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DEPENDENCY OF POLYCHLORINATED BIPHENYL AND POLYCYCLIC AROMATIC HYDROCARBON BIOACCUMULATION IN *MYA ARENARIA* ON BOTH WATER COLUMN AND SEDIMENT BED CHEMICAL ACTIVITIES

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Abstract—The bioaccumulation of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) by the filter-feeding soft-shell clam *Mya arenaria* was evaluated at three sites near Boston (MA, USA) by assessing the chemical activities of those hydrophobic organic compounds (HOCs) in the sediment bed, water column, and organisms. Polyethylene samplers were deployed to measure the activities of HOCs in the water column. Sediment activities were assessed by normalizing concentrations with sediment–water sorption coefficient values, including adsorption to black carbon in addition to absorption by organic carbon. Likewise, both lipids and proteins were considered in biota–water partition coefficients used to estimate chemical activities in the animals. Chemical activities of PAHs in *M. arenaria* were substantially less than those of the corresponding bed sediments in which they lived. In contrast, chemical activities of PCBs in *M. arenaria* often were greater than or equal to activities in the corresponding bed sediments. Activities of PAHs, such those of pyrene, in the water column were undersaturated relative to the sediment. However, some PCBs, such as congener 52, had higher activities in the water column than in the sediment. Tissue activities of pyrene generally were in between the sediment and water column activities, whereas activity of PCB congener 52 was nearest to water column activities. These results suggest that attempts to estimate bioaccumulation by benthic organisms should include interactions with both the bed sediment and the water column.

Keywords—Equilibrium partitioning Black carbon Chemical activity Polycyclic aromatic hydrocarbons Polychlorinated biphenyls

INTRODUCTION

In marine and freshwater systems, sediment is an important sink for hydrophobic organic compounds (HOCs). The presence of certain persistent toxic HOCs, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), can affect sediment quality long after their primary emissions have been terminated [1]. Consequently, the bioaccumulation of such HOCs by benthic organisms and bottom-dwelling fish is likely to be a long-standing problem unless steps are taken to remediate affected areas. Accurate understanding and prediction of the continuing risks to the benthos and other organisms, including humans that are connected to this bottom-dwelling community via food chains, is needed to assess the need for remedial actions.

Early progress in our understanding of HOC geochemistry and bioaccumulation led to the equilibrium partitioning (EqP) theory [2]. In this conceptualization, HOCs are assumed to distribute between the organic matter (OM) or organic carbon (OC) in sediments and the lipids in organisms, thus allowing a prediction of body concentrations at equilibrium

$$C_{\text{biota}} = (f_{\text{lipid}}K_{\text{LW}}/f_{\text{OC}}K_{\text{OC}})C_{\text{sed}} \quad (1)$$

where C_{biota} is the organism's tissue concentration (e.g., μg/g dry wt biota), f_{lipid} is the fraction of organism tissue consisting of lipids (g dry wt lipid/g dry wt biota), K_{LW} is the lipid–water partition coefficient for the HOC (ml/g dry wt lipid), f_{OC} is the fraction OC in the sediment (g dry wt OC/g dry wt sediment), K_{OC} is the OC–water partition coefficient for the HOC (ml/g OC), and C_{sed} is the HOC concentration in the sediment (e.g., μg/g dry wt sediment). However, the EqP concept has proved to be too simplistic to explain bioaccumulation observed at various field sites [3,4]. These results suggest the need for a more thorough understanding of the factors affecting bioavailability and bioaccumulation of HOCs.

Some of the discrepancy may result from using the assumption that HOC sorption to sediments involves only absorption into biogenic or diagenetic OM [5,6]. For example, investigators have long noted the inadequacy of this view when describing the distribution of PAHs between sediment and pore water [7–9]. This anomalous PAH behavior has been presumed to involve special interactions between the HOCs and a portion of the reduced carbon in sediments that is thermally altered OM (i.e., soot or char), herein referred to as black carbon (BC) [10]. Black carbon has a strong affinity for PAHs and other HOCs [11–15]. Further, PAHs in BC-amended sediments are less available to biota [16]. Thus, accounting for the presence of BCs in sediment beds reduces the expected pore-water concentration relative to assumptions based only on absorption to the biogenic or diagenetic OM.

Likewise, the idea that HOC bioaccumulation occurs only

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in the lipids of organisms might be erroneous. This may be especially problematic for organisms or their organs with relatively low lipid contents as compared to other abundant tissue components such as protein or lignin [17]. Previous investigations have shown that HOCs can partition from water into proteins as a function of the HOCs hydrophobicity (see Schwarzenbach et al. [17] and references therein). Because many benthic organisms contain more protein than fat, an accurate physicochemical prediction of HOC partitioning also might have to include consideration of uptake by proteinaceous materials.

For the EqP model of bioaccumulation to be accurate, the chemical activities of the HOCs in the sediment bed (a_{sed}) and in the biota (a_{biota}) must be equivalent. All of the important accumulating phases in each system (e.g., in the sediment bed or in the organism) should be represented. Hydrophobic organic compound chemical activities in the sediment are given by

$$a_{sed} = C_{sed}/(K_d C^{sat}_{W(L)}) \quad (2)$$

where K_d is the sediment–water sorption coefficient (ml/g dry wt) and $C^{sat}_{W(L)}$ is the aqueous solubility of the (hypothetical) liquid HOC (e.g., μg/ml). Here we hypothesize that the K_d for HOCs is more reliably predicted if the effects of absorption in the OC and adsorption onto BC are incorporated. Following Accardi-Dey and Gschwend [13,14], this idea suggests

$$K_d = f_{OC}K_{OC} + f_{BC}K_{BC}C_W^{n-1} \quad (3)$$

where f_{BC} is the fraction of BC in the sediment (g BC/g dry wt), K_{BC} is the BC–water adsorption coefficient ([μg/g BC]/[μg/ml]^n), C_W is the dissolved concentration of the HOC (e.g., μg/ml), and n is the Freundlich exponent needed because HOC adsorption isotherms are nonlinear. Likewise, HOC activity in the biota is given by

$$a_{biota} = C_{biota}/(K_{BW}C^{sat}_{W(L)}) \quad (4)$$

where K_{BW} is the biota–water partition coefficient (ml/g dry wt). As discussed, we hypothesize that including multiple media such as proteins would yield a more accurate expression for K_{BW}

$$K_{BW} = f_{lipid}K_{LW} + f_{protein}K_{PW} \quad (5)$$

where $f_{protein}$ is the protein content of the animal (g protein/g dry wt biota) and K_{PW} is the protein–water partition coefficient (ml/g protein). Taken together, this suggests a new EqP expression

$$C_{biota} = \left[\frac{(f_{lipid}K_{LW} + f_{protein}K_{PW})}{(f_{OC}K_{OC} + f_{BC}K_{BC}C_W^{n-1})}\right]C_{sed} \quad (6)$$

This expression includes HOC adsorption to BC in the sediment and absorption by proteins in the animals. The first objective of our study was to examine the effectiveness of this expanded sediment–biota equilibration model for an accurate estimation of bioaccumulation.

Another hypothesis forwarded to explain discrepancies between EqP predictions and bioaccumulation observations is that the animals exchange HOCs both with the bed sediments and with the water column [18]. Such is the case for filter-feeding bivalves, which are exposed to pollutants in the sediments through their diet and via dermal contact and also to pollutants in the water column as they pump water for respiration and feeding. Because HOCs in sediment beds and the overlying water column may not be at equilibrium with each other, the animals find themselves interacting with two environmental systems, each pulling the animal's body burdens toward different chemical activities. An effect of this type can be seen in the data of Morrison et al. [19], who looked at several benthic invertebrates living in Lake Erie. In each case, the animal body burdens were greater than expected based on equilibrium with the water column, but less than expected based on equilibrium with the sediments. Likewise, previous work suggested that HOC exchange with the water column in Boston Harbor explained the bioaccumulation observed in the soft-shelled clam, *Mya arenaria* (G. Ewald, Lund University, Lund, Sweden, personal communication). Thus, our second objective was to examine the importance of sediment activities versus water column activities for determining the uptake of HOCs by benthic organisms. Hence, we measured and compared HOC activities in the water column, as well as in the sediment beds, to what we found in a representative benthic organism, *M. arenaria*.

