# Quantification of the Dilute Sedimentary Soot Phase: Implications for PAH Speciation and Bioavailability

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Existing field data indicate that soot may significantly affect the environmental speciation of polycyclic aromatic hydrocarbons (PAHs). To expand hydrophobic partition models to include soot partitioning, we need to quantify $f_{sc}$, the soot fraction of the solid matrix, and $K_{sc}$, the soot-carbon-normalized partition coefficient. To this end, we have developed a method that allows quantification of soot carbon in dilute and complex sedimentary matrices. Non-soot organic carbon is removed by thermal oxidation, and inorganic carbonates are removed by acidification, followed by CHN elemental analysis of the residual soot carbon. The selectivity of the soot carbon method was confirmed in tests with matrices of known compostion. The soot quantification technique was applied to two sets of natural sediments, both previously analyzed for PAHs. The input histories of PAHs and soot recorded in a lacustrine sediment core followed the same general trends, and we thus infer a coupling between the two. Our measures of $f_{sc}$ and calculations of $K_{sc}$, approximated from studies of PAH sorption onto activated carbon, were applied to rationalize previously generated *in situ* $K_{oc}$ values. Intriguingly, we find that the elevated PAH $K_{d}$ values of two marine sediment−porewater systems are now quantitatively explainable through the extended, soot-partitioning inclusive, distribution model. The importance of the soot phase for PAHs in the environment has implications for how we perceive (and should test) *in situ* bioavailability and, consequently, also for the development of sediment quality criteria.

## Introduction

There are numerous indications in existing field data that soot-like phases may significantly affect the environmental PAH speciation. Socha and Carpenter (*4*) were not able to detect any porewater PAHs at a site contaminated by pyrogenic sources, despite expectations from $f_{oc}K_{oc}$ calculations ($f_{oc}$, the organic carbon fraction of the solid matrix, and $K_{oc}$, the organic-carbon-normalized partition coefficient; refs 5−7) of considerable porewater PAHs. They attributed this to the association of PAHs with soot. Several recent field investigations have reported $K_{oc}$ values for PAHs that are much larger than predictions based on organic matter partitioning

models (*5*−*7*) (Figure 1a). These studies were performed in many different settings, including lake (*8*), estuarine (*9*), and marine (*10*) surface waters, sediment pore waters (*2, 3*), and rain water (*11*). These results suggest the presence of a particulate phase like soot to which PAHs are significantly stronger associated than with natural organic matter. Since these data still indicate an influence of sorbate hydrophobicity (e.g., $K_{ow}$) on the reported $K_{oc}$ values, it may be concluded that an exchange between the "super-sorbent" and solution phases is taking place. In contrast, field-obtained $K_{oc}$ values for similarly hydrophobic polychlorinated biphenyls (PCBs) are typically lower and agree better with the organic-matter-based partition model predictions (*2, 3, 8, 11, 14*).

In order to rationalize the elevated $K_{d}$ values commonly observed for PAHs from the field, we suggest that the hydrophobic partitioning framework be expanded to also include partitioning with anthropogenic soot phases:

$$K_{d} = f_{oc}K_{oc} + f_{sc}K_{sc} \qquad (1)$$

where $f_{sc}$ is the soot carbon fraction of the solid matrix (g of soot carbon/g of solid) and $K_{sc}$ is the soot-carbon-normalized partition coefficient [(mol/g of soot) × (mol/mL of solution)$^{-1}$]. Hence, to model accurately the environmental fate of compounds like PAHs that appear to exhibit high affinities for soot, two new parameters, $f_{sc}$ and $K_{sc}$, may need to be constrained. While we know of no controlled investigations on soot−water partitioning of PAHs, sorption studies onto activated carbon have been reported (Figure 1b) (*1, 15*). Mass-normalized activated carbon−aqueous solution partition coefficients, $K_{ac}$, for PAHs, calculated from such studies, resemble the elevated partition coefficients observed in the environment for combustion-derived compounds like PAHs. If we thus assume that $K_{sc}$ can be reasonably approximated by the $K_{ac}$ values derived in Figure 1b, then the only other parameter required to investigate quantitatively the importance of soot partitioning for PAH speciation is the environmental soot abundance, $f_{sc}$.

It is the primary objective of this paper to describe a method that allows quantitative estimation of this dilute soot phase in complex environmental matrices. We then apply this method to natural sediments and demonstrate the potential importance of a soot sorbent phase to estimating the environmental behavior and effects of combustion-derived contaminants like PAHs.

## Experimental Section

**Background.** As pointed out by Ed Goldberg in his book, *Black Carbon in the Environment*, there is no unambigious definition of the highly condensed carbonaceous residue from incomplete combustion processes (*17*). The myriad of existing descriptors (soot, smoke, black carbon, carbon black, charcoal, spheroidal carbonaceous particles, elemental carbon, graphitic carbon, and charred particles) reflect either the functional processes studied or the operational techniques employed by different investigators. With the present objective of understanding PAH speciation, a method is warranted that quantitatively recovers the total mass of PAH-carrying soot carbon from dilute environmental matrices like sediments without inclusion of carbon from carbonates and biogenic organic matter.

