# PCB and PAH Speciation among Particle Types in Contaminated Harbor Sediments and Effects on PAH Bioavailability

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This research provides particle-scale understanding of PCB and PAH distribution in sediments obtained from three urban locations in the United States: Hunters Point, CA; Milwaukee Harbor, WI; and Harbor Point, NY. The sediments comprised mineral grains (primarily sand, silt, and clays) and carbonaceous particles (primarily coal, coke, charcoal, pitch, cenospheres, and wood). The carbonaceous sediment fractions were separated from the mineral fractions based on their lower density and were identified by petrographic analysis. In all three sediments, carbonaceous particles contributed 5-7% of the total mass and 60-90% of the PCBs and PAHs. The production of carbonaceous particles is not known to be associated with PCB contamination, and it is very unlikely that these particles can be the source of PCBs in the environment. Thus, it appears that carbonaceous particles preferentially accumulate PCBs acting as sorbents in the aqueous environment if PCBs are released directly to the sediment or if deposited as airborne soot particles. Aerobic bioslurry treatment resulted in negligible PAH loss from the carbonaceous coalderived material in Milwaukee Harbor sediment but resulted in 80% of the PAHs being removed from carbonaceous particles in Harbor Point sediment. Microscale PAH extraction and analysis revealed that PAHs in Harbor Point sediment were associated mainly with coal tar pitch residue. PAHs present in semisolid coal tar pitch are more bioavailable than PAHs sorbed on carbonaceous particles such as coal, coke, charcoal, and cenosphere. Results of this study illustrate the importance of understanding particle-scale association of hydrophobic organic contaminants for explaining bioavailability differences among sediments.

# Introduction

The management of sediments and the control of sediment contaminants are among the most challenging and complex problems faced by environmental engineers and scientists. Because of the strong binding of hydrophobic organic compounds (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), sediments serve as a long-term source of the contaminants to water bodies and biota, even long after the original source of contamination has been removed. While recent advances in analytical techniques make it possible to quantify even the smallest amount of anthropogenic contaminants present in sediment, our ability to relate sediment concentrations to water quality, biological availability, and toxicological effects is hindered by inadequate understanding of the binding and release of the contaminants in the sediment. This is due to the inherent heterogeneity of sediment material that defies organic geochemical generalizations based on bulk sediment physicochemical parameters such as total organic carbon content, surface area, and particle size distribution.

PCBs and PAHs sorb to the organic carbon fraction of sediment, and thus organic carbon fraction is taken as a measure of the sorption capacity for regulatory purposes. This enables normalization of the aqueous equilibrium relationship for sediments containing different amounts of organic carbon (1). However, a major problem with this approach is that organic carbon in sediment comes in different forms that may have very different sorption capacities for HOCs. For example, in addition to natural materials such as vegetative debris, decayed remains of plants and animals, and humic matter, sediment organic carbon also comprises particles such as coal, coke, charcoal, and soot that are known to have extremely high sorption capacities (2-6). Figure 1 shows a comparison of reported organic carbon-normalized phenanthrene partition coefficients (Koc) for different sorbents (5, 7-12). The  $K_{oc}$  values for different organic carbon forms span several orders of magnitude. On the basis of the partition coefficients presented in Figure 1, it is clear that HOCs associated with soot- or coal-type carbon may be orders of magnitude less available in the aqueous phase than HOCs associated with natural organic matter in soils and sediment. Thus, HOCs that end up in the sediment as contaminants may be of more or less concern depending on how weakly or strongly they are sorbed to the sediment organic matter.

