Distributed Sequestration and Release of PAHs in Weathered Sediment: The Role of Sediment Structure and Organic Carbon Properties

KARL J. ROCKNE,[†] LESLIE M. SHOR,[‡] L. Y. YOUNG,[§] GARY L. TAGHON,[#] AND DAVID S. KOSSON*,[‡]

Department of Civil and Materials Engineering, University of Illinois—Chicago, Chicago, Illinois 60607-7023, Department of Civil and Environmental Engineering, Vanderbilt University, Nashville, Tennessee 37235, and Biotechnology Center for Agriculture and the Environment and Institute of Marine and Coastal Sciences, Rutgers, The State University of New Jersey, New Brunswick, New Jersey 08901

Polycyclic aromatic hydrocarbon (PAH) contaminated sediments from Piles Creek (PC) and Newtown Creek (NC) in the NY/NJ Harbor estuary were separated into size fractions and further separated into low (<1.7 g cm^{-3}) and high (>1.7 g cm^{-3}) density fractions. The fractionated sediments were characterized for carbon content, pore structure, surface area, and PAH concentration. Most PAHs (50−80%) in both sediments were associated with the low-density fraction, which represents only 3−15% of total sediment mass, at levels greater than expected based on equilibrium partitioning. PC low-density sediment had 10 times greater organic carbon-normalized equilibrium partitioning coefficients (K_{oc}) than the other size fractions and whole sediment. Characterization of the sediment organic matter suggested that the preferential sequestration observed in PC sediment was not correlated with soot carbon but was likely due to the presence of detrital plant debris, an important food source for benthic animals. Fractional PAH desorption from whole PC sediment was significantly higher than from NC sediment after 3 months. For both sediments, a smaller percentage of the total PAHs was desorbed from the low-density fraction. However, because PAH concentrations were greatly elevated in these fractions, more PAH mass was desorbed than from the corresponding bulk and high-density fractions. These results demonstrate that PAHs are preferentially sequestered in a separable, low-density fraction at levels not predictable by equilibrium partitioning theory. Further, the low-density fraction apparently controls whole-sediment PAH release. Although plant debris appears to be an important sorbent for PAHs, this material may readily release PAHs into the aqueous phase.

* Corresponding author phone: (615)322-1064; fax: (615)322-3365; e-mail: David.Kosson@Vanderbilt.edu.
† University of Illinois-Chicago.
‡ Vanderbilt University.
§ Biotechnology Center for Agriculture and the Environment, Rutgers, The State University of New Jersey.
# Institute of Marine and Coastal Sciences, Rutgers, The State University of New Jersey.

Introduction

In recent years, much research has focused on the processes responsible for the limited availability of hydrophobic organic compounds (HOCs) in soil and sediment systems (*1−5*) and references therein. Processes such as "aging" (the decreased availability of HOCs with increasing contact time) and sorption nonlinearity occur in many systems. Mechanistic explanations for this behavior include hindered diffusion of HOCs in pores of molecular scale (*6, 7*) and interactions between sorbate and micropores in organic matter domains (the so-called "glassy" versus "rubbery" regions) in the dual-mode macromolecular model of soil organic matter (SOM) (*3, 8−10*).

Diagenetic age has been shown to correlate with the organic carbon/oxygen (C/O) ratio in some geosorbents; the higher the ratio, the more reduced and aged the organic matter. In dual mode theories, diagenetically aged materials (like coal or shale) are viewed as comprised of "glassy" organic matter responsible for strong HOC sorption, nonlinear adsorption behavior, and slow mass transfer rates (*9*). Soot particles also have high C/O ratios (*11*) and also are strong sorbents of cointroduced HOCs such as polycyclic aromatic hydrocarbons (PAHs) in sediments (*12*). Less diagenetically aged materials such as humic acid and other humic material are hypothesized to behave like a "rubbery" polymer with generally linear and reversible partitioning behavior (*9, 10*).

Many of the studies that have formed the basis for these theories were performed using soil material in which much of the organic matter was relatively diagenetically older, more reduced, or contained more soot (*2, 4, 5, 9, 13−16*). In organic-rich near shore sediments, particularly near emergent vegetation, much of the SOM is comprised of diagenetically young detritus from the breakdown of plants. This material is often present as a discrete phase from the mineral particles and can represent a preferred food source for detritivores (*17*). Because uptake of HOCs by sediment organisms can be a vector for human exposure through bioaccumulation and trophic transfer, accurate knowledge of the role this diagenetically young material plays in HOC fate is important from both an ecosystem and human health standpoint. At present, there are few studies of the role diagenetically young SOM like detritus plays in the sequestration of HOCs. Given the potential impact this material has on HOC exposure to higher organisms, investigation of the sequestration and partitioning behavior of HOCs in sediments rich in this material would lead to a better understanding of risk.

Understanding desorption from a given matrix is crucial for predicting bioavailability. In part because biota are size-excluded from the interior of sediment particles, and contaminants likely must be transported to the surface before they are available for biodegradation and/or biological uptake (*18*) and references therein, insight into bioavailability may be gained by narrowing our focus to the factors controlling desorption. A correlation between the rapidly desorbed fraction of PAH contamination and the achievable extent of biodegradation in a sediment has been demonstrated (*19*). However, predicting the rate and extent of desorption of HOCs from complex soil and sediment matrices depends on decoupling the contributions of many factors and a comprehensive understanding remains elusive.

To reduce complexity and facilitate understanding of slow desorption and bioavailability, model materials have often been used to study HOC sequestration. These include soil constituents (*20*), resins (*21*), porous silica beads (*22*), and porous glass beads (*6*). The advantage of using model materials is their structural simplicity, lack of heterogeneity,

and the resultant ease of interpreting results. However, such materials are necessarily a simplification of natural systems and comparability to natural systems is uncertain. Another limitation of some previous investigations is the reliance on materials that have been amended with contaminant and aged in the laboratory. Numerous studies have shown the dramatic effect that contaminant contact time with soil or sediment and exposure to actual environmental conditions have on extractability, toxicity, and bioavailability (23−26). Significant changes can still be observed in desorption and bioavailability after aging for up to 1 year (27). Because laboratory equilibration periods of many years are impractical, field-contaminated materials should be used to more accurately represent slow desorption and bioavailability in the environment and to establish comparability between model systems and field materials.

The purpose of this study was to better understand the factors controlling PAH sequestration and desorption in field-contaminated estuarine sediments and the role detritus plays in these processes. We focused on sediments collected from two sites located in the New York/New Jersey (NY/NJ) Harbor estuary. These sites were chosen because they had similar histories of long-term PAH contamination, but they were distinct in many of the physical and chemical properties likely to affect desorption, including the presence in one of the sites of detrital plant material.

Our approach to control for the complexity of studying weathered natural sediment was 3-fold. First, a large supply of well-homogenized parent material from each source location was separated into 18 size and density fractions. This fractionation strategy resulted in diminished heterogeneity within fractions and provided multiple points of comparison across and among fractions. Second, we developed a large data set of sediment physical and chemical characterization parameters focusing on factors likely to control PAH sequestration and desorption. Finally, we collected PAH partitioning and desorption data for several PAHs with a range of molecular properties for each of several sediment fractions in hopes of elucidating trends that may be obscured when focusing on total PAH behavior in whole sediment.

