AMENDMENT OF SEDIMENTS WITH A CARBONACEOUS RESIN REDUCES BIOAVAILABILITY OF POLYCYCLIC AROMATIC HYDROCARBONS

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Abstract—We evaluated the effectiveness of Ambersorb®, a carbonaceous resin, in reducing bioavailability of polycyclic aromatic hydrocarbons (PAHs) in contaminated sediments collected from the field. In laboratory studies, sediment pore-water concentrations of eight unsubstituted PAHs were significantly decreased after resin addition. Reduced PAH concentrations in oligochaete tissues from a laboratory bioaccumulation test, along with increased survival/reproduction and reduced photo-enhanced toxicity and sediment avoidance, also resulted from sediment treatment with Ambersorb. Ambersorb amendment also decreased pore-water PAH concentrations in field deployed sediments but did not improve benthic invertebrate colonization. Prediction of partitioning of PAHs between solid and aqueous phases in the test sediments was complicated by the presence of coal and soot. However, accurate predictions of bioavailability were achieved based on pore-water chemistry. Overall, these studies show that the addition of high affinity sorbents effectively reduces pore-water PAH concentrations and bioavailability and suggests that sorbent addition may serve as an option for in situ remediation of some contaminated sediments.

Keywords—Sediment Polycyclic aromatic hydrocarbons Bioavailability Remediation

INTRODUCTION

Sediments serve as the ultimate repository of a variety of persistent contaminants that can pose unacceptable risks to aquatic organisms. Various biological and analytical techniques exist to assess the potential risk of sediment-associated contaminants [1]. The most accurate of these are integrated approaches predicated, implicitly or explicitly, upon an understanding of processes controlling the bioavailability of contaminants in sediments. Prediction of bioavailability not only enables assessment of risk but can lend insight regarding the appropriate remediation options for uncontrollably contaminated sediments. To date, the most common (active) remediation option for contaminated sediment has consisted of removal followed by treatment and/or confined storage. However, the potential for more resource-efficient remediation (because of cost and logistic considerations) could make in situ approaches more desirable. One in situ approach consists of manipulating the bioavailability of sediment-associated contaminants.

Studies with inorganic and organic chemicals have shown a correlation between contaminant bioavailability and interstitial (pore) water chemical concentrations in sediments [2–5]. Research has demonstrated the role of organic carbon in controlling pore-water concentrations and the bioavailability of nonionic organic chemicals in sediments [2,6,7]. Understanding has been the basis for the development of chemical-specific guidelines for sediment-associated contaminants based on equilibrium partitioning [4]. Therefore, one approach to in situ remediation of sediments contaminated with nonionic compounds would be to reduce their bioavailability through addition of a material that has higher affinity for the contaminants than native organic carbon.

Initial studies conducted by our laboratory [8] evaluated the effects of a high-capacity resin (Ambersorb 1500®, Rohm and Haas, Spring House, PA, USA) on bioavailability of the polycyclic aromatic hydrocarbon fluoranthene spiked into freshwater sediment. Bioavailability of fluoranthene, as indicated both by partitioning to pore water and bioaccumulation by oligochaetes, was reduced in short-term (10-d) laboratory studies with Ambersorb-amended sediments. The purpose of the present study was to undertake a more comprehensive evaluation of capacity of the resin to alter bioavailability of polycyclic aromatic hydrocarbons (PAHs) in field-collected sediments using long-term studies conducted in both the laboratory and field.

METHODS

We utilized several approaches to examine bioavailability from both biological and chemical perspectives. In the laboratory, bioavailability was assessed by behavioral, toxicity, and bioaccumulation assays conducted with untreated and resin-amended sediments. These end points were assessed in conjunction with measurement of PAHs in the pore water. Complementary field experiments were conducted to determine whether resin addition would control pore-water chemistry under field conditions and whether decreases in PAH bioavailability would increase colonization of sediments by benthic organisms.

