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Supplemental Information

Impact of Dissolved Organic Matter on Hg and MeHg Sorption to Activated Carbon in Soils: Implications for Remediation

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Analytical Methods and QA

QA approach. Our quality control (QC) program for laboratory analyses consists of an initial demonstration of laboratory capability and the continued analysis of laboratory instrument blanks and calibration standard materials as a continuing check on performance. Appropriate lab and field blanks, continuing calibration standards, certified reference materials (where available), matrix spikes (for analyses without internal standards), and laboratory duplicates are all run at ~10% of the total sample number.

Elemental Analysis by ICP-OES. Solid samples were microwave digested Freeze-dried soil (0.100-0.125 g) was weighed into the digestion vessel, and 2.5 mL trace metal grade Nitric Acid, 1 mL trace metal grade concentrated Hydrochloric Acid, and 0.5 mL trace metal grade hydrofluoric acid were added to the vessel. The digestion vessel was capped immediately to prevent loss of S. The samples were digested with the method shown in Table S1. After the initial microwave digestion, 3 mL of cold-saturated Boric Acid (6 g/100 mL DI water) was added to each digestion vessel. The vessels were capped immediately, and the microwave digestion was run (step 2 in Table S1). The digestate was diluted with DI water prior to analysis via ICP-OES. The elemental analysis was carried out using an Optima 8300 ICP-OES (Perkin Elmer) coupled to an ESI SC-4 DX FAST sample introduction system. The ICP-OES method was a modification of EPA 200.7.¹

Anions Analysis. Anions in filtered slurry pore waters were measured using ion chromatography using an AnionPac AS18 Column on a Dionex ICS-2000 system.

Spectral analysis of dissolved organic matter. The character of DOM in pore water was assessed using proxy measures related to the UV spectrophotometric analysis of chromophoric dissolved organic matter (CDOM). These parameters included specific UV absorbance at 280 nm (SUVA₂₈₀) and the absorbance slope ratio (S_R), defined by Helms et al. (2008).² To characterize the DOM in our samples, UV absorbance was measured at wavelengths between 270 and 750 nm using clean 1 cm quartz cells on a Cary 4E UV visible spectrophotometer. SUVA₂₈₀ was calculated by dividing the UV absorbance measured at 280 nm by the concentration of DOC in the sample (units of L mg⁻¹ m⁻¹). S_R was calculated by dividing the fitted UV-absorbance slope between 275 and 295 nm by that between 350 and 400 nm (Helms et al. 2008). Both measures can be used as a first approximation of the molecular weight of DOM in the range of approximately 500–4000.^{2, 3} SUVA₂₈₀ is also related to percent aromaticity.³

Loss on Ignition. To determine loss on ignition (%LOI), triplicates of the soil sample were baked at 100 °C overnight to determine the dry weight of the soil. The dry soil sample was then baked at 450 °C overnight to obtain the weight of the ashed sample. The %LOI was calculated from the weight of sample lost via ashing.

Mercury	AC	Sequence of Spike	Initial Hg or MeHg	Initial DOM Concs.
Species		Addition	Concs. (ng/L)	(mg/L)
none	CAC-Coal	n/a	n/a	10, 40, 70, 100, 130
none	CAC-Coco	n/a	n/a	10, 40, 70, 100, 130
Hg	none	n/a	10, 40, 70, 100, 130	n/a
MeHg	none	n/a	10, 40, 70, 100, 130	n/a
Hg	CAC-Coal	Hg+DOM, then AC	10, 40, 70, 100, 130	10, 40, 70, 100, 130
Hg	CAC-Coco	Hg+DOM, then AC	10, 40, 70, 100, 130	10, 40, 70, 100, 130
Hg	CAC-Coal	AC+DOM, then Hg	10, 40, 70, 100, 130	10, 40, 70, 100, 130
Hg	CAC-Coco	AC+DOM, then Hg	10, 40, 70, 100, 130	10, 40, 70, 100, 130
MeHg	CAC-Coal	Hg+DOM, then AC	10, 40, 70, 100, 130	10, 40, 70, 100, 130
MeHg	CAC-Coco	Hg+DOM, then AC	10, 40, 70, 100, 130	10, 40, 70, 100, 130
MeHg	CAC-Coal	AC+DOM, then Hg	10, 40, 70, 100, 130	10, 40, 70, 100, 130
MeHg	CAC-Coco	AC+DOM, then Hg	10, 40, 70, 100, 130	10, 40, 70, 100, 130

Table S1. Design of mercury/SRHA/AC isotherm experiment.

