

# Evaluation of Biochars and Activated Carbons for In Situ Remediation Of Sediments Impacted With Organics, Mercury, And Methylmercury

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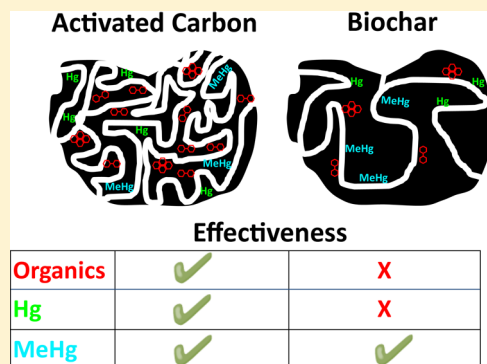
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## Supporting Information

**ABSTRACT:** In situ amendment of activated carbon (AC) to sediments can effectively reduce the bioavailability of hydrophobic organic contaminants. While biochars have been suggested as low-cost and sustainable alternatives to ACs, there are few comparative sorption data especially for mercury (Hg) and methylmercury (MeHg) at the low porewater concentrations in sediments. Here we compare the ability of a wide range of commercially available and laboratory synthesized ACs and biochars to sorb PAHs, PCBs, DDTs, inorganic Hg, and MeHg at environmentally relevant concentrations. Compared to natural organic matter, sorption capacity for most organic compounds was at least 1–2 orders of magnitude higher for unactivated biochars and 3–4 orders of magnitude higher for ACs which translated to sediment porewater PCB concentration reductions of 18–80% for unactivated biochars, and >99% for ACs with 5% by weight amendment to sediment. Steam activated carbons were more effective than biochars in Hg sorption and translated to modeled porewater Hg reduction in the range of 94–98% for sediments with low native  $K_d$  and 31–73% for sediments with high native  $K_d$  values for Hg. Unactivated biochars were as effective as the steam activated carbons for MeHg sorption. Predicted reductions of porewater MeHg were 73–92% for sediments with low native  $K_d$  and 57–86% for sediment with high native  $K_d$ . ACs with high surface areas therefore are likely to be effective in reducing porewater concentrations of organics, Hg, and MeHg in impacted sediments. Unactivated biochars had limited effectiveness for organics and Hg but can be considered when MeHg exposure is the primary concern.



## INTRODUCTION

In situ amendment of activated carbon (AC) to contaminated sediments effectively reduces organic contaminant bioavailability and has provided a new direction in contaminated sediment management.<sup>1</sup> Porewater concentration reductions of 70–99% have been reported for polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), dichlorodiphenyltrichloroethanes and metabolites (DDXs), dioxins, and furans.<sup>1</sup> Although some studies have explored the use of ACs to remediate metal contaminated sediments,<sup>2</sup> there is limited information available on the potential of ACs to sorb inorganic mercury (Hg) or methylmercury (MeHg) at the relatively low (ng- $\mu$ g/L) concentrations found in the porewater of contaminated sediments. To date, most AC sorption studies for Hg have focused on concentrations in the  $\mu$ g/L–mg/L level, more commonly found within a contaminated wastewater treatment context.<sup>3</sup> Like PCBs, MeHg concentrations bioamplify greatly in aquatic food webs, making fish the main risk driver for methylmercury (MeHg) exposure to people.<sup>4</sup>

Reducing the transfer of MeHg through food webs by limiting its uptake and release from contaminated sediment sources through in situ carbon amendments could therefore be greatly beneficial.

Recent studies have shown that biochars produced from pyrolysis of biomass such as wood chips, nut shells or poultry litter<sup>5,6</sup> can reduce the bioavailability of both organic<sup>7–9</sup> and inorganic contaminants.<sup>10</sup> Since high pyrolysis temperature biochar is relatively recalcitrant in the environment and can be used for carbon sequestration,<sup>11</sup> it is being pursued as a less expensive and more environmentally sustainable alternative to AC for the in situ remediation of contaminated soils.<sup>5,12</sup> However, biochars that have not been activated have

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Table 1. List of Carbon Used in the Study and Properties

carbon type	abbreviation	manufacturer	C (%) <sup>a</sup>	surface area (m <sup>2</sup> /g) <sup>b</sup>	skeletal density (g/cm <sup>3</sup> ) <sup>d</sup>	bulk density (g/cm <sup>3</sup> ) <sup>d</sup>
bituminous coal based AC	CAC-Coal	Calgon Corp.	80.9 ± 1.4	1116 ± 25	1.61	0.64
coconut shell based AC	CAC-Coco	Calgon Corp	90.8 ± 2.7	1305 ± 11	1.45	0.57
lignite coal based AC	CAC-Darco	Norit	72.8 ± 0.1	968 <sup>c</sup>	1.52	0.51
regenerated AC	CAC-RAC	Siemens	73.3 ± 0.8	1150 <sup>c</sup>	1.81	0.63
pine dust biochar	Bio-PD	Biochar Eng Corp.	22.1 ± 0.5	109 ± 2	0.98	0.43
peanut hull biochar	Bio-PH	Biochar Eng Corp.	31.9 ± 6.8	107 ± 2	1.28	0.60
barley straw biochar	Bio-BS	Biochar Eng Corp.	49.2 ± 2.5	26 ± 1	1.21	0.27
acai pit biochar	Bio-AP	Biochar Eng Corp.	77.2 ± 0.3	198 ± 6	1.23	0.65
hardwood lump charcoal	Bio-HW	Milazzo Industries	70.8 ± 0.3	224	1.29	0.64
steam activated turkey litter biochar	Lab-ATL	USDA-ARS	26.8 ± 1.2	300 ± 10	1.79	0.76
steam activated chicken litter biochar	Lab-ACL	USDA-ARS	26.9 ± 0.8	270 ± 3	1.97	0.92
pine dust biochar	Lab-PD	UMBC	77.9 ± 0.8	542	0.97	0.31
phragmites biochar	Lab-PHR	UMBC	69.6 ± 0.9	464	1.06	0.30
chemically activated pine dust biochar	Lab-APD	UMBC	71.0 ± 0.3	2266	1.16	0.27
chemically activated phragmites biochar	Lab-APHR	UMBC	64.6 ± 0.1	1579	1.14	0.31
iron oxide impregnated pine dust biochar	Lab-FePD	UMBC	77.1 ± 2.0	586	1.25	0.27
zero valent iron impregnated pine dust biochar	Lab-HW-ZVI	UMBC	38.4 ± 2.1	ND	1.43	0.81

