

Comparison of the *in Situ* and Desorption Sediment—Water Partitioning of Polycyclic Aromatic Hydrocarbons and Polychlorinated Biphenyls

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In situ sediment—porewater partitioning of polycyclic aromatic hydrocarbons (PAHs) measured in three cores from Boston Harbor, MA, has led us to suggest that only a fraction of the total measured sediment PAH concentration is available for equilibrium partitioning (AEP fraction). To test this, aqueous PAH concentrations were measured in laboratory desorption experiments using subsamples of the same Boston Harbor sediments. The observed concentrations were consistent with what we predicted from the field-derived AEP values: $C_{\text{aqueous}} = (C_{\text{sediment}} \times \text{AEP}) / (f_{\text{oc}} \times K_{\text{oc}})$ where f_{oc} is the fraction organic carbon in the sediment and K_{oc} is the organic carbon normalized sediment—water partition coefficient. Equilibrium partitioning models based on the total measured sediment PAH concentrations overestimated the measured aqueous PAH concentrations by as much as 100 times in some cases. Only a small fraction of the sediment phenanthrene and pyrene concentrations (1–40%) appeared to be available for equilibrium partitioning. Both *in situ* and laboratory desorption aqueous polychlorinated biphenyl (PCB) concentrations were consistent with equilibrium partitioning models and the assumption that 100% of these compounds was available for equilibrium partitioning. These results are particularly important to efforts to predict the environmental mobility and bioavailability of the PAHs.

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Introduction

The mobility and bioavailability of organic contaminants associated with sediment beds depend on the concentrations of these compounds in the porewater. These porewater concentrations, in turn, are controlled by sorption of the contaminants to the sediment solids. Nonpolar organic compounds are believed to sorb to sediment particles as a result of partitioning of the compounds between porewater and the sediment organic matter (1–4).

The presumption of sorptive equilibration for nonpolar organic compounds like polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) is, however, based on the concept that such molecules are introduced into the environment in an exchangeable form. Generally, the sources of PCBs are thought to be such that these molecules are readily available to move between phases. However, since PAHs have both pyrogenic and petroleum sources, and the PAHs associated with soot particles may not be readily exchangeable, it is not clear whether these aromatic hydrocarbons exhibit partitioning behavior like that shown when these compounds are added as solutes in sediment or soil suspensions (5–12). In our previous work (13), we showed that while PCBs in sediment beds from Boston Harbor distributed themselves between solution and solid phases in accordance with predictions based on the individual congeners' hydrophobicities, the PAHs in the same media did not do so. We hypothesized that this differential sorptive behavior arose because a substantial portion of the PAHs were associated with soot particles and therefore not in a form which was exchangeable on the time scale of decades (i.e., the age of the sediments examined.) Thus, we calculated what fraction of each PAH would need to be available for equilibrium partitioning (AEP) to explain the porewater concentrations we observed (13):

$$\text{AEP fraction} = \frac{(\text{measured porewater concn } (K_d'))}{(\text{measured sediment concn})} \quad (1)$$

where K_d' is an apparent partition coefficient calculated from measured partition coefficients (14) and accounting for the effects of porewater colloids (15, 16):

$$K_d' = f_{\text{ocs}} / (1 + f_{\text{occ}} K_{\text{occ}}) \quad (2)$$

where f_{ocs} is the sediment fraction organic carbon (g of C_{org} /g of sed), K_{ocs} is the sediment K_{oc} (mL/g of sediment C_{org}), f_{occ} is the colloidal fraction organic carbon (g of C_{org} /mL), K_{occ} is the colloidal K_{oc} (mL/g of colloidal C_{org}).

This study was designed to ascertain whether the apparent *in situ* porewater—sediment disequilibrium for partitioning of the PAHs that we observed in Boston Harbor sediments could be caused by such an AEP fraction. Aliquots of sediment were suspended in PAH- and PCB-clean artificial seawater, and the releases of these contaminants were observed. By comparing the desorption behavior of PCBs and PAHs of similar hydrophobicities and by using previous observations in which the extent of sorption for PAHs added to the sediment was observed (14), we directly discerned the importance of the non-exchanging fraction for PAHs at our study sites.

