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Mercury Complexation with Dissolved Organic Matter Released from Thirty-Six Types of Biochar

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Abstract
Previous studies show mercury (Hg) can be effectively removed from solution by biochar, but limited attention was paid on the complexation between Hg and components released from biochars, e.g. dissolved organic matter (DOM). Here, aqueous data from batch-style experiments were modeled using PHREEQC, incorporating thermodynamic constants between Hg and DOM, which was assumed to be composed of thiol, carboxylic, and phenolic functional groups. Modelling results suggest that > 99% Hg complexed with thiol groups in DOM. The modelled concentrations of Hg–DOM complexes from low-T (low-temperature, 300°C) biochars were greater than from high-T (600°C) biochars. The concentrations of Hg–DOM complexes were lower in wood-based than in agricultural residue- and manure-based biochars. Hg–DOM complexes may affect Hg speciation, bioavailability, transport, and methylation processes. This research describes a method to evaluate Hg–DOM interactions, and the results indicate extra caution regarding Hg–DOM complex formation is required in the selection of biochar for Hg remediation.

Keywords Mercury · Biochar · Dissolved organic matter · Complexes · PHREEQC

Biochar has been proposed as a reactive material for removing mercury (Hg) from aqueous solutions and as an additive to stabilize Hg in soils and sediments by co-blending (Bussan et al. 2016; Gomez-Eyles et al. 2013; Liu et al. 2017, 2016; Shu et al. 2016; Zhang et al. 2018). A number of studies have documented moderate to high rates of Hg uptake by biochars (Boutsika et al. 2014; Gomez-Eyles et al. 2013; Tang et al. 2015). However, primary concerns related to the application of biochar for Hg removal are the facilitated Hg transport and the conversion of inorganic Hg to more toxic methyl Hg (MeHg).

The process of producing biochars leads to the stabilization of carbon and other elements and also to the release of soluble constituents, including dissolved organic matter (DOM), anions, major cations, major nutrients, and trace elements (Jin et al. 2016; Liu et al. 2015, 2018; Xie et al. 2016; Yargicoglu et al. 2015; Zornoza et al. 2016). These components released from biochar may affect Hg speciation, distribution, transport, and bioavailability. Further understanding of the complexation between Hg and released components is required to assess the potential impacts of the use of biochar as a reactive material for removal of Hg and other contaminants.

Previous studies show DOC comprises < 0.1%–3% of the total C in biochar (Liu et al. 2015). These carbon forms can be utilized as electron donors by potential Hg methylators to convert Hg to MeHg (Desrochers et al. 2015; Kerin et al. 2006; Paulson et al. 2016). DOM is also widely known to form strong complexes with Hg^{2+} ions, a process that can affect Hg speciation (Benoit et al. 2001). DOM can potentially enhance the transport of Hg in flood plain soil, fresh water, and sediment pore water either by limiting adsorption onto solid phases or enhancing the solubility of Hg precipitates (Haitzer et al. 2002; Ravichandran 2004; Wallschläger et al. 1996). Therefore, improved understanding of the formation of Hg–DOM complexes can assist in understanding Hg complexation and bioavailability in aqueous solution.

Liu et al. (2015, 2016) evaluated a series of biochars produced from a variety of feedstocks at different pyrolysis

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temperatures. These studies focused on the effectiveness and mechanisms of Hg uptake by different groups of biochars, the forms of S and other functional groups in the biochars, and the release of soluble carbon and sulfur constituents from the biochars. The present study complements this previous work by modelling the potential formation of Hg–DOM and other complexes. These new findings are integrated with the results of Liu et al. (2015, 2016) with the overall goal of identifying biochar types that optimize Hg uptake but have minimal impacts on aqueous Hg speciation.