Previous analytical approaches may be divided into three broad categories: (i) particle counting of dilute sedimentary soot, (ii) thermal carbon determination of abundant atmospheric soot, and (iii) spectroscopical structural investigation of pure soot. Sedimentary soot studies characteristically involve an acid digestion and oxidation treatment, followed

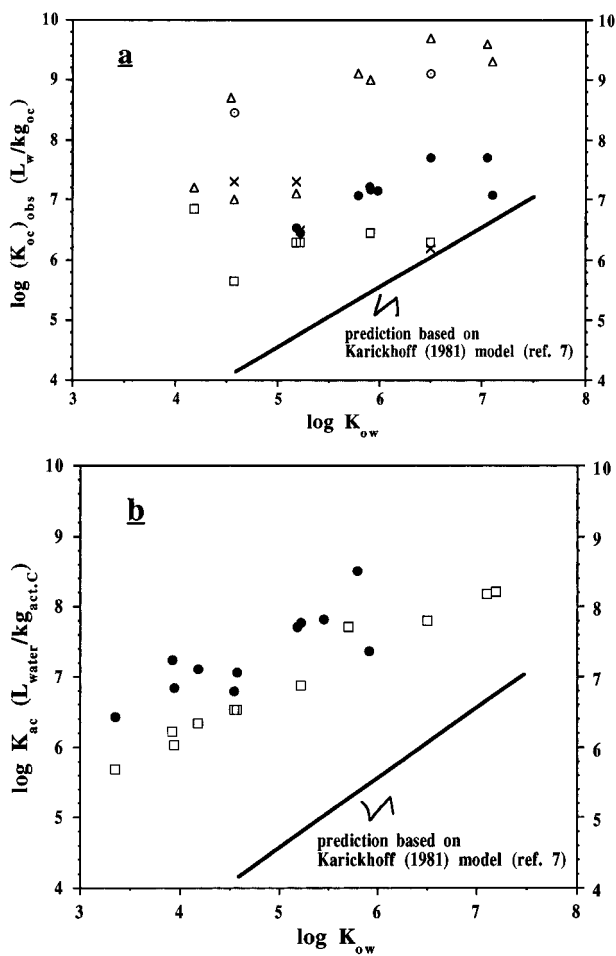* Corresponding author telephone: 617-253-1638; fax: 617-253-7395.

**FIGURE 1.** (a) *In situ* PAH $K_{oc}$ values observed in several different types of environmental regimes: estuarine (dotted open circles, ref 9), lacustrine (open squares, ref 8), and marine (filled circles, ref 10) surface waters, rainwater (open triangles, ref 11), and sediment porewater (crosses, refs 2 and 3). (b) Calculated activated-carbon partition coefficients ($K_{ac}$) for a range of PAHs (open squares, ref 15; filled circles, ref 1). The $K_{ac}$ values from ref 1 were calculated using the linearized Langmuir equation for the low equilibrium PAH concentration range; this case appears most applicable to environmental levels and Walters and Luthy (1) found this form to best represent their isotherm data. $K_{ow}$ values for both (a) and (b) are from refs 5, 12, 13, and 16).

by microscopical soot particle counting (*18−21*). Using this approach, Goldberg and co-workers have recreated the historical "charcoal" record of forest fires in cores from Lake Michigan and the pelagic ocean (*18, 22*). The spatial and temporal history of anthropogenic fossil fuel combustion has similarly also been investigated (*21−23*). In the only previous study to have investigated directly the importance of soot on PAH distribution in natural waters, a correlation between the particulate concentration of individual PAHs and the abundance of such large spheroidal carbonaceous particles was indeed found in an urban estuary (*24*). However, these microscopy-based methods are commonly limited to soot particles $>5−10 \mu$m. Since it has been shown that most soot particles in the atmosphere are smaller than a few microns (*25*), only analyzing the coarse fraction of soot prevents quantitative interpretation of such studies in terms of a PAH partition model.

The atmospheric soot methods are typically based on identifying the temperature conditions where organic carbon (OC) is thermally destabilized, while the soot carbon (SC) is still intact (*26, 27*). While a selective thermal approach may recover a substantial fraction of the whole SC mass, the current methods, developed primarily for atmospheric particles and

forest fire residues, are not directly applicable to a complex sedimentary matrix. It is important to consider the differences between soot-laden atmospheric particles and dilute sedimentary samples. Atmospheric particles contain high levels of SC, and the organic fraction is comprised primarily of sorbed low molecular weight molecules, which are easy to thermally degrade or volatilize. To determine accurately dilute SC in sediments using a thermal approach, the method needs to be developed and tested for its suitability in the presence of recalcitrant macromolecular organic matter, physically large solids, and large abundance of carbonate minerals (see Table 1).

Spectroscopical investigations of soot have been aimed at obtaining qualitative structural information (*28, 29*). Such techniques might reveal properties of the exterior of SC. They do not yield quantitative measures needed for the present investigation.

