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AC amendment to Phragmites marsh reduces PCB bioavailability

# Persistent Reductions in the Bioavailability of PCBs at a Tidally Inundated *Phragmites australis* Marsh Amended with Activated Carbon

James P. Sanders,[a] Natasha A. Andrade,[a] Charles A. Menzie,[b,c] C. Bennett Amos,[b,c] Cynthia C. Gilmour,[d] Elizabeth A. Henry,[e] Steven S. Brown,[f] and Upal Ghosh[a,c,*]

[a]Department of Chemical, Biochemical, and Environmental Engineering, University of Maryland, Baltimore, Maryland, USA

[b]Exponent, Alexandria, Virginia, USA

[c]Sediment Solutions, Ellicott City, Maryland, USA

[d]Smithsonian Environmental Research Center, Edgewater, Maryland, USA

[e]Anchor QEA, Saratoga Springs, New York, USA

[f]The Dow Chemical Company, Midland, Michigan, USA

* Address correspondence to ughosh@umbc.edu

**This article contains online-only Supplemental Data**



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**Abstract:** In situ amendment of sediments with highly sorbent materials like activated carbon (AC) is an increasingly viable strategy to reduce the bioavailability of persistent, sediment-associated contaminants to benthic communities. Because in situ sediment remediation is an emerging strategy, much remains to be learned about the field conditions under which amendments can be effective, the resilience of amendment materials toward extreme weather conditions, and the optimal design of engineered applications. Here we report the results of a multi-year, pilot-scale field investigation designed to measure the persistence and efficacy of AC amendments to reduce the bioavailability of polychlorinated biphenyls (PCBs) in an intertidal *Phragmites* marsh. The amendments tested were granular AC (GAC), GAC with a layer of sand, and a pelletized fine AC. Key metrics presented include vertically-resolved black carbon concentrations in sediment and PCB concentrations in sediment, porewater, and several invertebrate species. The results demonstrate that all three amendments withstood Hurricane Sandy and remained in place for the duration of the study, successfully reducing porewater PCB concentrations by 34–97%. Reductions in invertebrate bioaccumulation were observed in all amendment scenarios, with pelletized fine AC producing the most pronounced effect. Our findings support the use of engineered AC amendments in intertidal marshes, and can be used to inform amendment design, delivery, and monitoring at other contaminated sediment sites. This article is protected by copyright. All rights reserved

**Keywords:** PCB, Remediation, Sediment, Marsh, Phragmites, Activated Carbon

## INTRODUCTION

Hydrophobic organic compounds (HOCs) in sediments can be taken up by pelagic or benthic organisms through ingestion and dermal absorption and subsequently passed on to higher organisms and humans. For both of these pathways, the extent of uptake depends on the bioavailability of contaminants in sediment (Luthy and others 1997; NRC 2003). Work in the last two decades has demonstrated that black carbon (BC)—including soot, coal, and charcoal—strongly bind HOCs, and the presence of BC in sediments (both natural and anthropogenic) reduces uptake, often by an order of magnitude or more compared to natural organic matter (Ghosh and others 2000; Lohmann and others 2005). Contaminant sequestration in native sediments can be greatly enhanced by the addition of clean, manufactured carbonaceous materials such as activated carbon (AC) (Ghosh and others 2011). Laboratory tests with a variety of field sediments have shown that AC amendment in the range of 2–5% d.w. reduces equilibrium porewater concentrations of polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene) (DDT), dioxins, and furans in the range of 70–99%, thereby reducing the driving force for diffusive flux of HOCs into water and transfer into organisms (Ghosh and others 2011). Most studies using benthic organisms show a 70–90% reduction in biouptake of HOCs in AC-amended sediment compared to unamended controls (Ghosh and others 2011; McLeod and others 2007; Millward and others 2005; Sun and Ghosh 2007; Zimmerman and others 2005). These studies have collectively demonstrated that contaminant bioavailability in sediments can be reduced by engineered amendments.

In a recent pilot-scale study, application of AC to contaminated river sediments reduced biouptake of PCBs in benthic organisms (Beckingham and Ghosh 2011). After amendment with

AC at a target dose of 3.75% by dry weight, bioaccumulation in freshwater oligochaete worms was reduced by 69–99% compared to pre-amendment conditions, and concentrations of PCBs in water at equilibrium with sediment were reduced by more than 93% at all amended sites for up to three years of monitoring (Beckingham and Ghosh 2011).

Much is known about AC amendment in aquatic sediments in rivers, estuaries, mudflats, and lakes. However, no information is available on the persistence or efficacy of AC amendment in the sediment environment created within a *Phragmites australis* marsh, which can include densely structured root mats. To address this knowledge gap, we evaluated AC amendments in a *Phragmites* marsh impacted with legacy PCB and mercury contamination. While PCB and mercury investigations were conducted in parallel using the same experimental plots, this work reports only the PCB results. The study was conducted in the field as a pilot-scale demonstration to evaluate the persistence and efficacy of three different modes of application of AC on the sediment surface. Monitoring focused on sediment BC and key exposure pathways for PCBs into the food web (porewater and benthic organisms).

## MATERIALS AND METHODS

*Study Site Description.* This work was conducted at the Berry's Creek Study Area (BCSA) in Bergen County, New Jersey. Berry's Creek is an oligohaline tidal tributary (salinity 0–10 ppt; 4–5-ft tides) to the Hackensack River which is located in the Hackensack Meadowlands about five miles west of New York City. Marshes dominated by *Phragmites* constitute 306 hectares (~756 acres) and approximately 75% of the tidal area within the BCSA. This dense *Phragmites* marsh is supported by thick root mats that create a physically stable landscape, promoting consistent deposition (accretion) of new sediment (Weis and others 2005; Wright and Blauvelt 2010) and providing an important buffer against storm surge and flooding.

In fact, BCSA marshes experienced limited erosion from Superstorm Sandy in 2012, and helped substantially to limit damage to residential and commercial properties from an approximately 8-ft storm surge. BCSA comprises three distinct, federally-designated Superfund sites, and the surrounding region was formerly home to extensive industrial activity which resulted in contamination by mercury, PCBs, and other chemicals. This study was completed within Nevertouch Marsh, which is located in Upper Berry's Creek, adjacent to the Ventron/Velsicol Superfund Site. Nevertouch Marsh sediments are sulfidic and high in organic matter (Gilmour and others 2013). Invertebrate organisms native to the site include wolf spiders (*Lycosidae* spp.), which are found on *Phragmites* stems and on top of the marsh detrital layer, and the large, epibenthic amphipod *Orchestia grillus*.