Sediment collection and treatment

We collected sediment with a ponar dredge from two PAH-contaminated sites in the Duluth/Superior Harbor, near Superior, Wisconsin, USA (Hog Island [HI; see 9,10] and Su-
Controlling PAH bioavailability in sediment

Laboratory studies

Sediment avoidance assay. Colonization/avoidance of sediments by the oligochaete Lumbriculus variegatus was assessed using the laboratory sediment avoidance assay developed by West and Ankley [11]. The assay chamber consisted of an 800-ml beaker fitted with three removable 30-ml cups. Two cups were filled with inert glass beads (0.07–0.18 mm in diameter) and the third with test sediment; the space between the cups was filled with fine sand. Ten oligochaetes from onsite cultures [12] were added to each cup containing the test sediment or glass beads and allowed to burrow for 10 min prior to placing the cups into the chambers and the chambers into an automated water-renewal system [13]. Water overlying the sediments was replaced with two volume additions per day of clean Lake Superior water with the general characteristics of pH 7.3; dissolved oxygen, 7.4 mg/L; hardness, 44 mg/L as CaCO₃; and alkalinity, 45 mg/L as CaCO₃. Assays were conducted at 23 ± 1°C with a photoperiod of 16 h light:8 h dark. Animals were not fed during the course of the 72-h exposures. Laboratory sediment avoidance tests were terminated by removing chambers from the water renewal system and enumerating oligochaetes associated with the different substrates in the test system (i.e., sediment vs glass beads). The premise of the assay was that the oligochaetes would be found in the glass beads (which have no nutritive value and provide little shelter) only when the test sediment was unsuitable for habitation, presumably because of the presence of contaminants.

Bioaccumulation test. Twenty-eight–day bioaccumulation tests were conducted with L. variegatus using methods described elsewhere [12,14]. In addition to bioaccumulation, this assay indicates sediment toxicity in terms of survival/reproduction. Thirty animals were placed in replicate beakers containing 100 ml of sediment. Four replicates were used for each of the six treatments. A fifth replicate, without animals, was prepared for analysis of PAHs in the pore water at test initiation. Test beakers were held in an automated water-renewal system [13] providing two volume renewals of overlying Lake Superior water per day at 23 ± 1°C; animals were not fed during the exposure. Temperature, pH, and dissolved oxygen were measured daily in one replicate beaker of each treatment and stayed within acceptable limits [14]. At test termination, animals were sieved from two of the four replicates. Twenty-four worms were set aside for residue analysis, while six were used in the photo-enhanced toxicity tests described below. Prior to residue analysis, the oligochaetes were held in clean water for 24 h to allow gut clearance [14]. The two remaining replicates were used for pore-water PAH and dissolved organic carbon (DOC) analyses.

Field study

One-liter aliquots of Ambersorb-amended and untreated sediments from the two contaminated sites (HI, SH) were placed into sets of 11 shallow 1.3-L polypropylene trays with covers (Rubbermaid, Wooster, OH, USA) and stored at 4°C for 48 h. Trays were deployed in blocks of four, in a bay near the SH site, with each treatment placed randomly within each block. Once in the field, trays were uncovered, carefully lowered in the water to the bottom, and pressed into the surrounding sediment until even with the lip. Trays within a block were 0.4 to 0.7 m apart, with 0.8 to 1.1 m between blocks; water depth ranged from 0.46 to 0.55 m over the trays. After 55 d in the field (August 3–September 27, 1995), covers were carefully placed on the trays before they were lifted from the surrounding sediment. The trays were then placed on ice and transported back to the lab. Three sets of the recovered trays (i.e., three replicates per treatment) were used for chemical analysis. An additional seven sets of the recovered trays (seven replicates per treatment) were used for benthic community analysis.

Benthic community composition in the sediments was assessed by removing a 18.8 cm² core with a glass tube from each tray (277.4 cm² surface area). These subsamples were preserved in formalin and later sieved (number 40 mesh, 425 μm), sorted, and identified. Eleven different taxonomic groups were enumerated, including Diptera, Annelida, Cladocera, Copepoda, Ostracoda, Trichoptera/Ephemeroptera, Amphipoda, Gastropoda, Pelecypoda, Nematoda, and others [15].

Analytical procedures

Pore-water PAHs. Pore water was isolated from sediment samples by centrifugation at 10,000 g for 30 min at 4°C [16]. The supernatant was decanted through a fine stainless steel screen (230 mesh) to remove resin that remained suspended and then was centrifuged a second time to remove finer sus-
pended particulate matter from the pore water. The resulting pore-water samples were stored at 4°C prior to chemical analyses.

