Importance of Black Carbon to Sorption of Native PAHs, PCBs, and PCDDs in Boston and New York Harbor Sediments

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The solid−water distribution ratios (K_d values) of "native" PAHs, PCBs, and PCDDs in Boston and New York Harbor sediments were determined using small passive polyethylene samplers incubated for extended times in sediment-water suspensions. Observed solid−water distribution coefficients exceeded the corresponding $f_{oc}K_{oc}$ products by 1−2 orders of magnitude. It was hypothesized that black carbon (f_{BC}), measured in the Boston harbor sediment at about 0.6% and in the New York harbor sediment at about 0.3%, was responsible for the additional sorption. The overall partitioning was then attributed to absorption into the organic carbon and to adsorption onto the black carbon via $K_d = f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{n-1}$ with C_w in μg/L. Predictions based on published K_{oc}, K_{BC}, and n values for phenanthrene and pyrene showed good agreement with observed $K_{d,obs}$ values. Thus, assuming this dual sorption model applied to the other native PAHs, PCBs, and PCDDs, black carbon-normalized adsorption coefficients, K_{BC}s, were deduced for these contaminants. Log K_{BC} values correlated with sorbate hydrophobicity for PAHs in Boston harbor (log $K_{BC} \approx$ 0.83 log $\gamma_w^{sat} - 1.6$; $R^2 = 0.99$, $N = 8$). The inferred sorption to the sedimentary BC phase dominated the solid−water partitioning of these compound classes, and its inclusion in these sediments is necessary to make accurate estimates of the mobility and bioavailability of PAHs, PCBs, and PCDDs.

Introduction

The fate and effects of hydrophobic organic compounds (HOCs) in the environment are largely determined by their sorption to solid phases. For example, HOC releases to lake waters and coastal seawaters from contaminated sediment beds, accumulation by benthic animals, and biodegradation by microorganisms are processes that all depend on that HOC's sorption in the situation of interest (*1*). For many years now, investigators have noted that sorption of HOCs to natural sediments is not always consistent with predictions based on an absorption model ($f_{oc}K_{oc}$) that considers all organic matter as equally sorptive (*2−15*). Since investigators of polycyclic aromatic hydrocarbons (PAHs) long ago found

that these HOCs were commonly associated with "active carbon particles" in sediments (*16−18*), we have hypothesized that this sorption modeling discrepancy is often due to the presence of soots or chars (hereafter referred to as black carbon, BC particles) derived from combustion processes. This might be especially important for compounds such as PAHs and polychlorinated dibenzo-*p*-dioxins (PCDDs) that are co-generated with BC. Using spiking experiments, various workers have found that soots, as well as coal dust and naturally occurring coal and coaly particles, can be important for the sorption of PAHs (*10*, *11*, *19*, *20*). All these carbonaceous solids may also be important sorbents, analogous to granular activated carbon, for other HOCs like polychlorinated biphenyls (PCBs). This may be especially true for HOCs that can assume a planar conformation and thus maximize their contact with planar adsorbent surfaces (*21*).

In this paper, we examine the solid−water distributions of naturally incorporated ("native") PAHs, PCDDs, and PCBs, long present in sediment beds from Boston and New York harbors. By using the native sorbates, we sought to avoid the concern that spiked HOCs may not distribute into the solids in the same manner as the compounds long present in the environment. The Boston and New York harbor sediments were chosen to emphasize sorption to soots and chars since previous workers have shown the mostly pyrogenic origin of the PAHs in these locales (*4*, *22*). Coal shipping, storage, and use have not been prominent in these regions for the last 50 years, suggesting that the BC present in the top sediments is primarily composed of sootlike BC rather than coal. Using these harbor sediments in a series of laboratory experiments, we determined the overall solid−water distribution coefficients ($K_{d,obs}$) of such compounds without adding "spiked compounds" to the sediment slurries. Equilibrium dissolved concentrations were deduced by including small passive samplers, pieces of polyethylene (PE), in the incubations (*23−26*). The PE takes up organic compounds from the solid−water system until phase equilibrium is reached. At equilibrium, the measured PE concentrations, together with the corresponding PE−water partition coefficients (K_{PEw}), can be used to quantify the compounds' freely dissolved concentrations. While previous observations have long indicated the importance of BC to PAHs (*7*, *16−18*), we also sought to analyze other hydrophobic compounds in the same sediments including PCBs and PCDDs. Since these chlorinated, aromatic compounds differ in that PCDDs are planar molecules such as PAHs, while many PCB congeners often do not prefer planar conformations, we wanted to evaluate the role of sorbate shape.

Materials and Methods

Overview. PEs were deployed as passive in situ equilibrium samplers (*23−28*) in the sediment incubations. Low-density 51-μm-thick polyethylene sheet (Carlisle Plastics, Minneapolis, MN) was cut into small pieces and precleaned by extracting for 24 h in dichloromethane (DCM) twice, then methanol, and finally milli-RO water (AriesVaponics, Rockland, MA). When a piece of PE is placed in a sediment−water slurry, the HOCs accumulate within the PE until phase equilibrium occurs. In previous work in our laboratory (*23*, *24*), studies of the kinetics of the phenanthrene, pyrene, and 2,2′,5,5′-tetrachlorobiphenyl uptake into such cleaned PE from water revealed equilibration required less than a week, consistent with other literature reports (*27*). With this time frame in mind, the solvent-cleaned PE was characterized with respect to equilibrium partition constants for individual PAHs, PCBs, and PCDDs at room temperature (the same

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TABLE 1. Partition Coefficients of Selected Compounds: Octanol−Water (K_{ow}), Organic Carbon−Water (K_{oc}), Polyethylene−Water (K_{PEw}), and Aqueous Activity Coefficients at Saturation (γ_w^{sat})

compd	phen	pyr	bap	#44	#66	#95	2,7/8-Cl₂DD	2,3,7-Cl₃DD
log K_{ow}[a]	4.5	5.0	6.0	5.8	6.2	6.1	5.7	6.3
log γ_w^{sat} [b]	6.2	6.8	8.2	7.7	8.1	8.0	7.7	8.5
log K_{oc}[c]	4.2	4.7	5.7	5.1	5.5	5.4	5.4	6.0
log K_{PEw}[d]	4.5	5.0	6.3	5.3	6.1	5.9	5.5	6.2

[a] Mackay et al. (39) for PAHs. Hawker and Connell (37) for PCBs. Shiu et al. (38) for PCDDs. [b] Schwarzenbach et al. (1). log γ_w^{sat} (PAHs) = (log K_{ow} + 0.13)/0.75. log γ_w^{sat} (PCBs) = (log K_{ow} + 0.70)/0.85. log γ_w^{sat} (PCDDs) = (log K_{ow} + 0.79)/0.84. [c] Xia (36). log K_{oc} (PAHs, PCDDs) = 0.97 × log K_{ow} − 0.12. log K_{oc} (PCBs) = 0.97 × log K_{ow} − 0.50. [d] Adams (23). log K_{PEw} (PAHs) = 1.2 × log K_{ow} − 0.97. log K_{PEw} (PCBs) = 1.8 × log K_{ow} − 4.9. log K_{PEw} (PCDDs) = 0.99 × log K_{ow} − 0.09.

temperature used in our sediment−water incubations). The partition coefficients (K_{PEw}), defined as the ratio of the compound concentration in the PE (C_{PE}) over the dissolved concentration (Table 1):

$$K_{PEw} = C_{PE}/C_w \ (\text{mol/g PE})(\text{mol/mL water})^{-1} \quad (1)$$

were reproducible to within 0.1 log units (24). Knowledge of the HOC's PE−water partition coefficients allowed us to quantify the concentrations of the dissolved HOCs in equilibrium with the PE sampler and the sediments.

