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Environmental significance statement

Activated carbon is being developed as an *in situ* remediation treatment for mercury and methylmercury-contaminated soils. However, the effectiveness of activated carbon varies depending on the geochemical characteristics of the contaminated soil. A greater understanding of the impact of soil geochemistry on activated carbon efficacy for mercury and methylmercury is needed to guide the full-scale adoption of activated carbon as a remediation tool. This study is the first to employ laboratory experiments to examine how dissolved organic matter impacts mercury and methylmercury sorption to activated carbon under environmentally relevant conditions. The results show that in typical wetland soils, dissolved organic matter does not impact methylmercury sorption to activated carbon but decreases the sorption of mercury in a concentration dependent manner.

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

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ABSTRACT

Activated carbon (AC) amendments have shown promise in reducing inorganic mercury (Hg(II) complexes, “Hg”) and methylmercury (MeHg) risk in contaminated soils. However, the effectiveness of AC in Hg and MeHg immobilization has varied among studies, suggesting that site biogeochemistry might dictate efficacy. In this study, we examine the effect of dissolved organic matter (DOM) on MeHg and Hg sorption to AC. We evaluated the impact of Suwannee River Humic Acid (SRHA) on sorption to AC directly using an isotherm approach and in a soil/AC mixture using slurry microcosms. Aqueous sorption coefficients to AC (log K_{AC}) for Hg-SRHA and MeHg-SRHA complexes were one to two orders of magnitude lower (Hg-SRHA = 4.53, MeHgSRHA = 4.35) than those for chloride complexes ($HgCl_2$ = 6.55, MeHgCl = 4.90) and more closely resembled the log K_{AC} of SRHA (3.64). In anoxic, sulfidic soil slurries, the K_{AC} for sulfide species appears stronger than for chloride or SRHA species for both Hg and MeHg. AC significantly reduced porewater concentrations of both ambient MeHg and a fresh $Me^{199}Hg$ spike, and the addition of up to 60 mg/L SRHA did not reduce sorption to AC. The AC also reduced ambient Hg and ^{201}Hg porewater concentrations, but as SRHA concentration increased, the magnitude of solid phase sorption decreased. Speciation modeling revealed that SRHA may have impacted Hg distribution to the solid phase by reducing HgS precipitation. This study highlights the need for site-specific evaluation of AC efficacy and the value in developing biogeochemical models of AC performance for Hg.

INTRODUCTION

Until recently, remediation options for mercury-contaminated sediments and soils have mainly been limited to dredging or capping.[1] While these methods have successfully addressed mercury (Hg) exposure at many sites,[2-5] they can also be costly, ecologically destructive, and not always effective in permanently immobilizing contaminants.[2, 6-8] A potential alternative is the use of *in situ* sorbent amendments. Sorbents can increase the distribution of Hg and methylmercury (MeHg) to the solid phase, decreasing porewater concentrations, efflux, and bioaccumulation.[9-13]

Several amendments have been tested for *in situ* sediment and soil Hg and MeHg remediation, including ferrous and zero valent iron,[10, 11, 14] organoclays,[9] Thiol-SAMMS,[9] biochar,[9, 10, 13, 15] AC,[9-11, 16, 17] and sulfur-modified AC.[17] Under environmentally realistic conditions in sediments and soils, AC has outperformed most other sorbent amendments for Hg and MeHg sorption, the exception being sulfidized and thiolated sorbents,[9, 17] which can be more expensive. $HgCl_2$ and MeHgCl sorption to AC is higher (log K of ~6-7 and ~5, respectively)[18] than to ferric oxides (log K ~3-4),[19] manganese oxides (log K ~3-4),[19] and in most sediments (log K of ~3-6).[1, 19, 20]

AC is already a mainstream remediation tool for sediments contaminated with hydrophobic organic contaminants such as polychlorinated biphenyls and pesticides.[21] AC is manufactured from coal or biomass material. Activation by treatment at a high temperature under controlled oxidation creates a highly porous structure with desired surface functionality and a high sorption capacity.[22] AC provides an extensive internal surface area that can be very effective for adsorbing both hydrophobic and ionizable aromatic compounds through $\pi-\pi$ and $\pi^*-\pi$ interactions,[23] H-bonding, and van der Waals interactions.[24]

However, activated carbon amendment efficacy in Hg remediation varies with site geochemistry, presenting a barrier to widespread adoption as a remediation tool.[12, 13, 17] There is a critical need for research to determine the environmental parameters controlling AC effectiveness so that a rubric for AC application can be developed. For Hg and MeHg remediation in particular, there is a need to understand how the biogeochemical parameters that drive Hg and MeHg speciation in the environment (e.g. sulfide and dissolved organic matter (DOM) concentration) impact sorption onto AC.

While simple Hg and MeHg chloride complexes display equilibrium sorption coefficients to AC (K_{AC}, L/kg) that are similar to those for hydrophobic organic contaminants,[18] Hg and MeHg are commonly present in nature as complexes with organic matter or sulfides.[25] The sorption coefficients for these complexes with AC are unknown, and the influence of DOM on Hg and MeHg sorption to AC has not been evaluated. DOM could alter the K_{AC}, and/or the kinetics of sorption, in several ways. The K_{AC} for Hg- and MeHg-DOM complexes are likely to be lower than that the K_{AC} for Hg and MeHg chloride complexes.

Further, DOM sorption by AC could reduce the concentration of DOM complexes available for binding Hg and MeHg.[16] DOM coatings of mineral surfaces have been shown to enhance Hg and MeHg sorption and could have the same impact on AC.[19] Or, DOM may impact AC performance by blocking or “fouling” AC sorption sites. Reported attenuation factors for DOM fouling range between three and sixteen for PCB and phenanthrene sorption to AC in the presence of sediments.[26, 27] DOM sorption to AC is dependent on the AC pore size (bigger pores, more DOM sorption) and on the functional groups present on the DOM.[28] In this study, we specifically explore the influence of DOM on Hg and MeHg sorption to AC in simple aqueous systems, and in the more complex milieu of sediment.

Our endpoint for evaluating AC remediation efficacy is reduction of porewater Hg and MeHg. Although the speciation of porewater MeHg impacts its bioavailability, porewater contaminant concentrations are commonly been used as surrogates for bioavailability, and AC-mediated decreases in porewater MeHg concentration correlate with decreases in biotic uptake.[9, 11] To date, most experimental activated carbon amendments to Hg-contaminated sediments or soil microcosms have resulted in significant decreases in Hg and MeHg porewater concentrations. Reductions have ranged from little removal to better than 95%.[9-13, 16, 17] Efficacy in pore water reduction has varied with the type of carbon or biochar, the time since amendment, site chemistry and microbial processes. Amendment doses of 1-5% of the wet mass of sediment have been efficacious.