Materials and Methods

Source of Materials. Sediments from Piles Creek and Newtown Creek, two PAH-contaminated sites in the NY/NJ Harbor estuary, were used for these experiments. Piles Creek (40°36.53′ N, 74°13.60′ W) is an intertidal creek that runs through a salt marsh with abundant emergent vegetation, primarily *Spartina alterniflora*. Newtown Creek (40°44.28′ N, 73°56.75′ W) is a subtidal industrial waterway in Queens, NY with little or no vegetation. Piles Creek (PC) sediment was collected by shovel to a depth of approximately 20 cm from sediment exposed at low tide as described previously (28). Sediment was homogenized with an impeller (15 min) and stored immediately after homogenization at 4 °C in the dark. Newtown Creek (NC) sediment was collected from subtidal sediments using a Van Veen grab to a depth of approximately 20 cm, homogenized, and stored as above.

The sediments were size fractionated by wet sieving at 5−10 °C using sequential sieve sizes from 500 μm down to 63 μm, resulting in the following fractions: <63 μm, 63−125 μm, 125−300 μm, 300−500 μm, and >500 μm. Enough material was gathered in each fraction to perform the experiments described in this paper. Sediment was separated into density fractions by flotation in CsCl solution (1.7 ± 0.05 g cm^{-3}) as described in Mayer et al. (17). In all, 36 sediment fractions were prepared for this study (two sediments; whole and five size fractions; bulk, low-, and high-density). Based on biodegradation studies using these same sediments, it is unlikely that significant PAH biodegradation occurred under these conditions (27).

Physical Characterization. Particle size distribution analysis was performed by both wet sieving (particles >125 μm) and X-ray sedigraphy (particles <125 μm) using a Micromeritics model 5100 particle size analyzer as described previously (28).

Mesopore structure (pores 2−50 nm, IUPAC classification) and particle surface area was determined by nitrogen adsorption porisimetry using a Micromeritics ASAP 2010 accelerated surface area and porisimetry system (Micromeritics Instrument Corporation, Norcross, GA) as described previously (11). Macropore structure (pores >50 nm, IUPAC classification) and bulk and skeletal density as well as sediment porosity were measured using an automated mercury porisimetry system (Model 9320, Micromeritics Instrument Corporation, Norcross, GA) as in Rockne et al. (11).

Chemical Characterization. PAHs were extracted from the sediments using either a modification of the extraction procedure of Leeming and Maher (29) or a hot acetonitrile extraction method developed in this laboratory. For the Leeming and Maher protocol, dried sediment was extracted with methylene chloride, cleaned up with activated normal-phase silica gel cartridge, and concentrated as described (28).

For the hot acetonitrile method, a known mass of wet sediment was placed in a Teflon centrifuge tube. The tubes containing wet sediment were centrifuged (8000g, 20 min), and the supernatant was removed and discarded using a vacuum aspirator. Acetonitrile (20 mL) was added to the remaining dewatered sediment, and the sediment pellet was completely suspended by vortexing. Tightly capped extraction vessels were placed in a hot water bath and sonicated (85 °C, 2 h). Longer extraction periods (up to 48 h) did not give significantly higher extraction efficiencies. Following extraction, the tubes were centrifuged again (8000g, 20 min), and the supernatant was passed through a 0.2 μm nylon Acrodisc HPLC syringe filter (Pall Gelman, Ann Arbor MI) and transferred to autosampler vials (2 mL, Teflon lined caps) for analysis. PAH concentrations were normalized to the amount of extracted dry sediment mass (105 °C, 48 h). This extraction procedure was tested using a PAH-contaminated sediment standard from the National Institutes of Scientific Testing (Standard Reference Material 1941a, National Institutes of Standards and Technology (30)) and was found to give high extraction efficiencies similar to the Leeming and Mayer extraction protocol used above (data not shown).

PAHs were analyzed by high performance liquid chromatography (HPLC). Sample injections (5 μL) were separated on a 15 cm reverse-phase LC-PAH column (Supelco, Bellefonte, PA) during a 40-min run (1.5 mL min^{-1}, 35 °C) with the following gradient program: initial 55%/45% water/acetonitrile for 5 min, linear gradient to 100% acetonitrile at 30 min, hold for 10 min, and return to initial conditions. PAHs were quantified by digital diode array detection (Hewlett-Packard model 1050), photodiode array detection (Shimadzu Instruments model SPD-M10AVP), or programmable fluorescence detection (Shimadzu Instruments model RF-10AXL).

Total organic carbon and nitrogen in the sediments was measured using a Carlo Erba elemental analyzer (model NA1500) as described previously (11). Total carbon in the sediments was composed primarily of organic carbon because these sediments had negligible amounts of inorganic carbonates. Soot carbon was measured by a modification of the method of Gustafsson et al. (31) as described in Rockne et al. (11). We assumed the mass lost during low-temperature oxidation (375 °C, 24 h) of the sediment (termed "organic matter" in this study) was indicative of the nonsoot organic matter.

Statistical Regressions. Ordinary least squares linear regressions were performed using standard statistical techniques. "Strong correlation" implies significance at the 99%

level, "significant correlation" implies significance at the 95% level, and "weak correlation" implies significance at the 90% level. *P*-values reported in the text reflect the significance of the slope coefficient (*t*-test, one-tailed) in a linear model with PAH concentration as the dependent variable and the reported parameters as the independent variables.

Equilibrium Partitioning. Equilibrium PAH partitioning experiments were performed using selected size and density fractions. Sediment (1−10 g dry wt) was added to filtered (0.45 μm) seawater (4 l) poisoned with HgCl$_2$ (1% v/v of a saturated solution) in brown glass bottles previously baked (500 °C, 1 h) and incubated in the dark with occasional shaking. Following aging periods greater than 3 months, the sediment was allowed to settle, and the supernatant (approximately 3 l) was filtered through a solid phase extraction disk (3M Empore, 3M Corp., Saint Paul, MN) using manufacturer's specifications. The extraction disk retained PAHs present in the liquid phase during filtration, and these were subsequently extracted into hexane (4 mL) for analysis, resulting in a concentration of nearly 1000-fold over aqueous concentration. Even with this concentration step, not all PAHs were present at measurable concentrations in the aqueous phase. Mass recovery from the aqueous phase of known standards using this technique was 87 ± 19% for 3- to 5-ring PAHs (11 total). PAHs were extracted from the solid phase using the hot acetonitrile extraction procedure described above, and the ratio of the PAHs in each fraction was calculated and normalized to the organic carbon content in the solid phase for computation of the organic carbon-referenced partition coefficient (K_{oc}).

Hexane, acetone, and acetonitrile were Optima or high-performance liquid chromatography (HPLC) grade (Fisher Scientific, Pittsburgh, PA). ACS grade HgCl$_2$ was obtained from Sigma-Aldrich (Milwaukee, WI).

Desorption Studies. PAH desorption was measured for whole, high-density, and low-density fractions of each study sediment in duplicate using a modification of the method of Cornelissen et al. (*32*). A known mass of wet sediment and 0.3 g of Tenax-TA beads (60−80 mesh, Alltech Associates Inc., Deerfield, IL) were suspended in 100 mL of filtered seawater (0.45 μm) in 125-mL separatory funnels. HgCl$_2$ was added to prevent microbial growth (5% v/v of a saturated solution). Vessels were shaken (150 rpm) on a temperature-controlled orbital shaker (Brunswick Scientific, Edison, NJ) at 23 °C. At specified time intervals, the sediment/seawater slurry was separated from the beads, and fresh Tenax beads were added to the slurry. Separated beads were then extracted with 10 mL of hexane at 23 °C with shaking (150 rpm, 10 min). To determine the efficiency of this extraction procedure, Hungate tubes containing Tenax beads and an aqueous phenanthrene solution were incubated for time intervals ranging from 7 min to 7 days and extracted as above. Extraction efficiencies were 102 ± 5% and did not diminish with PAH-Tenax contact time. Before use, Tenax was washed three times each in acetone (50 mL g Tenax^{-1}), acetonitrile (50 mL g Tenax^{-1}), and hexane (50 mL g Tenax^{-1}). All glassware used in the experiments was baked at 500 °C for 5 h to remove organic contaminants.