Reaction	Log K	Reference
$H_2S \Leftrightarrow HS^- + H^+$	-7.02	4
$HS^{-} \Leftrightarrow S^{2^{-}} + H^{+}$	-17.4	4, 5
β -HgS _(s) + H ⁺ \Leftrightarrow Hg ²⁺ + HS ⁻	$\log K_{sp} = -38.7$	6
	$\log K_{sp} = -36.8$	7
$Hg^{2+} + HS^{-} \Leftrightarrow HgSH^{+}$	30.2	8
$Hg^{2+} + 2HS^{-} \Leftrightarrow Hg(SH)_2^{0}$	39.1	9
	37.7	10
$Hg^{2+} + 2HS^{-} \Leftrightarrow HgHS_{2}^{-} + H^{+}$	32.5	9
	31.53	10
$Hg^{2+} + 2HS^{-} \Leftrightarrow HgS_{2}^{2-} + 2H^{+}$	23.2	8
$Hg^{2+} + RS_2^{2-} \Leftrightarrow Hg(RS_2)$	42	7
$RS_2^{2-} + H^+ \Leftrightarrow RS_2H^-$	10	7
$Hg^{2+} + H_2O \Leftrightarrow HgOH^+ + H^+$	-3.4	4
$Hg^{2+} + 2H_2O \Leftrightarrow Hg(OH)_2^0 + 2H^+$	-6.2	4
$Hg^{2+} + 3H_2O \Leftrightarrow Hg(OH)_3^- + 3H^+$	-21.1	4
$Hg^{2+} + Cl^- \Leftrightarrow HgCl^+$	7.3	4
$Hg^{2+} + 2Cl^{-} \Leftrightarrow Hg(Cl)_2^0$	14	4
$Hg^{2+} + 3Cl^{-} \Leftrightarrow Hg(Cl)_{3}^{-}$	15	4
$Hg^{2+} + Cl^{-} + H_2O \Leftrightarrow HgOHCl^0 + H^+$	4.2	4
$Fe^{2+} + HS^{-} \Leftrightarrow FeS_{(s), mackinawite} + H^{+}$	3.6	4
$Fe^{2+} + HS^- \Leftrightarrow Fe(HS)^+$	5.62	11
$Fe^{2+} + 2HS^{-} \Leftrightarrow Fe(HS)_{2(aq)}$	8.95	4
$Fe^{2+} + 3HS^{-} \Leftrightarrow Fe(HS)_{3}^{-}$	10.99	4
$Fe^{2+} + H_2O \Leftrightarrow FeOH^+ + H^+$	-9.40	4
$Fe^{2+} + 2H_20 \Leftrightarrow Fe(OH)_{2(aq)} + 2H^+$	-20.49	4
$Fe^{2+} + 3H_20 \Leftrightarrow Fe(0H)_3^- + 3H^+$	-30.99	4
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$Fe^{2+} + Cl^- \Leftrightarrow FeCl^+$	-0.20	4

 Table S2. Stability constants for Hg speciation modeling

Reaction	Log K	Reference
$H_2S \Leftrightarrow HS^- + H^+$	-7.02	4
$HS^- \Leftrightarrow S^{2-} + H^+$	-17.4	4
$CH_3Hg^+ + SH^- \Leftrightarrow CH_3HgSH$	14.5	12
$CH_3Hg^+ + HS^- \Leftrightarrow H^+ + CH3HgS^-$	3.8	12
$2CH_3Hg^+ + HS^- \Leftrightarrow H^+ + (CH_3Hg)_2S$	20.1	12
$CH_3Hg+ + RS_2^{2-} \Leftrightarrow CH_3HgSR$	16.5	12
$RS_2^{2-} + H^+ \Leftrightarrow RS_2H^-$	10	13
$CH_3Hg^+ + Cl - \Leftrightarrow CH_3HgCl$	5.25	12
$CH_3Hg^+ + OH - \Leftrightarrow CH_3HgOH$	9.37	12
$Fe^{2+} + HS^{-} \Leftrightarrow FeS_{(s), mackinawite} + H^{+}$	3.6	4
	F (2)	11
$Fe^{2+} + HS^{-} \Leftrightarrow Fe(HS)^{+}$	5.62	11
$Fe^{2+} + 2HS^- \Leftrightarrow Fe(HS)_{2(aq)}$	8.95	4
$Fe^{2+} + 3HS^{-} \Leftrightarrow Fe(HS)_{3}^{-}$	10.99	4
$Fe^{2+} + H_2O \Leftrightarrow FeOH^+ + H^+$	-9.40	4
$Fe^{2+} + 2H_2O \Leftrightarrow Fe(OH)_{2(aq)} + 2H^+$	-20.49	4
$Fe^{2+} + 3H_20 \Leftrightarrow Fe(OH)_3^- + 3H^+$	-30.99	4
$Fe^{2+} + Cl^- \Leftrightarrow FeCl^+$	-0.20	4

Table S3. Stability constants for MeHg speciation

**Table S4.** Isotope spike values. Spikes were made to 1000 ml slurry bottles containing 100g wet sediment (equivalent to 13 g dry sediment).