Experimental Procedure. Wet sediment, water, and a small piece of PE were weighed into each of three foil-clad flasks and tumbled end-over-end in the dark for periods of up to 6 months. Each flask had a different size of PE (between 0.12 and 0.72 g). The masses of PE were chosen so that even the largest ones accumulated less than 5% of the individual sorbates at system equilibrium. At increasing time intervals, the PEs were removed, extracted, and analyzed for individual PAHs, PCBs, and PCDDs. After air-drying, the cleaned PEs were re-introduced into the flasks and subjected to further tumbling. In short incubations (less than 1 week), we saw that the smallest PEs exhibited greater HOC concentrations, C_{PE}, than the larger-PE replicates. This implied uptake by the PE was not limiting the rate of approach to system equilibration since all PEs had the same surface-area-to-mass ratio. Hence, like-C_{PE} values in small, medium, and large PE pieces were taken as evidence of sediment−water−PE equilibrium. Experiments were carried out with two different sediments: one from Quincy Bay in Boston Harbor (BH) and one from the Hudson River estuary in New York Harbor (NYH).

Boston Harbor. Grab samples of surface sediments were collected in North Quincy Bay, near Boston, MA, in December 1999. The sediment sample is described in more detail in Accardi-Dey and Gschwend (13). Three 500-mL glass flasks were used with same amount of sediment (20.9 g dry weight, determined from subsampled wet sediments) and water (450 mL), but increasing PE sizes (0.115, 0.262, and 0.642 g). A fourth glass flask served as a blank, consisting of 500 mL water and PE (0.35 g). The PEs were removed and analyzed after a succession of 3, 4, 17, 125, and 182 days of sediment−water exposures. After each extraction, the cleaned PEs were re-introduced into the flasks; this marked the beginning of a new tumbling experiment with the tumbling time set back to zero. The total amount removed by PE throughout the sequence of five tumbling experiments was around 10% for PAHs and 20% for PCBs.

New York Harbor. A 50 cm × 50 cm box corer was deployed from the M/V *Samantha Miller* to obtain a sediment core in the Hudson River (NYH) on October 4, 2000. The site was situated at the estuarine turbidity maximum zone (40°49′20.9′′ N, 73°58′26.2′′ W; more details are given in ref 29, in which the site is designated S11). A composite sample made up of the top 4 cm of the core was homogenized and subsampled for the tumbling experiment. For the NYH sediment tumbling, a higher sediment−water ratio than used for the BH

experiment was chosen to shorten the times to reach phase equilibrium. Three 250-mL glass flasks were used with same amounts of sediment (40.0 g dry weight) and water (200 mL) but increasing PE sizes (0.269, 0.434, and 0.722 g). A blank consisting of water and PE (0.38 g) was also run in parallel. The PEs were removed, extracted, and analyzed for PAHs, PCBs, and PCDDs after three consecutive 14-day sediment−water exposures. In the NYH sediment, the accumulated removals were around 20% of PAHs and PCBs and about 10% of PCDDs.

Analytical Procedure. Upon recovery of the PEs from the slurries, they were rinsed with milli-RO water, dried with Kimwipes, and extracted consecutively for 24 h in 60 mL DCM and again in 60 mL hexane. Internal standards (25 ng individual deuterated PAHs, 5 ng individual PCB congeners, and 1.25 ng ¹³C₁₂-labeled PCDDs per PE) were added prior to extraction.

Prior to tumbling, and again after each sediment's sequence of incubations, aliquots of sediment were analyzed for the PAHs, PCBs, and PCDDs. The sediment samples were Soxhlet-extracted consecutively for 24 h with hexane−acetone (90−10 v:v) followed by DCM. Internal standards (250 ng individual deuterated PAHs, 5 ng individual PCBs, and 12.5 ng individual ¹³C₁₂-labeled PCDDs per sample) were added to the sediments prior to extraction. The combined extracts were dried over anhydrous Na_2SO_4, concentrated to ca. 1 mL, and analyzed for PAHs and PCBs. For PCDD-analysis, sediment sample extracts were cleaned up using a mixed silica gel column (silica gel from Merck, grade 60; 2-cm-diameter column containing, from bottom to top: anhydrous Na_2SO_4, 2.5 g activated silica gel, 2.5 g basic silica gel (33% w:w 1 M NaOH), 2.5 g activated silica gel, 5 g acid silica gel (44% w:w concentrated H_2SO_4), 2.5 g activated silica gel, and anhydrous Na_2SO_4. Extracts were eluted with 125 mL hexane. All samples were then fractionated on a basic alumina column (1-cm-diameter column containing 4.5 g Super alumina 1 B from ICN) and eluted with 20 mL DCM−hexane (7:93 v:v, F₁) followed by 25 mL DCM/hexane (50:50 v:v, F₂-contained PCDDs). F₂ was spiked with 50 μL of deuterated *p*-terphenyl at 125 pg/μL in decane (injection standard) and reduced to its final volume before GC−MS analysis.

Quantification. All samples were analyzed by GC−MS. Analytes were separated on a 30 m × 250 μm i.d. DB5-MS capillary column with a 0.25-μm film thickness (J &W Scientific, Folsom, CA) in an HP 6890 GC connected to a JEOL GCmate MS operating at a resolving power of 500 (PAHs, PCBs) or 1000 (PCDDs). Samples (1 uL) were autoinjected in the splitless mode with the injection port held at 280 °C. The MS was operated in EI⁺ mode with selected ion monitoring (SIM). The following compounds were analyzed: phenan-threne (Phen), anthracene (An), sum of methylphenanthrenes (ΣMe-phen), fluoranthene (Fluo), pyrene (Pyr), benz[*a*]-anthracene (BaA), benzo[*b*]fluoranthene (BbF), benzo[*k*]-fluoranthene (BkF), benzo[*e*]pyrene (BeP), benzo[*a*]pyrene (BaP), perylene (Per), PCB congeners 2,2′,3,5′-tetrachloro-

TABLE 2. Sediment[a] (ng/gdw) and Dissolved Concentrations[b] (ng/L) Found in Laboratory Incubations of Boston Harbor (BH) and New York Harbor (NYH) Bed Sediments[d]

compd	phen	pyr	bap	PCB 44	PCB 66	PCB 95	2,7/8-Cl$_2$DD	2,3,7-Cl$_3$DD	f_{oc}[c]	f_{BC}[c]
					BH					
mean C_{sed}	9000	11000	3200	4300	8100	5400			3.1%	0.60%
SD	2000	4500	350	2100	2800	1000			0.64%	0.07%
mean C_w	1100	560	10	180	59	66				
SD	420	91	3	49	5	11				
					NYH					
mean C_{sed}	310	740	500	13	24	8.1	0.86	0.031	2.6%	0.34%
SD	13	63	43	<1	3	0.4	0.05	0.003	0.03%	0.02%
mean C_w	94	32	≥0.71	0.49	0.097	≥0.12	9.6E-03	5.1E-05		
SD	29	7	0.04	0.08	0.012	0.02	5.4E-04	1.5E-05		

