

Approval Sheet

Title of Dissertation: A Novel Equilibrium Passive Sampler for Methylmercury and
Other Advances in Monitoring and Activated Carbon Remediation
for Mercury and PCBs

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Abstract

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The ecological and human health risks posed by persistent sediment contaminants like polychlorinated biphenyls (PCBs) and methylmercury (MeHg) are often controlled by their bioavailability at low trophic levels. Benthic and epibenthic organisms can serve as a conduit for the contaminants to enter aquatic food webs, where they are subject to a large degree of biomagnification. As a result, benthic bioavailability is of central importance. This dissertation describes a series of projects linked by the common goal of advancing bioavailability science to improve the quality of contaminated site risk assessment and management.

First, a multi-year, pilot-scale study was performed to evaluate the persistence and efficacy of several different AC-based sediment amendments in an intertidal, estuarine marsh overrun with *Phragmites australis* reeds. Black carbon measurements showed that all three tested amendments remained in place through three years of daily tidal cycling and an unusually disruptive storm event. All three reduced bioaccumulation of PCBs by benthic and epibenthic organisms. The passive sampling effort employed several different polymer types and performance reference compound (PRC) adjustment

methods, enabling comparisons that can inform method development and standardization.

For mercury and MeHg remediation, a project was undertaken to explain the large variability observed in early tests of AC amendment for mercury-impacted sediments.

AC-water partitioning coefficients for mercury species complexed with dissolved organic matter (DOM) were measured and found to be far smaller than those previously reported for chloride complexes. Accordingly, the positive effect of AC on inorganic mercury partitioning in microcosms of slurried soil was attenuated by the addition of exogenous DOM. However, no effect on MeHg partitioning was observed. These results highlight the importance of considering site chemistry in remediation design.

Lastly, a novel passive sampling device for MeHg in sediment and soil porewaters was developed. This project seeks to address the need for a reliable, equilibrium sampling strategy capable of predicting MeHg bioavailability. Prospective materials were tested under increasingly realistic environmental conditions and several proved capable of concentrating aqueous MeHg by three to four orders of magnitude, permitting good prediction of porewater concentrations in a variety of matrices including salt marsh soils with and without AC amendment. One sampler, a suspension of AC particles in agarose gels, exhibited reasonably rapid, internally diffusive, and reversible MeHg accumulation. In a bioaccumulation study, sampler uptake was correlated with concentrations in the benthic amphipod *L. plumulosus*, which were reduced by amendment with AC. The project constitutes a successful proof of concept and provides the basis for further refinement. Future work will seek to optimize the design and preparation of samplers and develop a more detailed understanding of the dynamics of MeHg exchange among samplers and various ligands to facilitate interpretation of their measurements.

A Novel Equilibrium Passive Sampler for Methylmercury and Other Advances in
Monitoring and Activated Carbon Remediation for Mercury and PCBs

by

James Palmer Sanders

Dissertation submitted to the Faculty of the Graduate School of the
University of Maryland, Baltimore County in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy
2018

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Dedication

For Diane.

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I acknowledge The Dow Chemical Company, the National Institute of Environmental Health Sciences, and the Strategic Environmental Research and Development Program for funding my work. I thank all of my colleagues at UMBC and SERC, past and present, for help in the lab and in the field, for stimulating scientific conversations, and most importantly for their friendship. Thanks are also owed to all those who attended any of my conference presentations or gave an encouraging word along the way. Thank you to my committee members, including Dr. Lee Blaney, Dr. Claire Welty, and Dr. Steven Brown, all of whom made valuable contributions both to this work and to my personal development. Special thanks to Dr. Cynthia Gilmour, whose mentorship and expertise have been invaluable to my progress. I am also very grateful to Dr. Upal Ghosh, my distinguished advisor, and to Dr. Susan Kane Driscoll, both of whom have provided me with tremendous opportunities. Thank you for your belief in me.

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List of Abbreviations

AC	activated carbon
BAF	bioaccumulation factor
BC	black carbon
BCSA	Berry's Creek Study Area
BSAF	biota-sediment or -soil accumulation factor
C _{AC}	concentration in activated carbon
C _{org}	concentration in organism tissue
C _{pw}	concentration in sediment or soil porewater
C _s	concentration in sediment or soil
C _{sed}	concentration in sediment
C _w	concentration in water
DOC	dissolved organic carbon
DOM	dissolved organic matter
GAC	granular activated carbon
Hg _i	inorganic mercury
HOC	hydrophobic organic contaminant
K _d	sediment- or soil-water partitioning coefficient
K _{ow}	octanol-water partitioning coefficient
K _{ps}	passive sampler-water partitioning coefficient
MeHg	monomethylmercury
PAC	powdered activated carbon
PCB	polychlorinated biphenyl
PDMS	polydimethylsiloxane
PE	polyethylene
POM	polyoxymethylene-ethylene oxide copolymer
PRC	performance reference compound
ΣC	summed concentration of all measured PCB congeners
SRHA	Suwannee River Humic Acid

Chapter 1: Introduction

1.1. Activated Carbon Amendment to Reduce the Bioavailability of Polychlorinated Biphenyls

Polychlorinated biphenyls (PCBs) are a class of synthetic, chlorinated organic compounds that were widely used through much of the 20th century in various applications, including electrical transformers and capacitors.¹ They are associated with a number of adverse ecological and human health outcomes and have been deemed a probable human carcinogen by the USEPA.² Prior to a 1979 ban, they were produced and sold in formulations called Aroclors, which comprised different mixtures of the 209 possible PCB congeners. The properties that made PCBs useful—their hydrophobicity and resistance to degradation—have also contributed to making them a recalcitrant environmental contamination problem. They are dispersed throughout the environment and strongly associate with organic matter, particles, sediments, and soils.¹ In aquatic systems, their association with sediment or soil provides an exposure route for low-trophic level organisms including benthic and epibenthic invertebrates. Once taken up into an aquatic food web, PCBs are subject to a high degree of biomagnification, which often translates to ecological and human health risk through the vector of large, predatory fish. PCB-related fish consumption advisories are commonplace, particularly in the eastern United States. PCBs are a major driver of risk at many managed sites throughout the country, including dozens under the purview of the Superfund program.³ This has given rise to a fertile field of study in the risk assessment and remediation of the chemicals.

Historically, dredging has been the most widely implemented form of remediation for PCB-contaminated sediments and soils. However, concerns about resuspension and mobilization have led to the development of lower-impact, in situ remedies. Perhaps the most promising of these is the application of strongly sorbing amendment materials such as activated carbon (AC) to sequester PCBs in sediments and soils, thereby reducing their bioavailability to benthic and epibenthic consumers.^{4, 5} ACs are porous, extremely high-surface area materials generated by the high-temperature pyrolysis and activation of organic starting materials.⁴ Laboratory demonstrations of the potential utility of AC were followed by a number of successful pilot- and field-scale applications. These include Hunters Point Naval Shipyard in CA^{6, 7}, the lower Grasse River in NY⁸, and Mirror Lake in DE.⁹ Amendment of sediments with AC at these and other sites has produced reductions in PCB bioaccumulation in the range of 70–99%.⁴

1.2. Passive Sampling of Polychlorinated Biphenyls

The development of passive sampling for PCBs and other hydrophobic organics has proceeded roughly in parallel with that of AC remediation. The latter grew from the recognition that bulk concentrations in sediment are a poor surrogate for contaminant bioavailability because different geochemistries (e.g. those containing more black carbonaceous material) can exhibit vastly different partitioning behaviors in terms of both capacity and sorption kinetics.^{4, 10, 11} Instead, the concentrations of freely dissolved contaminants in porewaters (C_{pw}) were found to correlate much more closely with bioaccumulation. Despite the fact that the water phase is often only a minor contributor to total exposure for many animals, C_{pw} remains valuable because it gives an indication of the relative chemical activity of sediment-bound contaminants and their tendency to

move from one phase to another (e.g. from solid particles into an organism's digestive fluid).¹²⁻¹⁶

Early attempts to measure C_{pw} of PCBs and other persistent organic contaminants by filtering and extracting porewater were complicated by several factors. First, the analytical challenge of accurately measuring in the fg to pg range is nontrivial. Second, these contaminants are often associated with filter-passing, colloidal organic matter. While such material is often considered “dissolved” for operational purposes, in the context of strongly hydrophobic chemicals it can lead to large overestimates of the truly aqueous fraction.¹² Passive sampling techniques developed over the last 20–25 years have ameliorated these concerns. Passive sampling is based on the principle of concentrating more readily detectable amounts of target compounds from water into a high-affinity, diffusive sampling material. After a passive sampling device has been exposed to the sample matrix, its contaminant concentration is measured and C_{pw} is back-calculated from either a known and replicable sampler-water partitioning coefficient (in the case of equilibrium sampling) or a dynamic relationship such as Fick's first law of diffusion (in the case of kinetic sampling).^{12, 13, 16-20}

Passive sampling of PCBs is typically done using one of three organic polymers: polyethylene (PE), polyoxymethylene (POM, often a copolymer with ethylene oxide), or polydimethylsiloxane (PDMS).^{12, 21-23} These all function in an equilibrium mode, which means that the two most important considerations in the interpretation of their measurements are the accuracy of the relevant sampler-water partitioning coefficients (K_{ps}) and the timing of the sampler's approach to equilibrium. In a stagnant or low-flow system, large, hydrophobic analytes may not equilibrate with sampling polymers even

after a two- to four-week deployment. Methods have been developed to account for such nonequilibrium by measuring the loss from polymers of pre-loaded internal standards, or performance reference compounds (PRCs), whose diffusion out of polymers should closely mirror that of target analytes inward. The interpretation of PRC data has been approached in a number of different ways and remains among the most active areas of research in the passive sampling field.^{17, 18, 24-32}

Passive sampling has been remarkably successful for researchers and is increasingly drawing the interest of the regulatory community as a potential new tool to support contaminated site risk assessment and management decision-making. However, for it to do so, the field will need to undergo a process of standardization. All aspects, from selection of polymers and preparation of sampling devices to deployment, retrieval, analysis, and data interpretation should ultimately adhere to consensus best practices. In recent years, expert workshops and guidance documents have begun to give shape to the future implementation of passive sampling in a regulatory context.^{12, 13, 16, 33-36}

1.3. Activated Carbon Amendment to Reduce the Bioavailability of Mercury and Methylmercury

Mercury represents another major environmental contamination problem. Unlike PCBs, mercury is a naturally occurring element. It moves throughout the global environment in air, water, and soil in cycles of emission and deposition. However, anthropogenic activities including coal-fired power generation greatly enhance both the quantity and mobility of actively cycling and available mercury. This makes it a large and ongoing management challenge on the local, national, and international scales.³⁷ Against this backdrop, there are also numerous localized, point-source contamination problems

arising from artisanal gold mining (particularly in the developing world) and industrial activities. Elevated sediment and soil concentrations can be found at many current and former chloralkali plants, mines, paper mills, and other facilities, a large number of which are under active regulatory management.^{38, 39} Further, mercury contamination is present at many of the same sites impacted by PCBs, and is often responsible for driving risk, making it desirable to have viable in situ sampling and remediation options for both. Even more so than for PCBs, mercury risk is not well predicted by bulk solid concentrations. Instead, microbial conversion of inorganic mercury (Hg_i) to the more toxic and bioaccumulative methylmercury (MeHg) is of primary concern.⁴⁰⁻⁴³ Like PCBs, MeHg is responsible for many fish consumption advisories at the state and national levels.⁴⁴ Due to the central importance of MeHg, risk assessment typically focuses on the variables that control (a) microbial activity rates, (b) the bioavailability of Hg_i to methylators, and (c) that of MeHg to benthic consumers. These include solid-phase and porewater chemistry, particularly concentrations of organic matter, small thiols, and sulfide, all of which are strong ligands for Hg_i and MeHg, and iron, which strongly influences the availability and speciation of sulfur.^{40, 45-50}

Remediation strategies for aquatic mercury sites have included removal via dredging, sequestration via capping or immobilization, and various methods of modifying prevailing biogeochemical conditions with the aim of reducing methylation.^{38, 51, 52} More recently, spurred by the success of AC as a remediation tool for organics, some researchers have begun to investigate its potential use for mercury. One study found very strong partitioning of Hg_i and MeHg by ACs and biochars in water, and another demonstrated reductions in porewater concentrations and benthic bioaccumulation in AC-

amended sediment microcosms.^{51, 53} Two pilot-scale applications have been performed, in a Penobscot River (ME) salt marsh and at the Berry's Creek marsh in NJ.^{51, 52} In the aggregate, the results of these studies indicate significant promise but also a surprising amount of intersite variability in the effect on sediment- or soil-water partitioning (K_d) achieved by AC amendment.

1.4. Passive Sampling of Methylmercury

The bioavailability of MeHg to benthic invertebrates and other low-trophic level consumers is of interest to site assessors and managers because, as with PCBs, it gives an important indication of the overall risk to aquatic food webs.^{43, 54, 55} However, in contrast to PCBs, passive sampling for MeHg is considerably less well developed. This is largely due to the much greater complexity of aqueous MeHg chemistry. In environmental waters, free MeHg^+ ion is almost never present above nominal concentrations. Instead, it occurs predominantly in complexes with ligands such as chloride, sulfide, small thiols, and dissolved organic matter (DOM), depending on porewater chemistry.^{48, 56} These species occupy a wide range of size, mobility, diffusivity, and availability to biota and sampling devices. Further, the mechanisms of MeHg bioaccumulation remain poorly understood. Evidence has been found for both passive, diffusive cellular uptake of uncharged complexes and active internalization via protein channels.^{46, 57} The relative availabilities of various forms of MeHg for these processes, and for gut solubilization by benthic consumers, have not been established, making it unfeasible at present to design a chemoselective passive sampler as a direct biomimic.

Previous attempts at MeHg passive sampling have generally involved the adaptation of existing technologies originally designed to measure other analytes. A device developed

in the 1970s, the dialysis cell sampler (or peeper), operates on a size-exclusion principle. It has been used to sample metals and other ionic constituents including organic matter and sulfide.⁵⁸⁻⁶⁰ The challenge when using peepers for Hg_i and MeHg has been preserving speciation.⁶¹⁻⁶³ Of greater interest in recent years is the diffusive gradient in a thin film, or DGT, device, which is designed to function in a kinetic, rather than equilibrium, mode.^{20, 64} It has a successful history of sampling a variety of contaminant classes, but has not been widely accepted for Hg_i and MeHg. Ongoing sources of uncertainty include the device's potential to deplete porewater reserves, potentially resulting in oversampling⁶⁵⁻⁶⁸, the often confounding influences of DOM⁶⁹ and sulfide⁷⁰, and the danger of saturating binding sites within the device and diverging from kinetic uptake.⁷¹

1.5. Research Motivation

As activated carbon becomes an increasingly attractive option for in situ sediment remediation of hydrophobic organic contaminants (HOCs), several questions have yet to be answered. Even now, there have been relatively few applications at the pilot and field scales, and fewer still that have been monitored over the course of several years. It remains to be seen how effective the technology can be in diverse environmental systems, and how resilient it is to extreme weather and other perturbations. To expand the use of AC to mercury remediation, we need to characterize the biogeochemical factors that control its effectiveness, with the ultimate goal of developing a model to predict the “treatability” of contaminated sites.

Passive sampling of PCBs has matured to the point that it needs only refinement and standardization in order to be consistently implemented on a large scale. This will require

researchers and practitioners to agree on the most appropriate sampling materials and methods, and to reconcile the latest theoretical developments with the practical considerations involved in field deployments. For MeHg, an entirely new approach is needed to generate robust bioavailability measurements for this complex and challenging environmental contaminant.

The PCB-related research in this document enabled me to develop and implement the core concepts that I subsequently adapted to mercury bioavailability and passive sampling. The most significant intellectual contribution of the dissertation is based on the successful application of principles previously associated with hydrophobic pollutants to develop novel solutions for the mercury problem. The hypotheses that drove the mercury bioavailability research are as follows:

- *A passive sampling system based on some combination of chemical and size selectivity can be designed to provide input for a predictive model of MeHg bioaccumulation by the estuarine amphipod *Leptocheirus plumulosus*.*
- *Amendment of sediment with activated carbon will reduce porewater concentrations of bioavailable MeHg species, resulting in reduced MeHg accumulation by *L. plumulosus*. This reduction will coincide with reduced uptake by the sampling system developed for the previous hypothesis.*
- *Partitioning of Hg_i and MeHg to AC is substantially reduced in the presence of DOM, and can be predicted with equilibrium speciation calculations in tandem with AC-water partitioning coefficients for DOM.*

1.6. Outline of the Dissertation: Research Objectives and Contributions

This dissertation comprises seven chapters, including an introduction and a conclusion. Each of the intervening five chapters represents a manuscript prepared for a peer-reviewed journal.

Chapter 2 describes a pilot-scale field study comparing three different AC amendments in terms of their persistence and efficacy at reducing the bioavailability of PCBs in an intertidal *Phragmites* marsh at the Berry's Creek Study Area in Bergen County, NJ.

Sediment cores, passive samplers, and benthic organisms were collected during a number of field sampling events spanning more than three years. This represents the first successful demonstration of AC amendment in this type of system, and the results will be useful for the selection, design, and monitoring of future remediation projects. The study was a collaborative effort among UMBC, the Smithsonian Environmental Research Center (SERC), the consultancy firms Exponent, Anchor QEA, and Parsons, and The Dow Chemical Company. The resulting manuscript has nine authors, of whom I am the lead. In addition to drafting the manuscript, I also led the analytical effort and data interpretation, supervised an undergraduate lab assistant, and assisted with study design and field work. The passive sampling effort generated sufficiently interesting results to justify a separate manuscript, found in Chapter 3.

Chapter 3 covers the passive sampling effort carried out as part of the Berry's Creek pilot study described in Chapter 2. Three sampling polymers—PE, POM, and PDMS—were used, and in multiple thicknesses. Several ways of using PRC desorption data to adjust for sampler disequilibrium were compared, including methods based on first-order uptake kinetics and an assumption of aqueous boundary layer control on diffusion, as well as a

more generalizable method that takes into account compound- and site-specific properties. We found that all methods resulted in adjusted C_{pw} measurements that agreed well with one another for unamended sediment, but we also identified the potential for artifacts when the newer method is used for amended sediment. The use of multiple types of sampling polymers and PRC adjustment methods enabled direct, in situ comparisons that will help move the field toward consensus as it seeks to develop standard methods suitable for use within a regulatory context. This manuscript was written by three of the authors of the other Berry's Creek manuscript, of whom I was again the lead. The two papers were written as companions. My contribution to this work was the same as in Chapter 2.

The work described in Chapter 4 was conceived as an effort to characterize the effect of DOM on the sorption of mercury by AC. Previous studies had shown highly variable mercury-AC partitioning among diverse sediments and soils, and our working hypothesis was that this was largely driven by differences in aqueous mercury speciation, including DOM complexation. Addressing this variability is a necessary step toward developing a model of site treatability with AC, a central goal for mercury remediation. I performed a series of simple isotherm tests in water to generate AC partitioning coefficients for mercury-DOM complexes. This was an extension of previously published work by our colleagues that produced the coefficients for smaller complexes. My work lent theoretical support to a complementary study led by Dr. Grace Schwartz, then at SERC, in which mercury-DOM-AC interactions were tracked in anaerobic soil slurries. Along with the lab work associated with my portion of this project, I also performed chemical speciation

modeling, participated in the planning and interpretation phases, and helped draft the manuscript. It has six authors, of whom Dr. Schwartz is the lead and I am the second.

Chapter 5 outlines an effort to develop a novel passive sampling technology for MeHg in porewaters. Though MeHg is one of the most important and intensively studied environmental contaminants, there is currently no widely accepted passive sampling method to measure its bioavailability to aquatic food webs. The project developed and tested a series of prospective samplers under increasingly environmentally realistic conditions, culminating in soil microcosms. Several of the materials showed promise and merit further study, and one, a novel suspension of AC particles in agarose gels, is capable of generating useful predictions of MeHg porewater concentrations in sediment and soil. Crucially, the samplers appear capable of reversible, equilibrium sampling, which is the principle on which passive sampling of organic compounds has been successfully built but which has not been achieved for MeHg. I led the conceptual, experimental, and interpretive aspects of this study (with considerable analytical support from SERC personnel, particularly Alyssa McBurney). I am the first of five authors of the resulting manuscript.

In Chapter 6, two further soil microcosm studies with passive sampler deployments are described. This work provides further demonstrations of the AC-based sampler in realistic environmental matrices. I participated in the design, setup, analysis, and interpretation of both experiments, which were collaborative efforts among SERC, the U.S. Army Engineering Research and Development Center, The Dow Chemical Company, and Exponent, Inc. The decision to break these away from the manuscript in

Chapter 5 was based on a desire to focus on the samplers' ability to predict bioaccumulation. I am the first of eight authors of this manuscript.

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Chapter 2: Persistent Reductions in the Bioavailability of PCBs at a Tidally Inundated *Phragmites australis* Marsh Amended with Activated Carbon

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2.1. Abstract

In situ amendment of sediments with highly sorbent materials like activated carbon (AC) is an increasingly viable strategy to reduce the bioavailability of persistent, sediment-associated contaminants to benthic communities. Because in situ sediment remediation is an emerging strategy, much remains to be learned about the field conditions under which amendments can be effective, the resilience of amendment materials toward extreme weather conditions, and the optimal design of engineered applications. Here we report the results of a multi-year, pilot-scale field investigation designed to measure the persistence and efficacy of AC amendments to reduce the bioavailability of polychlorinated biphenyls (PCBs) in the unique environment of an intertidal *Phragmites* marsh. The amendments tested were granular AC (GAC), GAC with a layer of sand, and a pelletized, fine AC. Key metrics presented include vertically-resolved black carbon concentrations in sediment, and PCB concentrations in sediment, porewater, and several invertebrate species. The results demonstrate that all three amendments withstood Hurricane Sandy and remained in place for the duration of the study, successfully reducing porewater PCB concentrations by 34–97%. Reductions in invertebrate bioaccumulation were observed in all amendment scenarios, with pelletized fine AC producing the most pronounced effect. Our findings support the use of engineered AC amendments in intertidal marshes, and can be used to inform amendment design, delivery, and monitoring at other contaminated sediment sites.

2.2. Introduction

Hydrophobic organic compounds (HOCs) in sediments can be taken up by pelagic or benthic organisms through ingestion and dermal absorption and subsequently passed on to higher organisms and humans. For both of these pathways, the extent of uptake depends on the bioavailability of contaminants in sediment.¹ Work in the last two decades has demonstrated that black carbonaceous particles, including soot, coal, and charcoal, strongly bind HOCs, and the presence of black carbonaceous particles in sediments (both natural and anthropogenic) reduces uptake, often by an order of magnitude or more compared to natural organic matter.^{2, 3} Contaminant sequestration in native sediments can be greatly enhanced by the addition of clean, manufactured carbonaceous materials such as activated carbon (AC).⁴ Laboratory tests with a variety of field sediments have shown that AC amendment in the range of 2–5% d.w. reduces equilibrium porewater concentrations of polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons (PAHs), 1,1'-(2,2,2-trichloroethane-1,1-diyl)bis(4-chlorobenzene) (DDT), dioxins, and furans in the range of 70–99%, thereby reducing the driving force for diffusive flux of HOCs into water and transfer into organisms.⁴ Most studies using benthic organisms show a 70–90% reduction in biouptake of HOCs in AC-amended sediment compared to unamended controls.⁴ These studies have collectively demonstrated that contaminant bioavailability in sediments can be reduced by engineered amendments.

In a recent pilot-scale study, application of AC to contaminated river sediments reduced biouptake of PCBs in benthic organisms.⁵ After amendment with AC at a dose similar to the native sediment organic carbon content ($5.8 \pm 0.7\%$ d.w.), bioaccumulation in freshwater oligochaete worms was reduced compared to pre-amendment conditions by

69–99%, and concentrations of PCBs in water at equilibrium with sediment were reduced by more than 93% at all amended sites for up to three years of monitoring.⁵

While much is known about AC amendment in aquatic sediments in rivers, estuaries, mudflats, and lakes, no information is available on the persistence or efficacy of AC amendment in the unique sediment environment created within a *Phragmites australis* marsh. The site of this work was a *Phragmites* marsh impacted with legacy PCB and mercury contamination. While PCB and mercury investigations were conducted in parallel using the same experimental plots, this manuscript reports only the PCB results. The study was conducted in the field as a pilot-scale demonstration and involved three different modes of application of AC on the sediment surface followed by the monitoring of key exposure pathways for PCBs into the food web.

2.3. Materials and Methods

Study Site Description. This work was conducted at the Berry’s Creek Study Area (BCSA) in Bergen County, New Jersey. Berry’s Creek is a low-salinity tidal tributary to the Hackensack River and is located in the Hackensack Meadowlands about five miles west of New York City. Marshes dominated by *Phragmites* constitute 306 hectares (~756 acres) and approximately 75 percent of the tidal area within the BCSA. This dense *Phragmites* marsh is supported by thick root mats that create a physically stable landscape, thereby promoting consistent deposition (accretion) of new sediment^{6, 7} and providing an important buffer against storm surge and flooding of low-lying areas, including commercial buildings and residential neighborhoods. BCSA comprises three distinct, federally-designated Superfund sites, and the surrounding region was formerly home to extensive industrial activity, resulting in contamination by mercury, PCBs, and

other chemicals. This study was completed within Nevertouch Marsh, which is located in Upper Berry's Creek, adjacent to the Ventron/Velsicol Superfund Site. Nevertouch Marsh sediments are sulfidic and high in organic matter.⁸ Invertebrate organisms native to the site include wolf spiders (*Lycosidae* spp.), which are found on top of the marsh detrital layer, and the large, epibenthic amphipod *Orchestia grillus*.

Amendment Application. Four experimental plots were delineated within Nevertouch Marsh, each 10 m x 10 m and bounded by a 6-m buffer zone. Plot A was amended with SediMite™, a pelletized agglomerate of 50% powdered activated carbon (Siemens regenerated AC, < 30 mesh), sand, and clay (www.sedimite.com); Plot B served as an unamended control; Plot C was amended with coconut-shell based granular activated carbon (GAC; OLC WW 20 x 50 mesh from Calgon Corp.) topped by a 2–3 cm layer of sand; and Plot D was amended with GAC only. Previous work has shown pronounced amendment efficacy with a 5% dose of AC.^{5,9} The objective of application in the present study was to achieve this dose in the uppermost sediment layer, which represents the zone of greatest relevance to benthic organisms.¹⁰ In view of anticipated disruption of the amendment layer by tidal movement and bioturbation, a conservative application rate resulting in 5% AC in the top 10 cm assuming full mixing was calculated, and a further 25% safety factor was added for plot A resulting in a SediMite™ application rate of 5 kg m⁻² (2.5 kg AC m⁻²). For Plots C and D, where a coarser AC was used, the application rate was increased to 3.3 kg m⁻². The site was prepared by clearing *Phragmites* reeds from the plots and installing suspended metal planks a few inches above the sediment surface to facilitate access and sampling. The walkways also served to delineate nine subplots, each approximately 3 m x 3 m, within each plot. SediMite™ was applied using a

Vortex TR system (Vortex Granular Systems, Lighthouse Point, FL) that uses a flow of air to draw the pelletized material into an air stream and eject it to distances up to 12 m. Weight data from collection trays placed prior to SediMite™ application showed an average application rate of $4.8 \pm 1.0 \text{ kg m}^{-2}$, close to the target of 5 kg m^{-2} . GAC was applied as a water slurry to the surfaces of Plots C and D. The amount of GAC required to treat a subplot was loaded in large plastic containers and immersed in Berry's Creek surface water for a period of one hour, which hydrated the activated carbon and prevented it from being suspended in the water column during the first high tide following application. After an hour, the contents of the containers were thoroughly mixed and transferred into a 100-gallon tank. A gasoline-powered water pump was used to remove the slurry from the tank and eject it through a nozzle, which evenly distributed the slurry over the surface of the subplot. The thin sand layer placed over the activated carbon amendment in Plot C was moved from a staging area using a Telebelt conveyor. The sand was distributed over the plot by hand to a thickness of approximately 1".

Monitoring. Monitoring occurred at seven different time points, which for simplicity will hereafter be referred to by the number of months before or after the August 2012 amendment application: July 2012 (t_{-1}); October 2012, prior to Hurricane Sandy (t_{+2}); November 2012, after Sandy (t_{+3}); July 2013 (t_{+11}); November 2013 (t_{+15}); May 2014 (t_{+21}); and September 2015 (t_{+37}).

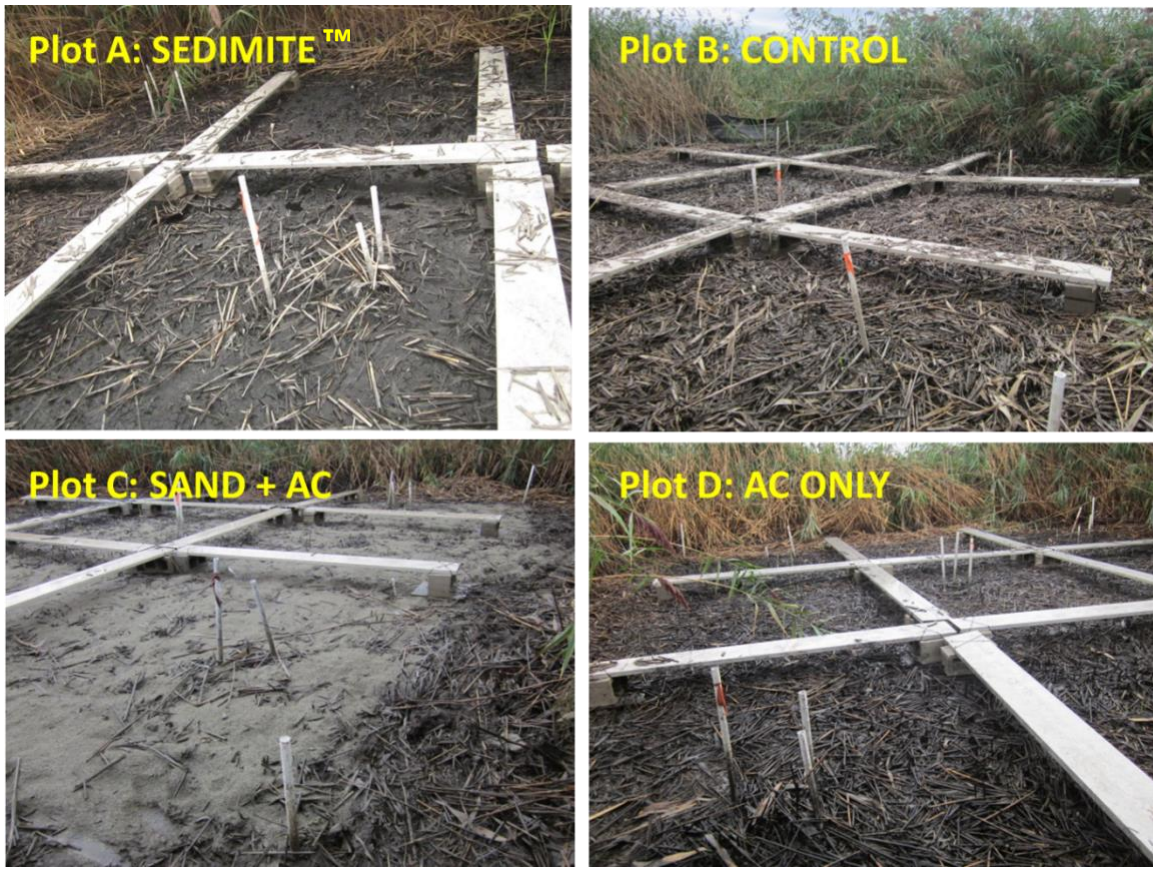


Figure 2.1. Appearance of the experimental plots two months after amendment application.

Sediment Collection. Sediment samples were collected using 4.8-cm i.d. boring core tubes from the 0- to 5-cm depth horizon at five randomly selected locations within each subplot and composited into a single sample. Collection occurred at low tide to minimize standing water. Soils were sampled using cutting/boring cores in an effort to capture root mass. The use of composite samples was intended to address anticipated spatial variability of contaminant concentrations within the plots. Processing of sediment core samples for vertical profiling changed throughout the monitoring period in response to a growing detritus layer developing on the marsh surface. Before AC application, most of

the detritus was cleared from the marsh surface. Sediment cores collected at t_{+2} were sectioned into a visible amendment layer followed by 0–5 cm and 5–10 cm sediment layers. This was done because of the differing thicknesses of the amendment layers among plots. For example, the GAC and sand amendment created the thickest layer of new material over the marsh surface and had to be accounted for during sample processing. An opportunistic sampling was performed one month after Hurricane Sandy (t_{+3}) to observe the effect of extreme weather on the persistence of amendment materials. In this effort, only the top 0–5 cm interval was sampled, including the detritus and amendment layers along with some sediment. In the subsequent two sampling events (t_{+11} and t_{+15}), a distinct new layer of detritus was observed on the surface and was sectioned separately from the amendment and underlying layers. Cores collected for the final two sampling events (t_{+21} and t_{+37}) were sectioned more finely, enabling generation of high-resolution vertical profiles of black carbon.

Passive Sampling. Porewater PCB concentrations (C_{pw}) were measured with passive sampling devices containing polyethylene (PE) or polyoxymethylene-ethylene oxide copolymer (POM). C_{pw} values were calculated with the standard equilibrium partitioning equation and partitioning coefficients.¹¹ When possible, PRC desorption data were used to adjust porewater concentrations for nonequilibrium. Adjusted concentrations are denoted C_{pw}' . More details on the passive sampling effort are provided separately.¹²

Materials. PCB solutions were prepared using individual congener and Aroclor standards in hexane purchased from Ultra Scientific (Kingstown, RI). All other chemicals and solvents were purchased from Fisher Scientific (Rockville, MD). Hexane and acetone were pesticide grade (CAS Nos. 110-54-3 and 67-64-1). Anhydrous sodium sulfate was

ACS grade (CAS No. 7757-82-6). Silica gel was 644 or 923 grade (CAS No. 112926-00-8 or 63231-67-4). Copper powder was lab grade (CAS No. 7440-50-8). Sulfuric acid was ACS Plus grade (CAS No. 7664-93-9). Potassium dichromate was ACS grade (CAS No. 7778-50-9).

Analytical Methods. The moisture content of wet sediment samples was determined by weighing representative subsamples (250 mg), drying in an oven overnight at 105 °C, and recording the difference in mass. Tissue and sediment samples were extracted by ultrasonication in 1:1 hexane:acetone according to U.S. EPA SW-846 method 3550C. Extracts were treated with activated copper powder to remove sulfur interference following U.S. EPA SW-846 method 3660B. Beginning with the t₊₁₁ sampling, activated copper was also added directly to wet sediment samples and mixed with a glass stir rod prior to extraction to address extensive sulfur interference. All extracts were cleaned up in deactivated silica gel columns following U.S. EPA SW-846 method 3630C. All PCB samples were analyzed by gas chromatography with electron capture detection (Agilent 6890N with a fused silica capillary column: Rtx-5MS, 60 m x 0.25 mm i.d., 0.25 µm film thickness from Restek, Bellefonte, PA, USA) according to an adapted version of U.S. EPA SW-846 method 8082A described by Beckingham and Ghosh.⁵ A total of 91 congeners or coeluting congener groups were quantified. PCB BZ #30 and 204 were used as internal standards. PCB BZ #14 and 65 were added as surrogates prior to all sample extractions to assess loss during processing. The total concentration of the 87 target congeners/congener groups (representing the commercial Aroclor mixtures 1232, 1248, and 1262) is hereafter denoted ΣC.

Black Carbon Determination. Sediment black carbon (BC) was measured with a chemical oxidation method.¹³ Briefly, dried sediment samples were treated with a solution of potassium dichromate in concentrated sulfuric acid to remove organic carbon, then thermally combusted and analyzed on a Shimadzu TOC-5000A with solid sample module SSM-5000A. A 5% BC sediment standard was processed alongside samples to quantify recovery.

In Situ Exposure Chambers. An in situ sediment exposure chamber was developed for this study. The chamber consisted of a 12" long, 6" i.d. tubular chamber with 500- μ m mesh-covered ports on one end. The exposure chamber was driven vertically into the sediment of each subplot to a depth of approximately 10", which left the bottom of the ports 1" above the sediment surface. The chambers were loaded with 125 3–5 mm, salinity-acclimated *Leptocheirus plumulosus*, an estuarine amphipod commonly used in toxicity testing, capped using a rubber pipe cap the center of which had been removed and replaced with 500- μ m mesh, and left in place for an exposure period of 14 d. After the exposure period, the upper 2–3" of sediment within the chambers was collected and sieved, and the surviving *L. plumulosus* individuals in this sieved material were collected and depurated for a period of 4–6 h in spring water. After depuration, the animals were blotted dry with filter paper, weighed, and immediately frozen for transport and analysis of PCBs, lipid content, and moisture content.

Several modifications were made to the in situ exposure chamber method following the first deployment of the chambers during the pre-application monitoring event. The modifications and rationale for making them are discussed in Appendix I.

Laboratory Bioaccumulation Assays. The recoveries and masses of *L. plumulosus* from the in situ exposure chambers were lower than anticipated during the t₋₁ and t₊₂ monitoring events, so for the t₊₁₁ monitoring event, intact cores were collected for use in laboratory bioaccumulation assays to provide an additional measure of bioaccumulation. The intact sediment cores were collected by driving 12” sections of 4” i.d. polycarbonate tubing into the sediment to a depth of 6”. The top of the core was capped, the core was extracted from the sediment, and then capped on the bottom. Four adjoining sediment cores were collected from each of the subplots. The samples were shipped on wet ice to EnviroSystems, Inc. (Hampton, NH) and used in bioaccumulation assays using the amphipod *Hyaella azteca* (salinity acclimated) according to a standard method.¹⁴

Native Invertebrate Tissue. Native invertebrate samples were collected from each of the plots. The target organism was *O. grillus*, which was observed during preliminary surveillance but became increasingly scarce during the study period. Organisms were collected from plot surfaces with forceps and placed in spring water for a depuration period of 4–6 h. After depuration, the animals were blotted dry with filter paper, weighed, and immediately frozen for transport and analysis of PCBs, lipid content, and moisture content.

O. grillus were difficult to find in the plots after application of amendments. This was likely due to the partial removal of detritus from the plots, as *O. grillus* rely upon detritus as a source of food and cover from predation. The scarcity of this organism was observed in Plot B as well, indicating that it was not caused by the presence of amendment materials. Spiders were collected as a supplementary native invertebrate during the t₊₁₁ monitoring event. Results are presented in Appendix I.

In this work, an organism “sample” (one n) refers to a composite of multiple individual organisms of a single species except in cases where individual spiders were sampled as discussed in Appendix I. Samples were homogenized with Na_2SO_4 using a glass stir rod and extracted in 1:1 hexane:acetone using an adaptation of EPA method 3550C. An aliquot equal to one tenth of the extract volume was quantitatively removed for lipid analysis, with the remainder proceeding to PCB analysis. Organism lipid content was measured using a method originally developed for mosquitos ¹⁵. In brief, each aliquot was evaporated to dryness, treated with a vanillin-phosphoric acid reagent to induce a color change, and analyzed on a Genesys 10S UV-visible spectrophotometer (ThermoScientific, Waltham, MA).

Quality Assurance/Quality Control. Surrogate recoveries in sediment extracts averaged $83 \pm 19\%$ for PCB BZ#14 and $79 \pm 12\%$ for PCB BZ#65 ($n = 163$). Average recoveries in passive sampler extracts were $92 \pm 9.7\%$ for PCB BZ#14 and $88 \pm 9.2\%$ for PCB BZ#65 ($n = 167$). Recoveries in organism extracts averaged $77 \pm 13\%$ for PCB BZ#14 and $74 \pm 12\%$ for PCB BZ#65 ($n = 67$). Data from PCB samples with less than 60% recovery of each surrogate compound are not reported. Standard recoveries in black carbon samples averaged $86 \pm 12\%$ ($n = 13$). No values were adjusted to account for standard recoveries.

2.4. Results and Discussion

Activated Carbon in Sediment. Activated carbon was measured as BC in sediment core samples collected in six distinct sampling events spanning more than three years after amendment application. While pre-application samples were not collected from the amended plots, the BC content in Plot B (control) was low at 0.1% ($n = 5$) in Sep 2012

and this was taken as representative of the background level in all plots. No background correction was applied. The BC content of the surface sediment and detritus layers in plot B increased to a value of 1.1% in 2013 samples, potentially due to redistribution of some AC from the adjacent treatment plots. As summarized in Figure 2.2, the data from all time points indicate elevated levels and persistence of AC in all three amended plots throughout the study period.

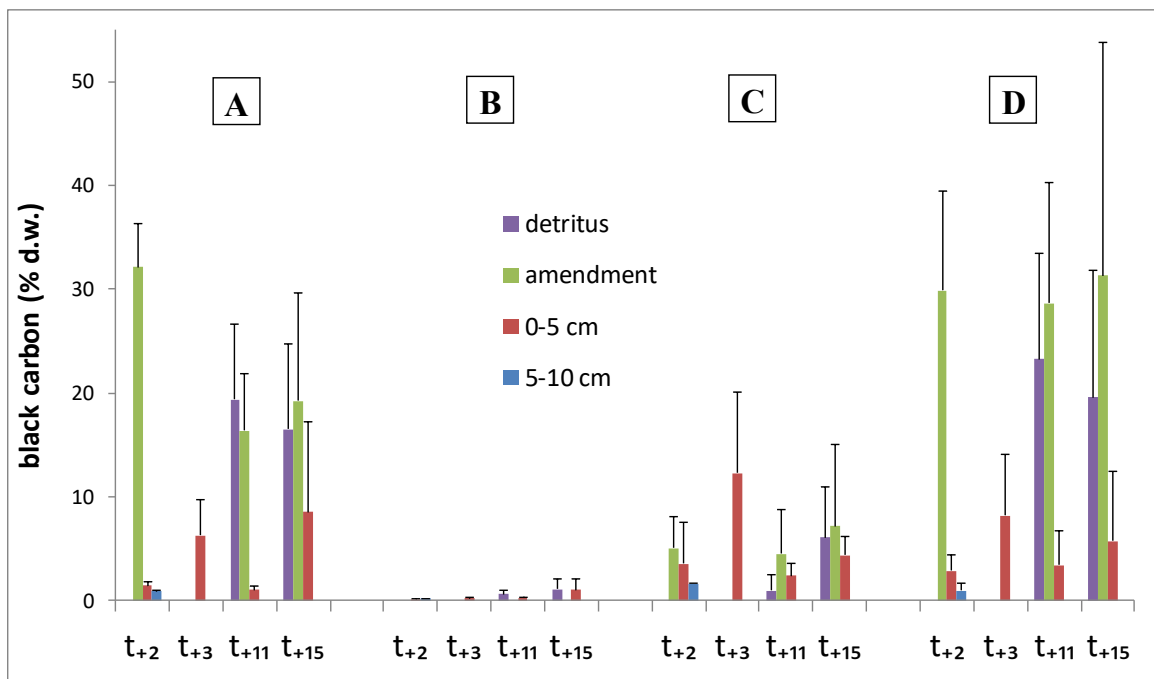


Figure 2.2. Dry-weight black carbon content of BCSA sediments, arranged by plot(A: SediMite™, B: unamended control, C: GAC and sand, D: GAC), layer, and date. Error bars show standard deviation among cores ($1 \leq n \leq 5$).

At t+2, high levels of BC in the amendment layers were measured. Plots A and D had the highest levels of BC, in the range of 30–32% ($n = 4$ and 5 , respectively, $p < 0.05$), while BC measured in Plot C was significantly lower at $5.0 \pm 3.0\%$ ($n = 5$, $p < 0.002$) due to the

dilution effect of the sand. At t_{+3} , AC was present in all amended plots at levels comparable to those measured before the storm, demonstrating the resilience of the amendments. In Plots A and D, where applied AC was exposed to the surface, the detritus layer defined for t_{+11} and t_{+15} would have included AC, while in Plot C, the detritus layer was dominated by sand. Thus, the apparently shallower penetration of AC below the amendment layer was likely an artifact of sample sectioning methods. At t_{+15} , the amendment layer in Plot A contained $19 \pm 10\%$ BC d.w. ($n = 5$), in Plot C $7.2 \pm 7.9\%$ ($n = 6$), and in Plot D $31 \pm 22\%$ ($n = 5$). Since duplicate analyses of individual samples were generally reproducible, the large variability in these measurements can be ascribed to a real phenomenon, i.e. a spatially heterogeneous distribution of amendment materials within each 100-m² plot. These results provide a basis for realistic anticipation of application uniformity and have important implications for the design of future remediation projects. The addition of a sand layer in Plot C was intended to prevent loss of AC, but it also served to dilute the AC in surface sediments, resulting in the lowest concentrations among the three amended plots.

Sediment below the amendment layer showed some integration of amendment materials over time. Compared to previous sampling events, this layer contained elevated BC levels at t_{+15} , with the highest measured in Plot A. However, the subjectivity involved in identifying and sectioning the amendment layer made precise quantification of downward AC migration into sediments difficult. To investigate vertical migration more carefully, samplings were performed at t_{+21} (Plot A only) and t_{+37} (Plots A, C, and D) in which cores were sectioned into 1-cm intervals in the uppermost 5 cm, and a 5-cm interval spanning the 5–10 cm horizon. Measurement of black carbon in these samples enabled

generation of high-resolution BC depth profiles (Figure 2.3). In plot A at t_{+21} , concentrations averaged $22 \pm 6.8\%$ d.w. ($n = 5$) in the top 1-cm layer and $23 \pm 6.6\%$ d.w. ($n = 5$) in the 1–2 cm layer. BC content was below the amendment target of 5% d.w. in the 3–4 cm interval ($2.0 \pm 1.6\%$ d.w. ($n = 5$)), and consistent with background levels in the 4–5 cm and 5–10 cm intervals. At t_{+37} , comparable BC profiles were observed in all three amended plots, with the exception of lower concentrations in the upper horizons of Plot C due to dilution by sand. These results indicate a vertical extent of mixing of 3–5 cm after three years. Such slow integration of amendment materials was likely due to low benthic activity and the presence of a dense *Phragmites* root mat that resisted sediment mixing. The fact that amendment materials in all three plots remained in place through more than three years of tidal cycling and a major storm event demonstrates the resilience required for a successful field application of these technologies. Because the amendments without a sand layer remained in place, the diluting effect and additional expense associated with the sand layer proved unnecessary.

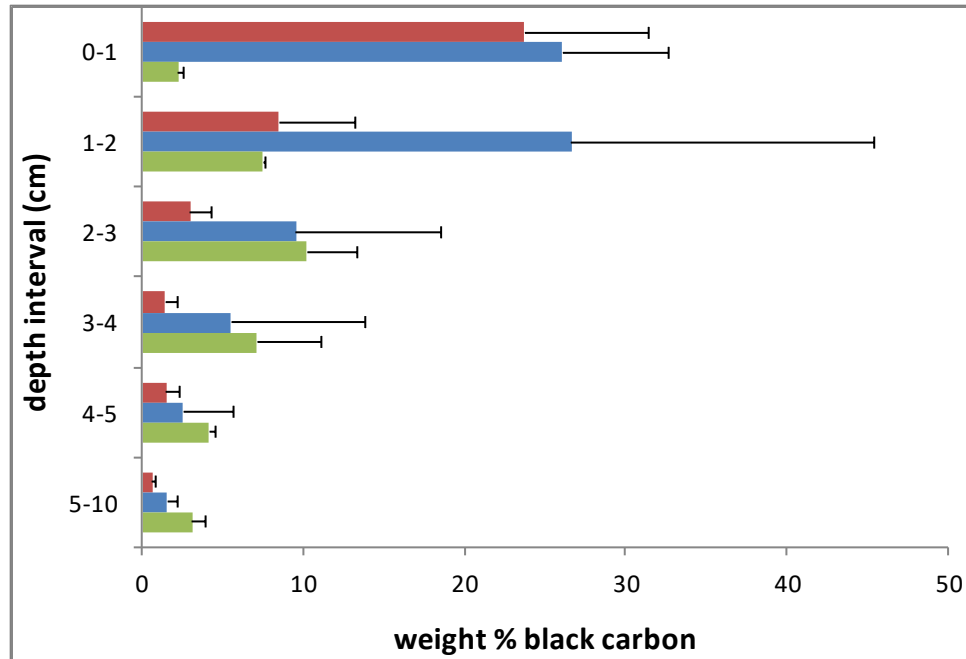


Figure 2.3. Depth profile of black carbon content (% d.w.) in BCSA sediment 37 months after amendment application. Red: SediMite™; blue, GAC; green, GAC and sand. Error bars show standard deviation among samples at each depth ($n = 5$ or 6).

Samples from the three treatment plots at t_{+37} can be used to compare the amount of AC remaining after 37 months with the original applied dose. In plot A, the applied SediMite™ had 15% moisture, and the BC content of the AC was 84%.¹³ Thus, the applied mass loading of BC was 1.8 kg BC m^{-2} . The recovered mass of BC at t_{+37} for plot A was $1.7 (\pm 0.5) \text{ kg BC m}^{-2}$. Plots C and D received GAC at an application rate of 3.3 kg AC m^{-2} which translates to a BC loading rate of 2.9 kg BC m^{-2} assuming 87% BC in the coconut GAC.¹³ For Plot C, which also received a sand layer (bulk density of 1.6 kg L^{-1}), the recovered mass of BC was $3.0 (\pm 0.4) \text{ kg m}^{-2}$ and for Plot D the recovered mass of BC was $3.1 (\pm 1.0) \text{ kg m}^{-2}$. Thus, after 37 months in the field and after a major storm that

flooded the area, the recovered mass of BC in the top 10 cm of sediment was close to the applied dose in each plot.

PCB Concentrations in Sediment. In all plots, a characteristic PCB homolog distribution was observed in sediment, with tetra- and penta-CB homologs dominating the distribution (Figure AI.S2). ΣC_{sed} in unamended sediment samples was in the range of 1.0–3.0 $\mu\text{g g}^{-1}$ d.w. at surficial and subsurficial depths throughout the study period ($n = 4$ or 5 for each sampling). At t_{+15} , detrital layer ΣC_{sed} ($0.53 \pm 0.29 \mu\text{g g}^{-1}$ d.w.) was 62% lower in Plot A compared to control ($1.4 \pm 0.12 \mu\text{g g}^{-1}$ d.w.). The largest reduction in total sediment concentration was observed in Plot C ($0.25 \pm 0.17 \mu\text{g g}^{-1}$, an 82% reduction) and the smallest in Plot D ($0.75 \pm 0.58 \mu\text{g g}^{-1}$, a 46% reduction). In general, surface placement of amendment materials was successful at reducing PCB concentrations in the new detritus collecting on the marsh surface. The observed recontamination of the fresh detritus collecting on the treated plot surface is likely from a combination of exposure to contaminated porewater in the treated layer combined with exposure to surface water at each tidal cycle. The tidal deposition of PCBs was evaluated using trays of clean topsoil placed on the marsh as described in the Supplemental Information. After exposure in the marsh environment through many tidal cycles over a period of three and a half months, the PCB concentration in the topsoil nearly doubled from $0.04 \mu\text{g g}^{-1}$ ($n = 2$) to $0.08 \mu\text{g g}^{-1}$ ($n = 3$; $p = 0.054$). The largest increases were observed in the tri- and tetrachloro congeners, pointing to sorption from the dissolved phase as the most likely mechanism of recontamination. Thus, for long-term effectiveness, any remedy implemented in the marsh will have to address the concentrations of PCBs in the water that overtops the marsh during tidal cycling.

PCB concentrations in the amendment layer of all three amended plots were lower than the concentrations measured in the 0–5 cm layer, with the lowest value found in Plot C (due to dilution with the sand layer). However, below the amendment layer, ΣC_{sed} in all plots remained close to $1.5 \mu\text{g g}^{-1}$ one year after amendment and within the range of 1.0– $3.0 \mu\text{g g}^{-1}$ through all sampling times. No temporal trends in sediment PCB concentrations were apparent across the three sampling events in the year after application.

PCB Concentrations in Sediment Porewater. Freely dissolved concentrations of PCBs in sediment porewater were measured by passive sampling with POM and PE. At t_{-1} , total PCBs in porewater (ΣC_{pw} ; unadjusted for nonequilibrium) were 1.0–4.0 ng L^{-1} in all plots in both the 0–2.5 cm and 5–7.5 cm depth intervals (Figure 2.4). At t_{+2} , ΣC_{pw} in the upper interval was decreased by 97% in Plot A (SediMiteTM), 48% in Plot B (control), 76% in Plot C (GAC and sand), and 86% in Plot D (GAC; $n = 5$ for Plots A, B, and D, $n = 3$ for Plot C). In all subsequent sampling events through t_{+15} , upper-interval ΣC_{pw} in amended plots remained low relative to both pre-amendment levels in the same plots and concurrently measured levels in Plot B. At t_{+15} , the smallest reduction (34%) was observed in Plot C. The largest proportional upper-interval reductions occurred in Plot A, where ΣC_{pw} was 91–97% lower than the initial value at all sampling events throughout the study. In the 5–7.5 cm depth interval, significant reductions in ΣC_{pw} were only observed in Plot A, where they were significant at all sampling events (t -test, $p < 0.05$). This finding is discussed at greater length separately.¹²

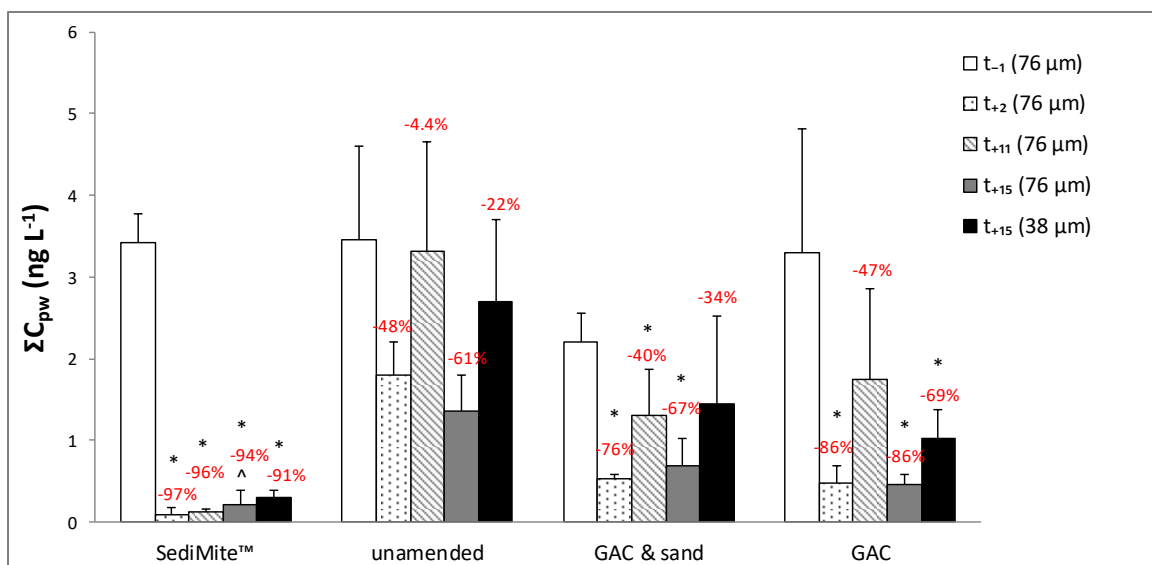


Figure 2.4. Average total PCB concentrations measured in sediment porewater using POM passive samplers in the 0–2.5 cm depth interval at BCSA. Values are unadjusted for fractional PRC loss. Error bars show one standard deviation among samplers in each plot ($n = 5$ except $^{\wedge} (n = 4)$). Percent decreases from each plot’s pre-amendment value are shown. Asterisks denote statistical significance ($p < 0.05$).