<sup>a</sup> ± standard error ( $n = 2$ ). <sup>b</sup> Based on N<sub>2</sub> adsorption at 77 K, ± standard deviation ( $n = 2$ ). <sup>c</sup> Obtained from ref 7. <sup>d</sup> Measured using carbons sieved to between 44 and 177 μm. ND = not determined.

considerably smaller surface areas than ACs, resulting in potentially lower sorption capacities for organic contaminants.<sup>5</sup>

This research therefore aims to answer two important questions that have recently arisen following the success of in situ AC amendment field trials for organic pollutants:<sup>1,13</sup>

- (1) Can biochars provide viable alternatives to ACs for the in situ remediation of sediments, based on partitioning behavior at environmentally relevant concentrations?
- (2) Which types of ACs and biochars are most suitable for the in situ treatment of Hg and MeHg impacted sediments?

To answer these questions, we evaluated the sorption potential of PCBs, PAHs, DDXs, Hg, and MeHg for a large range of commercially available and laboratory synthesized ACs and unactivated biochars. To our knowledge this is the first study that assesses Hg and MeHg sorption to carbon sorbents at the ng/L concentrations typical in contaminated sediment porewaters. These data are needed to help sediment remediation specialists better understand the potential effectiveness of carbon amendments to sediments and select the appropriate carbon on a site-specific basis.

## MATERIALS AND METHODS

**Carbon Selection and Synthesis.** The carbons tested in this study are listed in Table 1 and include commercially available activated carbons and biochars, steam activated poultry litter biochars obtained from the United States Department of Agriculture – Agricultural Research Service (USDA-ARS) Southern Regional Research Centre, and biochars synthesized in the laboratory at the University of Maryland Baltimore County (UMBC). At UMBC, the unactivated laboratory biochars were produced by pyrolyzing the source materials (pine dust and phragmites) at 600 °C for 2 h. Their activated analogues were chemically activated in the laboratory as described in Lim et al.<sup>14</sup> Briefly, phragmites and

pine dust source materials were mixed overnight with 65% phosphoric acid solution with an impregnation ratio of 3:1. Each source material was then dried at 100 °C before being pyrolyzed at 600 °C for 2 h. The resulting carbon was then thoroughly washed with DI water to remove residual acid. Iron oxide and zerovalent iron (ZVI) impregnated biochars were also synthesized in the laboratory as described in the Supporting Information (SI).

**Carbon Properties.** Total C analysis was performed using a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). Samples were combusted at 900 °C and the CO<sub>2</sub> produced was detected by a nondispersive infrared gas analyzer, following an operating procedure recommended by the manufacturer. The instrument was calibrated for carbon using reagent-grade dextrose. Surface area measurements were carried out by Particle Technology Laboratories (Chicago, Illinois), using a Micrometrics Tristar 3000 static pressure analyzer using nitrogen as the adsorbate. An aliquot portion of each carbon was heat conditioned for 2 h at 300 °C under vacuum before analysis. Surface areas were calculated from a five-point regression, based on the Langmuir model. Carbon density and settling characteristics were also examined in the laboratory to evaluate the physical stability of biochars and iron impregnated biochars relative to ACs, further details on this are provided in the SI.

**Organic Contaminant Sorption Isotherms.** To compare the organic sorption capacity of the different carbons, isotherm studies for organic contaminants were performed in deionized water (DI). Additionally, one of the biochars (Lab-PD) was tested in a saltwater matrix (10 ppt Instant Ocean salt in DI) to assess any salinity effects on organic contaminant sorption to carbon. The sorption of organics to the different carbons was determined by measuring aqueous equilibrium concentrations using polyoxymethylene (POM) strips. Briefly, 24 mg of each sorbent (particle diameter <250 μm) was added to amber glass jars containing 240 mL of sodium azide solution (100 mg/L) in

freshwater or saltwater. Each jar was then spiked with a known amount of PCB, PAH, and DDX stock solution to obtain four different spike levels (10  $\mu\text{L}$ , 50  $\mu\text{L}$ , 150  $\mu\text{L}$ , and 300  $\mu\text{L}$  of each stock solution) for each sorbent in duplicate. The PCB stock solution contained a 1:1 (vol) mixture of Aroclor 1242 and 1260 (Supelco, Bellefonte, PA) in methanol. The PAH stock contained acenaphthene (100 mg/L), phenanthrene (100 mg/L), and fluoranthene (80 mg/L) in acetone. The DDX solution contained 4,4'-DDE (20 mg/L) and 4,4'-DDD (10 mg/L) in methanol. The combined standard spike was always less than 1% by volume to avoid cosolvent effects. POM strips (76  $\mu\text{m}$  thick, CS Hyde Company, Lake Villa, IL, or 55  $\mu\text{m}$  thick, obtained from Gerard Cornelissen at the Norwegian Geotechnical Institute, Oslo, Norway) were then added to the jars and mixed at 32 rpm in the dark for 28 days. The POM samplers were then removed, rinsed briefly with water, wiped dry, and inspected to ensure they were visibly clean, and then extracted with a 1:1 hexane and acetone mixture (3  $\times$  24 h, with sequential extracts pooled). Prior to extraction PCB congeners BZ 14 and 65, and phenanthrene-d10 surrogates were added to assess the effectiveness of sample processing, and extracts with lower than 80% surrogate recoveries were discarded. The extracts were split into two equal parts for PCB and DDX analysis by GC-ECD,<sup>13</sup> and for PAH analysis by GC-MS.<sup>15</sup> The GC-ECD was an Agilent 6890N, and the GC-MS was an Agilent 6890 gas chromatograph coupled to an Agilent 5973N MS detector. PCB congeners BZ 30 and 204 were used as internal standards for PCB and DDX analysis, and 1-fluoronaphthalene and p-terphenyl-d14 internal standards were used for PAH analysis. Aqueous concentrations were then derived using the POM-fresh water partition coefficients ( $K_{\text{POMW}}$ ) values. POM-fresh water partition coefficients for PCBs with the 55  $\mu\text{m}$  POM used for the commercially available activated carbons were obtained from Beckingham and Ghosh (2013).<sup>16</sup> For the remainder of the carbons, 76  $\mu\text{m}$  thick POM was used and their  $K_{\text{POMW}}$  are specified in SI Table S1.<sup>17,18</sup> Details on how  $K_{\text{POMW}}$  values were corrected for isotherms conducted in a saltwater matrix are given in the SI. The sorption of PAHs, PCBs, and DDXs onto the carbons was nonlinear, so isotherms were fitted using the Freundlich equation ( $C_s = K_f C_w^n$ , where  $C_s$  is the sorbed concentration determined by mass balance,  $C_w$  is the water concentration measured using POM,  $K_f$  is the Freundlich sorption coefficient and  $n$  is the Freundlich parameter indicating isotherm nonlinearity).