Past work indicates the possible importance of soot carbon in sorption processes in sediment (2, 6, 13, 14). These studies measured soot carbon in sediment using partial thermal oxidation to remove non-soot organic carbon followed by treatment with acid to remove inorganic carbon and analysis of the remaining carbon. The soot carbon material isolated by partial thermal oxidation does not retain sorbed chemicals for further analysis. However, Gustafsson et al. (2) and Bucheli and Gustafsson (13) showed that elevated PAH partitioning in sediment samples could be explained on the basis of the soot carbon content and known high PAH sorption capacity of soot. They concluded that sorption of PAHs on a sootphase carbon in sediments may impact in situ bioavailability of PAHs. Accardi-Dev and Gschwend (6) performed PAH sorption studies with the isolated soot carbon and demonstrated that a modified, soot-partitioning inclusive, distribution model can better predict the observed PAH partitioning from sediment. Karapanagioti et al. (5) showed that sediments containing coaly particulates exhibited high  $K_{oc}$  values and nonlinear isotherms for phenanthrene sorption. Recently Salloum et al. (12) studied the sorption of phenanthrene on several aliphatic natural organic matter types (algae, cellulose, collagen, cuticle, lignin, kerogen, and humic acid) and concluded that aliphatic organic matter domains in soils and sediment may also play a significant role in the sorption of HOCs. However, none of these studies directly measured the levels of PAHs on natural organic matter particles, soot, or coal particles in field sediment, and as such, the conclusions are based on inference from equilibrium partitioning

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FIGURE 1. Organic carbon-normalized partition coefficient for phenanthrene for different types of organic carbon. Data sources: activated carbon (7); soot carbon (8); particulate coal, particulate charcoal, and amorphous organic matter (5); heavy fuel oil (9); several soils and sediments showing average and range (10, 11); Pula kerogen, collagen, humic acid, degraded algae, Green River kerogen, oxidized humic acid, cuticle, algae, lignin, and cellulose (12); coal tar (23).

and not on direct evidence of PAH association. Thus, from these studies it is not clear whether natural organic matter or black carbon in sediments comprise the predominant repository of hydrophobic contaminants such as PCBs and PAHs. In our earlier work, we demonstrated the predominant association of PAHs with coal-derived particles in Milwaukee Harbor sediments (4). We found from direct analysis of separated fractions and particle-scale microanalysis that the majority of PAHs in the sediment was associated with coalderived particles and that these PAHs were strongly bound, not easily desorbable, unavailable for biological treatment, and unavailable for uptake in earthworms (4, 15, 16).

The objective of this research is to extend particle-scale understanding of PCB and PAH distributions in sediment by comparing sediments from three different geographical locations and to illustrate the effect of PAH association with particle types on bioslurry treatment. We use three different aged, harbor sediment samples to investigate the importance of carbonaceous particles in the sequestration of PCBs and PAHs. The particulate organic carbon components in the sediments were separated by a density technique that preserves the physical and chemical integrity of the particles. Two of the sediments containing high levels of PAHs were subjected to aerobic bioslurry treatment to investigate PAH bioavailability to microorganisms. Microscale extraction and analysis were carried out to illustrate differences in PAH levels among carbonaceous particle types in sediment and to explain differences in PAH bioavailability.

#### Materials and Methods

Contaminated sediments often occur near harbors and old industrial establishments. Therefore, we selected three harbor/industrial locations across the country to study the extant distribution of PCBs and PAHs among particle classes. Three sediments used in this study were obtained from the following locations. All sediment samples were stored at 4  $^{\circ}$ C until used.

(*i*) Hunters Point, San Francisco Bay, CA. Sediment samples were collected from the intertidal zone in South Basin near the southern edge of the Hunters Point Naval Shipyard in January 2001 and screened through a 4 mm screen. Sampling took place during low tide along approximately 150 yards of shoreline within the intertidal zone. Historic shipyard and industrial activities in the adjacent region discharged PCBs,

PAHs, and heavy metals into the soil and sediment. Operations at the site included a former transformer storage yard, industrial landfills, fuel lines, a scrapyard, and an oil reclamation area. Between 1954 and 1974, nearly 250 gal of PCBs was estimated to have been released in the scrapyard parcel adjoining South Basin (*17*). Other PCB releases may have occurred as well. The Hunters Point South Basin Area is designated as a PCB hotspot in San Francisco Bay (*18*).

(*ii*) Milwaukee Harbor Confined Disposal Facility (CDF). Sediments in the CDF originated from Milwaukee Harbor during dredging operations to maintain waterway navigability. This 44 acre facility is operated by the Milwaukee Harbor Port Authority. Concerns have been raised about the potential for release of contaminants from such CDF sites and about closure requirements, as discussed by Bowman (*19*). Samples for this work were collected in fall 1996 at a depth of 4 m in the CDF. The sediment was sieved through a 1/4 in. screen in the field.