TABLE 1

Average Percent Recoveries of PAH and PCB Recovery Surrogates

	fluorene- d_{10}	terphenyl- d_{10}	perylene- d_{12}	CB29	CB143
Spectacle Island					
aqueous	61.3 \pm 24.6 (7) ^a	95.6 \pm 22.8 (8)	78.8 \pm 12.3 (2)	95.8 \pm 6.92 (8)	86.3 \pm 11.3 (8)
sediment	101 \pm 14.7(8)	111 \pm 10.1 (8)	89.3 \pm 19.8 (5)	93.2 \pm 15.0 (8)	72.7 \pm 12.1 (8)
Fort Point Channel					
7–9 cm aqueous	69.0 \pm 21.3 (5)	103 \pm 21.3 (7)	88.2 \pm 18.1 (2)	74.8 \pm 14.4 (8)	74.9 \pm 12.3 (8)
7–9 cm sediment	96.7 \pm 22.6 (7)	111 \pm 13.6 (5)	85.8 \pm 7.89 (2)	79.2 \pm 11.5 (8)	76.1 \pm 20.0 (8)
15–17 cm aqueous	56.7 \pm 6.72 (4)	104 \pm 12.7 (6)	nq ^b	84.3 \pm 3.80 (3)	78.8 \pm 8.70 (3)
15–17 cm sediment	97.6 \pm 1.64 (5)	117 \pm 16.7 (5)	92.8 \pm 0.93 (2)	108 \pm 2.35 (3)	85.6 \pm 22.9 (3)

^a Number of samples in parentheses. ^b nq, not quantitated due to poor peak resolution.

Materials and Methods

Sediment samples were taken from 0.25 m² box cores obtained at two sites in Boston Harbor: (1) Fort Point Channel (42°21'22" N, 71°02'41" W), and (2) Spectacle Island (42°19'46" N, 70°59'34" W) as previously described (13). Three core section samples that had been stored frozen at –40 °C were selected for the desorption experiments [the same samples examined previously by Chin and Gschwend (14) for phenanthrene and pyrene sorption]. Three replicate experiments were conducted for each sediment sample for each of three time periods: 24 h, 48 h, and 2 wk. The sediment samples were thawed and homogenized manually using a stainless steel spatula prior to sampling.

The 24-h and 48-h experiments were conducted in 750-mL glass centrifuge tubes (Bellco Inc.) with Teflon-lined screw caps. The 2-wk experiments were conducted in 500-mL amber glass bottles with Teflon-lined screw caps. Defrosted wet sediment samples were weighed (0.224–1.15 g dry wt of sediment, masses chosen to try to have 20–80% of the sorbates in each phase after equilibration) and added to each tube, followed by bicarbonate-buffered (1 mM) saline solution (0.6 M NaCl). All experiments were poisoned with approximately 1 mL of a saturated aqueous mercuric chloride.

Prior to use, all glassware was solvent rinsed and then combusted overnight at 500 °C. The NaCl and bicarbonate were Soxhlet extracted in 1:1 methanol/toluene and then dichloromethane for 24 h each. In addition, the NaCl was heated to 500 °C for 24 h.

The sediment–water suspensions were agitated on a shaker table for 24 h, 48 h, and 2 wk. The glass centrifuge tubes were covered in aluminum foil to protect the samples from direct light. At the end of the experiments, the tubes were centrifuged at 500g for 20 min to separate the aqueous phase from the solid phase.

A subsample of the aqueous phase (approximately 1.5 mL) was reserved for dissolved organic carbon analysis. The total dissolved organic carbon concentration was measured in Dr. W. Martin's laboratory at WHOI using a high-temperature platinum-catalyzed method (17). The remaining aqueous phase was immediately extracted four times with 50 mL each of dichloromethane (DCM), and the four extracts were combined (18).

Sediment samples were extracted in the same bottles used for incubations on a shaker-table using 1 \times 30 mL of methanol and 3 \times 20 mL of DCM. The methanol fraction was combined with 100 mL of double-distilled water. The methanol–water solution was extracted with hexane, and the hexane extract was combined with the DCM extracts (19). Prior to extraction, both sediment and aqueous

samples were spiked with deuterated PAH recovery surrogates (fluorene- d_{10} , terphenyl- d_{10} and perylene- d_{12}) and PCB recovery surrogates [2,4,5-trichlorobiphenyl (CB29) and 2,2',3,4,5,6'-hexachlorobiphenyl (CB143)]. Other aspects of the extraction and concentration procedures have been described more fully elsewhere (13).

