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Activated Biochars with Iron for In-Situ Sequestration of Organics, Metals, and Carbon

SERDP Project ER-2136

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List of Acronyms

Activated Carbon	(AC)
Polycyclic Aromatic Hydrocarbons	(PAHs)
Polychlorinated Biphenyls	(PCBs)
Dichlorodiphenyltrichloroethanes	(DDTx)
Total Organic Carbon	(TOC)
Zero Valent Iron	(ZVI)
Polyoxymethylene	(POM)
Tetrachloroethylene	(PCE)
Trichloroethylene	(TCE)
Mercury	(Hg)
Methylmercury	(MeHg)

Keywords

Biochar, Activated Carbon, PCBs, PAHs, Mercury, Methylmercury, contaminant, sediment, sequestration, bioavailability

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Abstract

Objectives

This research follows from previous work that has demonstrated that suitable sorbent amendments to sediments can lead to contaminant sequestration and reduction of contaminant bioavailability for in-situ management of impacted sites. The primary objective of this research was to test a range of available biochars and especially formulated biochars that can reduce the bioavailability and leaching of toxic chemicals like PAHs, PCBs, DDTs, mercury and methylmercury in sediments. To address this objective five key research questions were addressed:

1. Are biochars effective sorbents for PAHs, PCBs, DDT, mercury and methyl mercury?
2. Do biochars need activation to increase specific surface area and be effective sorbents for PAHs, PCBs, DDT, mercury and methyl mercury?
3. Can addition of zero valent iron in biochars enhance the dechlorination of chlorinated organic compounds?
4. Can incorporation of iron oxide in biochars enhance the metal binding capacity of biochars?
5. Can incorporation of iron and iron oxides increase the density of biochars to make them more stable in the sediment environment and allow separation for mass transfer calculations?

Technical Approach

A range of biochars made from a number of agricultural residues, phragmites, and hardwoods were evaluated in this research. In addition, the biochars were activated either physically or chemically to enhance their organic contaminant sorption properties, impregnated with zero valent iron to evaluate their potential for the dechlorination of chlorinated compounds, and with iron oxides to evaluate the enhancement of sorption of mercury and methylmercury. Contaminant sorption to the carbons was evaluated in the aqueous phase by conducting sorption isotherms and pH edge sorption studies, followed by effectiveness testing in the sediment phase. The impregnation of iron/iron-oxides created a denser carbon so the increased stability of iron amended biochars was also assessed. The magnetic properties of these iron amended carbons also allowed for the separation of the carbon after contact with sediment enabling contaminant mass transfer assessments.

Results

Biochars were able to sorb organic contaminants, Hg and MeHg, making them attractive alternatives to ACs in sites contaminated with both organic and inorganic contaminants. However, due to their lower surface area, unactivated biochars have a lower affinity for organic contaminants than ACs, so activation is necessary for their performance to match that of ACs. Unactivated biochars were able to reduce PCB porewater concentration by 18-80%, while the activated carbons and activated biochars consistently reduced organic contaminant porewater concentration by >99% in a DoD impacted sediment. Hg isotherms and pH edge sorption experiments indicate that some of the ACs were the most effective in removing Hg from solution at low concentrations. However, they also suggest that these ACs could have a limited amount of sorption sites available for inorganic contaminants relative to the biochars as their performance dropped with increasing Hg concentrations. The biochars, particularly poultry litter derived

chars, were able to remove more Hg from solution at higher Hg concentrations compared to other carbons (>99% Hg removal in pH edge study). It is possible that the high phosphate content of these poultry litter biochars are responsible for this enhanced Hg sorption. These biochars are therefore attractive from an Hg remediation standpoint, but the stability of the phosphate within the carbon needs to be evaluated before field application. Iron oxide amended chars could be separated magnetically to assess PCB mass transfer from sediment to carbon. The use of iron to impregnate the carbons was effective in improving their density and settling characteristics but had limited success in improving the sorption capacity of the carbons to Hg and MeHg or in enhancing the dechlorination of chlorinated organic compounds. Refinement of the iron amendment technique and longer-term studies are required to fully explore the potential of iron amended chars.

Benefits

This study provides the proof-of-concept that can lead to further development of biochars for full-scale sediment remediation through scale-up to large-scale production of the synthesized biochars, evaluation of full-scale economics of the manufacturing, and finally benthic organism bioavailability and toxicity studies to evaluate the impact of the new sorbents in aquatic ecosystems. Activated biochars produced from waste biomass can provide strong sorbents for the remediation of contaminated sediments, reducing treatment costs and possibly reversing the carbon footprint of the remediation strategy. This could be particularly attractive in contaminated wetlands invaded by Phragmites, as the Phragmites itself could be used to produce the activated biochars necessary for sediment remediation on site.

Objectives

Previous work by us and others has demonstrated that contaminant exposure pathways in contaminated sediments can be controlled by modifying and enhancing the binding capacity of natural sediments with sorbent amendments. The primary objective of this research was to test a range of available biochars and especially formulated biochars that can reduce the bioavailability and leaching of toxic chemicals like PAHs, PCBs, DDTs, mercury and methyl mercury in sediments. Utilization of biomass-derived as opposed to fossil carbon-derived black carbons affords the additional opportunity for carbon storage in sediments along with the sequestration of toxic contaminants.

To address the primary objective of this study, five key research questions were addressed:

1. Are biochars effective sorbents for PAHs, PCBs, DDT, mercury and methyl mercury in freshwater and saltwater matrices?
2. Do biochars need activation to increase specific surface area and be effective sorbents for PAHs, PCBs, DDT, mercury and methyl mercury in freshwater and saltwater matrices?
3. Can addition of zero valent iron in biochars enhance dechlorination of chlorinated organic compounds?
4. Can incorporation of iron oxide in biochars enhance the metal binding capacity of biochars?
5. Can incorporation of iron and iron oxides increase the density of biochars to make them more stable in the sediment environment and allow separation for mass transfer calculations?

A range of biochars and activated biochars derived from agricultural residues and other biomass source materials were evaluated to achieve this objective. These biochars are commercially available or have been developed by other research groups. In addition, a series of enhanced biochars were produced in the laboratory. The properties of these biochars were modified by activating them chemically to improve their organic contaminant sorption properties, and also by impregnating them with iron oxides to enhance the sorption of mercury and methyl mercury. Biochars impregnated with zero valent iron were also synthesized to evaluate their potential for the dechlorination of chlorinated compounds. The impregnation of iron/iron-oxides can create a denser carbon so the increased stability of iron amended biochars was also evaluated. The magnetic properties of these iron amended carbons also allow for the separation of the carbon after contact with the sediment enabling contaminant mass transfer assessments.

Since there are several recently concluded and ongoing studies that have advanced the technology of in-situ sorbent amendment to sediments (ER-1491, ER-0510, CU-1207; Grasse River Activated Carbon Pilot Study), we anticipate that the most effective sorbents tested or synthesized in this project will require only little effort to be included in potential field demonstration or full-scale remediation efforts. The additional studies will require scale-up to large-scale production of the synthesized biochars, evaluation of full-scale economics and carbon budget of the manufacturing process, and finally benthic organism bioaccumulation and toxicity studies to evaluate impact of the new sorbents to aquatic ecosystems.

Relevance to SERDP

This proposal responds to SERDP FY 2011 SEED Statement of Need (SON): In-situ Remediation of Contaminated Aquatic Sediments. Specifically, this proposal addresses three of the four issues that were suggested for addressing in the SON as explained below:

1) Ability to achieve contaminant degradation or sequestration: This study evaluates the use of biomass based chars and activated chars with amendments designed to enhance the sequestration of organic compounds, mercury and methyl mercury and achieve the degradation of chlorinated organic compounds.

2) Bioavailability of sequestered contaminants: The research evaluated the bioavailability of sequestered contaminants through aqueous equilibrium partitioning studies using sediment samples from a DoD site.

3) Amendment placement, distribution, and stability: As mentioned previously, sorbents synthesized in this project included biochars impregnated with iron that will make the material denser thereby enhancing its stability in the sediment environment compared to regular biochars.

In addition, the proposed research evaluated the effectiveness of the sorbents in both freshwater and saltwater environments, and the focus was on contaminants of most concern in sediments including PAHs, PCBs, DDT, mercury and methyl mercury.

Background

Remediation of PCB-impacted sediment. The cleanup process of sediment sites is complex and creates unique challenges due to expensive cleanup strategies, large and diverse sediment sites, and presence of ecologically valuable resources or legislatively protected species or habitats (USEPA, 2005). As indicated in USEPA (2005), removal options such as dredging and excavation have certain clear advantages, especially in situations where hot spots exist and there is a desire to reduce sources and risks quickly and to insure a permanent solution. However, the limitations and disadvantages of these methods have also become better understood. Dredging and disposal can be expensive and disruptive to existing ecosystems (USEPA, 2005). Moreover, contaminants can be released into the water and air environments during sediment dredging, transportation, and storage (USEPA, 1996; Valsaraj et al., 1998; NRC, 2002). Capping with clean sediments may not be practicable in sensitive ecosystems and at sites where there is concern with changing the sediment bathymetry. New developments in in-situ remediation approaches are needed that are less energy-intensive, less expensive, less disruptive of the environment, able to reduce human and ecosystem exposure, and defensible through well-grounded scientific understanding of contaminant fate processes and bioavailability in field conditions.

In-situ control of PCB bioavailability in sediment. Recent findings indicate that the bioavailability and leachability of contaminants in sediment are affected strongly by the nature of binding of the contaminants to the sediment particle types (Cornelissen et al., 1997; Kraaij et al., 2002; Ghosh et al., 2003a; Kukkonen et al., 2004; Lohmann et al., 2005; Moermond et al., 2005). For example, Jonker and Koelmans (2002) found that soot and soot-like materials have very high affinities for PCBs and PAHs and that the presence of these materials can lower aqueous concentrations of the contaminants, implying a reduction in the potential uptake by aquatic organisms. In our earlier work (Ghosh et al., 2000; Talley et al., 2002; Ghosh et al., 2003a), we demonstrated that PAHs associated with coal-derived particles are much less available for biological uptake. These findings suggest that the presence of black carbonaceous particles in sediments naturally reduces contaminant availability. McLeod et al (2004) showed in clam particle feeding studies that the assimilation efficiency for a tetrachloro-PCB was only 1-2% via ingestion if the PCB was sorbed to activated carbon, compared to > 90% for PCBs sorbed to diatoms.

In our recent work with PCB-contaminated sediments we have demonstrated that addition of activated carbon reduces PCB bioavailability greatly. Reductions in total PCB bioaccumulation of 69% by Macoma clams, 72% by Leptocheirus amphipods, and 83% by Neanthes worms were observed in laboratory tests on sediment treated for one month with activated carbon (Ghosh et al., 2003b; Millward et al., 2005). We also find that sediment treated with activated carbon attains aqueous equilibrium PCB concentrations 85 and 92% lower than untreated sediment in one month and six-month contact experiments, respectively (Zimmerman et al., 2004). For freshwater sediments we have demonstrated that biouptake in oligochaetes decreased after the addition of 2.6% activated carbon (amounting to half the sediment TOC). Based on total PCB concentration in wet tissue, the mean bioaccumulation reductions were 70% for placement of activated carbon as a layer without mixing, 70% for placement and mixing of activated carbon for 2 minutes, and 90% for the placement and slow mixing of activated carbon for one month prior to worm addition (Sun and Ghosh, 2007). This demonstrates the potential for application of activated carbon to the biologically active layer of PCB-contaminated sediment to be an effective in situ stabilization method to reduce contaminant bioavailability to sediment organisms at the base of the aquatic food web. In situ bioavailability reduction using carbon amendment may be applicable at sites where reducing bioaccumulation can limit exposures and consequent risk to acceptable levels and is being demonstrated through several pilot-scale field trials (Beckingham and Ghosh, 2011; Ghosh et al., 2011).

Potential use of biochars and carbon sequestration. While, activated carbon made from coal has been demonstrated to work as a suitable sorbent for bioavailability reduction, carbons manufactured from biomass waste products offer an exciting opportunity for efficient resource utilization with the added potential opportunity for carbon sequestration in the process of sediment remediation (Beesley et al., 2010; Beesley et al., 2011). Additionally, new types of activated carbons made from renewable resources such as biomass waste and poultry litter are being developed and are claimed to have superior metal sorption characteristics (Fitzmorris et al., 2006; Cao et al., 2009; Cao et al., 2011). Black carbons from natural sources (such as forest fires) and man-made sources are known to persist naturally in soils and sediments and form the basis for carbon dating of soil and sediment cores. Also, recent findings indicate that carbon storage opportunities exist for black carbon introduction in soils because in this form the carbon is stable and not prone to microbial oxidation processes (Marris, 2006; Lehmann, 2007). In addition, the US EPA’s new Green remediation strategy aims to minimize the environmental footprints of a cleanup (http://www.epa.gov/superfund/greenremediation/). Therefore, technologies that can reduce or reverse the carbon footprint while reducing risks will likely be favored in the future. A major unknown currently is whether biochars or activated biochars can be effective in reducing organic and metal contaminant bioavailability in sediments. Further, it is not known if amendment of the biochars with iron and iron oxides can enhance sorption capacity for metals, allow dechlorination of chlorinated organics, make the carbon denser and enhance stability, and allow separation for mass transfer evaluations. We aim to address each of these knowledge gaps in this study.

Activated carbons have been impregnated by various salts, elements, and oxides to attribute unique sorption properties in other studies. Activated carbon impregnated with Fe(III) oxides have been investigated for the removal of several anionic and catonic metals (Reed, 2000; Vaughan and Reed, 2005). Metal removal increased significantly over that observed for the virgin carbon and also was a strong function of pH. Impregnation of the carbon decreased the surface area (21%), total pore volume (23%), and iodine number (20%). Recent work by Choi et al. (2009) demonstrated that zero valent iron impregnated activated carbons can dechlorinate PCBs in aqueous systems. They found that the reaction rate can be enhanced by including palladium as a catalyst. However, the wet chemistry method of impregnation used by these researchers and the use of a noble metal (Pd) increases the cost of the final product.

Development of iron/ironoxide amended Activated Carbon. Recent development of a magnetic activated carbon offers a wonderful opportunity as a sorbent in contaminated sediments that may be retrieved from the sediment after repartitioning along with the toxic contaminants. The iron amended carbon is produced by mixing a carbon source (agricultural waste) with a magnetic precursor (Miller et al., 2004). After a series of heat treatments under controlled conditions, an activated carbon with magnetic properties is obtained. The product carbon has residual iron in various states of oxidation that can be controlled by the nature of impregnating iron, pyrolysis process, and the activation process. Typically some zero valent iron and a mixture of iron oxides, including magnetite remains embeded in the carbon imparting the material a diamagnetic behavior. A simple schematic process flowsheet for the production of the magnetic activated carbon in shown in Figure 1. The manufacturing steps are quite similar to a traditional process for the manufacture of activated carbons, except for the inclusion of an iron salt (typically $FeCl_3$). The final product consists primarily of carbon (87-97 %), as well as other elements (e.g., H, O, S and N) that form surface functional groups. Surface areas are typically in the range of 500-800 m^2/g as measured by the nitrogen BET method. Tests in our laboratory has demonstrated that even at low additions of the magnetic precursor to the activated carbon, greater than 98% recovery of the carbon is possible as demonstrated in Figure 1b. Embedding of iron and iron oxides in the carbon offer the following new opportunities: 1) the zero valent iron may be utilized in the reductive dechlorination of chlorinated organics that are sorbed to the carbon, 2) iron oxides may act to enhance the sorption capacity of certain metal contaminants, 3) the impregnation of iron/iron-oxides will increase carbon density and also allow separation of the carbon after contact with sediment for contaminant mass transfer assessments and potential contaminant removal in a field application.

