DEVELOPMENT OF IN-SITU MERCURY REMEDIATION APPROACHES BASED ON METHYLMERCURY BIOAVAILABILITY

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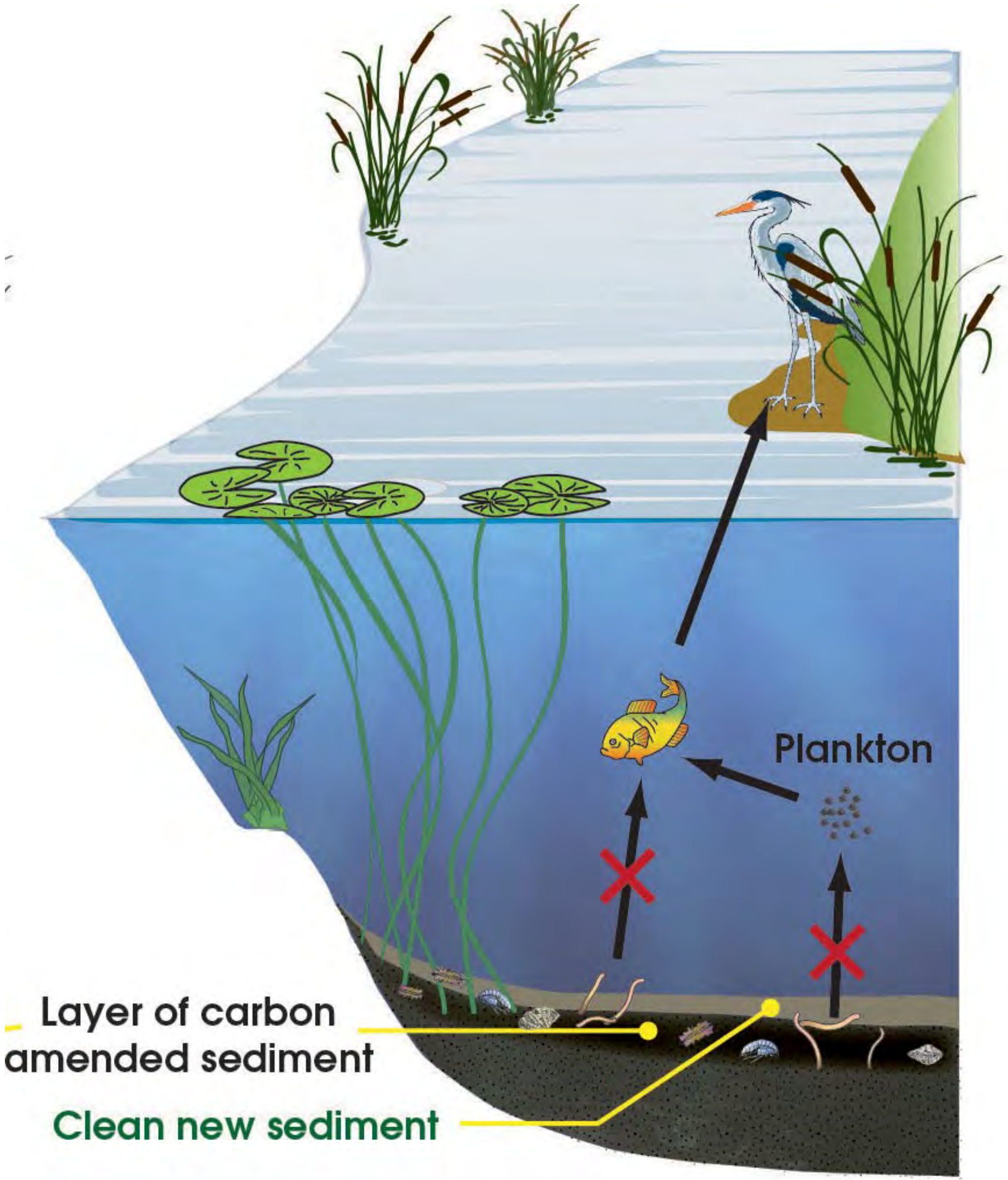
RESEARCH BACKGROUND



Activated carbon amended to surficial sediments reduces uptake of bioaccumulative pollutants in the food chain through:

1) Reduced porewater concentrations
2) Reduced bioaccumulation in benthic organisms
3) Reduced flux into water column and uptake in the pelagic food web.

Demonstrated for PCBs in several pilot studies

Q: Can AC or biochar sequester Hg/MeHg and reduce bioavailability?

See Feature Article : In-situ sorbent amendments: A new direction in contaminated sediment management. Ghosh et al. *Environ. Sci. Technol*. 45, 1163–1168. 2011.

SPECIFIC AIMS OF NIEHS PROJECT

Specific Aim 1: Develop in situ remediation tools for Hg and MeHg impacted sediments

- Evaluate how black carbons impact Hg methylation and MeHg degradation rates, and microbial community structure and activity, particularly the activity of hgcA.
- Test the effectiveness across a broader range of biogeochemical conditions and sediment types.
- Identify characteristics that make sites suitable for in situ remediation, by developing a model for AC/biochar effectiveness across biogeochemical conditions.