Hexane samples were analyzed directly by HPLC with photodiode array and fluorescence detection as previously described. Alternatively, for samples with low PAH concentration, hexane samples were concentrated under a N$_2$ stream at 60 °C, adjusted to 300 μL with acetonitrile, stored in conical HPLC vials (Chromachol LTD, Trumball, CT), capped with Teflon-lined silica septa (National Scientific Company, Lawrenceville, GA), and stored in the dark at 4 °C until analyzed. The mass recovery of this concentration procedure was 96 ± 11%. For the sediment desorption studies, the total recovery of PAHs initially present in the sediment were 99 ± 22% and 95% ± 24% for whole PC and NC sediments,
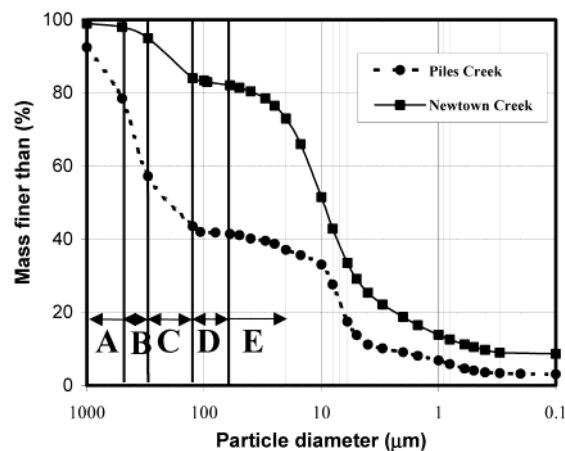

FIGURE 1. Particle size distribution of Piles Creek and Newtown Creek sediment. Vertical lines represent the sieved size fractions used in this study: (A) >500 μm, (B) 300−500 μm, (C) 125−300 μm, (D) 63−125 μm, and (E) <63 μm.

respectively. No discernible trend in recovery efficiency based on molecular weight was observed.

Results and Discussion

Characterization of the Test Sediments. PC sediment had a broad range of particles from sand to clays (Figure 1). In contrast, NC sediment was composed primarily of silt- and clay-sized particles with few sand-sized particles. NC sediment also had a substantially higher fraction of clay-sized particles than Piles Creek (25% vs 10%, respectively). NC sediment had generally higher organic carbon concentrations, organic matter content, and soot carbon concentrations than PC sediment (Table 1). Under microscopic examination, both bulk sediments appeared fairly homogeneous, while the low-density fractions showed large heterogeneity in particle type and size (Figure S1, Supporting Information). Plant fragments, soot-like particles, and charcoal-like particles were apparent in the PC sediment low-density fraction. The plant fragments were probably debris from *Spartina alterniflora*, the dominant macrophyte in the salt marsh through which Piles Creek flows. In contrast, low-density NC sediment fractions did not appear to contain plant fragments but were instead dominated by dark material that appeared to contain small mineral particles (fine silt or clay-sized) in a conglomeration (Figure S1, Supporting Information).

PAHs Concentrations were Greatly Elevated in Coarse and Low-Density Fractions. The total PAH content (sum of the 16 EPA priority pollutants) of PC and NC sediment was 100 and 50 mg kg^{-1}, respectively (Table 1). PAHs were not distributed evenly among size and density fractions; for both sediments, PAH concentrations in the coarsest size fraction (>500 μm) were four times higher than in the whole sediment (Table 1), and the smallest size fraction had the lowest PAH concentration.

The most dramatic differences in PAH content were generally found between density fractions. PAH concentrations in low-density whole PC sediment were 100 times higher than the corresponding high-density portion (Figure 2A); as high as 3000 mg kg^{-1} in the >500 μm fraction, much greater than impaired sediment action levels outlined by the EPA (*33*). Similarly high ratios were observed between the high- and low-density portions of each size fraction (25:1 to nearly 200:1). Similar results were obtained in the NC sediment, but the trend was not nearly as pronounced (Figure 2B). The PAH concentration of low-density NC sediment was five times higher than the complementary high-density fraction. The ratio of PAH concentration between corresponding low- and

TABLE 1. Summary of Selected Physical and Chemical Properties of the Sediment Fractions Used in This Study[a]

sediment fraction	total PAH (mg kg^{-1})	surface area[b] (m^2 g^{-1})	organic carbon (mg g^{-1})	organic matter[c] (mg g^{-1})	soot carbon[d] (mg g^{-1})	soot/OC (% of total OC)	OM to[e] nonsoot C ratio (mass basis)	fraction low-density (%)
				Piles Creek				
bulk	100	5.4	44	60	5.9	13	1.6	3.6
low-density	1900	1.9	280	390	47	17	1.7	N/A
high-density	20	6.3	41	53	4.3	11	1.4	N/A
<63 μm	15	9.3	51	92	6.1	12	2.0	0.63
63−125 μm	42	4.1	76	100	18	24	1.7	4.9
125−300 μm	29	1.8	27	43	7.4	26	2.2	4.8
300−500 μm	25	1.2	29	34	5.1	18	1.5	2.3
>500 μm	410	1.0	22	52	6.2	12	1.2	9.3
				Newtown Creek				
bulk	50	14	57	93	7.7	12	1.9	15
low-density	160	10	145	230	12	8	1.7	N/A
high-density	31	9.1	42	79	3.5	8	2.0	N/A
<63 μm	40	15	51	95	3.8	8	2.0	14
63−125 μm	120	7.0	110	150	20	19	1.8	9.3
125−300 μm	170	7.9	130	170	27	21	1.6	18
300−500 μm	130	3.9	120	290	56	46	4.3	7.9
>500 μm	200	4.6	230	360	32	14	1.8	45

