



Enhanced biochars can match activated carbon performance in sediments with high native bioavailability and low final porewater PCB concentrations



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HIGHLIGHTS

- An enhanced biochar consistently matched AC reductions in PCB bioaccumulation.
- Sorption isotherms indicated AC has superior sorptive properties than the biochar.
- Matching performance attributed to low final porewater concentrations and sorption nonlinearity.
- Bioaccumulation was well predicted from freely dissolved porewater concentrations.

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ABSTRACT

A bench scale study was conducted to evaluate the effectiveness of *in situ* amendments to reduce the bioavailability of pollutants in sediments from a site impacted with polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and cadmium. The amendments tested included fine and coarse coal-based activated carbons (AC), an enhanced pinewood derived biochar (EPB), organoclay, and coke dosed at 5% of sediment dry weight. Strong reductions in total PCB porewater concentrations were observed in sediments amended with the fine AC (94.9–99.5%) and EPB (99.6–99.8%). More modest reductions were observed for the coarse AC, organoclay, and coke. Strong reductions in porewater PCB concentrations were reflected in reductions in total PCB bioaccumulation in fresh water oligochaetes for both the fine AC (91.9–96.0%) and EPB (96.1–96.3%). Total PAH porewater concentrations were also greatly reduced by the fine AC (>96.1%) and EPB (>97.8%) treatments. EPB matched or slightly outperformed the fine AC throughout the study, despite sorption data indicating a much stronger affinity of PCBs for the fine AC. Modeling EPB and fine AC effectiveness on other sediments confirmed the high effectiveness of the EPB was due to the very low final porewater concentrations and differences in the native bioavailability between sediments. However, low bulk density and poor settling characteristics make biochars difficult to apply in an aquatic setting. Neither the EPB nor the fine AC amendments were able to significantly reduce Cd bioavailability.

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1. Introduction

Aquatic sediments form the ultimate repositories of past and ongoing discharges of hydrophobic organic compounds (HOCs) such as polychlorinated biphenyls (PCBs) and polycyclic aromatic

hydrocarbons (PAHs), as well as some heavy metals. Work in the last two decades has demonstrated that black carbonaceous particles in sediments such as soot, coal, and charcoal very strongly bind HOCs, and their presence in sediments (both natural and anthropogenic) reduces exposure (Ghosh et al., 2000; Lohmann et al., 2005), often by one order of magnitude or more compared to natural organic matter. The “natural” contaminant sequestration in native sediments can be greatly enhanced by the addition of clean, manufactured carbonaceous materials into sediments, such as activated carbon (AC) (Ghosh et al., 2011).

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Due to the success of AC amendment field pilots and full-scale sediment treatment project studies (Patmont et al., 2015), *in situ* remediation with carbon amendments is being considered as part of the remedy for increasingly larger areas of sediment remediation sites. However, AC is an expensive material and application in large sediment sites can be costly. The use of less expensive materials that can achieve similar levels of risk reduction can be of great benefit for the sediment remediation industry. Other materials have been pursued as sorbent amendments to reduce contaminant bioavailability or introduced into active caps to reduce contaminant mobility like biochars, coke or organoclays (Gomez-Eyles et al., 2011; Knox et al., 2008; Meric et al., 2012; Murphy et al., 2006; Ulrich et al., 2015).

Interest in biochars for soil fertility amendment has soared over the last decades (Ercikson, 2016), and methods of characterization standardized (Bachmann et al., 2016). Life cycle assessment studies suggest the use of biomass derived carbons could reduce the overall impact of a remediation strategy by sequestering carbon dioxide (Sparrevik et al., 2011). However, researchers have yet not been able to grapple with the wide range of sorption properties generated from various manufacturing processes of biochars, and how these different types of biochars end up impacting effectiveness in an application involving soil/sediment remediation. There has been little experimental investigation that directly compares biochars with activated carbon in sediment amendment studies. Recent work by Ulrich et al. (2015) compared two biochars with an activated carbon for performance in a stormwater infiltration media to retard pollutant transport. They found that overall, the breakthrough times were the longest for the activated carbon by about an order of magnitude.

Previous studies have shown that due to their superior sorption capacity for HOCs relative to other materials (Ghosh et al., 2003), ACs are more effective than these alternative amendments for sediments and soils impacted with HOCs (Hale et al., 2011; Zimmerman et al., 2004; Gomez-Eyles et al., 2013a, 2013b). This is primarily due to the considerably higher surface area of ACs ($1000\text{--}2000\text{ m}^2\text{g}^{-1}$) relative to any other low-cost black carbons like biochars ($10\text{--}400\text{ m}^2\text{g}^{-1}$). For example, compared to natural organic matter in sediments, HOC sorption was found to be 3–4 orders of magnitude stronger for ACs compared to 1–2 orders of magnitude stronger for biochars (Gomez-Eyles et al., 2013a). However, many studies have shown how biochar sorption can be enhanced by increasing the pyrolysis production temperature (Gomez-Eyles et al., 2013b) and/or adding an activation step in their manufacture to produce an activated biochar (or biomass-based AC) (Gomez-Eyles et al., 2013a).

Recent work by Lattao et al. (2014) indicated that sorption to biochar peaked at a pyrolysis temperature of $500\text{ }^\circ\text{C}$. However, the final sorption characteristics were not easily predictable based on physical attributes of the char such as the specific surface area alone. They concluded that sorption was a complex function of char properties and solute molecular interaction, and not very predictable based on easily measured properties of the char. In further work, Xiao and Pignatello (2016) demonstrated that post pyrolysis air oxidation of the biochar can greatly enhance sorption of a large range of compounds by up to a factor of 100. They attributed this enhancement of oxidation to a 'reaming' effect, whereby the pores on the biochar are made more accessible for sorption by the oxidation of tarry deposits that were generated during pyrolysis and were not totally volatilized initially. However, this process of enhancing pore access and adding functionality to chars is not much different from the traditional activation process that typically involves some combination of air/steam at high temperature or the use of chemical oxidation to achieve a similar enhancement of sorption. These activation processes come at an energy and carbon

cost however, which reduces yield, increases the price of the biochar, and reduces its value as a method of greenhouse gas abatement.

