

## Activated Carbon Mitigates Mercury and Methylmercury Bioavailability in Contaminated Sediments

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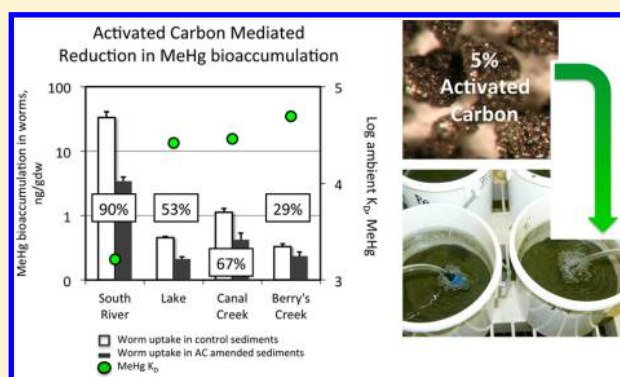
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### Supporting Information

**ABSTRACT:** There are few available in situ remediation options for Hg contaminated sediments, short of capping. Here we present the first tests of activated carbon and other sorbents as potential in situ amendments for remediation of mercury and methylmercury (MeHg), using a study design that combined 2 L sediment/water microcosms with 14 day bioaccumulation assays. Our key end points were pore water concentrations, and bioaccumulation of total Hg and MeHg by a deposit-feeding oligochaete *Lumbriculus variegatus*. Four amendments were tested: an activated carbon (AC); CETCO Organoclay MRM (MRM); Thiol-SAMMS (TS), a thiol-functionalized mesoporous silica; and AMBERSEP GT74, an ion-exchange resin. Amendments were tested in four separate microcosm assays using Hg-contaminated sediments from two freshwater and two estuarine sites. AC and TS amendments, added at 2–7% of the dry weight of sediments significantly reduced both MeHg concentrations in pore waters, relative to unamended controls (by 45–95%) and bioaccumulation of MeHg by *Lumbriculus* (by between 30 and 90%). Both amendments had only small impacts on microcosm surface water, sediment and pore water chemistry, with the exception of significant reductions in pore water dissolved organic matter. The effectiveness of amendments in reducing bioaccumulation was well-correlated with their effectiveness in increasing sediment:water partitioning, especially of MeHg. Sediments with low native sediment:water MeHg partition coefficients were most effectively treated. Thus, in situ sediment sorbent amendments may be able to reduce the risk of biotic Hg and MeHg uptake in contaminated sediments, and subsequent contamination of food webs.



### INTRODUCTION

In-situ sorbent amendments have attracted recent attention as a relatively low-cost, low-impact approach for remediation of contaminated sediments.<sup>1</sup> Sorbent amendments are designed to increase contaminant binding to sediments, rather than removing the contaminants per se. Sorbent materials, such as activated carbon, biochar, organoclays, and functionalized substrates can be physically mixed into contaminated sediments, added to capping materials, or applied directly to sediment or marsh surfaces.

Sorbent amendments have been effective, both in laboratory and field trials, in reducing bioaccumulation and thus risk of hydrophobic organic contaminants (HOCs).<sup>2–8</sup> In the field trials, sorbents have generally been tested at 2–5% of sediment dry weight based on mixing depths ranging from 10 to 30 cm.<sup>1</sup> The main mode of action is stronger binding to solids and a reduction in the pore water concentration of the toxicant.

This in turn results in reduced uptake by benthic organisms. For HOCs, pore water concentrations are strong predictors of bioavailability. The application of activated carbon (AC) to contaminated sediment appears to be the most efficient and cost-effective amendment for mitigation of HOC bioavailability, both in coastal and freshwater sediments.<sup>5</sup> In laboratory trials, ACs have generally reduced sediment pore water concentrations of PCBs, PAHs, dioxins and DDT by 70–99%, and bioaccumulation by benthic test organisms by 70–90%.<sup>1</sup>

Pilot-scale field trials at Hunters Point, CA<sup>5,6</sup> and Grasse River, NY<sup>7</sup> confirmed the effectiveness of ACs for PCB risk remediation over several years. In both field studies, there was

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no observed impact of AC amendment on existing benthic community. Although some negative impacts have been reported,<sup>9</sup> a recent literature review noted that adverse response to AC exposure are only observed in about 20% of studies.<sup>10</sup> Subsequent work has confirmed the efficacy of in situ AC amendments in remediation of risk from other chlorinated organics<sup>11,12</sup>

To date, in situ amendments have not been widely tested for the remediation of sediment contaminants other than HOCs. Inorganic mercury (Hg<sub>i</sub>) and methylmercury (MeHg) are obvious potential targets. MeHg is highly bioaccumulative, and the main goal in Hg remediation is often to reduce risk from this form of Hg.<sup>13,14</sup> Like PCBs, the sediment:water partition coefficient for MeHg can be a strong predictor of bioavailability to benthic fauna.<sup>15,16</sup> Activated carbon is commonly used in treatment of Hg-contaminated waters, and can reduce the level of extractable Hg in soils.<sup>17</sup> If sorbent amendments can reduce pore water total Hg and MeHg concentrations, and/or enhance partitioning to sediments, they should be effective in reducing bioavailability to organisms.

The strong sorption of Hg<sub>i</sub> and MeHg to natural organic matter in sediments and soils supports the idea that AC could be effective in reducing their concentrations in pore waters. The concentration of natural organic matter in sediments is a strong predictor of total Hg and MeHg partitioning between the bulk phase and pore water ( $K_D$ ).<sup>18–21</sup> Further, the bioaccumulation of MeHg by benthic organisms such as polychaetes,<sup>15</sup> amphipods<sup>22</sup> and sipunculans<sup>23</sup> has also been negatively related to sediment organic content.