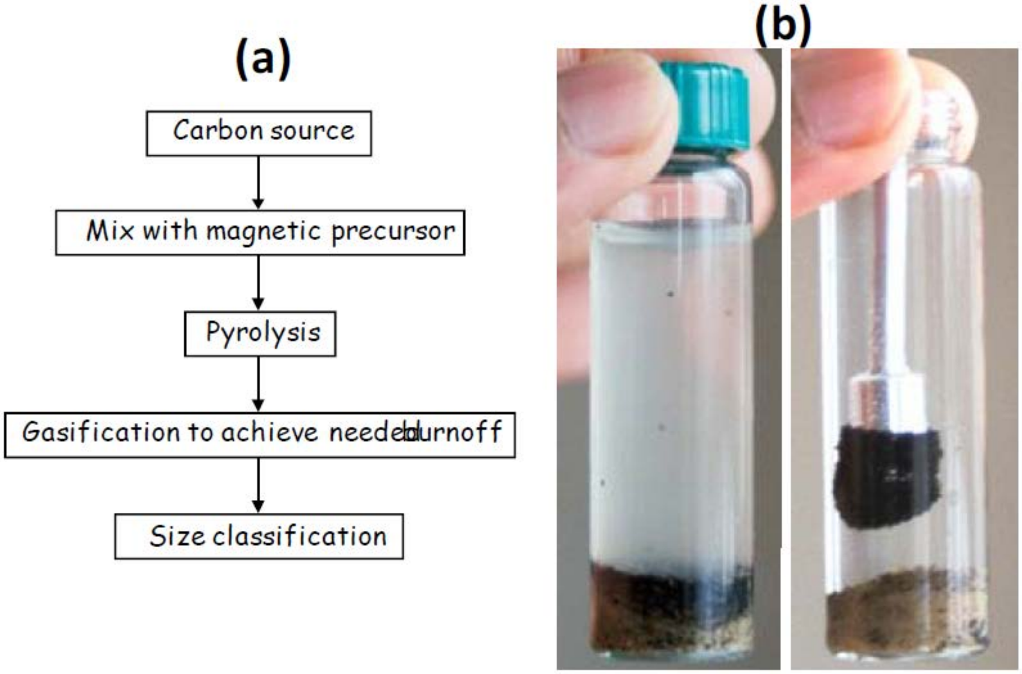

Figure 1. a) Steps involved in the production of magnetic activated carbon and b) demonstration of magnetic activated carbon added to sediment (left) and retrieved using a permanent magnet (right).

Material and Methods

Task 1: Selection/synthesis of biochars and testing of freshwater and saltwater isotherms for PAHs, PCBs, DDT, mercury and methyl mercury

Carbon Selection. The carbons tested in this study are listed in Table 1 and include commercially available activated carbons and biochars, biochars obtained from the US Department of Agriculture through an existing cooperative agreement and laboratory produced biochars.

Table 1. List of carbons

Carbon Type	Abbreviation	Manufacturer	Cost ($/lb)
Bituminous coal based AC	CAC-Coal	Calgon Corp.	3-4
Coconut shell based AC	CAC-Coco	Calgon Corp	1
Lignite coal based AC	CAC-Darco	Norit	3-4
Regenerated AC	CAC-RAC	Siemens	0.50
Pine dust biochar	Bio-PD	BEC	<1
Peanut hull biochar	Bio-PH	BEC	<1
Barley straw biochar	Bio-BS	BEC	<1
Acai pit biochar	Bio-AP	BEC	<1
Hardwood lump Charcoal	Bio-HW	Milazzo Industries	<1
Activated turkey litter biochar	Act Bio-CL	USDA	NA
Activated chicken litter	Act Bio-TL	USDA	NA
Pine dust biochar	Lab-PD	UMBC	<1
Phragmites biochar	Lab-PHR	UMBC	<1
Activated pine dust biochar	Lab-APD	UMBC	<1
Activated Phragmites biochar	Lab-APHR	UMBC	<1
Iron oxide impregnated pine dust biochar	Lab-FePD	UMBC	NA
Zero valent iron impregnated pine dust biochar	Lab-HW-ZVI	UMBC	NA
Iron amended granulated biochar	Bio-GFe	Pilot production	NA

Carbon characterization. Total C analysis was performed using a Shimadzu TOC analyzer with a solids sample module (TOC-5000A and SSM-5000A). Surface area measurements were carried out by Particle Technology Labs (Chicago, Illinois). The continuous flow method at 77 K was employed for quantification of adsorbed and desorbed N_2, using a QUANTACHROME QUANTASORB QS-13 Surface- Area Particle-Size Analyzer and ultra-high purity gaseous nitrogen (99.999%, from BOC Gases). Surface areas were calculated from a five-point regression, based on the Langmuir equation.

PAH, PCB and DDT isotherm studies. Isotherm studies were performed in freshwater and saltwater matrices to compare the organic sorption capacity of the different carbons. This was tested by measuring aqueous equilibrium concentrations using polyoxymethylene (POM) strips. Briefly, 24 mg of each sorbent (<250μm) 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 DDT stock solution to obtain 4 different spike levels for each sorbent. The PCB stock solution contained a 1:1 (vol) mixture of Aroclor 1242 and 1260

(Supelco, Bellefonte, PA, USA), the PAH stock contained acenapthene, phenanthrene and fluoranthene, and the DDT solution contained 4,4'-DDE and 4,4'-DDD. POM strips (90 µm thick) 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 to ensure they were visibly clean, wiped dry and extracted with a 1:1 hexane and acetone mixture. The extracts were split into two equal parts for PCB and DDT analysis by GC-ECD, and for PAH analysis by GC-MS.

Mercury pH-edge sorption isotherms. Hg pH-edge sorption isotherm studies in freshwater matrices were performed to compare the Hg sorption capacity of the various carbons. A known mass of the different sorbents carbons (<250µm) was added to a range of mercury feed solutions. The concentrated stock solutions of mercury were prepared by dissolving mercury chloride ($HgCl_2$) salt into freshwater. The initial concentration of mercury was 20 mg/L. While stirring rapidly, a wide-mouth pipette was used to remove 40 ml aliquots of the adsorbent slurry, which were then placed in 50 ml plastic vials. The pH of the vials was then adjusted using either 0.1 N sodium hydroxide or 0.1 N nitric acid, obtaining solutions ranging from 3 to 10 in pH. The samples were then shaken for 48 hours. Upon removal from the shaker, sample pH was measured; filtered using a 0.45 µm filters, and preserved using concentrated nitric acid. Samples were then analyzed for divalent metal concentration using an inductively coupled plasma mass spectrometer (ICP-MS).

Mercury and methylmercury sorption isotherms. Mercury and methylmercury sorption isotherms were carried out in a saltwater matrix. A known mass of each sorbent was added to PTEG bottle containing 50ml of water. Each jar was then spiked with a known amount of mercury or methylmercury solution to obtain 5 different spike levels for each sorbent. The bottles were then allowed to equilibrate for 1 week at 4° C, after which they were filtered and the solutions analyzed by ICP-MS.

Mercury and methylmercury analysis were performed at the Smithsonian Environmental Research Center. Total mercury analysis (EPA Method 1631) was performed following digestion, reduction, and gold-trapping. Methylmercury analysis (EPA Method 1630) was done by distillation, ethylation, and gas chromatographic separation. Methylmercury samples were distilled (Horvat et al., 1993) and then derivatized using sodium tetraethylborate. After distillation and ethylation, volatile mercury species are purged and concentrated onto traps filled with Tenax®, thermally desorbed, separated on an OV 3/Chromasorb column, and directly introduced on a stream of argon into an inductively coupled plasma-mass spectrometer (ICP-MS) (Perkin-Elmer Elan DRC II) for detection. For quantification, SERC used isotope dilution techniques (Hintelmann et al., 1995; Hintelmann and Ogrinc, 2002), in which trace amounts of enriched methyl199 mercury are added to each sample as an internal standard. For each batch of total mercury or methylmercury samples, a suite of quality assurance and quality control (QA/QC) measures are run and reported. These include the analysis of blanks, analytical duplicates, and certified reference materials (CRMs) where available and appropriate. Typical detection limits for total mercury are <1 ng/L for pore waters, <0.5 ng/L for surface waters, and 0.1 ng/g for sediments and tissue. Typical detection limits for methylmercury are <0.5 ng/L for pore waters, <0.25 ng/L for surface waters, and <0.1 ng/g for sediments and tissue. Details of SERC methods and quality assurance can be found in recent publications (Mitchell and Gilmour, 2008; Hollweg et al., 2009).

Task 2: Synthesizing and testing chemically activated biochars and biochars with iron and iron oxides embedded.

Synthesis of activated and iron impregnated biochars. Chemically activated biochars were produced as described in (Lim et al., 2010). Briefly, Phragmites and pine dust source materials were mixed 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.

Iron oxide impregnated biochar was produced following the methods described by Miller et al. (2004). Briefly, pine dust was soaked in an $FeCl_3$ solution (0.024M) and homogenized for 24 hours in an orbital shaker. The material was then dried at 100° C for 24 hours before being pyrolyzed at 600° C for 2 hours.

Zero valent iron (ZVI) impregnated biochar was produced following the incipient wetness method described by Choi et al. (2008). Here a hardwoord derived biochar (Milazzo Industries) was impregnated with ZVI by melting $Fe(NO_3)_3{}^{\cdot}9H_20$ at 55-60° C with a small quantity of water (5 mL) onto the carbon. The slurry was then dried at room temperature, put in an oven overnight (at 105° C), and further calcined in a muffle furnace at 300° C for 4 hours to remove nitrate ions. The iron oxide impregnated onto the biochar was then reduced to elemental Fe using a $NaBH_4$ solution.

Dechlorination studies. To assess the dechlorination potential of the ZVI impregnated biochar an aqueous PCE solution was prepared in previously boiled and nitrogen purged distilled water. The carbon was contacted with the solution for a month, and aliquots of the solution were analyzed at different timepoints (0, 1, 2 and 4 weeks) for dechlorination products (TCE) by GC-ECD. The aqueous PCE solution was also contacted with the unamended hardwood derived biochar and iron filings in separate treatments.

Effectiveness testing in the sediment phase. Carbons were tested using a PCB impacted sediment from a DoD site (Upper Canal Creek, Aberdeen Proving Grounds, MD). The sediment was mixed with the carbons at a dosing rate of 5% by mass of dry sediment, and equilibrated for a month in the presence of polyoxymethylene (POM) passive sampling strips to evaluate PCB porewater concentrations using methods presented in Sun and Ghosh (2008). Changes in PCB porewater concentrations can be related to changes in PCB bioavailability in the sediment (Beckingham and Ghosh, 2011), and can therefore give an indication of the success of the carbon amendment.

Task 3: Test density, settling, and separation characteristics of biochars with or without iron amendments.

Density and settling characteristics. Skeletal and bulk density of carbons were measured in the laboratory by a gravimetric method. For skeletal density measurement, the carbon was first filled in tared 10 ml volumetric flasks and then filled with acetone up to the volumetric mark. The volume of acetone required was calculated from the mass and density of acetone and used to calculate by difference the volume occupied by the carbon. Bulk density of the carbons was measured by filling up a known volume with the carbon and measuring the mass. To evaluate the effect of adding iron amendments to biochars settling test were performed on a selection of carbons. Settling tests consisted of measuring the time taken for replicates of 10 carbon particles (500um-600um) to fall through a 1m column of freshwater and 10 ppt seawater.

Measurement of mass transfer kinetics of target contaminants from sediment into iron-amended biochars. The previously mentioned PCB impacted sediment from Upper Canal Creek was amended (5% by weight) with an iron amended granulated biochar. The magnetic properties of the biochar enabled a separation of the carbon from the sediments at different timepoints (0, 1, 2 and 4 weeks). The carbon and the sediment were then extracted and tested for PCBs using EPA standard methods for extraction, clean up and analysis.

Results and Discussion

Carbon characterization

The results of the carbon characterization are displayed in Table 2. As expected the commercially available activated carbons and the biochars activated chemically in the laboratory had a larger surface area than the unactivated biochars. The steam activation of the poultry litter biochars produced by the USDA only had a moderate impact on their surface area.

Table 2. Carbon properties

Carbon Type	C (%)	Surface area (m^2/g)
CAC-Coal	80.9±1.4	1116.1±18.0
CAC-Coco	90.8±2.7	1305±8.4
CAC-Darco	ND	ND
CAC-RAC	ND	ND
Bio-PD	22.1±0.5	109.4±0.8
Bio-PH	31.9±6.8	107.3±1.3
Bio-BS	49.2±2.5	26.1±0.2
Bio-AP	77.2±0.3	197.9±4.4
Bio-HW	70.8±0.3	223.6
Act Bio-CL	26.8±1.2	300.4±6.7
Act Bio-TL	26.9±0.8	270.4±1.7
Lab-PD	77.9±0.8	542.2
Lab-PHR	69.6±0.9	464.3
Lab-APD	71.0±0.3	2265.6
Lab-APHR	64.6±0.14	1578.8
Lab-FePD	77.1±2.0	586.2
Lab-HW-ZVI	38.4±2.1	ND
Bio-GFe	59.6±0.1	ND

PAH, PCB and DDT sorption

Aqueous equilibrium isotherms

Isotherms studies were carried out in two batches. The first set was carried out using the already available biochars and ACs while the methods for synthesizing the biochars in the laboratory were being optimized. Once the laboratory biochars were synthesized a second set of isotherms was performed. Due to the large amounts of carbons tested, graphs and tables displaying these results are split into these two categories (readily available carbons and laboratory synthesized carbons) for clarity.

The sorption of PAHs, PCBs and DDTs onto the carbons was mostly non-linear, so isotherms were fitted using the Freundlich equation. Activated carbons consistently removed more organic contaminants from solution than the unactivated biochars at the environmentally relevant concentrations tested. The difference in sorption capacity between activated carbons and unactivated biochars was around 2 orders of magnitude for the readily available carbons. This is illustrated in Figures 2-5 showing the sorption of two PCB congeners (PCB 18 and PCB 158 as representative tri- and hexachloro PCBs) to the different carbons, and additionally Figures 6 and 7 displaying the sorption of fluoranthene and 4,4'-DDE to the laboratory synthesized carbons. The figures also include the expected sorption of the contaminants to natural organic matter (OM), derived using generic K_{ow} to K_{oc} relationships obtained from the literature (Schwarzenbach et al., 2003).