[a] Based on sum of extraction at the end of experiments plus amounts removed in PEs. [b] Calculated as C_{PE}/K_{PEw}. [c] BH data from ref 13. [d] Standard deviations (SD) reflect variation of triplicates. Values preceded by a greater than or equal sign represent cases in which system equilibration may not have been achieved.

biphenyl (no. 44), 2,2′,5,5′-tetrachlorobiphenyl (no. 52), 2,3′,4,4′-tetrachlorobiphenyl (no. 66), 2,2′,3,5′,6-pentachlorobiphenyl (no. 95); and PCDDs, 2,7/8-Cl$_2$DD and 2,3,7-Cl$_3$DD. PAHs and PCDDs were quantified using the isotope dilution method relative to isotope-labeled internal standards (d_{10}-acenaphthene, d_{10}-Phen, d_{14}-p-terphenyl, d_{12}-BaA, d_{12}-Per; and $^{13}C_{12}$-2,7/8-Cl$_2$DD). Calibration standards, chosen to bracket the sample concentrations of PAHs or PCDDs, were used to derive response factors of the analytes relative to the appropriate isotope-labeled internal standards. PCBs were quantified relative to internal standards (PCBs 69 and 143). In the later BH PE-samples, PAHs and PCBs were analyzed in dilutions which were quantified externally.

Quality Assurance/Quality Control. Mean recoveries of the added internal standards (±1 RSD), calculated relative to the GC injection standards, ranged from 78 ± 23% (d_{10}-Ace) to 99 ±35% (d_{12}-BaA) for the PAHs, from 73 ± 41% (no. 69) to 80 ± 27% (no. 143) for the PCBs, and were 88 ± 17% for $^{13}C_{12}$-2,7/8-Cl$_2$DD. The isotope dilution method corrects the analytes' concentration in the sample for recoveries of the internal standards. Blank values for PAHs in the PEs were in general below 1% of the amount of PAHs retrieved by the PEs. The concentrations of the other PAHs, PCBs, and PCDDs in the blanks were calculated from the noise of the baseline and did not exceed 1 ng/sample (PAHs), a few hundred pg/sample (PCBs), and less than 10 pg/sample (PCDDs). This was equivalent to less than 10% of the amount of analytes detected in the samples. The results were not blank-corrected.

In the BH sediments, the mass balance after five equilibrations lasting a total time of almost 1 year was 84% ± 30% for the PAHs ($N = 24$). For PCBs 44, 66, and 95, the mean mass balance was 85% ± 31% ($N = 9$). In the NYH sediments, an average of 99 ± 29% of PAHs ($N = 33$) could be accounted for in the mass balances, with a range of 63% (BkF, BaP) up to 129% (Me-Phen). For PCBs, an average mass balance of 66 ± 7% ($N = 12$) was calculated. For the Cl$_{2-3}$DDs, mass balances yielded 80% ± 6% ($N = 6$). These results indicate that whatever losses, if any, occurred in the incubations over the weeks and months would not have caused significant sorptive disequilibrium (i.e., an undersaturated dissolved phase).

Organic Carbon (f_{oc}) and Black Carbon (f_{BC}) Determinations. The organic carbon (f_{oc}) and black carbon (f_{BC}) contents of the BH and NYH samples were also measured as reported previously (30, 31). Subsamples were oxidized for 24 h at 375 °C under air in a muffle furnace. Coal particles do not survive this treatment (30). Subsequently, untreated and heat-treated samples were acidified with HCl to remove carbonates and analyzed with a Perkin-Elmer 2400 CHN Elemental Analyzer (Norwalk, CT). The 375 °C heat-treated sample yielded the f_{BC}. The organic carbon content (f_{oc}) was

calculated as the difference between the untreated and heat-treated samples. This chemothermal oxidation method (CTO-375) potentially errs in two ways: (i) charring of OC during the 24-h thermal oxidation may lead to an overestimation of BC and (ii) oxidation of the BC present during that same step may result in an underestimation of the naturally present soot/char fraction. Accardi-Dey (31) found that additions of proteins lead to OC charring, and this artifact was indicated by elevated "black nitrogen"—the nitrogen measured during the BC determination in the CHN. In both of our cases, the black nitrogen was very small (≪0.1 wt %), indicating little OC charring. Additionally, a round-robin study showed that the CTO-375 method gave consistently lower BC concentrations than other methods (32). Hence, we conclude that charring was not substantially inflating our f_{BC} values. In contrast, there is as yet no indicator established to assess the oxidation of BC during CTO-375—potentially leading to an underestimation of f_{BC} and a corresponding overestimation of the resulting K_{BC} values (see below).

Results

Sediment Concentrations. The Quincy Bay site in Boston Harbor (BH) generally exhibited greater levels of contamination than the Hudson River site in New York Harbor (NYH) (Table 2). In the BH sediment, PAH concentrations were thousands of ng/gdw, whereas PAH concentrations were only hundreds of ng/gdw in the NYH sediment. PCB concentrations were in the thousands ng/gdw in the BH sediment, but only in the tens ng/gdw in the NYH sediment. Only the PCDD concentrations were similar in both sediments, with OCDD near 1 ng/gdw and other targeted congeners at only hundreds of pg/gdw (data not shown). Our data are consistent with earlier reports concerning that part of the Boston Harbor displaying somewhat elevated PAH and PCB concentrations (33, 34). We know of no other PCDD data for the BH sediments. The PCDD concentrations we found in the NYH sediment match other reported data from the lower Hudson River within a factor of 3 (35, 36).

In the BH sediment, the f_{oc} was 3.1% ± 0.64 and the f_{BC} was 0.60% ± 0.07 of the sediment's dry weight (13). In the NYH sediment, the f_{oc} was 2.6% ± 0.03 and the f_{BC} was 0.34% ± 0.02 of the dry weight. These values are similar to those reported by Adams (24) and Mitra et al. (22) for other sites in this estuary.

