DIFFERENCES IN PAH DESORPTION AND SEDIMENT ORGANIC MATTER COMPOSITION BETWEEN NON-VEGETATED AND RECENTLY VEGETATED FUEL-OILED SEDIMENTS

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We assessed the desorption behavior of pyrene, chrysene, phenanthrene, and tri-alkylated (C_3) phenanthrene/anthracenes for non-vegetated and recently vegetated (< 2 yrs) fuel-oiled sediments collected from the Indiana Harbor Canal (IHC), Gary, IN. Bulk sediment and humin were analyzed for PAH concentrations, organic matter composition, and PAH desorption behavior. PAH desorption isotherms and kinetics were determined using batch aqueous extractions and a two compartment, first-order kinetic model. Vegetated sediments contained more plant carbon and were more nonpolar and less oxidized than non-vegetated sediments. Desorption kinetics indicated that PAH desorption was primarily controlled by a slow PAH-desorbing fraction (F_2) of IHC sediments. However, in vegetated sediments, particularly humin, PAH release from a faster PAH-desorbing fraction (F_1) increased as did the rates (k_2) of PAH desorption from the dominant slow PAH-desorbing fraction (F_2). We propose that vegetation provides aliphatic, nonpolar carbon to IHC sediments that facilitates more rapid PAH desorption from bulk sediment and humin.

KEY WORDS PAH, sediments, *Phragmites*, desorption, humin

INTRODUCTION

Although many polycyclic aromatic hydrocarbons (PAHs) are toxic, their sorption to sediment organic matter (SOM) can reduce their toxicity and availability for biodegradation. The “bioavailable fraction” is often described as those PAHs that desorb into solution or pore water where they are more accessible for uptake by organisms (Alexander, 2000). The bioavailability of PAHs can be evaluated by examining PAH desorption behavior from sediment organic matter (SOM) using biphasic systems of sediment and water to evaluate the amount of PAH(s) desorbed into water over time (Pignatello, 1990; White and Pignatello, 1999). Desorption behavior is generally assumed to control PAH bioavailability (Kukkonen *et al.*, 2003), bioremediation (Cornelissen *et al.*, 1998), and phytoremediation (Ahn *et al.*, 2005).

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The type of SOM and contaminant residence times in SOM can influence the rate and extent of PAH desorption (White *et al.*, 1997; Johnson *et al.*, 2001). Cornelissen *et al.* (1997b) observed that contaminant desorption 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 emanated from “rubbery” pores within condensed SOM while the very slow desorbing PAHs derived from fixed sites within the glassy matrix of SOM. This concept of different PAH mobility in SOM is based on a polymer dual-mode sorption model whereby two domains, glassy and rubbery, simultaneously exist in SOM (Mao and Schmidt-Rohr, 2006). Predominant mechanisms for sorption in the glassy domain include adsorption and absorption while rubbery domains involve primarily linear partitioning or absorption.

Desorption studies may utilize lab-contaminated or weathered, field-contaminated materials. Evaluating contaminant desorption from field soils or sediments better represents how environmental processes alter contaminant uptake, association, and release (Rockne *et al.*, 2002). Prior studies have observed that sediment characteristics such as porosity, organic matter concentration, and specific surface area can influence the fast and slow diffusion of PAHs from field sediments (Shor *et al.*, 2003). In sediments containing plant detrital materials, porosity and PAH, hydrophobicity were observed to influence PAH diffusion from the rapid-release domains of sediment while specific surface area influenced PAH diffusion from slow-release domains of sediment (Shor *et al.*, 2003).

Specific SOM structures may also influence PAH desorption behavior. Aromatic carbon (Gunasekara and Xing, 2003; Yang *et al.*, 2004), aliphatic carbon (Chefetz *et al.*, 2000; Salloum *et al.*, 2002; Mao *et al.*, 2002), black carbon (Oen *et al.*, 2006; Cornelissen *et al.*, 2005), diagenetically-aged carbon (Johnson *et al.*, 2001; Rockne *et al.*, 2002), and polarity (Rutherford *et al.*, 1992; Kile *et al.*, 1999; Xing *et al.*, 1994) may impart disparate desorption behavior ranging from rapidly desorbing, slow desorbing, very slow desorbing, to desorption resistant fractions of contaminant (Cornelissen *et al.*, 1997b; Shor *et al.*, 2003; Saffron *et al.*, 2006). Diagenetically-aged SOM, such as coke, coals, and kerogen, exhibit slow or resistant PAH desorption behavior due to weathering processes that remove polar functional groups while increasing the condensed, aromatic carbon domains of SOM (Johnson *et al.*, 2001; Gunasekara and Xing, 2003). Less mature geosorbents may slow or enhance PAH desorption due to either rigid, crystalline (glassy) or more amorphous, mobile (rubbery) aliphatic carbon domains, respectively (Gunasekara and Xing, 2003; Oren and Chefetz, 2005; Chen and Xing, 2005; Salloum *et al.*, 2002). The presence or absence of polar functional groups within SOM domains appears to correlate with faster and slower PAH desorption behavior, respectively (Chen *et al.*, 2005).