Materials and Methods

Thirty-six biochar samples were evaluated for Hg complexation in batch-style experiments. The feedstocks included corn cobs (CC), corn stover (CS), cocoa husk (CA), cotton seed husk (CT), wheat shaft (GR2), spent hops (GR3), switchgrass (GR4), pine mulch and bark (SW), poultry (MP) and cattle (MB) manures, and mushroom soils (MU). The feedstocks were pyrolyzed at 300°C (low-T) or 600°C (high-T). In addition, three commercial products were purchased from Wicked Good Charcoal Co. (CL1), Cowboy Charcoal Co. (CL2), and Biochar Engineering Corp. (CL5). Two batches of activated carbon (AC1 and AC2) were used as benchmark materials (Sigma-Aldrich Corp.). The experiment was conducted by mixing 2 g of biochar with 150 mL (mass ratio as 1:75) of 10 μg L^{-1} Hg-spiked water, representative of environmental Hg concentrations (Ranchou-Peyruse et al. 2009). The ratio is selected to differentiate the removal percentages of Hg using different biochars (Liu et al. 2016). No other metals were added and the mixture was reacted for 2 days. At the termination of the experiment, aqueous phase was analyzed for total Hg, anions, cations, DOC, nutrient, and trace elements. The ionic strength of the majority of the solutions were < 0.004 mol L^{-1}. Details of the biochar preparation method and experiments are described elsewhere (Liu et al. 2015, 2016).

Speciation modeling was conducted to assess the extent of complexation of Hg with inorganic species and thiol, carboxylic, and phenolic functional groups of DOM. The model calculations were executed with PHREEQCi (Parkhurst and Appelo 1999) using the MINTEQA2 database (Allison et al. 1991). The database was modified by adding thermodynamic reaction constants for Hg^{2+} and other metals (Al^{3+}, Mg^{2+}, Ca^{2+}, Cu^{2+}, Zn^{2+}, Fe^{3+}, and Fe^{2+}) with thiol, carboxylic, and phenolic ligands (Table 1). The pH, Eh, and concentrations of cations, anions, alkalinity, OAs, and DOC (Liu et al. 2015, 2016) were used as model inputs.

The following equations were used to estimate the concentrations of thiol (Eq. 1), carboxylic (Eq. 2), and phenolic (Eq. 3) ligands in DOM using DOC concentrations:

$$[DomsH] = [DOM] \times F_1 \times F_2 \times F_3 / W_S, \tag{1}$$

$$[DomcooH] = C_1 \times [DOC]/1000, \tag{2}$$

$$[DomoH] = C_2 \times [DOC]/1000, \tag{3}$$

where [DomsH], [DomcooH], and [DomoH] respectively represent the concentrations of thiol, carboxylic, and phenolic ligands in mmol L^{-1}; and [DOM] and [DOC] respectively represent the concentrations of DOM and DOC in mg L^{-1}. DOM concentrations are considered to be two times DOC concentrations by mass (Dong et al. 2010). In Eq. 1, F_1 is the total sulfur content percentage in DOM by mass, F_2 is the percentage of reduced sulfur content (thiol ligand) in total sulfur, F_3 is the percentage of reactive thiol ligand in the reduced sulfur content, and W_S is the atomic weight of sulfur. In Eqs. 2 and 3, C_1 and C_2 are the conversion factors for carboxylic and phenolic ligands from DOM, respectively. F_1, F_2, and F_3 are taken to be 0.86% (Benoit et al. 2001; Dong et al. 2010; Haitzer et al. 2003), 50% (Haitzer et al. 2003; Skyllberg et al. 2006), and 2% (Skyllberg et al. 2006), respectively. C_1 and C_2 are taken to be 9.5 and 4.1 mmol g^{-1} DOC (Lu and Allen 2002). For samples with concentrations below the method detection limit (MDL), a value of half MDL was entered for modelling purposes (Ettler et al. 2007).

