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Activated Carbon and Biochar Reduce Mercury Methylation Potentials in Aquatic Sediments

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Abstract Much of the toxic methylmercury (MeHg) that biomagnifies in the aquatic food chain and accumulates in fish and seafood is believed to originate from microbial methylation of inorganic Hg^{+2} in anoxic sediments. We examined the effect amending wetland sediments with activated carbon and biochar on Hg methylation potentials using microcosms and Hg stable isotope tracers. The inorganic $^{200}Hg^{+2}$ spike was methylated at ~0.37 %/day in the untreated sediment, but that rate decreased to <0.08 %/day for the amended sediments, with 80 % and 88 % reductions in methylation rates for activated carbon and biochar amendments, respectively. Demethylation rates were relatively unchanged. Our key finding is that amending contaminated sediment with activated carbon and biochar decreases bioavailable Hg, and thus may also decrease Hg transfer into food webs. However, further research is needed to evaluate exactly how the sorbents impact Hg methylation rates and for related field studies.

Keywords Mercury · Methylmercury · Methylation · Wetland sediment · Activated carbon · Biochar · In situ remediation

Mercury (Hg), a pervasive global contaminant that is dispersed through the atmosphere, has no known role in biological systems (Clarkson and Fitzgerald 1991). While it occurs naturally in the environment, anthropogenic activities, such as mining, fossil fuel burning, and certain industrial processes have increased the amount of Hg present in atmospheric, aquatic, and terrestrial systems (Selin 2009). Mercury deposits to the earth's surface primarily as Hg^{+2} via wet precipitation (Prestbo and Gay 2009). Mercury can also adsorb onto aerosols, such as soot, which occur chiefly over land where aerosols are more abundant, and this promotes deposition near point sources (Zhang et al. 2009). Once deposited, Hg^{+2} can be reduced to Hg^0 by certain microorganisms and re-emitted to the atmosphere, or it can be microbially converted to methylmercury (MeHg) (Driscoll et al. 2013). Further, Hg^{+2} deposited in watersheds is transported via runoff to lakes, where methylation is enhanced in anoxic sediments by sulfate reducing bacteria (Compeau and Bartha 1985). The resultant MeHg, a neurotoxin and teratogen, is incorporated into primary producers and biomagnifies in the aquatic food chain reaching high concentrations in large predatory fish (Sunderland 2007; Pickhardt and Fisher 2007). This is of particular concern for humans that rely on fish for a major component of their diet (Zahir et al. 2005).

Sediments are complex deposits of inorganic and organic matter that serve as a natural storage system many anthropogenic contaminants, such as heavy metals and hydrophobic organic compounds (HOCs). Within sediments, naturally occurring carbonaceous particles, such as coal and soot, have been shown to harbor organic contaminants and reduce their bioavailability (Ghosh et al. 2000). This has led to the study of in situ sorbent amendments as an alternative to traditional approaches for remediation of contaminated sediments because traditional approaches, such as dredging and disposal, can be costly, resuspend and mobilize contaminants, and have uncertain outcomes (Ghosh et al. 2011; Gilmour et al. 2013). When mixed with sediments sorbents can strongly bind with contaminants effectively reducing their pore water concentrations and bioavailability (Gilmour et al. 2013). Most

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in situ sorbent remediation work has focused on HOCs, with activated carbon (AC) showing promise as a cost-effective amendment for HOCs, including classes of notorious pollutants such as PCBs and PAHs (Ghosh et al. 2011).

Activated carbon is composed of defective graphene layers, which are formed by selective gasification of carbon atoms via thermal activation or treatment with chemicals; it is also filled with pores that greatly increase surface area and intensify van der Waals forces, which enhances its ability to adsorb a wide range of molecular species (Marsh and Reinoso 2006).

Biochar is another sorbent that has reduced the bioavailability and/or mobility of contaminants in sediments (Gomez-Eyles et al. 2013). It is attractive as a potential remediation material because it is becoming more readily available (and less costly) as biomass fuels are explored as a component of renewable energy. Biochar can be described as a carbon-rich, porous, fine-grained substance produced by thermally decomposing biomass under low oxygen concentrations and temperatures between 300 and 1000°C. The major difference between AC and biochar is that the former has undergone treatment specifically to increase its porosity.

Inorganic Hg and MeHg strongly sorb to organic matter in sediments reducing partitioning to the pore water and decreasing bioaccumulation by benthic organisms (Schartup et al. 2013; Gilmour et al. 2013). Yet few studies evaluating carbonaceous sorbents for in situ remediation of contaminated sediments have targeted Hg species. Recently, biochar and AC carbon were shown to mitigate Hg and MeHg bioavailability in contaminated sediments in microcosm assays (Gilmour et al. 2013). In another study, sorption capacities for inorganic Hg were found to be 1–2 orders of magnitude higher for AC compared to biochar, but were similar for MeHg (Gomez-Eyles et al. 2013). However, further research is needed to understand and evaluate this potential remediation approach, and to assess the impact these sorbents have on Hg methylation/demethylation rates.

