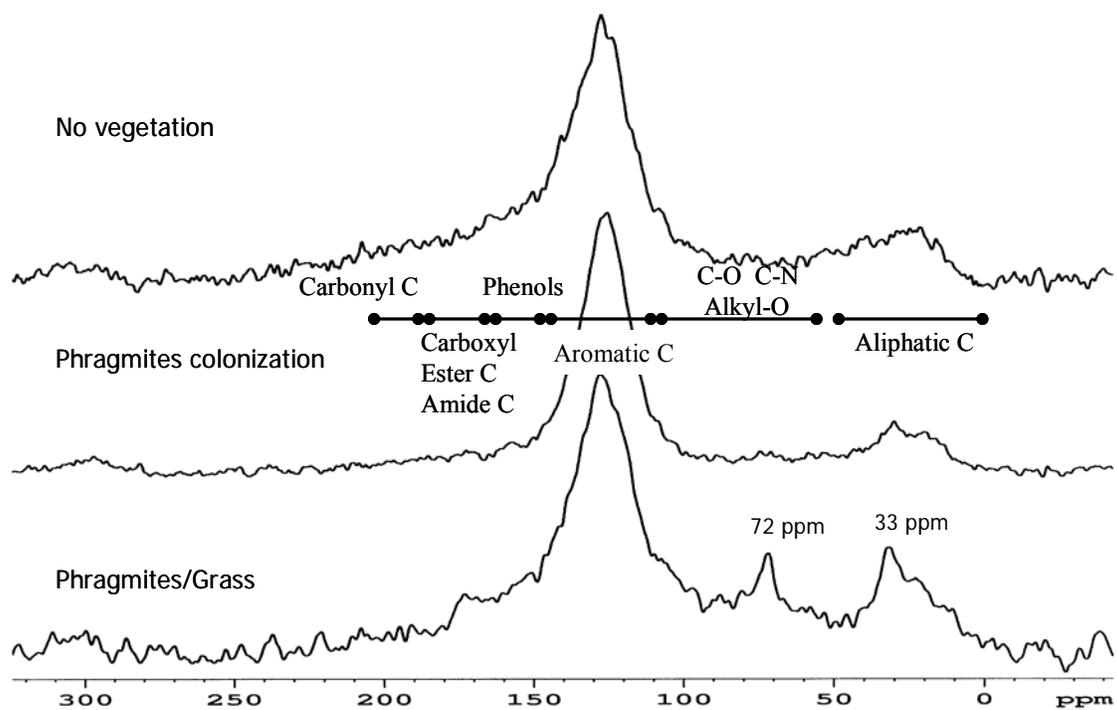


Figure 4-1. Cross-polarization magic angle spinning (CPMAS) ^{13}C nuclear magnetic resonance spectra of RP HF/HCl humin fractions for non-vegetated, *Phragmites* colonization, and *Phragmites* with mixed grass areas (Gregory et al., 2005)