This study assessed PAH desorption behavior from heavily contaminated fuel-oiled near shore sediments collected from the Indiana Harbor Canal (IHC), Gary, IN. IHC sediments were either not vegetated or recently colonized by *Phragmites australis*, the common reed plant (<2 yrs). We evaluated the organic matter composition of IHC sediment fractions and determined PAH desorption isotherms for pyrene, phenanthrene, chrysene, and C₃-phenanthrene/anthracenes. The amount and extent of PAH desorption and PAH desorption kinetics were assessed in light of differences between vegetated and non-vegetated sediment organic matter composition. We hypothesized that vegetation

would alter sediment organic matter composition and PAH desorption behavior relative to non-vegetated sediment fractions.

MATERIALS AND METHODS

Sediment Sampling, Fractionation, and Characterization

The Indiana Harbor Canal (IHC) is a heavily industrialized area with historic petroleum contamination of soils and sediments. Diesel fuel is the dominant contaminant source at the site and a petroleum sheen persists in canal waters (Sand Creek Consultants, Inc., 2002). Total petroleum hydrocarbon (TPH) concentrations range from 2% to 43% of sediment mass. Disturbance of the site in 2002 resulted in colonization by *Phragmites australis*, the common reed plant.

Sediment samples were collected by removing approximately 10 cm of sediment by hand trowel or shovel within a 2-m-diameter circle of vegetated or non-vegetated sediments. Sediment samples were collected at 6 to 9 locations for each plant species and 3 locations of non-vegetated sediments. Non-vegetated sediments were composited at the site prior to storage and transport. In vegetated areas, plant litter and debris were removed from the sediment surface after which sediments with plants roots were removed *in toto*. Visible plant roots and plant material were removed from sediments prior to mixing sediments together for each plant species. Sediments were transported in plastic bags at 0°C. Prior to chemical fractionation and analyses, small visual root residuals were removed, and sediments were sieved (2mm) and homogenized again in ceramic bowls.

The original composite sediments samples are referred to as bulk sediment fractions. Aliquots of bulk sediments (10–15 g) were freeze-dried then chemically fractionated to obtain de-ashed humin fractions according to previously described methods in Gregory *et al.*, (2005, 2008). Briefly, sediments were lipid-extracted twice then extracted with sodium hydroxide under a nitrogen headspace to remove humic and fulvic acids. Humin was de-ashed using hydrochloric acid (HCl) and hydrofluoric acid (HF). To evaluate our fractionation and extraction procedures, diluted Alaskan north slope crude oil (ANS) was spiked with deuterated chrysene (CHY-d₁₂, 3.5 µg/mL) and added to a soil with no known petrogenic contamination. Recovery was 100% (Gregory *et al.*, 2005). Humin represents the sediment organic matrix after extraction with dichloromethane (DCM) and alkaline salts to remove lipids and humic/fulvic acids, respectively. De-ashed humin represents humin after extraction with HF/HCl to remove the mineral matrix.

Bulk sediment and de-ashed humin fractions were analyzed for black carbon (BC) content by acidification of freeze-dried samples with 1.2 M hydrogen chloride vapor then thermal oxidation at 375°C for 24 hours followed by total organic carbon measurement (Gelinas *et al.*, 2001; Wakeham *et al.*, 2004). Elemental analyses of carbon, hydrogen, nitrogen, and oxygen were determined by high-temperature combustion and/or pyrolysis techniques on a ConFlo III Elemental Analyzer (Thermo Electron North America LLC, West Palm Beach, FL). One sediment fraction and a set of duplicate sediment fractions, making up 25% of samples analyzed, were sent to Huffman Labs (Golden, CO) for quality assurance and quality control. Standard methods ASTM D-4129 (C and H), ASTM D-5373 (N), and ASTM D-5622 (O) were used. Percent relative standard deviation (RSD) was within 10% for samples analyzed.

Desorption experiments. Desorption experiments used an aqueous batch technique that was adapted from Cornelissen *et al.* (1997a). Three replicate PAH desorption

measurements were taken at seven time points over a 120-day period. A mixture of sediment (≈ 5 g dry weight), mercuric chloride (HgCl_2 ; biocide, 2 g/L), and distilled, deionized water was added to 50 mL Teflon Oak Ridge centrifuge tubes. Samples were capped, sealed with TeflonTM tape, and allowed to shake for time periods ranging from 24 hours to 120 days at $20 \pm 2^\circ\text{C}$.

