Mechanisms of Mercury Removal by Biochars Produced from Different Feedstocks Determined using X-ray Absorption Spectroscopy

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Abstract

Thirty-six biochars produced from distinct feedstocks at different temperatures were evaluated for their potential to remove mercury (Hg) from aqueous solution at environmentally relevant concentrations. Concentrations of total Hg (THg) decreased by >90% in batch systems containing biochars produced at 600 and 700 °C and by 40-90% for biochars produced at 300 °C. Elevated concentrations of SO₄²⁻ (up to 1000 mg L⁻¹) were observed in solutions mixed with manure-based biochars. Sulfur X-ray absorption near edge structure (XANES) analyses indicated the presence of both reduced and oxidized S species in both unwashed and washed biochars. Sulfur XANES spectra obtained from biochars with adsorbed Hg were similar to those of washed biochars. Micro-X-ray fluorescence mapping results indicate that Hg was heterogeneously distributed across biochar particles. Extended X-ray absorption fine structure modeling indicates Hg was bound to S in biochars with high S content and to O and Cl in biochars with low S content. The predominant mechanisms of Hg removal are likely the formation of chemical bonds between Hg and various functional groups on the biochar. This investigation provides information on the effectiveness and mechanisms of Hg removal that is critical for evaluating biochar applications for stabilization of Hg in surface water, groundwater, soils, and sediments.

Key Words

Mercury; biochar; black carbon; sulfur; X-ray absorption spectroscopy

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1. Introduction

Large volumes of solid-phase reactive materials are required in treatment systems to control the release of metals and other contaminants to the environment. For example, construction of permeable reactive barriers [1, 2], containerized treatment systems [3, 4], and alternative treatment wetlands [5-7] all require use of large volumes of adsorbents, reductants, or other treatment materials.

Biochar and other carbonaceous materials are widely used as treatment materials to remove a range of metals (e.g., As, Cd, Cr, Cu, Ni, Pb, Zn) and organic contaminants from aqueous solutions [8-13]. Biochar has also been evaluated with respect to Hg stabilization [14-16]. The majority of Hg removal studies have focused on the determination of sorption isotherms, kinetic rate constants, or factors influencing sorption. Most of the studies have been conducted in experimental systems with relatively high initial Hg concentrations (5-2000 mg L⁻¹) [16-19], which is typical of industrial wastewater but much higher than commonly observed in the environment. Additional studies have been conducted for Hg removal at environmental concentrations [20-24]. For example, Klasson et al. [23] and Hollerman et al. [22] reported that Hg concentrations decreased from 1 µg L⁻¹ to <12 ng L⁻¹ in batch experiments [23] and to <51 ng L⁻¹ in column experiments [22] using functionalized resins.

Speciation of Hg in the environment is strongly dependent on the presence of thiol functional groups [25]. Therefore, understanding the sulfur (S) speciation in biochars is important with respect to potential removal approaches. X-ray absorption near-edge structure (XANES) spectroscopy is a non-destructive technique widely used for the characterization and quantification of sulfur species in various materials [26-31]. XANES analysis of biochar produced from corn stover and oak has indicated the presence of both organic and inorganic forms of sulfur [32, 33]. Micro X-ray fluorescence (µ-XRF) maps and extended X-ray absorption

fine structure (EXAFS) are powerful techniques for providing spatial localization of Hg, its correlation with other elements of interest, and local structural information including binding elements, bond distances, and coordination numbers. Hg L_{III} edge EXAFS analysis has been used to evaluate mechanisms of Hg removal using various treatment media, including brominated biomass ash [31], cupric chloride-impregnated sorbents [34], granular iron [35], activated carbon, thiol-containing materials, and modified attapulgite clay [36].

As described in Liu et al. [37], the biochar samples investigated in this study release different masses and forms of soluble carbon, including short-chain organic acids, total dissolved organic carbon, and alkalinity. The current study describes the removal of Hg from aqueous solution by these biochars and the release of additional components that could influence Hg cycling and methylation or limit the use of the biochars for environmental applications. To evaluate the binding mechanisms, X-ray absorption spectroscopy (XAS) was applied to determine the distribution of Hg and the local coordination geometry of Hg bound to biochar particles. Combined, these analyses assist in understanding how Hg is bound to biochar, and what substances might co-occur in the biochar to potentially influence transformation of Hg in field applications.

2. Methods

2.1 Biochars employed

Thirty-six biochar samples were prepared from three groups of feedstocks: wood, agricultural residue, and manure (Table 1). The feedstocks were air dried and pyrolyzed using a kiln at either 300 °C (low T) or 600 °C (high T) for 2-3 h under limited O₂ conditions. The biochars were cooled overnight to room temperature. Liu et al. [37] provide detailed methods used for preparation of the biochars.

Table 1. Abbreviations, sources of feedstock, and pyrolysis temperatures for biochar samples.

Abbreviation ^a	Feedstock	T (°C)	Abbreviation	Feedstock	T (°C)
Wood			Agricultural residue		
AC1	activated carbon	- ^b	CS1H	corn stovers	600
AC2	activated carbon	- ^b	CS1L	corn stovers	300
CL1	Wicked Good Charcoal	~700	CS2H	corn stovers	600
CL2	Cowboy Charcoal	~700	CS2L	corn stovers	300
CL5	Biochar Engineering Charcoal	~700	CC1H	corn cob	600
SW1H	mulch	600	CC1L	corn cob	300
SW1L	mulch	300	CC2H	corn cob	600
SW2H	pine bark	600	CC2L	corn cob	300
SW2L	pine bark	300	CA1H	cocoa husk	600
Manure			CA1L	cocoa husk	300
MB1H	cow manure	600	CT1H	cotton seed husk	600
MB1L	cow manure	300	CT1L	cotton seed husk	300
MP1H	chicken manure	600	GR2H	wheat shaft	600
MP1L	chicken manure	300	GR2L	wheat shaft	300
MP2L	chicken manure	300	GR3H	spent hops	600
MP3H	chicken manure	600	GR3L	spent hops	300
MU1H	mushroom soil	600	GR4H	switchgrass	600
MU1L	mushroom soil	300	GR4L	switchgrass	300
MU2H	mushroom soil	600			
MU2L	mushroom soil	300			
MU3H	mushroom soil	600			

^a Number after the first two letters indicates different sources; H and L at the end represent biochar preparation at high (600 °C) vs. low (300 °C) temperature, respectively.