The approach taken in this study to determine the dilute sedimentary soot phase is based on thermal oxidation of OC, followed by release of inorganic carbonates (IC) via *in situ* acidification. The residual SC is then quantified by CHN elemental analysis.

**Removal of OC.** Samples were dried in covered containers at 60 °C and ground to $<500 \mu$m individual particle size. About 50 mg of each sample was weighed into pretared porcelain crucibles with a silica glaze surface (Coors Ceramics, Golden, CO). A rack of up to eight crucibles, covered with precombusted aluminum foil, was placed inside a muffle furnace (Thermolyne Model F-A1730 equipped with an auxiliary temperature controller Thermolyne Furnatrol 133, Sybron Corp., Dubuque, IA). All samples were oxidized at 375 °C for 24 h in the presence of excess oxygen (air).

**Removal of IC.** The cooled samples were subsampled and weighed (1−10 mg, depending on availability of residue and expected C content) into pretared Ag capsules (D2029, 8 × 5 mm; Elemental Microanalysis Ltd., Manchester, NH) using an electrical microbalance (Cahn 25 Automatic Electrobalance; Ventron Corp., Cerritos, CA). Throughout the acidification procedure, the Ag capsules were kept in a home-built Al tray with 32 positions. Several method blanks and standards (acetanilide) were included in each batch of samples. A microdispenser with a glass capillary tube was used in adding low-C water (Aries Vaponics, Vaponics Corp., Rockland, MA) and acid for the *in situ* removal of IC. After wetting each sample with 25 $\mu$L of water, 25 $\mu$L of 1 M HCl was added into each Ag capsule. Then, the samples were allowed to sit for 1 h at room temperature covered with clean Al foil. When the capsules had cooled, another 50 $\mu$L of 1 M HCl was added, followed by 30 min of cooling. The Al tray with samples was then placed in an oven and dried at 60 °C. The last three steps were repeated until effervescence upon acid addition ceased, indicating complete removal of carbonates. As pointed out by Nieuwenhuize *et al.* (*30*), this type of carbon determination, using *in situ* acidification, is advantageous in that it eliminates reweighing procedures, consumes only about 10 mg of sample per analysis, and importantly, avoids losses of acid-soluble organic material to transitory containers.

**CHN Elemental Analysis.** The composition of the prepared samples was determined using a PE 2400 CHN elemental analyzer (Perkin Elmer Corp., Norwalk, CT). The detection limit of the analyzer (i.e., instrument blank) was about 4 $\mu$g of C. Response factors were determined using an acetanilide standard (relative standard deviation within batches was ca. 0.3%). Sample preparation blanks were determined with each batch (for entire project: 9.6 ± 4.4 $\mu$g of C, $n = 19$) and subtracted from raw sample data. Tests in which temperature and duration of combustion were varied verified that the same set of standard operating procedures could be used for quantitative C determination of all samples, irrespective of the soot content. Quantitative oxidation of

**TABLE 1. Results of Testing the Soot Carbon Method with Matrices of Known Composition**

| sample | OC + SC (g of C/g of sample) | SC (g of C/g of sample) | SC / (OC + SC) |
|---|---|---|---|
| NIST diesel particulate matter | $0.822 \pm 0.019$ | $0.777 \pm 0.031$ | 0.95 |
| humic acid | $0.455 \pm 0.014$ | $0.00069 \pm 0.00025$ | 0.0015 |
| acetanilide | $0.715 \pm 0.003$ | no residue | <0.0001 |
| polystyrene | $0.914 \pm 0.007$ | no residue | <0.0001 |
| polyethylene | $0.862 \pm 0.005$ | no residue | <0.0001 |
| oak | $0.466 \pm 0.013$ | $0.00008 \pm 0.00006$ | 0.0002 |
| fuel oil, diesel no. 2 | (0.8) ? | no residue | <0.0001 |
| crude oil, Gullfax North Sea | (0.8) ? | no residue | <0.0001 |
| corn pollen, starchy | $0.344 \pm 0.016$ | 0.28 | 0.82 |
| corn pollen, waxy | 0.37 | 0.10 | 0.28 |
| Green River Shale kerogen | 0.75 | no residue | <0.0001 |
| Kimberlite kerogen | 0.65 | <0.0001 | <0.0002 |
| Beulah-Zap lignite | $0.535 \pm 0.003$ | 0.00016 | 0.00031 |
|    Argonne Nat'l Lab Coal no. 8 vitrinite reflectance 0.28 | | | |
| Pittsburgh seam coal | $0.712 \pm 0.036$ | 0.0028 | 0.0039 |
|    Argonne Nat'l Lab Coal no. 4 vitrinite reflectance 0.81 | | | |
| Pocahontas anthracite | $0.762 \pm 0.052$ | 0.0034 | 0.0045 |
|    Argonne Nat'l Lab Coal no. 5 vitrinite reflectance 1.42 | | | |
| activated carbon (mesh 4−12) | 0.67 | 0.068 | 0.10 |
| activated carbon (mesh 12−20) | $0.82 \pm 0.05$ | 0.14 | 0.17 |
| activated carbon (mesh 20−40) | $0.66 \pm 0.03$ | 0.35 | 0.53 |
| activated carbon (100+ mesh) | $0.899 \pm 0.004$ | $0.54 \pm 0.04$ | 0.60 |
| car tire (Cooper, 30 ± 2% carbon black) | $0.862 \pm 0.003$ | $0.33 \pm 0.3$ | 0.38 |

soot by this instrumental method was indicated by a yield of 82% C upon analysis of weighed standard soot (Table 1), well within the 75−90% range commonly found on soot particles (*31*).