Sediment-Water Partitioning. PCB sediment-water partitioning coefficients (K_d) were calculated for the t_{+11} sampling data by dividing C_{sed} by C_{pw}' (adjusted using the k_e - K_{ps} PRC method).¹² Because C_{sed} was measured in the upper 5 cm of sediment while C_{pw}' represented only the upper 2.5 cm in that sampling event, the resulting K_d values should be interpreted with care, particularly in the amended plots. The discrepancy is less relevant for Plot B, where no significant vertical trend in C_{pw} was found in subsequent high-resolution measurements.¹²

In all plots, PCB K_d exhibited a log-log correlation with K_{ow} across individual congeners (Figure 2.5). Despite significant reductions in C_{pw} in Plots C and D as a result of

amendment, there was no evident increase in K_d in these plots relative to Plot B (control). This may be due in part to the discrepancy between porewater and sediment sampling horizons, as well as the potential for artificially low C_{sed} as a result of reduced extractability from amended sediment (31–34% on average and more pronounced for lower-chlorinated congeners; see Appendix I). Trends in K_d were evaluated with reference to a simple partitioning model based on the assumption that organic carbon was the dominant binding phase for PCBs:

$$K_d = f_{oc}K_{oc} \quad (1)$$

where f_{oc} is the fraction of sediment comprising organic carbon and K_{oc} is the organic carbon-water equilibrium partitioning coefficient for each congener or coeluting group.

In the absence of a directly measured value, f_{oc} was set at 11% by multiplying the average measured loss-on-ignition (LOI) in the plots (31%) by a correction factor of 0.36.^{8, 16} K_{oc} values for all congeners were derived from a model for sorption of hydrophobic chemicals to sediment¹⁷:

$$\log K_{oc} = 1.00 \times \log K_{ow} - 0.21 \quad (2)$$

Measured K_d values in Plots B, C, and D were higher than predicted by this simple model, which is sensitive to imprecision in LOI and f_{oc} values and does not take into account partitioning to black carbon, present even in Plot B at low background concentrations.² While the fraction of BC in each plot varied, the influence of BC in overall K_d was accounted for as follows^{18, 19}:

$$K_d = (f_{oc} - f_{bc})K_{oc} + f_{bc}K_{bc} \quad (3)$$

where f_{bc} , the mass fraction of black carbon in sediment, was set at 5% (the application target for the amended plots), and K_{bc} , the partitioning coefficient for black carbon, varies linearly with K_{ow} in the concentration ranges measured in this work²⁰:

$$\log K_{bc} = 0.91 \times \log K_{ow} + 1.37 \quad (4)$$

With this model, a good fit for the observed data in Plots B, C, and D was obtained. In Plot A, K_d was elevated compared to the other three plots by roughly one order of magnitude across the range of hydrophobicities. This can be attributed to the more strongly sorbing, higher-surface area, fine-grained AC used in the amendment materials in this plot, and helps to explain the larger reductions in PCB ΣC_{pw} and bioaccumulation (next section) observed in the plot. Increases in K_d were more pronounced at the lower end of the K_{ow} range, and the Plot A results exhibited greater scatter due to the larger relative error in C_{pw} measurements near our lower analytical detection limits.

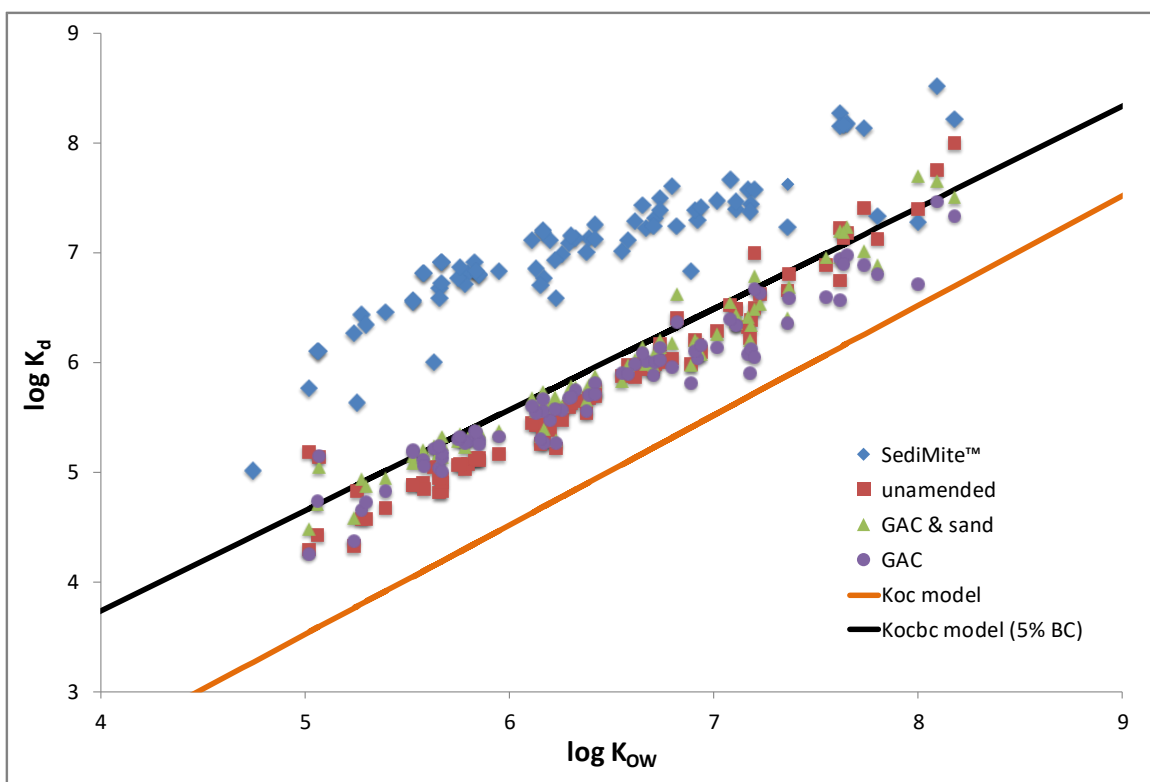


Figure 2.5. Logarithmic sediment-water partitioning coefficients for individual PCB congeners or congener groups. Data are from the t_{+11} sampling. Each K_d value is calculated from an average C_{sed} value ($n = 5$) for the 0–5 cm horizon and an average C_{pw} value ($n = 5$) for the 0–2.5 cm horizon. C_{pw} was adjusted with the k_e - K_{ps} PRC method.¹ Orange line: organic carbon model; black line: organic carbon and black carbon model (see text for descriptions).

PCB Bioaccumulation in Field and Laboratory Exposures. All three amendments effected reductions in PCB bioaccumulation compared to unamended sediment. A summary of amphipod bioaccumulation results from both field and laboratory exposures can be found in Table 2.1. At t_{+2} , both caged and native, free-ranging amphipods

contained reduced PCB body burdens (ΣC_{org}) in all three amended plots relative to Plot B (control).

Table 2.1. Summary of amphipod bioaccumulation data.

Event	Metric	Lab Control Sediment	Plot A (SediMite™)	Plot B (unamended)	Plot C (GAC & sand)	Plot D (GAC)
t ₊₂	sediment BC, wt %*	n.d.	1.5 ± 0.42 (5)	0.15 ± 0.017 (5)	3.6 ± 3.9 (5)	2.9 ± 1.5 (5)
	ΣC_{pw} , ng L ⁻¹ **	n.d.	0.091 ± 0.086 (5)	1.8 ± 0.39 (5)	0.54 ± 0.046 (3)	0.47 ± 0.21 (5)
	caged <i>L. plumulosus</i> ΣC_{org} , ng g ⁻¹ w.w.	n.d.	17 (1)	1000 ± 100 (2)	330 (1)	240 (1)
	native <i>O. grillus</i> ΣC_{org} , ng g ⁻¹ w.w.	n.d.	420 (1)	2100 (1)	490 (1)	500 (1)
t ₊₁₁	sediment BC, wt %*	n.d.	1.0 ± 0.34 (5)	0.26 ± 0.042 (5)	2.4 ± 1.2 (5)	3.4 ± 3.3 (5)
	ΣC_{pw} , ng L ⁻¹ **	n.d.	0.12 ± 0.041 (5)	3.3 ± 1.3 (5)	1.3 ± 0.56 (5)	1.8 ± 1.1 (5)
	lab <i>L. plumulosus</i> ΣC_{org} , ng g ⁻¹ w.w.	25 ± 14 (3)	46 (1)	280 ± 110 (2)	n.d.	n.d.
	lab <i>H. azteca</i> ΣC_{org} , ng g ⁻¹ w.w.	6.7 ± 6.0 (3)	10 ± 2.9 (3)	300 ± 37 (3)	30 (1)	86 ± 35 (3)
t ₊₁₅	sediment BC, wt %*	n.d.	8.6 ± 8.7 (5)	1.0 ± 1.0 (5)	4.1 ± 1.9 (6)	5.7 ± 6.8 (5)
	ΣC_{pw} , ng L ⁻¹ **	n.d.	0.20 ± 0.19 (4)	1.4 ± 0.44 (5)	0.69 ± 0.33 (5)	0.47 ± 0.11 (5)
	lab <i>H. azteca</i> ΣC_{org} , ng g ⁻¹ w.w.	22 ± 8.9 (3)	n.d.	240 ± 74 (3)	87 (1)	55 ± 17 (3)

* 0–5 cm depth interval; ** 0–2.5 cm depth interval measured with POM-76 and unadjusted for nonequilibrium; *n* given in parentheses

For caged *L. plumulosus*, reductions of 98%, 68%, and 76% were observed in Plots A (SediMite™), C (GAC and sand), and D (GAC), respectively. Similarly, ΣC_{org} in native, free-ranging *O. grillus* collected in Plots A, C, and D was 78% ($p < 0.05$), 48% (not statistically significant), and 68% ($p < 0.05$) lower, respectively, than in Plot B. Overall, reductions in bioaccumulation in amended plots were more pronounced for caged versus native organisms. This can be explained by a combination of two factors. First, native organisms collected from the plots were free-ranging and could have been washed into or out of unamended buffer zones by the tide, thereby diluting the effect of amendment. Second, native organisms could have spent part of their early lives in unamended, contaminated sediments whereas caged organisms were cultured in clean sediment and went in with minimal prior exposure. Beginning with t_{+3} , native *O. grillus* became too scarce to collect sufficient tissue for PCB analysis. Indeed, general benthic activity in both control and amended plots was lower than expected during these sampling events, and survival and recovery of caged organisms was also inconsistent, probably due to poor habitat within enclosed chambers that did not provide adequate shelter during low tide and recovery from large amounts detritus.

In 10-d laboratory exposures to intact sediment cores, *L. plumulosus* ΣC_{org} was 84% lower in Plot A sediment than in unamended sediment. Tissue recoveries from Plot C and D laboratory exposures were insufficient for analysis. Two separate experiments were performed with *H. azteca*. In the first, ΣC_{org} was reduced by 96%, 90%, and 71% in Plot A, C, and D sediment, respectively ($p < 0.01$ for all three). In the second, 64% and 77% reductions in Plot C and D sediments were observed, but only the latter was statistically significant ($p = 0.05$). Insufficient tissue was available for Plot A. All three amendments

led to reduced bioaccumulation in laboratory exposures, with fine-grained AC in the form of SediMite™ producing the most pronounced effect.

Implications. Previous pilot-scale demonstration projects with in situ amendment of AC to sediments have targeted marine mudflats²¹, rivers⁵, and deep ocean deployments²². Results from this field study provide new insights into the technical feasibility and effectiveness of in situ remediation for a *Phragmites*-dominated, intertidal marsh with PCB contamination. AC amendments applied in a *Phragmites* marsh were stable over the three-year period of observation through multiple tidal cycles and a major storm. All three amendment types demonstrated reductions in the concentration of PCBs in surface sediment porewaters (34–97%) and in benthic organisms (48–98%), with the largest reductions associated with the use of a pelletized, fine-grained activated carbon (as SediMite™). Many coastal ecosystems have been historically impacted by the deposition of contaminated sediments and are difficult to remediate using the common approaches of sediment removal or capping. In situ amendments as described in this paper provide an alternative that is capable of reducing exposure of pollutants to the food web without significantly impacting the existing ecosystem in the marsh by dredging or other, more disruptive methods.

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UG is a co-inventor of two patents related to the technology described in this paper for which he is entitled to receive royalties. One invention was issued to Stanford University (US Patent # 7,101,115 B2), and the other to the University of Maryland Baltimore County (UMBC) (U.S. Patent No. 7,824,129). In addition, UG is a partner in a startup company (Sediment Solutions) that has licensed the technology from Stanford and UMBC and is transitioning the technology in the field.

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Chapter 3: Evaluation of Passive Sampling Polymers and Non-Equilibrium Adjustment Methods in a Multi-Year Surveillance of Sediment Porewater PCBs

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3.1. Abstract

Polymeric passive sampling devices are increasingly used to measure low-level, freely dissolved concentrations of hydrophobic organic contaminants in environmental waters. A range of polymers have been used for this purpose, and several different methods of accounting for nonequilibrium using performance reference compounds (PRCs) have been proposed. This study explores the practical impacts of these decisions in an applied context using results from a multi-year passive sampling surveillance of polychlorinated biphenyl (PCB) concentrations in sediment porewater at a contaminated marsh amended with activated carbon sorbent materials. In a series of five sampling events spanning almost two years, we deployed polyoxymethylene (POM), polyethylene (PE), and polydimethylsiloxane (PDMS) samplers and calculated porewater concentrations with four different PRC adjustment methods. The results provide a basis for evaluating amendment performance by showing reductions of 34–97% in amended sediment porewater concentrations. They also provide a quantitative underpinning for discussions of the differences between sampling polymers, selection of PRCs, generation of high-resolution vertical profiles of porewater concentrations, and a comparison of PRC adjustment methods.

3.2. Introduction

Hydrophobic polymers are in wide use as passive sampling devices for organic pollutants like polychlorinated biphenyls (PCBs) in sediment porewaters. Their measurements of freely dissolved contaminant concentrations provide a useful metric of bioavailability to benthic organisms.¹ The advantage provided by passive samplers lies in their ability to sample target chemicals, which typically exist in extremely low aqueous concentrations, to analytically detectable levels, and to do so in a time-integrative fashion. During sampler deployment, contaminants diffuse into the polymer toward a thermodynamic equilibrium with the external water phase. This can be modelled as a diffusion process whose rate is controlled by the sampler's geometry, the concentration gradient between sampler and water, and an overall mass transfer coefficient representing the resistances to transfer in the sampling polymer and the external, aqueous boundary layer.² The relative importance of each source of mass transfer resistance can be described in terms of the target compound's octanol-water partitioning constant. When passive samplers are deployed in static sediments, mass transfer is limited by the sediment side for most hydrophobic compounds.³ In practice, this means that samplers in stagnant sediments may be kinetically inhibited from reaching equilibrium with highly hydrophobic contaminants during a typical deployment time of months. To account for this nonequilibrium, performance reference compounds (PRCs) can be loaded into samplers prior to deployment. PRCs are compounds with chemical characteristics similar to those of the target contaminants but not present in the field at detectable levels. Loss of PRCs from samplers is used to characterize sampler equilibration during the period of deployment, and to adjust measured contaminant concentrations accordingly.⁴

Ideally, the kinetics of PRC desorption should be identical to those of target compound absorption. In practice, such isotropic kinetics can be realized by the use of stable isotope-labelled versions of the target compounds as PRCs. However, when this strategy is not viable (as in the present study, in which a suite of dozens of PCB congeners was measured and the use of an isotope-labelled version of each would have been cost prohibitive), desorption data from a small selection of PRCs must be extrapolated to estimate the equilibration state of all target compounds.⁵ Currently, there exists no standardized method of carrying out such extrapolations, with numerous variants having been reported in the literature. In the past, most of these relied on correlations (either linear or nonlinear) between measured sampler uptake rate (k_e) and a physicochemical property of the PRCs like molar volume (V_m), molecular weight (MW), octanol-water partitioning (K_{ow})⁶ or sampler-water partitioning (K_{ps}).⁷ The latter two are to some extent interchangeable because K_{ps} values for most congeners are derived from literature-reported correlations with K_{ow} .¹ All of these methods are based on the model of a first-order, exponential approach to sampler equilibrium. Most investigators have found this approximation suitable for conditions in which contaminant mass transfer is controlled primarily by the aqueous boundary layer. This includes low-flow or stagnant sediments, thin sampling polymers ($< 100 \mu m$), and highly hydrophobic target compounds ($\log K_{ow} > 4.5$).^{3, 8} Recently, more general PRC adjustment methods have been proposed. These are based on modeling of Fickian diffusion by contaminants into and out of sediment beds and they take into account not only compound- but site-specific properties.^{2, 8}

In the present work, passive sampling data were generated as part of a multi-year monitoring effort for a pilot-scale sediment remediation project, which is described in

greater detail elsewhere.⁹ Several widely-used sampling polymers were employed and their measurements are compared, including contrasting congener accumulation profiles and PRC desorption rates. Finally, a comparison is made of several of the most commonly used methods for adjusting measured porewater concentrations for nonequilibrium.

3.3. Materials and Methods

Study Site. All measurements were performed at the Berry's Creek Study Area (BCSA) in Bergen County, NJ. The area chosen is a tidal marsh overrun by *Phragmites australis* reeds and impacted by legacy contamination with mercury and PCBs. The marsh study area was divided into four plots, designated A–D. Plot A was amended with SediMite™, a pelletized agglomerate of 50% powdered activated carbon (Siemens regenerated AC, < 30 mesh), sand, and clay (www.sedimite.com); Plot B served as an unamended control; Plot C was amended with coconut-shell based granular activated carbon (GAC; OLC WW 20 x 50 mesh from Calgon Corp.) topped by a 2–3 cm layer of sand; and Plot D was amended with GAC only. In addition to passive sampling of sediment porewater, monitoring consisted of measuring black carbon and extractable PCBs from sediments, measuring bioaccumulation in the field using both caged and native benthic organisms, and laboratory bioaccumulation assays. Those results are reported separately.⁹ Passive sampling was performed at five different time points, which for simplicity will be referred to by the number of months before or after amendment application: t-1, t+2, t+11, t+15, and t+21.

Passive Sampling. Sampling polymers used in this study include polyethylene (PE; Husky, Bolton, Ontario) in 17.7 and 25 µm thicknesses, hereafter denoted PE-18 and PE-

25, and polyoxymethylene (POM; CS Hyde, Lake Villa, IL) in 38 and 76 μm thicknesses, hereafter denoted POM-38 and POM-76. Prior to use, polymer sheets were cut into strips and cleaned by soaking in a 1:1 mixture of hexane and acetone for approximately 12 h. Strips were impregnated with performance reference compounds (PRCs) in a 4:1 mixture of methanol and deionized water.¹⁰ Initially, five PRCs were to be employed: PCB BZ #s 29, 69, 103, 155, and 192, representing the tri- through hepta-substituted homolog groups. However, in early chromatographic tests, PCB BZ #103 was found to coelute with another compound present in BCSA sediment and was excluded from subsequent work. After impregnation, strips were removed from solution and blotted gently. For the t_{-1} , t_{+2} , t_{+11} , and t_{+15} deployments, one strip from each impregnation solution was removed and analyzed, with the results used as a proxy measure of initial PRC concentrations in all other strips from that solution. For t_{+21} , a 4-cm portion of each PE sheet to be deployed was cut off, placed in 25 mL 1:1 hexane:acetone, and refrigerated for subsequent extraction and direct measurement of initial PRC concentrations.

POM samplers were assembled by enfolding the strips with stainless steel mesh and placed in a frame assembled by fastening two 8" galvanized steel corner brackets (Home Depot model #16077) with 3/8" screws and nuts. For t_{-1} , t_{+2} , t_{+11} , and t_{+15} , two 2.5 cm strips of POM-76 were fixed horizontally across the 14.5 cm width of the frame's open area and arranged to sample the 0–2.5 cm and 5–7.5 cm depth intervals discretely (Figure 3.1). PE samplers for t_{+21} were assembled in a similar fashion with two corner brackets, but with an additional 10" zinc mending plate (Home Depot model #15390) to create an inner open area 18 cm wide x 14.5 cm high. One contiguous sheet of PE-25 was fixed across this entire area (Figure 3.1). For t_{+15} , one strip of PE-18 and one strip of POM-76

were arranged end to end across the 14.5 cm open width and spanning the 0–2.5 cm depth interval. After assembly, all samplers were wrapped in aluminum foil and kept refrigerated or on ice prior to deployment. One field blank sampler was transported in the same fashion as the deployed devices, briefly exposed to the air at the site, and returned to the lab for analysis. Each sampler was placed in one of nine subsections of a plot, and sampler locations were varied between events. Each device was deployed by cutting a slot into the root mat with a hacksaw, placing the sampler into the slot, and gently tapping it down until the polymer strips were aligned with the intended sampling depth (Figure 3.1). After 28 d of exposure, samplers were removed from sediment and disassembled. All strips were gently rinsed with deionized water, blotted dry with paper towels, placed in individual borosilicate vials, and kept cold until processing. Contiguous PE sheets used at t_{+21} were sectioned into five 1-cm strips corresponding to the uppermost 5 cm of sediment, and one 5-cm strip corresponding to the 5–10 cm depth interval.



Figure 3.1. Passive samplers enclosed in metal frames for deployment in marsh sediment. Top left: POM strips arranged to sample two discrete depth intervals; top right: contiguous PE sheet for high resolution measurement of vertical porewater concentration profiles; bottom: passive sampling frame (denoted with arrow) embedded in sediment alongside in situ organism exposure cages.

Chemicals. PCB solutions were prepared using individual congener and Aroclor standards in hexane purchased from Ultra Scientific (Kingstown, RI). All other chemicals and solvents were purchased from Fisher Scientific (Pittsburgh, PA). Hexane and acetone

were pesticide grade (CAS Nos. 110-54-3 and 67-64-1). Anhydrous sodium sulfate was ACS grade (CAS No. 7757-82-6). Silica gel was 644 or 923 grade (CAS No. 112926-00-8 or 63231-67-4). Copper powder was lab grade (CAS No. 7440-50-8).

Analytical Methods. Passive sampling polymers were extracted three times overnight in 1:1 hexane:acetone with 60 rpm orbital shaking. The pooled extracts were reduced to 2 mL with a gentle nitrogen stream in a water bath at 35–40 °C, treated with activated copper, and cleaned up using a miniaturized version of the silica gel procedure described in U.S. EPA SW-846 method 3630C, performed in 5.75” Pasteur pipets. All samples were analyzed by gas chromatography with electron capture detection using an adaptation of U.S. EPA SW-846 method 8082A.¹¹ PCB BZ #30 and 204 were used as internal standards. Surrogate standards (PCB BZ #14 and 65) were added prior to all sample extractions to assess loss during processing. The analytical method measured 87 target congeners/congener groups that were summed based on homolog groups or total PCBs (hereafter denoted ΣC).

Quality Assurance/Quality Control. Average surrogate recoveries in passive sampler extracts were $92 \pm 9.7\%$ for PCB BZ#14 and $88 \pm 9.2\%$ for PCB BZ#65 ($n = 167$). PCB samples with less than 60% recovery of each surrogate compound are not reported. No values were adjusted to account for surrogate recoveries.

Calculation of PCB Porewater Concentrations. Unadjusted porewater concentrations (C_{pw}) were calculated according to the equilibrium partitioning equation:

$$C_{pw} = \frac{C_{ps}}{K_{ps}} \quad (3.1)$$

where C_{ps} is the measured concentration in the passive sampling material (g kg^{-1} polymer) and K_{ps} is the polymer-water partitioning coefficient specific to each congener/polymer combination (L kg^{-1}). K_{ps} values for POM were derived using an empirical relationship with octanol-water partitioning coefficients (K_{ow})¹²:

$$\log K_{ps} = 0.791 \times \log K_{ow} + 1.018 \quad (3.2)$$

PCB K_{ow} values were taken from.¹³ Average values were used for groups of two or more coeluting congeners. K_{ps} values for PE were derived with the following empirical relationship¹⁴:

$$\log K_{ps} = 1.18 \times \log K_{ow} - 1.26 \quad (3.3)$$

K_{ps} for PE has been found to be independent of polymer thickness, so one set of values was used for both PE-18 and PE-25.¹⁵ K_{ps} values for PDMS were derived as follows¹⁴:

$$\log K_{ps} = 0.947 \times \log K_{ow} - 0.017 \quad (3.4)$$

PRC depletion data were used to adjust porewater concentrations for nonequilibrium using four different methods (summarized in Table 3.1). The first three are based on the sampling rate approach where the overall exchange rate of PCBs between sediment porewater and sampling polymers was approximated as a first-order kinetic process. An exchange rate coefficient ($k_{e,PRC}$, d^{-1}) was computed for each PRC in each sampler strip (i.e., each PRC at each depth interval in each sampler location) with the following equation:

$$k_{e,PRC} = \ln \left(\frac{C_{ps,PRC}(0)}{C_{ps,PRC}(t)} \right) \left(\frac{1}{t} \right) \quad (3.5)$$

where $C_{ps,PRC}(0)$ is the measured concentration of PRC in the sampler prior to deployment and $C_{ps,PRC}(t)$ is the measured concentration following deployment.¹⁶ In this work, $t = 28$ d for all experiments. The first adjustment method consisted of establishing log-linear correlations between measured $k_{e,PRC}$ and K_{ps-w} , and extrapolating k_e for target PCBs.¹⁷ In the second method, log k_e values were extrapolated from linear correlations with molar volume (V_m , $\text{cm}^3 \text{mol}^{-1}$). V_m was taken from published values or homolog group averages for unreported congeners.¹⁸ With k_e values for each congener or congener group, adjusted porewater concentrations (C_{pw}') can be computed:

$$C_{pw}' = \frac{C_{ps}}{K_{ps}(1-e^{-k_e t})} \quad (3.6)$$

The third method was the molar volume adjustment procedure, which is based on an empirically derived, nonlinear relationship between apparent sampling rate (R_s , L d^{-1}) and V_m .⁵ $R_{s,PRC}$ for each PRC was calculated as follows¹⁶:

$$R_{s,PRC} = k_{e,PRC} K_{ps} M_{ps} \quad (3.7)$$

where M_{ps} is the mass of the sampling material. This sampling rate was adjusted for the V_m of target PCBs with the following relationship⁵:

$$R_s = R_{s,PRC} \left(\frac{V_{m,PRC}}{V_m} \right)^{0.39} \quad (3.8)$$

With R_s and k_e , C_{pw}' for target PCBs can be calculated as above. For all methods mentioned thus far, PCB BZ #29 was used to adjust mono- through tri-CBs, BZ # 69 was used for tetra- and penta-CBs, BZ # 155 was used for hexa-CBs, and BZ # 192 was used for hepta- and higher CBs.

The final correction method applied was a diffusion-based model.² Calculations were carried out using the associated PRC Correction Calculator software.¹⁹ The software's compound database was updated to include coeluting PCB congener groups with averaged literature values for K_{ow} and diffusivity in PE.^{7, 13} A porosity value of 0.72, representing an average of volumetrically measured sediment samples, was used in the calculations.

Table 3.1. Summary of PRC adjustment methods employed.

Abbreviation	Summary	Relevant Equation	Reference
k_e - K_{ps}	linear regression of exchange rate vs. sampler partitioning	$k_{e,PRC} = \ln \left(\frac{C_{ps,PRC}(0)}{C_{ps,PRC}(t)} \right) \left(\frac{1}{t} \right)$	15, 16
k_e - V_m	linear regression of exchange rate vs. molar volume	$k_{e,PRC} = \ln \left(\frac{C_{ps,PRC}(0)}{C_{ps,PRC}(t)} \right) \left(\frac{1}{t} \right)$	15, 16
MVA	adjustment of sampling rate based on empirical molar volume dependence	$R_s = R_{s,PRC} \left(\frac{V_{m,PRC}}{V_m} \right)^{0.39}$	5
diffusion	fixed-bed diffusive mass transfer model	$\frac{\partial C_{PE}}{\partial t} = D_{PE} \frac{\partial^2 C_{PE}}{\partial x^2} \text{ for } -l < x < l$	2

3.4. Results and Discussion

PCB Concentrations in Sediment Porewater. At t_{-1} , unadjusted concentrations of freely dissolved total PCBs (ΣC_{pw}) measured with POM were in the range of 1.0–4.0 ng L⁻¹ in all plots and in both the 0–2.5 cm (Figure 3.2) and 5–7.5 cm depth intervals. At t_{+2} , ΣC_{pw} in the upper interval had decreased by 97% in Plot A, 48% in Plot B, 76% in Plot C, and

86% in Plot D ($n = 5$ for Plots A, B, and D, $n = 3$ for Plot C). In all subsequent sampling events up to t_{+15} , upper-interval ΣC_{pw} in amended plots remained low relative to both pre-amendment levels in the same plots and concurrently measured levels in the unamended plot. At t_{+15} , the smallest reduction was observed in the granular AC and sand-treated plot (34%). The largest relative upper-interval reductions were measured in Plot A, where ΣC_{pw} was 91–97% lower than the initial value at all sampling events throughout the study. In the 5–7.5 cm depth interval, significant reductions in ΣC_{pw} were only observed in Plot A, where they were significant at all sampling events ($p < 0.05$). Significant reductions relative to pre-application values ($p < 0.05$) were observed in all three amended plots and at all time points except the 38- μm POM measurement at t_{+15} in Plot C.

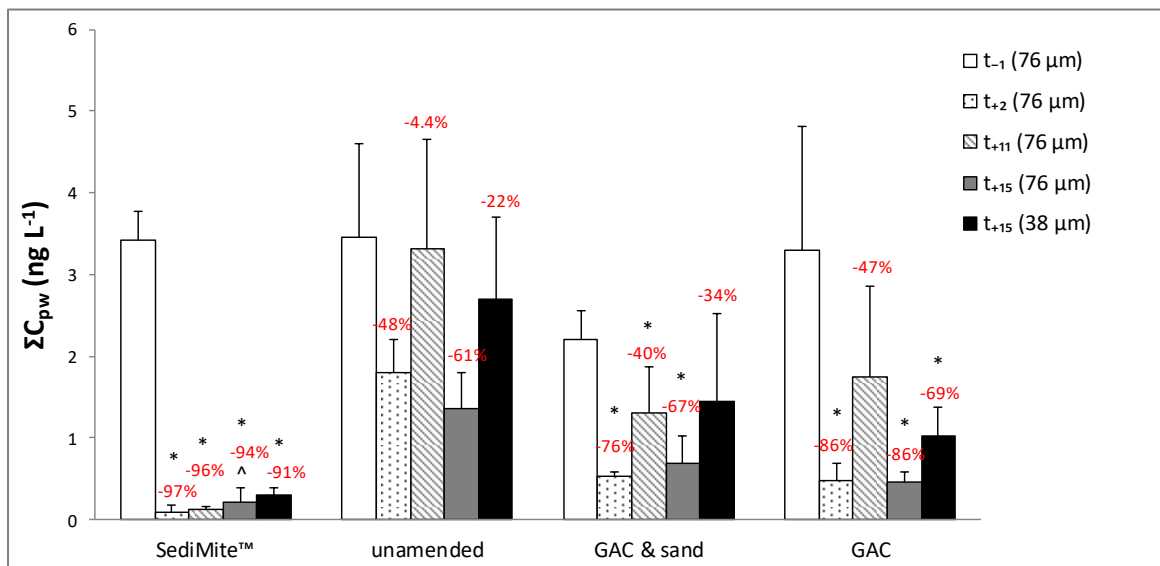


Figure 3.2. Average total PCB concentrations measured in sediment porewater using POM passive samplers in the 0–2.5 cm depth interval at BCSA. Values are unadjusted for fractional PRC loss. Error bars show one standard deviation among samplers in each plot

($n = 5$ except * ($n = 4$)). Percent decreases from each plot's pre-amendment value are shown.

Observed changes in ΣC_{pw} in the amended plots generally remained consistent throughout the study period. Following amendment application, within-plot variability from one sampling event to another was modest and can be explained by some combination of experimental error, temperature effects (sampling events occurred in summer and fall alternately), and the fact that sampling devices were placed in different locations within plots for each event. This means that any spatial variations in AC levels, microbial dechlorination activity, sediment geochemistry, hydrology, and other variables potentially influencing porewater concentrations were not controlled across sampling events.

To account for the equilibrium state of passive samplers after 28-d deployments, performance reference compounds (PRCs) were added prior to use. When initial concentrations in POM strips were obtained from a separate strip taken from the same impregnation solution, $C_{0,PRC}$ was more variable and, in a few cases, lower than $C_{f,PRC}$ for the two heaviest PRCs. In these cases, PRC adjustments were not possible. The use of a small piece cut off of each sampling strip to represent $C_{0,PRC}$ for that strip led to much more predictable patterns of PRC loss. This highlights a potentially significant degree of variability in the extent of PRC loading among POM strips in a single solution jar, even with orbital shaking. Because reliable PRC loss measurements were available for some, but not all, sampling events, only unadjusted ΣC_{pw} values were used to compare porewater concentrations among sampling events and compute fractional decreases following AC amendment. While these unadjusted concentrations are likely substantially

lower than the true values in an absolute sense, their use for comparison between plots and across sampling events is still instructive. This is because, when PRC data were applied, the relative magnitudes of the resulting adjustments were remarkably consistent between plots, thereby preserving the proportionality of the C_{pw} data. To the extent that sub-equilibrium values might bias such comparisons, it would be toward a slight underestimation of amendment efficacy as described later.

High Resolution Depth Profile of Porewater PCBs. Data from contiguous PE samplers collected at t_{+21} enabled generation of 1-cm vertical profiles of freely dissolved PCBs in porewater for Plots A and B (Figure 3.3). Plots C and D were not sampled for this event. This deployment produced useful PRC data which enabled calculation of adjusted C_{pw} values. In Plot B, ΣC_{pw} values (computed using the k_e - K_{ps} adjustment method) were in the range of 11–16 ng L⁻¹ ($n = 3$) at all depth intervals, and in Plot A ΣC_{pw} values were in the range of 0.52–3.7 ng L⁻¹ ($n = 3$). No trend with depth was apparent in Plot B. In Plot A, ΣC_{pw} values were higher at each successive depth interval below 1 cm, suggesting a profile in loose accord with that of black carbon, measured separately.⁹ However, no statistically significant trend with depth could be determined due to variability in the data. At each depth, ΣC_{pw} values were significantly lower in Plot A than Plot B (t-test, $p < 0.05$). Because black carbon concentrations at depths greater than 3 cm did not differ significantly between the plots, reduced PCB concentrations in these intervals invite closer scrutiny. It is possible that during installation, surficial black carbon was inadvertently introduced into the slots cut to accommodate passive sampling devices, leading to artificially reduced concentrations immediately adjacent to the samplers. This may also explain the decreased ΣC_{pw} in the 5–10 cm interval found in prior sampling

events. As described above, this was not observed in Plots C and D, perhaps owing to the coarser (and thus both less mobile and less sorptive) granular AC applied in those plots. Thus, care must be taken when placing in situ passive samplers within a layered treatment zone such as reactive caps or in situ amendments.

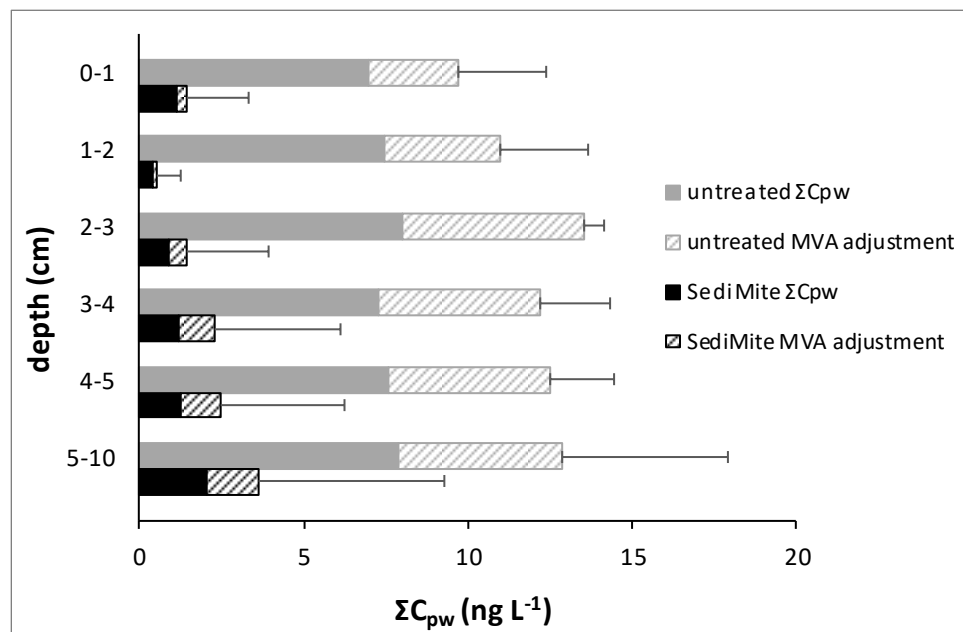


Figure 3.3. Total PCB concentrations in BCSA sediment porewater measured in situ at discrete depth intervals using PE passive samplers (t_{+21}). Solid bars show unadjusted ΣC_{pw} . Hatched bars show adjustments for PRC loss using the MVA method. Error bars show standard deviation in total adjusted values among samplers in each plot ($n = 3$).

Nonequilibrium Assessment with Performance Reference Compounds. In all deployments, PCB 29 and 69 (tri- and tetra-substituted congeners, respectively) were depleted from passive sampling strips to a greater extent than were PCB 155 and 192 (hexa- and hepta-). This agrees with the findings of another group, who observed an

inverse relationship between PCB molecular weight and diffusivity in several sampling polymers.⁷ At t_{+21} , PRCs were depleted by $92 \pm 8.7\%$ (PCB-29), $84 \pm 16\%$ (PCB-69), $29 \pm 7.1\%$ (PCB-155), and $30 \pm 6.1\%$ (PCB-192) in Plot A ($n = 18$), and $69 \pm 6.8\%$, $58 \pm 7.1\%$, 25 ± 8.4 , and $23 \pm 7.0\%$ in Plot B ($n = 18$). This indicates that the samplers were far from equilibrium with respect to more hydrophobic PCBs after their 28-d deployments. By extension, this also implies a larger adjustment of C_{pw} for larger PCBs regardless of the PRC correction method employed, and a concomitantly larger degree of uncertainty in C_{pw}' . For example, with the k_e - K_{ps} method, mono-CBs were adjusted upward by 7.4%, while deca-CB was adjusted upward by 2300%. However, even after PRC adjustment, hepta- through deca-chlorinated congeners accounted for only 2.1% of $\Sigma C_{pw}'$. This can be attributed in part to their much lower water solubilities, and also to the compositions of the original contaminant mixtures; Aroclors up to 1254 comprise less than 3% by weight hepta-substituted or higher congeners.²⁰ In this sampling, tri-, tetra-, and penta-CBs accounted for 98% of $\Sigma C_{pw}'$ (Figure 3.4). Since the objective of amendment was to decrease total PCB concentrations in porewater, the incremental error from PRC adjustments of the heaviest PCB congeners was of negligible importance. However, when the target reductions are for benthic organism tissue concentration, the higher chlorinated homologs gain significance due to the strong partitioning into lipids. In general, selection of PRCs should be made in consideration of the expected congener distribution in the medium to be sampled. However, heavier, less diffusive PRCs can be problematic if they do not dissipate to a quantifiable extent.²¹

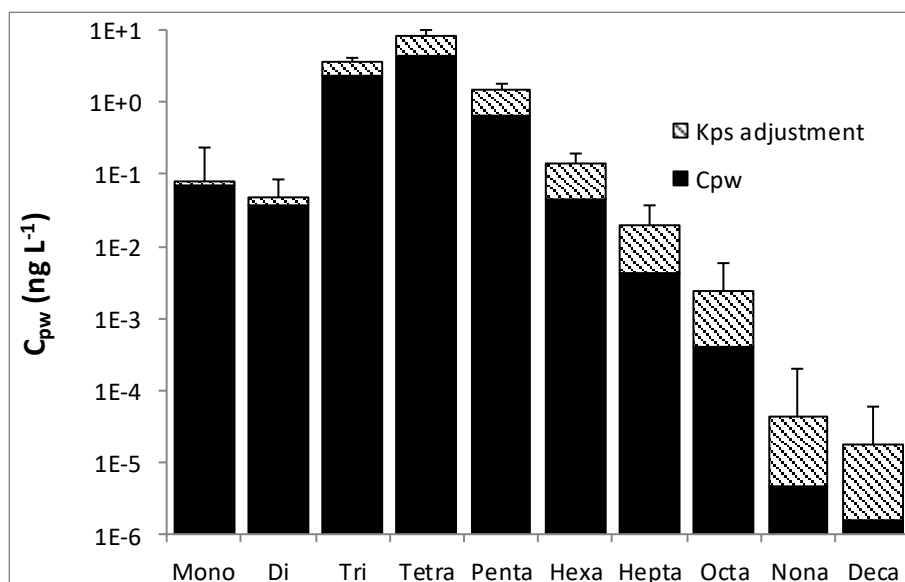


Figure 3.4. Vertically averaged (0–10 cm) PCB porewater concentrations in unamended BCSA sediment at t_{+21} as measured by PE passive samplers, shown by degree of chlorination. PRC adjustments made using k_e - K_{ps} linear regression. Error bars show standard deviation in adjusted value among samplers ($n = 3$). Note logarithmic scale.

Greater PRC loss was observed in AC-amended sediment than in unamended sediment. This is to be expected, since amendment with AC increases sediment K_d , resulting in faster kinetics of desorption.² This may imply that unadjusted C_{pw} values tend to underestimate amendment efficacy because the difference between amended- and unamended-plot concentrations is made larger by PRC adjustment. PRC loss data also pointed to differences in polymer uptake behavior. At t_{+11} , PE-18 equilibrated with lighter PCBs much more quickly than did simultaneously and adjacently deployed POM-76. Because the bulk of PCB contamination in BCSA porewater comprises mono- through tetra-substituted congeners, this contrast in kinetic profiles led to sharp differences in total uptake between the two polymer types: the unadjusted estimate of ΣC_{pw} given by the

POM samplers ($n = 5$) was 30% of the PE value ($n = 4$). However, accounting for kinetic differences by applying the k_e - K_{ps} PRC method brought the POM-reported value of $\Sigma C_{pw}'$ to 83% of the PE value (Figure 3.5). While $\Sigma C_{pw}'$ was comparable between the two polymer types, it is likely that the PE value is more accurate because the degree of uncertainty in each measurement is related to the degree of polymer-porewater nonequilibrium and the magnitude of the resulting PRC adjustment. Oen et al. reported agreement within a factor of two in PRC-corrected porewater concentrations of PCBs measured by 51- μm PE and 17- μm POM. Notably, their POM-measured values were still lower than the PE-measured values, despite the advantage of thinner POM and thicker PE relative to those used in the present work.²² Another group observed a similar factor-of-two discrepancy between the two polymers' measurements in ex situ sediments. They proposed the use of a PE/POM correction factor in lieu of PRCs, but noted that POM hadn't fully equilibrated even after 96 d in their experimental systems.²³ Total uptake by adjacently-deployed PDMS was comparable to POM, and the site's characteristic PCB homolog signature was preserved. However, the extent of PRC desorption from PDMS was quite low and in some cases within analytical error margins, so no adjustments were made to PDMS-measured concentrations. These concentrations were likely far from equilibrium. While PDMS is in wide use for passive sampling, it is typically used in the form of a solid-phase microextraction (SPME) fiber coating or thin (ca. 25 μm) sheet.^{24, 25} In our deployment, the tradeoff between sufficient mass for PCB uptake and limited space alongside two other polymers within the sampling frames led to the selection of a thick sheet. The resulting kinetic deficiency made it a poor alternative to the other sampling materials used. SPME fibers deployed by Fernandez et al. greatly

underpredicted porewater PCB concentrations in the absence of PRC correction, although the authors noted that this may have been due in part to mass transfer limitations.²⁶ Considering ease of use, equilibration rate, and reproducibility of PRC desorption, PE proved to be the most effective among the sampling materials evaluated in the present study.

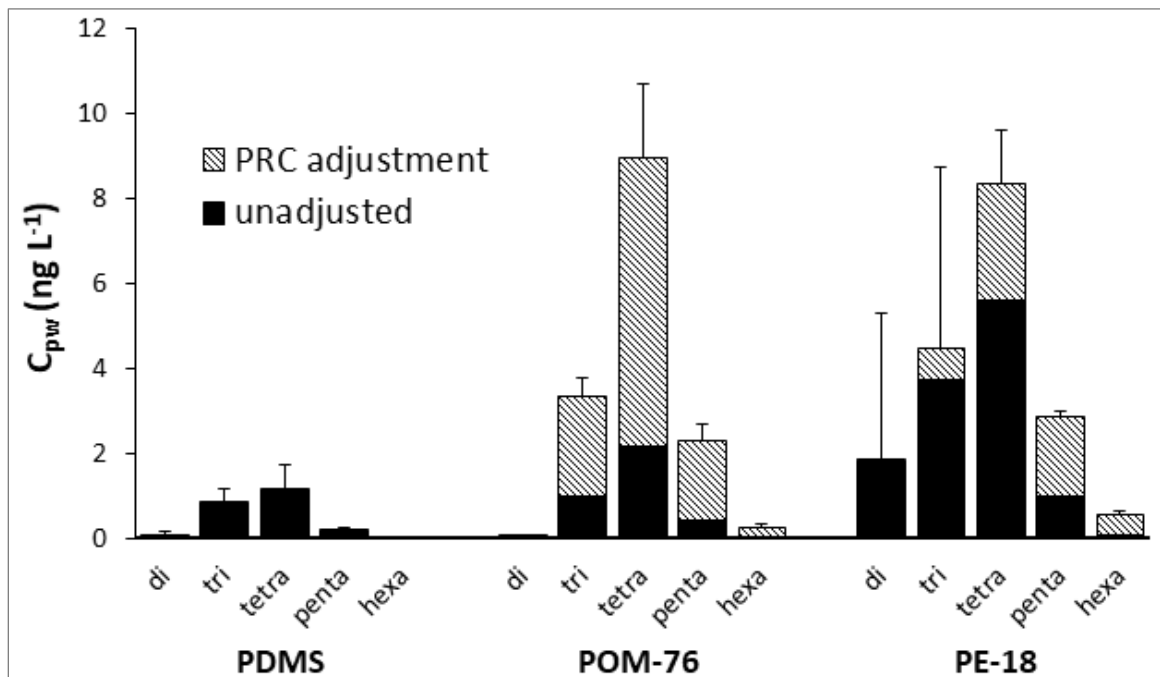


Figure 3.5. PCB homolog concentrations in the uppermost 2.5 cm of unamended BCSA sediment porewater measured at t_{+11} in a simultaneous deployment of 0.5-mm PDMS, 76- μ m POM, and 18- μ m PE. PRC adjustments were performed using the k_e - K_{ps} method. Error bars show standard deviation of total adjusted values among samplers (unadjusted for PDMS; $n = 5$ each for PDMS and POM-76, $n = 4$ for PE-18).

Comparison of PRC Adjustment Methods. The k_e - K_{ps} correlation method was applied to sampling events for which the average coefficient of determination among samplers

was 0.70 or greater. In most cases r^2 was greater than 0.85. At t_{+15} , r^2 for POM-38 averaged 0.76 ± 0.30 , but only 0.42 ± 0.21 for POM-76. This was due to slower desorption of PRCs from the thicker polymers, resulting in larger relative error in pre- vs. post-deployment measurements. At t_{+21} , a comparison of results using two sets of K_{ps} values revealed a large influence of K_{ps} on both the strength of correlation with k_e and the magnitude of adjustment to C_{pw} . In this deployment, r^2 for k_e vs. K_{ps} averaged 0.68 ± 0.13 using K_{ps} values derived from a published correlation with K_{ow} .¹⁴ A SETAC Pellston Workshop recommended that these values be used for consistency across laboratories.¹ However, as an exercise, we also computed C_{pw}' using K_{ps} either taken directly or, where necessary, interpolated from another set of published values.¹⁸ With these, r^2 with k_e averaged 0.91 ± 0.08 . Further, $\Sigma C_{pw}'$ in Plots A and B was on average 20% higher using the Choi et al. (2013) values than with those from Smedes et al. (2009). Nonetheless, the relative effect of the amendment was independent of the choice of K_{ps} values; $\Sigma C_{pw}'$ in Plot A was 86% lower than in Plot B using either set. In cases where greater certainty in absolute C_{pw} measurements is needed, the accuracy of K_{ps} and K_{ow} values would be more critical. K_{ps} for PRCs is the largest source of error in C_{pw} measurements. An interlaboratory variability of 0.2–0.5 log units has been found in PCB K_{ps} , potentially leading to errors in C_{pw} up to a factor of three.²⁷

Correlation coefficients for the k_e - V_m method were similar to, and in most cases slightly higher than, those for k_e - K_{ps} . $\Sigma C_{pw}'$ values calculated with this method were also quite similar, including comparable homolog distributions. The MVA method produced similar $\Sigma C_{pw}'$ values, with homolog distributions shifted slightly away from lighter PCBs in favor of penta- and hexa-substituted congeners.

The diffusion-based adjustment method was applied to the t_{+21} porewater data. The calculated relationships between K_d and K_{ow} were consistent among samples from Plot B (unamended), with an average r^2 value of 0.89 ± 0.09 . The average slope was 1.6 ± 0.2 and the average intercept was -4.4 ± 1.1 . The resulting fractional equilibration values produced remarkably similar C_{pw} results to those obtained with the other methods, including both total concentration and homolog distribution (Figure 3.6). Thus, the first-order, rate-based adjustment methods are able to provide a reasonably accurate correction for nonequilibrium as is the more rigorous diffusion-based method.

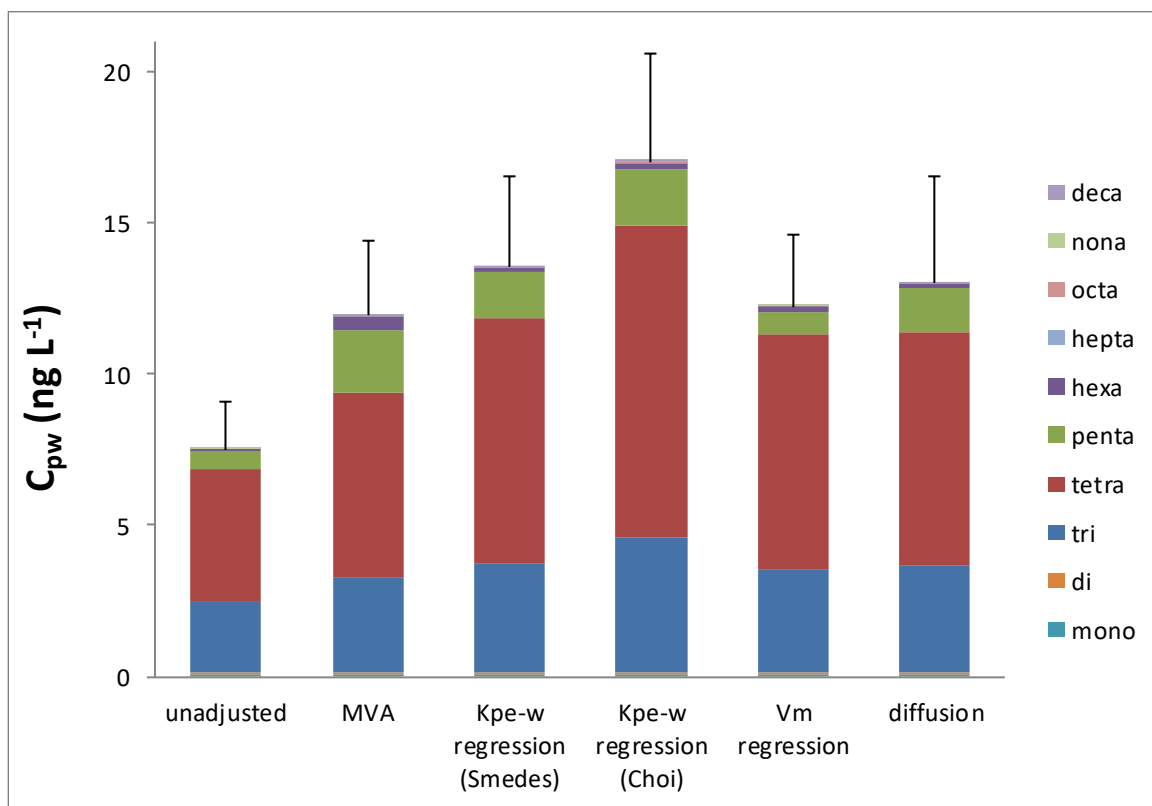


Figure 3.6. Comparison of PRC adjustment methods. Bars show vertically averaged porewater PCB concentrations in the uppermost 2.5 cm of unamended BCSA sediment, arranged by homolog group. Concentrations were measured in situ with PE passive

samplers at t_{+21} . Included are unadjusted values and values adjusted with each of the PRC methods discussed. Error bars show standard deviation in ΣC_{pw} among samplers ($n = 3$).

By contrast, the diffusion-based method did not work well when applied to the sampler data from Plot A (SediMite™). An average $\log K_d$ - $\log K_{ow}$ correlation coefficient of 0.50 ± 0.31 was obtained, with widely varying slopes and intercepts among individual samples. The method was therefore not used to calculate C_{pw}' for this plot. The distinction was most likely due to the presence of activated carbon amendment in Plot A. On average, the amendment increased sediment K_d by one to two log units. However, this effect was stronger for the lower molecular weight compounds because mass transfer into AC can be faster compared to the strongly hydrophobic compounds as observed previously.¹¹ Thus, the altered K_d observed after fresh amendment of AC has a weaker relationship with compound $\log K_{ow}$. This likely confounded PRC calculations across sampler locations and depth intervals in the presence of AC.

Apart from the challenges with the diffusion method for Plot A, $\Sigma C_{pw}'$ values from all PRC adjustment methods agreed closely with one another and preserved trends in unadjusted ΣC_{pw} measurements and homolog distributions across all plots, sampling times, and depth intervals (Figure 3.6). This is perhaps unsurprising as all are based on intrinsic physical properties of PCB molecules either directly (molecular volume) or indirectly (diffusivity or sorption affinity for a polymer, which themselves depend on characteristics such as molecular volume, flexibility, planarity, and hydrophobicity).^{3, 7} The extent of agreement among all methods lends confidence in both the absolute values of $\Sigma C_{pw}'$ and the ratios among plots in the study, enabling comparison of the efficacy of

tested amendments. However, the difficulty we experienced in applying the diffusion method to the AC-amended plot highlights the importance of interpreting PRC results carefully to ensure that they make physical and chemical sense. Here, the use of multiple, complementary PRC adjustment methods proved helpful. The use of four PRCs spanning the predominant homolog range present at the site strengthened all of the adjustment calculations and minimized the error associated with extrapolating fractional equilibration. Of the three polymers used, PE provided the most reliable porewater concentration measurements.

3.5. Acknowledgements

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UG is a co-inventor of two patents related to the “SediMite™” technology described in this paper for which he is entitled to receive royalties. One invention was issued to Stanford University (US Patent # 7,101,115 B2), and the other to the University of Maryland Baltimore County (UMBC) (U.S. Patent No. 7,824,129). In addition, UG is a partner in a startup company (Sediment Solutions) that has licensed the technology from Stanford and UMBC and is transitioning the technology in the field.

