

Reinterpreting Literature Sorption Data Considering both Absorption into Organic Carbon and Adsorption onto Black Carbon

AMYMARIE ACCARDI-DEY AND PHILIP M. GSCHWEND*

Ralph M. Parsons Laboratory, MIT 48-415, Department of Civil and Environmental Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

We hypothesized that the sorption of polycyclic aromatic hydrocarbons (PAHs) to natural sediments and soils should consider both *absorption* into a biogenic/diagenetic organic carbon (OC) fraction and *adsorption* onto a combustion-derived, black carbon (BC) fraction. Here, two sets of literature data were reevaluated to illustrate that an OC adsorbent and a BC adsorbent together can (1) account for sediment–pore-water distribution coefficients observed in the field that are greater than predicted by a simple $f_{oc}K_{oc}$ partitioning model and (2) explain a group of nonlinear phenanthrene isotherms observed in the laboratory with a single value for the BC-normalized distribution coefficient ($\log K_{BC} = 6.1 \pm 0.04$) and a Freundlich exponent ($n \approx 0.6$ if $\log K_{oc} = 4.0$) that is strongly dependent on the K_{oc} value selected.

Introduction

Current research has demonstrated that sediments contain at least two reduced carbon fractions: (1) a biogenic/diagenetic organic carbon (OC) fraction and (2) a combustion-derived, black carbon (BC) fraction (1–7). Both of these carbon fractions can act as sorbents of hydrophobic organic compounds, such as polycyclic aromatic hydrocarbons (PAHs). Thus, we hypothesized that PAH sorption in sediments and soils and the associated solid–water distribution coefficient (K_d , L/kg_{sediment}) must consider both an OC *adsorbent* and a BC *adsorbent* acting in parallel (6)

$$K_d = f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{n-1} \quad (1)$$

Here, the absorption term is the product of the OC fraction (f_{oc} , kg_{oc}/kg_{sediment}) and the OC-normalized distribution coefficient (K_{oc} , L/kg_{oc}). The adsorption term is the product of the BC fraction (f_{BC} , kg_{BC}/kg_{sediment}), the BC-normalized distribution coefficient [K_{BC} , ($\mu\text{g}/\text{kg}_{BC}$)/($\mu\text{g}/\text{L}$)^{*n*}], and a function of the dissolved concentration (C_w , $\mu\text{g}/\text{L}$), where *n* is the Freundlich exponent that describes the distribution of adsorption sites on BC. Because the OC fraction (f_{oc}) has traditionally reflected the sum of OC and BC (8, 9), we note that, in this paper, the f_{oc} parameter includes only the OC adsorbent and is calculated as the difference between the total organic carbon (TOC) content in the solid phase and the BC fraction.

* Corresponding author phone: (617)253-1638; fax: (617)253-7395; e-mail: pmgshwe@mit.edu.

This combined sorption model (eq 1) is mathematically similar to other models reported in the literature that describe sorption as a combination of absorption into “soft carbon” and adsorption onto “hard carbon” (10–12). In these models, the OC adsorption term is expressed as a linear model with low sorption enthalpies, noncompetitive exchange, and rapid kinetics. Meanwhile, the nonlinear component of sorption is assigned to adsorption onto a non-OC fraction. Although a multiparameter model that apportions nonlinearity to both the OC and BC terms (13) is plausible and more versatile, a model with fewer adjustable parameters is more economical. Therefore, we sought to ascertain whether reported nonlinear PAH sorption could be understood by considering only a three-parameter model in which all nonlinear interactions are proportional to the presence of BC.

Our combined model can account for many of the shortcomings present in the traditional $f_{oc}K_{oc}$ model (8, 9, 14, 15). Unlike a simple partitioning scheme, our new model is tunable in accord with the presence of more than one reduced carbon fraction in sediments and soils exhibiting distinct chemical affinities. This alternative sorption approach now enables us to explain observations of widely varying K_{oc} values for single sorbates interacting with diverse organic matter (16–18) and observations of deduced K_{oc} values that exceeded their corresponding K_{ow} values (19–22).

To assess the effectiveness of our combined sorption model (eq 1), we reinterpreted two sets of literature observations. These data sets include (1) field observations by McGroddy and Farrington, who measured $\log K_d$ values for PAHs in cores that were greater than those predicted by the $f_{oc}K_{oc}$ model (19, 20), and (2) laboratory observations by Huang et al. (17), who found a group of nonlinear phenanthrene isotherms for diverse sediments and soils used in earlier efforts to establish the $f_{oc}K_{oc}$ model. We postulated that these recently reported $\log K_d$ values and this group of nonlinear isotherms could be explained by considering both an OC adsorbent and a BC adsorbent. Our investigation implies that three sorbate parameters (K_{oc} , K_{BC} , and *n*) and two measured sorbent factors (f_{oc} and f_{BC}) are needed to estimate sorption for any natural solid/PAH combination of interest.

Methods

Sample Site: Boston Harbor. In 1990, investigators from the University of Massachusetts at Boston (20) and MIT (23, 24) retrieved three box cores from Boston Harbor at (1) Fort Point Channel (FPC) from the Inner Harbor, (2) Spectacle Island (SI) from the Northwest Harbor, and (3) Peddocks Island (PI) from the Southeast Harbor. In general, the Inner Harbor is the most polluted area in Boston Harbor mainly because of local combined sewer overflow sites and effluent discharge from former primary treatment plants (25, 26). The Southeast Harbor is the least polluted area because of its distance from the urban center. Sewage discharge [>150 tons of solids per day in 1990 (27)] had severely affected the benthic communities in the harbor and limited bioturbation in the sediment to <1 cm at FPC and <10 cm at SI and PI (24, 28). Sediments and pore waters from the retrieved box cores were analyzed for percent TOC, pore-water organic colloidal concentrations, pore-water PAHs, and sediment-sorbed PAHs (19, 23). With a sedimentation rate of millimeters per year in the Inner and Northwest Harbors, core horizons below the depth of bioturbation reflect deposits that are years to decades old (19), allowing protracted times for sorptive equilibration.

Sample Site: U.S. EPA Survey. Sediment and soil samples were collected in the late 1970s in collaboration with the U.S. Environmental Protection Agency (EPA) to investigate the sorption of several organic compounds (29). Most of the samples were located in the watersheds of the Missouri, Mississippi, Illinois, Wabash, and Ohio Rivers and were chosen on the basis of their depositional characteristics and proximity to potential energy-generating facilities (15, 29). Recently, Huang et al. used these archived sediments and soils to remeasure phenanthrene sorption over wide concentration ranges and extended incubation times (17). In brief, they measured final dissolved phenanthrene concentrations (between 1 and 1000 $\mu\text{g/L}$) after 14–28 days of incubation with the EPA sorbents in solutions containing 0.005 M CaCl_2 and 100 mg/L NaHCO_3 . The final sorbed concentrations were then back-calculated by Huang et al. assuming no other losses of phenanthrene.