At each designated time point, samples were removed from the shaker table and centrifuged for 20 minutes at 2500 rpm. The aqueous portion (~ 35 mL) was decanted into a new 50 mL TeflonTM Oak Ridge tube and allowed to sit for 24 hours. The aqueous phase of each sample was replaced with a fresh aliquot of 40 mL of HgCl_2 solution and shaken until the next time point. An aliquot of the decanted aqueous phase was removed with a 10 mL pipette, transferred to another 50 mL TeflonTM Oak Ridge centrifuge tube, and extracted with 5 mL of dichloromethane (DCM); the DCM layer was removed and transferred to a 40 mL amber EPA vial with anhydrous sodium sulfate (Na_2SO_4) to remove any residual water. DCM extracts were evaporated under a gentle stream of N_2 gas to approximately 1 mL and transferred to a gas chromatography/mass spectrometry (GC/MS) vial using a 500 μL syringe. Sample volumes were adjusted to 1 mL, sealed, and stored at 0°C until GC/MS analysis. DCM extracts of bulk sediment and de-ashed humin were first loaded onto neutral activated alumina columns prior to analysis by GC/MS. DCM extracts of sediments were concentrated to 5 mL.

GC/MS SIM. Both DCM extracts of sediments and aqueous desorption samples were spiked with deuterated phenanthrene (d_{10} , 500 ng/mL) and benzo[*a*]pyrene (d_8 , 505 ng/mL) as internal standards prior to GC/MS analysis. Extracts were analyzed for 42 PAHs using a modified method of EPA 8270 (USEPA, 1986) as described in Luellen and Shea (2002). GC/MS select ion monitoring (SIM) mode analyses were conducted on a HP5890 Series II GC equipped with electronic pressure control connected to an HP5970 or HP5972 MSD using a Restek 30 m $\times$ 0.25 mm Rtx-5 (film thickness 0.25 μm) MS w/Integra-Guard column.

Data analysis. Desorption from sediment can be described by the following two compartment, first-order kinetic model shown in Equation 1 (Oen *et al.*, 2006; Cornelissen *et al.*, 1997b and 1998):

$$\frac{S_t}{S_0} = F_1 e^{-k_1 \cdot t} + F_2 e^{-k_2 \cdot t} \quad (1)$$

S_t and S_0 are the observed sediment-sorbed amounts at time t (days) and at the start of the experiment. F_1 and F_2 represent two kinetically different desorbing fractions of the contaminant present in the sediment. F_1 represents a faster PAH-desorbing fraction in sediment, and F_2 represents a second, slower PAH desorbing fraction. The first-order rate constants for F_1 and F_2 are noted as k_1 and k_2 (days^{-1}). Because PAHs should desorb from the F_1 fraction at a faster rate (k_1) than their rate of desorption (k_2) from the slower F_2 fraction, one assumption of the model is that $k_1 \gg k_2$. The model was fitted to observed PAH desorption data to estimate rate constants (k_1 , k_2) and desorbing compartments (F_1 and F_2) by minimizing the cumulative squared residuals between observed and calculated values of $\ln(S_t/S_0)$ in Equation 1 under the boundary condition that $F_1 + F_2 = 1$. The best-fit adjustable parameter values were found using the solver function in Microsoft Excel[®] 7.0 (Denton, 2000).

Concentrations of select PAHs between vegetated (*Phragmites australis*) and non-vegetated sediment fractions (Table 1) were compared to determine if vegetation

Table 1 Individual PAH concentrations ($\mu\text{g/g}$ sediment) for fuel-oiled sediments at Indiana Harbor Canal, Gary, IN

	Indiana Harbor Canal (IHC)			
	Bulk sediment		De-ashed humin	
	Non-vegetated	<i>Phragmites</i>	Non-vegetated	<i>Phragmites</i>
Phenanthrene ^a	8.2 $\pm$ 0.51	7.2 $\pm$ 0.58	0.10 $\pm$ 0.002 ^B	0.15 $\pm$ 0.011 ^B
Pyrene ^a	457 $\pm$ 36.7 ^A	361 $\pm$ 23.6 ^A	0.42 $\pm$ 0.014 ^B	0.2 $\pm$ 0.002 ^B
Chrysene ^a	229 $\pm$ 33.9	205 $\pm$ 15.7	0.09 $\pm$ 0.01 ^B	0.47 $\pm$ 0.087 ^B
C ₃ -Phen/anth ^{a,b}	346 $\pm$ 27.2 ^A	229 $\pm$ 19.07 ^A	0.12 $\pm$ 0.01	0.12 $\pm$ 0.01

^aValues are means ($n = 3$) $\pm$ one standard deviation.

^bC₃-phenanthrene/anthracenes

^A denotes mean values that are significantly different [Student *t*-test ($p < 0.05$)] between non-vegetated and *Phragmites* bulk sediments.

^BDenotes mean values that are significantly different [Student *t*-test ($p < 0.05$)] between non-vegetated and *Phragmites* de-ashed humin.

significantly altered PAH concentrations in sediments. 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. Correlations between individual PAH concentrations and the distribution ratios between (F_2/F_1) were determined by linear regression.

