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Bioavailability of PAHs: Effects of Soot Carbon and PAH Source

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The bioavailability of 38 individual polycyclic aromatic hydrocarbon (PAH) compounds was determined through calculation of biota–sediment-accumulation factors (BSAF). BSAF values were calculated from individual PAH concentrations in freshwater mussel, marine clam, and sediment obtained from field and laboratory bioaccumulation studies. Sediment that was amended with different types of soot carbon (SC) was used in some of the bioaccumulation experiments. BSAF values for petrogenic PAH were greater than those for pyrogenic PAH (e.g., 1.57 ± 0.53 vs 0.25 ± 0.23, respectively), indicating that petrogenic PAH are more bioavailable than pyrogenic PAH ($p < 0.05$). This trend was consistent among marine and freshwater sites. Increased SC content of sediment resulted in a linear decrease in the bioavailability of pyrogenic PAHs ($r^2 = 0.85$). The effect of increasing SC content on petrogenic PAH was negligible. SC was considered as an additional sorptive phase when calculating BSAF values, and using PAH–SC partition coefficients from the literature, we obtained unreasonably large BSAF values for all petrogenic PAH and some pyrogenic PAH. This led us to conclude that a quantitative model to assess bioavailability through a combination of organic carbon and soot carbon sorption is not applicable among field sites with a wide range of soot carbon fractions and PAH sources, at least given our current knowledge of PAH–SC partitioning. Our data offer evidence that many factors including analysis of a full suite of PAH analytes, PAH hydrophobicity, sediment organic carbon content, sediment soot carbon content, and PAH source are important to adequately assess PAH bioavailability in the environment.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment, produced primarily as a result of anthropogenic activities, and are known to cause adverse human and ecological health effects (*1–6*). PAHs can be broadly separated into three nonexclusive categories based on their source (*2*): biogenic, petrogenic, and pyrogenic PAHs. Biogenic PAHs are formed from natural biological processes including diagenesis; petrogenic PAHs are derived from petroleum and usually enter the aquatic environment dissolved in water, air, or a cosolvent such as crude oil; and pyrogenic PAHs are formed as a result of incomplete combustion of fuels and largely enter the environment tightly sorbed to particulate matrixes (*1*). Pyrogenic PAHs are also produced in tandem with combustion products such as soot (*1, 7, 8*). Petrogenic PAHs include the unsubstituted parent and alkyl homologues of naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes where the alkyl homologues are more abundant than the parent PAH (*2*). Pyrogenic PAHs are generally represented by greater abundances of parent compounds and a predominance of the 3–5-ring PAHs such as anthracene and benzo[*a*]pyrene (*2*). This simple classification is often useful but in reality is complicated by overlap among the three classes and by different PAH sources having varying relative abundances of individual PAH analytes.

Due to their hydrophobic nature, all PAHs are preferentially associated with carbon phases of particles, and thus adverse health effects are often evident with sediment exposure. The extent to which PAHs accumulate in a sediment-dwelling organism depends primarily on the ratio of the PAH uptake rate to the depuration rate, the capacity of the organism to metabolize PAHs (e.g., cytochrome P450 activity), the mobility of the organism, and various physical–chemical properties of the individual compounds. For example, bivalves are frequently used as sentinel organisms because of their low capability to metabolize PAHs (*9*) and their relatively sessile character, thereby providing a time-integrated measurement of PAH contamination. Bioaccumulation potential also depends on the desorption rate of the PAHs from the sediment or particle matrix (*10–14*). If desorption kinetics are fast relative to the co-occurrence of the PAH and the organism, the PAH will be available for uptake. However, if desorption rates are slow, the contaminant may be less available for uptake. Therefore, it is important to consider the bioavailability of PAHs when assessing their bioaccumulative potential.

Others have reported that PAHs may exhibit low chemical and biological availability (*1, 14–18*). This low availability has been described by field-derived solid–water partition coefficient (K_D) values being greater than predicted (*19–21*), as fractions available for equilibrium partitioning (AEP) being less than predicted (*22*), and culminates in toxicities that are less than predicted based on equilibrium partitioning theory. When identifying the potential for toxicity of sediment to aquatic organisms, determining sediment PAH concentration is only one aspect of evaluation. Particularly when investigating PAHs, it is important to assess the availability of individual PAHs to organisms. High total sediment PAH concentrations may not confer toxic levels to organisms if individual analytes are sequestered or tightly sorbed and are unavailable for desorption and uptake into the organism (*16, 17*). One way to assess the bioavailability of PAHs in the environment is to compare individual PAH concentrations in benthic organisms to individual PAH concentrations in sediment. This approach is described as the biota–sediment accumulation factor (BSAF) model (*14, 18, 23, 24*):

$$\mathrm{BSAF} = (C_m/f_l)/(C_s/f_{oc}) \quad (1)$$

where C_m is the individual PAH concentration in mussel tissue (ng of PAH/g of mussel dry weight), f_l is the organism lipid fraction (g of lipid/g of mussel dry weight), C_s is the individual PAH concentration in sediment (ng of PAH/g of sediment dry weight.), and f_{oc} is the mass fraction of organic carbon (g of organic C/g of sediment dry weight). The BSAF models the partitioning of PAHs between the hydrophobic (sorptive) phases present in a benthic organism and sediment. These sorptive phases are traditionally the lipid fraction in the

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TABLE 1. Outline of Study Treatments, Sediment PAH Concentrations, and Carbon Content

study	treatment	total sediment PAH concn (38 analytes) (ng/g)	f_{sc}	% SC	% OC
freshwater *Elliptio* sp.	6-month bioaccumulation study: field	326	0.03	0.02	0.64
marine *Mya* sp.	14-d bioaccumulation studies: field	30,000	0.19	0.88	3.74
marine *Mya* sp.	14-d bioaccumulation studies: lab, using unamended and soot carbon-amended sediments[a]	892, unamended	0.04 (unamended); 0.29–0.30 (amended)	0.23 (unamended); 0.85–0.89 (amended)	2.14

[a] Amended with diesel soot, urban dust, and oil-fired power plant soot.

organism and the organic carbon fraction in sediment. One must consider specific assumptions when using the BSAF model, including

(i) The organism possesses minimal capability to metabolize PAHs (BSAF values of <1 may suggest metabolism has occurred).

(ii) Sorption/desorption kinetics are fast relative to uptake kinetics so that PAHs are bioavailable (BSAF values may be <1 if bioavailability is decreased).

(iii) The affinity of PAHs for organism lipid and sediment organic carbon are equivalent [i.e., octanol–water partition coefficient (K_{ow}) is equivalent to organic carbon-normalized partition coefficient (K_{oc})].

(iv) Organic carbon (OC) is the only sorptive phase present in sediment.