(*iii*) Harbor Point Sediment, NY. This sediment sample was collected in 1999 from a freshwater harbor site located near a former manufactured gas plant in Utica, NY. The sediment was collected using 1–2 ft cores and sieved through 3/8 in. mesh and composited on site. High levels of PAHs in the sediment are thought to have originated from a historic gas manufacturing facility in the vicinity.

Size and Density Separation. Wet sieving was performed to separate the sediment into four size fractions (<63, 63-250, 250-1000, and  $>1000 \,\mu$ m). The larger size fractions (>63  $\mu$ m) were composed primarily of sandy grains, carbonaceous particles, and woody material. The lighter carbonaceous particles were washed off from the heavier sand particles by swirling with water in a beaker and draining off the entrained lighter particles, giving two separate fractions that we define as "light" and "heavy". As a final step, a saturated cesium chloride solution with a specific gravity of 1.8 was used to remove the remaining lighter density particles. Materials in the fine fraction (<63  $\mu$ m) were density-separated using the cesium chloride solution. Five grams of wet sediment and 40 mL of cesium chloride solution were mixed and centrifuged at 2000g for 10 min in 50 mL glass centrifuge tubes. Separated particles were washed with water to remove cesium chloride (4).

**Coal Petrography Analysis.** Coal petrography analysis of sediment particles was performed according to ASTM standard methods for coal analysis: D2797 (Preparing Coal Samples for Microscopic Analysis by Reflected Light), D2798 (Microscopic Determination of the Reflectance of Vitrinite in a Polished Specimen of Coal), and D2799 (Microscopic Determination of Volume Percent of Physical Components of Coal).

PCB/PAH Analysis. Soil PCBs and PAHs were extracted following U.S. EPA Method 3550B using 3 volumes of 40 mL each of an acetone-hexane mixture (1:1) and sonicating the slurry for 6 min (pulsing for 15 s on and 15 s off). Pesticidegrade hexane and acetone were used for all extractions. EPA Method 3630C was followed for sample cleanup where the dried and concentrated extracts are passed through a deactivated silica gel column to remove organic interferences and to separate the PCBs and PAHs. PCB congener-specific analysis was performed using a modified EPA Method 8082. An Agilent gas chromatograph (model 6890) with a fused silica capillary column (HP-5, 60 m  $\times$  0.25 mm i.d.) and an electron capture detector was used for analysis. PCB standards for calibration were purchased as hexane solutions from Ultra Scientific (North Kingstown, RI) and also obtained from the U.S. EPA's National Health and Environmental Effects Research Laboratory in Grosse Ile, MI. A multi-level calibration table was prepared using a PCB mixture containing 250 µg/L of Aroclor 1232, 180 µg/L of Aroclor 1248 and 180  $\mu$ g/L of Aroclor 1262 yielding a total PCB concentration

of  $610 \mu g/L$  (20). Concentrations of individual PCB congeners in the mixture were obtained from Mullin (20). Two internal standards were used: 2,4,6-trichlorobiphenyland2,2',3,4,4',5,6,6'octachlorobiphenyl, which are not present in commercial Aroclor mixtures. Using this protocol, 86 PCB congeners or congener groups could be identified and quantified. With this analytical method, there are some coeluting peaks in the analysis. Where this occurs, coeluting peaks are calibrated as the sum of congeners. PAH analysis was performed using an Agilent gas chromatograph (model 6890) with a fusedsilica capillary column (HP-5, 30 m  $\times$  0.25 mm i.d.) and a flame ionization detector based on U.S. EPA Method 8100 for PAHs. A standard U.S. EPA mixture of 16 PAH compounds obtained from Ultra Scientific was used for calibration.