*Amendment Application.* Four experimental plots were delineated within Nevertouch Marsh, each 10 m x 10 m and bounded by a 6-m buffer zone (Figure S7). Plot A was amended with SediMite™, a pelletized agglomerate of 50% powdered activated carbon (Siemens regenerated AC, < 30 mesh), sand, and clay (www.sedimite.com); Plot B served as an unamended control; Plot C was amended with coconut-shell based granular activated carbon (GAC; OLC WW 20 x 50 mesh from Calgon Corp.) topped by a 2–3 cm layer of sand; and Plot D was amended with GAC only. Previous work has shown pronounced amendment efficacy with a 5% dose of AC (Beckingham and Ghosh 2011; Fagervold and others 2010). The objective of application in the present study was to achieve this dose in the uppermost sediment layer, which represents the zone of greatest relevance to benthic organisms (USEPA 2005). In view of anticipated disruption of the amendment layer by tidal movement and bioturbation, a conservative application rate resulting in 5% AC in the top 10 cm assuming full mixing was calculated, and a further 25% safety factor was added for plot A resulting in a SediMite™

application rate of 5 kg $m^{-2}$ (2.5 kg AC $m^{-2}$). For Plots C and D, where a coarser AC was used, the application rate was increased to 3.3 kg $m^{-2}$. The site was prepared by clearing *Phragmites* reeds from the plots and installing suspended metal planks a few inches above the sediment surface to facilitate access and sampling. The walkways also served to delineate nine subplots, each approximately 3 m x 3 m, within each plot. SediMite™ was applied using a Vortex TR system (Vortex Granular Systems, Lighthouse Point, FL) that uses a flow of air to draw the pelletized material into an air stream and eject it to distances up to 12 m. Weight data from collection trays placed prior to SediMite™ application showed an average application rate of 4.8 ± 1.0 kg $m^{-2}$, close to the target of 5 kg $m^{-2}$. GAC was applied as a water slurry to the surfaces of Plots C and D. The amount of GAC required to treat a subplot was loaded in large plastic containers and immersed in Berry's Creek surface water for a period of one hour, which hydrated the activated carbon and prevented it from being suspended in the water column during the first high tide following application. After an hour, the contents of the containers were thoroughly mixed and transferred into a 100-gallon tank. A gasoline-powered water pump was used to remove the slurry from the tank and eject it through a nozzle, which evenly distributed the slurry over the surface of the subplot. The thin sand layer placed over the activated carbon amendment in Plot C was moved from a staging area using a Telebelt conveyor. The sand was distributed over the plot by hand to a thickness of approximately 1".

*Monitoring.* Monitoring occurred at seven different time points, which for simplicity will hereafter be referred to by the number of months before or after the August 2012 amendment application: July 2012 ($t_{-1}$); October 2012, prior to Hurricane Sandy ($t_{+2}$; see Fig. 1); November 2012, after Sandy ($t_{+3}$); July 2013 ($t_{+11}$); November 2013 ($t_{+15}$); May 2014 ($t_{+21}$); and September 2015 ($t_{+37}$).

*Sediment Collection.* Sediment samples were collected using 4.8-cm i.d. boring core tubes from the 0- to 5-cm depth horizon at five randomly selected locations within each subplot and composited into a single sample. Collection occurred at low tide to minimize standing water. Soils were sampled using cutting/boring cores in an effort to capture root mass. The use of composite samples was intended to minimize the confounding effect of anticipated spatial variability of contaminant concentrations within the plots. Processing of sediment core samples for vertical profiling changed throughout the monitoring period in response to a growing detritus layer developing on the marsh surface. Before AC application, most of the detritus was cleared from the marsh surface. Sediment cores collected at $t_{+2}$ were sectioned into a visible amendment layer followed by 0–5 cm and 5–10 cm sediment layers. This was done because of the differing thicknesses of the amendment layers among plots. For example, the GAC and sand amendment created the thickest layer of new material over the marsh surface and had to be accounted for during sample processing. An opportunistic sampling was performed one month after Hurricane Sandy ($t_{+3}$) to observe the effect of extreme weather on the persistence of amendment materials. In this effort, only the top 0–5 cm interval was sampled, including the detritus and amendment layers along with some sediment. In the subsequent two sampling events ($t_{+11}$ and $t_{+15}$), a distinct new layer of detritus was observed on the surface and was sectioned separately from the amendment and underlying layers. Cores collected for the final two sampling events ($t_{+21}$ and $t_{+37}$) were sectioned more finely, enabling generation of high-resolution vertical profiles of BC.

*Passive Sampling.* Porewater PCB concentrations ($C_{pw}$) were measured with passive sampling devices containing polyethylene (PE; Husky, Bolton, Ontario) in either 17.7 or 25 µm thicknesses or polyoxymethylene-ethylene oxide copolymer (POM; CS Hyde, Lake Villa, IL) in either 38 or 76 µm thicknesses. $C_{pw}$ values were calculated with the standard equilibrium

partitioning equation and constants (Ghosh and others 2014). When possible, performance reference compound (PRC) desorption data were used to adjust porewater concentrations for nonequilibrium. Adjusted concentrations are denoted $C_{pw}$'. More details on the passive sampling effort are provided in (Sanders and others 2018 (in review)).

*Materials.* PCB solutions were prepared using individual congener and Aroclor standards in hexane purchased from Ultra Scientific (Kingstown, RI). All other chemicals and solvents were purchased from Fisher Scientific (Rockville, MD). Hexane and acetone were pesticide grade (CAS Nos. 110-54-3 and 67-64-1). Anhydrous sodium sulfate was ACS grade (CAS No. 7757-82-6). Silica gel was 644 or 923 grade (CAS No. 112926-00-8 or 63231-67-4). Copper powder was lab grade (CAS No. 7440-50-8). Sulfuric acid was ACS Plus grade (CAS No. 7664-93-9). Potassium dichromate was ACS grade (CAS No. 7778-50-9).

*Analytical Methods.* The moisture content of wet sediment samples was determined by weighing representative subsamples (250 mg) of homogenized sediment, drying in an oven overnight at 105 °C, and recording the difference in mass. Tissue and sediment samples were extracted by ultrasonication in 1:1 hexane:acetone according to U.S. EPA SW-846 method 3550C. Extracts were treated with activated copper powder to remove sulfur interference following U.S. EPA SW-846 method 3660B. Beginning with the $t_{+11}$ sampling, activated copper was also added directly to wet sediment samples and mixed with a glass stir rod prior to extraction to address extensive sulfur interference. All extracts were cleaned up in deactivated silica gel columns following U.S. EPA SW-846 method 3630C.

All PCB samples were analyzed by gas chromatography with electron capture detection (Agilent 6890N with a fused silica capillary column: Rtx-5MS, 60 m x 0.25 mm i.d., 0.25 μm film thickness from Restek, Bellefonte, PA, USA) according to an adapted version of U.S. EPA

SW-846 method 8082A (Beckingham and Ghosh 2011). A total of 91 congeners or coeluting congener groups were quantified. PCB BZ #30 and 204 were used as internal standards. PCB BZ #14 and 65 were added as surrogates prior to all sample extractions to assess loss during processing. The total concentration of the 87 remaining target congeners/congener groups (representing the commercial Aroclor mixtures 1232, 1248, and 1262) is hereafter denoted ΣC. All statistical tests were performed in Microsoft Excel.

