SETAC PRESS

Environmental Toxicology and Chemistry, Vol. 26, No. 7, pp. 1380–1385, 2007
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Printed in the USA
0730-7268/07 $12.00 + .00

THE USE OF COARSE, SEPARABLE, CONDENSED-PHASE ORGANIC CARBON PARTICLES TO CHARACTERIZE DESORPTION RESISTANCE OF POLYCYCLIC AROMATIC HYDROCARBONS IN CONTAMINATED SEDIMENTS

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(*Received* 3 *January* 2006; *Accepted* 12 *February* 2007)

Abstract—Physical separations were employed to characterize the source of desorption-resistant behavior for polycyclic aromatic hydrocarbons (PAHs) in laboratory- and field-contaminated sediments. Size and density separation of laboratory-contaminated sediments did not effectively separate the amorphous-phase (volatile) and condensed-phase (nonvolatile) organic carbon as measured by thermal oxidation at 375°C. These separations also did not result in sediment fractions with significantly different desorption characteristics as measured by apparent partition coefficients. Coarse particles from a field-contaminated sediment from Utica Harbor (UH; Utica, NY, USA), however, could be directly separated into sandy fractions and organic fractions that were composed of woody organic matter, charcoal or charred vegetative matter, and coal-like and coal-cinder particles. Chemical analysis showed that coal-like (glassy, nonporous) and coal-cinder (porous, sintered) particles exhibited very high PAH concentrations and high apparent partition coefficients. These particles also exhibited significantly higher condensed-phase (nonvolatile) organic carbon contents as defined by thermal oxidation at 375°C. The apparent partition coefficients of PAHs in the coal-cinder particles were a good indication of the apparent partition coefficients in the desorption-resistant fraction of UH sediment, indicating that the coarse particles provided a reasonable characterization of the desorption-resistance phenomena in these sediments even though the coarse fractions represented less than 25% of the organic carbon in the whole sediment.

Keywords—Hydrophobic organic contaminants Condensed-phase organic matter Sediments Desorption resistance

INTRODUCTION

Desorption resistance of hydrophobic organic contaminants in sediments has been widely ascribed to the heterogeneity of organic matter in sediments and soils [1–4]. Condensed-phase organic carbon, denoted by such synonyms as hard carbon, black carbon, soot carbon, and coal-derived carbon, has been considered to be responsible for the sequestration of hydrophobic organic contaminants in sediments. For example, Ghosh et al. [5,6] suggested that desorption resistance is associated with slow diffusion for coal-derived particles. Huang and Weber [7] believed that entrapment of sorbing molecules within the hard carbon (i.e., condensed-phase sediment organic matter matrices) contributes to desorption resistance. Xing and Pignatello [8] attributed the desorption resistance to glassy-phase organic matter. Gustafsson et al. [9] developed a method to quantify the sedimentary soot phase, and that definition is used herein to describe the volatile (lost during combustion at 375°C) and nonvolatile (refractory after combustion at 375°C) organic carbon and to provide an operational definition of the amorphous-phase (volatile) and condensed-phase (nonvolatile) organic carbon.

Because desorption resistance is apparently correlated with the condensed-phase (nonvolatile) organic carbon [10–12], the current efforts are focused on the isolation of the condensed-phase (nonvolatile) organic matter from sediment. Separation of sediment into different fractions has been attempted previously [1,6,11], but complete separation of the amorphous-phase (volatile) and condensed-phase (nonvolatile) fractions has not been successful. Size and density fractionation leads to incomplete separation of these fractions, and this problem is demonstrated herein with a laboratory-inoculated sediment from a freshwater bayou in Baton Rouge (LA, USA). Sediment collected from Utica Harbor (UH; Utica, NY, USA), however, contained a variety of coarse particles, both mineral and organic, exceeding 2 mm in size. The large particle size allowed separation of these particles into similar fractions based on visual observation. The desorption of polycyclic aromatic hydrocarbons (PAHs) from particles of like character in these large fractions is evaluated to identify the desorption characteristics of the various particles. The ability to achieve complete separation of like particles allows evaluation of the relationship between the fraction of nonvolatile organic carbon and desorption resistance as defined by larger effective partition coefficients (i.e., lower extents of desorption) and slow sorption or desorption kinetics. The desorption of PAHs from these coarse particles also is compared with that of the bulk sediment to evaluate the representativeness of using these large particles to characterize sorption or desorption phenomena.