Sediment distribution coefficients (K_d, L/kg) for Hg and MeHg are useful indicators in determining the success of AC application.[9, 10] Many environmental parameters affect Hg and MeHg K_d. Distribution to the solid phase is highly dependent on the identity, concentration, and character of solid phase ligands (e.g. sulfide, iron, natural organic matter) and dissolved phase ligands (e.g. DOM). Hg and MeHg K_d values are lowest in environments with high concentrations of dissolved ligands, such as DOM.[29-35] The impact of DOM on K_d is particularly pronounced for Hg as DOM has been shown to inhibit the precipitation and aggregation of cinnabar ($HgS_{(s)}$),[36] thus holding Hg in solution and enhancing Hg availability for microbial methylation.[9, 37, 38] AC may be more effective in reducing pore water Hg and MeHg concentrations in environments where DOM concentrations are high. High DOM concentrations can lead to higher porewater concentrations of Hg and MeHg.[9, 10] When AC is applied in these environments, distribution of Hg and MeHg out of the porewater onto the solid phase is greatly improved, leading to greater apparent efficacy in the AC treatment compared to environments where distribution to the solid phase is already naturally high. [9, 10]

The objective of this study was to determine the impact of DOM concentration on Hg and MeHg distribution in a soil-AC mixture. To establish a baseline for DOM effects on sorption to AC, a series of aqueous isotherm tests were set up to determine the sorption of Hg and MeHg to AC in oligohaline water in the presence of Suwannee River Humic Acid (SRHA). To test the impact of SRHA on sorption under more environmentally relevant conditions, anoxic slurries were constructed using oligohaline, Hg-contaminated marsh soil from Berry's Creek in New Jersey. The slurries were amended with AC and spiked with varying concentrations of SRHA. The slurries were also amended with a$HgCl_2$ or MeHgCl enriched stable isotope spike to assess the distribution of newly-spiked Hg and MeHg to the solid phase. Porewater and solid phase Hg and MeHg concentrations were monitored over 21 days along with other geochemical parameters.

MATERIALS AND METHODS

Isotherm Experiments. Two commercially available ACs were chosen, both from Calgon Carbon Corporation (Moon Township, PA), one derived from bituminous coal (hereafter CAC-Coal) and the other from coconut shell (CAC-Coco). Both have been reported to exhibit strong sorption of Hg (log K_d = 6.6 for both) and MeHg (log K_d = 4.9 for CAC-Coal and 5.4 for CAC-Coco) in 3 ppt Instant Ocean water.[18] Bituminous coal-based and coconut shell-based ACs are the two most common forms of ACs available in the commercial market. Coconut shell-derived materials have been reported to have smaller pore size distributions,[39] but previous researchers have found both to perform well for sorption of PCBs.[18] Thus, these two materials were selected with a reasonable expectation that both would perform well, but with the additional possibility of a pore-size effect for contrast. Both ACs were sieved to a mesh size of 80 x 325. The CAC-Coal had a %C of 80.9, a surface area of 1116 m^2/g, a skeletal density of 1.61 g/cm^3, and a bulk density of 0.64 g/cm^3.[18] The CAC-Coco had a %C of 90.8, a surface area of 1305 m^2/g , a skeletal density of 1.45 g/cm^3, and a bulk density of 0.57 g/cm^3.[18] The DOM used was Suwannee River Humic Acid II (SRHA; International Humic Substances Society), a well-characterized, organic-rich isolate with a high degree of aromaticity that has been shown to hold Hg in solution under environmentally relevant conditions .[40] Hg and MeHg were spiked as enriched stable isotopes in the forms of $^{201}HgCl_2$ and $Me^{199}HgCl$ (Oak Ridge National Laboratories). $Me^{199}Hg$ was synthesized in-house by reacting methylcobalamin with 91.95% enriched $^{199}HgCl_2$.[41] The $^{199}HgCl_2$ and $^{201}HgCl_2$ solutions were made by dissolving ^{199}Hg and ^{201}Hg (98.11% enriched) powder in 0.1% HCl. The deionized water (DI) used in our experiments was produced via a whole-house, re-circulating deionization, RO, UV, and filtration system to a final conductivity of >22MΩ.

Sample bottles were prepared with 50 mL DI water adjusted to 3 ppt salinity with Instant Ocean™ (Spectrum Brands) to mimic the oligohaline conditions prevalent at the Hg-contaminated site where the soil for the slurry experiments was collected[42] and to be consistent with previous AC isotherm experiments.[18] Instant Ocean™ blanks were tested for Hg and MeHg as well as DOC (blank value = 0.6 mg C/L). Sodium bicarbonate (7.5 mM) was added to buffer sample pH against acidification by SRHA. AC, SRHA, and Hg or MeHg in different combinations of concentration, AC type, and sequence of addition were measured into separate 60-mL polyethylene terephthalate glycol (PETG) bottles as summarized in Table S1. To determine the importance, if any, of the sequence of addition, the constituents for each bottle were added in one of two ways: mercury and SRHA first, followed by overnight incubation at

4°C and subsequent addition of AC, or AC and SRHA first, followed by overnight incubation at 4°C and subsequent addition of mercury. Varying the sequence of DOM and Hg/MeHg addition is a way to assess whether fouling of the AC by DOM interferes with Hg and MeHg adsorption to AC. Bottles receiving AC were amended with 10 mg of the AC type indicated in Table S1. SRHA additions were selected to maintain an environmentally realistic DOM:Hg mass ratio of 10^6 in each sample. This was done to avoid saturating thiol sites on DOM, which control mercury-DOM complexation under normal conditions.[43] The SRHA was spiked over a range of 10 to 130 mg DOM/L. The ^{201}Hg and Me^{199}Hg spike additions ranged from 10 to 130 ng/L.

After the initial additions of Hg, MeHg, and DOM, all samples were incubated for 14 d with orbital shaking at 120 RPM. Incubations were carried out at 4 °C to minimize confounding effects of microbial activity. Following incubation, water was collected by filtration (0.45 μm glass microfiber filters) using disposable plastic syringes. Experimental results were interpreted by comparing measured sorption coefficients (K_{AC}, L/kg) to predicted values for DOM alone and for Hg or MeHg chloride complexes. K_{AC} for each isotherm sample was predicted by modeling equilibrium mercury speciation using MINEQL[44] (Tables S2 and S3, Supplemental Spreadsheet). Isotherm Hg, MeHg, and pH data are listed in the Supplemental Spreadsheet.

Soil Slurry Experiment Design. The slurry experiment was designed to evaluate the impact of DOM on Hg and MeHg sorption to AC in soil, using a range of Suwannee River Humic Acid II (SRHA, International Humic Substances Society) concentrations from 0 to 60 mg/L (Table 1 and Figure S1). The experiment was conducted at 4 °C to minimize confounding effects of microbial activity. The study consisted of five treatments and a total of 50 slurry bottles. One of the treatments contained no AC or SRHA. All other treatments were amended with AC at 5% of the sediment dry weight and with varying concentrations of SRHA. Half of the bottles for each treatment were spiked with $^{201}HgCl_2$ at ~10% of the ambient Hg in the soil to track Hg distribution and the other half of the bottles for each treatment were spiked with $Me^{199}HgCl$ at ~50% of the ambient MeHg of the soil to track MeHg distribution (Table S4). Hg and MeHg spike levels were chosen to provide enough mass to detect while minimizing changes in overall concentrations.