Mya arenaria remains an important commercial species and is part of the New England diet. *Mya arenaria* is a filter-feeding bivalve and has been used in numerous studies as a test organism to assess the availability and toxicity of sediment-bound contaminants [20–24]. Because of its life history, a siphon-utilizing bivalve such as *M. arenaria* is unlikely to be solely exposed to contaminants in the sediment [20]. The clam can be exposed to pollutants passively through direct contact with sediment, or actively through intake of water and near-bottom particles for respiration and filter-feeding, or both. Elimination half-lives of 45 to 111 d were reported for dioxin congeners in *M. arenaria* transplanted from contaminated sites to clean sediments [23], indicating both the role of the bed in controlling HOC exchanges and the months-long periods of time for such transfers. For the present investigation, we collected *M. arenaria* for analysis of their tissues for PAH and PCB concentrations and activities, and for determination of their lipid and protein contents. We also collected a sample of the sediment immediately surrounding the animal(s) at each site so that we could quantify PAHs and PCBs, determine f_{OC} and f_{BC}, and calculate chemical activities. Concurrently, we assessed the chemical activities of PAHs and PCBs in the water column by deploying passive, polyethylene (PE) samplers [25]. Finally, to empirically assess the applicable K_ds for PAHs and PCBs, we performed desorption experiments with PE samplers tumbled with site sediment samples.

MATERIALS AND METHODS

Field sampling

Two field sampling campaigns focused on three areas where previous collections showed widely varying HOC levels in sediments and soft-shelled clams [24]. The first site, sampled in October 2001, was east of Squantum Marina in Dorchester Bay (DB) (Boston, MA, USA), centered at 42°17.90′N, 71°01.02′W (Fig. 1). Two stations were located at the inner side of a tidally exposed mudflat sheltered from wave-induced erosion. The sediments were fine grained, dark colored, and rich in OM (see below). Four other stations were located on the outer, wave-exposed side of that same mudflat. These sediments were coarse grained and, with the exception of one location, had low OM contents (see below).

The second site was in the Saugus River (SR) estuary (Lynn, MA, USA), centered at 42°26.70′N, 70°57.80′W. This area was sampled in June 2002 (Fig. 1). *Mya arenaria* was collected at five stations within 50 m of each other on the

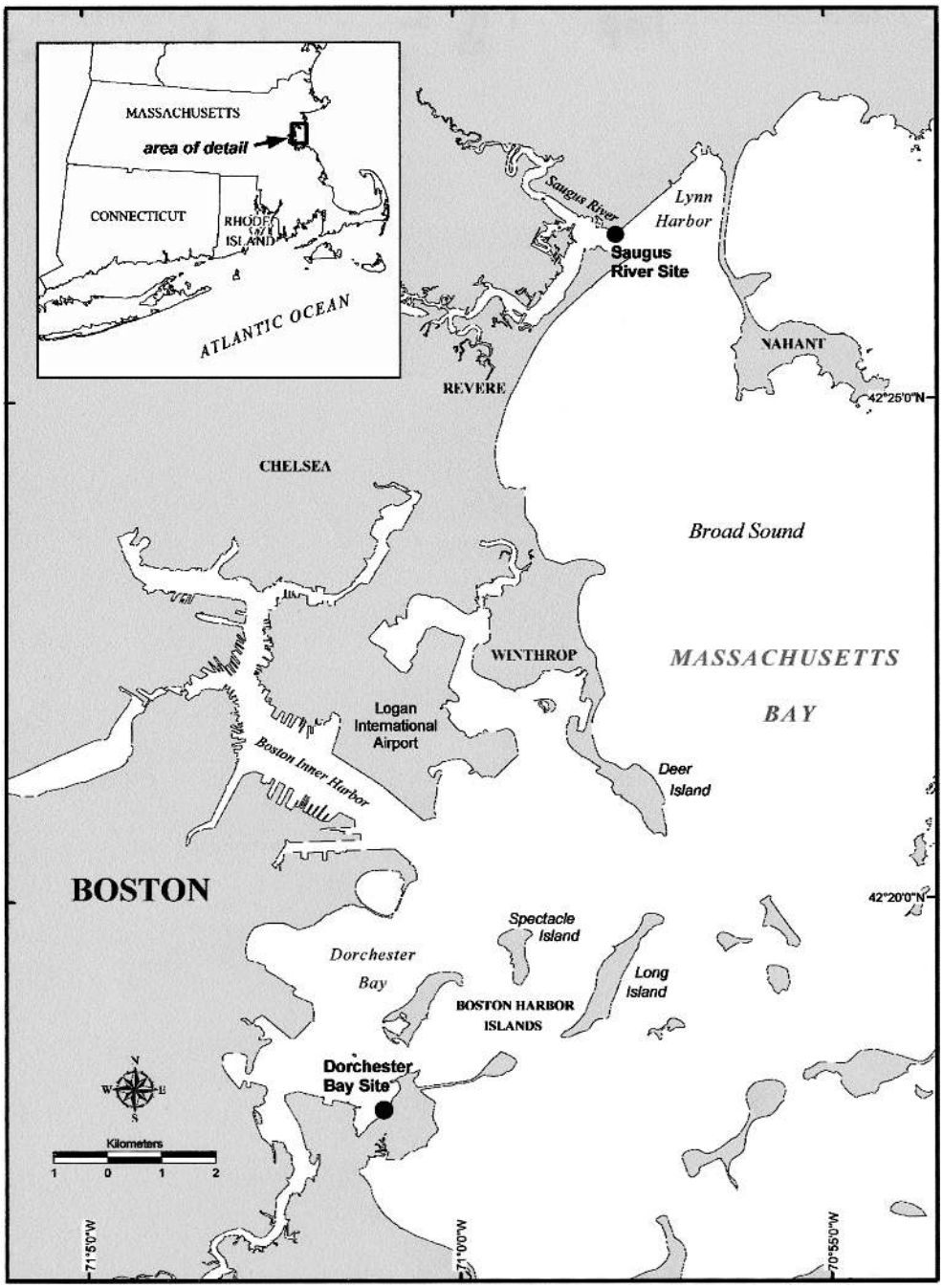

Fig. 1. Study sampling sites: Dorchester Bay (Boston, MA, USA) and the Saugus River (Lynn, MA, USA).

northern bank of the estuary. Sediments from this site were dark colored, fine grained, and rich in OM (see below).

In all cases, the clams were collected during low tide from sections of the exposed intertidal zone. Siphon holes of *M. arenaria* were located and the clams were excavated with a pitch spade, together with the immediately surrounding sediments. The clams (in water) and sediment samples were stored in plastic bags on ice until arrival in the laboratory. The clams were rinsed in tap water and frozen at −20°C within 4 h of collection. Sediments also were frozen at −20°C until thawed for analysis.

Sample extraction

Clams were shucked, their gut contents were removed, and remaining tissues were homogenized in organic solvents by using a 360-ml stainless steel container mounted on a Waring commercial blender (Waring Products, Torrington, CT, USA). Before extraction, 100 μl of PAH and PCB recovery-standards mix were added to the sediment and tissue samples. Each PAH (D_{10}-phenanthrene [D_{10}-Phen], D_{12}-benz[*a*]anthracene [D_{12}-B*a*A], and D_{12}-perylene) was at a concentration of 10 ng/μl. The PCB recovery standard was congener 198 (1.1 ng/μl). The individual clams were extracted according to the methods of Bligh and Dyer [26] by using chloroform and methanol (chloroform:methanol:water, 1:2:0.8, v/v/v). All solvents were Ultra resi-analyzed (J.T. Baker, Philipsburg, NJ, USA). After phase separation and transferring the chloroform phase to a clean test tube, the methanol:water phase was reextracted twice by adding new chloroform. The combined extract volume was then reduced to approximately 1 ml with a gentle stream of N_2.

About 10 to 20 g of sediment (wet wt) also were extracted by shaking with chloroform:methanol, followed by ultrasonication for 30 min. The solids were allowed to settle for 24 h before phase separation. This procedure was repeated twice by adding new parts of chloroform to the aqueous phase. The final volume of the extracts in chloroform was reduced to approximately 1 ml under N_2.