*Black Carbon Determination.* BC in sediment was measured with a chemical oxidation method (Grossman and Ghosh 2009). Briefly, dried sediment samples were treated with a solution of potassium dichromate in concentrated sulfuric acid to remove organic carbon, then thermally combusted and analyzed on a Shimadzu TOC-5000A with solid sample module SSM-5000A. A 5% BC sediment standard was processed alongside samples to quantify recovery.

*In Situ Exposure Chambers.* An in situ sediment exposure chamber was developed for this study. The chamber consisted of a 12” long, 6” i.d. tubular chamber with 500-µm mesh-covered ports on one end. The exposure chamber was driven vertically into the sediment of each subplot to a depth of approximately 10”, which left the bottom of the ports 1” above the sediment surface. The chambers were loaded with 125 3–5 mm, salinity-acclimated *Leptocheirus plumulosus*, an estuarine amphipod commonly used in toxicity testing, capped using a rubber pipe cap the center of which had been removed and replaced with 500-µm mesh, and left in place for an exposure period of 14 d. Organism loading was based on the tissue masses required to support mercury, PCB, and lipid analysis and an anticipated recovery rate of 50% due to the inherent difficulties of in situ exposures. After the exposure period, the upper 2–3” of sediment within the chambers was collected and sieved, and the surviving *L. plumulosus* individuals (100–400 mg tissue weight from each chamber) in this sieved material were collected and depurated

for a period of 4–6 h in spring water. Following depuration, the organisms were blotted dry with filter paper, weighed, and immediately frozen for transport and analysis of moisture, lipid content and PCB concentrations.

Due to low organism recoveries, several modifications were made to the in situ exposure chamber method following the first deployment of the chambers during the pre-application monitoring event. The modifications were intended to enhance air and water exchange and provide additional shade. Further details can be found in the Supporting Information.

*Laboratory Bioaccumulation Assays.* The recoveries and masses of *L. plumulosus* from the in situ exposure chambers were lower than anticipated during the $t_{-1}$ and $t_{+2}$ monitoring events due to impaired water exchange within the chambers ($t_{-1}$) and installation of the organisms into the amendment materials ($t_{+2}$), so for the $t_{+11}$ monitoring event, intact cores were collected for use in laboratory bioaccumulation assays to provide an additional measure of bioaccumulation. The intact sediment cores were collected by driving 12” sections of 4” i.d. polycarbonate tubing into the sediment to a depth of 6”. The top of the core was capped, the core was extracted from the sediment, and then capped on the bottom. Four adjoining sediment cores were collected from each of the subplots. The samples were shipped on wet ice to EnviroSytems, Inc. (Hampton, NH) and used in bioaccumulation assays with *L. plumulosus* and the amphipod *Hyalella azteca* (salinity acclimated) according to ASTM E-1706 (ASTM 2010).

*Native Invertebrate Tissue.* Native invertebrate samples were collected from each of the plots. The target organism was *O. grillus*, which was observed during preliminary surveillance but became increasingly scarce during the study period. Organisms were collected from plot surfaces with forceps and placed in spring water for a depuration period of 4–6 h. After

depuration, the animals were blotted dry with filter paper, weighed, and immediately frozen for transport and analysis of PCBs, lipid content, and moisture content.

*O. grillus* were difficult to find in the plots after application of amendments. This was likely due to the partial removal of detritus from the plots, as *O. grillus* rely upon detritus as a source of food and cover from predation. The scarcity of this organism was observed in Plot B as well, indicating that it was not caused by the presence of amendment materials. Spiders were collected as a supplementary native invertebrate during the $t_{+11}$ monitoring event. Results are presented in the Supporting Information.

In this work, an organism "sample" (one *n*) refers to a composite of multiple individual organisms of a single species except in cases where individual spiders were sampled (see Supporting Information). Composites were assembled to achieve analytically detectable PCB masses and typically consisted of 200–500 mg wet tissue weight. Samples were homogenized with $Na_2SO_4$ using a glass stir rod and extracted in 1:1 hexane:acetone using an adaptation of EPA method 3550C. An aliquot equal to one tenth of the extract volume was quantitatively removed for lipid analysis, with the remainder proceeding to PCB analysis. Organism lipid content was measured using a method originally developed for mosquitos (Van Handel 1985). In brief, each aliquot was evaporated to dryness, treated with a vanillin-phosphoric acid reagent to induce a color change, and analyzed on a Genesys 10S UV-visible spectrophotometer (ThermoScientific, Waltham, MA).

*Quality Assurance/Quality Control.* Surrogate recoveries in sediment extracts averaged 83 ± 19% for PCB BZ#14 and 79 ± 12% for PCB BZ#65 ($n$ = 163). Average recoveries in passive sampler extracts were 92 ± 9.7% for PCB BZ#14 and 88 ± 9.2% for PCB BZ#65 ($n$ = 167). Recoveries in organism extracts averaged 77 ± 13% for PCB BZ#14 and 74 ± 12% for

PCB BZ#65 ($n$ = 67). Data from PCB samples with less than 60% recovery of each surrogate compound are not reported. Standard recoveries in black carbon samples averaged 86 ± 12% ($n$ = 13). No values were adjusted to account for standard recoveries.

**RESULTS AND DISCUSSION**

*Activated Carbon in Sediment.* Activated carbon was measured as BC in sediment core samples collected in six distinct sampling events spanning more than three years after amendment application. While pre-application samples were not collected from the amended plots, the BC content in Plot B (control) was low at 0.1% (n = 5) in Sep 2012 and this was taken as representative of the background level in all plots. No background correction was applied. The BC content of the surface sediment and detritus layers in plot B increased to a value of 1.1% in 2013 samples, potentially due to redistribution of some AC from the adjacent treatment plots. As summarized in Figure 2, the data from all time points indicate elevated levels and persistence of AC in all three amended plots throughout the study period.

At $t_{+2}$, high levels of BC in the amendment layers were measured. Plots A and D had the highest levels of BC, in the range of 30-32% ($n$ = 4 and 5, respectively, $p < 0.05$), while BC measured in Plot C was significantly lower at 5.0 ± 3.0% ($n$ = 5, $p < 0.002$) due to the dilution effect of the sand. At $t_{+3}$, AC was present in all amended plots at levels comparable to those measured before the storm, demonstrating the resilience of the amendments. In Plots A and D, where applied AC was exposed to the surface, the detritus layer defined for $t_{+11}$ and $t_{+15}$ would have included AC, while in Plot C, the detritus layer was dominated by sand. Thus, the apparently shallower penetration of AC below the amendment layer was likely an artifact of sample sectioning methods. At $t_{+15}$, the amendment layer in Plot A contained 19 ± 10% BC d.w. ($n$ = 5), in Plot C 7.2 ± 7.9 % ($n$ = 6), and in Plot D 31 ± 22% ($n$ = 5). Since duplicate analyses

of individual samples were generally reproducible, the large variability in these measurements can be ascribed to a real phenomenon, i.e. a spatially heterogeneous distribution of amendment materials within each 100-$m^2$ plot. These results provide a basis for realistic anticipation of application uniformity and have important implications for the design of future remediation projects. The addition of a sand layer in Plot C was intended to prevent loss of AC, but it also served to dilute the AC in surface sediments, resulting in the lowest concentrations among the three amended plots.