This study therefore evaluated a biochar that was especially produced by a commercial manufacturer to physically enhance its sorptive properties. To our knowledge this is the first study comparing the performance of a commercially available enhanced biochar for the remediation of sediments against already established AC products. In this paper we report the results of a laboratory treatability study conducted to assess the effectiveness of different amendments including a commercially available enhanced biochar and AC at reducing contaminant bioavailability in sediments collected from a site where PCBs are the main risk driver, but that also contained significant levels of Cd and PAHs. All sorbents were evaluated in a first round of tests, where their ability at reducing PCB and PAH porewater concentrations was tested using passive samplers. The most effective sorbents at reducing PCB porewater concentration were then evaluated in a second round of tests where reductions in Cd porewater concentrations were assessed, and bioaccumulation studies were carried out to confirm if reductions in PCB porewater concentrations translated into reduced tissue concentrations in freshwater oligochaetes.

To help interpret the observed results, sorption data for the different amendments were used to model reductions in PCB porewater concentrations after amendment and predict the uptake in a benthic organism based on measured porewater concentrations. As well as modeling reductions in the sediments used in this study, reductions were also predicted in a sediment of contrasting properties used in a previous study to evaluate AC and biochar performance (Gomez-Eyles et al., 2013a).

2. Materials and methods

2.1. Sediments and sorbents

Sediments were collected from four locations (S1, S2, S3 and S4) within an estuarine location in Dark Head Cove, Middle River, a PCB-impacted site in Maryland. Sediment samples S1 and S2 were selected for the PCB treatability study, as they had PCB concentrations in the range of what would potentially be considered for remediation by *in situ* treatment with carbon amendments. S4 was used for the Cd study as the porewater of this sediment sample was the only one that exceeded the National Recommended Water Quality Criteria (NRWQC) for Cd after correcting for hardness (Table 1). The commercially available sorbent amendments tested in the treatability study included a fine and a coarse bituminous coal-derived AC (Calgon Corporation), an enhanced pinewood-derived powdered biochar (EPB) (Biochar Solutions, Inc), Organoclay[®] PM-199 (CETCO), and coke (Ispat Inland, Inc., East Chicago, IL). The EPB and coke were sieved to the same particle size as the fine AC (80×325 mesh) to enable fair performance comparisons (Table S1). As described by the manufacturer, the EPB was produced in a controlled oxidation environment in a thermal conversion unit without the use of any chemical activation agents. Exothermic heat from the controlled oxidation provided the energy required for the conversion process maintained at a temperature ranging from 700 to $1000\text{ }^\circ\text{C}$ over a maximum 10 min period. The commercial manufacturing process provides limited control and monitoring of the pyrolysis temperature relative to smaller scale biochar bench-scale studies reported in the literature (Chen et al., 2008). After the conversion, the materials were treated with water for quenching and dust control and held in fire safe containers to cool down. The overall yield of biochar in this process was low and reported at less than 10% of original biomass, which reduces some of the carbon sequestration benefits of these type of amendments.

Table 1
Bulk sediment Cd, porewater Cd, TOC and BC contents of sediment (n = 2).

Sample	Cd in sediment (mg/kg) ^a	Cd in porewater (ug/l) ^b	Hardness (mg/l)	NRWQC corrected for Hardness (ug/l)	TOC (%)	BC (%)
S1	8.93	0.23	770	1.04	2.74	0.31
S2	6.88	0.20	941	1.21	2.78	0.34
S3	8.66	0.64	855	1.13	n.m.	n.m.
S4	9.70	1.21	513	0.77	n.m.	n.m.

n.m. = not measured.

^a HNO₃ extraction.

^b Values in bold exceed NRWQC.

The resulting biochar had a high mineral content of 21%, mostly made of calcium salts.

2.2. Sediment characterization

The initial sediment characterization included analysis of bulk sediment concentrations of PCBs, PAHs and Cd, porewater Cd concentrations, sediment porewater hardness, total organic carbon (TOC) and native black carbon (BC).

Sediment PCBs and PAHs were extracted following EPA publication SW-846 (Test Methods for Evaluating Solid Waste, Physical/Chemical Methods) method 3550B using three volumes of 40 mL each of acetone-hexane mixture (50:50) and sonicating the slurry for 6 min (pulsing for 30 s on and 30 s off). PCB extracts were then cleaned up based on EPA methods 3630C (silica gel cleanup) and 3660B (sulfur removal with copper). In the silica gel cleanup process, the dried and concentrated extracts are passed through a 3% deactivated silica gel column. PAH extracts were also cleaned up using EPA method 3630C, with dried concentrated extracts passed through an activated silica gel column.

Bulk sediment extractable Cd was determined by acid digestion with 10% nitric acid solution. The resultant digestate was then diluted and filtered. To measure dissolved Cd concentrations, sediment samples were centrifuged to separate sediment porewater from the bulk sediment. The porewater was then filtered using 0.45 μm PTFE filters, and preserved using concentrated nitric acid to pH < 2. Filtered samples were analyzed for Cd using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS) using Indium as an internal standard. Sediment porewater hardness was measured using a Total Hardness Test Kit, Model HA-71A (Hach, CO, USA).

The TOC analysis was performed using a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). Sediment BC was measured by pre-combusting the sample at 375 °C to remove non-black carbon, followed by the measurement of the residual BC in the sample by combustion at 900 °C (Gustafsson et al., 1997).