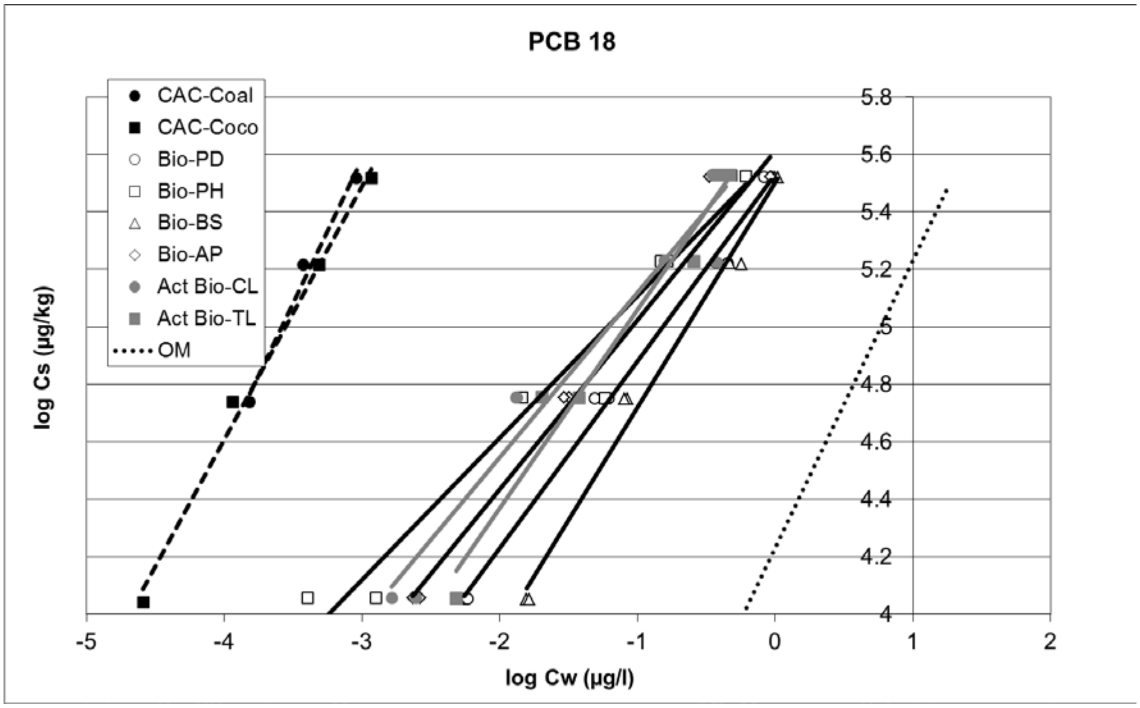

Figure 2. PCB 18 isotherms for the readily available carbons. Isotherms are plotted with dashed lines for the activated carbons, with straight grey lines for the activated poultry litter biochars and with straight black lines for the remainder of the biochars. Modeled isotherms for organic matter are plotted with black dotted lines.

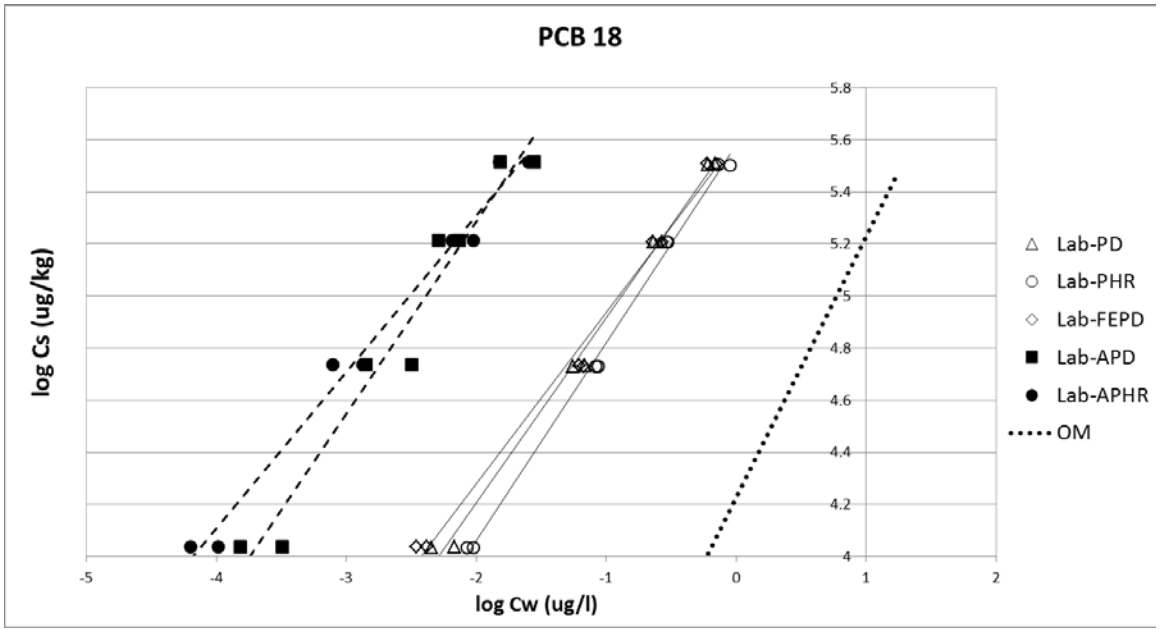

Figure 3. PCB 18 isotherms for the laboratory synthesized carbons. Isotherms are plotted with dashed lines for the biochars activated chemically in the laboratory, and with straight black lines for the remainder of the biochars. Modeled isotherms for organic matter are plotted with black dotted lines.

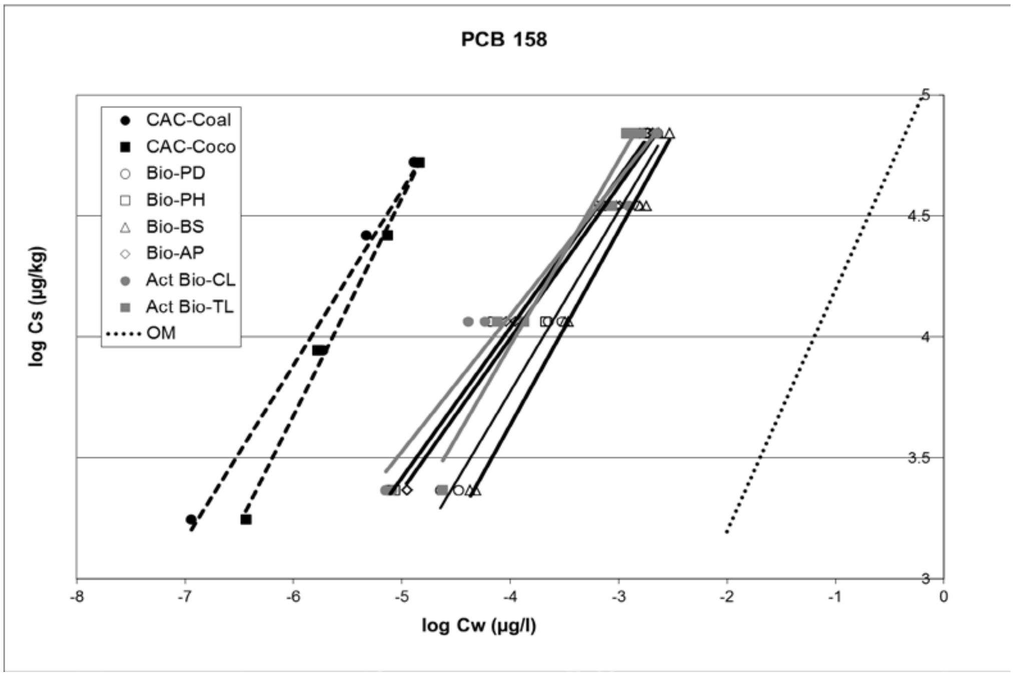

Figure 4. PCB158 isotherms for the readily available carbons. Isotherms are plotted with dashed lines for the activated carbons, with straight grey lines for the activated poultry litter biochars and with straight black lines for the remainder of the biochars. Modeled isotherms for organic matter are plotted with black dotted lines.

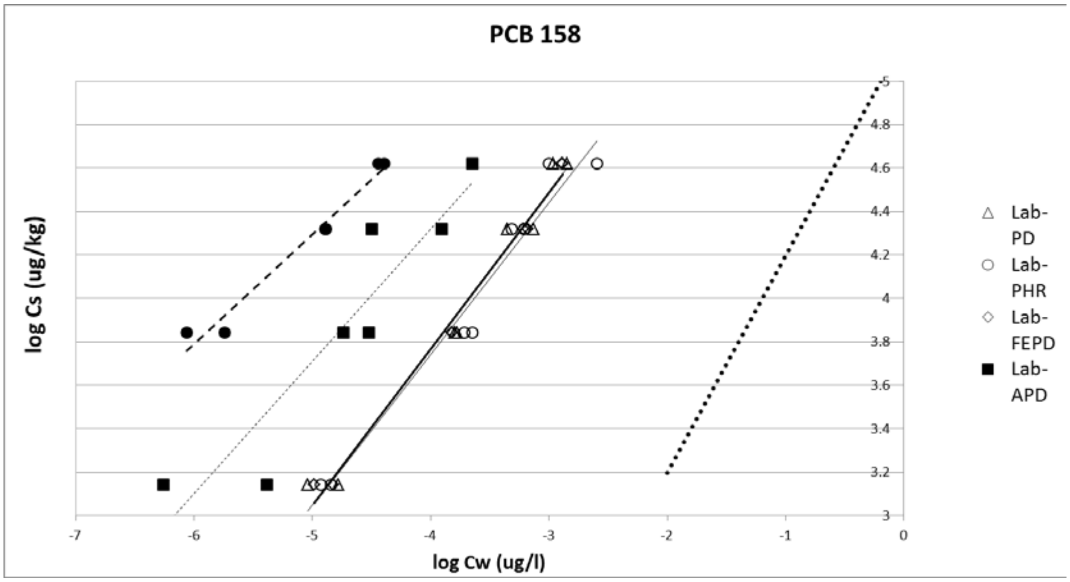

Figure 5. PCB158 isotherms for the laboratory synthesized carbons. Isotherms are plotted with dashed lines for the biochars activated chemically in the laboratory, and with straight black lines for the remainder of the biochars. Modeled isotherms for organic matter are plotted with black dotted lines.

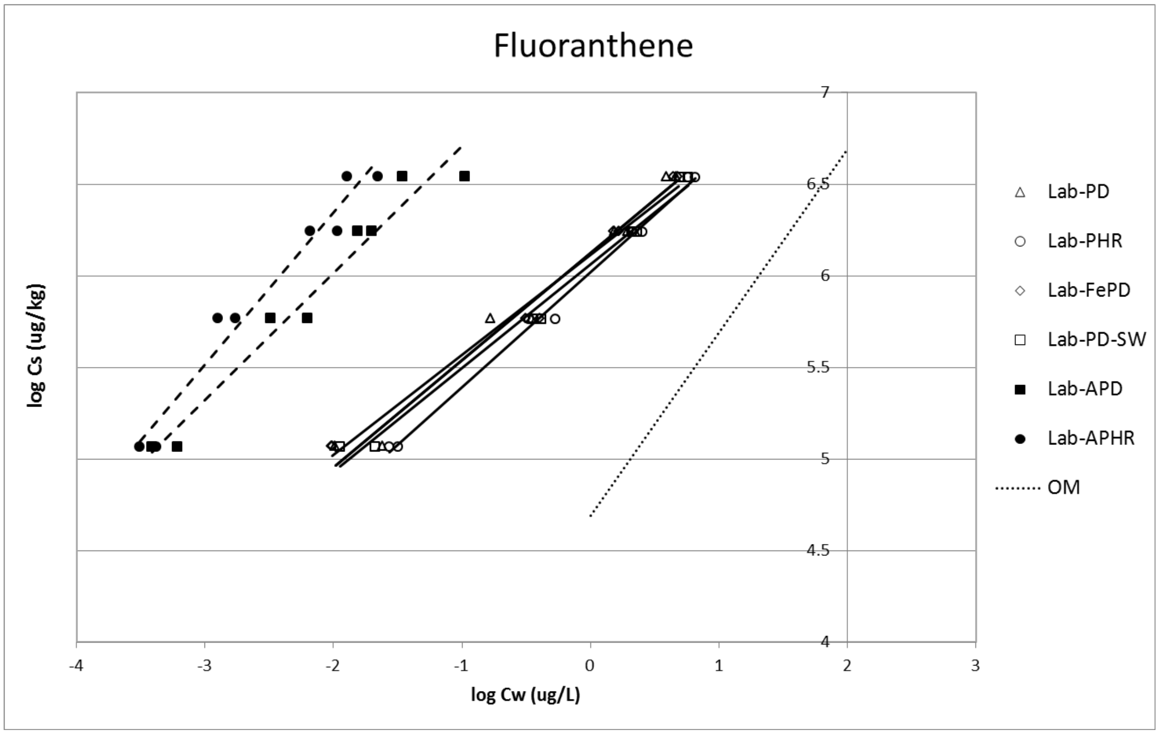

Figure 6. Fluoranthene isotherms for the laboratory synthesized carbons. Isotherms are plotted with dashed lines for the biochars activated chemically in the laboratory, and with straight black lines for the remainder of the biochars. Modeled isotherms for organic matter are plotted with black dotted lines.