Polycyclic aromatic hydrocarbons were extracted from pore water using a solid-phase extraction disk technique. A 47-mm C$_{18}$ AR Spec® disk (Ansys, Irvine, CA, USA) was precleaned with methylene chloride and acetonitrile before conditioning with methanol and distilled deionized water. Pore water (50–100 ml) was passed through the disk and analytes eluted with 5 ml of acetonitrile followed by two 5-ml aliquots of methylene chloride. The combined extracts were passed through granular sodium sulfate to remove residual water and were concentrated by evaporation to 0.5 to 1.0 ml under a stream of nitrogen gas. Procedural blanks and matrix spike recovery samples were processed similarly.

Pore-water extracts were analyzed for eight target PAHs (naphthalene, phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo[b]fluoranthene, and benzo[a]pyrene) on a HP (Hewlett-Packard, Fremont, CA, USA) 1050 high-pressure liquid chromatograph (HPLC) equipped with a HP 1046A fluorescence detector. Fluorescence detector wavelengths for excitation and emission, respectively, were, for naphthalene, 220 and 325 nm; for phenanthrene and anthracene, 250 and 390 nm; for fluoranthene and pyrene, 237 and 420 nm; for chrysene, 277 and 376 nm; and for benzo[b]fluoranthene and benzo[a]pyrene, 255 and 420 nm. One hundred microliters of sample was injected onto an Adsorbosphere ultrahigh surface area C$_{18}$ column (4.6 mm × 150 mm; Alltech Associates, Deerfield, IL, USA) and eluted with a gradient program starting at 60% acetonitrile/water and linearly ramped to 100% acetonitrile at a flow rate of 1.5 ml/min. The data were collected by evaporation to 0.5 to 1.0 ml under a stream of nitrogen gas. Procedural blanks and matrix spike recovery samples were processed similarly.

The supernatant (extract) was transferred to a volumetric flask, the tissue pellet resuspended in acetonitrile, reconstituted, and the additional supernatant combined with the initial extract. Tissue extracts were analyzed by HPLC as described previously and were also analyzed by GC/MS to confirm identity of analytes quantified by HPLC.

**Sediment PAHs.** Untreated sediment samples were extracted using a procedure modified from Dong et al. [17] (Ambersorb-treated sediments were not analyzed because of uncertainties associated with PAH extraction from the Ambersorb). Five grams of wet sediment was homogenized with 30 g of anhydrous sodium sulfate in a glass jar. Twenty milliliters of methylene chloride was added and the jar was tightly covered with a Teflon®-lined cap and sonicated in a water bath maintained at 35°C for 15 min. Upon cooling to room temperature, the extract was removed, passed through a funnel containing sodium sulfate (prerinised with methylene chloride), and collected in a glass centrifuge tube. An additional 20 ml of methylene chloride was added to the glass jar and the sonication/sodium sulfate steps repeated. The combined extracts were concentrated by evaporating under a nitrogen stream and diluted to appropriate volumes using acetonitrile. The extracts were analyzed by HPLC and GC/MS using the same conditions as above. Percent moisture of sediments was determined by drying 5 g wet weight of sediment overnight at 105°C.

**Quality assurance for PAH analyses.** Procedural blanks, matrix-spiked recovery samples and duplicate samples comprised 10% or more of all samples analyzed. Chromatographic peaks were not detected in blanks at retention times associated with target PAHs. Recovery correction of PAH measurements was performed utilizing the matrix spikes. Polycyclic aromatic hydrocarbon recoveries ranged from 45.5 to 94.3% for pore water, 94.3 to 115.7% for tissue, and 70.0 to 84.9% for sediment. The percentage agreement among duplicate samples ranged from 73 to 94% for sediments and 67 to 100% for pore water. No additional tissue samples were available for duplicate analysis.

**Organic carbon.** Dissolved organic carbon was determined for selected pore-water samples with nondispersive infrared detection following a catalytic oxidation with a Dohrmann DC-190 total organic carbon analyzer (Rosemount Analytical, Santa Clara, CA, USA). The analyzer was calibrated using one-point calibration and samples run simultaneously with a set of quality control standards; agreement of replicate standards was within 10%. Whole sediment samples (sediment both with and without the resin) were analyzed for total organic carbon using the same instrument according to manufacturer’s instructions. The DOC and total organic carbon values were corrected based on recoveries varying from 100.8% to 114.0%, with duplicates agreeing within 8.9%.