^b not applicable

2.2 Batch experiments for Hg removal

A stock solution of 200 mg L⁻¹ of Hg²⁺ was prepared by dissolving reagent-grade HgCl₂ in ultra-pure water (Milli-Q purification system). The stock solution was diluted with river water (South River, Waynesboro, VA) to a concentration of ~10 µg L⁻¹, representative of environmental levels [38]. A series of batch-style experiments was conducted by adding 2 g of biochar to 150 mL of Hg(II)-spiked water. The mixtures were shaken thoroughly and allowed to equilibrate at room temperature for 2 d. Ultrapure water was used as a control to assess potential Hg contamination during laboratory procedures. Samples containing river water only and biochar mixed with unspiked river water were also used as controls.

At the termination of the experiment, water samples were filtered using 0.45 μm cellulose-acetate filters (Pall Corp.). For a subset of samples, six sequential aliquots (5@1 mL followed by 1@15 mL) of filtrate were analyzed, and concentrations of THg were observed to stabilize after the third aliquot. Therefore, for the majority of the samples, the first 5 mL aliquot of sample was discarded and subsequent aliquots were placed in an amber borosilicate glass bottle for analysis of total Hg (THg). These samples were acidified to pH <2 using ultra-pure HNO_3 . Additional samples were collected in polypropylene bottles and left unacidified for anion analyses. All samples were stored at 4 °C until analysis. The anion samples were analyzed within 72 h of collection.

2.3 Water analyses

THg concentrations were determined by cold vapor atomic fluorescence spectroscopy (Tekran Instruments) after digestion following US-EPA Method 1631 [39]. The method detection limit (MDL) was 0.19 ng L^{-1} as determined following the EPA procedure (40 CFR, Part 136). Quality assurance/quality control steps taken included analysis of laboratory blanks (<MDL), duplicate samples for each set of 10 samples (0-20% relative standard deviation, most < 5%), one matrix spike sample for each set of 10 samples (85-115% recovery, most 95-105%), and a NIST standard (80-120% recovery, most 95-105%) for each run. Concentrations of anions were determined on unacidified samples using ion chromatography (Dionex DX-600) with an IonPac AS9-HC 4 $\times$ 250 mm column.

2.4 Sulfur content

Solid-phase S content of the biochar samples was measured using a resistance furnace (Eltra CS-2000). Samples were oven-dried at 105 °C for 24 h before analysis and were analyzed three times; mean values of these analyses are reported.

2.5 X-ray Absorption Spectroscopy (XAS)

Eight unwashed and washed biochars without Hg and five biochars with adsorbed Hg were analyzed using S K-edge XANES. Thin-sections of five biochars with adsorbed Hg were characterized by μ -XRF mapping and Hg L_{III}-edge EXAFS.

2.5.1 Reference materials

Organic S reference compounds included dibenzyl disulfide (DibDis), L-cysteine, dibenzyl sulfide (DibSu), dibenzo thiophene (DibTh), and butyl sulfone (BuSu) (all from Sigma-Aldrich); tetramethylene sulfoxide (TeSu) (from Acros Organics); and sodium methane sulfonate (NaMeSu) (from Alfa Aesar). Pyrrhotite, cinnabar (α -HgS, Excalibur Mineral), metacinnabar (β -HgS), pyrite, Na tetrathionate ($\text{Na}_2\text{S}_4\text{O}_8$), NaS_2O_3 , K_2SO_4 , and HgSO_4 were selected as inorganic reference materials. The spectrum of thianthrene was obtained from an online database [40]. Mercury reference materials included cinnabar, HgO (Sigma-Aldrich), and HgCl_2 (Fisher Scientific). The spectra of Hg_2Cl_2 was obtained from an online database [41] and metacinnabar from the Hephaestus utility of the Demeter software package [42].

2.5.2 Hg EXAFS

Hg EXAFS analysis was conducted on the batch test samples; however, the concentrations of adsorbed Hg were too low to collect high quality spectra. To obtain improved EXAFS spectra, additional Hg was loaded onto the biochar samples by mixing 0.8 g biochar with 200 mL of a 50 mg L^{-1} Hg(II) solution. The mixture was separated onto a filter after 48 h and the solid phase freeze-dried for polished thin-section preparation. The thin-sections were prepared by mounting grains of biochar within epoxy cement on a quartz slide 26×26 mm in size to a thickness of 30 μm (Vancouver Petrographics Ltd., Canada).

EXAFS spectra were collected for samples and reference materials on Beamline 13-ID-E (GSECARS) and Beamline 20-ID-B (PNC/XSD) at the Advanced Photon Source (APS; Illinois, USA). A focused beam approximately $2 \times 2 \mu\text{m}$ in size was used for XAS data collection. The μ -XRF maps were collected with a photon energy for excitation of 12.6 keV. The step size (pixel) was $2 \times 2 \mu\text{m}$ for fine maps and $25 \times 25 \mu\text{m}$ for coarse maps. Areas with elevated Hg intensity were identified for acquisition of EXAFS spectra.

The XRF mapping was analysed using X-ray Microprobe Map Viewer [43] for data from the GSECARS beamline and 2D QScanPlot for data from the PNC/XSD beamline. The XAS spectra were analysed using Athena, and EXAFS model calculations were made using Artemis [42]. The modeling was performed following the method described by Gibson et al. [36]. Briefly, the crystal structures of reference materials were obtained from the American Mineralogist Crystal Structure database [44] and ATOMS.INP website [45]. Weak oscillations in the EXAFS data were enhanced by applying a k weighting of 3 to the spectra. Coordination numbers (CNs) were considered as a constant during refinement of the first shell for the reference materials to obtain the amplitude reduction factor (S_0^2) and static disorder (σ^2). S_0^2 and σ^2 were then kept invariant for refinement of the first shell of Hg bound to biochar to model the CNs.

2.5.3 S XANES

Preliminary XANES analysis indicated a pronounced intensity for sulfate and suppression of the intensity for other reduced S peaks; therefore, a separate set of biochar samples was washed to lessen the intensity of the sulfate signal. The biochar samples were mixed with ultrapure water at a 1:10 mass ratio following the same procedure as the batch experiment, except that the mixtures were filtered after 2 h; this procedure was repeated for a total of 6 or 12 times. Liu et al. [37] provide details of the washing steps. Biochar samples after washing and

samples after contact with Hg were freeze-dried and ground into fine powders to decrease self-adsorption effects.