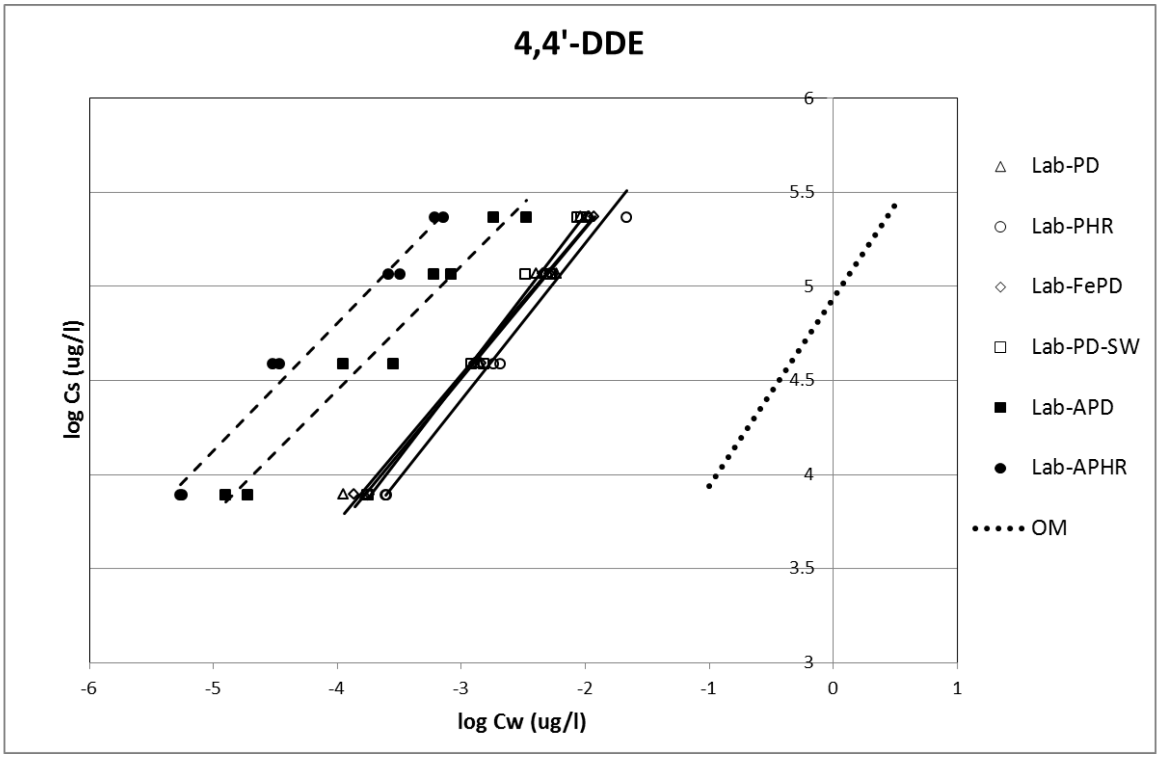

Figure 7. 4,4'-DDE isotherms for the laboratory synthesized carbons. Isotherms are plotted with dashed lines for the biochars activated chemically in the laboratory, and with straight black lines for the remainder of the biochars. Modeled isotherms for organic matter are plotted with black dotted lines.

Isotherms like the ones in the figures above were plotted for individual PCBs, PAHs and DDTs for all the carbons, and their Freundlich isotherms parameters are summarized in Table 3 and 4. A representative PCB congener from a selection of the different PCB homolog groups is presented together with the PAHs and DDTs tested. The fact that the K_f values for the different sorbents was higher for the commercially available activated carbon and the biochars chemically activated in the laboratory, suggests the surface area of the carbon has a major influence on organic contaminant sorption. This increased sorption with increasing carbon surface area has been previously reported for organic compounds (Bornemann et al., 2007; Zhou et al., 2009; Wang et al., 2010). 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, so their pyrolysis and activation process could be optimized further to improve their organic contaminant sorption characteristics. Also, as shown in Table 2, the carbon content of poultry litter biochars is much smaller (27%) compared to commercial activated carbons. The poultry litter likely contains other inorganic constituents that are not very effective sorbents for organic compounds.

Table 3. Freundlich isotherm parameters for the readily available carbons

Contaminant	Kow	Bio-PD		Bio-PH		Bio-BS		Bio-AP		Bio-HW		Act Bio-CL		Act Bio-TL		CAC-Coal		CAC-Coco	
		Kf	n	Kf	n	Kf	n	Kf	n	Kf	n	Kf	n	Kf	n	Kf	n	Kf	n
PCB 8+5	5.02	5.6	0.52	5.78	0.44	5.7	0.49	5.6	0.47	5.4	0.64	5.8	0.53	5.9	0.64	8.4	0.91	7.9	0.78
PCB 18	5.24	5.5	0.65	5.6	0.49	5.7	0.50	5.6	0.59	5.6	0.76	5.7	0.57	5.8	0.69	8.6	1.0	8.1	0.88
PCB 47	5.85	6.8	0.67	6.4	0.53	6.6	0.61	6.6	0.59	5.9	0.77	6.6	0.57	7.1	0.70	8.0	0.82	8.6	0.96
PCB 99	6.39	6.0	0.75	7.1	0.66	7.1	0.68	7.1	0.68	6.3	0.79	6.9	0.61	6.2	0.75	7.7	0.71	8.8	0.94
PCB 158	7.02	6.8	0.75	7.6	0.62	7.9	0.70	6.5	0.63	6.6	0.70	7.3	0.56	7.0	0.76	8.2	0.72	9.1	0.9
PCB 180	7.36	7.3	0.83	7.0	0.65	8.6	0.77	8.3	0.68	7.9	0.79	6.9	0.56	9.0	0.85	9.1	0.82	9.5	0.93
Acenapthene	3.92	5.4	0.47	5.8	0.49	5.1	0.63	5.6	0.43	6.3	0.55	5.9	0.59	5.8	0.69	7.9	0.89		
Phenanthrene	4.46	5.6	0.52	5.9	0.60	5.3	0.70	5.7	0.50	6.3	0.51	6.1	0.61	6.0	0.63	8.3	1.1		
Fluoranthene	4.95	5.9	0.55	6.3	0.64	5.8	0.72	6.1	0.49	7.1	0.57	6.5	0.60	6.4	0.61	10.4	1.1		
4,4'-DDE	6.51	6.7	0.74	6.5	0.58	6.8	0.83	6.6	0.63	6.9	0.83	6.5	0.57	7.0	0.82	8.46	0.69		
4,4'-DDD	6.02	6.2	0.76	6.0	0.55	6.3	0.86	6.1	0.60	6.3	0.81	6.2	0.58	6.4	0.72	8.3	0.73		

Table 4. Freundlich isotherm parameters for the laboratory synthesized carbons

Contaminant	Kow	Lab-PD		Lab-PD-SW		Lab-PHR		Lab-FePD		Lab-APD		Lab-APHR	
		Kf	n	Kf	n	Kf	n	Kf	n	Kf	n	Kf	n
PCB 8+5	5.02	5.5	0.59			5.4	0.63	5.5	0.52	6.6	0.63	6.3	0.49
PCB 18	5.24	5.6	0.71			5.6	0.76	5.6	0.66	6.8	0.74	6.5	0.60
PCB 47	5.85	5.9	0.76			5.9	0.78	5.9	0.74	6.6	0.73	5.9	0.44
PCB 99	6.39	6.4	0.83			6.3	0.80	6.3	0.80	6.8	0.73	6.9	0.68
PCB 158	7.02	6.7	0.72			6.5	0.70	6.6	0.72	6.7	0.61	6.8	0.50
PCB 180	7.36	7.8	0.87			7.6	0.82	7.7	0.85	8.1	0.72	8.5	0.78
Acenapthene	3.92	5.6	0.43	5.9	0.42	5.6	0.52	5.9	0.39	8	0.65	7.1	0.66
Phenanthrene	4.46	5.9	0.5	6.3	0.55	5.8	0.52	5.9	0.44	8.1	0.8	7.2	0.7
Fluoranthene	4.95	6.9	0.59	7.3	0.66	6.9	0.63	6.9	0.54	8.6	0.69	9.2	0.84
4,4'-DDE	6.51	6.9	0.78	7.1	0.86	6.9	0.83	6.9	0.8	7.1	0.67	7.52	0.68
4,4'-DDD	6.02	6.3	0.75	6.4	0.78	6.3	0.81	6.3	0.74	6.8	0.65	7.24	0.68

The non-linearity of the isotherms as indicated by the Freundlich *n* term displayed in Table 3 and 4 gives an indication of how the sorption capacity changes (typically decreases) with increasing aqueous concentration. As Freundlich *n* values get lower than 1 they indicate more sorption non-linearity suggesting the carbon is less sorbing at higher aqueous concentrations. A Freundlich *n* value of 1 indicates linear sorption. To illustrate the difference in n values between carbons more clearly, the n values for the isotherms of PCBs 18 and 158 are graphed in Figures 8 and 9 for the readily available carbons. The fact that the *n* term is generally lower for the biochars than the activated carbons suggests strong sorption sites are more limited in the biochars, and that they are getting saturated at high contaminant concentrations. The Freundlich *n* term for activated carbons is closer to 1 especially for the lower chlorinated PCBs indicating strong sorption affinity even at the high aqueous concentration tested.

Although these sorption experiments were not designed to investigate competition effects, it is likely for the competition for sorption to be much greater in the biochars than in the CACs due to the large differences in surface area between them. This issue of pore blocking and sorption site saturation could limit the effectiveness of biochar as an organic contaminant remediation amendment. The blocking of sorption sites in activated carbons by organic matter (Rhodes et al., 2010), and a reduced efficiency of biochars sorbents due to competition between contaminants (Cao et al., 2009) has been previously reported. These factors are the likely causes for the diminished capability of aged biochar to adsorb organic contaminants (Zhang et al., 2010). This may raise questions on the long term effectiveness of sediment remediation strategies using biochars. However, a recent study where biochars were contacted with soils and artificially aged in the laboratory found they were still effective at reducing pyrene pore water concentrations after ageing (Hale et al., 2011). The fact that the unactivated biochars sorb all the organic contaminants more strongly than natural organic matter (OM) by at least 1-2 orders of magnitude (Figures 2-7) suggests that they can increase sediment Koc considerably and hence reduce contaminant porewater concentrations after amendment. Also due to the benefits biochar offers in terms of lower cost and carbon sequestration re-applying fresh biochar could be a feasible solution to this lower capacity problem.

Taking a closer look at the Freundlich parameters in Table 3 it is apparent that the difference in sorption between the high surface area carbons and the biochars was larger for the less chlorinated PCBs (K_f values approximately 3 orders of magnitude apart) than for the more heavily chlorinated ones (K_f values approximately 2 orders of magnitude apart). The decreased sorption for the higher molecular weight PCBs have been attributed to the slower kinetics of internal mass transfer for these heavier compounds (Werner et al., 2006). In short-term experiments, activated carbons have been shown to be very effective for reducing porewater concentrations of lower chlorinated PCBs with longer time required to show similar effectiveness for the higher chlorinated PCBs (Zimmerman et al., 2004; Sun and Ghosh, 2008). Beckingham and Ghosh (2011) showed that in a pilot demonstration of AC amendment to sediment, reduction in porewater PCBs were lower for the higher chlorinated PCBs after 1 year.

However, three years after treatment, the reductions in porewater PCBs were the same for all homolog levels.

To investigate if the salinity had an effect on the sorption capacity of the biochars the laboratory, sorption isotherms were carried out in 10 ppt salt water using the laboratory synthesized pine dust biochar (Lab-PD-SW). K_f values were generally not affected or were slightly increased in saline conditions (Table 3). Similarly impregnating the carbon with iron oxides (Lab-FePD) had no apparent effect on the organic contaminant sorption properties of its analogous unimpregnated biochar (Lab-PD) (Table 3).

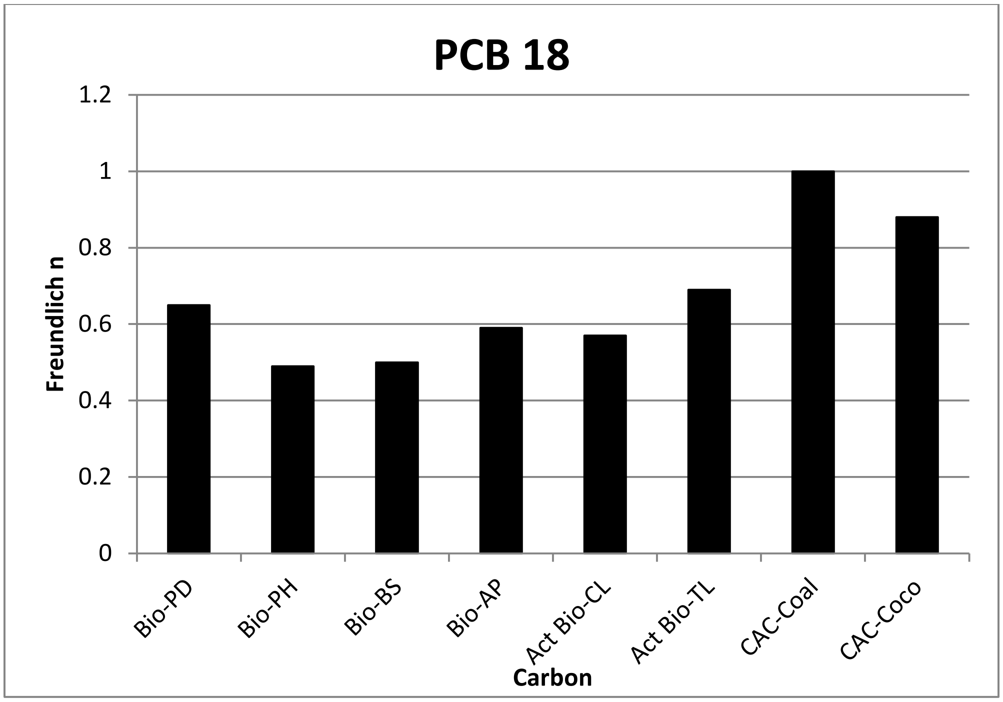

Figure 8. Freundlich *n* parameters for the readily available carbons in the PCB 18 isotherms

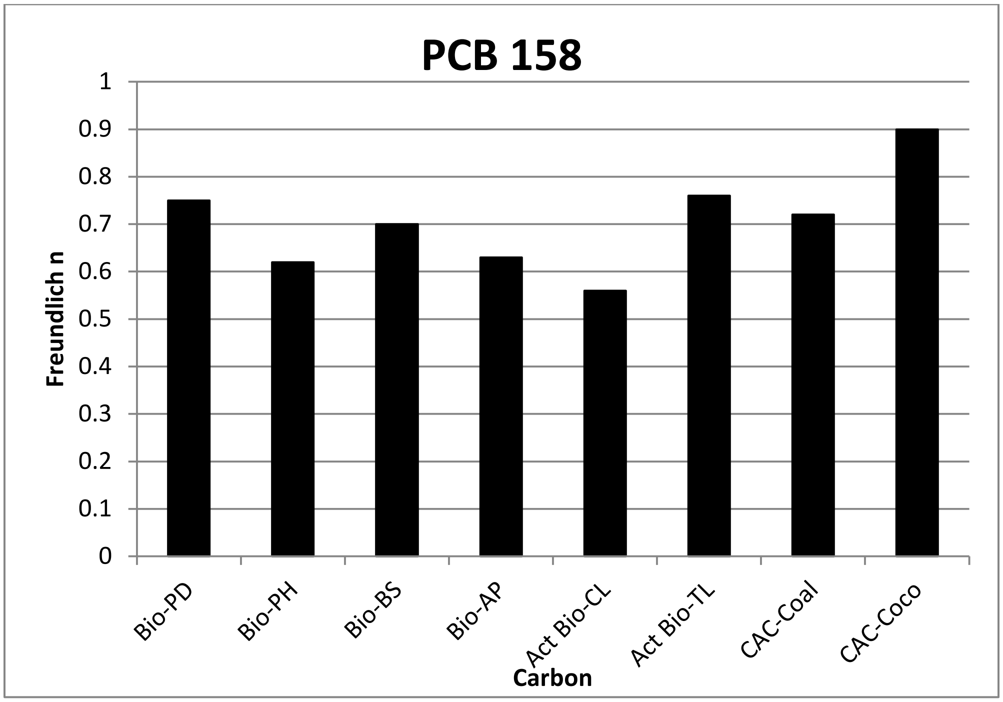

Figure 9. Freundlich *n* parameters for the readily available carbons in the PCB 158 isotherms.