Subsamples were collected from all tissue extracts for weight determination of lipids with a Cahn microbalance (El Cerrito, CA, USA). Clean-ups for the clam extracts were performed with wet-packed activated silica columns (6 g, Silica Gel 100–200 Mesh, EM Science, Gibbstown, NJ, USA). Four fractions were obtained from each sample: fraction 1 eluted with 6 ml of hexane, followed by fraction 2 with 44 ml of hexane containing the PCBs. Fraction 3 was eluted with 50 ml of hexane:dichloromethane (9:1, v/v) and contained the PAHs. Fraction 4 (30 ml dichloromethane:methanol, 9:1, v/v) contained polar compounds and was retained in case of breakthrough of PAHs from fraction 3. The fractions were reduced in volume to about 1 ml before analysis. Aliquots of the samples were then transferred into gas chromatograph (GC) vials and shipped overnight to the U.S. Environmental Protection Agency (U.S. EPA) ORD/NHEERL Atlantic Ecology Division in Narragansett (RI, USA) for analysis of PAHs and PCBs.

Deployment of PE samplers

The PE samplers were cut from sheets that were 51 ± 3 μm thick (mean ± 1 standard deviation; Carlisle Plastic, Minneapolis, MN, USA). The PE samplers were deployed as passive in situ equilibrium samplers [25,27] in DB. Dissolved HOCs accumulate in PE by diffusion until phase equilibrium occurs. Knowledge of the PE–water partition coefficients (K_{PEW}s) of the HOCs allowed us to quantify the concentrations of the dissolved HOCs (see below). Before field exposure, the PE samplers were cleaned twice with dichloromethane for 48 h and exchanged to Milli-RO® water (Aries Vaponics, Rockland, MA, USA). The PE samplers were deployed in the water column at DB from June 2001 through June 2002 in consecutive deployments, each of which lasted approximately four weeks. The one PE sampler corresponding to the sediment and tissue samples discussed here was deployed during September and October 2001 and covered a period of six weeks. Each time, two PE strips were mounted on precleaned metal wire loops, which attached to a rope about 2 m above the sediment. After exposure, the PE samplers were stored in prerinsed amber glass jars at 4°C. Field blanks were obtained by transporting additional PE samplers to the field sites, where they were transferred into amber glass jars. For extraction, PEs were rinsed briefly with Milli-RO water and dried with Kimwipes® (Kimberly-Clark, Roswell, GA, USA). Massachusetts Institute of Technology (MIT, Cambridge, MS, USA) recovery standards were added (for PAHs 100 μl of deuterated PAHs: D_{10}-acenapthene, D_{14}-*para*-terphenyl, and D_{12}-B*a*A, all at 2 ng/μl, and D_{10}-Phen at 1 ng/μl; and for PCBs 100 μl of PCB congeners 69, 97, 143, and 191 at 100 pg/μl). The PE samplers were extracted twice with 60 ml of dichloromethane. Combined extracts were reduced in volume to approximately 1 ml by using a rotavap (Brinkman, Westbury, NY, USA) and transferred into GC vials. Injection standards were then added (25 μl *m*-terphenyl at 3 ng/μl for PAHs and 50 μl of PCB congener 114 at 200 pg/μl for PCBs), and samples were analyzed directly by gas chromatography–mass spectrometry (GC-MS) at MIT.

Water samples were collected from DB in May 2002 and the SR in June 2002. These samples were collected in cleaned, foil-clad, 20-L, glass carboys and in three 4-L amber glass jugs. They were transported to the laboratory and stored at 4°C for up to 2 d before filtration (125 mm, glass fiber filter/C Whatman, Maidstone, UK). A small circle of PE (~10 mg) was added to each 20-L carboy to determine directly dissolved concentrations. The water in the carboys was stirred with a Teflon® stir bar for four weeks at 24°C. Then the PE was removed and extracted. A blank value was taken by extracting approximately 10 mg of PE. The 4-L water samples were liquid–liquid extracted with dichloromethane four times. The 4 L of Milli-RO water were extracted as the water blank. These four extracts were combined, dried over anhydrous sodium sulfate, reduced by rotary evaporation to approximately 1 ml, and transferred into GC vials. The HOC concentrations measured in these water samples agreed within a factor of two to four for the lower molecular weight PAHs (pyrene [Pyr] and B*a*A) and PCBs (congeners 52 and 66) as determined by the PE measurement. Phenanthrene blank concentrations were comparable to the samples, so this analyte was not considered further.

Determination of OC, BC, and protein fractions

Sediment OC and BC contents were measured with a PE 2400 CHN elemental analyzer (Perkin-Elmer, Norwalk, CT, USA). The carbon of nonsoot character was removed by combusting the dried, ground sediment samples for 24 h at 375°C. Sediment samples were then acidified to remove carbonates before determining BC [28]. Protein content for one clam was estimated by measuring the nitrogen content with the CHN elemental analyzer. All nitrogen was assumed to be part of an average protein ($C_{10}H_{15}N_4O_2$) [29]. Thus, we assumed the N contribution of nucleic acids and other nitrogenous compounds is either negligible or that these compounds absorb HOCs similarly to proteins.

Analytical procedures

The following compounds, covering a range of well-described physicochemical properties, were measured by both the MIT and U.S. EPA laboratories: Phen, Pyr, B*a*A, benzo[*a*]pyrene (B*a*P), and PCB congeners 2,2′5,5′-tetrachlorobiphenyl (PCB 52), 2,3′,4,4′-tetrachlorobiphenyl (PCB 66), 2,3,3′,4,4′-pentachlorobiphenyl (PCB 105), and 2,2′,3,3′,4,4′-hexachlorobiphenyl (PCB 128). Analytes were quantified relative to the most similar recovery standards. Multipoint calibration standards were used to derive response factors of the analytes relative to the appropriate recovery standards.

At the U.S. EPA laboratory, tissue and sediment PAHs were analyzed by gas chromatography–mass selective detection with a Hewlett-Packard 5890 Series II GC equipped with a 7673A autosampler, electronic pressure control, and 5971A mass selective detector (Hewlett-Packard, Wilmington, DE, USA). Sample extracts (2.0 μl) were injected in the splitless mode with septum purge (3:1) after 0.8 min. The injection port was maintained at 270°C and column head pressure was set to maintain constant flow at 1.1 ml/min. The GC oven temperature was held at 60°C for 1 min after injection, then ramped at 5°C/min to a final temperature of 310°C, and held for 4 min. The mass selective detector was operated in selected-ion monitoring mode. Ions at 188, 240, and 264 (recovery standards D_{10}-Phen, D_{12}-B*a*A, and D_{12}-perylene, respectively) and target PAH mass units were monitored. Polycyclic aro-

matic hydrocarbons were then quantified by using peak areas from calibration standards of authentic compounds (Supelco, Belafonte, PA, USA) and recovery standards, and comparing the results of the standards to those obtained from the sample extracts.

At the U.S. EPA laboratory, tissue and sediment PCBs were also analyzed by using a Hewlett-Packard 5890 Series II GC equipped with a 7673A autosampler and electronic pressure control for determination of environmental concentration distribution. Analysis involved injecting 1.0 μl of sample in the splitless mode with inlet purge after 1.0 min onto a 30-m DB-5 fused silica capillary column (J & W Scientific, Folsom, CA, USA). Helium was the carrier gas at a flow rate of 1.5 ml/min. The flow of a 95:5 (v/v) mixture of argon:methane to the detector was maintained at 35 ml/min. Oven temperature was held at 100°C for 1.0 min; it was then programmed to increase to 140°C at 5°C/min and held at 140°C for 1 min; to increase to 230°C at 1.5°C/min and held for 20 min; and finally to increase to 300°C at 10°C/min and held for 5 min. Injection port temperature was 270°C and the detector temperature was kept constant at 325°C. Data were collected and analyzed on a MicroVax-based computer software system (PE-Nelson, San Jose, CA, USA). Polychlorinated biphenyls were quantified by peak areas from calibration standards of authentic compounds (National Institute of Standards and Technology [NIST] Standard Reference Material [SRM] 2262 *Chlorinated Biphenyls Congeners in Isooctane* [Gaithersburg, MD, USA]), the recovery standard (congener 198), and comparison to those obtained from the sample extracts.