BC Determinations. BC contents from archived EPA survey samples and Boston Harbor sediments were determined by us as described previously (1). The dry EPA samples were powders and used as received. The frozen Boston Harbor samples were dried overnight at 80 °C, ground with a mortar and pestle, and sieved to remove coarse mineral grains > 425 μm . Less than 50 mg of each sample was spread in precombusted crucibles, covered with precombusted aluminum foil, and combusted under air for 24 h at 371–372 °C in a Sybron F-A1730 Thermolyne muffle furnace (Dubuque, IA).

A Perkin-Elmer 2400 CHN elemental analyzer (Norwalk, CT) was then used to measure the BC fractions in the combusted samples. A 15-mg subsample of combusted sediment was wetted with 100 μL of low-carbon water (Aries Vaponic, Rockland, MA) in silver capsules and then acidified in situ with 100 μL sulfurous acid (Fischer Scientific, Fairlawn, NJ, 6% assay) to remove the inorganic carbon fraction. Once the sediment had dried, the silver capsules were wrapped in tin capsules to catalyze the oxidation reaction in the CHN analyzer. The elemental weight percentages were accepted only when standard acetanilide samples were within ± 0.3 wt % of the known acetanilide values (71.09 wt % C). The carbon blank for the CHN analysis was $14.9 \pm 0.9 \mu\text{g}$ of carbon ($N = 13$). The signal-to-noise ratio was > 3:1 for most of the combusted samples. In three EPA samples, this ratio was 2:1 ($N = 6$). Instrumental blanks were run after each sample to verify that previous samples were completely combusted. The OC fraction was then estimated by subtracting the measured BC weight percentage from the originally reported TOC content ($\text{OC} = \text{TOC} - \text{BC}$). Reported TOC values for the EPA samples were verified by independent measurements of the TOC content in three samples. All reported weight percentages represent the mean \pm one standard deviation.

Phenanthrene Sorption onto Boston Harbor Sediments. Phenanthrene sorption onto BC in sediments from south Dorchester Bay in Boston Harbor (6) was measured to compare with best-fit log K_{BC} values deduced from the Huang et al. data set. Combusted sediments (40–80 mg) were mixed with ~ 100 mL of low-carbon water containing phenanthrene at 3.62 or 8.54 $\mu\text{g/L}$ using methods described previously (6). After 28 days of tumbling, a Perkin-Elmer LS50B luminescence spectrofluorometer (Buckinghamshire, England) was used to measure phenanthrene remaining in test and control solutions. (Fluorescence quenching was determined to be negligible.) Individual K_d values were then calculated from the fraction of phenanthrene remaining in the test solutions, and these values were normalized to the BC fraction in the sediment.

Data Analysis

For the reported Boston Harbor PAH data, pore-water and sediment-sorbed concentrations were corrected for losses

during analysis using reported recoveries (19). All pore-water concentrations were further corrected for the fraction of PAHs bound to colloids. For this correction, measured K_{colloid} values for pyrene were used (19, 23), whereas K_{colloid} values for other PAHs were estimated from $\log K_{\text{colloid}} = 1.02 \log K_{\text{ow}} - 0.53$ (30). For the McGroddy data examined here, field log K_d values for pyrene were calculated using the combined sorption model (eq 1), our measured BC and OC fractions, and measured pore-water concentrations. In our calculations, we assumed a log K_{oc} value of 4.7 (31), a log K_{BC} value of 6.25 ± 0.14 , and an n value of 0.62 ± 0.12 for pyrene (6). Distribution coefficients were adjusted with a Setschenow factor, $10^{(0.3/M)(0.5 M)}$, to accommodate for 0.5 M salt, but no temperature adjustments were made. The reported log K_{oc} value of 4.7 might overestimate the true K_{oc} value because early investigators did not consider adsorption onto BC. However, at field concentrations considered here (nanograms per liter), the $f_{\text{oc}}K_{\text{oc}}$ term contributes <26% of the sum K_d values, and minor adjustments of the K_{oc} value will not substantially affect our estimates.

Next, SigmaPlot (version 4.0, Scientific Graphing Software, Inc.) was utilized along with our measured BC and OC fractions for each core section to extract optimal K_{BC} values for 17 other PAHs from the McGroddy data. All reported K_{BC} values derived from SigmaPlot had a coefficient of variation between 15 and 50% (13 nonbioturbated, sediment layers from FPC, SI, and PI). In our analysis, K_{oc} values for individual PAHs were calculated from $\log K_{\text{oc}} = 0.989 \log K_{\text{ow}} - 0.346$ (9). Because of past experimental protocols (high sorbate concentrations and short incubation) that emphasized absorption (12, 18), we do not believe that reported K_{oc} values were grossly overestimated. For example, in the pyrene sorption experiment by Means et al. [$C_w = 100\text{--}1000 \mu\text{g/L}$ with EPA 4 (15)], absorption accounted for 76–88% of the total sorption phenomena. Likewise, in the phenanthrene experiment by Karickhoff et al. [$C_w = 100\text{--}500 \mu\text{g/L}$ with EPA 4 (14)], the $f_{\text{oc}}K_{\text{oc}}$ term accounted for 54–69% of the overall sorption.

For the reported phenanthrene data, each isotherm was fit using SigmaPlot and our measured BC and OC fractions to extract K_{BC} and n values ($N = 12$). The phenanthrene log K_{oc} value was fixed at 4.0 for these optimizations in accordance with previous measurements by Karickhoff using the same EPA samples (9). All errors in the K_{BC} and n values deduced from SigmaPlot are reported in terms of coefficients of variation. For completeness, each isotherm was also fit with the combined sorption model and three adjustable parameters: K_{oc} , K_{BC} , and n . However, because the $f_{\text{oc}}K_{\text{oc}}$ term does not significantly contribute to the overall sorption value at equilibrium for much of the concentration range examined, the coefficient of variation was >80% for the K_{oc} value and no conclusions could be made on the true K_{oc} value. Note that, for EPA 22, the OC fraction was estimated using our own measured TOC value of 2.6 wt % carbon because a BC/TOC ratio of 96% was unreasonable when considering the TOC value of 1.6 wt % carbon reported by Huang et al. (17).

In our second approach, we used MATLAB (version 6.1.0.450 R12.1, The MathWorks, Inc., Natick, MA) to solve simultaneously for single values of K_{BC} and n for phenanthrene sorption onto 11 EPA samples using the Levenberg–Marquardt nonlinear least-squares function. For this optimization, a suite of likely K_{oc} values was investigated [3.7–4.3 (31)]. Errors were minimized between the predicted and observed values of the logarithm of the dissolved concentration (in micrograms per liter) to have equal weighting of low and high dissolved concentrations. All reported MATLAB errors represent \pm one standard deviation. All isotherms were fit using sorbed concentrations in micrograms per gram and dissolved concentrations in micrograms per liter to be consistent with the original work by Huang et al. (17).

However, K_{BC} values and K_d values were converted to units of $(\mu\text{g}/\text{kg}_{BC})/(\mu\text{g}/\text{L})^n$ and liters per kilogram, respectively, for comparison with previously reported literature results.