[a] Average of triplicate measurements (except fraction low-density). Generally the standard error of the mean was <7%. [b] For all surfaces with pore widths >2 nm. [c] Dry mass loss after heating (375 °C, 24 h). [d] Organic carbon after heating (375 °C, 24 h). [e] Ratio of organic matter to nonsoot organic carbon (total organic carbon minus soot carbon).
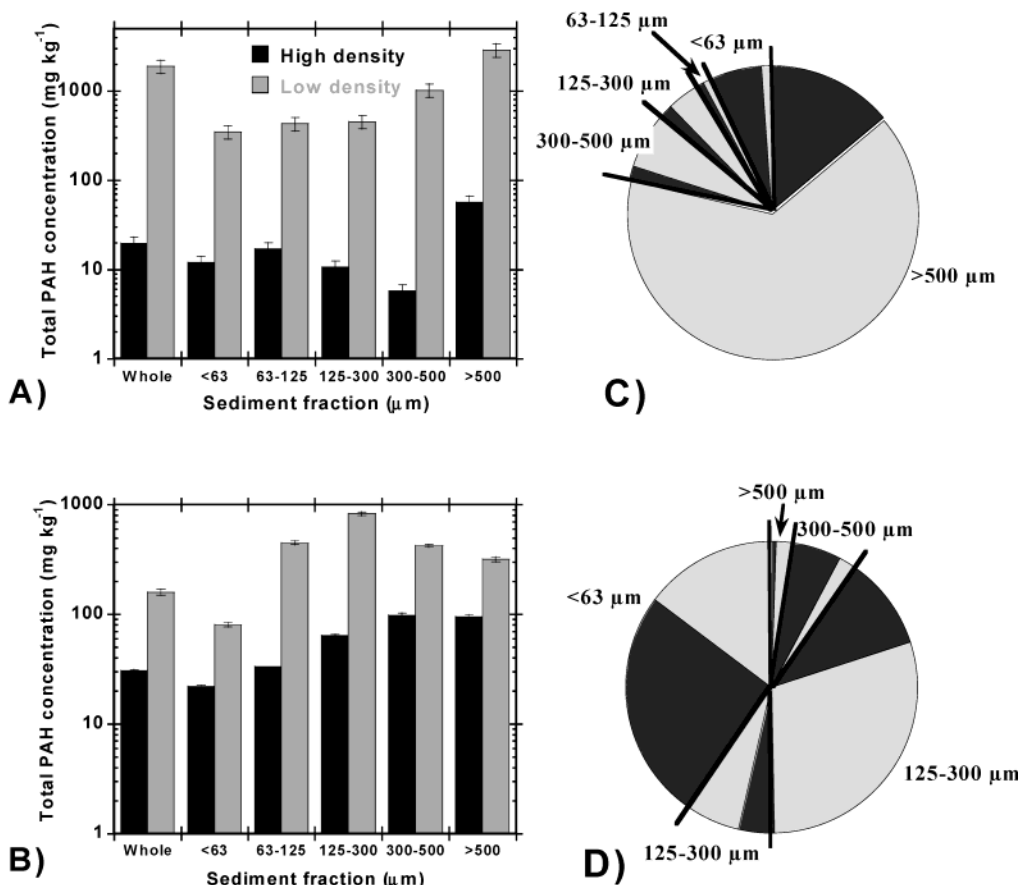

FIGURE 2. Total PAH distribution in Piles Creek (A, C) and Newtown Creek (B, D) sediments. Shown are the total PAH concentration in each fraction (A, B) and the fraction of the total PAH mass in each size and density fraction (C, D). Mean of duplicates or triplicates ± SEM.

high-density components of each NC sediment size fraction ranged from 3:1 to 13:1.

In PC sediment, 85% of the total PAHs were found in the low-density fractions (Figure 2C), despite the fact that the low-density components comprised only 4% of the total sediment mass. Interestingly, even though a greater fraction of NC sediment was comprised of low-density material (15%) as compared to PC sediment, the fraction of PAHs in the low-density NC sediment was not as high as in low-density PC sediment (54%, Figure 2D). Within each size fraction, PAH mass was generally greater in the low-density portions (Figure 2C,D) with the exception of the <63 μm fraction of

NC and PC sediment (which had the highest mineral fraction specific surface area) and the 300−500 μm fraction of NC sediment.

The fact that the majority of the total PAH mass was present in a separable fraction has potentially encouraging implications for sediment management. The technology currently exists to separate sediment particles by density on a large scale using a hydrocyclone (*34*), and our results suggest that the use of this technology may have promise in sediment remediation of PAHs by targeted removal of a small volume accounting for a majority of the contaminant mass. Whether other priority sediment pollutants (such as polychlorinated biphenyls) also preferentially sequester in low-density material remains to be seen.

PAH Sequestration Correlations with Sediment Characteristics. To understand factors controlling PAH distribution in the test sediments, we regressed the physical and chemical characterization data with the independent variable PAH concentration among the size- and density-fractions of each sediment. Not surprisingly, there were strong positive correlations between PAH concentration and organic carbon concentration in both PC ($p < 0.001$) and NC sediments ($p < 0.001$) (Table S2, Supporting Information). Similarly, there were also strong correlations between PAH concentration and organic matter concentration ($p < 0.001$ and $p = 0.004$, respectively, for PC and NC sediments). In both sediments there were also significant correlations between PAH concentration and organic carbon/nitrogen ratio ($p = 0.024$ and $p = 0.030$ for PC and NC sediment, respectively). A significant inverse correlation was found between total PAH concentration and specific surface area and porosity in NC sediment ($p = 0.028$ and $p = 0.042$, respectively), but no such correlation was observed for PC sediment. PAH distribution was also not correlated with organic matter to nonsoot carbon ratio (a measure of the degree of oxidation of the organic matter) in either sediment. This result contrasts with recent reports in the literature that HOCs exhibit stronger sorption in less oxidized organic matter (*9*).

Because the role of soot in PAH sequestration has received much attention in recent literature reports (*31*, *35−37*), we examined the soot data more closely. The soot content of PC and NC sediment fractions ranged widely, varying from 8% to as high as 46% of total organic carbon (Table 1). Soot was found in all size fractions, which is consistent with recent studies that found soot associated with particle sizes spanning from <1 μm into fine sand sizes (*11*, *38*, *39*). Soot was found in both high- and low-density fractions; a result not surprising given that soot densities are reported to be near the density separation cutoff used in this study (*11*) and could thus be found in either density fraction. Although there was a strong positive correlation between soot carbon concentration and PAH concentration in the fractions of PC and NC sediment, this correlation can be attributed to the interdependence between soot carbon concentration and organic carbon concentration. No significant correlation was found between PAH concentration and soot carbon when expressed as a percentage of total organic carbon ($p = 0.459$ and $p = 0.217$ for PC and NC sediment, respectively) in separate one-independent variable regressions (Table S2, Supporting Information). Furthermore, the correlation of PAH concentration with soot carbon concentration was not significant ($p = 0.468$ and $p = 0.215$ for PC and NC sediment, respectively) in a two-independent variable regression model including both organic carbon and soot carbon concentration (Table S3, Supporting Information). These findings indicate that soot carbon is not the primary sequestration material for PAHs in these sediments.

Study sediments and fractions were extensively characterized for physical parameters likely to affect sequestration and desorption. PC sediment specific surface area (5.4 m²

g⁻¹) was less than half that of NC sediment (14 m² g⁻¹). Even within each size fraction, NC sediment had a greater specific surface area than the respective PC sediment fractions (Table 1), suggesting that NC sediment was more porous or had smaller pores than PC sediment. This was confirmed by the pore structure analysis of the sediments, where NC sediment had generally higher porosity for all the size fractions, ranging from 61 to 72%, compared to 47−67% for PC sediment (Table 1). The trend in mesopore structure (2−50 nm, intraparticle) was more similar between the two sediments (Figure S2, Supporting Information). For both sediments, there was a general trend of increasing mesoporosity with decreasing particle size (Figure S2A,C, Supporting Information), with only the magnitude differing between the sediments. Although the <63 μm fraction pore size distribution was similar in pattern and magnitude for both sediments, every other size fraction of NC sediment had significantly higher mesoporosity than in PC sediment, particularly true for the smallest pores in the mesopore domain, where hindered pore diffusion is most likely to occur.