2.3. Measuring reductions in freely dissolved PCB and PAH porewater concentrations

To test the effectiveness of the sorbents, sediment samples S1 and S2 were amended with a 5% by dry weight dose of fine AC, coarse AC, EPB, organoclay or coke. The fine AC was also amended into both sediments at a lower dose level of 2%. Briefly, 250 g of sediment (wet weight) were thoroughly mixed with the corresponding amendment in triplicate. To measure porewater concentrations, the amended sediments were made into a slurry (80% moisture content) and a 25 μm polyethylene (PE) passive sampler was then added to each treatment (USEPA et al., 2017). The bottles were packed in cardboard boxes and allowed to equilibrate for 28 days in an orbital shaker. The PE strips were then removed, wiped dry, and extracted in an acetone-hexane solution (3 × 24 h, with

sequential extracts pooled). The extract was then cleaned up and analyzed for PCBs and PAHs. Freely dissolved PCB and PAH concentrations were calculated from the sorbate concentration in the PE using concentration independent PE-water distribution ratios (K_{PE}), that have been presented in previous studies (Ghosh et al., 2014).

2.4. Laboratory bioaccumulation study

Laboratory bioaccumulation assays were conducted using a freshwater oligochaete (*Lumbriculus variegatus*, Aquatic Research Organisms, Hampton, New Hampshire), following methods described in Beckingham and Ghosh (2011) which is based on standard test guidelines for this organism (USEPA, 2000). The bioaccumulation studies evaluated the effectiveness of the selected carbon amendments in reducing biological uptake of PCBs near the base of the benthic food chain. Based on the freely dissolved PCB concentration reduction results (described later), the fine AC and EPB were selected as the two amendments to investigate for bioaccumulation reduction. Each of the two sediment samples (S1 and S2) was dosed with the selected sorbents at a single dosing rate (5% by dry weight).

Organisms were exposed to the sediments in 1 L glass beakers (300 g sediment and 0.5 g organisms per beaker; 4 replicates per sample) for 28 days and maintained at room temperature of 20–23 °C with a 16 h light:8 h dark photoperiod. At the termination of the experiment, organisms were removed from the sediments and allowed to depurate for 7 h in a clean beaker containing deionized water. The depurated organisms were then weighed, homogenized with excess sodium sulfate, and extracted with a 50:50 mixture of hexane and acetone under sonication. The final extract was cleaned using the previously mentioned EPA method 3630C (silica gel cleanup) coupled with EPA method 3665A (sulfuric acid cleanup) to ensure there was no lipid interference in the analyses. Before cleanup a subsample of this extract was taken to determine worm lipid content using a spectrophotometric method described in previous studies (Sun and Ghosh, 2007; Van Handel, 1985). Basic water quality parameters such as temperature, pH, hardness, dissolved oxygen, ammonia, and alkalinity were monitored before and throughout the bioaccumulation experiment.

2.5. PCB and PAH analysis

PCB analysis of the sediment, PE and worm tissue extracts were performed on an Agilent 6890 N gas chromatograph (Restek, Bellefonte, PA, USA) with an electron capture detector and a fused silica capillary column (Rtx-5MS, 60 m × 0.25 mm i.d., 0.25 μm film thickness). PCB standards for calibration were purchased as hexane solutions from Ultra Scientific (North Kingstown, RI, USA). A 4 point annual calibration ($r^2 > 0.97$ for every congener) was prepared using a PCB mixture containing 250 μg/L of Aroclor 1232, 180 μg/L of Aroclor 1248 and 180 μg/L of Aroclor 1262. 2,4,6-trichlorobiphenyl (PCB 30) and 2,2',3,4,4',5,6,6'-octachlorobiphenyl (PCB 204) were

added to all samples as internal standards. Standard checks were run every 10 samples to ensure GC-ECD calibration holds. In some cases where congener peaks coelute, they are identified and reported as the sum of congeners. Congener identification is performed based on congener relative retention times and based on the comparison of a standard chromatogram with a sample chromatogram obtained from Mullin (1994).

PAH analysis of the sediment and PE extracts were performed on an Agilent gas chromatograph (Model 6890) with a fused silica capillary column (HP-5, 30 m × 0.25 mm i.d.) and a mass spectrometer detector was used for analysis of PAHs based on EPA method 8270. A standard mixture of 16 EPA-priority pollutant PAH compounds obtained from Ultra Scientific was used for calibration. 1-fluoronaphthalene, deuterated-p-terphenyl, deuterated benzo(a)pyrene and deuterated dibenzo(a,h)anthracene were used as internal standards. A fresh 5-point calibration was performed for every sample batch ($r^2 > 0.95$ for every PAH).

2.6. QA/QC for PCB and PAH extractions

PCBs 14 and 65 (for PCBs) and deuterated phenanthrene (for PAHs) were used as surrogates to check for analyte recovery in all sediment, PE and organism extractions. Recoveries for all passive sampler and sediment extracts were above 70%, except for one sediment extract which was discarded. Recoveries for the organism extractions were generally lower due to the extra cleaning steps involved in the analyses, but ranged between 62.0 and 83.1% for all extractions. Data presented have not been corrected for surrogate recovery.

2.7. Modeling reductions in PCB porewater concentrations using sorption data

PCB sorption in sorbent amended sediment was modeled based on the following 2-carbon model (Gomez-Eyles et al., 2013a) assuming that the native organic carbon and the added black carbon were the dominant sorption domains:

$$C_s = (f_{OC} K_{OC} C_w) + (f_{BC} K_f C_w)$$

Where C_s is the total sorbed concentration, f_{OC} is the fraction of native organic carbon in the sediment, K_{OC} is the measured organic carbon to water partition coefficient of the native sediment, f_{BC} is the fraction of amended carbon in the sediment. PCB sorption data for the fine AC were obtained from Gomez-Eyles et al. (2013a), and a batch sorption study was conducted to fully characterize PCB sorption to the EPB used in this study following the same method. Coke was omitted from this modeling exercise as no sorption data for this specific coke is available in the literature, and due to its poor performance relative to the other carbons in the study.