**Elucidation of Optimal Combustion Temperature.** The first analytical objective was to constrain the temperature where natural organic matter was thermally unstable while soot mass was preserved intact. As SC, we employed National Institute of Standards & Technology (NIST) Standard Reference Material 1650: diesel particulate matter (NIST, Gaithersburg, MD). Initial characterization of this soot standard using photon correlation spectroscopy (N4 submicron particle analyzer, Coulter Electronics, Hialeah, FL) yielded an average soot size in sonicated ethanol suspensions of $180 \pm 20$ nm. Scanning electron microscopy (SEM) of this standard indicated a primary particle size of 30 nm, with aggregates up to 400 nm. To represent natural OC, we used humic acid (Aldrich Chemical Co.; Milwaukee, WI). Based on the recoveries of these two standards, the optimal temperature selectivity was elucidated through a set of runs where the combustion temperature was systematically varied while keeping all other parameters constant.

**Method Testing with Well-Characterized Matrices.** The suitability of the method to sedimentary SC quantification was assessed through testing with several rather well-characterized substances, which could be considered as representing different components of complex sedimentary organic matter or anthropogenic combustion "phases" (see Table 1). Two organic polymers, polystyrene and polyethylene, were obtained by the fine-shredding of a coffee cup and a milk bottle, respectively. Fine dust of oak wood was similarly prepared from a cleaned piece of lumber. Starchy and waxy corn pollen were from Carolina Biological Supply (Burlington, NC). Fuel oil (diesel no. 2) and crude oil (Gullfax field, North Sea) were both tested. We also analyzed an unused car-tire (vulcanized rubber) sample containing $30 \pm 2\%$ carbon black (Bernard Chien, Cooper Tire, Findlay, OH, personal communication). A number of coal matrices of increasing maturity were tested. Two well-studied kerogens, Green River shale and Kimberlite (e.g., ref 32), were analyzed. Three samples were also tested from the well-characterized Argonne National Laboratory's Premium Coal Series: Beulah-Zap (a lignite), Pittsburgh seam, and Pocahontas (an anthracite). As an indicator of the maturity of the coal, the

vitrinite reflectances of these samples were 0.28, 0.81, and 1.42, respectively (*Users' Handbook for Argonne Premium Coals*; L. Eglinton, Woods Hole Oceanographic Institution, Woods Hole, MA, personal communication). Finally, we analyzed the OC−SC distribution of four activated carbon samples of decreasing particle size: mesh 4−12, 12−20, 20−40 (Darco; Aldrich Chemical Co.), and mesh 100+ (Norit A; Aldrich Chemical Co.).

**Method Application to Natural Sediments.** As a final test of the the soot quantification technique, we applied the method to two sets of natural sediments, both previously analyzed for PAHs. First, SC was determined in two Boston Harbor sediment subsamples (0−2 cm near Spectacle Island at 42°20′N 71°00′ W and 7−9 cm of Fort Point Channel at 42°21′ N 71°03′ W), in which McGroddy and co-workers (*2, 3*) had previously found peculiarly elevated PAH partition coefficients (Figure 1a). Second, a profile of sedimentary SC was obtained from an Upper Mystic Lake (42°26′ N 71°06′ W) sediment core, which has been radiometrically dated (*33*), and for which we have measured individual PAHs. For PAH analysis, 5−10 g of the extruded wet sediment was spiked with deuterated PAH recovery standards. The recoveries were phenanthrene-$d_{10}$ $96 \pm 20\%$, terphenyl-$d_{14}$ $101 \pm 30\%$, and perylene-$d_{12}$ $80 \pm 26\%$. Following a 1-h $CH_3OH$ soak in the Soxhlet, the sediment was Soxhlet-extracted for 24 h in 90:10 $CH_2Cl_2$−$CH_3OH$, followed by 24 h in pure $CH_2Cl_2$. The concentrated and combined extracts were eluted on gravity columns containing $NaSO_4$ (anhydrous) and neutral alumina. The PAHs were eluted in the second fraction with 50 mL of hexane−$CH_2Cl_2$ and quantified by GCMS (HP 5995B).

In response to the potential interference of pollen (Table 1), independent quantification of pollen and spores in the sediment samples was conducted by Richard Orson (Environmental Consulting, Branford, CT). Pollen analysis (sediment digestion, mounting, counting, and identification) followed published methods (*34, 35*).