Microscale PAH Extraction and Analysis. To investigate differences in PAH abundances among particle types in Harbor Point sediment, a small quantity of lighter density particles in the 250–1000  $\mu$ m size fraction were manually separated under the microscope into five particle types: wood, coal/coke, charcoal, coal tar pitch, and cenosphere (see Figure S1 in Supporting Information). These particle types were identified by visual observation under a light microscope. The wood and charcoal were identified based on grain structure and color. The cenospheres appeared as black hard rounded shells. Coal appeared as hard, black, and shiny particles, and coke had a porous look. The coal tar pitch was confirmed from its softness under the tweezers and by observing particle melting upon contact with the heated tip of a spatula (see Figure S2 in Supporting Information). Five particles of each kind were weighed and extracted in 1.5 mL glass vials with Teflon-lined caps using a 50:50 mixture of methylene chloride and acetone. The capped vials were placed in a sonicator bath and warmed to 50 °C for 3 min for the extraction. Following three sequential extractions, the solvent was exchanged into cyclohexane and cleaned up in a silica gel microcolumn prepared in a disposable glass pipet. The cleanup procedure was a scaled down version of the standard U.S. EPA Method 3630C. The final extract was concentrated to 150 µL before analysis. Lighter density particles in Milwaukee Harbor sediment were also separated into the two primary components (coalderived, and wood) and analyzed for PAHs.

Aerobic Bioslurry Experiments. Aerobic slurry reactors using Harbor Point sediment were prepared in separate 4 L glass flasks. A total of 2.4 L of minimal medium was added with 1.33 kg of Harbor Point sediment. The minimal medium contained 0.4 g of K<sub>2</sub>HPO<sub>4</sub>, 0.317 g of NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, 0.216 g of NH<sub>4</sub>Cl, 0.1 g of MgSO<sub>4</sub>, 1.0 mg of FeSO<sub>4</sub>·7H<sub>2</sub>O, and 1.0 mL of trace elemental substances (TES)/L of deionized water, and pH was adjusted to 7.0 with NaOH. TES consisted of 0.15 g of ZnNO<sub>3</sub>·6H<sub>2</sub>O, 0.1 g of MnCl<sub>2</sub>·4H<sub>2</sub>O, 0.062 g of H<sub>3</sub>BO<sub>3</sub>, 0.19 g of CoCl<sub>2</sub>·6H<sub>2</sub>O, 0.035 g of CuSO<sub>4</sub>·5H<sub>2</sub>O, 0.027 g of NiSO<sub>4</sub>· 6H<sub>2</sub>O, 0.026 g of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O, and 5.2 g of EDTA/L of deionized water. Oxygen was supplied to the reactors through an air pump (1.6 L/min). The reactors were homogeneously mixed by Lightnin General Purpose mixer (Rochester, NY) and operated for 60 d at 24 °C. Polyurethane foam traps were used to test for volatilization of PAHs during the bioslurry process. Only naphthalene was detected in the trap and accounted for 0.8% of naphthalene present in the sediment added to the bioslurry reactor.

**Light Microscopy Imaging.** A Leica WILD M3Z microscope  $(65-400 \times magnification)$  was used for light microscopy imaging of sediment particles. A Kodak DX3900 digital camera was attached to the imaging tube of the microscope to collect pictures.

**PAH Desorption Study.** PAH desorption kinetic studies were conducted using separated lighter fractions. Desorption tests followed previously used procedures (*15*). Tenax beads (0.5 g) and sediment sample (0.2 g) were added to a 12 mL

glass vial containing 10 mL of water and continuously mixed in a rotator. Sodium azide (1000 mg/L) was added to the mixture to prevent biological growth. At sampling times, the Tenax beads were harvested by allowing the sediment to settle and the Tenax beads to float up. The Tenax beads were scooped out of the test tube, and fresh Tenax was added. PAHs were extracted from the Tenax beads and analyzed by GC-FID.

### **Results and Discussion**

Sediment Particle Characterization. Sediments from the three locations were separated into four size classes: <63, 63-250, 250-1000, and >1000  $\mu$ m. Light microscopy illustrates the diversity of particles and identifies prominent particle classes in the sediment samples. As shown in the microscopic image of sediments from the three locations in Figure 2, the 250–1000  $\mu$ m size sediments comprise mineral grains (primarily sand) and organic particles of various kinds such as wood, charcoal, coal, coke, pitch, and cenosphere. An exact identification of the nature of organic particles was performed through petrographic analysis. Petrographic analysis involves preparation of a polished particle surface followed by visualization under a microscope using normal or polarized light. This technique has been used historically to identify coal maceral structures, rank coals, identify different stages of coal pyrolysis and coke formation, determine coal tar and pitch quality, and identify chars and cenospheres (21). Karapanagioti et al. (5) used petrographic techniques to identify types of organic matter including coals in different size fractions of aquifer material. In our earlier work, we used similar techniques to identify coal-derived particles in Milwaukee Harbor sediment (4).