For Organoclay[®] PM-199 a linear sorption model was used, as the sorption coefficients for selected PCBs provided by the manufacturer were linear:

$$C_s = (f_{sed} K_d C_w) + (f_{OCL} K_{OCL} C_w)$$

Where f_{sed} is the fraction of native sediment, K_d is the native sediment distribution coefficient, f_{OCL} is the fraction of organoclay in sediment (5%) and K_{OCL} is the distribution coefficient of the organoclay. To help interpret the results the same modeling exercise was repeated using parameters of a previously characterized PCB impacted sediment of contrasting properties (Upper Canal Creek, Aberdeen Proving Grounds, MD) used in Gomez-Eyles et al. (2013a).

2.8. Measuring reductions in porewater Cd concentrations

The Cd treatability studies were conducted using the two sorbents found to be most effective for PCBs; fine AC and EPB. Each of the sorbents were amended and mixed into the sediment sample S4 in triplicate at a single dosing level of 5% by dry weight. The mixtures were then placed in bottles and mixed end over end in a tumbler for 1 month. Porewater Cd and hardness measurements were performed at the end of the test.

3. Results and discussion

3.1. Sediment characterization

Bulk sediment total PCB concentrations ranged from 1.81 to 59.2 mg/kg (Fig. S1). PCB homolog distribution profiles had a different pattern compared to usual Aroclor profiles and were dominated by tetrachloro-PCBs. Further analysis by GC-MS and congener comparison with typical dechlorination pathways confirmed that the tetrachloro-PCBs are primarily comprised of dechlorination products of Aroclor 1260, namely, PCB 47, 49, 51, and 52. These four tetrachloro PCB congeners have been identified as major dechlorination products that persist in Baltimore Harbor sediments (Fagervold et al., 2007).

Bulk sediment total PAH concentrations ranged from 8.0 to 15.4 mg/kg (Fig. S2), which is in the range of typical PAH concentrations found in urban sediments. DiBlasi et al. (2008) reported total PAHs in the range of 13–23 mg/kg in urban stormwater suspended solids trapped on the surface of bioretention facilities.

Bulk sediment and porewater Cd concentrations are displayed in Table 1. After correcting for hardness, only S4 porewater concentrations exceeded United States National Recommended Water Quality Criteria (NRWQC) for Cd. This sediment sample was therefore selected for use in the Cd treatability study. TOC and BC measurements were performed on the sediment samples used in the PCB treatability study (S1 and S2) as carbon phases in sediments are known to play a dominant role in controlling PCB partitioning and bioavailability (Table 1). The TOC value of this sediment was relatively low at about 2.7% compared to sediments used in other carbon amendment studies (5.8% for Grasse River sediments; Beckingham and Ghosh, 2011). The native BC in sediments at 0.3% is in the range of values reported for Grasse River (0.2%; Beckingham and Ghosh, 2011).

3.2. Freely dissolved porewater PCB and PAH concentrations

All amended treatments reduced porewater PCB concentrations in both sediments. However, the EPB and the fine AC were particularly effective with total PCB porewater concentration reductions of over an order of magnitude (Fig. 1). Differences between fine AC and EPB treatments were not statistically significant for either S1 or S2 (t-test, $p > 0.05$). The organoclays and coke also reduced concentrations but not to the same degree. Previous sorption studies have shown that the sorption of hydrophobic organic contaminants to organoclays and coke is only moderately higher (<1 order of magnitude) than their sorption to native sediment organic matter (Knox et al., 2008; Murphy et al., 2006). Amending these materials at a 5% dose level is therefore not going to provide the reductions of bioavailability usually observed when treating sediments with AC.

Coarse AC was also effective at reducing porewater PCB concentrations, but as previously reported (Zimmerman et al., 2005), the shorter inter- and intraparticle diffusive path lengths and larger external surface area provided by the greater number of smaller fine AC particles enhances the effectiveness of the finer particle size carbon amendment. For the carbon to be effective, the PCBs have to

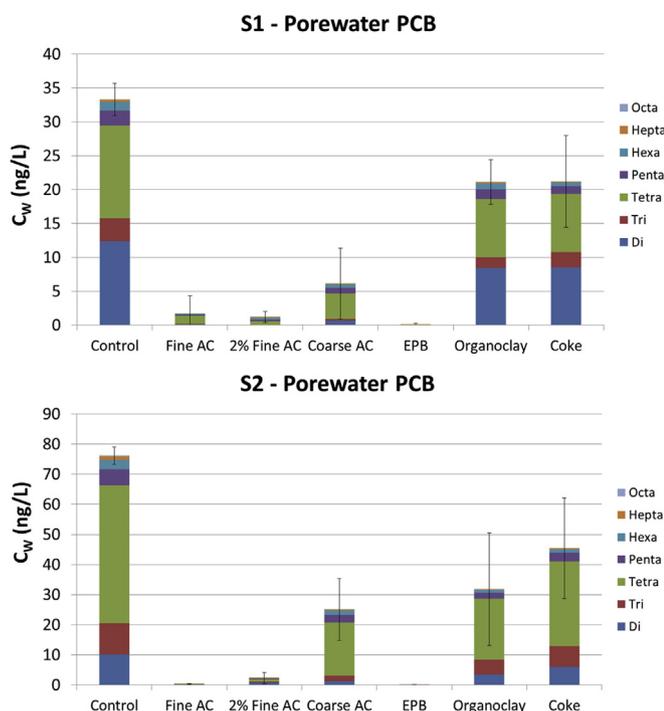


Fig. 1. Reductions in PCB homolog porewater concentrations in S1 and S2. All amendments were added at a 5% dry weight dose, except for the 2% fine AC. Error bars represent standard deviations ($n = 3$).

diffuse out of the organic matter in the sediment into the porewater and from the porewater onto the carbon surface. These diffusion processes are slow (from days up to several years in static systems), especially for the larger and more hydrophobic PCBs, so minimizing diffusion distances and increasing external surface area increases the kinetics of PCB mass transfer onto the carbon.