## Results and Discussion

**Optimization of Temperature Conditions for SC−OC Separation.** The combustion temperature with optimal selectivity between OC and SC was found by comparing the recovered C mass in samples of NIST soot or Aldrich humic acid over the temperature range 275−450 °C. The humic acid OC was
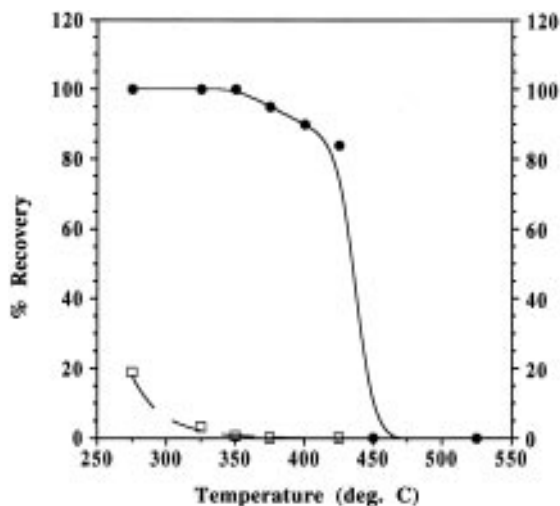
FIGURE 2. Recoveries of soot C (dark circles) and humic acid organic C (open squares) as a function of increasing oxidation temperature.

found to be significantly more labile than SC (Figure 2). For the humic acid, only one-fifth of the OC was preserved at 275 °C, and a mere 0.15% of the carbon mass was recovered at 375 °C. The soot was significantly more recalcitrant with 95% preserved at 375 °C, and 84% still remained at 425 °C. SC was only quantitatively oxidized at 450 °C (0.06% recovered C). Based on these results, we chose to use 375 °C to distinguish between OC and SC. While a very small amount of OC still may be included in this operational SC (≈0.15% of humic OC preserved) and a small amount of soot-matrix carbon may be excluded (≈5% of NIST diesel particle C lost), these conditions appear suitable to minimize interference of OC matrices on SC while giving an estimate of SC applicable to investigation of its role in PAH speciation. A similar temperature (340 °C) was found in a previous study to be suitable for the oxidative thermal separation of OC from black carbon residues of forest fires (27).

**Method Testing with Well-Characterized Matrices.** Due to the complexity of aquatic sediments and the interference potential of some of their constituents, the method was tested with several known matrices (Table 1). These samples may be divided into two categories. First, samples whose reduced carbon content may be classified as exclusively OC; in addition to humic acid and acetanilide, this group includes plastic polymers, oak wood, pollens, oils, and coals. Second, samples that contain carbon of soot-like structure; in addition to the NIST diesel particulate matter, this includes the activated carbon samples and the car tire (containing a significant amount of carbon black). In Table 1, the results are presented for each sample's total reduced carbon content prior to the thermal treatment (i.e., OC + SC) as well as after the complete pretreatment procedure (i.e., SC). The ratio SC/(OC + SC) reflects the potential of a component of the natural organic matter category to be included in the SC pool. For the OC samples, this "interference potential" would also indicate if an organic matter matrix was significantly "charred" by the method to produce SC.

The precision of the data was typically in the range of 1–3% (expressed as the relative standard deviation). For the organic matter samples, interference potentials were 0–0.5% (except for pollen; see discussion below). This result is quite sufficient since we find that SC/OC in coastal marine sediments is about 10% and in a historical lacustrine sediment is 2–6% (see below).

The significant interference potential of corn pollen inspired us to obtain an independent estimate of pollen abundance in the natural sediments where we were measuring SC in order to evaluate whether such results could be compromised by pollen. The recalcitrancy of pollen observed

over geological time scales has been traced to sporopollenin, oxidized polymers of carotenes and carotene esters, present in the pollen wall (36). The 48–50 cm depth Mystic Lake sediment sample was found to contain 87 000 pollen grains/g dry weight. Dominant species were oak, birch, pine, fern, and ambrosia, with an average upper diameter of 35 μm. Using the measured carbon content of corn pollen (ca. 35%), a specific gravity of pollen at 1.4 (ref 35), and assuming a spherical shape, we can estimate that this lacustrine sediment contains about 0.0010 g of pollen C in each gram of dry sediment. Assuming that half of the pollen C may be quantified as SC (Table 1), we estimate that such pollen levels may account for one-quarter to one-tenth of the SC measured in Mystic Lake (see below). Thus, we conclude that the presence of pollen does not appear to compromise appreciably the dilute SC quantification at this lacustrine site. In the 7–9 cm Fort Point Channel sediment (Boston Harbor), two samples gave pollen counts of 23 000 and 22 000 grains/g of dry sediment, respectively. This represents over 1 order of magnitude lower pollen C than SC concentrations in this marine sediment and thus no risk of interference from pollen on the SC findings.