MATERIALS AND METHODS

Sediments

Laboratory-spiked sediment from Bayou Manchac (BM), a freshwater bayou in Baton Rouge, was used for the size- and density-separation experiments. Analysis showed that the sediment contained much less than 1 mg/kg of phenanthrene (PHE). The sediment was prepared following procedures de-

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scribed previously [13]. Briefly, the sediment was spiked with PHE (Sigma-Aldrich Chemical, Milwaukee, WI, USA) at its saturation concentration after being passed through a 2-mm sieve. Phenanthrene was dissolved in hexane, transferred into a 4-L glass jar, and then evaporated under a stream of ultrahigh-purity nitrogen while rotating the jar until PHE uniformly deposited on the internal wall. Preweighed sediment with known moisture content (45–55%, water/wet sediment wt) was added into the glass jar, and sodium azide (3,000 mg/kg dry sediment wt) was added to inhibit microbial activities. The glass jar was then tumbled for five weeks to ensure that PHE partitioned homogeneously to the matrices of sediment. At the conclusion of tumbling, the spiked sediment was washed (desorbed) sequentially by isopropanol diluted with electrolyte solution (0.01 M NaCl and 0.01 M $CaCl_2$ in tap water; 1:1, v/v). As a result, five BM sediments labeled BM1 through BM5 with PHE concentrations of 50.0, 39.0, 13.4, 10.2, and 3.81 mg/kg, respectively, were prepared to provide an increasing desorption-resistant fraction of PHE [13]. Kan et al. [4] has shown previously that washing sediments in this manner will preferentially remove rapidly desorbable contaminants, leaving an increasing desorption-resistant fraction of PHE. A field-contaminated sediment, UH sediment, was used to obtain coarse particles in the present study. Utica Harbor was contaminated over many decades during the operation of a coal gasification plant.

Size and density separation of laboratory-spiked sediment

Fractionation of BM sediments using wet sieving for size separation and a high-density solution for density separation was performed in a manner similar to the procedures reported by Mayer et al. [14] and by Ghosh et al. [5]. One-hundred grams of wet sediment and 200 ml of water were added into a 500-ml glass jar and mixed thoroughly using a spatula. After settling for 3 min, the suspended material was collected and passed through a series of sieves (63, 150, and 250 μm). This step was repeated until the water became clear. Then, 100 ml of CsCl (Fisher Scientific, Pittsburgh, PA, USA) solution with a specific gravity of 1.8 were added into the jar and mixed. After settling for 3 min, the floating material and the CsCl solution were collected and passed through the same series of sieves. At this point, the sediment had been separated into five fractions, including one residual heavy fraction consisting mostly of sand, three light fractions on sieves, and one light fine fraction (particle size, <63 μm). The first four fractions were rinsed with water three times to remove residual CsCl. The light fine fraction was centrifuged (2,000 *g* for 20 min) and washed with water three times to remove CsCl. The heavy fraction was passed through a 63-μm sieve and split into two fractions. Thus, the sediment was separated into six fractions: Four light fractions that were less than 63 μm light (mostly clay, silt, and organic matter), 63 to 150 μm light (mainly organic matter), 150 to 250 μm light (mainly organic matter), and greater than 250 μm light (mainly organic matter); and two heavy fractions that were less than 63 μm heavy (mainly sand) and greater than 63 μm heavy (mainly sand). The weight of each fraction, the PHE concentration in each fraction, and the apparent partition coefficient of PHE in each fraction were determined.