Sediment below the amendment layer showed some integration of amendment materials over time. Compared to previous sampling events, this layer contained elevated BC levels at $t_{+15}$: 8.6 ± 8.7%, 1.0 ± 1.0%, 4.1 ± 1.9%, and 5.7 ± 6.8% in plots A–D, respectively. However, the variability in the data and the subjectivity involved in identifying and sectioning the amendment layer made precise quantification of downward AC migration into sediments difficult. To investigate vertical migration more carefully, samplings were performed at $t_{+21}$ (Plot A only) and $t_{+37}$ (Plots A, C, and D) in which cores were sectioned into 1-cm intervals in the uppermost 5 cm, and a 5-cm interval spanning the 5–10 cm horizon. Measurement of black carbon in these samples enabled generation of high-resolution BC depth profiles (Fig. 3). In plot A at $t_{+21}$, concentrations averaged 22 ± 6.8% d.w. ($n$ = 5) in the top 1-cm layer and 23 ± 6.6% d.w. ($n$ = 5) in the 1–2 cm layer. BC content was below the amendment target of 5% d.w. in the 3–4 cm interval (2.0 ± 1.6% d.w. ($n$ = 5)), and consistent with background levels in the 4–5 cm and 5–10 cm intervals. At $t_{+37}$, comparable BC profiles were observed in all three amended plots, with the exception of lower concentrations in the upper horizons of Plot C due to dilution by sand. These results indicate a vertical extent of mixing of 3–5 cm after three years with very little AC penetrating below 5 cm. Such slow integration of amendment materials likely owed to low

benthic activity and the presence of a dense *Phragmites* root mat that resisted sediment mixing. We observed similarly shallow vertical integration in a salt marsh in Penobscot, ME (Gilmour and others 2018). This contrasts with an observed penetration below 8 cm observed in Grasse River sediments 3 years after a layered application of AC (Beckingham and Ghosh 2011). Insofar as the benthic zone is of greatest relevance, this outcome of slow penetration was not entirely negative, but the possibility should be taken into account in future applications in sediments with dense rooted vegetation. In cases where greater pollutant loads exist at lower depths, limited vertical mixing could be desirable. The fact that amendment materials in all three plots remained in place through more than three years of tidal cycling and a major storm event demonstrates the resilience required for a successful field application of these technologies. Because the amendments without a sand layer remained in place, the diluting effect and additional expense associated with the sand layer proved unnecessary.

Samples from the three treatment plots at $t_{+37}$ can be used to compare the amount of AC remaining after 37 months with the original applied dose. In plot A, the applied SediMite™ had 15% moisture, and the BC content of the AC was 84% (Grossman and Ghosh 2009). Thus, the applied mass loading of BC was 1.8 kg BC $m^{-2}$. The recovered mass of BC at $t_{+37}$ for plot A was 1.7 (±0.5) kg BC $m^{-2}$ (94% of the applied mass). Plots C and D received GAC at an application rate of 3.3 kg AC $m^2$ which translates to a BC loading rate of 2.9 kg BC $m^{-2}$ assuming 87% BC in the coconut GAC[13]. For Plot C, which also received a sand layer (bulk density of 1.6 kg $L^{-1}$), the recovered mass of BC was 3.0 (±0.4) kg $m^{-2}$ (103% recovery) and for Plot D the recovered mass of BC was 3.1 (±1.0) kg $m^{-2}$ (107% recovery). Thus, after 37 months in the field and after a major storm that flooded the area, the recovered mass of BC in the top 10 cm of sediment was

close to the applied dose in each plot. It is likely that the *Phragmites* reeds and roots sheltered amendment materials from the erosive effects of tidal and storm activity.

*PCB Concentrations in Sediment.* In all plots, a characteristic PCB homolog distribution was observed in sediment, with tetra- and penta-CB homologs dominating the distribution (Figure S2). Total PCB concentrations ($\Sigma C_{sed}$) in unamended sediment samples were in the range of 1.0–3.0 µg $g^{-1}$ d.w. at surficial and subsurficial depths throughout the study period ($n$ = 4 or 5 for each sampling). At $t_{+15}$, detrital layer $\Sigma C_{sed}$ (0.53 ± 0.29 µg $g^{-1}$ d.w.) was 62% lower in Plot A compared to control (1.4 ± 0.12 µg $g^{-1}$ d.w.). The largest reduction in total sediment concentration was observed in Plot C (0.25 ± 0.17 µg $g^{-1}$, an 82% reduction) and the smallest in Plot D (0.75 ± 0.58 µg $g^{-1}$, a 46% reduction). In general, surface placement of amendment materials was successful at reducing PCB concentrations in the new detritus collecting on the marsh surface. The observed recontamination of the fresh detritus collecting on the treated plot surface is likely from a combination of exposure to contaminated porewater in the treated layer combined with exposure to surface water at each tidal cycle. The tidal deposition of PCBs was evaluated using trays of clean topsoil placed on the marsh as described in the Supplemental Information. After exposure in the marsh environment through many tidal cycles over a period of three and a half months, the PCB concentration in the topsoil nearly doubled from 0.04 µg $g^{-1}$ ($n$ = 2) to 0.08 µg $g^{-1}$ ($n$ = 3; $p$ = 0.054). The largest increases were observed in the tri- and tetrachloro congeners, pointing to sorption from the dissolved phase as the most likely mechanism of recontamination. Thus, for long-term effectiveness, any remedy implemented in the marsh will have to address the concentrations of PCBs in the water that overtops the marsh during tidal cycling. Final homolog distributions were similar to those in native marsh sediments, but final $\sum C_{sed}$ was much lower.

PCB concentrations in the amendment layer of all three amended plots were lower than the concentrations measured in the 0–5 cm layer, with the lowest value found in Plot C (due to dilution with the sand layer). However, below the amendment layer, $\Sigma C_{sed}$ in all plots remained close to 1.5 µg $g^{-1}$ one year after amendment and within the range of 1.0–3.0 µg $g^{-1}$ through all sampling times. No temporal trends in sediment PCB concentrations were apparent across the three sampling events in the year after application.

*PCB Concentrations in Sediment Porewater.* Freely dissolved concentrations of PCBs in sediment porewater were measured by passive sampling with POM and PE. At $t_{-1}$, total PCBs in porewater ($\Sigma C_{pw}$; unadjusted for nonequilibrium) were 1.0–4.0 ng $L^{-1}$ in all plots in both the 0–2.5 cm and 5–7.5 cm depth intervals (Fig. 4). At $t_{+2}$, $\Sigma C_{pw}$ in the upper interval was decreased by 97% in Plot A (SediMite™), 48% in Plot B (control), 76% in Plot C (GAC and sand), and 86% in Plot D (GAC; $n$ = 5 for Plots A, B, and D, $n$ = 3 for Plot C). In all subsequent sampling events through $t_{+15}$, upper-interval $\Sigma C_{pw}$ in amended plots remained low relative to both pre-amendment levels in the same plots and concurrently measured levels in Plot B. At $t_{+15}$, the smallest reduction (34%) was observed in Plot C. The largest proportional upper-interval reductions occurred in Plot A, where $\Sigma C_{pw}$ was 91–97% lower than the initial value at all sampling events throughout the study. In the 5–7.5 cm depth interval, significant reductions in $\Sigma C_{pw}$ were only observed in Plot A, where they were significant at all sampling events (t-test, $p < 0.05$). This finding is discussed at greater length separately (Sanders and others 2018 (in review)).