**Data analysis**

**Partitioning calculations.** To aid in interpretation of PAH bioavailability in the test system, freely dissolved PAH concentrations in pore water ($c_{pw}^{fd}$) were estimated as:

$$c_{pw}^{fd} = c_{pw}^{total}(1 + K_{DOC}[DOC])$$  (1)

where $c_{pw}^{total}$ is the measured PAH concentration in pore water, [DOC] is the measured pore-water DOC concentration (kg/L), and $K_{DOC}$ is assumed to be 0.1 $K_{OC}$ [18]. The $K_{OC}$ was calculated from $K_{OW}$ as described by Di Toro et al. [4]. The DOC concentration in the Ambersorb-treated SH sample was not measured because of insufficient sample; this concentration was...
Controlled PAH bioavailability in sediment

RESULTS AND DISCUSSION

Laboratory studies

Sediment avoidance. Oligochaetes actively avoided untreated HI sediment, with no animals recovered from the sediment, compared with 93.8% recovered from untreated WBS (Table 1). Although not statistically significant due to high variability, addition of Ambersorb to HI sediment increased mean recovery from 0% to 54.1%, suggesting an improvement in sediment condition. Recovery of oligochaetes from untreated SH and WBS sediments was significantly higher (78.9 and 93.8%, respectively) than in untreated HI sediment (0%). Addition of resin to WBS and SH sediments did not result in significantly different utilization of sediments by *L. variegatus* when compared with untreated WBS and SH.

Bioaccumulation study. Although dissolved oxygen concentrations (5.3–7.3 mg/L) and to a lesser extent pH (7.0–7.5) were higher in Ambersorb-treated sediments than untreated sediments, both parameters remained within acceptable limits for *L. variegatus* during laboratory tests [14]. At the conclusion of the 28-d bioaccumulation test, pore-water DOC was significantly higher in untreated WBS (27.3 ± 0.4 µg/ml) and HI (42.7 ± 1.2 µg/ml) than in treated sediments (7.5 ± 0.5 µg/ml and 11.6 ± 0.2 µg/ml, respectively). Pore water from untreated SH had a DOC concentration of 15.6 ± 0.7 µg/ml. Insufficient pore-water volumes were recovered from the resin-amended SH replicates for DOC analysis.

Mean (standard deviation) percent survival/reproduction of oligochaetes during the 28-d bioaccumulation test were, for WBS, 123 (5.8); for WBS + resin, 121.1 (5.1); for SH, 154.9 (2.3); for SH + resin, 130.1 (6.5); for HI, 95.5 (6.9); and for HI + resin, 119.9 (5.8). A significantly greater number of oligochaetes were recovered from the Ambersorb-treated HI samples compared with the untreated HI sediment. In contrast, the SH samples had significantly more oligochaetes recovered from the untreated sample than sediment with Ambersorb addition, although both were higher than the WBS control. There was no significant difference between untreated and amended WBS sediments.

A subset of animals recovered from the 28-d test were subsequently exposed to UV light in clean water for 24 h. There was no UV-induced mortality of animals from untreated or resin-amended WBS samples. Animals from the untreated SH sediment had 100% mortality after 6.5 h, while those from the Ambersorb-amended SH sediment did not exhibit 100% mortality until after 24 h. All animals from both the untreated and amended HI sediment died within 3.7 h of UV exposure.

Concentrations of PAHs in bulk sediment, pore water, and oligochaete tissue from the bioaccumulation test are provided in Table 2. Percent total organic carbon was 2.6 ± 0.6 and 7.7 ± 0.4 for untreated and treated SH sediment, respectively, and 4.4 ± 0.2 and 6.8 ± 1.2 for untreated and treated HI sediment, respectively. All measured PAHs were at higher concentrations in SH sediment than in HI; none were detected in the WBS sediment. However, amendment of SH and HI sediments with Ambersorb reduced concentrations of PAHs that were detected in pore water and, in the case of HI, reduced PAHs below the analytical quantitation or detection limits. Trends in tissue concentrations in *L. variegatus* of PAHs closely tracked those observed in the pore water (Table 2). Specifically, treatment with Ambersorb significantly reduced measured concentrations of all PAHs detected in animals from treated samples.