The importance of the kinetics of mass transfer is also reflected in the fact that reductions in PCB porewater concentrations after fine AC or EPB amendment were larger for less-chlorinated PCBs (Tables S1 and S2). The lighter, more mobile, less chlorinated PCBs sorb onto the carbons more quickly, so larger reductions in porewater concentrations are observed for these compounds in short-term experiments (Oen et al., 2011). In the longer-term the higher chlorinated PCBs are expected to show similar reductions as observed in a 3 year field pilot study in Grasse River (Beckingham and Ghosh, 2011). It is also likely for this mass transfer limitation to favor EPB performance relative to the fine AC in the short term (Fig. 1). As the bulk density of EPB is small (0.36 g/cm^3) compared to the fine AC (0.64 g/cm^3), there are larger numbers of EPB particles per unit mass, reducing the distance PCB molecules have to travel to the nearest carbon sorption site and also increasing the overall external surface area for mass transfer. Kinetics of mass transfer are therefore likely to be quicker onto the EPB than onto the fine AC. However, these initial kinetic limitations are expected to become less significant over longer periods of exposure in the environment.

Similar trends were observed for PAHs, with the biggest reductions in porewater concentration again occurring with the EPB and fine AC treatments (Fig. 2). The coarse AC, organoclays, and coke treatments were generally more effective at reducing PAHs than PCBs. It is likely for this to be due to the planar nature of PAHs. The sorption of planar molecules like PAHs to black carbons is known to be favored relative to the sorption of non-planar molecules like most PCBs (Cornelissen et al., 2005). There was no apparent trend in PAH porewater concentrations with increasing

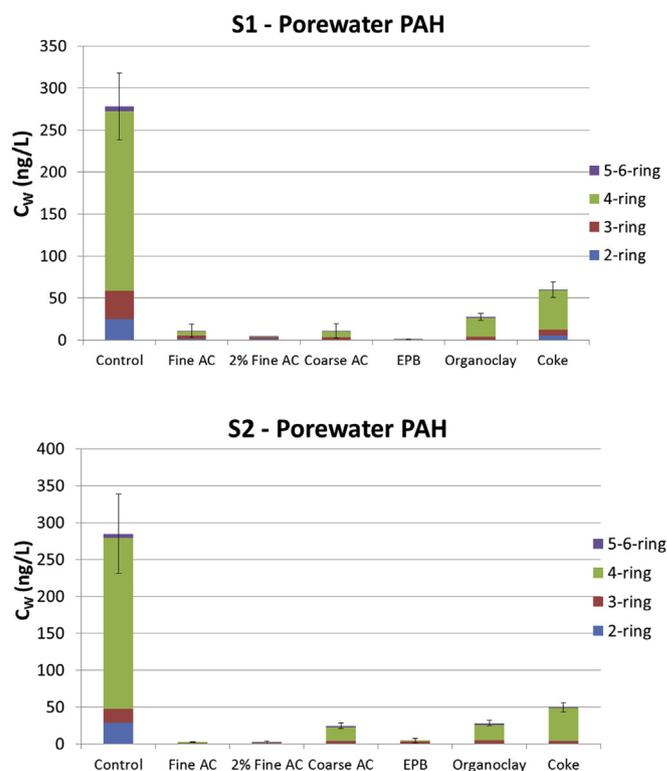


Fig. 2. Reductions in PAH porewater concentrations in S1 and S2. All amendments were added at a 5% dry weight dose, except for the 2% fine AC. Error bars represent standard deviations ($n = 3$).

hydrophobicity as there was with PCBs (Tables S3 and S4). Any trend may have been masked by the fact that PAH porewater concentrations after amendment were all very low and close to GC-MS detection limits in most carbon treatments.

3.3. PCB bioaccumulation in freshwater oligochaetes

Both the EPB and the fine AC strongly reduced PCB bioaccumulation relative to the untreated controls reflecting the porewater concentration reductions presented before (Fig. 3). This was expected as freely dissolved porewater concentrations have been shown to be indicative of PCB bioaccumulation in the tissue of benthic organisms (Werner et al., 2009). PCB bioaccumulation in worm tissue in this study was well estimated using porewater PCB concentrations using the following relationship with K_{OW} (Fig. 4):

$$\log(C_{\text{lipid}}) = 0.91 \cdot \log(K_{OW}) + 0.50 + \log(C_W) \quad (\text{Werner et al., 2009})$$

Where C_{lipid} is the PCB concentration in worm lipid ($\mu\text{g/g}$), and K_{OW} is the octanol to water partition coefficient. The relationship between estimated concentration in worms and measured concentration did not change with treatment, indicating that the porewater concentration remains a good predictor of equilibrium uptake in lipids irrespective of treatment.