Here we present results from preliminary tests evaluating the impact of biochar and AC amendments on net MeHg production in wetland sediments at environmentally relevant concentrations. Using a species specific stable isotope technique, we traced the formation of MeHg in sediment from a wetland previously found to have relatively high levels of Hg in fish. The study design included microcosms grouped into four categories: (1) no amendments, (2) autoclaved with no amendments, (3) amended with biochar, and (4) amended with AC. This initial work focused solely on methylation rates and did not include pore water measurements or microbial techniques.

Materials and Methods

Sediment was collected from the top 10 cm from a ~2 acre wetland near the University of Mississippi campus, in Oxford, MS, USA. The wetland was previously found to have largemouth bass (*Micropterus salmoides*) exceeding 1 μg/kg of Hg in their skeletal muscle (unpublished data). The sediment was immediately brought back to the laboratory, homogenized using gloved hands, and dispensed in ~100 g aliquots into twenty 125 mL acid-washed amber glass jars. The water content of the sediment was ~20 %. No additional water was added to the sediment.

Biochar from gasification of pinewood at ~830°C was obtained from the Mlsna research group at Mississippi State University. Activated carbon prepared from coconut shells was purchased from Sargent-Welch (Rochester, NY). The sorbents were further ground with a mortar and pestle and sieved, with particles in the 250–500 μm being used in this study. To drive off surface-bound Hg from the sorbents, amendments were "heat cleaned" in a vacuum oven at 170°C for 24 h and stored in plastic bags prior to use.

Enriched isotopes of ^{199}HgO and ^{200}HgO were purchased from Oak Ridge National Laboratory and dissolved in 10 % optima grade nitric acid. Me^{199}Hg was synthesized using methylcobalamin (Martín-Doimeadios et al. 2002). Concentrations of the spike solutions were determined using reverse isotope dilution analysis. The Me^{199}Hg^{+} and ^{200}Hg^{2+} spikes were prepared by diluting a portion of the stock solutions with bottom water from the wetland site.

Sample jars containing the sediment were grouped into four categories (each with five replicates): (1) no amendments, (2) autoclaved with no amendments, (3) biochar amended, and (4) AC amended. Sorbents were added to the amended samples to attain a 5 % mixture (dry weight). All samples were spiked with Me^{199}Hg and ^{200}Hg^{2+} at ~80 % of the ambient levels in the sediment (spike preparation is discussed below). Spiked samples were homogenized by mixing with a plastic spatula. Samples for autoclaving were covered with aluminum foil and were twice heated at 121°C for 20 min, with treatments separated by 24 h. All samples were placed into a vacuum oven, which was continually purged with nitrogen, and allowed to incubate in the dark for 2 weeks. The samples were then placed in a freezer at −80°C for a day and subsequently lyophilized for 7 days. The freeze-dried samples were stored in a freezer until analysis.

Methylmercury in the sediment was determined after being extracted and distilled following U.S. EPA Method 1630. The MeHg was derivatized by ethylation and analyzed by purge and trap GC-ICP-MS. This was accomplished by coupling a Tekran 2700 MeHg analyzer to a sector field inductively coupled plasma mass spectrometer

(ICP-MS) (Element-XR, Thermo). For isotope measurements, we monitored ^{199}Hg, ^{200}Hg, and ^{202}Hg in low resolution mode with a 5 % mass window and 100 points per peak. Recoveries for MeHg in estuarine sediment reference material (CC-580; IRMM, Belgium) were within 15 % of certified values. Total-Hg was determined by isotope dilution using a direct mercury analyzer coupled to the same ICPMS as described elsewhere (Bussan et al. 2015). Recoveries of DORM-3 reference material (NRC, Canada) were within 5 % of certified values.

Mercury methylation and demethylation rates were determined using species-specific enriched stable isotopes following procedures developed for sediment assays (Hintelmann and Evans 1997; Hintelmann et al. 2000; Martín-Doimeadios et al. 2004; Heyes et al. 2004). Briefly, three isotopes of Hg were monitored: one represented the newly produced MeHg from the added inorganic Hg tracer; another the demethylation of the added MeHg tracer; and a third the changes in the MeHg concentrations derived from the Hg originally present in the sample. Specific rate calculations followed the approach used by Heyes et al. (2006).