Chromatographic Separations. The extracts were solvent-exchanged into approximately 1 mL of hexane, and the entire extract was applied to a 1.0 \times 30 cm glass chromatography column packed with 7 g of 5% deactivated silica gel (100–200 mesh). The following elution scheme was used: 20 mL of hexane (fraction 1), 15 mL of 25% dichloromethane (DCM) in hexane followed by 5 mL of 50% DCM in hexane (fraction 2), and 15 mL of DCM (fraction 3). The PCBs were isolated in fraction 1. The PAHs were isolated in fraction 2. Each fraction was reduced in volume by rotary evaporation to a final volume of approximately 1 mL and stored in amber vials in the freezer.

PAH Quantitation. The PAH fractions were analyzed by gas chromatography with a flame ionization detector on a Carlo Erba 4160 gas chromatograph with an on-column injector, a 30-m DB5 column, and hydrogen as a carrier gas (13). Procedural blanks were analyzed concurrently with the samples. Detectable concentrations of PAHs were not measured in any of the blanks analyzed. The aqueous phase detection limit depends on the volume of sample. We estimated a range of detection limits from 8.0 ng/L for a 0.50-L sample to 2.5 ng/L for a 1.0-L sample. The sediment sample limit of detection was approximately 20 ng/g sediment.

The recoveries for the deuterated PAH recovery surrogates are summarized in Table 1. The recoveries of the fluorene- d_{10} in the aqueous samples are less than those for the corresponding sediment samples, probably due to volatilization. None of the reported PAH concentrations were corrected for recoveries.

PCB Quantitation. The aqueous extract fractions were brought up in 20–50 μ L of external standard solution [octachloronaphthalene (OCN) at 16 pg/ μ L]. The sediment extract fractions were brought up in 500 μ L–1 mL of external standard solution (OCN at 16 pg/ μ L). The PCB congeners were analyzed by gas chromatography with a Ni-63 electron capture detector (ECD) on a Carlo Erba 2150 GC with a 30-m DB5 fused silica column operated with hydrogen as the carrier gas and nitrogen as the ECD makeup gas. The following chromatographic conditions were used: 1.0 μ L on-column injection; 1 min at 90 °C; temperature programming at 5 °C/min to 170 °C and then 1 °C/min to 275 °C where the temperature was held for 15 min. Congener concentrations were determined from relative response factors generated by calibration with a quantitative solution

TABLE 2

Measured and Predicted Aqueous-Phase Concentrations (ng/L)

compd	log K_{oc}	AEP ^a	concentrations (ng/L)		
			measured aqueous	predicted from AEP sediment	predicted from total sediment
FPC ^b 15–17 cm ($f_{oc} = 0.0519$)					
phenanthrene	4.30 ^c	4.2	17 ± 8.7 $n = 9$	64 ± 27 $n = 9$	1500 ± 630 $n = 9$
pyrene	5.18 ^c	39	220 ± 51 $n = 9$	310 ± 71 $n = 9$	800 ± 180 $n = 9$
CB101	5.79, 5.93 ^d	100	0.44 ± 0.12 $n = 8$	0.87 ± 0.38 $n = 8$	0.87 ± 0.38 $n = 8$
CB138	6.16 ^{d,e}	100	0.43 ± 0.15 $n = 5$	0.49 ± 0.19 $n = 7$	0.49 ± 0.19 $n = 7$
FPC ^b 7–9 cm ($f_{oc} = 0.0547$)					
phenanthrene	4.30 ^c	0.78	7.1 ± 2.0 $n = 6$	14 ± 7.4 $n = 8$	1800 ± 950 $n = 8$
pyrene	5.20 ^c	27	84 ± 36 $n = 8$	150 ± 55 $n = 8$	550 ± 203 $n = 8$
CB101	5.79, 5.93 ^d	100	1.3 ± 0.56 $n = 8$	2.9 ± 1.3 $n = 8$	2.9 ± 1.3 $n = 8$
CB138	6.16 ^{d,e}	100	1.0 ± 0.35 $n = 8$	1.7 ± 0.90 $n = 8$	1.7 ± 0.90 $n = 8$
SI ^b 14–16 cm ($f_{oc} = 0.0334$)					
phenanthrene	4.30 ^c	0.067	8.57 ± 4.66 $n = 6$	1.14 ± 0.87 $n = 9$	1703 ± 1230 $n = 9$
pyrene	5.23 ^c	2.77	20.7 ± 9.12 $n = 7$	17.8 ± 12.9 $n = 9$	642.2 ± 465 $n = 9$
CB101	5.79, 5.93 ^d	100	0.56 ± 0.15 $n = 8$	0.94 ± 0.56 $n = 8$	0.94 ± 0.56 $n = 8$
CB138	6.16 ^{d,e}	100	0.59 ± 0.25 $n = 7$	0.58 ± 0.29 $n = 7$	0.58 ± 0.29 $n = 7$

^a Percent of the sediment concentration available for equilibrium partitioning McGroddy and Farrington (13). ^b FPC, Fort Point Channel core; SI, Spectacle Island core. ^c Chin and Gschwend (14). ^d Gschwend and Wu (29) and unpublished data. ^e Assuming the same log K_{oc} value for congeners CB153 and CB138.

prepared from a National Research Council of Canada standard solution (standard: CLB-1D).