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Chapter 4: Impact of Dissolved Organic Matter on Mercury and Methylmercury Sorption to Activated Carbon in Soils: Implications for Remediation

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4.1. Abstract

In situ sorbent amendments like activated carbon (AC) have shown promise as a low-impact method to reduce inorganic mercury (Hg) and methylmercury (MeHg) risk in contaminated sediments and soils. However, the effectiveness of AC in contaminant immobilization varies widely among soils, suggesting that soil biogeochemistry might dictate the efficacy of AC for Hg and MeHg remediation. In this study, we evaluated the impact of dissolved organic matter (DOM) on MeHg and Hg partitioning to AC directly using an isotherm approach and also evaluated DOM impacts on AC sorption in the complex milieu of soil, using slurry microcosms. In water, partition coefficients (K_d) for Hg-DOM and MeHg-DOM complexes (Suwannee River Humic Acid, SRHA) to AC were one to two orders of magnitude lower than those for chloride complexes and more closely resembled the K_d of DOM. In the anaerobic soil slurry experiments, the addition of SRHA did not significantly impact the partitioning of either ambient MeHg or a fresh Me¹⁹⁹Hg spike onto AC. For inorganic Hg (both ambient Hg and fresh ²⁰¹Hg spike), AC was effective in reducing porewater Hg at all levels of the SRHA addition. However, the SRHA affected the magnitude of Hg partitioning (both ambient Hg and fresh ²⁰¹Hg spike) to AC in soils in a concentration-dependent manner. AC efficacy in MeHg sorption was not impacted by DOM addition up to 60 mg/L, suggesting that AC may be valuable in reducing MeHg risk even in high-DOM soils like marshes. Results suggest that DOM impacted Hg sorption, but not MeHg sorption, to AC in soils by interfering with HgS

precipitation and/or by changing aqueous HgS speciation. For both Hg and MeHg, the sorption of sulfide species appears stronger than the sorption of chloride or DOM species. This study highlights the need to evaluate AC efficacy for remediation in the matrix being considered for treatment and to develop models of AC efficacy based on site biogeochemistry.

4.2. Introduction

There is a need for in situ treatment approaches for mercury-contaminated sediments and soils. In situ activated carbon (AC) amendments are effective in sequestering and immobilizing hydrophobic organic contaminants¹⁻³ and show promise for treatment of mercury (Hg) and methylmercury (MeHg).⁴⁻⁶ AC is manufactured from coal or biomass material that has been treated at a high temperature under controlled oxidation, creating a highly porous structure with desired surface functionality and a high sorption capacity.⁷ AC provides an extensive internal surface area that can be very effective for adsorbing both hydrophobic and ionizable aromatic compounds through π - π and π^* - π interactions,⁸ H-bonding, and van der Waals interactions.⁹ When AC is applied to sediments, contaminants in porewater preferentially bind to the activated carbon particles, reducing chemical activity in the sediment phase, thereby reducing contaminant bioavailability and contaminant flux into the water column.

Previous work has demonstrated strong sorption of Hg and MeHg to a range of ACs and biochars. Hg and MeHg have log K_{ds} of 6–7 and 4.5–5.5 for sorption onto AC in water, respectively, while PCB log K_{ds} ranged from 4.5 to 7.5.¹ Laboratory studies have found that AC amendments to sediment resulted in significant reductions in Hg and MeHg porewater concentrations.^{5, 6} These porewater reductions have also been shown to

correlate with reductions in biotic uptake. AC at roughly 2–7% of sediment dry weight was effective in reducing MeHg uptake by oligochaetes (*Lumbriculus variegatus*) in laboratory microcosms containing 0.02 to 14 ng MeHg gdw⁻¹ in soils.⁵ After 14 days, the AC amendment achieved 90% and 50% reductions in *Lumbriculus* MeHg uptake in the two freshwater sediments tested and 30% reduction of uptake in the estuarine sediments tested. Another microcosm study using freshwater wetland sediment found that granular AC reduced MeHg uptake by pond snails (*Lymnaea stagnalis*) by ~50%. Snails were exposed to intact clumps of contaminated sediment (~6 ng gdw⁻¹ MeHg) in microcosms over 41 days.⁶ AC was added to the top 3 cm of soil at 1% of the estimated soil dry weight. These uptake experiments, and additional ongoing work in our group, show that AC amendments consistently decrease Hg and MeHg porewater concentrations and bioaccumulation factors, but the magnitude of the reduction in the few soils tested to date has been highly variable. The variability of AC impact across different soils indicates that site geochemistry may control the effectiveness of AC amendments.

K_d may be a useful predictor of MeHg bioavailability that could be used as a guiding parameter for AC application. While some studies have shown a relationship between MeHg K_d and biotic uptake,¹⁰⁻¹² only two have examined the relationships between MeHg K_d, bioavailability, and AC efficacy. In these biouptake studies, K_d was a good predictor of MeHg uptake,^{5, 6} and AC was most effective in sediments with low native K_d values.⁵ MeHg and Hg K_ds tend to be highest in soils that have high concentrations of ligands, such as natural organic matter (NOM), sulfide, and iron.¹³⁻¹⁷ Soil Hg and MeHg K_ds are also greatly influenced by the concentration of dissolved ligands, particularly sulfides¹⁷ and the concentration and character of dissolved organic matter (DOM).^{15, 18}

DOM has been shown to inhibit the precipitation and aggregation of cinnabar ($\text{HgS}_{(s)}$)¹⁹, thus enhancing Hg availability for microbial methylation.²⁰⁻²² Larger, more aromatic^{20, 21} or sulfidized²³ DOM was most effective in enhancing MeHg production.

The presence of DOM may also influence the sorption of Hg and MeHg onto AC by creating a ligand complex that sorbs to AC by a different mechanism. Additionally, DOM can block sorption sites through ‘fouling’ of the active sites on AC. While the former mechanism has not been studied well, the issue of AC fouling in the presence of DOM and other sorbates in sediments has been investigated for organics.^{24, 25} Reported attenuation factors for DOM fouling have ranged between three and sixteen for PCB and phenanthrene sorption to AC in the presence of sediments.^{26, 27}

The objective of this study was to determine the impact of DOM concentration on Hg and MeHg partitioning in a soil-AC mixture. To establish a baseline for DOM effects on partitioning, a series of aqueous isotherm tests were set up to determine the partitioning of Hg and MeHg to AC in water in the presence and absence of Suwannee River Humic Acid. To test the impact of DOM on partitioning under more environmentally relevant conditions, anaerobic slurries were constructed using 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 an inorganic Hg or MeHg enriched stable isotope spike to assess the partitioning of newly-spiked Hg and MeHg to the solid phase and to monitor methylation and demethylation in the microcosms. Porewater and solid phase Hg and MeHg concentrations were monitored over 21 days along with other geochemical parameters.

4.3. 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 inorganic Hg(II) ($\log K_d = 6.6$ for both) and MeHg ($\log K_d = 4.9$ for CAC-Coal and 5.4 for CAC-Coco).¹ Both ACs were sieved to a mesh size of 80 x 325 μm . The CAC-Coal had a %C of 80.9, a surface area of 1116 $\text{m}^2 \text{g}^{-1}$, a skeletal density of 1.61 g cm^{-3} , and a bulk density of 0.64 g cm^{-3} .¹ The CAC-Coco had a %C of 90.8, a surface area of 1305 $\text{m}^2 \text{g}^{-1}$, a skeletal density of 1.45 g cm^{-3} , and a bulk density of 0.57 g cm^{-3} .¹ 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 tends to make it reactive toward mercury.²⁰ Hg and MeHg were spiked as enriched stable isotopes in the forms of $^{201}\text{HgCl}_2$ and $\text{Me}^{199}\text{HgCl}$ (Oak Ridge National Laboratories). Me^{199}Hg was synthesized in-house by reacting methylcobalamin with 91.95% enriched $^{199}\text{HgCl}_2$.²⁸ The $^{199}\text{HgCl}_2$ and $^{201}\text{HgCl}_2$ solutions were made by dissolving ^{199}Hg and ^{201}Hg (98.11% enriched) powder in 0.1% HCl.

A total of thirty combinations of AC, DOM, and Hg or MeHg were measured into separate 60-mL PETG bottles as summarized in Table 4.1. 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 DOM first, followed by overnight incubation and subsequent addition of AC, or AC and DOM first, followed by overnight incubation and subsequent addition of mercury. Sample bottles were prepared with 50 mL deionized water adjusted to 3 ppt salinity with Instant Ocean (Spectrum Brands). Sodium bicarbonate (7.5 mM)

was added to buffer sample pH against acidification by DOM. Bottles receiving AC were amended with 10 mg of the AC type indicated in Table 4.1. 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 thiolic sites on DOM, which control mercury-DOM complexation under normal conditions.²⁹ The SRHA was spiked over a range of 10 to 130 mg L⁻¹. The ²⁰¹Hg and Me¹⁹⁹Hg spike additions ranged from 10 to 130 ng L⁻¹.

Table 4.1. Design of mercury/DOM/AC isotherm experiment.

Mercury Species	AC	Sequence of Spike Addition	Initial Hg or MeHg Concs. (ng L⁻¹)	Initial DOM Concs. (mg L⁻¹)
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

After the initial equilibration step, 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 K_{AC} to predicted values. K for each isotherm sample was predicted by modeling equilibrium mercury speciation using MINEQL (Appendix II).

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.³⁰⁻³² Briefly, total Hg was determined by digesting samples in hot 7:4 v/v HNO₃/H₂SO₄ (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). Samples for MeHg analysis were analyzed via ethylation, purge and trap, gas chromatography, also using a MERX system, and ID-ICP-MS, following distillation. QC data are provided in Tables AII.S2 and AII.S3.

Soil Slurry Experiment Design. The microcosm experiment was designed to evaluate the impact of DOM on Hg and MeHg partitioning to AC in soils, using a range of SRHA II concentrations from 0 to 60 mg L⁻¹ (Table 4.2 and Figure AII.S1). The main experiment was conducted at 4 °C to minimize confounding effects of microbial activity. The study consisted of seven treatments and a total of 66 slurry bottles. One of the

treatments contained no AC or DOC. All other treatments were amended with AC at 5% of the sediment dry weight and with varying concentrations of SRHA II. Half of the bottles for each treatment were spiked with $^{201}\text{HgCl}_2$ at ~10% of the ambient Hg in the soil to track methylation and the other half of the bottles for each treatment were spiked with $\text{Me}^{199}\text{HgCl}$ at ~50% of the ambient MeHg of the soil to track demethylation (Table AII.S3). Hg and MeHg spike levels were chosen to provide enough mass to detect while minimizing changes in overall concentrations.

Table 4.2. Design of microcosm experiment.

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

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 4 °C slurry bottles were refrigerated, protected from light during incubation, and kept on icepacks during time point disassembly.

Slurry Construction. Anaerobic soil slurries were constructed at a 10 to 1 liquid to solid ratio. Hg-contaminated soil (~20 µg gdw⁻¹) was obtained in November 2015 from a *Phragmites* marsh at roughly 5 ppt salinity in Berry's Creek, New Jersey.³³ Surface soil (0-15 cm) was collected by Parsons Corporation and transferred into two-gallon plastic buckets with locking lids. The buckets were filled completely to minimize headspace.

The soil was stored at 4 °C for three months prior to the experiment. The soil consisted of fine-grained clay trapped by *Phragmites* roots. Details of the soil chemistry are shown in Table AII.S2. The soil was initially homogenized at the U.S. Army Engineer Research and Development Center by removing large *Phragmites* roots and mixing in a blender with 40% w w⁻¹ addition of deionized water. 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 N₂) under anaerobic conditions (Coy Anaerobic Chamber) and then incubated anaerobically for two weeks prior to splitting for treatment amendments to ensure fully anaerobic conditions.

The slurry was divided for the “No DOM/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.¹ The regenerated AC was 73.3% C, had a surface area of 1150 m² g⁻¹, a skeletal density of 1.81 g cm⁻³, and a bulk density of 0.63 g cm⁻³.¹ The slurry was then further divided into containers for DOM and isotope spike amendments. These amendments were done immediately prior to the start of the experiment. SRHA II was added to the designated slurries at 15 mg L⁻¹, 30 mg L⁻¹, and 60 mg L⁻¹ (final concentration in slurry). For the addition, the SRHA was weighed into a small container and mixed with ~1 mL of ultrapure RO/DI water to dissolve. This 1 mL SRHA solution was added to the slurry and mixed well by end over end shaking. The ²⁰¹Hg and Me¹⁹⁹Hg 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 aliquots were parsed and preserved for total Hg, MeHg, metals, 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 total Hg and MeHg analysis. 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. The sulfide aliquot was preserved 1:1 with sulfide antioxidant buffer and analyzed via an ion-specific electrode calibrated with Pb-titrated standards.³⁴ Sulfide samples were analyzed within 6 h of the time point. Specific UV absorbance $\lambda = 280 \text{ nm}$ (SUVA₂₈₀) 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 $\lambda = 280 \text{ nm}$ with a Cary 4E UV-vis spectrophotometer.

Hg and MeHg Speciation Modeling. Hg and MeHg speciation modeling was performed using MINEQL v. 4.62.3 and Visual Minteq v. 13.1.³⁵ Stability constants, inputs, and outputs are tabulated in Appendix II. 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⁻¹) provided by the International Humic Substances Society, and by the measured percentage of exocyclic sulfur (23.6%) for SRHA.³⁶ We also assumed that native DOC in these soils taken from highly sulfidic marsh soils in the BCSA would have been sulfurized²³ 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.³⁷ for soils in the sulfidic regions of the Everglades. Thiol density calculations are shown in Table AII.S10.

Statistical Analyses. All statistical analyses were performed using the statistical software package JMP.³⁸ The data were assessed for normality and log₁₀ 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 AII.S6.

4.4. Results and Discussion

Isotherm Experiments. Previous work by Gomez-Eyles et al. reported strong partitioning of HgCl₂ and MeHgCl to several AC types in DI water isotherms.¹ However, in a typical estuarine marsh soil, organic matter is much more likely than chloride to dominate Hg and MeHg speciation.³⁹ In our isotherm experiments, we approximated an estuarine system with the addition of DOM to a 3 ppt Instant Ocean matrix, using environmentally realistic DOM:Hg mass ratios. Equilibrium speciation calculations (using MINEQL) indicated that DOM complexes accounted for ~100% of Hg and MeHg in the experimental solutions. We found that partitioning of the HgDOM and MeHgDOM complexes to AC was substantially lower than the published values for Hg and MeHg

chloride complexes.¹ Further, the log K for the HgDOM and MeHgDOM complexes closely resembled the log K of DOM alone (Figure 4.1). This was true for both CAC-Coal and CAC-Coco and occurred regardless of whether DOM or mercury was added first and pre-equilibrated with the AC (data not shown). Because the order of addition did not impact partitioning, we hypothesize that the DOM-mediated reduction in partitioning was due to a fundamental change in the interactions between Hg, MeHg, and AC, and not to a general fouling of the ACs by DOM.

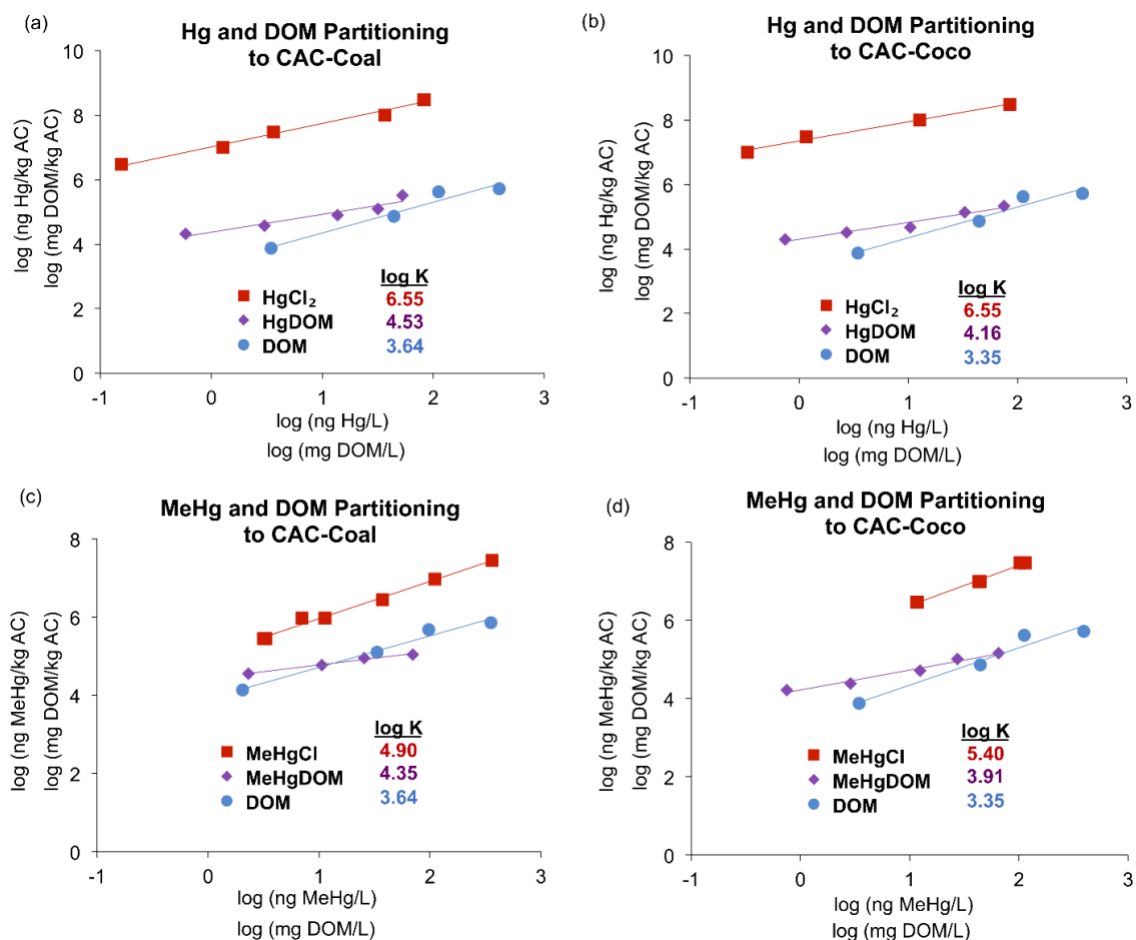


Figure 4.1. Sorption isotherms for Hg (top) and MeHg (bottom) onto two types of AC, in the presence and absence of DOM, plotted along with sorption isotherms for DOM. Left, coal-based AC; right, coconut shell-based AC. ACs are described in text.

We also observed that the effect of DOM on sorption to AC was greater for Hg than MeHg. Log K for HgDOM was about two log units lower than HgCl₂, while log K for MeHgDOM was only 0.5 to 1 log unit lower than MeHgCl. Interestingly, log K for HgDOM and MeHgDOM were similar (roughly 4 to 4.5) across all permutations of AC type and sequence of addition. For comparison, log K for SRHA DOM alone was 3.64 on CAC-Coal and 3.35 on CAC-Coco.

Soil Slurry Partitioning Experiment. *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, with significant oxygen demand. These estuarine soils, incubated with 3 ppt Instant Ocean water (containing 2.4 mM SO₄) became highly sulfidic following incubation, with concentrations rising above 1 mM after 21 d (Figure AII.S2). High porewater sulfide levels kept dissolved Fe concentrations at, or just above, the instrument detection limit (0.06 mg L⁻¹) (Figure AII.S3). However, neither AC nor SRHA amendments had any significant impact on porewater Fe or sulfide concentrations (Figures AII.S2 and AII.S3). Slurry pH remained circumneutral during the incubations (Figure AII.S4). Soil samples from time zero contained Fe in molar excess of S, suggesting an accumulation of pyrite in the original soil. 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 AII.S2.

Impact of AC on DOC. The background DOC level in slurries without AC amendment was roughly 9 mg L^{-1} , comparable to published values for the Berry's Creek marsh site (Figure 4.2).³³ The addition of 5% AC reduced ambient DOC concentrations in slurries without SRHA addition by about two thirds. AC also reduced total DOC in SRHA-spiked slurries by 70%, 50%, and 40% for the 15, 30 and 60 mg L^{-1} SRHA treatments, respectively. With the exception of the highest DOM addition, DOM levels stayed generally constant or declined moderately over the course of the experiment (Figure AII.S6).

AC amendments also changed the chemical character of DOC in slurries with and without SRHA spikes. SUVA_{280} was reduced in AC amended soils, although the reduction was relieved at the highest SRHA spike levels (Table AII.S9). The SUVA_{280} for the High DOM spike was 4.31, which is similar to values previously reported for SRHA.²¹

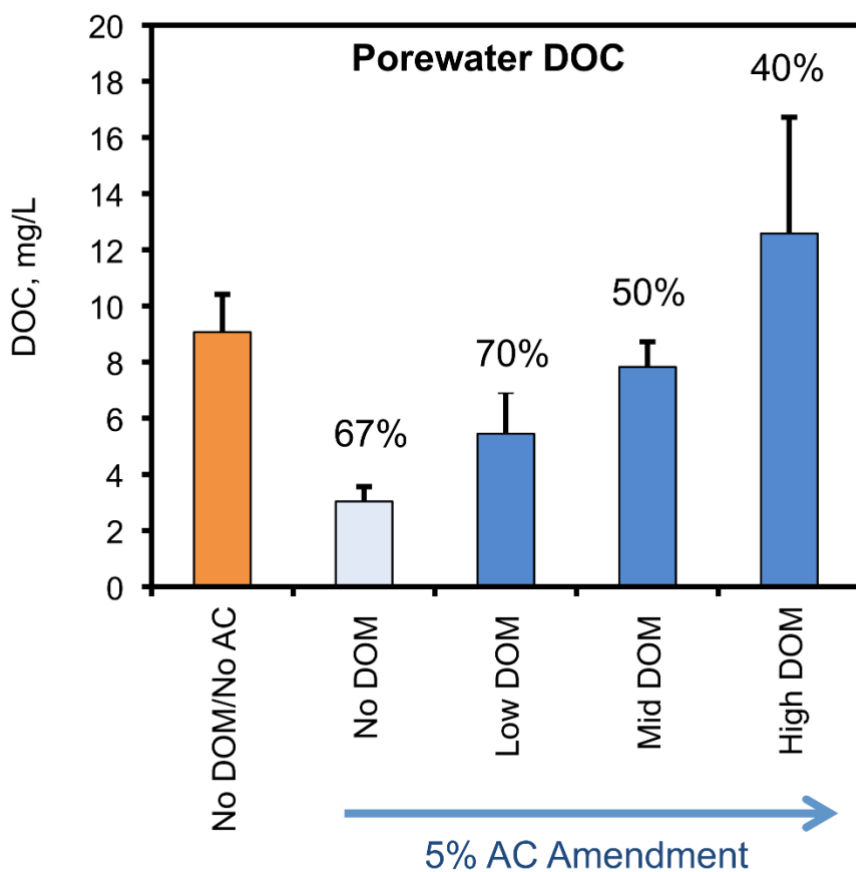


Figure 4.2. Average dissolved organic carbon concentrations in sediment/AC microcosms across all time points. SRHA addition levels were 15, 30 and 60 mg L⁻¹ respectively in Low-, Mid-, and High-DOM treatments. Error bars show the standard deviation of the concentrations measured. Percentages show the percent reduction (No DOM relative to No DOM/No AC, Low-, Mid-, and High-DOM relative to expected DOC concentration). Time series data are shown in Figure AII.S5.

Impact of DOM on Hg Partitioning to AC. DOM additions reduced the partitioning of inorganic Hg to AC in soil slurries in a concentration-dependent way. The effect was stronger for a freshly added ²⁰¹Hg spike than for ambient Hg. The AC amendment reduced ambient porewater Hg concentrations to ~10 ng L⁻¹, a roughly 75% reduction

from unamended slurries. At the highest DOM addition level, AC reduced porewater Hg to $\sim 20 \text{ ng L}^{-1}$, a reduction of only 50% (Figure 4.3a). For the fresh ^{201}Hg spike, AC reduced porewater Hg from 285 ng L^{-1} in unamended slurries to $\sim 5 \text{ ng L}^{-1}$ (comparable to the concentration of ambient Hg in the same treatment), a 98% reduction (Figure 4.3b). The addition of DOM significantly decreased ^{201}Hg sorption to AC, allowing up to $\sim 90 \text{ ng L}^{-1}$ of ^{201}Hg to stay in solution. At the highest DOM concentration, AC sorbed only $\sim 40\%$ of ^{201}Hg from porewater.

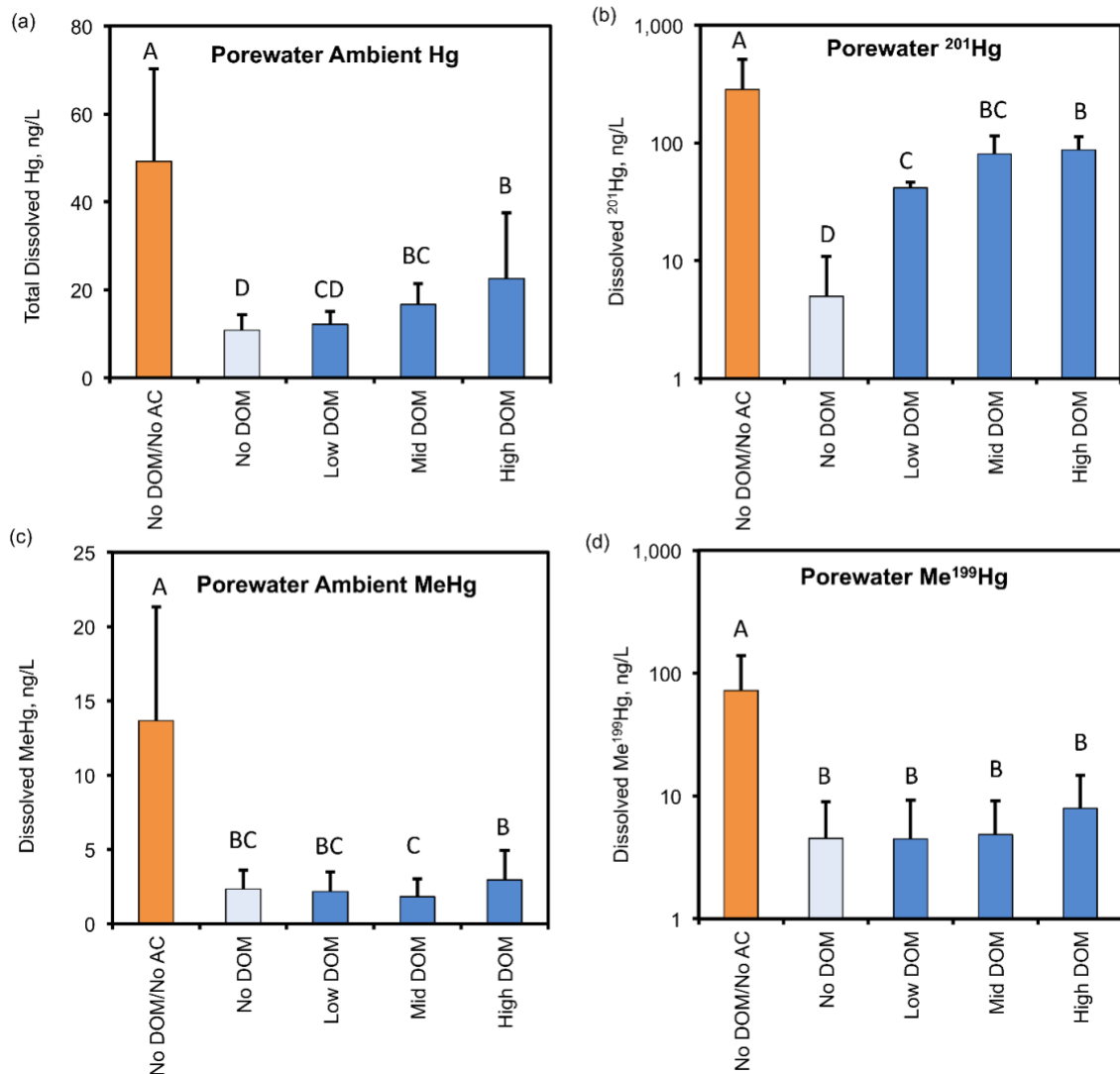


Figure 4.3. Effect of added DOM on porewater total Hg and MeHg concentrations in AC-treated soils. Bars are the average dissolved concentrations in the soil microcosms over all time points: (a) total ambient Hg; (b) ^{201}Hg ; (c) ambient MeHg; and (d) Me^{199}Hg . Error bars represent the standard deviation 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. All linear models used $\text{Hg or MeHg} \sim \text{Treatment, Day, and Treatment*Day}$. Time series data are shown in Figure AII.S6. Note the log scales for the enriched isotope spikes.

The trends in porewater concentration for both ambient Hg and spiked ^{201}Hg were reflected in the soil:water partition coefficients (Figure 4.4a and b). AC increased ambient Hg partitioning to the solid phase by about an order of magnitude compared to the unamended slurries (Figure 4.4a). With the exception of the High DOM treatment, the addition of DOM to the AC-amended microcosms did not significantly impact the K_d of ambient Hg. The fresh ^{201}Hg spike was, as expected, more reactive toward both AC and DOM. AC increased the average K_d almost 50-fold (Figure 4.4b), and all levels of the SRHA DOM addition significantly decreased the ^{201}Hg K_d by one to two orders of magnitude. Added DOM in large part negated the positive impact of the AC on spike Hg partitioning; the K_d s of the AC + SRHA treatments were statistically indistinguishable from the unamended slurries.

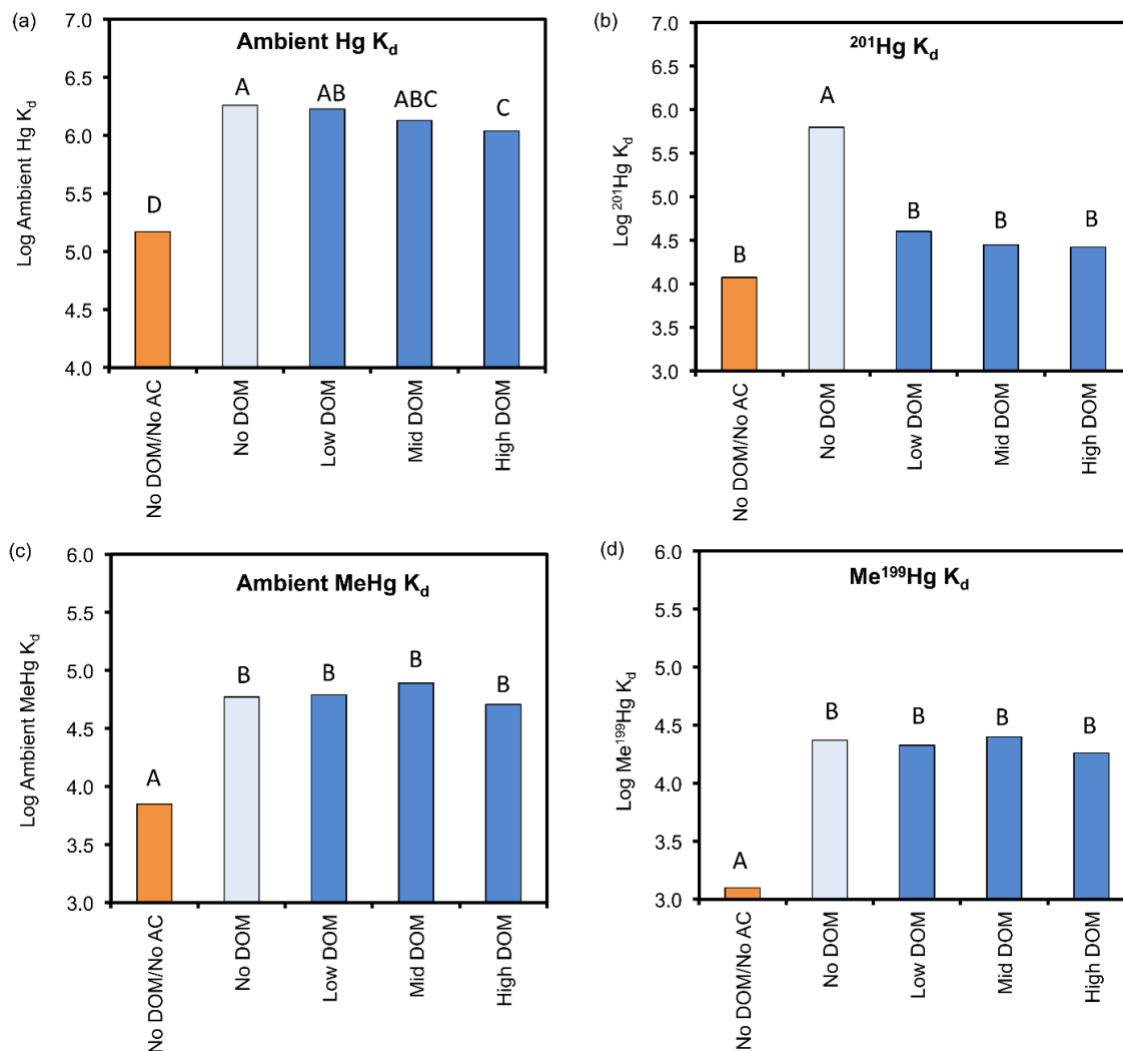


Figure 4.4. Average sediment:water partition coefficients for Hg and MeHg over all time points: (a) ambient Hg; (b) ^{201}Hg ; (c) ambient MeHg; (d) Me^{199}Hg . Sediment:water partition coefficients (K_d) were calculated as the sediment concentration in $\text{ng k}^{-1}\text{g}$ divided by the porewater concentration in ng L^{-1} . Shared letters signify that the treatments were not statistically different. Linear models were as follows: ambient Hg $K_d \sim \text{Isotope Spike} + \text{Treatment} + \text{Day} + \text{Treatment} * \text{Day} + \text{Treatment} * \text{Isotope Spike}$; ambient MeHg $K_d \sim \text{Treatment} + \text{Day} + \text{Isotope Spike}$; and for both $^{201}\text{Hg}K_d$ and Me^{199}Hg : $K_d \sim \text{Treatment} + \text{Day}$. Time series data are shown in Figure AII.S7.

Impact of DOM on MeHg partitioning to AC. Unlike inorganic Hg, SRHA DOM spikes at any concentration (up to 60 mg L⁻¹) did not significantly impact MeHg sorption to AC in the soil slurries. Activated carbon additions were effective in sequestering MeHg, reducing ambient porewater MeHg from ~14 to about 2 ng L⁻¹ (~85% reduction) and reduced a fresh Me¹⁹⁹Hg spike from ~72 to ~5 ng L⁻¹ (~95%) (Figure 4.3c and 4.3d). Soil:water ambient and spike MeHg partition coefficients were 1 and 1.5 orders of magnitude higher, respectively, in AC-amended slurries relative to unamended slurries (Figure 4.4c and 4.4d).

DOM Influence on Hg and MeHg Complexation and Sorption to AC. In the slurry experiments, DOM reduced 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 DOM changed Hg speciation in a way that reduced AC sorption but did not do so for MeHg.

We hypothesized that DOM might impact Hg (but not MeHg) sorption to AC by slowing the formation of metacinnabar,^{20-22, 40} therefore slowing Hg partitioning to the solid phase. Unlike inorganic Hg, 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 DOM (Fig. 3) supports this idea. Modeled HgS precipitation in the slurries was borderline, depending on the choice of K_{sp} and of the formation constants for aqueous mercuric sulfides (HgS₂⁻², HgHS⁻², Hg(HS)₂) (Figure 4.5, Figure AII.S9), with either metacinnabar or aqueous mercuric sulfides dominating species of inorganic Hg in porewaters in these slurries that produced high μ M sulfide. 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 taking into account potential increases in thiol content from in situ sulfurization of DOM, because DOM concentrations were several orders of magnitude less than sulfide. If lower formation constants for HgHS_2^- and $\text{Hg}(\text{HS})_2^{41}$ and precipitation of HgS^{42} are used in modeling, metacinnabar precipitates in all of the microcosm treatments. The predicted amount of HgS formation increased across the DOM gradient in the slurries (reflecting higher total Hg concentrations in porewater). ^{201}Hg speciation followed similar trends as the ambient Hg (Figure AII.S10), with HgS precipitation borderline, depending on the choice of K_{sp} and of the formation constants for aqueous mercuric sulfides.

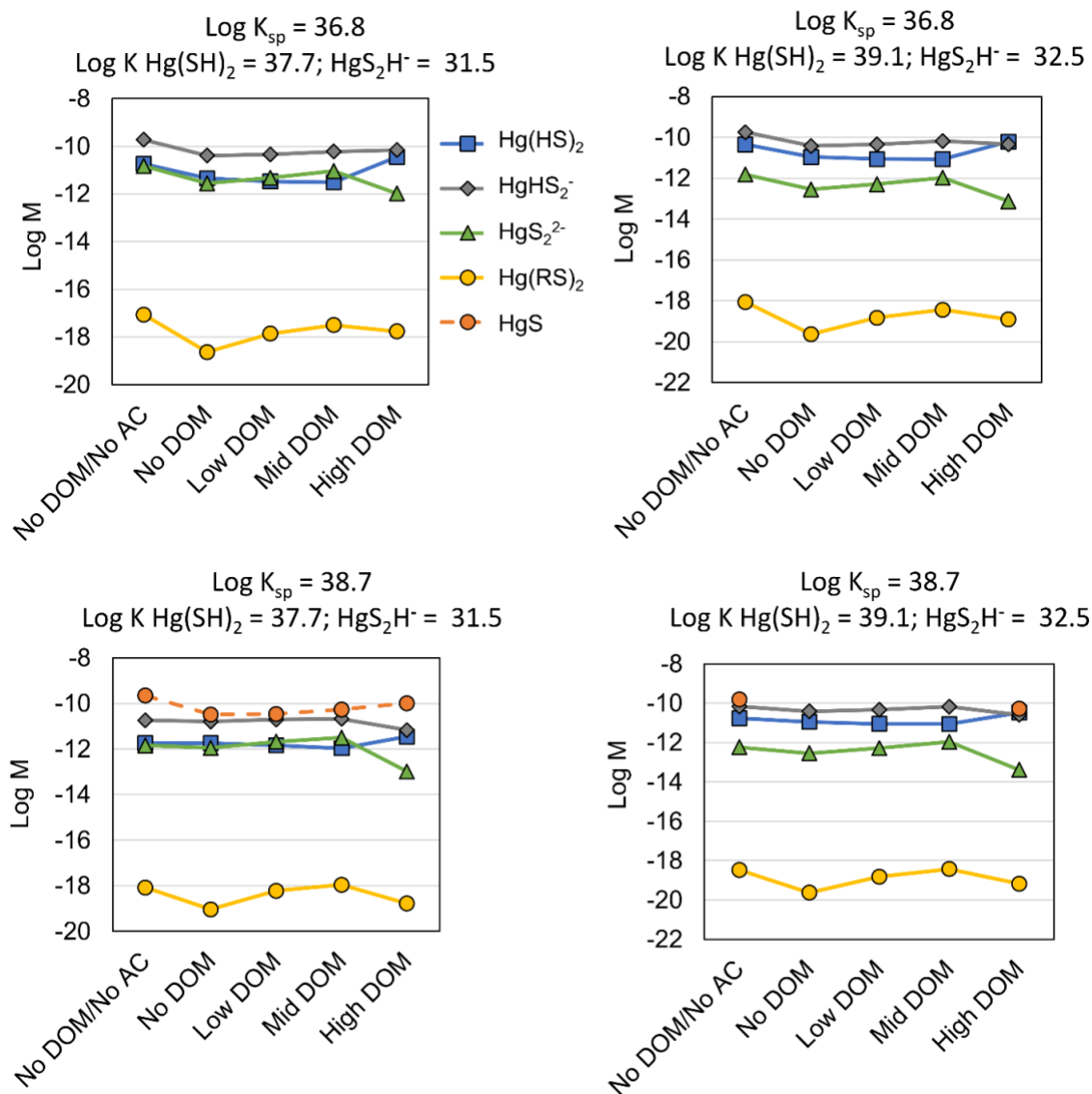


Figure 4.5. Calculated filter-passing inorganic Hg(II) speciation in the microcosms.

Stability constants are listed in Table AII.S4. Speciation calculation inputs and outputs are shown in Appendix II. Calculations were performed using two values of the solubility product (K_{sp}) for the reaction $\text{Hg}^{2+} + \text{HS}^- = \beta\text{-HgS}_{(\text{s})} + \text{H}^+$ and two values for the stability constants for $\text{Hg}(\text{SH})_2$ and HgS_2^{2-} .⁴⁰⁻⁴³

An alternative hypothesis is that HgS species have higher affinity for AC than do DOM-Hg complexes, and that HgS species distribution changed across the DOM gradient. Inorganic Hg was present almost 100% as Hg-S (either metacinnabar or aquo species) in the slurries, and with the high K_{sp} models, the fraction of total Hg precipitated as HgS increased with increasing DOM amendment (reflecting higher total aqueous Hg concentrations). This hypothesis is also supported by our estimates of $\log K_{AC}$ in the slurries. Using the known fraction of AC in the slurries and the K_{ds} from the “Sediment-Only” and “No DOM” treatments, we back-calculated a K_{AC} for the microcosms for comparison to the isotherm study K_{ACs} (Table AII.S17). $\log K_{AC}$ for Hg and ^{201}Hg in the slurries were 6.02 and 7.09, respectively. These are substantially higher than the ones obtained in the isotherm experiments for either chloride or DOM species (HgCl_2 $\log K_{AC} = 6.55$, HgDOM $\log K_{AC} = 4.53$). The key difference between the two experiments was the presence of sediment and high- μM sulfide in the slurries.

Both modeled aqueous MeHg and Me^{199}Hg speciation was dominated by MeHg-S species (Figures AII.S11 and AII.S12), though MeHg-thiols were the second most abundant MeHg species. MeHg does not form sulfide precipitates, and unlike inorganic Hg, the formation constants for MeHg thiols are somewhat higher than for MeHgSH . Thus, thiols in DOM can compete with bisulfide as ligands for MeHg . Because MeHg was already complexed with DOM even in slurries without added DOM, the addition of the SRHA did not observably impact the distribution of MeHg among species or MeHg sorption to AC. Like Hg, however, the K_{AC} for $\text{MeHgS aquo species}$ appears higher than K_{AC} for MeHg-DOM or MeHgCl . $\log K_{AC}$ for MeHg and Me^{199}Hg were 6.02 and 5.65,

respectively, compared to MeHgCl $\log K_{AC} = 4.89$ and MeHgDOM $\log K_{AC} = 4.35$ in the isotherm experiments.

To summarize, we speculate that DOM impacted Hg sorption, but not MeHg sorption, to AC in soils by interfering with HgS precipitation and/or by changing aqueous HgS speciation. The sorption of HgS and MeHgS species to AC also appears stronger than the sorption of chloride and sulfide species. Resolution of the mechanism of DOC impacts on Hg sorption to AC in sulfidic sediments will require the direct determination of $\log K_{ACs}$ for Hg and MeHg sulfides, and the distinction between HgS precipitation and AC sorption.

Implications for Contaminated Site Remediation. Our results show that the addition of SRHA did not significantly impact the efficacy of AC for reducing ambient and newly-spiked MeHg porewater concentrations. Thus, in typical wetland environments like those of our slurries, with high organic carbon content in the soil and high ambient dissolved sulfide concentrations, DOM is not expected to directly impact AC efficacy for the remediation of MeHg contamination.

SRHA DOM concentrations impacted inorganic Hg porewater reductions in a concentration-dependent manner for both the ambient and newly-spiked pools, reducing the extent of sorption onto AC. Our slurries contained relatively high concentrations of dissolved sulfide and soil organic carbon, both of which favor greater partitioning of Hg to the solid phase. It is likely that DOM would have an even greater impact on Hg sorption to AC in environments with lower soil ligand content and lower dissolved sulfide concentrations. The reduction in AC efficacy by DOM was much more significant

for newly-spiked Hg. Though MeHg production from the ^{201}Hg spike was reduced in the presence of AC, DOM clearly enhances the mobility of the spike. Therefore, at sites where new Hg inputs are the target of the AC amendment, DOM concentration should be a concern for site remediation. It may be necessary to increase the AC dose in areas receiving new Hg inputs. 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.

Further exploration is needed of the impact of DOM character on Hg and MeHg partitioning to AC. Previous experiments have shown that SRHA is effective in increasing Hg bioavailability for methylation because it is able to inhibit the growth and aggregation of metacinnabar due to its large size and aromatic character.²⁰ However, SRHA has a relatively low sulfur content (0.5%) compared to other DOM isolates.²⁰ It is possible that this lower sulfur content would impact SRHA reactivity towards MeHg and Hg species due to a lower amount of thiol ligand binding sites on the DOM. High sulfide environments (like those in our slurries) could also result in the sulfurization of both DOM and AC surfaces.²³ Increased DOM thiol content would likely decrease the sorption of both Hg and MeHg to AC, with more pronounced impact on Hg. Sulfurization of the AC surface would create more binding sites for Hg and MeHg and potentially enhance sorption of Hg and MeHg.

For more confident predictions of how DOM might impact AC performance across ecosystems, further study is needed to determine how DOM isolates of varying character impact Hg and MeHg partitioning onto AC. Isotherm experiments are needed to measure the impact of sulfide on MeHg and Hg partitioning 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. HgCl₂ vs HgDOM) sorbed are equal, or if the percent reduction in porewater 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. Though several questions remain, overall, our data indicate that DOM, sulfide, and Hg age are important parameters controlling AC sorption and should be considered in amendment design and assessment. We will be better able to parameterize a model for AC amendment efficacy as more data from field trials are published.

4.5. Acknowledgements

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Chapter 5: Development of a Novel Equilibrium Passive Sampling Device for Methylmercury in Sediment and Soil Porewaters

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5.1. Abstract

In recent years, passive sampling has emerged as a viable method for estimating the bioavailability of hydrophobic organic contaminants like PCBs and PAHs in sediments and soils. However, passive sampling methods for methylmercury (MeHg), another persistent and bioaccumulative contaminant that drives ecological and human health risk at many managed sites, have not achieved comparable acceptance. Here, we describe the identification and testing of a suite of candidate materials for a novel equilibrium sampling device specifically designed for MeHg. The materials' partitioning coefficients for MeHg complexed with HO^- and with dissolved organic matter were measured in isotherm tests, and many were in a desirable range ($10^{3.5}$ – $10^{4.0}$), comparable to typical sediment-water partitioning coefficients. A subset of the materials was tested in slurries of contaminated soils and sediments, and separately in stagnant sediment microcosms. In both experiments samplers made good predictions of directly measured porewater concentrations. Sampler equilibration time in water and in sediments/soils was approximately one to two weeks. We investigated the mechanism of accumulation by one sampler, a suspension of activated carbon particles in an agarose gel. Sampling was kinetically influenced by interactions with AC particles and not limited by diffusion through the agarose gel. We also demonstrated desorption of Hg and MeHg from AC, indicating that this sampler is capable in principle of equilibrium sampling. As such, it

may represent an alternative to the diffusive gradient in a thin film (DGT) device, which is designed to function in a kinetic mode.

5.2. Introduction

Mercury is a bioaccumulative, neurotoxic pollutant that pervades the global environment. It is a naturally occurring element, but anthropogenic activities, especially coal-fired power generation and artisanal gold mining, greatly enhance the availability and mobility of global mercury stores.¹ Inorganic mercury (Hg_i) is converted to the more toxic and bioaccumulative methylmercury (MeHg) by ubiquitous microorganisms including sulfate reducers, iron reducers, methanogens, and others.² Because of the specific conditions required by methylators, their activity is often localized in redox transition zones near solid-water interfaces³, making MeHg readily available for uptake by benthic and epibenthic fauna.⁴ These organisms are important for site risk assessment because they serve as a conduit for the transfer of MeHg into pelagic food webs, where it can be biomagnified to levels of concern for both human and ecological receptors.⁵⁻⁹ Benthic bioavailability provides an indication of the risk posed by persistent, sediment-associated contaminants and can be used to monitor the effects of emissions reductions and sediment remediation efforts.¹⁰⁻¹² However, MeHg bioavailability predictions are confounded by a number of factors. Bioaccumulation depends to a large extent on organism feeding behavior and life history, along with environmental variables including sediment organic carbon and sulfide content.¹³⁻¹⁶ MeHg in sediments is also subject to significant temporal and spatial variation based on temperature, redox, and hydrologic conditions, all of which affect Hg_i complexation and microbial activity.¹⁷ This means that

a strategy based on opportunistic “grab” sampling of native organisms and sediment cores risks obscuring important trends.

Increasingly, passive sampling of sediment and soil porewaters is used as a time-integrative and cost-effective method to measure the bioavailability of legacy contaminants.^{18, 19} Polymeric passive samplers have been extensively investigated as a tool to measure freely dissolved porewater concentrations (C_{pw}) of hydrophobic organic contaminants including polychlorinated biphenyls and polycyclic aromatic hydrocarbons. Dissolved concentrations of these hydrophobic compounds are typically very low, and sediment ingestion is more likely to represent the dominant exposure route for benthic fauna than dermal diffusion or ingestion of water. Even so, C_{pw} measurements are useful under the assumption that contaminants are in thermodynamic equilibrium among water, sediment, animal, and sampler compartments.¹⁹⁻²¹ This chemical activity-based approach permits the use of equilibrium partitioning coefficients to calculate unknown concentrations or to predict the outcome of a perturbation such as the addition of an engineered sediment amendment or an ongoing contaminant input. In this way, porewater passive sampling measurements can serve as a useful proxy for benthic bioavailability. Sampler accumulation generally represents a first-order exchange process that proceeds through a linear uptake phase before approaching equilibrium. The degree of equilibration achieved during a deployment can be assessed with performance reference compounds, permitting adjustments to measured water concentrations to account for nonequilibrium.¹⁹

While equilibrium passive samplers are increasingly well established for organics, no comparable device has achieved wide acceptance for measuring MeHg. The best-studied

is the diffusive gradient in a thin film, or DGT, device.²²⁻³⁰ In contrast to the equilibrium samplers just described, DGT operates in a kinetic mode, i.e., it accumulates analytes linearly for as long as it is deployed. This introduces the potential for oversampling by depleting the analyte in porewater and inducing resupply from sediment. Modeling approaches to account for sediment resupply have been proposed, but for MeHg this question is particularly complicated by the large potential variability in solid-phase concentrations arising from microbial activity.³¹⁻³⁴ Uncertainty also surrounds the identities of the MeHg species sampled by DGT and the extent to which they represent the bioavailable fraction. Recently, concerns have also been raised about the ability of DGT gels to become saturated and diverge from linear uptake kinetics.³⁵ Additionally, it has been reported that metal-sulfide nanoparticles can deposit on DGT membranes, slowing diffusion into the samplers.³⁶ DGT sampling is most likely to be a good proxy for bioavailability in marine surface waters, where the small and readily diffusive MeHgCl complex can dominate MeHg speciation. However, in typical estuarine and fresh porewaters, MeHg is more likely to be complexed with sulfide, small organic thiols, or bulky dissolved organic matter (DOM) molecules.^{37, 38} These species occupy a wide range of sizes, diffusivities, and bioavailabilities, greatly increasing uncertainty when extrapolating from DGT to organism accumulation. Additionally, the physiological mechanisms of benthic MeHg uptake are currently not well understood. MeHg may diffuse across membranes as uncharged complexes, or it may exchange with other ligands on biological surfaces; evidence of both has been found.^{14, 39} The appeal of equilibrium passive sampling is that, if the sampling material is properly designed, it should approach a steady-state concentration analogous and in proportion to the steady

state reached by benthic animals, irrespective of mechanism.¹⁸ The work described here seeks to develop such a device, with the goal of enabling reproducible measurements of bioavailable MeHg and improving risk assessment and management for mercury-contaminated sites.

Our approach to developing a novel sampler began empirically, by identifying a suite of materials with affinity for MeHg sufficient to concentrate it to a desirable extent. For our purposes, this entailed a target range for logarithmic sampler-water partitioning constants ($\log K_{ps}$) of 3.0 to 4.5. This range was selected in part to ensure accumulation of analytically detectable masses of MeHg in a reasonably-sized sampler. It was also chosen to avoid perturbing native sediment-water partitioning (K_d), which is often in or near this range.⁴⁰ More than 30 materials were screened in isotherms for MeHgOH and MeHgDOM, with the most successful chosen to proceed to further, more environmentally realistic tests, first in slurried soils and sediments, then in stagnant sediment microcosms. One particularly promising material, activated carbon embedded in agarose, was subjected to additional experiments to investigate its kinetics of MeHg uptake and release.

5.3. Materials and Methods

Material Selection and Preparation. The materials tested in this work can be divided into three categories: (1) standard laboratory polymers not specifically designed for metal sorption; (2) polymers containing activated carbon; and (3) polymers with reduced sulfur chemical functionality. Agarose gels were prepared with an existing method⁴¹, but suspensions of sorbent materials in agarose were based on custom formulations. Sulfur-functionalized polymers were identified in the biomedical (^{42,43,44}) or water treatment (⁴⁵)

literature. A method for embedding AC in a polyvinylidene fluoride (PVDF) polymer was adapted from an electrochemistry application.⁴⁶ A complete list of tested materials and references to preparation methods is presented in Table 5.1, and photos of selected samplers appear in Figure AIII.S1. For all experiments except initial screening isotherms, agarose gels were prepared with uniform thickness (800 μm except where noted) by casting between glass plates separated by spacers. Spacer and gel thicknesses were verified with a 0-1” digital micrometer (iGaging, San Clemente, CA).

Table 5.1. Summary of materials screened in MeHg isotherm experiments. Correlation coefficients are for log-transformed C_{ps} vs. C_{w} .

abbreviation	material	ref.	MeHgOH		MeHgDOM	
			log K_{ps}	r^2	log K_{ps}	r^2
ag	agarose	41	2.59	0.96		
ag+AC	activated carbon suspended in agarose	41	3.45	>0.99	2.83	0.92
ag+Cys	L-cysteine dissolved in agarose	41	2.94	0.98		
ag+Cys-alg	L-cysteine-functionalized alginate suspended in agarose	42	3.59	0.92		
ag+Cys-xylo	L-cysteine-functionalized xyloglucans suspended in agarose	44	3.45	0.95		
ag+MAA-chit	mercapto-functionalized chitosan suspended in agarose	47	3.21	0.98		
ag+MPTMS-DE	mercapto-functionalized diatomaceous earth suspended in agarose	45	3.82	0.99	3.11	0.99
ag+SAMMS	thiol-SAMMS suspended in agarose	41	5.07	0.96	3.31	0.92
agPEG	agarose doped with polyethylene glycol and glycerol	48	2.68	0.72		
agPEG+AC	activated carbon suspended in PEG-doped agarose	48	3.55	0.98	3.02	0.90
agPEG+SAMMS	thiol-SAMMS suspended in PEG-doped agarose	48	3.93	>0.99	2.98	>0.99
CA	cellulose acetate	n/a	2.58	0.99		
CA+MA	mercapto-functionalized cellulose acetate	49	2.36	0.99		
CN	cellulose nitrate	n/a	2.95	0.91		
DE	diatomaceous earth	n/a	2.96	0.93		
MPTMS-DE	mercapto-functionalized diatomaceous earth	45	5.65	0.98		
Parafilm	paraffin	n/a	2.06	0.96		
PDMS	polydimethylsiloxane	n/a	2.14	0.99		

PE	polyethylene	n/a	2.35	0.92		
PES	polyethersulfone	n/a	2.72	0.72		
PET+Cys	L-cysteine-functionalized polyethylene terephthalate	43	3.73	0.94	3.29	0.99
POM38	polyoxymethylene (38 μ m thick)	n/a	2.05	0.93		
PTFE	polytetrafluoroethylene	n/a	2.19	0.97		
PU+Cys	L-cysteine-functionalized polyurethane	43	1.92	0.46		
PVDFm+AC	activated carbon suspended in PVDF prepared with 1:1 methanol:water nonsolvent	46	3.39	0.84		
PVDFw	polyvinylidene fluoride prepared with water nonsolvent	46	2.29	0.90		
PVDFw+AC	activated carbon suspended in PVDF prepared with water nonsolvent	46	3.24	0.98	3.21	0.99
PVDFw+Cys	L-cysteine dissolved in PVDF	46	4.36	0.97		
PVDFw+SAMMS	thiol-SAMMS suspended in PVDF	46	4.11	0.98	3.00	0.98
SAMMS	thiol-SAMMS	n/a	5.52	0.97		

Screening Isotherms. *MeHgOH Isotherms.* Small pieces of test material were cleaned, dried, weighed, and placed in 60-mL polyethylene terephthalate glycol copolymer (PETG) bottles containing 50 mL deionized water adjusted to 3 ppt salinity with Instant Ocean (Spectrum Brands, Blacksburg, VA). All experiments in this work were run at low salinity for consistency and to mimic the conditions at our primary field site, an oligohaline, estuarine marsh. In this experiment, $[\text{Cl}^-]$ was sufficiently low and pH sufficiently high (approximately 9 as predicted by MINEQL and verified by direct measurement) that MeHg was predominantly complexed with HO^- rather than Cl^- . The solutions were spiked with MeHg at a series of concentrations chosen in consideration of analytical detection limits and anticipated partitioning. Samples were incubated for 14 d in the dark at 4 °C with orbital shaking at 120 rpm. Following incubation, sample waters were passed through 0.45- μ m GDX filters (Whatman plc, Maidstone, Kent, UK) with disposable plastic syringes. Filtrates were processed and analyzed for MeHg. In screening isotherms only, the mass-normalized sampler concentration, C_{ps} , was calculated from the

difference between spiked and recovered MeHg in water. In all other experiments, samplers were directly distilled and analyzed. Sampler-water partitioning coefficients, K_{ps} , were calculated as the ratio of C_{ps} to C_w . Control bottles with no sampler were used to assess MeHg degradation and loss to bottle walls. Bottle sorption was significant in sampler-free controls, but negligible relative to partitioning by enhanced polymers.