State of Equilibrium in Tumbling Experiments. To assess each incubation's approach to sorption equilibrium, tumbling experiments were carried out for times sufficient to have the same C_{PE} values in all three PE samplers. For the BH sediment after 182 days, all three had the same PE-mass-normalized concentrations, despite their divergent sizes. Further, these concentrations were higher than those seen

TABLE 3. Individual and Average Solid−Water Distributions ($K_{d,obs}$) for BH (182 days) and NYH Sediment (14 days)[a]

	phen	pyr	bap	PCB 44	PCB 66	PCB 95	2,7/8-Cl$_2$DD	2,3,7-Cl$_3$ DD
BH								
log $K_{d,obs}$ (0.12 g of PE)	3.9	4.4	5.5	4.4	5.3	5.0		
log $K_{d,obs}$ (0.26 g of PE)	4.0	4.3	5.4	4.2	5.0	4.7		
log $K_{d,obs}$ (0.64 g of PE)	3.8	4.1	5.8	4.2	4.9	4.7		
mean	3.9	4.3	5.5	4.3	5.1	4.8		
SD	0.1	0.2	0.2	0.1	0.2	0.2		
NYH								
log $K_{d,obs}$ (0.27 g of PE)	3.4	4.2	5.8	4.4	5.4	4.8	4.9	5.7
log $K_{d,obs}$ (0.43 g of PE)	3.6	4.4	5.9	4.4	5.3	4.8	4.9	5.8
log $K_{d,obs}$ (0.72 g of PE)	3.6	4.4	5.9	4.5	5.4	4.9	4.9	5.9
mean	3.5	4.4	≤5.9	4.4	5.4	≤4.8	4.9	5.8
SD	0.1	0.1	0.1	0.1	0.0	0.1	0.0	0.1

[a] Values preceded by a less than or equal sign represents cases in which system equilibration may not have been achieved.

in the previous shorter term incubations of 3, 4, 17, and 125 days (this latter incubation may have been equilibrated, but problems with some of the HOC analyses caused us to rerun the experiment). This indicated that each PE was equilibrated with the rest of the sediment−water system in this 182-day data set.

For the NYH tumbling experiments, the sediment mass-to-water volume ratio was increased by about a factor of 4 and the tumbling time cut to 14 days. Three successive incubations gave indistinguishable K_d values, implying that we were not depleting the readily available pollutants (27). Assuming that such a readily available fraction was equilibrated with a slower exchanging fraction in the field, this result implies the PE values also represent equilibrium with the whole sediment. Also, on the basis of earlier laboratory experiments, 14-day incubations were sufficient to achieve equilibrium for PAHs up to pyrene, the Cl$_4$Bs and Cl$_{2−3}$DDs. For the higher molecular weight compounds, equilibrium may not have been achieved; in these cases, the C_w values reported here are flagged as minimum estimates of the equilibrium values (preceded with ≥) and $K_{d,obs}$ as maximum estimates (≤).

Solid−Water Distribution Ratios ($K_{d,obs}$) in the Sediment−Water Slurries. Using our knowledge of the equilibrium partitioning of PAHs, PCBs, and PCDDs between the dissolved phase and PE at the experimental temperatures (24; Table 1), we calculated the truly dissolved HOC concentrations for each suspension ($C_w = C_{PE}/K_{PEw}$; Table 2). Aqueous PAH and PCB concentrations for the NYH sample were generally much lower than those found using the BH sediment. Using the measured sediment concentrations and the dissolved concentrations inferred from the PE samplers, we calculated $K_{d,obs}$ values for the 182-day BH sediment−water incubation and the first 14-day NYH sediment−water incubation (Table 3). For the BH sediment, average $K_{d,obs}$ values for PAHs after 182 days of tumbling increased with chemical hydrophobicity from Phen (8.6E3 L/kg) to BaP (3.7E5 L/kg). For PCBs, the solid−water distributions went from a low value of 2.0E4 L/kg for PCB 44 up to 1.2E5 L/kg for the mono-*ortho*-substituted (coplanar) tetrachlorobiphenyl (no. 66). Increasing $K_{d,obs}$ values with increasing hydrophobicity were also observed for PAHs in NYH. PCB 66 consistently displayed a higher $K_{d,obs}$ than PCB 44. The PCDDs in NYH displayed high $K_{d,obs}$ values, comparable to the more hydrophobic PAHs and PCB #66 (Table 3).

Discussion

Comparison of $K_{d,obs}$ Values and $f_{oc}K_{oc}$. Since PEs of different sizes exhibited the same C_{PE} values, we concluded that our tumbling experiments had approached sorptive equilibria. Therefore, solid−water distributions could be interpreted using equilibrium models. To begin, we compared our observations of sediment−water partitioning (Table 3) to equilibrium expectations on the basis of each sediment's organic carbon content (f_{oc}) and each sorbate's organic carbon-normalized partition coefficient (K_{oc}, Table 1). Reported K_{oc} values from earlier studies could be inaccurate for two reasons: the unrecognized presence of f_{BC} would result in erroneously elevated K_{oc} and the particle concentration effect would have an opposite effect and result in erroneously low K_{oc} values. Recent investigations have provided better controls to eliminate this latter artifact. So, it is more likely that recent K_{oc} estimates are biased high, causing the products ($f_{oc}K_{oc}$) to also err to the high side. We used K_{oc} for PAHs and PCDDs on the basis of the correlation with K_{ow} established by Xia for aquatic sediments (37):

$$\log K_{oc} \text{ (PAHs, PCDDs)} = 0.97 \log K_{ow} - 0.12 \quad (2)$$

For PCBs, we chose the relationship from Xia (37):

$$\log K_{oc} \text{ (PCBs)} = 0.97 \log K_{ow} - 0.50 \quad (3)$$

These correlations are close to those originally developed by Karickhoff et al. (38) and Chiou et al. (39) and were reviewed to try to represent partitioning of apolar organic contaminants to the bulk of organic matter absent any black carbon. The K_{ow} values were taken from Mackay et al. (40) for PAHs, from Hawker and Connell (41) for PCBs, and from Shiu et al. (42) for PCDDs (Table 1).

The predicted K_d values ($K_{d,pred} = f_{oc}K_{oc}$) were always much less than our experimental $K_{d,obs}$ values (Figure 1), despite the possibility that literature values of K_{oc} are biased high. The divergence of $K_{d,obs}$ values from such predictions was highest for PAHs and exceeded $f_{oc}K_{oc}$ products by about 1.5−2 log units. The $K_{d,obs}$ values for PCBs were higher than predicted by about 1 log unit. We interpret this as strong evidence that absorption within organic carbon ($f_{oc}K_{oc}$) is not sufficient to explain the sorption of native organic contaminants in these two sediments. This highlights the need to consider another sedimentary phase to account for the observed, stronger retention of the compounds investigated.

Considering OC Absorption Plus BC Adsorption. Since the PAHs in the recent sediments at these harbor sites are chiefly pyrogenic (4, 22), and because coal has not been used widely in recent years in Boston and New York, we hypothesized that combustion-derived BC was responsible for the additional equilibrium sorptive capacity of the sediments. The additional effect of the dilute BC phase on the sorption of organic compounds can be parametrized using a minimum of fitting parameters as (13)

$$K_d = f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{n-1} \quad (4)$$
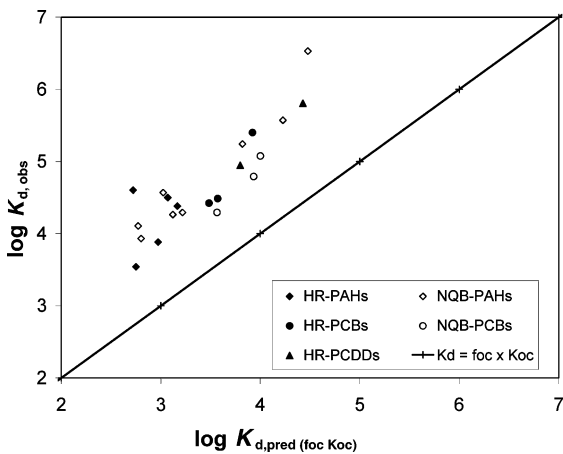
FIGURE 1. Measured solid−water distribution coefficients ($K_{d,obs}$) vs predictions ($K_{d,pred}$) based on $f_{oc}K_{oc}$ for PAHs, PCBs, and PCDDs from BH (North Quincy Bay, NQB) and NYH (Hudson River, HR) sediments.