XANES spectra were collected on samples and reference materials at both the GSECARS beamline and at the Soft X-ray Microcharacterization Beamline (SXRMB) at the Canadian Light Source (CLS; Saskatchewan, Canada). At GSECARS, homogenized powders of samples and reference materials (mixed with high-purity graphite with a S content of ~5%) were placed into an acrylic holder covered with 2.5- μm thick Mylar film (Chemplex Industries). Sample holders were placed in a He bag during analysis. A Si(111) monochromator was detuned to 70% to reduce higher-order harmonics. An unfocused beam of $\sim 50 \times 50 \mu\text{m}$ was employed and data were collected using a Vortex ME4 silicon drift diode array detector. At the CLS-SXRMB, homogenized samples and pure reference materials were smeared as a thin film on conductive double-side tape mounted to a copper sample holder. The holder was placed inside a chamber under vacuum. Spectra were collected using fluorescence yield for biochar samples and total electron yield for the reference materials.

One to six scans were collected for biochars and reference materials. Data processing was performed with Athena [42]. The spectra of the samples were compared with reference materials, and spectra of reference materials with peaks at the same peak energy were selected for linear combination fitting (LCF) in Athena to calculate the relative percentages of S species in a given sample.

2.6 Statistical analysis

Statistically significant correlations among feedstock type, pyrolysis temperature, THg, anion concentrations, and S content were determined using a two-fractional ANOVA. Correlation analyses were evaluated by Pearson product-moment correlation coefficients.

3. Results and Discussion

3.1 Removal of Hg

Biochar treatment reduced concentrations of THg in river water from 9800 ng L⁻¹ to as low as 21 ng L⁻¹, for a removal of up to 99.8% (Fig. 1). THg concentrations in the water treated by most high-T biochars were lower than the 2000 ng L⁻¹ US-EPA drinking water standard and 73% of the high-T biochars were lower than the 770 ng L⁻¹ concentration recommended by the US-EPA to protect aquatic life [46, 47]. Concentrations of THg decreased by >95% in the batch mixtures containing charcoals, activated carbons, low-T biochars produced from poultry manure and mushroom soils, and high-T biochars produced from corn cobs, corn stover, mixed grass, hop grass, switchgrass, pine mulch, pine bark, poultry manure, and mushroom soils. The highest THg concentration (5800 ng L⁻¹) was observed for biochar produced from pine bark prepared at 300 °C. The THg concentration decreased by 29% for the Hg-spiked river water after 2 d; possibly due to uptake of Hg by organic matter. The THg concentrations in other controls containing ultrapure water alone, river water alone, and biochar mixed with river water were less than 10 ng L⁻¹.

Fig. 1. THg concentrations and % Hg removal from aqueous solution in batch tests containing biochar and river water spiked with Hg. C represents the control containing Hg-spiked river water with no biochar added.

THg concentrations of the aqueous solution equilibrated with high-T biochars were significantly lower than those observed for low-T biochars ($P < 0.05$). No significant differences

in THg concentrations were observed among different biochar groups and from the interaction of pyrolysis temperatures and different groups. Mercury removal efficiencies were consistently greater than 80% (majority >90%) in samples treated by manure-based biochars and high-T wood-based biochars. These treatment efficiencies are comparable to those reported for other carbonaceous materials. For example, Hg removal efficiencies of 86 to 75% using 2 to 250 $\mu\text{g L}^{-1}$ $^1\text{Hg}^{2+}$ were observed for a biochar produced from soybean stalk [48].

3.2 Sulfate

Sulfate concentrations in the mixtures with biochars ranged from 6.0 to 1000 mg L^{-1} (Fig. 2), all of which exceed the concentration in the control (5.9 mg L^{-1}). The highest concentrations of SO_4^{2-} (range 72-1000 mg L^{-1} , median >400 mg L^{-1}) were consistently observed in river water mixed with mushroom soil and poultry manure biochars, whereas lower concentrations were observed with wood-based biochars. The concentrations of SO_4^{2-} in mixtures containing Cowboy Charcoal (CL2), high-T pine bark (SW2H), corn cob (CC2H), and spent hops (GR3H) biochars were only slightly higher than those measured in river water (range 6.0-7.1 mg L^{-1}).

Fig. 2. Concentrations of SO_4^{2-} in river water (control C) versus concentrations in batch mixtures containing river water and biochar.

The elevated concentrations in the poultry manure and mushroom soil biochars are consistent with earlier studies [49] and likely due to high inorganic S content in the feedstocks [50]. The statistical analysis indicated no significant differences of sulfate concentrations

between the low-T and high-T biochars, whereas the SO_4^{2-} concentrations of manure-based biochars were significantly higher than the agricultural residue-based biochars.

The elevated concentrations of SO_4^{2-} released from the biochar may be problematic for applications of biochar for Hg stabilization at contaminated sites if reducing conditions are established, because the added SO_4^{2-} can be utilized as an electron acceptor by sulfate-reducing bacteria known to be major Hg methylators [51] and MeHg is much more toxic than other forms of Hg. Liu et al. [37] report that organic acids and dissolved organic carbon (DOC) are released by some of the biochars. In combination with SO_4^{2-} , these organic acids and other forms of DOC may act as electron donors further stimulating growth of Hg methylators. The elevated SO_4^{2-} concentrations released from the biochar may affect the aqueous-phase speciation of Hg, especially for biochar samples prepared from the mushroom soil and poultry manure. The released DOC can also affect the aqueous-phase speciation of Hg, because Hg can strongly bind to DOC [52]. Speciation calculations were made for all batch samples using PHREEQCi. For these calculations, thermodynamic constants for Hg-Dissolved organic matter (Hg-DOM) [53-56] were added into the database. These calculations indicate that the aqueous solutions for all the samples were strongly undersaturated with respect to HgSO_4 , HgO , HgCl_2 phases, and that the Hg-DOM complexes accounted for >90% of the THg.