Sediment phase testing

The results obtained from the isotherms studies translated well when testing the carbons in the sediment phase. Figures 10 and 11 show how the commercially activated carbons and the chemically activated biochars produced in the laboratory were able to reduce PCB pore water concentrations further than the other carbons for a selected range of PCB congeners. In terms of total PCBs, the commercially activated carbons and the chemically activated biochars produced in the laboratory, reduced aqueous PCBs by >99% relative to the control sediment. The other carbons on the other hand only reduced between 18-54% to the total PCB in the porewater 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 have been previously reported after applying activated carbons in soils and sediments (Millward et al., 2005; Brändli et al., 2008; Cho et al., 2009; Fagervold et al., 2010). Although the effect of biochars on organic contaminant bioavailability has not been studied so extensively, the more modest reductions by biochars in this study are also in line with previous studies reporting >40% reduction in the rapidly desorbing PAH fraction (Beesley et al., 2010), >30% reduction in PAH bioaccumulation in earthworms (Gomez-Eyles et al., 2011) and >40% reduction in organic pesticide degradation (Yu et al., 2009) after biochar amendment. Recent work with dioxin contaminated soils showed that carbons with finer particle sizes or more macropores showed higher reduction efficiencies (Chai et al., 2012). In their study, powdered regenerated AC and powdered coconut AC demonstrated to be the most effective and the two biochars performed less effectively but reasonably well especially in the powdered form.

The results of this study show that biochars are able to reduce organic contaminant bioavailability to some degree, but they are not as effective in doing so as activated carbons. However, it is possible to synthesis biochars with high enough surface areas for them to be able to reduce organic contaminant bioavailability to the same degree or higher than regular coal derived activated carbons. Studies have shown that increasing the pyrolysis temperature at which biochars are produced can increase biochar surface area dramatically (Chen et al., 2008). A number of studies have shown that increasing biochar surface area can increase their ability to adsorb organic contaminants (Yu et al., 2006; Zhou et al., 2009; Kasozi et al., 2010; Wang et al., 2010), optimizing the pyrolysis and activation processes would increase the potential of biochars for the remediation of sediments impacted with organic contaminants.

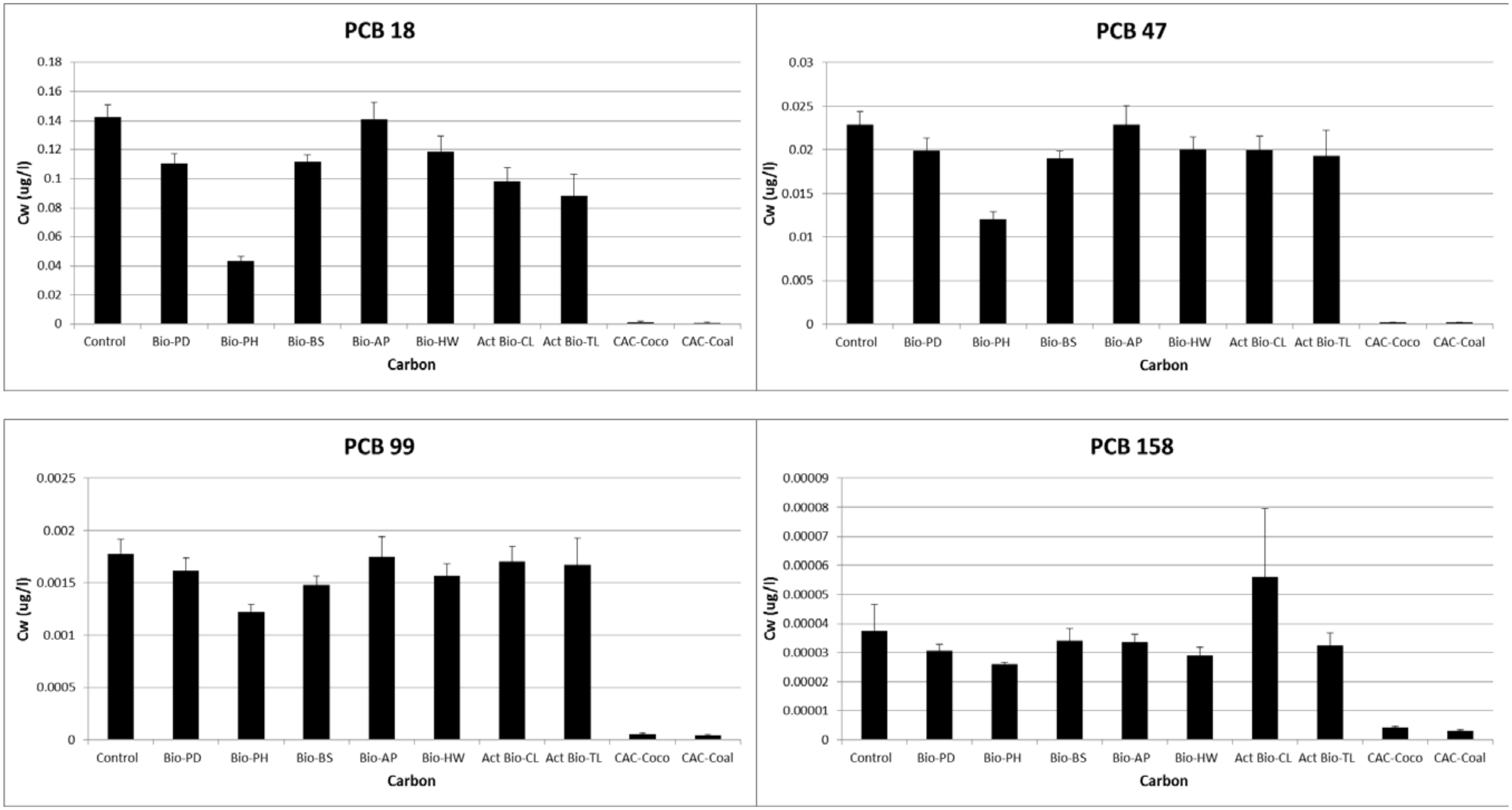

Figure 10. Porewater PCB concentrations in sediments amended with the readily available carbons. Error bars represent the standard error (n=3).

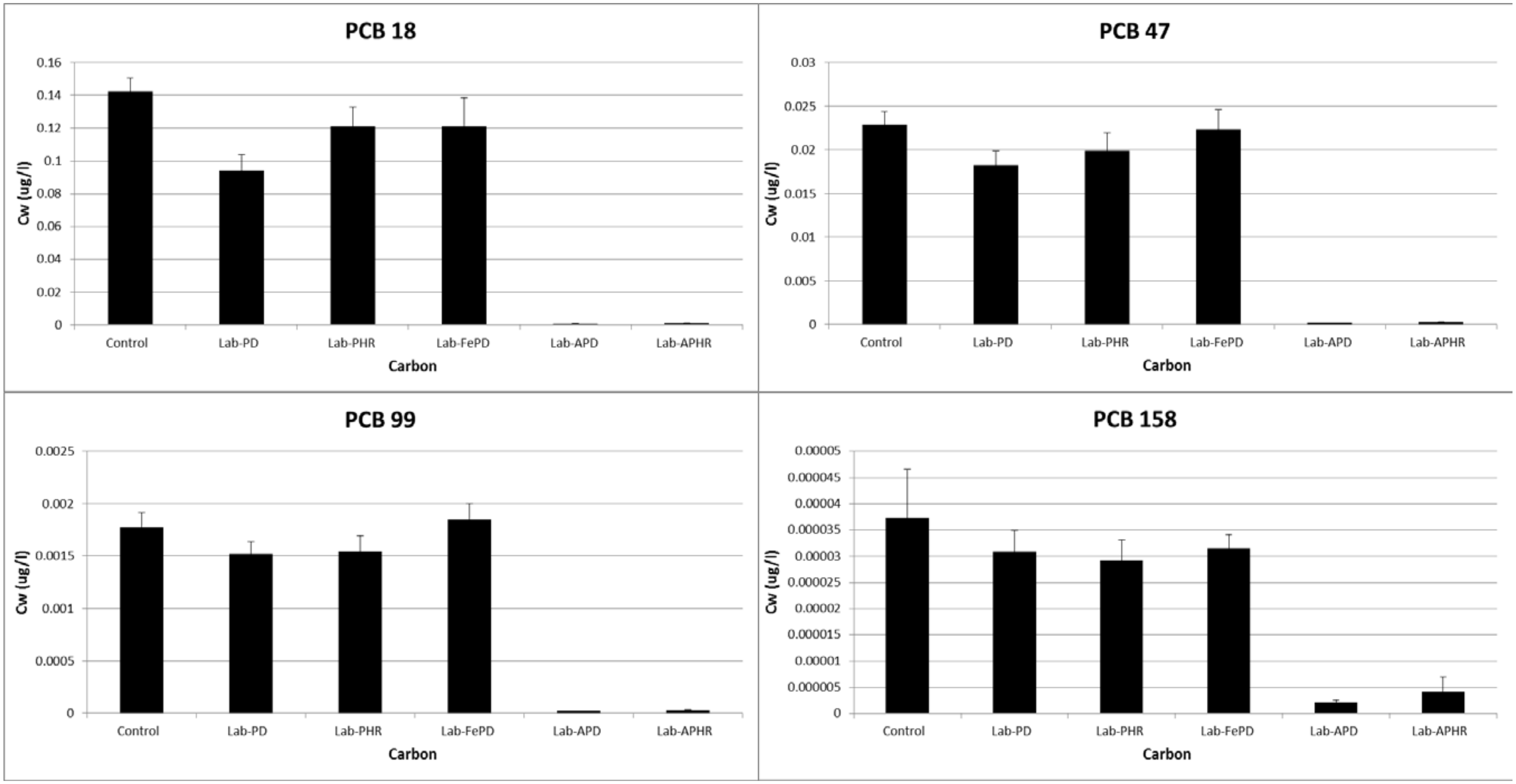

Figure 11. Porewater PCB concentrations in sediments amended with the laboratory synthesized carbons. Error bars represent the standard error (n=3).

PCB mass transfer kinetics

Figure 12 shows the reductions in PCB concentrations in the sediment phase after being amended over one month exposure with the iron amended granulated biochar.

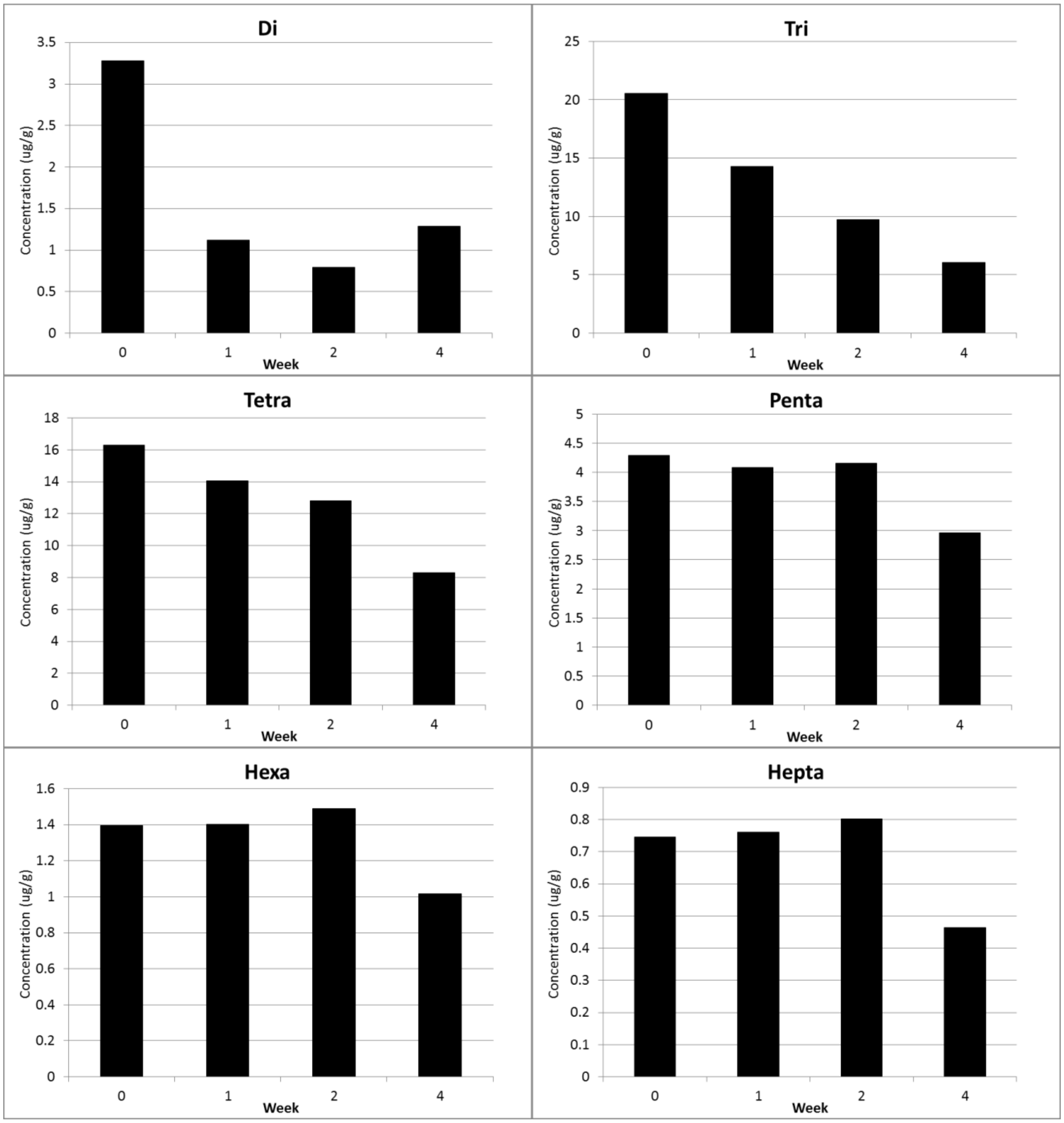

Figure 12. Reductions in PCB homolog concentrations in sediment showing contaminant mass transfer out of the sediment phase.