Field study

Trends in concentrations of pore-water PAHs in untreated versus amended SH and HI sediments at conclusion of the field study were similar to those observed in the laboratory bioaccumulation study (Table 3). Concentrations of all eight measured PAHs were reduced in resin-amended HI sediment pore water compared with pore water from untreated HI (Table 3). Reductions ranged from 65% for naphthalene to 98% for pyrene. Concentrations of pore-water PAHs were also significantly reduced in pore water from Ambersorb-amended SH sediment when compared with pore water from the untreated samples (Table 3). Reductions ranged from 28% for naphthalene to 98% for fluoranthene.

Benthic community composition in trays retrieved after the 55-d field exposure was similar among treatments (Table 4). Mean number of organisms recovered ranged from 8.6 × 10⁴ organisms/m² in the amended SH to 1.4 × 10⁴ organisms/m² in untreated HI. Trays containing resin-treated sediments often contained fewer organisms than those with untreated sediment; however, these differences were not significant. Mean percent

<table>
<thead>
<tr>
<th>Table 1. Results from laboratory sediment avoidance assays (± standard deviation) using untreated and resin treated sediments</th>
</tr>
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<tbody>
<tr>
<td>Site</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>West Bearskin</td>
</tr>
<tr>
<td>Superior Harbor</td>
</tr>
<tr>
<td>Hog Island</td>
</tr>
</tbody>
</table>

*a = 2.  
*b = 3.*
Synthesis of study results

Several, though not all, biological measures indicated that resin addition reduced bioavailability of the specific PAHs measured and improved the biological suitability of sediments. Resin treatment of HI sediment decreased avoidance by oligochaetes in the laboratory sediment avoidance assay and increased the number of worms recovered following the 28-d bioaccumulation test, a response sensitive to sediment contamination at other sites [22]. Ultraviolet light-induced mortality of oligochaetes exposed to SH sediment was also reduced by Ambersorb addition. However, other responses suggest that the eight measured PAHs may not have been the only toxicants of significance in these sediments. For example, oligochaetes exposed to Ambersorb-amended sediments generally had nondetectable concentrations of the measured PAHs yet still exhibited photo-enhanced toxicity under UV light exposure. Although time to death was increased by resin treatment of SH sediment, HI samples did not show the same improvement despite comparable reductions in measured tissue PAHs.

Table 3. Sediment and pore-water polycyclic aromatic hydrocarbon (PAH) concentrations at conclusion of 55-d field experiment with and without Ambersorb® resin treatment

*ND = not detected; BQL = below quantitation limits (sediment = 70 ng/g for all PAHs) (pore water analyzed by GC/MS = 1.0 ng/ml for benzo[a]pyrene, 0.5 ng/ml for benzo[b]fluoranthene and chrysene, 0.1 ng/ml for all other PAH; pore water analyzed by high-performance liquid chromatography = 0.1 ng/ml for all PAHs; tissue = 124 ng/g for all PAHs).

*a Significantly different from corresponding untreated sample (p ≤ 0.05).

*b One or more replicates were BQL.

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Sediment dry weight (ng/g)</th>
<th>Pore water (ng/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(untreated/treated)</td>
<td>(untreated/treated)</td>
</tr>
<tr>
<td>Superior Harbor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>925 ± 1,434</td>
<td>0.08 ± 0.04/0.06 ± 0.02</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>22,269 ± 22,114</td>
<td>0.31 ± 0.19/0.03 ± 0.02b</td>
</tr>
<tr>
<td>Anthracene</td>
<td>7,667 ± 9,153</td>
<td>0.29 ± 0.17/0.04 ± 0.03b</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>25,537 ± 26,727</td>
<td>2.02 ± 0.65/0.03 ± 0.02b</td>
</tr>
<tr>
<td>Pyrene</td>
<td>19,687 ± 19,469</td>
<td>1.20 ± 0.24/0.05 ± 0.03b</td>
</tr>
<tr>
<td>Chrysene</td>
<td>17,430 ± 16,471</td>
<td>1.14 ± 0.31/0.16 ± 0.03b</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>6,158 ± 5,879</td>
<td>0.09 ± 0.04/0.02 ± 0.01b</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>11,748 ± 11,683</td>
<td>0.15 ± 0.06/0.03 ± 0.02b</td>
</tr>
<tr>
<td>Hog Island</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Naphthalene</td>
<td>BQL</td>
<td>0.13 ± 0.06/0.05 ± 0.01</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>297 ± 232</td>
<td>0.07 ± 0.03/0.01 ± 0.01bc</td>
</tr>
<tr>
<td>Anthracene</td>
<td>BQL</td>
<td>0.01 ± 0.02/ND</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>872 ± 200</td>
<td>0.07 ± 0.07/ND</td>
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<tr>
<td>Pyrene</td>
<td>974 ± 145</td>
<td>0.45 ± 0.19/0.01 ± 0.01bc</td>
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<tr>
<td>Chrysene</td>
<td>516 ± 72</td>
<td>0.11 ± 0.11/0.01 ± 0.01c</td>
</tr>
<tr>
<td>Benzo[b]fluoranthene</td>
<td>463 ± 154</td>
<td>0.11 ± 0.03/0.01 ± 0.01bc</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>636 ± 213</td>
<td>0.12 ± 0.04/0.01 ± 0.01bc</td>
</tr>
</tbody>
</table>