TABLE 4. Measured Solid−Water Distributions ($K_{d,obs}$) for Phenanthrene and Pyrene and Predictions ($K_{d,pred}$)[a] Based on Measured f_{oc}, f_{BC}, and Literature Values for K_{oc}, K_{BC}, and n

log $K_{d,obs}$	log $K_{d,pred}$	% deviation[b]
	Phenanthrene	
3.9	3.6	53%
3.5	3.7	31%
	Pyrene	
4.3	4.2	24%
4.4	4.4	2%

[a] Phenanthrene: log K_{BC} = 5.6, n = 0.7 (15); pyrene: log K_{BC} = 6.3, n = 0.62 (13). [b] % deviation = abs(($K_{d,pred}$ − $K_{d,obs}$)/$K_{d,obs}$).

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where K_{BC} is the adsorption coefficient to BC [(mol kg$_{bc}^{-1}$)/(mol/L)^n], n is the Freundlich exponent for adsorption onto BC, and C_w is the dissolved concentration (µg/L).

Using BH sediment, thermally pretreated to remove the non-BC organic matter, and spiking additions of pyrene to develop isotherms, Accardi-Dey and Gschwend (13) found a log K_{BC} of 6.25 ± 0.14 (mol kg$_{bc}^{-1}$)/(mol/L)^n with n of 0.62 for this PAH. For both BH and NYH sediments, our observed solid−water distributions for pyrene were in good agreement with what was predicted using eq 4 and these values from spiking additions (Table 4). Accardi-Dey and Gschwend (15) also found that log K_{BC} for phenanthrene is between 5.3 and 5.9 (mol kg$_{bc}^{-1}$)/(mol/L)^n in laboratory incubations of thermally treated BH sediment with varying concentrations of added phenanthrene. Assuming phenanthrene's log K_{BC} to be 5.6 (mol kg$_{bc}^{-1}$)/(mol/L)^n with a Freundlich n of 0.7, one estimates its solid−water distribution coefficients within less than a factor of 2 of our $K_{d,obs}$ values (Table 4). This correspondence between estimates using the dual f_{oc} absorption plus f_{BC} adsorption model reflected by eq 4 is very good, and it supports the hypothesis that carbonaceous particles capable of surviving thermal oxidation at 375 °C were responsible for the enhanced HOC sorption in these harbor sediments.

Deducing K_{BC} Values for Other PAHs, PCBs, and PCDDs. Since inclusion of BC in the sorption model for pyrene and phenanthrene greatly improved the match between measured and predicted K_d values for these harbor sediments, we used our $K_{d,obs}$ values to deduce K_{BC} values for the other PAHs, PCBs, and PCDDs measured in the PEs and sediments. In each case, the overall distribution coefficient, $K_{d,obs}$, was split up into the partitioning to the OC ($f_{oc}K_{oc}$) and the BC ($f_{BC}K_{BC}C_w^{n-1}$) fractions. This was done by subtracting the

product of the literature K_{oc} value (see above) times the corresponding f_{oc} from the $K_{d,obs}$ values. The term representing the affinity to BC was divided by f_{BC} to yield $K_{BC}C_w^{n-1}$. Finally, estimates of each compound's K_{BC} were obtained by assuming n values of 0.4, 0.7, and 1.0 for n (Table 5). The n-value of 0.7 is a typical value for fitted isotherms for phenanthrene and pyrene (11, 13, 15, 19). The estimated log K_{BC} values for any given sorbate were the same within 0.6 log units (factor of 4) for the BH and NYH sediments. These results indicate the BC from both sediments had comparable sorbent properties; although given the potential diversity of BC sources, this need not be true. However, both sediments reflect deposition of solids from strongly urbanized watersheds, and thus a similarity of BC origins seems reasonable.

For PAHs up to pyrene in BH, the influence of n on the fitted K_{BC} values was relatively small (within 0.5 log units) because C_w was close to 1 µg/L. However, for the more hydrophobic PAHs and PCBs from BH, and most analytes from the NYH sediments, the resulting K_{BC} values were much more sensitive to the choice of n. It has been suggested in a review by Allen-King et al. (43) that the Freundlich coefficient n can be estimated on the basis of a sorption measurement at low C_w and the assumption that for C_w close to saturation, K_d can be approximated through $f_{oc}K_{oc}$ (43). However, because of the ratio of f_{BC} to f_{oc} in our cases, we find that even with C_w approaching aqueous phase saturation, adsorption onto BC is approximately as important as absorption into the OC matrix. This prevents use of their approach for estimating n values from our data.

Uncertainty in log K_{BC} Values. For each K_{BC} estimation, uncertainties stem from (a) the precision in the quantification of C_{PE} and C_{sed}; (b) the precision of our knowledge of the corresponding K_{PEw}; (c) the precision and accuracy of f_{oc} and f_{BC} measurements; and (d) the precision and accuracy of the K_{oc} estimates.

Precision. The analytical uncertainty in C_{PE} and C_{sed} (Table 2) is about 10−30% (ca. ±0.1 log units for log K_{BC}). The analytical reproducibilities in determining f_{oc} and f_{BC} (Table 2) are about 10−20%. The uncertainty in the K_{PEw} values are within 30% (ca. ±0.1 log units for log K_{BC}). To account for the natural variability of natural organic matter, a factor of 2 uncertainty was assumed for the K_{oc} term for our given sediments (44). However, as will be detailed further below, the $f_{oc}K_{oc}$ term is of minor importance for the overall sorption in our tests. Propagating these imprecisions in our data according to standard procedures (45), the combined uncertainties limit the overall precision of the log K_{BC} values (for n = 0.7) to within a factor of 1.5 (i.e., ±0.2 log units). Possibly of more concern are matters of K_{BC} accuracy.