The various kinds of organic particles identified in the three sediments in this study by petrographic analysis are shown in Figure 3. A striking common feature in the analysis of the three sediments is the abundance of coal and coalderived particles in all three sediments. Possible sources of coals in these sediments are coal transportation activities in harbors near the sampling locations, historic coal use in the local area, and coal gas manufacturing facilities in the vicinity. All three sediments showed the presence of wood particles. Hunters Point and Harbor Point sediment showed significant presence of lignite and cenospheres. Cenospheres are more or less spherical, porous semicoke or coked particles formed during the rapid heating of unconfined coal (21). These particles appear as hollow carbon spheres often broken into pieces in the sediment. A special feature of the Harbor Point sediment was the presence of pitch, a likely residue and waste product from former manufactured gas operations. The Milwaukee Harbor sediment was unique in showing a preponderance of coal-derived particles. The Hunters Point sediment showed significant presence of charcoal, which was not observed in abundance in the other sediment samples. Oil-soot particles were not seen abundantly in the two size fractions that were studied in detail: 63-250 and  $250-1000 \,\mu\text{m}$ . Oil-soot particles are typically nanometer sized globules, often in grape-like clusters several micons in size. On the basis of the size of oil-soot particles, these may be present in the study sediments in the  $< 63 \,\mu m$  lighter density fraction. In our petrography analysis for Hunters Point sediment, we found an oil-soot cluster in the 63–250  $\mu$ m size range among more prevelant black carbonaceous particle types described above. Although there were differences in carbonaceous particle types found in the three sediment samples, a common characteristic is the abundance of highly sorbing carbon substrates in all three sediments.

**PCB and PAH Concentrations in Sediment.** PCB homologue and PAH concentrations in the three sediments are shown in Figures S3 and S4, respectively, in the Supporting Information. Among the three sediments, Hunters Point had



Harbor Point, NY

Milwaukee Harbor, WI

Hunters Point, CA

FIGURE 2. Light microscopy images of particles in sediment from three locations showing the different geochemical types in the size range of  $250-1000 \mu$ m. The relevant particle types identified are sd, sand; sh, shell; co, coal; ch, charcoal; pi, coal tar pitch; ce, cenosphere; and wd, wood.

the highest levels of PCBs at 9.9  $\pm$  0.9 mg/kg with predominantly higher chlorinated congeners and resembling Aroclor 1260 in congener distribution. The most abundant PCB homologues were hexa- and heptachlorobiphenyls. The PCB concentrations at this site are approximately 3 orders of magnitude higher than background PCB levels (25  $\mu$ g/kg) in the sediment in San Francisco Bay (18). Total PCB concentration in Milwaukee Harbor sediment was 1 mg/kg with tetra- and pentachlorobiphenyls being the most abundant homologues. Although PCBs were detected in Harbor Point sediment, a detailed study of the PCB distribution in this sediment was not conducted as part of this investigation. Research with Harbor Point sediments focused on PAHs, which were the primary contaminant of concern at this site at  $262 \pm 25$  mg/kg total PAHs. This sediment also appears to be the least weathered based on the relatively higher levels of lower molecular weight PAHs such as phenanthrene. Total PAH concentration in Milwaukee Harbor sediment was 90  $\pm$  7 mg/kg. Hunters Point sediment had the lowest levels of PAHs at 8 mg/kg.

It is well-known that hydrophobic organic compounds such as PCBs and PAHs partition into organic carbon on soils and sediments. However, this partitioning process may vary greatly if the organic carbon present in soils and sediments comprises various forms such as humic matter particles, humic matter sorbed on mineral surfaces, animal and vegetative debris, and products of coal and wood use and combustion. Our earlier work with Milwaukee Harbor sediment showed the importance of coal-derived particles in sorption of PAHs. The following compares the distribution of PCBs and PAHs among particle sizes and density classes for three different sediments.