Reductions in porewater concentrations following sediment amendment therefore translated into reductions in PCB bioaccumulation in worm tissue. As shown in Tables S5 and S6, the percent reductions in lipid and aqueous concentrations in both treatments are greater than 90% for PCB homologs up to hexachlorobiphenyls. However, for the hepta-, octa-, and nonachlorobiphenyls, the percent reductions in lipids were less than the observed reductions in aqueous concentration. This has been

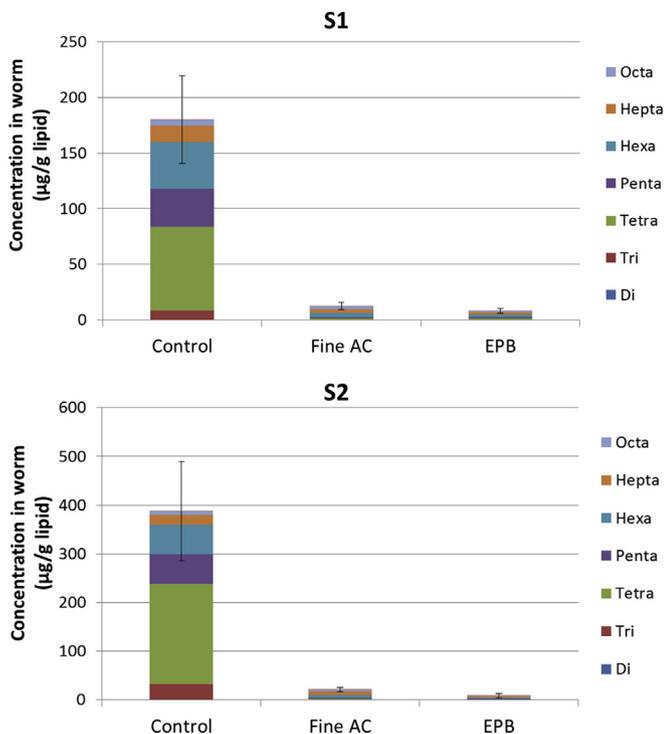


Fig. 3. Reductions in total PCB bioaccumulation in S1 and S2. Error bars represent standard deviations ($n = 4$).

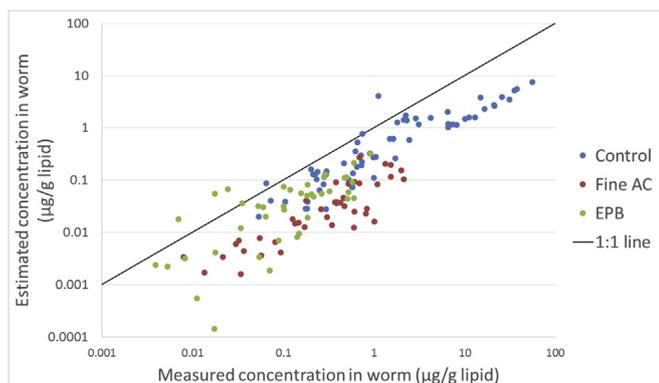


Fig. 4. Comparison of measured PCB concentrations in worm lipid in S2 with those estimated from porewater concentrations as in Werner et al. (2009).

observed in previous studies and is likely related to disequilibrium of the strongly hydrophobic compounds that have not quite reached a state of thermodynamic equilibrium with the introduced black carbon phase. However, these higher chlorinated congeners only represent 9% of total PCBs accumulated in the benthic organism.

Overall, these observations demonstrate that reductions observed in freely dissolved porewater concentrations are also manifested in uptake in freshwater worms that ingest sediment. Since ingestion of sediment is the dominant pathway for exposure of PCBs for this type of benthic organisms, reductions in uptake by worms demonstrate that strong binding of the PCBs to the added AC or biochar is also reducing exposure through the ingestion pathway.

The EPB and fine AC were both very effective at reducing PCB bioaccumulation and porewater concentrations. The EPB slightly

outperformed the fine AC throughout the study, although reductions in total PCB concentrations were only statistically significant between the fine AC and EPB treatments in the S1 worm tissues (t -test, $p < 0.01$). This was unexpected due to the considerably higher surface area of ACs ($1000\text{--}2000\text{ m}^2\text{g}^{-1}$) relative to any other black carbon amendments like biochars ($10\text{--}400\text{ m}^2\text{g}^{-1}$), as surface area has been shown to strongly correlate with the affinity of carbons for hydrophobic organic compounds like PCBs (Beesley et al., 2011; Gomez-Eyles et al., 2013b). For example, compared to natural organic matter in sediments, HOC sorption was found to be 3–4 orders of magnitude stronger for ACs compared to 1–2 orders of magnitude stronger for biochars (Gomez-Eyles et al., 2013a). This EPB has a high surface area ($358\text{ m}^2\text{g}^{-1}$) relative to other commercially available biochars (Gomez-Eyles et al., 2013a), but it is still lower than the fine AC ($1116\text{ m}^2\text{g}^{-1}$). We therefore decided to fully characterize PCB sorption in this EPB and compare it to PCB sorption on other biochars and the fine AC using the same methods followed in Gomez-Eyles et al. (2013a). The sorption data were then used to help interpret why the EPB was able to match the fine AC performance in this study.

3.4. Comparison of PCB sorption isotherms

Both the fine AC and the EPB have superior sorptive properties to that of natural sediment organic matter (Table S7, Fig. 5). The EPB isotherm was highly non-linear and EPB sorption capacity for PCBs is at least 2–3 orders of magnitude higher than sediment organic matter, whereas fine AC sorption is 3–4 orders of magnitude higher and relatively less non-linear than the EPB isotherm over the