Polyethylene and water samples were analyzed for PAHs and PCBs at MIT by GC-MS in selective-ion monitoring. Analytes were quantified relative to MIT recovery standards. Analytes were separated on a 30-m DB5-MS capillary column with a 0.25-μm film thickness (J &W Scientific) in an HP 6890 GC connected to a JEOL GCmate MS (Peabody, MA, USA), operating at a resolving power of 500. Samples (1 μl) were autoinjected in the splitless mode with the injection port held at 280°C. For PCBs, the injection port was at 300°C, and the GC temperature program started at 70°C, ramped at 20°C/min to 180°C, increased by 4°C/min to 260°C, and reached 280°C in 1.0 min, where it was held for 4 min. For PAHs, the injection port was at 280°C, and the GC was temperature programmed from 70°C to 180°C at 20°C/min before continuing to 300°C at a rate of 6°C/min.

Quality control

Recoveries were calculated by assuming a final volume of 1 ml. Mean recoveries ranged from 72 to 87% for deuterated PAHs in the sediments ($n = 15$), and from 78 to 86% in the tissue samples ($n = 24$). For PCBs, recovery of 198 averaged 87% for the tissue samples ($n = 24$) and 127% in the sediment samples ($n = 16$). Recoveries >100% could result from inaccurate estimation of the solvent volumes at the time of injection (e.g., evaporation in autoinjection vials). An NIST SRM 1974a (*Organics in Mussel Tissue*) was included in the analytical procedure in both laboratories. For PAHs analyzed at the U.S. EPA, the results were on average 109% of the certified values (range 58–192%) with recovery standard recoveries of 46 to 61%. For PCBs analyzed at the U.S. EPA, on average 71% (64–78%) of the certified values were obtained, with 68% standard recovery. Detection limits were approximately 1 ng/sample for Phen and Pyr and approximately 2 ng/sample for B*a*A and B*a*P. For PCBs, detection limits were approximately 0.1 ng/sample. Blank values were 5 to 30 ng/sample for PAHs. In general, this was ≤10% of the amount detected in the samples. For PCBs, blank values were ≤0.5 ng in the tissue blanks and 1 to 2 ng/sample in the sediments, also ≤10% of the amount detected in the samples. The greatest concentrations of PAHs (Phen and fluoranthene) were measured in the two solvent blanks processed together with the DB tissue samples. These samples had high ratios of Phen to methyl-Phen (>2). Similarly elevated concentrations of Phen and fluoranthene, and of Phen relative to methyl-Phen (>2:1) were measured for two samples of *M. arenaria* from DB. These samples were likely contaminated by the same source and their data were excluded from further analysis. In the OC-poor sediments from DB ($n = 4$), concentrations of several HOCs were less than five times the concentrations found in the blanks. For Phen, Pyr, and PCB 52, one result each was excluded and two results for PCB 66 were excluded from further data treatment. Mean recoveries in the PE samples analyzed at MIT ranged from 71 to 92% for deuterated PAHs ($n = 39$), and from 96 to 117% for PCBs ($n = 37$); PCB 97 was excluded because of interferences. In the liquid–liquid extractions, mean recoveries ranged from 55 to 92% for deuterated PAHs and from 60 to 70% for PCBs. Detection limits for the PE samples were approximately 0.5 ng/sample for PAHs and 0.1 ng/sample for PCBs. Mean concentrations in the PE field blanks were 12 ng/sample for Phen, 0.8 ng/sample for Pyr, and 0.3 ng/sample for PCBs 52 and 66.

The accuracies of our measurements were estimated based on the results of analyzing the NIST SRM 1974a. The PCBs analyzed in this study were within 50% (or a factor of 1.5) or better of the certified result. For PAHs, the accuracy was at worst within a factor of two of the certified result. These accuracies reflect cumulative errors due to subsampling NIST SRM 1974a, the spiking procedures, the multiple extractions, clean-up and volume reduction steps, shipment to the U.S. EPA laboratory, and the resulting GC quantification. Several PE samples were split between the U.S. EPA and the MIT laboratories and analyzed for PAHs as described above. On average, the results agreed within 30%, with individual PAHs differing by up to a factor of two. These data inaccuracies also imply that the inputs to our estimates of bioaccumulation were within a factor of two for PAHs and 1.5 for PCBs. We believe this level of data accuracy is sufficient for examining bioaccumulation (see below) but one should keep this level of precision in mind when observations are compared to theory.

Partitioning coefficients and aqueous solubilities

We used partition coefficients and (liquid) solubilities from the literature to transform concentration data to corresponding chemical activities (Table 1). Mean values for PAH K_{OW}s were calculated based on all experimental K_{OW}s tabulated in Mackay et al. [30]. For PCBs, K_{OW}s were taken from Hawker and Connell [31]. The K_{OC} values were calculated by using correlations from Karickhoff [32]

$$\log K_{OC}(\text{PAHs}) = 0.989 \times \log K_{OW} - 0.346 \quad (7)$$

$$\log K_{OC}(\text{PCBs}) = 0.88 \times \log K_{OW} + 0.03 \quad (8)$$

The partitioning of a given contaminant between proteins and water was estimated as [17]

$$\log K_{PW} = 0.7 \times \log K_{OW} \quad (9)$$

The PAH solid aqueous solubilities ($C^{sat}_{W(S)}$ in units of kg/L)

Table 1. Partition constants for selected polycylic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), including octanol–water (K_{OW}), organic carbon–water (K_{OC}), protein–water (K_{PW}), black carbon–water (K_{BC}), polyethylene–water (K_{PEW}), and $C^{sat}_{W(L)}$ (liquid water solubility, in mol/L)

Compound[a]	Log K_{OW}[b]	Log K_{OC}[c]	Log K_{PW}[d]	Log K_{BC}[e]	Log K_{PEW}[f]	Log $C^{sat}_{W(L)}$[g]
Phen	4.5	4.1	3.2	6.1	4.3	−10.7
Pyr	5.0	4.6	3.5	6.4	5.0	−11.2
B*a*A	5.6	5.2	3.9	6.9	5.8	−12.0
B*a*P	6.0	5.6	4.2	7.1	6.4	−12.8
PCB 52	5.8	5.2	4.1	5.9	5.4	−12.4
PCB 66	6.2	5.5	4.3	6.9	6.1	−12.8
PCB 105	6.7	5.9	4.7	7.1	6.9	−13.4
PCB 128	6.7	6.0	4.7	7.0	7.0	−13.5

[a] Phen = phenanthrene; Pyr = pyrene; B*a*A = benz[*a*]anthracene; B*a*P = benzo[*a*]pyrene; PCB 52 = 2,2′,5,5′-tetrachlorobiphenyl; PCB 66 = 2,3′,4,4′-tetrachlorobiphenyl; PCB 105 = 2,3,3′,4,4′-pentachlorobiphenyl; PCB 128 = 2,2′,3,3′,4,4′-hexachlorobiphenyl.
[b] K_{OW} values for PAHs and PCBs from Mackay et al. [30] and Hawker and Connell [31], respectively.
[c] K_{OC} values from Karickhoff [32].
[d] K_{PW} values from Schwarzenbach et al. [17].
[e] From this study, assuming Freundlich $n = 0.7$.
[f] K_{PEW} values from Adams [25].
[g] Calculated based on solid solubilities for PAHs and PCBs from de Maagd et al. [33] and Huang and Hong [34], respectively.

were taken from De Maagd et al. [33] and those for PCBs were from Huang and Hong [34]. These were converted into liquid aqueous solubilities ($C^{sat}_{W(L)}$; Table 1) according to

$$C^{sat}_{W(L)} = C^{sat}_{W(S)}\exp(+\Delta_{fus}G_i/RT) \quad (10)$$

where $\Delta_{fus}G_i$ is the chemical's free energy of fusion, R is the universal gas constant, and T is the temperature in K. The term $\Delta_{fus}G_i$ was estimated as a function of the compound's melting temperature, molecular shape, and symmetry (for more details, see chapter 5 of Schwarzenbach et al. [17]).