*a ND = not detected; BQL = below quantitation limits (sediment = 70 ng/g for all PAHs) (pore water = 0.01 to 0.02 ng/ml for Superior Harbor [WL, USA], and 0.025 to 0.05 ng/ml for Hog Island).

*b Significantly different from corresponding untreated sample.

*c One or more replicates were BQL.
wise, survival/reproduction responses in the bioaccumulation test differed between the SH and HI sediments even though tissue concentrations of measured PAHs were similar. This suggests that at least some of the biological responses observed in our studies were caused by toxics other than the measured PAHs; work by Kosian et al. [10] suggested that the UV-enhanced toxicity of pore waters from HI sediments was partially attributable to substituted and heterocyclic PAH structures not measured in the present study. Without knowing the identity of the additional chemicals causing toxicity and their responses to Ambersorb treatment, it is difficult to fully evaluate the ability of Ambersorb to improve overall biological suitability of these specific contaminated sediments.

In field deployments, Ambersorb-amended sediments did not result in increased colonization by benthic invertebrates despite decreased PAH concentrations in pore water. Several potential explanations for this lack of improvement exist. Although reductions in contaminant concentrations in pore-water quality were substantial, it is possible that the Ambersorb treatment did not effectively reduce the bioavailability of PAHs sufficiently to affect colonization potential. Alternatively, other contaminants that do not partition strongly to Ambersorb may have influenced colonization. Aspects of the experimental design may also have affected colonization; because the trays containing the untreated and Ambersorb-amended sediments were placed in an environment with background contamination (near the SH site), the local pool of benthic organisms available for colonization may have been limited. Colonization might be expected via pelagic drift [23,24], but 55 d may not have been adequate to detect animals entering the trays via this route or the comparatively small refugia offered by the trays may not have been sufficient to foster colonization.

Finally, it may be that there are characteristics of the resin and/or interaction of the resin with the sediment that result in suboptimal conditions for benthic animal colonization and reproduction. For instance, Ambersorb amendment substantially reduced pore-water DOC concentrations (72% in measured samples); other studies have shown that dissolved organic material can serve as a direct or indirect source of nutrition for benthic invertebrates [e.g., 25–27]. Hence, resin-induced decreases in pore-water DOC could affect benthic invertebrate reproduction (bioaccumulation test with SH + resin) and/or desirability of benthic habitats (field study colonization and laboratory sediment avoidance with SH + resin).

### Partitioning behavior

While the focus of this study was to evaluate the effect of Ambersorb on PAH bioavailability, peculiarities in the chemical partitioning within untreated sediments caught our attention. Partitioning of nonionic organic chemicals in sediments is often described as approximating equilibrium between pore water and the organic carbon phase of the sediment [4]. This approach generally assumes that all sources of organic carbon are sufficiently comparable in their partitioning properties that they can be effectively described with a single partition coefficient, $K_{OC}$, which can be estimated from $K_{ow}$ [4]. However, recent papers have documented unusual partitioning behavior of PAHs in sediments, which has been attributed to the presence of soot particles [28,29]. Bulk sediment and pore-water chemistry data collected in the present study also indicate that the observed partitioning to pore water is one to two orders of magnitude lower than would be predicted from literature $K_{OC}$ values (Fig. 1), suggesting that either (1) a portion of the PAHs in the sediment is in forms that are functionally unavailable for partitioning [28] or (2) a portion of the organic carbon in the sediment has a much higher partitioning coefficient [29].