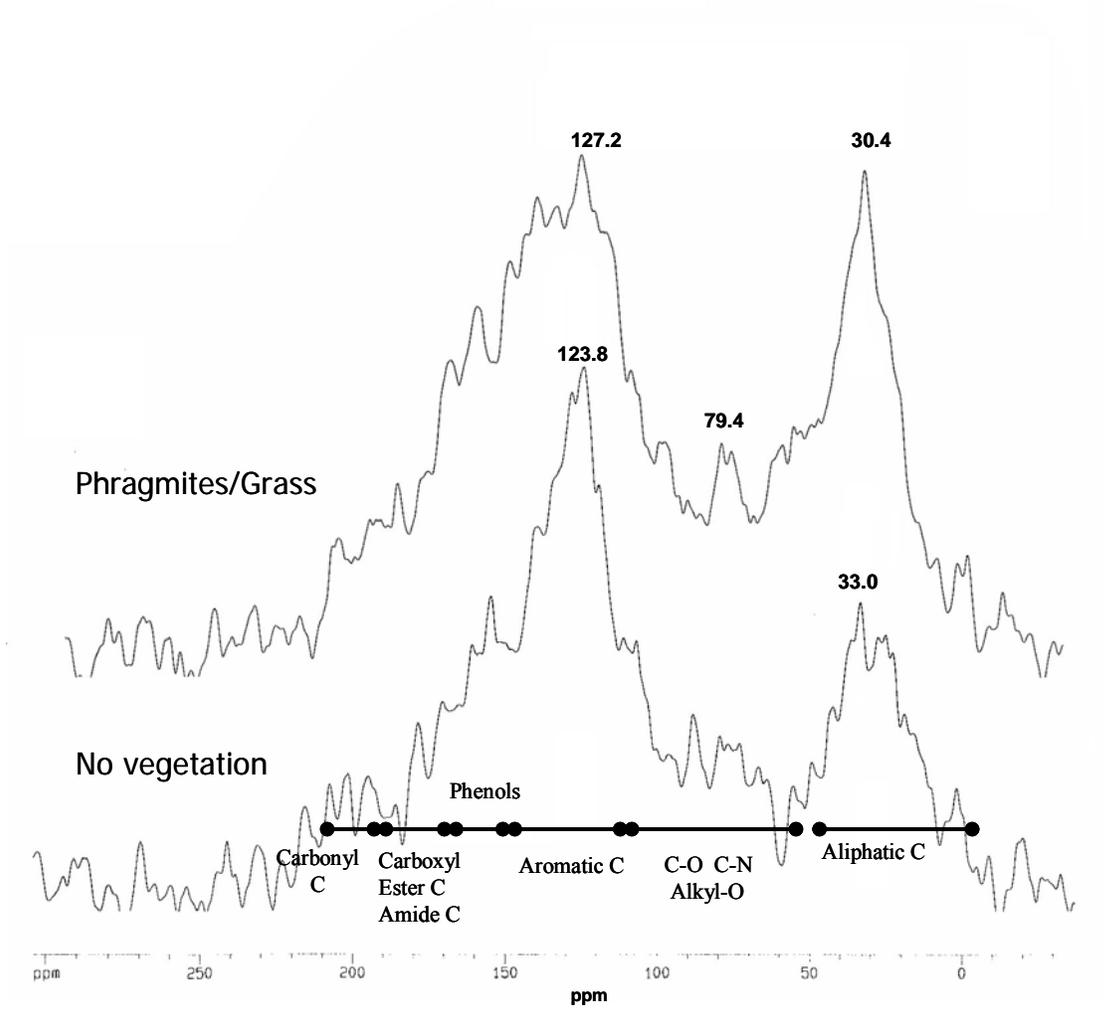


Figure 4-2. Cross-polarization magic angle spinning (CPMAS) ¹³C nuclear magnetic resonance spectra of IH HF/HCl humin fractions for non-vegetated and *Phragmites* sediments (personal communication, E.G. Nichols).

