Stabilization of Mercury and Methyl Mercury by Biochars in Water/Sediment Microcosms

Peng Liu, Carol Ptacek, David Blowes, Krista Paulson, Jing Ma, and Alana Ou Wang

Department of Earth and Environmental Sciences
University of Waterloo
Waterloo, Ontario, Canada

Introduction

Previous studies have focused on the addition of biochar to South River sediments as an amendment to control dissolved Hg concentrations and to limit the production of methyl mercury (MeHg). These studies were either conducted as short-term laboratory experiments in a controlled environment, or as longer-term field experiments in a less controlled setting. The studies described here focus on evaluating the effectiveness of biochar amendments for controlling Hg and MeHg in saturated, anaerobic microcosm experiments in a laboratory setting over longer time-frames than has previously been investigated. The effectiveness of amending South River sediment with multiple sources of biochars also was evaluated over these longer time frames to provide a direct comparison of treatment effectiveness for different biochar materials.

Specific Questions Addressed

1) Will the amendment of sediments with biochar promote Hg binding over an extended time period?
2) What is the nature of the binding mechanism between Hg and biochar?
3) Will net MeHg production increase due to the release of elevated sulfate, dissolved organic carbon (DOC), and organic acids (OA) associated with the addition of biochar?
4) Are there differences in Hg stabilization and MeHg production for the difference biochar sources?

Experiments

Cowboy charcoal (CL2), low- and high-T switchgrass biochar (GR4L and GR4H), high-T poultry manure (MP1H), and activated carbon (AC) were selected as amendments to South River sediment collected from RRM 3.5 (labelled SRD). The biochar, sediment, and South River water (SRW) were mixed at a ratio of 1:20:80 by mass (5 g, 100 g, and 800 mL) (Figure 1). Mixtures containing SRW and biochar only, and SRW and sediment only, were used as controls. The microcosm experiments were conducted in an anaerobic glovebox.
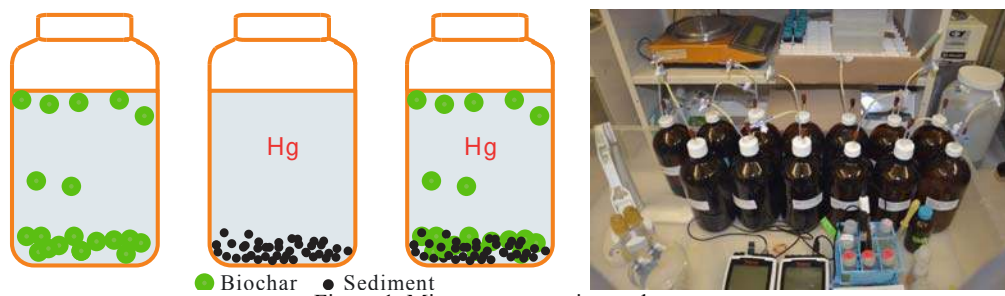
Biochar   Sediment
Figure 1. Microcosm experimental setup.

The aqueous phase was sampled as a function of time for analyses of pH, Eh, alkalinity, total Hg (tHg), MeHg, anions, cations, NH_3-N, PO_4-P, organic acids (OAs), and DOC. The solid phase was sampled as a function of time for analyses of tHg, MeHg, Hg sequential extraction, and pyrosequencing analyses. The biochar particles were separated and prepared for thin-sections. The thin-sections were analyzed for X-ray fluorescence (XRF) mapping of S, Hg, Cu, Fe, and Mn and X-ray spectroscopy (XAS) of S, Hg, Cu, and Fe.

Results

Chemical composition of aqueous solutions:

Determinations of aqueous concentrations of tHg as a function of time showed elevated concentrations of tHg in the sediment control, reaching values of approximately 40 µg L^{-1} (Figure 2). During the first few weeks of the experiment, there was little difference in tHg between the control and the mixtures containing biochar. Reductions in tHg concentrations of 50% relative to the control were observed after 30 days for the activated carbon (AC), after 90 days for the high-T poultry manure biochar (MP1H), and 120 days for the low-T switchgrass biochar (GR4L) and the high-T switchgrass biochar (GR4H) amendments. Similar decreases in aqueous concentrations of tHg were not observed in the duplicate amendment systems containing Cowboy Charcoal (CL2) over the duration of the experiment. The concentrations of tHg in the control and amendment systems were highly variable over the duration of the experiments, especially in the mixtures containing low-T switchgrass biochar (GR4L) and high-T switchgrass biochar (GR4H). The tHg concentrations in the duplicate amendment systems containing Cowboy Charcoal (CL2) were more variable than those observed in the high-T poultry manure biochar (MP1H) amendment. The tHg concentrations in the high-T switchgrass biochar (GR4H) amendment were lower than the low-T switchgrass biochar (GR4L) amendment during the first 120 days, and then increased at later times. The observed reductions in tHg in the aqueous phases were: activated carbon (AC) > high-T poultry manure biochar (MP1H) > low-T switchgrass biochar (GR4L) > high-T switchgrass biochar (GR4H) > Cowboy Charcoal (CL2).
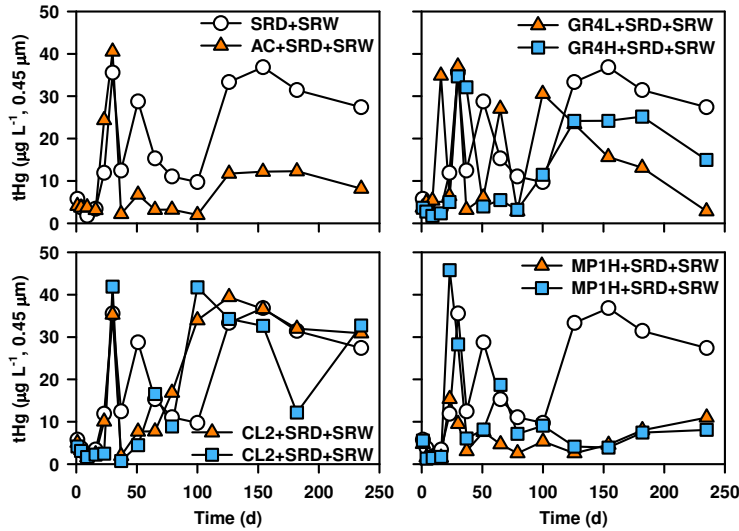
Figure 2. Aqueous concentrations of tHg (0.45 µm filtered) in SRD control (open circles) and amendment systems (triangles and squares) versus time.

Concentrations of MeHg as a function of time reached maximum values of close to 40 ng L^{-1} in the sediment control (Figure 3). Similar or lower concentrations of MeHg were observed in the mixtures containing biochar. The peak concentration in activated carbon (AC) amendment system was higher than the control. The MeHg concentrations in the duplicate Cowboy Charcoal (CL2) amendment systems were the lowest compared to the control and the other amendment systems. The MeHg concentrations in the low-T switchgrass biochar (GR4L) and high-T switchgrass biochar (GR4H) were lower than those in the control during the first 100 days, but higher after 180 days. The peak concentrations in the high-T poultry manure biochar (MP1H) amendments were lower than that in the control, but persisted at elevated concentrations for longer. The MeHg concentrations in the mixtures containing activated carbon (AC) and high-T poultry manure biochar (MP1H) were lower than the control after 90 and 150 days, respectively. The rank in order of removal efficiency of MeHg was: Cowboy Charcoal (CL2) > high-T switchgrass biochar (GR4H) > low-T switchgrass biochar (GR4L) > activated carbon (AC) > high-T poultry manure biochar (MP1H).
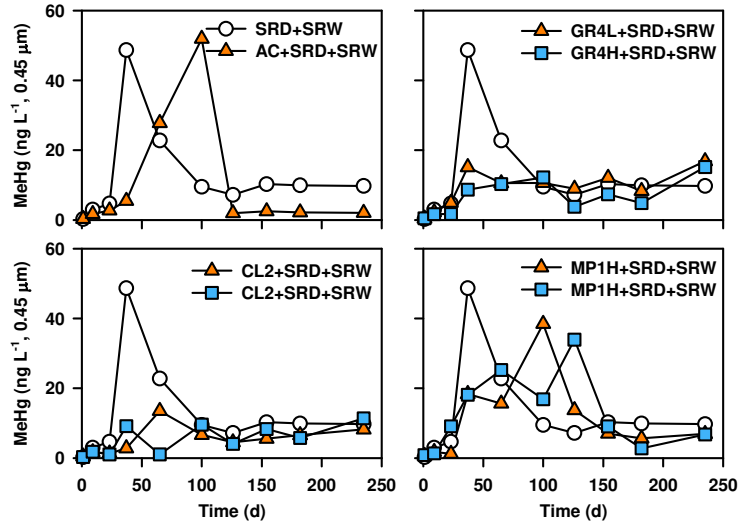
Figure 3. Aqueous concentrations of MeHg (0.45 μm filtered) in SRD control (open circles) and amendment systems (triangles and squares) versus time.