**Modeling and Measuring Pore Water Reductions for Organics in the Sediment Phase.** Porewater concentration reductions were modeled in a PCB impacted sediment (Upper Canal Creek, Aberdeen Proving Grounds, MD) using the following two-carbon model:<sup>19</sup>

$$C_s = (f_{\text{OC}} K_{\text{OC}} C_w) + (f_{\text{BC}} K_f C_w^n)$$

Where  $f_{\text{OC}}$  is the fraction of organic carbon in the sediment,  $K_{\text{OC}}$  is the measured organic carbon to water partition coefficient of the native sediment,  $f_{\text{BC}}$  is the fraction of amended carbon in the sediment (assumed at 5%). The effectiveness of the carbons to reduce organic contaminant porewater concentrations was also measured experimentally for this PCB impacted sediment. The sediment was mixed with the carbons at a dosing rate of 5% by mass of dry sediment in triplicate, and equilibrated for a month in the presence of POM passive sampling strips (76  $\mu\text{m}$ ) to evaluate PCB porewater

concentrations. A triplicate set of unamended sediment samples were equilibrated in the same way to serve as a control.

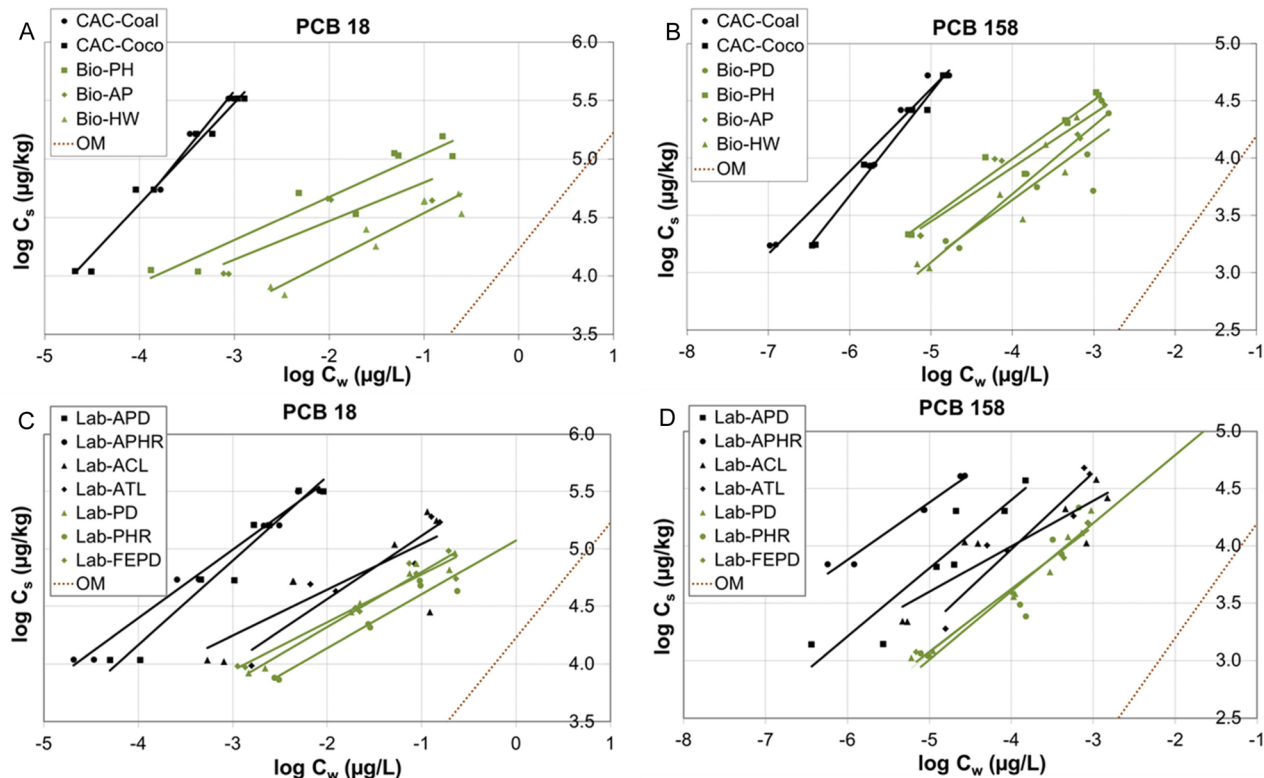
**Hg and MeHg Sorption Isotherms.** Hg and MeHg sorption isotherms were carried out at 3 ppt salinity (3 ppt Instant Ocean salt in trace-metal grade RO/DI water). A known mass of each sorbent (10 mg) was added to PETG bottles containing 50 mL of water. Vials were first placed in a 65 °C water bath for 15 min to degas the carbons. Each jar was then spiked with a known amount of Hg or MeHg solution to obtain five different spike levels for each sorbent. Spike levels were chosen based on estimated distribution coefficient ( $K_d$ ) values to yield final aqueous concentrations at equilibrium between 0.1 and 100 ng/L. Spikes were added as enriched stable isotopes in order to quantify spikes separately from any Hg present in the ACs and biochars. Enriched stable <sup>201</sup>Hg (98.1%) and <sup>199</sup>Hg (92.0%) in the form of HgCl<sub>2</sub> were obtained from Oak Ridge National Laboratory. Me<sup>199</sup>Hg and Me<sup>201</sup>Hg were synthesized in-house by reaction of methylcobalamin with enriched <sup>199</sup>HgCl<sub>2</sub> or <sup>201</sup>HgCl<sub>2</sub>.<sup>20</sup> The bottles were then allowed to equilibrate for 15 days at 4 °C, with shaking, after which they were filtered to 0.2  $\mu\text{m}$  using a stacked Whatman GD/X filter. Filtrates were acidified to 0.5% HCl and stored at 4 °C and analyzed for Hg and MeHg based on methods described previously<sup>21</sup> and in the SI.