The experiment was carried out over 21 d. Bottles were destructively sampled at 0 h, 1 d, 3 d, 7 d, and 21 d. The slurry bottles were refrigerated, protected from light during incubation, and kept on icepacks during time point disassembly.

Slurry Experiment Activated Carbon. The sediment slurries were amended with a regenerated AC manufactured by Siemens. Gomez-Eyles et al. previously determined log K_{AC} values for Hg (7.28) and MeHg (5.5), which were higher than those determined for the CAC-Coal and CAC-Coco used in our isotherm experiments.[18] Gomez-Eyles et al. also used AC isotherm data in a series of modeling exercises to predict the most efficacious AC for amendment to soils with varying loss on ignition (%LOI) values.[18] Of all the amendments tested, the regenerated AC was predicted to remove the most Hg and MeHg from porewater across a range of %LOI soils. Because of its predicted performance in these models and its higher K_{AC} values for both Hg and MeHg, the regenerated AC was chosen as the amendment for our slurry microcosms. The regenerated AC was 73.3% C, had a surface area of 1150 m^2/g, a skeletal density of 1.81 g/cm^3, and a bulk density of 0.63 g/cm^3.[18] We dosed the slurry microcosms at 5% of the soil dry weight as this amendment strength was shown to be successful in previous field and laboratory studies by our group.[9, 10]

Slurry Construction. Anoxic soil slurries were constructed at a 10 to 1 liquid to solid ratio. Hg-contaminated soil (~20 μg/gdw) was obtained in November 2015 from a *Phragmites* marsh in Berry's Creek, New Jersey (salinity 0.8 to 12 ppt).[42] Surface soil (0-15 cm) was collected by shovel and transferred into two-gallon plastic buckets with locking lids. The buckets were filled completely to minimize headspace. The soil consisted of fine-grained clay trapped by *Phragmites* roots. Details of the soil chemistry are shown in Table S5. The soil was initially homogenized shortly after collection at the U.S. Army Engineer Research and Development Center by removing large *Phragmites* roots and mixing in a blender with 40% w/w addition of deionized water. The soil was stored at 4 °C for three months prior to the experiment. Immediately prior to use in the microcosm experiment, the soil was homogenized again by hand-stirring under ambient lab conditions. For slurry bottle construction, the homogenized soil was mixed with 3 ppt Instant Ocean™ water (degassed for 30 min with high-purity N_2) under anaerobic conditions (Coy Anaerobic Chamber) and then incubated anaerobically at room temperature for two weeks prior to splitting for treatment amendments to ensure fully anoxic conditions.

The slurry was divided into separate aliquots for the "No SRHA/No AC" control and AC-amended treatments six days prior to the experiment. The slurry designated for AC amendment was amended at 5% of dry weight with Siemens regenerated AC.[18] The slurry was then further divided into containers for SRHA and isotope spike amendments. These amendments were done immediately prior to the start of the experiment. SRHA was added to the designated slurries to achieve the following total DOM concentrations per liter of slurry water: 15 mg DOM/L (7.5 mg C/L), 30 mg DOM/L (15 mg C/L), and 60 mg DOM/L (30 mg C/L). For the addition, the SRHA was weighed into a small container and mixed with ~1 mL of DI water to dissolve. This 1 mL SRHA solution was added to the slurry, and the small container was rinsed twice with a small amount DI water to ensure maximum transfer of humic acid to the slurry. The slurry was mixed well by end over end shaking for approximately 2 min. The ^{201}Hg and Me^{199}Hg spikes were added immediately following the SRHA addition to start the experiment.

In the glove bag, the different slurry treatments were poured into pre-marked, acid-cleaned serum bottles. The bottles were sealed in the anaerobic chamber and then stored outside the chamber as described above. The bottles were shaken every other day to mix the contents thoroughly.

Slurry Deconstruction and Sampling. To stop the incubations at each time point, bottles were allowed to settle and then opened in a glove box. Overlying water (henceforth designated “porewater”) was immediately filtered through a 0.45-μm glass microfiber syringe filter and the filtrate was parsed and preserved for total Hg, MeHg, metals, dissolved organic carbon (DOC), anions, and sulfide measurements. An unfiltered aliquot was taken for pH measurement. The solid remaining in the bottle was frozen and then freeze-dried for elemental content and total Hg and MeHg analysis, following the methods described below and in the Supplemental Information. Total Hg, MeHg, and metals porewater aliquots were preserved at 1% (v/v) with 50% (v/v) trace metal grade HCl. The aliquot for DOC and anions was frozen until analysis. DOC was measured as mg C/L. The sulfide aliquot was preserved 1:1 with sulfide antioxidant buffer and analyzed via an ion-specific electrode calibrated with Pb-titrated standards.[45] Sulfide samples were analyzed within 6 h of the time point. Specific UV absorbance $\lambda = 280$ nm (SUVA$_{280}$) for the time zero microcosm samples was determined by measuring porewater DOC with a Shimadzu TOC-V$_{CSH}$ total organic carbon analyzer and UV absorbance at $\lambda = 280$ nm with a Cary 4E UV-vis spectrophotometer.

Hg and MeHg analyses. Hg and MeHg samples were processed and analyzed according to methods adapted from EPA methods 1630 and 1631 and previously described by Mitchell and

Gilmour (2008).[46-48] Briefly, total Hg was determined by digesting samples in hot 7:4 v/v HNO_3/H_2SO_4 (1:2 v/v sample digest acid) until sample vapors turned colorless, then further digested overnight with 1% BrCl. Stannous chloride was added to reduce Hg(II) to Hg(0) using an automated Brooks-Rand MERX system, and the sample was analyzed via isotope dilution inductively coupled plasma mass spectrometry (ID-ICP-MS). MeHg samples were distilled and analyzed via ethylation, purge and trap, gas chromatography, also using a MERX system, and ID-ICP-MS. QC data are provided in Tables S7 and S8.

Hg and MeHg Speciation Modeling. Hg and MeHg speciation modeling was performed using MINEQL v. 4.62.3[44] and Visual MINTEQ v. 3.1.[49] Stability constants are listed in Tables S2 and S3, and inputs and outputs are shown in the Supplemental Spreadsheet. DOC inputs into our models were based on thiol density estimates. For SRHA, we estimated thiol density by multiplying DOC concentrations by the molar S:C ratio (4.41 mmol/mol) provided by the International Humic Substances Society, and by the measured percentage of exocylic sulfur (23.6%) for SRHA.[50] We also assumed that native DOC in these samples taken from highly sulfidic marsh soils in the Berry's Creek marsh would have been sulfurized,[51] increasing their thiol content. To estimate sulfurization, we assumed the higher end of the ranges of S:C and exocyclic S measured by Poulin, et al. (2017)[52] for soils in the sulfidic regions of the Everglades. Thiol density calculations are shown in the Supplemental Spreadsheet.