RESULTS AND DISCUSSION

PAH Concentrations and Sediment Organic Matter Composition

We evaluated phenanthrene, pyrene, and chrysene desorption behavior and kinetics so that results could be compared to other published PAH desorption data for field-contaminated sediments. We included C₃-phenanthrenes/anthracenes in this study because petrogenic PAH sources, such as petroleum, contain alkylated PAHs that are not often studied for their toxicity, fate, and transport. Alkylated PAHs are useful indicators of PAH attenuation and weathering (Gregory *et al.*, 2005) and are certainly present at phytoremediation sites contaminated with petroleum wastes.

Of the four PAHs evaluated in this desorption study (Table 1), only pyrene had lower mean concentrations in both vegetated bulk and humin fractions relative to non-vegetated sediment fractions (Student *t* test, $p < 0.05$). Phenanthrene and chrysene concentrations were similar for bulk sediment fractions but significantly higher for vegetated humin. Mean C₃-phenanthrenes/anthracenes concentrations were significantly lower in vegetated bulk sediments but similar for both vegetated and non-vegetated humin (Table 1; Student *t* test, $p < 0.05$).

The same sediments used for this desorption study were also characterized by Gregory *et al.* (2008). We previously reported total PAH concentrations of 42 alkylated and non-alkylated PAHs for the same IHC sediment fractions (Gregory and Nichols, 2008). Overall, *Phragmites* bulk sediment fractions had lower mean concentrations of TPAH than non-vegetated bulk sediments; whereas, total PAH concentrations in humin fractions were similar.

Table 2 Percent organic carbon (OC), percent modern carbon (MC)^b, percent black carbon (BC), elemental analyses, atomic ratios, and polarity index for fuel-oiled sediments at Indiana Harbor Canal, Gary, IN

	Indiana Harbor Canal (IHC)			
	Bulk sediment		De-ashed humin	
	Non-vegetated	<i>Phragmites</i>	Non-vegetated	<i>Phragmites</i>
% Organic C ^{a,c}	14 ± 0.96	13 ± 0.14	4.6 ± 0.31 ^B	3.7 ± 0.12 ^B
% Modern C ^{a,c}	8.2 ± 0.075 ^A	21 ± 0.11 ^A	4.4 ± 0.073 ^B	8.2 ± 0.075 ^B
% C ^a	17 ± 0.17	16 ± 0.51	0.97 ± 0.028 ^B	0.31 ± 0.0035 ^B
% H ^a	2.5 ± 0.0079 ^A	2.0 ± 0.086 ^A	0.10 ± 0.01 ^B	0.06 ± 0.01 ^B
% N ^a	0.18 ± 0.003 ^A	0.21 ± 0.001 ^A	0.02 ± 0.001 ^B	0.01 ± 0.001 ^B
% O	5.1 ± 0.29 ^{a,A}	2.8 ± 0.026 ^{a,A}	1.2 ± 0.24 ^b	0.29 ± 0.021 ^b
H/C ^a	0.14 ± 0.002 ^A	0.13 ± 0.001 ^A	0.08 ± 0.023 ^B	0.17 ± 0.009 ^B
O/C	0.29 ± 0.009 ^{a,A}	0.17 ± 0.004 ^{a,A}	1.2 ± 0.22 ^b	0.93 ± 0.063 ^b
Polarity index ^b PI = (O+N)/C	0.30 ± 0.01	0.19 ± 0.004	1.5 ± 0.19	0.92 ± 0.06
% BC ^{a,d}	17 ± 3.0	21 ± 2.9	7.1 ± 1.3 ^B	4.5 ± 0.31 ^B

^aValues are means of triplicates ± one standard deviation;^bValues are means of duplicates ± one standard deviation;^cGregory *et al.*, 2008; and^d% black carbon of total organic carbon; organic carbon after heating (375 C, 24 h).^ADenotes mean values that are significantly different [Student *t*-test (*p* < 0.05)] between non-vegetated and *Phragmites* bulk sediments.^BDenotes mean values that are significantly different [Student *t*-test (*p* < 0.05)] between non-vegetated and *Phragmites* de-ashed humin.

We also previously reported differences in the organic matter composition (modern carbon and percent organic carbon) between vegetated and non-vegetated IHC sediments in Gregory *et al.* 2008 and have provided those data in Table 2 as they are relevant to interpretation of PAH desorption behavior. *Phragmites* IHC sediment contained more modern carbon, or plant-derived carbon, than non-vegetated IHC sediment fractions. Natural abundance radiocarbon carbon measurements determine the amount of ¹⁴C present in a sample to “age date” or “carbon-date” a particular material. Modern plants fix ¹⁴CO₂ from the atmosphere and, therefore, have a modern ¹⁴C signature as do their consumers. Petroleum, derived from ancient plants, is old and no longer contains ¹⁴C-photosynthate due to radioactive decay; thus, petroleum products have 0% modern carbon content in contrast to modern plants (100%). This relationship can be exploited at sites with significant petrogenic contamination and vegetation to evaluate how much plant carbon (modern carbon) is present in contaminated media (Gregory *et al.*, 2005).