Results and Discussion

Reinterpreting PAH Sorption onto Boston Harbor Sediment in the Environment. To evaluate the combined sorption model, we began by seeking to explain the unusually large K_d values observed for Boston Harbor sediments. McGroddy and Farrington previously reported that sorbed PAH concentrations observed in Boston Harbor sediments were much greater than predicted by the $f_{oc}K_{oc}$ model using measured pore-water concentrations (20). For example, the observed $\log K_d$ values for pyrene at FPC, SI, and PI (Figure 1, open squares) were approximately 1 logarithm unit greater than the $f_{oc}K_{oc}$ -based $\log K_d$ values (Figure 1, filled circles). Although petroleum in the sediments can contribute to large distribution coefficients, lipid contents, and PAH ratios in the sediments at FPC, SI, and PI did not indicate any excessive presence of oils. For example, the average phenanthrene/ Σ methylphenanthrene ratio was greater than 2, and the average pyrene/1-methylpyrene ratio was greater than 5, implying pyrogenic sources (19, 32, 33). In addition, the percentage of extractable lipids at these sites was small [$0.7 \pm 0.3\%$ at FPC, $0.4 \pm 0.1\%$ at SI, and $0.3 \pm 0.1\%$ at PI (19)].

McGroddy and Farrington suggested that the presence of BC in the sediments could explain this discrepancy for PAHs. They proposed that a certain percentage of PAHs was occluded within BC particles and was unavailable for equilibrium partitioning (20). Because of the urban surroundings of Boston Harbor, the BC particles that accumulated in these near-shore sites were likely derived from atmospheric fallout (34), roadway runoff (35), and local combined sewer overflow sites (36). Recent flux estimations by Gustafsson and Gschwend (2) suggest that Boston Harbor receives approximately 10^6 kg of BC annually. Our analysis of core sections studied by McGroddy and Farrington showed that the measured BC weight percentages ($\text{kg}_{BC}/\text{kg}_{\text{sediment}}$) were 0.7–1.2 wt % in FPC, 0.3–0.4 wt % in SI, and approximately 0.2 wt % in PI (Table 1).

Our previous studies have shown that pyrene sorption onto Boston Harbor sediments is approximated well when simultaneous absorption into an OC fraction and adsorption onto a BC fraction is considered (6). Likewise, for the McGroddy core sections examined here, the eq-1-based $\log K_d$ values (Figure 1, filled triangles) are much better approximations of the observed data than the values obtained by the traditional $f_{oc}K_{oc}$ approach. In general, the combined sorption model underpredicted the observed $\log K_d$ values in the upper core sections by 0.4 ± 0.2 logarithm units ($N = 6$). We attribute the discrepancy in the upper cores of SI and PI to pore-water flushing and bioturbation. PI and SI had substantial infaunal abundance (37, 38), and measurements of naturally occurring ^{222}Rn activity suggested that mixing and irrigation were present at both sites. Pore-water flushing (either by wave mixing, bioturbation, or gas production) penetrated to 9 cm at SI (10^{-7} s^{-1}) and to 12 cm at PI (10^{-6} s^{-1}) (24). In addition, excess ^{232}Th activity was also detected at both PI and SI down to 10 cm, implying a bioturbation flux of $1.2 \times 10^{-5} \text{ cm}^2/\text{s}$ at PI and $6.3 \times 10^{-6} \text{ cm}^2/\text{s}$ at SI (24). The corresponding bioturbation flux at FPC was less intense at $2.0 \times 10^{-7} \text{ cm}^2/\text{s}$ for depths of <1 cm (28), but this flux might contribute to the $\log K_d$ discrepancies observed in surficial sediment at FPC. In light of our observation that the combined sorption model consistently underestimated the observed $\log K_d$ values in the bioturbated portions of these cores, we suspect that dissolved PAH

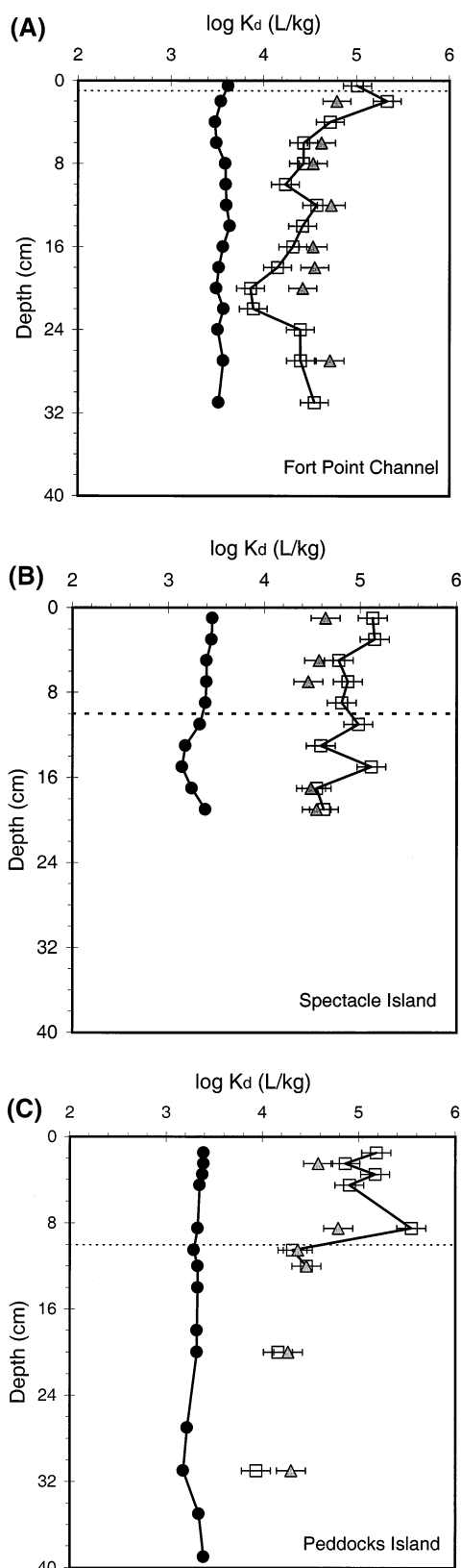


FIGURE 1. Depth profile (cm) of $\log K_d$ values (L/kg) for pyrene at (a) Fort Point Channel (FPC), (b) Spectacle Island (SI), and (c) Peddocks Island (PI). Each panel includes the $\log K_d$ values predicted by $K_d = f_{oc}K_{oc}$ (filled circles; assuming $\log K_{oc} = 4.7$), the $\log K_d$ value observed by McGroddy and Farrington [open squares (19)], and the $\log K_d$ value calculated by the model $K_d = f_{oc}K_{oc} + f_{BC}K_{BC}C_w^{n-1}$ (filled triangles; eq 1 assuming $\log K_{oc} = 4.7$, $\log K_{BC} = 6.25$, and $n = 0.62$). The dotted lines at 1 cm (FPC) and 10 cm (SI and PI) mark the approximate depth of bioturbation.