Given these assumptions, if the PAHs are in equilibrium with the OC then BSAF values should be close to 1. Often, BSAF values greater than 1 are observed for some contaminants (*18*), perhaps due to $K_{ow} > K_{oc}$ (i.e., assumption iii is not correct). Alternatively, BSAF values are sometimes less than 1 (*24*), indicating a decreased bioavailability. This decreased bioavailability may be a result of a secondary sorptive phase that is not accounted for in eq 1. While the traditional form of the BSAF model considers only OC as the sorptive phase, others have recently suggested that soot carbon (SC) may provide an additional sorptive phase for PAHs and other planar compounds (*7, 19–21*). In this paper, we present PAH bioavailability estimates using both the traditional and "modified" BSAF, which includes a term for the mass fraction of SC in sediment (f_{sc}), as well as a quantity that accounts for the greater affinity of PAHs for SC relative to OC (K_{sc}/K_{oc}, where K_{sc} is the soot carbon–water distribution coefficient):

$$\mathrm{BSAF} = (C_m/f_L)/(C_s/(f_{oc} + f_{sc}(K_{sc}/K_{oc}))) \qquad (2)$$

The K_{sc} values were estimated from a quantitative structure–activity relationship (QSAR) calculated from existing laboratory-derived activated carbon–water distribution coefficient (K_{ac}) values (*20, 25*), extrapolated for 38 PAH. The objectives of this study were to present BSAF values for 38 individual PAH using both marine and freshwater bivalves, assess potential differences in accumulation related to putative PAH source (petrogenic vs pyrogenic), and evaluate the applicability among field sites of a modified BSAF model (eq 2) including SC as an additional sorptive phase in sediment.

Experimental Section

Sample Collection–Freshwater Sites (Table 1). Mussels (*Elliptio complanata*) were taken from a relatively uncontaminated site [total mussel PAH concentration (sum of 38 analytes) was less than 100 ng/g] in West-Central North Carolina (Catawba River Basin) and deployed in polyethylene crates lined on the bottom with fine-mesh (5 mm opening) at a relatively rural forested site in Gaston County, NC (f_{sc} = 0.03). Following a 6-month exposure period, mussels were collected and composited for analysis. Surficial (top 2 cm) sediment samples were collected in triplicate.

Sample Collection–Marine Sites (Table 1). Marine clams (*Mya arenaria*) were sampled from multiple sites in the vicinity of Boston and Cape Cod, MA, and a 14-d field bioaccumulation study was performed (f_{sc} = 0.19). Additional 14-d laboratory bioaccumulation studies were conducted using field-collected unamended sediment (f_{sc} = 0.04), and the same field sediment amended with SC (f_{sc} = 0.29–0.30) from different sources (diesel soot, urban dust, and oil-fired power plant soot). All f_{sc} values are the mass fraction of total carbon in the sediment. Amended sediments were mixed in rotating drums at 15 rpm in the dark for 30 d prior to conducting the bioaccumulation studies. Except for data in Table 4, all marine data are from the 14-d field bioaccumulation study. Figure 4 includes data from all bioaccumulation studies.

Sample Extraction. Mussel, clam, and sediment samples were extracted as described by Short et al. (*26*) with the following modifications: samples were lyophilized and shaker-extracted (200 rpm) for 24 h, and sediment samples were extracted with methylene chloride:acetone (1:1) (v:v). Mass fraction of OC in sediment was determined by carbon, hydrogen, and nitrogen (CHN) analysis with an elemental analyzer. Content of SC was also determined with CHN analysis, following combustion of lyophilized sediment at 375 °C to remove the thermally labile fraction (*20*). Mussel and clam lipid content was determined by passing extracts through a gel permeation chromatography (GPC) column, collecting the lipid fraction, evaporating, and weighing.

PAH Analysis. Sediment and bivalve samples were analyzed for 38 PAH analytes (Table 2) with an HP5890 series II GC equipped with electronic pressure control connected to an HP5970 MSD operated in the selected ion monitoring (SIM) mode and utilizing a Restek 30 m × 0.25 mm Rtx-5 (film thickness 0.25 μm) MS w/Integra-Guard column. Analysis was run using 1-μL injections and the following temperature program: injection port, 300 °C; transfer line, 280 °C; initial temperature, 40 °C; initial hold, 1 min; ramp rate, 6 °C/min; final temperature, 290 °C; final hold, 30 min. Recovery internal standards (phenanthrene-d_{10}, benzo[*a*]-pyrene-d_{12}) were used to derive response factors and to quantify samples. Data quality was assessed using procedural blanks, replicate analyses, matrix spikes, and surrogate internal standards (naphthalene-d_8, acenaphthene-d_{10}, perylene-d_{12}, chrysene-d_{12}). Surrogate internal standard and matrix spike recoveries were 55–105%, lab replicate RSDs were <15%, and method blanks were either not detected or were <10% of the measured value. Method detection limits were 0.2–0.5 ng/g dry weight.

TABLE 2. Properties of PAH Analytes with Traditional (T) and Modified (M) BSAF Values, with and without Soot Carbon Correction, Respectively, from Freshwater and Marine Field Sites

analyte	symbol	log K_{ow}[a]	log K_{ac}[b]	log K_{sc}[c]	freshwater T BSAF	marine T BSAF	freshwater M BSAF	marine M BSAF
naphthalene	N0	3.37	5.63	5.23, 4.63	2.11	1.31	13.97	56.86
C1-naphthalenes	N1	3.87	6.03		2.19	1.87	12.01	65.12
C2-naphthalenes	N2	4.37	6.43		2.44	2.14	11.20	59.88
C3-naphthalenes	N3	5.00	6.94		2.96	1.95	10.94	41.53
C4-naphthalenes	N4	5.55	7.38		2.49	2.07	7.72	34.84
acenaphthylene	AY	4.07	6.19		2.15	0.31	10.97	9.89
acenaphthene	AC	3.92	6.07		1.96	0.17	10.56	5.79
fluorene	F0	4.18	6.28	5.40, 6.03	4.07	0.40	19.95	12.16
C1-fluorenes	F1	4.97	6.91		5.53	1.65	20.64	35.60
C2-fluorenes	F2	5.20	7.10		2.71	2.30	9.38	44.95
C3-fluorenes	F3	5.50	7.34		2.26	2.11	7.11	36.27
dibenzothiophene	D0	4.49	6.53		2.85	1.74	12.51	46.21
C1-dibenzothiophenes	D1	4.86	6.82		3.52	1.39	13.64	31.44
C2-dibenzothiophenes	D2	5.50	7.34		2.18	1.70	6.86	29.22
C3-dibenzothiophenes	D3	5.73	7.52		1.53	1.21	4.50	18.87
phenanthrene	P0	4.57	6.59	5.82, 6.62	1.77	0.16	7.54	4.10
C1-phenanthrenes/anthracenes	P1	5.14	7.05		1.20	1.48	4.22	29.68
C2-phenanthrenes/anthracenes	P2	5.51	7.35		1.45	1.52	4.55	26.02
C3-phenanthrenes/anthracenes	P3	6.00	7.74		2.46	1.49	6.67	20.73
C4-phenanthrenes/anthracenes	P4	6.51	8.15		1.56	1.63	3.70	18.35
anthracene	AN	4.54	6.57		0.75	0.06	3.23	1.56
fluoranthene	FL	5.22	7.11		0.47	0.28	1.61	5.42
C1-fluoranthenes/pyrenes	FP1	5.72	7.51		0.43	0.34	1.27	5.32
pyrene	PY	5.18	7.08	6.59, 7.03, 6.25[d]	0.76	0.92	2.66	18.13
benz[*a*]anthracene	BaA	5.91	7.67		0.27	0.05	0.77	0.72
chrysene	C0	5.86	7.63		0.50	0.55	1.40	8.12
C1-chrysenes	C1	6.42	8.08		0.77	0.72	1.85	8.41
C2-chrysenes	C2	6.88	8.45		0.41	0.84	0.88	8.13
C3-chrysenes	C3	7.44	8.90		0.74	0.89	1.40	6.89
benzo[*b*]fluoranthene	BbF	5.80	7.58		0.35	0.18	1.01	2.72
benzo[*k*]fluoranthene	BkF	6.00	7.74		0.30	0.21	0.83	2.92
benzo[*e*]pyrene	BeP	6.20	7.90		0.58	0.30	1.48	3.84
benzo[*a*]pyrene	BaP	6.04	7.77		0.18	0.12	0.49	1.64
perylene	PE	6.30	7.98		0.18	0.11	0.44	1.35
indeno[1,2,3-*c,d*]pyrene	IP	7.00	8.54		0.27	0.04	0.56	0.37
dibenz[*a,h*]anthracene	DA	6.75	8.34		0.41	0.07	0.91	0.71
benzo[*g,h,i*]perylene	BgP	6.50	8.14		0.29	0.34	0.70	3.84
coronene	CO	7.64	9.06		0.26	0.15	0.46	1.07
fraction organic carbon (f_{oc})					0.64	3.74	0.64	3.74
fraction soot carbon (f_{sc})					0.03	0.19	0.03	0.19