The pH in the isotherm experiments was not buffered, although all bottles were initially adjusted to pH 7. After 15 days (at take-down), the pH in the treatment bottles was between 5 and 8 for all carbons except for the hardwood lump charcoal biochar (BioHW, pH 8–9), and the activated chicken litter biochar (Act Bio-CL, pH 9–10). The sorption isotherms for Hg and MeHg were then fitted with a linear model to derive carbon specific  $K_d$  values.

**Modeling Pore Water Reductions for Hg and MeHg in the Sediment Phase.** The native  $K_d$  for Hg in sediments spans a wide range and depends on many biogeochemical factors, but is strongly associated with organic matter content.<sup>4,22</sup> Published relationships between sediment organic matter content and total Hg or MeHg  $K_d$  for Chesapeake Bay and mid-Atlantic shelf sediments (CB/M-Atl)<sup>4</sup> and New York/New Jersey Harbor sediments (NY/NJ)<sup>22</sup> were used for modeling the sediment phase. Average CB/M-Atl have lower native  $K_d$  than the NY/NJ sediments, so the effect of carbon amendment on a low organic matter content CB/M-Atl sediment (5% loss on ignition (LOI)) was compared with the effect of carbon amendment in a NY/NJ sediment with high organic matter content (10% LOI). Reductions were modeled for a typical Hg impacted sediment concentration of 10 mg/kg. MeHg sediment concentrations of 0.1 mg/kg were assumed as MeHg generally represents 0.1% to 1% of the total Hg concentration in moderately contaminated sediments.<sup>22–24</sup> Reductions after amendment were predicted using the following linear model, since sorption was found to be linear within this low concentration range:

$$C_s = (f_{\text{sed}} K_d C_w) + (f_{\text{BC}} K_{d-\text{BC}} C_w)$$

Where  $C_s$  is the total sorbed concentration,  $f_{\text{sed}}$  is the fraction of native sediment,  $K_d$  is the native sediment distribution coefficient,  $f_{\text{BC}}$  is the fraction of amended carbon in sediment, and  $K_{d-\text{BC}}$  is the distribution coefficient of the amended carbon. A typical amendment dose of 5% carbon by weight was assumed.



**Figure 1.** Sorption isotherms for PCB 18 and PCB 158. Carbons are split into commercially available carbons (A,B) and laboratory synthesized carbons (C,D). Isotherms are plotted with black lines for the activated carbons and biochars, and with green lines for the unactivated biochars. A dotted brown line is used for the predicted sorption to natural organic matter (OM).<sup>26</sup> Carbon abbreviations are given in Table 1.

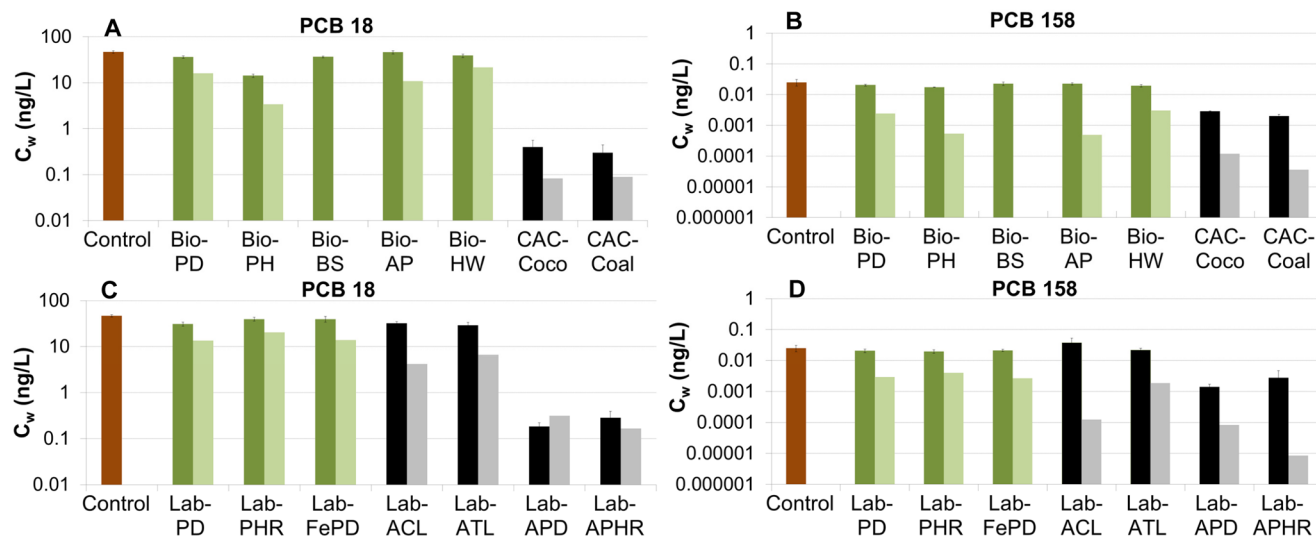
## RESULTS AND DISCUSSION

**Carbon Surface Area Characterization.** The carbons tested ranged over two orders of magnitude in surface area (Table 1). The commercially available activated carbons (both coal and coconut shell based) and the biochars chemically activated in the laboratory (especially pine dust based) had the highest surface areas, typically greater than 1000 m<sup>2</sup>/g. The two poultry litter biochars, produced by steam activation by the USDA, had relatively low surface areas for an activated carbon (270–300 m<sup>2</sup>/g) likely due to the high inorganic content. However, measurement by N<sub>2</sub> adsorption at 77° K may underestimate the surface areas of some of the carbons with smaller pores <15 Å, as the diffusion of N<sub>2</sub> into micropores is severely limited at 77° K.<sup>25</sup> These small micropores unaccounted for by N<sub>2</sub> adsorption are likely to be less relevant for the sorption of bulky PCB, PAH, and DDX molecules (generally 7–13 Å wide), but could play some role in the sorption of MeHg (≈3 Å) and Hg (<2 Å), depending on their complexation.