Analysis of the five coal samples with our methodology yielded an insignificant return of SC but did indicate an influence of coal maturity on the SC results. Consistent with their degree of condensation, as indicated by increasing vitrinite reflectances, the lignitic samples produced the lowest apparent SC recovery and the anthracite produced the highest (Table 1).

The activated carbon sample series also provided a notable trend. While these samples contained both OC and SC, the smaller the grain size, the higher the relative soot content. If charring were occurring, as a result of reaction-limiting diffusional transport of oxygen during our thermal treatment, the opposite trend would have been expected; larger grain sizes with smaller surface area to volume ratios would have resulted in incomplete OC oxidation/volatilization. We found the opposite trend and interpret it to be related to how the activated carbon is produced. In activated carbon manufacturing, some woody tissues (e.g., coconut shells) are fragmented and pyrolyzed. It is likely that there will be more complete conversion to SC for smaller fragments (larger the mesh number) as a result of larger surface area to volume ratios. Hence, the activated carbon results suggest that charring is insignificant with our method and that, to simulate soot partitioning using activated carbon sorbents, the smallest particle size should be employed.

In summary, testing of our method with substances representative of complex sedimentary components demonstrate that our SC measurements are likely free of significant interference from either charring or recalcitrant OC. These results with well-characterized matrices lend credence to the suitability of this method for quantifying dilute soot in natural regimes.

**Application to Natural Samples.** The developed soot method was used to investigate two natural sediments with previously determined (a) historical PAH input (Mystic Lake) and (b) PAH partitioning behavior (Boston Harbor).

*Mystic Lake.* The PAH depositional history, as recorded in the Mystic Lake core (Figure 3a), is temporally similar to previous sediment core observations of historical PAH loadings (37–40). The concentrations of individual PAHs range from a maximum around 10 μg/g to less than 10 ng/g at the core bottom. The relative compound abundances are indicative of combustion being the dominant source throughout the core. For example, the (methylfluoranthenes + methylpyrenes)/fluoranthene ratio was relatively consistent at 0.29 ± 0.06. A value for this ratio of 0.24 has been measured on pure soot (41). In contrast, this ratio would be expected to be above unity if the source was direct petroleum contamination (42, 43).
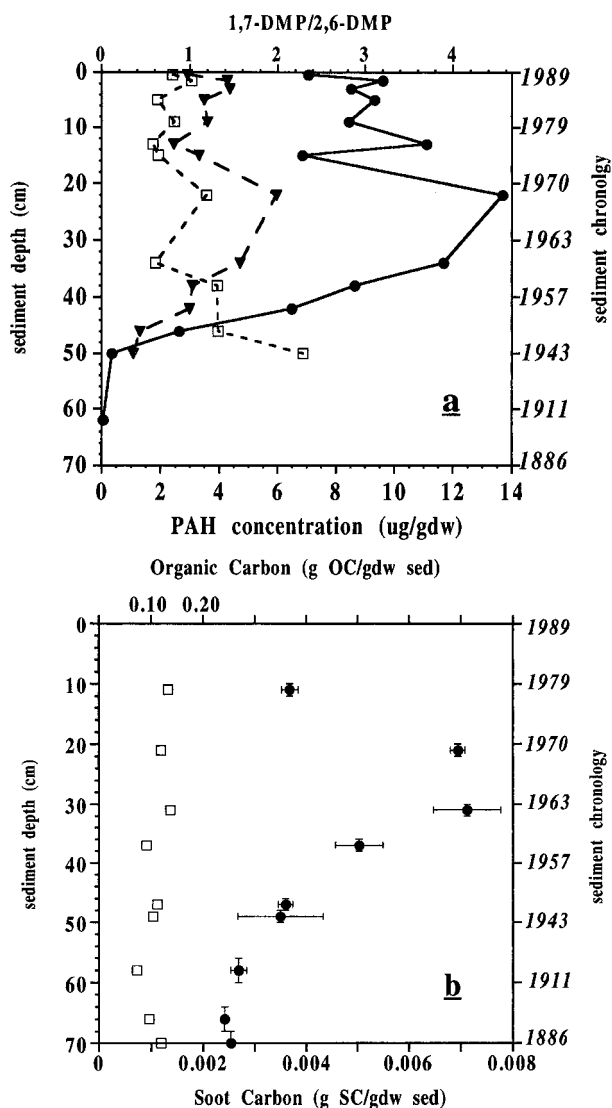
FIGURE 3. (a) Upper Mystic Lake profiles of pyrene (dark circles), benzo[a]pyrene (dark inverted triangles), and the ratio of the 1,7- to 2,6-dimethylphenanthrene isomers (open squares). (b) Mystic Lake profiles of soot carbon (dark circles) and organic carbon (open squares).