Statistical Analyses. All statistical analyses were performed using the statistical software package JMP.[53] The data were assessed for normality and $\log_{10}$ transformed as necessary. Differences between microcosm treatments were assessed using general linear models that included time, treatment, isotope spike (and two-way interaction terms) as appropriate. Details of the models used can be found in the figure captions and in Supplemental Table S9.

RESULTS AND DISCUSSION

Isotherm Experiments

Previous work by Gomez-Eyles et al. (2013) reported strong sorption of $HgCl_2$ and MeHgCl to several AC types in 3 ppt Instant Ocean isotherms.[18] However, in a typical estuarine marsh soil, organic matter is much more likely than chloride to dominate Hg and MeHg speciation.[25]. In isotherm experiments designed to mimic oxic, non-sulfidic, estuarine waters, we found that sorption of the Hg and MeHg DOM complexes (specifically Suwannee River Humic Acid II) to AC was substantially lower than sorption of the corresponding Hg and MeHg chlorides. The experiments were carried out using environmentally realistic DOM:Hg mass ratios.[43] Equilibrium speciation calculations (using MINEQL) indicated that SRHA complexes accounted for ~100% of Hg and MeHg in the experimental solutions with added SRHA.

Further, HgSRHA and MeHgSRHA sorption onto AC (K_{AC}) was more similar to the K_{AC} for DOM alone than to the K_{AC} values of $HgCl_2$ and MeHgCl. This was true for both types of AC tested, CAC-Coal (Figure 1) and CAC-Coco (Figure S2) and occurred regardless of the order in which SRHA or mercury were exposed to AC (data not shown). Because the order of addition did not impact sorption, we hypothesize that the SRHA-mediated decrease in sorption was due to a fundamental change in the interactions between Hg/MeHg and AC, and not to a general fouling of the ACs by SRHA. The similarity of K_{AC} for HgSRHA and MeHgSRHA to that of SRHA alone suggests that the sorption process is mechanistically controlled by DOM-AC interactions, particularly at higher concentrations of DOM.

We also found that the effect of SRHA on sorption to AC was greater for Hg than MeHg. K_{AC} for HgSRHA was about two log units lower than $HgCl_2$, while log K_{AC} for MeHgSRHA was only 0.5 to 1 log unit lower than MeHgCl. Interestingly, log K_{AC} for HgSRHA and MeHgSRHA were similar (roughly 4 to 4.5) across all permutations of AC type and sequence of addition . For comparison, log K_{AC} for SRHA alone was 3.64 on CAC-Coal and 3.35 on CAC-Coco (Gomez-Eyles et al., unpublished data). These results imply that remedy design calculations based on K_{AC} for chloride complexes risk significantly overestimating the efficacy of AC in systems dominated by DOM.

Soil Slurry Experiment

In a soil slurry experiment conducted under the more complex, reducing conditions of estuarine salt marsh soils, we found that SRHA additions up to 60 mg/L had minimal impact on MeHg distribution to the solid phase, but significantly reduced inorganic Hg K_d. The 21-day study was conducted anaerobically and run at 4 ^oC to slow microbial transformations of Hg.

Slurry Geochemistry. The *Phragmites* soil used in the slurries consisted of fine-grained mineral matter and clay trapped by roots. The soil was highly organic (%LOI = 37.6), with significant oxygen demand. These estuarine soils, incubated with 3 ppt Instant Ocean water (containing 2.4 mM SO_4) became highly sulfidic during the experimental incubations, with concentrations rising above 1000 μM after 21 d (Figure S3), indicating microbial sulfate-reducing activity. High porewater sulfide levels led to Fe-S precipitation, explaining the low dissolved Fe concentrations, which were at, or just above, the instrument detection limit (0.06 mg/L) (Figure S4). However, neither AC nor SRHA amendments had any significant impact on porewater Fe or sulfide concentrations. Slurry pH remained circumneutral during the incubations (Figure S5). Soil samples from time zero contained Fe in molar excess of S. Mn in slurry soil was very low, indicating that the soil was sampled from a site with a generally reduced oxidation state. Details of soil chemistry are shown in Table S5. Under the sulfidic conditions in the experiments, the dominant Hg and MeHg complexes in slurry water were sulfide species (see below for a detailed discussion of complexation and precipitation).

Impact of AC on DOM. DOM dynamics in the microcosms were assessed by measuring DOC concentrations. The addition of 5% AC to the soil slurry microcosms decreased porewater DOC concentrations (Figure 2) and changed the chemical character of the DOC in solution. However, the addition of SRHA up to 60 mg/L did not reduce the ability of AC to sorb DOC.

The background DOC level in slurries without AC amendment (orange bars) was roughly 9 mg/L, comparable to published values for the Berry's Creek marsh site.[42] AC amendment alone, without SRHA addition (grey bars), significantly decreased DOC concentrations in slurries without SRHA, by 66 ± 11%. Three different concentrations of SRHA were added to slurries with AC to assess the impacts of DOM on Hg and MeHg binding to AC (blue bars). SRHA additions increased the total DOC in slurry porewaters proportionally to the addition level. However, AC removed the same fraction of DOC at all three added SRHA concentrations (67 ± 15%), statistically the same fraction removal as ambient DOM in the slurries. AC rapidly removed DOC from solution and with the exception of the highest SRHA addition, DOC levels stayed generally constant or declined moderately over the course of the experiment (Figure S6). The consistent DOC removal indicates that the AC was not saturated with DOM.

AC amendment also reduced DOC aromaticity (as measured by $SUVA_{280}$) in slurries with and without SRHA spikes, although the decrease was relieved at the highest SRHA spike levels (Table S10). The $SUVA_{280}$ for DOC in the high SRHA (60 mg/L) spike was 4.31, which is similar to values previously reported for SRHA.[40] The changes in aromaticity across the SRHA gradient reflect the different characters of the starting materials, but also selective removal of aromatic DOC by AC.

Impact of DOM on Hg Sorption to AC. The addition of SRHA to the slurries significantly reduced inorganic Hg sorption to AC, in a concentration dependent manner. In slurries without added SRHA, AC amendment lowered ambient porewater Hg concentrations to ~10 ng/L, a significant, roughly 80% decrease from unamended slurries. However, at the highest SRHA addition level, AC only reduced porewater Hg by ~50% (Figure 3a). A fresh Hg spike, added to slurries as $^{201}HgCl_2$, was more reactive toward both AC and SRHA than the ambient Hg in the slurries. AC reduced porewater ^{201}Hg by 98% in slurries without SRHA but provided only ~70% reduction at the highest SRHA concentration (Figure 3b). On average across all dates and treatments, 94 ± 12 % of the added ^{201}Hg was recovered in the slurries.