Obtaining coarse particles from field-contaminated sediment

The UH sediment was coarsely sieved to obtain coarse particles with a size greater than 2 mm that could be separated on the basis of visual characteristics. Unfortunately, this was not possible with the already-sieved sediments used for size and density separation. These particles, constituting less than 5% of the total mass of the initial sediments, were air-dried at room temperature and sorted manually. Four main categories of particles rich in organic matter were collected, and these were denoted as coal-like, coal-cinder, woody, and charcoal. Black, shiny, and nonporous particles were identified as coal-like particles. Gray-black, porous particles were identified as coal-cinder particles because of their sintered coal-like appearance. Woody particles, charred wood, and charcoal-like particles were readily identifiable. Inorganic silica, sandy particles, which represented approximately half the total coarse particle fraction, also were readily identifiable. These mineral particles were discarded, because they contained minimal organic matter and were not expected to contribute significantly to the sorption of hydrophobic organics. The concentrations of PAHs were determined in each of the coarse organic particle fractions. Total organic carbon contents as well as amorphous-phase (volatile at 375°C) and condensed-phase (nonvolatile at 375°C) organic carbon contents were determined from each of the fractions with a PerkinElmer (Wellesley, MA, USA) 2400 series II carbon-hydrogen-nitrogen elemental analyzer [13].

Measurement of PAHs and apparent partition coefficients

For sediment samples and their fractions, ultrasonic extraction (U.S. Environmental Protection Agency Method 3550B, SW-846 [15]) was used to extract PAHs from sediment matrix. The extraction efficiency for PHE was 96.6 ± 5.0% (mean ± standard deviation) from freshly spiked laboratory sediments. An Agilent (Palo Alto, CA, USA) 1100 Series high-performance liquid chromatograph (HPLC) equipped with ultraviolet–diode array detector and fluorescence detector was used to determine the concentrations of PAHs in the extract following the method suggested by the U.S. Environmental Protection Agency (Method 8310, SW-846 [16]). The concentration of contaminant in aqueous phase was determined with the HPLC after centrifugation (2,000 *g* for 20 min). The apparent sediment/water partition coefficients for PAHs were measured following procedures described elsewhere [10]. Briefly, the sediment/water partition coefficient was measured under conditions of a water to sediment ratio of 25:1 and 10-d equilibration time [13]. The organic carbon–based partition coefficient (K_{OC}) was defined by normalizing the measured partition coefficient with the total organic carbon in the solid fraction. The background solution used for the apparent partition coefficients measurement was an electrolyte solution of 0.01 M NaCl, 0.01 M $CaCl_2{\cdot}2H_2O$, and 0.01 M NaN_3 in deionized water.

RESULTS AND DISCUSSION

Size and density separation of sediment

Sediment mass distribution, PHE concentration, and PHE distribution in each fraction for the five BM sediments are shown in Figure 1. As shown in Figure 1C, approximately 38 to 43% of the sediment mass and 55 to 73% of the PHE in the corresponding whole sediment was associated with the light fine fraction (<63 μm light). Three light fractions rich in organic matter (63–150 μm light, 150–250 μm light, and >250 μm light) were almost 3% of the sediment mass, but 17 to 36% of the PHE in the corresponding whole sediment resided in these fractions. Phenanthrene concentrations in these