MeHgDOM Isotherms. We also evaluated partitioning of MeHg complexed with DOM (MeHgDOM) to several samplers. Isotherms were set up as above, but with the addition of Suwannee River Humic Acid Standard II (SRHA; International Humic Substances Society) in a 10^6 :1 SRHA:MeHg mass ratio in each sample and 7.5 mM NaHCO_3 to buffer pH at 8. A high SRHA:MeHg mass ratio was chosen to avoid saturating thiolic sites on DOM, which control MeHg-DOM complexation under normal environmental conditions.⁵⁰ To ensure a stable MeHg distribution, solutions were incubated overnight after addition of SRHA but before addition of samplers. The assumption of an overnight equilibrium between MeHg and DOM was based on the work of Luengen et al.¹⁵

Sampler Kinetics and Mechanism of Accumulation. In an initial, range-finding experiment, two samplers, ag+AC and PET+Cys, were exposed to MeHgOH or MeHgDOM solutions for 7 h, 1 d, 7 d, 14 d, or 28 d. Solutions were sampled destructively at each time point and water filtrates and samplers were processed and analyzed for MeHg.

In a subsequent experiment, pieces of ag+AC of identical composition but contrasting thicknesses (0.80 x 5 x 5 mm vs. 0.17 x 10 x 10 mm) were exposed to MeHgDOM to determine whether it diffuses into the sampler or is restricted to surface adsorption. A solution of 3 ppt Instant Ocean, 7.5 mM NaHCO_3 , and 5 mg L⁻¹ SRHA was prepared and

passed through a 0.7- μm AQFA filter apparatus. The filtrate was spiked to 50 ng L^{-1} MeHg and allowed to equilibrate overnight before being apportioned to exposure bottles. Samplers were added to bottles and exposed in the dark at 4 $^{\circ}\text{C}$ with orbital shaking at 60 rpm. Samples were collected destructively after 6 min, 2.4 h, 7 h, 1 d, 3 d, 7 d, 21 d, and 58 d. Waters and samplers were collected, preserved, and analyzed. Results from the 21- and 58-d time points are not reported because C_{pw} had dropped substantially in both sampler and control bottles due to MeHg degradation.

Activated Carbon Kinetics and Desorption. Granular activated carbon (Calgon 80 x 325 TOG LF, CAS #7440-44-0, sieved to $> 53 \mu\text{m}$ prior to use) was weighed into PETG bottles containing 50 mL of deionized water with 3 ppt Instant Ocean and 5000 ng L^{-1} Hg or 250 ng L^{-1} MeHg. Control bottles without AC contained 50 ng L^{-1} Hg or 20 ng L^{-1} MeHg. Bottles were incubated for 5 min, 30 min, 6 h, or 2 d, after which shaking was halted and AC particles were allowed to settle. Waters were carefully removed by pipet while minimizing withdrawal of AC, filtered, preserved, and analyzed. Fresh solution without mercury spike was added to the original exposure bottles up to the 50-mL mark, and the bottles were incubated for the same amounts of time as in the exposure step. Bottle weights were collected before and after each step to track solution volumes, and exposure times were recorded to the minute. Each adsorption and desorption time point was run in duplicate (controls) or triplicate (AC).

Soil and Sediment Slurries. A natural soil and sediment were used to test the predictive capabilities of select samplers in a more complex chemical setting. Soil from the upper 15 cm of a Berry's Creek (Bergen County, NJ) *Phragmites* marsh was collected in June 2015 in a location containing about 30 ppm total Hg. Estuarine sediment was collected

from the Rhode River dock at the Smithsonian Environmental Research Center in Edgewater, MD. It contained about 0.1 ppm solid-phase Hg and less than 5 ppb MeHg. Sediment and soil chemistry can be found in Table AIII.S8. Slurries of each were prepared with degassed, deionized water containing 3 ppt Instant Ocean in a 9:1 weight ratio with solids. All subsequent handling was performed in an anaerobic glove bag. Slurries were spiked with unlabeled Hg equal to 10% (soil) or 20% (sediment) of the native, dry-weight Hg content to encourage additional MeHg formation. Slurries were incubated for 7 d with a gentle shake once per day before apportionment to sample jars. Three sampler types were tested in duplicate: ag+AC, ag+SAMMS, and PET+Cys. Samplers were cleaned, dried, weighed, measured, and placed in small baskets prepared by folding strips of polypropylene mesh and sewing edges together with nylon thread (Figure AIII.S1c). Mesh and thread were washed with 1 M HNO₃ followed by deionized water prior to use. Samplers in baskets were placed in wide-mouth, glass sample jars containing 50 mL equilibrated soil or sediment slurry. Two additional “canary” jars of each slurry were prepared without samplers but with 2 mg L⁻¹ resazurin to monitor redox status. Jars were kept on ice for 20 d to minimize further MeHg production and were gently swirled once per day. After exposure, samplers were removed from jars and baskets, gently rinsed with deionized water, blotted with lab wipes, weighed, and frozen. An aliquot of overlying water was collected from each jar for pH measurements, and the remaining jar contents were transferred to tubes and centrifuged at 4200 rpm for 7 min. Supernatants were passed through 0.45 µm glass microfiber syringe filters with disposable plastic syringes into clean, 60-mL PETG bottles. Aliquots were set aside for analysis of sulfide and DOC. Remaining filtrates were acidified with 0.5% HCl and

refrigerated, then processed and analyzed for MeHg and a suite of standard chemical constituents. Pelleted solids were lyophilized until weights were replicable, then processed and analyzed for MeHg.

Sediment Microcosms. Bottom sediment was collected to a depth of 15 cm from a tidal creek in the upper part of Berry's Creek. The sediment was silty mud with solid-phase Hg concentrations of 40–50 ppm. Sediments were collected in May 2016 in 5-gal buckets, shipped on ice to SERC and maintained at 4 °C until the start of the experiment in August. Sediment chemistry is summarized in Table AIII.S9. Sediments were mixed by hand and a portion was amended with 5 wt% activated carbon (Calgon Type 3055, 80 x 325 mesh, CAS #7440-44-0). For microcosms, 200 g sediment with or without AC was combined with 225 mL overlying water (5 ppt Instant Ocean) in 800-mL plastic beakers. Beakers were loosely lidded, gently aerated, and kept at room temperature (Figure AIII.S5). Microcosms equilibrated 14 d prior to sampler insertion. In each beaker, one ag+AC sampler in a protective basket was fully submerged in the uppermost 0.5 cm of sediment, spanning the visually apparent redox transition zone). Samples were collected destructively at 0, 8, 14, 21, and 28 d of exposure. Samplers were removed from baskets, preserved, and analyzed as before. Sediment and porewater were separated by centrifugation at 4000 rpm for 5 min and handled as in the slurry experiment. Sediment and porewater measurements reflected vertical averages of the entire depth of sediment in the microcosms (2–3 cm). Overlying water was gently replaced in remaining beakers on sampling days.

Analytical Methods. MeHg in all matrices was measured by isotope dilution mass spectrometry after separation and cleanup by distillation.⁵¹ Total Hg was also measured

using ID-ICP-MS following SnCl_2 reduction to Hg^0 . Water samples were digested with BrCl and sediment samples with 7:4 $\text{HNO}_3\text{:H}_2\text{SO}_4$. Further details and quality assurance data are found in Table AIII.S2.

Equilibrium Speciation Calculations. The chemical modeling program MINEQL+ v.4.6 (Environmental Research Software, Hallowell, ME) was used to calculate aqueous MeHg speciation in all experimental systems. Conditional stability constants for a variety of MeHg complexes were obtained from literature sources and added to the software's database as outlined in Table AIII.S1. All other thermodynamic constants were software defaults.

5.4. Results and Discussion

Screening Isotherms. *MeHgOH* Isotherms. Initial isotherm tests demonstrated greatly enhanced sorptive capabilities of both AC- and thiol-modified polymers relative to unmodified hydrophobic polymers, and permitted the selection of a subset of enhanced polymers to proceed to subsequent tests. In the first set of experiments, equilibrium speciation modeling indicated that MeHg was complexed to HO^- . Partitioning of MeHgOH by eight unmodified hydrophobic polymers, while log-linear (average $r^2 = 0.92$), was one to two orders of magnitude below our target range for $\log K_{\text{ps}}$ of 3.0 to 4.5. This outcome was to be expected given the low hydrophobicity of MeHgOH ($\log K_{\text{ow}} = -1.2$).³⁹ By contrast, many of the AC- and thiol-modified polymers fell comfortably within our target range, and sorption isotherms remained log-linear over multiple orders of magnitude (Table 5.1 and Figure 5.1a). We fitted partitioning data to Freundlich isotherms and found exponents less than one for some tested materials. However, curves only diverged from linearity at unrealistically high C_w (Figure AIII.S2), so reported K_{ps}

represents the average partitioning for each isotherm. A discussion of polymer permeability is found in the SI and supported by Table AIII.S3.

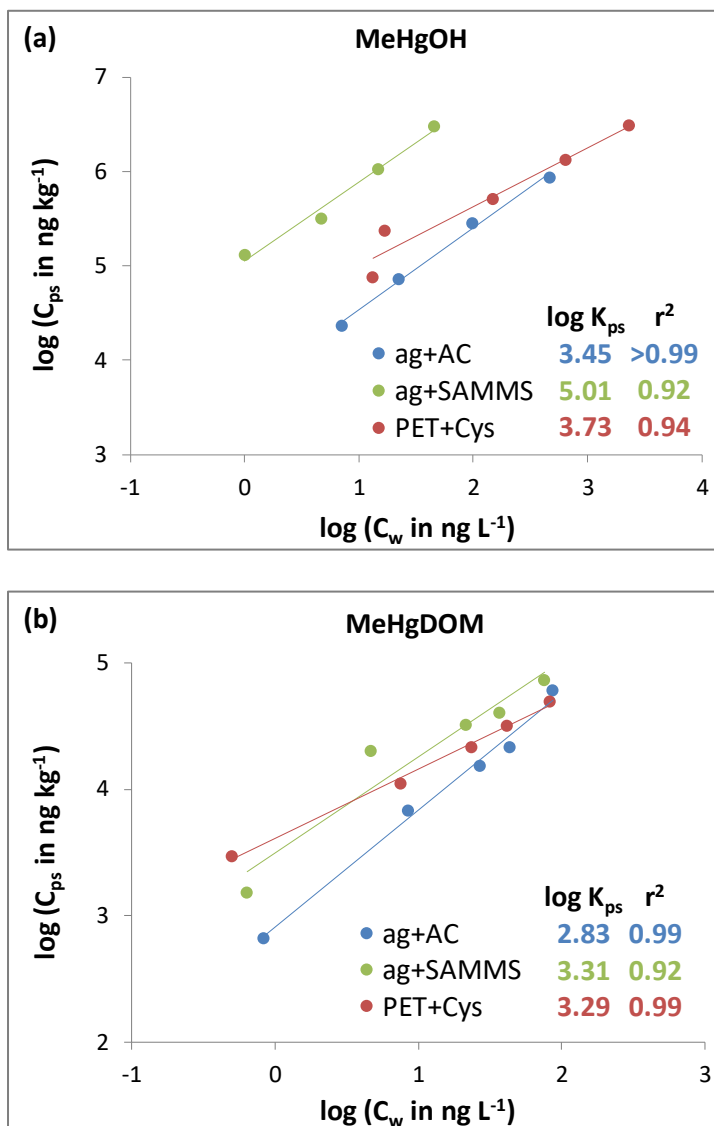


Figure 5.1. Partitioning of (a) MeHgOH and (b) MeHgDOM to select samplers in 14-d aqueous isotherm tests. Note different axis scales.

Three samplers, ag+AC, ag+SAMMS, and PET+Cys, were identified as the most promising based on the strength and proportionality of their partitioning in combination

with their physical attributes. The sulfur-functionalized biomedical polymers (“thiomers”)—including thiolated chitosan and cysteinylated alginate and xyloglucans—lacked mechanical strength as prepared and were suspended in agarose to confer stability in isotherm tests. Though they also partitioned well, they were excluded from further consideration due to the additional complexity involved in their preparation and the availability of several viable alternatives.

MeHgDOM Isotherms. Partitioning of MeHgDOM was reduced compared to MeHgOH for all tested samplers (Figure 5.1b). Speciation modeling for isotherms run with added SRHA predicted virtually complete complexation of MeHg with DOM. Compared to smaller MeHg complexes, MeHgDOM is both less diffusive and less bioavailable.⁵²⁻⁵⁴ This experiment therefore represents an important contrast to the idealized scenario in the previous set of isotherms. However, in all cases partitioning remained in or near our target range and was proportional across a range of C_w ($r^2 \geq 0.92$). The lowest K_{ps} was measured for ag+AC, which in one sense is not surprising in light of recent findings by our group that partitioning of aqueous MeHg to AC is sharply reduced in the presence of SRHA.⁵⁵ However, under true, diffusively unconstrained equilibrium conditions, one might expect MeHg to establish consistent partitioning with AC particles irrespective of the other ligands present. That this didn’t occur suggests that, as in our other study, the MeHgDOM-AC interaction may have effectively reflected a DOM-AC interaction with MeHg incidentally associated.⁵⁵ This will be addressed in future work. Generally, positive results for samplers in both the HO^- and DOM isotherms were encouraging and indicated their potential to function across a variety of water chemistries and MeHg species.

Sampler Kinetics and Mechanism of Accumulation. In a range-finding kinetics experiment in aqueous solution, both ag+AC and PET+Cys approached equilibrium partitioning of MeHgOH after two weeks (Figure 5.2a and Table AIII.S4). Partitioning at this time point was slightly lower for both samplers than in 14-d screening isotherms. For PET+Cys, the 95% confidence interval in this experiment (power fit) was not statistically different from its isotherm K_{ps} value, but for ag+AC the 95% CI was higher than isotherm K_{ps} . Absolute accumulation of MeHgDOM was depressed compared to MeHgOH, with lower partitioning at each time point. The shape of the MeHgDOM kinetic curve was also flatter, making equilibration difficult to verify.

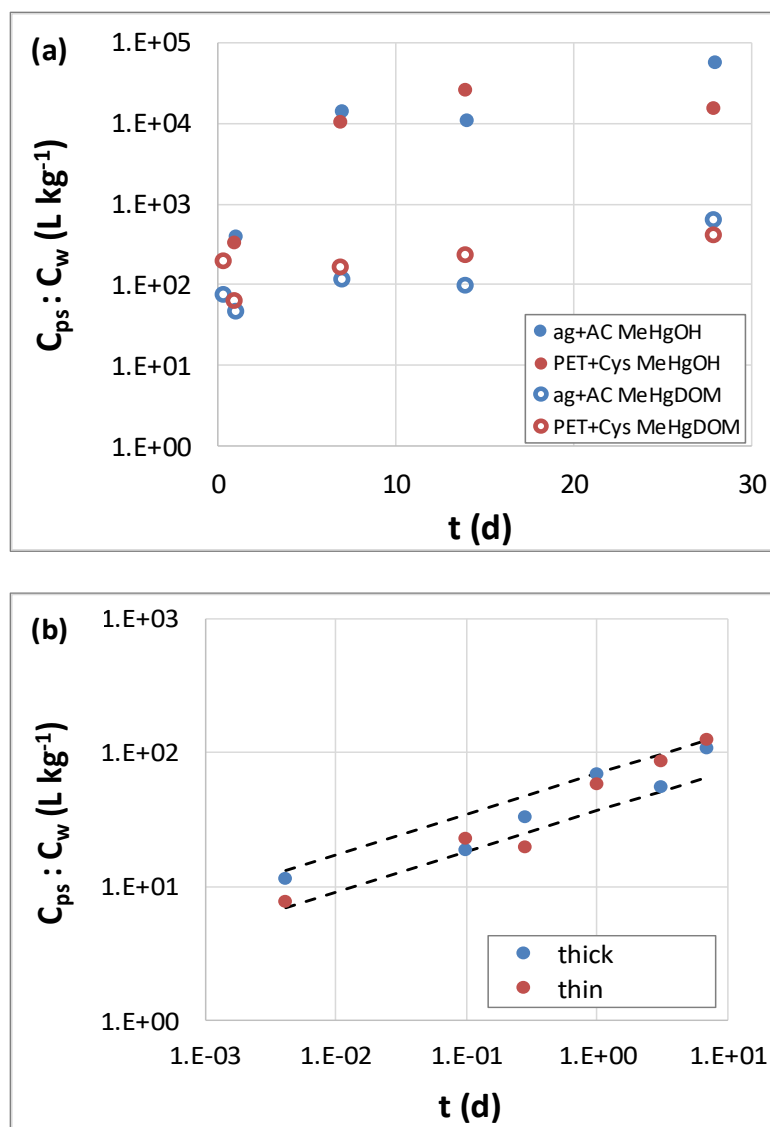


Figure 5.2. (a) Kinetic curves for polymer-water partitioning of MeHgOH (filled circles) and MeHgDOM (open circles) by ag+AC (blue) and PET+Cys (red). (b) Kinetic curves for partitioning of MeHgDOM by ag+AC with two contrasting surface area-to-volume ratios: 3.3 mm^{-1} ("thick", blue) and 12.2 mm^{-1} ("thin", red). Dotted lines: upper and lower 95% confidence intervals for power fit of thick data. Note arithmetic vs. logarithmic abscissae.

In addition to kinetics, the mechanisms of MeHg accumulation by samplers are an important consideration in sampler development. An understanding of where and how sorption occurs is required to interpret sampler concentrations and optimize form factors. PET is a relatively impermeable polymer, so both the cysteinylolation of PET and the accumulation of MeHg by PET+Cys can be assumed to occur mostly on the material's surface. By contrast, agarose is permeable and readily permits diffusion of MeHg even in the presence of DOM.⁵⁴ To verify a permeation-based mechanism of accumulation by ag+AC, pieces of the material with contrasting surface area-to-volume ratios were exposed to aqueous MeHgDOM and sampled along a time course. If internal diffusion were substantially inhibited relative to diffusion to sampler surfaces, accumulation would increase with increasing surface area-to-volume ratio. However, this was not the case. Aside from one point, the uptake curves of the two thicknesses were indistinguishable (power fit, $p = 0.05$; Figure 5.2b). This strongly suggests that even large MeHg complexes (SRHA has an average molecular weight of 1399 daltons⁵⁶) readily permeate the agarose matrix of ag+AC, in contrast to PVDF. A simple modeling exercise supports this contention. The diffusion coefficient of MeHgDOM into agarose is $2.68 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, only 15% lower than that of MeHg without DOM.⁵⁴ With this value of D , a Fickian diffusion calculation predicts greater than 90% equilibration by agarose within 1 d at a depth of 400 μm (the half-thickness of our sampler). For comparison, our kinetic curves indicate an approach to equilibrium over several days to a week or more. It should also be borne in mind that the average pore size in our agarose gels, though not directly measured, is probably about 400 nm, while the DOM used would have been on the order of 1 nm and subject to only limited aggregation.⁵⁷⁻⁵⁹ These considerations suggest that

both the kinetics and equilibrium partitioning capacity of ag+AC are controlled by the included AC particles and not the agarose gel. This opens the possibility of tuning the sampler's performance by adjusting the concentration and properties of the AC used in its formulation. Mass balance data for this experiment are found in Table AIII.S5.

Activated Carbon Kinetics and Desorption. A separate experiment was performed to characterize adsorption and desorption onto bare AC particles. Partitioning of MeHgOH to AC was rapid (Figure AIII.S3a), approaching the previously published log K_{AC} value of 4.89 within 5 h and slightly surpassing it (5.11) by 2 d.⁶⁰ When MeHg-loaded AC was exposed to clean water, re-equilibration to a log K_{AC} of 5.09 occurred within 3.6 h (details in Table AIII.S6). Because complete removal of the original exposure solutions was impossible without also removing AC, some MeHg-spiked water carried over into desorption solutions (< 5%). However, the masses of MeHg carried over were accounted for and amounted to only 15–30% of the totals measured in water after desorption, confirming that MeHg indeed desorbed from AC. These findings support the notion of a rapid and at least partially reversible equilibrium between AC and water and, by extension, between ag+AC and water. In a field deployment, the extent and rate of this reversibility will determine the sampler's ability to respond to changing porewater concentrations in a time-integrative fashion, and will depend on the nature of the sorption process. (A model fit of MeHg adsorption is shown in Figure AIII.S3b. Hg_i adsorption data are found in Figure AIII.S4 and Table AIII.S7.)

The kinetics of sorption by porous media are characterized by multiple mechanistic steps, including diffusion to sorbent surfaces and intraparticle diffusion.⁶¹ The rates and relative importance of these steps are modulated by the extent of mixing, sorbate concentration,

sorbent particle size, and sorption affinity, and are often analyzed quantitatively by means of the Weber-Morris procedure.^{62, 63} The temporal resolution of the present experiment was insufficient to support such an analysis, but given the shape of the kinetic curve it is reasonable to assume that, in our well-mixed systems, intraparticle diffusion was rate-limiting at later time points. However, in a passive sampler deployment in stagnant sediment, film diffusion would be slower and exert a greater impact on overall rate. In that case, equilibration could be slower.⁶³ Sorption of contaminants to AC is often characterized by operationally distinguished fast- and slow-desorbing fractions.^{64, 65} Further work is needed to understand the kinetics of sorption by polymers relative to those of MeHg ligand exchange in porewater and, for sulfur-based polymers, at sampler sorbent sites. This will determine the extent to which polymers are capable of true dynamic equilibrium sampling of dissolved MeHg.

Soil and Sediment Slurries. In the more chemically complex and realistic milieu of slurries, all three tested sampler types successfully predicted MeHg C_{pw} , giving an early indication that they may be viable for use in field conditions. All samplers were retrieved intact after 20 d of exposure. The two experiments provided a test across sharply contrasting porewater MeHg concentrations and speciation. Porewater MeHg in the sediment slurries was extremely low due to oxidizing conditions during the pre-incubation phase, as indicated by low initial sulfide concentrations ($0.69 \mu\text{M}$) and a resazurin color change in the canary jars. Sulfide concentrations, already low at the outset, declined further during the sampler exposure period, to a final value of $0.07 \pm 0.01 \mu\text{M}$. As a result, aqueous MeHg concentrations at the end of the exposure were extremely low ($0.12 \pm 0.043 \text{ ng L}^{-1}$). Both aqueous and sampler MeHg measurements

were close to method detection limits and highly variable (one outlying value was excluded for failing a Dixon's Q-test). In comparison, the soil porewaters were initially reducing and contained high sulfide concentrations ($269 \pm 1.96 \mu\text{M}$), but declined to $0.78 \pm 0.21 \mu\text{M}$ by the end of the exposure. The contrast in redox status drove a change in MeHg speciation. Modeling results for the soil slurries indicated that the sulfide complex predominated at d 0 but the balance had shifted to DOM by d 20. (In sediment slurries, DOM predominated at both time points.) No color change was observed in the corresponding soil canary jars. Despite the change in redox conditions, final aqueous concentrations of MeHg were considerably higher than in sediment slurries ($8.7 \pm 1.5 \text{ ng L}^{-1}$), permitting more reproducible measurements of both water and samplers. Measured $\log K_{\text{ps}}$ values in soil slurries were 3.41 (ag+AC), 3.12 (ag+SAMMS), and 3.11 (PET+Cys), all within our target range.

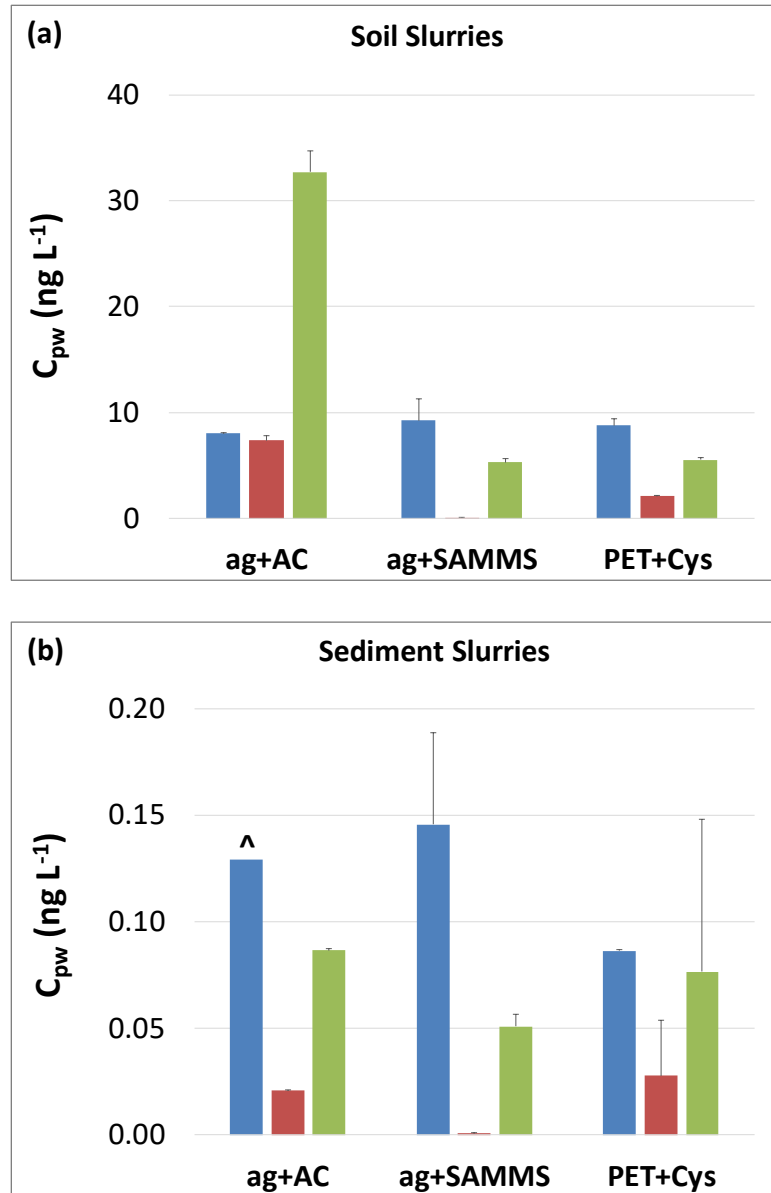


Figure 5.3. Porewater MeHg concentrations in (a) slurried soil and (b) sediment. Blue bars: directly measured in centrifuged porewater; red bars: predicted by dividing measured polymer concentrations (C_{ps}) by K_{ps} values from MeHgOH isotherm experiment. Green bars: predicted by dividing C_{ps} by K_{ps} from MeHgDOM isotherm experiment. Error bars show +1 standard error ($n = 2$ except [^], $n = 1$). Note different axis

scales. In (b), lower detection limits were 0.05–0.13 ng L⁻¹ for porewater and 1.03–92.16 ng kg⁻¹ for samplers.

To contextualize these results, we used sampler accumulation in slurries in combination with partitioning coefficients generated in screening isotherms to calculate “predicted” C_{pw} in slurries. Figure 5.3 presents a comparison of the sampler-predicted values with directly measured concentrations in centrifuged porewater. In general, sampler predictions agreed with direct measurements in both soil and sediment slurries. Predictions were within a factor of two in four cases and within a factor of four in the remaining two. Precision was greater in soil slurries, where both porewater and sampler concentrations were further above detection limits.

Sediment Microcosms. As they did in well-mixed soil slurries, ag+AC samplers again made good predictions of MeHg concentrations in sediment porewater, here at low C_{pw} and under stagnant, poorly mixed conditions (Figure 5.4). MeHg partitioning by ag+AC in unamended Berry’s Creek sediment was comparable to that in slurries ($\log K_{ps} = 3.59$ vs. 3.41). Activated carbon added to sediment produced a strong effect. Over the 28-d exposure period, sediment amended with AC contained significantly less MeHg in both the solid phase ($p < 0.001$, $n = 10$) and porewater ($p < 0.001$, $n = 10$) compared to unamended sediment. C_{pw} in amended beakers remained below 1 ng L⁻¹ throughout the study, comparable to background levels in uncontaminated sediments and soils.

Sediment-water partitioning, $\log K_d$, was 4.06 without amendment and 4.72 with AC. Sampler partitioning in amended sediment was somewhat stronger ($\log K_{ps} = 4.09$) than in unamended sediment, and led to overpredictions of C_{pw} in a relative sense, but even

these were within 2 ng L^{-1} of direct measurements. It should also be noted that direct measurements represent snapshots while sampler measurements are time integrative, so some of the observed divergence could be due to temporal fluctuations. To explain the apparent effect of AC on K_{ps} , we considered the possibility that AC scavenged DOM, resulting in a smaller fraction of MeHg complexed by DOM and an accordingly higher availability of MeHg to polymers. In fact, at d 14, 21, and 28, DOC was somewhat lower (not statistically significant) in AC-amended sediment, but our speciation modeling still predicted complete complexation to DOM in all beakers. However, due to the uncertainties inherent in the modeling approach—the most important of which surround the stability constants used for complexation with sulfide and DOM, as well as the fraction of -RSH groups on DOM (see Table AIII.S1 for details)^{55, 66, 67}—the hypothesis that AC may alter MeHg speciation by reducing DOC and/or sulfide concentrations shouldn't be discarded at this time. Despite the modeled dominance of MeHgDOM, better C_{pw} predictions were obtained from ag+AC using its K_{ps} for MeHgOH. This could be due to differences between the DOM used in isotherm experiments and the DOM native to these estuarine sediments. SRHA is a terrestrially-derived DOM occupying the high range of both aromaticity and molecular weight, which could have caused lower diffusivity or sorbability for MeHgDOM in isotherm tests.^{56, 68} Across all time points and both amendments, sampler accumulation was reasonably well correlated with directly measured C_{pw} ($r^2 = 0.69$; Figure AIII.S6).

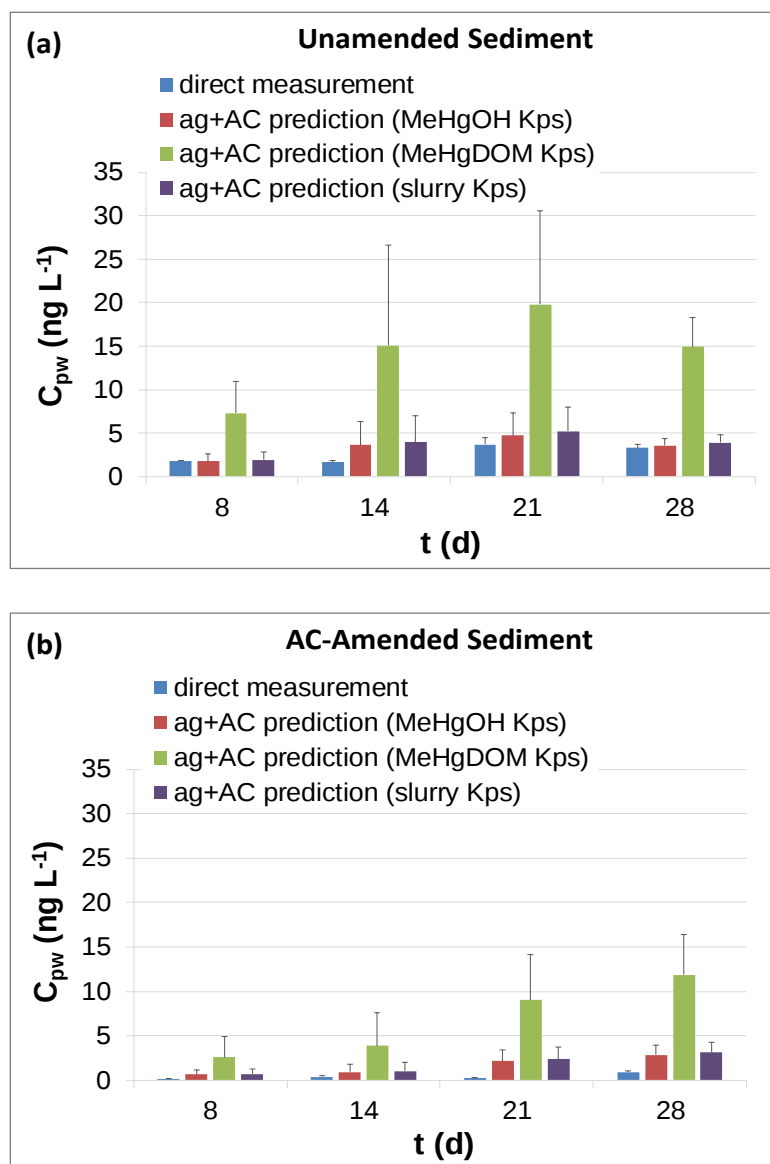


Figure 5.4. Porewater MeHg concentrations in sediment microcosm experiment.(a) Unamended sediment; (b) sediment amended with 5% dw activated carbon. Values were directly measured (blue) or predicted by ag+AC with K_{ps} from MeHgOH isotherm (red), MeHgDOM isotherm (green), or soil slurry experiment (purple). Error bars show +1 standard error ($n = 2$).

The microcosm experiment also provided the first temporal results for our samplers in environmentally representative matrices (Figure 5.4). In both amendment scenarios, there was no trend in the accuracy of sampler-predicted C_{pw} with time. There was a slight increase in C_{pw} with time that was reflected in both direct and sampler measurements. In unamended sediment, the most accurate prediction was made at 8 d, the first time point sampled. This gives another indication that ag+AC may achieve equilibrium with porewater in a stagnant deployment on the order of one to two weeks, in agreement with measured kinetics in water (Figure 5.2a).

Implications. We report the identification and testing of several sorbent materials with strong potential as passive samplers for MeHg in soil and sediment porewaters, including at least one, ag+AC, which appears capable of functioning in a dynamic equilibrium mode. This sampler, along with others designed for chemisorption at reduced sulfur sites, made accurate measurements of dissolved MeHg in environmentally realistic matrices. The partitioning coefficients of these samplers are such that a square piece approximately 1 cm on a side will accumulate a readily detectable mass of MeHg at a water concentration as low as 1 ng L^{-1} . Importantly, sampler partitioning in soil slurries and sediment microcosms was generally within about half a log unit of K_d . This helps to ensure that neither sampler nor soil/sediment will outcompete the other to the point of introducing measurement artifacts, as DGT can do by depleting porewater MeHg.³⁴ In DGT theory, MeHg complexes diffuse in a Fickian fashion toward sites of strong chemisorption, the assumption being that the complexes dissociate during diffusion in the gel so that only free metal ion sorbs to the binding resin and is ultimately measured.⁶⁹ In this strictly kinetic mode, accumulation remains linear with time provided that the

binding capacity of the resin is not exhausted and that the external water concentration is maintained.³⁵ In contrast, some of our samplers appear to behave in an equilibrium mode. For ag+AC, we hypothesize that accumulation of MeHg is kinetically controlled not by diffusion through the agarose gel but rather by a more complex process of sorption to included AC particles. We characterized the kinetics of sampler accumulation in well-agitated water and stagnant sediment, as well as those of sorption onto bare AC particles. Together, these predict an approach to equilibrium on the order of one to two weeks. We also demonstrated desorption of MeHg from AC into water, which supports the concept of reversible, equilibrium sampling with an AC-based material. Samplers underwent no apparent degradation or fouling during deployment in sediments and soils, indicating that they should not require a potentially interfering membrane.³⁶

For the sulfur-based samplers, further investigation of mechanism is required. In the case of PET+Cys, the polymer itself is relatively nonporous and impermeable. Not only should it be largely resistant to internal diffusion by MeHg, but the nature of the cysteinylation process ensures that the strongly sorptive sites are localized primarily on the polymer's surface. The plateauing kinetic profiles we measured for PET+Cys could have been due to a gradual occupation of available surface sites by MeHg exchanging from other ligands, even stronger ones like DOM. The formation constants involved leave open this possibility: MeHg's log K_f for cysteine is 16.67 while those for the thiol binding sites in SRHA range from 10.39 to 14.84.^{70, 71}

Several lines of future investigation are available. Sampler design and fabrication must be optimized and professionalized. The potential use of stable MeHg isotopes as performance reference compounds to measure and account for nonequilibrium should be

explored. The dynamics of MeHg exchange among samplers, water, and soil/sediment and among different complexing ligands must be elucidated to identify the pools accessed by the samplers and to determine the ability of samplers to respond to fluctuating C_{pw} . This will help to explain why K_{ps} was depressed in the presence of DOM. Because the utility of the devices will ultimately be determined by their ability to predict benthic bioavailability in diverse field conditions, tests alongside organisms in both the lab and the field will be necessary. These should be accompanied by a robust modeling effort to support risk assessment calculations based on passive sampling data. Finally, the sorbents in our samplers have affinity for other metals, including Hg, Cd, Pb, Zn, and others. With additional experimentation, it should be possible to adapt them for the measurement of these contaminants.

5.5. Acknowledgements

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Chapter 6: Using an Activated Carbon-Based Passive Sampler to Predict Methylmercury Porewater Concentrations and Bioaccumulation by *L. plumulosus* in Sediment and Soil

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6.1 Abstract

Methylmercury (MeHg) is a persistent, bioaccumulative contaminant that drives risk at many managed sediment and soil sites. It is formed by the methylation of inorganic mercury by anaerobic microorganisms in redox transition zones. MeHg can be taken up by benthic and epibenthic organisms and enter aquatic food webs, where it is subject to biomagnification up to several orders of magnitude. There remains a need for a reliable method to measure the benthic bioavailability of MeHg, an important indication of overall risk. Recently, we reported the development of a novel equilibrium passive sampling device based on the concept of a sorbent embedded in a polymer. In that work, the sampler was subjected to limited testing in environmentally relevant matrices, including one sediment microcosm, where it successfully predicted independently measured porewater concentrations. In the present work, we report the results of two further microcosm studies with a different soil mix containing higher MeHg concentrations. One of the two studies also included the benthic amphipod *L. plumulosus* to measure a key biological exposure. Measurements by our sampler correlated with both porewater concentrations and bioaccumulation by the amphipod, although absolute sampler accumulation was diminished in the presence of the animals. This work further supports the utility of the novel passive sampler for bioavailability assessment but also suggests possible site-specific or conditional effects that would need to be considered in a model of bioaccumulation based on sampler measurements.

6.2. Introduction

Methylmercury (MeHg) is a neurotoxic and bioaccumulative pollutant found at elevated concentrations in many freshwater and oligohaline systems.¹ It occurs as a result of the methylation of inorganic mercury (Hg_i) by ubiquitous, anaerobic microorganisms in redox transition zones.² MeHg in sediments and soils can enter aquatic food webs through benthic and epibenthic organisms and be biomagnified at higher trophic levels.^{3, 4} For other sediment-bound, bioaccumulative contaminants like PCBs and PAHs, passive sampling has emerged as a useful method for providing time-integrative measures of benthic bioavailability.⁵⁻¹¹ By contrast, for MeHg, passive sampling efforts have been challenged by additional complexities, including its more complicated biogeochemistry, temporal changes with redox fluctuations, and less well-defined mechanisms of bioaccumulation.¹²⁻¹⁵ As a result, no sampling strategy has achieved widespread acceptance.

In a previous study we reported the development of a novel passive sampler (ag+AC) designed explicitly for MeHg.¹⁶ The sampler consists of a suspension of activated carbon particles in an agarose gel. In slurried sediments and soils and in stagnant sediment microcosms, it established sampler-water partitioning (K_{ps}) in the range of about $10^{3.5}$ to $10^{4.0}$ L kg⁻¹, comparable to native sediment-water partitioning (K_d) at many sites.¹⁷ Its kinetics and basic mechanism of accumulation in water were also characterized. However, for its measurements to be useful in risk assessments as a proxy for benthic bioavailability, several additional steps are required. One is to develop a more thorough understanding of the dynamics of sampler behavior in more chemically complex matrices like sediment porewaters. Another is to test the sampler in a wider variety of sediments

and soils and, most importantly, alongside benthic organisms, with the ultimate aim of developing and calibrating a robust model linking sampler measurements to bioaccumulation.

This work reports the results of two further microcosm experiments similar to the one previously reported¹⁶ but using soil taken from a different location. In one of the two, samplers were deployed alongside the benthic amphipod *L. plumulosus*. The results are compared across all three microcosm studies to date.

6.3. Materials and Methods

Passive Samplers. ag+AC samplers (Figure AIV.S1a) were prepared by casting agarose¹⁸ containing 5 wt% activated carbon (Calgon 80 x 325 TOG LF, CAS #7440-44-0) between glass plates separated by spacers to achieve a thickness of 800 μm , verified with a 0-1" digital micrometer (iGaging, San Clemente, CA). Gels were placed in small baskets prepared by folding strips of polypropylene mesh and sewing edges together with nylon thread (Figure AIV.S1b). Mesh and thread were washed with 1 M HNO_3 followed by deionized water prior to use.

Activated Carbon. Siemens regenerated activated carbon was used in both experiments. AC was 73.3% C, had a surface area of $1150 \text{ m}^2 \text{ g}^{-1}$, a skeletal density of 1.81 g cm^{-3} , and a bulk density of 0.63 g cm^{-3} .¹⁹

Soil Microcosms. A previous microcosm experiment was described elsewhere¹⁶ and is referenced herein as Experiment 1. In the present study, two further experiments (2 and 3) were conducted and the relevant differences are listed in the following paragraph. In both, soil was permitted to equilibrate in beakers for 14 d prior to sampler exposure.

Before use, samplers were cleaned, dried, weighed, measured, and placed in small baskets prepared by folding strips of polypropylene mesh and sewing edges together with nylon thread (Figure AIV.S1b). Mesh and thread were washed with 1 M HNO₃ followed by deionized water. At d 0, one ag+AC sampler was added to each beaker. Samplers were inserted vertically so as to span the visually apparent oxic-anoxic interface with overlying water (5 ppt artificial sea salt). Exposure beakers were loosely lidded, gently aerated, and kept at room temperature (Figures AIV.S2a and AIV.S3). Overlying water was gently replaced in remaining beakers on sampling days. Sulfide was measured in Experiment 2 only; values were used in MeHg speciation modeling for both experiments. After exposure, sampler baskets were gently removed from beakers and polymers were removed from baskets, rinsed with deionized water, blotted with lab wipes, weighed, and frozen. Overlying water was decanted and the remaining beaker contents (approximately 3–4 cm wet soil) were transferred to tubes and centrifuged at 4000 rpm for 5 min. Supernatants were passed through 0.45 µm glass microfiber syringe filters with disposable plastic syringes into clean, 60-mL PETG bottles. Aliquots were set aside for analysis of sulfide and DOC. Remaining filtrates were acidified with 0.5% HCl and refrigerated, then processed and analyzed for MeHg, total mercury (THg), and a suite of standard chemical constituents. Pelleted solids were lyophilized until weights were replicable, then processed and analyzed for MeHg.

Experiment 2. Oligohaline soils were collected from a *Phragmites* marsh in upper Berry's Creek and combined with *Phragmites* marsh soils collected from SERC's Global Change Research wetland to achieve a Hg concentration of approximately 20 µg g⁻¹. Soil chemistry data are summarized in Tables AIV.S3-S5. Prior to this study, the mixed soil

was used with or without 5 wt% AC amendment for 18 months in a *Phragmites* mesocosm study in a tidal creek at SERC. 400 mL of soil was combined with 550 mL overlying water in 1-L glass beakers (Figure AIV.S2). Microcosms were constructed with unamended soils, soils amended with AC at the outset of the preceding mesocosm experiment, or soils freshly amended with 5 wt% AC immediately prior to this experiment. Samples were collected at 0, 4, 8, 15, and 25 d. Exposures and analysis were performed at the Smithsonian Environmental Research Center in Edgewater, MD.

Experiment 3. This exposure was conducted at the Environmental Laboratory of the U.S. Army Engineering Research and Development Center (ERDC) in Vicksburg, MS. Soils were taken from the same starting batches as those used in Experiment 2, but had aged an additional six weeks. Soil chemistry data are summarized in Tables AIV.S6-S8. Setup was similar to Experiment 2, except that beakers were immersed in a water bath to maintain temperature at 23.0 ± 1.0 °C (Figure AIV.S3) and 50 salinity-acclimated *L. plumulosus* (Aquatic Biosystems, Fort Collins, CO) were placed into each beaker at sampler exposure d 0 (soil equilibration d 14). Twice weekly, 20 mg ground TetraMin was added as food to each beaker in the form of a seawater slurry. Samples were collected at 0, 7, 14, and 21 d. A parallel set of beakers was set up and maintained identically except without passive samplers. *L. plumulosus* for MeHg analysis were collected from these beakers. Organisms were sieved from soil, blotted dry, weighed, placed in small cryovials, and frozen immediately. All MeHg and THg samples were shipped to SERC for analysis. Other chemical analyses were performed at ERDC.

Analytical Methods. MeHg in all matrices was measured by isotope dilution mass spectrometry after separation and cleanup by distillation.²⁰ Total Hg was also measured

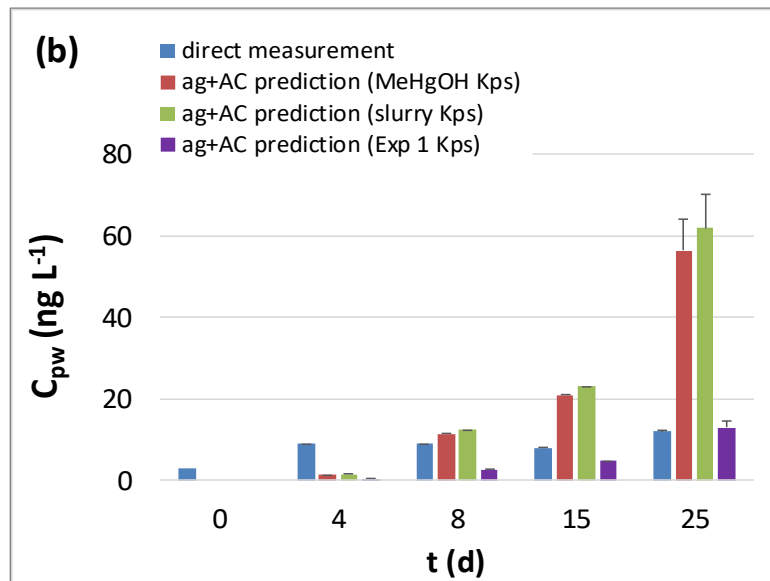
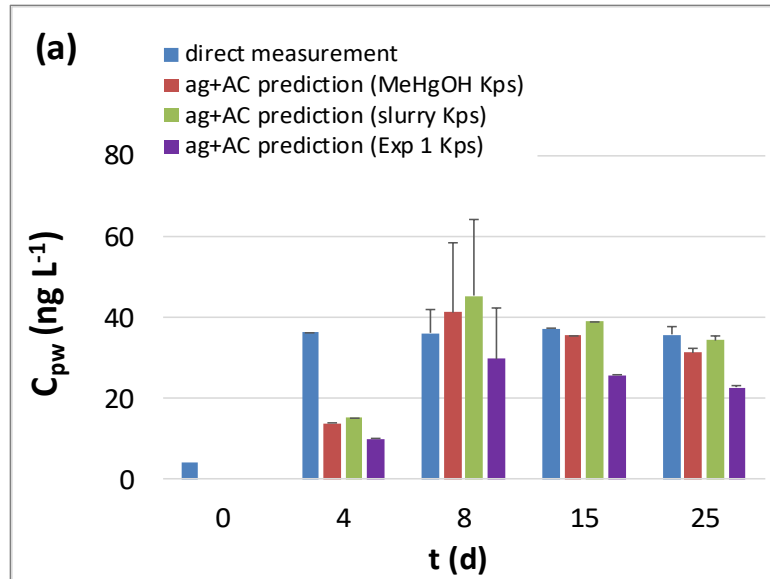
using ID-ICP-MS following SnCl_2 reduction to Hg^0 . Water samples were digested with BrCl and sediment samples with 7:4 $\text{HNO}_3\text{:H}_2\text{SO}_4$. Further details can be found in the Supplemental Information. Quality assurance data are summarized in Table AIV.S2.

Equilibrium Speciation Calculations. The chemical modeling program MINEQL+ v.4.6 (Environmental Research Software, Hallowell, ME) was used to calculate aqueous MeHg speciation in all experimental systems. Conditional stability constants for a variety of MeHg complexes were obtained from literature sources and added to the software's database as outlined in Table AIV.S1. All other thermodynamic constants were software defaults.

6.4. Results and Discussion

Experiment 2. In a soil mix with relatively high concentrations of MeHg dominated by complexes with dissolved organic matter (DOM), ag+AC again made consistently accurate measurements of C_{pw} (Figure 6.1). In unamended soil, both solid-phase and porewater MeHg concentrations were roughly one order of magnitude higher than those in Experiment 1, resulting in similar $\log K_d$ values (ca. 3.5–4.0). The effect of fresh AC amendment was more pronounced in Experiment 2, with increases in K_d of 1.5–2.0 log units at every time point beginning at 4 d. This was driven almost entirely by reductions in C_{pw} , which reached the same sub-ng L^{-1} range attained in Experiment 1 following amendment despite much higher pre-amendment levels. The AC amendment was markedly less effective after aging than fresh but still resulted in approximately factor-of-three reductions in C_{pw} . MeHg was again predominantly complexed by DOM, although porewater DOC concentrations were somewhat lower than in Experiment 1, resulting in a small (ca. 1–5%) fraction of MeHg complexed by sulfide. Accordingly, partitioning by

ag+AC was similar to Experiment 1, with $\log K_{ps}$ again around 3.5 in unamended soil and 4.2 in soil amended with fresh AC. K_{ps} in aged AC-amended soil was intermediate between the two. The slope of $\log C_{ps}$ vs. $\log C_{pw}$ in unamended soils across Experiments 1 and 2 was 0.89, and in AC-amended soils was 0.80 (Figure 6.2), although they were not statistically distinguishable (ANCOVA). As in Experiment 1, we considered the possibility that AC scavenged DOM, resulting in a smaller fraction of MeHg complexed by DOM and an accordingly higher availability of (sulfide-complexed) MeHg to samplers. Here, DOC concentrations were indeed significantly different among the three amendments (t -tests, $p < 10^{-6}$; Figure AIV.S2c) but speciation modeling still predicted predominance of the DOM complex in all three. However, due to the uncertainties in the modeling—the most important of which surround the stability constants used for complexation with sulfide and DOM, as well as the fraction of $-RS^-$ groups on DOM^{21-23} —the hypothesis shouldn't be discarded. The fact that both slopes were below one may be due to nonlinear partitioning effects at higher C_{pw} . However, this should not be taken as an indication that the sampler approaches its absolute capacity in an environmentally plausible C_{pw} range. Freundlich-type adsorption with an exponent less than one is common for ACs and other materials and owes to the complex nature of the sorption process. We fitted ag+AC sorption data to Freundlich isotherms and showed divergence from linearity only at unrealistically high MeHg concentrations (100s to 1000s of $ng\ L^{-1}$). The presence of DOM can also be expected to depress adsorption via competitive binding, or fouling.^{24, 25}



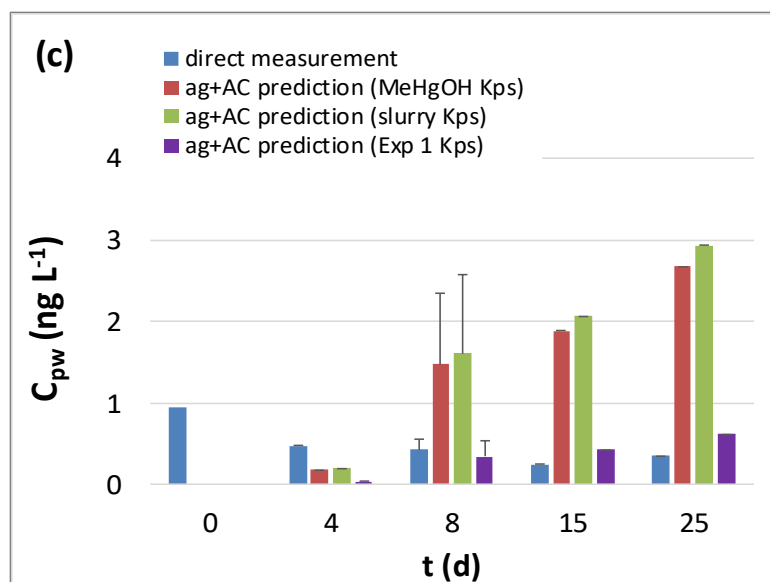


Figure 6.1. Porewater MeHg concentrations in soil microcosm Experiment 2. (a) Unamended soil; (b) soil amended with aged activated carbon; (c) soil amended with fresh activated carbon. Values were directly measured (blue) or predicted by ag+AC with K_{ps} from MeHgOH isotherm (red), soil slurry experiment (green), or soil microcosm Experiment 1 (purple). Error bars show +1 standard error ($n = 2$). No error bar denotes $n = 1$. Note different abscissa scales.

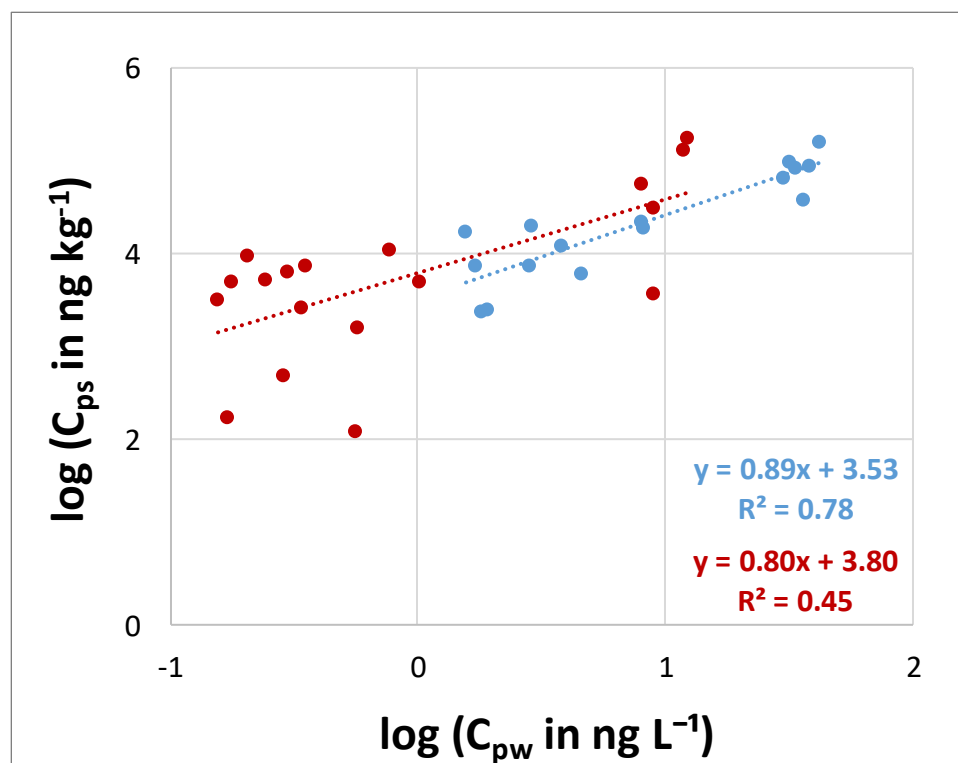


Figure 6.2. Sampler-water partitioning of MeHg by ag+AC in soil microcosm

Experiments 1 and 2. Each point represents one beaker. Blue: unamended soil ($n = 14$);

red: AC-amended soil ($n = 18$).