[a] Log K_{ow} values from Neff and Burns (*44*). [b] K_{ac} values calculated from QSAR using Gustafsson et al. (*45*) and Luehrs et al. (*25*). [c] Experimentally derived K_{sc} values: Bucheli and Gustafsson (*46*). [d] Experimentally derived K_{sc} value: Accardi-Dey and Gschwend (*20*).

Results and Discussion

Calculation of BSAF Values and Assessment of Bioavailability. BSAF values were calculated for 38 individual PAH analytes (Table 2) with eq 1. These values are referred to as "traditional" (T) BSAF, in which OC is considered the only sorptive phase in sediment. Figure 1a,b represents the BSAF values plotted against individual PAHs, in order of increasing hydrophobicity (log K_{ow}) along the *x*-axis, calculated for freshwater and marine sites, respectively. Petrogenic PAH had BSAF values equal to or greater than 1 in most cases, whereas pyrogenic PAH generally had BSAF values less than 1. For example, the petrogenic PAHs parent naphthalene (N0) and its alkylated homologues (C1−C4 naphthalenes, N1−N4) had BSAF values that ranged from 1.3 to greater than 2. These analytes were available for uptake by the freshwater mussels and marine clams. However, anthracene (AN), fluoranthene (FL), benz[*a*]anthracene (BaA), indeno-[1,2,3-*c,d*]pyrene (IP), and coronene (CO) among other pyrogenic PAHs had BSAF values that were less than 1 and in some cases were as low as 0.04 (i.e., IP). The difference in accumulation between petrogenic and pyrogenic PAHs observed was consistent between the freshwater and marine sites. The observation that petrogenic PAHs were more bioavailable than pyrogenic PAHs at both the freshwater and marine sites is somewhat surprising because of the difference in site characteristics. The freshwater site was relatively unpolluted (total sediment PAH concentration = 326 ng/g) and had a low organic carbon content (f_{oc}= 0.64%), whereas the marine site was highly polluted (total sediment PAH concentration > 30 000 ng/g) and had a greater organic carbon content (f_{oc}= 3.74%). There were, however, differences in the relative abundance of individual analytes at each of the sites. At the freshwater site, acenaphthylene (AY) and acenaphthene (AC) were available (Figure 1a), but the BSAF values are questionable due to concentrations for these analytes being lower than our nominal detection limit. At the marine site, AY and AC were less available (Figure 1b), suggestive of a pyrogenic source or influence of sediment characteristics. The relative abundances of fluorene (F0) also differed at each site, where F0 was available to mussels at the freshwater site and less available to clams at the marine site. Regardless of location, it appears that petrogenic PAHs were nearly all more bioavailable than pyrogenic PAHs. Using the data from Figure 1, the average petrogenic PAH BSAF values were greater than 1 [2.44 ± 1.15 (freshwater) and 1.57 ± 0.53 (marine)], and the average pyrogenic BSAF values were less than 1 [0.63 ± 0.60 (freshwater) and 0.25 ± 0.23 (marine)]. It should be noted, however, that the average petrogenic

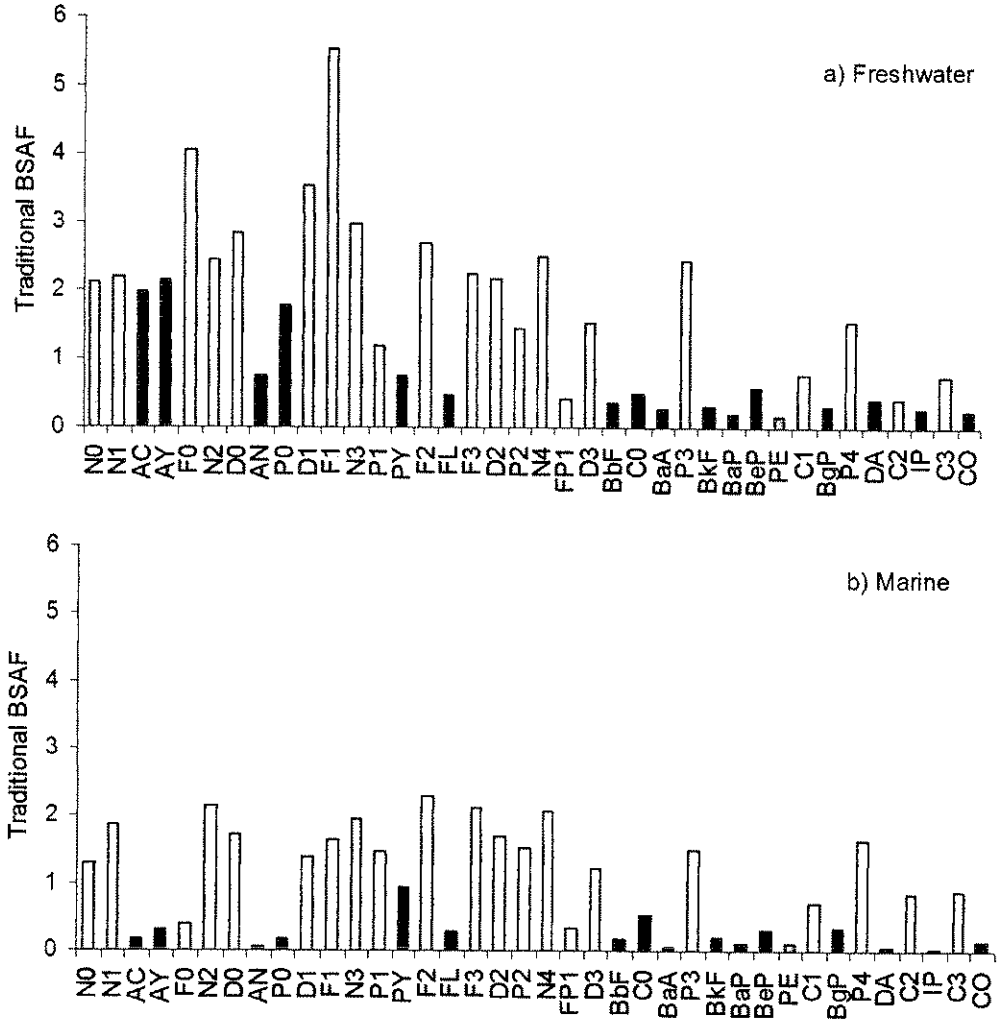

FIGURE 1. Traditional BSAF values (no soot carbon corrections) for individual PAH at a freshwater (a) and marine (b) site. White bars represent petrogenic PAH; solid black bars represent pyrogenic PAH [perylene (PE), the only biogenic PAH, is solid gray]. A BSAF of 1 indicates 100% bioavailability. Note that the petrogenic PAH have BSAF values that are on average equivalent to or greater than 1, whereas nearly all of the pyrogenic PAH have BSAF values that are less than 1. PAH analytes are all listed on the *x*-axis in order of increasing hydrophobicity; symbol codes are given in Table 2.