Results and Discussion

The results of the batch experiments in terms of DOC, SO$_4^{2-}$, total Hg (tHg) concentrations and Hg removal are presented in Liu et al. (2015, 2016). Overall, Hg removal of > 95% was observed for the majority of the biochars. Sulfate concentrations ranged from 6.0 to 1000 mg L^{-1} in solutions mixed with the biochars and were elevated compared with the control. Concentrations of DOC varied as a function of pyrolysis temperature and raw materials. The highest concentration of DOC (148 mg L^{-1}) was observed in the batch mixture containing high-T corn stover (CS1) biochar. Relatively high concentrations of DOC were observed in the batch mixtures containing low-T agricultural residue- and manure-based biochars.

The modelling results indicate that most of the Hg in the solution was bound to thiol groups (Doms$^-$ or DomscooDoms^{2-}, > 99%) of DOM (Fig. 1). The modelled concentrations of Hg–DOM complexes were greater for low-T than for high-T biochars. The concentrations of Hg–DOM complexes were lower in charcoal and activated carbon than in other biochars as a result of low concentrations of both Hg in the spiked river water samples and DOC in the charcoal and activated carbon biochars (Liu et al. 2015, 2016). The only samples with Hg(OH)$_{2(aq)}$ as a major species were the control (river water) and high-T poultry

Table 1 Selected thermodynamic constants for Hg^{2+} and other metals with thiol, carboxylic, and phenolic ligands at a temperature of 25°C, ionic strength of 0, and pressure of 10^5 Pa

Reactions	log K	References
$DomsH^a = Doms^{-,b} + H^+$	−10	Smith et al. (2004)
$DomcooH^c = Domcoo^{-,d} + H^+$	−5.12	Temminghoff et al. (2000)
$DomoH^e = Domo^{-,f} + H^+$	−9.78	Temminghoff et al. (2000)
$Hg^{2+} + Doms^- = HgDoms^-$	28.0	Dong et al. (2010)
$Hg^{2+} + 2Doms^- = Hg(Doms)_2$	34.0	Dong et al. (2010)
$Hg^{2+} + Domcoo^- = HgDomcoo^+$	10.0	Dong et al. (2010), Gismera et al. (2007)
$Hg^{2+} + Domo^- = HgDomo^+$	8.78	Gismera et al. (2007)
$Hg^{2+} + Domcoo^- + Doms^- = DomcooHg\text{-}Doms$	31.6	Dong et al. (2010)
$Doms^- + Ca^{2+} = CaDoms^+$	2.5	Smith et al. (2004)
$Doms^- + Mn^{2+} = MnDoms^+$	4.75	Smith et al. (2004)
$Doms^- + Fe^{2+} = FeDoms^+$	6.60	Smith et al. (2004)
$Doms^- + Co^{2+} = CoDoms^+$	8.14	Smith et al. (2004)
$Doms^- + Ni^{2+} = NiDoms^+$	9.79	Smith et al. (2004)
$Doms^- + Zn^{2+} = ZnDoms^+$	9.11	Smith et al. (2004)
$Doms^- + Cd^{2+} = CdDoms^+$	10.1	Smith et al. (2004)
$Doms^- + Cu^{2+} = CuDoms^+$	14.1	Laglera and van den Berg (2003)
$Doms^- + Mg^{2+} = MgDoms^+$	2.75	Smith et al. (2004)
$Doms^- + Pb^{2+} = PbDoms^+$	12.2	Smith et al. (2004)
$Fe^{3+} + Doms^- = FeDoms^{2+}$	12.3	Berthon (1995)
$Mg^{2+} + Domcoo^- = MgDomcoo^+$	1.1	Bryan et al. (2002)
$Al^{3+} + Domcoo^- = AlDomcoo^{2+}$	2.5	Bryan et al. (2002)
$Ca^{2+} + Domcoo^- = CaDomcoo^+$	3.57	Temminghoff et al. (2000)
$Cu^{2+} + Domcoo^- = CuDomcoo^+$	5.4	Temminghoff et al. (2000)
$Fe^{2+} + Domcoo^- = FeDomcoo^+$	1.6	Bryan et al. (2002)
$Fe^{3+} + Domcoo^- = FeDomcoo^{2+}$	2.4	Bryan et al. (2002)
$Zn^{2+} + Domcoo^- = ZnDomcoo^+$	1.6	Bryan et al. (2002)
$Mg^{2+} + Domo^- = MgDomo^+$	2.58	Bryan et al. (2002)
$Al^{3+} + Domo^- = AlDomo^{2+}$	7.33	Bryan et al. (2002)
$Fe^{2+} + Domo^- = FeDomo^+$	4.27	Bryan et al. (2002)
$Fe^{3+} + Domo^- = FeDomo^{2+}$	6.99	Bryan et al. (2002)
$Zn^{2+} + Domo^- = ZnDomo^+$	4.27	Bryan et al. (2002)
$Ca^{2+} + Domo^- = CaDomo^+$	5.05	Temminghoff et al. (2000)
$Cu^{2+} + Domo^- = CuDomo^+$	10.5	Temminghoff et al. (2000)