TABLE 1. Measured BC Weight Percentages (Mean $\pm 1\sigma$), Reported TOC (BC + OC) Weight Percentages, and BC/TOC Ratios for McGroddy and Farrington (19, 20) Boston Harbor, MA, Cores

sample	BC wt %	TOC wt %	BC \times 100/TOC
Fort Point Channel			
1–3 cm	0.70 \pm 0.14	4.92	14
5–7 cm	0.84 \pm 0.09	4.40	19
7–9 cm ^a	0.66 \pm 0.08	5.47	12
11–13 cm	1.2 \pm 0.13	5.65	22
15–17 cm	0.84 \pm 0.05	5.19	16
17–19 cm	0.86 \pm 0.09	4.67	18
19–21 cm	0.67 \pm 0.07	4.39	15
25–29 cm	0.96 \pm 0.12	5.23	18
Spectacle Island			
0–2 cm ^a	0.27 \pm 0.04	4.06	7
4–6 cm	0.29 \pm 0.07	3.54	8
6–8 cm	0.26 \pm 0.05	3.53	7
16–18 cm	0.40 \pm 0.12	2.48	16
18–20 cm	0.44 \pm 0.16	3.43	13
Peddocks Island			
2–3 cm	0.21 \pm 0.04	3.46	6
7–8 cm	0.18 \pm 0.02	3.24	6
10–11 cm	0.22 \pm 0.03	2.78	8
13–15 cm	0.24 \pm 0.02	3.01	8
19–21 cm	0.18 \pm 0.01	2.97	6
29–33 cm	0.23 \pm 0.01	2.16	11

^a Literature value for BC wt % measured previously in our laboratory by the same method (7).

concentrations do not reflect sorption equilibrium in the upper sections of these cores.

Recent reports suggest that PAH sorption is a combination of both fast and slow sorption (18, 39–41). For example, Weber and Huang showed that, for the same sediments and soils used by Means et al. (15) and Karickhoff (9), the ratio of sorbed-to-dissolved phenanthrene concentrations [$C_s/C_w^n = K_F$, in units of ($\mu\text{g/g}$)/($\mu\text{g/L}$)ⁿ] increased continuously over a 2-week study (40). In some instances, the C_s/C_w^n ratio after 1 day was 58–82% of the C_s/C_w^n ratio attained after 2 weeks. Recent work by Accardi-Dey and Gschwend also showed that the adsorption of pyrene onto combusted sediments in the laboratory took several days to reach an apparent equilibrium (6). If PAH desorption rates from BC are limited by the surface detachment process, then these rates can be estimated as the ratio of our observed sorptive rate to the BC distribution coefficient. Consequently, when processes such as bioturbation deplete pore-water sorbate concentrations in the field, desorption and reequilibration of PAHs can take weeks to months. Thus, PAH sorption at SI and PI might occur on the same time scale as (or possibly on a longer time scale than) pore-water irrigation and bed mixing (24).

The combined sorption model also tended to overestimate the observed K_d values in deeper nonbioturbated horizons by 0.3 ± 0.2 logarithm units ($N = 10$), especially at FPC. For example, the model does not explain the dip in the observed $\log K_d$ values at FPC between 18 and 22 cm corresponding chronologically to the late-1970s. This dip might reflect changes in the sorptive strength of the BC in these horizons (e.g., due to changing fuel usage in response to the oil embargo). Alternatively, elevated estimates of field K_d values might have been due to our overcorrection for colloid-bound PAHs. Nonetheless, we conclude that tuning to measured values of f_{oc} and f_{bc} and using estimates of K_{oc} , K_{bc} , and n for pyrene allowed reasonable a priori estimates of field K_d values for PAHs.

Extracting in Situ $\log K_{BC}$ Values for PAHs. Similarly to pyrene, other PAHs in Boston Harbor sediments were observed to exhibit K_d values that were much greater than

predicted by a simple partitioning scheme (19). If PAH sorption is the sum of absorption into the OC fraction and adsorption onto the BC fraction, then the underestimated sorption was due to PAH adsorption onto BC. If this assumption is true, then best-fit K_{BC} values can be extracted for other PAHs from the remaining adsorption data using the combined sorption model and our measured BC fractions (for nonbioturbated layers).

Because we do not know how the Freundlich exponent changes for the various PAHs and BC in the environment, a K_{BC} value was calculated for each case of $n = 0.6, 0.7,$ and 0.8 [Table 2 (19)]. This exponent range is supported by recent reports of Freundlich exponents varying from 0.6 to 0.8 for activated carbon (42), black carbon (6, 43), sediments, and soil (10, 18, 40) for a range of organic chemicals. In general, the extracted K_{BC} values varied by less than ± 0.3 logarithm units in this range. The coefficient of variation on the K_{BC} values (ranging from 15 to 50%) increased for each PAH as the Freundlich exponent increased from 0.6 to 0.8, implying that lower Freundlich exponents yielded a better fit to the data. Our SigmaPlot-derived $\log K_{BC}$ values compared well with other reported values for the sorption of PAHs onto NIST diesel particulate matter [SRM 1650 (43)] and combusted Boston Harbor sediment (6) (Table 2).

These K_{BC} values derived from in situ concentrations and conditions need to be regarded with caution, however, because the field data might reflect other environmental factors in addition to sorption. For example, colloids might have a stronger effect on the dissolved concentration of high-molecular-weight PAHs than predicted (23, 30, 44); thus, the field K_d values for these compounds might actually be higher than reported. Sorption competition, arising because PAHs in the environment occur as mixtures, can also have a pronounced effect on the K_d values. As favorable adsorption sites become occupied, the adsorbed concentration of other competing PAHs decreases (11). In this case, the field data might reflect K_d values that are lower than would be expected for single-compound testing. Furthermore, anaerobic degradation of low-molecular-weight PAHs by sulfate reducers can potentially increase the apparent distribution coefficients by lowering the dissolved PAH concentration (45, 46) if this removal mechanism is faster than desorptive replacement. Finally, the BC matrix might change with sediment depth, reflecting a change in BC source over time and thus affecting the adsorption capacity and $\log K_{BC}$ values.

With these caveats in mind, the data fitting showed larger BC distribution coefficients for more hydrophobic PAHs, where $\log K_{ow}$ is used as a metric of hydrophobicity (Figure 2). Although we are not implying a linear dependency between octanol–water partitioning and BC adsorption, the increasing trend for $\log K_{BC}$ values is expected because larger, more hydrophobic PAHs are less compatible with water. However, we note that this trend in hydrophobicity does not exclude the possibility of an occlusion mechanism, assuming that occluded means chemically extractable but not water-exchangeable. If McGroddy extracted both the sorbed and occluded PAHs from the BC in the sediment, then, for a given PAH, we would observe a larger K_{BC} value in our SigmaPlot analysis of the McGroddy data than we do in laboratory spiking experiments that do not involve any chemical extractions. Previous work in our laboratory with pyrene and native Boston Harbor sediment suggest that the $\log K_{BC}$ value for spiked pyrene is approximately 6.3 ± 0.1 (6), which compares very well with the SigmaPlot-estimated $\log K_{BC}$ value of 6.2–6.4 for pyrene (Table 2). Therefore, reversible adsorption onto the BC fraction as represented by spiked compounds (as opposed to PAH occlusion) explains much of the reported high $\log K_d$ values observed in these sediments and others.