Currently, there are few remediation options for sediment Hg contamination short of dredging and capping. Dredging can achieve mass removal<sup>24,25</sup> but may resuspend and mobilize contaminants.<sup>26,27</sup> In-situ capping can be a low cost remediation practice and imposes less adverse environmental impact compared to dredging.<sup>28,29</sup> However, buried contaminants may be transported through the capping layer and enter into the overlying water through bioturbation, tidal pumping, and groundwater flow.<sup>30</sup> Regulations may not permit changes in marsh or sediment elevation, and where they do, elevation changes may alter community structure. Capping may also impact the magnitude and depth of MeHg production.<sup>31</sup> Recent field studies show that thin-layer caps that include AC, and AC mixed into surface sediments have limited impact on benthic community structure and density, especially after some recolonization time.<sup>10</sup>

Here we present the first tests of AC and other sorbents as potential in situ amendments for remediation of mercury and methylmercury (MeHg), using a study design that combined sediment/water microcosms with 14 day bioaccumulation assays. Our key end points were pore water concentrations and bioaccumulation of total Hg and MeHg. The deposit-feeding oligochaete *Lumbriculus variegatus* was chosen as a test organism, because of its reported salinity tolerance up to 4.2 ppt,<sup>32</sup> and because it is a head-down feeder that ingests sediments and detritus. Sediments from four contaminated sites were tested, including two estuarine and two freshwater sediments. The effect of amendments on both sediment chemistry and bioaccumulation were examined concomitantly. This design allowed us to evaluate impacts of the amendments on net MeHg production and sediment biogeochemistry. It also allowed us to examine multiple lines of evidence for exposure reduction including pore water concentrations, sediment water partitioning, and bioaccumulation.

## MATERIALS AND METHODS

**Contaminated Sediments Tested.** Sediments from four sites were examined. Sites were selected to provide a range of

salinity and biogeochemistry. and based on remediation needs. Shallow river-bottom sediments from South River, VA, were provided by DuPont in October 2008. Bottom sediments from a Hg-contaminated temperate shallow freshwater mid-Atlantic lake were collected in fall 2009. Rohm and Haas Company provided sediment from creek bottom in upper Berry's Creek marsh in New Jersey in fall 2008. Sediments from Canal Creek, MD, adjacent to Aberdeen Proving Grounds, were collected by our group in fall 2008. The top 15 cm of sediments were collected and refrigerated until use in the microcosms.

**Sediment Water Microcosms.** Sediment/water microcosms (Supporting Information (SI) Figure S1) were used to simultaneously assess the impact of amendments on Hg and MeHg partitioning behavior, mercury methylation, and bioaccumulation. The study design was based on the U.S. Environmental Protection Agency (EPA) standard protocol for bioaccumulation using the oligochaete worm, *Lumbriculus variegatus*.<sup>33</sup> This design allowed us to test the effects of amendments on various aspects of the biogeochemical mercury cycle simultaneously with bioavailability.

Four sets of microcosm studies were conducted, one each from each study site, beginning within weeks of sample collection. In each study, three sorbent amendments were tested. The sorbents tested varied among sites (Table 1), although AC was

**Table 1. Amendments to Microcosm Sediments, Based on Physical Measurements of Freshly Collected Sediments<sup>a</sup>**

site	bulk density (g dry/cc)	porosity (ml/cc)	LOI (%)	amendment	amendment amount as:	
					% of dry weight	% of organic matter <sup>b</sup>
South River	0.56	0.72	9.8	none		
				TS	5%	51%
				MRM	5%	51%
Lake	0.26	0.85	12.2	none		
				TS	5%	41%
				MRM	5%	41%
Canal Creek	0.44	0.79	13.1	none		
				AC low <sup>c</sup>	2.4%	19%
				AC med <sup>c</sup>	4.8%	37%
Berry's Creek	0.33	0.83	14.5	none		
				TS	4.4%	31%
				GT74	4.4%	31%
				AC	4.4%	31%

<sup>a</sup>TS = Thiol-SAMMS (Steward Environmental Solutions; a thiol-functionalized mesoporous silica), MRM = CETCO Organoclay Mercury Reduction Medium, AC = Calgon Carbon particulate activated carbon (TOG 80 × 235 mesh), GT74 = AMBERSEP GT74 (an ion exchange resin). <sup>b</sup>Calculated as the mass of added sorbent as a percentage of the dry mass of organic matter in sediments, as measured by LOI. <sup>c</sup>Added as SediMite containing 60% AC by weight.

used in each study. Other amendments were chosen to represent different classes of sorbents. Each study included five replicate microcosms per amendment, plus five unamended control microcosms ( $n = 20$  microcosms per study). Four liter buckets were filled with approximately 750 cc of sediment. Sorbents were added to the sediments and well mixed by

gloved hands. For South River, Lake, and Berry's Creek sediments, the target dose of amendments was 5% by dry weight of sediments, based on physical measurements of fresh sediments (Table 1). For Canal Creek, a range of AC amendment doses was tested (Table 1), as part of preparation for a field trial of AC at the site.