We were surprised to observe significant increases of plant carbon in vegetated IHC sediment and humin after only two years of *Phragmites* growth. In contrast, total organic carbon (% OC) did not change or was actually lower in *Phragmites* sediments than non-vegetated sediments (Gregory *et al.*, 2008; see Table 2). Increased plant carbon content with negative or similar organic carbon content suggests increased biogenic carbon turnover, or humification, in vegetated sediment fractions. As plant organic matter undergoes humification and diagenesis, H/C and O/C atomic ratios decline as SOM is biologically processed, physically condensed, and chemically reduced (Johnson *et al.*, 2001; Yang *et al.*, 2004). O/C and H/C ratios were lower for vegetated bulk sediments

(Table 2), which indicates that vegetated bulk sediments were less oxidized, more reduced, and more “humified” than non-vegetated bulk sediments. Vegetated humin was also less oxidized (O/C) than non-vegetated humin but also less reduced (H/C). These mixed results are not unexpected given that aliphatic carbon, such as plant and microbial lipids, are preserved in humin via humification processes (Salloom *et al.*, 2002).

Elemental analyses can be used to describe the degree of SOM condensation and to evaluate the polarity of vegetated and non-vegetated sediment fractions (Huang and Weber, 1997; Mao *et al.*, 2002; Kang and Xing, 2005). Elemental data in Table 2 was used to calculate a polarity index (PI) that is the weight ratio of O + N to C (Rutherford *et al.*, 1992; Xing *et al.*, 1994). Polarity indices were lower for vegetated fractions than non-vegetated fractions and indicate that *Phragmites* sediment and humin were more nonpolar than non-vegetated sediment and humin.

Black carbon generally has low atomic ratios and low polarity and is an important component of SOM that influences PAH desorption and bioavailability (Corneillesen *et al.*, 2005). Black carbon may comprise 1 to 20% (median of 9%) of the total organic carbon present in sediment (Corneillesen *et al.*, 2005). BC content was similar between vegetated and non-vegetated bulk sediment fractions, but BC content was greater for non-vegetated humin than *Phragmites* humin (Table 2). BC content of bulk sediments (17–21%) was two to three times greater than BC content of humin fractions (4–7%) which may explain why bulk sediment fractions were more nonpolar and reduced than humin fractions. However, greater BC content of non-vegetated sediment fractions does not explain increased atomic ratios and polarity indices for non-vegetated sediments relative to vegetated sediment fractions.

Phragmites australis is known to translocate oxygen and a significant portion of its photosynthate carbon to sediments via its roots (Minchinton, 2002), and we observed more plant carbon in vegetated IHC sediment (Gregory *et al.*, 2008). Fifty percent of *Phragmites* litter becomes substrate material for soils and sediments (Asaeda *et al.*, 2002), and this material would be more polar and oxidized than weathered fuel-oil. We also observed that *Phragmites* bulk sediments contained more weathered PAHs than non-vegetated bulk sediments (Gregory *et al.*, 2008) which should contribute more oxidized and polar PAH metabolites to the SOM matrix. Thus, we anticipated that vegetated SOM composition would be more polar and oxidized than non-vegetated SOM and were surprised that elemental data and atomic ratios indicated otherwise. Vegetated SOM was actually less oxidized and more nonpolar than non-vegetated SOM.

Recently, Cofield *et al.* (2007) evaluated the effect of vegetation on manufactured, gas plant soil hydrophobicity and observed that vegetated, manufactured gas plant soils were more hydrophobic (nonpolar) than unplanted soils after one year of phytoremediation. Their research indicated that plant residues and microbially-derived lipids were the primary factors controlling soil hydrophobicity not contamination (Cofield *et al.*, 2007, references therein). Their findings suggest that more reduced and nonpolar *Phragmites* IHC sediment reflect *Phragmites* carbon influx, plant carbon turnover, and associated rhizosphere microbial activity.