3.3 Sulfur content

The solid-phase S content of the biochar samples ranged from <0.01 to 3.4% (Table 2). Solid-phase S content was highest for the manure-based biochars, at 0.48-3.40%, and lowest for the wood-based biochars, at <0.01-0.18%. These observations are consistent with SO_4^{2-} concentrations in the aqueous phase (Fig. 2). The S content of two high-T corn stover biochars

(CS1H, 0.82%; CS2H, 0.37%) are close to the value reported for a corn stover biochar produced at 500 °C (~0.8%) [33].

Table 2. Sulfur content of biochars as a function of pyrolysis temperature.

Group	Biochar	S (%)	
		Low-T	High-T
Wood	AC2	-	0.18±0.02
	AC1	-	0.18±0.01
	CL5	-	<0.01
	CL2	-	<0.01
	CL1	-	0.14±0.01
	SW1	0.04±0.01	<0.01
	SW2	0.03±0.01	0.04±0.01
Agricultural residue	CS1	0.10±0.02	0.82±0.03
	CS2	0.11±0.02	0.37±0.02
	CC2	0.04±0.01	0.02±0.01
	GR4	0.10±0.01	0.55±0.02
	GR2	0.21±0.02	0.36±0.02
	GR3	0.13±0.02	0.34±0.02
	CC1	0.05±0.01	0.03±0.01
	CT1	0.02±0.01	0.03±0.01
	CA1	0.16±0.02	0.20±0.02
Manure	MP1	0.54±0.02	0.48±0.02
	MU2	2.4±0.05	2.4±0.04
	MU3	-	0.58±0.02
	MP2	0.67±0.02	-
	MP3	-	1.9±0.02
	MU1	3.1±0.05	3.4±0.06
	MB1	0.14±0.02	0.09±0.02

The statistical analysis indicated differences in S content between low-T and high-T biochar are insignificant. Generally, light elements (e.g., hydrogen) are vaporized as pyrolysis temperature increases, leading to enrichment of S [57], i.e., S content of high-T biochars is greater than for low-T biochars [33, 58]. The lack of correlation here may be due to the variety of biochar samples evaluated. A significant difference in S content among the three groups is evident, i.e., the S content of manure-based biochar is significantly greater than for agricultural residue-based biochar, which is consistent with a previous study [33]. Correlation analysis indicated that SO_4^{2-} concentrations in the aqueous phase are not significantly correlated with S

content in the biochars. This observation suggests that other forms of S are likely present in the biochars.

3.4 S XANES analyses

Due to the complexity of sulfur species in nature, a variety of sulfur reference materials were characterized. The XANES spectra collected (Fig. 3a,b) are consistent with the presence of reduced sulfur (v1 - v5) and oxidized sulfur (v6, SO_4^{2-}) species in all biochar samples (Fig. 3c,d), in agreement with other studies [33]. The peak positions of v3 (thianthrene-like) and v4 (thiophene-like) are at the same energy (2474.3 eV), and therefore are expressed as v3/4. The presence of v3/4 and v6 (sulfate-like, 2482.5 eV) peaks is evident in all samples. Elemental sulfur-like peaks (v2, 2472.7 eV) are evident in unwashed and washed activated carbon (AC) and high T mushroom soil (MU1H) biochars, which is consistent with reduced sulfur peaks occurring in the energy range of 2472 to 2473 eV for brominated and non-brominated activated carbon [31]. Spectra consistent with the presence of thiophene-like (2nd peak) or sulfoxide-like (v5, 2476.2 eV) species were collected for CL2 and GR4H biochars. Evidence of sulfide-like S species (v1, 2470.4 eV) is present in the spectra of washed MP1H.

Comparison of the spectra obtained for the low-T and high-T biochars indicates that the intensity and percentage of peaks are consistent with the presence of reduced S (Table 3). In addition, new peaks of reduced S phases are observed in the spectra for the high-T biochars, e.g., v2 for the MU1H biochar and v5 for the GR4H biochar. The intensities of reduced S peaks in washed high-T biochars are also higher than for washed low-T biochars (Fig. 3c,d). These results indicate that a portion of inorganic sulfur (sulfate) was likely leached into the aqueous phase through the washing step relative to reduced sulfur species, which is consistent with the elevated SO_4^{2-} data in the batch experiment (Fig. 2).

Fig. 3. ^{a,b} S XANES spectra for 17 sulfur standards. ^{c,d} S XANES spectra for unwashed and washed biochars; the number after the sample name indicates the number of times that the sample was washed. The dashed blue line indicates the fitted curves for samples using LCF. Spectra identifications displayed on the left side of subplots b, c, and d indicate samples where the spectra were reduced by half for ease of display. ^e S XANES spectra for activated carbon and biochars with adsorbed Hg(II).

An LCF process was conducted to determine the similarity between the spectra of biochars and reference materials (Fig. 3c,d). A combination of K₂SO₄ and thiophene provides the best fit for CL2, GR4L, and GR4H biochars (Table 3). Addition of thianthrene and elemental S was required to provide the best fit for AC and addition of pyrrhotite was required for washed MP1H. The increase in the percentage of reduced S species in the biochar samples after washing is consistent with the intensity increase of the spectra (Fig. 3c,d). The percentage of reduced S species in high-T switchgrass biochar (GR4H) increased in comparison with GR4L, which is consistent with the peak intensity increase (Fig. 3c d).

Table 3. Percentage (%) of different S forms calculated by LCF

Standards	AC	AC-6 ^a	CL2	CL2-6	GR4L	GR4L-6	GR4H	GR4H-6	MP1H	MP1H-12
K ₂ SO ₄	27	26	29	16	36	53	18	13	91	62
Dibenzo thiophene	44	23	71	84	64	47	82	87	9	27
Thianthrene	11	27	-	-	-	-	-	-	-	-
S	18	24	-	-	-	-	-	-	-	-
Pyrrhotite	-	-	-	-	-	-	-	-	-	11

Reduced χ^2	0.11	0.08	0.03	0.03	0.13	0.15	0.02	0.02	0.39	0.04
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^a labels -6 and -12 indicate number of washes

S XANES spectra collected for pyrolyzed carbonaceous material indicate that the majority of S bonded to C is thermally decomposed during pyrolysis at 450 °C [32, 33]. Ester-S, and to a small extent inorganic sulfate, also accumulate [32]. The transformation of sulfate to reduced S occurs at pyrolysis temperatures above 500-600 °C when hydrocarbon molecules (in pyrolysis vapor and syngas) and/or H₂ (present in syngas) are present [33]. The sulfur transformed from sulfate is retained in the char and is presumably bound to the organic char matrix. As the biochar in this study was prepared at 300 and 600 °C, part of the sulfate was likely transformed to reduced and organic bound sulfur at 600 °C.