In contrast to Experiment 1, this experiment included a 4-d time point, which clearly showed nonequilibrium by ag+AC in all three soil types. After 4 d, K_{ps} was roughly one order of magnitude lower than the apparent equilibrium levels achieved at 8 d and maintained through the 15- and 25-d sampling events. This provides further insight into the kinetics one can expect from ag+AC in this type of exposure and agrees with the curves we generated separately in water.¹⁶ However, the kinetic analysis is complicated by the fact that C_{pw} was also not at equilibrium during the first week of sampler exposure, particularly in unamended soil, where it climbed from an average value of 4.02 to 36.29

ng L⁻¹ between d 0 and d 4. Sampler exchange kinetics may therefore have been more favorable than they appeared. Further investigation into sampler uptake and release under a variety of scenarios (including both increasing and decreasing C_{pw}) will help to establish their ability to respond to changing conditions in a time-integrative fashion. One of the challenges in characterizing the kinetics of MeHg sampling or sorption is maintaining a constant concentration of this highly reactive and unstable compound.

Experiment 3. Uptake by samplers was slowed in the presence of benthic organisms, but still predictive of bioaccumulation. Porewater MeHg speciation was again dominated by DOM (95–99%), and both solid-phase and porewater concentrations in unamended soil were consistent with those in Experiment 2. By contrast, solid-phase concentrations in the freshly amended soil reached a higher maximum by d 21, and in aged AC soil were roughly twice as high as those in Experiment 2, remaining so throughout the duration of the study. The soil for these two experiments was sourced from the same batch, with the only operative difference being the roughly six-week lag between the two experimental start dates. C_{pw} in all three soil types was very consistent between the two experiments, meaning that the additional MeHg was formed and retained on the solid phase in AC-amended soils, leading to higher K_d. This could have been due to an accumulation of organic matter on AC surfaces, stimulating microbial activity, or decreased degradation of MeHg sorbed to AC (unpublished data). After 21 d, bioaccumulation of MeHg by *L. plumulosus* averaged 5.90 ng gww⁻¹ in unamended soil, 2.93 ng gww⁻¹ with fresh AC amendment, and 20.70 ng gww⁻¹ with aged AC (*n* = 5 tissue composites each). The 50% reduction by fresh AC was comparable to reductions achieved in the polychaete *L. variegatus* in a previous study.²⁰ On the other hand, the unexpected threefold increase in

bioaccumulation caused by aged AC was apparently driven by a combination of elevated solid-phase concentrations and C_{pw} .

Accumulation by ag+AC was substantially depressed compared to previous experiments; K_{ps} was roughly one order of magnitude lower than in Experiment 2 through the first 14 d of exposure. Not only soils but also the samplers themselves were sourced from the same batches and handled identically. By elimination, the presence of *L. plumulosus* seems the most credible explanation. We hypothesize that bioturbation oxidized the upper 1 cm of soils, resulting in lower MeHg in porewater. This is the same depth horizon to which samplers were exposed. (In contrast, directly measured C_{pw} values represent vertical averages of the entire depth of soil in the beaker, or about 4–5 cm, which would have obscured reductions at the interface with water.) Perhaps tellingly, sampler accumulation was considerably slower than in Experiment 2, only approaching that experiment's 8-d partitioning by d 21. As such, concentrations in samplers (C_{ps}) were only weakly correlated with those in organisms (C_{org} ; $r^2 = 0.53$; Figure 6.3a) when viewed across all time points, but this relationship was considerably tighter for the d 21 sampling in isolation ($r^2 = 0.97$; Figure 6.3b), implying that a longer exposure time might have strengthened the results.

Because of the close similarity between Experiments 2 and 3 (the main difference being the presence of the amphipods), we sought correlations not only within but across the two data sets. Importantly, C_{ps} in Experiment 2 was a strong predictor of C_{org} in Experiment 3 ($r^2 = 0.61$; Figure 6.3c). Again, the correlation was considerably tighter at d 21, as one would expect with an equilibrium sampler ($r^2 = 0.98$; Figure 6.3d). This is the first demonstration of a proportional response of equilibrium passive sampler measurement

with a biological exposure assessment for MeHg. The slopes of the d-21 $C_{org}-C_{ps}$ prediction lines were nearly identical for C_{ps} from Experiments 2 and 3 (0.43 vs. 0.45, respectively), but the intercept was sharply increased for Experiment 3 (1.92 vs. 0.89) due to a difference in the depth horizons sampled by direct measurement and by the passive samplers. This implies that, in Experiment 3, accumulation by ag+AC was proportional to our relevant endpoint of benthic organism bioaccumulation. However, the absolute concentration estimated using passive sampling did not match the directly measured porewater concentration because the direct measurement was performed across the entire 4–5 cm of sediment depth while the passive samplers and epibenthic *Leptocheirus* were exposed to near-surface soil. To clarify this, future exposures would benefit from the use of larger polymer pieces to span a greater depth interval reflecting the relevant exposure zone and generating vertical profiles of C_{pw} where necessary.

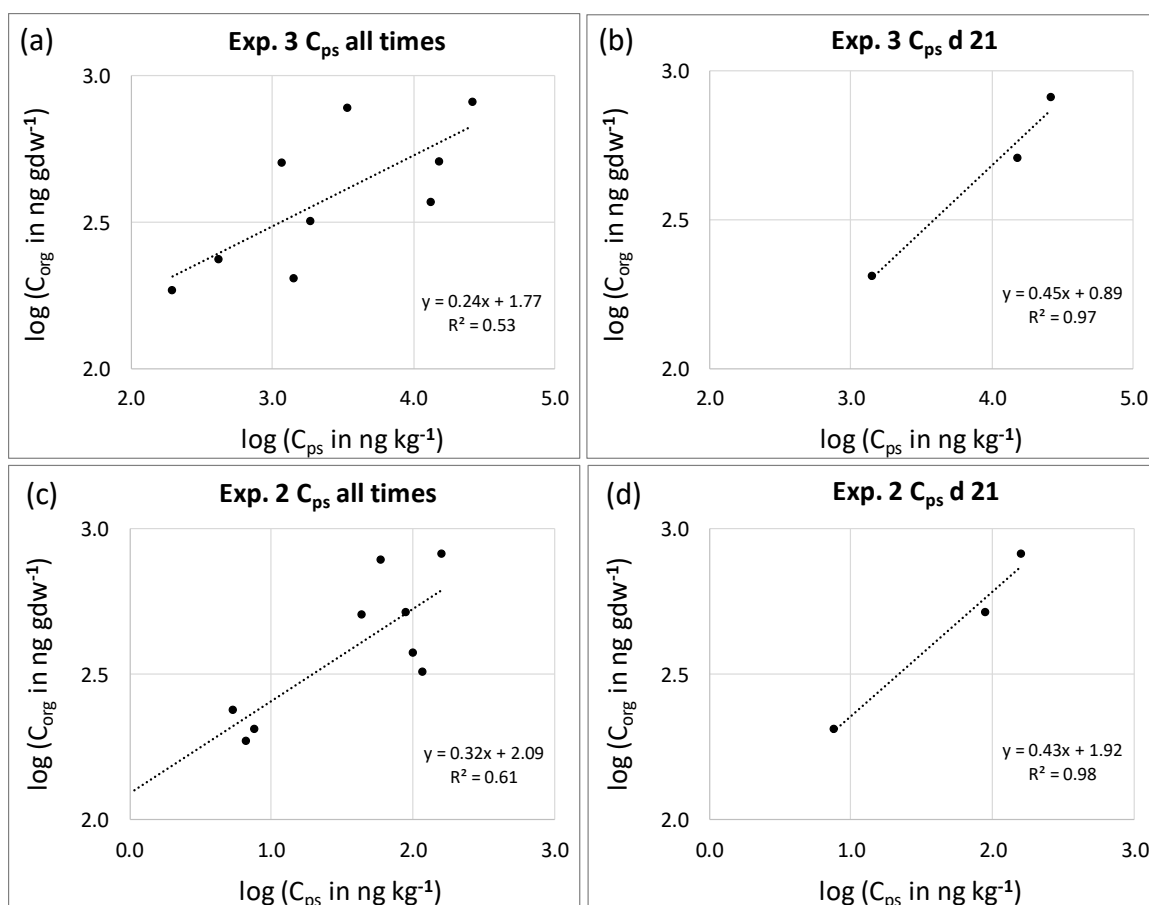


Figure 6.3. Passive sampler predictions of MeHg bioaccumulation by *L. plumulosus* in soil microcosms. All C_{org} data are from Experiment 3. (a) C_{ps} from Experiment 3, all three time points; (b) C_{ps} from Experiment 3, d 21 only; (c) C_{ps} from Experiment 2, all three time points; (d) C_{ps} from Experiment 2, d 21 only. Each point represents an average of triplicate measurements of both C_{ps} and C_{org} .

Implications. Taken together, the three microcosm passive sampling experiments to date, including the two outlined here, demonstrate the capability of ag+AC passive samplers to make useful predictions of MeHg bioaccumulation. As illustrated in Figure 6.2, partitioning by ag+AC was remarkably consistent across the first two soil microcosm experiments despite variable conditions (particularly the presence of AC amendment).

The change in sampler partitioning in the presence of benthic amphipods may indicate that further study is needed to understand the influence of varying site conditions on sampling kinetics and absolute accumulation by samplers. Still, the fact that observed correlations generally had similar slopes and differed mainly in their intercepts suggests that the sampler should, in principle, be effective under diverse conditions, but may require some degree of calibration. Since samplers and amphipods were exposed to a similar depth interval in soils, it may be that the lower concentrations measured by samplers provided an accurate indication of exposure. MeHg is a highly redox-sensitive compound that often exhibits substantial vertical concentration gradients, and our samplers appear capable of generating the necessary vertically resolved and time-integrated measurements needed to characterize benthic and epibenthic exposure.

6.5. Acknowledgements

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Chapter 7: Research Summary and Recommendations

7.1. Conclusions for Motivating Research Questions

The original aim of the study described in Chapters 2 and 3 was to evaluate the persistence and efficacy of three different types of activated carbon amendment in an intertidal *Phragmites* marsh. A key component of the research also involved refining and implementing an appropriate passive sampling program to measure freely dissolved PCB concentrations in the sediment porewater. The three-year surveillance generated several lines of evidence of the persistence of AC in the field and its performance in reducing the bioavailability of PCBs. Significantly elevated black carbon concentrations in sediment cores demonstrated that the amendment materials remained in place at or above target levels for the duration of the study, in spite of daily tidal inundation and an unusually violent storm event. Depth-resolved measurements showed less-than-anticipated vertical incorporation of amendment materials due to low benthic activity and a dense root mat. Porewater PCB concentrations measured by passive samplers were reduced by 34–97% across all amended sediment plots and sampling events. All three amendment types reduced PCB bioaccumulation, though low organism recoveries limited our statistical power. In addition to successfully answering the original study questions, I expanded the contribution of the research by developing a detailed analysis and comparison of passive sampling materials and data treatment methods.

My involvement in the PCB study helped advance our understanding of pollutant bioavailability and passive sampling, both of which are more well developed for PCBs compared to mercury. The work laid the foundation for the development of my key research questions concerning mercury bioavailability and measurement. The formal

research hypotheses from my Ph.D. proposal are now discussed in the sequence in which they were addressed in this document.

Partitioning of Hg_i and MeHg to AC is substantially reduced in the presence of DOM, and can be predicted with equilibrium speciation calculations in tandem with AC-water partitioning coefficients for DOM.

As described in Chapter 4, isotherm experiments verified that K_{AC} for DOM-complexed MeHg is roughly one half to one and a half log units lower than the corresponding value for the smaller Cl^- complex. For Hg_i , the difference is roughly two to three log units, depending on the type of AC. In both cases, the new values are much closer to those of DOM alone, which strongly suggests that DOM molecules control the sorption process. The modeling approach whereby speciation predictions are used to generate “hybrid” or weighted K_{AC} values is theoretically sound and capable of semiquantitative estimates of partitioning, but its utility is currently limited by a substantial amount of propagated uncertainty due to inputs—stability constants and partitioning coefficients—that span many orders of magnitude.

*A passive sampling system based on some combination of chemical and size selectivity can be designed to provide input for a predictive model of MeHg bioaccumulation by the estuarine amphipod *Leptocheirus plumulosus*;*

*Amendment of sediment with activated carbon will reduce porewater concentrations of bioavailable MeHg species, resulting in reduced MeHg accumulation by *L. plumulosus*. This reduction will coincide with reduced uptake by the sampling system developed for the previous hypothesis.*

These hypotheses were addressed in Chapters 5 and 6. In support of the first hypothesis, a number of sampling polymers with the ability to predict MeHg porewater concentrations were identified, and one of these (ag+AC) did so consistently across multiple experiments representing different environmental conditions. Its partitioning coefficients in several different matrices were on the order of $\log K_{ps} = 3-4$, in our target range and similar to typical sediment K_d . Its uptake kinetics were consistent with standard passive sampling deployment times, and its mechanism of accumulation was shown to be internal diffusion followed by reversible sorption to included AC particles. The second hypothesis was verified when both bioaccumulation by *L. plumulosus* and polymer uptake were reduced in sediment microcosms as a result of AC amendment.

The first-principles bioaccumulation model originally proposed to support the first hypothesis could not be applied because of incomplete parameterization, including details of chemical controls on MeHg sorption by AC and by soils, as well as input parameters related to organism feeding that either were not or could not be measured. Instead, as described in Chapter 6, we developed correlations both within and across multiple experiments that show that concentrations in ag+AC predict both C_{pw} and C_{org} .

7.2. Implications of Research

The PCB remediation work contributed to the knowledge base by providing useful information on the selection, design, and monitoring of in situ activated carbon amendments in the special environment of a tidally inundated *Phragmites* marsh. The results proved that AC amendments can remain in place for years even without the added expense and dilutive effect of a sand layer, and they also highlighted the importance of AC grain size to sorptive performance. A side experiment implicated tidally deposited

detritus as a source of ongoing contamination in this marsh, improving our conceptual model of the entire site and informing future study design and, potentially, management decisions. The passive sampling effort not only supported the conclusions drawn about amendment performance but also generated a large amount of data to compare different polymer types and thicknesses and different PRC adjustment methods, all of which may be useful in developing consensus best practices for in situ sediment porewater sampling. The critical findings of the study were (a) the agreement among several disparate PRC adjustment methods for measurements in unamended sediment and (b) the failure of the most recently developed method to account for AC amendment.

The establishment of mercury-DOM partitioning coefficients for AC represents an important contribution to the mercury remediation field. The values have already proved useful in modeling and interpreting the slurry experiment in this project and the sediment and soil exposures in the MeHg passive sampler project. The fact that they are so much lower than those for smaller mercury complexes emphasizes the importance of considering aqueous speciation in the design of an AC amendment; a difference in partitioning of an order of magnitude or more could hinge on speciation. The large disparities also appear to indicate fundamental mechanistic differences in the sorption of different species (i.e., complexes with DOM vs. those with smaller ligands) to AC.

Development of a novel passive sampler for MeHg was, and remains, a large undertaking that will require substantial additional effort by many laboratories to bring to a stage of wide acceptance comparable to that achieved by HOC samplers. This project serves as a proof of concept for equilibrium MeHg passive sampling, which could represent a promising alternative to kinetic samplers like DGT that work well for some types of

analytes but have important shortcomings for mercury. The novel, activated-carbon based sampler ag+AC was successful in both fundamental and applied experiments and merits ongoing and active study. It provided the first demonstration of proportional equilibrium passive sampling response correlating with bioaccumulation, and appears to represent a convenient method for generating time-integrative and vertically resolved measurements of MeHg bioavailability. We also showed several different sampling materials to be potentially useful, making them candidates for further testing by our colleagues or others. In addition to the manuscripts in this dissertation, I also coauthored a successful proposal for the U.S. Strategic Environmental Research and Development Program that secured funding for an additional three years of study on this and a related research project.

7.3. Recommendations for Future Work

The ability of AC amendment to effect local reductions in PCB C_{pw} and bioavailability had been convincingly established by several previous studies and was again confirmed here. What remains to be determined is the precise extent of bioaccumulation reductions that can be expected, particularly at higher trophic levels. In this project, low organism recovery and small sample sizes made it difficult to detect statistically significant amendment effects, let alone to use these low-trophic level measurements in a wider model of accumulation throughout the food web. Yet it is ultimately the upper-trophic level effects of intervention that are of interest to decision makers. To predict these in a complex system like BCSA will require a more integrated understanding of the site's ecology and hydrologic components to develop a working model of contaminant fate, transport, and trophic transfer.

In the PCB passive sampling work, the failure of the diffusion-based PRC adjustment method for AC-amended sediment was noteworthy, particularly given the good agreement between it and the other methods when applied to unamended sediment. The method may require modification to account for large, artificial increases in K_d caused by sediment amendment. Another finding in this and other contemporaneous work in our group is that PE appears to be easier to use and provides more kinetically favorable sampling than POM. It could be that PE will gradually emerge as the consensus polymer of choice for this type of passive sampling. However, if POM is to remain in use, it will be necessary to develop K_{ps} values for different thicknesses of the polymer. Unlike PE, K_{ps} for POM depends on polymer thickness, and it was a shortcoming of the study described in Chapter 3 that one set of K_{ps} values was used for two different polymer thicknesses. It would be interesting to revisit that study with more appropriate values to determine what effect, if any, they have on the results.

The most important gap in the DOM study is the lack of K_{AC} values for mercuric and methylmercuric sulfides. These could be established in similar aqueous isotherm experiments, and would improve model predictions of partitioning in future studies. The use of other types of DOM should also be considered. SRHA is near the upper extremes of both molecular weight and aromaticity, and it seems likely that a contrasting DOM such as Williams Lake hydrophobic acid or Pacific Ocean fulvic acid would produce different effects that would not only facilitate broader predictive capability but may also provide important mechanistic insights. Additionally, the relative kinetics of AC sorption by different mercuric complexes should be determined. If the differences are sufficiently

large, this could cause disproportionate effects on sorption and bioavailability that would need to be taken into account for remediation design.

For the MeHg passive sampling project, many of the next steps have already been delineated and funded by an additional three-year grant. These are aimed at continued advancement of the ag+AC concept and include further optimizing and professionalizing the design and fabrication of the polymer, more thoroughly characterizing the exchange dynamics of various MeHg species among polymer, water, and sediment, and more tests in different types of sediments, including alongside animals. The most important outstanding questions for this project concern the precise species accessible to samplers, their relevance to bioavailability, and the extent and timing of sampler response to external changes in speciation and concentration. In particular, it will be important to characterize the interactions of DOM-bound MeHg with AC particles or other sorbent sites in samplers. This may help explain why polymer accumulation was depressed in the presence of DOM, in opposition to strict equilibrium partitioning theory.

While ag+AC was the most successful implementation of the equilibrium sampling concept in this work, other materials might be able to perform as well or better. Here, collaboration between environmental scientists and materials engineers or polymer chemists could prove fruitful. Also, because other metallic contaminants such as Hg_i, Cd, Pb, and Zn have affinity for AC and reduced sulfur moieties, the sampling concepts we have employed here may be applicable to these as well given additional experimentation. For any novel passive sampler to be accepted for wide use by practitioners, its preparation and implementation must be standardized and the measurements it generates should bear a readily quantifiable relationship to a useful endpoint like bioavailability.

This will require a more robust modeling effort than has been achieved thus far, built on a wider data set and a more complete conceptual model of MeHg speciation, partitioning, and kinetics.

Appendix I: Supplemental Information for Chapter 2

Supplemental Information to the Article:

Persistent reductions in the bioavailability of PCBs at a tidally inundated

***Phragmites australis* marsh amended with activated carbon**

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Reductions in Bioaccumulation Pathways. Bioaccumulation of PCBs by benthic organisms occurs through two distinct pathways: diffusion from porewater and extraction from ingested sediment.¹ The addition of AC to sediments addresses both by greatly enhancing the sorptive capacity of the solid phase. This reduces diffusive flux across biological membranes by decreasing equilibrium concentrations in porewater. It also makes sorbed PCBs on ingested food more resistant to extraction in the gut. Previous work using selective extraction techniques has given rise to a conceptual model of bioavailability in which two empirically distinct pools of PCB congeners, more and less readily desorbed, are associated with contaminated sediment.² In this model, the latter pool, typically attributed to sorption to BC in sediments, is also less bioavailable. It has been found that PCBs associated with AC particles are extracted much less efficiently in the clam gut than PCBs associated with natural organic matter.³

To explore whether observed reductions in bioaccumulation could be explained solely by decreased porewater concentrations, bioaccumulation factors (BAFs) were compared across the amendment plots at t_{+11} . A BAF for each PCB congener or group of coeluting congeners in the deposit feeder *H. azteca* was calculated as the ratio of lipid-normalized tissue concentration to PRC-adjusted C_{pw} . BAFs were closely correlated with K_{ow} for Plots B, C, and D (Figure AI.S1). By contrast, most of the C_{pw} data from Plot A were near or below detection limits, leading to large scatter in BAF values. Generally, observed BAFs lay within an order of magnitude of K_{ow} and followed no clear trends with amendment type. The lack of a strong amendment effect on BAFs indicates that the reductions in bioaccumulation observed in the amended plots were largely driven by reductions in C_{pw} . However, while gut assimilation efficiencies were not independently

measured in this study, it is known that most of the uptake of mid- to high-molecular weight PCBs in benthic organisms occurs through ingestion of sediments. For example, an earlier study demonstrated that an average of nearly 80% of PCB congeners ($\log K_{ow} > 6$) were taken up through ingestion by the deposit feeder *L. variegatus*.⁴ This suggests that both uptake pathways were likely reduced. To the extent that bioaccumulation was lower in amended sediments, one might posit a reduction in gut extractability analogous to reduced sediment extractability as described elsewhere in Appendix I. However, the scatter in the BAF data is such that no clear, interplot differences in the BAF vs. K_{ow} relationship (which might indicate differentially available “pools” of congeners) can be discerned.

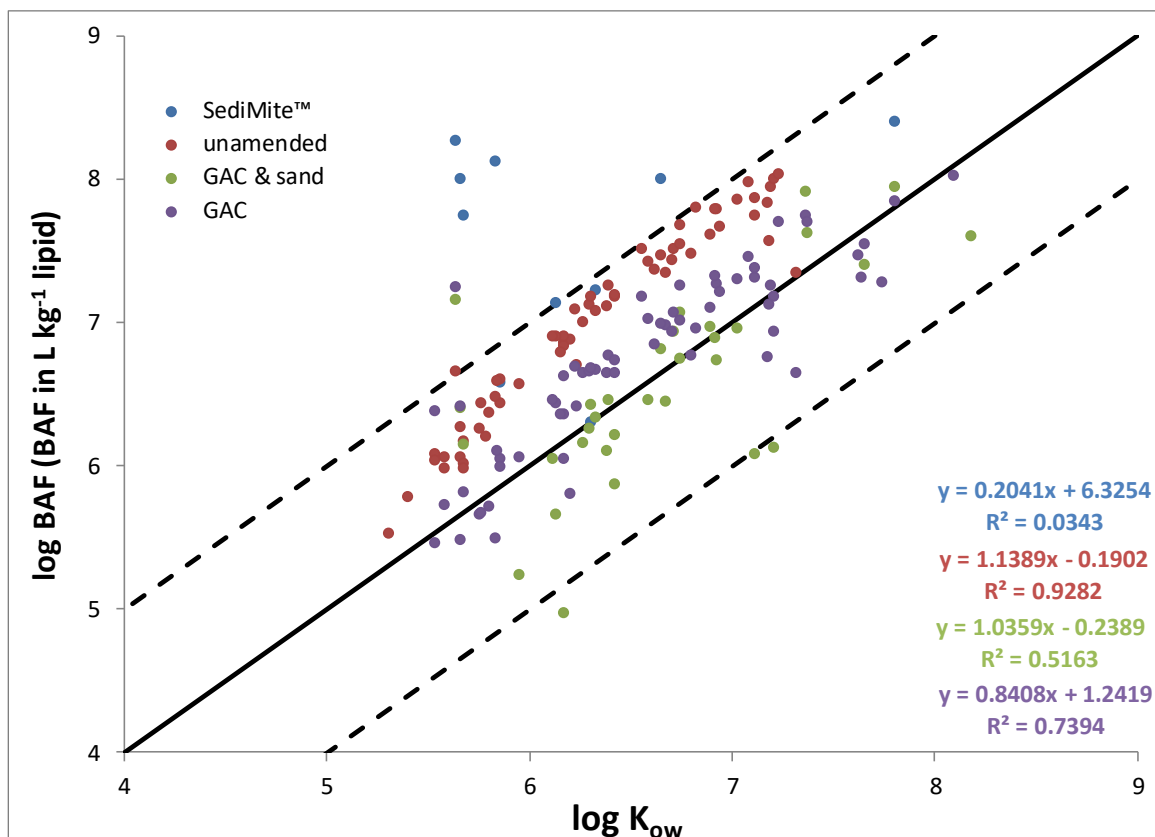


Figure AI.S1. Logarithmic, lipid-normalized BAFs for all analyzed PCB congeners or coeluting groups of congeners in native *H. azteca* plotted against logarithmic octanol-water partitioning constants. Porewater concentrations were corrected for nonequilibrium by linear regression of $\log k_{e,PRC}$ with $\log K_{ps-w}$. Lines show the one-to-one relationship (solid) plus or minus one log unit (dashed).

Additional Details on Exposure Chambers. The in situ exposure chambers were deployed in Plots A and B with modifications to the chamber body and the placement of the chambers within the plots. The ports located at the top of the chamber body were increased in height and width to enhance air and water exchange. The chambers were placed below the raised walkways and strips of landscaping mesh were stretched over and perpendicular to the walkways and staked into place. These methods were intended to provide the chambers with shade during the exposure period, which was in response to low recoveries from the chambers during monitoring rounds with elevated temperatures. The exposures did provide an additional sample point of invertebrate tissue for analysis, but these modifications did not significantly increase recoveries from the chambers.

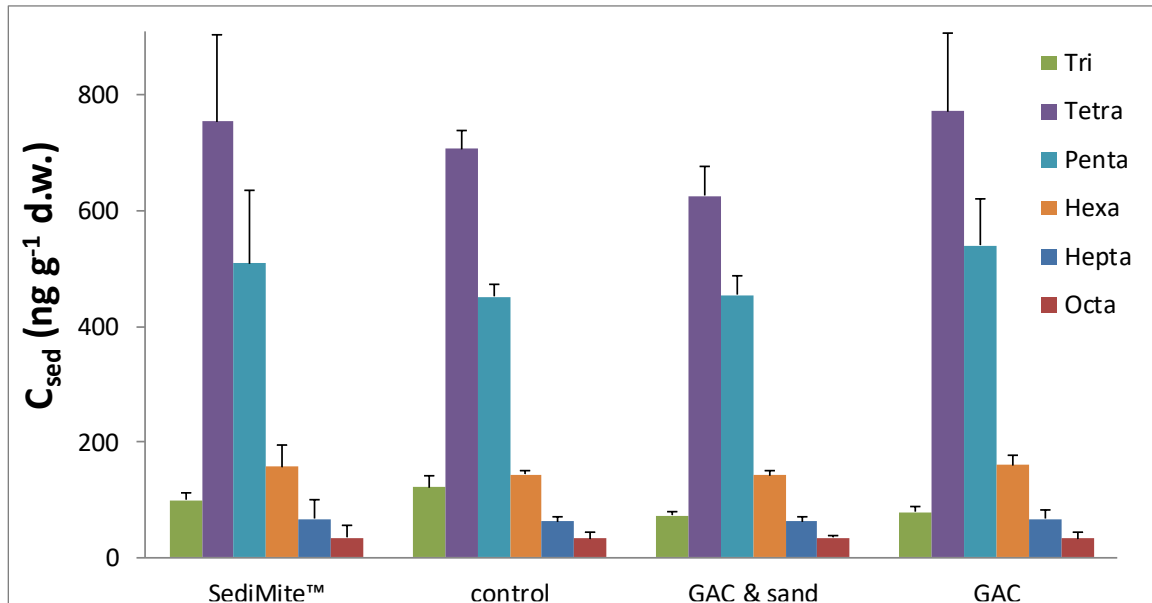


Figure AI.S2. Homolog distributions of PCBs extracted from BCSA sediments in the 0–5 cm depth interval, collected at t_{+15} . Mono-, di-, nona-, and deca-substituted congeners were all present at low concentrations (data not shown). Error bars show standard deviation among samples ($n = 5$ for each plot).

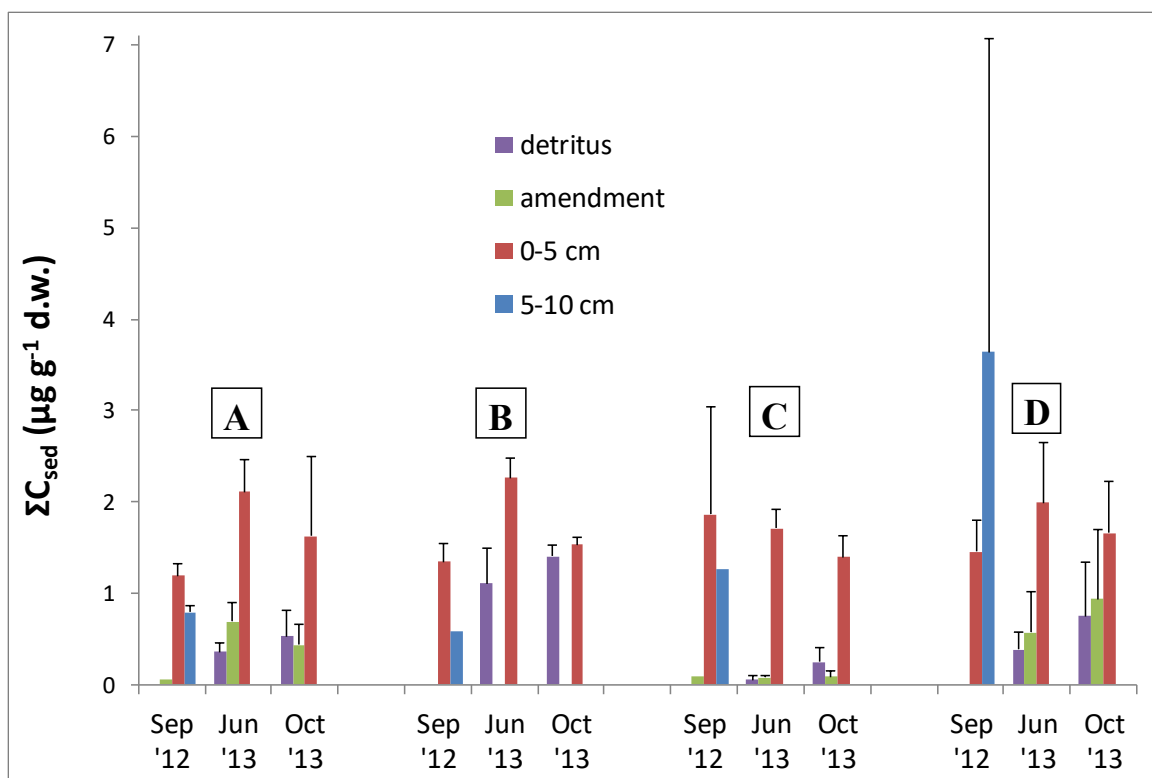


Figure AI.S3. Total extractable PCB concentrations in BCSA sediment arranged by plot (A: SediMite™, B: unamended control, C: GAC and sand, D: GAC), sampling time, and layer. Error bars show standard deviation ($1 \leq n \leq 5$).

Reductions in Extractable Sediment PCBs. Because amendment materials were not designed to degrade or remove PCBs, decreases in measured surficial sediment concentrations suggest a matrix effect of the AC and/or sand, acting through a combination of two mechanisms. The first is simple mass dilution; adding clean materials to a matrix will decrease contaminant concentrations regardless of any other benefits provided by the amendment. ΣC_{sed} was consistently lower in Plot C than in Plot D and the only difference in amendment between the two was a layer of sand (which can be expected to be largely inert toward PCB molecules). This implies a significant

contribution of the dilution mechanism to observed interplot differences. The other potential factor is a reduction in PCB extractability. A separate experiment was conducted to assess the influence of AC on extraction efficiency of PCBs from BCSA sediment. Control surficial sediments were amended in the laboratory with 0, 5, or 10% d.w. AC, homogenized, allowed to equilibrate, and extracted. Measured concentrations were 31% lower in sediment amended with 5% AC ($n = 4$), and 34% lower with a 10% AC dose ($n = 4$). Extractability was reduced to a greater extent for smaller PCBs, with extracted di- and tri-substituted congeners reduced by greater than 70% and 50%, respectively. Previous workers reported a 45% reduction in total PCB extractability with either 5% or 10% AC added to river sediment, including greater reductions for lower-chlorinated congeners.⁵ Together, these results suggest that a substantial fraction of PCB molecules can become associated with AC particles strongly enough to resist extraction by ultrasonication in hexane:acetone, and that the effect is more pronounced for smaller PCBs that are able to penetrate more deeply into the porous AC matrix. It further suggests that the observed shift toward a heavier homolog distribution in sediments compared to porewater may have been due in part to such disproportional extractability.

Tidal Deposition of PCBs on Marsh Surface. In a side experiment, sediment trays were placed in the plots to evaluate PCB input to the marsh surface from deposition by tidal water. The trays were filled with clean topsoil with a starting concentration of about 40 ng g⁻¹ ($n = 2$). After exposure in the marsh environment through many tidal cycles over a period of three and a half months, the PCB concentration in the topsoil nearly doubled to 80 ng g⁻¹ ($n = 3$; $p = 0.054$) but remained much lower than the 1000–3000 ng g⁻¹ present in native marsh sediments. While this demonstrates some ongoing PCB deposition on the

marsh surface with the tides, the extent of recontamination was relatively low during the sampling period. The PCB homolog signatures in the post-exposure topsoil differed significantly from those in the initial clean topsoil used to fill the trays (Figure AI.S4). Concentrations of tetra-substituted congeners were more than fourfold higher, and of tri-substituted congeners more than twentyfold higher. This proportional enrichment of smaller, more water-soluble congeners suggests absorption of dissolved PCBs from overlying water, not deposited sediment, as the source of additional contamination in these samples.

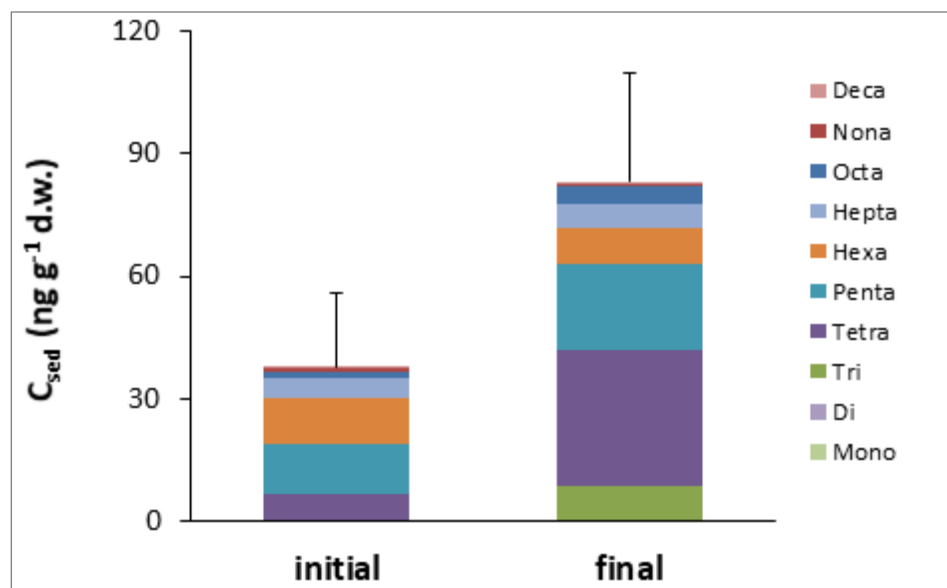


Figure AI.S4. PCB concentrations by homolog group in topsoil deployed in collection trays (initial) and collected from the same trays 3.5 months after deployment (final).

Error bars show standard deviation in ΣC_{sed} (initial $n = 2$ and final $n = 3$).

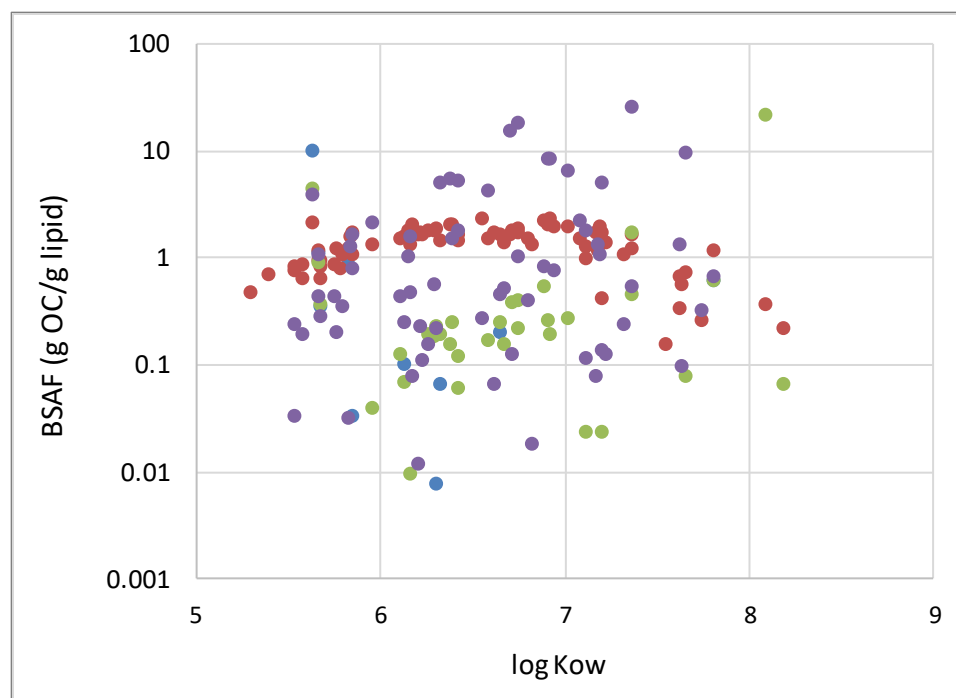


Figure AI.S5. Biota-sediment accumulation factors for PCBs. Data are from the t_{+11} sampling. Each BSAF value is calculated from an average C_{sed} value ($n = 5$) for the 0–5 cm horizon and an average, lipid-normalized C_{org} value ($n = 5$) for the 0–2.5 cm horizon.

PCBs in Wolf Spiders. Native wolf spiders (*Lycosidae* spp.) collected at BCSA for the t_{+11} sampling were dichotomous in size. The large majority of individuals had wet masses of 25–50 mg ($n = 157$), while a few were in the range of 150–300 mg ($n = 4$). Further, some sample composites included egg sacs ($n = 9$), while others did not ($n = 4$). Together, these factors introduced a large degree of variability to PCB and lipid content measurements. Lipid-normalized ΣC_{org} in all spider composites was 71 ± 54 ng g⁻¹ in Plot A ($n = 3$), 50 ± 14 ng g⁻¹ in Plot B ($n = 3$), 1000 ± 1500 ng g⁻¹ in Plot C ($n = 4$), and 18 ± 1.7 ng g⁻¹ in Plot D ($n = 3$). The outlying value for Plot C is due to two of the larger spiders with far higher ΣC_{org} . If large spiders are ignored (Figure AI.S6), lipid-normalized

ΣC_{org} was 15 ng g^{-1} for spiders collected in Plot A ($n = 1$), $50 \pm 14 \text{ ng g}^{-1}$ in Plot B ($n = 3$), $79 \pm 35 \text{ ng g}^{-1}$ in Plot C ($n = 2$), and $18 \pm 1.7 \text{ ng g}^{-1}$ in Plot D ($n = 3$). These data appear to suggest a reduction in spider lipid-normalized ΣC_{org} in Plots A and D, though the small number of sample composites preclude a statistically significant finding. Across all plots, lipid-normalized ΣC_{org} in large spiders was $1000 \pm 1500 \text{ ng g}^{-1}$ and in small spiders was $42 \pm 29 \text{ ng g}^{-1}$. The large differences in PCB concentration observed in small versus large wolf spiders could be due to different feeding habits (larger spiders may prey upon higher-trophic level organisms with larger PCB burdens) and mobility (larger spiders are more likely to move outside of the amended area and be exposed to unamended sediment). As with amphipods, free-ranging native spiders may have shown weaker correlations than laboratory organisms due to differences in mobility and exposure history.

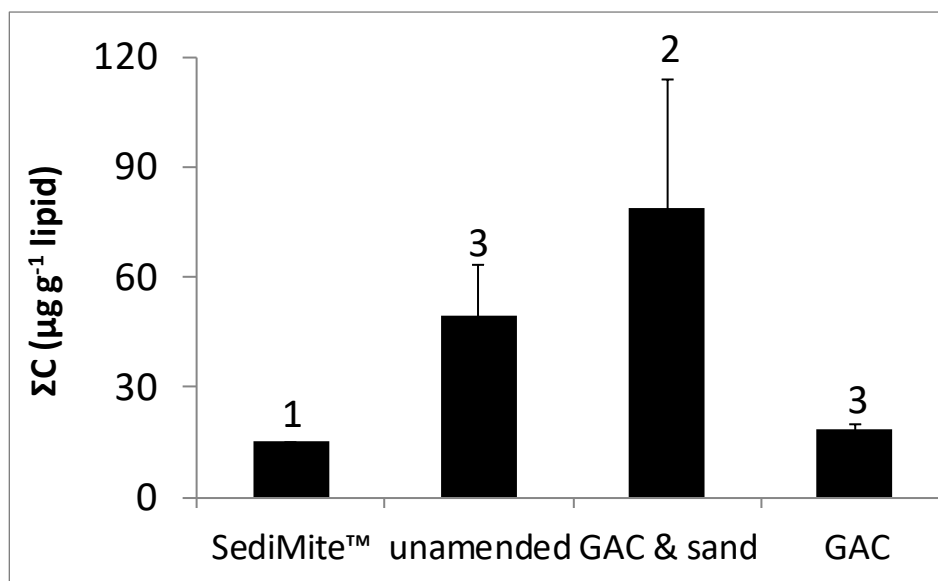


Figure AI.S6. Total lipid-normalized PCB concentrations in native small wolf spiders collected at BCSA. Error bars show standard deviation (n shown above each bar). Large spiders with high outlier concentrations are excluded.

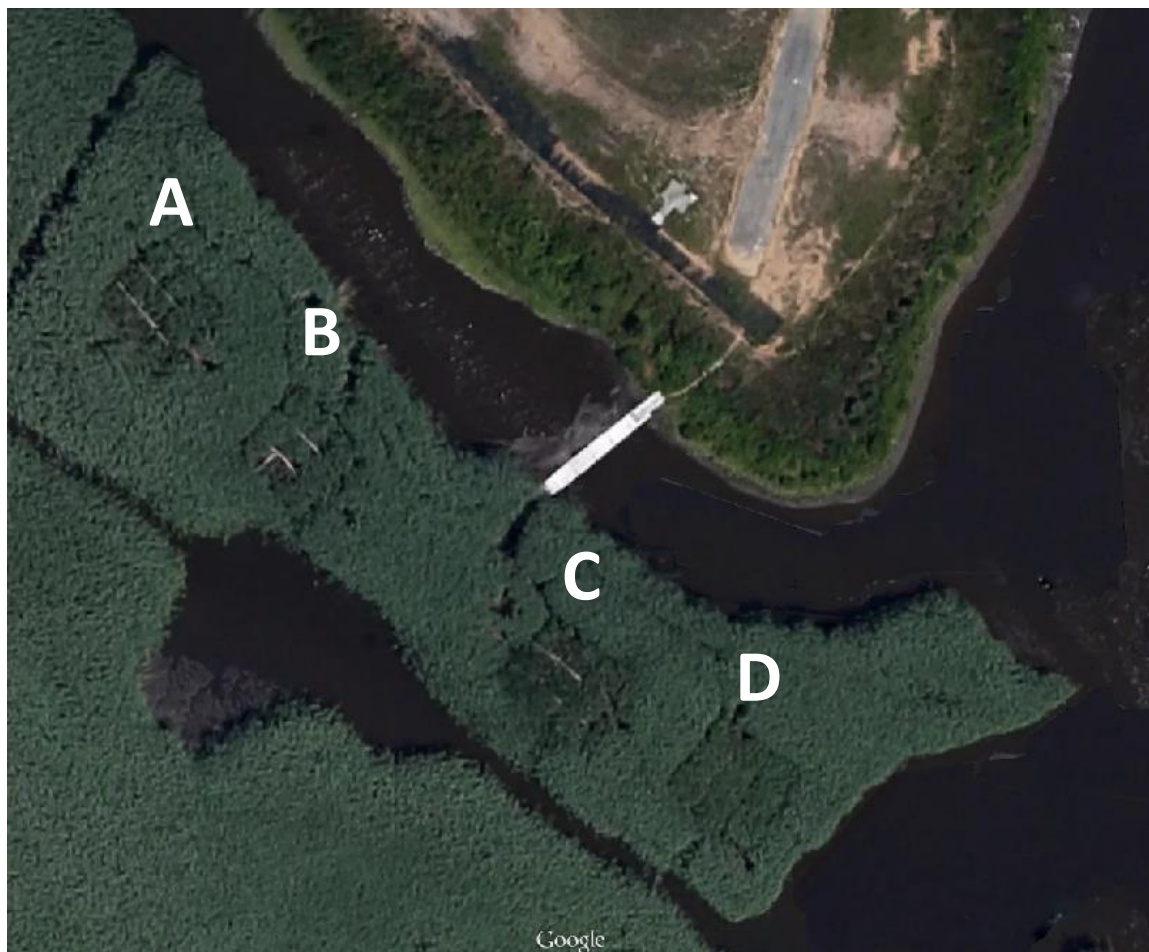


Figure AI.S7. Google satellite image of study area taken approximately one year after amendment application. Letters denote plot locations.

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Supplemental Information to the Article:

**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 AIV.S1. After the initial microwave digestion, 3 mL of cold-saturated Boric Acid (6 g in 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 AIV.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 porewaters 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 porewater 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 (SR), defined by Helms et al.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). SR was calculated by dividing the fitted UV-absorbance slope between 275 and 295 nm by that between 350 and 400 nm.² 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.

Table AII.S1. Microwave digestion method for soil samples.

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 AII.S2. QC summary for filterable MeHg (FMeHg) and MeHg 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 ⁻¹
Detection Limit	0.56 ng L ⁻¹
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 ⁻¹
Detection Limit	0.45 ng g ⁻¹

Table AII.S3. QC summary for filterable total Hg (FTHg) 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.

FTHg 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 ⁻¹
Detection Limit	1.76 ng L ⁻¹
Hg in Soils QC Summary	
QC Parameter	Average of Runs
CRM (MESS-4 Marine Sediment)	128%
ID Recovery	Recovery = 91%
RPD between duplicate samples	RPD = 1.5%
Digestion Blank	0.73 µg L ⁻¹
Detection Limit	0.18 µg g ⁻¹

Table AII.S4. Stability constants for Hg speciation modeling.

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

Table AII.S5. Stability constants for MeHg speciation.

Reaction	Log K	Reference
$\text{H}_2\text{S} \rightleftharpoons \text{HS}^- + \text{H}^+$	-7.02	4
$\text{HS}^- \rightleftharpoons \text{S}^{2-} + \text{H}^+$	-17.4	4
$\text{CH}_3\text{Hg}^+ + \text{SH}^- \rightleftharpoons \text{CH}_3\text{HgSH}$	14.5	12
$\text{CH}_3\text{Hg}^+ + \text{HS}^- \rightleftharpoons \text{H}^+ + \text{CH}_3\text{HgS}^-$	3.8	12
$2\text{CH}_3\text{Hg}^+ + \text{HS}^- \rightleftharpoons \text{H}^+ + (\text{CH}_3\text{Hg})_2\text{S}$	20.1	12
$\text{CH}_3\text{Hg}^+ + \text{RS}_2^{2-} \rightleftharpoons \text{CH}_3\text{HgSR}$	16.5	12
$\text{RS}_2^{2-} + \text{H}^+ \rightleftharpoons \text{RS}_2\text{H}^-$	10	13
$\text{CH}_3\text{Hg}^+ + \text{Cl}^- \rightleftharpoons \text{CH}_3\text{HgCl}$	5.25	12
$\text{CH}_3\text{Hg}^+ + \text{HO}^- \rightleftharpoons \text{CH}_3\text{HgOH}$	9.37	12
$\text{Fe}^{2+} + \text{HS}^- \rightleftharpoons \text{FeS}_{(s), \text{mackinawite}} + \text{H}^+$	3.6	4
$\text{Fe}^{2+} + \text{HS}^- \rightleftharpoons \text{Fe}(\text{HS})^+$	5.62	11
$\text{Fe}^{2+} + 2\text{HS}^- \rightleftharpoons \text{Fe}(\text{HS})_{2(aq)}$	8.95	4
$\text{Fe}^{2+} + 3\text{HS}^- \rightleftharpoons \text{Fe}(\text{HS})_3^-$	10.99	4
$\text{Fe}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^+ + \text{H}^+$	-9.40	4
$\text{Fe}^{2+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_{2(aq)} + 2\text{H}^+$	-20.49	4
$\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_3^- + 3\text{H}^+$	-30.99	4
$\text{Fe}^{2+} + \text{Cl}^- \rightleftharpoons \text{FeCl}^+$	-0.20	4

Table AII.S6. Soil characteristics (all elemental concentrations in mg g⁻¹).

	Amendment amount as:	
	% of dry weight	% of organic matter
Berry's Creek <i>Phragmites</i> Soil	5	13

Table AII.S7. Isotope spike values.

Isotope Composition	Spike Solution Concentration	Target Spike Concentration
²⁰¹ HgCl ₂	20 µg mL ⁻¹	2 µg gdw ⁻¹ in slurry bottle
Me ¹⁹⁹ HgCl	1.5 µg mL ⁻¹	67.5 ng gdw ⁻¹ in slurry bottle

Table AII.S8. SUVA₂₈₀ 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 ± 0.23
No DOM	*
Low DOM	0.47 ± 0.26
Mid DOM	0.57 ± 0.34
High DOM	4.31 ± 0.95

Table AII.S9. General linear models used to assess Hg and MeHg porewater and solid phase data. *CDOM₂₈₀ reading was below the blank.

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 _d	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 $K_d \sim$ Treatment + Day + Isotope Spike
Me ¹⁹⁹ Hg K_d	Me ¹⁹⁹ Hg $K_d \sim$ Treatment + Day
Ambient MeHg in Soils	MeHg $\sim$ Treatment + Day + Isotope Spike + Treatment*Isotope Spike
Me ²⁰¹ Hg in Soils	Me ²⁰¹ Hg $\sim$ Treatment + Day + Treatment*Day
Me ¹⁹⁹ Hg in Soils	Me ¹⁹⁹ Hg $\sim$ Treatment + Day + Treatment*Day

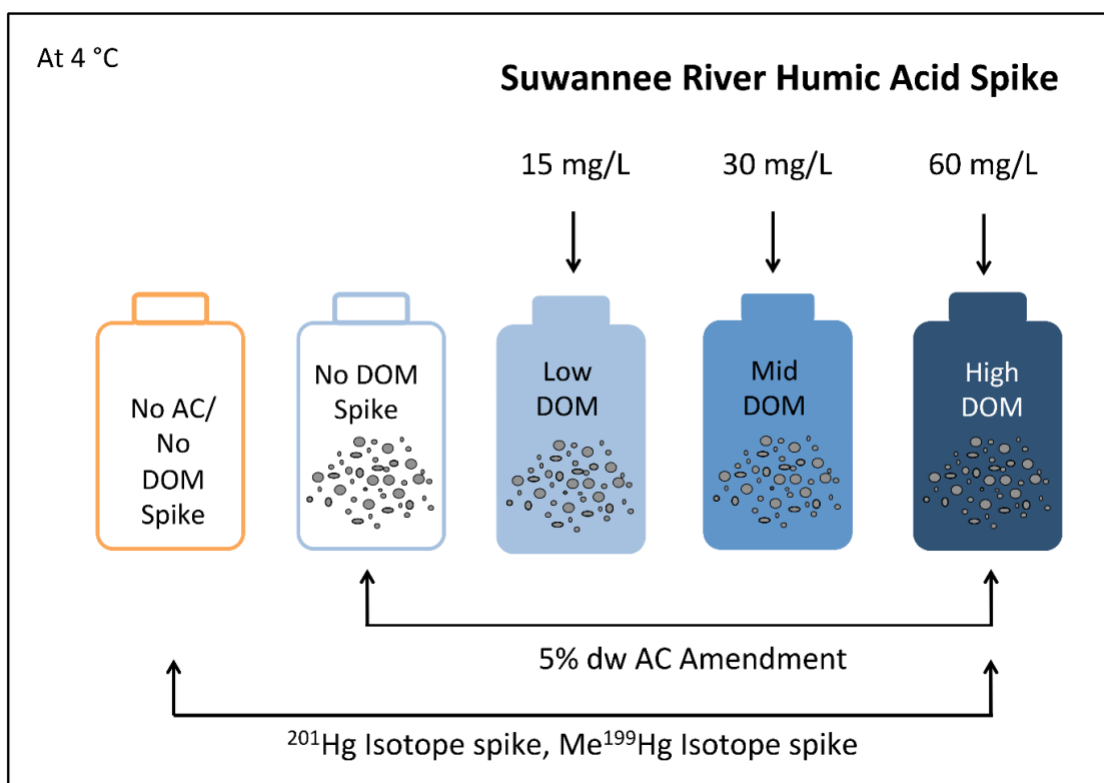


Figure AII.S1. Experimental design schematic for the slurry experiment.