Procedural blanks were analyzed concurrently with the samples. No detectable concentrations of PCBs were present in any of the procedural blanks. The estimated detection limits for the aqueous samples depended on the volume of the samples and ranged from 0.20 ng of individual congener/L for a 0.50-L sample to 0.10 ng of individual congener/L for a 1.0-L sample. The estimated limit of detection for the sediment samples was 0.25 ng of individual congener/g of sediment. The percent recoveries of the two PCB recovery surrogates are reported in Table 1. None of the reported PCB congener concentrations have been corrected for recoveries.

Complete resolution of all PCB congeners on a single capillary column is not yet possible. Closely related congeners have a strong tendency to coelute under standard chromatographic conditions. Therefore, the possibility that the measured PCB congener concentrations have been affected by the presence of coeluting congeners cannot be ignored. The congeners reported here (CB101, CB138) do not have coeluting congeners that are present in appreciable concentrations in commercial Arochlor mixtures.

Results and Discussion

Sediment and Site Characteristics. The Fort Point Channel site is located in Inner Boston Harbor. Ship traffic, fueling, and docking are extensive in the vicinity, and nearby combined sewer overflows occasionally allow inputs of street runoff and sewage. Oily sheens appeared on the surface of porewaters isolated from this core, and the high

“pentane-extractable” content of the sediment appears to make the sediment organic matter an especially effective sorbent for PAHs (14). Individual PAHs were measured by us in surficial sediments of this area at 1–10 ppm (13). In contrast, the Spectacle Island site is located somewhat farther offshore (ca. 1 mi). Spectacle Island has been used as a dump site in the past. The sediment PAH concentrations measured in the Spectacle Island core sediments were markedly lower than those of the Fort Point Channel core (about 1 ppm for each PAH). Moreover, the Spectacle Island core yielded porewater concentrations that appeared to be far below those expected from equilibrium partitioning. We hypothesized that the dominant source of PAH to these sediments may have been pyrogenic PAH associated with soot particles (13). The AEP fractions calculated for phenanthrene and pyrene in the three sediment samples used in our desorption experiments suggest that only small fractions of the measured sediment phenanthrene and pyrene concentrations were available for exchange with the aqueous phase (Table 2). A significantly smaller AEP fraction was calculated for the Spectacle Island sediment phenanthrene and pyrene concentrations than the Fort Point Channel sediment PAH concentrations.

Desorbed Concentrations vs Predictions Based on Field AEPs. To assess whether the observed desorbed concentrations in our laboratory experiments were consistent with the concept that one portion of the PAHs was available for equilibrium partitioning (1–4), while the remainder was effectively irreversibly bound on time scales of 50–100 yr (although organic solvent extractable), we used the AEPs calculated from our field data for the core sections tested