Reduced sulfur plays an important role in the binding of Hg because Hg-S complexes form with disulfide/disulfane in addition to thiol S [59]. Binding of Hg to reduced S is usually favored over binding to other functional groups, e.g., hydroxyl and carboxyl groups [31, 60, 61]. In this study, the S XANES spectra of biochars adsorbed with Hg are similar to the spectra of washed biochars with no adsorbed Hg; no obvious change in the intensity of the reduced and oxidized sulfur peaks is evident (Fig. 3c-e). The similarity indicates that S components in the biochar are not altered by the adsorbed Hg.

3.5 μ -XRF mapping

The μ -XRF results indicate Hg is distributed on the edges, inside the pores, and even inside the pore walls of the particles in all thin sections (Fig. 4). These observations indicate that Hg penetrates into the interior of biochar particles and does not simply sorb to the surface and pore walls. The Hg is unevenly distributed, as the greatest enrichments are close to the particle edges and within the pores in all particles. Low intensity areas on the Hg μ -XRF map are also evident within particles, especially within the low-T switchgrass (GR4L) and high-T poultry

manure (MP1H) biochars. The Hg enrichment area displays a cross-channel pattern in the high-resolution mapping area on CL2-Coarse. The Hg $L_{\alpha 1}$ peaks in the XRF spectra confirm the existence of Hg in Hg-rich areas of the maps for AC-Coarse and CL2-Coarse.

Fig. 4. Microscope photos under reflection mode (left) and Hg L_{α} line μ -XRF maps (right) in thin sections. The white bars represent 100 μ m. The EXAFS spectra for modeling were collected at the locations indicated by white arrows. Note: For AC-Coarse and CL2-Coarse, a high resolution mapping area is displayed directly below each map. The XRF spectra displayed on the right side were collected over the areas identified by white squares in the maps directly to the left of the XRF spectra.

The results indicate Hg is present on the edges of and inside the particles. However, this is inconsistent with a previous study that reported Hg concentrated 0-100 μ m from the exterior of the polysulfide-rubber-coated activated carbon [62]. The XRF K_{α} or K_{β} lines of other elements (K, Ca, Mn, Fe, Ni, and Cu) were also collected, but their intensity is not distinguishable from

the background. The S K_{α} line was filtered by Al foil because the detector was saturated without a filter.

3.6 Hg XANES analysis and EXAFS modelling

The threshold E_0 (ionization energy) of the XANES indicates the Hg oxidation state in the five samples is similar to HgCl_2 , HgO , and cinnabar, suggesting the Hg is present as Hg^{2+} (Fig. 5a). The XANES spectra show the absence of a distinct shoulder on the edge in the samples, in contrast to the shoulder (12.29 keV) observed for HgCl_2 and HgO reference materials.

Fig. 5. ^a Normalized Hg XANES spectra. ^b First-derivative spectra, where IPD is the inflection point difference. ^c k^3 -weighted chi spectra (black line) and best fit (light blue-dash line). ^d Fourier-transformed magnitude spectra. ^e Fourier-transformed real part.

Inflection point difference (IPD) is defined as the energy difference of two distinct peaks in the first derivatives of the spectra [63]. IPD can be used as a screening method to estimate the

Hg binding environment [31]. The IPDs of AC, CL2, and GR4L samples ranged from ~8.1 to ~8.4 eV, which are close to that of HgCl₂ (Fig. 5b). IPDs of the GR4H and MP1H samples were 7.6 and 7.7 eV, close to that of cinnabar.

EXAFS spectra were modeled against the first shell of HgCl₂, Hg₂Cl₂, HgO, metacinnabar, cinnabar, and their combinations. The best fit was obtained using HgO as a model compound for AC and GR4L, HgCl₂ for CL2, and cinnabar for GR4H and MP1H (Fig. 5c-e; Table 4). The EXAFS modeling R-factors range from 0.006 to 0.04 for the reference materials and 0.005 to 0.16 for the biochar samples.

Table 4. Mercury EXAFS fitting results ^a

sample	path	CN	R (Å)	S ₀ ²	σ ² (Å ²)	ΔE ₀ (eV)	R-factor
AC	Hg-O	1.15 (±0.16)	2.08 (±0.02)	1.058 ^b	0.005 ^b	0.76	0.09
CL2	Hg-Cl	0.55 (±0.06)	2.26 (±0.01)	0.967 ^b	0.002 ^b	-6.9	0.013
GR4L	Hg-O	1.51 (±0.23)	2.11 (±0.06)	1.058 ^b	0.005 ^b	8.9	0.16
GR4H	Hg-S	0.83 (±0.18)	2.24 (±0.05)	0.841 ^b	0.005 ^b	-2.5	0.064
MP1H	Hg-S	1.17 (±0.07)	2.26 (±0.03)	0.841 ^b	0.005 ^b	-1.5	0.005
Cinnabar	Hg-S	2	2.37	0.841 (±0.123)	0.005 (±0.001)	3.51	0.015
HgO	Hg-O	2	2.05	1.058 (±0.299)	0.005 (±0.004)	-1.1	0.044
HgCl ₂	Hg-Cl	2	2.29	0.967 (±0.107)	0.002 (±0.001)	-0.6	0.006

^a CN = coordination number, R = bond length, and R-factor = fitting statistic.