Sediment Mass Distribution among Particle Classes. The carbonaceous sediment fraction comprising coal, coke, charcoal, pitch, cenospheres, and wood are separable from the mineral fraction based on their lower density. The three sediments were separated into size and density fractions and analyzed for PCBs and PAHs in each fraction. Results of sediment mass distribution by size and density shown in Figure 4 reveal for each size fraction that the lighter density fraction has much smaller mass as compared to the heavier mineral fraction. For all three sediments 5–7% of the total sediment mass is contributed by the lighter density carbonaceous particles. The two freshwater sediment samples, Milwaukee Harbor and Harbor Point, have clay/silt (<63  $\mu$ m heavy) as the predominant sediment component. The Hunters Point sediment is coarser in grain size with fine and coarse sands comprising the majority of the sediment.

Sediment PCB and PAH Distribution among Particle Classes. PCB and PAH analyses of the lighter and heavier density fractions reveal that the majority of the contaminants are associated with the small quantity of lighter density carbonaceous particles. As shown in Figure 5, the fraction of total PAHs associated with the lighter density carbonaceous particles in Hunters Point, Milwaukee Harbor, and Harbor Point sediments are 89%, 68%, and 62%, respectively. We find that the fraction of total PCBs associated with lighter density carbonaceous particles in Hunters Point and Milwaukee Harbor sediments are 68% and 58%, respectively (Figure 6). Thus, for all three sediments, PAHs and PCBs are predominantly associated with the carbonaceous particles. Earlier work by us for Milwaukee Harbor sediment (4) and recent work by Rockne et al. (22) for NY/NJ harbor sediments has shown that PAHs can be found predominantly in the lighter density fraction of sediments. As with PAHs, our data for two sediments are the first reporting of the distribution of PCBs among sediment particle density classes.

PAH and PCB analyses by size and density fractions shown in Figures 5 and 6 reveal that except for the fine grained (<63  $\mu$ m) sediment fraction, for every size fraction, the lighter density material contributes to the majority of PAHs and PCBs in the sediment. For the fine size fraction (<63  $\mu$ m), in all three sediments the heavier density particles contributed more PCBs and PAHs than the lighter density particles. Possible reasons for the difference with the finest size fraction are the much larger surface area of the finer size fraction and the comparatively larger overall mass of heavy particles in this size fraction. For example, in the case of Harbor Point



Harbor Point, NY

Milwaukee Harbor, WI

Hunters Point, CA

FIGURE 3. Petrographic identification of organic carbon particles in sediment from three locations reveals the presence of coal, partially oxidized coal, coke, lignite, wood, charcoal, cenospheres, char, and pitch. Petrography images shown are under reflected light in oil at  $500 \times$  magnification.

sediment, only 1% by mass in the  $\,{}^{<}63~\mu{\rm m}$  size fraction comprises light particles.

**Implications of PCB Speciation in Carbonaceous Particles.** Since combustion and pyrolysis processes are associated with the production of PAHs as a byproduct, there is a possibility that the coal- and combustion-derived particles reach the sediment with PAHs already sorbed to the particles. In our current work, we analyzed PCB distribution in two of the sediments. Results of PCB analysis by sediment density fractions reveal a strikingly similar story wherein the majority of the PCBs are associated with the lighter density carbon-aceous particles. Since the production of coal, coke, charcoal, and cenosphere is in no way associated with PCB use, it is unlikely that these particles can be the source of PCBs in the environment. For the  $< 63 \ \mu$ m size light fraction, if airborne soot particles are present, those may have picked up some



FIGURE 4. Sediment mass distribution by size and density, heavy (Hv) and light (Li), for Hunters Point, CA; Milwaukee Harbor, WI; and Harbor Point, NY, sediments.

of the PCBs from the atmosphere before depositing in the sediment. For the larger sized particles such as coal, coke, and charcoal, it appears that over a long period of time, PCBs in the sediment tend to preferentially accumulate in these carbonaceous particles where they may be strongly bound. Such migration of PCBs and possibly PAHs into a more strongly sorbing matrix has significant implications for assessment of sediment quality criteria and for possible in situ stabilization approaches. For example, addition of sorbent carbonaceous material like activated carbon to the sediment may enhance the sequestration of these hydrophobic compounds in the sediment, making them less available for biological uptake and release into the overlying water.