PAH BSAF values for the freshwater and marine sites did not include the alkylated homologues of chrysene (C0) because the origin (petroleum vs coal source) of these analytes is uncertain. Additionally, the biogenic PAH perylene (PE) has been excluded from all BSAF averages; phenanthrene (P0) and C0 have been excluded from the pyrogenic BSAF averages at both sites; AC and AY have been excluded at only the freshwater site; and pyrene (PY) has been excluded at only the marine site. The reasons for these exclusions are discussed later but take into account differing sources of PAH to both sites. On the basis of these results, bioavailability appears to be influenced by the source of PAHs where petrogenic PAHs are more available than pyrogenic PAHs by about a factor of 5.

As we have just shown, PAH source can yield a prediction of PAH bioavailability, but PAH bioavailability can also offer information a priori on PAH source. Although nearly all petrogenic PAHs were bioavailable and nearly all pyrogenic PAHs exhibited lesser availability, there were several exceptions to this classification. From this arises our logic in determining which PAHs to consider when calculating average petrogenic and pyrogenic BSAF values for this study. For example, PAHs that enter the environment associated with neat or dissolved petroleum would be expected to exhibit greater availability than PAHs that enter tightly sorbed to a particulate phase, such as soot. In Figure 1a, P0 is available (BSAF = 1.77), indicating that it may be in a more readily exchangeable state, perhaps associated with a refined diesel oil source rather than a high-temperature combustion source. However, the alkylated homologues of chrysene (C1–C3 chrysenes) have BSAF values that are slightly less than 1, suggesting lowered bioavailability. These alkylated chrysenes at the freshwater site may be bound in a coal or tar matrix and are not as readily available for equilibrium partitioning. In contrast, P0 exhibited lesser availability (BSAF = 0.16) at the marine site (Figure 1b), suggesting a different source of P0, perhaps of pyrogenic origin, to this system as compared to the freshwater system. Moreover, PY and parent C0 were more available at the marine site, which may suggest the presence of creosote, providing a more available source of PY and C0. This pattern of response suggests that the type of PAH entering the system influences bioavailability in different ways and that source may be an important factor when examining PAH bioavailability.

Influence of PAH Hydrophobicity. The differences in PAH bioavailability according to PAH source (petrogenic vs pyrogenic) that occurred in both the freshwater and marine systems (Figure 1a,b) suggests that bioavailability is to some

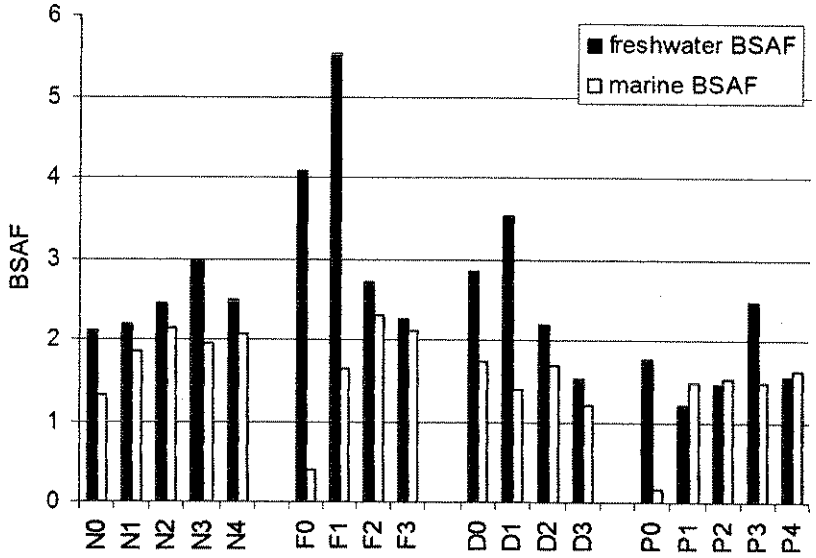

FIGURE 2. Alkyl homologue series plotted in sets of increasing hydrophobicity (log K_{ow} for naphthalene series ranges from 3.37 to 5.55; for fluorene series, it ranges from 4.18 to 5.55; for dibenzothiophene series, it ranges from 4.86 to 5.73; for phenanthrene/anthracene series, it ranges from 4.57 to 6.51). Note that the BSAF values do not decrease to less than 1, even though hydrophobicity increases, except for the marine BSAF values for fluorene and phenanthrene (where decreases are more likely the result of sediment soot carbon influence or PAH source than log K_{ow} value). For example, the analytes naphthalene and C4-phenanthrene are similarly bioavailable in both systems regardless of the fact that C4-phenanthrene is 3 orders of magnitude more hydrophobic than naphthalene.

extent independent of K_{ow}. Specifically, petrogenic PAHs with log K_{ow} values greater than 5 still exhibit BSAF values close to or greater than 1. For example, at the freshwater site, the petrogenic C3- and C4-phenanthrenes (P3 and P4) are available to mussels, with BSAF values of 2.46 and 1.56, respectively, despite having log K_{ow} values of 6.0 and 6.5, higher than the K_{ow} values for pyrogenic PAHs that have lesser availability (e.g., benzo[*k*]fluoranthene (BkF), with log K_{ow} of 6.0 and BSAF value of 0.30). Similarly, at the marine site, the petrogenic PAHs P3 and P4 and the C2- and C3-chrysenes (C2 and C3) are available to clams (BSAF values of 1.49, 1.63, 0.84, and 0.89, respectively) even though their log K_{ow} values are all greater than 6.0. Although the log K_{ow} of petrogenic C3 (7.44) is comparable to that of pyrogenic coronene (CO, 7.64), the BSAF values of CO (0.26, 0.15) are less than those for C3 (0.74, 0.89) at both the freshwater and marine sites. The influence of PAH source is consistent for the less hydrophobic pyrogenic PAHs as well: if hydrophobicity were the dominant factor in predicting bioavailability, we would expect the pyrogenic PAHs AN and FL to be available. However, AN (log K_{ow} of 4.54) is less bioavailable to both mussels and clams, with BSAF values of 0.75 (freshwater) and 0.06 (marine), and FL (log K_{ow} of 5.22, comparable to those for available petrogenic PAH listed above) has BSAF values of 0.47 (freshwater) and 0.28 (marine). Furthermore, when the BSAF values for alkyl homologue groups are compared (Figure 2), they are for the most part consistently equal to or greater than 1, regardless of K_{ow}. Across a range of log K_{ow} values from 3.37 to 6.51, most BSAF values are greater than 1 for the petrogenic alkyl homologues. Therefore, based on these data, we believe that the PAH source is a more important indicator of bioavailablity than hydrophobicity alone.