^b fixed values from model compounds

Although the IPDs of activated carbon (AC) and low-T switchgrass biochar (GR4L) are closer to HgCl₂ than HgO, negative values of coordination numbers were obtained when HgCl₂ was used as a model compound. The modeled bond distances of Hg-O in AC and GR4L are between 2.08 and 2.11 Å, which is close to the theoretical value (2.05 Å, Table 4) and in agreement with a previous study [36]. The O atoms bound to Hg are likely from the O-containing functional groups identified in Fourier transform infrared spectra [37] or H₂O sorbed to surfaces of activated carbon particles [64]. However, a study by Bisson et al. [31] shows Hg is primarily bound to S in activated carbon used for capturing Hg from coal-fired power plants. The

coordination number of Cl bound to Hg for Cowboy Charcoal (CL2) is ~0.55, which is less than the Cl in the HgCl₂ reference compound. The modeled Hg-Cl distance is ~2.26 Å, which is close to the expected 2.29 Å for HgCl₂ but shorter than ~2.36 Å for Hg-Cl in cupric chloride-impregnated sorbents [34]. The Cl likely originated from the solution or possibly the biochar. The best fitting results for high-T switchgrass biochar (GR4H) and high-T poultry manure biochar (MP1H) were obtained when cinnabar was used a model compound. The coordination numbers of S bound to Hg for GR4H and MP1H are between 0.79 and 1.17, which are in the range of published values [31, 36]. The modeled Hg-S distances are ~2.24 and ~2.26 Å, shorter than 2.37±0.04 Å for the cinnabar and previous studies [31, 34]. The poor fitting against Hg-S for AC, CL2, and GR4L is likely due to the low S content in these samples compared with GR4H and MP1H (Table 2).

The S XANES data also indicate that Hg is likely bound to S in AC, CL2, and GR4L, but the percentage of Hg-S in AC, CL2, and GR4H appears to be low as Hg-S is not well represented in the EXAFS modeling for Hg. The Hg removal mechanisms by carbonaceous sorbents include coordination between Hg and functional groups on/within sorbents, reduction of Hg²⁺ to Hg(I) and precipitation [65], and co-precipitation with anions. The predominant removal mechanisms appear to be chemical binding of Hg to functional groups (e.g., thiol, hydroxyl, carboxylic, chloride) on the surface of and within the biochars. Based on the S XANES and Hg EXAFS analyses, and published studies [36], the following Hg removal mechanisms are proposed:

The relative importance of these individual mechanisms appears to be dependent on the biochar source material and pyrolysis temperature.

4. Conclusions

The majority of the biochars studied were highly effective with respect to the removal of Hg from aqueous solution and highlight the potential of biochars for this purpose. Hg distribution maps indicate that Hg is unevenly distributed across the biochar particles. Hg binds to S functional groups of the investigated biochars with elevated S content and binds to O and Cl functional groups of the biochar with low S content.

Sulfur speciation plays an important role in Hg speciation. The presence of S in the biochar samples is variable, with contents ranging from less than the analytical detection limit to greater than 3%. The S in the biochar samples is present in both reduced and oxidized species. Variable concentrations of sulfate leach from the biochars.

In some aquatic environments, elevated concentrations of sulfate and labile organic matter might promote growth of sulfate-reducing bacteria, the primary group of methylating bacteria. Of the biochars studied, elevated concentrations of sulfate and labile organic compounds are evident in manure-based biochars and biochars produced from cocoa husk. The lowest concentrations of these components are released from wood-based biochars and biochars produced from cotton seed husk, corn cob and stover, and grasses, suggesting these biochars may have a lower potential to stimulate growth of sulfate-reducing bacteria. The presence of dissolved organic matter also might promote complexation reactions with Hg, potentially increasing Hg mobility. These results suggest that, in addition to considering the extent of Hg uptake by biochars, the presence of dissolved components that are known to promote Hg complexation and methylation reactions should be considered when selecting biochars for different environmental applications.

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References

- [1] D.W. Blowes, C.J. Ptacek, S.G. Benner, C.W.T. McRae, T.A. Bennett, R.W. Puls, Treatment of inorganic contaminants using permeable reactive barriers, *J. Contam. Hydrol.*, 45 (2000) 123-137.
- [2] D.W. Blowes, C.J. Ptacek, J.L. Jambor, In-situ remediation of Cr(VI)-contaminated groundwater using permeable reactive walls: Laboratory studies, *Environ. Sci. Technol.*, 31 (1997) 3348-3357.
- [3] W.D. Robertson, C.J. Ptacek, S.J. Brown, Rates of nitrate and perchlorate removal in a 5-year-old wood particle reactor treating agricultural drainage, *Ground Water Monit. Remediat.*, 29 (2009) 87-94.
- [4] S.I. Hussain, D.W. Blowes, C.J. Ptacek, D. Olding, Phosphorus removal from lake water using basic oxygen furnace slag: System performance and characterization of reaction products, *Environ. Eng. Sci.*, 31 (2014) 631-642.
- [5] S.I. Hussain, D.W. Blowes, C.J. Ptacek, J.H. Jamieson-Hanes, B. Wootton, G. Balch, J. Higgins, Mechanisms of phosphorus removal in a pilot-scale constructed wetland/BOF slag wastewater treatment system, *Environ. Eng. Sci.*, 32 (2015) 340-352.
- [6] C. Barca, S. Troesch, D. Meyer, P. Drissen, Y. Andreis, F. Chazarenc, Steel slag filters to upgrade phosphorus removal in constructed wetlands: Two years of field experiments, *Environ. Sci. Technol.*, 47 (2013) 549-556.
- [7] Z.M. Easton, M. Rogers, M. Davis, J. Wade, M. Eick, E. Bock, Mitigation of sulfate reduction and nitrous oxide emission in denitrifying environments with amorphous iron oxide and biochar, *Ecol. Eng.*, 82 (2015) 605-613.
- [8] J. Lehmann, S. Joseph, *Biochar for Environmental Management: Science and Technology*, Earthscan Publishers, London, UK, 2009.
- [9] X. Dong, L.Q. Ma, Y. Li, Characteristics and mechanisms of hexavalent chromium removal by biochar from sugar beet tailing, *J. Hazard. Mater.*, 190 (2011) 909-915.
- [10] J. Jiang, R.K. Xu, T.Y. Jiang, Z. Li, Immobilization of Cu(II), Pb(II) and Cd(II) by the addition of rice straw derived biochar to a simulated polluted Ultisol, *J. Hazard. Mater.*, 229-230 (2012) 145-150.
- [11] P. Zhang, H. Sun, L. Yu, T. Sun, Adsorption and catalytic hydrolysis of carbaryl and atrazine on pig manure-derived biochars: Impact of structural properties of biochars, *J. Hazard. Mater.*, 244-245 (2013) 217-224.
- [12] X. Hu, Z. Ding, A.R. Zimmerman, S. Wang, B. Gao, Batch and column sorption of arsenic onto iron-impregnated biochar synthesized through hydrolysis, *Water Res.*, 68 (2015) 206-216.