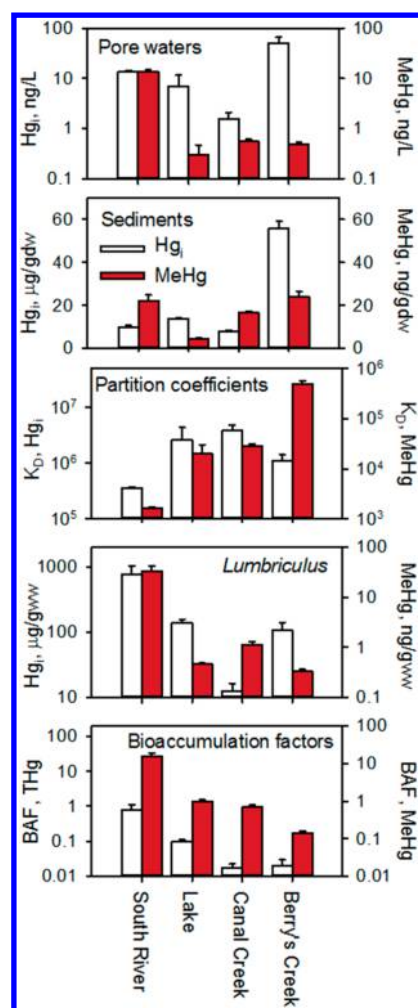
After sorbents were mixed in, sediments were gently covered with 1 L of water. Microcosms were held for several days prior to introduction of worms, in order to allow vertical sediment redox gradients to re-establish. Re-establishment of anoxia within sediments was assessed by following dissolved oxygen and  $\text{NH}_4$  in overlying water. Overlying water for the microcosms was taken from a stream at the Smithsonian Environmental Research Center (W101; water chemistry in SI Table S1).<sup>34</sup> Water was collected fresh and diluted or amended with Instant Ocean to approximate the ionic strength and sulfate concentration of surface water at the contaminated sites (diluted 3:1 and 1:1, respectively, with laboratory DI/RO water for South River and Lake; and amended with Instant Ocean to 2 or 1.5 ppt salinity for estuarine Canal Creek and Berry's Creek). To support the worms, water overlying the sediments was aerated and changed every 2–3 days with minimal disturbance to sediments. Basic water chemistry, including DO, pH, anions, hardness, alkalinity, conductivity, and ammonium ion, was followed in the overlying water. Worms were not added to the microcosms until ammonium levels dropped below 2 mg/L, and DO was above 5 mg/L.

Worms were added as a known weight (~1g wet) to each microcosm chamber. Microcosms with worms were incubated for 14 days in a constant temperature room of approximately 25 °C on a 12 h light, 12 h dark schedule. During the 14 day exposure trial, we continued to replace overlying water every 2–3 days, and to monitor surface water chemistry (SI Figures S2–5). Worms were monitored visually to make sure they were alive and active, watching for burrowing in sediments, and live tails moving in the overlying water.

At the end of the 14 day exposure time, water quality was measured for a final time, and water samples were preserved for additional analysis. The remaining overlying water was removed, and sediments were separated into two portions, one to assess sediment chemistry, the other for recovery of worms. Worms were sieved from sediment, depurated for 8 h in clean spring water, then weighed and frozen in glass vials for total Hg and MeHg analysis.

To avoid sample oxidation—which can result in changes in sediment and pore water chemistry and Hg or MeHg partitioning—the other portion of sediments was processed inside a anaerobic glovebox ( $\text{H}_2/\text{N}_2$  mix) equipped with  $\text{O}_2$ -removal catalysts. Pore waters were separated from solids by centrifugation followed by filtration using 0.22  $\mu\text{m}$  polycarbonate membrane filter units. Pore water analytes included total Hg, MeHg, anions, base cations, pH, sulfide, and DOC. A portion of the bulk sediment was frozen for analysis of total Hg, MeHg, bulk density, and loss on ignition (LOI).

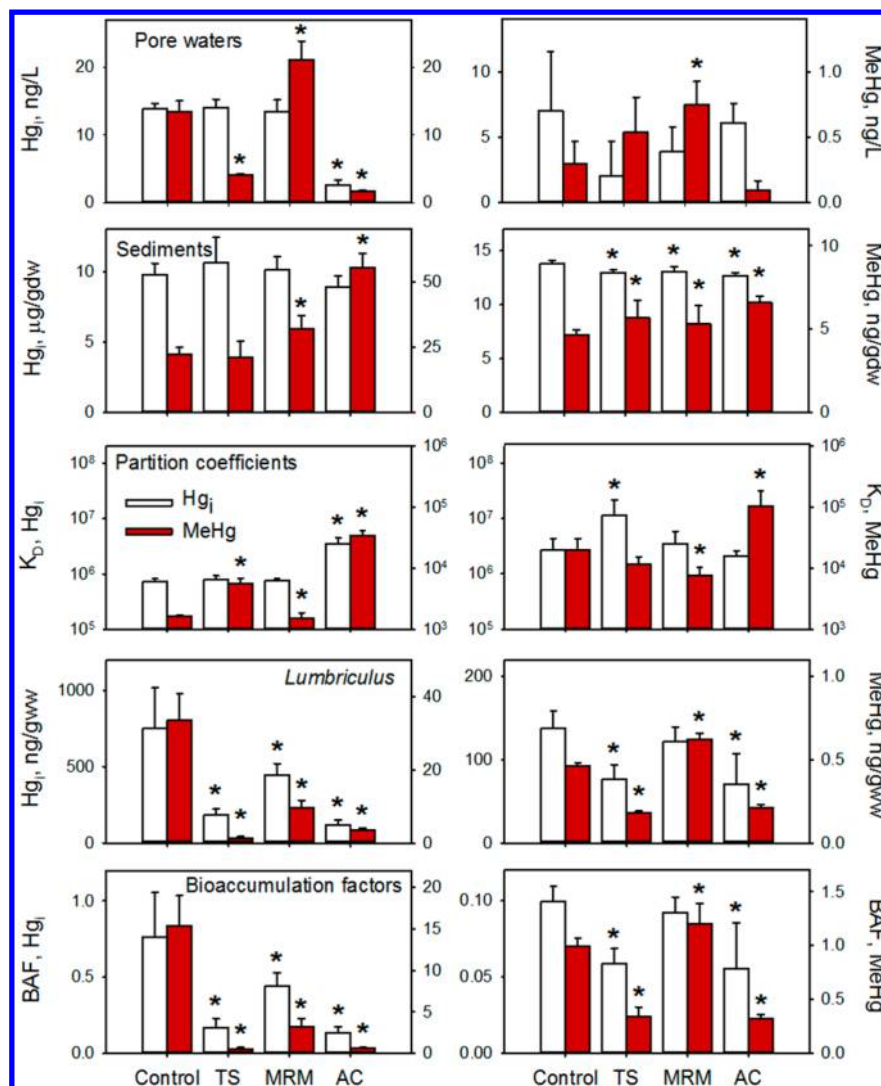
**Sorbents.** The sorbents tested (Table 1) included particulate activated carbon, an organoclay, and proprietary sorbents designed for commercial Hg removal. Particulate activated carbon (TOG 80  $\times$  235 mesh; particle size 75–300  $\mu\text{m}$ ), referred to here as AC, was obtained from Calgon Carbon Corporation. A granular filtration medium developed for Hg sequestration, Organoclay MRM, was purchased from CETCO. Thiol-SAMMS (TS), is a thiol-functionalized mesoporous silica purchased from Steward Environmental Solutions and used in a powder form