BSAF and log K_{ow} were not significantly correlated in regression analysis ($r^2 = 0.42$, $p < 0.05$, and negative slope) where hydrophobicity only explained 42% of the variation in the BSAF values (Figure 3). It is important to note that while the *average* trend is a negative slope, the data points are divided into two sections: those that are primarily petrogenic PAHs (log BSAF values ≥ 0) and those that are primarily pyrogenic PAHs (log BSAF values < 0). The influence of PAH source, as discussed above is the more dominating factor controlling bioavailability. Other studies have demonstrated conflicting information for log BSAF versus log K_{ow} relationships; some demonstrating a maximal BSAF at log K_{ow} 5.5–6 (ref *12*, using an amphipod), whereas others had positive slopes (ref *27*, using a deposit feeding clam) that are in contrast to our negative slope. The difference appears to arise when only a small subset of PAHs are used or when different log K_{ow} values are used [e.g., Landrum (*12*) used a higher log K_{ow} value for AN (4.5) than for P0 (4.3), whereas our log K_{ow} value was larger for P0 (AN = 4.53, P0 = 4.57)]. However, if the same PAH analytes were used from our study, similar results would be obtained (i.e., maximal and positive slope with fewer compounds).

When a full suite of PAH analytes, including alkylated homologues, is used in the analysis (as was done in this study), a more robust data set is obtained for which a more descriptive relationship between log BSAF and log K_{ow} can be determined. Ferraro et al. (*14*), and Krauss et al. (*28*) also reported an independent relationship between log BSAF and log K_{ow} for PAH in clams and earthworms, respectively, and their corresponding BSAF values for individual PAHs agreed well with ours (Table 3). Moreover, Maruya et al. (*24*) reported a negative slope for log BSAF versus log K_{ow}, and the BSAF values also compared well to ours (Table 3), suggesting that hydrophobicity alone is not a good predictor of bioavailability and that additional factors such as the source of individual PAHs may be a better predictor of bioavailability.

Other Factors Influencing BSAF Values. Other factors, in addition to decreased bioavailability, should be considered to potentially explain the decreased BSAF values of pyrogenic PAH. These include differences in hydrophobic character between mussel lipid and sediment OC, a lack of steady-state condition for mussels, the sediment phase, and the water column, and a preferential capacity of mussels to metabolize 3+ ring PAH analytes. While there is evidence that organism lipid quality may be more "lipid-like" than sediment OC [i.e., $K_{ow} = 0.41\ K_{oc}$ (*29*)], because OC can contain hydrophilic components, any difference would have presumably affected our entire suite of analytes equally and would not have resulted in decreased availability unasso-

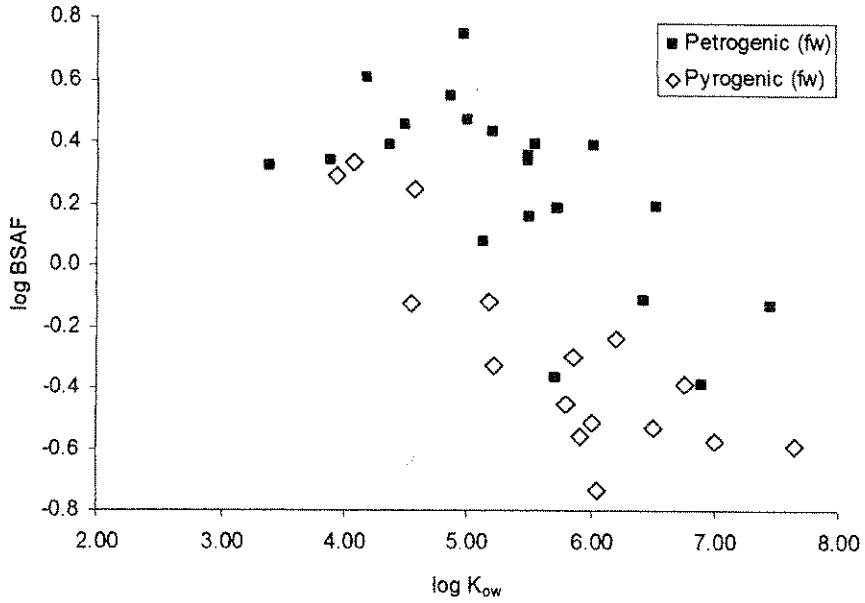

FIGURE 3. Plot of log BSAF vs log K_{ow} values from this study (freshwater data, fw). The majority of the petrogenic PAH (black squares) are clustered together with log BSAF values greater than 0, while nearly all the pyrogenic PAH (open diamonds) are clustered together with log BSAF values less than 0. This suggests that hydrophobicity is not solely governing PAH bioavailability.

TABLE 3. Comparison of BSAF Values for Bivalves in This Study to Other Organisms

species	PY	BaA	C0	Bb,k,jF	BaP	literature cited
Elliptio complanata	0.76	0.27	0.50	0.30–0.35	0.18	this study
Mya arenaria	0.92	0.05	0.55	0.18–0.21	0.12	this study
Macoma nasuta	0.37–0.53	0.15–0.62	0.21–0.61	0.21–1.02	0.05–0.85	Ferraro et al. (*14*)
Lumbricus terrestris	0.16	0.2	0.18	0.16	0.16	Krauss et al. (*28*)[a]
Potamocorbula amurensis	0.12–1.50	0.09–2.48	0.13–0.97	0.08–1.20	0.06–0.19	Maruya et al. (*24*)

[a] Values approximated from Figure 4 in Krauss et al. (*28*). C0 represents both chrysene and triphenylene.

ciated with PAH hydrophobicity. For example, if all PAH analytes were available for equilibrium partitioning, they should have preferentially partitioned into mussel lipid based on their individual affinity for adipose tissue unless steric problems existed or particular analytes remained unavailable for equilibrium partitioning due to surface association with particulates, micropore sediment association, or occlusion (*17*). Although lipid pool inequality could explain part of our data, it is potentially masked by a larger effect; notably, decreased bioavailability of the pyrogenic compounds. Therefore, lipid pool inequalities do not seem to explain the difference between petrogenic and pyrogenic PAH BSAFs that we observe in Figure 1a,b.

Bioaccumulation experiments with *Mytilus edulis* have shown rapid uptake of organic compounds and that steady state is reached on average within 8 d (*30*). Additionally, Obana et al. (*31*) reported that clams (*Tapes japonica*) reached steady state with the water column in 2 d and with the sediment in 7 d. This included the high K_{ow} compounds B(b)F, B(k)F, IP, and B(g)P. While Pruell et al. (*32*) reported steady state was reached in *M. edulis* at 20 d, an *apparent* steady state appeared to be reached at 10 d for the 4-ring PAH. Based on results from a separate PAH bioaccumulation study performed by this laboratory, unionid mussels appeared to reach steady state within 4 d of exposure (*33*). Therefore, we believe that the 14-d (*Mya*) and 180-d (*Elliptio*) exposure durations for data presented in this paper are more than sufficient to reach steady state between the bivalves and the rapidly reversible sediment PAH pool. The distinction between steady state levels is important especially for the sediment-sorbed PAH available for rapid exchange with the water column and those sediment-associated PAHs that are only slowly reversible and not as available for equilibrium partitioning (*12*). The lack of accumulation of pyrogenic PAH in bivalves from this study may be from lack of a steady state between the bivalves and the slowly reversible PAH pool in the sediment or the pool associated with an additional sorptive phase, such as soot carbon (SC). The apparent steady state that has been reached for PAH analytes with high log K_{ow} values (P4, 6.51) suggests that the lower BSAF values were not related to a lack of equilibrium but rather to a lack of bioavailability.