- [13] M. Ahmad, Y.S. Ok, A.U. Rajapaksha, J.E. Lim, B.Y. Kim, J.H. Ahn, Y.H. Lee, M.I. Al-Wabel, S.E. Lee, S.S. Lee, Lead and copper immobilization in a shooting range soil using soybean stover- and pine needle-derived biochars: Chemical, microbial and spectroscopic assessments, *J. Hazard. Mater.*, 301 (2016) 179-186.
- [14] D. Mohan, A. Sarswat, Y.S. Ok, C.U. Pittman Jr, Organic and inorganic contaminants removal from water with biochar, a renewable, low cost and sustainable adsorbent - A critical review, *Bioresour. Technol.*, 160 (2014) 191-202.
- [15] M. Bundschuh, J.P. Zubrod, F. Seitz, M.C. Newman, Effects of two sorbents applied to mercury-contaminated river sediments on bioaccumulation in and detrital processing by *Hyalomma azteca*, *J. Soils Sediments*, 15 (2015) 1265-1274.
- [16] L.G. Boutsika, H.K. Karapanagioti, I.D. Manariotis, Aqueous mercury sorption by biochar from malt spent rootlets, *Water Air Soil Poll.*, 225 (2014) 1-10.
- [17] S.K. Das, A.R. Das, A.K. Guha, A study on the adsorption mechanism of mercury on *Aspergillus versicolor* biomass, *Environ. Sci. Technol.*, 41 (2007) 8281-8287.
- [18] K. Kadirvelu, M. Kavipriya, C. Karthika, N. Vennilamani, S. Pattabhi, Mercury(II) adsorption by activated carbon made from sago waste, *Carbon*, 42 (2004) 745-752.
- [19] C. Namasivayam, K. Kadirvelu, Uptake of mercury (II) from wastewater by activated carbon from an unwanted agricultural solid by-product: Coirpith, *Carbon*, 37 (1999) 79-84.
- [20] K.T. Klasson, K. Kosny, S.R. Drescher, G.R. Southworth, J.F. Hensley, Reaching parts per trillion clean-up criterion for mercury in water, in: *Waste Management 2003 Symposium*, Tucson, AZ, 2003, pp. 23-27.
- [21] K. Klasson, D. Bostick, L. Farr, D. McTaggart, P. Taylor, Demonstration of mercury sorbents to meet DOE customer needs (Report#: ORNL/TM-2000/12), Oak Ridge National Laboratory, TN, 2000.
- [22] W. Hollerman, L. Holland, D. Ila, J. Hensley, G. Southworth, T. Klasson, P. Taylor, J. Johnston, R. Turner, Results from the low level mercury sorbent test at the Oak Ridge Y-12 Plant in Tennessee, *J. Hazard. Mater.*, 68 (1999) 193-203.
- [23] K.T. Klasson, D.T. Bostick, Trace-level mercury removal from surface water (Report#: ORNL/CP-98108), Oak Ridge National Laboratory, TN, 1998.
- [24] D. Bostick, K. Klasson, Multi-weight isotherm results for mercury removal in upper East Fork Popular Creek water (Report#: ORNL/TM--13582), Oak Ridge National Laboratory, TN, 1998.
- [25] Y. Yin, H.E. Allen, C.P. Huang, D.L. Sparks, P.F. Sanders, Kinetics of mercury(II) adsorption and desorption on soil, *Environ. Sci. Technol.*, 31 (1997) 496-503.

- [26] M.J. Wang, Y.F. Hu, J.C. Wang, L.P. Chang, H. Wang, Transformation of sulfur during pyrolysis of inertinite-rich coals and correlation with their characteristics, *J. Anal. Appl. Pyrol.*, 104 (2013) 585-592.
- [27] J. Prietzel, J. Thieme, U. Neuhausler, J. Susini, I. Kögel-Knabner, Speciation of sulphur in soils and soil particles by X-ray spectromicroscopy, *Eur. J. Soil Sci.*, 54 (2003) 423-433.
- [28] T. Zeng, W.A. Arnold, B.M. Toner, Microscale characterization of sulfur speciation in lake sediments, *Environ. Sci. Technol.*, 47 (2013) 1287-1296.
- [29] M.E. Fleet, XANES spectroscopy of sulfur in Earth materials, *Can. Mineral.*, 43 (2005) 1811-1838.
- [30] A. Manceau, K.L. Nagy, Quantitative analysis of sulfur functional groups in natural organic matter by XANES spectroscopy, *Geochim. Cosmochim. Acta*, 99 (2012) 206-223.
- [31] T.M. Bisson, L.C.W. MacLean, Y. Hu, Z. Xu, Characterization of mercury binding onto a novel brominated biomass ash sorbent by X-ray absorption spectroscopy, *Environ. Sci. Technol.*, 46 (2012) 12186-12193.
- [32] S. Churka Blum, J. Lehmann, D. Solomon, E.F. Caires, L.R.F. Alleoni, Sulfur forms in organic substrates affecting S mineralization in soil, *Geoderma*, 200-201 (2013) 156-164.
- [33] S. Cheah, S.C. Malone, C.J. Feik, Speciation of sulfur in biochar produced from pyrolysis and gasification of oak and corn stover, *Environ. Sci. Technol.*, 48 (2014) 8474-8480.
- [34] X. Li, J.Y. Lee, S. Heald, XAFS characterization of mercury captured on cupric chloride-impregnated sorbents, *Fuel*, 93 (2012) 618-624.
- [35] C.G. Weisener, K.S. Sale, D.J.A. Smyth, D.W. Blowes, Field column study using zerovalent iron for mercury removal from contaminated groundwater, *Environ. Sci. Technol.*, 39 (2005) 6306-6312.
- [36] B.D. Gibson, C.J. Ptacek, M.B.J. Lindsay, D.W. Blowes, Examining mechanisms of groundwater Hg(II) treatment by reactive materials: An EXAFS study, *Environ. Sci. Technol.*, 45 (2011) 10415-10421.
- [37] P. Liu, C.J. Ptacek, D.W. Blowes, W.R. Berti, R.C. Landis, Aqueous leaching of organic acids and dissolved organic carbon from various biochars prepared at different temperatures, *J. Environ. Qual.*, 44 (2015) 684-695.
- [38] M. Ranchou-Peyruse, M. Monperrus, R. Bridou, R. Duran, D. Amouroux, J.C. Salvado, R. Guyoneaud, Overview of mercury methylation capacities among anaerobic bacteria including representatives of the sulphate-reducers: Implications for environmental studies, *Geomicrobiol. J.*, 26 (2009) 1-8.