Accuracy. We believe that the K_{oc} estimations by Xia (37) are the best available as the authors critically reviewed the partitioning of organic contaminants to soils/sediments and only took data into consideration which had high f_{oc} and low f_{BC}. However, even if we assume a 50% inaccuracy, the overall uncertainty of the K_{BC} values is barely affected (as the $f_{oc}K_{oc}$ terms are much smaller in absolute values than the corresponding K_d values). The f_{BC} term is more important for the overall accuracy in K_{BC} values. Unfortunately, the accuracy of any method used to obtain this BC parameter remains unknown, although it is recognized that some procedures cause charring of non-BC organic matter to give artificially high f_{BC} results while others may result in the unintended destruction of some portion of the BC and give low f_{BC} values (31, 32). In light of intercomparison studies (32), our methods are more likely to yield f_{BC} values that are biased low. Since our experimental sorption data fix the value of the product ($f_{BC}K_{BC}$) if f_{BC} is low by a factor of 2, then the fitted K_{BC} values must be a factor of 2 too high (i.e., 0.3 log units, Table 5). Here, our best-fit results for pyrene's log K_{BC} in BH was 6.4 ± 0.26 (mol kg$_{bc}^{-1}$)/(mol/L)$^{-0.3}$ and in NYH it

TABLE 5. Derived Mean Black Carbon−Water Partitioning Coefficientents (log K_{BC}) from $K_{d,obs}$ Values

compd	BH log K_{BC} ($n = 0.7$)	SD[a]	BH log K_{BC} ($n = 0.4$)	BH log K_{BC} ($n = 1.0$)	NYH log K_{BC} ($n = 0.7$)	SD[a]	NYH log K_{BC} ($n = 0.4$)	NYH log K_{BC} ($n = 1.0$)
phenanthrene	6.1	0.24	6.1	6.1	5.6	0.26	5.3	5.9
anthracene	6.1	0.22	5.8	6.3	6.4	0.24	5.6	7.1
∑Me-Phen	6.5	0.27	6.2	6.7	5.9	0.26	5.5	6.3
fluoranthene	6.4	0.25	6.3	6.4	6.5	0.22	6.0	7.0
pyrene	6.4	0.26	6.3	6.4	6.4	0.23	5.9	6.8
BaA	6.9	0.23	6.5	7.4	≤6.9[d]	0.24	≤6.0	≤7.8
BbFA	na[b]				≤7.3	0.21	≤6.4	≤8.1
BkFA	na				≤7.3	0.21	≤6.4	≤8.2
BeP	na				≤6.8	0.24	≤6.0	≤7.6
BaP	7.1	0.28	6.5	7.7	≤7.4	0.21	≤6.4	≤8.3
perylene	7.4	0.72	6.4	8.4	≤7.3	0.22	≤6.4	≤8.1
PCB 52	nc[c]				5.9	0.23	5.0	6.9
PCB 44	6.2	0.28	6.0	6.4	5.8	0.23	4.8	6.8
PCB 66	6.9	0.28	6.5	7.2	6.7	0.21	5.4	7.9
PCB 95	6.6	0.28	6.2	6.9	≤6.1	0.23	≤4.9	≤7.3
2,7/ 8-Cl$_2$DD	nc				5.9	0.22	4.4	7.4
2,3,7-Cl$_3$ DD	nc				6.1	0.23	3.9	8.3

[a] On the basis of the overall precision of the analysis and an accuracy of 50% for f_{BC} and K_{oc}. [b] na, not analyzed. [c] nc, not considered because of unaccounted losses in mass balance. [d] Values preceded by a less than or equal sign may represent cases in which system equilibration may not have been achieved.

was 6.4 ± 0.23 (mol kg$_{bc}$$^{-1}$)/(mol/L)$^{-0.3}$. These are consistent with published values using diesel soot in the laboratory (*12*). Our K_{BC} values deduced from the tumbling incubations for native pyrene and phenanthrene are also consistent with values obtained using additions of these PAHs to thermally pretreated Boston Harbor sediments, supporting the conclusion that these results are accurate (*13, 15*). Despite this concordance, it is possible that our results on native compounds give a K_{BC} applicable to the environment which is biased high by inaccurately low f_{BC} values. This environmental K_{BC} may match those seen in spiking experiments on pure BC (*12, 13, 15*) because competitive sorbates have been removed under those conditions. Importantly, getting the same result by desorbing or adsorbing these PAHs suggests that such compounds may be free to establish new solid water equilibria as the conditions change (e.g., after deposition in a bed or particle uptake by a deposit-feeding organism.)

It is more difficult to assess the accuracy of the log K_{BC} values for PCBs and PCDDs. First, the trends that we see within compound groups, with higher K_{BC} values for less soluble compounds, are like the trends reported by Bärring et al. (*46*). For the Cl$_{2−3}$DDs, our fitted log K_{BC} values were around 6 (mol kg$_{bc}$$^{-1}$)/(mol/L)^{n}. Because of their low dissolved concentrations, the choice of the n value affects these fitted K_{BC}'s by up to ± 2 log units. These native-derived log K_{BC}'s were lower than those of Bärring et al. (*46*) who tested pure diesel soot in the laboratory and found log K_{BC} 7 (mol kg$_{bc}$$^{-1}$)/(mol/L)^{n}. This may suggest that the value of n for this compound in the field may be between 0.7 and 1. Despite this uncertainty, these results all support the hypothesis that the sedimentary BC phase exhibits a high affinity for PCDDs.

Dependency of K_{BC} on Compound Properties. The K_{BC} values for all three compound classes show the importance of sorbate hydrophobicity. For example, focusing on the PAHs from the BH sediments (for Freundlich $n = 0.7$) and using the log K_d values for all PAHs at a constant sorbate chemical activity of 10^{-3}, one finds a correlation (Figure 2):

$$\log K_{d,BC} \approx 0.83 \log \gamma_w^{sat} - 1.58 \quad (r^2 = 0.99, N = 8) \quad (5)$$

Since (log γ_w^{sat}) reflects the sorbate's free energy of dissolution in water, this strong correlation implies that this sorption phenomenon depends on the sorbate's incompatibility with the water.
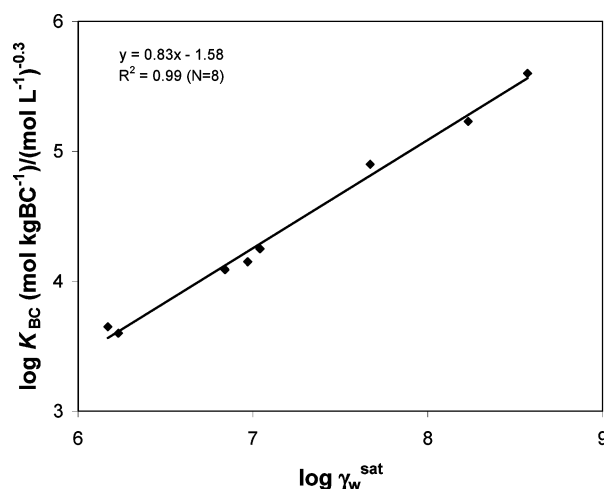
FIGURE 2. Deduced black carbon−water partitioning coefficients (log K_{BC}) as a function of the aqueous activity coefficients at saturation (log γ_w^{sat}) for PAHs from the BH sediment.

For the tetrachlorobiphenyls (Cl$_4$B), the highest mean log K_{BC} values were derived for PCB 66. PCB 66 is mono-*ortho*-substituted and therefore capable of maximizing its surface adsorption by adopting a planar configuration (*21*). A similar separation of K_{BC} values of coplanar and nonplanar PCBs was presented by Bärring et al. (*46*). The PCB results indicate that K_{BC} values are substitution dependent (higher for coplanar PCBs).