Isotope Composition	Spike Solution Concentration	mL spike/bottle	Spike concentration in slurry bottles	Target Spike Concentration
²⁰¹ HgCl ₂	20 µg/mL	1.3	26 µg/L	2 μg/gdw in slurry bottle
Me ¹⁹⁹ HgCl	1.5 μg/mL	0.585	0.878 μg/L	67.5 ng/gdw in slurry bottle

 Table S5.
 Homogenized soil characteristics.

			Amendment amount as:							
	LOI (%)	% of dry weight	% of organic matter	Al (mg/g)	Ca (mg/g)	Fe (mg/g)	Mg (mg/g)	Mn (mg/g)	Na (mg/g)	S (mg/g)
Homogenized Berry's Creek <i>Phragmites</i> Soil	37.6	5	13	39.3	4.92	26.2	8.79	0.452	15.2	12.5

Microwave Digestion Step 1					
Power (W)	Temp (°C)	Ramp (min)	Hold (min)	Fan	
1400		5		1	
1400			20	1	
1400			28	2	
0	60			3	
Microwave Digestion Step 2					
Power (W)	Temp (°C)	Ramp (min)	Hold (min)	Fan	
1400			5	1	
1400			15	1	
0	55		0	3	

Table S6.	Microwave	digestion	method	for soil	samples.
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**Table S7.** QC summary for filterable MeHg (FMeHg), filterable total Hg (FHg), MeHg in soils, and Hg in soils analyses. Notes: No CRM is available for MeHg in water at appropriate concentration. Sample analysis was done using isotope dilution (ID), in which a spike is added to every sample and used to calculate sample concentrations.

FMeHg QC Summary				
QC Parameter	Average			
CRM (NIST 1566b Oyster Tissue)	Recovery = 96%			
ID Recovery	Recovery = $40\%$			
RPD between duplicate samples	RPD = 13.4%			
Distillation Blank	0.14 ng/L			
Detection Limit	0.56 ng/L			
MeHg in Soils QC Summary				
QC Parameter	Average			
CRM (NIST 1566b Oyster Tissue)	Recovery = 102.3%			
ID Recovery	Recovery = 87%			
RPD between duplicate samples	RPD = 7.5%			
Distillation Blank	0.52 ng/L			
Detection Limit	0.45 ng/g			

**Table S8.** QC summary for filterable total Hg (FHg) and Hg in soils analyses. Sample analysis was done using isotope dilution (ID), in which a spike is added to every sample and used to calculate sample concentrations.

FHg QC Summary				
QC Parameter	Average			
CRM (ORMS-5 Hg in River Water)	Recovery = 99%			
ID Recovery	Recovery = 96%			
RPD between duplicate samples	RPD = 4.3%			
Digestion Blank	0.71 ng/L			
Detection Limit	0.15ng/L			
Hg in Soils QC Summary				
QC Parameter	Average			
CRM (MESS-4 Marine Sediment)	128%			
ID Recovery	Recovery = 91%			
RPD between duplicate samples	RPD = 1.5%			
Digestion Blank	0.73 μg/L			
Detection Limit	0.18 µg/g			

**Table S9.** General linear models used to assess Hg and MeHg porewater and solid phase data.

Data Assessed	Model
Ambient Hg in Porewater	Hg ~ Treatment + Day + Treatment*Day
²⁰¹ Hg in Porewater	²⁰¹ Hg ~ Treatment + Day + Treatment*Day
Ambient MeHg in Porewater	MeHg ~ Treatment + Day + Treatment*Day
Me ¹⁹⁹ Hg in Porewater	Me ¹⁹⁹ Hg ~ Treatment + Day +
	Treatment*Day
Ambient Hg K	Hg K _d ~ Isotope spike + Treatment + Day +
	Treatment*Day + Treatment*Isotope Spike
²⁰¹ Hg K _d	201 Hg K _d ~ Treatment + Day
Ambient MeHg K _d	MeHg K _d ~ Treatment + Day + Isotope Spike
Me ¹⁹⁹ Hg K _d	$Me^{199}Hg K_d \sim Treatment + Day$
Ambient Molla in Soile	MeHg ~ Treatment + Day + Isotope Spike +
Alliblent Meng III Solis	Treatment*Isotope Spike
Mo ²⁰¹ II.g in Soile	Me ²⁰¹ Hg ~ Treatment + Day +
	Treatment*Day
Me ¹⁹⁹ Hg in Soils	Me ¹⁹⁹ Hg ~ Treatment + Day + Treatment*Day

**Table S10.**  $SUVA_{280}$  values from sediment-AC microcosm porewater at the 0h time point. Values represent the average of readings from two microcosms. Uncertainties represent the range of the samples.