**Figure 1.** Cross-site comparison of Hg (white) and MeHg (red) concentrations and bioaccumulation in unamended sediments for the four study sites. Data are from control microcosms after 14 day incubations. Each bar shows the average values plus standard deviation for the five control microcosms in each study. Sediment:water partition coefficients ( $K_D$ ) were calculated as the concentration in sediments in ng/kg divided by the concentration in sediment pore waters in ng/L. BAF was calculated as the concentration in worms (per g dry weight) divided by the concentration in bulk sediments (per g dry weight). Note that all data except Hg and MeHg in sediments are shown on log scales.

(<45  $\mu\text{m}$ ). The uptake capacity of mercury by Thiol-SAMMS is high, approximately 600 mg/g.<sup>35</sup> AMBERSEP GT74, is a commercial ion-exchange resin manufactured by Rohm and Haas Company for mercury removal from solutions and gaseous streams. For the microcosm study, GT74 was crushed with a mortar and pestle and then sieved through a 60  $\mu\text{m}$  sieve. Isotherm studies were conducted separately to ascertain the effectiveness of Hg and MeHg sorption by each amendment (Gomez-Eyles et al. in review). In most cases, the binding capacity was enhanced at lower particle sizes.

**Culturing of *Lumbriculus variegatus*.** Adult mixed-age *L. variegatus* (Aquatic Research Organisms, Hampton, NH) were temporarily held in an aquarium with spring water (pH 7.5) obtained from a small stream located on the campus of the University of Maryland Baltimore County (Baltimore, MD). Worms were cultured following the culturing procedure outlined by the U.S. EPA.<sup>33</sup> On the start day of test, the *L. variegatus* were



**Figure 2.** Results from freshwater microcosm experiments, South River (left) and Lake (right). Inorganic Hg data are on the left axes in white, MeHg data on the right axes in red. Each bar is the average + SD of five replicate microcosms after 14 day incubations. Starred values are significantly different from controls based on ANOVA ( $\alpha < 0.05$ ) and Student-Newman-Keuls comparisons. Note log scales for most data, and different scales across sites.

transferred to a glass pan and counted and weighed before addition to bioassay beakers. Prior to the microcosm uptake studies, 10 day acute toxicity assessments were performed on sediments from Berry's Creek, the freshwater lake and Canal Creek, to test whether *Lumbriculus* would survive exposure in these contaminated sediments. All demonstrated good survival of the organisms ( $\geq 100\%$  recovery of worms added as some reproduced by asexual fragmentation).