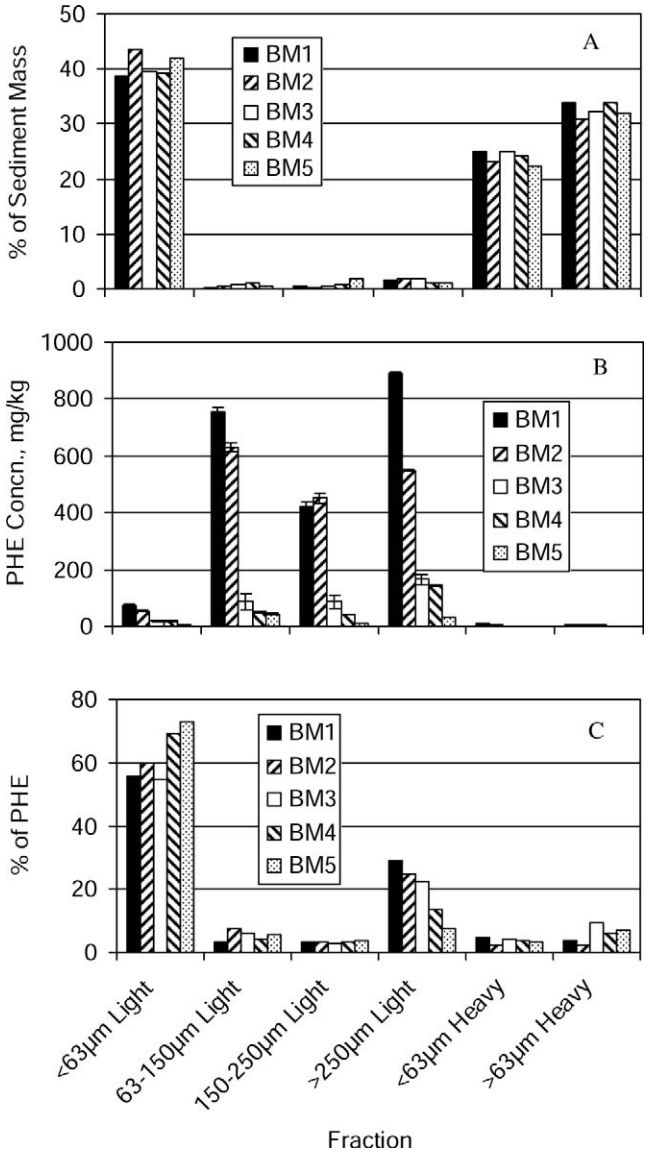

Fig. 1. Phenanthrene distribution in fractionated Bayou Manchac (BM; Baton Rouge, LA, USA) sediments. Phenanthrene concentration in BM1, BM2, BM3, BM4, and BM5 were 50.0, 39.0, 13.4, 10.2, and 3.81 mg/kg, respectively. (**A**) The sediment mass distribution in each fraction. (**B**) Phenanthrene concentration in each fraction. (**C**) Phenanthrene distribution in each fraction.

three fractions were as much as 18-fold higher than the corresponding whole-sediment loading. Phenanthrene concentrations in heavy fractions were much less than those in the corresponding whole sediment. Approximately 90% of the total PHE was found in the four light fractions. These findings were consistent with the observations reported in literature. Ghosh et al. [11] found that carbonaceous particles, constituting only 5 to 7% of the sediment by weight, contained 60 to 90% of the total polychlorinated biphenyls and PAHs in three sediments. Rockne et al. [1] observed that 50 to 80% of the PAHs in two sediments were associated with the low-density fractions that represents only 3 to 15% of total sediment.

Although it was possible to separate most of the organic matter and most of the PHE into the light fraction, little or no separation of condensed-phase organic matter from amorphous-phase organic matter occurred. The fraction of condensed-phase carbon, as estimated using the method of Gustafsson et al. [9], was 49% in the less-than-63-μm light fraction and 46% in the other light fractions. The greater proportion of PHE in the larger light fractions was simply a result of the higher organic carbon content in these fractions rather than a differentiation based on organic carbon quality. This was substantiated by the fact that the total organic carbon–normalized concentrations of PHE in different size fractions were very close to each other and to that of the corresponding whole sediment. Table 1 shows that the organic carbon–normalized partition coefficient in each of the light or heavy fractions were effectively identical, although a tendency of an increased partition coefficient at lower sediment concentrations (i.e., moving from sediment BM1 to BM5) was observed. The preparation of the various sediments by sequential washing with dilute isopropanol solution likely resulted in preferential removal of more readily available PHE, resulting in the observed increases in apparent partition coefficient. In summary, the size and density fractionation was not successful in separating the more strongly held PHE fractions from the weakly held fractions.

Characterization of different coarse particles

In an attempt to achieve a more effective separation of types of organic matter and the strongly and weakly associated organic contaminants, the very large particles (>2 mm) of UH sediment were visually separated into different fractions as described previously. The organic carbon contents of these particles ranged from 28.82 to 83.13%, as shown in Table 2. This compares to the organic carbon content of the whole

Table 1. Apparent partition coefficients (log K_{OC}) for fractionated Bayou Manchac (Baton Rouge, LA, USA) sediment with different concentrations of phenanthrene[a]