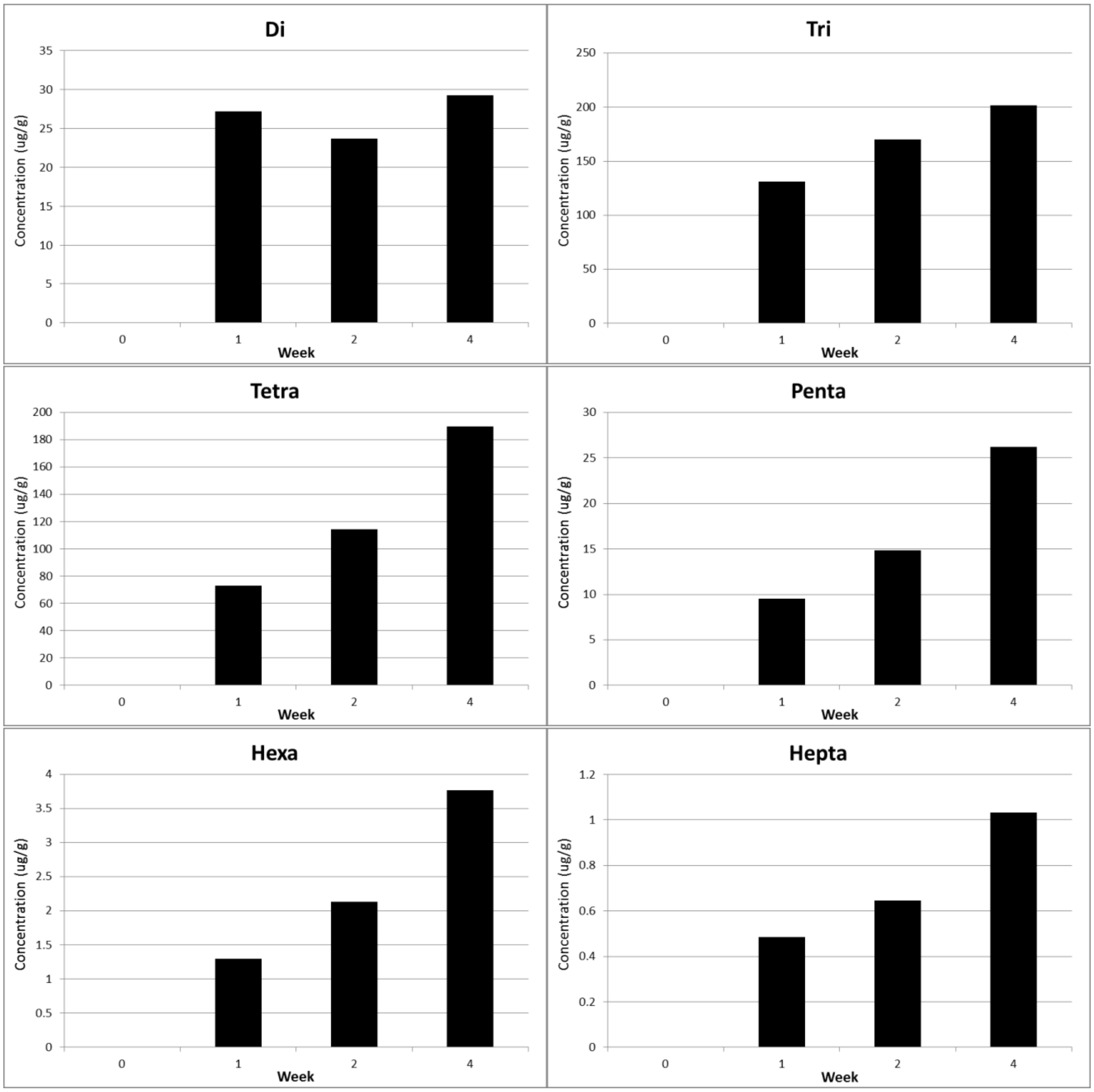

Figure 13. Mass transfer of PCBs into the carbon phase.

These reductions in PCB concentration in the sediment were accompanied with increases in the PCB concentration in the carbon with time (Figure 13).

These findings are in line with the previously mentioned short-term experiments using activated carbons that found quick reductions in porewater concentrations of lower chlorinated PCBs with a longer time required to show similar reductions for the higher chlorinated PCBs (Zimmerman et al., 2004; Sun and Ghosh, 2008). The mass transfer kinetics are quicker for the more water soluble less chlorinated PCBs, as they will more readily leave the sediment to enter the solution and become available for sorption by the carbons. Apart from being less water soluble, the more heavily chlorinated PCBs are likely to be more recalcitrant and more tightly bound up within the sediment, and this could also contribute towards the slower mass transfer of these more chlorinated compounds.

Dechlorination studies

Although the oxidation of the ZVI impregnated carbon surface was visually apparent we were unable to detect any TCE in the aqueous PCE solution after 1 month. There was also visual evidence of oxidation in the surface of the iron filings, and although it was below quantitation limits, there was evidence of TCE formation in the chromatograms. The intermediate TCE may have also formed in the ZVI impregnated carbon treatment but it could be sorbed to the carbon reducing its concentration in the aqueous phase. It could have also been dechlorinated further compromising its detection using our current liquid-phase injection GC-ECD method. Other workers have reported PCB dechlorination using a ZVI impregnated activated carbon containing palladium (Choi et al., 2008; Choi et al., 2009), and a longer study is therefore needed to optimize the production of a dechlorinating zero valent iron impregnated biochar.

Mercury and methylmercury sorption

Plots for the Hg (Figures 14 and 15) and MeHg (Figures 17 and 18) isotherms have been separated into readily available and laboratory synthesized carbons for clarity, as was done for the organic contaminants isotherms. The isotherms were fitted with a linear model and the resulting K_d values are summarized in Table X below.

Table 5. K_ds for Hg and MeHg sorption isotherms

Carbon	Hg K_d	MeHg K_d	Hg K_d : MeHg K_d
Bio-PH	7.83E+05	2.19E+05	3.58
Bio-BS	2.69E+04	9.61E+04	0.28
Bio-AP	2.36E+05	2.17E+05	1.09
Bio-HW	1.11E+05	2.72E+05	0.41
Act Bio-CL	8.30E+06	2.25E+05	36.83
CAC-Coco	3.64E+06	2.64E+05	13.74
CAC-Coal	3.55E+06	7.85E+04	45.22
CAC-Darco	1.59E+07	2.56E+05	62.3
CAC-RAC	1.92E+07	3.53E+05	54.4
Lab-PD	6.40E+04	2.62E+05	0.24
Lab-PHR	1.96E+05	1.30E+05	1.51
Lab-FePD	6.09E+04	3.24E+05	0.19
Lab-APD	4.16E+03	1.44E+04	0.29
Lab-APHR	5.92E+03	7.51E+03	0.79

The pH in these isotherms was not buffered, but it was adjusted to near neutral at the beginning of the experiments. When the isotherms were taken down the pH was re-measured before Hg and MeHg analysis. pH values at the end of the experiment were consistently between 5-7 for all carbons except for the peanut hull biochar (BioPH, pH 7-8) and for the activated chicken litter biochar (Act Bio-CL, pH 9-10).

The Hg isotherms show that the commercially available activated carbons tested were the most effective at removing Hg from solution at the lowest concentrations. This could occur due to the presence of high energy sorption sites in the activated carbon surface for the Hg to sorb to. However the trends in the Hg isotherm plots suggest an experimental artifact could have contributed to the performance of the readily available biochars to be underestimated at the low Hg concentrations. Some of these carbons (specifically Bio-PH, Bio-BS, Bio-AP and Act Bio-CL) were sieved to a different particle size (<250µm) than the other carbons (44µm - 177µm), and therefore contained some finer particles that may have not been removed during the filtration process at the end of the isotherm study. Even though the amount of particles getting through the filter is believed to be very small they could still have an impact on the Hg concentrations measured in the solution after filtration due to their relatively higher Hg concentration. This artifact only has a significant effect at the lower Hg concentrations when lower levels of Hg are being measured.

Despite this artifact, the trends in the isotherm plots suggest that the number of sorption sites in the activated carbons may be more limited than in the biochars, as the difference between the carbons gets smaller with increasing Hg concentrations (Figure 14). This could be problem when applying activated carbons in the field as their sorption sites could become saturated by other competing species in the sediment porewater.

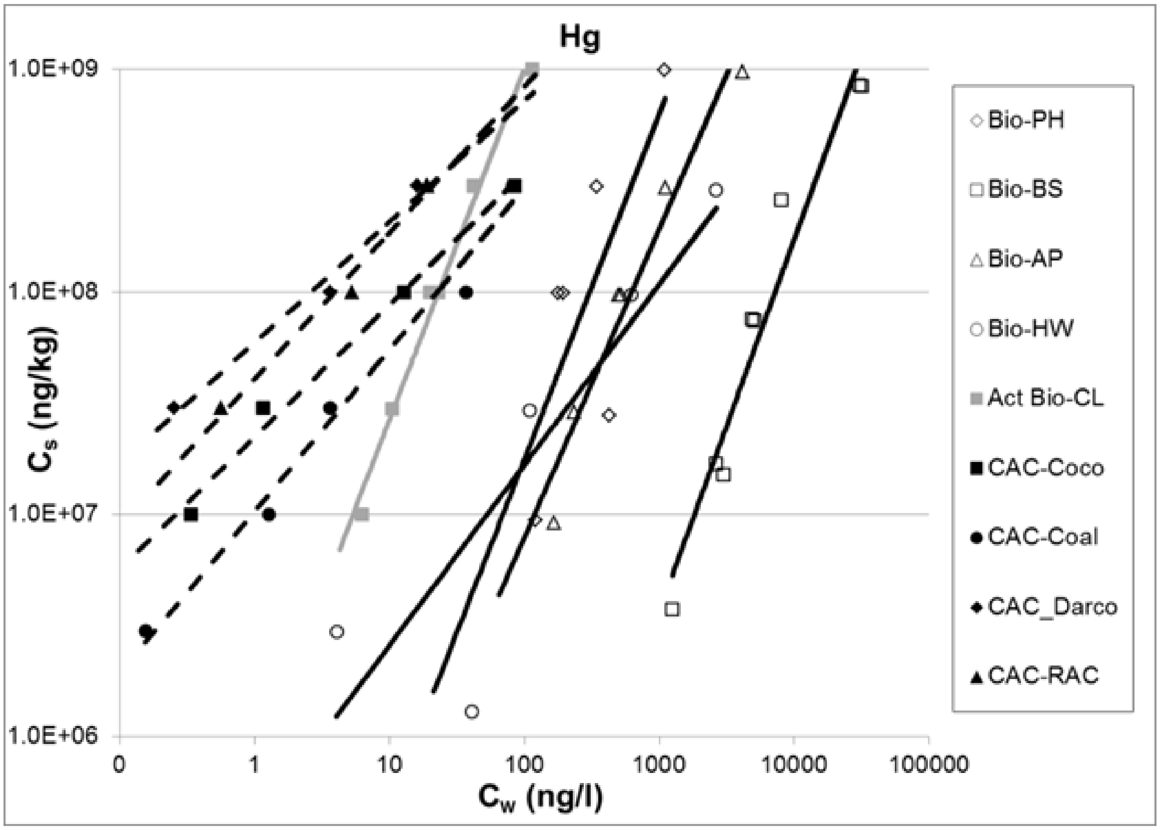

Figure 14. Mercury sorption isotherms for commercially available carbons. Isotherms are plotted with dashed lines for the activated carbons, with a straight grey line for the activated chicken litter biochar and with straight black lines for the remainder of the biochars.

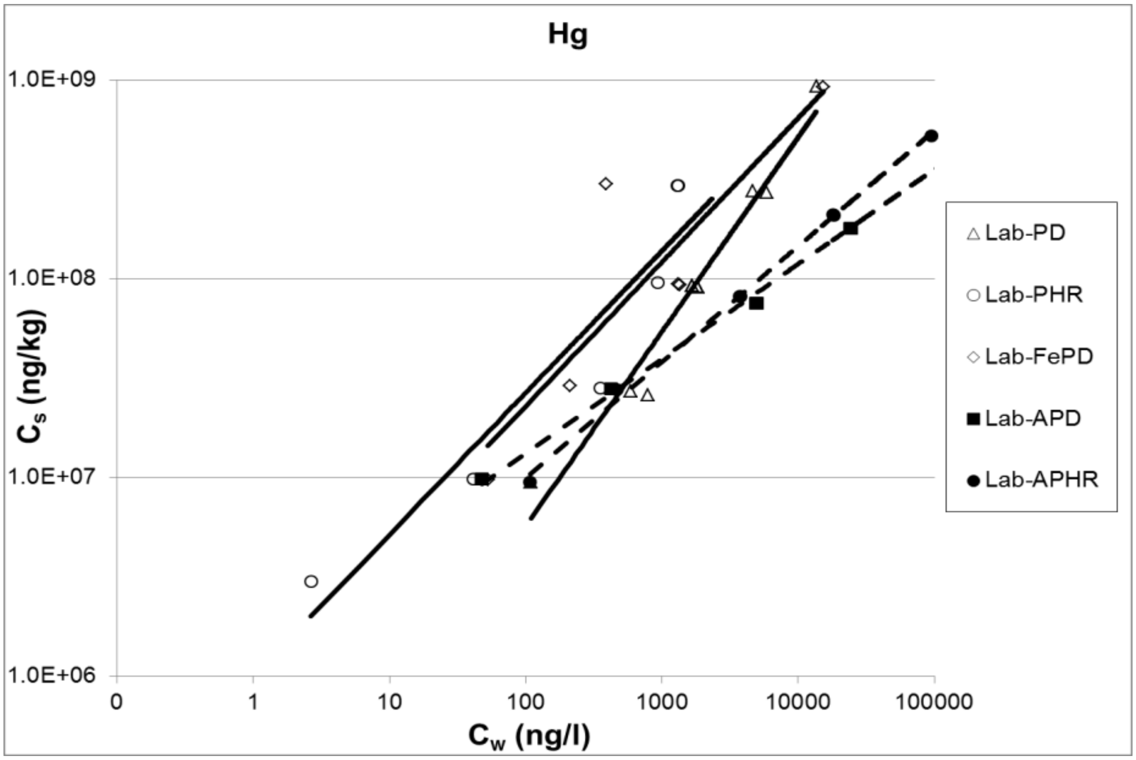

Figure 15. Mercury sorption isotherms for laboratory synthesized carbons. Isotherms are plotted with dashed lines for the biochars activated chemically in the laboratory, and with straight black lines for the remainder of the biochars.

This lower capacity of the ACs to remove high concentrations of Hg from solution was also apparent in the high Hg concentration pH edge sorption experiment Figure 16. Here the poultry litter biochar consistently removed >99% of the Hg from solution over the whole pH range. The other biochars also consistently removed more Hg than the ACs from solution throughout the whole pH range. Carbons were generally less effective at higher and lower pHs except the poultry litter ones.