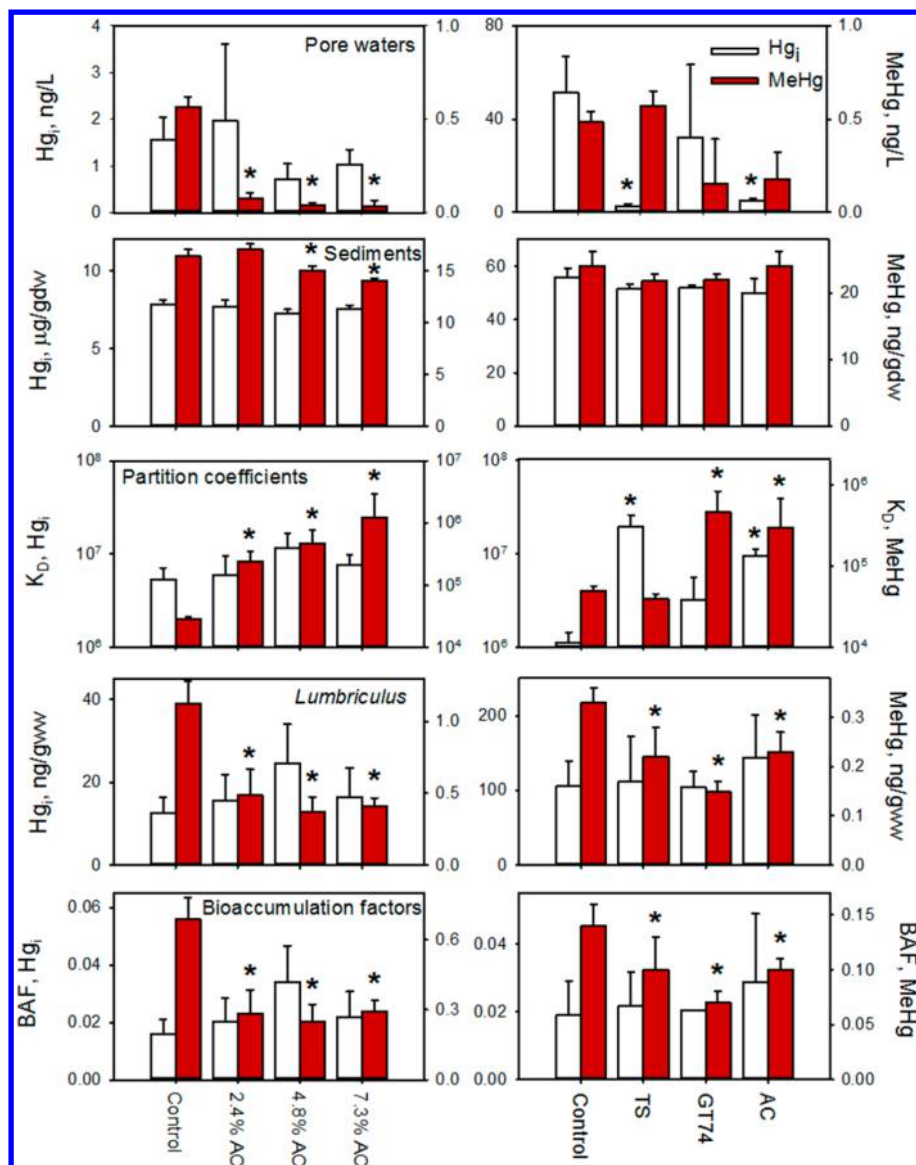
**Mercury and Methylmercury Analyses.** All total Hg and MeHg analyses were carried out using a Perkin-Elmer Elan DRC II ICP-MS after sample preparation by digestion or distillation as described in detail in prior publications.<sup>36,37</sup> These methods are adaptations of EPA Methods 1630 and 1631. Briefly, total Hg samples were digested (hot 7:4 v/v  $\text{HNO}_3/\text{H}_2\text{SO}_4$ ) and introduced into the ICP-MS following  $\text{SnCl}_2$  reduction in a Perkin-Elmer flow-injection/gas stripping system. For MeHg in all matrices, samples were distilled prior to ethylation, purging and trapping onto Tenax, thermal desorption, separation by gas chromatography, and detection with ICP-MS. Inorganic Hg concentrations ( $\text{Hg}_i$ ) were calculated by subtracting measured MeHg from total Hg.

All MeHg analyses were carried out using isotope dilution ICP-MS, significantly improving accuracy and precision of these multistep methods. Isotope dilution spikes were added prior to distillation. Blanks and suitable certified reference materials were run with every batch. Quality assurance data for total Hg and MeHg in various matrices in the study are given in SI Table S2. Detailed methods for other chemical analyses are given in the SI.

**Statistical Analyses.** Differences among treatments were assessed by analysis of variance (ANOVA), with an alpha of 0.05, using SAS 9.1. All variables tested were distributed normally or log transformed to achieve normal distribution.

## RESULTS AND DISCUSSION

**Study Sediment Characteristics.** We examined two contaminated freshwater sediments and two low-salinity estuarine sediments. The sediments ranged in total Hg (THg) concentration from about 10 to 50  $\mu\text{g/g}$  dry weight (Figure 1), well above sediment quality guidelines (SQG) for inorganic Hg toxicity, specifically above the consensus Probable Effect Concentration (PEC) of 1.06  $\mu\text{g/g}$  dry weight.<sup>38</sup> However, the toxicity and



**Figure 3.** Results from estuarine sediment microcosm experiments, Canal Creek (left) and Berry's Creek (right). Inorganic Hg data are on the left axes in white, MeHg data on the right axes in red. Each bar is the average + SD of five replicate microcosms after 14 day incubations. Starred values are significantly different from controls based on ANOVA ( $\alpha < 0.05$ ) and Student-Newman-Keuls comparisons. Note log scales for most data, and different scales across sites.

bioaccumulation of inorganic and methyl mercury are dependent on sediment chemistry and organismal feeding behavior.<sup>15,16</sup> Detailed characteristics of the site are given in SI Table S3.

The total Hg contamination level in the study sediments was not a good predictor of MeHg concentration (SI Figure S6) or pore water Hg or MeHg concentrations among the sites. Typical of contaminated sediments, MeHg accounted for much less than 1% of THg in the bulk phase; MeHg as a percent of THg in sediments (% MeHg) generally declines as THg rises.<sup>39</sup> Among our study sites, the highest %MeHg was found in the least contaminated sediments (SI Figure S6). However, the site with the highest THg (Berry's Creek) also contained the highest concentration of MeHg. The higher %MeHg values were found in the less sulfidic and lower organic carbon sediments.

As is typical of most sediments, MeHg accounted for a much larger percentage of THg in pore waters than in the solid phase (Figure 1). This reflects the commonly observed lower

partitioning of MeHg to solids. Sediment:water partition coefficients ( $K_D$ ) for MeHg varied by almost 2 orders of magnitude, and were 1–2 orders of magnitude less than  $K_D$ s for inorganic Hg ( $Hg_i$ ). As typically observed,<sup>20,37,40,41</sup>  $K_D$ s for both  $Hg_i$  and MeHg tended to increase with sediment organic matter content and porosity, and with pore water conductivity, iron and sulfide (SI Figure S7). The mechanism of Hg binding to NOM is primarily through ligand–ligand interactions with thiols in OM,<sup>42</sup> although once thiols are saturated, Hg may bind other moieties in NOM, or interact via other mechanisms.