Black carbon–water partition coefficients

The sediment–water partitioning coefficients (K_ds) for PAHs and PCBs were determined by prolonged tumbling of sediments from Quincy Bay (MA, USA) with water and PE samplers. Experiments were monitored for up to six months to attain sorptive equilibrium in the subsystems, namely water, sediment OM, sediment BC, and PE. The overall partitioning was then attributed to absorption into the OC and adsorption onto BC (see Eqn. 3). Values for the Freundlich coefficient (n) have been reported to range from 0.6 to 0.8 [13,14,35]. We used $n = 0.7$ as a default value and solved for K_{BC} (Table 1).

Polyethylene–water partition coefficients

Concentrations of dissolved HOCs in the water column at each site were calculated by applying measured K_{PEW}s (log K_{PEW}; see Table 1) [25]. In brief, K_{PEW} values were measured in the laboratory for several PAHs and PCBs. The partition coefficients (K_{PEW}) were defined as the ratio of the compound concentration in the PE (C_{PE}, in mol/g PE) over the dissolved concentration (in mol/ml water). The K_{PEW} values also were adjusted for their temperature dependencies and the influence of salinity as determined by Adams [25]. Values of the excess enthalpy of solvation (ΔH^{exc}_{solv}) were calculated as the difference between the enthalpies of solvation and melting, with the physicochemical values taken from Shiu and Ma [36]. Because of decreasing temperatures during the fall and winter, K_{PEW}s increased by 30 to 50% for most PAHs. For PCBs, ΔH^{exc}_{solv} was estimated to be approximately 20 kJ/mol per congener, which increased K_{PEW}s by 40%. The salinity in DB was 28‰ (corresponding to ~0.5 M NaCl). Xie et al. [37] concluded that for aromatic hydrocarbon, a value of 0.3 for K^s, the Setschenow constant (M^{-1}), is reasonable. Considering this approximation and the measured salinity, K_{PEW} values were estimated to be about 40% higher in the seawater than in the laboratory freshwater.

RESULTS AND DISCUSSION

Contaminant distributions in sediments

In DB sediment samples, concentrations of individual PAHs varied by more than a factor of 10 (Table 2). Hundreds of nanograms per gram dry weight of individual PAHs were present in the OC-rich sediments from the depositional area, whereas concentrations decreased to a few nanograms per gram dry weight in the erosional, low-OC nearshore sediments of DB. In sediment samples from the SR, mean individual PAH concentrations were consistently greater than the DB values, averaging in the hundreds of nanograms per gram dry weight and varying by factors of three to five among sampling stations (Table 2). Previous investigators found that concentrations of Phen and Pyr in a sediment sample from the SR were near 1,000 ng/g dry weight [38].

The PCB concentrations also varied among the DB samples, with concentrations as high as 10 ng/g dry weight in sediments from the depositional area to about 0.1 ng/g dry weight in the nearshore, low-OC sediments (Table 2). The SR sediments had a narrower range of concentrations, with average values of a few nanograms per gram dry weight. McDowell et al. [38] also reported PCB concentrations near 1 ng/g dry weight per congener for a composite sediment sample from the SR in 1995.

The range and mean f_{OC} and f_{BC} were comparable at the two sampling areas, with f_{OC} near 1% (Table 2). However, at DB, the depositional sediments had greater f_{OC} values (1.3 and 1.5%), and the erosional shore sediments had f_{OC} values of only 0.2 to 0.3%. At one DB station, which was enriched with a wooden, organic matrix, the f_{OC} was 1.8%. Values of f_{BC} were about 0.1% at both sampling areas, although the lowest values were seen at the low-OC sites.

Table 2. Concentrations (ng/g dry wt) of selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls (PCBs) and organic carbon fractions (f_{OC}s) and black carbon fractions (f_{BC}s) in sediments from Dorchester Bay (DB) (Boston, MA, USA) and the Saugus River (Lynn, MA, USA)

	DB, OC-rich (n = 2)			DB, OC-poor (n = 4)			Saugus River (n = 5)		
Compound	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Phen	200	180	220	17[b]	<3.3	26	440	210	630
Pyr	460	440	480	40[b]	<5.4	42	950	320	1,500
B*a*A	210	200	220	14	8	18	300	150	520
B*a*P	220	200	240	14	10	16	240	81	460
PCB 52	5.5	5.3	5.6	0.21[b]	<0.10	0.28	1.8	0.41	3.1
PCB 66	9.2	8.9	9.5	0.21[c]	<0.12	0.52	1.1	0.60	1.8
PCB 105	5.3	5.1	5.5	0.20	0.05	0.37	0.88	0.49	1.4
PCB 128	2.4	2.3	2.4	0.12	0.03	0.19	0.41	0.21	0.74
f_{OC} (%)	1.4	1.3	1.5	0.64	0.21	1.8	0.75	0.34	1.3
f_{BC} (%)	0.16	0.13	0.19	0.13	0.03	0.39	0.14	0.08	0.20

[a] Phen = phenanthrene; Pyr = pyrene; B*a*A = benz[*a*]anthracene; B*a*P = benzo[*a*]pyrene; PCB 52 = 2,2′,5,5′-tetrachlorobiphenyl; PCB 66 = 2,3′,4,4′-tetrachlorobiphenyl; PCB 105 = 2,3,3′,4,4′-pentachlorobiphenyl; PCB 128 = 2,2′,3,3′,4,4′-hexachlorobiphenyl.
[b] n = 3.
[c] n = 2.

Contaminant distributions in tissues

Tissue samples from DB and the SR had narrow ranges of PAH concentrations, with minima and maxima differing by only two to four times (Table 3). In general, individual PAHs were approximately tens of nanograms per gram dry weight. Pyrene had the highest concentrations (75 ng/g dry wt in DB and 230 ng/g dry wt in the SR); lowest measured concentrations were determined for B*a*P (<5 ng/g dry wt in DB and 7 ng/g dry wt in the SR). Tissue samples from the high- and low-OC regions of DB displayed similar concentrations of PAHs. McDowell et al. [38] reported PAH concentrations in composite samples of *M. arenaria* from the SR, in which Pyr also dominated with a concentration near 1,000 ng/g dry weight; B*a*A and Phen displayed concentrations of about 300 ng/g dry weight. Gardner and Pruell [21] reported concentrations in *M. arenaria* near 20 ng/g for individual PAHs in 1988 from Quincy Bay, which borders DB. These values are similar to the concentrations measured in the current study, although they were seen about 15 years earlier.

Polychlorinated biphenyl concentrations in tissues of *M. arenaria* were in the tens of nanograms per gram dry weight in DB, but only a few nanograms per gram dry weight in the SR samples (Table 3). Similar to the PAH results, PCB concentrations displayed narrow ranges in the clams from DB and the SR (i.e., within two to three times) and similar results for the high- and low-OC regions of DB. Interestingly, McDowell et al. [38] reported PCB concentrations for composite samples of *M. arenaria* from the SR were 2 to 5 ng/g dry weight for congener 52 in 1995. This value compares well to the concentrations measured in this study in DB. Concentrations in *M. arenaria* were reported to be about 10 to 20 ng/g dry weight for individual PCBs by Gardner and Pruell [21], which, like the PAH results for the clams, is comparable to what we measured 15 years later.

Lipid fractions for the clams ranged from 5.3 to 9.0% at DB and from 5.8 to 7.6% at the SR (Table 3). These are comparable to other measurements for *M. arenaria* in Boston Harbor, where McDowell and Shea [24] measured f_{lipids} of 3.7 to 6.1% and Ewald and Gschwend determined f_{lipids} of 5.6 to 11.6% (G. Ewald, Lund University, Lund, Sweden, personal communication). The protein content was estimated to be 48% on a dry mass basis for *M. arenaria*.