TABLE 2. $\log K_{BC}$ Values $[(\mu\text{g}/\text{kg}_{BC})/(\mu\text{g}/\text{L})^n]$ at Given Freundlich Exponents (n) for the BC Fraction Measured from McGroddy Non-Bioturbated Samples (19) for 17 Co-occurring PAHs in Boston Harbor, MA

ID ^a	PAH	$\log K_{ow}$	SigmaPlot-derived $\log K_{BC}$				N^c	$\log K_{BC}^d$		
			$n = 0.6$	% CV ^b	$n = 0.7$	% CV				
1	naphthalene	3.3	5.1	21	5.2	24	5.4	26	5	5.2
2	acenaphthene	4.0	5.4	24	5.6	26	5.9	27	6	
3	acenaphthylene	4.1	4.8	30	5.0	30	5.3	30	4	
4	fluorene	4.2	6.0	33	6.2	39	6.4	46	7	5.3
5	phenanthrene	4.5	6.3	24	6.4	27	6.5	30	14	5.7, 5.4
6	anthracene	4.5	6.1	27	6.3	31	6.5	35	11	
7	1-methylphenanthrene	5.0	6.2	34	6.4	41	6.6	49	9	
8	fluoranthene	5.1	6.7	15	6.9	15	7.1	15	14	
9	pyrene	5.1	6.2	25	6.3	28	6.4	32	13	6.6, 6.3
10	1-methylpyrene	5.7	6.1	21	6.3	26	6.4	32	12	
11	chrysene	5.7	6.8	36	7.0	38	7.1	39	8	
12	benz[a]anthracene	5.8	6.9	38	7.1	40	7.3	41	9	
13	benzo[b]fluoranthene	5.9	6.0	15	6.2	18	6.3	20	4	
14	benzo[k]fluoranthene	6.0	6.8	2	7.0	2	7.2	5	2	
15	benzo[a]pyrene	6.2	6.9	18	7.2	20	7.4	21	10	
16	benzo[e]pyrene	6.3	6.9	25	7.1	27	7.3	29	10	
17	dibenz[a,h]anthracene	6.8	6.8	43	7.1	46	7.4	50	8	

^a ID number for individual PAH corresponding to Figure 2. ^b % CV represents the coefficient of variation as a percentage for each Freundlich exponent. ^c Population size from McGroddy data set (19). ^d Literature values for BC-normalized distribution coefficients (6, 43, and our study).

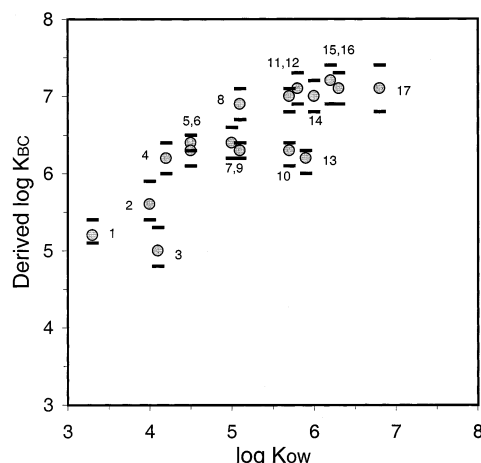


FIGURE 2. Derived $\log K_{BC}$ values $[(\mu\text{g}/\text{kg}_{BC})/(\mu\text{g}/\text{L})^n]$ from the McGroddy field data (19) versus $\log K_{ow}$ ($L_{\text{octanol}}/L_{\text{water}}$) used here only as a metric of PAH hydrophobicity. Filled circles represent the best-fit $\log K_{BC}$ values for nonbioturbated sediment layers from all three cores ($N = 13$) when the Freundlich exponent (n) is fixed at 0.7 and the relation $K_{BC} = K_d - f_{oc}K_{oc}/(f_{BC}C_w^{n-1})$ is assumed. Tabs above and below the filled circle show the variability in $\log K_{BC}$ when $n = 0.8$ (tabs above circles) and $n = 0.6$ (tabs below circles). ID numbers for the PAHs are listed in Table 2.

Reinterpreting PAH Sorption onto EPA Samples in the Laboratory. To continue the assessment of our hypothesis that PAH sorption reflects both OC adsorption and BC adsorption, we attempted to explain nonlinear phenanthrene sorption onto EPA sediments and soils using our model and single values of K_{BC} and n . To explain the nonlinear isotherms observed by Huang et al., the BC fractions in all of the EPA samples were first measured. BC weight percentages ranged from 0.03 ± 0.01 to 1.6 ± 0.02 among the 12 samples (Table 3). The two soil samples (i.e., EPA 14 and EPA 20) were among the lowest values both exhibiting a BC weight percent of 0.03 ± 0.01 , but an insufficient amount of data exists to determine whether soils usually contain lower BC contents than sediments. These observations, combined with previous measurements (2, 6), suggest that BC often contributes up to 20% of the TOC (Tables 1 and 3). Higher BC/TOC ratios (such as 65% BC/TOC for EPA 22) are uncommon, but they have been reported for surface sediments of the North Sea and in estuaries of The Netherlands (3).

No correlation between BC and TOC existed within our EPA data set ($R^2 = 0.08$, $N = 12$), indicating that our measurements were not affected by charring or other artifacts. Low correlation coefficients between BC and TOC have also been observed for coastal sediments in the New England region [$R^2 = 0.25$, $N = 15$ (2)]. These results contradict recent claims that the thermal oxidation method creates BC from the incomplete combustion of organic matter (5). Instead, reported linear correlation between BC and TOC might reflect similar depositional conditions encouraging accumulation of both types of carbon at the same loci rather than analytical error (3, 5).

We used SigmaPlot and our combined sorption model to extract the best-fit n and $\log K_{BC}$ parameters for each isotherm generated by Huang et al. (17). The average of the 12 $\log K_{BC}$ values for phenanthrene was 5.9 ± 0.5 ($N = 12$; Table 3), and the average n value was 0.65 ± 0.08 ($N = 12$). Our average $\log K_{BC}$ value approximated the reported value of 5.7 for the sorption of phenanthrene onto NIST diesel particulate matter (43). It also compared reasonably well with our measured $\log K_{BC}$ value, which ranged from 5.3 to 5.9 ($N = 4$) for the sorption of phenanthrene onto combusted sediments from Boston Harbor (Table 4). However, our average, SigmaPlot n value [0.65 ± 0.08 ($N = 12$)] did not compare well with the n values (0.87–1.00) reported by Bucheli and Gustafsson in the same NIST experiment (43), and an insufficient amount of data existed in our laboratory to construct an isotherm for comparison.