<table>
<thead>
<tr>
<th>Organisms/m²</th>
<th>Superior Harbor</th>
<th>Hog Island</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Composition</td>
<td>Untreated</td>
<td>Treated</td>
</tr>
<tr>
<td>Dipera</td>
<td>$51.1 \pm 14.3$</td>
<td>$47.0 \pm 23.8$</td>
</tr>
<tr>
<td>Amelida</td>
<td>$18.0 \pm 5.4$</td>
<td>$24.7 \pm 7.2$</td>
</tr>
<tr>
<td>Cladocera</td>
<td>$3.3 \pm 1.5$</td>
<td>$4.6 \pm 2.9$</td>
</tr>
<tr>
<td>Copepoda</td>
<td>$6.2 \pm 3.2$</td>
<td>$3.3 \pm 1.5$</td>
</tr>
<tr>
<td>Ostracoda</td>
<td>$9.2 \pm 3.1$</td>
<td>$10.7 \pm 7.5$</td>
</tr>
<tr>
<td>Trichoptera/Ephemeroptera</td>
<td>$0.8 \pm 0.9$</td>
<td>$0.5 \pm 0.9$</td>
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<tr>
<td>Amphipoda</td>
<td>$0$</td>
<td>$0$</td>
</tr>
<tr>
<td>Gastropoda</td>
<td>$1.0 \pm 1.1$</td>
<td>$0.7 \pm 0.7$</td>
</tr>
<tr>
<td>Pylcopoda</td>
<td>$1.4 \pm 0.8$</td>
<td>$1.5 \pm 1.0$</td>
</tr>
<tr>
<td>Nematoda</td>
<td>$8.3 \pm 4.5$</td>
<td>$6.5 \pm 2.8$</td>
</tr>
<tr>
<td>Other</td>
<td>$0.8 \pm 0.7$</td>
<td>$0.5 \pm 0.4$</td>
</tr>
</tbody>
</table>

![Fig. 1. Ratio of apparent organic carbon coefficient ($K_{OC}$) to $K_{OW}$ predicted from $K_{OC}$ for sediments from two sites in the Duluth/Superior Harbor (near Superior, WI, USA).](image)
though small pieces of coal were visible in the SH sediment. Bender et al. [30] showed very low biological availability of PAHs to oysters exposed to coal dust slurries. Research is needed to rigorously determine which of the proposed reasons for unusual partitioning behavior in the presence of soot/coal is correct and to modify the equilibrium partitioning expression accordingly, either by quantifying and subtracting the sediment PAH unavailable for partitioning or quantifying the PAH partitioning to these additional carbon matrices.

As organisms that ingest whole sediment, oligochaetes should be exposed to sediment PAHs via both ingestion and pore water. Equilibrium partitioning theory asserts that the route of exposure to PAHs is irrelevant because the solid and pore water. Equilibrium partitioning theory asserts that the solid and pore water phases are in approximate equilibrium; hence, the chemical activity in both is the same regardless of the actual concentrations in each medium. Concentrations of PAHs in oligochaete tissues measured in this study support this contention. Tissue concentrations predicted from pore-water PAHs are closely (within a factor of 10) to measured values (Fig. 2), while tissue concentrations predicted from bulk sediment are generally much lower than would ordinarily be associated with this level of pore-water exposure, apparent bioavailability corresponded to chemical activity in the sediment (as indexed by freely dissolved pore-water PAHs) rather than to PAH concentration in the sediment. This finding opposes the views of organism, its interaction with sewage sludge. Mar Environ Res 18:133–153.


Summary
Addition of 4% Ambersorb resin to two field-collected sediments consistently reduced pore-water PAH concentrations in both a 28-d laboratory bioaccumulation assay and a 55-d field study. The PAH concentrations measured in tissues from the bioaccumulation test provided evidence that pore-water concentrations correctly predict bioavailability of PAH regardless of exposure routes or sediment concentration. The addition of resin also reduced sediment avoidance by L. variegatus and improved their survival/reproduction in HI sediment and reduced phototoxicity in SH sediment. While biological results at times were less than conclusive, these data support the conceptual utility of in situ remediation of sediment-associated contaminants by the addition of high-capacity partitioning materials. This remediation approach has been used successfully to treat contaminated water samples [e.g., 32–34] but has not received significant attention for sediment-associated contaminants.

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