Affinities to BC

After the tumbling equilibrations, observed K_ds for PAHs, normalized to the f_{OC} values, exceeded the corresponding K_{OC}s

Table 3. Concentrations (ng/g dry wt) of selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls (PCBs) and lipid fractions (f_{lipids}) and protein fractions ($f_{proteins}$) in *Mya arenaria* from Dorchester Bay (DB) (Boston, MA, USA) and the Saugus River (Lynn, MA, USA)[a]

	DB, OC-rich (n = 5)			DB, OC-poor (n = 4)			Saugus River (n = 6)		
Compound	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Phen	33	24	51	21[b]	16	25	51	34	66
Pyr	65	48	75	52[b]	47	57	160	95	230
B*a*A	23	16	37	22[b]	20	24	42	31	56
B*a*P	24	<5	39	16[b]	16	17	11	7.3	18
PCB 52	14	9.4	24	15	13	17	4.2	2.7	6.5
PCB 66	22	14	36	19	16	22	4.2	2.6	6.5
PCB 105	9.2	5.9	15	8.6	6.6	10	2.5	1.7	3.6
PCB 128	3.6	2.2	6.6	4.1	3.0	5.1	1.5	1.0	1.9
f_{lipid} (%)	6.3	5.3	7.2	7.9	6.5	9.0	6.9	5.8	7.6
$f_{protein}$ (%)	48	—	—	48	—	—	48	—	—

[a] OC = organic carbon; Phen = phenanthrene; Pyr = pyrene; B*a*A = benz[*a*]anthracene; B*a*P = benzo[*a*]pyrene; PCB 52 = 2,2′,5,5′-tetrachlorobiphenyl; PCB 66 = 2,3′4,4′-tetrachlorobiphenyl; PCB 105 = 2,3,3′,4,4′-pentachlorobiphenyl; PCB 128 = 2,2′,3,3′,4,4′-hexachlorobiphenyl.
[b] n = 2.

Table 4. Dissolved concentrations of selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls (PCBs) based on liquid–liquid extraction and polyethylene (PE)[a] equilibrations. Blank concentrations are given in parentheses

	Dorchester Bay (MA, USA), October 2001			Dorchester Bay, May 2002		Saugus River, June 2002			
Compound[b]	PE-based[c]	(Blank)	Liquid–liquid[d]	(Blank)	PE-based[e]	Liquid–liquid[f]	(Blank)	PE-based[e]	(Blank)
Pyr (ng/L)	2.3	(5×10^{-3})	2.2 ± 0.4	(0.07)	4.5	6.4 ± 0.8	(0.92)	6.0	(0.1)
B*a*A (ng/L)	0.04	(2×10^{-4})	0.33 ± 0.21	(0.01)	0.09	0.36 ± 0.05	(0.04)	0.07	(0.05)
PCB 52 (pg/L)	92	(1.1)	130 ± 21	(20)	160	70 ± 4	(42)	210	(77)
PCB 66 (pg/L)	20	(0.13)	83 ± 22	(4.9)	41	35 ± 15	(13)	39	(2.9)

[a] PE-based dissolved concentrations were corrected for salinity and temperature.
[b] Pyr = pyrene; B*a*A = benz[*a*]anthracene; PCB 52 = 2,2′,5,5′-tetrachlorobiphenyl; PCB 66 = 2,3′,4,4′-tetrachlorobiphenyl.
[c] Field deployment ($n = 1$).
[d] $n = 3$.
[e] Carboy deployment ($n = 1$).
[f] $n = 2$.

by ≥100 times (data not shown). The enhanced sorption was attributed to interactions with BC, and so K_{BC} values were inferred assuming Freundlich exponents of 0.7. The resulting K_{BC}s increased with sorbate hydrophobicity (Table 1). The dominance of the sedimentary BC phase has been reported for PAHs in other studies [8,9,11–15]. For PCBs, the affinity to BC seems to depend on congener conformation. For noncoplanar PCB congeners 52 and 128, for example, K_{BC}s exceeded the corresponding K_{OC}s by <10 times. However, for the mono-ortho-substituted PCBs 66 and 105, affinity to BC was greater, with K_{BC}s exceeding K_{OC}s by >10 times (Table 1). Similar results have been reported by others [39,40]. Atmospheric aerosols also seem to show preferential interactions with planar PCBs, compared to nonplanar PCBs [41].

HOC concentrations in the water column

In DB in October, the PE-deduced concentrations of dissolved HOCs (C_{diss}) were limited to those of Pyr, B*a*A, PCB 52, and PCB 66. As discussed earlier, Phen was excluded because of high concentration in the field blanks. For the larger molecular weight compounds, PE-based concentrations were much lower (e.g., B*a*P) or not detected in the PE extracts (e.g., PCB 105), whereas liquid–liquid extractions still indicated the presence of heavier compounds (data not shown). This result could indicate the importance of colloid-bound compounds that would be extractable but not accumulated by PE [42]. Alternatively, slow diffusive uptake of the heavier compounds may limit the accuracy of the PE results because we assumed PE–water equilibration. Hence, we limited PE-based results to those smaller compounds that certainly approach PE–water equilibrium in the field within four weeks and that were not affected by blank values [25]. We found C_{diss} for Pyr at 2 ng/L, for B*a*A at 0.04 ng/L, for PCB 52 at 92 pg/L, and for PCB 66 at 20 pg/L in DB in October 2001 (Table 4). Similar levels were found again in May 2002. Dissolved concentrations of PAHs in the SR were based on the PE results from the 20-L carboy. They were dominated by Pyr (~6 ng/L); the highest concentrations for the PCBs were approximately 70 to 210 pg/L for PCB 52 and between 20 and 40 pg/L for the other congeners.

Rudnick and Chen [43] reported Pyr concentrations in Boston Harbor ranging from <10 to >100 ng/L in 1997. Luellen and Shea [44] measured C_{diss} in DB in June 1999, and reported aqueous concentrations of 4 to 30 ng/L (Phen), 4 to 65 ng/L (Pyr), and approximately 1 ng/L (B*a*A and B*a*P). The data reported by Luellen and Shea [44] were dominated by Pyr, similar to the results reported here (D. Shea, North Carolina State University, Raleigh, NC, USA, personal communication). However, a marked decrease in aqueous concentrations seems to have occurred over the last three years, perhaps because of the change in sewage discharge into Boston Harbor to a new site 15 km into Massachusetts Bay in 2000.

Chemical activities

One objective of this study was to elucidate the relative sources of PAHs and PCBs accumulated by benthic clams by using analysis of the both the local sediments and the water column. As detailed further in Schwarzenbach et al. [17], a convenient way to calculate a chemical's activity in a given environmental medium (e.g., sediment or tissue) is to apply partition coefficients to derive the corresponding dissolved phase in equilibrium, then normalize the results to the chemical's liquid solubility (Table 1). This approach was chosen for the following sections discussing chemical activities, and thus the state of equilibrium between sedimentary, water column, and bioaccumulated contaminants.

To determine the importance of BC and protein in the calculations, we first assumed that the HOC activities in the sediments only represented equilibrium with the sedimentary OC. Thus, $a_{sed(OC)}$ in each case was calculated according to

$$a_{sed(OC)} = C_{sed}/[(f_{OC}K_{OC})C^{sat}_{W(L)}] \quad (11)$$

Similarly, the animals' body burden activities were estimated by assuming that the measured contaminants were only stored in the lipid fraction

$$a_{biota(lip)} = C_{biota}/[(f_{lipid}K_{OW})C^{sat}_{W(L)}] \quad (12)$$

We assumed that octanol is a suitable representative of the animal's lipid fraction. Expected HOC activities in *M. arenaria* at equilibrium with the sediments based on this EqP approach exceeded the observed tissue activities by one to two orders of magnitude for almost every chemical or site case (Table 5 and Fig. 2). Predicted $a_{sed(OC)}$s for PAHs always differed more than $a_{sed(OC)}$s for PCBs from $a_{biota(lip)}$ at all three sites (Fig. 2).