A closer inspection of the 12 SigmaPlot $\log K_{BC}$ values reveals a 2-logarithm-unit range of values from 4.5 to 6.4 (Table 3). Unlike in our previous discussion that focused on Boston Harbor sediments, the EPA samples considered here represent a diverse suite of sites and might include BC from a variety of sources (e.g., engine-derived soot, incinerator fly ash, chars from biomass burns, and carbon black from tire wear). Each source might produce a BC adsorbent with a different affinity for PAHs. Contributions from diverse surface chemistry (considering crystalline graphite versus oxygen moiety substituted activated carbons) and surface area might account for the range of $\log K_{BC}$ values observed. However, we are suspicious that EPA 22, with the highest BC weight percentage, had the lowest $\log K_{BC}$ value. An alternative explanation for the low distribution coefficient for EPA 22 might be that the incubation period chosen by Huang et al. was not long enough for this particular sample because of the large BC fraction. Thus, equilibrium might not have been

TABLE 3. Measured BC Weight Percentages (Mean \pm 1 σ), Reported TOC Weight Percentages (BC + OC, Mean \pm 1 σ), and BC/TOC Ratios for Huang et al. (17) EPA Sediments and Soils, along with Best-Fit log K_{BC} Values [$(\mu\text{g}/\text{kg}_{BC})/(\mu\text{g}/\text{L})^n$] and Freundlich Exponents (n) for Phenanthrene

sample	BC wt %	TOC wt %	BC \times 100/TOC	SigmaPlot-derived values ^a			
				log K_{BC}	% CV ^d	n	% CV ^d
EPA 4 (river sediment, ND)	0.11 \pm 0.01	2.28 \pm 0.05	5	6.0	3.8	0.61	2.9
EPA 5 (river sediment, ND)	0.05 \pm 0.01	2.07 \pm 0.14	2	6.4	3.3	0.60	2.6
EPA 13 (river sediment, WV)	0.15 \pm 0.01	4.50 \pm 0.10	3	6.3	2.9	0.62	2.2
EPA 14 (soil, WV)	0.03 \pm 0.01 ^b	0.446 \pm 0.031	7	5.6	1.2	0.79	5.4
EPA 15 (river sediment, IN)	0.20 \pm 0.08	1.24 \pm 0.09	16	5.6	2.5	0.63	1.8
EPA 18 (river sediment, KY)	0.05 \pm 0.02	0.543 \pm 0.030, 0.64 \pm 0.05 ^c	9, 8 ^c	5.9	2.7	0.64	1.9
EPA 20 (soil, IL)	0.03 \pm 0.01 ^b	1.18 \pm 0.03	3	6.3	4.2	0.59	3.4
EPA 21 (river sediment, IL)	0.34 \pm 0.08	2.36 \pm 0.16	14	5.9	1.6	0.63	1.2
EPA 22 (river sediment, IL)	1.6 \pm 0.22	1.65 \pm 0.06, 2.6 \pm 0.27 ^c	96, 62 ^c	4.5	0.5	0.85	0.2
EPA 23 (lake sediment, IL)	0.09 \pm 0.01	2.57 \pm 0.08	4	6.3	3.3	0.61	2.6
EPA 26 (river sediment, IL)	0.05 \pm 0.01	1.50 \pm 0.01	3	6.2	2.9	0.65	2.0
EPA B2 (stream sediment, GA)	0.03 \pm 0.01 ^b	1.07 \pm 0.03, 1.49 \pm 0.29 ^c	3, 2 ^c	6.3	5.0	0.56	4.5

^a SigmaPlot-derived values assuming a phenanthrene log K_{oc} value of 4.0. ^b Signal-to-noise ratio was 2:1 with $N=6$. ^c Independent measurements of TOC wt % (mean \pm 1 σ) by our laboratory and corresponding BC/TOC \times 100 ratios. ^d % CV represents the coefficient of variation as a percentage.

TABLE 4. Measured Phenanthrene Sorption (Mean \pm 1 σ) to Combusted Sediment (Boston Harbor, MA) in the Laboratory

sediment ^a (mg)	volume ^a (L)	initial concentration ($\mu\text{g}/\text{L}$)	final concentration ($\mu\text{g}/\text{L}$)	measured K_d (L/kg)	estimated log K_{BC}^b [($\mu\text{g}/\text{kg}$)/($\mu\text{g}/\text{L}$) ^{n}]
40.6	0.102	3.62 \pm 0.14	2.97 \pm 0.14	550 \pm 170	5.5–5.6
41.6	0.104	8.54 \pm 0.34	7.77 \pm 0.33	250 \pm 160	5.3–5.4
79.8	0.103	3.62 \pm 0.14	1.96 \pm 0.12	1100 \pm 130	5.8–5.9
80.2	0.105	8.54 \pm 0.34	6.38 \pm 0.29	450 \pm 100	5.5–5.7

^a Error in sediment mass and volume is $<1\%$. ^b BC-normalized distribution coefficient (log K_{BC}) assuming that $K_{BC} = K_d/f_{BC}(C_{final}^{n-1})$, where $f_{BC} = 0.2 \pm 0.02$ wt % for $n = 0.6$ and $n = 0.8$.

established, so that the BC distribution coefficient was underestimated.

In addition to examining these 12 log K_{BC} values separately, all of the isotherms were fit collectively using the combined sorption model. To this end, we used MATLAB to solve simultaneously for the best-fit log K_{BC} and n values for the 11 EPA isotherms with a fixed log K_{oc} value of 4.0. EPA 22 was not included in this fit because of its unusual BC/TOC ratio and low log K_{BC} value. The MATLAB optimization yielded a single best-fit log K_{BC} value for phenanthrene of 6.1 ± 0.04 and an n value of 0.55 ± 0.03 with an R^2 of 0.95. Remarkably, when BC adsorption and OC absorption were considered together, single values for log K_{BC} and n could explain the phenanthrene sorption onto this diverse array of sediments and soils. In addition, our model parameters for phenanthrene sorption compared well with an independent sorption experiment performed by Karapanagioti et al., who examined the sorption of phenanthrene in synthetic groundwater onto a soil subsample (0.5–0.25 mm grain size, nonmagnetic) dominated by isolated coal particles (18). In their work, the best-fit Freundlich exponent was 0.55 ± 0.02 with a log K_{BC} value of $6.3\text{--}6.4$ at $1 \mu\text{g}/\text{L}$ [assuming that all of the carbon (1.60 wt % C) is attributed to the coal particles].

In our optimization, the log K_{BC} value was affected only slightly by the choice of log K_{oc} value, whereas the n value was extremely sensitive to log K_{oc} . Because the Freundlich exponent (n) reflects the curvature of the isotherm, the n value decreased to compensate for the higher log K_{oc} values. For example, as the log K_{oc} values for phenanthrene were adjusted from 3.7 to 4.3 (31), the best-fit n value decreased from 0.66 to 0.27, whereas the log K_{BC} value remained virtually the same (decreased slightly from 6.1 to 6.0). The constancy of the log K_{BC} term throughout this fitting suggests that, at low dissolved concentration where adsorption dominates (12, 18), only one BC distribution coefficient can reasonably fit all of these isotherms. Furthermore, these results suggest that observed nonlinear isotherms are dominated by BC adsorption, and therefore, minor manipulations in the

nonlinear/linear nature of the OC fraction will have minor implications on the predicted log K_d values for low phenanthrene concentrations.