What, then, are the potential impacts of more nonpolar OM matrices on PAH attenuation and desorption? Generally, more reduced, nonpolar OM strongly sorbs PAHs, slows PAH desorption, and reduces PAH bioavailability (Huang and Weber, 1997; Johnson *et al.*, 2001; Wang *et al.*, 2005). However, we and Cofield *et al.* (2007) observed significant attenuation of PAHs in more nonpolar, vegetated contaminated SOM relative to more polar, non-vegetated SOM controls. Greater PAH weathering and reductions in PAH

Table 3 Mass amounts and percent PAH desorbed from bulk sediment and humin fractions of non-vegetated and vegetated IHC sediments

	Non-vegetated		<i>Phragmites</i>	
	Total desorbed (ng/g)	% Total PAH	Total desorbed (ng/g)	% Total PAH
Bulk sediments				
Phen ^a	17 ± 0.15	0.20 ± 0.0019	17 ± 0.29	0.24 ± 0.0040
Pyrene ^a	74 ± 11 ^A	0.02 ± 0.002	40 ± 3.4 ^A	0.01 ± 0.001
Chy ^a	28 ± 3.2 ^A	0.01 ± 0.001	6.5 ± 0.45 ^A	0.003 ± 0.0002
C ₃ -Phen ^{a,b}	42 ± 4.1 ^A	0.01 ± 0.001 ^A	20 ± 2.0 ^A	0.01 ± 0.001 ^A
De-ashed humin				
Phen ^a	23 ± 1.8	22 ± 1.7	26 ± 0.46	17 ± 0.31
Pyrene ^a	7.0 ± 0.41	1.7 ± 0.10	7.9 ± 0.29	3.9 ± 0.14
Chy ^a	3.2 ± 0.35	3.6 ± 0.39	2.6 ± 0.44	0.6 ± 0.09
C ₃ -Phen ^{a,b}	7.6 ± 0.79	6.4 ± 0.66	7.2 ± 0.76	5.9 ± 0.63

% Total PAH refers to the amount of each individual PAH desorbed divided by the its total extractable concentration in that sediment fraction.

^aValues are means (n = 3) ± one standard deviation.

^bC₃-phenanthrene/anthracenes.

^ADenotes mean values that are significantly different [Student *t*-test (*p* < 0.05)] between non-vegetated and *Phragmites* bulk sediments.

concentrations for vegetated sediments suggest enhanced PAH release from vegetated sediments relative to non-vegetated sediments.

PAH desorption. To normalize PAH desorption data to PAH concentrations in sediments, we determined the percent PAH desorbed which is defined as the total cumulative PAH desorbed in 120 days divided by the total sediment PAH concentration. Consistent trends among all PAHS were not observed. C₃-phenanthrene desorbed similar percentages for vegetated and non-vegetated sediment fractions (Table 3; Student *t* test, *p* < 0.05). Percent chrysene desorbed was greater for non-vegetated bulk sediment and humin fractions. Percent pyrene desorption was greater for non-vegetated bulk sediments and vegetated humin, and percent phenanthrene desorption was greater for *Phragmites* bulk sediment and non-vegetated humin.

Total PAH desorbed was less than 0.24% for bulk sediments and between 0.6 and 22% for humin fractions. Other studies have observed PAH desorption from 1 to 90% for field-contaminated sediments (Oen *et al.*, 2006). Differences in desorption behavior among different sediments can also be attributed to organic matter composition, sources of PAH contamination, and the extent of weathering (Shor *et al.*, 2003; Oen *et al.*, 2006).

A greater percent of PAH desorbed from humin fractions than bulk sediment fractions. Results also show that more phenanthrene desorbed (% desorbed) from bulk sediment and humin than the other PAHs (Table 3). Other studies have observed that more hydrophilic PAHs desorb less than more hydrophobic PAHs due to the release or degradation of lower molecular weight PAHs in highly weathered sediments (Oen *et al.*, 2006; Shor *et al.*, 2003). Phenanthrene desorption did not follow this trend which would suggest that IHC fuel-oiled sediments retain a significant, non-weathered fuel-oil fraction.

Desorption rate constants and desorbing fractions. To better evaluate differences in rates of PAH desorption between vegetated and non-vegetated sediment

fractions, rate constants for PAH desorption from fast and slow PAH desorbing-sediment compartments were calculated using Equation 1. The observed fractional desorption data for bulk sediments (Figure 1) and humin (Figure 2) of each PAH show a change in slope that indicates a more rapid then slower phase of PAH release over time. Biphasic desorption isotherms are commonly observed for PAH desorption from field-contaminated sediments.

The solid data points in Figures 1 and 2 represent means of observed desorption measurements ($n = 3$; $\pm$ one standard deviation) at specific time points over 120 days. Lines were obtained by exponential curve fitting and represent calculated values using the empirical, first-order, two-compartment model described in equation 1. Fitting the observed data to Equation 1 provides rate constants (k_1 , k_2) and the faster (F_1) and slower (F_2) PAH desorbing- fractions in the sediment.