**Organic Contaminant Sorption Isotherms.** Activated carbons consistently removed more organic contaminants from solution than the unactivated biochars at the environmentally relevant concentrations tested. Figure 1 shows the sorption of two PCB congeners (PCB 18 and PCB 158 as representative tri- and hexachloro PCBs) to the different carbons tested. Due to the large number of carbons tested, graphs and tables displaying these results are split into two categories for clarity: (1) commercially available carbons and (2) laboratory synthesized carbons. For comparison, the sorption of the contaminants to natural organic matter (OM) is also plotted, using values predicted from published  $K_{ow}$  to  $K_{oc}$  relation-

ships.<sup>26</sup> Trends in sorption strength among carbons shown for PCBs were similar for PAHs and DDXs (SI Figure S2). These isotherm results illustrate that sorption of hydrophobic contaminants to commercial activated carbons is about 3–4 orders of magnitude stronger than OM, while the sorption to unactivated biochar is 1–2 orders of magnitude stronger than OM. The implication of this finding is that biochars with lower sorption capacity can still provide enhancement of sorption capacity in sediments but to a limited extent compared to commercial activated carbons.

Isotherms like the ones in the Figure 1 and SI Figure S2 were plotted for individual PCB congeners, PAHs and DDXs for all carbons, and their Freundlich isotherm parameters are summarized in SI Tables S2 and S3. To assess the effect of contaminant hydrophobicity on sorption to the carbons, log  $K_d$  ( $C_w = 1$  ng/L) values were plotted against logarithmic octanol–water partitioning coefficients (log  $K_{ow}$ ) for a selection of PCB congeners, PAHs, and DDXs (SI Figure S3). For CAC-Coal, there is a small trend of increasing sorption with increasing  $K_{ow}$ . However, especially for the activated and unactivated biochars, there appears to be a dip in apparent  $K_d$  values around log  $K_{ow}$  of 6. A hypothesis for the lower  $K_d$  values in the midrange of  $K_{ow}$  is the conflicting influence of increasing hydrophobicity with increasing  $K_{ow}$  (stronger affinity for carbon) and simultaneous increase in size and difficulty in accessing interior pores of the carbons at least for short-term experiments. There are other possible mechanisms that could explain the trend observed for PCBs like the possibility of increasing numbers of chlorine atoms interfering with  $\pi$ – $\pi$  bonds, but verifying the dominant mechanisms for these trends was outside of the scope of the study.



**Figure 2.** Porewater concentrations of PCB 18 and 158 in Upper Canal Creek sediments amended with commercially available (A,B), and laboratory-synthesized (C,D) unactivated biochars (dark green), and activated carbons/biochars (black bars). Error bars represent standard error ( $n = 3$ ). Modeled concentrations derived using the Freundlich parameters in SI Tables S2 and S3 are shown in light green (unactivated biochars) and gray bars (activated carbons and biochars). The differences to measured values reflect a sorption attenuation factor. Model results for Bio-BS are not displayed, as there are no Freundlich parameters available for this carbon. Carbon abbreviations are given in Table 1.

To investigate the effect of salinity on the sorption capacity of the biochars, sorption isotherms were carried out in 10 ppt salt water using the laboratory synthesized pine dust biochar (Lab-PD-SW). Examining the salinity effect is important as *in situ* carbon amendments are considered for saline sites, especially in estuarine environments. In a 10 ppt salt water matrix  $K_f$  values increased due to lower solubility of hydrophobic organic contaminants in saline solutions.<sup>27</sup> This increase was larger for the more hydrophobic organic compounds (SI Table S3 and Figure S4). This confirms that carbon amendments are likely to be as effective or more in saline than in freshwater systems in terms of reducing organic contaminant porewater concentrations.

**Modeling and Measuring Pore Water Reductions for Organics in Sediment.** Predicted and measured porewater reductions in the sediment phase confirmed that the commercially available ACs and the chemically activated biochars produced in the laboratory are able to reduce PCB pore water concentrations more effectively than the other carbons (Figure 2 and SI Figure S5). In terms of total PCBs, the commercially available ACs and the chemically activated biochars produced in the laboratory reduced porewater PCBs by >99%. Unactivated biochars on the other hand only reduced total PCBs in porewater between 18 and 54% relative to the control, with the exception of the peanut hull char that removed close to 80%.