Pore water concentrations of  $Hg_i$  and MeHg were significant predictors of uptake by *Lumbriculus* among the sites tested (SI Figure S8) while the level of total Hg in sediments was not (SI Figure S9). In the untreated control microcosms, worm uptake varied by almost 2 orders of magnitude among the four sediments tested, despite a less than 5-fold difference in THg concentrations (Figure 1). As expected,<sup>15,43</sup> tissue:sediment bioaccumulation factors (BAFs) for MeHg were roughly 10–50

times higher than BAFs for Hg. Sediment:water partitioning behavior was a significant predictor of BAF (SI Figure S8).

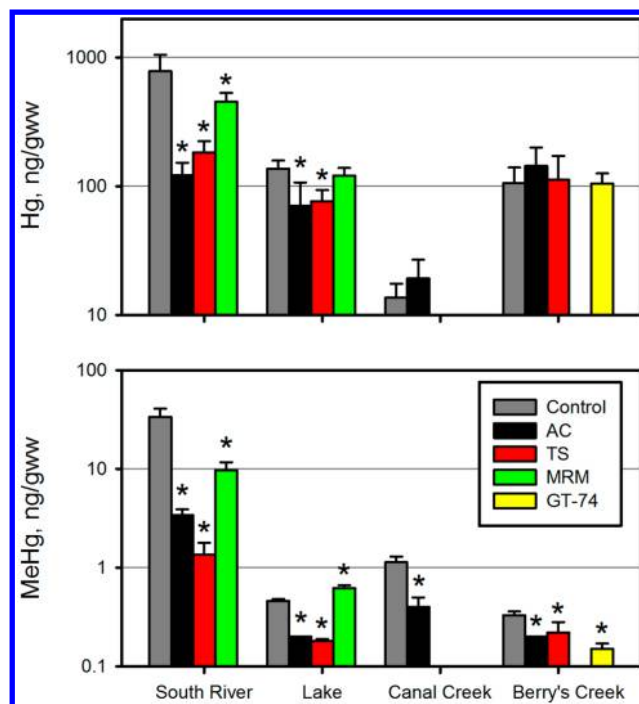
**Effect of Amendments on Hg and MeHg Partitioning and Bioaccumulation.** Both activated carbon (AC) and/or Thiol-SAMMS (TS) amendments, added at about 5% of the dry weight of sediments, were effective in reducing MeHg uptake, and to a lesser extent Hg<sub>i</sub> uptake, by *Lumbriculus* during the 14 day microcosm experiments (Figures 2 and 3). The most effective treatments reduced 14 day MeHg uptake by *Lumbriculus* by about an order of magnitude (Figure 4). On average, amendments were twice as effective in reducing MeHg uptake as Hg<sub>i</sub> uptake.

The effectiveness of the amendments varied substantially among the sorbents and sediments tested (Figure 4; also SI Table S4 lists the % reductions), and was not correlated with THg in sediments (SI Figure S10). Both AC and TS amendments were highly effective in reducing MeHg uptake in both freshwater sediments (~90% in South River, and ~50% in Lake). In the most highly contaminated sediment, Berry's Creek, AC and TS reduced MeHg uptake by about 30%. Both AC and TS significantly reduced Hg<sub>i</sub> uptake from the two freshwater sediments, but did not significantly affect Hg<sub>i</sub> uptake from either estuarine sediment. The Organoclay MRM amendment, tested only in the freshwater sites, significantly reduced Hg<sub>i</sub> and MeHg uptake from South River, but increased MeHg uptake from Lake sediments. The ion-exchange resin, GT74, significantly reduced MeHg but not Hg<sub>i</sub> uptake at the one site where it was tested (Berry's Creek).

In order to assess how sorbent amendments reduced Hg and MeHg risk and exposure, we examined their impact on bulk phase and pore water Hg and MeHg concentrations, sediment:water partitioning, and bioaccumulation factors (Figures 2 and 3). Mechanisms by which amendments could reduce Hg<sub>i</sub> and MeHg uptake by worms include reduced bioavailability, reduced MeHg production from Hg<sub>i</sub>, enhanced MeHg degradation or flux, and reduced metabolism or feeding rate of the worms.

In most of the study sediments, AC and TS amendments reduced pore water MeHg and sometimes Hg<sub>i</sub> concentrations, and increased partitioning to bulk sediments ( $K_D$ ). Across the sites, AC was the most consistently effective, significantly reducing pore water MeHg concentrations, and increasing the MeHg  $K_D$  in all four test sediments. Addition of organo-clay, MRM, resulted in increased pore water MeHg concentrations in both freshwater sediments, but was not tested in the estuarine sediments. The ion-exchange resin GT74 increased the  $K_D$  for MeHg but not Hg<sub>i</sub> in the Berry's Creek sediments, one site where it was tested.