Sediment	BM1	BM2	BM3	BM4	BM5
PHE concn. (mg/kg)	50.0	39.0	13.4	10.2	3.81
Whole sediment	4.51 ± 0.01	4.59 ± 0.01	4.72 ± 0.01	4.79 ± 0.01	4.92 ± 0.02
<63 μm light	4.60 ± 0.02	4.64 ± 0.01	4.88 ± 0.03	5.05 ± 0.02	5.02 ± 0.02
63–150 μm light	4.60 ± 0.02	4.74 ± 0.03	4.51 ± 0.02	4.47 ± 0.02	4.95 ± 0.03
150–250 μm light	4.47 ± 0.03	4.60 ± 0.03	4.52 ± 0.02	4.48 ± 0.01	4.57 ± 0.03
>250 μm light	4.67 ± 0.01	4.64 ± 0.02	4.84 ± 0.02	4.99 ± 0.03	4.90 ± 0.02
<63 μm heavy	4.60 ± 0.02	4.40 ± 0.02	4.90 ± 0.02	4.89 ± 0.03	4.83 ± 0.03
>63 μm heavy	4.25 ± 0.02	4.28 ± 0.02	4.82 ± 0.01	4.85 ± 0.02	4.86 ± 0.01

[a] Values are presented as the mean ± standard deviation. Organic carbon contents (f_{OC}) were 1.95% for <63 μm light, with condensed-phase organic carbon content (f_{OC}^{C}/f_{OC}) of 49%;. The f_{OC} values were 18.81% for 63–150 μm light, 150–250 μm light, and >250 μm light, with f_{OC}^{C}/f_{OC} of 46%, and f_{OC} values were 0.40% for heavy fractions. PHE = phenanthrene.

Table 2. Organic carbon content (%) of different particles from Utica Harbor sediment (Utica, NY, USA)[a]

Particles	f_{OC}	f_{OC}^{C}	f_{OC}^{C}/f_{OC}
Coal-like	80.9 ± 0.23	41.5 ± 0.62	51.3 ± 0.79
Coal-cinder	28.8 ± 0.12	21.4 ± 0.19	74.3 ± 0.73
Wood	56.0 ± 0.38	0.00	0.00
Charcoal	83.1 ± 0.33	0.41 ± 0.01	0.50 ± 0.01
Bulk sediment	2.10 ± 0.02	0.82 ± 0.02	39.1 ± 1.0

[a] f_{OC} = total organic carbon content of sediment; f_{OC}^{C} = condensed phase or nonvolatile organic carbon content.

sediment of 2.1%. Although the separated coarse organic particles represented only 1 to 2% of the original sediment, it constituted approximately 25% of the organic carbon in the original sediment.

The high content of organic carbon in the separated coarse particles was comparable to the organic carbon contents reported by Jonker and Koelmans [17]: Coal-like particles, 90.8%; coal soot, 32.2%; and charcoal, 82.2%. As indicated in Table 2, the only particle fractions that exhibited significant condensed-phase organic carbon (nonvolatile fractions as measured by thermal oxidation at 375°C [9]) were the coal-like and coal-cinder particles.

Concentrations of contaminants in the various coarse particles and contaminants in the corresponding whole sediment are listed in Table 3. The concentrations of PAHs in the coal-like particles and coal-cinder particles were significantly higher than those in the corresponding whole sediment, with the total PAH concentration being approximately 22- and 25-folder higher, respectively. The concentrations of PAHs in wood particles, however, were only approximately twice those in the bulk sediment, and the concentrations of PAHs in charcoal particles were even less than the average in bulk sediment. On an organic carbon–normalized basis, only the coal-cinder particles exhibited above-average sorption (i.e., above that of the overall sediment). The concentrations of compounds with less molecular weight in wood and charcoal particles were approximately the same as or higher than those in the bulk sediment, whereas the concentrations of compounds with larger molecular weight in wood and charcoal particles generally were less than those in bulk sediment. This may suggest that the wood and charcoal were introduced to the sediments relatively recently, such that the generally more rapidly sorbing, low-molecular-weight contaminants might be closer to equilibrium than the high-molecular-weight PAHs or be the result of different sorption characteristics for the compounds.

The apparent partition coefficients for PAHs in coal-like particles and coal-cinder particles are presented in Table 4. The apparent partition coefficients of PAHs in both coal-like and coal-cinder particles were significantly greater than conventional literature K_{OC} values as predicted from octanol/water partition coefficient [18] using correlations reported by Karickhoff et al. [19]. The literature K_{OC} values indicate the expected partition coefficient associated with that compound if sorption is fast and reversible. The average difference of log K_{OC} values was approximately 0.6 for coal-like particles and approximately 0.8 for coal-cinder particles. The elevated partition coefficient is substantiated by previous reports that the partition coefficients as a measure of sorption capacity in various black carbon particles may be orders of magnitude higher than conventional literature values [11,17,20]. Recently, Hawthorne et al. [21] reported that the partition coefficients of PAHs in 114 historically contaminated sediments typically are as much as two orders of magnitude higher than the commonly used literature K_{OC} values.