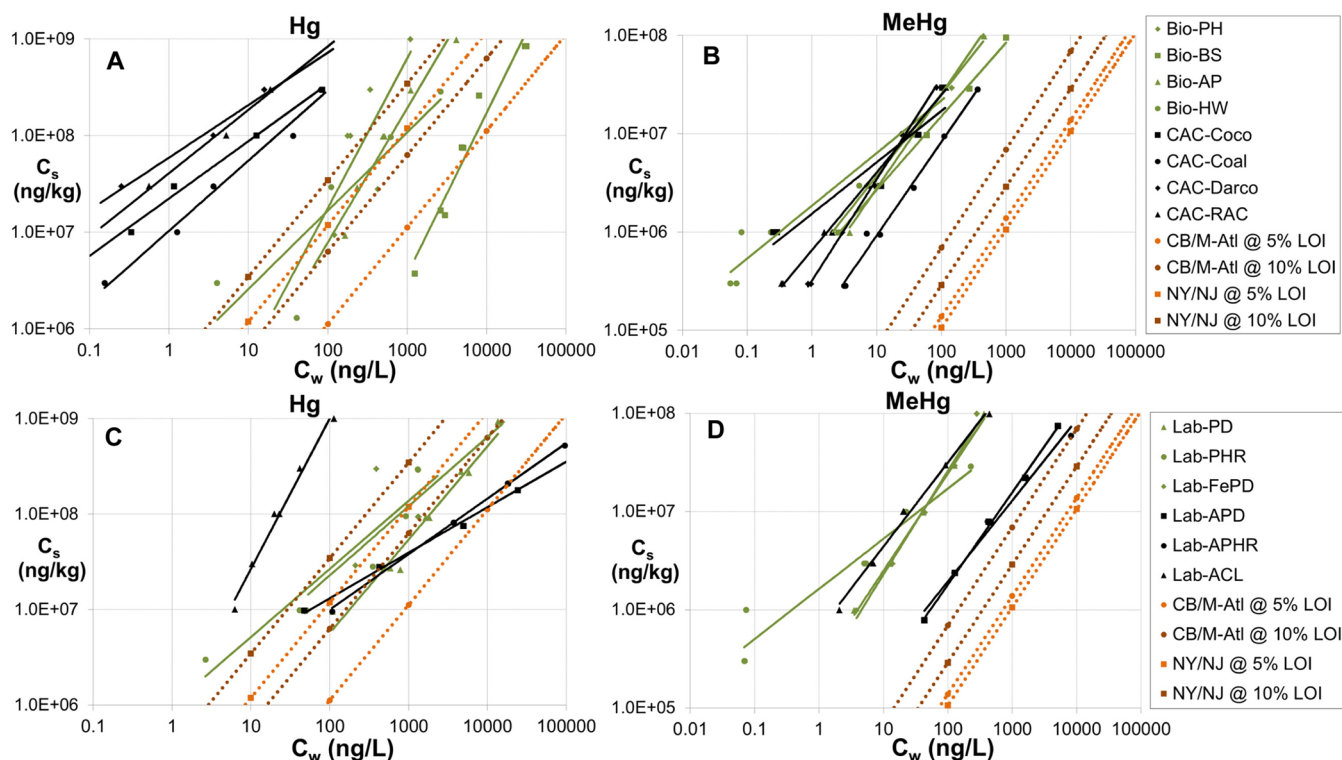
Large reductions in organic contaminant pore water concentration after applying activated carbons in soils and sediments have been previously reported.<sup>28,29</sup> Although the effect of biochars on organic contaminant bioavailability has not been studied as extensively, the more modest reductions by biochars in this study are also in line with previous studies in soils reporting 50% reduction in the rapidly desorbing PAH fraction<sup>10</sup> and a 45% reduction in total PAH bioaccumulation in earthworms after 56 days (biochar amended at 10% by weight).<sup>8</sup>

Modeled porewater reductions generally over predict the actual reductions in porewater concentrations (Figure 2 and SI

Figure S5). The blocking of sorption sites in black carbons by organic matter has been previously reported as a potential cause.<sup>5,30</sup> The magnitude of this sorption attenuation has not been extensively studied for either AC or biochar amendments, but it has been reported that black carbon  $K_d$  can be reduced by close to an order of magnitude in the environment relative to their measured  $K_d$  in clean water.<sup>13,30,31</sup> The extent of attenuation may be related to sediment properties such as OM type, the relative content of OM compared to sorbent dose, and kinetics of mass transfer.<sup>32</sup> A drop of 1 order of magnitude in the  $K_d$  of carbon amendments still leaves ACs and activated biochar  $K_d$  well above the  $K_d$  of OM. This is not the case for unactivated biochars, so their application may not always provide a sufficient improvement to the sorptive properties of the native sediment. However, a recent study where biochars and ACs were contacted with soils and artificially aged in the laboratory found that AC sorption was attenuated by an average factor of 8, whereas the attenuation in biochar sorption was not statistically significant.<sup>9</sup> This was hypothesized to be related to an influence of pore size distribution on fouling by OM, but could also be reflective of the smaller amounts of OM that are likely to sorb on unactivated biochars relative to ACs.

Previous work has reported that coconut shell based AC with smaller pore sizes may be more prone to fouling and perform poorly in the sediment environment.<sup>25</sup> In the present study we find that compared to coal based AC, the coconut shell based AC performed nearly as well for PCBs. While carbon raw material type has influence on the pore size distribution achieved after activation, it is well-known in the carbon industry that the activation process itself can be tailored to achieve a desired distribution of pore sizes.<sup>33</sup> Thus, activated carbons from the same starting materials may have different properties, and selection needs to take into account the sorption characteristics of the final activated product.

The fact that the commercially available activated carbons and the biochars chemically activated in the laboratory reduced PCB porewater concentrations more effectively confirms that



**Figure 3.** Sorption isotherms for mercury and methylmercury. Carbons are split into commercially available carbons (A,B) and laboratory synthesized carbons (C,D). Isotherms are plotted with black lines for the activated carbons and biochars and with green lines for the unactivated biochars. Dotted lines represent average sediment  $K_d$  values for Hg and MeHg in Chesapeake Bay and mid-Atlantic shelf (CB/M-Atl)<sup>4</sup> and New York/New Jersey harbor (NY/NJ)<sup>22</sup> sediments containing 5% (orange) and 10% (brown) loss-on-ignition.

the surface area of the carbon has a major influence on organic contaminant sorption. This is well-known for adsorption processes. Increased sorption with increasing carbon surface area has been previously reported for organic compounds.<sup>5</sup> This is also illustrated in SI Figure S6 where we plot measured reductions in sediment porewater concentrations against sorbent surface area. The activated carbons were consistently more effective, except for the activated poultry litter biochars. The steam activation of the poultry litter biochars did not increase the surface area of these biochars to the levels of the commercially activated carbons and the chemically activated biochars produced in the laboratory. Additionally, the poultry litter ACs had very low carbon content (27%) and are largely made up of inorganic solids that do not contribute to sorption of organics and possibly occlude carbon surfaces.