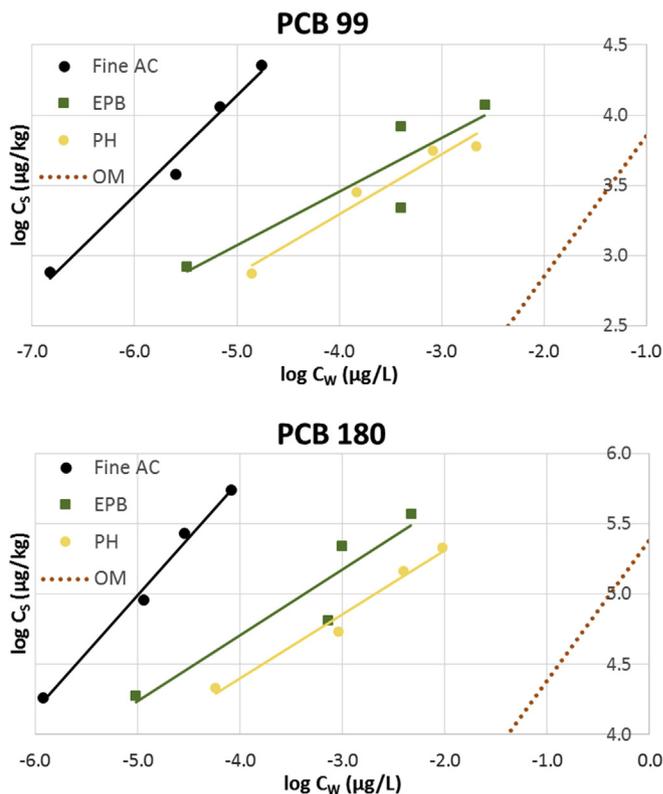


Fig. 5. Sorption isotherms for PCB congeners 99 and 180 plotted using data presented in Table S7 for fine AC and biochar. PH is a peanut hull biochar that was found to be amongst the most sorptive biochars in a previous study (Gomez-Eyles et al., 2013a, b). A dotted brown line is used for the predicted sorption to natural organic matter (OM) (LaGrega et al., 1994). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

concentration range tested. Their addition into sediments at small doses can therefore greatly enhance PCB sorption, drastically reducing freely dissolved concentrations. A peanut hull derived biochar that was the most sorptive out of 8 unactivated biochars characterized by Gomez-Eyles et al. (2013a) is included in Fig. 5, to illustrate how the EPB used in this study has superior sorptive qualities. The biochar industry has therefore been able to optimize biochar production parameters for superior sorption in its commercially available products.

3.5. Modeling reductions in PCB porewater concentrations using sorption data

Observed reductions in PCB porewater concentrations in S1 were generally well predicted using sorption data for fine AC, EPB, and organoclays (Fig. S3). However, for the carbons model predictions overestimated performance. Overprediction of reductions have been reported previously and is a function of the sorption attenuation of the carbons by dissolved organic matter in the sediment (Werner et al., 2006), and the slow kinetics of mass transfer for the more hydrophobic PCBs (Oen et al., 2011). After 28 days of shaking in the laboratory the system is still unlikely to be at equilibrium for the more hydrophobic PCBs. Both of these processes are reflected in Fig. S4 where we evaluate the ratio of modeled K_d in S1, after amendment predicted using the sorption parameters in Table S7 and accounting for the sorption of the native sediment organic carbon, against the effective K_d measured in this study. Ratios are consistently higher for the fine AC than EPB, indicating the fine AC is more prone to fouling or slow mass transfer than EPB in this sediment. Increased fouling in AC relative to biochars has been reported by others (Hale et al., 2011), and is likely influenced by the higher sorption of dissolved organic matter onto the AC surface due to its higher sorption capacity. Other factors like the pore size distribution of the carbons and the concentration of dissolved organic matter in the sediment will also have an impact, and deserve further study to improve our ability to predict the long term effectiveness of carbon amendments. Modeled K_d to effective K_d ratios also increased with PCB K_{ow} , especially for EPB, indicating the amended sediments may not be at equilibrium, or that the larger PCB congeners are more prone to sorption attenuation effects, but most likely a combination of the two. It is also important to note that the sorption attenuation effect was particularly large in these sediments. AC sorption attenuation factors typically range from 5 to 100 (e.g. Choi et al., 2012; McDonough et al., 2008; or Canal Creek MD, Fig. S4), but were generally in the range of 100–5000 in the sediments in the present study despite not having a particularly high concentration of organic carbon (Table 1).

Both the observed (Fig. 1) and modeled (Fig. S5) reductions after EPB amendment to S1 match or exceed reductions after fine AC amendment. This result is surprising given the 1–2 orders of magnitude superior sorption affinity of PCBs for the fine AC relative to the EPB (Table S7, Fig. 5), and results reported in previous studies using other sediments (Gomez-Eyles et al., 2013a), and for other hydrophobic organic contaminants in soils and sewage sludge (Brennan et al., 2014; Oleszczuk et al., 2012). For example Gomez-Eyles et al. (2013a) reported two different ACs reduced total PCB porewater concentrations by >99%, whereas 8 different unactivated biochars only reduced concentrations by 18–80%.

There are two main reasons for the differences observed in this specific study relative to others, besides the previously mentioned enhanced mass transfer kinetics onto the EPB relative to the fine AC due to its lower bulk density. The first is that the EPB used in this study is more sorptive than others characterized previously (Fig. 5). The second is that the sediment used in this study has a relatively high native PCB bioavailability (i.e. the PCBs are not tightly bound to

the sediment matrix, relative to other sediments). For example, the K_d values for PCB congeners in S1 are relatively low compared to those in other sediments used in prior AC amendment investigations (e.g. Canal Creek, MD Fig. S6). When contaminants are less tightly bound to the sediment, the addition of a sorptive phase will have a bigger effect on sorption than in sediments where the contaminants are already tightly bound (Gilmour et al., 2013). This results in very low final porewater concentrations in sediments. As seen in Fig. 5, at very low (pg/L) concentrations of individual PCB congeners, the isotherms of AC and EPB approach each other due to nonlinearity. The importance of the native bioavailability of the PCBs in the sediment is illustrated in Figs. S5 and S7. Both EPB and the fine AC are predicted to consistently reduce PCB porewater concentration by more than 97% in S1, but this is not the case for Canal Creek sediments. The fine AC is still predicted to consistently reduce PCB porewater concentration by more than 97% in Canal Creek, but reductions as low as 50% are predicted for EPB. The big difference between the two sediments is that after carbon amendment, the final porewater concentration is much higher in Canal Creek sediment compared to sediment S1. Given the usual overestimation of carbon efficacy due to carbon fouling and mass transfer limitations illustrated in Fig. S4, sorptive biochars like EPB may therefore not provide a sufficient enhancement to sediment sorption in sediments unless the final porewater concentrations remain low in the pg/L levels. On the other hand, ACs are likely to be consistently effective for the remediation of HOCs in most sediments.