It is unlikely that bivalves possess preferential metabolic capacity for breaking down 3+ ring PAHs. Narbonne et al. (*34*) reported that the number of rings in a PAH compound influences their metabolic rates. However, the relationship between the number of rings and metabolic rate is reported as a shorter half-life for fewer ringed PAHs (5 h for N0 and 8 h for BaP in *M. edulis*), which is the opposite of our data. If metabolism is occurring, one might expect lower BSAF values for the lower molecular weight (e.g., N0, N1, etc.) PAH analytes. Additionally, because bivalves exhibit minimal enzymatic capacity for metabolizing PAHs (*1*, *9*), it is highly unlikely that the bivalves in our study were selectively metabolizing the 3+ ring analytes.

Influence of SC as an Additional Sediment Sorptive Phase. In an attempt to understand the underlying mechanisms to explain our observations, we hypothesized that SC in test sediment may be responsible for the decreased bioavailability of pyrogenic PAHs. Although PAHs partition (absorb) into OC, they also adsorb to SC (*20*), and this may help explain where the unavailable pool of PAHs reside. When we applied eq 2 to our data, we found that the modified BSAF values unreasonably overestimated bioavailability for

petrogenic PAH (Table 2) but increased the BSAF values for the pyrogenic PAHs so that most approached 1 and some exceeded 1. The few overpredictions of bioavailability for the pyrogenic PAH may be due to using K_{ac} to estimate soot carbon–water partition coefficients (K_{sc}), which may have over-estimated PAH affinity for SC. Correcting for SC content may only be necessary for pyrogenic rather than petrogenic PAHs. For example, the uncorrected BSAF value for the petrogenic PAH N0 at the freshwater site is 2.11 and for the marine site is 1.31, but once these values are corrected for SC, the BSAF values increase to 13.97 and 56.86, respectively; an increase of nearly 7–50-fold. However, when pyrogenic analytes are corrected for SC, BSAF values increase from 0.27 to 0.77 for BaA at the freshwater site and from 0.05 to 0.72 at the marine site. This suggests that petrogenic PAH may be less affected by SC in sediment and that K_{ac} values may be overestimating K_{sc} values. K_{ac} values may not reflect K_{sc} values in field-collected sediments if competitive sorption interactions are involved. Moreover, if other hydrophobic organic contaminants (HOCs) such as pesticides and polychlorinated biphenyls (PCBs) and natural organic matter (NOM) compete for active surface sorption sites on the exterior of the SC particles, laboratory-derived K_{sc} values may not adequately estimate field interactions. Also, different types of SC used in the laboratory, such as National Institute of Standards and Technology, Standard Reference Materials, and SC present in field sediment, which can be as high as 30% of total organic carbon (*35*), may possess different affinities for PAHs. Thus, potential differences in binding affinity will likely remain uncertain until competitive sorption studies in laboratory and field settings are conducted.

The SC fractions at the freshwater and marine sites studied here were different, with an f_{sc} at the freshwater site of 0.03 and an f_{sc} at the marine site of 0.19 (f_{sc} values are reported as g of SC/g of TOC). In Figure 1a,b, the overall relative petrogenic PAH BSAF values did not differ between the two sites (BSAF values are ≥ 1), even though the SC fraction at the marine site was six times that of the freshwater site (Figure 1a,b). However, there was a marked difference in the availability of the pyrogenic PAH at the two sites, particularly for P0, AN, FL, BaA, BbF, BkF, BaP, IP, and CO. At the freshwater site, which had less SC, the BSAF values for the pyrogenic PAH were, for the most part, greater than those at the marine site. For example, AN had a BSAF value of 0.75 at the freshwater site; however, in contrast with the increased soot carbon fraction at the marine site, AN had a BSAF value of 0.06. Therefore, these data suggest that as f_{sc} values increase, the bioavailability of pyrogenic PAHs decreases, but the bioavailability of the petrogenic PAHs remains essentially unaffected. It should be noted that while different bivalve species can exhibit different feeding mechanisms, which could influence the amount of contaminant exposure, both *Mya* and *Elliptio* species tend to burrow in sediment (*36, 37*). As our data agree at both sites, it is unlikely that species differences are exerting any substantial variation in the data.

This difference between petrogenic and pyrogenic PAHs and their interaction with SC may offer indirect evidence about the mechanism(s) of PAH sorption onto SC active sites. For example, petrogenic PAHs may not be affected by SC because pyrogenic PAHs are formed in tandem with SC and might enter the environment already associated with SC (i.e., they are native to the SC), whereas petrogenic PAHs are more likely to enter the environment dissolved in water or sorbed to OC and may only encounter the SC after binding sites are largely saturated. This interaction may further depend on the type of soot (e.g., some soots can contain petrogenic PAHs). Others have reported that PAHs are associated primarily with the exterior of the SC particle (*38, 39*). This association has been shown by a similarity in 2D and 3D surface areas of soot (*40, 41*) and by the use of cryomicrotome sectioning techniques that found most PAHs are present on the external surfaces of coal particles (*38*). Additionally, contrasting evidence exists for external versus internal sorption; Gustafsson and Gschwend (*41*) reported that slow gas sorption kinetics suggested internal interactions, whereas Ghosh et al. (*38*) suggested desorption models with a "rind" type outer layer of PAHs on coal-derived particles best explains PAH interaction. To understand why SC appears to only influence the bioavailability of pyrogenic PAHs, the microscale mechanism(s) behind the interaction must be resolved.

Ideally, accounting for the SC fraction and affinity of PAHs for soot carbon, as modeled in eq 2, would result in adequate predictions of bioavailability among field sites with varying organic carbon and SC fractions and among different PAH sources. However, when we incorporated an additional marine site with a different SC fraction and this same sediment amended with various sources of soot carbon (Figure 4, Table 1), the effect of increasing SC and decreasing bioavailability persisted, but high f_{sc} sediments still contained similar ranges of pyrogenic BSAF values as those for low f_{sc} sediments. For example, in the unamended sediment with an f_{sc} of 0.04, the range of pyrogenic BSAF values (BSAF range from 0.25 to 1.25) was similar to those for the sediment that had been amended with SC, increasing the f_{sc} values to 0.29–0.30 (BSAF range from 0.08 to 0.98). Even with high SC contents, individual analytes still exhibited BSAF values that were at or near 1. If the effect of SC on bioavailability was as influential as expected, one might observe substantially lower BSAF values in sediments with very high SC content. Therefore, other, yet unknown contributing factors seem to be important for controlling bioavailability of PAH among sites differing in SC.