*Sediment-Water Partitioning.* PCB sediment-water partitioning constants ($K_d$) were calculated for the $t_{+11}$ sampling data by dividing $C_{sed}$ by $C_{pw}$' (adjusted using the $k_e$-$K_{pw}$ PRC method described separately (Sanders and others 2018 (in review))). Because $C_{sed}$ was measured in the upper 5 cm of sediment while $C_{pw}$' represented only the upper 2.5 cm in that sampling

event, the resulting $K_d$ values should be interpreted with care, particularly in the amended plots. The discrepancy is less relevant for Plot B, where no significant vertical trend in $C_{pw}$ was found in subsequent high-resolution measurements (Sanders and others 2018 (in review)).

In all plots, PCB $K_d$ exhibited a log-log correlation with $K_{ow}$ (Hawker and Connell 1988) across individual congeners (Fig. 5). In Plot A, $K_d$ was elevated compared to the other three plots by roughly one order of magnitude across the range of hydrophobicities. This can be attributed in part to the more strongly sorbing, higher-surface area, fine-grained AC used in the amendment materials in this plot, and helps to explain the larger reductions in PCB $\Sigma C_{pw}$ and bioaccumulation (next section) observed in the plot. Increases in $K_d$ were more pronounced at the lower end of the $K_{ow}$ range, and the Plot A results exhibited greater scatter due to the larger relative error in $C_{pw}$ measurements near our lower analytical detection limits. Despite some reductions in $C_{pw}$ in Plots C and D as a result of amendment, there was no evident increase in $K_d$ in these plots relative to Plot B (control). This may owe to the much smaller reductions in $C_{pw}$ in plots C and D compared to plot A, the discrepancy between porewater and sediment sampling horizons, as well as the potential for artificially low $C_{sed}$ as a result of reduced extractability from amended sediment (31–34% on average and more pronounced for lower-chlorinated congeners; see Supporting Information). Trends in $K_d$ were evaluated with reference to a simple partitioning model based on the assumption that organic carbon was the dominant binding phase for PCBs:

$$K_d = f_{oc} K_{oc} \tag{1}$$

where $f_{oc}$ is the fraction of sediment comprising organic carbon and $K_{oc}$ is the organic carbon-water equilibrium partitioning constant for each congener or coeluting group. In the absence of a

directly measured value, $f_{oc}$ was set at 11% by multiplying the average measured loss-on-ignition (LOI) in the plots (31%) by a correction factor of 0.36 (Costello and others 2011; Gilmour and others 2013). $K_{oc}$ values for all congeners were derived from a model for sorption of hydrophobic chemicals to sediment (Karickhoff and others 1979):

$$\log K_{oc} = 1.00 \times \log K_{ow} - 0.21 \quad (2)$$

Measured $K_d$ values in Plots B, C, and D were higher than predicted by this simple model, which is sensitive to imprecision in LOI and $f_{oc}$ values and does not take into account partitioning to black carbon, present even in Plot B at low background concentrations (Lohmann and others 2005). While the fraction of BC in each plot varied, the influence of BC in overall $K_d$ was accounted for as follows (Fadaei and others 2015; Werner and others 2010a):

$$K_d = (f_{oc} - f_{bc})K_{oc} + f_{bc}K_{bc} \quad (3)$$

where $f_{bc}$, the mass fraction of black carbon in sediment, was set at 5% (the application target for the amended plots), and $K_{bc}$, the partitioning coefficient for black carbon, varies linearly with $K_{ow}$ in the concentration ranges measured in this work (Werner and others 2010b):

$$\log K_{bc} = 0.91 \times \log K_{ow} + 1.37 \quad (4)$$

With this model, a good fit for the observed data in Plots B, C, and D was obtained (Figure 5). For Plot A, the BC-inclusive model still underpredicted $K_d$, probably because the fine-grained AC used in Plot A is a much stronger sorbent than the modeled BC.

*PCB Bioaccumulation in Field and Laboratory Exposures.* All three amendments effected reductions in PCB bioaccumulation compared to unamended sediment. A summary of amphipod bioaccumulation results from both field and laboratory exposures can be found in Table 1. At $t_{+2}$, both caged and native, free-ranging amphipods contained reduced PCB body burdens ($\Sigma C_{org}$) in all three amended plots relative to Plot B (control). For caged *L. plumulosus*, reductions of 98%, 68%, and 76% were observed in Plots A (SediMite™), C (GAC and sand), and D (GAC), respectively. Similarly, $\Sigma C_{org}$ in native, free-ranging *O. grillus* collected in Plots A, C, and D was 78% ($p < 0.05$), 48% (not statistically significant), and 68% ($p < 0.05$) lower, respectively, than in Plot B. Overall, reductions in bioaccumulation in amended plots were more pronounced for caged versus native organisms. This can be explained by a combination of two factors. First, native organisms collected from the plots were free-ranging and some could have been washed into or out of unamended buffer zones by the tide, thereby diluting the effect of amendment. Second, native organisms could have spent part of their early lives in unamended, contaminated sediments whereas caged organisms were provided as lab-cultured organisms and presumably began with minimal prior exposure. Beginning with $t_{+3}$, native *O. grillus* became too scarce to collect sufficient tissue for PCB analysis. Indeed, visually apparent benthic organisms in both control and amended plots were generally more scarce than expected during these sampling events, and survival and recovery of caged organisms was also inconsistent, probably due to the large amounts of detritus and poor habitat within enclosed chambers that did not provide adequate shelter during low tide.

In 10-d laboratory exposures to intact sediment cores, *L. plumulosus* $\Sigma C_{org}$ was 84% lower in Plot A sediment than in unamended sediment (Table 1). Tissue recoveries from Plot C and D laboratory exposures were insufficient for analysis. Two separate experiments were performed with *H. azteca*. In the first, $\Sigma C_{org}$ was reduced by 96%, 90%, and 71% in Plot A, C, and D sediment, respectively ($p < 0.01$ for all three). In the second, 64% and 77% reductions in Plot C and D sediments were observed, but only the latter was statistically significant ($p = 0.05$). Biota-sediment accumulation factors for *H. azteca* are presented in Figure S5. Insufficient tissue was available for Plot A in the second experiment. Overall, all three amendments led to reduced bioaccumulation in laboratory exposures, with fine-grained AC in the form of SediMite™ producing the most pronounced effect.