Using the deposition rates derived in this and a parallel core from radionuclide data and knowledge of local industrial events (33), the historical variations in PAH input were assessed (Figure 3a). The deepest section of our core analyzed for PAHs represents approximately the turn of the century. The very low fluxes at this time, prior to the onset of heavy industrialization and the associated fossil-fuel combustion, may be indicative of PAHs from natural processes such as forest fires as well as residential and agricultural wood-burning. In fact, the downcore ratio of 1,7-dimethylphenan-threne to 2,6-dimethylphenanthrene (1,7-DMP/2,6-DMP; Figure 3a), an indicator of the relative contribution to pyrogenic PAH from woody vs fossil fuel combustion (44), suggests that wood/forest burning may have been a dominant PAH contributor to the deepest core sections. However, such sources appear to become less significant at shallower depths in this core, as the dramatic increase in PAH fluxes likely reflects the rapid acceleration of industrial activities in this part of the world during the first half of the 1900s. Consistent with results from the aforementioned four studies (37−40), the dramatic increase of sedimentary PAH flux reached a maximum around 1960, after which a slight decrease followed. This may reflect the switchover from coal as the primary energy source to gas and oil, which occurred in the United

States during this period (45). While the total energy consumption was increasing, widespread switchover to oil and gas, which produce less PAHs per btu than coal (46), apparently resulted in a net decrease in PAH production during this transitory period.

We used our SC method to develop a corresponding profile of soot input to Mystic Lake (Figure 3b). The dilute sedimentary soot was found in the concentration range 0.002−0.007 (g of SC/g of dry sediment), corresponding to a maximum SC flux of 2.3 (g m$^{-2}$ yr$^{-1}$). The soot profile was found to mimic the combustion-derived PAH profiles described above. While the SC abundances were only several percent of the OC levels ($0.11 \pm 0.02$ g of OC/g of dry sediment), the SC and OC profiles were completely decoupled (OC showed no clear trend with depth; Figure 3b), further supporting the contention that interferences from pollen or charring are negligible. The increasing value of 1,7-DMP/2,6-DMP in the deeper sections (Figure 3a) indicates that soot may have different sources and properties (e.g., PAH content) over time. Our quantitative historical record of total soot input exhibits the same qualitative temporal trend as the microscopy-counted Lake Michigan sedimentary charcoal record (18, 20). The PAH−soot coupling recorded in this sediment core adds confidence to the applicability of the proposed method for quantifying dilute soot in such complex sedimentary environments.

*Boston Harbor.* Finally, we applied our soot method to two Boston Harbor sediment samples, in which anomalously elevated *in situ* PAH partition coefficients have been found (2, 3). While the OC contents of these marine sediments (0.04−0.05 g of OC/g of dry sediment) were lower than in the Mystic Lake sediments, the SC contents were similar (see footnotes of Table 2). This resulted in SC/OC ratios near 0.10 in this anthropogenically influenced urban harbor. An important finding of McGroddy and co-workers in the aforementioned work was that the environmental PAH speciation deduced by measuring the actual *in situ* phase distribution did not comply with the expectations from existing sorption models (i.e., refs 5−7). These workers observed $K_d$ values several orders of magnitude above the predictions from such a commonly applied hydrophobic partition framework (Table 2), which is based on the presumption of natural organic matter being the sole (or dominant) sorbent for hydrophobic compounds in the environment. To explain the elevated $K_d$ values, McGroddy et al. (2, 3) hypothesized that the PAHs were existing in an apparent disequilibrium due to a significant fraction of the bound PAHs being sequestered in a physical−chemical form (e.g., soot), making them unavailable for equilibrium partitioning on the decadal time scale of these accreting sediments. An alternative, or further development of the above, interpretation is that the inferred soot is a much stronger PAH sorbent than natural organic matter and thus causes equilibrium *in situ* $K_d$ values to be elevated as compared to the simple organic matter partitioning scenario. Our ability to quantify the dilute sedimentary soot phase makes it possible to now investigate whether such a sorbent is present in sufficient amounts to explain the elevated partition coefficients observed. Using our measures of $f_{sc}$ and calculating $K_{sc}$ from ref 1 (Figure 1b), the extended hydrophobic partitioning framework (eq 1) was applied to rationalize the *in situ* PAH speciation (Table 2). It is seen that the $K_d$ predictions of the product $f_{oc}K_{oc}$ are orders of magnitude lower than the $K_d$ values actually observed. In contrast, the extended framework, which includes a term for soot partitioning, appears successful in predicting the actual PAH distribution (Table 2). Of course, we should emphasize that it is possible that some fractions of the soot-associated PAHs are held within the aromatic planes of the soot structure (28, 29, 48) such that they may not desorb to reach equilibrium with the surrounding water on time scales of interest for certain

**TABLE 2. Different PAH Partitioning Models Applied to Boston Harbor Sediments**

| | log $K_d$ ($L_{porewater}/kg_{drysed}$) | |
| --- | --- | --- |
| | phenanthrene | fluoranthene |
| **Fort Point Channel (7−9 cm)[a]** | | |
| actual distributions measured *in situ* (2) | 5.0 | 5.4 |
| distributions predicted from $K_d = f_{oc}K_{oc}$[b] | 2.9 | 3.6 |
| distributions predicted when including a soot phase[c] (eq 1) | 4.9 | 5.6 |
| **Spectacle Island (0−2 cm)[d]** | | |
| actual distributions measured *in situ* (2) | 5.9[e] | 5.2 |
| distributions predicted from $K_d = f_{oc}K_{oc}$[b] | 2.8 | 3.4 |
| distributions predicted when including a soot phase[c] (eq 1) | 4.5 | 5.2 |