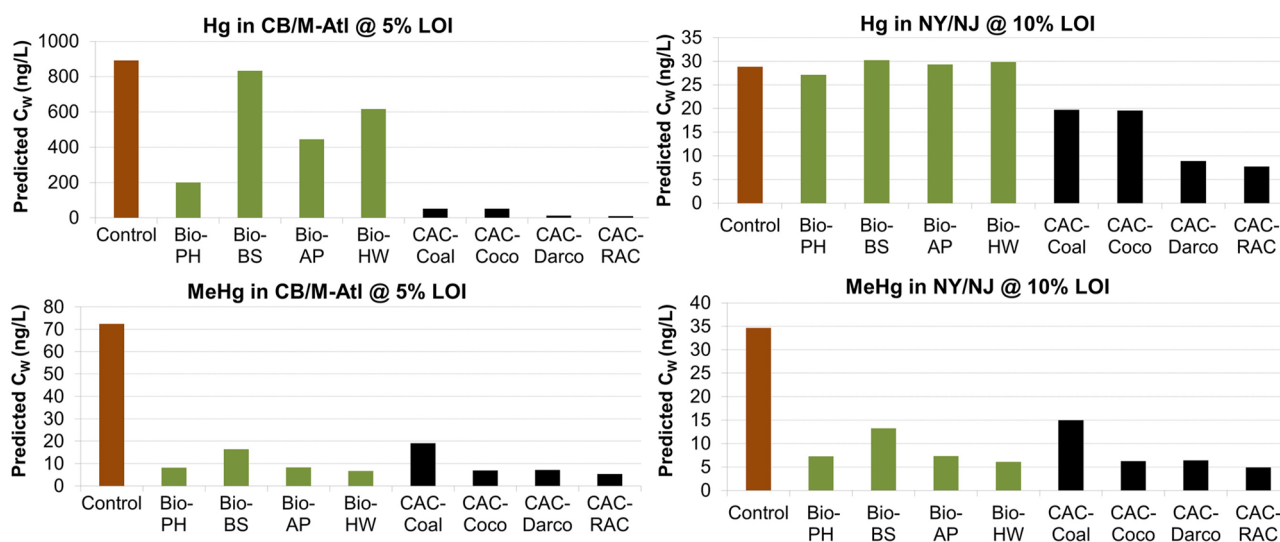
Reduced organic contaminant bioavailability due to the presence of native black carbon material (e.g., soot, coke) is very common in contaminated sediments and soils, especially those impacted with PAHs.<sup>15,34</sup> This, coupled with sorptive attenuation effects, could result in unactivated biochar amendments having little or no effect on organic contaminant bioavailability in sediments and soils with high levels of native black carbon. However, increasing pyrolysis temperatures and including activation steps in their manufacture increases their surface area.<sup>5</sup> These high surface area biochars have been shown to reduce organic contaminant bioavailability to the same degree or higher than regular coal derived ACs in this study and others.<sup>25</sup> Higher pyrolysis temperatures and activation increases the cost and limits the carbon sequestration potential of biochars. Conversely, increased effectiveness means less activated material is needed for an application. The use of biomass derived ACs is more sustainable than the use of coal-

based ACs, as shown by a recent complete life-cycle analysis of sediment remediation methods.<sup>35</sup>

**Hg and MeHg Sorption Isotherms.** Commercially available activated carbons were approximately 2–3 orders of magnitude stronger sorbents for both inorganic Hg and MeHg than CB/M-Atl<sup>4</sup> and NY/NJ<sup>22</sup> sediments (Figure 3). Interestingly, biochars—both activated and not activated—were almost equally effective sorbents for MeHg as the commercial ACs. However, biochars were no better sorbents for inorganic Hg than natural sediments.

The isotherms were fitted with a linear model and the resulting  $K_d$  values are summarized in SI Table S4. Linear models provided good fits for all carbons ( $r^2 > 0.94$  for all Hg isotherms, and  $r^2 > 0.97$  for all MeHg isotherms). The inorganic Hg isotherms show that the commercially available ACs tested were the most effective at removing Hg from solution, particularly the regenerated activated carbon ( $K_d = 1.92 \times 10^7$ ) and the lignite coal derived activated carbon ( $K_d = 1.59 \times 10^7$ ) (Figure 3). Based on sorption capacity alone, these results suggest that commercially available ACs are the most effective material (among those tested here) for the in situ remediation of Hg-contaminated sediments.

However, MeHg produced from inorganic Hg is generally the toxin of most concern, and is always present at some level in Hg contaminated sediments. Most of the carbons tested were roughly equally effective (except the phosphoric acid activated biochars) in MeHg sorption (Figure 3). The activation of biochars did not enhance MeHg sorption, in fact chemical activation of *Phragmites* and pine dust biochars decreased their affinity for MeHg. In many ways, MeHg sorption to carbons did not behave like sorption of either inorganic Hg or PCBs/PAHs/DDXs. For example, the steam



**Figure 4.** Modeled Hg and MeHg porewater concentrations in hypothetical contaminated sediments (10 mg/kg Hg, and 1 mg/kg MeHg) after amendment with commercially available carbons. Left, predictions for average sediments from Chesapeake Bay and the mid-Atlantic shelf (CB/M-Atl) containing 5% LOI; right, predictions for average New York/New Jersey harbor sediments (NY/NJ) with 10% LOI. Predictions were obtained by using carbon specific  $K_d$  values from SI Table S4. Modeled predictions are shown in dark green (unactivated biochars) and black bars (activated carbons and biochars).

activated carbons and biochars were 13–62 times better at removing Hg from solution than MeHg, whereas the difference in Hg and MeHg sorption was not that pronounced for other carbons (SI Table S4.) This suggests that Hg and MeHg sorption to carbons involve different sorption mechanisms. Further characterization of the sorption of Hg and MeHg to carbon surfaces at low concentrations is needed to understand mechanisms and inform remediation options.

For the two biochars treated with phosphoric acid (Lab-PD and Lab-PHR) activation enhanced the carbon surface area and the sorption of organics, but Hg and MeHg sorption was diminished. Thus steam activation may be a more favorable method of activation when considering Hg sorption.