*Implications.* Previous pilot-scale demonstration projects with in situ amendment of AC to sediments have targeted marine mudflats (Cho and others 2009), rivers (Beckingham and Ghosh 2011), and deep ocean deployments (Cornelissen and others 2012). Results from this field study provide new insights into the technical feasibility and effectiveness of in situ remediation for a *Phragmites*-dominated, intertidal marsh with PCB contamination. AC amendments applied in a *Phragmites* marsh were stable over the three-year period of observation through multiple tidal cycles and a major storm. All three amendment types demonstrated reductions in the concentration of PCBs in surface sediment porewaters (34–97%) and in benthic organisms (48–98%), with the largest reductions associated with the use of a pelletized, fine-grained activated carbon (as SediMite™). Many coastal ecosystems have been historically impacted by the deposition of contaminated sediments and are difficult to remediate using the common approaches of sediment removal or capping. In situ amendments as described in this paper provide an alternative that can reduce exposure of pollutants to the food web without

significantly impacting the existing ecosystem in the marsh by dredging or other, more disruptive methods. Future studies in this type of marsh environment should take into account our observation of extremely low and highly variable benthic community density. Any studies including sampling of native organisms should perform an exhaustive survey. In situ exposures should take measures to ensure organism survival by minimizing heat and dryness within the chambers.

*Supplemental Data*—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

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*Disclaimer*—U. Ghosh is a co-inventor of two patents related to the technology described in this paper for which he is entitled to receive royalties. One invention was issued to Stanford University (US Patent # 7,101,115 B2), and the other to the University of Maryland Baltimore County (UMBC) (U.S. Patent No. 7,824,129). In addition, UG and CAM are partners in a startup company (Sediment Solutions) that has licensed the technology from Stanford and UMBC and is transitioning the technology in the field.

*Data availability*— Data, associated metadata, and calculation tools are available from the corresponding author (ughosh@umbc.edu).

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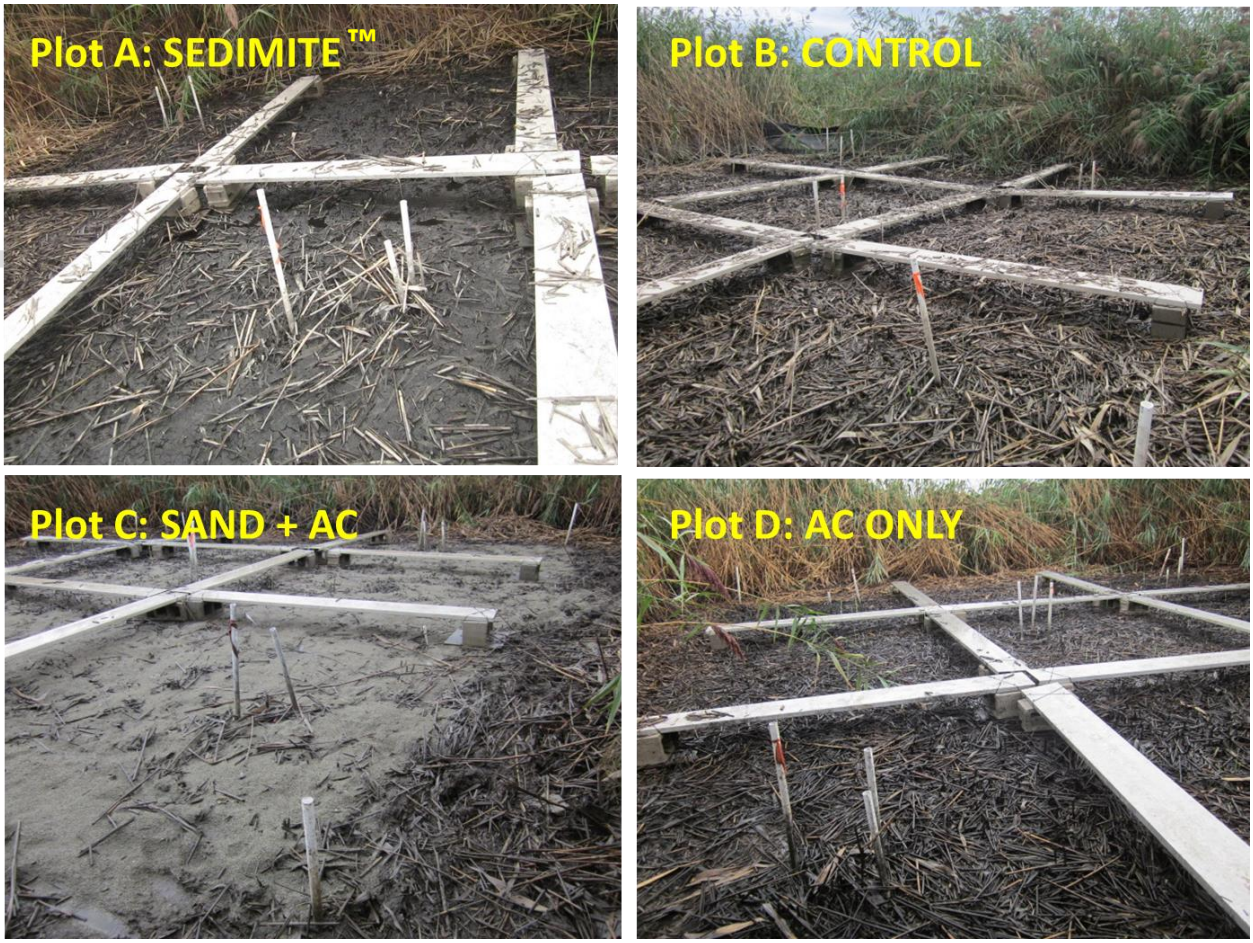
Figure 1. Appearance of the experimental plots two months after amendment application.

Figure 2. Dry-weight black carbon content of BCSA sediments, arranged by plot (A: SediMite™, B: unamended control, C: GAC and sand, D: GAC), layer, and date. Error bars show standard deviation among cores ($1 \leq n \leq 5$).

Figure 3. Depth profile of black carbon content (% d.w.) in BCSA sediment 37 months after amendment application. Red: SediMite™; blue, GAC; green, GAC and sand. Error bars show standard deviation among samples at each depth ($n$ = 5 or 6).

Figure 4. Average total PCB concentrations measured in sediment porewater using POM passive samplers in the 0-2.5 cm depth interval at BCSA. Values are unadjusted for fractional PRC loss. Error bars show one standard deviation among samplers in each plot ($n$ = 5 except ^ ($n$ = 4)). Percent decreases from each plot's pre-amendment value are shown. Asterisks denote statistical significance ($p < 0.05$).

Figure 5. Logarithmic sediment-water partitioning coefficients for individual PCB congeners or congener groups. Data are from the $t_{+11}$ sampling. Each $K_d$ value is calculated from an average $C_{sed}$ value ($n$ = 5) for the 0–5 cm horizon and an average $C_{pw}$' value ($n$ = 5) for the 0–2.5 cm horizon. $C_{pw}$ was adjusted with the $k_e$-$K_{ps}$ PRC method (Sanders and others 2018 (in review)). Orange line: organic carbon model; black line: organic carbon and black carbon model (see text for descriptions).