We reconstructed all 11 EPA isotherms using the combined sorption model with a log K_{oc} value of 4.0, a log K_{BC} value of 6.1, and an n value of 0.55. These model isotherms were then compared to the observed isotherms reported by Huang et al. (17). Our model estimated the observed sorbed concentration well at high dissolved concentrations ($>10 \mu\text{g}/\text{L}$); however, at lower concentrations ($<10 \mu\text{g}/\text{L}$), the model either overestimated or underestimated the observed sorbed concentrations. The equal scattering of data above and below the observed isotherms is expected, however, because of the modeling optimization scheme. (For simplicity, only three representative isotherms are shown in Figure 3 – one that is overestimated, one that is underestimated, and one that is predicted well.) In general, the combined sorption model was able to predict the K_d values observed by Huang et al. within a factor of 3. To illustrate this approximation differently, a compilation of data along all 11 isotherms was made for the predicted log K_d values (eq 1) versus observed log K_d values (17) at three different dissolved concentrations (2, 20, and 400 $\mu\text{g}/\text{L}$; Figure 4). As noted above, the data are more scattered at the lower concentrations (2 $\mu\text{g}/\text{L}$, filled circles) than the higher concentrations (400 $\mu\text{g}/\text{L}$, filled squares). The difference between the predicted log K_d values at 2 $\mu\text{g}/\text{L}$ and the one-to-one line was 0.3 ± 0.4 logarithm units, whereas the difference at 400 $\mu\text{g}/\text{L}$ was only 0.1 ± 0.2 logarithm units. We noticed no correlation between the BC fraction of the samples and the accuracy of these estimates. Hence, our model and our best-fit parameters allow for reasonable estimates of phenanthrene sorption onto a diverse set of sediments and soils.

Our work suggests that the simple OC absorption model does not capture all sorption phenomena influencing PAHs in natural solids that contain BC, especially at ambient concentrations. We expect that similar behaviors will apply to the planar congeners in other important hydrophobic

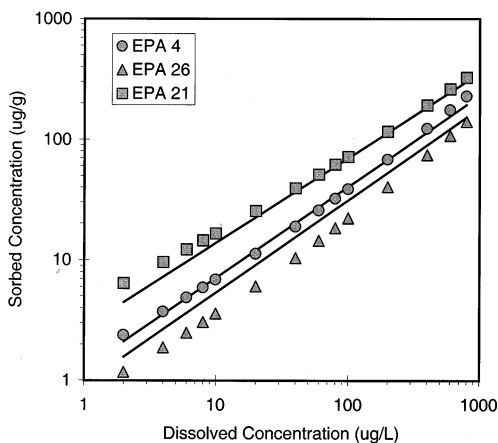


FIGURE 3. Comparison of observed phenanthrene isotherms [solid line; $C_s (\mu\text{g/g}) = K_d C_w (\mu\text{g/L})^n$] from Huang et al. (17) and model isotherms [filled symbols; $C_s (\mu\text{g/g}) = f_{oc} K_{oc} C_w (\mu\text{g/L}) + f_{bc} K_{bc} C_w (\mu\text{g/L})^n$, assuming $\log K_{oc} = 4.0$, $\log K_{bc} = 6.1$, and $n = 0.55$] for three representative EPA samples (EPA 4, 26, and 21). For the sorbed concentration ($\mu\text{g/g}$), the propagated error was approximately 20% for the observed isotherm by Huang et al. (17) and 50% for the model isotherm. Samples correspond to data listed in Table 3.

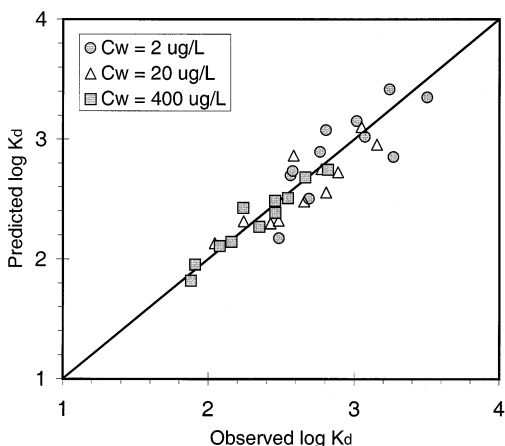


FIGURE 4. $\log K_d$ values (L/kg) predicted from eq 1 ($K_d = f_{oc} K_{oc} + f_{bc} K_{bc} C_w^{n-1}$ assuming $\log K_{oc} = 4.0$, $\log K_{bc} = 6.1$, and $n = 0.55$) versus the $\log K_d$ values (L/kg) observed by Huang et al. (17) at the dissolved concentrations (C_w) of 2 $\mu\text{g/L}$ (filled circles), 20 $\mu\text{g/L}$ (open triangles), and 400 $\mu\text{g/L}$ (filled squares) along 11 isotherms. The approximate errors for all data are ± 0.2 logarithm units for the predicted $\log K_d$ value (y axis) and ± 0.1 logarithm units for the observed $\log K_d$ value (x axis). The solid line marks the one-to-one line.

compound classes [e.g., PCBs, dioxins, DDE (22)] where BC is the dominant sorbent. Therefore, remediation programs and risk-management teams need to consider the implication of both a BC adsorbent and an OC adsorbent in sediments and soils. These BC sorptive interactions might explain the limited desorption (47) and limited bioavailability of PAHs in the environment (48–51).

Acknowledgments

This work was supported by NSF Grant BES-9800485. The project, number RC-70, was also funded (in part) by the MIT Sea Grant College Program under Federal Grant NA86RG0074 from the National Sea Grant College Program, National Oceanic and Atmospheric Administration, U.S. Department of Commerce. We especially thank Wayne Banwart, Suresh Rao, and Ryan Hultgren for locating and donating the EPA samples and John Farrington, Tim Eglinton, and Chris Reddy for locating and donating the McGroddy cores. Special thanks

go to John MacFarlane of MIT for his continuous support in the laboratory, Dave Glover of WHOI for help on the MATLAB modeling, and Richard Bopp for his useful discussions on this project.