The highest sulfate concentrations were observed in the duplicate batch with high-T poultry manure biochar (MP1H) as an amendment (Figure 4), which is consistent with previously reported results showing elevated aqueous sulfate concentrations in short-duration batch systems containing high-T poultry manure biochar (Ptacek et al., 2013). The concentrations of sulfate in the amendment containing Cowboy Charcoal (CL2) decreased at a rate similar to the control. The concentrations of sulfate in the activated carbon (AC) and high-T switchgrass biochar (GR4H) mixtures were higher than in the control. The higher sulfate concentrations in the activated carbon (AC) amendment system are attributed to the leaching of sulfate from activated carbon (AC) (Ptacek et al., 2013). The relatively rapid decrease in sulfate concentrations in the low-T switchgrass biochar (GR4L) may be due to the activity of SRB coupled to the presence of elevated acetate in the low-T switchgrass biochar (GR4L) amendments.
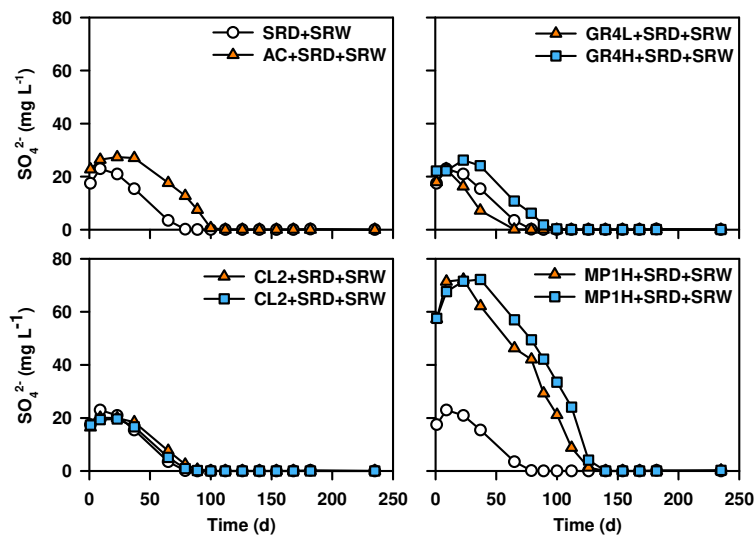

Figure 4. Aqueous sulfate concentrations in the SRD control (open circles) and amendment systems (triangles and squares) versus time.

Sulfate-reducing bacteria are the major contributors to Hg methylation (Benoit et al., 2001; Gilmour et al., 1992). The low MeHg concentrations in Cowboy Charcoal (CL2), high-T switchgrass biochar (GR4H), and low-T switchgrass biochar (GR4L) are consistent with the low sulfate concentrations in these amendments (Figure 3). The elevated sulfate concentrations observed in activated carbon (AC) and high T poultry manure biochar (MP1H) amendment systems correlate to elevated MeHg concentrations. The low tHg concentrations in these amendments also may partly be due to the elevated concentrations of sulfate which can be converted to sulfide. Sulfide can scavenge Hg by forming mercury sulfide precipitates.

Solid-phase characterization:

The X-ray fluorescence (XRF) mapping is an elemental analysis technique which allows the examination of the distribution of an element of interest in a particle or a small area of a particle. The XRF mapping can simultaneously illustrate the spatial distribution of several elements at one time, which can help to define the binding environment and hot spots of an element of interest. The XRF maps are presented for Hg and Fe in a fresh SRD particle (Figure 5, top) and for Hg, S, Fe, Cu, and Mn in a reacted particle of Cowboy Charcoal (Figure 5, bottom) at day 235 of the experiment. Maps for S, Cu, and Mn in the fresh SRD particle were also collected, however the signals were poor, which indicates that the concentrations of these elements also were low in this particle. The results indicate that the particle of fresh SRD had an elevated Fe content and the Hg hot spot was near the surface of this particle. This particle was likely iron oxide. The Hg on the surface was not associated with S, given that a low S content was observed.
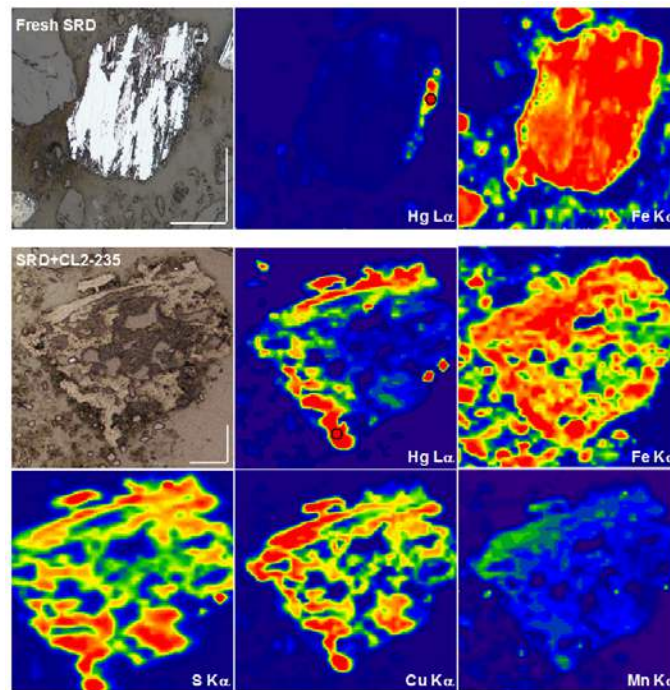

Figure 5: Top: Microscope photo of fresh SRD sediment and X-ray fluorescence maps for Hg Lα and Fe Kα X-ray fluorescence (XRF), and Bottom: Microscope photo and XRF maps for Hg Lα, Fe Kα, S Kα, Cu Kα, and Mn Kα for a grain of Cowboy Charcoal (CL2) after 235 days i in thin-sections. The white bars in the microscope photo represent 0.1 mm. The EXAFS spectra for modeling were collected inside the black circles.

The Hg in the particle of Cowboy Charcoal in the CL2 amendment were observed to co-exist with S, Fe, Cu, and Mn. The Hg, Cu, and Fe were likely in sulfide forms as high S contents were observed. The Cu and Fe were also likely in reduced forms. The thin-section samples of activated carbon (AC), low-T switchgrass biochar (GR4L), high-T switchgrass biochar (GR4H), and high-T poultry manure biochar (MP1H) amendments and the control at day 235 were also mapped with XRF, however similar particles were not observed.

X-ray Absorption Near-Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) are regions of the spectra acquired from X-ray absorption spectroscopy (XAS). XANES spectra can help to define the oxidation state of an element and its primary binding environment. EXAFS spectra can help to define the local structural information (binding elements, coordination number, bond length, etc.) of the atom of interest. The EXAFS spectra were modeled for Hg in the hot spot observed in the fresh SRD sediment and for Hg and Cu in the Cowboy Charcoal (CL2) particle (Figure 6). The best fit of the Hg spectra collected for fresh SRD was obtained using Hg_2Cl_2 as the model compound, whereas the best fit of the Hg spectra collected for the Cowboy Charcoal (CL2) particle was obtained using cinnabar as a model compound. The best fit for the Cu spectra was obtained using Cu_2S as a model compound. The Hg spectra for the particle in the Cowboy Charcoal (CL2) amendment is consistent with cinnabar, which is relatively stable in the environment. These observations suggest the potential transformation of Hg as Hg_2Cl_2 to Hg in cinnabar. This transformation to a more stable form of Hg within the biochar grain may be associated with a decrease in bioavailability of Hg in Cowboy Charcoal (CL2) amendment.
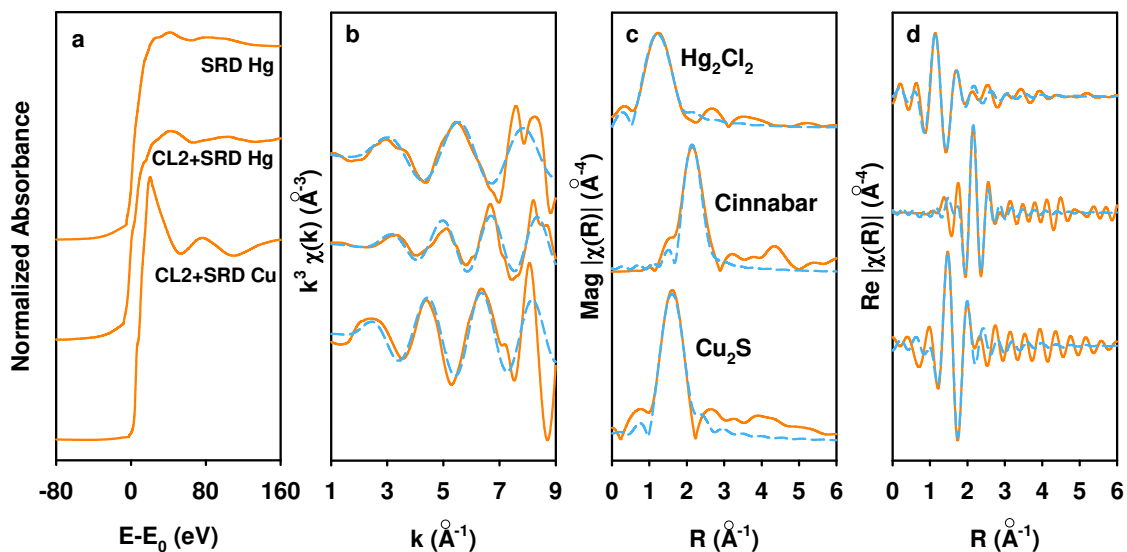