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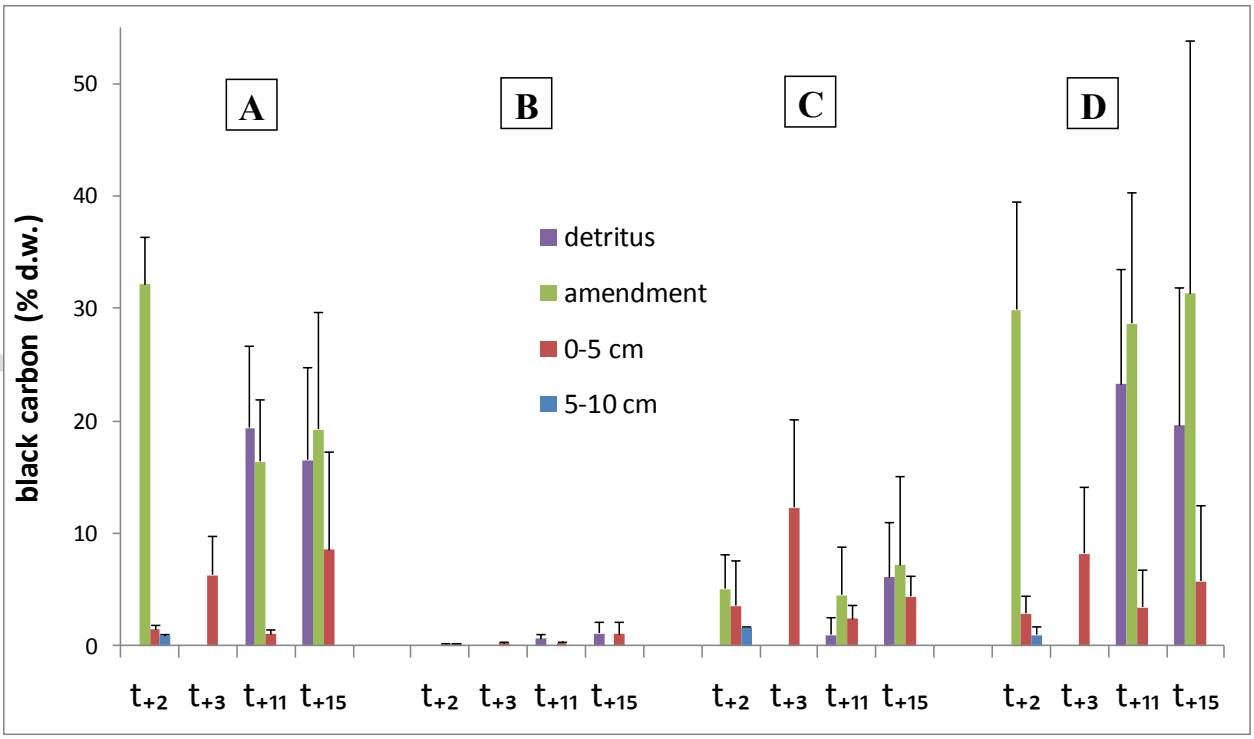


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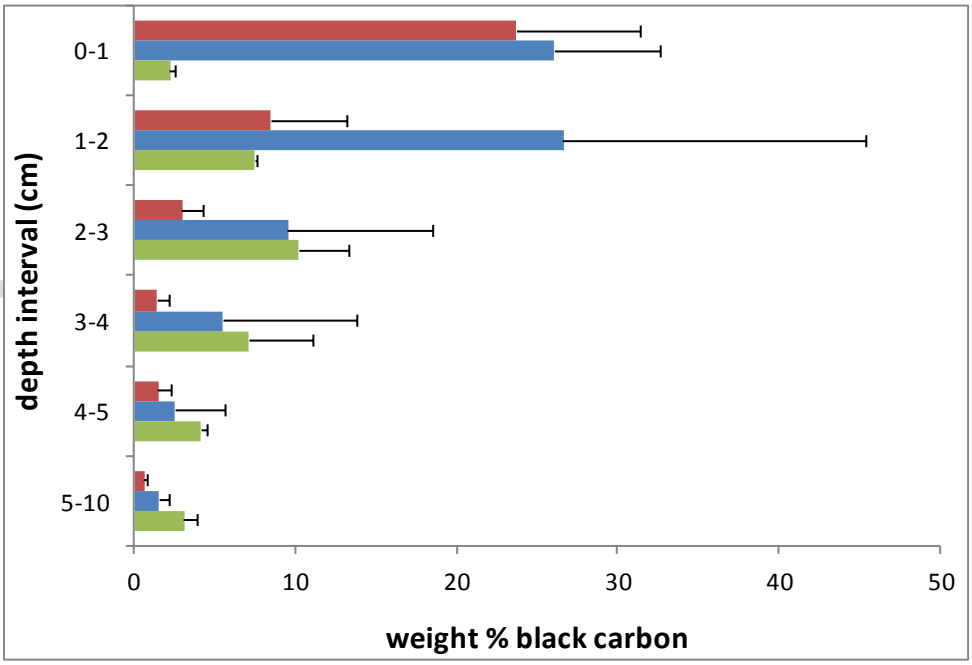


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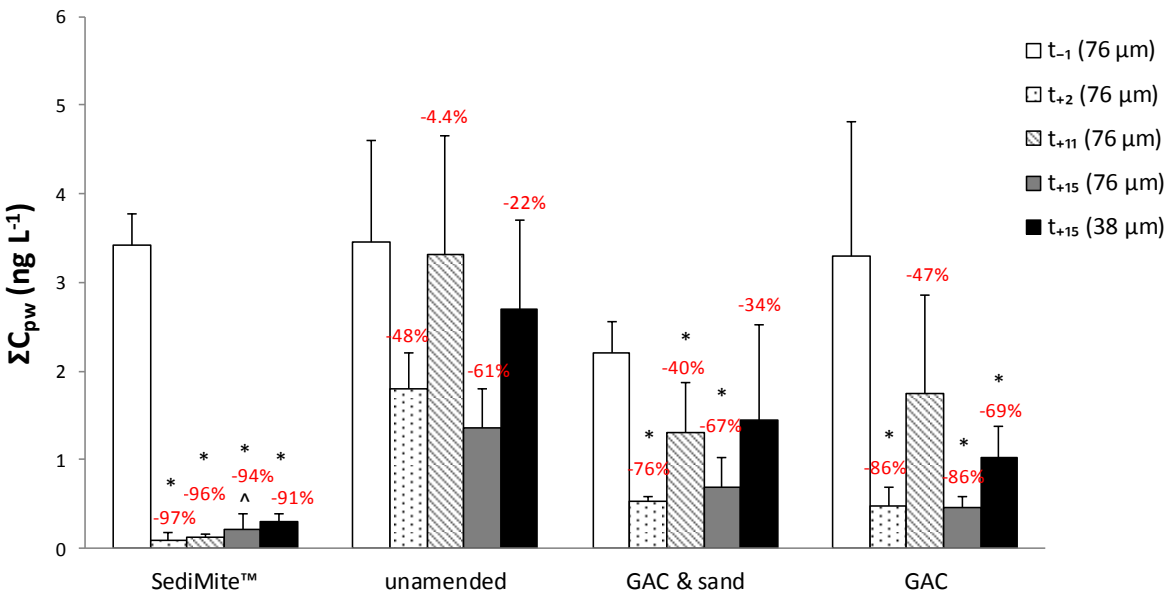