Influence of PAH Source and Subsequent Effect on Bioavailability. Because the effect of increasing soot carbon concentration and decreasing bioavailability was not overtly apparent (Figure 4), we evaluated other factors such as the PAH source on BSAF values. We examined the effect of PAH source on bioavailability using the amended sediment, with constant SC content (0.29–0.30). We found that the effect of SC content on PAH bioavailability was overwhelmed by the change in PAH source (Table 4), although the effect was still only observed with pyrogenic PAHs rather than for petrogenic PAHs. While there was some decrease in petrogenic BSAF values as f_{sc} was increased, the effect was not as marked as for pyrogenic PAHs. For example, with the unamended marine sediment (collected from a source different from that presented in Figure 1b), the difference between the availability of petrogenic and pyrogenic PAHs was consistent; however, the pyrogenic PAHs were more bioavailable in the unamended sediment than in sediment amended with SC. As the fraction of SC was increased from the unamended sediment (0.04) to each of the three amended sediments (0.29–0.30), the bioavailability of the pyrogenic PAHs decreased, but the lower BSAF values did not remain consistent as the PAH source changed and the f_{sc} was held constant. This relation was described best by the BSAF of the pyrogenic PAH BeP varying from 0.57 in low SC, unamended sediment, to 0.28 in high SC sediment amended with diesel soot. However, when PAH source changed with no change in f_{sc}, the BSAF decreased to 0.09 for sediment amended with urban dust and sediment amended with oil-fired power plant soot. This result was particularly interesting because urban dust can contain diesel soot or diesel-based combustion products (e.g., from diesel vehicles; *42*). The variation in BSAF values that occurred when the source of the amended quantity changed but SC content remained constant suggests that PAH source is an important factor influencing bioavailability, perhaps more than both f_{sc} and PAH hydrophobicity. The

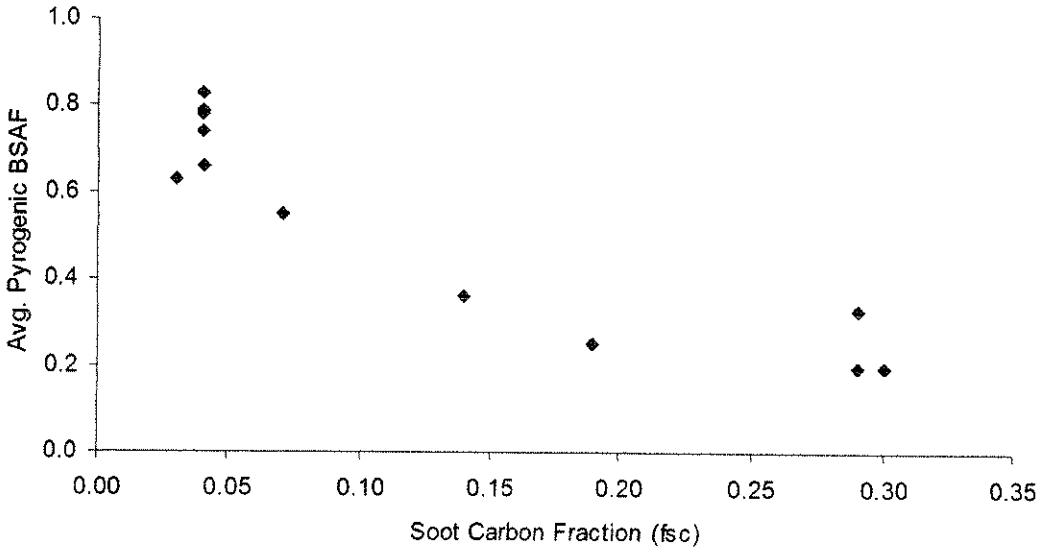

FIGURE 4. Average BSAF values for pyrogenic PAH vs soot carbon content for all freshwater and marine sites. The relationship between BSAF value and increasing soot carbon content was weaker than expected, suggesting that the PAH source may also contribute to the decreased bioavailability of pyrogenic PAH.

TABLE 4. BSAF Values for *M. arenaria* as a Function of Differing Soot Carbon Content of Sediment and PAH Source

	unamended	diesel soot[a]	urban dust[a]	oil-fired power plant soot[a]
f_{sc}	0.04	0.29	0.29	0.30
N0	1.51	1.28	1.29	1.03
N1	1.24	1.27	1.32	0.90
N2	1.64	1.23	1.09	0.82
N3	1.77	1.55	1.21	0.92
N4	1.62	1.44	1.14	0.88
AY	0.42	0.31	0.22	0.16
AC	0.51	0.26	0.09	0.14
F0	1.36	1.51	1.05	0.84
F1	1.75	1.53	1.46	1.22
F2	1.48	1.18	1.29	1.07
F3	1.30	1.42	1.38	1.18
D0	1.57	1.15	1.05	0.91
D1	1.49	1.21	1.36	0.82
D2	1.33	1.07	1.27	0.93
D3	1.20	1.19	0.94	1.04
P0	0.42	0.47	0.11	0.08
P1	1.36	1.41	1.36	0.99
P2	1.44	1.20	1.06	1.08
P3	1.59	1.65	0.96	0.88
P4	1.57	0.95	1.14	1.16
AN	0.60	0.12	0.08	0.08
FL	0.73	0.27	0.13	0.13
FP1	0.89	0.39	0.20	0.15
PY	1.25	1.15	1.01	0.97
BaA	0.72	0.28	0.17	0.17
C0	1.03	0.84	0.33	0.38
C1	1.18	0.88	0.72	0.49
C2	1.27	1.07	0.82	0.58
C3	1.34	1.12	1.15	0.72
BbF	0.62	0.26	0.13	0.14
BkF	0.57	0.37	0.24	0.17
BeP	0.57	0.28	0.09	0.09
BaP	0.45	0.17	0.08	0.07
PE	0.46	0.21	0.17	0.14
IP	0.29	0.14	0.08	0.06
DA	0.49	0.18	0.12	0.12
BgP	0.78	0.24	0.16	0.17
CO	0.90	0.14	0.11	0.10

[a] Source of soot carbon used for sediment amendment.

differences in BSAF values that were observed with changes in PAH source were most likely related to differing compositions of starting material, combustion temperature, and weathering. For example, diesel soot is formed at lower burning temperatures than urban dust and oil-fired power plant soot. Moreover, diesel soot PAH signatures exhibit less weathering than urban dust PAH patterns (*43*). These unique properties make establishing a quantitative BSAF model that accounts for f_{sc}, as previously presented in eq 2, difficult among environmental sites. Measuring SC content of field collected sediments may be helpful only in a qualitative sense for evaluating bioavailability because SC appears to have little effect on the bioavailability of petrogenic PAH and its overall effect on pyrogenic PAH can be overridden by the specific source of the PAH or SC.

Applicability of Modified BSAF Model among Ecosystem Types. Due to the greater influence of PAH source relative to SC content or PAH hydrophobicity in bioavailability assessments in this study, the use of the modified BSAF model as presented in this paper may not be applicable among a wide range of ecosystem types, including those with differing f_{sc} values and PAH sources. The utility of a model requires that variables existing among different locations be accounted for in a reasonable and simplistic way. For example, the traditional method of normalizing sediment HOC concentrations to sediment organic carbon allows comparison of HOC concentrations among different sites (though PAHs are frequently an exception to this). Based on the data presented in this paper, it is uncertain whether a PAH–SC bioavailability model can be developed that can be applied universally among sites with differing SC concentrations and sources of PAH. However, additional research on determining actual K_{sc} values and the applicability of laboratory-derived K_{sc} values to field settings must be considered. Competitive interactions in the environment, such as those between other HOCs and NOM for SC active sites, should be studied to advance our overall understanding of the mechanisms involved between contaminants and SC in the environment. Our data show only moderate decreases in bioavailability with subsequent increases in SC content in sediment, typically with BSAF values declining by factors of 2–3 with substantial increases in SC (e.g., nearly an 8-fold increase in f_{sc}, Table 4). This brings into question the toxicological relevance of SC as a major player in site hazard assessment and remediation technologies.