[a] The $f_{oc}$ was 0.0547 g of OC/gdw (2); the soot content, $f_{sc}$, of this sediment was determined to be 0.0066 ± 0.0008 g of SC/g dw. [b] We used log $K_{oc}$ values for phenanthrene and fluoranthene of 4.12 and 4.79, calculated from log $K_{ow}$ values in ref 12 using the relationship of ref 7. [c] Soot partition coefficients were calculated from data in ref 1 (shown in Figure 1b), and the log $K_{sc}$ were for phenanthrene 7.1 and for fluoranthene 7.8. [d] The $f_{oc}$ was 0.0406 g of OC/g dw (2), and the $f_{sc}$ was determined to be 0.0027 ± 0.0004 g of SC/g dw. [e] This reported value (2) deviates from the commonly observed trend of hydrophobicity-driven *in situ* $K_d$ values. Since this surficial sediment sample is well-oxidized, it is possible that this value reflects biodegradation of porewater phenanthrene being faster than desorption (i.e., non-equilibrium) as significant biotransformation rates of spiked phenanthrene to oxidized Boston Harbor sediments have been observed (47).

processes. However, the good agreement between total (gas adsorption) and external (electron microscopy) surface areas (48) may suggest that soot has limited internal pore structures to occlude PAHs.

The implications of an association between PAH and soot in natural sediments are intriguing. These findings quantitatively support the inclusion of specific combustion phases in environmental speciation models of hydropohobic contaminants (i.e., eq 1). The large number of studies reporting peculiarly elevated partition coefficients for PAHs (e.g., Figure 1a) but not for PCBs may now be explained by the presence of anthropogenic soot controlling the PAH distribution. Soot particles appear to consist of a highly conjugated and condensed carbonaceous matrix, and their structure may be thought of as a multi-layered macro-PAH (28, 29, 48, 49). Hence, it may be expected that strong $\pi-\pi$ interactions are established between the often co-introduced flat PAH molecules and the soot particles. Interestingly, it was recently reported that coplanar PCBs exhibited 0.5 log unit of elevated affinities to urban aerosols as compared to predictions from their vapor pressures while this was not seen for congeners of larger dihedral angles (51). Dioxins and other planar aromatic molecules may similarly establish favorable dispersion interactions with soot, which could affect their environmental speciation. The present results suggest that the chemical exchange of PAHs between these strongly sorbing, but dilute, anthropogenic phases and the surrounding aqueous solution may be at or near equilibrium (at least in this decade-old sediment−porewater system initially evaluated).

Our results support the hypothesis forwarded by Farrington and co-workers in reflection of the results from the U.S. Mussel Watch Survey (52) that, unlike petroleum-spilled PAHs, pyrogenic PAHs may be less available for biological uptake as a result of presumed strong associations with combustion particles. This finding is particularly important as the recently elucidated geographical fallout pattern and relative compound abundances of PAH fluxes into the northwestern Atlantic suggest that pyrogenic sources are dominating the PAH input to the ocean (53). The tremendous influence of PAH−soot associations on the bioavailable fraction should be taken into account in the establishment of sediment quality criteria (SQC), currently being developed by the U.S. EPA (e.g., ref 54). The basis of these SQC is to ensure that the porewater concentration, in *equilibrium* with the sediment, is not exceeding the *final chronic water quality criteria values* (FCV). Since the soot phase may be dominating the environmental PAH speciation, we propose that the SQC may need to be redefined as

$$SQC(PAH_i) = (f_{oc}K_{oc} + f_{sc}K_{sc})FCV(PAH_i) \qquad (2)$$

If some fraction of the PAHs are so occluded within soot so as to be practically non-exchangeable on time scales of interest, then eq 2 would also need to include a factor for the fraction that is *a*vailable for *e*quilibrium *p*artitioning (AEP; refs 2 and 3):

$$SQC(PAH_i) = \left(\frac{f_{oc}K_{oc} + f_{sc}K_{sc}}{AEP}\right)FCV(PAH_i) \qquad (3)$$

In either case, it appears necessary to quantify not only $f_{oc}$ but also $f_{sc}$ to derive such a first-order approximation of the exposed contaminant levels.

One further implication of the environmental soot-associated PAH speciation is that current laboratory-based practices, using liquid PAH solutions and extracts in sorption and toxicity testing, may not realistically reflect the actual availability of *in situ* PAHs to participate in such processes. To further constrain the proposed extension of the hydrophobic partitioning model to include soot-phase partitioning, $K_{sc}$ should be evaluated under controlled conditions. This first direct investigation on the quantitative relationship between *in situ* PAH distribution and the presence of soot phases indicates that understanding this link may prove crucial to elucidating the biogeochemical cycling of such combustion-derived compounds.

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