[a] DomsH thiol functional group in DOM

[b] $Doms^-$ deprotonated thiol functional group in DOM

[c] DomcooH carboxylic functional group in DOM

[d] $Domcoo^-$ deprotonated carboxylic functional group in DOM

[e] DomoH phenolic functional group in DOM

[f] $Domo^-$ deprotonated phenolic functional group in DOM

manure and mushroom soil biochars, likely due to low concentrations of DOC and high pH (Liu et al. 2015).

The predominance of Hg–DOM complexes is likely due to the low Hg concentrations and the presence of abundant thiol functional groups (Liu et al. 2016). The greater concentrations of Hg–DOM complexes in solutions mixed with low-T biochars vs. high-T biochars are likely due to the much greater DOC concentrations released by low-T biochars (Liu et al. 2015). The relative prevalence of $Hg(OH)_{2(aq)}$ species in high-T biochars may be due to the high pH values and low DOC concentrations. When biochar is used in the field for contaminated water remediation, the geochemical parameters, solid to solution ratio, and concentrations of tHg, DOC, cations, and anions are different than considered here. Therefore, the speciation of Hg in the resulting remediated water may also be different and must be modeled using the field data.
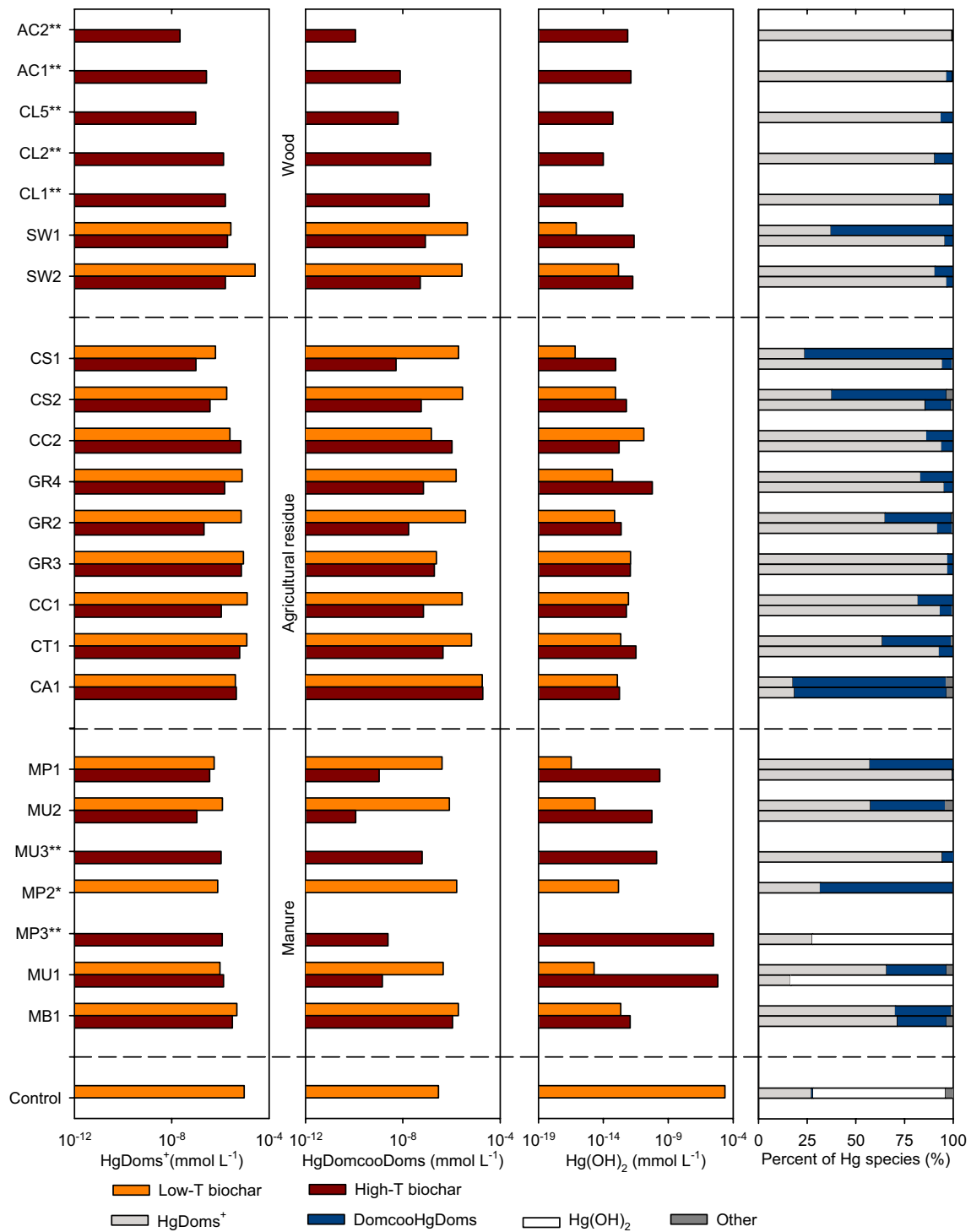
Fig. 1 PHREEQC modeling results of Hg and DOM complexes in aqueous solution in batch tests containing biochar and river water spiked with Hg. Control represents Hg-spiked river water with no biochar added. * and ** Data not available for high-T and low-T biochar, respectively