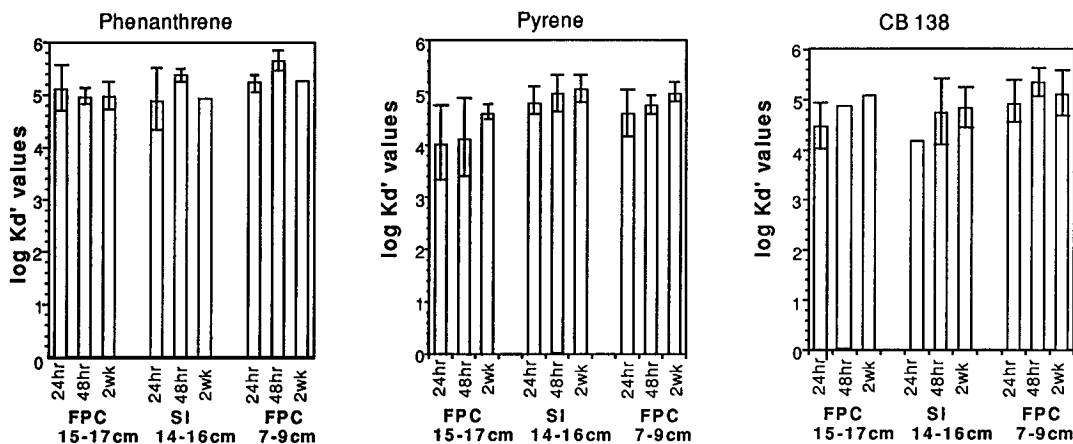


FIGURE 1. Log K_d' values for phenanthrene, pyrene, and CB138 at 24 h, 48 h, and 2 weeks for each of the three sediment samples. Error bars represent 1 SD deviation around the mean of three replicates.

for PAH desorption in the laboratory to predict the corresponding solution concentrations. This approach is only valid if the laboratory desorption experiments allowed enough time for the PAHs to reach sorptive equilibrium. Pyrene has been reported to be equilibrated in sorption experiments with these sediments within 24 h (14). In the experiments described here, there were no reproducible temporal trends observed in our measured apparent partition coefficients (K_d') for periods of up to 2 weeks (Figure 1). This is consistent with the results of previous studies (14, 20).

Our calculations also require consideration of any colloiddally bound PAHs in our desorption supernatants. However, the dissolved organic carbon concentrations measured for aqueous samples from the desorption experiments were generally quite low (1.85–2.75 mg of C_{org} /L). Since these concentrations suggest organic colloid-to-water ratios much less than 10^{-5} , and we only examined sorbates with $K_{oc} \leq 10^6$, our predicted aqueous concentrations were based on the assumption that the aqueous concentration was composed entirely of dissolved PAH.

Thus aqueous concentrations were calculated from two different sediment concentrations, the AEP fraction and the total measured sediment concentrations of pyrene and phenanthrene:

predicted from AEP fraction

$$\text{aqueous concentration} = (\text{sediment concentration} \times \text{AEP fraction}) / (K_{ocs} f_{ocs}) \quad (3)$$

predicted from total measured sediment PAH

$$\text{aqueous concentration} = (\text{sediment concentration}) / (K_{ocs} f_{ocs}) \quad (4)$$

where K_{ocs} is the compound's organic normalized sediment partition coefficient and f_{ocs} is the sediment fraction organic carbon.

The aqueous pyrene concentrations measured in our desorption tests were well predicted from the AEP sediment pyrene concentrations used in combination with K_{ocs} reported previously by Chin and Gschwend (14). The aqueous pyrene concentrations predicted from the measured sediment pyrene concentrations were a factor of 3.7 higher than the measured aqueous pyrene concentrations. The measured aqueous phenanthrene concentrations were

also better predicted from the AEP fraction of the sediment phenanthrene concentration than from the total measured phenanthrene concentration (Table 2). The aqueous phenanthrene concentrations predicted from the measured sediment phenanthrene concentration were approximately 2 orders of magnitude higher than the actual measured aqueous phenanthrene concentrations.

In order to test the validity of our hypothesis that PAH partitioning behavior is controlled by the source of these compounds, we compared the *in situ* and desorption partitioning behavior of the PAH compounds, phenanthrene and pyrene, and two PCB congeners, CB101 and CB138. The results of the field study (21) suggested that the sediment PCB concentrations appeared to be completely available for exchange with the surrounding porewaters (100% AEP). Aqueous concentrations of CB101 and CB138 measured in our desorption experiments were well predicted from the measured sediment concentrations (Table 2).

Partition Coefficients for PAHs vs PCBs. The *in situ* and desorption sediment–water partitioning of phenanthrene, pyrene, CB101, and CB138 are illustrated in terms of the observed partition coefficients (Figure 2). The desorption sediment log K_{oc} values are the average of the values obtained in the three time periods. The desorption sediment log K_{oc} values and the *in situ* sediment log K_{oc} values calculated for CB101 and CB138 agree quite well with the literature log K_{oc} values reported for these compounds. In contrast, both the desorption sediment log K_{oc} values and the *in situ* sediment log K_{oc} values calculated for phenanthrene and pyrene are significantly higher than the literature values for these compounds. The PAH compounds present in our contaminated sediments do not appear to be available for exchange with the aqueous phase while the PCB congeners appear to equilibrate completely in both the *in situ* and desorption studies.