We found a weak inverse relation between PAH concentration and both surface area and porosity for NC sediment, but no correlation for PC sediment. However, for PC sediment both a positive correlation of PAH concentration with organic matter concentration and a negative correlation with specific surface area were significant ($p < 0.001$ and $p = 0.036$, respectively, Table S3, Supporting Information). Similarly, two-independent parameter regressions between PAH concentration and organic matter concentration with either porosity (negative correlation, $p = 0.013$) or particle diameter (positive correlation, $p = 0.004$) were also observed in PC sediment (Table S3, Supporting Information). The negative correlations of PAH concentrations with porosity and specific surface area were expected because PAH concentrations tended to increase with increasing particle diameter (especially for NC sediment), and both porosity and surface area decreased with increasing particle size in both sediments.

Given the hydrophobicity of PAHs, it is not surprising that the amount and composition of the organic matter dominated PAH sequestration trends, and physical characteristics were less important as a determinant of sequestration. However, these results may provide information about the location and physical structure of sediment organic matter in these test sediments. If sediment organic matter existed as a thin uniform coating on solid surfaces, we would expect to see a positive correlation of PAHs with surface area. Instead there was a weak negative correlation, suggesting that sediment organic matter was not evenly distributed on the sediment particle surfaces. Although SOM dominated sequestration (an equilibrium process), physical properties such as surface area and pore structure may figure prominently in the kinetic mass transport mechanisms controlling desorption and bioavailability.

SOM Structure Affects PAH Sequestration and Partitioning. The result that PAH content was strongly correlated with organic carbon content raises the question whether the high PAH concentrations in the low-density fractions were simply due to the higher organic carbon content of the low-density material, which contained 25−40% of the total organic carbon in the test sediments (Figure S3, Supporting Information, Table 1). However, as can be seen by comparison of the organic carbon-referenced PAH concentrations in each fraction, preferential sequestration of PAHs in the low-density fraction was not simply the result of higher organic carbon content (Figure 3). If partitioning of PAHs were simply the result of the increased organic carbon in the low-density fraction, the ratio of the organic carbon-referenced PAH concentration in the low-density and high-density fractions would fall on a 1:1 line. As can be seen from the PC sediment data, organic carbon-referenced PAH concentrations in the
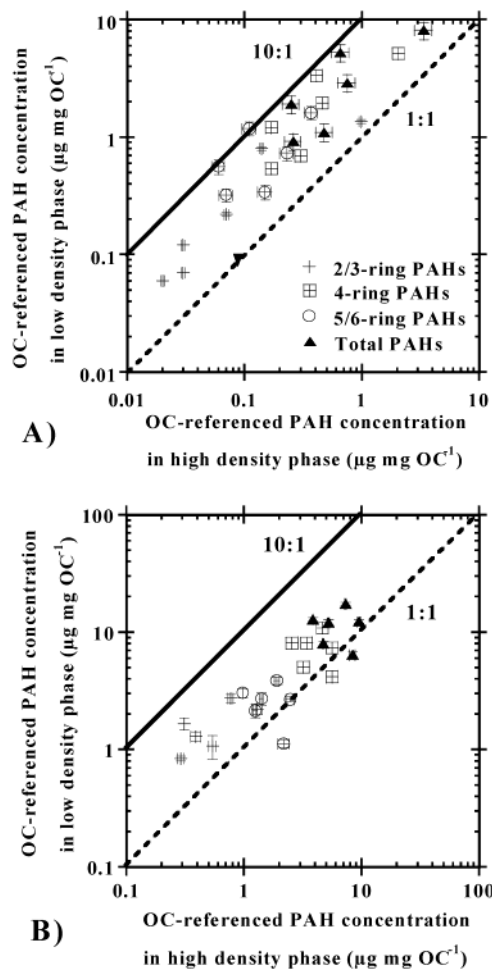
FIGURE 3. Comparison of the organic carbon-referenced PAH concentration in the low-density versus high-density fractions of (A) Piles Creek and (B) Newtown Creek sediments. Dashed line and solid line represents a 1:1 and 10:1 ratio, respectively, of organic carbon-referenced PAH concentration in the low-density fraction versus the high-density fraction. Note different scales. Mean of duplicate or triplicate determinations ± SEM.

FIGURE 4. Comparison of the equilibrium organic carbon-normalized sediment-water partitioning coefficients (K_{oc}) for PAHs in the various sediment fractions versus bulk Piles Creek sediment. Dashed line and solid line represents a 1:1 and 10:1 ratio, respectively, between the partition coefficients in the sediment fractions and the bulk sediment.

low-density fraction were 2–10 times higher than in the high-density fraction (Figure 3A). In general, this behavior was stronger for higher molecular weight PAHs than for 2–3 ring PAHs. A similar, but less pronounced trend was observed in the NC sediment, where low-density organic carbon-referenced PAH concentrations were generally 2–3 times greater than in the high-density fraction (Figure 3B).

Given the extent to which PAHs sequester in the low-density fraction of PC sediment, we wanted to determine whether this behavior was reflected in equilibrium aqueous-solid partitioning. Comparison of the organic carbon-normalized partition coefficients (log K_{oc}) in the bulk PC sediment to those in each fraction indicates that the low-density fraction was a strong sorbent for PAHs (Figure 4). The trend of higher partition coefficients in the low-density fraction was also observed in NC sediment but was not nearly as pronounced as in PC sediment (data not shown). Comparing the log K_{oc} for those PAHs with measurable partition coefficients (2–4 ring PAHs) in the sediment size fractions to those measured in the bulk sediment shows that the partitioning was similar (i.e. they followed a 1:1 ratio compared to the bulk sediment). In contrast, the partition coefficients were nearly 10 times higher for the low-density fraction, as shown by the data that trend along the 10:1 line. These results are consistent with the sequestration data discussed earlier and further demonstrate that the low-
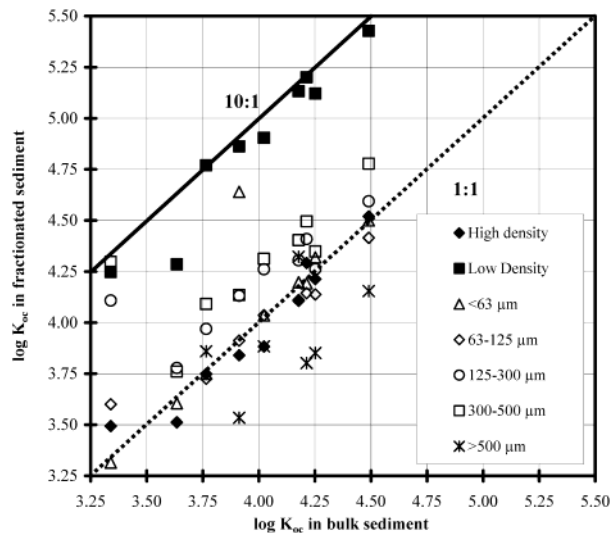
density sediment fraction was a preferential sorbent in which PAHs sequester and partition at levels greater than expected based on organic carbon-normalized equilibrium partitioning theory.

It is apparent from both the site histories and the physical and chemical characterizations of these two sediments that the SOM was fundamentally different in NC and PC sediments. One of these sites, PC, is particularly rich in vascular plant debris, a material common in many coastal environments. We conclude that this material is an important sorbent for PAHs based on (1) the absence or only weak correlation between PAH content and soot content and various physical parameters, (2) the dramatic PAH enrichment in the coarse, low-density fraction of PC sediment, and (3) the differences observed between PAH sequestration in PC and NC sediment given that detrital material was largely absent from NC sediment. Some studies have also reported high concentrations of PAHs in low-density particles from estuarine and coastal environments (40–42), although none of these studies characterized the sediments to the extent we have here. This enrichment is beyond what can be explained based on higher organic carbon concentration. In the next sections we explore how the rate and extent of PAH desorption differ in various fractions of the study sediments.