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Literature Cited

(1) Neff, J. M. *Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*; Applied Science: London, UK, 1979.
(2) Page, D. S.; Boehm, P. D.; Douglas, G. S.; Bence, A. E.; Burns, W. A.; Mankiewicz, P. J. *Mar. Pollut. Bull.* **1999**, *38*, 247.
(3) Baumard, P.; Budzinski, H.; Garrigues, P. *Environ. Toxicol. Chem.* **1998**, *17*, 765.
(4) Dickerson, R. L.; Hooper, M. J.; Gard, N. W.; Cobb, G. P.; Kendall, R. J. *Environ. Health Perspect.* **1994**, *102* (Suppl.), 65.
(5) Trust, K. A.; Fairbrother, A.; Hooper, M. J. *Environ. Toxicol. Chem.* **1994**, *13*, 821.
(6) Ward, E. C.; Murray, M. J.; Lauer, L. D.; House, R. V.; Irons, R.; Dean, J. H. *Toxicol. Appl. Pharmacol.* **1984**, *75*, 299.
(7) Goldberg, E. D. *Black Carbon in the Environment*; Wiley: New York, 1985.
(8) Broman, D.; Naf, C. *Chemosphere* **1990**, *21*, 69.
(9) James, M. O. In *Metabolism of Polycyclic Aromatic Hydrocarbons in the Aquatic Environment*; Varanasi, U., Ed.; CRC Press: Boca Raton, FL, 1989; p 78.
(10) Chung, N.; Alexander, M. *Environ. Sci. Technol.* **1999**, *33*, 3605.
(11) Alexander, M. *Environ. Sci. Technol.* **2000**, *34*, 4259.
(12) Landrum, P. F. *Environ. Sci. Technol.* **1989**, *23*, 588.
(13) Landrum, P. F.; Hayton, W. L.; Lee, H., II; McCarty, L. S.; Makay, D.; McKim, J. M. In *Bioavailability: Chemical, Physical and Biological Interactions*; Hamelink, J. L., Ed.; Lewis Publishers: Boca Raton, FL, 1994; p 203.
(14) Ferarro, S. P.; Lee, H. II.; Ozretich, R. J.; Specht, D. T. *Arch. Environ. Contam. Toxicol.* **1990**, *19*, 386.
(15) Krauss, M.; Wilcke, W.; Zech, W. *Environ. Sci. Technol.* **2000**, *34*, 4335.
(16) Alexander, M. *Environ. Sci. Technol.* **1995**, *29*, 2713.
(17) Luthy, R. G.; Aiken, G. R.; Brusseau, M. L.; Cunningham, S. D.; Gschwend, P. M.; Pignatello, J. J.; Reinhard, M.; Traina, S. J.; Weber, W. J., Jr.; Westall, J. C. *Environ. Sci. Technol.* **1997**, *31*, 3341.
(18) Wong, C. S.; Capel, P. D.; Nowell, L. H. *Environ. Sci. Technol.* **2001**, *35*, 1709.
(19) Bucheli, T. D.; Gustafsson, O. *Environ. Sci. Technol.* **2000**, *34*, 5144.
(20) Accardi-Dey, A.; Gschwend, P. M. *Environ. Sci. Technol.* **2002**, *36*, 21.
(21) Gustafsson, O.; Haghseta, F.; Chan, C.; Macfarlane, J.; Gschwend, P. M. *Environ. Sci. Technol.* **1997**, *31*, 203.
(22) McGroddy, S. E.; Farrington, J. W.; Gschwend, P. M. *Environ. Sci. Technol.* **1996**, *30*, 172.
(23) Boese. B. L.; Lee, H., II; Specht, D. T.; Pelletier, J.; Randall, R. *Environ. Toxicol. Chem.* **1996**, *15*, 1584.
(24) Maruya, K. A.; Risebrough, R. W.; Horne, A. J. *Environ. Toxicol. Chem.* **1997**, *16*, 1087.
(25) Luehrs, D. C.; Hickey, J. P.; Nilsen, P. E.; Godbole, K. A.; Rogers, T. N. *Environ. Sci. Technol.* **1996**, *30*, 143.
(26) Short, J. W.; Jackson, T. J.; Larsen, M. L.; Wade, T. L. In *Proceedings of The Exxon Valdez Oil Spill Symposium*; Rice, S. D., Spies, R. B., Wolfe, D. A., Eds.; American Fisheries Society: Bethesda, MD, 1996.
(27) Lamoureux, E. M.; Brownawell, B. J. *Environ. Toxicol. Chem.* **1999**, *18*, 1733.
(28) Krauss, M.; Wilcke, W.; Zech, W. *Environ. Sci. Technol.* **2000**, *34*, 4335.
(29) Karickhoff, S. W. *Chemosphere* **1981**, *10*, 833.
(30) Geyer, H.; Sheehan, P.; Kotzias, D.; Feitag, D.; Korte, F. *Chemosphere* **1982**, *11*, 1121.
(31) Obana, H.; Nakamura, S.; Kashimoto, T. *Water Res.* **1983**, *17*, 1183.
(32) Pruell, R. J.; Lake, J. L.; Davis, W. R.; Quinn, J. G. *Mar. Biol.* **1986**, *91*, 497.
(33) Thorsen, W. A. Ph.D. Dissertation, North Carolina State University, 2003.
(34) Narbonne, J. F.; Djomo, J. E.; Ribera, D.; Ferrier, V.; Garrigues, P. *Ecotoxicol. Environ. Saf.* **1999**, *42*, 1.
(35) Bucheli, T. D.; Gustafsson, O. *Environ. Toxicol. Chem.* **2001**, *20*, 1450.
(36) Downs, C. A.; Shigenaka, G.; Fauth, J. E.; Robinson, C. E.; Huang, A. *Environ. Sci. Technol.* **2002**, *36*, 2987.
(37) McMahon, R. F.; Bogan, A. E. In *Ecology and Classification of North American Freshwater Invertebrates*, 2nd ed.; Thorp, J. H., Covich, A. P., Eds.; Academic Press: New York, 2001; Chapter 11.
(38) Ghosh, U.; Talley, J. W.; Luthy, R. G. *Environ. Sci. Technol.* **2001**, *35*, 3468.
(39) Ghosh, U.; Gillette, J. S.; Luthy, R. G.; Zare, R. N. *Environ. Sci. Technol.* **2000**, *34*, 1729.
(40) Gustafsson, O.; Gschwend, P. M. In *Molecular Markers in Environmental Geochemistry*; Eganhouse, R. P., Ed.; American Chemical Society: Washington, DC, 1997; p 365.
(41) Gustafsson, O.; Gschwend, P. M. In *Bioavailability of Organic Xenobiotics in the Environment: Practical Consequences for the Environment*; Baveye, P., Block, J. C., Goncharuk, V. V., Eds.; Kluwer Academic Publishers: Norwell, MA, 1999; p 327.
(42) Fernandes, M. B.; Skemstad, J. O.; Johnson, B. B.; Wells, J. D.; Brooks, P. *Chemosphere* **2003**, *51*, 785.
(43) Burns, W. A.; Mankiewicz, P. J.; Bence A. E.; Page, D. S.; Parker, K. R. *Environ, Toxicol, Chem.* **1997**, *16*, 1119.
(44) Neff, J. M.; Burns, W. A. *Environ. Toxicol. Chem.* **1996**, *15*, 2240.
(45) Gustafsson, O.; Haghseta, F.; Chan, C.; Macfarlane, J.; Gschwend, P. *Environ. Sci. Technol.* **1997**, *31*, 203.
(46) Bucheli, T. D.; Gustafsson, O. *Environ. Sci. Technol.* **2000**, *34*, 5144.

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