Treatment	SUVA ₂₈₀ at 0h (L(mg C) ^{-1 m-1} )
No DOM/No AC	$1.45 \pm 0.23$
No DOM + AC	*
Low DOM +AC	$0.47 \pm 0.26$
Mid DOM + AC	0.57 ± 0.34
High DOM +AC	4.31 ± 0.95
SRHA#	4.26

*CDOM₂₈₀ reading was below the blank.

[#] Graham et al. 2012.



Figure S1. Experimental design schematic for the slurry experiment.



**Figure S2.** Sorption isotherms for Hg (top) and MeHg (bottom) onto coconut-based AC. Chloride species (squares) are plotted along with SRHA alone (circles) and along with Hg and MeHg in the presence of SRHA (diamonds).



**Figure S3.** Porewater sulfide in soil/AC microcosms. Data points represent the average of duplicate microcosms.



**Figure S4.** Average total dissolved iron concentrations in the soil/AC microcosms across all time points. Error bars represent the standard deviation of the sample measurements. There were no significant differences in porewater iron among treatment based on general linear model using appropriately transformed data.



**Figure S5.** Average pH in the soil/AC microcosms across all time points. Error bars represent the standard deviation of the sample measurements. There were no significant differences in porewater pH among treatment based on a general linear model.



**Figure S6.** Porewater DOC concentrations in the soil/AC microcosms. Data points represent the average of duplicate microcosms.



**Figure S7.** Effect of added SRHA on porewater total Hg and MeHg concentrations in ACtreated soils: (a) Ambient Total Hg; (b) ²⁰¹Hg; (c) Ambient MeHg; and (d) Me¹⁹⁹Hg. Note that the ²⁰¹Hg and Me¹⁹⁹Hg concentrations are shown on the log scale. Ambient data points are the average of two bottles; spike data points are from individual bottles. The average RPD between paired ambient Hg and MeHg bottles were 42% and 10% respectively.



**Figure S8.** Effect of added SRHA on sediment total Hg and MeHg concentrations in AC-treated soils. Ambient data points are the average of two bottles; spike data points are from individual bottles. The average RPD between paired ambient Hg and MeHg bottles were 8% and 34% respectively



**Figure S9.** Soil:water distribution coefficients for Hg and MeHg in AC-treated soils: (a) Ambient Total Hg; (b)  201 Hg; (c) Ambient MeHg; and (d) Me 199 Hg. Ambient data points are the average of two bottles; spike data points are from individual bottles. Sediment:water partition coefficients (K_d) were calculated as the sediment concentration in ng/kg divided by the pore water concentration in ng/L. The average RPD between paired ambient Hg and MeHg bottles were 55% and 29% respectively



**Figure S10.** Calculated filter-passing inorganic ²⁰¹Hg(II) speciation in the microcosms. Stability constants are listed in Tables S4. Speciation calculation inputs and outputs are shown in the supplemental spreadsheet. Calculations were performed using two values of the solubility product (Ksp) for the reaction Hg²⁺ + HS⁻ =  $\beta$ -HgS_(s) + H⁺ (Drott et al. 2013, Smith and Martell 1993); and two values for the stability constants for Hg(SH)₂ and HgS₂²⁻ (Drott et al. 2013, Schwarzenbach and Widmer 1963). RS represents thiol moieties on DOM.



**Figure S11.** Calculated filter-passing MeHg speciation in the microcosms. Stability constants are listed in Table S5. Speciation calculation inputs and outputs are shown in the supplemental spreadsheet. RS represents thiol moieties on DOM.



**Figure S12.** Calculated filter-passing Me¹⁹⁹Hg speciation in the microcosms. Stability constants are listed in Table S5. Speciation calculation inputs and outputs are shown in the supplemental spreadsheet. RS represents thiol moieties on DOM.



**Figure S13.** Calculated filter-passing inorganic Hg(II) speciation as a function of total Hg concentration and total sulfide concentration ([H₂S]T) under the average conditions in the experimental bottles (pH 7.2, total Fe 4E-6M, Cl- 2E-2M, RSH 2E-6M. In this model RS represents thiol moieties on DOM. Metacinnabar ( $\beta$ -HgS(s)) precipitates in the area below the diagonal lines. Above the line metacinnabar is undersaturated and dissolved Hg–S species ( $\Sigma$ HgS_(aq)), particularly Hg(SH)₂ and HgS₂²⁻ predominate. Red bars show the range of experimental conditions. Calculations were performed using two values of the solubility product (K_{sp}) for the reaction Hg²⁺ + HS⁻ =  $\beta$ -HgS_(s) + H⁺ (Drott et al. 2013, Smith and Martell 1993); and two values for the stability constants for Hg(SH)₂ and HgS₂²⁻ (Drott et al. 2013, Schwarzenbach and Widmer 1963).

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