Table 4. Apparent partition coefficients (log K_{OC}) of polycyclic aromatic hydrocarbons in coal-like and coal-cinder particles from Utica Harbor (Utica, NY, USA) sediment

Compound	Literature value[a]	Coal-like[b]	Coal-cinder[b]
Phenanthrene	4.36	5.23 ± 0.01	5.10 ± 0.01
Anthracene	4.33	5.40 ± 0.02	5.07 ± 0.02
Pyrene	4.97	5.01 ± 0.01	5.25 ± 0.02
Chrysene	5.65	6.35 ± 0.03	6.62 ± 0.01
Benzo[*b*]fluoranthene	5.59	6.23 ± 0.02	6.79 ± 0.02
Benzo[*k*]fluoranthene	5.79	6.14 ± 0.02	6.56 ± 0.03
Benzo[*a*]pyrene	5.83	6.32 ± 0.02	6.86 ± 0.02

[a] Literature values of log K_{OC} were calculated from log K_{OW} compiled in Mackay et al. [18] using correlation log K_{OC} = log K_{OW} − 0.21 reported by Karickhoff et al. [19]. The total organic carbon content of sediment (f_{OC}) for coal-like particles from Utica Harbor sediment is 80.9%, and the condensed-phase organic carbon content (f_{OC}^{C}/f_{OC}) is 0.51. The f_{OC} for coal-cinder particles from Utica Harbor sediment is 28.8%, and the f_{OC}^{C}/f_{OC} is 0.74.

[b] Values are presented as the mean ± standard deviation.

Coal-cinder particles and desorption resistance in bulk sediments

The coal-cinder particles showed the greatest sorption and the highest fraction of condensed-phase organic carbon. The importance of this fraction on reducing the physicochemical availability of contaminants can be illustrated by comparing the apparent partition coefficients in coal-cinder particles with that in the bulk sediment. A polymeric sorbent, XAD-2 (Supelco, Bellefonte, PA, USA), was used effectively to remove

Table 3. Concentrations of polycyclic aromatic hydrocarbons (PAHs) in coarse particles from Utica Harbor (Utica, NY, USA) sediment[a]

PAH compound	Whole sediment (mg/kg)	Coal-like particles (mg/kg)	Coal-cinder particles (mg/kg)	Wood particles (mg/kg)	Charcoal particles (mg/kg)
Phenanthrene	6.53 ± 0.22	177 ± 9.5	287 ± 14	49.1 ± 2.3	25.7 ± 0.94
Anthracene	5.80 ± 0.10	74.4 ± 1.3	334 ± 11	25.4 ± 0.75	9.92 ± 0.35
Pyrene	23.8 ± 0.45	227 ± 5.0	290 ± 8.7	78.1 ± 1.4	5.88 ± 0.16
Chrysene	24.3 ± 1.0	550 ± 20	347 ± 10	5.90 ± 0.23	12.3 ± 0.27
Benzo[*b*]fluoranthene	8.91 ± 0.31	347 ± 13	348 ± 15	8.63 ± 0.31	—
Benzo[*k*]fluoranthene	4.15 ± 0.05	149 ± 5.2	147 ± 4.9	0.64 ± 0.05	0.26 ± 0.02
Benzo[*a*]pyrene	12.7 ± 0.36	334 ± 13	358 ± 7.8	10.3 ± 0.42	0.67 ± 0.03
ΣPAH Compounds	86.1	1,860	2,110	178	54.7
ΣPAH Compounds/f_{OC}	4,100	2,300	7,490	317	65.8

[a] Values are presented as the mean ± standard deviation. ΣPAH = sum of PAHs; f_{OC} = total organic carbon content of sediment.