The recognition of sedimentary BC as a high-affinity phase for organic contaminants suggested that OC-based estimates of pore-water activities may overestimate HOC activities. Thus, sediment BC was included in a combined absorption and adsorption model and the HOC activities in the bed sediment were calculated as

$$a_{sed(OC,\,BC)} = C_{sed}/[(f_{OC}K_{OC} + f_{BC}K_{BC}C_W^{0.3})C^{sat}_{W(L)}] \quad (13)$$

Including BC reduced the estimated a_{sed} values by >10 times (the SR and high-OC region in DB) to 100 times (low-OC

Table 5. Calculated chemical activities (*a* values, all ppm) for selected polycyclic aromatic hydrocarbons and polychlorinated biphenyls (PCB) in sediments (sed), *Mya arenaria* (lipid [lip] and protein [prot]), and the overlying water column (WC) in Dorchester Bay (DB) (Boston, MA, USA) and the Saugus River (Lynn, MA, USA)[a]

	$a_{sed\ (OC)}$		$a_{sed\ (OC,\ BC)}$		$a_{biota\ (lip)}$		$a_{biota\ (lip,\ prot)}$		a_{WC}
Compound	Mean	Range	Mean	Range	Mean	Range	Mean	Range	Mean
DB OC-rich									
Phen	400	380–420	13	11–14	5.9	5.0–8.9	4.4	3.6–6.7	—
Pyr	830	820–850	49	39–59	10	8.3–11	8.3	6.5–9.2	2.3
B*a*A	640	630–650	18	14–21	6.1	3.9–9.0	5.2	3.4–7.8	0.3
B*a*P	1,280	1,230–1,330	50	43–56	13	<2.2–19	11	<2.0–17	—
PCB 52	31	30–32	3.8	3.1–4.6	3.8	2.8–6.1	3.4	2.4–5.4	1.1
PCB 66	73	71–75	1.3	1.0–1.6	7.3	5.2–12	6.6	4.7–11	0.7
PCB 105	52	51–53	0.7	0.6–0.9	3.4	2.4–5.5	3.1	2.2–5.1	—
PCB 128	25	24–25	0.5	0.4–0.6	1.4	0.8–2.4	1.3	0.8–2.3	—
DB OC-poor									
Phen	100	<44–160	1.1	<0.4–1.6	3.4	2.3–4.4	2.6	1.8–3.3	—
Pyr	270	<63–440	6.7	<1.5–10	7.2	5.8–8.6	5.9	4.9–7.0	2.3
B*a*A	180	39–290	1.9	0.1–3.1	5.0	4.1–5.9	4.4	3.6–5.1	0.3
B*a*P	380	53–640	5.7	0.2–8.9	7.2	6.9–7.5	6.5	6.3–6.8	—
PCB 52	6.8	<0.4–10	0.29	<0.02–0.39	3.2	2.5–3.6	2.9	2.3–3.3	1.1
PCB 66	21	<0.7–24	0.13	<0.004–0.13	5.2	3.7–5.9	4.8	3.5–5.4	0.7
PCB 105	10	0.5–21	0.05	0.0004–0.10	2.5	1.9–3.0	2.4	1.8–2.9	—
PCB 128	5.9	0.7–13	0.04	0.001–0.09	1.3	1.0–1.5	1.2	0.9–1.4	—
Saugus River									
Phen	1,700	1,200–2,050	54	13–140	8.4	6.1–11	5.9	2.1–9.5	—
Pyr	3,050	2,300–4,120	200	27–520	23	13–36	16	0.88–29	5.9
B*a*A	1,710	1,150–2,060	44	9.3–140	9.9	6.7–14	8.9	5.8–13	0.5
B*a*P	2,530	1,960–2,970	93	11–310	5.1	3.1–7.9	4.5	3.1–7.1	—
PCB 52	18	9.4–29	1.3	0.10–3.6	1.0	0.70–1.5	0.89	0.63–1.3	2.4
PCB 66	17	9.1–23	0.10	0.02–0.30	1.3	0.76–1.8	1.2	0.70–1.7	1.3
PCB 105	17	11–20	0.09	0.02–0.27	0.83	0.54–1.1	0.76	0.51–1.1	—
PCB 128	8.3	3.5–11	0.06	0.02–0.22	0.52	0.36–0.62	0.49	0.34–0.59	—

[a] OC = organic carbon; BC = black carbon; Phen = phenanthrene; Pyr = pyrene; B*a*A = benz[*a*]anthracene; B*a*P = benzo[*a*]pyrene; PCB 52 = 2,2′,5,5′-tetrachlorobiphenyl; PCB 66 = 2,3′,4,4′-tetrachlorobiphenyl; PCB 105 = 2,3,3′,4,4′-pentachlorobiphenyl; PCB 128 = 2,2′3,3′,4,4′-hexachlorobiphenyl.

region in DB) for PAHs and by about 10 to >100 times for PCBs (Table 5 and Fig. 3).

Similar to the sedimentary phase, the contaminant's activities in the tissues ($a_{biota(lip,\ prot)}$) were recalculated, taking into account both the lipid and protein content of the animals (Table 5)

$$a_{biota(lip,\ prot)} = C_{biota}/[(f_{lipid}K_{LW} + f_{protein}K_{PW})C^{sat}_{W\,(L)}] \quad (14)$$

Including proteins decreased $a_{biota(lip,\ prot)}$ by about 30% for Phen, and by about 20% for the other PAHs. The effect was less pronounced for PCBs, where $a_{biota(lip,\ prot)}$ decreased by about 15% for congener 52, but reduced $a_{biota(lip,\ prot)}$ for the heavier congener (PCB 128) by about 10% (Table 5 and Fig. 3).

Comparing these new estimates of chemical activities in

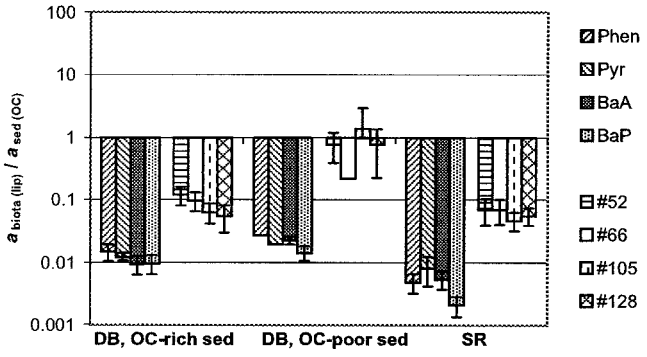

Fig. 2. Ratio of calculated chemical activities (mean ± 1 standard deviation) in *Mya arenaria* ($a_{biota(lip)}$) and sediment ($a_{sed(OC)}$) when assuming equilibrium absorption only into the animal's lipid fraction and the sedimentary organic matter for selected polycyclic aromatic hydrocarbons (phenanthrene [Phen], pyrene [Pyr], benz[*a*]anthracene [B*a*A], and benzo[*a*]pyrene [B*a*P]) and polychlorinated biphenyls in Dorchester Bay (DB) and the Saugus River (SR, Lynn, MA, USA). OC = organic carbon. Note: *y*-axis is on a log scale.

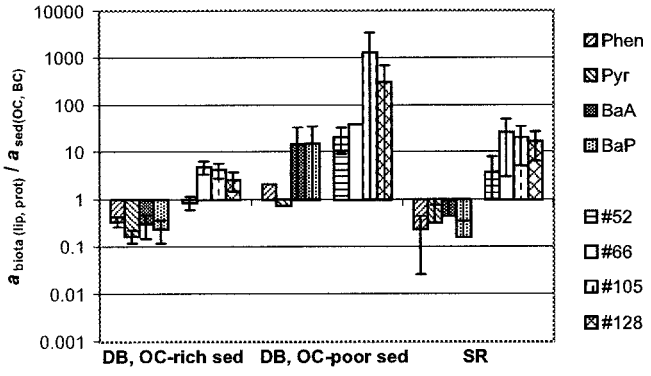

Fig. 3. Ratio of calculated chemical activities (mean ± 1 standard deviation) in *Mya arenaria* ($a_{biota(lip,prot)}$) and sediment ($a_{sed(OC,\ BC)}$) when assuming equilibrium absorption into the animal's lipid and protein and the sediment's organic carbon (OC) and black carbon (BC) fractions for selected polycyclic aromatic hydrocarbons (phenanthrene [Phen], pyrene [Pyr], benz[*a*]anthracene [B*a*A], and benzo[*a*]pyrene [B*a*P]) and polychlorinated biphenyls in Dorchester Bay (DB) and the Saugus River (SR, Lynn, MA, USA). Note: *y*-axis is on a log scale.