In many coastal and estuarine areas, it is reasonable to assume that a significant portion of pyrogenic PAH is introduced to the sediments in association with soot particles. Other sources would be pyrogenic PAH contained in used crankcase oil and creosote. PAH compounds associated with a soot matrix may be less available to exchange with the porewaters than petroleum-derived PAH (8).

Our discussion of “available” and “unavailable” fractions of the total measured sediment PAH concentrations may

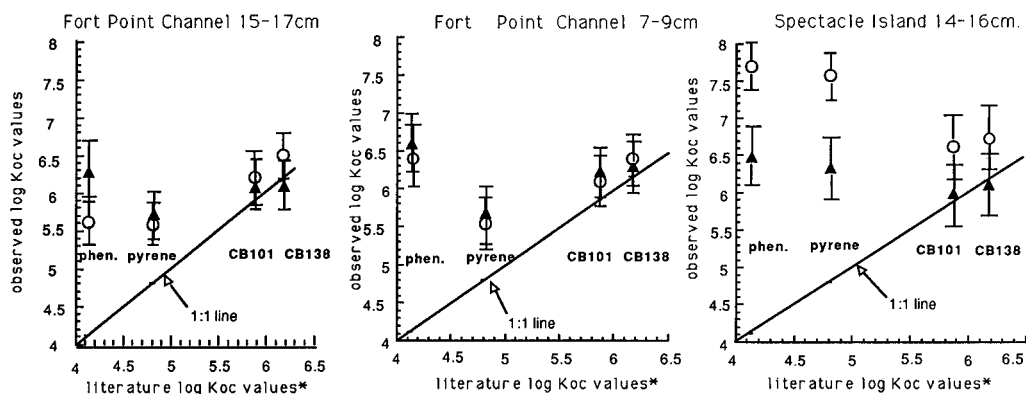


FIGURE 2. Literature log K_{oc} values plotted against observed log K_{oc} values for phenanthrene, pyrene, CB101, and CB138. The triangles represent desorption log K_{oc} values, and the circles represent *in situ* log K_{oc} values. Note: The error bars on the desorption log K_{oc} values represent 1 SD of the average of the measurements at all three time points ($n = 9$). The error bars on the *in situ* log K_{oc} values represent an estimate of the uncertainty associated with the literature sediment and colloid K_{oc} values for these compounds used in calculating our *in situ* log K_{oc} values. An asterisk indicates that you should see Table 2 for references.

be a simplification of a wide range of interactions. Diffusion of PAH through the soot matrix may be extremely slow, resulting in PAH that appear to be unavailable on the time scales represented by these sediment cores (30–50 yr). The kinetics of PAH desorption from soot particles to high purity nitrogen have been measured (11). The desorption into nitrogen of PAHs and *n*-alkanes from soot particles collected on a Teflon membrane filter was measured over 28 days. The effective diffusion coefficients calculated for several PAH (9-fluorenone, fluorene, and phenanthrene) were approximately 6 log units lower than expected (11). One possible explanation for these values was slow transport through the soot matrix (11).

Incomplete desorption of naphthalene, phenanthrene, and *p*-dichlorobenzene from a low carbon content sediment has recently been reported (22). The authors suggest that the observed hysteresis may be due to a physical alteration of the sediment organic matter resulting in irreversibly bound contaminant. We would expect an alteration in the sediment organic matter to affect the observed desorption behavior of both PAHs and PCBs in a similar manner. Therefore, we cannot explain the discrepancy we observed between the partitioning behavior of PCBs and PAHs in both our *in situ* and desorption studies in terms of an alteration in the sediment organic matter.

Implications for Sediment Quality Criteria. The U.S. EPA is currently developing sediment quality criteria (SQC) to complement the existing water quality criteria (23). These SQCs are being calculated from available final chronic water quality criteria values (FCV) using an equilibrium partitioning approach. That is, assuming that

$$\text{equilibrated porewater concentration} = \frac{\text{measured sediment concentration}}{(f_{ocs} K_{ocs})} \quad (5)$$

SQCs are those sediment levels equilibrated with porewater concentrations equal to the FCVs:

$$\text{SQC}(\text{compound } i) = f_{ocs} K_{ocs} \text{FCV}(\text{compound } i) \quad (6)$$

If a significant fraction of measured sediment PAHs are unavailable to partition into the surrounding porewater within decades, then the porewater concentrations predicted by an equilibrium partitioning approach will obviously tend to overestimate the actual porewater concen-

trations. For the sediments studied here, this would result in errors as large as 100 (e.g., pyrene at Spectacle Island; Table 2).