The trends in porewater concentration for both ambient Hg and spiked ^{201}Hg were reflected in the sediment:water distribution coefficient (K_d) (Figures 4a and b). AC increased ambient Hg distribution to the solid phase roughly tenfold compared to the unamended slurries (Figure 4a). Apart from the High SRHA treatment, the addition of SRHA to the AC-amended microcosms did not significantly reduce the distribution of ambient Hg to the solid phase. AC increased the distribution of the fresh, more reactive ^{201}Hg spike to solids by about 50-fold (Figure 4b), but all levels of the SRHA addition significantly reduced the ability of AC to sorb ^{201}Hg, reducing K_d by one to two orders of magnitude. Added SRHA in large part negated the positive impact of the AC on spike ^{201}Hg sorption; the K_d values of the AC + SRHA treatments were statistically indistinguishable from the unamended slurries. Overall, the porewater and K_d data for both ambient Hg and ^{201}Hg would at first suggest that SRHA had a fouling effect on the AC. However, the MeHg data do not support this hypothesis.

AC and DOM impacts on K_d reflect changes in both porewater and sediment Hg and MeHg concentrations. There was no significant net change in sediment ambient MeHg or total Hg concentration over time in the incubations, indicating that methylation and demethylation were at roughly steady state. $Me^{201}Hg$ was produced slowly from the ^{201}Hg spike, and $Me^{199}Hg$ was lost from some bottles, indicating a low level of active methylation and demethylation (Figure S8).

Impact of SRHA on MeHg sorption to AC. SRHA spikes up to 60 mg/L did not significantly reduce the ability of AC to sorb MeHg in the soil slurries. AC additions were effective in sequestering MeHg, lowering ambient porewater MeHg from ~14 to about 2 ng/L (~85% decrease) and decreasing a fresh $Me^{199}Hg$ spike from ~72 to ~5 ng/L (~95%) (Figure 3c and 3d). The addition of SRHA did not change porewater MeHg concentrations or distribution coefficients relative to slurries without added SRHA. Soil:water distribution coefficients for ambient and spike MeHg were 1 and 1.5 orders of magnitude higher, respectively, in AC-amended slurries relative to unamended slurries (Figure 4c and 4d). On average across all dates and treatments, 89 ± 15 % of the added $Me^{199}Hg$ was recovered in the slurries.

SRHA Influence on Hg and MeHg Complexation and Sorption to AC. In the slurry experiments, SRHA appeared to reduce the ability of AC to sorb inorganic Hg but had little effect on sorption of MeHg by AC. The simplest explanation for the difference is that SRHA changed Hg speciation in a way that decreased its distribution to the solid phase but did not do so for MeHg. Equilibrium speciation modeling showed that both aqueous inorganic Hg (Figure 5 and S10) and MeHg (Figures S11 and S12) were dominantly complexed with sulfide in these highly sulfidic slurries, and that speciation did not change appreciably across a gradient of DOM (modeled as thiols). However, we hypothesize that DOM might impact Hg (but not MeHg) distribution to the solid phase by slowing the formation of metacinnabar ($HgS_{(s)}$).[54, 55] This non-equilibrium interaction is not captured by equilibrium speciation models. Previous studies have shown that SRHA is effective in increasing Hg bioavailability for methylation through its ability to inhibit the growth and aggregation of metacinnabar.[40] MeHg-sulfides do not form insoluble species and would not be affected by this interaction. The observed increase in total aqueous Hg concentration with increasing SRHA (Fig. 3) supports this hypothesis. However, speciation modeling gave mixed predictions of whether metacinnabar precipitation occurred, depending on the choice of solubility product constant (K_{sp}) for metacinnabar and formation constants for aqueous mercuric sulfides (HgS_2^{-2}, $HgHS^{2-}$, $Hg(HS)_2$) (Figure 5, Figure S13). If lower formation constants for $HgHS_2^-$ and $Hg(HS)_2$[56] and high values for precipitation of HgS[57] are used in modeling, metacinnabar is predicted to precipitate in all of the microcosm treatments. Regardless of the stability constants and formation constants used, modeling predicts that either metacinnabar or aqueous mercuric sulfides were the dominant species of inorganic Hg in the pore waters. The amount of inorganic Hg predicted to be bound to thiols in DOM was several orders of magnitude less than aqueous Hg-S species predictions, even considering potential increases in thiol content from *in situ* sulfurization of DOM.[51] ^{201}Hg speciation followed similar trends as the ambient Hg (Figure S10).

Modeling showed that both MeHg and Me^{199}Hg speciation in all slurry treatments were dominated by MeHg-S species (Figures S11 and S12). MeHg-DOM complexes (modeled as –RS) represented less than 0.25% of the total MeHg yet were the second most abundant MeHg species. The proposed formation constants for MeHg organic thiols (MeHgSR) are somewhat higher than for MeHgSH (Table S3), and thus, thiols in DOM can compete with bisulfide as ligands for MeHg, depending on their relative concentrations. However, at the high sulfide levels in the experiment, MeHgSH was the dominant complex. The addition of SRHA did not impact speciation (Figures S11 and S12) and did not impact distribution (Figure 4), as MeHg does not form sulfide precipitates.

The slurry incubation results also indicated that AC sorbs Hg-S and MeHg-S complexes more strongly than the chlorides. Using the known fraction of AC in the slurries and the K_d values from the "No SRHA/no AC" (sediment only) and "No SRHA + AC" (sediment +AC, but without added SRHA) treatments, we estimated sorption to the AC alone (K_{AC}) (Supplemental Spreadsheet). Log K_{AC} for Hg and ^{201}Hg in the slurries were 7.6 ± 0.1 and 7.3 ± 0.2, respectively, calculated from the average values across all time points, excluding T0. The log K_{AC} for Hg was higher than the isotherm-derived value[18] of 7.2 ± .02 for $HgCl_2$. Similarly, log K_{AC} for MeHg and Me^{199}Hg were 6.1 ± 0.1 and 6.1± 0.1, respectively, compared to 5.4 ± 0.02 for MeHgCl in isotherm experiments.[18] The key differences between the two experiments were the presence of sediment and high-μM sulfide in the slurries.

Alternative explanations for our observation of DOM impacts on Hg sorption to AC include the formation of unknown DOM-Hg-S complexes, competition for sulfide between DOM and Hg, and binding other than the ligand-ligand interactions modeled here, including sorption of uncharged HgS complexes. Further, we performed these tests with one type of DOM, SRHA, an aged isolate with a relatively low sulfur content (0.5%).[51, 52] It is possible that fresh natural organic matter[58] or DOM with a higher sulfur content would have a stronger impact on Hg and MeHg binding to AC. High sulfide environments (like those in our slurries) can result in the sulfurization of both DOM and AC surfaces,[51] and the balance of those effects on K_{AC} are unknown. Different types of DOM have also shown different propensities to adsorb to AC,[28] which could influence sorption, depending on what proportion of the Hg and MeHg is present in DOM complexes.