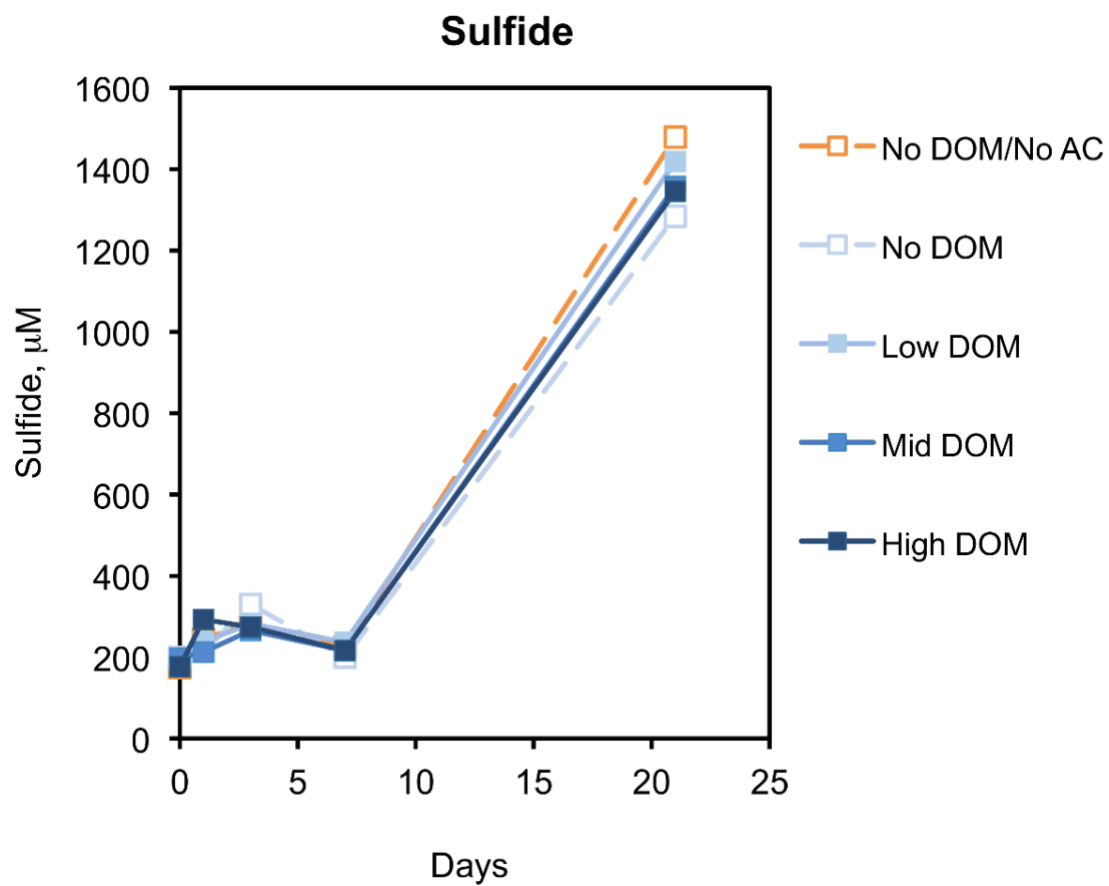


Figure AII.S2. Porewater sulfide in soil/AC microcosms. Data points represent the average of duplicate microcosms.

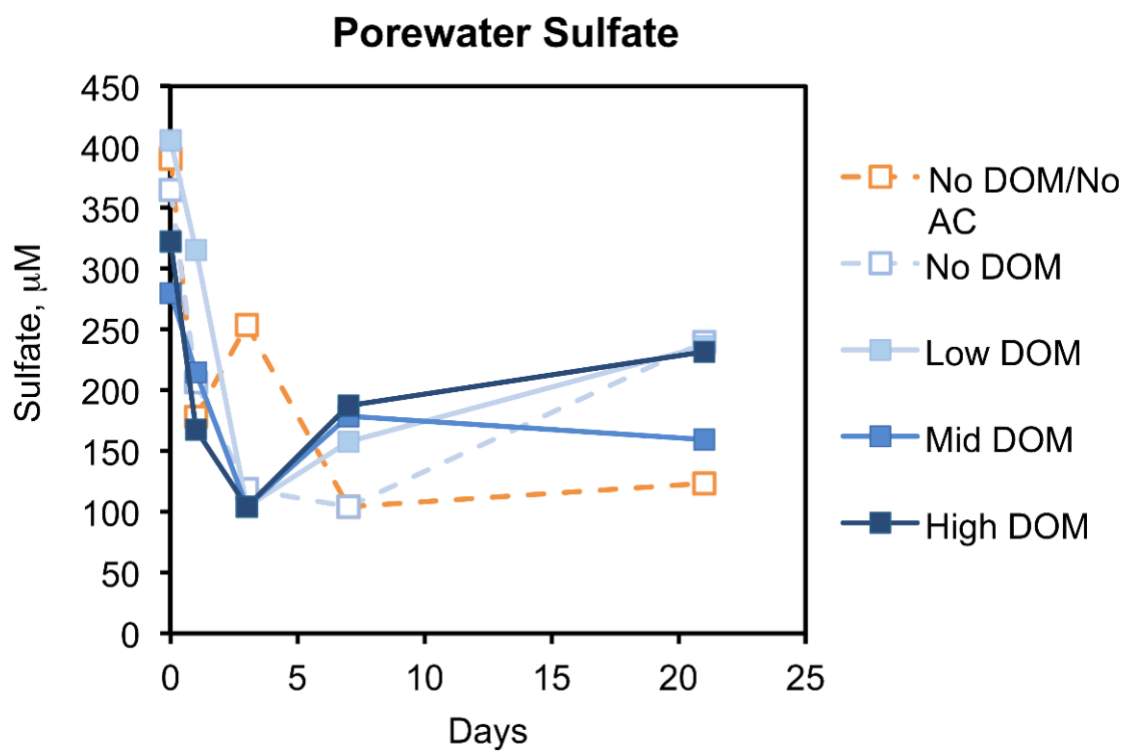


Figure AII.S3. Porewater sulfate in soil/AC microcosms. Data points represent the average of duplicate microcosms.

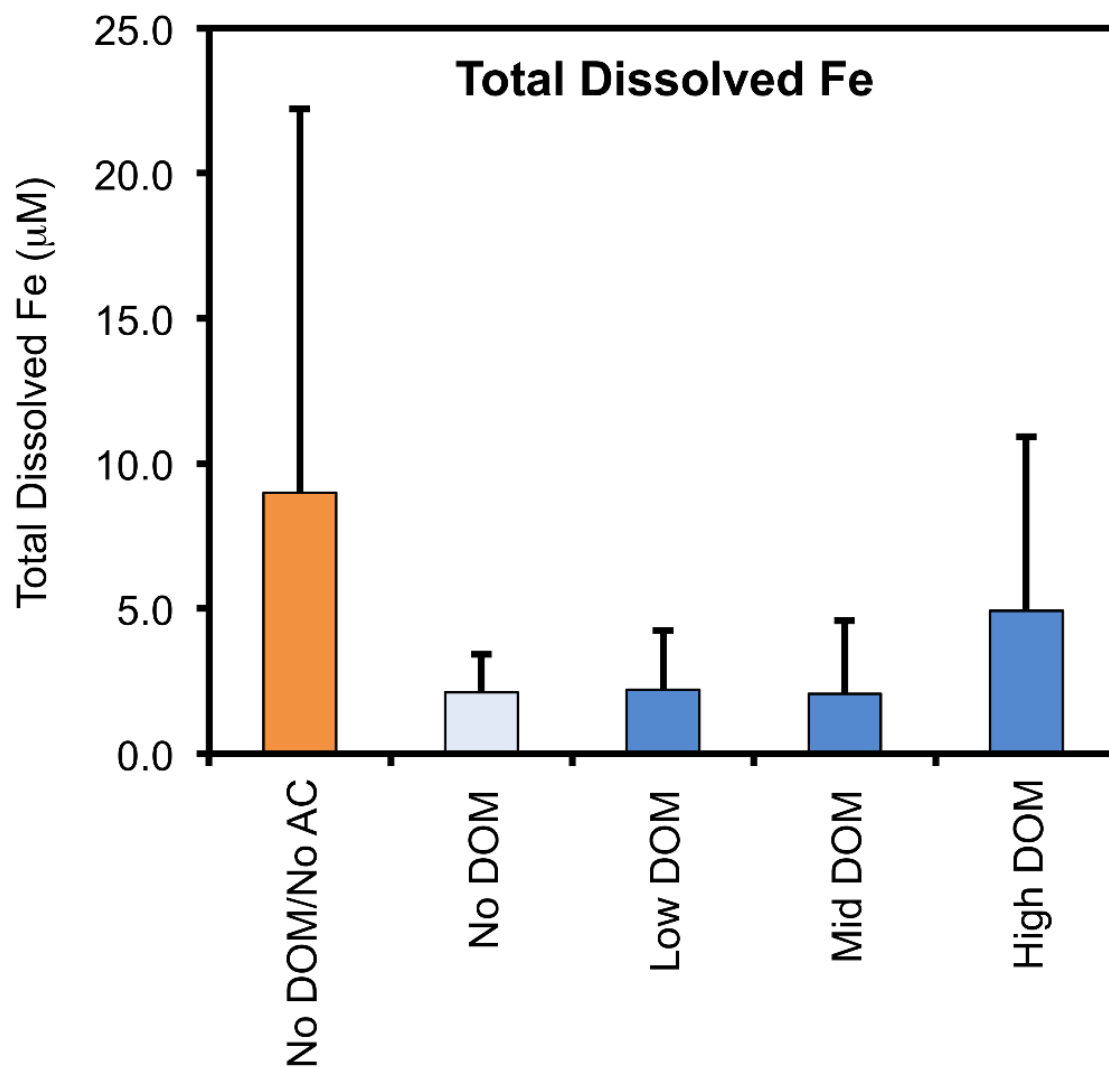


Figure AII.S4. Average total dissolved iron concentrations in soil/AC microcosms across all time points. Error bars represent the standard deviation of the sample measurements.

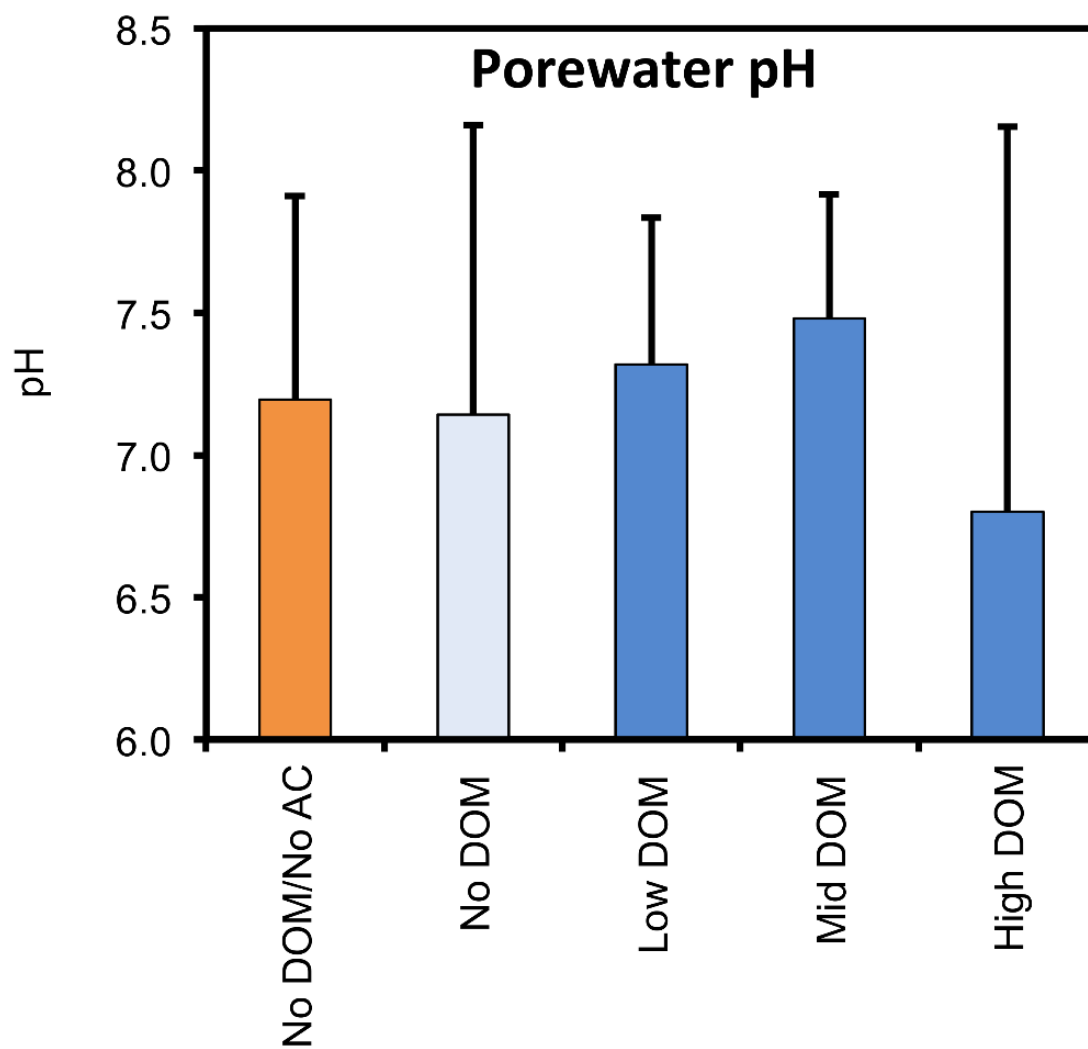


Figure AII.S5. Average pH in the soil/AC microcosms across all time points. Error bars represent the standard deviation of the sample measurements.

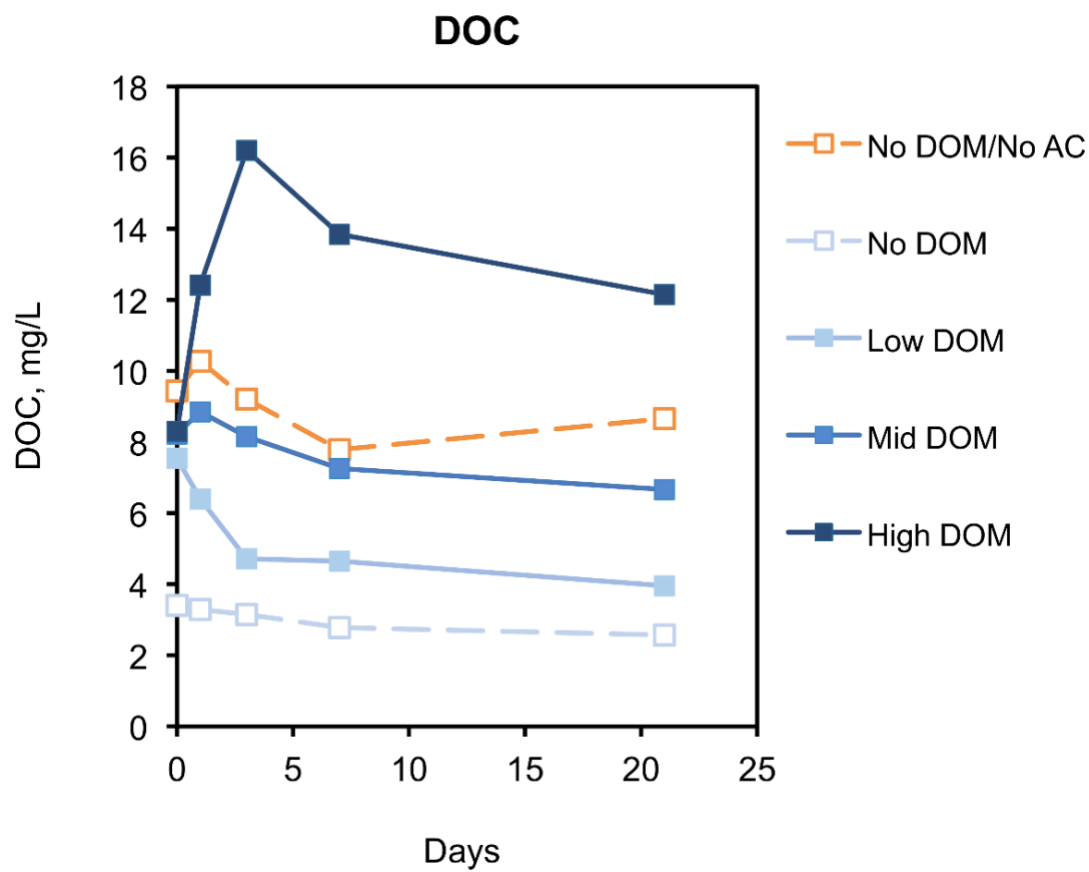


Figure AII.S6. Porewater DOC concentrations in the soil/AC microcosms. Data points represent the average of duplicate microcosms.

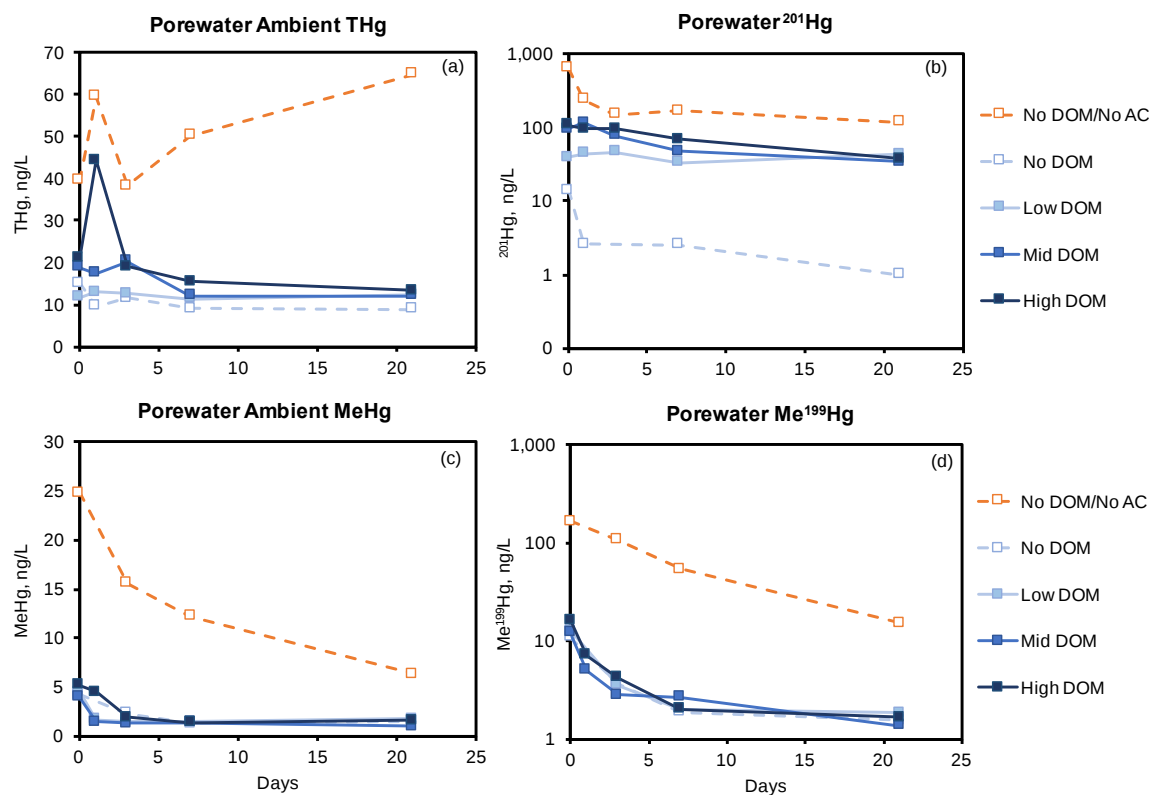


Figure AII.S7. Effect of added DOM on porewater total Hg and MeHg concentrations in AC-treated soils: (a) Ambient Total Hg; (b) ²⁰¹Hg; (c) Ambient MeHg; and (d) Me¹⁹⁹Hg. Note that the ²⁰¹Hg and Me¹⁹⁹Hg concentrations are shown on the log scale. Ambient data points are the average of two bottles; spike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

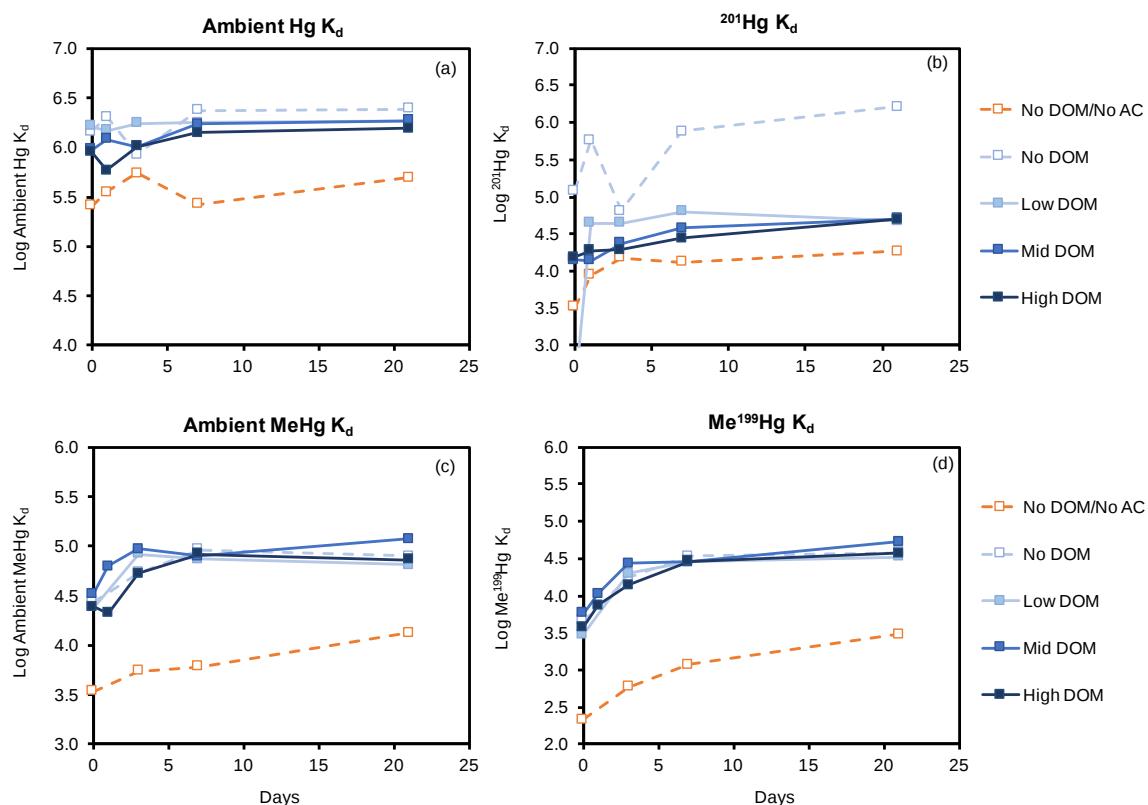


Figure AII.S8. Sediment:water partition coefficients for Hg and MeHg in AC-treated soils: (a) Ambient Total Hg; (b) ^{201}Hg ; (c) Ambient MeHg; and (d) Me ^{199}Hg .

Sediment:water partition coefficients (K_d) were calculated as the sediment concentration in ng kg^{-1} divided by the porewater concentration in ng L^{-1} .

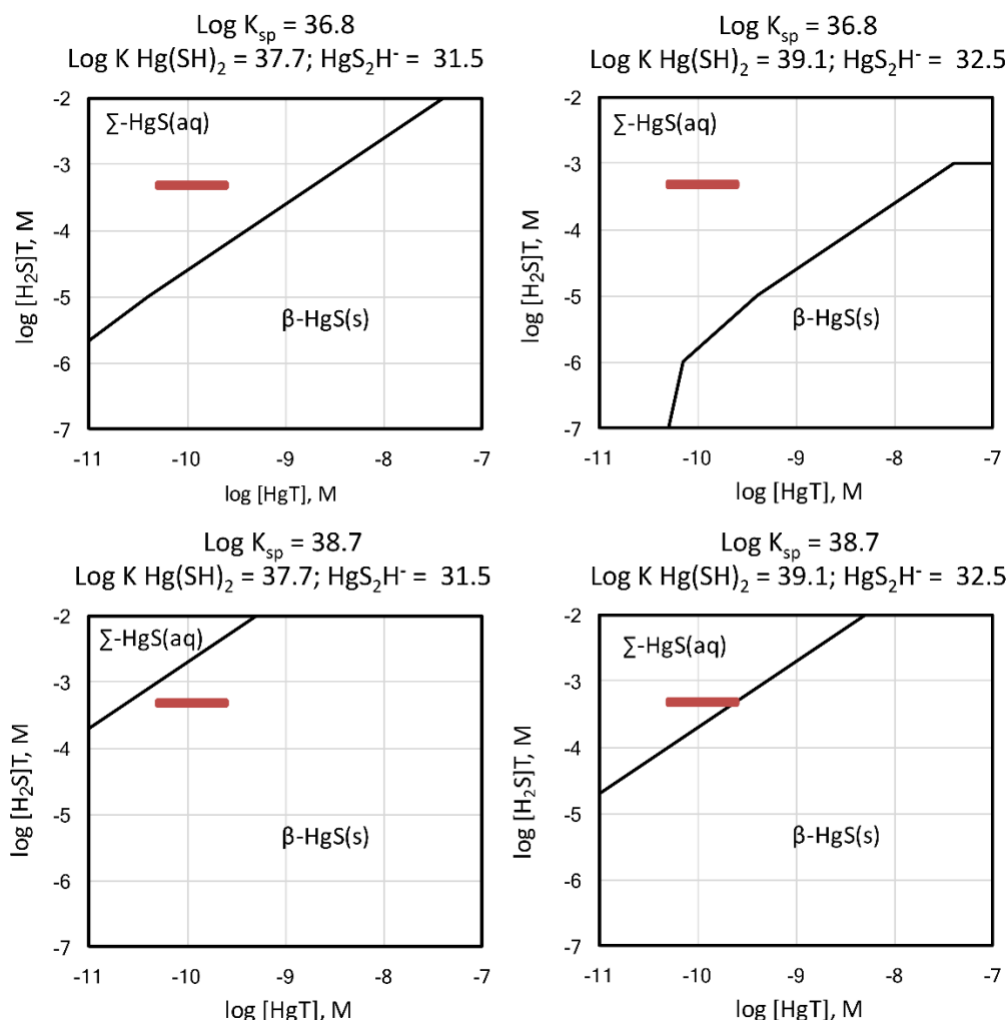


Figure AII.S9. Calculated filter-passing inorganic Hg(II) speciation as a function of total Hg concentration and total sulfide concentration ($[H_2S]T$) under the average conditions in the experimental bottles (pH 7.2, total Fe 4E-6M, Cl- 2E-2M, RSH 2E-6M.

Metacinnabar ($\beta\text{-HgS(s)}$) precipitates in the area below the diagonal lines. Above the line metacinnabar is undersaturated and dissolved Hg–S species ($\Sigma\text{HgS(aq)}$), particularly Hg(SH)_2 and HgS_2^{2-} predominate. Red bars show the range of experimental conditions. Calculations were performed using two values of the solubility product (K_{sp}) for the reaction $\text{Hg}^{2+} + \text{HS}^- = \beta\text{-HgS(s)} + \text{H}^+$ and two values for the stability constants for



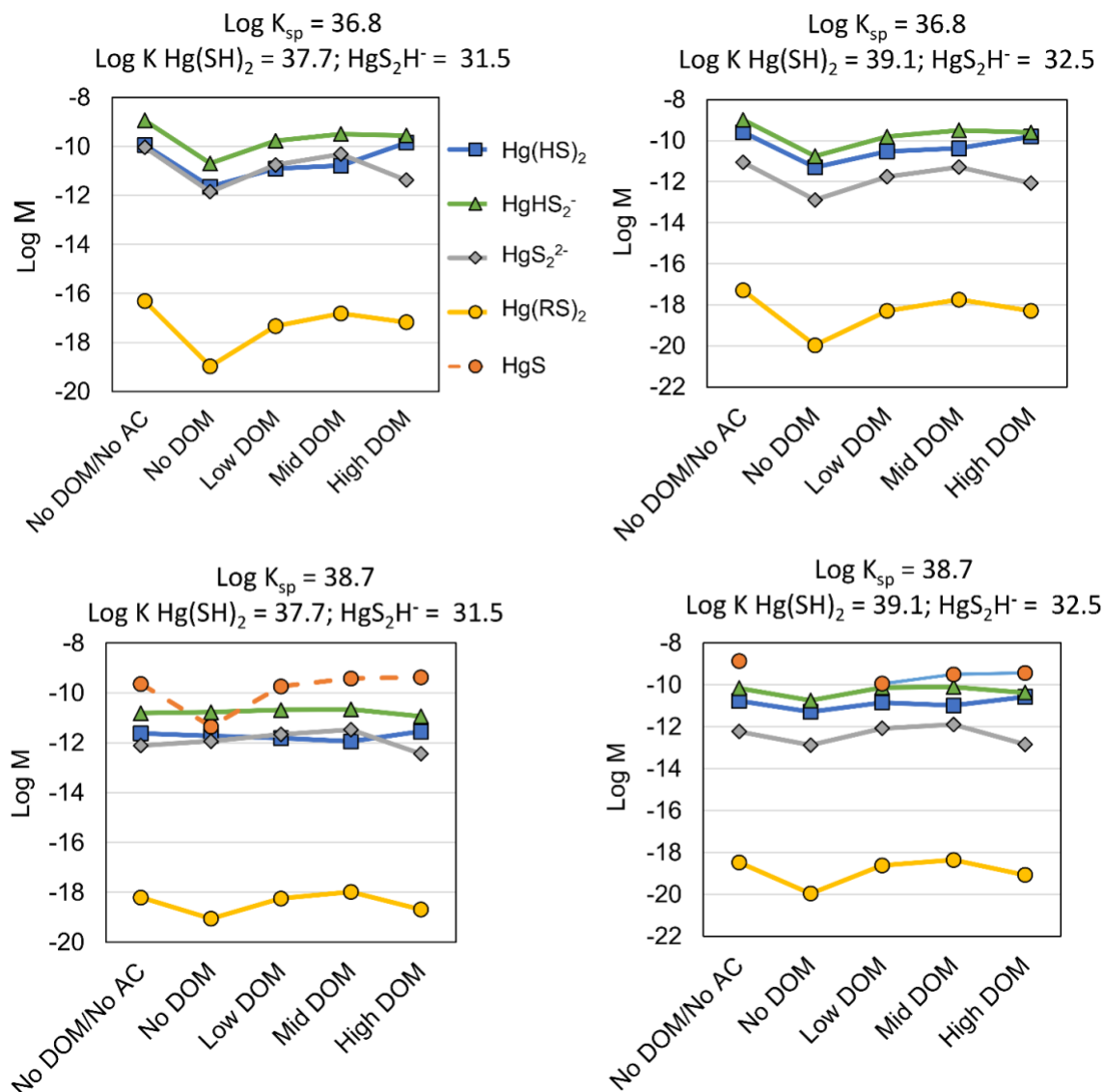


Figure AII.S10. Calculated filter-passing inorganic $^{201}\text{Hg(II)}$ speciation in the microcosms. Stability constants are listed in Tables AII.S4. Speciation calculation inputs and outputs are shown in Appendix II. Calculations were performed using two values of the solubility product (K_{sp}) for the reaction $\text{Hg}^{2+} + \text{HS}^- = \beta\text{-HgS}_{(\text{s})} + \text{H}^+$ and two values for the stability constants for Hg(SH)_2 and HgS_2^{2-} .⁴⁰⁻⁴²

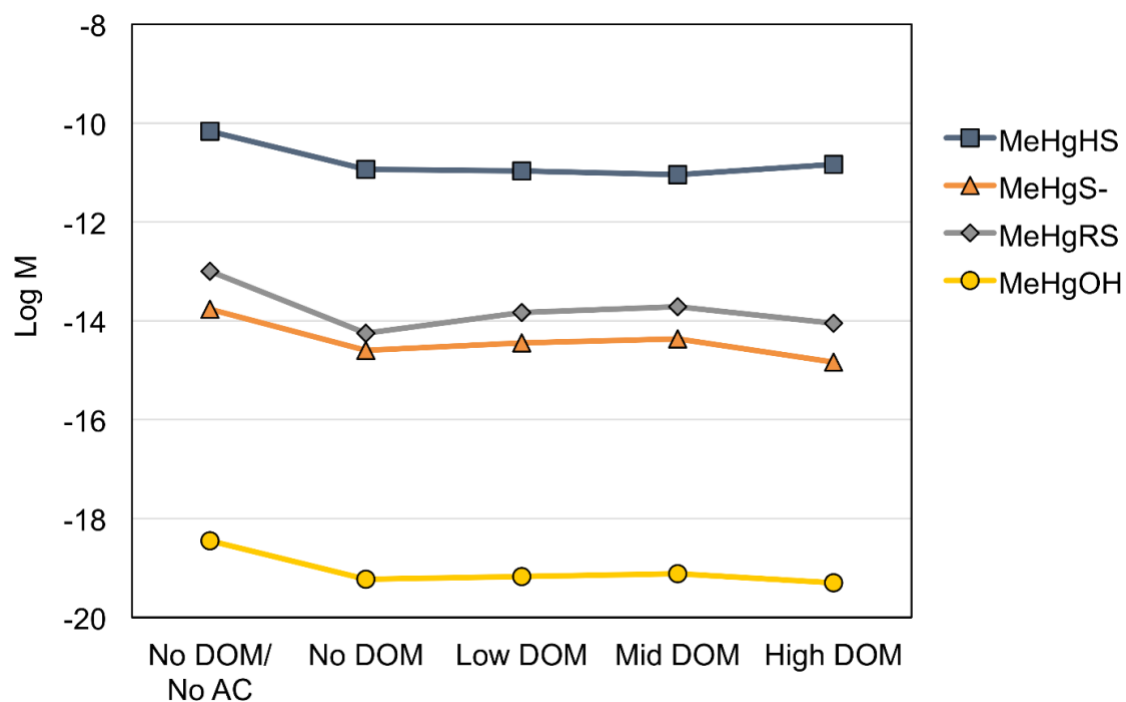


Figure AII.S11. Calculated filter-passing MeHg speciation in the microcosms. Stability constants are listed in Table AII.S5. Speciation calculation inputs and outputs are shown in Appendix II.

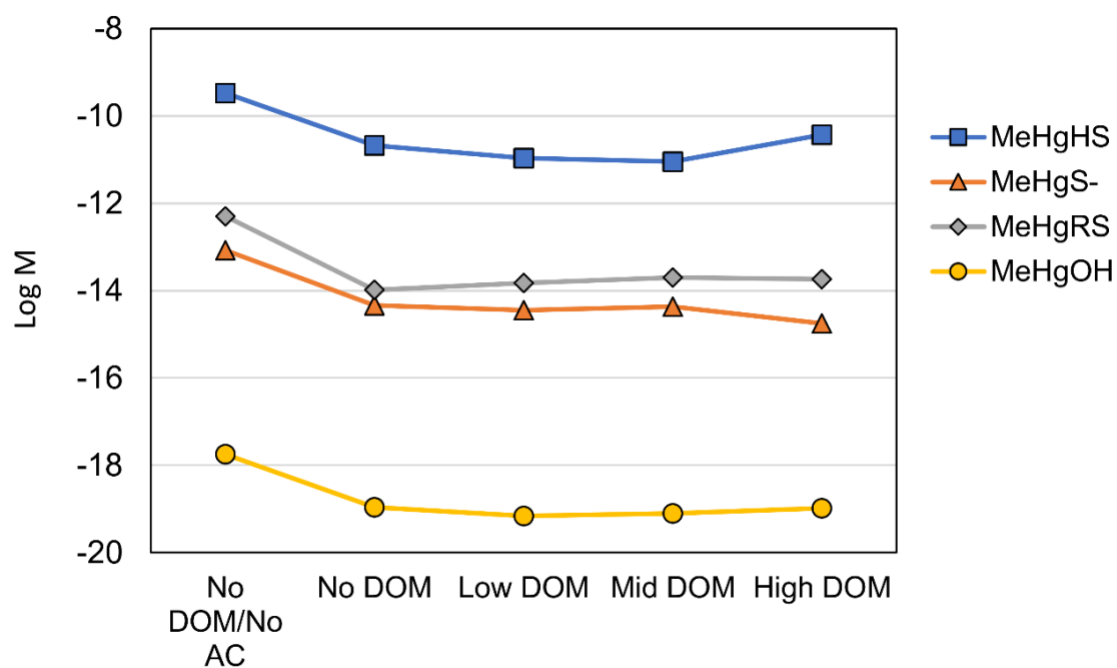


Figure AII.S12. Calculated filter-passing Me¹⁹⁹Hg speciation in microcosms. Stability constants are listed in Table AII.S5. Speciation calculation inputs and outputs are shown in Appendix II.

Table AII.S10. Estimation of SR content of soil DOM and soil+SRHA.

			mmol S mol C ⁻¹													
DOM S content (Poulin, et al. 2017)			low SO ₄ :	9	fraction of S as exocyclic increases with SO ₄ /HS concentration of site											
for hydrophobic acid fraction only			hi SO ₄ :	14												
for Everglades porewater DOM																
HPOA fraction of Everglades NOM is 46–52%																
For Berry's Creek soils:																
For these 5 ppt salinity, highly sulfidic soils I think we can assume we are at the top end of the Everglades range																
So,			14	mmol S mol C ⁻¹												
			50	% exocyclic C												
These values reflect the already sulfidized nature of BCSA soil DOM																
Then assume that HPOA is half of all NOM; and that the residual NOM has NO S content (a conservative assumption to balance using the highest S values in the Everglades data set)																
SRHA	SRHA S:C		(Graham et al. 2017)													
	IHSS															
	mmol/mol		4.14													
	percent		23.6													
	exocyclic S															
			SRHA				Native BCSA soil NOM									
			Corrected to 23.6													
			measured		from SRHA	from SRHA	DOC									
			mg L ⁻¹	mg L ⁻¹	mol C L ⁻¹	mol SR L ⁻¹	mg L ⁻¹	mol C L ⁻¹	mol S L ⁻¹	mol RS L ⁻¹						
Hg SPIKE	DOC Conc	Time Pt.	Total DOC	SRHA DOC	SRHA DOC	SRHA	Native DOC	Native DOC	Native DOC	Native DOC						
²⁰¹ Hg	High DOC Cold	T0	8.90	5.62	4.68E-04	4.57E-07	3.28	2.73E-04	1.91E-06	9.56E-07						
²⁰¹ Hg	High DOC Cold	T1	18.67	15.29	1.27E-03	1.24E-06	3.38	2.82E-04	1.97E-06	9.86E-07						
²⁰¹ Hg	High DOC Cold	T2	16.62	12.83	1.07E-03	1.04E-06	3.79	3.16E-04	2.21E-06	1.10E-06						
²⁰¹ Hg	High DOC Cold	T3	14.89	12.67	1.06E-03	1.03E-06	2.23	1.86E-04	1.30E-06	6.49E-07						
²⁰¹ Hg	High DOC Cold	T4	13.89	11.29	9.41E-04	9.19E-07	2.60	2.17E-04	1.52E-06	7.59E-07						
²⁰¹ Hg	Low DOC Cold	T0	6.95	3.68	3.06E-04	2.99E-07	9.19	7.66E-04	5.36E-06	2.68E-06						
²⁰¹ Hg	Low DOC Cold	T1	7.46	4.08	3.40E-04	3.32E-07	12.33	1.03E-03	7.19E-06	3.60E-06						
²⁰¹ Hg	Low DOC Cold	T2	4.50	0.71	5.90E-05	5.78E-08	9.77	8.14E-04	5.70E-06	2.85E-06						
²⁰¹ Hg	Low DOC Cold	T3	4.50	2.27	1.89E-04	1.85E-07	8.10	6.75E-04	4.73E-06	2.36E-06						
²⁰¹ Hg	Low DOC Cold	T4	4.16	1.56	1.30E-04	1.27E-07	8.83	7.36E-04	5.15E-06	2.57E-06						

²⁰¹ Hg	Mid DOC Cold	T0	7.99	4.72	3.93E-04	3.84E-07	7.70	6.42E-04	4.49E-06	2.25E-06
²⁰¹ Hg	Mid DOC Cold	T1	8.55	5.17	4.31E-04	4.21E-07	6.16	5.13E-04	3.59E-06	1.80E-06
²⁰¹ Hg	Mid DOC Cold	T2	7.66	3.87	3.22E-04	3.15E-07	15.78	1.31E-03	9.20E-06	4.60E-06
²⁰¹ Hg	Mid DOC Cold	T3	6.81	4.59	3.82E-04	3.74E-07	12.79	1.07E-03	7.46E-06	3.73E-06
²⁰¹ Hg	Mid DOC Cold	T4	6.43	3.83	3.19E-04	3.12E-07	10.40	8.67E-04	6.07E-06	3.03E-06
²⁰¹ Hg	No DOC Cold	T0	3.28	0	0.00E+00	0.00E+00	3.28	2.73E-04	1.91E-06	9.56E-07
²⁰¹ Hg	No DOC Cold	T1	3.38	0	0.00E+00	0.00E+00	3.38	2.82E-04	1.97E-06	9.86E-07
²⁰¹ Hg	No DOC Cold	T2	3.79	0	0.00E+00	0.00E+00	3.79	3.16E-04	2.21E-06	1.10E-06
²⁰¹ Hg	No DOC Cold	T3	2.23	0	0.00E+00	0.00E+00	2.23	1.86E-04	1.30E-06	6.49E-07
²⁰¹ Hg	No DOC Cold	T4	2.60	0	0.00E+00	0.00E+00	2.60	2.17E-04	1.52E-06	7.59E-07
²⁰¹ Hg	No DOC/No AC	T0	9.19	0	0.00E+00	0.00E+00	9.19	7.66E-04	5.36E-06	2.68E-06
²⁰¹ Hg	No DOC/No AC	T1	12.33	0	0.00E+00	0.00E+00	12.33	1.03E-03	7.19E-06	3.60E-06
²⁰¹ Hg	No DOC/No AC	T2	9.77	0	0.00E+00	0.00E+00	9.77	8.14E-04	5.70E-06	2.85E-06
²⁰¹ Hg	No DOC/No AC	T3	8.10	0	0.00E+00	0.00E+00	8.10	6.75E-04	4.73E-06	2.36E-06
²⁰¹ Hg	No DOC/No AC	T4	8.83	0	0.00E+00	0.00E+00	8.83	7.36E-04	5.15E-06	2.57E-06
Me ¹⁹⁹ Hg	High DOC Cold	T0	7.70	4.17	3.48E-04	3.40E-07	3.53	2.94E-04	2.06E-06	1.03E-06
Me ¹⁹⁹ Hg	High DOC Cold	T1	6.16	2.97	2.47E-04	2.42E-07	3.19	2.66E-04	1.86E-06	9.31E-07
Me ¹⁹⁹ Hg	High DOC Cold	T2	15.78	13.27	1.11E-03	1.08E-06	2.51	2.09E-04	1.46E-06	7.32E-07
Me ¹⁹⁹ Hg	High DOC Cold	T3	12.79	9.45	7.88E-04	7.70E-07	3.34	2.78E-04	1.95E-06	9.73E-07
Me ¹⁹⁹ Hg	High DOC Cold	T4	10.40	7.86	6.55E-04	6.40E-07	2.54	2.12E-04	1.48E-06	7.41E-07
Me ¹⁹⁹ Hg	Low DOC Cold	T0	8.14	4.61	3.84E-04	3.75E-07	3.53	2.94E-04	2.06E-06	1.03E-06
Me ¹⁹⁹ Hg	Low DOC Cold	T1	5.34	2.15	1.79E-04	1.75E-07	3.19	2.66E-04	1.86E-06	9.31E-07
Me ¹⁹⁹ Hg	Low DOC Cold	T2	4.93	2.42	2.01E-04	1.97E-07	2.51	2.09E-04	1.46E-06	7.32E-07
Me ¹⁹⁹ Hg	Low DOC Cold	T3	4.80	1.46	1.22E-04	1.19E-07	3.34	2.78E-04	1.95E-06	9.73E-07
Me ¹⁹⁹ Hg	Low DOC Cold	T4	3.75	1.21	1.00E-04	9.81E-08	2.54	2.12E-04	1.48E-06	7.41E-07
Me ¹⁹⁹ Hg	Mid DOC Cold	T0	8.45	4.92	4.10E-04	4.00E-07	3.53	2.94E-04	2.06E-06	1.03E-06
Me ¹⁹⁹ Hg	Mid DOC Cold	T1	9.15	5.96	4.96E-04	4.85E-07	3.19	2.66E-04	1.86E-06	9.31E-07
Me ¹⁹⁹ Hg	Mid DOC Cold	T2	8.64	6.13	5.11E-04	4.99E-07	2.51	2.09E-04	1.46E-06	7.32E-07
Me ¹⁹⁹ Hg	Mid DOC Cold	T3	7.70	4.36	3.63E-04	3.55E-07	3.34	2.78E-04	1.95E-06	9.73E-07
Me ¹⁹⁹ Hg	Mid DOC Cold	T4	6.90	4.36	3.63E-04	3.55E-07	2.54	2.12E-04	1.48E-06	7.41E-07
Me ¹⁹⁹ Hg	No DOC Cold	T0	3.53	0	0.00E+00	0.00E+00	3.53	2.94E-04	2.06E-06	1.03E-06

Me ¹⁹⁹ Hg	No DOC Cold	T1	3.19	0	0.00E+00	0.00E+00	3.19	2.66E- 04	1.86E- 06	9.31E- 07
Me ¹⁹⁹ Hg	No DOC Cold	T2	2.51	0	0.00E+00	0.00E+00	2.51	2.09E- 04	1.46E- 06	7.32E- 07
Me ¹⁹⁹ Hg	No DOC Cold	T3	3.34	0	0.00E+00	0.00E+00	3.34	2.78E- 04	1.95E- 06	9.73E- 07
Me ¹⁹⁹ Hg	No DOC Cold	T4	2.54	0	0.00E+00	0.00E+00	2.54	2.12E- 04	1.48E- 06	7.41E- 07
Me ¹⁹⁹ Hg	No DOC/No AC	T0	9.68	0	0.00E+00	0.00E+00	9.68	8.07E- 04	5.65E- 06	2.82E- 06
Me ¹⁹⁹ Hg	No DOC/No AC	T1	8.21	0	0.00E+00	0.00E+00	8.21	6.84E- 04	4.79E- 06	2.39E- 06
Me ¹⁹⁹ Hg	No DOC/No AC	T2	8.64	0	0.00E+00	0.00E+00	8.64	7.20E- 04	5.04E- 06	2.52E- 06
Me ¹⁹⁹ Hg	No DOC/No AC	T3	7.47	0	0.00E+00	0.00E+00	7.47	6.22E- 04	4.36E- 06	2.18E- 06
Me ¹⁹⁹ Hg	No DOC/No AC	T4	8.49	0	0.00E+00	0.00E+00	8.49	7.07E- 04	4.95E- 06	2.48E- 06

Table AII.S11. Modeling inputs for Hg_i speciation in isotherms.

Sample	Description	Note	Cl ⁻	HCO ₃ ⁻	Hg	Hg	SRHA	DOMRS	O/C	solids	pH
			(M)	(M)	(ng L ⁻¹)	(M)	(mg L ⁻¹)	(M)			
JS16_0121	PETG control	n/a	4.65E-02	7.50E-03	4.96	2.47E-11	0.00	0.00E+00	C	OFF	8.16
JS16_0122	PETG control	n/a	4.65E-02	7.50E-03	9.65	4.80E-11	0.00	0.00E+00	C	OFF	8.15
JS16_0123	PETG control	n/a	4.65E-02	7.50E-03	24.04	1.20E-10	0.00	0.00E+00	C	OFF	8.08
JS16_0124	PETG control	n/a	4.65E-02	7.50E-03	51.20	2.55E-10	0.00	0.00E+00	C	OFF	8.07
JS16_0125	PETG control	n/a	4.65E-02	7.50E-03	99.02	4.93E-10	0.00	0.00E+00	C	OFF	7.84
JS16_0151	²⁰¹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	4.87	2.42E-11	4.21	1.67E-07	C	OFF	8.38
JS16_0152	²⁰¹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	9.89	4.92E-11	8.91	3.54E-07	C	OFF	8.28
JS16_0153	²⁰¹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	25.51	1.27E-10	25.74	1.02E-06	C	OFF	8.20
JS16_0154	²⁰¹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	48.72	2.42E-10	49.15	1.95E-06	C	OFF	8.05
JS16_0155	²⁰¹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	95.81	4.77E-10	86.30	3.43E-06	C	OFF	7.92
JS16_0156	²⁰¹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	5.07	2.52E-11	4.39	1.74E-07	C	OFF	8.38
JS16_0157	²⁰¹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	9.71	4.83E-11	8.75	3.48E-07	C	OFF	8.26
JS16_0158	²⁰¹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	24.23	1.21E-10	24.45	9.72E-07	C	OFF	8.21
JS16_0159	²⁰¹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	49.71	2.47E-10	50.15	1.99E-06	C	OFF	8.04
JS16_0160	²⁰¹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	97.88	4.87E-10	88.17	3.50E-06	C	OFF	7.93
JS16_0171	AC+DOC first, then ²⁰¹ Hg	coal	4.65E-02	7.50E-03	5.03	2.50E-11	4.35	1.73E-07	C	OFF	8.50
JS16_0172	AC+DOC first, then ²⁰¹ Hg	coal	4.65E-02	7.50E-03	9.68	4.82E-11	8.72	3.47E-07	C	OFF	8.38
JS16_0173	AC+DOC first, then ²⁰¹ Hg	coal	4.65E-02	7.50E-03	24.10	1.20E-10	24.31	9.66E-07	C	OFF	8.31
JS16_0174	AC+DOC first, then ²⁰¹ Hg	coal	4.65E-02	7.50E-03	48.76	2.43E-10	49.19	1.95E-06	C	OFF	8.22
JS16_0175	AC+DOC first, then ²⁰¹ Hg	coal	4.65E-02	7.50E-03	98.17	4.88E-10	88.42	3.51E-06	C	OFF	8.08
JS16_0176	AC+DOC first, then ²⁰¹ Hg	coco	4.65E-02	7.50E-03	4.98	2.48E-11	4.31	1.71E-07	C	OFF	8.47
JS16_0177	AC+DOC first, then ²⁰¹ Hg	coco	4.65E-02	7.50E-03	10.26	5.10E-11	9.24	3.67E-07	C	OFF	8.45

JS16_0178	AC+DOC first, then ^{201}Hg	coco	4.65E-02	7.50E-03	24.69	1.23E-10	24.90	9.90E-07	C	OFF	8.35
JS16_0179	AC+DOC first, then ^{201}Hg	coco	4.65E-02	7.50E-03	49.38	2.46E-10	49.82	1.98E-06	C	OFF	8.22
JS16_0180	AC+DOC first, then ^{201}Hg	coco	4.65E-02	7.50E-03	96.69	4.81E-10	87.09	3.46E-06	C	OFF	8.11

Table AII.S12. Modeling outputs for Hg_i speciation in isotherms (results are split into two tables).

Sample ID	Description	Note	Hg(OH) ₂	HgClOH	HgCl ₄ ²⁻	HgCl ⁺	HgCl ₂	HgCl ₃ ⁻	HgHCO ₃ ⁺	Hg(CO ₃) ₂ ²⁻
JS16_012 1	PETG control	n/a	9.43E-13	6.50E-12	8.40E-13	5.27E-17	1.13E-11	5.16E-12	5.39E-19	9.03E-16
JS16_012 2	PETG control	n/a	1.76E-12	1.24E-11	1.64E-12	1.03E-16	2.20E-11	1.01E-11	1.06E-18	1.69E-15
JS16_012 3	PETG control	n/a	3.36E-12	2.78E-11	4.32E-12	2.71E-16	5.79E-11	2.66E-11	2.77E-18	3.21E-15
JS16_012 4	PETG control	n/a	6.85E-12	5.81E-11	9.24E-12	5.80E-16	1.24E-10	5.68E-11	5.93E-18	6.55E-15
JS16_012 5	PETG control	n/a	5.17E-12	7.45E-11	2.01E-11	1.26E-15	2.70E-10	1.24E-10	1.28E-17	4.86E-15
JS16_015 1	²⁰¹ Hg+DO C first, then AC	coal	8.99E-27	3.73E-26	2.91E-27	1.83E-31	3.90E-26	1.79E-26	1.87E-33	8.58E-30
JS16_015 2	²⁰¹ Hg+DO C first, then AC	coal	3.71E-27	1.94E-26	1.90E-27	1.19E-31	2.55E-26	1.17E-26	1.22E-33	3.55E-30
JS16_015 3	²⁰¹ Hg+DO C first, then AC	coal	1.08E-27	6.81E-27	8.03E-28	5.04E-32	1.08E-26	4.93E-27	5.16E-34	1.04E-30
JS16_015 4	²⁰¹ Hg+DO C first, then AC	coal	5.14E-28	4.57E-27	7.60E-28	4.77E-32	1.02E-26	4.68E-27	4.88E-34	4.91E-31
JS16_015 5	²⁰¹ Hg+DO C first, then AC	coal	3.08E-28	3.69E-27	8.29E-28	5.20E-32	1.11E-26	5.10E-27	5.30E-34	2.92E-31
JS16_015 6	²⁰¹ Hg+DO C first, then AC	coco	8.63E-27	3.58E-26	2.79E-27	1.75E-31	3.74E-26	1.71E-26	1.79E-33	8.23E-30
JS16_015 7	²⁰¹ Hg+DO C first, then AC	coco	3.71E-27	2.03E-26	2.08E-27	1.31E-31	2.79E-26	1.28E-26	1.34E-33	3.55E-30
JS16_015 8	²⁰¹ Hg+DO C first, then AC	coco	1.15E-27	7.04E-27	8.10E-28	5.08E-32	1.09E-26	4.98E-27	5.21E-34	1.10E-30
JS16_015 9	²⁰¹ Hg+DO C first, then AC	coco	5.01E-28	4.56E-27	7.76E-28	4.87E-32	1.04E-26	4.77E-27	4.98E-34	4.79E-31
JS16_016 0	²⁰¹ Hg+DO C first, then AC	coco	3.04E-28	3.55E-27	7.80E-28	4.89E-32	1.05E-26	4.80E-27	4.99E-34	2.88E-31
JS16_017 1	AC+DOC first, then ²⁰¹ Hg	coal	9.91E-27	3.12E-26	1.84E-27	1.16E-31	2.47E-26	1.13E-26	1.18E-33	9.39E-30
JS16_017 2	AC+DOC first, then ²⁰¹ Hg	coal	4.15E-27	1.72E-26	1.34E-27	8.42E-32	1.80E-26	8.24E-27	8.60E-34	3.96E-30
JS16_017 3	AC+DOC first, then ²⁰¹ Hg	coal	1.25E-27	6.08E-27	5.57E-28	3.49E-32	7.46E-27	3.42E-27	3.57E-34	1.19E-30
JS16_017 4	AC+DOC first, then ²⁰¹ Hg	coal	5.76E-28	3.46E-27	3.89E-28	2.44E-32	5.21E-27	2.39E-27	2.50E-34	5.52E-31
JS16_017 5	AC+DOC first, then ²⁰¹ Hg	coal	3.25E-28	2.70E-27	4.19E-28	2.63E-32	5.62E-27	2.58E-27	2.69E-34	3.11E-31
JS16_017 6	AC+DOC first, then ²⁰¹ Hg	coco	9.70E-27	3.27E-26	2.07E-27	1.30E-31	2.78E-26	1.27E-26	1.33E-33	9.22E-30
JS16_017 7	AC+DOC first, then ²⁰¹ Hg	coco	4.00E-27	1.59E-26	9.37E-28	5.88E-32	1.59E-26	7.30E-27	3.67E-31	1.12E-24

JS16_017 8	AC+DOC first, then ²⁰¹ Hg	coco	1.24E-27	5.77E-27	4.61E- 28	2.89E -32	6.74E- 27	3.09E -27	1.54E-31	2.96E-25
JS16_017 9	AC+DOC first, then ²⁰¹ Hg	coco	5.72E-28	3.31E-27	3.87E- 28	2.43E -32	4.81E- 27	2.20E -27	1.04E-31	1.04E-25
JS16_018 0	AC+DOC first, then ²⁰¹ Hg	coco	3.45E-28	2.43E-27	3.87E- 28	2.43E -32	4.30E- 27	1.97E -27	8.55E-32	4.71E-26

Table AII.S13. Modeling outputs for Hg_i speciation in isotherms (second of two parts).