PAH Desorption Varied Greatly by Sediment and Sediment Fraction. The rate of PAH desorption is of critical importance to risk assessment. Under a given set of conditions, the mass of contaminant released in a finite period of time is relevant to predict exposure magnitude as well as the expected efficacy of potential remediation strategies. In general for our test sediments, PAHs desorbed more rapidly from PC sediment than from NC sediment (Figure 5A). For example, 50% of the labile phenanthrene (defined as the mass that can be desorbed in 3 months using an infinite-sink desorption apparatus) was desorbed in the first 6 h from whole PC sediment compared to 8 days in NC sediment (Figure S4A, Supporting Information). Other PAHs showed similar, although less pronounced, trends. For pyrene, 50% desorption was achieved in less than 2 h for PC sediment, compared to 6 h for NC sediment (Figure S4B, Supporting Information). For chrysene, 50% desorption occurred in 6 h for PC sediment but almost 2 days in NC sediment (Figure S4C, Supporting Information). Finally, benzo[a]pyrene was
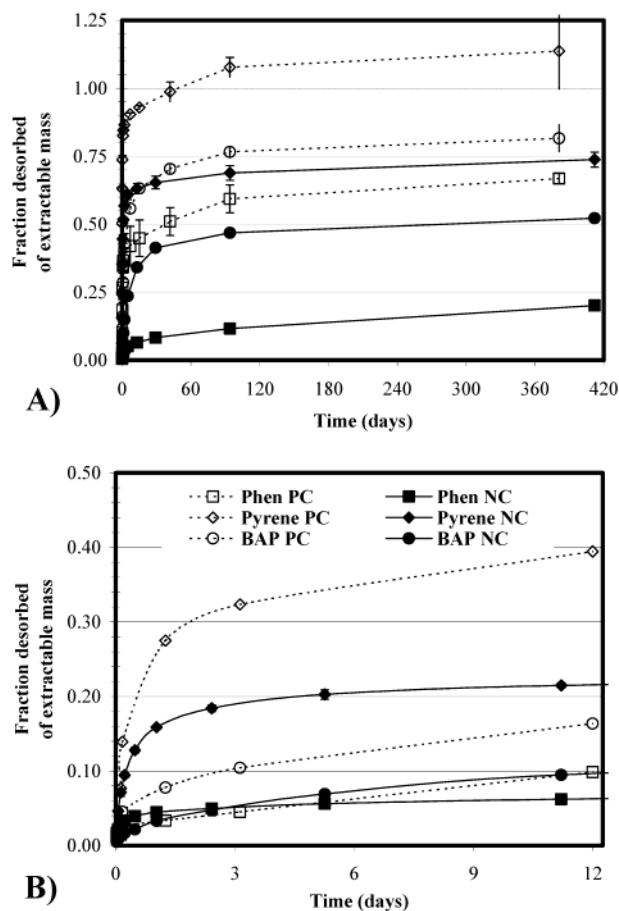
A)

B)

FIGURE 5. Cumulative PAH mass desorbed as a fraction of extractable mass. Shown are phenanthrene (Phen), pyrene and benzo[*a*]pyrene (BAP) in (A) whole Piles Creek (PC) and Newtown Creek (NC) sediments and (B) low-density PC and NC sediment fractions. Average $\pm$ range of duplicates.

50% desorbed in approximately 1 day from PC sediment, compared to nearly 5 days in NC sediment (Figure S4D, Supporting Information).

In addition to desorption rate, the extent of desorption is important to determine the fraction of the total contamination present in a sediment that can be removed under certain experimental conditions and may be an indicator for bioavailability (*19*). In our study, PAHs were desorbed more extensively from PC sediment than from NC sediment (Figure 5A). Averaged by compound, nearly 70% of the PAHs were desorbed from PC sediment within 3 months, compared to only 36% of the PAHs desorbed from NC sediment (Table 2). Relative extent of desorption between the sediments varied significantly based on PAH molecular structure. For example, phenanthrene was five times more extensively desorbed from PC sediment than from NC sediment (59% vs 12%) at three months, whereas the fraction of pyrene and benzo[*a*]pyrene desorbed from PC sediment was less than twice that of NC sediment (108% vs 69% and 76% vs 47%, respectively).

We have shown that PAHs in PC sediment were found primarily in coarse, nonporous plant detrital material. It is also important to take note of the relatively rapid and extensive release of PAHs from the sediment containing this material, including large hydrophobic compounds such as benzo[*a*]pyrene. These findings are in contrast with a recent study by Gosh et al. (*43*) that reported that only 40% of the PAHs desorb from whole Milwaukee Harbor sediment under similar experimental conditions within a similar 3-month period. Interestingly, the findings reported by Gosh et al. are quite similar to the data reported here for the fraction of

TABLE 2. Cumulative Mass Desorbed (at 3 Months) for Selected Sediment Fractions Expressed as Sediment Concentration Decrease and as a Percent of Total PAH Content

	whole PC		whole NC		low-density NC	
	mg kg^{-1}	% of total	mg kg^{-1}	% of total	mg kg^{-1}	% of total
phenanthrene	0.40	59	0.24	12	0.75	9
anthracene	0.41	58	0.26	22	0.44	11
pyrene	3.74	108	4.31	69	4.12	24
benzo[*a*]anthracene	1.47	75	1.27	40	2.08	22
chrysene	1.90	53	0.80	24	2.37	16
benzo[*b*]fluoranthene	1.03	60	1.52	37	2.16	15
benzo[*k*]fluoranthene	0.45	65	0.69	41	1.03	17
benzo[*a*]pyrene	0.78	76	1.44	47	1.73	15
indeno[1,2,3-cd]pyrene	ND	ND	1.15	61	ND	ND
average recovery[a] (%)		69		36		16

[a] Indeno[1,2,3-cd]pyrene is not included because this compound was not determined for all fractions. ND - - not determined.

PAHs desorbed from whole NC sediment (36%). In contrast to PC sediment, neither the Milwaukee Harbor sediment nor NC sediment contained appreciable amounts of vascular plant debris.

Differences in the average extent of PAH desorption may also be accounted for by differences in physical properties between NC sediment and PC sediment. A much greater fraction of PAH mass was found in fine particles of NC sediment versus PC sediment. These fine NC sediment particles also had the highest specific surface area and mesoporosity of any of the sediment fractions in this study (Table 1, Table S1, Supporting Information). These physical properties could have inhibited mass transport of PAHs from NC sediment.

Given the large differences in PAH sequestration and physical and chemical properties between the high- and low-density sediment fractions, we investigated further the desorption kinetics from the density-fractions to determine whether similar large differences in mass transfer would be observed. More PAH mass was desorbed from each low-density fraction than the corresponding whole or high-density fractions. For example, the cumulative mass of benzo[*a*]-pyrene desorbed in 3 months was 1.7 mg kg^{-1} from low-density NC sediment, 1.4 mg kg^{-1} from whole NC sediment (Table 2), and 0.82 mg kg^{-1} from high-density NC sediment (data not shown). This trend held for every compound reported except pyrene, which had approximately the same mass desorbed from the low-density fraction as from whole NC sediment (4.1 and 4.3 mg kg^{-1}, respectively). From an ecological risk standpoint, our results indicate that the low-density fraction represents a greater risk for PAH exposure to biota contacting this material. Not only did this fraction contain higher PAH concentrations, but a much greater PAH mass was desorbed from these fractions.