To summarize, we hypothesize that SRHA impacted Hg distribution to the solid phase in our soil slurries by interfering with HgS precipitation. MeHg distribution was not affected. The apparent sorption of HgS and MeHgS species to AC also appears stronger than the sorption of the chlorides. Resolution of the mechanism of DOM impacts on Hg sorption to AC in sulfidic sediments will require the direct determination of log K_{AC} values for Hg and MeHg sulfides, and the distinction between HgS precipitation and AC sorption.

Implications for remediation. In typical wetland environments like those represented by our slurries, DOM is not expected to directly impact AC efficacy for the remediation of MeHg contamination. However, at sites where new Hg inputs are the target of AC amendment, DOM concentration should be factored into AC amendment level decisions. Also, seasonal influxes of organic matter may impact how well AC performs in areas receiving new Hg inputs, so amendments might be timed for maximum effect. Isotherm experiments are needed to measure the impact of sulfide on MeHg and Hg sorption to AC in a simple water matrix. This would allow for the eventual modeling and prediction of AC efficacy in real ecosystems, and in the presence and absence of metacinnabar precipitation. Future work should also determine whether the fractions of different Hg and MeHg species (e.g. $HgCl_2$ vs HgDOM) sorbed are equal, or if the percent decrease in porewater concentration differs greatly for one species over another. In the latter case, the time needed to reestablish an equilibrium species distribution in porewater following AC amendment would be of importance. These questions have important implications for bioavailability assessments. Overall, our data indicate that AC is an effective remediation tool for both Hg and MeHg, but DOM, sulfide, and Hg age are important parameters controlling AC sorption that should be considered in amendment design and assessment.

CONFLICT OF INTEREST

There are no conflicts to declare.

ACKNOWLEDGEMENTS

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SUPPLEMENTAL INFORMATION

The Supplemental Information section contains the inputs for speciation calculations for the isotherm and slurry experiments, time course data for Hg and MeHg in soils and porewaters, additional figures on microcosm geochemistry, and additional figures on Hg and MeHg speciation in the microcosms.

Table 1. Microcosm Experiment design. Slurry bottles contained estuarine marsh soil in 1:10 ratio to artificial estuarine seawater. Ten replicate bottles were set up initially for each of the five treatments. Half of the bottles received $^{201}HgCl_2$ spike to 26 ug/L (~10% of ambient soil concentration) and half of the bottles received $Me^{199}HgCl$ spike to 0.88 ng/L (~50% of ambient soil concentration). Bottles were sampled destructively over time, at 0, 1, 3, 7 and 21 days. Total number of bottles = 50. AC was a regenerated AC manufactured by Siemens. Slurries were incubated with occasional shaking at 4^{o}C.

Treatment	**AC**	**SRHA Added**	**Expected organic C addition from SRHA**	**Storage**
1. No SRHA/No AC	None	None	None	4 °C
2. No SRHA	5% dw	None	None	4 °C
3. Low SRHA	5% dw	15 mg/L	7.9 mg/L	4 °C
4. Mid SRHA	5% dw	30 mg/L	15.8 mg/L	4 °C
5. High SRHA	5% dw	60 mg/L	31.6 mg/L	4 °C

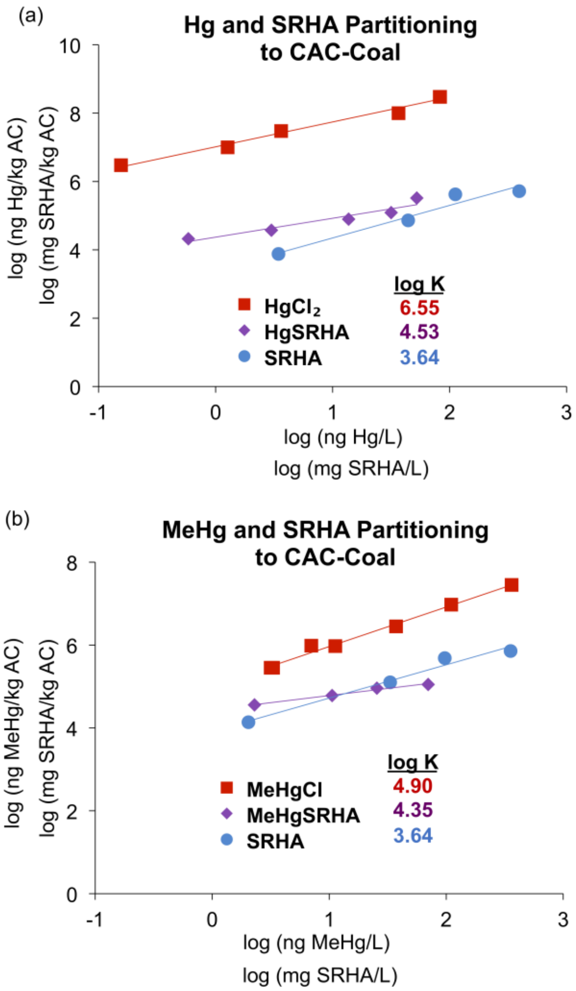

Figure 1. Sorption isotherms for Hg (top) and MeHg (bottom) onto coal-based AC. Chloride species (squares) are plotted along with SRHA alone (circles) and along with Hg and MeHg in the presence of SRHA (diamonds). SRHA isotherm from Gomez-Eyles et al., unpublished data.

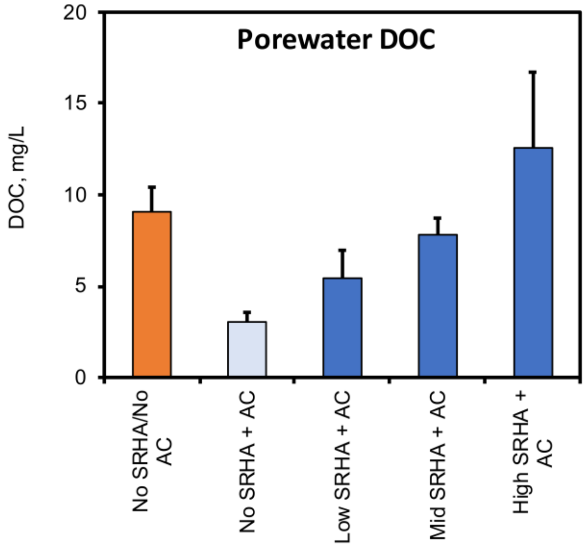

Figure 2. Average dissolved organic carbon concentrations in sediment slurry microcosms across all time points, with standard deviations. The orange bar is the average value for slurries without any added AC or SRHA. The grey bar is sediment slurry with 5% added AC, but no added SRHA. Blue bars are slurries with 5% AC plus SHRA addition at 15, 30 and 60 mg DOM/L respectively in Low-, Mid-, and High treatments. SRHA is ~50% carbon, so we expect DOM concentrations to be ~2x DOC mg/L. There were no significant differences among treatments in the fraction of DOM removed by AC. AC removed ~66% ± 14% of DOM in all treatments Time series data are shown Figure S6.