Time, weathering, and sorption to organic matter reduce PAH bioavailability; hence, PAH desorption is primarily controlled by the slower desorbing PAH fraction (F_2) in weathered, field-contaminated sediments. The F_2 fraction is typically quite large (0.997) relative to the faster desorbing fraction, F_1 (0.0032), in field sediments, and PAH release from the F_2 fraction is much slower (10^{-4} /day; k_2) than from the F_1 fraction (10^{-0} /day; k_1). Larger F_1 fractions suggest more PAH release from sediment. Faster PAH release from either F_1 or F_2 fractions would be evident by increases in their respective rate constants, (k_1 , k_2). If vegetation increases PAH desorption from IHC sediments, then values of F_1 , its rate constant (k_1), and the rate constant of F_2 (k_2) should also increase. For purposes of clarity, we show only the relative size of the faster desorbing PAH fractions (F_1) in vegetated and non-vegetated sediments in Table 4. The slower desorbing sediment compartment (F_2) can be readily determined by $F_2 = 1 - F_1$.

Larger F_1 values were generally observed more for vegetated fractions than their respective non-vegetated fractions (Table 4). F_1 values in vegetated bulk sediment were greater for all PAHs except phenanthrene, and F_1 values in vegetated humin were greater for all PAHs except C₃-phenanthrenes. Both vegetated and non-vegetated humin appear to contain a larger F_1 fraction than their respective bulk sediments. F_1 values for humin were greater than bulk sediment F_1 values for all PAHs; hence, a greater percent of each PAH was released from humin than bulk sediment as summarized in Table 3.

The rate of PAH release (k_1) from F_1 fractions did not differ between vegetated and non-vegetated bulk sediments, and F_1 desorption rate constants (k_1) were on the order of 10^{-1} /day (Table 4). Thus, vegetated bulk sediments had greater F_1 fractions but the same PAH release rates as non-vegetated bulk sediments. The rate of PAH release (k_2) from F_2 , the fraction that primarily controls PAH desorption, was greater in vegetated bulk sediments.

For humin fractions, phenanthrene and chrysene k_1 values were greater in non-vegetated humin while pyrene and C₃-phenanthrenes k_1 values were greater in vegetated humin (Table 4). As observed in bulk sediments, the rate of PAH release (k_2) from F_2 was greater in vegetated humin. F_1 desorption rate constants (k_1) were on the order of 10^0 to 10^{-2} /day for humin fractions and were more variable than bulk sediment values. F_2 desorption rate constants (k_2) were on the order of 10^{-4} to 10^{-5} /day and often 5 to 10 times greater than bulk sediment values.

As expected, F_2 desorption rate constants (k_2) of 10^{-4} to 10^{-5} /day were much lower F_1 desorption rate constants (k_1). IHC (k_2) rate constants were lower than other published values (10^{-3} /day) (Kan *et al.*, 2000). Translating our data to compare to other published rate constants (h^{-1}) yielded rate constants for bulk sediments that ranged from 10^{-2} /h for

Figure 1 Desorption of PAHs from vegetated ($\blacksquare$, *Phragmites*) and non-vegetated ($\blacktriangle$) bulk sediments. Observed values are means of triplicates $\pm$ one standard deviation. Lines were obtained by exponential curve fitting to the two compartment first-order kinetic model (Equation 1). Estimated rate constants and desorbing fractions for observed values are presented in Table 4.

Figure 2 Desorption of PAHs from vegetated (■, *Phragmites*) and non-vegetated (▲) de-ashed humin. Observed values are means of triplicates $\pm$ one standard deviation. Lines were obtained by exponential curve fitting to the two compartment first-order kinetic model (Equation 1). Estimated rate constants and desorbing fractions for observed values are presented in Table 4.

Table 4 Desorption rate parameters for Four PAHs in sediment fractions from non-vegetated and *phragmites* sediment fractions at Indiana Harbor Canal, Gary, IN

Indiana Harbor Canal (IHC)											
Bulk sediment						De-ashed humin					
Non-vegetated			<i>Phragmites</i>			Non-vegetated			<i>Phragmites</i>		
F_1 (10^{-3})	k_1 d^{-1}	k_2 ($10^{-4}/d$)	F_1 (10^{-3})	k_1 d^{-1}	k_2 ($10^{-4}/d$)	F_1 (10^{-3})	k_1 d^{-1}	k_2 ($10^{-4}/d$)	F_1 (10^{-3})	k_1 d^{-1}	k_2 ($10^{-4}/d$)
Phen	3.2	0.76	1.1	2.9	0.76	1.2	1.5	6.5	45	0.07	8.9
Pyrene	3.5	0.76	0.76	12	0.76	1.2	0.35	1.1	17	1.9	2.1
Chy	1.1	0.76	0.42	3.0	0.76	0.12	2.1	0.85	3.9	1.1	1.0
C ₃ -Phen ^a	0.58	0.76	0.46	1.9	0.76	0.53	0.04	3.0	3.2	2.0	5.2

^aC₃-phenanthrene/anthracenes. F_1 denotes the a more rapidly desorbing PAH fraction in sediment. A boundary condition of the model is that $F_1 + F_2 = 1$. k_1 & k_2 denote rate constants for PAH desorption from the faster (F_1) and slower (F_2) PAH-desorbing fractions.