Literature Cited

- Gustafsson, Ö.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 203–209.
- Gustafsson, Ö.; Gschwend, P. M. *Geochim. Cosmochim. Acta* **1998**, *62*, 465–472.
- Middelburg, J. J.; Nieuwenhuize, J.; Breugel, P. *Mar. Chem.* **1999**, *65*, 245–252.
- Zhou, J. L.; Fileman, T. W.; Evans, S.; Donkin, P.; Readman, J. W.; Mantoura, R. F. C.; Rowland, S. *Sci. Total Environ.* **1999**, *244*, 305–321.
- Gelinas, Y.; Prentice, K. M.; Baldock, J. A.; Hedges, J. I. *Environ. Sci. Technol.* **2001**, *35*, 3519–3525.
- Accardi-Dey, A.; Gschwend, P. M. *Environ. Sci. Technol.* **2002**, *36*, 21–29.
- Mitra, S.; Bianchi, T. S.; McKee, B. A.; Sutula, M. *Environ. Sci. Technol.* **2002**, *36*, 2296–2302.
- Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979**, *206*, 831–832.
- Karickhoff, S. W. *Chemosphere* **1981**, *10*, 833–846.
- Weber, W. J.; McGinley, P. M.; Katz, L. E. *Environ. Sci. Technol.* **1992**, *26*, 1955–1962.
- Xing, B. S.; Pignatello, J. J.; Gigliotti, B. *Environ. Sci. Technol.* **1996**, *30*, 2432–2440.
- Xia, G. S.; Ball, W. P. *Environ. Sci. Technol.* **1999**, *33*, 262–269.
- Laor, Y.; Rebhun, M. *Environ. Sci. Technol.* **2002**, *36*, 955–961.
- Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241–248.
- Means, J. C.; Wood, S. G.; Hassett, J. J.; Banwart, W. L. *Environ. Sci. Technol.* **1980**, *14*, 1524–1528.
- Grathwohl, P. *Environ. Sci. Technol.* **1990**, *24*, 1687–1693.
- Huang, W. L.; Young, T. M.; Schlautman, M. A.; Yu, H.; Weber, W. J. *Environ. Sci. Technol.* **1997**, *31*, 1703–1710.
- Karapanagioti, H. K.; Kleinedam, S.; Sabatini, D.; Grathwohl, P.; Ligouis, B. *Environ. Sci. Technol.* **2000**, *34*, 406–414.
- McGroddy, S. E. Ph.D. Thesis. Sediment–Pore Water Partitioning of PAHs and PCBs in Boston Harbor, Massachusetts. University of Massachusetts at Boston, Boston, MA, 1993; pp 1–255.
- McGroddy, S. E.; Farrington, J. W. *Environ. Sci. Technol.* **1995**, *29*, 1542–1550.
- Chiou, C. T.; McGroddy, S. E.; Kile, D. E. *Environ. Sci. Technol.* **1998**, *32*, 264–269.
- Bucheli, T. D.; Gustafsson, Ö. *Environ. Toxicol. Chem.* **2001**, *20*, 1450–1456.
- Chin, Y.; Gschwend, P. M. *Environ. Sci. Technol.* **1992**, *26*, 1621–1626.
- Wong, C. S. Assessing the Flux of Organic Pollutants from the Sediments of Boston Harbor. M.S. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1992; pp 1–138.
- Shiaris, M. P.; Jambard-Sweet, D. *Mar. Pollut. Bull.* **1986**, *17*, 469–472.
- Eganhouse, R. P.; Sherblom, P. M. *Mar. Environ. Res.* **2000**, *51*, 51–74.
- Rex, A. C. *The State of Boston Harbor 1997–1998: Beyond the Boston Harbor Project*; Enquad Technical Report No. 00-05; Massachusetts Water Resources Authority: Boston, MA, 2000; pp 1–24.
- Stolzenbach, K. D.; Adams, E. E. In *Contaminated Sediments in Boston Harbor*; Marine Center for Coastal Processes, MIT Sea Grant Program, MIT: Cambridge, MA, 1998; pp 45–74.
- Hassett, J. J.; Means, J. C.; Banwart, W. L.; Woods, S. G. *Sorption Properties of Sediments and Energy-Related Pollutants*; U.S. Environmental Protection Agency, U.S. Government Printing Office: Washington, DC, 1980.
- Mitra, S.; Dickhut, R. M. *Environ. Toxicol. Chem.* **1999**, *18*, 1144–1148.
- Gawlik, B. M.; Sotiriou, N.; Feicht, E. A.; Schulte-Hostede, S.; Kettrup, A. *Chemosphere* **1997**, *34*, 2525–2551.
- Youngblood, W. W.; Blumer, M. *Geochim. Cosmochim. Acta* **1975**, *39*, 1303–1314.
- Gschwend, P. M.; Hites, R. A. *Geochim. Cosmochim. Acta* **1981**, *43*, 2359–2367.
- Windsor, J. G.; Hites, R. A. *Geochim. Cosmochim. Acta* **1979**, *43*, 27–33.
- Miguel, A. M.; Kirchstetter, T. W.; Harley, R. A. *Environ. Sci. Technol.* **1998**, *32*, 450–455.

- (36) Lefkowitz, L.; Dahlen, D.; Hunt, C.; Ellis, B. *1998 CSO Sediment Study Synthesis Report*; Enquad Technical Report No. 99-12, Massachusetts Water Resources Authority: Boston, MA, 2000; pp 1–54.
- (37) Gallagher, E. D.; Keay, K. E. In *Contaminated Sediments in Boston Harbor*; Stolzenback, K. D., Adams, E. E., Eds.; Marine Center for Coastal Processes, MIT Sea Grant Program, MIT: Cambridge, MA, 1998; pp 89–132.
- (38) Leo, W. S.; Alber, M.; Connor, M. S.; Keay, K. E.; Rex, A. C. *Contaminated Sediments in Boston Harbor*; Enquad Technical Report No. 93-9; Massachusetts Water Resources Authority: Boston, MA, 1994; pp 1–53.
- (39) Pignatello, J. J.; Xing, B. S. *Environ. Sci. Technol.* **1996**, *30*, 1–11.
- (40) Weber, W. J.; Huang, W. L. *Environ. Sci. Technol.* **1996**, *30*, 881–888.
- (41) ten Hulscher, T. E. M.; Vrind, B. A.; van den Heuvel, H.; van der Velde, L. E.; van Noort, P. C. M.; Beurskens, J. E. M.; Govers, H. A. J. *Environ. Sci. Technol.* **1999**, *33*, 126–132.
- (42) Crittenden, J. C.; Luft, P.; Hand, D. W.; Oravitz, J. L.; Loper, S. W.; Art, M. *Environ. Sci. Technol.* **1985**, *19*, 1037–1043.
- (43) Bucheli, T. D.; Gustafsson, Ö. *Environ. Sci. Technol.* **2000**, *34*, 5144–5151.
- (44) Masiello, C. A.; Druffel, E. R. M. *Science* **1998**, *280*, 1911–1913.
- (45) Coates, J. D.; Woodward, J.; Allen, J.; Philp, P.; Lovley, D. R. *Appl. Environ. Microbiol.* **1997**, *63*, 3589–3593.
- (46) Hayes, L. A.; Nevin, K. P.; Lovley, D. R. *Org. Geochem.* **1999**, *30*, 937–945.
- (47) Lamoureux, E. M.; Brownawell, B. J. *Environ. Toxicol. Chem.* **1999**, *18*, 1733–1741.
- (48) Tracey, G. A.; Hansen, D. J. *Arch. Environ. Contam. Toxicol.* **1996**, *30*, 467–475.
- (49) Tang, J.; Garcia, R.; Holden, K. M. L.; Mitchell, S. C.; Pis, J. J. *Environ. Sci. Technol.* **1998**, *32*, 3586–3590.
- (50) Alexander, M. *Environ. Sci. Technol.* **2000**, *34*, 4259–4265.
- (51) Krauss, M.; Wilcke, W.; Zech, W. *Environ. Pollut.* **2000**, *110*, 79–88.

Received for review January 31, 2002. Revised manuscript received October 14, 2002. Accepted October 18, 2002.

ES020569V