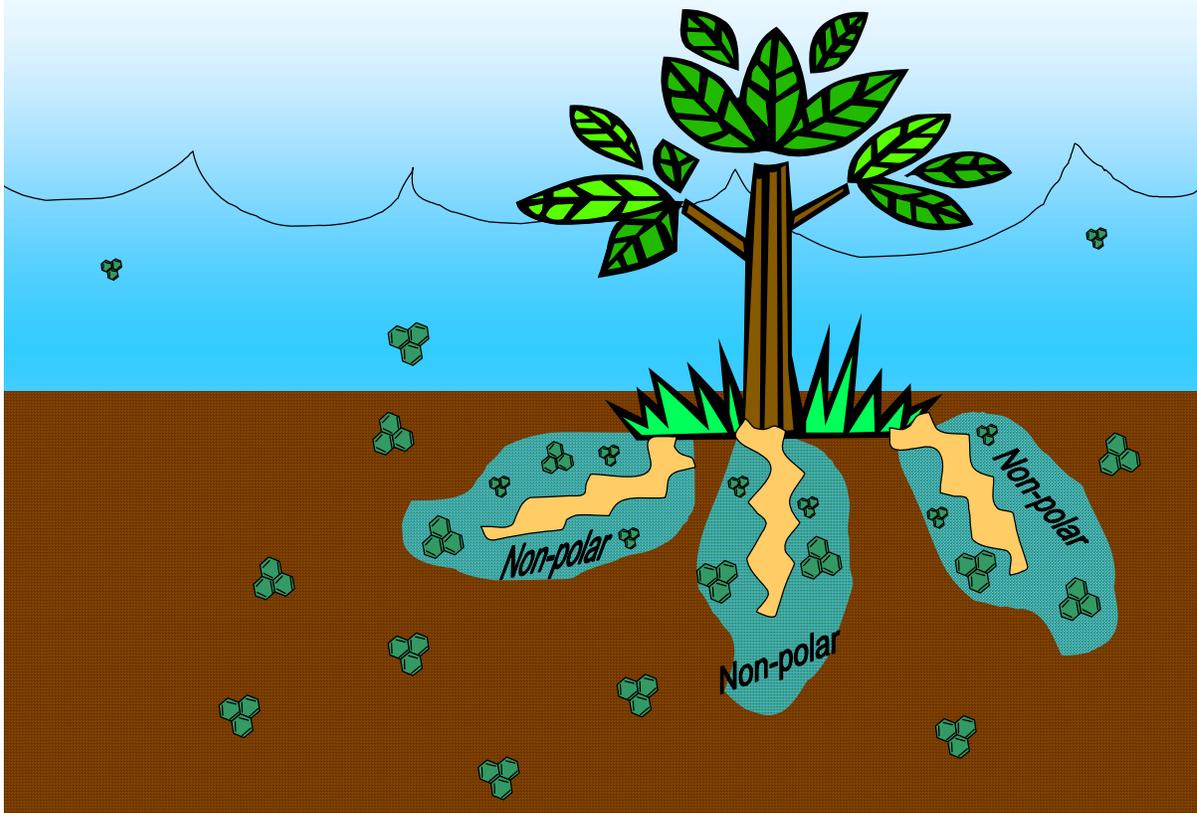


Figure 4-3. Schematic of PAH desorption behavior in vegetated IH sediment. *Phragmites* has been present for 3-4 years. Plant organic matter initially retards PAH bioavailability by making SOM more non-polar due to the presence of aliphatic carbon.