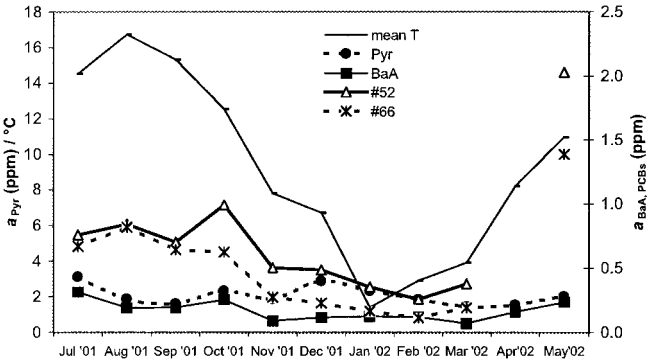

Fig. 4. Temporal variations of measured chemical activities in the water column (a_{WC}) of Dorchester Bay (Boston, MA, USA) for pyrene (Pyr), benz[*a*]anthracene (B*a*A), and polychlorinated biphenyl congeners 52 and 66.

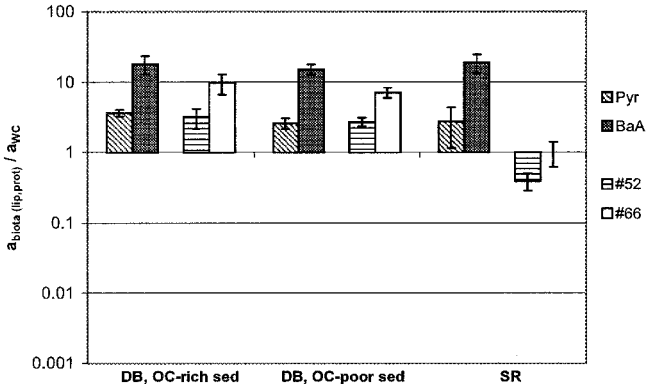

Fig. 5. Ratio of chemical activities (mean ± 1 standard deviation) in *Mya arenaria* ($a_{biota(lip, prot)}$) and the overlying water column (a_{WC}) for pyrene (Pyr), benz[*a*]anthracene (B*a*A), and polychlorinated biphenyl congeners 52 and 66 when using October 2001 water data for Dorchester Bay (DB) and June 2002 water data for the Saugus River (SR, Boston, MA, USA). Note: *y*-axis is on a log scale. OC = organic carbon.

M. arenaria and the sediments, we found that for PAHs at the high-OC DB site and the SR, the mean $a_{sed(OC, BC)}$ values were always greater than the mean $a_{biota(lip, prot)}$ values (Table 5). Interestingly, the low-OC DB site now indicates that the clams exhibited some greater PAH chemical activities than the sediments in which they live. The $a_{sed(OC, BC)}$s estimated for all the sediments stations ranged more than 10-fold, compared to a range of only two to three found in $a_{biota(lip, prot)}$ values of *M. arenaria*. The sedimentary $a_{sed(OC, BC)}$ values for the PCBs were 1 to 10 times lower than $a_{biota(lip, prot)}$. A wider range of calculated $a_{sed(OC, BC)}$ values (factor of 10–100) also was found for PCBs in the sediments compared to in the animal tissues (e.g., factor of three in DB and five in the SR). These discrepancies suggest that sediment bed activities do not, by themselves, dictate the corresponding animal body burdens. It appears that the sediments are a source of PAHs to the clams, but the same deposits also may be sinks for PCBs from the animals.

Seasonal water column activities in DB

At this stage, it is appropriate to examine the state of sediment–water column equilibria. As suggested by others [19], activity of a given HOC in the clam may be between the activities encountered in the sediments and the water column. Water column activities (a_{WC}s) were deduced for PCB congeners 52 and 66, Pyr, and B*a*A based on PE deployments in DB. These analytes equilibrate with PE in less than four weeks (the deployment period we used), and their temperature-dependent K_{PEW} and $C^{sat}_{W(L)}$ values were known [25]. For all analytes, a_{WC}s decreased from high values in the summer of 2001 to low values at the beginning of 2002 (Fig. 4). A discrete water sample taken in May 2002 suggested an increase in a_{WC} (Fig. 4). For Pyr, BaA, and congener 52, a_{WC} decreased by factors of approximately two to four from summer to winter. Congener 66 displayed an even stronger seasonal cycle, with a_{WC} being lower by a factor of seven at the beginning of 2002 compared to values in the summer of 2001 (Fig. 4). These results imply that benthic organisms may be subject to strong changes in a_{WC} over the course of a year. Consequently, benthic organisms could experience the water column as a source of organic contaminants during the summer, but the same water column could serve as a sink for contaminants during the winter months.

Sediment–water column equilibrium

For Pyr and B*a*A at the study sites, a_{sed} values exceeded a_{WC} values (Table 5). This outcome was more pronounced at the SR (factors of 20). These distinctions seem reasonable because we expect the SR area to be more intensively flushed than DB. In general, the activities for *M. arenaria* fell between the values of a_{sed} and a_{WC}, the only exception being for B*a*A at the low-OC DB site where one may argue the clams' activities were indistinguishable from those of the bed (i.e., within a factor of two).

A different picture emerged for the state of sediment–water equilibrium for PCBs (Table 5). The a_{WC} values for congeners 52 and 66 were greater than or equal to a_{sed} values at the low-OC DB site and at the SR. The opposite was true at the high-OC DB area. We should note that our corrections for BC sorption of the PCBs may be inaccurate because these compounds have not been examined widely in this regard. More work is needed to assess such BC sorption.

Factors governing the bioaccumulation of PAHs and PCBs by M. arenaria

Ratios of $a_{biota(lip, prot)}$ to a_{WC} for Pyr, B*a*A, and congeners 52 and 66 were calculated (Fig. 5). Activity ratios were >1 for Pyr and BaA at both sites. The clam–sediment ratios were <1 for these compounds (Fig. 3 and Table 5), indicating that clam uptake is from the bed and release is to the water column. For congeners 52 and 66, the water was undersaturated with respect to the clams in DB, but supersaturated at the SR site. Given the relatively large disparity in activities found in the clams and sediments in DB, this result supports the idea that PCB exchange presently involves uptake from high-OC beds at DB and release to the overlying seawater. However, at the SR site, the clams appear to take up these PCBs from the water and release them to the bed. This observation is consistent with earlier findings by Foster et al. [20], who reported negligible uptake of sedimentary pollutants by *M. arenaria* at the site they studied.

Several explanations are available to explain the additional differences between these new, activity-based estimates of PAH and PCB bioaccumulation. First, $a_{biota(lip, prot)}$ does not consider the role of contaminant metabolism by the organism. *Mya arenaria* can metabolize PAHs such as Pyr and B*a*P [45,46]. Interestingly, B*a*P exhibited lower chemical activity in the DB clams than was observed in either the sediment or the water column (data not shown). If metabolism occurs at a

rate that is significant relative to exchange with the environment, a reduction in $a_{biota(lip, prot)}$ would occur. In contrast, it is unlikely that effective pathways are present in *M. arenaria* for metabolizing PCBs [47]. Second, based on the similar PCB activities (ranges) we found in animals from a wide range of sediments, wider-scale factor(s) such as horizontally homogenized water column activities may dominate as a factor controlling the observed pattern of PCB bioaccumulation.

In summary, benthic organisms such as *M. arenaria* appear to reflect chemical exchanges with both the sediment bed in which they live and the water column from which they respire and feed. Results of our comparisons of observed versus estimated bioaccumulations may be better understood if one includes the adsorptive effects of BC along with the absorptive effects of OC. Similarly, the role of protein absorption in explaining bioaccumulation of HOCs, although relative small, likely improves estimates. Overall, the use of activities for describing the partitioning and bioavailability of PAHs and PCBs in aquatic systems may simplify the interpretation of these often complex processes. To expand upon these findings, future work needs to explore the possibly different activities between planar and nonplanar PCBs and the effects of organism life style (e.g., filter feeders versus deposit feeders).

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