Although more PAH mass was released from the low-density fractions, this trend was driven by the much higher PAH concentrations in low-density sediment. When scaled to the initial concentrations, a smaller percentage of PAHs were desorbed from the low-density fractions than from the corresponding whole and high-density fractions. For example, 69% of the initial pyrene was desorbed in 3 months from whole NC sediment, while only 24% was desorbed from the NC low-density fraction (Table 2). Similarly, 47% of the benzo[*a*]pyrene mass was desorbed in 3 months from whole NC sediment, while only 15% was desorbed from low-density NC sediment.

A direct comparison of the desorption kinetics of the two low-density fractions indicates that a much greater mass
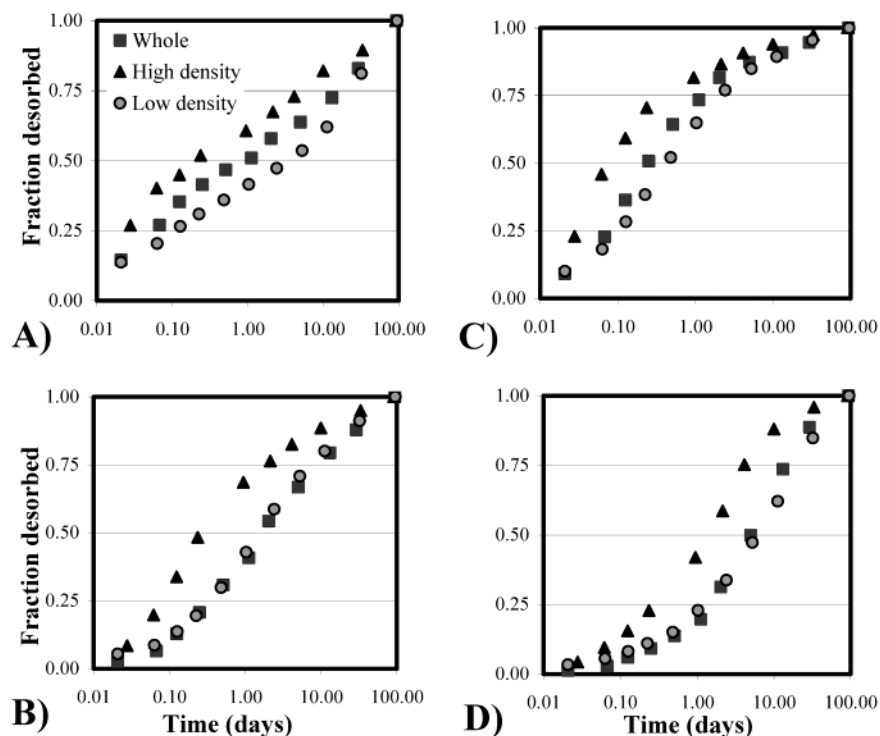
FIGURE 6. Fractional PAH mass desorption normalized to total PAH mass desorbed after three months from whole, high-density, and low-density fractions of Newtown Creek sediment. Shown are (A) anthracene, (B) chrysene, (C) pyrene, and (D) benzo[a]pyrene.

fraction was desorbed from low-density PC sediment as compared to low-density NC sediment (Figure 5B). For example, at day 12, approximately 40% of the pyrene had desorbed from low-density PC sediment, but only 21% had desorbed from low-density NC sediment. Similarly, more benzo[a]pyrene desorbed from the low-density PC sediment than from NC sediment (16% versus 10%, respectively) over the same time period. Given that 70% of the PAHs in PC sediment were desorbable and the vast majority of PAHs were found in the coarse low-density fraction, PAHs contained within this material must be readily desorbed from the vascular plant material to account for the observed results. In contrast, the PAHs sequestered within the low-density fraction of NC sediment were much less readily desorbed.

Desorption from Low-Density Fraction was Rate-Limiting. While constituting only 15% of the NC sediment mass, the low-density fraction had a disproportionately large impact on the rate of high molecular weight PAH desorption. For chrysene and the 5-ring PAHs in particular, the desorption profile from whole NC sediment (the characteristic shape of the curve describing fractional desorption as a function of time) was virtually coincident with the desorption profile for low-density NC sediment (Figure 6, Figure S5, Supporting Information). When the low-density fraction is removed from whole sediment, as in the case of the high-density sediment fraction, PAHs desorb much faster and to a greater extent, relative to the initial PAH concentration. These results suggest that the presence of a low-density fraction controls the release of high molecular weight PAHs.

We conceptualize that PAHs are sequestered in various organic matter-rich regions within heterogeneous sediment aggregates. As PAHs partition from organic matter regions, and/or from solid surfaces, or diffuse through liquid-filled pores, they reversibly partition back into the low-density organic material. For hydrophobic PAHs, desorption from the low-density fraction of NC sediment is the rate-limiting step in the aggregate desorption process. From a contaminated sediment management standpoint, these results are significant because not only could removing the low-density

fraction significantly decrease the whole sediment concentration of PAHs but also it may enhance the rate of PAH desorption from the remaining sediment.

Given the differences between the sequestration and desorption data for the low-density fractions of the two study sediments, two conclusions may be drawn: (1) sediments rich in plant debris (like PC sediment) may represent an increased potential for PAH release, and thus ecological exposure and (2) researchers should be cautioned from generalizing the results from one study site, as two locations within the same estuary system exhibited dramatically different behavior in sequestration and rate and extent of desorption.

Implications

We have shown that PAH-contaminated sediments from two environments with different physical and chemical characteristics contain low-density fractions that sequester a majority of the PAH mass present in the sediments. These results are in agreement with a recent report of PAH sequestration in size and density fractions of Milwaukee Harbor sediments (43). In that report, PAHs were found to preferentially sequester in what the authors termed "coal/wood material". Our results extend this observed phenomenon to estuarine systems. Further, we have demonstrated the importance of SOM structure on the preferential sequestration in the low-density fraction, and the lack of a correlation between PAH concentration and soot demonstrates that soot is not important at all sites, particularly in sediments where soot deposition is not a primary source of PAHs. Although the majority of PAHs were present in the low-density fraction for both NC and PC sediments, the extent to which PAHs sequestered in this fraction was dependent on SOM structure. Preferential partitioning (greatly in excess of organic carbon-referenced values) was more prevalent in PC sediment. The preferential sorbent in this sediment was likely low-density plant fragment detritus. Further, we present the first detailed investigations of the sequestration and equilibrium partitioning behavior of PAHs in this diagenetically young detrital material. Given the role detrital material

plays in the benthic food chain (i.e., the potential for exposure to higher animals through trophic transfer), our results lend support for the growing emphasis placed on toxicity-based approaches for determining sediment quality criteria, rather than total sediment contaminant concentrations (*44*).

Although we have not focused this study on contaminated sediment management, the results of this study and the recent work of Ghosh et al. (*43*) raise some important considerations for contaminated sediment managers. From a remediation standpoint, preferential partitioning suggests that a treatment targeted at removal of the low-density fraction (containing the bulk of the desorbable PAHs) may be a cheaper alternative than treatment of the entire sediment and may facilitate desorption of PAHs in the remaining high-density fraction. From a risk characterization standpoint, it is apparent that calculating the risk posed by contaminated sediments based on bulk sediment PAH concentrations is supported neither by the actual PAH sequestration behavior in the field nor by the differences in the rate and extent of PAH desorption in sediment fractions compared with whole sediments. Our results indicate that preferential partitioning in different fractions will affect exposure (negatively or positively) depending on to which sediment fraction the organism is exposed.