The presence of Hg–DOM complexes may affect the speciation, transformation, and bioavailability of Hg. Complexation between Hg and DOM may inhibit Hg^{2+} sorption onto surfaces of minerals and facilitate the transport of Hg from polluted soils and sediments to rivers, lakes,

and groundwater (Haitzer et al. 2002, Hsu-Kim et al. 2013; Liang et al. 2013; Wallschläger et al. 1996). For example, a study on Hg at Matagami Lake, Québec (Canada) shows an increase of tHg content correlated well with an increase of organic matter in the sediment cores (Moingt et al. 2014).

With respect to the biogeochemical role of DOM in Hg methylation, early findings indicate the bioaccumulation of Hg in food webs may be decreased by lowering the bioavailability of Hg(II) for methylation (Benoit et al. 2001), because the DOM molecules are generally too large for microbial uptake. More recent findings suggest Hg–DOM complexes promote Hg methylation by increasing the solubility of Hg compounds (Hsu-Kim et al. 2013) and providing carbon sources for Hg methylators (Chiasson-Gould et al. 2014).

Constants, including F_1, F_2, F_3, C_1, and C_2, were applied in the current study to calculate the concentrations of thiol, carboxylic and phenolic functional groups using the concentrations of DOM. The elemental composition of DOM from different sources (e.g. different types of biochar) may vary (Jamieson et al. 2014; Mancinelli et al. 2017), and the constants may also vary among the different DOM types. Therefore, future studies are required to characterize DOM and provide more data to measure or calculate the concentrations of the functional groups.

In combination with the results of Hg removal and DOC release from previous batch experiments, wood- and agricultural residue-based high-T biochars are promising reactive media for Hg removal from aqueous solution. These biochars showed high Hg removal percentages, limited release of DOC, and lower Hg–DOM complexes than the other biochars evaluated in this study.

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