Effect of PAH Association with Particle Types on Bioavailability. Aerobic bioslurry experiments were carried out using the two sediments that had high levels of PAHs: Milwaukee Harbor (90 mg/kg) and Harbor Point (262 mg/ kg). We reported in an earlier study for Milwaukee Harbor sediment that PAH biodegradation was achieved mainly within the <63  $\mu$ m heavy fraction comprising the clays and silt, for which there was 75% reduction in PAHs (16). The coal-derived material from Milwaukee Harbor sediment showed no significant reduction in PAH concentrations during the biotreatment process. Thus PAHs associated with the lighter density fraction of Milwaukee Harbor sediment, which was primarily coal-derived particles, appear to be strongly bound and not available for biological degradation.

A similar aerobic bioslurry treatment study was conducted using Harbor Point sediment to compare with the finding from the Milwaukee Harbor study. As shown in Figure 7, nearly 75% reduction of total PAHs was achieved during 2 months of aerobic bioslurry treatment of Harbor Point



FIGURE 5. Sediment PAH distribution by size and density, heavy (Hv) and light (Li), for the contaminated sediments from urban areas. The lighter density fractions comprise 89%, 68%, and 62% of the total PAHs for Hunters Point, CA; Milwaukee Harbor, WI; and Harbor Point, NY, sediments, respectively.



FIGURE 6. PCB distribution in Hunters Point sediment and Milwaukee Harbor sediment by size and density, heavy (Hv) and light (Li). The less dense fractions of the sediment comprise 68% and 58% of the total PCBs for Hunters Point, CA, and Milwaukee Harbor, WI, respectively.

sediment. Greater than 90% reduction was achieved for the low molecular weight PAHs  $(2-3 \operatorname{ring})$  and 20-50% reduction was achieved for the high molecular weight PAHs  $(5-6 \operatorname{rings})$ . PAH analysis by particle size and density revealed that, although reductions of PAHs associated with the heavy sand/silt/clay fractions were high (69%), significant PAH reductions were also achieved for PAHs associated with the lighter density fractions comprising coal, charcoal, char, cenospheres, and coal tar pitch (80%). As shown in Figure 8, the four size classes of the lighter density fraction of Harbor Point sediment underwent significant losses of PAHs during the bioslurry treatment process.



FIGURE 7. Change in PAH concentration during 2 months of aerobic bioslurry treatment of Harbor Point sediment.



FIGURE 8. PAH loss from Harbor Point sediment for size and density fractions during 2 months of aerobic bioslurry treatment showing losses from heavy (Hv) mineral fractions as well as light (Li) organic particle fractions.

PAH Desorption Kinetics. Abiotic desorption studies using Tenax resin were conducted with two size fractions  $(63-250 \text{ and } 250-1000 \ \mu\text{m})$  of the lighter density particles in Milwaukee Harbor and Harbor Point sediments. Results of these desorption studies are shown in Figure 9 where the fraction of PAHs released from the sediment particles after different times of desorption are plotted over a 8-10 day period. For the three most prominent PAHs that were degraded during biotreatment (phenanthrene, fluoranthene, and pyrene), 10-20% of the PAHs are desorbed in Milwaukee Harbor sediment as compared to 40-70% for Harbor Point sediment in the same time period. Thus, mass transfer of PAHs from the lighter density particles is much faster in Harbor Point sediment as compared to that in Milwaukee Harbor sediment. The striking difference in PAH desorption rates in the lighter density fraction of the two sediments explains the differences in extents of PAH biodegradation observed.

**Microscale PAH Extraction from Organic Particle Types.** Microscale extraction and analysis was performed on the different particle classes in Harbor Point and Milwaukee Harbor sediments to investigate further the association of PAHs with the lighter density carbonaceous particles in these two sediments. Individual particles of the lighter density fraction particles ( $250-1000 \ \mu$ m) were separated manually using a pair of fine-point tweezers under a microscope. The five types of carbonaceous particles separated out as shown in Figure S1 in the Supporting Information are coal tar pitch,



FIGURE 9. Desorption of PAHs from light-density fractions showing faster release of PAHs from Harbor Point sediment as compared to the Milwaukee Harbor sediment. The dashed lines and open symbols represent data for Harbor Point. Full lines and closed symbols represent data for Milwaukee Harbor. Triangles represent particle size 63–250  $\mu$ m, and squares represent size 250–1000  $\mu$ m.