Sample ID	HgCO ₃	Hg ²⁺	HgOH ⁺	Hg(OH) ₃ ⁻	Hg-(DOMRS) ₂	HgCl ₂ (s)	Hg ₃ -O ₂ CO ₃	mon-troydite	total Hg
JS16_0121	3.57E-15	1.35E-22	4.82E-18	2.01E-19	7.79E-20	1.30E-10	8.16E-28	4.11E-09	2.47E-11
JS16_0122	6.84E-15	2.64E-22	9.23E-18	3.67E-19	1.19E-19	2.54E-10	5.46E-27	7.69E-09	4.80E-11
JS16_0123	1.53E-14	6.94E-22	2.06E-17	5.95E-19	1.74E-19	6.68E-10	4.42E-26	1.46E-08	1.20E-10
JS16_0124	3.19E-14	1.48E-21	4.31E-17	1.19E-18	2.35E-19	1.43E-09	3.86E-25	2.99E-08	2.55E-10
JS16_0125	4.06E-14	3.23E-21	5.52E-17	5.28E-19	2.20E-19	3.11E-09	2.79E-25	2.26E-08	4.93E-10
JS16_0151	2.05E-29	4.68E-37	2.77E-32	3.18E-33	2.42E-11	4.49E-25	4.26E-70	3.93E-23	2.42E-11
JS16_0152	1.07E-29	3.06E-37	1.44E-32	1.04E-33	4.92E-11	2.94E-25	3.77E-71	1.62E-23	4.92E-11
JS16_0153	3.75E-30	1.29E-37	5.06E-33	2.53E-34	1.27E-10	1.24E-25	1.13E-72	4.73E-24	1.27E-10
JS16_0154	2.51E-30	1.22E-37	3.39E-33	8.52E-35	2.42E-10	1.18E-25	1.71E-73	2.25E-24	2.42E-10
JS16_0155	2.02E-30	1.33E-37	2.74E-33	3.78E-35	4.77E-10	1.28E-25	4.94E-74	1.35E-24	4.77E-10
JS16_0156	1.97E-29	4.49E-37	2.66E-32	3.05E-33	2.52E-11	4.31E-25	3.76E-70	3.77E-23	2.52E-11
JS16_0157	1.12E-29	3.35E-37	1.51E-32	9.95E-34	4.83E-11	3.22E-25	3.94E-71	1.62E-23	4.83E-11
JS16_0158	3.87E-30	1.30E-37	5.22E-33	2.74E-34	1.21E-10	1.25E-25	1.30E-72	5.00E-24	1.21E-10
JS16_0159	2.50E-30	1.25E-37	3.38E-33	8.11E-35	2.47E-10	1.20E-25	1.62E-73	2.19E-24	2.47E-10
JS16_0160	1.95E-30	1.25E-37	2.64E-33	3.81E-35	4.87E-10	1.21E-25	4.61E-74	1.32E-24	4.87E-10
JS16_0171	1.71E-29	2.97E-37	2.32E-32	4.63E-33	2.50E-11	2.85E-25	4.31E-70	4.33E-23	2.50E-11
JS16_0172	9.46E-30	2.16E-37	1.28E-32	1.47E-33	4.82E-11	2.07E-25	4.18E-71	1.81E-23	4.82E-11
JS16_0173	3.34E-30	8.95E-38	4.52E-33	3.76E-34	1.20E-10	8.60E-26	1.34E-72	5.44E-24	1.20E-10
JS16_0174	1.90E-30	6.25E-38	2.57E-33	1.41E-34	2.43E-10	6.01E-26	1.62E-73	2.51E-24	2.43E-10
JS16_0175	1.48E-30	6.73E-38	2.00E-33	5.77E-35	4.88E-10	6.48E-26	4.04E-74	1.42E-24	4.88E-10
JS16_0176	1.79E-29	3.34E-37	2.43E-32	4.23E-33	2.48E-11	3.20E-25	4.34E-70	4.23E-23	2.48E-11
JS16_0177	5.33E-27	9.37E-38	9.32E-33	1.48E-33	5.10E-11	1.84E-25	2.19E-68	1.75E-23	5.10E-11
JS16_0178	1.65E-27	6.21E-38	3.92E-33	3.92E-34	1.23E-10	7.77E-26	6.54E-70	5.41E-24	1.23E-10
JS16_0179	7.63E-28	7.23E-38	2.65E-33	1.46E-34	2.46E-10	5.54E-26	6.43E-71	2.50E-24	2.46E-10
JS16_0180	4.60E-28	9.01E-38	2.17E-33	7.19E-35	4.81E-10	4.96E-26	1.40E-71	1.50E-24	4.81E-10

Table AII.S14. Modeling inputs for MeHg speciation in isotherms.

Sample ID	Description	Note	Cl ⁻	HCO ₃ ⁻	MeHg	MeHg	SRHA	DOMRS	O/C	solids	pH
			(M)	(M)	(ng L ⁻¹)	(M)	(mg L ⁻¹)	(M)			
JS16_0126	PETG control	n/a	4.65E-02	7.50E-03	5.02	2.35E-11	0.00	0.00E+00	C	OFF	8.32
JS16_0127	PETG control	n/a	4.65E-02	7.50E-03	10.34	4.83E-11	0.00	0.00E+00	C	OFF	8.30
JS16_0128	PETG control	n/a	4.65E-02	7.50E-03	25.18	1.18E-10	0.00	0.00E+00	C	OFF	8.23
JS16_0129	PETG control	n/a	4.65E-02	7.50E-03	50.33	2.35E-10	0.00	0.00E+00	C	OFF	8.20
JS16_0130	PETG control	n/a	4.65E-02	7.50E-03	103.86	4.85E-10	0.00	0.00E+00	C	OFF	8.19
JS16_0161	Me ¹⁹⁹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	4.90	2.29E-11	4.24	1.69E-07	C	OFF	8.36
JS16_0162	Me ¹⁹⁹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	9.91	4.63E-11	8.93	3.55E-07	C	OFF	8.28
JS16_0163	Me ¹⁹⁹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	24.88	1.16E-10	25.10	9.98E-07	C	OFF	8.35
JS16_0164	Me ¹⁹⁹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	49.04	2.29E-10	49.47	1.97E-06	C	OFF	8.31
JS16_0165	Me ¹⁹⁹ Hg+DOC first, then AC	coal	4.65E-02	7.50E-03	99.52	4.65E-10	89.64	3.56E-06	C	OFF	8.18
JS16_0166	Me ¹⁹⁹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	5.09	2.38E-11	4.40	1.75E-07	C	OFF	8.44
JS16_0167	Me ¹⁹⁹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	10.09	4.72E-11	9.09	3.61E-07	C	OFF	8.45
JS16_0168	Me ¹⁹⁹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	24.28	1.13E-10	24.49	9.73E-07	C	OFF	8.38
JS16_0169	Me ¹⁹⁹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	48.65	2.27E-10	49.08	1.95E-06	C	OFF	8.33
JS16_0170	Me ¹⁹⁹ Hg+DOC first, then AC	coco	4.65E-02	7.50E-03	96.52	4.51E-10	86.94	3.46E-06	C	OFF	8.25
JS16_0181	DOC+AC first, then Me ¹⁹⁹ Hg	coal	4.65E-02	7.50E-03	5.00	2.33E-11	4.32	1.72E-07	C	OFF	8.51
JS16_0182	DOC+AC first, then Me ¹⁹⁹ Hg	coal	4.65E-02	7.50E-03	10.12	4.73E-11	9.12	3.62E-07	C	OFF	8.37
JS16_0183	DOC+AC first, then Me ¹⁹⁹ Hg	coal	4.65E-02	7.50E-03	24.59	1.15E-10	24.81	9.86E-07	C	OFF	8.36
JS16_0184	DOC+AC first, then Me ¹⁹⁹ Hg	coal	4.65E-02	7.50E-03	49.52	2.31E-10	49.96	1.99E-06	C	OFF	8.29
JS16_0185	DOC+AC first, then Me ¹⁹⁹ Hg	coal	4.65E-02	7.50E-03	100.49	4.70E-10	81.72	3.25E-06	C	OFF	8.28
JS16_0186	DOC+AC first, then Me ¹⁹⁹ Hg	coco	4.65E-02	7.50E-03	4.88	2.28E-11	4.22	1.68E-07	C	OFF	8.52
JS16_0187	DOC+AC first, then Me ¹⁹⁹ Hg	coco	4.65E-02	7.50E-03	9.85	4.60E-11	8.87	3.53E-07	C	OFF	8.50
JS16_0188	DOC+AC first, then Me ¹⁹⁹ Hg	coco	4.65E-02	7.50E-03	24.12	1.13E-10	24.33	9.67E-07	C	OFF	8.45
JS16_0189	DOC+AC first, then Me ¹⁹⁹ Hg	coco	4.65E-02	7.50E-03	49.29	2.30E-10	49.73	1.98E-06	C	OFF	8.44
JS16_0190	DOC+AC first, then Me ¹⁹⁹ Hg	coco	4.65E-02	7.50E-03	100.79	4.71E-10	81.96	3.26E-06	C	OFF	8.31

Table AII.S15. Modeling outputs for MeHg speciation in isotherms.

Sample ID	Description	Note	CH ₃ Hg ⁺	CH ₃ Hg-HCO ₃ ⁻	CH ₃ Hg-CO ₃ ²⁻	CH ₃ Hg-OH	(CH ₃ Hg) ₂ -OH ⁺	CH ₃ Hg-Cl	CH ₃ Hg-DOMRS	(CH ₃ H) ₂ S	total CH ₃ Hg
JS16_0126	PETG control	n/a	2.07E-15	4.60E-15	1.59E-13	1.09E-11	5.40E-24	1.25E-11	9.04E-19	4.17E-32	2.35E-11
JS16_0127	PETG control	n/a	4.34E-15	9.67E-15	3.19E-13	2.18E-11	2.27E-23	2.61E-11	9.50E-19	1.84E-31	4.83E-11
JS16_0128	PETG control	n/a	1.14E-14	2.54E-14	7.13E-13	4.87E-11	1.33E-22	6.85E-11	9.78E-19	1.26E-30	1.18E-10
JS16_0129	PETG control	n/a	2.33E-14	5.20E-14	1.36E-12	9.31E-11	5.21E-22	1.40E-10	9.88E-19	5.30E-30	2.35E-10
JS16_0130	PETG control	n/a	4.86E-14	1.08E-13	2.78E-12	1.90E-10	2.21E-21	2.93E-10	9.94E-19	2.30E-29	4.85E-10
JS16_0161	Me ¹⁹⁹ Hg+ DOC first, then AC	coal	3.83E-20	8.54E-20	2.19E-18	1.49E-16	1.37E-33	2.31E-16	2.29E-11	1.43E-41	2.29E-11
JS16_0162	Me ¹⁹⁹ Hg+ DOC first, then AC	coal	3.10E-20	6.91E-20	2.18E-18	1.49E-16	1.11E-33	1.87E-16	4.63E-11	9.37E-42	4.63E-11
JS16_0163	Me ¹⁹⁹ Hg+ DOC first, then AC	coal	2.43E-20	5.40E-20	2.00E-18	1.37E-16	7.98E-34	1.46E-16	1.16E-10	5.75E-42	1.16E-10
JS16_0164	Me ¹⁹⁹ Hg+ DOC first, then AC	coal	2.62E-20	5.82E-20	1.97E-18	1.34E-16	8.44E-34	1.57E-16	2.29E-10	6.66E-42	2.29E-10
JS16_0165	Me ¹⁹⁹ Hg+ DOC first, then AC	coal	3.77E-20	8.39E-20	2.10E-18	1.44E-16	1.30E-33	2.27E-16	4.65E-10	1.38E-41	4.65E-10
JS16_0166	Me ¹⁹⁹ Hg+ DOC first, then AC	coco	2.42E-20	5.37E-20	2.45E-18	1.68E-16	9.76E-34	1.46E-16	2.38E-11	5.71E-42	2.38E-11
JS16_0167	Me ¹⁹⁹ Hg+ DOC first, then AC	coco	2.29E-20	5.07E-20	2.37E-18	1.62E-16	8.91E-34	1.38E-16	4.72E-11	5.10E-42	4.72E-11
JS16_0168	Me ¹⁹⁹ Hg+ DOC first, then AC	coco	2.30E-20	5.11E-20	2.03E-18	1.39E-16	7.66E-34	1.38E-16	1.13E-10	5.15E-42	1.13E-10
JS16_0169	Me ¹⁹⁹ Hg+ DOC first, then AC	coco	2.52E-20	5.62E-20	1.99E-18	1.36E-16	8.23E-34	1.52E-16	2.27E-10	6.20E-42	2.27E-10
JS16_0170	Me ¹⁹⁹ Hg+ DOC first, then AC	coco	3.28E-20	7.31E-20	2.15E-18	1.47E-16	1.16E-33	1.98E-16	4.51E-10	1.05E-41	4.51E-10
JS16_0181	DOC+AC first, then Me ¹⁹⁹ Hg	coal	2.14E-20	4.74E-20	2.54E-18	1.74E-16	8.96E-34	1.29E-16	2.33E-11	4.46E-42	2.33E-11
JS16_0182	DOC+AC first, then Me ¹⁹⁹ Hg	coal	2.63E-20	5.86E-20	2.27E-18	1.55E-16	9.83E-34	1.59E-16	4.73E-11	6.75E-42	4.73E-11
JS16_0183	DOC+AC first, then Me ¹⁹⁹ Hg	coal	2.39E-20	5.32E-20	2.02E-18	1.38E-16	7.93E-34	1.44E-16	1.15E-10	5.58E-42	1.15E-10
JS16_0184	DOC+AC first, then Me ¹⁹⁹ Hg	coal	2.71E-20	6.04E-20	1.95E-18	1.33E-16	8.66E-34	1.63E-16	2.31E-10	7.15E-42	2.31E-10
JS16_0185	DOC+AC first, then Me ¹⁹⁹ Hg	coal	3.44E-20	7.66E-20	2.42E-18	1.65E-16	1.36E-33	2.07E-16	4.70E-10	1.15E-41	4.70E-10
JS16_0186	DOC+AC first, then Me ¹⁹⁹ Hg	coco	2.11E-20	4.67E-20	2.56E-18	1.76E-16	8.90E-34	1.27E-16	2.28E-11	4.33E-42	2.28E-11
JS16_0187	DOC+AC first, then Me ¹⁹⁹ Hg	coco	2.09E-20	4.64E-20	2.43E-18	1.67E-16	8.38E-34	1.26E-16	4.60E-11	4.27E-42	4.60E-11
JS16_0188	DOC+AC first, then Me ¹⁹⁹ Hg	coco	2.05E-20	4.54E-20	2.12E-18	1.45E-16	7.12E-34	1.23E-16	1.13E-10	4.07E-42	1.13E-10
JS16_0189	DOC+AC first, then Me ¹⁹⁹ Hg	coco	2.07E-20	4.59E-20	2.09E-18	1.43E-16	7.12E-34	1.24E-16	2.30E-10	4.17E-42	2.30E-10
JS16_0190	DOC+AC first, then Me ¹⁹⁹ Hg	coco	3.25E-20	7.24E-20	2.45E-18	1.67E-16	1.30E-33	1.96E-16	4.71E-10	1.03E-41	4.71E-10

Table AII.S16. Modeling inputs for speciation in slurry microcosms

Treatment	pH	H ⁺ (M)	Fe (M)	HS ⁻ (M)	Cl ⁻ (M)	Hg (M)	MeHg (M)	RS (thiols) (M)	²⁰¹ Hg (M)
No DOM/No AC	7.20	6.38E-08	9.00E-06	4.81E-04	1.77E-02	2.46E-10	6.83E-11	2.65E-06	1.423E-09
No DOM	7.14	7.21E-08	2.11E-06	4.45E-04	2.23E-02	5.40E-11	1.16E-11	8.86E-07	2.493E-11
Low DOM	7.32	4.80E-08	2.20E-06	4.71E-04	2.07E-02	6.08E-11	1.08E-11	2.04E-06	2.074E-10
Mid DOM	7.48	3.32E-08	2.06E-06	4.50E-04	1.84E-02	8.31E-11	9.06E-12	2.37E-06	4.041E-10
High DOM	6.80	1.58E-07	4.92E-06	4.61E-04	1.62E-02	1.13E-10	1.46E-11	1.66E-06	4.353E-10

Table AII.S17. Solid-water partitioning in slurry microcosms.

Treatment	Hg K _d	Hg log K _d	²⁰¹ Hg K _d	²⁰¹ Hg log K _D	native MeHg K _d	native MeHg log K _d	Me ¹⁹⁹ Hg K _d	Me ¹⁹⁹ Hg log K _d
No DOC/No AC	1.48E+05	5.17	1.18E+04	4.07	7.06E+03	3.85	1.25E+03	3.10
No DOC Cold	1.82E+06	6.26	6.28E+05	5.80	5.92E+04	4.77	2.35E+04	4.37
Low DOC Cold	1.69E+06	6.23	3.99E+04	4.60	6.18E+04	4.79	2.12E+04	4.33
Mid DOC Cold	1.35E+06	6.13	2.80E+04	4.45	7.76E+04	4.89	2.50E+04	4.40
High DOC Cold	1.09E+06	6.04	2.62E+04	4.42	5.10E+04	4.71	1.82E+04	4.26

Table AII.S18. Estimates of K_{AC} in slurry microcosms.

		K _d	log K _d
native MeHg	unamended	7.06E+03	3.85
	amended	5.92E+04	4.77
	K _{AC}	1.05E+06	6.02
native Hg	unamended	1.48E+05	5.17
	amended	1.82E+06	6.26
	K _{AC}	3.35E+07	7.53

		K _d	log K _d
Me ¹⁹⁹ Hg	unamended	1.25E+03	3.10
	amended	2.35E+04	4.37
	K _{AC}	4.45E+05	5.65
²⁰¹ Hg	unamended	1.18E+04	4.07
	amended	6.28E+05	5.80
	K _{AC}	1.23E+07	7.09

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Supplemental Information to the Article:

Development of a novel equilibrium passive sampling device for methylmercury in sediment and soil porewaters

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Contains: 23 pages of material, including detailed analytical methods, 11 tables, six figures, and references.

Table AIII.S1. Additional reactions used in MINEQL+ equilibrium speciation modeling.

Two components were added to the software's database: MeHg (+1 charge), and DOMRS, representing a model reduced exocyclic sulfur binding site in Suwannee River Humic Acid (-1 charge). DOMRS site densities were estimated from DOC measurements with the following equation, under the assumption that DOM characteristics were similar to SRHA¹⁻³:

$$[\text{DOMRS}] = \frac{\text{mg DOC}}{\text{L}} \times \frac{\text{mg SRHA}}{0.5263 \text{ mg DOC}} \times \frac{0.0054 \text{ mg S}}{\text{mg SRHA}} \times \frac{0.236 \text{ mg reduced exocyclic S}}{\text{mg S}} \times \frac{\text{mol reduced exocyclic S}}{32065 \text{ mg reduced exocyclic S}}$$

Reaction	log K	Reference
$\text{H}^+ + \text{DOMRS}^- \rightleftharpoons \text{DOMRSH}$	9.000	4, 5
$\text{MeHg}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{MeHgSO}_4^-$	0.940	6
$\text{MeHg}^+ + \text{Br}^- \rightleftharpoons \text{MeHgBr}$	6.620	7
$\text{MeHg}^+ + \text{Cl}^- \rightleftharpoons \text{MeHgCl}$	5.400	8
$\text{MeHg}^+ + \text{F}^- \rightleftharpoons \text{MeHgF}$	1.500	7
$\text{MeHg}^+ + \text{DOMRS}^- \rightleftharpoons \text{MeHgDOMRS}$	17.500	4, 5, 9, 10
$2\text{MeHg}^+ + \text{H}_2\text{O} \rightleftharpoons (\text{MeHg})_2\text{OH}^+ + \text{H}^+$	-2.150	11
$\text{MeHg}^+ + \text{H}_2\text{O} \rightleftharpoons \text{MeHgOH} + \text{H}^+$	-4.500	8
$\text{MeHg}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{MeHgCO}_3^-$	6.100	6
$\text{MeHg}^+ + \text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{MeHgHCO}_3$	12.950	8
$\text{MeHg}^+ + \text{HS}^- \rightleftharpoons \text{MeHgS}^- + \text{H}^+$	7.300	7
$\text{MeHg}^+ + \text{HS}^- \rightleftharpoons \text{MeHgSH}$	14.500	12
$2\text{MeHg}^+ + \text{HS}^- \rightleftharpoons (\text{MeHg})_2\text{S} + \text{H}^+$	23.600	7, 8

Analytical Methods. MeHg samples were distilled in H₂SO₄ as described by Horvat et al.¹³ and analyzed following the method outlined by Mitchell and Gilmour.¹⁴ Briefly, a spike consisting of enriched, stable Hg isotope (Oak Ridge National Laboratories) was added, the samples were buffered with acetate, derivatized with sodium tetraethylborate to facilitate volatilization, purged and concentrated on a Tenax trap with a Brooks/Rand autosampler, thermally desorbed, separated on an OV-3/Chromosorb column, and introduced into a Perkin Elmer Elan DRC II ICP-MS for detection. THg was also measured as in Mitchell and Gilmour.¹⁴ Concentrations were determined by digesting samples in 7:4 HNO₃:H₂SO₄, heating to achieve loss of color, oxidizing organics with BrCl, reducing Hg(II) to Hg(0) with SnCl₂, and analyzing via ICP-MS. Isotopic dilution calculations were performed to enhance the accuracy and precision of MeHg and THg measurements.¹⁴ MeHg quality assurance data are summarized in Table AIII.S2. Sulfide was measured by mixing samples 1:1 with sulfide antioxidant buffer (2.0 M NaOH, 0.2 M ascorbic acid, and 0.2 M Na₂EDTA in deoxygenated, deionized water prepared anaerobically) and analyzing with a sulfide ion-selective electrode calibrated by lead titration of a saturated sulfide standard. DOC was measured on a Shimadzu organic carbon analyzer. Cations were measured on a Perkin Elmer Optima 8300 ICP-OES. Where not directly measured, major ion concentrations used in speciation modeling were estimated from the chemical composition of Instant Ocean provided by the manufacturer.¹⁵

Table AIII.S2. Quality assurance data for MeHg analyses in this work. Analysis was done by isotope dilution ICP-MS, i.e. with internal stable isotope standards. Relative percent differences (RPD) are for duplicate analyses of the same prepared sample. CRMs were NIST 1566b oyster tissue. Detection limits were estimated as three times the standard error of blanks across samples.

matrix	RPD duplicates	CRM recovery	ID spike recovery	distillation blanks	DL	units
water	$6.2 \pm 2.4\%$	$95.8 \pm 1.9\%$	$70.3 \pm 1.1\%$	0.52 ± 0.28	1.02 ± 0.27	ng L ⁻¹
sediment/ soil	$22.6 \pm 0.7\%$	$105.1 \pm 4.2\%$	$59.8 \pm 3.8\%$	0.51 ± 0.13	66.3 ± 11.2	ng kgdw ⁻¹
ag+AC	n/a	$97.3 \pm 2.2\%$	$54.8 \pm 2.3\%$	0.06 ± 0.01	228.66 ± 52.53	ng kgww ⁻¹
PET+Cys	n/a	$99.7 \pm 4.4\%$	$61.1\% \pm 3.4\%$	0.05 ± 0.01	188.63 ± 27.84	ng kgww ⁻¹

Polymer Permeability. Using MeHg partitioning coefficients for bare AC¹⁶ and Thiol-SAMMS (this work), we conducted a simple, mass-weighted partitioning analysis for the samplers containing suspensions of these sorbent materials, as follows:

$$K_{ps,predicted} = f_{polymer}K_{polymer} + f_{sorbent}K_{sorbent} \quad (AIII.S1)$$

where f is the fractional contribution of each component to the total mass of the material. Because these calculations involved K values separated by multiple orders of magnitude, they were accompanied by substantial uncertainty. Even so, a comparison of measured K_{ps} to $K_{ps,predicted}$ provided a semiquantitative indication of the relative contributions of internal diffusion and surface adsorption to the overall mechanisms of sampler accumulation (Table AIII.S3). Notably, the agarose-based samplers performed more closely to model predictions than did the PVDF-based samplers, indicating that the former were more permeable and amenable to suffusion by MeHgOH. Indeed, MeHg species are known to pass readily through agarose, which is sometimes used as the diffusive gel in DGT samplers.^{17, 18} A diffusive mechanism for ag+AC was confirmed in a subsequent kinetics experiment.

In an attempt to enhance the permeability of PVDF samplers, variants were prepared with either water or 1:1 methanol:water as nonsolvent to produce contrasting membrane pore structures.¹⁹ The measured partitioning by the methanol:water-prepared sampler, which was formulated to encourage a more globular microstructure with fewer macrovoids, was somewhat greater than that of the water-prepared sampler ($\log K_{ps} = 3.58$ vs. 3.24). However, both remained well below their model-predicted partitioning, likely due to the dense outer skin that is characteristic of PVDF membranes regardless of the nonsolvent used in preparation.¹⁹ Thus, it appears likely that partitioning by all of the PVDF

samplers in this study was dominated by surface adsorption, and that most of the included sorbent particles were not accessed by MeHgOH. An analogous method to modulate the permeability of agarose was also explored. Alternate versions of ag+AC and ag+SAMMS were prepared with a polyethylene glycol dopant to promote macroporosity in the gel (agPEG+AC and agPEG+SAMMS).²⁰ The effects of this modification on isotherm partitioning were ambiguous. While their measured and predicted K_{ps} values were in better agreement than those of ag+AC and ag+SAMMS, this was due to increased partitioning by agPEG+AC on one hand and decreased partitioning by agPEG+SAMMS on the other; no overall trend was apparent. Additionally, the agPEG gels themselves were slushier and less mechanically robust than standard agarose, making them poorly suited for deployment in sediment and soil, so the idea was abandoned.

Table AIII.S3. Comparison of measured sampler partitioning in isotherms to mass-weighted predictions based on fractional compositions.

abbreviation	material	ref.	$\log K_{ps}$	r^2	f_{polymer}	f_{sorbent}	$\log K_{ps,\text{predicted}}$	$K_{ps}:$ $K_{ps,\text{predicted}}$
ag	agarose	21	2.59	0.96	n/a	n/a	n/a	n/a
agPEG	agarose doped with polyethylene glycol and glycerol	20	2.68	0.98	n/a	n/a	n/a	n/a
PVDFw	poly(vinylidene fluoride) prepared with water nonsolvent	22	2.29	0.13	n/a	n/a	n/a	n/a
AC	activated carbon	n/a	5.48	0.97	n/a	n/a	n/a	n/a
ag+AC	activated carbon suspended in agarose	21	3.45	1.0	0.96	0.04	4.1	0.23
agPEG+AC	activated carbon suspended in PEG-doped agarose	20	3.55	0.98	0.97	0.03	3.5	1.26
PVDFw+AC	AC suspended in PVDF prepared with water nonsolvent	22	3.24	0.98	0.89	0.11	4.5	0.05
PVDFm+AC	AC suspended in PVDF prepared with 1:1 methanol:water nonsolvent	22	3.58	0.98	0.89	0.11	4.5	0.11

Table AIII.S4. Raw data and calculations for initial passive sampler kinetics experiment.

All concentrations are of MeHg. Mass balances in samples showed loss of MeHg over time, especially in isotherms without added DOM. This resulted in artificially reduced C_w at later time points and partitioning that surpassed the 14-d K_{ps} values generated in screening isotherms. Mass balances in MeHgDOM samples were somewhat more favorable, indicating a preservative effect of either the DOM or the accompanying buffer.

sorbate	sampler	t (min)	C_w (ng L^{-1})	C_{ps} (ng kg^{-1})	ng on ps	ng in water	mass bal.	% recov.	$C_{ps}:C_w$	log ($C_{ps}:C_w$)	frac. equil. vs. isotherm
MeHgOH	ag+AC	1411	1.75	666	0.018	0.087	0.106	46%	381	2.58	0.14
MeHgOH	ag+AC	10029	0.16	2210	0.021	0.008	0.028	12%	13984	4.15	4.96
MeHgOH	ag+AC	20077	0.10	1042	0.017	0.005	0.021	9%	10582	4.02	3.75
MeHgOH	ag+AC	40250	0.03	1799	0.010	0.002	0.012	5%	56340	4.75	19.99
MeHgOH	PET+Cys	1390	3.13	977	0.017	0.159	0.176	76%	312	2.49	0.06
MeHgOH	PET+Cys	10008	0.12	1184	0.021	0.006	0.026	11%	9937	4.00	1.85
MeHgOH	PET+Cys	20056	0.06	1559	0.025	0.003	0.028	12%	25002	4.40	4.66
MeHgOH	PET+Cys	40231	0.09	1281	0.017	0.004	0.021	9%	14575	4.16	2.71
MeHgDOM	ag+AC	433	11.22	806	0.010	0.566	0.576	58%	72	1.86	0.11
MeHgDOM	ag+AC	1405	6.42	287	0.007	0.330	0.337	34%	45	1.65	0.07
MeHgDOM	ag+AC	10018	12.56	1370	0.024	0.634	0.657	66%	109	2.04	0.16
MeHgDOM	ag+AC	20067	8.69	813	0.016	0.442	0.458	46%	93	1.97	0.14
MeHgDOM	ag+AC	40240	3.43	2049	0.034	0.175	0.209	21%	597	2.78	0.88
MeHgDOM	ag+AC	79404	0.85	554	0.012	0.043	0.055	5%	651	2.81	0.96
MeHgDOM	PET+Cys	429	11.30	2155	0.048	0.569	0.617	62%	191	2.28	0.10
MeHgDOM	PET+Cys	1389	15.00	899	0.020	0.767	0.787	79%	60	1.78	0.03
MeHgDOM	PET+Cys	10001	2.57	400	0.009	0.129	0.138	14%	155	2.19	0.08
MeHgDOM	PET+Cys	20050	6.40	1441	0.019	0.328	0.347	35%	225	2.35	0.12
MeHgDOM	PET+Cys	40223	2.14	825	0.017	0.104	0.121	12%	386	2.59	0.20
MeHgDOM	PET+Cys	79388	0.48	1997	0.022	0.024	0.047	5%	4139	3.62	2.12

Table AIII.S5. Mass balance data for ag+AC thick/thin sampler kinetics experiment. All concentrations are of MeHg. All samples were spiked to an initial concentration of 50 ng L⁻¹. Average fractional recovery was 102 ± 7% (s.d. among all 30 samples).

time pt.	ag+AC	g water	final C _w (ng L ⁻¹)	ng in water	ng in sampler	total ng	frac. recov.
0	none	37.437	45.77	1.713	0.000	1.713	92%
0	thick	40.317	48.76	1.966	0.018	1.984	98%
0	thin	39.320	49.78	1.957	0.022	1.979	101%
1	none	36.519	48.25	1.762	0.000	1.762	97%
1	thick	38.434	47.71	1.834	0.028	1.862	97%
1	thin	37.636	48.59	1.829	0.040	1.869	99%
1	none	39.413	48.92	1.928	0.000	1.928	98%
1	thick	39.840	45.99	1.832	0.028	1.860	93%
1	thin	37.262	46.44	1.730	0.037	1.767	95%
2	none	35.790	51.99	1.861	0.000	1.861	104%
2	thick	38.035	50.68	1.928	0.031	1.958	103%
2	thin	39.596	50.66	2.006	0.050	2.056	104%
3	none	37.717	48.47	1.828	0.000	1.828	97%
3	thick	39.623	49.97	1.980	0.066	2.046	103%
3	thin	38.236	47.71	1.824	0.096	1.920	100%
4	none	36.918	49.62	1.832	0.000	1.832	99%
4	thick	38.405	51.84	1.991	0.165	2.156	112%
4	thin	39.172	50.90	1.994	0.222	2.216	113%
5	none	39.288	48.11	1.890	0.000	1.890	96%
5	thick	39.138	42.42	1.660	0.240	1.900	97%
5	thin	39.306	49.67	1.952	0.432	2.384	121%
5	none	39.027	51.73	2.019	0.000	2.019	103%
5	thick	40.596	52.98	2.151	0.237	2.388	118%
5	thin	39.471	44.78	1.768	0.293	2.060	104%
6	none	37.938	45.68	1.733	0.000	1.733	91%
6	thick	40.371	39.30	1.586	0.518	2.104	104%
6	thin	39.435	36.16	1.426	0.607	2.033	103%
7	none	40.326	49.90	2.012	0.000	2.012	100%
7	thick	38.901	32.21	1.253	0.297	1.550	80%
7	thin	38.012	33.87	1.288	0.308	1.596	84%

Table AIII.S6. Raw data and calculations for MeHg AC kinetics and desorption experiment. All concentrations are of MeHg.

sorbent	time pt.	rep	t (h)	C _w (ng L ⁻¹)	mtot (ng)	m in water (ng)	frac. as carry-over	ng on AC	mg AC	C _{AC} (ng kg ⁻¹)	C _{AC} :C _w (L kg ⁻¹)	avg. log K
none	a1	1	0.08	6.60	0.976	0.32	n/a	n/a	n/a	n/a	n/a	
none	a1	2	0.08	10.44	0.989	0.52	n/a	n/a	n/a	n/a	n/a	
CAC-Coal	a1	1	0.10	90.81	11.762	4.27	n/a	7.490	10.70	699961	7708	
CAC-Coal	a1	2	0.10	61.80	13.103	3.24	n/a	9.864	11.61	849629	13749	4.03
none	a2	1	0.60	8.42	0.986	0.41	n/a	n/a	n/a	n/a	n/a	
none	a2	2	0.60	9.84	1.037	0.51	n/a	n/a	n/a	n/a	n/a	
CAC-Coal	a2	1	0.57	33.52	12.505	1.68	n/a	10.828	10.75	1007266	30054	
CAC-Coal	a2	2	0.58	69.52	12.658	3.52	n/a	9.138	11.89	768530	11055	4.31
none	a3	1	4.60	7.74	0.982	0.38	n/a	n/a	n/a	n/a	n/a	
none	a3	2	4.62	9.94	1.013	0.50	n/a	n/a	n/a	n/a	n/a	
CAC-Coal	a3	1	4.67	17.57	12.916	0.91	n/a	12.008	10.90	1101662	62691	
CAC-Coal	a3	2	4.67	19.64	12.732	1.00	n/a	11.732	11.33	1035469	52715	
CAC-Coal	a3	3	4.68	21.98	12.606	1.11	n/a	11.498	10.84	1060663	48262	4.74
none	a4	1	47.63	10.12	0.987	0.50	n/a	n/a	n/a	n/a	n/a	
none	a4	2	47.65	10.05	1.009	0.51	n/a	n/a	n/a	n/a	n/a	
CAC-Coal	a4	1	47.67	7.42	12.670	0.38	n/a	12.294	10.31	1192438	160639	
CAC-Coal	a4	2	47.68	9.97	12.872	0.51	n/a	12.359	9.95	1242066	124554	
CAC-Coal	a4	3	47.68	9.88	12.378	0.49	n/a	11.888	11.74	1012640	102455	5.11
none	d1	1	0.08	0.22	0.657	0.01	0.27	n/a	n/a	n/a	n/a	
none	d1	2	0.08	0.23	0.476	0.01	0.34	n/a	n/a	n/a	n/a	
CAC-Coal	d1	1	0.08	3.73	7.694	0.19	1.10	7.509	10.70	701737	188322	
CAC-Coal	d1	2	0.10	5.77	10.044	0.29	0.61	9.749	11.61	839700	145601	5.27
none	d2	1	0.57	0.23	0.574	0.01	0.25	n/a	n/a	n/a	n/a	
none	d2	2	0.57	0.26	0.531	0.01	0.32	n/a	n/a	n/a	n/a	
CAC-Coal	d2	1	0.53	3.37	10.878	0.17	0.29	10.710	10.75	996271	295649	
CAC-Coal	d2	2	0.53	8.86	9.259	0.46	0.26	8.796	11.89	739792	83479	5.28
none	d3	1	3.58	0.29	0.606	0.01	0.26	n/a	n/a	n/a	n/a	
none	d3	2	3.60	0.30	0.513	0.01	0.23	n/a	n/a	n/a	n/a	
CAC-Coal	d3	1	3.58	6.49	12.043	0.31	0.11	11.731	10.90	1076277	165899	
CAC-Coal	d3	2	3.60	10.06	11.777	0.49	0.09	11.284	11.33	995906	98970	
CAC-Coal	d3	3	3.60	10.08	11.536	0.50	0.08	11.041	10.84	1018515	101051	5.09
none	d4	1	43.28	0.24	0.493	0.01	0.43	n/a	n/a	n/a	n/a	
none	d4	2	43.28	0.27	0.505	0.01	0.26	n/a	n/a	n/a	n/a	
CAC-Coal	d4	1	43.30	1.62	12.312	0.08	0.22	12.231	10.31	1186325	733212	
CAC-Coal	d4	2	43.32	1.96	12.376	0.10	0.18	12.278	9.95	1233927	630749	
CAC-Coal	d4	3	43.33	1.26	11.906	0.07	0.25	11.835	11.74	1008112	798736	5.86

Table AIII.S7. Raw data and calculations for Hg_i AC kinetics and desorption

experiment. All concentrations are of Hg_i.

sorbent	time pt.	rep	t (h)	C _w (ng L ⁻¹)	mtot (ng)	m in water (ng)	frac. as carry-over	ng on AC	mg AC	C _{AC} (ng kg ⁻¹)	C _{AC} :C _w (L kg ⁻¹)	avg. log K
none	a1	1	0.08	11.50	2.411	0.55	n/a	1.857	n/a	n/a	n/a	
none	a1	2	0.08	16.79	2.578	0.87	n/a	1.713	n/a	n/a	n/a	
CAC-Coal	a1	1	0.08	275.81	249.045	13.74	n/a	235.307	10.85	21687300	78631	
CAC-Coal	a1	2	0.12	123.07	244.370	6.01	n/a	238.355	11.90	20029845	162754	
CAC-Coal	a1	3	0.08	46.75	255.985	2.39	n/a	253.591	15.53	16329124	349250	5.29
none	a2	1	0.52	7.00	2.465	0.35	n/a	2.119	n/a	n/a	n/a	
none	a2	2	0.52	7.24	2.536	0.37	n/a	2.169	n/a	n/a	n/a	
CAC-Coal	a2	1	0.48	5.43	249.790	0.27	n/a	249.519	10.78	23146463	4264877	
CAC-Coal	a2	2	0.48	3.94	242.045	0.19	n/a	241.854	10.47	23099726	5858536	
CAC-Coal	a2	3	0.50	6.07	250.410	0.30	n/a	250.106	9.46	26438249	4353121	6.68
none	a3	1	4.32	11.63	2.497	0.58	n/a	1.916	n/a	n/a	n/a	
none	a3	2	4.32	19.26	2.523	0.97	n/a	1.552	n/a	n/a	n/a	
CAC-Coal	a3	1	4.33	9.51	255.325	0.49	n/a	254.839	11.28	22592138	2375327	
CAC-Coal	a3	2	4.35	11.97	249.750	0.60	n/a	249.152	12.24	20355561	1700461	
CAC-Coal	a3	3	4.38	16.34	249.340	0.82	n/a	248.525	10.89	22821393	1396340	6.26
none	a4	1	47.57	4.68	2.432	0.23	n/a	2.204	n/a	n/a	n/a	
none	a4	2	47.58	15.43	2.554	0.79	n/a	1.766	n/a	n/a	n/a	
CAC-Coal	a4	1	47.57	1.71	246.040	0.08	n/a	245.956	13.23	18590770	10876228	
CAC-Coal	a4	2	47.57	1.36	247.125	0.07	n/a	247.058	9.36	26395060	19401360	
CAC-Coal	a4	3	47.60	8.40	255.055	0.43	n/a	254.626	10.16	25061642	2981984	7.04
none	d1	1	0.08	1.18	1.861	0.06	0.07	n/a	n/a	n/a	n/a	
none	d1	2	0.10	0.89	1.719	0.05	0.13	n/a	n/a	n/a	n/a	
CAC-Coal	d1	1	0.08	10.72	236.095	0.57	1.38	235.526	10.85	21707439	2024606	
CAC-Coal	d1	2	0.10	10.76	238.690	0.60	0.55	238.086	11.90	20007199	1859099	
CAC-Coal	d1	3	0.10	29.23	253.730	1.57	0.09	252.155	15.53	16236656	555568	6.17
CAC-Coal	d2	1	0.58	17.11	249.526	0.85	0.01	248.676	10.78	23068300	1347896	
CAC-Coal	d2	3	0.60	6.12	250.116	0.29	0.04	249.828	9.46	26408852	4316890	6.45
none	d3	1	3.78	0.59	1.920	0.03	0.06	n/a	n/a	n/a	n/a	
none	d3	2	3.82	0.69	1.559	0.03	0.04	n/a	n/a	n/a	n/a	
CAC-Coal	d3	1	3.82	8.19	254.864	0.45	0.03	254.413	11.28	22554311	2754905	
CAC-Coal	d3	2	3.83	8.01	249.185	0.40	0.08	248.781	12.24	20325208	2538295	
CAC-Coal	d3	3	3.82	14.17	248.582	0.73	0.09	247.853	10.89	22759688	1606712	6.36
none	d4	1	43.22	0.73	2.206	0.04	0.12	n/a	n/a	n/a	n/a	
none	d4	2	43.23	0.97	1.773	0.05	0.11	n/a	n/a	n/a	n/a	
CAC-Coal	d4	2	43.28	0.56	247.061	0.03	1.24	247.034	9.36	26392487	47329082	
CAC-Coal	d4	3	43.30	0.66	254.640	0.04	0.19	254.600	10.16	25059095	38016674	7.63

Table AIII.S8. Raw data and calculations from sediment and soil slurry experiment at d
0. All concentrations are of MeHg.

matrix	rep	sampler	sulfide	pH	C _s	C _{pw}	log K _d
			(μM)		(ng kgdw ⁻¹)	(ng L ⁻¹)	log (L kgdw ⁻¹)
sediment	1	n/a	0.69	7.06	945	0.5	3.31
sediment	2	n/a	0.69	6.98	1149	0.3	3.55
sediment	3	n/a	0.69	6.80	993	0.5	3.33
soil	1	n/a	267.00	7.04	74877	93.1	2.91
soil	2	n/a	270.92	7.07	45118	90.6	2.70
soil	3	n/a	268.95	7.04	44690	79.6	2.75

Table AIII.S9. Raw data and calculations from sediment and soil slurry experiment at d
20. All concentrations are of MeHg. *Excluded from calculations for failing Q-test.

matrix	rep	sampler	sulfide	pH	C _s	C _{pw}	log K _d	C _{ps}	pw pred. w. K _{DOM}	avg.	std. error	log K _{ps}
			(μM)		(ng kgdw ⁻¹)	(ng L ⁻¹)	log (L kgdw ⁻¹)	(ng kg ⁻¹)	(ng L ⁻¹)	(ng L ⁻¹)	(ng L ⁻¹)	log (L kg ⁻¹)
sediment	1	ag+AC	0.09	6.88	554	0.58*	n.d.	58	0.09			n.d.
sediment	2	ag+AC	0.05	7.10	562	0.13	3.64	59	0.09	0.09	0.00	2.66
sediment	1	ag+SAMMS	0.07	7.24	518	0.19	3.44	116	0.06			2.79
sediment	2	ag+SAMMS	0.08	7.30	614	0.10	3.78	92	0.05	0.05	0.01	2.95
sediment	1	PET+Cys	0.07	7.25	587	0.09	3.83	289	0.15			3.52
sediment	2	PET+Cys	0.05	7.13	623	0.09	3.86	10	0.00	0.08	0.07	2.05
soil	1	ag+AC	0.54	7.14	44049	8.07	3.74	19433	28.74			3.38
soil	2	ag+AC	0.87	7.10	48468	7.96	3.78	22123	32.72	30.73	1.99	3.44
soil	1	ag+SAMMS	0.95	7.15	45573	7.17	3.80	12227	5.99			3.23
soil	2	ag+SAMMS	0.65	7.11	41233	11.30	3.56	10791	5.29	5.64	0.35	2.98
soil	1	PET+Cys	1.06	7.21	46701	9.41	3.70	11546	5.92			3.09
soil	2	PET+Cys	0.62	7.17	47668	8.14	3.77	10761	5.52	5.72	0.20	3.12

Table AIII.S10. Porewater chemistry in unamended sediment used in microcosm experiment. (Final two rows are solid-phase concentrations.) Sediment was a silty mud collected to a depth of 15 cm from a tidal creek in the upper part of Berry's Creek in Bergen County, NJ. Sediment was either unamended (this page) or amended with 5 wt% activated carbon (Calgon Type 3055, 80 x 325 mesh, CAS #7440-44-0) (next page). Values represent averages $\pm$ one s.d. (no s.d. denotes $n = 1$).

parameter	units	0 d	8 d	14 d	21 d	28 d
Al	mg L ⁻¹	2.06 $\pm$ 0.65	1.7 $\pm$ 0.57	1.31	1.03 $\pm$ 0.57	0.55 $\pm$ 0.4
B	mg L ⁻¹	0.98 $\pm$ 0.04	1 $\pm$ 0.12	1.1	1.13 $\pm$ 0.04	1.37 $\pm$ 0.16
Ba	mg L ⁻¹	1.15 $\pm$ 0.02	0.83 $\pm$ 0.25	0.79	1 $\pm$ 0.14	0.85 $\pm$ 0.46
Ca	mg L ⁻¹	81 $\pm$ 7	89 $\pm$ 18	111	125 $\pm$ 19	152 $\pm$ 16
DOC	mg L ⁻¹	n.d.	19.09 $\pm$ 1.92	17.02 $\pm$ 1.74	15.18 $\pm$ 1.01	35.91 $\pm$ 33.2
Fe	mg L ⁻¹	2.11 $\pm$ 0.34	3.44 $\pm$ 2.13	8.5	10.45 $\pm$ 8.7	14.08 $\pm$ 9.22
FMeHg	ng L ⁻¹	1.97 $\pm$ 0.19	1.8 $\pm$ 0.14	1.68 $\pm$ 0.17	3.71 $\pm$ 1.16	3.29 $\pm$ 0.67
FTHg	ng L ⁻¹	473.65 $\pm$ 145.59	414.37 $\pm$ 0.61	367.82	244.75 $\pm$ 59.89	143.69 $\pm$ 86.71
K	mg L ⁻¹	62.03 $\pm$ 7.83	54.1 $\pm$ 2.83	78.9	60.1 $\pm$ 9.48	91.05 $\pm$ 1.06
Mg	mg L ⁻¹	157 $\pm$ 7	167 $\pm$ 17	185	195 $\pm$ 22	254 $\pm$ 41
Mn	mg L ⁻¹	0.8 $\pm$ 0.1	0.92 $\pm$ 0.37	1.3	1.51 $\pm$ 0.65	2 $\pm$ 0.77
Na	mg L ⁻¹	1427 $\pm$ 21	1460 $\pm$ 14	1440	1495 $\pm$ 7	1935 $\pm$ 205
P	mg L ⁻¹	4.84 $\pm$ 0.18	5.94 $\pm$ 1.21	4.97	5.66 $\pm$ 0.64	5.61 $\pm$ 1.05
pH		6.95 $\pm$ 0.01	7.01 $\pm$ 0.47	6.54 $\pm$ 0.02	6.53 $\pm$ 0.18	6.45 $\pm$ 0.24
S	mg L ⁻¹	43.07 $\pm$ 10.29	55.85 $\pm$ 18.88	77.2	97.2 $\pm$ 37.9	138.15 $\pm$ 54.94
Si	mg L ⁻¹	15.33 $\pm$ 0.21	16.9 $\pm$ 0.42	16.9	15.4 $\pm$ 0.57	16.65 $\pm$ 0.78
Sr	mg L ⁻¹	1.22 $\pm$ 0.09	1.29 $\pm$ 0.21	1.56	1.7 $\pm$ 0.22	2.15 $\pm$ 0.3
sulfide	μ M	0.44	0.82	1.42 $\pm$ 0.08	2.52 $\pm$ 0.35	1.32 $\pm$ 0.43
Zn	mg L ⁻¹	0.32 $\pm$ 0.02	0.3 $\pm$ 0.05	0.35	0.34 $\pm$ 0.03	0.36 $\pm$ 0.01
MeHg (solid)	ng gdw ⁻¹	33.64 $\pm$ 0.07	26.41 $\pm$ 2.56	20.52	21.13 $\pm$ 0.12	24.75 $\pm$ 0.76
THg (solid)	μ g gdw ⁻¹	45.71 $\pm$ 0.59	48.22 $\pm$ 0.58	46.78 $\pm$ 0.54	47.89 $\pm$ 1.56	49.25 $\pm$ 1.26

Table AIII.S11. Porewater chemistry in AC-amended sediment used in microcosm experiment. (Final two rows are solid-phase concentrations.) Sediment was a silty mud collected to a depth of 15 cm from a tidal creek in the upper part of Berry's Creek in Bergen County, NJ. Sediment was amended with 5 wt% activated carbon (Calgon Type 3055, 80 x 325 mesh, CAS #7440-44-0) (next page). Values represent averages $\pm$ one s.d. (no s.d. denotes $n = 1$).

parameter	units	0 d	8 d	14 d	21 d	28 d
Al	mg L ⁻¹	0.79 $\pm$ 0.3	0.2 $\pm$ 0.1	0.57 $\pm$ 0.08	0.13 $\pm$ 0.1	0.57 $\pm$ 0.16
B	mg L ⁻¹	1 $\pm$ 0.02	0.99 $\pm$ 0.05	1.1 $\pm$ 0.04	1.22 $\pm$ 0.13	1.21 $\pm$ 0.07
Ba	mg L ⁻¹	0.84 $\pm$ 0.26	0.71 $\pm$ 0.36	0.46 $\pm$ 0.06	0.47 $\pm$ 0.1	0.53 $\pm$ 0.15
Ca	mg L ⁻¹	84 $\pm$ 3	94 $\pm$ 14	122 $\pm$ 18	143 $\pm$ 13	146 $\pm$ 20
DOC	mg L ⁻¹	n.d.	28.3 $\pm$ 19.34	6.77 $\pm$ 0.14	6.42 $\pm$ 0.35	17.02 $\pm$ 8.66
Fe	mg L ⁻¹	2.56 $\pm$ 0.79	2.96 $\pm$ 2.45	7.48 $\pm$ 2.35	18.3 $\pm$ 6.22	16.96 $\pm$ 14.91
FMeHg	ng L ⁻¹	0.44 $\pm$ 0.13	0.16 $\pm$ 0.01	0.37 $\pm$ 0.27	0.27 $\pm$ 0.09	0.89 $\pm$ 0.17
FTHg	ng L ⁻¹	259.85 $\pm$ 108.12	87.33 $\pm$ 18.03	251.98 $\pm$ 2.5	65.78 $\pm$ 35.19	168.25 $\pm$ 23.26
K	mg L ⁻¹	103.7 $\pm$ 15.99	105.1 $\pm$ 8.34	107.5 $\pm$ 7.78	138 $\pm$ 12.73	126 $\pm$ 14.14
Mg	mg L ⁻¹	164 $\pm$ 3	173 $\pm$ 16	197 $\pm$ 21	259 $\pm$ 1	249 $\pm$ 16
Mn	mg L ⁻¹	0.92 $\pm$ 0.05	1.03 $\pm$ 0.3	1.34 $\pm$ 0.21	2.16 $\pm$ 0.45	1.95 $\pm$ 0.95
Na	mg L ⁻¹	1457 $\pm$ 23	1450 $\pm$ 28	1545 $\pm$ 120	1895 $\pm$ 64	1875 $\pm$ 92
P	mg L ⁻¹	4.98 $\pm$ 0.12	4.28 $\pm$ 0.64	4.01 $\pm$ 0.4	3.16 $\pm$ 0.04	5.25 $\pm$ 1.34
pH		6.75 $\pm$ 0.01	6.78 $\pm$ 0.11	6.61 $\pm$ 0.06	6.42 $\pm$ 0.11	6.46 $\pm$ 0.26
S	mg L ⁻¹	58.03 $\pm$ 10.71	68.35 $\pm$ 15.63	112.15 $\pm$ 19.59	181 $\pm$ 4.24	154.5 $\pm$ 55.86
Si	mg L ⁻¹	14.6 $\pm$ 0.52	14.7 $\pm$ 0.57	15.2 $\pm$ 0.14	16.3 $\pm$ 0.57	16.8 $\pm$ 1.13
Sr	mg L ⁻¹	1.25 $\pm$ 0.03	1.37 $\pm$ 0.16	1.69 $\pm$ 0.23	2.03 $\pm$ 0.26	2.06 $\pm$ 0.32
sulfide	μ M	0.28	0.45 $\pm$ 0.03	0.66 $\pm$ 0.15	0.65 $\pm$ 0.17	1.81 $\pm$ 0.32
Zn	mg L ⁻¹	0.35 $\pm$ 0.01	0.27	0.35 $\pm$ 0.01	0.38 $\pm$ 0.02	0.32 $\pm$ 0.03
MeHg (solid)	ng gdw ⁻¹	16.82	15.99 $\pm$ 1.3	16.34	15.35 $\pm$ 1.34	15.2 $\pm$ 0.17
THg (solid)	μ g gdw ⁻¹	46.24 $\pm$ 0.74	47.88 $\pm$ 2.43	47.91 $\pm$ 3.34	47.45 $\pm$ 0.81	47.61 $\pm$ 1.85

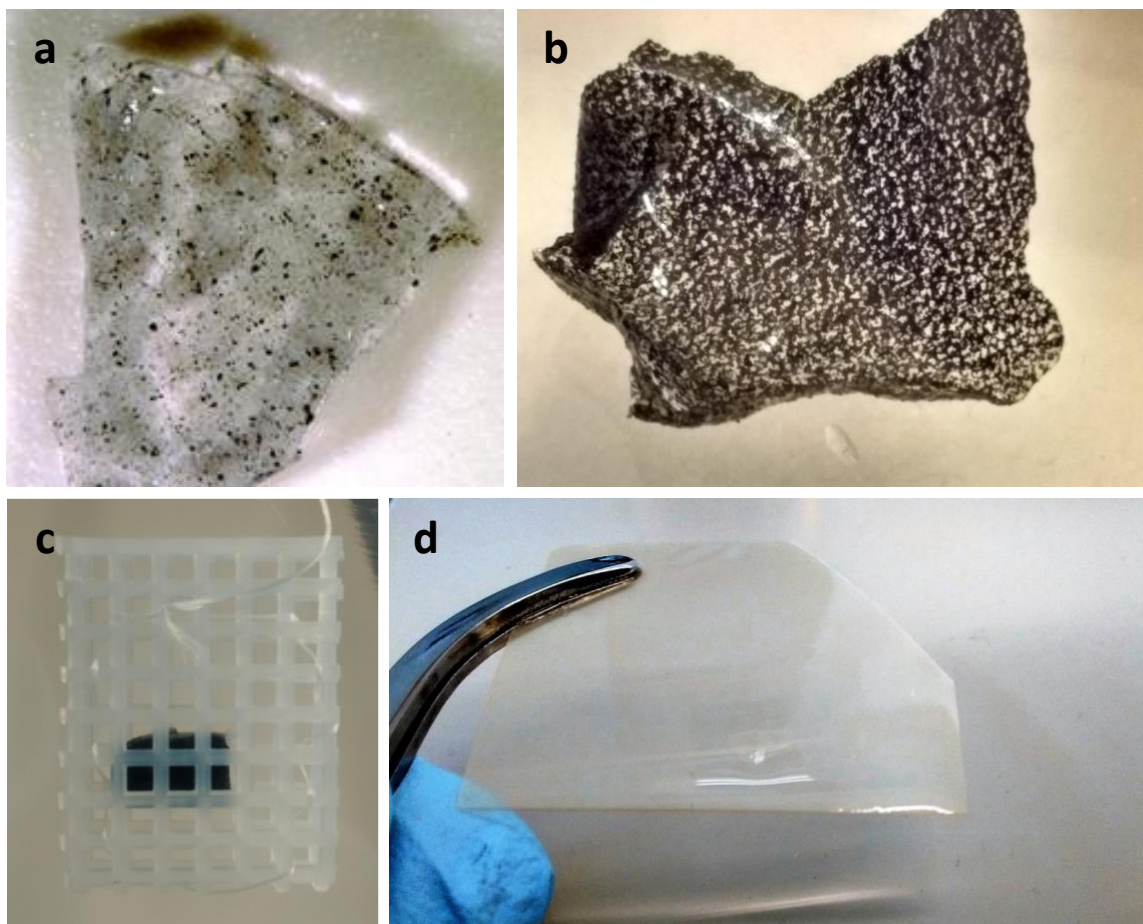


Figure AIII.S1. Photos of selected sampling materials. (a) ag+AC under light microscope; (b) PVDF+AC; (c) ag+AC in protective basket; (d) PET+Cys.