**Modeling Pore Water Reductions for Hg and MeHg in Sediment.** The commercially available activated carbons are predicted to be considerably more effective than the unactivated biochars at reducing Hg porewater concentrations (Figure 4). Reductions of 94–98% in Hg porewater concentrations were predicted after 5% amendment with commercially available activated carbon in the CB/M-Atl sediment with low organic matter content. However, the predicted effectiveness of these carbons in the NJ/NY sediment with higher organic matter content and stronger native sorption was lower (31–73% reductions in porewater Hg). Therefore, commercial ACs could be effectively used as in situ sediment remediation agents to reduce pore water inorganic Hg concentrations and hence bioaccumulation risk, but the benefit would be significantly lower in sediments with already high native  $K_d$ . Amendment with unactivated biochars would only have very modest impacts on Hg bioavailability.

For MeHg however, both steam activated and unactivated carbons are predicted to effectively reduce porewater concentrations in the hypothetical sediments modeled. Reductions of 73–92% were predicted after 5% amendment of these carbons to relatively low OM CB/M-Atl sediment. Predicted reductions were lower (57–86%) for the higher OM NJ/NY sediments. Although unactivated biochars are unlikely to have a significant impact on Hg porewater concentrations in

most sediments, they have the potential to be effective amendments in sediments where MeHg is the primary driver for risk. Biochars can be less expensive than AC, especially when sourced locally and when activation is not required.<sup>9</sup> Due to the large variability in Hg and MeHg  $K_d$  values across different sediments, and the poorly understood sorption behavior of MeHg with ACs and biochars, site-specific assessments will need to be carried out as part of any potential Hg remediation plan involving carbon sorbents.

These modeled results for Hg/MeHg were not validated with measured reductions in this study as they were with organics. However, the impact of AC on porewater Hg and MeHg concentrations in contaminated natural sediments was tested in a recent related microcosm study.<sup>36</sup> The isotherm data provided reasonable predictions of observed reductions in pore water MeHg in the three of four tested sediments (SI Figure S7). However, the isotherm model under predicted observed reductions in inorganic Hg in three of four sediments. The under-prediction of inorganic Hg removal may be explained by the interaction between AC and pore water dissolved organic matter (DOM). Importantly, AC amendments to sediments can significantly reduce porewater DOM concentrations,<sup>36</sup> and this has critical impact on inorganic Hg complexation and partitioning. DOM helps to keep Hg in the aqueous phase through sorption, and also by “capping” the growth of precipitation of HgS nanoparticles.<sup>37</sup> Thus removal of DOM from porewaters by black carbon may additionally enhance the removal of inorganic Hg and sometimes MeHg from pore waters, as observed in our laboratory microcosm studies.<sup>36</sup> This provides a mechanism for AC effectiveness in sediment Hg/MeHg remediation above what might be expected based solely on fairly low sorption. Porewater DOM also enhances the bioavailability of Hg for microbial methylation,<sup>38,39</sup> so AC amendments could potentially reduce MeHg risk via reductions by this mechanism. Thus, these sorption parameters need to be used with caution for prediction of porewater concentration reductions. However, these

sorption parameters are useful as a guide in the selection of the most effective carbon for sediment remediation.

**Implications for Sediments Impacted with Both Organics and Inorganics.** Results of this study provide a rational basis for selecting carbons for use in in situ treatment of sediments. For most sites where MeHg, Hg, and potentially other organics are contaminants of concern, commercially available activated carbons will likely be the preferred option.

If carbon sequestration provides an added and important benefit for an application, the use of biochars can be considered. An added benefit of biochars is the lower cost compared to commercial activated carbons allowing higher dose to be used if necessary and appropriate. However, the difference between ACs and biochars in terms of Hg, PCB, PAH, and DDX sorption were consistently above 1 order of magnitude (closer to 2 orders of magnitude for the organics). This implies that at least a 50% amendment of biochar by weight would be needed for a reduction in bioavailability of these contaminants comparable to what a 5% AC amendment would achieve. Such high doses would negate the benefits of using carbon amendments as a minimally invasive in situ treatment. Furthermore, as documented in the SI, biochars have lower density and settling rates than ACs. Therefore, their application and stability in sediment is also going to present an engineering challenge.

The sediment-water partitioning of Hg and MeHg in natural sediments is highly variable. Additionally, for Hg and MeHg, the difference in  $K_d$  values between typical sediment and ACs tested is not as high as for hydrophobic organic contaminants. This suggests that the performance of AC treatments for Hg and MeHg remediation is likely to be variable (as shown in Figure 4) and site specific. Initial treatability studies, as described in a related paper,<sup>36</sup> will be needed on a site-specific basis to determine whether a specific sorbent will provide a target improvement to the native sediment sorption characteristics. The sorption data presented here can be used to select an initial set of carbons for treatability studies.

Further research is needed to evaluate how sediment geochemistry and redox impact the efficacy of ACs and biochars in remediating Hg and MeHg. The study described here is one of the necessary first steps in understanding and modeling this potential remediation approach. The interactions between black carbons, dissolved organic matter, iron, sulfur, and Hg/MeHg are especially important. Additional information is needed to understand the mechanisms of Hg and MeHg binding to black carbons at low concentrations, to evaluate how sorption is affected by carbon fouling, and to assess how amendments impact net MeHg production in sediments. This information will enable a better understanding of the efficacy of in situ sorbent amendments as potential remediation tools for Hg and MeHg. It will also provide information on the long-term stability of carbon amendments with regard to Hg and MeHg remediation, and will inform material manufacturing to produce sorbents with favorable characteristics for enhanced Hg and MeHg sorption. Ultimately, selection for a site application, either a single sorbent or a combination, entails optimizing for effective risk reduction with consideration to efficacy, ecosystem response, costs, large-scale commercial availability, and sustainability.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Additional information as noted in the text. 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 (U.S. Patent # 7,101,115 B2), and the other to the University of Maryland Baltimore County (UMBC) (U.S. Patent #7,824,129). In addition, U.G. is a partner in a startup company (Sediment Solutions) that has licensed the technology from Stanford and UMBC and is transitioning the technology in the field.

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