k_1 and $10^{-6}/\text{h}$ to $10^{-5}/\text{h}$ for k_2 . PAH desorbing fractions in natural sediments can have average rate constants that range from 10^{-1} to $10^{-0}/\text{h}$ for “fast”, 10^{-3} to $10^{-2}/\text{h}$ for “slow,” and 10^{-5} to $10^{-4}/\text{h}$ for “very slow” (Johnson *et al.*, 2001; Jonker *et al.*, 2005; Oen *et al.*, 2006). Comparison of our observed rate constants to literature values suggest that PAH release is controlled by both a “slow” (F_1) and “very slow” (F_2) desorbing PAH fraction, but that the “very slow” (F_2) fraction primarily controls PAH release. “Fast” desorbing PAH fractions are no longer present. However, the rate of PAH desorption from the “very slow,” controlling F_2 fraction was greater in vegetated bulk sediment and, particularly, vegetated humin fractions than non-vegetated bulk and humin fractions.

We regressed individual PAH concentrations to their respective desorbing fractions, $\text{Log}(F_2/F_1)$, to evaluate if PAH concentrations were associated with PAH kinetics (Oen *et al.*, 2006). For bulk sediments, desorption was not associated with PAH concentrations ($r^2 < 0.001$). For humin, faster desorption behavior was weakly associated with increased PAH concentrations ($r^2 = 0.43$). Oen *et al.* (2006) observed no correlation ($r^2 < 0.02$) to weak correlations ($r^2 < 0.29$; $p < 0.01$) between PAH desorption kinetics and PAH concentrations in sediments. Prior studies also observed that the quantity of organic matter is a poor predictor for desorption (Shor *et al.*, 2003; Oen *et al.*, 2006; Kukkonen *et al.*, 2003, Cornelissen *et al.*, 2005) relative to other sediment characteristics. Significant correlations have been observed between desorption and either particle size or the black carbon content of sediments (Cornelissen *et al.*, 2005), but similar BC content between vegetated and non-vegetated sediment fractions do not explain their observed differences in PAH desorption.

Shor *et al.* (2003) observed that PAHs rapidly diffused through sediment fractions rich in vascular plant debris, and Kukkonen *et al.* (2003) observed that the size of the faster desorption compartment (F_1) was directly related to the amount of plant pigment per amount of organic carbon. Li *et al.* (2005) also observed that indigenous microorganisms facilitate increased PAH desorption which is of interest to this study given the “rhizosphere effect” of plants on microbial abundance and activity. We observed that vegetated IHC sediments contained more plant carbon and increased PAH desorption kinetics even though these sediments were more reduced, non polar, and less oxidized than non-vegetated fractions. We propose that nonpolar, plant-derived carbon released into IHC sediments altered PAH desorption behavior and increased PAH desorption kinetics.

Plant-derived *aliphatic* carbon materials are integral and persistent components of SOM, particularly humin, and are preserved in soils and sediments through humification (Salloum *et al.*, 2002). These materials have large sorptive affinities for PAHs (Chefetz *et al.*, 2000; Salloum *et al.*, 2002) that are correlated to their polymethylene-rich (nonpolar) content (Mao *et al.*, 2002). Aliphatic plant carbon is thought to represent “rubbery mobile” domains of SOM into which PAHs can partition (Mao and Schmidt-Rohr, 2006). We postulate that these plant-derived aliphatic domains more rapidly sorb and desorb PAHs relative to other SOM domains present in sediment. Accordingly, the presence of these plant materials increased the faster-desorbing PAH fraction (F_1) as well as PAH desorption kinetics (k_2) from the dominant slower desorbing PAH fraction (F_2) in IHC bulk sediment and humin.

CONCLUSION

This study emphasizes the broader chemical and physical impact of plant organic matter on contaminated organic matter composition and PAH bioavailability. We

hypothesized that plant carbon released into IHC sediments would alter PAH desorption behavior. This study examined whether this process can occur after only a few years of plant growth. After two years of *Phragmites* growth in fuel-oiled sediments, vegetated sediment fractions were more reduced and non polar than non-vegetated sediments, yet PAH ratios were more weathered and PAH desorption kinetics were faster, particularly for vegetated humin. Other studies have observed that plant materials can increase soil hydrophobicity yet still enhance PAH dissipation (Cofield *et al.* 2007).

Our findings suggest that aliphatic plant carbon contributes nonpolar “rubbery” domains to IHC sediments that facilitate more rapid PAH desorption kinetics (Kukkonen *et al.*, 2003; Mao and Schmidt-Rohr, 2006). This study highlights that other indices, such as overall carbon transfer from plant to soils/sediments and desorption kinetics, may indicate initial changes to organic contamination attenuation when concentration data shows little change. Rapid characterization, such as a 24 h desorbed fraction of PAHs (Shor *et al.*, 2003), may be useful indices to assess the early phases of phytoremediation.

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