Statistical evaluation was done using STAT PLUS 2009. Analysis of variance (ANOVA) and Tukey's HSD test were used test for differences among groups. Differences were deemed significant at the $p < 0.05$ level.

Results and Discussion

Activated carbon and biochar decreased Hg methylation rates by 80 % and 88 %, respectively (Table 1). These reductions were statistically significant compared to the control (no amendment) group. The sorbents in effect halted production of MeHg to levels that nearly matched the autoclaved samples. The non-zero methylation rate for the autoclaved samples may suggest that some methylating microorganisms survived the process, or that a slight amount of abiotic methylation occurred, or both. Demethylation rates were relatively unchanged, with no statistical difference between the sorbent-amended sediment and the untreated sediment.

The methylation rate reductions observed for AC and biochar were similar in magnitude (Table 1). This is perhaps not surprising because while there appears to be greater sorption capacity for inorganic Hg for AC compared to unactivated biochar, the latter has been shown to be as effective as steam-AC for MeHg sorption (Gomez-Eyles et al. 2013). If the reduction between AC and biochar is indeed similar, and remains so in field studies, then this is a positive development for potential in situ remediation because biochar is lower in cost than AC. Also, many Hg-contaminated sites have high levels of other contaminants, such as HOCs. Because in situ carbon sequestration is an effective means of remediation for HOCs (Gomez-Eyles et al. 2013), the approach has the added benefit of reducing bioavailability of both types of contaminants.

As discussed, both AC and biochar effectively bind Hg and MeHg in sediments reducing their bioavailability (Gilmour et al. 2013). The sorbents contain surface-active functional groups such as carboxyl, hydroxyl, and phenolic groups that can bind with charged heavy metal species through electrostatic interactions via an ion exchange mechanism (Uchimiya et al. 2011). This suggests that some portion of the enriched isotope spikes may be incorporated into the sorbents, effectively removing them from the native sediment particles, its pore water, and their associated bacterial communities; this potentially confounds the methylation and demethylation rate analyses. The addition of the biochar or AC may also affect the community of microorganisms or alter their activity, which in turn could impact methylation rates. Others have shown that biochar can have both positive and negative effects on microbial-mediated carbon mineralization/decomposition (Zimmerman et al. 2011; Kuzyakov et al. 2009). The sorbents can also alter the pH of the water–sediment system, with biochar generally having a neutral to slightly alkaline effect (Ahmad et al. 2014). Changes in pH can, in turn, affect aqueous Hg speciation.

Until future work addresses whether and how these factors impacts the methylation and demethylation rate determinations, rates obtained by this method should be considered operationally defined. In any case, the amount of extractable (available) MeHg decreased >80 %, from ~0.0092 to <0.0016 nmol/g, suggesting that the amount of bioavailable MeHg decreased by at least that amount (Fig. 1). While the MeHg that is produced by microorganisms within the sediment during the incubation period could also be adsorbed on the amendments, the extraction

Table 1 Mercury methylation and demethylation rates in wetland sediment under different experimental conditions

Amendment	Rate constant (day^{-1})		M/D	% of tracer methylated (day^{-1})
	Methylation	Demethylation		
Untreated	0.00366	0.082	0.045	0.37
Autoclaved	0.00031	0.059	0.005	0.03
Biochar	0.00046	0.074	0.006	0.05
Activated carbon	0.00074	0.092	0.008	0.07

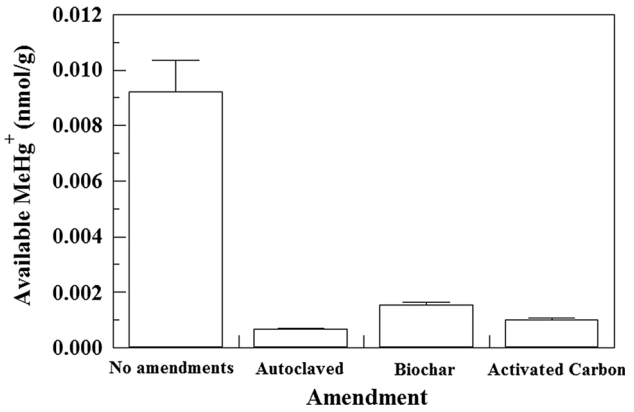

Fig. 1 Mean concentration of methylmercury recovered from each of the treated sediments (*error bars* are 1 SD)

procedures used in the analysis are believed to be sufficiently strong to retrieve this MeHg.

In summary, this preliminary study has shown that both biochar and activated carbon were effective in reducing Hg methylation rates by >80 %, without much impact on demethylation rates. These promising results deserve further attention to better understand exactly how these sorbents impact net MeHg production in sediments, and to test this potential remediation approach under field conditions.

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