Implications. No matter what the K_{BC} and n values are, most of the HOC sorption in the two sediments we examined was not due to absorption into OC as represented by the model ($f_{oc}K_{oc}$). Coal or coaly organic matter could also contribute strongly to the overall sorption at other sites containing these carbonaceous solids (*11, 19, 20*). Assuming the overall $K_{d,obs}$ can be apportioned into the terms representing OC-absorption and BC-adsorption in our harbor sediments, we find that BC was responsible for over 90% of the total PAH sorption (i.e., $K_{d,obs}$) in BH and over 80% in NYH. For PCBs, adsorption to BC was dominant for all congeners in BH and NYH, ranging from over 80% to roughly 90%. Adsorption to BC explained 90% or more for the PCDDs considered here. Further, if the Freundlich coefficients are

near 0.7, extrapolations of our observations to sorbate concentrations approaching their solubilities indicate this BC-adsorption would contribute at least half of the total sorption in these two harbor sediments.

Over 20 sediment samples from Quincy Bay, MA, were analyzed for the abundance of OC and BC by Ewald (47). OC averaged 2.5% (0.6−7.3%) of the sediment dry weight, and BC was about a factor of 10 lower (mean 0.3%, range 0.07−0.7%) in those samples. However, the affinities to BC (see above), especially at dissolved concentrations below 1 μg/L, are higher by orders of magnitude than the absorption into OC. Hence, the putative sedimentary BC phase dominates the solid−water partitioning, mobility, and bioavailability of PAHs, PCBs, and PCDDs in these sediments, despite this reduced carbon's relatively low environmental abundance. This result helps explain the lower-than-expected bioaccumulation of these HOCs by infauna such as the soft-shell clam *Mya arenaria* (48).

The low dissolved HOC concentrations at many field sites present field research with immense problems in measuring truly dissolved concentrations without interference by colloidal particles. The use of passive samplers, such as the PEs used here, can potentially overcome these analytical problems. Thus, such methods are necessary to advance our understanding of phase partitioning of HOCs in aqueous systems. Our results further stress the need for measuring sorption isotherms at environmentally relevant concentrations and to natural particles, as recently demonstrated by Cornelisson and Gustafsson (49). A combination of comparative sediment and sorbate studies is needed to better characterize the distribution and availability of sedimentary HOCs.

Acknowledgments

Literature Cited

(1) Schwarzenbach, R. P.; Gschwend, P. M.; Imboden, D. M. *Environmental Organic Chemistry*, 2nd ed.; Wiley-Interscience: New York, 2003; 1313 pp.

(2) Grathwohl, P. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: implications on K_{oc} correlations. *Environ. Sci. Technol.* **1990**, *24*, 1687−1693.

(3) Weber, W. J.; McGinley, P. M.; Katz, L. E. A distributed reactivity model for sorption by soils and sediments. 1. Conceptual basis and equilibrium assessments. *Environ. Sci. Technol.* **1992**, *26*, 1955−1962.

(4) McGroddy, S. E.; Farrington, J. W. Sediment porewater partitioning of polycyclic aromatic-hydrocarbons in 3 cores from Boston Harbor, Massachusetts. *Environ. Sci. Technol.* **1995**, *29*, 1542−1550.

(5) McGroddy, S. E.; Farrington, J. W.; Gschwend, P. M. Comparison of the in situ and desorption sediment-water partitioning of polycyclic aromatic hydrocarbons and polychlorinated biphenyls. *Environ. Sci. Technol.* **1996**, *30*, 172−177.

(6) Xing, B. S.; Pignatello, J. J.; Gigliotti, B. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environ. Sci. Technol.* **1996**, *30*, 2432−2440.

(7) Gustafsson, Ö.; Gschwend, P. M. In *Molecular Markers in Environmental Geochemistry*; Eganhouse, R. P., Ed.; ACS Symposium Series 671; American Chemical Society: Washington, DC, 1997; pp 365−381.

(8) Chiou, C. T.; McGroddy, S. E.; Kile, D. E. Partition characteristics of polycyclic aromatic hydrocarbons on soils and sediments. *Environ. Sci. Technol.* **1998**, *32*, 264−269.

(9) Xia, G. S.; Ball, W. P. Adsorption−partitioning uptake of nine low-polarity organic chemicals on a natural sorbent. *Environ. Sci. Technol.* **1999**, *33*, 262−269.

(10) Kleineidam, S.; Rugner, H.; Ligouis, B.; Grathwohl, P. Organic matter facies and equilibrium sorption of phenanthrene. *Environ. Sci. Technol.* **1999**, *33*, 1637−1644.

(11) Karapanagioti, H. K.; Kleineidam, S.; Sabatini, D.; Grathwohl, P.; Ligouis, B. Impacts of heterogeneous organic matter on phenanthrene sorption: Equilibrium and kinetic studies with aquifer material. *Environ. Sci. Technol.* **2000**, *34*, 406−414.

(12) Bücheli, T. D.; Gustafsson, Ö. Ubiquitous observations of enhanced solid affinities for aromatic organochlorines in field situations: Are in situ dissolved exposures overestimated by existing partitioning models? *Environ. Toxicol. Chem.* **2001**, *20*, 1450−1456.

(13) Accardi-Dey, A.; Gschwend, P. M. Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environ. Sci. Technol.* **2002**, *36*, 21−29.

(14) Jonker, M. T. O.; Koelmans, A. A. Extraction of polycyclic aromatic hydrocarbons from soot and sediment: Solvent evaluation and implications for sorption mechanism. *Environ. Sci. Technol.* **2002**, *36*, 4107−4113.

(15) Accardi-Dey, A.; Gschwend, P. M. Reinterpreting literature sorption data considering both absorption into organic carbon and adsorption onto black carbon. *Environ. Sci. Technol.* **2003**, *37*, 99−106.

(16) Youngblood, W. W.; Blumer, M. Polycyclic aromatic hydrocarbons in the environment−Homologous series in soils and recent marine sediments. *Geochim. Cosmochim. Acta* **1975**, *39*, 1303−1314.

(17) Prahl, F. G.; Carpenter, R. PAH-phase associations in Washington coastal sediment. *Geochim. Cosmochim. Acta* **1983**, *47*, 1013−1023.

(18) Socha, S. B.; Carpenter, R. Factors affecting pore water hydrocarbon concentrations in Puget Sound sediments. *Geochim. Cosmochim. Acta* **1987**, *51*, 1273−1284.

(19) Kleineidam, S.; Schüth, C.; Grathwohl, P. Solubility-normalized combined adsorption-partitioning sorption isotherms for organic pollutants. *Environ. Sci. Technol.* **2002**, *36*, 4689−4697.

(20) Ghosh, U.; Zimmerman, J. R.; Luthy, R. G. PCB and PAH speciation among particle types in contaminated harbor sediments and effects on PAH bioavailability. *Environ. Sci. Technol.* **2003**, *37*, 2209−2217.

(21) Jonker, M. T. O.; Smedes, F. Preferential sorption of planar contaminants in sediments from Lake Ketelmeer, The Netherlands. *Environ. Sci. Technol.* **2000**, *34*, 1620−1626.

(22) Mitra, S.; Dellapenna, T. M.; Dickhut, R. M. Polycyclic aromatic hydrocarbon distribution within lower Hudson River estuarine sediments: Physical mixing vs sediment geochemistry. *Estuarine Coastal Shelf Sci.* **1999**, *49*, 311−326.