In some cases the amendments resulted in changes in bulk MeHg concentration. Sediment bulk MeHg concentrations were 10–40% higher in most sorbent-amended South River and Lake sediments than in controls at the end of the 14 day study, and more than double in AC-amended South River sediments. This observed increase in bulk MeHg could have arisen from higher rates of gross MeHg production, declines in MeHg degradation, or reduced MeHg efflux to overlying water. We had initially hypothesized that sorptive amendments might reduce the net production of MeHg in sediments by reducing the bioavailability of inorganic Hg for methylation, but this was not the case. Sorbents appear to increase MeHg partitioning more than Hg<sub>i</sub> partitioning, suggesting that the amendments may disproportionately decrease the availability of MeHg for demethylation or abiotic losses. Direct study of gross methylation, demethylation



**Figure 4.** Comparison across treatments and sediments of inorganic Hg (top) and MeHg (bottom) uptake by *Lumbriculus* in 14 day microcosm studies. Starred values are significantly different from uptake in unamended control microcosms based on ANOVA ( $\alpha < 0.05$ ) and Student-Newman-Keuls comparisons. Bars show the means (+ 1 SD) of five replicate treatment microcosms, except Canal Creek, where bars show the average of 15 microcosms across three AC treatment levels.

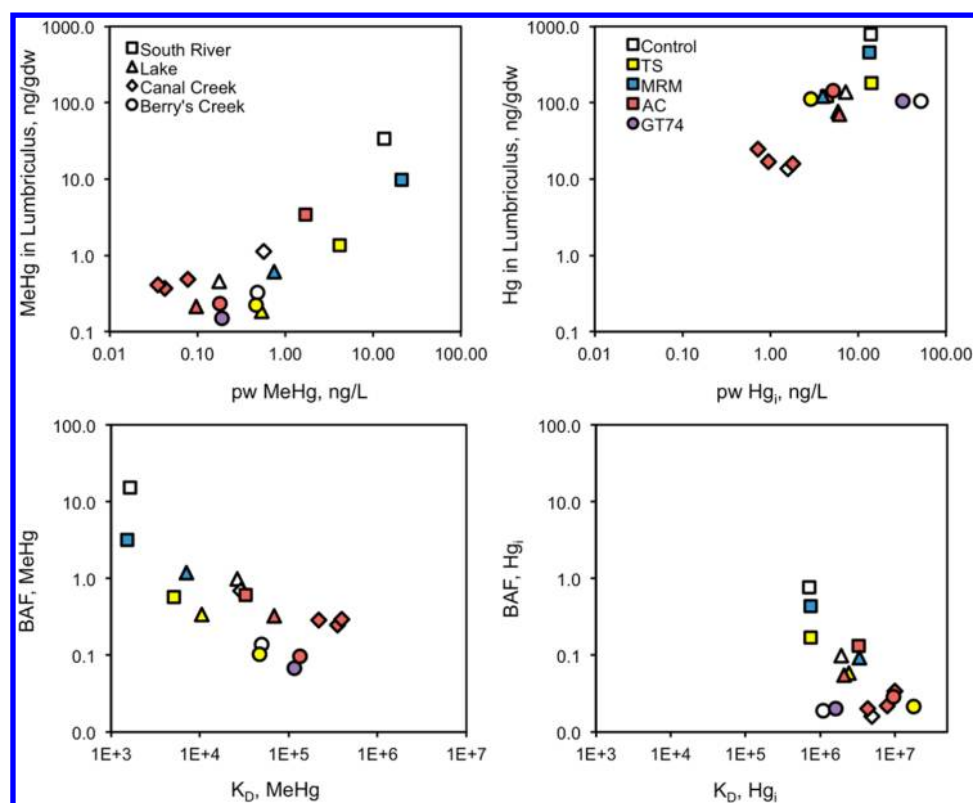
and flux rates will be needed to sort this out. Nevertheless, in the cases where amendments resulted in higher bulk MeHg concentrations, amendments still significantly reduced pore water MeHg concentrations, and reduced uptake by *Lumbriculus*.

#### Sediment Amendments Reduce Biotic Uptake by Reducing Hg and MeHg Bioavailability to Organisms.

Across all control and amended sediments, pore water concentrations of Hg and MeHg strongly predicted 14 day Hg and MeHg uptake by *Lumbriculus* (Figure 5). Similarly, sediment:water partitioning ( $K_D$ ) was a strong predictor of BAF. The amendments most effective in reducing pore water Hg and MeHg concentrations were also most effective in reducing worm uptake. Comparison of BAFs and  $K_D$ s among the amendment types (Figure 5) shows that AC was generally the most effective of the tested amendments in reducing BAFs and increasing  $K_D$ s, especially for MeHg.

All of the amendments were most effective in sediments with the lowest native  $K_D$  values (SI Figure S8). This makes simple sense, as the sorbent amendments effectively compete with the existing binding capacity of sediments for Hg and MeHg. Across the four sites examined,  $K_D$ s for both Hg<sub>i</sub> and MeHg were lowest in sediments with geochemical characteristics that minimize sediment Hg sorption, including low organic matter content, high porosity, and low concentrations of solid phase iron and sulfide (SI Figure S7). The amendments were most effective in South River sediments, where sediment water Hg and MeHg partition coefficients were lowest.

The strong relationship between  $K_D$  and BAF may not mean simply that animals take up MeHg directly from pore water. Partition coefficients also may provide a measure of absorption



**Figure 5.** Comparison of Hg<sub>i</sub> and MeHg uptake by *Lumbriculus* with sediment:water partitioning in the microcosm studies. Top: Sediment pore water concentrations for MeHg (left) and Hg<sub>i</sub> (right) vs uptake by *Lumbriculus*. Bottom: Sediment:water partition coefficients ( $K_D$ ) vs BAF for *Lumbriculus*. Data include all four sediments studied and all 16 amendment treatments. Each data point is the average value for the five microcosms in each (sediment X amendment) treatment ( $n = 16$ ), after 14 days incubation. In this graphic, shapes identify sites, and colors identify treatments (amendments). Scales are the same between Hg and MeHg for comparison.

efficiency (AE) for contaminants in the solid phase. For example, McLeod et al.<sup>44</sup> demonstrated for a PCB and a PAH that strong sorption in carbons is related to greatly reduced AE. For MeHg, the importance of sediment vs pore water as a source to benthic organisms depends on feeding behavior and  $K_D$ ,<sup>15,16</sup> however, exposure through either pathway is reduced by strong sorption. In this study, the test organisms were head-down feeders that ingest sediment and detritus, and no additional food was provided.