- [39] U. EPA, Method 1631, Revision E: Mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry, US Environmental Protection Agency Washington, DC, (2002).
- [40] ID21 Sulfur XANES Spectra Database of European Synchrotron Radiation Facility. <http://www.esrf.eu/UsersAndScience/Experiments/Imaging/ID21/php> (accessed April 2015).
- [41] EXAFS Database of Standard Materials at NSLS. <http://www.bnl.gov/ps/x18b/data.asp> (accessed April 2015).
- [42] B. Ravel, M. Newville, ATHENA, ARTEMIS, HEPHAESTUS: Data analysis for X-ray absorption spectroscopy using IFEFFIT, J. Synchrotron Radiat., 12 (2005) 537-541.
- [43] M. Newville Larch: X-ray Data Analysis. <http://cars.uchicago.edu/xraylarch/contents.html>.
- [44] American Mineralogist Crystal Structure Database. <http://rruff.geo.arizona.edu/AMS/amcsd.php> (accessed April 2015).
- [45] The Atoms.inp Archive. <http://cars.uchicago.edu/~newville/adb/search.html>.
- [46] US-EPA US-EPA National Primary Drinking Water Regulations. <http://water.epa.gov/drink/contaminants/index.cfm> (accessed April 2015).
- [47] US-EPA National Recommended Water Quality Criteria. <http://water.epa.gov/scitech/swguidance/standards/criteria/current/index.cfm> (accessed April 2015).
- [48] H. Kong, J. He, Y. Gao, H. Wu, X. Zhu, Cosorption of phenanthrene and mercury(II) from aqueous solution by soybean stalk-based biochar, J. Agric. Food Chem., 59 (2011) 12116-12123.
- [49] A. Hass, J.M. Gonzalez, I.M. Lima, H.W. Godwin, J.J. Halvorson, D.G. Boyer, Chicken manure biochar as liming and nutrient source for acid appalachian soil, J. Environ. Qual., 41 (2012) 1096-1106.
- [50] M. Guo, J. Chorover, Leachate migration from spent mushroom substrate through intact and repacked subsurface soil columns, Waste Manage., 26 (2006) 133-140.
- [51] H. Hsu-Kim, K.H. Kucharzyk, T. Zhang, M.A. Deshusses, Mechanisms regulating mercury bioavailability for methylating microorganisms in the aquatic environment: A critical review, Environ. Sci. Technol., 47 (2013) 2441-2456.
- [52] D. Wallschläger, M.V.M. Desai, R.D. Wilken, The role of humic substances in the aqueous mobilization of mercury from contaminated floodplain soils, Water Air Soil Poll., 90 (1996) 507-520.

- [53] A.E. Martell, R.M. Smith, Critically Selected Stability Constants of Metal Complexes, Version 8.0; NIST Standard Reference Database 46. National Institute of Standards and Technology: Washington DC, USA, 2004
- [54] E.J.M. Temminghoff, A.C.C. Plette, R. Van Eck, W.H. Van Riemsdijk, Determination of the chemical speciation of trace metals in aqueous systems by the Wageningen Donnan Membrane Technique, *Anal. Chim. Acta*, 417 (2000) 149-157.
- [55] W. Dong, L. Liang, S. Brooks, G. Southworth, B. Gu, Roles of dissolved organic matter in the speciation of mercury and methylmercury in a contaminated ecosystem in Oak Ridge, Tennessee, *Environ. Chem.*, 7 (2010) 94-102.
- [56] M.J. Gismera, J.R. Procopio, M.T. Sevilla, Characterization of mercury-Humic acids interaction by potentiometric titration with a modified carbon paste mercury sensor, *Electroanal.*, 19 (2007) 1055-1061.
- [57] T. Bandoz, Activated Carbon Surfaces in Environmental Remediation, Academic Press, Amsterdam, The Netherlands, 2006.
- [58] J.W. Gaskin, C. Steiner, K. Harris, K.C. Das, B. Bibens, Effect of low-temperature pyrolysis conditions on biochar for agricultural use, *Trans. ASABE*, 51 (2008) 2061-2069.
- [59] K. Xia, U.L. Skjellberg, W.F. Bleam, P.R. Bloom, E.A. Nater, P.A. Helmke, X-ray absorption spectroscopic evidence for the complexation of Hg(II) by reduced sulfur in soil humic substances, *Environ. Sci. Technol.*, 33 (1999) 257-261.
- [60] D. Hesterberg, J.W. Chou, K.J. Hutchison, D.E. Sayers, Bonding of Hg(II) to reduced organic sulfur in humic acid as affected by S/Hg ratio, *Environ. Sci. Technol.*, 35 (2001) 2741-2745.
- [61] M. Haitzer, G.R. Aiken, J.N. Ryan, Binding of mercury(II) to dissolved organic matter: The role of the mercury-to-DOM concentration ratio, *Environ. Sci. Technol.*, 36 (2002) 3564-3570.
- [62] E.A. Kim, Y. Masue-Slowey, S. Fendorf, R.G. Luthy, Intra-particle migration of mercury in granular polysulfide-rubber-coated activated carbon (PSR-AC), *Chemosphere*, 86 (2012) 648-654.
- [63] F.E. Huggins, N. Yap, G.P. Huffman, C.L. Senior, XAFS characterization of mercury captured from combustion gases on sorbents at low temperatures, *Fuel Process. Technol.*, 82 (2003) 167-196.
- [64] Y.H. Li, C.W. Lee, B.K. Gullett, The effect of activated carbon surface moisture on low temperature mercury adsorption, *Carbon*, 40 (2002) 65-72.
- [65] E.I. El-Shafey, Removal of Zn(II) and Hg(II) from aqueous solution on a carbonaceous sorbent chemically prepared from rice husk, *J. Hazard. Mater.*, 175 (2010) 319-327.