(23) Adams, R. G. Sediment-Water Exchange of Polycyclic Aromatic Hydrocarbons in the Lower Hudson Estuary. M.S. Thesis, Department of Civil and Environmental Engineering, MIT, 2000, 112 pp.

(24) Adams, R. G. Polyethylene Devices and the Effects of Sediment Resuspension on the Cycling of PAHs and PCBs in the Lower Hudson Estuary. Ph.D. Thesis, Department of Civil and Environmental Engineering, MIT, 2003, 184 pp.

(25) Mayer, P.; Tolls, J.; Hermens, J. L. M.; Mackay, D. Equilibrium sampling devices. *Environ. Sci. Technol.* **2003**, *37*, 3A−9A.

(26) Müller, J. F.; Manomanii, K.; Mortimer, M. R.; McLachlan, M. S. Partitioning of polycyclic aromatic hydrocarbons in the polyethylene/water system. *Fresenius J. Anal. Chem.* **2001**, *371*, 816−822.

(27) Booij, K.; Hofmans, H. E.; Fischer, C. V.; Van Weerlee, E. M. Temperature-dependent uptake rates of nonpolar organic compounds by semipermeable membrane devices and low-density polyethylene membranes. *Environ. Sci. Technol.* **2003**, *37*, 361−366.

(28) Vinturella, A. E.; Burgess, R. M.; Coull, B. A.; Thompson, K. M.; Shine, J. P. Use of passive samplers to mimic uptake of polycyclic aromatic hydrocarbons by benthic polychaetes. *Environ. Sci. Technol.* **2004**, *38*, 1154−1160.

(29) Woodruff, J. D.; Geyer, W. R.; Somerfield, C. K.; Driscoll, N. W. Seasonal variation of sediment deposition in the Hudson River estuary. *Mar. Geol.* **2001**, *179*, 105−119.

(30) Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J. K.; Gschwend, P. M. Quantification of the dilute sedimentary soot phase: Implications for PAH speciation and bioavailability. *Environ. Sci. Technol.* **1997**, *31*, 203−209.

(31) Accardi-Dey, A. M. Black carbon in marine sediments: quan-itifcation and implications for the sorption of polycyclic aromatic hydrocarbons. Ph.D. Thesis, Department of Civil and Environmental Engineering, MIT, 2003, 279 pp.

(32) Currie, L. A.; Benner, B. A.; Kessler, J. D.; Klinedinst, D. B.; Klouda, G. A.; Marolf, J. V.; Slater, J. F.; Wise, S. A.; Cachier, H.; Cary, R.; Chow, J. C.; Watson, J.; Druffel, E. R. M.; Masiello, C. A.; Eglinton, T. I.; Pearson, A.; Reddy, C. M.; Gustafsson, O.; Quinn, J. G.; Hartmann, P. C.; Hedges, J. I.; Prentice, K. M.; Kirchstetter, T. W.; Novakov, T.; Puxbaum, H.; Schmid, H. A critical evaluation of interlaboratory data on total, elemental, and isotopic carbon in the carbonaceous particle reference material, NIST SRM 1649a. *J. Res. N.I.S.T.* **2002**, *107*, 279−298.

(33) McDowell, J. E.; Shea, D. *Population Processes of Mya arenaria from Contaminated Habitats in Massachusetts Bays*; Report to the Massachusetts Bays Program, 1997, MBP-97-01.

(34) Gardner, G. R.; Pruell, R. J. *A Histopathological and Chemical Assessment of Winter Flounder, Lobster and Soft-Shelled Clam Indigenous to Quincy Bay, Boston Harbor and an In Situ Evaluation of Oysters Including Sediment (Surface and Cores) Chemistry;* U.S. EPA, Environmental Research Laboratory: Narragansett, RI, 1988; 108 pp.

(35) Bopp, R. F.; Chillrud, S. N.; Shuster, E. L.; Simpson, H. J.; Estabrooks, F. D. Trends in chlorinated hydrocarbon levels in Hudson River basin sediments. *Environ. Health Perspect.* **1998**, *106*, 1075−1081.

(36) Lohmann, R.; Nelson, E.; Eisenreich, S. J.; Jones, K. C. Evidence for dynamic air−water exchange of PCDD/Fs: A study in the Raritan Bay/Hudson River Estuary. *Environ. Sci. Technol.* **2000**, *34*, 3086−3093.

(37) Xia, G. S. Sorption behaviour of nonpolar organic chemicals on natural sorbents. Ph.D. Thesis, The Johns Hopkins University, Baltimore, MD, 1998.

(38) Karickhoff, S.; Brown, D. S.; Scott, T. A. Sorption of hydrophobic pollutants on natural sediments. *Water Res.* **1979**, *13*, 241−248.

(39) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. Partition equilibriums of nonionic organic compounds between soil organic matter and water. *Environ. Sci. Technol.* **1983**, *17*, 227−231.

(40) Mackay, D.; Shiu, W.-Y.; Ma, K.-C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate of Organic Compounds*; Lewis Publishers: Boca Raton, FL, 1992; Vol. 2.

(41) Hawker, D. W.; Connell, D. W. Octanol−water partition coefficients of polychlorinated biphenyl congeners. *Environ. Sci. Technol.* **1988**, *22*, 382−387.

(42) Shiu, W. Y.; Doucette, W.; Gobas, F. A. P. C.; Andren, A.; Mackay, D. Physical-chemical properties of chlorinated dibenzo-*p*-dioxins. *Environ. Sci. Technol.* **1988**, *22*, 651−658.

(43) Allen-King, R. M.; Grathwohl, P.; Ball, W. P. New modeling paradigms for the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter in soils, sediments, and rocks. *Adv. Water Resour.* **2002**, *25*, 985−1016.

(44) Kile, D. E.; Chiou, C. T.; Zhou, H.; Li, H.; Xu, O. Partition of nonpolar organic pollutants from water to soil and sediment organic matters. *Environ. Sci. Technol.* **1995**, *29*, 1401−1406.

(45) Skoog, D. A.; West, D. M.; Holler, F. J. *Fundamentals of Analytical Chemistry*, 7th ed.; Saunders College Publishing: Philadelphia, 1996.

(46) Bärring, H.; Bucheli, T. D.; Broman, D.; Gustafsson, Ö. Soot-water distribution coefficients for polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polybrominated diphenyl ethers determined with the soot cosolvency-column method. *Chemosphere* **2002**, *49*, 515−523.

(47) Ewald, G. Chemical Engineering II, Lund University, Sweden. Personal communication.

(48) Lohmann, R.; Burgess, R. M.; Cantwell, M. G.; Ryba, S. A.; MacFarlane, J. K.; Gschwend, P. M. Dependency of polychlorinated biphenyl and polycyclic aromatic hydrocarbon bioaccumulation in *Mya arenaria* on both water column and sediment bed chemical activities. *Environ. Toxicol. Chem.* **2004**, *11*, 2551−2562.

(49) Cornelissen, G.; Gustafsson, O. Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates. *Environ. Sci. Technol.* **2004**, *38*, 148−155.