To apply this result to the issue of identifying sediment beds that exceed such SQCs, especially for PAHs, it appears that we need to correct measured sediment concentrations by the AEP. Thus, unacceptable sediment deposits would be established when

$$\text{measured sediment concentration (PAH)}_i > \text{SQC}(\text{PAH})_i \quad (7)$$

or

$$\text{measured sediment concentration (PAH)}_i > (f_{ocs} K_{ocs} \text{FCV}(\text{PAH})_i) / \text{AEP} \quad (8)$$

The EPA (24, 25) has proposed specific organic carbon-normalized SQCs for phenanthrene (freshwater: 180 $\mu\text{g/g}$ of C_{org} , salt water: 240 $\mu\text{g/g}$ of C_{org}) and fluoranthene (freshwater: 620 $\mu\text{g/g}$ of C_{org} , salt water: 300 $\mu\text{g/g}$ of C_{org}). We compared the proposed criteria with the highest sediment concentrations of these compounds we measured in the sediments just outside Fort Point Channel: phenanthrene at 58 $\mu\text{g/g}$ of C_{org} and fluoranthene at 200 $\mu\text{g/g}$ of C_{org} . These maximum sediment concentrations are much lower than the proposed sediment quality criteria for these compounds. If our estimates of the relevant AEPs were also utilized [AEP (phenanthrene, Fort Point Channel) ≈ 0.3 and AEP (fluoranthene, Fort Point Channel) ≈ 0.3], these sediments would be even farther below the SQCs. The fact that the Inner Boston Harbor sediments are in compliance with the proposed sediment quality criteria for these compounds suggests that these criteria will be exceeded only by sediments that have been heavily affected by a point source discharge of petroleum or other fossil fuel hydrocarbons [e.g., within Fort Point Channel itself where individual PAHs occur at 10–100 $\mu\text{g/g}$ (26)].

Sediments as Sources of Contamination to Overlying Water Column. The mobility of PAH compounds in marine sediments may depend on the source of the specific compounds. Pyrogenic PAH may be tightly associated with soot particles and transported via sediment transport processes. PCB congeners and petroleum-derived PAH compounds will be present in the sediment porewaters as freely dissolved compounds as well as associated with

porewater organic colloids. Sediment resuspension events as well as active bioturbation could result in the rapid transport of these compounds to the overlying water column.

Our data are limited to three cores, but our results suggest that the release of PAH associated with sediments and porewaters will not result in water column concentrations that will exceed the current water quality criteria for these compounds. This follows from the fact that the concentrations in porewaters do not exceed water quality criteria, and therefore any exchange into the overlying water from porewater fluxes or desorption from resuspended sediments would be diluted relative to porewater concentrations. However, the prevalence of biological indications of contaminant exposure such as hepatic lesions in winter flounder from Boston Harbor (27, 28) suggest that the contaminants associated with sediments are affecting the benthic organisms. The observed biological effects may be due to the presence of compounds other than the PAH compounds or may be due to synergistic effects resulting from the suite of organic and metal contaminants that the organisms are exposed to throughout their lifetimes.

Further research will be required to determine the specific routes of exposure to these organisms as well as the specific compounds responsible for the observed biological impacts. Without this type of information, we cannot assume that our current water quality and sediment quality criteria are truly protective of benthic and pelagic ecosystems and of public health.

Conclusions

Equilibrium partitioning models provided accurate descriptions of the partitioning behavior of PCB congeners in both the *in situ* study and the desorption experiments. The partitioning behavior of the PAH compounds associated with contaminated sediments from Boston Harbor was not well described by equilibrium partitioning models in either the *in situ* study or the desorption experiments. Equilibrium partitioning models greatly overestimated both the porewater and the desorption aqueous-phase concentrations. A comparison of the observed desorption behavior for PAHs and PCBs suggest that the hysteresis observed for the PAHs is due to factors unique to the PAH compounds, not physical or chemical alterations in the sediment organic matter.

We believe that only a fraction of the total measured sediment PAH concentration was available for equilibrium partitioning. The aqueous PAH concentrations predicted from the AEP fraction of the sediment PAH concentration were much more accurate predictors of the measured desorption aqueous-phase concentrations than the concentrations predicted from the total measured PAH concentration. This has important implications for modeling the fate and transport of these compounds in benthic ecosystems.