Additionally, the strong relationship between the sediment:organism BAF and sediment:water  $K_D$  supports the idea that AC amendments resulted in lower MeHg concentrations in *Lumbriculus* because of changes in bioavailability rather than changes in feeding behavior. Janssen and Beckingham<sup>10</sup> recently reviewed this literature and noted that adverse response to AC exposure are only observed in about 20% of studies, and are more likely at smaller particles sizes and higher doses than used in our study.

**Dose:Response for Activated Carbon Additions in Canal Creek Sediments.** Using Canal Creek sediments, we explored the relative effectiveness of AC amendments at various levels. AC amendments were made at three different dosing levels (Table 1) and compared to unamended control microcosms (Figure 3). AC amendments significantly reduced 14 day MeHg uptake by *Lumbriculus* at all three concentrations, although Hg<sub>i</sub> uptake was not reduced. The carbon amendments also resulted in significantly decreased pore water MeHg and increased MeHg  $K_D$  at all three amendment levels. However, there was no significant relationship between the AC dose and any response variable, including MeHg uptake. For this

estuarine sediment, AC was equally effective at 2.4% of sediment dry mass as at 7.3%, at least in the short run.

**Impact of Amendments on Sediment Chemistry.** The positive effect of sediment amendments on exposure to contaminants must be balanced against any negative impacts the amendments may have on ecosystem biogeochemistry and ecology. The impacts could potentially include decreased productivity via reduced nutrient bioavailability, altered feeding rate of benthic organisms due to physical changes in sediment structure, and changes in recruitment. We examined surface water, sediment and pore water chemistry in the microcosms as one way to help evaluate potential impacts of amendments.

Activated carbon, TS, and GT-74 amendments generally had only small impacts on microcosm surface water, sediment, and pore water chemistry (SI Figures S11–16). One exception was a consistent decrease in pore water DOC in AC-amended sediments (SI Figure S14). The other amendments had mixed or no impact on DOC. DOC has a major role in Hg partitioning, complexation, and bioavailability.<sup>45–47</sup> Sorption of DOC onto AC could affect Hg in a variety of ways. DOC is a strong ligand for Hg, holding it in the aqueous phase<sup>48,49</sup> and increasing the bioavailability of Hg in sulfidic sediments for microbial methylation.<sup>50,51</sup>

The Organoclay MRM amendment led to significant increases in conductivity, sulfate, nitrate and iron in the microcosms (SI Figures S13, S15), suggesting that this material released salts to the sediments. In MRM-amended sediments, MeHg production may have been enhanced by the additional sulfate.<sup>52</sup> Changes in ionic strength may also have effects on Hg and MeHg partitioning and bioavailability.

**Implications for In Situ Sediment Treatment.** These microcosm studies showed that sorbent amendments can be effective in reducing pore water Hg and MeHg concentrations and their uptake by *Lumbriculus variegatus*. Thus, sorbent amendments may be able to reduce the risk of biotic Hg and MeHg uptake in contaminated sediments, and subsequent contamination of food webs. The use of sorbents in Hg and MeHg remediation is worth testing in the field.

Evaluation of a Hg-contaminated site for potential remediation with in situ amendments might begin with a measurement of the native  $K_D$  for Hg and MeHg. Sediments with low native sediment:water partition coefficients for Hg and MeHg should be most effectively treated. It will be important to compare the sorption efficiency of potential sorbents with the  $K_D$  and concentration of natural organic matter (NOM) in any site considered for remediation.

There is potential to improve remediation efficiency through the choice of sorbent, and its surface area and chemistry. Here we evaluated only one type of AC, which yielded a maximum observed benefit of roughly an order of magnitude decrease in MeHg uptake. Initial assessments of  $K_D$ s for other AC chemistries are 2–3 orders of magnitude higher than  $K_D$ s for most NOMs (Gomez-Eyles et al. in review). In the short term microcosm trials, activated carbon and Thiol-SAMMS (TS) were the most consistently and strongly effective amendments, and resulted in only relatively minor changes in sediment chemistry. Other sorbents may be effective, but will need to be evaluated for unintended effects, like the increase in sulfate we observed in MRM-amended freshwater sediments. A major advantage of AC is the additional effectiveness for a range of common organic pollutants in sediments such as PCBs and PAHs.

Limitations of the in situ amendment approach could include declining effectiveness as amendment materials are buried by ongoing sedimentation, changes in net MeHg production or accumulation, and AC “fouling” or reduced sorption capacity over time. Based on this study, AC amendments should be most appropriate for field trials at sites where a 50–90% reduction in MeHg uptake is sufficient to achieve remediation goals. We have field trials underway at three such sites.

## ■ ASSOCIATED CONTENT

### ■ Supporting Information

Chemical characteristics of study sediments and water used in microcosms, photos of microcosms, QA for Hg and MeHg analyses, detailed analytical methods, supporting figures, and impacts of amendments on microcosm chemistry. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare the following competing financial interest(s): U.G. is a co-inventor of two patents related to the in-situ remediation of sediments 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) and Menzie Cura and Associates (U.S. Patent No. 7,824,129). In addition, U.G. and C.A.M. are partners in a

startup company (Sediment Solutions) that has licensed the technology and is transitioning the technology in the field.

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