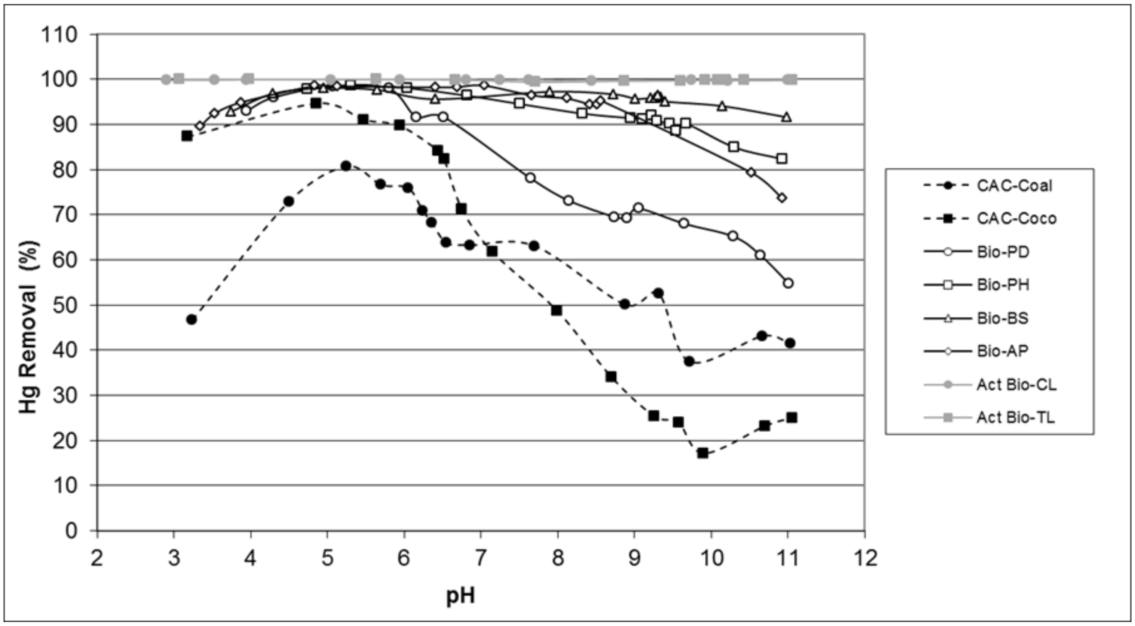

Figure 16. Mercury removal by the readily available carbons at different pHs. Activated carbons are plotted with dashed lines, poultry litter activated biochars with grey lines and the remainder of the biochars are plotted with solid black lines.

Despite the experimental artifact potentially underestimating the sorption of the chicken litter derived biochar, it still was one of the most effective carbons at removing Hg from solution in the Hg isotherms studies (K_d = 8.30E+06) and they were consistently the most effective carbon at removing high Hg concentrations from solution in the pH edge study. Apart from having relatively high levels of sulfur, broiler litter biochars have been reported to have relatively higher phosphorus contents (3.7%) than chars produced from other source materials like coal, coconut shell or wood (<0.2%) (Lima et al., 2009). It has been postulated that the presence of phosphorus, primarily in the form of phosphate, can create a negative charge on the carbon that can ionically bind positively charge metal ions like Hg^{2+} (Lima and Marshall, 2007; Lima et al., 2009). Cao et al., (2009) found that low temperature cow manure derived biochars were more effective at immobilizing Pb^{2+} than a CAC. The authors confirmed by X-ray diffraction that the main mechanism behind this increased Pb^{2+} immobilization by the biochars was the formation of a Pb-phosphate precipitate. It is therefore likely for the presence of phosphate groups on the poultry litter char surface to be at least in part responsible for their increased Hg^{2+} removal relative to the other carbons. It is important to note that their steam activation may have also improved their surface area relative to the other biochars which may have also been a contributing factor to this increased sorption. Also the fact that they increased the pH concentration to a much high level than the other biochars should not be overlooked as this could have also had an impact on the amount of Hg removal from solution.

Although the exact mechanism by which this poultry litter char is removing Hg from solution cannot be identified in the current study, these results are particularly encouraging with respect to the use of these kinds of chars for the remediation of Hg impacted sediments. Further studies to elucidate this sorption mechanism would enable the identification of the necessary characteristics needed in a carbon to improve its Hg binding properties, which could in turn provide the necessary information for the synthesis of biochars especially adapted for Hg sorption. However, it will also be important to quantify the amount of phosphate that could be leached from these biochars if released to the sediment environment as this could create an environmental impact of its own.

The chemical activation of the laboratory produced biochar was counterproductive in terms of Hg sorption (Figure 15) and it was these chemically activated biochars that had the weakest Hg binding properties. Despite their large surface areas they did not appear to have the higher energy sorption sites that seemed to be present in the commercially available steam activated carbons favoring Hg sorption at low concentration. It therefore seems like steam activation is a more favorable method of activation when considering Hg sorption. One issue we found with phosphoric acid chemical activation is the challenge of washing the acid off after activation and the resulting low pH of the carbon that can impact sorption of Hg. Activation with steam could also potentially produce more oxygen containing functional groups in the carbon surface than a chemical activation would. As occurred with the steam activated carbons, the performance of these chemically activated biochars also dropped relative to that of the other biochars with increasing Hg concentrations. This again suggests their sorption potential could be reduced substantially further in the field due to competition effects. ACs have been shown to have a relatively low affinity to other heavy metal cations like Cu^{2+} or Pb^{2+} despite their high surface areas (Cao et al., 2009; Jaramillo et al., 2009). The governing role of surface functional groups over that of surface area has been reported when applying biochars to soil to sequester heavy metals (Uchimiya et al., 2011). ACs are usually produced at higher temperatures than the biochars used in this study, which together with their activation process contributes to their increased surface area relative to the biochars. However, using Fourier transform infrared spectra Uchmiya et al, (2011) showed that as pyrolysis temperature are increased above 350° C the presence of surface carboxyl and other functional groups that could enhance Hg^{2+} sorption is reduced. In increasing the potential of the carbon to sorb organic contaminants the ability of the carbon to sorb inorganic contaminants could therefore be compromised (Beesley et al., 2011). A better understanding of how biochar manufacturing parameters (e.g source material, pyrolysis temperature or activation process) impact the sorption of inorganic contaminants like Hg could enable the synthesis of a carbon suited for the remediation of sediments impacted with both organic and inorganic contaminants.

Despite the success of impregnating activated carbons with iron oxides for the treatment of waters contaminated with inorganic contaminants (Reed, 2000; Vaughan and Reed, 2005), the impregnation of iron oxides onto the biochar in this study has a negligible effect on the sorption capacity of the carbon for mercury (Figure 15). In another study Reed et al. (2000) found that iron impregnated ACs were substantially more effective at removing arsenic from solution than virgin activated carbon, however they were only slightly more effective than the virgin AC at removing Pb(II) and Hg(II) at high aqueous concentrations.

Differences in sorption capacity for MeHg were not as large between carbons relative to Hg (Figures 17 and 18). The commercial activated carbons (coconut, reactivated carbon, and lignite based Darco) performed quite well for MeHg adsorption. However, the chemically activated carbons prepared in the laboratory were not as effective in removing MeHg from solution, again suggesting this form of activation may not be the most appropriate when considering carbons for the remediation of MeHg impacted sediments. Interestingly the steam activated commercial 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 (see Kd Hg Kd : MeHg Kd ratio in Table 5.) This suggests Hg and MeHg could have different sorption mechanisms, and that activation using steam may contribute to an enhanced sorption of Hg relative to MeHg. Further characterization of the sorption of Hg and MeHg to the carbon surface is needed to inform about what these different sorption mechanisms could be.

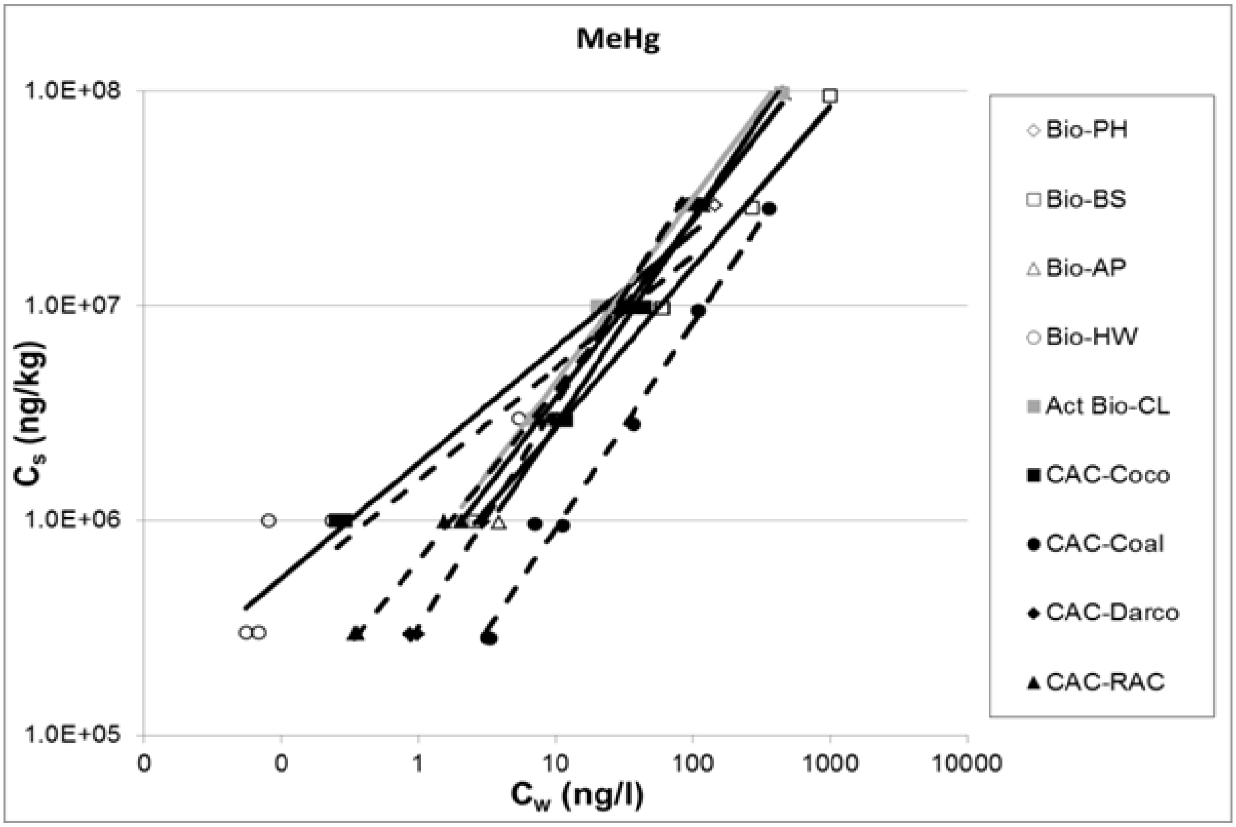

Figure 17. Methyl mercury sorption isotherms for commercially available carbons. Isotherms are plotted with dashed lines for the activated carbons, with a straight grey line for the activated chicken litter biochar and with straight black lines for the remainder of the biochars.

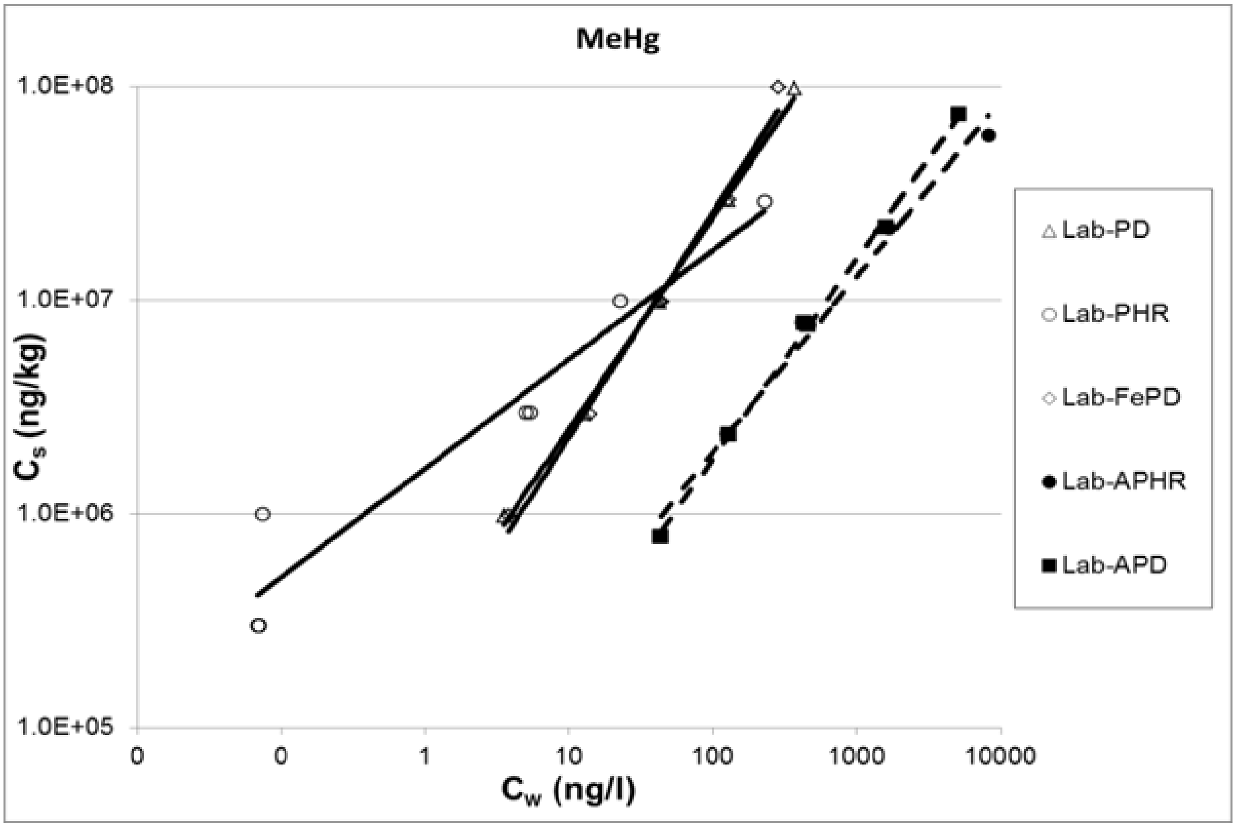

Figure 18. Methyl mercury sorption isotherms for laboratory synthesized carbons. Isotherms are plotted with dashed lines for the biochars activated chemically in the laboratory, and with straight black lines for the remainder of the biochars.

Carbon structural and settling characteristics

The structural properties of a selection of carbons are displayed in Table 6.

Table 6. Structural properties of the carbons

Carbon	Skelatal density (g/cm^3)	Avg Bulk Density (g/cm^3)
Bio-HW	1.29	0.638
Bio-PH	1.28	0.598
Bio-AP	1.23	0.653
Act Bio-CL	1.97	0.920
CAC-Coal	1.61	0.640
Lab-HW-ZVI	1.43	0.807

The unactivated biochars have a skeletal density between 1.2-1.3 g/cm^3. Thus all biochars after becoming wet should settle in water. However, the density of the biochars is smaller compared to the activated carbons tested. The raw material used for making the carbons has a significant impact on the final density and hardness of the product. For this reason, most commercially available activated carbons are made from either coal or coconut shell which is a very dense form of biomass. The bulk density of all carbons tested was less than 1 g/cm^3 due to the high internal porosity of the carbons and also inter-particle porosity of the packed materials. These inter-particle and intra-particle pores are filled with water upon contact allowing the carbon to settle in water. Among the carbons tested, the chicken litter activated carbon and the iron amended activated carbon had the highest bulk density.