charcoal, cenosphere, coal/coke, and wood (56%, 9%, 18%, 5%, and 12%, respectively, by weight). Coal petrography analysis performed on another set of particles confirmed the presence of these particle types (see Figure 3). Results of



FIGURE 10. Microextraction and analysis of major organic particles classes in the 250-1000- $\mu$ m size fraction showing the predominance of PAH association with coal-derived particles in Milwaukee Harbor and coal tar pitch particles in Harbor Point sediment.

extraction and microanalysis of carbonaceous particles from Milwaukee Harbor and Harbor Point sediment are shown in Figure 10. For Milwaukee Harbor, coal-derived particles (coal, partially oxidized coal, and coke) contributed 95% of the PAHs in the lighter density fraction (250–1000  $\mu$ m). In contrast, coal tar pitch particles contributed 96% of the total PAHs in the Harbor Point sediment light density fraction  $(250-1000 \ \mu m)$ . Contributions from the other types of particles amount to the remaining 4% of the PAHs. Although the individual particle separation and microscale PAH analyses were not possible for the smaller size fractions, visual observation under a microscope revealed a similar nature of particle distribution across particle sizes in the lighter density fraction. Thus, for Harbor Point sediment, the predominance of PAHs in the lighter density particles is due to the presence of PAH containing coal tar pitch particles. The implications from these observations are as follows:

PAHs sorbed on coal-derived particles and aged for years in the field (as seen in Milwaukee Harbor sediment) are strongly bound and not available for biodegradation, whereas PAHs associated with semisolid, coal tar pitch (as seen in Harbor Point sediment) are largely bioavailable. In the first case, PAHs are sorbed on highly aromatic, hard, coal-derived particles; in the second case, PAHs are partitioned into a softer coal tar pitch matrix and therefore more easily available for desorption. Our results from abiotic desorption tests show that PAHs desorb much faster when associated with pitch particles as compared to coal/coke particles. Log  $K_{oc}$  values for phenanthrene sorption on coals are reported to be 6.3-6.4 (5) as compared to a log  $K_{oc}$  of 5 for phenanthrene partitioning from coal tars (23) (assuming carbon content of coal tar to be 95%). Thus, based on equilibrium partitioning, PAHs associated with coal tar are much more available in the aqueous phase than PAHs sorbed on coals. The semisolid matrix of coal tar pitch may inhibit mass transfer rates but not as much as polymer-like diffusion in coals. Work by Ortiz et al. (24) reports solid-phase diffusivities for phenanthrene through solid paraffin in the order of  $10^{-10}$  cm<sup>2</sup>/s, which is orders of magnitude higher than estimated diffusivities of PAHs in coal matrix reported by us of  $10^{-17}$  cm<sup>2</sup>/s (15) and

those reported by Karapanagioti et al. (5) of  $10^{-14}$  cm<sup>2</sup>/s. On the basis of the large differences in equilibrium partitioning and desorption rates between hard coal versus the softer semisolid pitch matrix and the fact that during bioslurry treatment some of the soft coal tar pitch particles may also undergo breakdown, it is not surprising that we see significantly higher extent of biotreatment in Harbor Point sediment as compared to Milwaukee Harbor sediment.

Several recent studies suggest the predominant role of soot carbon or black carbon in the sequestration of PAHs in sediments (2, 3, 6, 8, 14). Most of these studies use two separate observations: high sorption capacity of soot carbon and identification of soot carbon in sediments to infer that PAHs in sediment are actually associated primarily with the soot carbon, as equilibrium conditions would dictate. Nonetheless, there is little direct evidence that soot carbon in sediment indeed contains a major fraction of PAHs. Results of this study illustrate the importance of direct measurements at the particle scale to understand the nature of PCB and PAH distribution in contaminated sediments. We show here that black carbon particles in aged, field sediments may accumulate PCBs. Furthermore, as shown in the case of Harbor Point sediment, even in the presence of black carbon (coal, coke, cenospheres, and charcoal), PAHs may remain primarily associated with original source materials such as coal tar pitch and may be available to microorganisms for biodegradation.

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## Supporting Information Available

Additional light microscopy images of representative organic particle types in Harbor Point sediment and additional data on PCB and PAH distributions in the three sediments. This material is available free of charge via the Internet at http:// pubs.acs.org.

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