Figure 6. [a] Edge-step normalized Cu K-edge and Hg LIII-edge XANES spectra of fresh SRD and Cowboy Charcoal (CL2) in an amendment after 235 days. [b] k3-weighted chi spectra (orange solid line) and the best fit data (light blue dash line). [c] Fourier-transfor m magnitude spectra and the best fit data. The spectra were best fitted by these reference materials. Fourier transform data were not corrected for a phase shift. [d] Fourier-transform real part and the best fit data. The Hg and Cu XANES spectra are plotted relative to *E0* of 12 284 and 8 979 eV, respectively.

Summary and Implications

Long-term batch experiments were conducted to evaluate the effectiveness of biochar as an amendment for controlling Hg in South River sediments. Different biochar materials were co-blended with the sediments and maintained under saturated conditions in an anoxic environment. These mixtures were periodically sampled to determine the aqueous concentrations of Hg, MeHg and other geochemical parameters. Solid-phase samples were periodically collected and analysed for mineralogical and geochemical parameters. Large reductions in aqueous Hg concentrations were not observed at early times, but were followed by larger reductions in total Hg as the experiments progressed. Concentrations of MeHg in Cowboy Charcoal (CL2) and low- and high-T switchgrass (GR4L and GR4H) were lower than the sediment control. The sulfate concentration decreased in the sediment control and amendments as the experiments progressed. The XAS studies indicated Hg in Hg_2Cl_2 form was near the surface of a Fe-bearing particle in fresh SRD sediment. Hg in cinnabar form was observed to be co-precipitated with S, Fe, Cu, and Mn in a particle from Cowboy Charcoal (CL2) amendment. Similar particles were not isolated from other biochar mixtures.

The decrease in Hg and sulfate concentrations from aqueous solution and the characterization of Hg in the XAS studies suggest a potential transformation pathway for Hg from a soluble form to the insoluble cinnabar during long-term contact with Cowboy Charcoal biochar. A possible pathway leading to this transformation was: 1) After Hg_2Cl_2-bearing sediment, Fe(III) oxide particles and Cowboy Charcoal (CL2) particles were blended, the system became progressively reduced causing dissolution of the Fe(III) oxide phases, possibly releasing Cu and Hg into solution, 2) Meanwhile sulfate from the sediment was reduced to form sulfide. 3) A suitable environment was provided within the Cowboy Charcoal (CL2) particle for the co-precipitation of Hg, S, Fe, Cu, and Mn.

The occurrence of cinnabar within the biochar particle indicates that the accumulation of Hg is within the biochar structure. This result suggests that in addition to Hg being present as an insoluble phase, it is present within the biochar structure. Biochar contains reduced C which may provide a geochemical environment where cinnibar may be more resistant to reoxidation.

This document describes the major findings of this study to date. Additional analyses are currently being conducted using XAS and other techniques to evaluate whether the phases identified occur elsewhere in the biochar or are relatively sparse.

References

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