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Literature Cited

- (1) Karickhoff, S. W.; Brown, D. S.; Scott, T. A. *Water Res.* **1979**, *13*, 241–248.
- (2) Chiou, C. T.; Peters, L. J.; Freed, V. H. *Science* **1979**, *206*, 831–832.
- (3) Schwarzenbach, R. P.; Westall, J. *Environ. Sci. Technol.* **1981**, *15*, 1360–1367.
- (4) Chiou, C. T.; Porter, P. E.; Schmedding, D. W. *Environ. Sci. Technol.* **1983**, *17*, 847–858.
- (5) Farrington, J. W.; Goldberg, E. D.; Risebrough, R. W.; Martin, J. H.; Bowen, V. T. *Environ. Sci. Technol.* **1983**, *17*, 490–496.
- (6) Prahl, F. G.; Carpenter, R. *Geochim. Cosmochim. Acta* **1983**, *47*, 1013–1023.
- (7) Readman, J. W.; Mantoura, R. F. C.; Rhead, M. M. *Fresenius Z. Anal. Chem.* **1984**, *319*, 126–131.
- (8) Socha, S. B.; Carpenter, R. *Geochim. Cosmochim. Acta* **1987**, *51*, 1273–1284.
- (9) Pankow, J. F. *Atmos. Environ.* **1988**, *22*, 1405–1409.
- (10) Ligocki, M. P.; Pankow, J. F. *Environ. Sci. Technol.* **1989**, *23*, 75–83.
- (11) Rounds, S. A.; Tiffany, B. A.; Pankow, J. F. *Environ. Sci. Technol.* **1993**, *27*, 366–377.
- (12) Steiner, D.; Burtcher, H. K. *Environ. Sci. Technol.* **1994**, *28*, 1254–1259.
- (13) McGroddy, S. E.; Farrington, J. W. *Environ. Sci. Technol.* **1995**, *29*, 1542–1550.
- (14) Chin, Y. P.; Gschwend, P. M. *Environ. Sci. Technol.* **1992**, *26*, 1621–1626.
- (15) Brownawell, B. J.; Farrington, J. W. *Geochim. Cosmochim. Acta* **1986**, *50*, 157–169.
- (16) Baker, J. E.; Capel, P. D.; Eisenreich, S. J. *Environ. Sci. Technol.* **1986**, *20*, 1136–1143.
- (17) Martin, W. R.; McCorkle, D. C. *Limnol. Oceanogr.* **1993**, *38*, 1464–1479.
- (18) Brownawell, B. J. Ph.D. Dissertation, Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography, Cambridge, MA, 1986.
- (19) Sherblom, P. M. Ph.D. Dissertation, University of Massachusetts, Boston, MA, 1990.
- (20) Means, J. C.; Wood, S. G.; Hassett, J. J.; Banwart, W. L. *Environ. Sci. Technol.* **1980**, *14*, 1524–1528.
- (21) McGroddy, S. E. Ph.D. Dissertation, University of Massachusetts, Boston, MA, 1993.
- (22) Kan, A. T.; Fu, G.; Tomson, M. B. *Environ. Sci. Technol.* **1994**, *28*, 859–867.
- (23) Di Toro, D. M.; Zarba, C. S.; Hansen, D. J.; Berry, W. J.; Swartz, R. C.; Cowan, C. E.; Pavlou, S. P.; Allen, H. E.; Thomas, N. E.; Paquin, P. R. *Environ. Toxicol. Chem.* **1991**, *10*, 1541–1583.
- (24) U.S. EPA. *Sediment quality criteria for the protection of benthic organisms: Phenanthrene*; EPA 822-R-93-014; Offices of Water, Research and Development, and Science and Technology: Washington DC, 1993.
- (25) U.S. EPA. *Sediment quality criteria for the protection of benthic organisms: Fluoranthene*; EPA 822-R-93-012; Offices of Water, Research and Development, and Science and Technology: Washington DC, 1993.
- (26) Shiaris, M. P.; Jambard-Sweet, D. *Mar. Poll. Bull.* **1986**, *17*, 469–472.
- (27) Moore, M. J. Ph.D. Dissertation, Massachusetts Institute of Technology/Woods Hole Oceanographic Institution Joint Program in Oceanography, Cambridge, MA, 1991.
- (28) NOAA. *National Benthic Surveillance Project: Northeast Coast Fish Histopathology and Relationships between Lesions and Chemical Contaminants (1987–89)*; Technical Memorandum NMFS-NWFSC-4; NOAA: Seattle, 1992.
- (29) Gschwend, P. M.; Wu, S. *Environ. Sci. Technol.* **1985**, *19* (1), 90–96.

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