3.6. Measuring reductions in porewater Cd concentrations

No significant reductions in porewater Cd were observed after amending S4 with the fine AC or EPB (Fig. S8). However, porewater Cd concentrations in the controls after 1 month of mixing were much lower (0.34 $\mu\text{g/l}$) than the initial concentrations reported when characterizing the fresh sediment (1.21 $\mu\text{g/l}$). These low Cd concentrations are below the NRWQC that ranged between 1.13 and 1.21 $\mu\text{g/l}$ after correcting for hardness (between 855 and 940 mg/l). It is likely that redox conditions changed during the 1 month of mixing in a closed bottle, and unlike PCBs, redox is known to play a major role in determining metal speciation and bioavailability. The mixed sediment samples were therefore aerated for 1 week and Cd porewater concentrations were re-determined. Again, there was no significant difference between the treatments and the controls, but the Cd concentrations in the controls (0.97 $\mu\text{g/l}$) were closer to the initially determined concentrations (1.21 $\mu\text{g/l}$) (Fig. S8).

Our results suggest that carbon amendments are not likely to have an effect on porewater Cd concentrations in these sediments, while other factors like redox conditions in the sediment are likely to play a much more important role in determining Cd bioavailability. Reductions in organic contaminant (e.g. PCB, PAH or DDTs) porewater concentrations between 70 and 90% have been previously reported after AC amendments to sediments (Beckingham and Ghosh, 2011; Ghosh et al., 2011; Tomaszewski et al., 2007; Zimmerman et al., 2004). However, there are a more limited number of studies examining the effect of carbon amendments in reducing heavy metal porewater concentrations in sediments. Kwon et al. (2010) reported 40–70% reductions in Cd porewater concentrations after amendment with activated carbon, however the Cd had been freshly spiked into the sediment and porewater concentrations were therefore 30-fold higher. In the same study AC amendments had a negligible effect on native Pb concentrations in the sediment, as the native Pb bioavailability was low. The native K_d of Cd in S4 is close to an order of magnitude higher than the laboratory spiked sediments used in Kwon et al. (2010), explaining the difference in effectiveness of the carbon amendments between

studies. The effectiveness of carbon amendments to reduce Hg bioavailability has also been shown to depend on how strongly bound the Hg is within the native sediment before amendments. Porewater Hg concentration reductions after AC amendment ranged from 15 to 90% depending on the sediment being tested, with smaller reductions reported in sediments with high native sediment-porewater partition coefficients (K_d) for Hg (Gilmour et al., 2013).

3.7. Amendment effects on worm lipid content

No significant differences in worm lipid content were detected between fine AC, EPB and control treatments (Fig. S9). However, it is important to note lipid content was the only toxicity endpoint assessed in this study, and previous studies have shown some limited deleterious effects on benthic organisms on these and other biological endpoints (Jonker et al., 2009; Fagervold et al., 2007; Kupryianchyk et al., 2012; Nybom et al., 2016). A review examining the ecotoxicological effects of AC amendments concluded these effects depended on the characteristics of the sedimentary environment and the AC amendment strategy (e.g., AC dose and particle size) (Janssen and Beckingham, 2013). More limited studies have been conducted in sediments with biochar, but weight loss effects have been reported in earthworms (Gomez-Eyles et al., 2011). Further investigation would therefore be required to fully assess the potential impact of biochars on benthic communities, but results from this study are encouraging in that regard.

3.8. Implications

Both fine AC and EPB amendments strongly reduced PCB and PAH porewater concentrations (>95%), and PCB bioaccumulation (>93%) in sediments S1 and S2. Amending these sediments in the field with either fine AC or EPB would therefore greatly reduce the amount of PCBs entering at the base of the aquatic food chain and PCB flux out of the sediments into the overlying water. However, although the EPB can be less expensive (\$1000 per ton vs \$2500 per ton) and was at least as effective as the fine AC, concerns about the physical stability of the carbon in the sediment due to its lower density need to be addressed before recommending wide scale field application. Biochar made from soft woods have very low density and are difficult to handle and apply in large-scale, especially in an aquatic environment.

Care must be taken with the interpretation of the positive results reported for the biochar used in this study. The superior sorptive properties of the EPB relative to other unactivated biochars are due to the special thermal conversion process involved in its manufacture. Additionally, the thermal conversion process used to manufacture this enhanced biochar results in a very low yield of carbon (<10%) which reduces the carbon sequestration benefit and raises the cost of the final product. Enhanced biochars may be a valid alternative to ACs in specific sediments, but traditional ACs made from coal or coconut shell can guarantee a better performance than biochars in a wider range of sediment characteristics. It is unlikely for organoclays and coke to provide a suitable alternative to AC for the *in situ* remediation of sediments impacted with HOCs by direct application. Although not specifically addressed in this study, this reduced sorption relative to AC should not preclude any of the amendments in this study from being considered in a reactive cap scenario where a less sorptive material could also effectively isolate underlying contaminants. Finally, neither the fine AC nor the biochar were found to be suitable for Cd remediation in the sediments used in this study.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.chemosphere.2018.03.132>.

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