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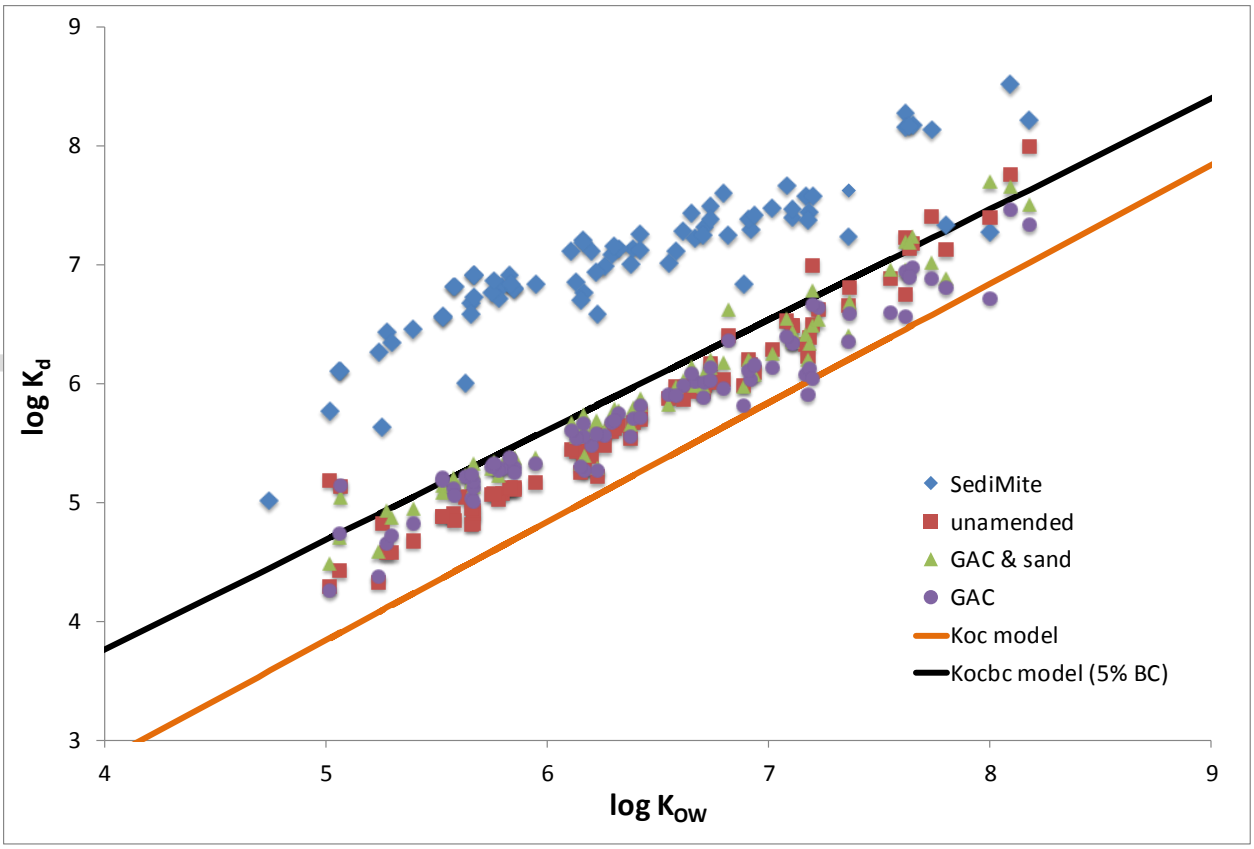


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**Table 1.** Summary of amphipod bioaccumulation data.

| Monitoring Event | Metric | Lab Control Sediment | Plot A (SediMite™) | Plot B (unamended) | Plot C (GAC & sand) | Plot D (GAC) |
|---|---|---|---|---|---|---|
| $t_{+2}$ | sediment BC, wt %* | n.d. | 1.5 ± 0.42 (5) | 0.15 ± 0.017 (5) | 3.6 ± 3.9 (5) | 2.9 ± 1.5 (5) |
| | $\Sigma C_{pw}$, ng $L^{-1}$** | n.d. | 0.091 ± 0.086 (5) | 1.8 ± 0.39 (5) | 0.54 ± 0.046 (3) | 0.47 ± 0.21 (5) |
| | caged *L. plumulosus* $\Sigma C_{org}$, ng $g^{-1}$ w.w. | n.d. | 17 (1) | 1000 ± 100 (2) | 330 (1) | 240 (1) |
| | native *O. grillus* $\Sigma C_{org}$, ng $g^{-1}$ w.w. | n.d. | 420 (1) | 2100 (1) | 490 (1) | 500 (1) |
| $t_{+11}$ | sediment BC, wt %* | n.d. | 1.0 ± 0.34 (5) | 0.26 ± 0.042 (5) | 2.4 ± 1.2 (5) | 3.4 ± 3.3 (5) |
| | $\Sigma C_{pw}$, ng $L^{-1}$** | n.d. | 0.12 ± 0.041 (5) | 3.3 ± 1.3 (5) | 1.3 ± 0.56 (5) | 1.8 ± 1.1 (5) |
| | lab *L. plumulosus* $\Sigma C_{org}$, ng $g^{-1}$ w.w. | 25 ± 14 (3) | 46 (1) | 280 ± 110 (2) | n.d. | n.d. |
| | lab *H. azteca* $\Sigma C_{org}$, ng $g^{-1}$ w.w. | 6.7 ± 6.0 (3) | 10 ± 2.9 (3) | 300 ± 37 (3) | 30 (1) | 86 ± 35 (3) |
| $t_{+15}$ | sediment BC, wt %* | n.d. | 8.6 ± 8.7 (5) | 1.0 ± 1.0 (5) | 4.1 ± 1.9 (6) | 5.7 ± 6.8 (5) |
| | $\Sigma C_{pw}$, ng $L^{-1}$** | n.d. | 0.20 ± 0.19 (4) | 1.4 ± 0.44 (5) | 0.69 ± 0.33 (5) | 0.47 ± 0.11 (5) |
| | lab *H. azteca* $\Sigma C_{org}$, ng $g^{-1}$ w.w. | 22 ± 8.9 (3) | n.d. | 240 ± 74 (3) | 87 (1) | 55 ± 17 (3) |

* 0–5 cm depth interval; ** 0–2.5 cm depth interval measured with POM-76 and unadjusted for nonequilibrium; *n* given in parentheses