These results shown in Table 6 confirm that unactivated biochars are less dense than activated carbons. Biochar stability in the sediment environment may therefore be compromised in high energy systems. However, impregnating hardwood biochar with iron (Lab-HW-ZVI) increased the density reducing the differences relative to activated carbons in terms of skeletal density and actually making them denser than commercially available activated carbons (CAC-Coal) in terms of bulk density.

This increase in density by iron impregnation was also tested using carbon settling tests. Figures 19 and 20 show how the biochar settles at considerably lower rates than the activated carbons in both fresh and salt water, but after the biochar is impregnated with iron its settling rates are similar to those of the AC. These results suggest that impregnating biochars with iron could be a feasible way of improving their stability in sediment environments.

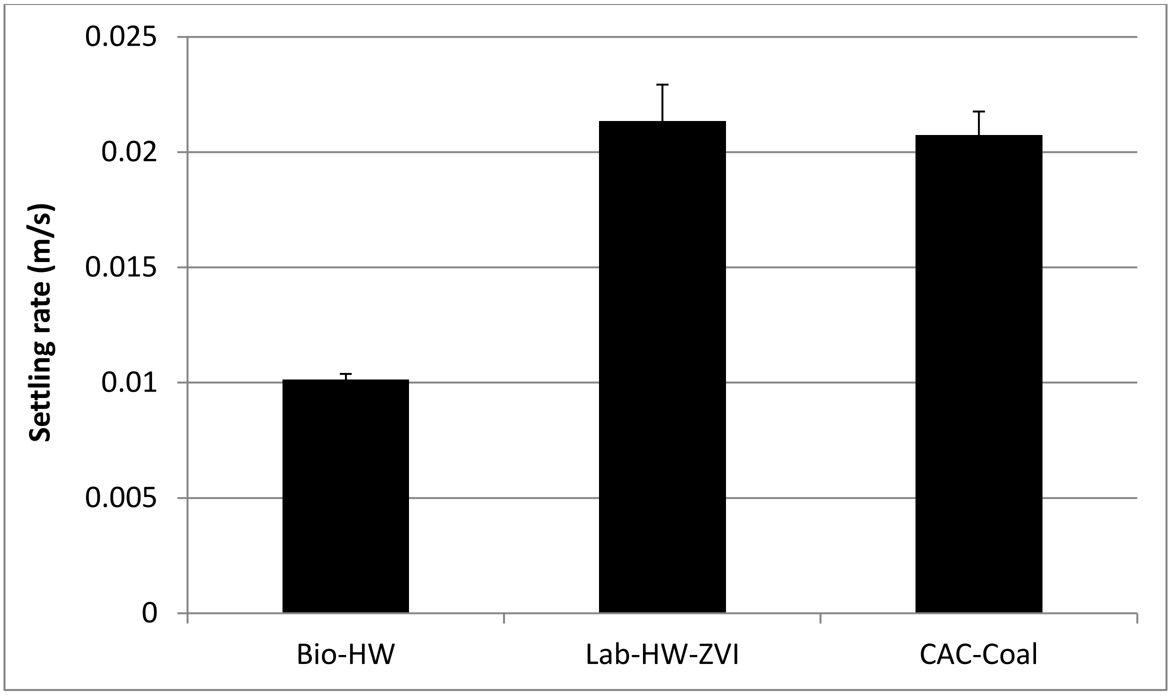

Figure 19. Carbon settling rates in freshwater. Error bars represent the standard error (n=5).

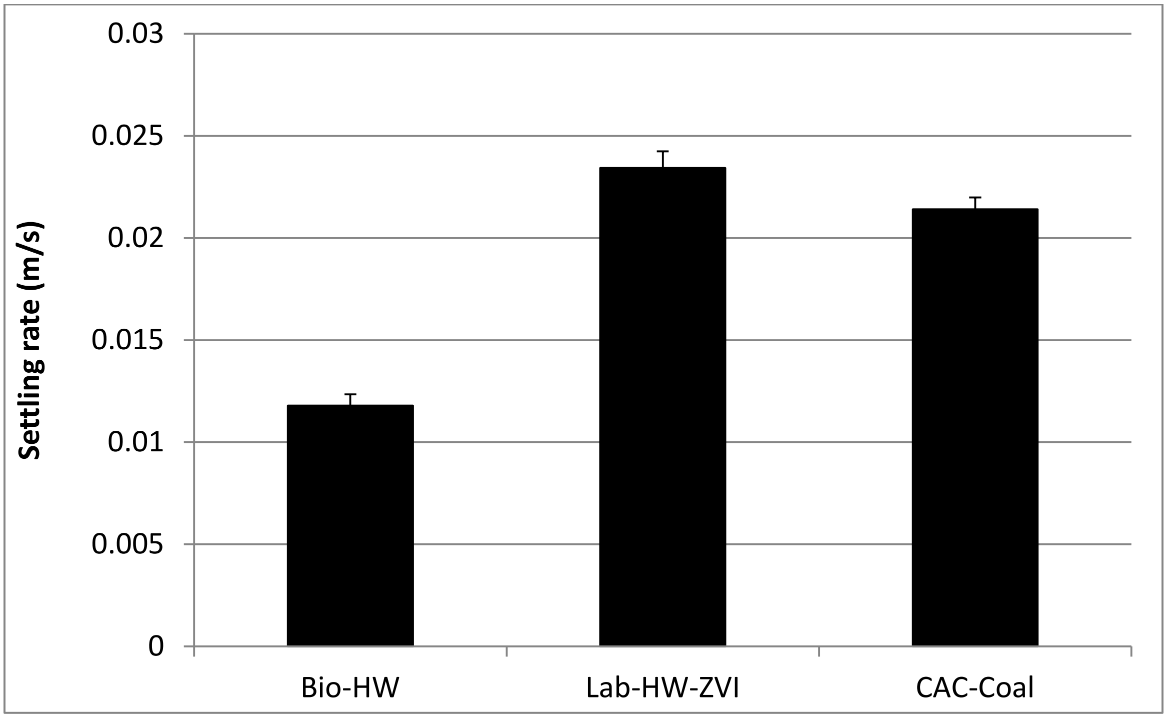

Figure 20. Carbon settling rates in saltwater (10ppt). Error bars represent the standard error (n=5).

Conclusion and Implications for Future Research

Conclusions and Implications

Biochars were able to sorb organic contaminants, Hg, and MeHg, making them attractive alternatives to ACs in sites contaminated with both organic and inorganic contaminants. However, due to their lower surface area, unactivated biochars have a lower affinity for organic contaminants than ACs. The results of this study suggest that waste biomass products could be used for the in-situ remediation of sediments impacted with organic contaminants, but including an activation step in their manufacture is needed to enable a reduction in porewater concentrations to the level close to what is achieved using commercially available ACs. To our knowledge this study is the first comprehensive assessment of sorption isotherms at low environmentally relevant concentrations of PCBs, PAHs, DDx, Hg, and MeHg for a large range of biochars and activated carbons.

Commercial steam activated carbons showed strong sorption of Hg and MeHg from solution at environmentally relevant low concentrations in the range of tens of ng/L. Laboratory activation of two biochars using phosphoric acid treatment was not successful in enhancing the sorption characteristics for Hg and MeHg. It was in fact the biochars (especially poultry litter activated carbon) that was able to remove more Hg from solution than any other carbons at high Hg concentrations.

The ability of the poultry litter carbons was particularly encouraging with respect to Hg sorption. We hypothesize this could be due to their high phosphate content. Identifying the exact mechanism by which Hg binds to the carbons by X-ray diffraction would enable the identification of the desirable carbon properties to maximize Hg sorption, enabling the production of carbons with optimized Hg binding properties. The results of the Hg isotherms and pH edge sorption studies suggest it is challenging to find a carbon with both a high surface area, and therefore high organic contaminant sorption potential, and a large capacity for Hg sorption. However, improving our understanding of the mechanisms by which Hg sorbs to carbon could enable the synthesis of carbons that combine optimized organic and inorganic contaminant biding properties. The production of these carbons will therefore require a detailed investigation of how the activation and pyrolysis processes can be adjusted to maximize carbon surface area without compromising the specific surface functionality necessary for inorganic contaminant sorption. Alternatively, a combination of biochars could be used at the same time. This could include an activated biochar derived from waste biomass (e.g Phragmites activated biochar) for organic contaminant sorption and a poultry litter biochar for Hg sorption.

If it is indeed the high phosphate content in the biochars that enables this enhanced sorption, it will be important to understand the stability of this phosphate within the biochar and the risk associated with its deployment in the field in terms of phosphate nutrient contamination.

The use of iron to impregnate the carbons was effective in improving their density and settling characteristics but had limited success in improving the sorption capacity of the carbons to Hg and MeHg or in enabling the dechlorination of chlorinated organic compounds. The density of the unactivated biochars was lower than that of the activated carbons before impregnation, so their amendment in high energy systems could be problematic unless their settling characteristics are improved by techniques likes the one described in this study. Other workers have been successful in dechlorinating PCBs using ZVI amended activated carbons (Choi et al., 2008; Choi et al., 2009), so longer term focused experiments are needed to optimize the production of ZVI impregnated biochars that are able to enhance PCB dechlorination as well as improving their density and settling characteristics.

Leveraged funding and technology transition.

<u>1. Low level sorption isotherm studies for MeHg.</u> Low-level (1- 100 ng/L) sorption isotherm studies with MeHg was not planned as a part of the proposed SEED project but was made possible through additional leveraged support from DuPont and the Dow Chemical Company. This allowed collaboration with Dr. Cindy Gilmour at the Smithsonian Environmental Research Center and further exploration of MeHg sorption characteristics of the biochars. The high cost of low level MeHg analysis would not have allowed us to perform these isotherm studies within the scope of the SEED project.

<u>2. Feasibility of using biochars for dioxin and furan impacted soils.</u> Sorption of dioxins and furans on biochars was not planned as a part of the proposed SEED project primarily due to the high cost of analysis of these chemicals at environmentally relevant low concentrations. Collaboration with Dow Chemical Company and internal funding from Dow allowed the comparison of commercial activated carbons (coal, lignite, coconut shell based, and regenerated) and biochars (pine and corn stover based) for the sorption of dioxins and furans using test methods similar to the ones adopted in this study. Results of these laboratory studies with dioxins and furans were recently published (Chai et al. 2012). A pilot study has been initiated at Dow Chemical facilities to evaluate the effectiveness of selected activated carbons biochar for the reduction of bioavailability of dioxins and furans in floodplain soils.

Future research

This SEED project explored a range of biochars and activated/amended biochars for the potential use in sediment amendment for reducing the bioavailability of PCBs, PAHs, DDTx, Hg, and MeHg. Based on the results from this study, the following future research areas are proposed:

1. Further exploration of the use of native phragmites activated biochar for the treatment of marshes impacted with organics.

   - Investigate pilot-scale production of phragmites activated biochar maximizing contaminant sorption properties
   - Investigate biomass/unit area in a phragmites marsh and evaluate carbon sequestration potential

2. Further exploration of the mercury sorption of poultry litter activated biochar.

   - Investigate mechanism of Hg adsorption in poultry litter activated biochar
   - Collaborate with USDA and a carbon manufacturer (Calgon pilot facilities) to test feasibility and scale up production
   - Explore the extent of and ways to reduce nutrient leaching from poultry litter activated biochar
   - Explore the potential of reducing methylation rates of Hg with poultry litter activated biochars

3. Explore combination of Phragmites and poultry litter activated biochars to achieve sequestration of organics and Hg. While the product made from phragmites has excellent organic sorption capability as demonstrated in the SEED project, the poultry litter based product has superior mercury sorption characteristics. The combination of the two products either before or after the activation process may yield a biomass derived activated carbon that is suitable for organics and Hg sequestration.

4. Evaluate the feasibility and cost of pilot-scale production of iron amended biochars to enhance settling characteristics. Work will involve collaboration with an activated carbon manufacturing industry. We believe longer-term focused experiments are necessary to fully understand the capability of iron-amended biochars to induce dechlorination of low molecular weight chlorinated organics.

5. Perform laboratory treatability and bioaccumulation studies with two DoD field site sediments containing organics and mercury (Aberdeen Proving Grounds, Quantico) and evaluate the feasibility of using selected biochars in the field.

Publications and Presentations

Publications

The potential of biochar amendments to remediate contaminated soils. Gomez-Eyles, J.L., Beesley, L., Moreno-Jiménez, E., Ghosh U., and Sizmur, T. (in press). In Ladygina N. & Rineau F. [eds.]. Biochar and soil biota. Science Publishers, Enfield, New Hampshire 03748, USA/Jersey, British Isles.

(*Some of the literature review for this study was used to write this book chapter*)

Effectiveness of Activated Carbon and Biochar in Reducing the Availability of Polychlorinated Dibenzo-p-dioxins/dibenzofurans in Soils. Yunzhou Chai, Rebecca J. Currie, John W. Davis, Michael Wilken, Greg D. Martin, Vyacheslav N. Fishman, and Upal Ghosh. Environ. Sci. Technol., 46, 1035-1043, 2011.

(*Leveraged funding and effort by Dow Chemical Company resulted in this publication*)

Presentations

Biochars and activated carbons for the in-situ sequestration of organic contaminants and mercury in sediments. Gomez-Eyles J.L., Yupanqui, C., Xia, H., Beckingham B., Kwon, S.J., Riedel, G., Gilmour, C. and Ghosh, U. Society of Environmental Toxicology and Chemistry (SETAC) – Chesapeake Bay Chapter, College Park, MD. April 2012 – Platform presentation.

Sorption of Priority Pollutants to Biochars and Activated Carbons For Application to Soil and Sediment Remediation. Beckingham B., Gomez-Eyles J.L., Riedel, G., Gilmour, C. and Ghosh, U. European Geosciences Union (EGU) General Assembly 2012 Vienna, Austria. April 2012 – Poster presentation.

Biochars and activated carbons for the in-situ sequestration of organic contaminants and mercury in sediments. Gomez-Eyles J.L., Beckingham B., Kwon, S.J., Riedel, G., Gilmour, C. and Ghosh, U. Society of Environmental Toxicology and Chemistry (SETAC) – North America Annual Meeting, Boston, MA. November 2011 – Platform presentation.

Activated biochars with iron for in-situ sequestration of organics, metals, and carbon. U. Ghosh and J. L. Gomez-Eyles. SERDP/ESTCP Annual Symposium, Washington, DC, December 1, 2010.

Evaluating the potential of biochars for the in situ remediation of sediments contaminated with organic contaminants, mercury and methylmercury. Jose L. Gomez-Eyles, Carmen Yupanqui, Barbara Beckingham, Seokjoon Kwon, Georgia Riedel, Cynthia Gilmour and Upal Ghosh. Gordon Research Conference: Environmental Sciences – Water. June, 2012. Poster presentation and best poster award winner.

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