To understand the risk posed by PAH-contaminated sediments it is necessary to not only characterize the distributed sequestration of PAHs but also to determine the release rates of PAHs from various sediment fractions. A comprehensive understanding of PAH desorption from sediments requires consideration of physical and chemical sediment properties, molecular properties of PAHs, and special attention to SOM structure and properties. The large effort necessary to measure PAH release from all of the sediment fractions, as done in this study, is clearly not feasible for all contaminated sites. Therefore, the ultimate goal of this endeavor is to develop a predictive model of PAH release behavior and bioavailability based on fundamental physical, chemical, and biological parameters that are more readily measured than long-term desorption release rates.

Acknowledgments

Supporting Information Available

Five figures and three tables that supplement the discussion in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Pignatello, J. J. *Environ. Toxicol. Chem.* **1990**, *9*, 1117−1126.
(2) Luthy, R. G.; Aiken, G. R.; Brusseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Rheinhard, M.; Traina, S. J.; Weber, W. J.; Westall, J. C. *Environ. Sci. Technol.* **1997**, *31*, 3341−3347.
(3) Huang, W.; Young, T. M.; Schlautman, M. A.; Hong, Y.; Weber, W. J. *Environ. Sci. Technol.* **1997**, *31*, 1703−1710.
(4) Pignatello, J. J.; Xing, B. *Environ. Sci. Technol.* **1996**, *30*, 1−11.
(5) Huang, W.; Weber, W. J. *Environ. Sci. Technol.* **1997**, *31*, 3238−3243.
(6) Farrell, J.; Grassian, D.; Jones, M. *Environ. Sci. Technol.* **1999**, *33*, 1237−1243.
(7) Farrell, J.; Reinhard, M. *Environ. Sci. Technol.* **1994**, *28*, 53−62.
(8) Huang, W.; Weber, W. J. *Environ. Sci. Technol.* **1997**, *31*, 3238−3243.
(9) Xia, G.; Pignatello, J. J. *Environ. Sci. Technol.* **2001**, *35*, 84−94.
(10) Xing, B.; Pignatello, J. J. *Environ. Sci. Technol.* **1997**, *31*, 792−799.
(11) Rockne, K. J.; Taghon, G. L.; Kosson, D. S. *Chemosphere* **2000**, *41*, 1125−1135.
(12) McGroddy, S. E.; Farrington, J. W.; Gschwend, P. M. *Environ. Sci. Technol.* **1996**, *30*, 172−177.
(13) Pignatello, J. J. *Environ. Toxicol. Chem.* **1990**, *9*, 1107−1115.
(14) Nam, K.; Alexander, M. *Environ. Sci. Technol.* **1998**, *32*, 71−74.
(15) White, J. C.; Alexander, M. *Environ. Toxicol. Chem.* **1996**, *15*, 1973−1978.
(16) Hatzinger, P. B.; Alexander, M. *Environ. Sci. Technol.* **1995**, *29*, 537−545.
(17) Mayer, L. M.; Jumars, P. A.; Taghon, G. L.; Macko, S. A.; Trumbore, S. *J. Mar. Res.* **1993**, *51*, 373−389.
(18) Shor, L. M.; Kosson, D. S. In *Bioremediation*; Valdes, J. J., Ed.; Kluwer Academic Publishers: Dordrecht, 2000; pp 15−43.
(19) Cornelissen, G.; Rigterink, H.; Ferdinandy, M. M. A. *Environ. Sci. Technol.* **1998**, *32*, 966−970.
(20) Knaebel, D. B.; Federle, T. W.; McAavoy, D. C.; Vestal, J. R. *Appl. Environ. Microbiol.* **1994**, *60*, 4500−4508.
(21) Carroll, K.-M.; Harkness, M.-R.; Bracco, A.-A. *Environ. Sci. Technol.* **1994**, *28*, 253−256.
(22) Cornelissen, G.; Van-Noort, P.-C. M.; Govers, H.-A. J. *Environ. Sci. Technol.* **1998**, *32*, 3124−3132.
(23) Nash, R. G.; Woolson, A. E. *Science* **1967**, *157*, 924−927.
(24) Scribner, S. L.; Benzing, T. R.; Sun, S.; Boyd, S. A. *J. Environ. Qual.* **1992**, *21*, 115−120.
(25) MacLeod, C.; Semple, K. *Environ. Sci. Technol.* **2000**, *34*, 4952−4957.
(26) Hatzinger, P. B.; Alexander, M. *Environ. Sci. Technol.* **1995**, *29*, 537−545.
(27) Liang, W. Ph.D. Dissertation, Rutgers University, New Brunswick, NJ, 2001.
(28) Rockne, K. J.; Taghon, G. L.; Young, L. Y.; Kosson, D. S. *In Situ On-Site Bioremediation* **1999**, *5*, 271−276.
(29) Leeming, R.; Mayer, W. *Org. Geochem.* **1994**, *18*, 647−655.
(30) Schantz, M. M.; Benner, B. A.; Hays, M. J.; Kelly, W. R.; Vocke, R. D.; Demiralp, R.; Greenberg, R. R.; Schiller, S. B.; Lauenstein, G. G.; Wise, S. A. *Fresenius J. Anal. Chem.* **1995**, *352*, 166−173.
(31) Gustafsson, O.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 203−209.
(32) Cornelissen, G.; van Noort, P. C. M.; Govers, H. A. *Environ. Toxicol. Chem.* **1997**, *16*, 1351−1357.
(33) U.S. EPA. *Sediment quality criteria for the protection of benthic organisms: phenanthrene*; EPA 822-R-93-012; Offices of Water, Research and Development, and Science and Technology: Washington, DC, 1993.
(34) NRC. *Contaminated Sediments in Ports and Waterways*; National Academy Press: Washington, DC, 1997.
(35) Burns, W. A.; Mankiewicz, P. J.; Bence, A. E.; Page, D. S.; Parker, K. R. *Environ. Toxicol. Chem.* **1997**, *16*, 1119−1131.
(36) Goss, K. U.; Eisenreich, S. J. *Atmos. Environ.* **1997**, *31*, 2827−2834.
(37) Dachs, J.; Eisenreich, S. J. *Environ. Sci. Technol.* **2000**, *34*, 3690−3697.
(38) Griffin, J. J.; Goldberg, D. E. *Environ. Sci. Technol.* **1983**, *17*, 244−245.
(39) Masiello, C. A.; Druffel, E. R. M. *Science* **1998**, *280*, 1911−1913.
(40) Prahl, F. G.; Carpenter, R. *Geochim. Cosmochim. Acta* **1983**, *47*, 1013−1023.
(41) Readman, J. W.; Mantoura, R. F. C.; Rhead, M. M. *Fresenius J. Anal. Chem.* **1984**, *319*, 126−131.
(42) Raoux, C. Y.; Garrigues, P. In *Organic Geochemistry, Advances and Applications in the Natural Environment*; Manning, D. A. C., Ed.; Manchester University Press: 1991; pp 552−556.
(43) Ghosh, U.; Gillette, J. S.; Luthy, R. G.; Zare, R. N. *Environ. Sci. Technol.* **2000**, *34*, 1729−1736.
(44) U.S. EPA. *Methods for Measuring the Toxicity and Bioaccumulation of Sediment-Associating Contamination with Freshwater Invertebrates*; EPA 600/R-99/064; U.S. EPA Office of Water: Washington, DC, 2000.