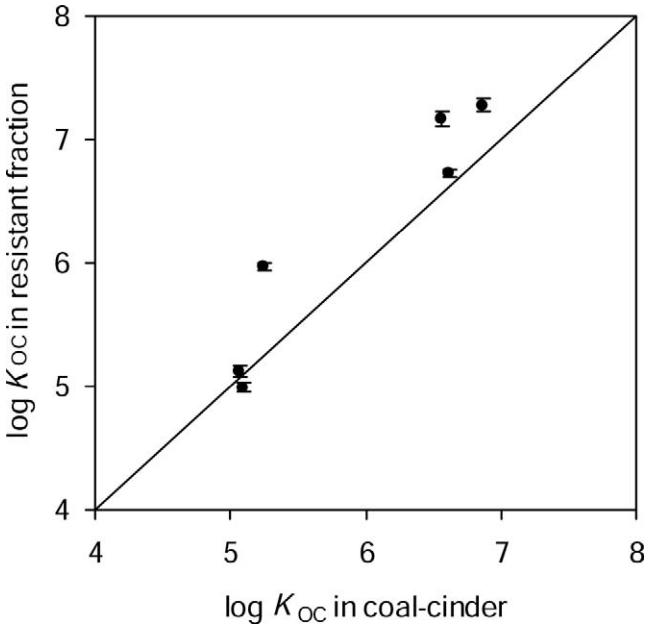

Fig. 2. Comparison of apparent partition coefficients in desorption-resistant fraction and in coal-cinder particles in Utica Harbor (UH, Utica, NY, USA) sediment.

the entire readily desorbable fraction from the bulk sediment according to procedures described elsewhere [10]. The apparent partition coefficient of this residual sediment was then compared to the measured partition coefficient in the coal-cinder particles. Figure 2 shows the resistance-dominated sediment partition coefficient versus the partition coefficient measured on coal-cinder particles. The coal-cinder partition coefficient measured on the coarse particles reasonably approximated the observed desorption-resistant contaminant partition coefficient in sediment. There is a small tendency for the coal-cinder partition coefficient to underpredict partition coefficients observed in the partially desorbed sediments, although this may simply represent incomplete desorption of the rapidly desorbable contaminants with the XAD-2. The coarse particles rich in nonvolatile or condensed-phase organic carbon thus appear to provide a good representation of that fraction of sediment responsible for slow or equilibrium-limited desorption. Our previous work has shown that a higher slow-desorbing fraction, or desorption resistance, of PAHs in two field sediments was related to higher condensed-phase organic carbon contents [10] as determined by an operational method (i.e., partial thermal oxidation of the sediment at 375°C) [9]. The coarse coal-cinder particles isolated in the present study provided additional evidence to support the idea that the presence of condensed-phase organic carbon in sediments reduces the available fraction of hydrophobic organic contaminants for partitioning into aqueous phase, and the aqueous-phase concentration has been found to reflect bioavailability and uptake in organisms [22,23].

CONCLUSIONS

Size and density separation of laboratory-contaminated sediments did not effectively separate the amorphous-phase (volatile) and condensed-phase (nonvolatile) organic carbon as measured by thermal oxidation at 375°C in a laboratory-inoculated freshwater sediment from BM. Neither did size and density separation result in sediment fractions with significantly different desorption characteristics as measured by apparent partition coefficients. Coarse fractions of field-contaminated sediments from UH, however, could be directly separated into sandy fractions and organic fractions that were composed of woody organic matter, charcoal or charred vegetative matter, and coal-like and coal-cinder particles. Chemical analysis showed that coal-like (glassy, nonporous) and coal-cinder (porous, sintered) particles exhibited very high PAH concentrations and apparent partition coefficients. These particles also exhibited significantly higher condensed-phase (nonvolatile) organic carbon contents as defined by thermal oxidation at 375°C. The apparent partition coefficients of PAHs in the coal-cinder particles were a good indication of the apparent partition coefficients in the desorption-resistant fraction of UH sediment (as defined by the residual contaminants after treatment with XAD-2), suggesting that these particles provided a good model for the desorption resistance behavior of the whole sediment.

Acknowledgement—The authors thank three anonymous reviewers for their valuable comments. The present study received financial support from the Hazardous Substance Research Center/South and Southwest funded by the U.S. Environmental Protection Agency.

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