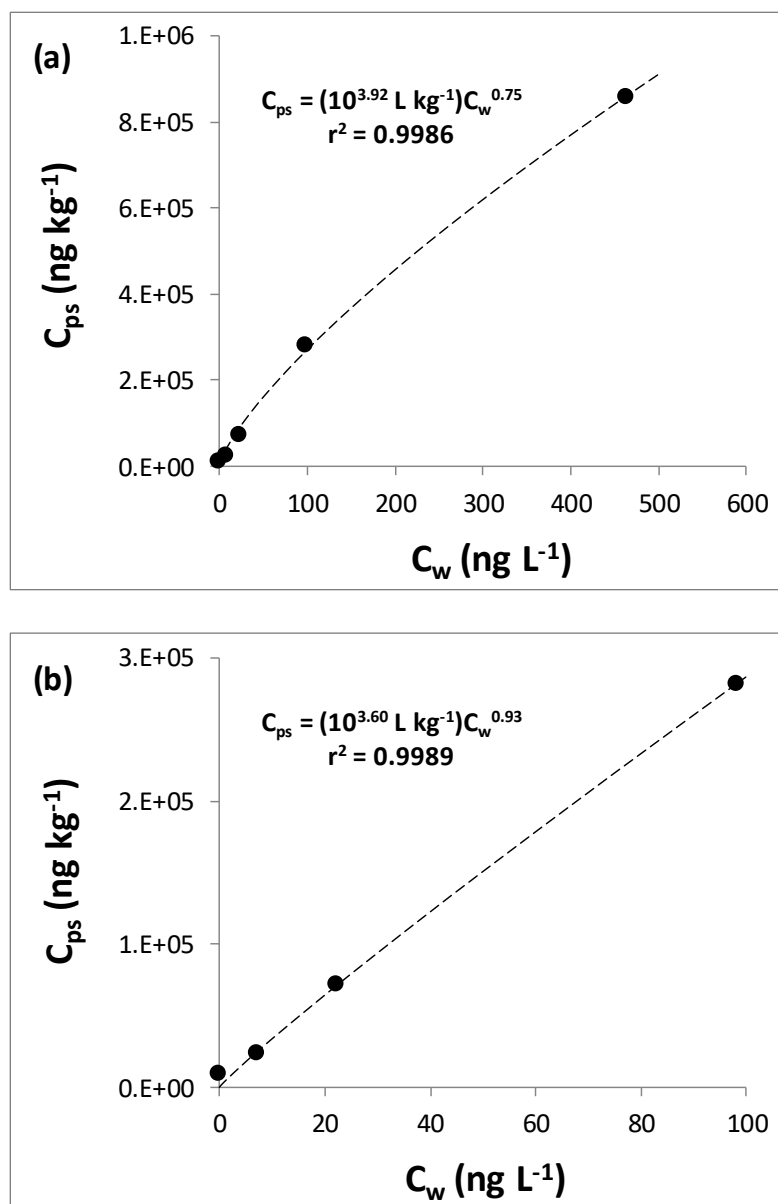


Figure AIII.S2. Freundlich model fits of sorption isotherm data for MeHgOH on ag+AC.

Points: measured data. Dashed lines: model fits (equations shown on plots). (a) All five points; (b) first four points only.

Activated Carbon Kinetics Modeling. The MeHg-AC kinetic data (Figure AIII.S3a) were fitted with pseudo-first order²³ and pseudo-second order²⁴ (Figure AIII.S3b) kinetic models. Both models provided good fits of the data ($r^2 = 0.98$ and 1.0 , respectively), suggesting a Langmuir-type adsorption mechanism.²⁵ The apparent sorption rate constants, which depend on experimental conditions including initial C_w , were $k_1 = 0.31 \text{ h}^{-1}$ and $k_2 = 2.1 \times 10^{-4} \text{ kg ng}^{-1} \text{ h}^{-1}$. The equilibrium C_{AC} predicted by the pseudo-second order model was $1.2 \times 10^6 \text{ ng kg}^{-1}$. It should be emphasized that this does not represent this AC's maximum adsorptive capacity. In Gomez-Eyles et al., the MeHg sorption isotherm of this carbon remained log-linear for initial C_w values up to 6000 ng L^{-1} under conditions nearly identical to ours. There, the final C_{AC} was $2.8 \times 10^7 \text{ ng kg}^{-1}$.¹⁶ This, along with the proportionality of our screening isotherms, indicates that there is little danger of saturating an ag+AC sampler with MeHg at environmentally realistic C_{pw} . We also evaluated the kinetics of inorganic mercury sorption to AC (Table AIII.S7 and Figure AIII.S4).

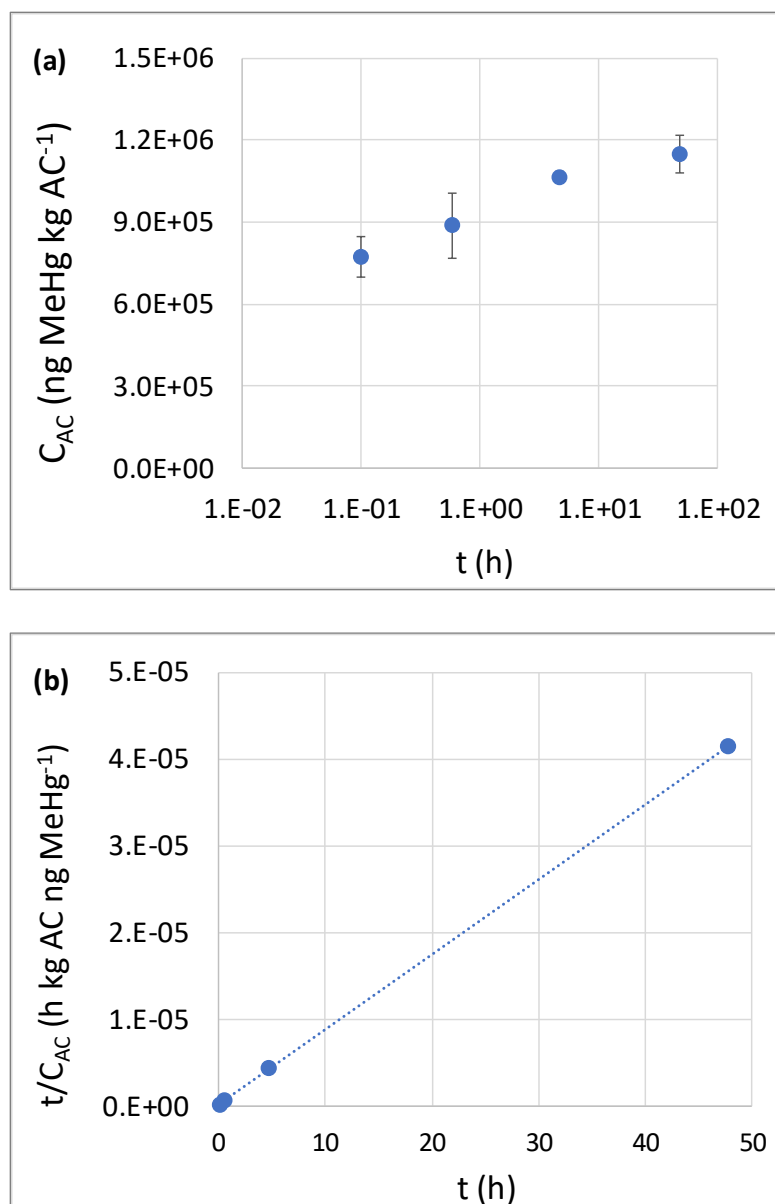


Figure AIII.S3. Kinetics of MeHgOH adsorption to a coal-derived activated carbon (initial $C_w = 250 \text{ ng L}^{-1}$). (a) MeHg concentrations on AC over time; error bars show ± 1 standard error. (b) Pseudo-second order model fit. $k_2 = 2.1 \times 10^{-4} \text{ kg ng}^{-1} \text{ h}^{-1}$; $C_{AC,eq} = 1.2 \times 10^6 \text{ ng kg}^{-1}$.

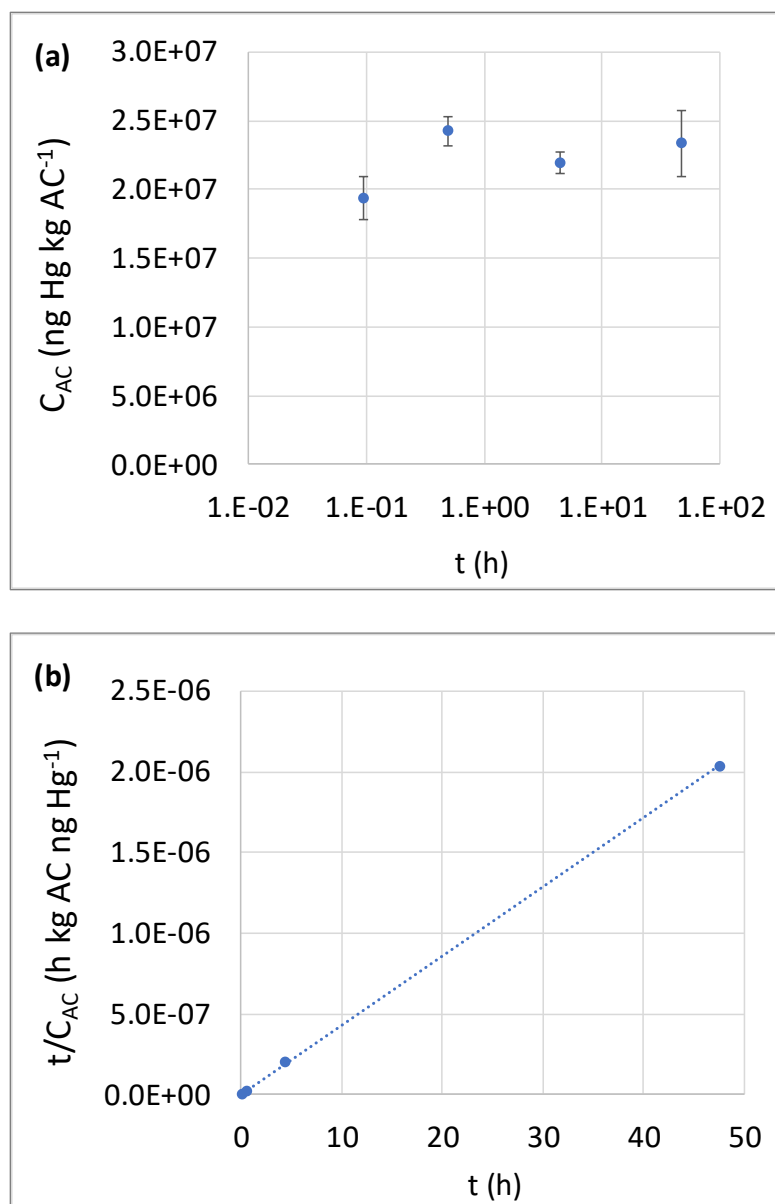


Figure AIII.S4. Kinetics of $\text{Hg}(\text{OH})_2$ adsorption to a coal-derived activated carbon (initial $C_w = 5000 \text{ ng L}^{-1}$). (a) Hg concentrations on AC over time; error bars show ± 1 standard error. (b) Pseudo-second order model fit. $k_2 = 1.1 \times 10^{-5} \text{ kg ng}^{-1} \text{ h}^{-1}$; $C_{\text{AC,eq}} = 2.3 \times 10^7 \text{ ng kg}^{-1}$.

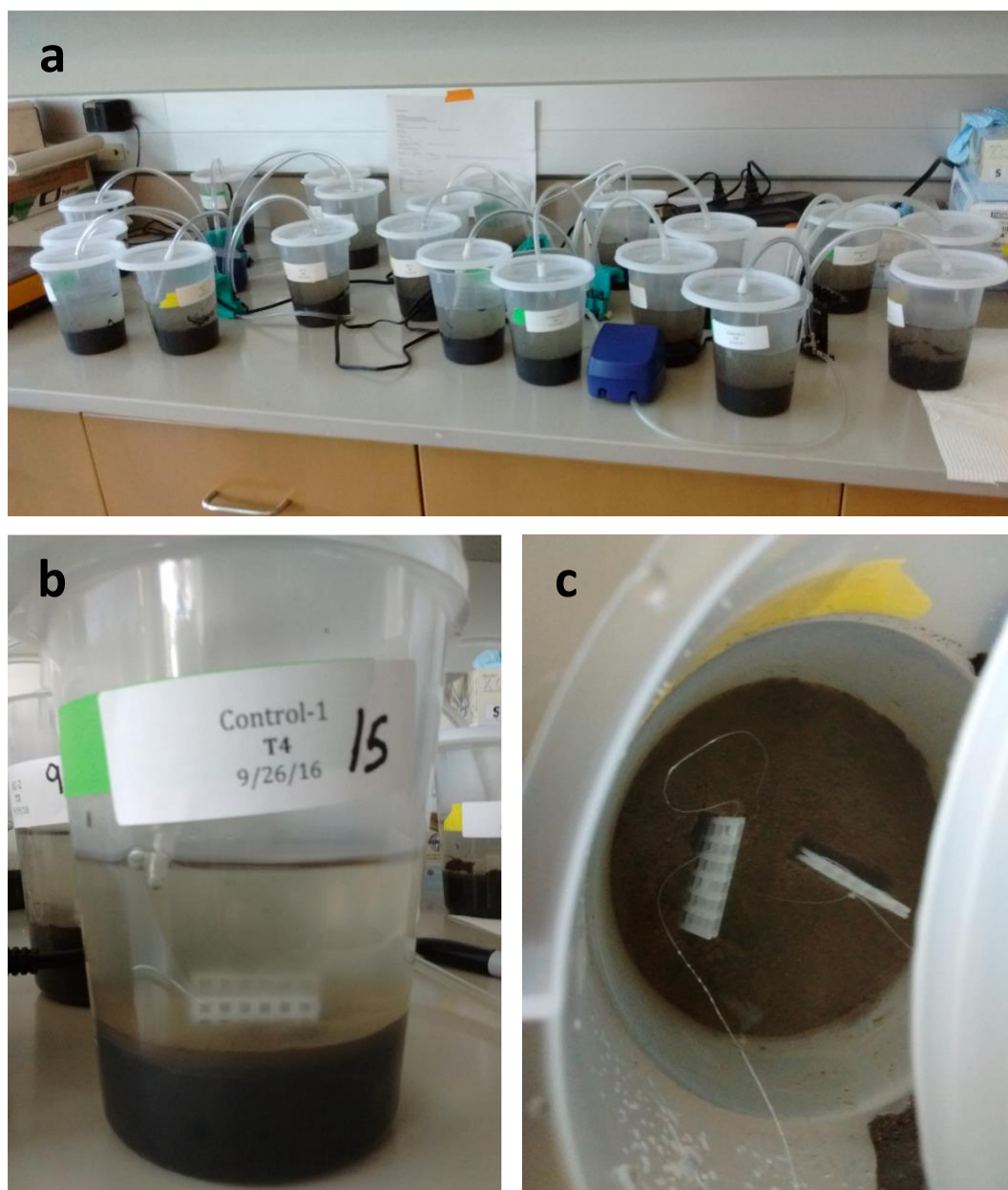


Figure AIII.S5. Photos of soil microcosm experiment. (a) Overview of setup; (b, c) detail views of one beaker from the side and above. Note placement of baskets to expose passive samplers to visibly apparent redox transition zone.

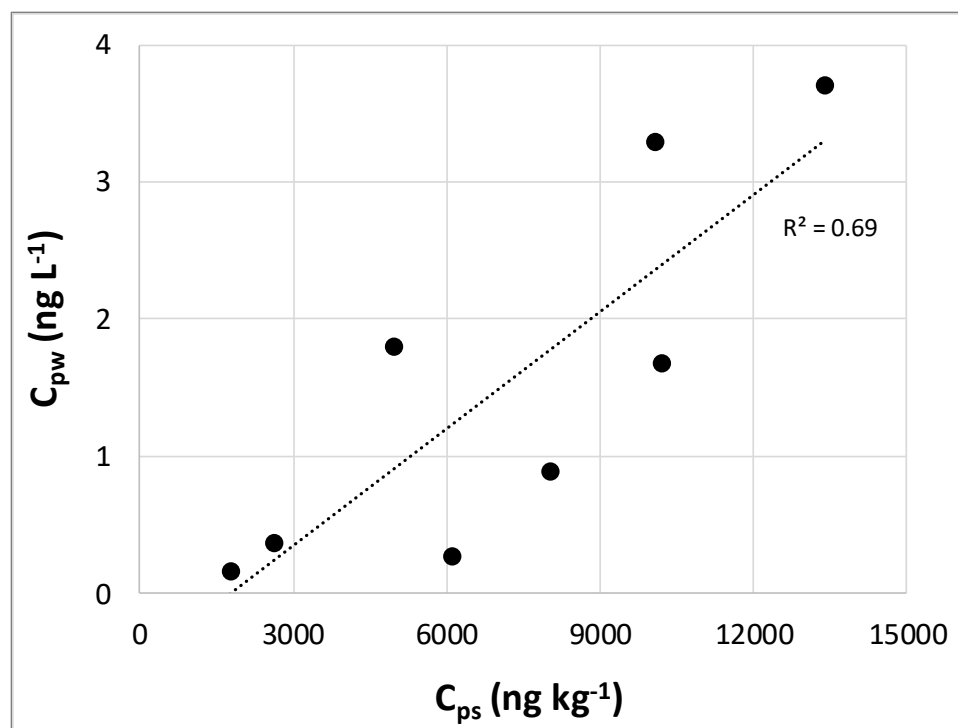


Figure AIII.S6. Predictions of directly measured C_{pw} by passive samplers in sediment microcosm experiment across both amendment types and all time points.

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Supplemental Information to the Article:

Using an activated carbon-based passive sampling device to predict methylmercury porewater concentrations and bioaccumulation by *L. plumulosus* in sediment and soil

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Contains: 34 pages of material, including detailed analytical methods, three figures, eight tables, and references.

Table AIV.S1. Additional reactions used in MINEQL+ equilibrium speciation modeling.

Two components were added to the software's database: MeHg (+1 charge), and DOMRS, representing a model reduced exocyclic sulfur binding site in Suwannee River Humic Acid (-1 charge). DOMRS site densities were estimated from DOC measurements with the following equation, under the assumption that DOM characteristics were similar to SRHA¹⁻³:

$$[\text{DOMRS}] = \frac{\text{mg DOC}}{\text{L}} \times \frac{\text{mg SRHA}}{0.5263 \text{ mg DOC}} \times \frac{0.0054 \text{ mg S}}{\text{mg SRHA}} \times \frac{0.236 \text{ mg reduced exocyclic S}}{\text{mg S}} \times \frac{\text{mol reduced exocyclic S}}{32065 \text{ mg reduced exocyclic S}}$$

Reaction	log K	Reference
$\text{H}^+ + \text{DOMRS}^- \rightleftharpoons \text{DOMRSH}$	9.000	4, 5
$\text{MeHg}^+ + \text{SO}_4^{2-} \rightleftharpoons \text{MeHgSO}_4^-$	0.940	6
$\text{MeHg}^+ + \text{Br}^- \rightleftharpoons \text{MeHgBr}$	6.620	7
$\text{MeHg}^+ + \text{Cl}^- \rightleftharpoons \text{MeHgCl}$	5.400	8
$\text{MeHg}^+ + \text{F}^- \rightleftharpoons \text{MeHgF}$	1.500	7
$\text{MeHg}^+ + \text{DOMRS}^- \rightleftharpoons \text{MeHgDOMRS}$	17.500	4, 5, 9, 10
$2\text{MeHg}^+ + \text{H}_2\text{O} \rightleftharpoons (\text{MeHg})_2\text{OH}^+ + \text{H}^+$	-2.150	11
$\text{MeHg}^+ + \text{H}_2\text{O} \rightleftharpoons \text{MeHgOH} + \text{H}^+$	-4.500	8
$\text{MeHg}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{MeHgCO}_3^-$	6.100	6
$\text{MeHg}^+ + \text{H}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{MeHgHCO}_3$	12.950	8
$\text{MeHg}^+ + \text{HS}^- \rightleftharpoons \text{MeHgS}^- + \text{H}^+$	7.300	7
$\text{MeHg}^+ + \text{HS}^- \rightleftharpoons \text{MeHgSH}$	14.500	12
$2\text{MeHg}^+ + \text{HS}^- \rightleftharpoons (\text{MeHg})_2\text{S} + \text{H}^+$	23.600	7, 8

Table AIV.S2. Quality assurance data for MeHg analyses in this work. Analysis was done by isotope dilution ICP-MS, i.e. with internal stable isotope standards. Relative percent differences (RPD) are for duplicate analyses of the same prepared sample. CRMs were NIST 1566b oyster tissue. Detection limits were estimated as three times the standard error of blanks across samples.

matrix	RPD duplicates	CRM recovery	ID spike recovery	distillation blanks	DL	units
water	4.8 ± 2.2%	100.9 ± 1.8%	73.0 ± 1.8%	0.87 ± 0.54	0.22 ± 0.01	ng L ⁻¹
soil	9.5 ± 2.9%	95.5 ± 4.0%	83.2 ± 1.0%	0.85 ± 0.54	1343 ± 62	ng kgdw ⁻¹
ag+AC	n/a	98.6 ± 1.8%	74.1 ± 5.5%	0.53 ± 0.42	218 ± 82	ng kgww ⁻¹

Analytical Methods. MeHg samples were distilled in H₂SO₄ as described by Horvat et al.¹³ and analyzed following the method outlined by Mitchell and Gilmour.¹⁴ Briefly, a spike consisting of enriched, stable Hg isotope (Oak Ridge National Laboratories) was added, the samples were buffered with acetate, derivatized with sodium tetraethylborate to facilitate volatilization, purged and concentrated on a Tenax trap with a Brooks/Rand autosampler, thermally desorbed, separated on an OV-3/Chromosorb column, and introduced into a Perkin Elmer Elan DRC II ICP-MS for detection. THg was also measured as in Mitchell and Gilmour.¹⁴ Concentrations were determined by digesting samples in 7:4 HNO₃:H₂SO₄, heating to achieve loss of color, oxidizing organics with BrCl, reducing Hg(II) to Hg(0) with SnCl₂, and analyzing via ICP-MS. Isotopic dilution calculations were performed to enhance the accuracy and precision of MeHg and THg measurements.¹⁴ MeHg quality assurance data are summarized in Table AIV.S2. Sulfide was measured by mixing samples 1:1 with sulfide antioxidant buffer (2.0 M NaOH, 0.2 M ascorbic acid, and 0.2 M Na₂EDTA in deoxygenated, deionized water prepared anaerobically) and analyzing with a sulfide ion-selective electrode calibrated by lead titration of a saturated sulfide standard. DOC was measured on a Shimadzu organic carbon analyzer. Cations were measured on a Perkin Elmer Optima 8300 ICP-OES. Anions were measured using ion chromatography (AnionPac AS18 column, ICS-2000, Dionex Corp). Where not directly measured, major ion concentrations used in speciation modeling were estimated from the chemical composition of Instant Ocean provided by the manufacturer.¹⁵

Table AIV.S3. Porewater chemistry in unamended soil used in microcosm Experiment 2.

(Final two rows are solid-phase concentrations.) Oligohaline soil was collected from a *Phragmites* marsh in upper Berry's Creek and combined with *Phragmites* marsh soil collected from the SERC Global Change Research wetland to achieve a Hg concentration of approximately 20 $\mu\text{g g}^{-1}$. Prior to this study, the mixed soil was used for 18 months in a *Phragmites* mesocosm study in a tidal creek at SERC. Values represent averages $\pm$ one s.d. (no s.d. denotes $n = 1$).

parameter	units	0 d	4 d	8 d	15 d	25 d
ammonia	ppm	n.d.	n.d.	1.5 $\pm$ 0.07	1.49	2.23 $\pm$ 0.31
DOC	mg L ⁻¹	24.7 $\pm$ 1.5	27.3	27.9 $\pm$ 0.6	25.6	34.2 $\pm$ 2.5
FTHg	ng L ⁻¹	1778 $\pm$ 247	1531	810 $\pm$ 150	562	518 $\pm$ 142
FMeHg	ng L ⁻¹	4.02 $\pm$ 0.01	36.29	36.05 $\pm$ 8.28	34.42 $\pm$ 4.07	35.07 $\pm$ 2.42
IC-Br	μM	89.5 $\pm$ 2.2	77.7	76.8 $\pm$ 4.9	76.2	72 $\pm$ 7.6
IC-Cl	μM	93678 $\pm$ 419	78887	78305 $\pm$ 587	72989	69880 $\pm$ 2229
IC-F	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-NO2	μM	695 $\pm$ 7	760	732 $\pm$ 43	745	615 $\pm$ 192
IC-NO3	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-PO4	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-SO4	μM	8249 $\pm$ 31	5834	4753 $\pm$ 18	3012	1357 $\pm$ 2
pH		5.98 $\pm$ 0.08	6.44	6.26	6.45	7.43 $\pm$ 0.02
sulfide	μM	0.98 $\pm$ 0.05	0.2	0.88 $\pm$ 0.09	0.61	1.39 $\pm$ 0.15
Hg	$\mu\text{g gdw}^{-1}$	20 $\pm$ 1	20.1	18 $\pm$ 2.4	20	16 $\pm$ 1.9
MeHg	ng gdw ⁻¹	80	191	205 $\pm$ 27	203	172 $\pm$ 1

Table AIV.S4. Porewater chemistry in aged AC-amended soil used in microcosm

Experiment 2. (Final two rows are solid-phase concentrations.) Oligohaline soil was collected from a *Phragmites* marsh in upper Berry's Creek and combined with *Phragmites* marsh soil collected from the SERC Global Change Research wetland to achieve a Hg concentration of approximately 20 $\mu\text{g g}^{-1}$. Prior to this study, the mixed soil was used with 5 wt% AC amendment for 18 months in a *Phragmites* mesocosm study in a tidal creek at SERC. Values represent averages $\pm$ one s.d. (no s.d. denotes $n = 1$).

parameter	units	0 d	4 d	8 d	15 d	25 d
ammonia	ppm	n.d.	n.d.	1.38 $\pm$ 0.14	1.18	1.47 $\pm$ 0.11
DOC	mg L ⁻¹	15.5 $\pm$ 0.2	12.5	13.3 $\pm$ 2.4	12.2	14.3 $\pm$ 1.7
FTHg	ng L ⁻¹	1214 $\pm$ 73	567	321 $\pm$ 70	253 $\pm$ 1	206 $\pm$ 26
FMeHg	ng L ⁻¹	3.07 $\pm$ 0.48	8.97	9.11 $\pm$ 0.73	7.98	12.06 $\pm$ 0.4
IC-Br	μM	84 $\pm$ 2.3	76.4	74.7 $\pm$ 8.5	76.4 $\pm$ 0.9	79.6 $\pm$ 7.9
IC-Cl	μM	92106 $\pm$ 222	78083	77655 $\pm$ 542	72625 $\pm$ 73	69912 $\pm$ 2038
IC-F	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-NO2	μM	687 $\pm$ 72	692	734 $\pm$ 52	647 $\pm$ 38	433 $\pm$ 97
IC-NO3	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-PO4	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-SO4	μM	8487 $\pm$ 90	6592	5713 $\pm$ 18	3925 $\pm$ 5	2382 $\pm$ 121
pH		6.06 $\pm$ 0.01	6.37	6.31 $\pm$ 0.01	6.47	7.52 $\pm$ 0.3
sulfide	μM	0.45 $\pm$ 0.03	0.06	0.26 $\pm$ 0.06	0.25	0.43
Hg	$\mu\text{g gdw}^{-1}$	23.7 $\pm$ 1.5	18.4	22.2 $\pm$ 0.4	18.9	17.9 $\pm$ 0.4
MeHg	ng gdw ⁻¹	122 $\pm$ 16	131 $\pm$ 16	235 $\pm$ 22	247 $\pm$ 39	339 $\pm$ 88

Table AIV.S5. Porewater chemistry in fresh AC-amended soil used in microcosm Experiment 2. (Final two rows are solid-phase concentrations.) Oligohaline soil was collected from a *Phragmites* marsh in upper Berry's Creek and combined with *Phragmites* marsh soil collected from the SERC Global Change Research wetland to achieve a Hg concentration of approximately 20 $\mu\text{g g}^{-1}$. Prior to this study, the mixed soil was used for 18 months in a *Phragmites* mesocosm study in a tidal creek at SERC. The soil was amended with 5 wt% AC immediately prior to Experiment 1. Values represent averages $\pm$ one s.d. (no s.d. denotes $n = 1$).

parameter	units	0 d	4 d	8 d	15 d	25 d
ammonia	ppm	n.d.	n.d.	1.17 $\pm$ 0.06	1.59	1.48 $\pm$ 0.18
DOC	mg L ⁻¹	5.8 $\pm$ 1.2	4.9	4.4 $\pm$ 0.2	3.9	3.9 $\pm$ 0.9
FTHg	ng L ⁻¹	1237 $\pm$ 48	376	323 $\pm$ 94	141	95 $\pm$ 17
FMeHg	ng L ⁻¹	0.95 $\pm$ 0.19	0.38 $\pm$ 0.13	0.43 $\pm$ 0.19	0.24	0.36 $\pm$ 0.01
IC-Br	μM	102.6 $\pm$ 8.5	82.2	83.2 $\pm$ 1	81.4	67.1 $\pm$ 2.4
IC-Cl	μM	94117 $\pm$ 17	80025	79126 $\pm$ 2377	77604	69832 $\pm$ 93
IC-F	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-NO2	μM	796 $\pm$ 1	839	749 $\pm$ 34	773	441 $\pm$ 89
IC-NO3	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-PO4	μM	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-SO4	μM	9856 $\pm$ 46	7048	6382 $\pm$ 168	4865	3123 $\pm$ 443
pH		6.25 $\pm$ 0.02	6.49	6.34	6.54	7.34 $\pm$ 0.21
sulfide	μM	0.37 $\pm$ 0.03	0.03	0.18 $\pm$ 0.01	0.17	0.28 $\pm$ 0.02
Hg	$\mu\text{g gdw}^{-1}$	19.8 $\pm$ 0.3	18.6	18.6 $\pm$ 1.2	13.8	15.6 $\pm$ 1
MeHg	ng gdw ⁻¹	74 $\pm$ 8	96	128 $\pm$ 3	176	183 $\pm$ 32

Table AIV.S6. Porewater chemistry in unamended soil used in microcosm Experiment 3.

(Final two rows are solid-phase concentrations.) Soil was taken from the same starting batch used in Experiment 1, but had aged an additional six weeks. Values represent averages $\pm$ one s.d. (no s.d. denotes $n = 1$).

parameter	units	-7 d	0 d	7 d	14 d	21 d
DOC	mg L ⁻¹	15.13 $\pm$ 0.85	16.42 $\pm$ 0.19	11.34 $\pm$ 1.04	21.4 $\pm$ 1.72	20.81 $\pm$ 5.23
F-Al	mg L ⁻¹	0.24 $\pm$ 0.07	0.43 $\pm$ 0.03	0.61 $\pm$ 0.17	0.83 $\pm$ 0.17	0.55 $\pm$ 0.06
F-B	mg L ⁻¹	0.76 $\pm$ 0.07	0.73 $\pm$ 0.02	0.74 $\pm$ 0.01	0.76 $\pm$ 0.02	0.7 $\pm$ 0.01
F-Ba	mg L ⁻¹	1.37 $\pm$ 0.09	1.15 $\pm$ 0.06	1.01 $\pm$ 0.14	1.13 $\pm$ 0.05	1.12 $\pm$ 0.05
F-Ca	mg L ⁻¹	86.63 $\pm$ 1.11	68.26 $\pm$ 2.37	60.89 $\pm$ 0.2	55.33 $\pm$ 1.02	48.6 $\pm$ 0.45
F-Fe	mg L ⁻¹	97.32 $\pm$ 3.85	63.48 $\pm$ 3.65	40.19 $\pm$ 2.47	30.15 $\pm$ 5.33	24.99 $\pm$ 2.44
F-K	mg L ⁻¹	78.44 $\pm$ 9.36	67.7 $\pm$ 5.15	61.22 $\pm$ 7.94	58.64 $\pm$ 2.29	56.07 $\pm$ 1.33
F-Mg	mg L ⁻¹	214.43 $\pm$ 12.47	180.1 $\pm$ 10.13	165.05 $\pm$ 9.64	154.43 $\pm$ 2.57	154.5 $\pm$ 1.15
F-Mn	mg L ⁻¹	13.13 $\pm$ 0.68	9.59 $\pm$ 0.56	8.09 $\pm$ 0.47	7.03 $\pm$ 0.5	6.41 $\pm$ 0.16
F-Na	mg L ⁻¹	1789 $\pm$ 120	1609 $\pm$ 113	1591 $\pm$ 118	1534 $\pm$ 60	1549 $\pm$ 7
F-P	mg L ⁻¹	1.21 $\pm$ 0.36	2.54 $\pm$ 0.31	1.23 $\pm$ 0.03	1.48 $\pm$ 0.5	1.04 $\pm$ 0.42
F-S	mg L ⁻¹	190.75 $\pm$ 15.98	121.85 $\pm$ 11.66	101.32 $\pm$ 4.7	93.23 $\pm$ 6.76	91.78 $\pm$ 14.76
F-Si	mg L ⁻¹	10.3 $\pm$ 0.35	12.13 $\pm$ 0.16	12.06 $\pm$ 0.33	12.79 $\pm$ 0.93	11.99 $\pm$ 0.9
F-Zn	mg L ⁻¹	0.97 $\pm$ 0.08	0.53 $\pm$ 0.03	0.42 $\pm$ 0.06	0.48	0.49 $\pm$ 0.01
FMeHg	ng L ⁻¹	18.64 $\pm$ 0.53	54.29 $\pm$ 5.56	35.19 $\pm$ 1.14	30.3 $\pm$ 6.84	19.5 $\pm$ 0.54
FTHg	ng L ⁻¹	951 $\pm$ 61	860 $\pm$ 31	656 $\pm$ 46	559 $\pm$ 54	339 $\pm$ 71
IC-Br	μ M	82.4 $\pm$ 3.32	89.37 $\pm$ 5.17	89.85 $\pm$ 1.48	89.7 $\pm$ 3.91	86.44 $\pm$ 2.49
IC-Cl	μ M	90729 $\pm$ 1763	82628 $\pm$ 953	81664 $\pm$ 369	79657 $\pm$ 923	77863 $\pm$ 402
IC-F	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-NO3	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-PO4	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-SO4	μ M	7928 $\pm$ 677	4570 $\pm$ 165	4040 $\pm$ 162	3648 $\pm$ 395	3343 $\pm$ 795
pH		126 $\pm$ 7	210 $\pm$ 16	236 $\pm$ 8	212 $\pm$ 21	211 $\pm$ 27
salinity	ppt	6.69 $\pm$ 0.01	6.73 $\pm$ 0.06	6.73 $\pm$ 0.07	6.86 $\pm$ 0.14	6.86 $\pm$ 0.16
temperature	$^{\circ}$ C	9	7.33 $\pm$ 0.58	7	6	5
total ammonia	mg N L ⁻¹	22 $\pm$ 0.1	21.2 $\pm$ 0.1	21.6 $\pm$ 0.1	21.5 $\pm$ 0.1	21.2 $\pm$ 0.2
THg	μ g gdw ⁻¹	13.23 $\pm$ 0.35	8.79 $\pm$ 0.38	4.86 $\pm$ 0.27	3.16 $\pm$ 0.51	2.66 $\pm$ 0.97
MeHg	ng gdw ⁻¹	17	17 $\pm$ 1	17 $\pm$ 1	17	17 $\pm$ 1

Table AIV.S7. Porewater chemistry in aged AC-amended soil used in microcosm

Experiment 3. (Final two rows are solid-phase concentrations.) Soil was taken from the same starting batch used in Experiment 1, but had aged an additional six weeks. Values represent averages $\pm$ one s.d. (no s.d. denotes $n = 1$).

parameter	units	-7 d	0 d	7 d	14 d	21 d
DOC	mg L ⁻¹	7.42 $\pm$ 0.67	8.72 $\pm$ 0.29	5.58 $\pm$ 0.63	11.26 $\pm$ 1	20.88 $\pm$ 1.72
F-Al	mg L ⁻¹	0.1 $\pm$ 0.03	0.18 $\pm$ 0.09	0.26 $\pm$ 0.08	0.23 $\pm$ 0.04	0.21 $\pm$ 0.04
F-B	mg L ⁻¹	0.72 $\pm$ 0.01	0.78 $\pm$ 0.01	0.78 $\pm$ 0.03	0.78 $\pm$ 0.03	0.71 $\pm$ 0.01
F-Ba	mg L ⁻¹	1 $\pm$ 0.05	0.99 $\pm$ 0.07	0.84 $\pm$ 0.1	0.98 $\pm$ 0.09	0.94 $\pm$ 0.04
F-Ca	mg L ⁻¹	85.93 $\pm$ 1.3	71.12 $\pm$ 1.65	65.25 $\pm$ 1.17	58.46 $\pm$ 0.26	51.31 $\pm$ 0.86
F-Fe	mg L ⁻¹	90.62 $\pm$ 3.74	64.95 $\pm$ 0.96	42.03 $\pm$ 3.38	34.02 $\pm$ 1.97	24.52 $\pm$ 1.88
F-K	mg L ⁻¹	85.05 $\pm$ 1.97	72.86 $\pm$ 3.57	61.49 $\pm$ 2.45	60.82 $\pm$ 2.04	53.77 $\pm$ 4.31
F-Mg	mg L ⁻¹	231.5 $\pm$ 3.97	192.53 $\pm$ 3.09	173.33 $\pm$ 3.12	167.2 $\pm$ 6.24	150.5 $\pm$ 6.46
F-Mn	mg L ⁻¹	24.27 $\pm$ 0.78	18.76 $\pm$ 0.2	16.85 $\pm$ 0.27	15.5 $\pm$ 0.49	12.42 $\pm$ 0.63
F-Na	mg L ⁻¹	1905 $\pm$ 25	1731 $\pm$ 28	1634 $\pm$ 73	1596 $\pm$ 42	1482 $\pm$ 87
F-P	mg L ⁻¹	0.29 $\pm$ 0.25	0.52 $\pm$ 0.27	0.42 $\pm$ 0.19	0.42 $\pm$ 0.13	0.35 $\pm$ 0.1
F-S	mg L ⁻¹	224.63 $\pm$ 6.45	155.03 $\pm$ 6.05	127.77 $\pm$ 6.72	115.9 $\pm$ 5.09	104.3 $\pm$ 7.93
F-Si	mg L ⁻¹	7.92 $\pm$ 0.2	9.5 $\pm$ 0.26	9.23 $\pm$ 0.39	9.55 $\pm$ 0.06	9.01 $\pm$ 0.19
F-Zn	mg L ⁻¹	0.68 $\pm$ 0.01	0.51 $\pm$ 0.06	0.44 $\pm$ 0.05	0.51 $\pm$ 0.06	0.46 $\pm$ 0.01
FMeHg	ng L ⁻¹	6.81 $\pm$ 1.51	13.06 $\pm$ 0.4	10.58 $\pm$ 0.66	9.77 $\pm$ 0.99	9.12
FTHg	ng L ⁻¹	777 $\pm$ 54	440 $\pm$ 104	417 $\pm$ 66	271 $\pm$ 27	190 $\pm$ 4
IC-Br	μ M	84.82 $\pm$ 2.83	93.12 $\pm$ 4.62	91.98 $\pm$ 8.13	89.53 $\pm$ 4	85.65 $\pm$ 1.77
IC-Cl	μ M	91377 $\pm$ 1324	83751 $\pm$ 224	80877 $\pm$ 1147	79788 $\pm$ 829	77389 $\pm$ 152
IC-F	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-NO3	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-PO4	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-SO4	μ M	9038 $\pm$ 168	6108 $\pm$ 64	5004 $\pm$ 211	4489 $\pm$ 219	4231 $\pm$ 86
pH		6.69	6.68 $\pm$ 0.01	6.72 $\pm$ 0.02	6.83 $\pm$ 0.02	6.81 $\pm$ 0.07
salinity	ppt	8	7	7	6	5
temperature	°C	21.9 $\pm$ 0.1	21.3 $\pm$ 0.1	21.7 $\pm$ 0.1	21.5 $\pm$ 0.1	21.3 $\pm$ 0.1
total ammonia	mg N L ⁻¹	12.4 $\pm$ 0.1	8.41 $\pm$ 0.16	4.77 $\pm$ 0.48	3.99 $\pm$ 0.3	2.16 $\pm$ 0.15
THg	μ g gdw ⁻¹	19 $\pm$ 1	19	19 $\pm$ 1	19 $\pm$ 1	18
MeHg	ng gdw ⁻¹	257 $\pm$ 5	385 $\pm$ 10	512 $\pm$ 30	502 $\pm$ 39	574 $\pm$ 42

Table AIV.S8. Porewater chemistry in fresh AC-amended soil used in microcosm

Experiment 3. (Final two rows are solid-phase concentrations.) Soil was taken from the same starting batch used in Experiment 1, but had aged an additional six weeks. Values represent averages $\pm$ one s.d. (no s.d. denotes $n = 1$).

parameter	units	-7 d	0 d	7 d	14 d	21 d
DOC	mg L ⁻¹	3.89 $\pm$ 1.3	3.06 $\pm$ 0.22	1.5 $\pm$ 0.19	8.53 $\pm$ 0.78	5.39 $\pm$ 0.6
F-Al	mg L ⁻¹	0.03 $\pm$ 0.01	0.02	0.02	0.03 $\pm$ 0.01	0.03 $\pm$ 0.02
F-B	mg L ⁻¹	1.13 $\pm$ 0.07	0.98 $\pm$ 0.01	0.91 $\pm$ 0.02	0.88 $\pm$ 0.01	0.79 $\pm$ 0.02
F-Ba	mg L ⁻¹	0.63 $\pm$ 0.07	0.49 $\pm$ 0.12	0.41 $\pm$ 0.01	0.75 $\pm$ 0.04	0.45 $\pm$ 0.03
F-Ca	mg L ⁻¹	134.33 $\pm$ 2.15	102.15 $\pm$ 2.11	86.01 $\pm$ 2.55	81.96 $\pm$ 1.36	72.89 $\pm$ 0.31
F-Fe	mg L ⁻¹	53.48 $\pm$ 1.72	37.2 $\pm$ 0.23	23.23 $\pm$ 1.85	26.87 $\pm$ 1.05	21.36 $\pm$ 0.13
F-K	mg L ⁻¹	96.44 $\pm$ 5.32	76.92 $\pm$ 2	66.38 $\pm$ 4.05	62.82 $\pm$ 1.59	58.75 $\pm$ 0.92
F-Mg	mg L ⁻¹	228.57 $\pm$ 2.66	198.1 $\pm$ 2.08	171.87 $\pm$ 7.15	174.63 $\pm$ 6.67	164.03 $\pm$ 5.4
F-Mn	mg L ⁻¹	17.74 $\pm$ 0.18	13.95 $\pm$ 0.05	11.62 $\pm$ 0.25	11.94 $\pm$ 0.17	11.1 $\pm$ 0.08
F-Na	mg L ⁻¹	1933 $\pm$ 2	1730 $\pm$ 11	1680 $\pm$ 64	1627 $\pm$ 7	1572 $\pm$ 21
F-P	mg L ⁻¹	0.13 $\pm$ 0.09	0.09 $\pm$ 0.05	0.07 $\pm$ 0.03	0.23 $\pm$ 0.12	0.17 $\pm$ 0.05
F-S	mg L ⁻¹	246.57 $\pm$ 7.65	185.33 $\pm$ 5.73	154.83 $\pm$ 10.54	133.63 $\pm$ 4.75	130.8 $\pm$ 14.35
F-Si	mg L ⁻¹	9.4 $\pm$ 0.24	9.88 $\pm$ 0.05	8.88 $\pm$ 0.12	10.38 $\pm$ 0.31	10.06 $\pm$ 0.09
F-Zn	mg L ⁻¹	0.64 $\pm$ 0.1	0.31 $\pm$ 0.01	0.29 $\pm$ 0.01	0.43 $\pm$ 0.01	0.31
FMeHg	ng L ⁻¹	0.46 $\pm$ 0.06	0.5 $\pm$ 0.42	0.33 $\pm$ 0.05	0.54 $\pm$ 0.3	0.42 $\pm$ 0.11
FTHg	ng L ⁻¹	640 $\pm$ 71	262 $\pm$ 22	146 $\pm$ 16	118 $\pm$ 11	87 $\pm$ 5
IC-Br	μ M	102.42 $\pm$ 1.47	95.35 $\pm$ 1.46	98.87 $\pm$ 5.25	91.78 $\pm$ 2.33	88.11 $\pm$ 4.04
IC-Cl	μ M	93902 $\pm$ 486	83711 $\pm$ 804	81735 $\pm$ 656	80137 $\pm$ 159	79385 $\pm$ 577
IC-F	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-NO3	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-PO4	μ M	b.d.l.	b.d.l.	b.d.l.	b.d.l.	b.d.l.
IC-SO4	μ M	9745 $\pm$ 67	7205 $\pm$ 59	6277 $\pm$ 244	5306 $\pm$ 221	5088 $\pm$ 351
pH		51 $\pm$ 2	130 $\pm$ 3	198 $\pm$ 11	246 $\pm$ 16	332 $\pm$ 37
salinity	ppt	6.8 $\pm$ 0.01	6.84 $\pm$ 0.05	6.89 $\pm$ 0.01	6.97 $\pm$ 0.03	6.96 $\pm$ 0.06
temperature	°C	9	7	7	6	5.33 $\pm$ 0.58
total ammonia	mg N L ⁻¹	21.9 $\pm$ 0.1	21.4 $\pm$ 0.1	21.7 $\pm$ 0.1	21.6 $\pm$ 0.1	21.5 $\pm$ 0.1
THg	μ g gdw ⁻¹	11.77 $\pm$ 0.06	6.92 $\pm$ 0.17	3.68 $\pm$ 0.79	3.98 $\pm$ 0.84	2 $\pm$ 0.32
MeHg	ng gdw ⁻¹	15 $\pm$ 1	16 $\pm$ 1	15 $\pm$ 1	16	15 $\pm$ 1

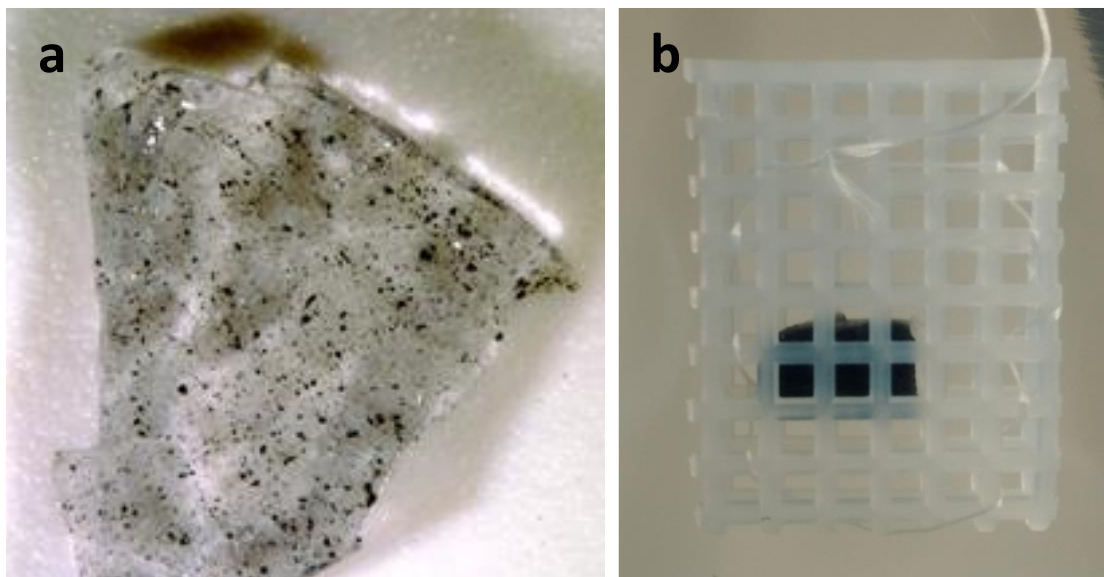


Figure AIV.S1. Photos of ag+AC passive sampler. (a) Sampling polymer under light microscope; (b) polymer suspended in a protective polypropylene basket for deployment in soil.

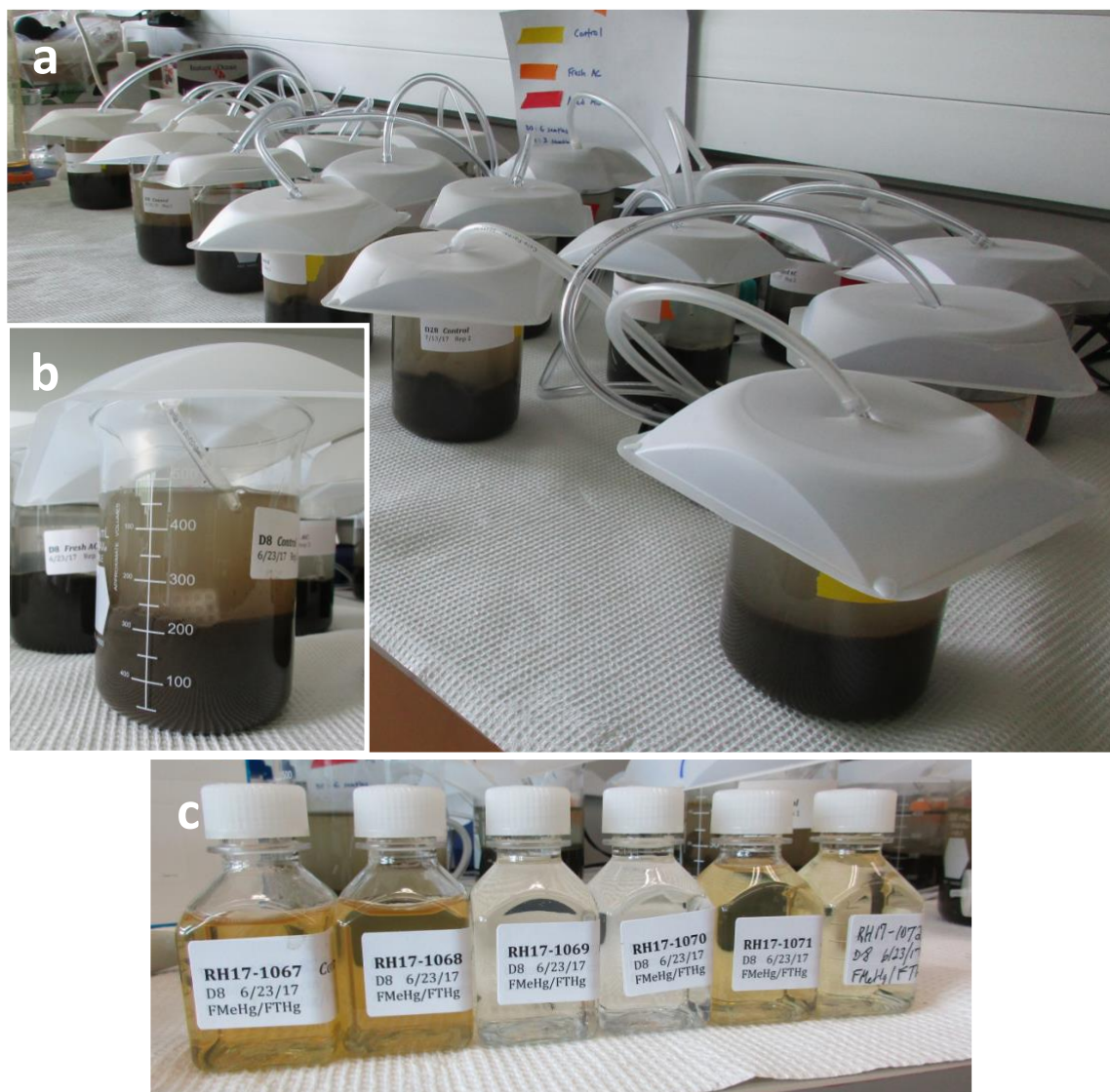


Figure AIV.S2. Photos of soil microcosm Experiment 2. (a) Overview of experimental setup; (b) detail view of one beaker showing passive sampler in basket deployed at soil-water interface; (c) filtered porewaters showing effect of AC on DOM concentration—left pair, unamended; center pair, amended with fresh AC; right pair, amended with aged AC.

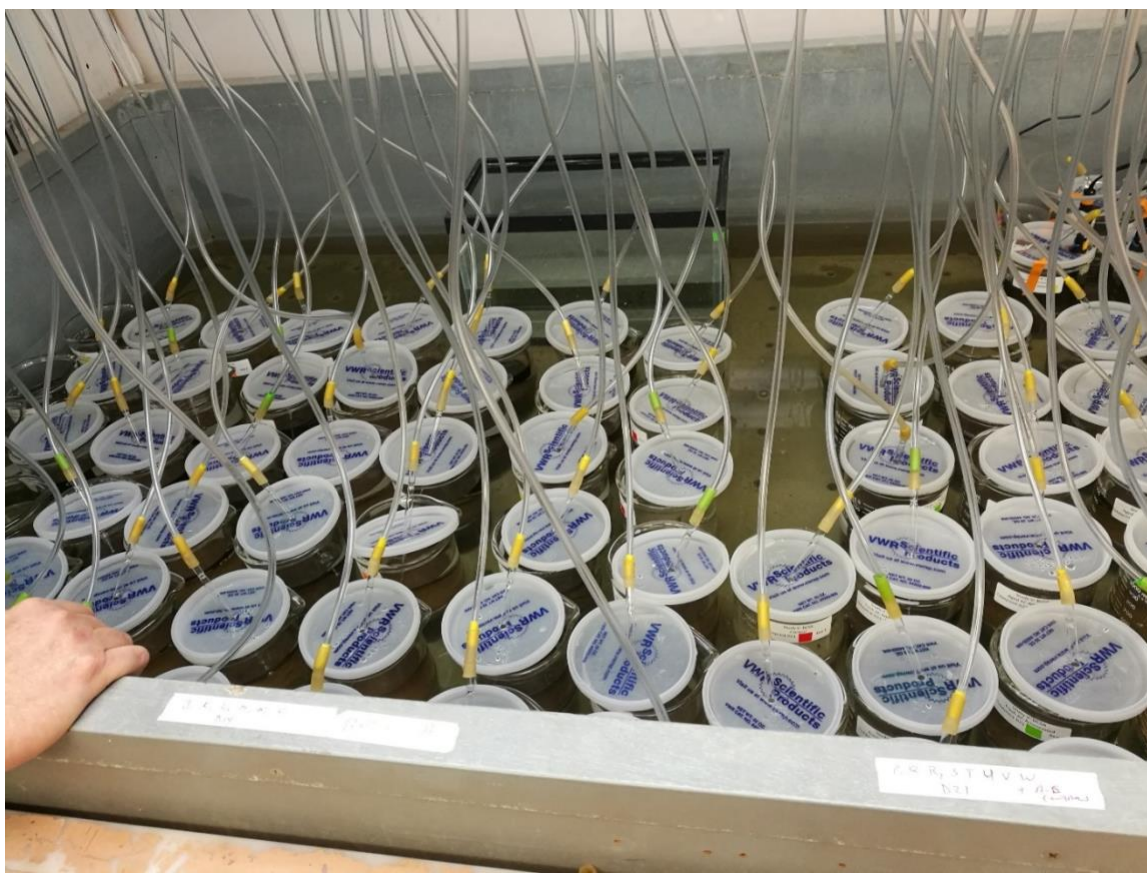


Figure AIV.S3. Photo of soil microcosm Experiment 3. Glass beakers were immersed in a water bath and loosely lidded, and overlying water was gently aerated.

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