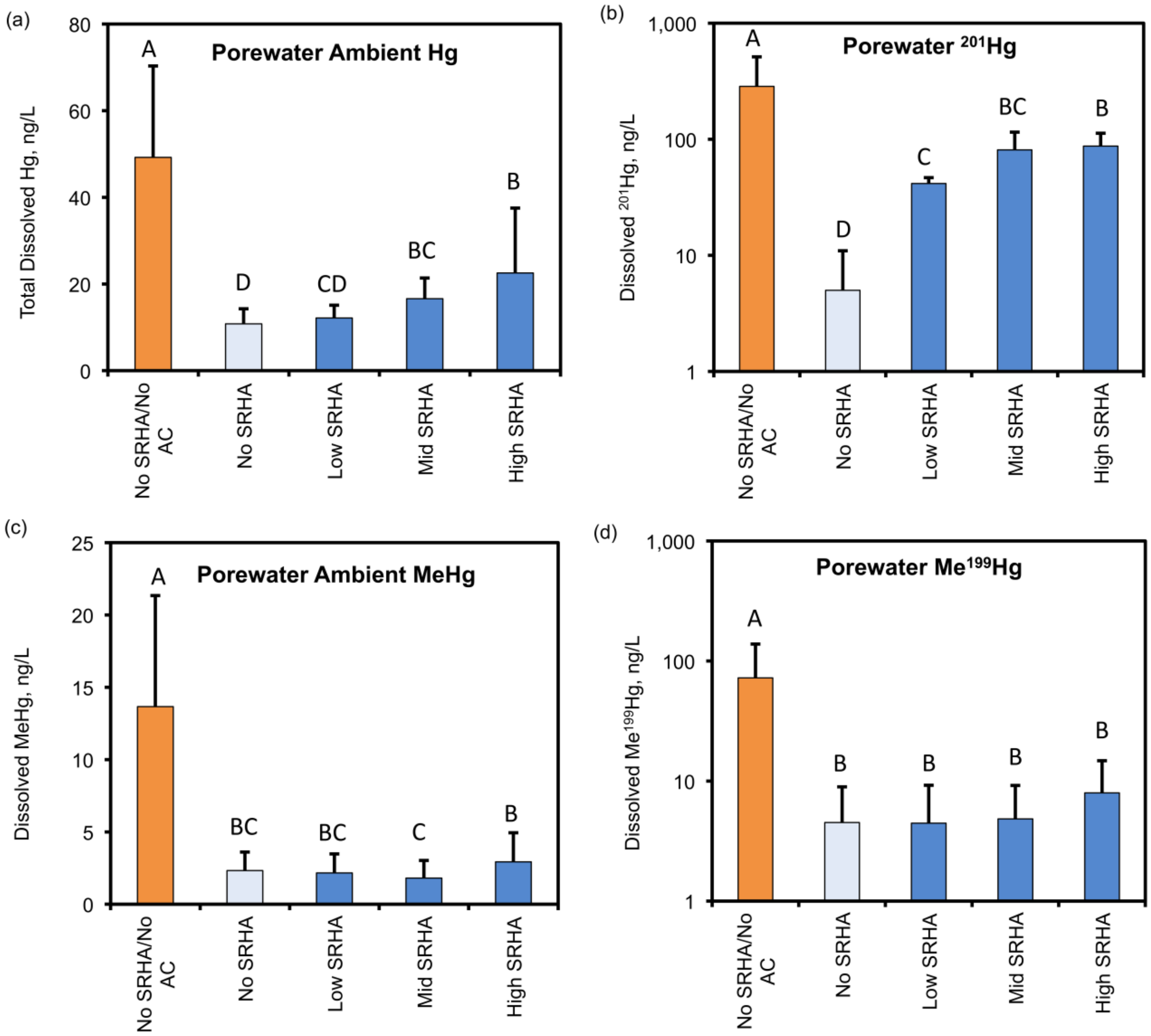

Figure 3. Effect of added SRHA on porewater total Hg and MeHg concentrations in AC-treated soils. Bars are the average dissolved concentrations in the soil microcosms over all time points: (a) total ambient Hg; (b) ^{201}Hg; (c) ambient MeHg; and (d) Me^{199}Hg. Error bars represent the standard deviation of the sample values. Note that the ^{201}Hg and Me^{199}Hg concentrations are shown on the log scale. Shared letters signify that the treatments were not statistically different based on Students t-test (α=0.05) of least square means from general linear models that included date and treatment effects, and the interaction term where significant. Time series data are shown in the SI (Figure S7).