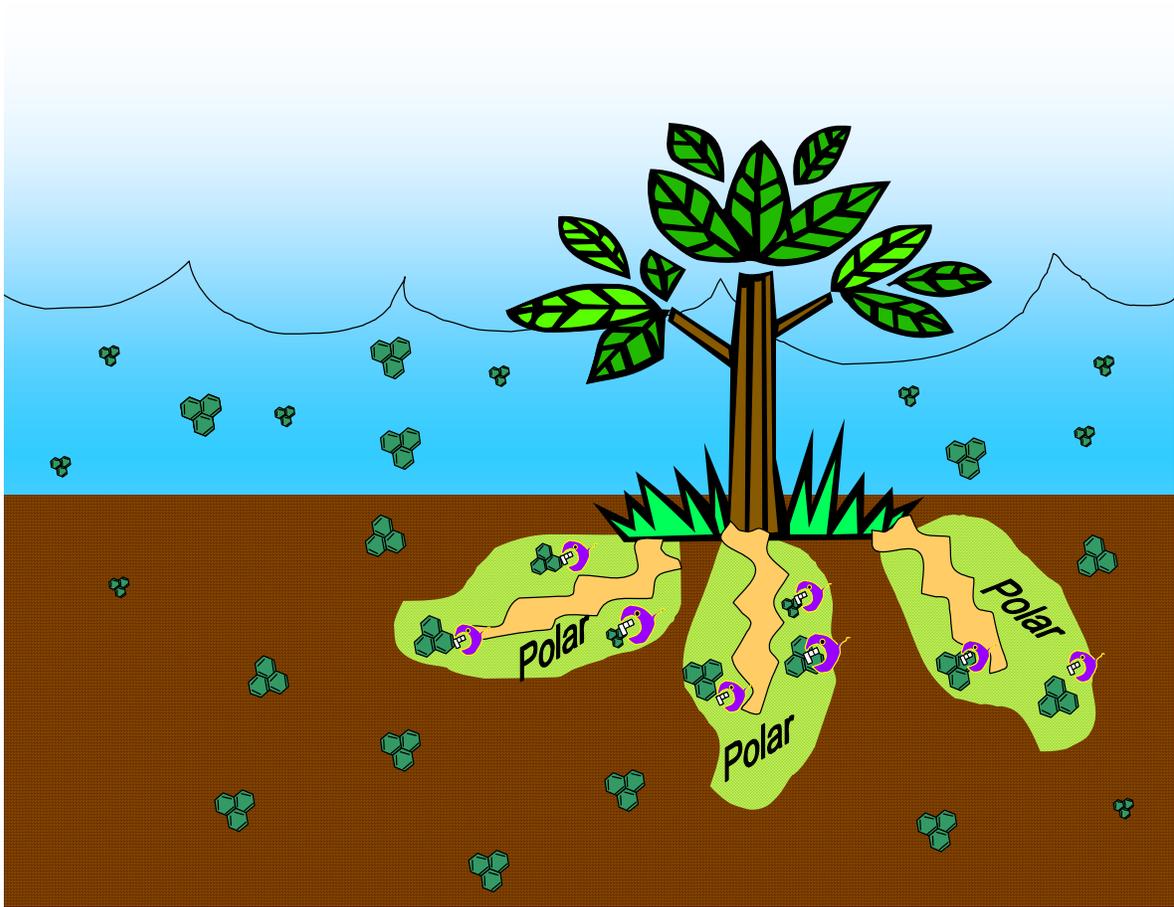


Figure 4-4. Schematic of PAH desorption behavior in vegetated RP sediment. *Phragmites* has been present for over 30 years. Over time, plant organic matter reverses SOM condensation in sediments and increases PAH bioavailability by making SOM more polar. Polarity enhances PAH release while desorbed PAHs are attenuated by the *Phragmites* affiliated microbial community.

Chapter 5 – CONCLUSION

Contaminated sites are fairly common in highly industrialized areas and they pose health risks to both humans and other organisms. Phytoremediation is an effective, relatively inexpensive, and aesthetically pleasing method for reclaiming impacted sites from industrial contaminants, such as PAHs. Studies show that vegetation influences PAH concentrations in soils and sediments; however, the mechanisms by which this occurs are enigmatic. To elucidate these processes, I studied the PAH desorption behavior for vegetated and non-vegetated sediment fractions from two petrogenic-polluted sites. My hypotheses were: 1) if *Phragmites australis* augmented PAH bioavailability, then greater PAH concentrations should desorb from vegetated weathered, petrogenic-polluted compared to non-vegetated weathered, petrogenic-polluted sediments; and that 2) if vegetation enhanced PAH desorption from sediments, then additional vegetative contact should further enhance PAH desorption compared to non-vegetated weathered, petrogenic-polluted sediments.

The exposure of organisms to PAHs occurs when these compounds are released into soil or sediment solution or to the adjacent aqueous environment. The sorption of PAHs to soil or sediment organic matter can reduce PAH bioavailability and mitigate toxic effects. Results from this study show that the introduction of modern organic carbon by *Phragmites australis* initially retards PAH desorption from vegetated compared to non-vegetated sediment fractions by increasing the amount of amorphous aliphatic carbon in vegetated sediment organic matter. Extensive vegetative exposure seems to induce the opposite result as greater PAH desorption occurs in vegetative compared to non-vegetated sediment fractions. As suggested by CPMAS ^{13}C NMR spectra, this observation is likely due to increased polarity and more crystalline aliphatic carbon in vegetated versus non-vegetated

sediment fractions, both of which would contribute to enhanced PAH desorption. Findings also illustrate noticeably lower PAH concentrations in vegetated compared to non-vegetated sediment fractions with extensive vegetative exposure; suggesting that in addition to enhancing PAH desorption, plant introduced modern carbon stimulates microbial activity and thus metabolism or co-metabolism of existing PAHs. These findings are relevant because they suggest that certain vegetation could provide a cost-effective, minimally invasive, in-situ method to attenuate carcinogenic contaminants, such as PAHs, in sediments. However, future work needs to be performed to further clarify the impact of vegetation on the structure of sediment organic matter.

Chapter 6 – FUTURE WORK

Future research is needed to better understand how vegetation alters sediment organic matter (SOM) structure and impacts PAH desorption. While cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance (CPMAS ^{13}C NMR) spectra illustrate the presence of certain functional groups, they do not adequately quantify sediment fraction polarity, which may greatly influence PAH desorption. Both Fourier transform infrared (FTIR) spectroscopy as well as SOM polarity indices can elucidate the impact of SOM polarity on desorption. FTIR spectroscopy enables further scrutiny of SOM and aides in quantifying relative abundance of polar versus non-polar functional groups. SOM fractions could additionally be analyzed for components such as C, H, N, and O, which can be used to ascertain a polarity index $((\text{O}+\text{N})/\text{C})$. This information could be used in tandem with FTIR data to clarify PAH desorption behavior in vegetated petrogenic-polluted sediments.

Additional suggestions for future research include:

- Further examination of Indiana Harbor (IH) sediment fractions. As IH *Phragmites* is relatively immature compared to refinery pit (RP) vegetation, it would be interesting to determine if PAH desorption behavior in IH sediment fractions mirrors that observed in RP sediment fractions as IH vegetation matures. In addition, it could be beneficial to extend IH desorption isotherms beyond 120 days to determine when steady state conditions have been achieved.
- Comparing vegetative influence on PAH desorption behavior in weathered petrogenic-polluted sediments to ascertain if vegetative variety impacts desorption rates and fraction of PAHs desorbing.

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