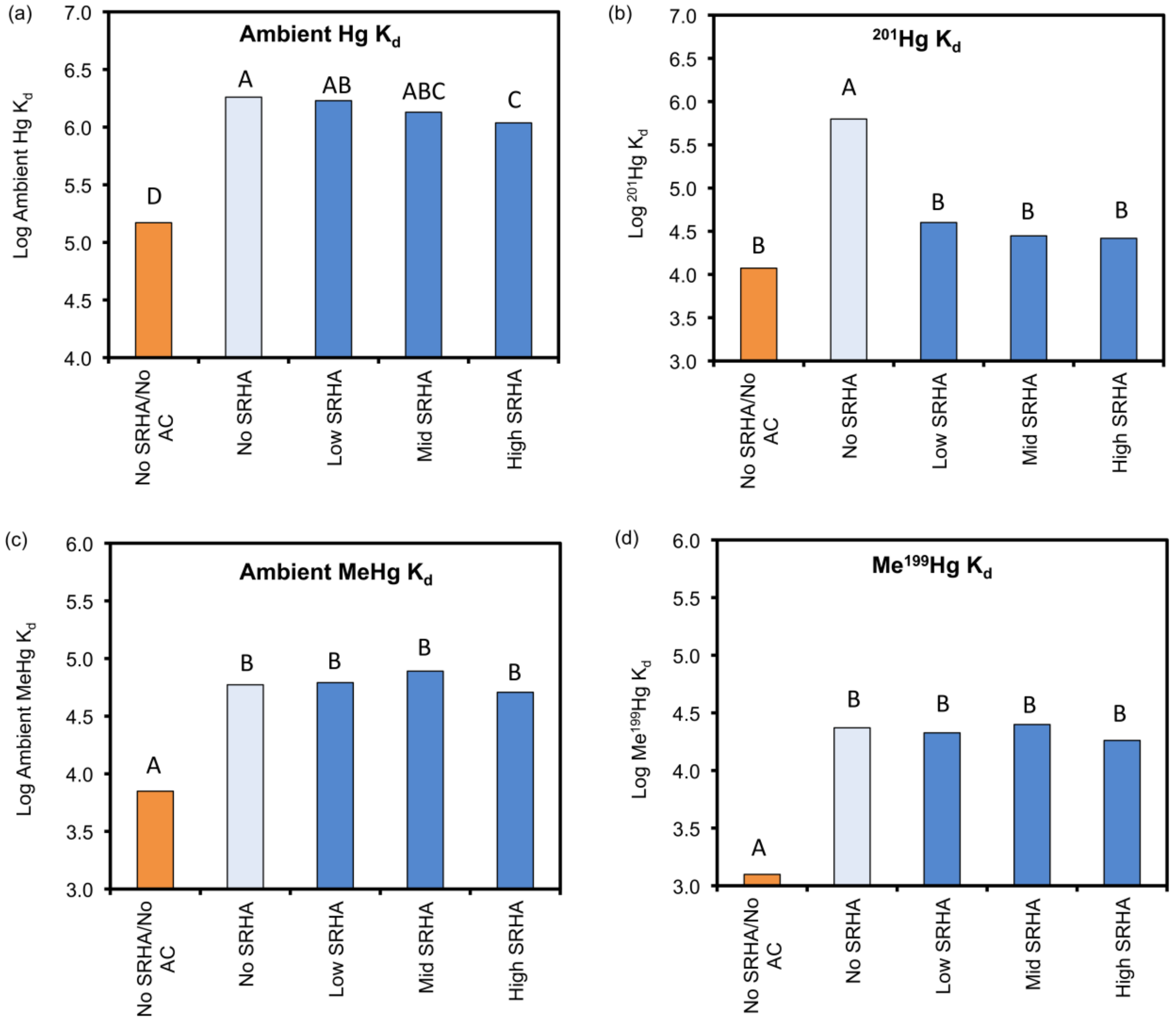

Figure 4. Average sediment:water distribution coefficients for Hg and MeHg over all time points: (a) ambient Hg; (b) ^{201}Hg; (c) ambient MeHg; (d) Me^{199}Hg. Sediment:water distribution coefficients (K_d) were calculated as the sediment concentration in ng/kg divided by the porewater concentration in ng/L. Shared letters signify that the treatments were not statistically different based on Students t-test (α=0.05) of least square means from general linear models that included date and treatment effects, and the interaction term where significant. Time series data are shown in the SI (Figure S9).

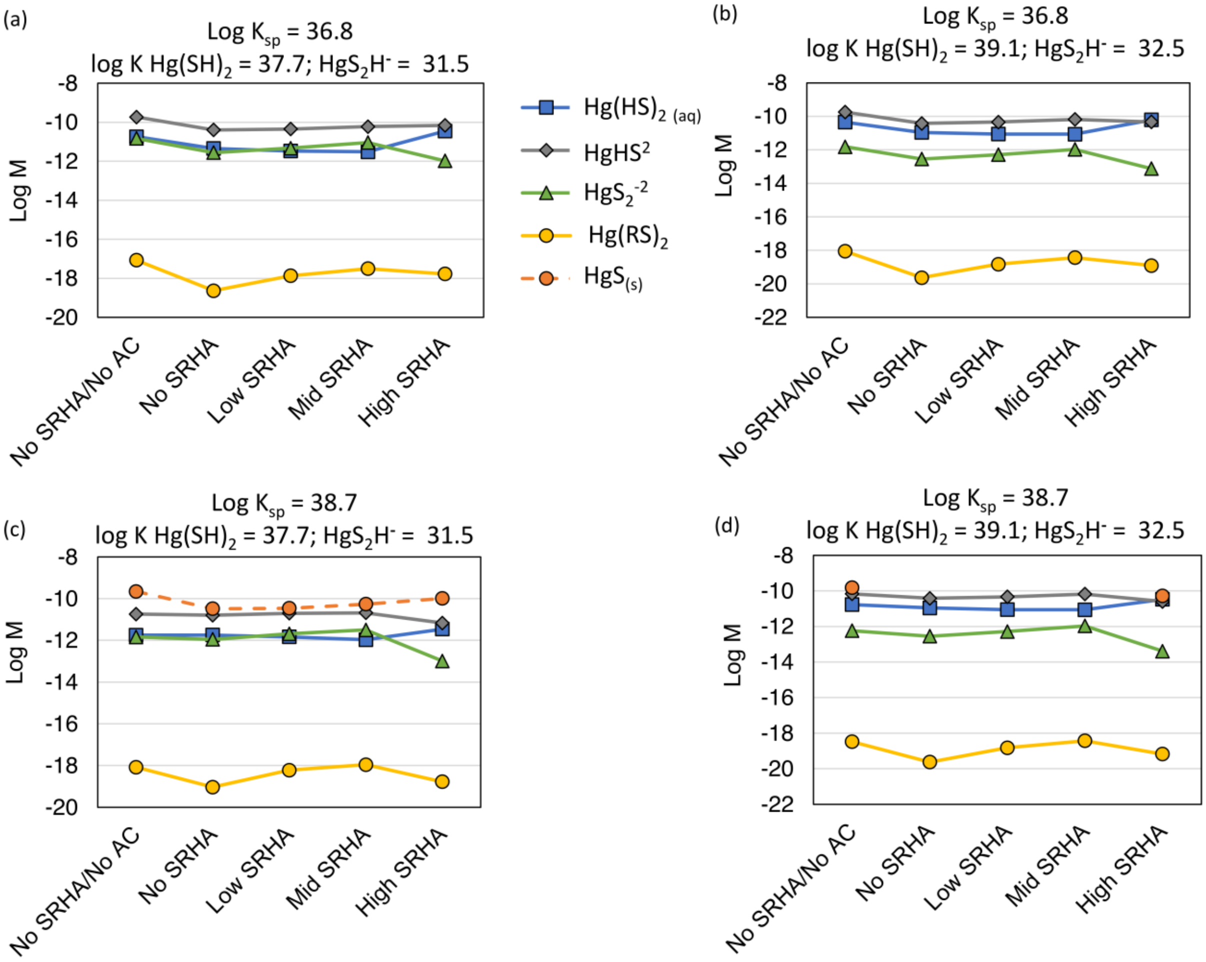

Figure 5. Calculated filter-passing inorganic Hg(II) speciation in the microcosms. Stability constants are listed in Tables S4. Speciation calculation inputs are shown in the supplemental spreadsheet. Calculations were performed using two values of the solubility product (K_{sp}) for the reaction $Hg^{2+} + HS^{-} = \beta\text{-}HgS_{(s)} + H^{+}$ (Drott et al. 2013, Smith and Martell 1993);[59, 60] and two values for the stability constants for $Hg(SH)_2$ and HgS_2^{2-} (Drott et al. 2013, Schwarzenbach and Widmer 1963).[56, 59] In this model RS represents thiol moieties on DOM.

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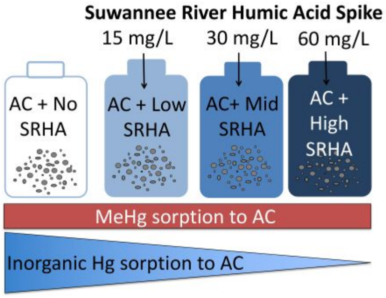

In sulfidic soil, increasing concentrations of dissolved organic matter decreased Hg sorption to AC but did not impact MeHg sorption.