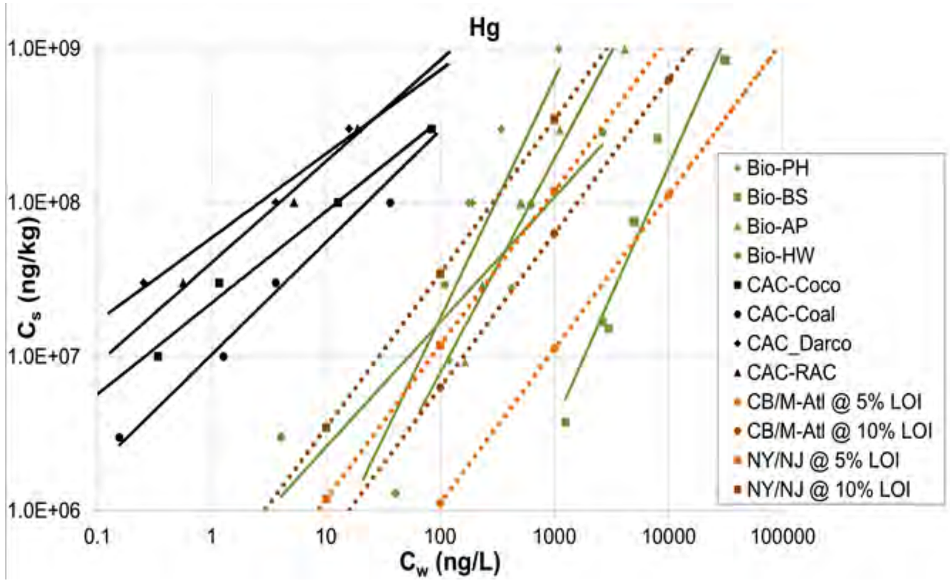
Specific Aim 2: Fill key knowledge gaps needed to develop a biogeochemical model for MeHg production and degradation in contaminated sediments and soils:

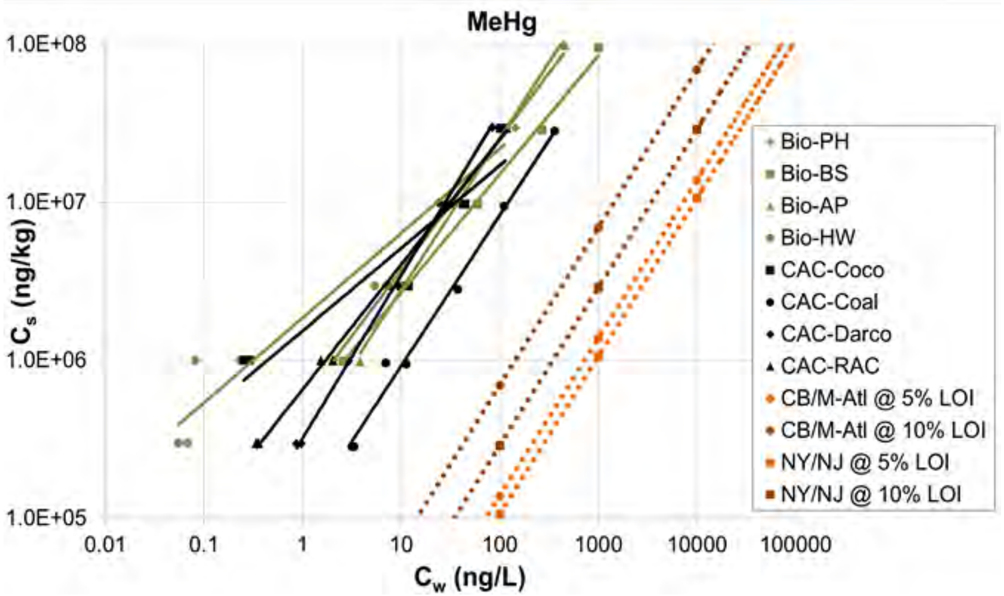
- Determine the role of microbial community structure in MeHg production, using genetic probes for the newly-identified microbial Hg-methylation genes.
- Assess the relative roles of MeHg production and degradation in net MeHg accumulation, using novel analytical methods.
- Determine and correlate vertical profiles of methylation and demethylation rates, with *hgcAB* abundance and expression in sediment cores and evaluate how different sorbent amendment strategies can influence overall MeHg bioavailability.

APPROACH TO EVALUATING AC AS A TOOL FOR Hg RISK REDUCTION

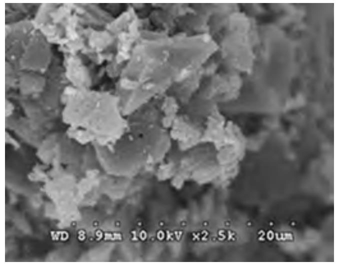
- Isotherm studies to evaluate potential AC and biochars
- Lab studies to evaluate efficacy across soil types
- Small-scale field and mesocosm trials
  - Penobscot River, ME
  - Berry's Creek, NJ
  - SERC marsh
- Lab work to examine mechanisms and parameterize models

MERCURY ISOTHERM STUDIES FOR SELECTED BIOCHARS AND ACTIVATED CARBONS

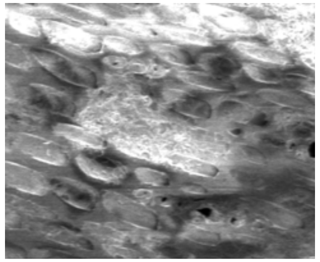




AC



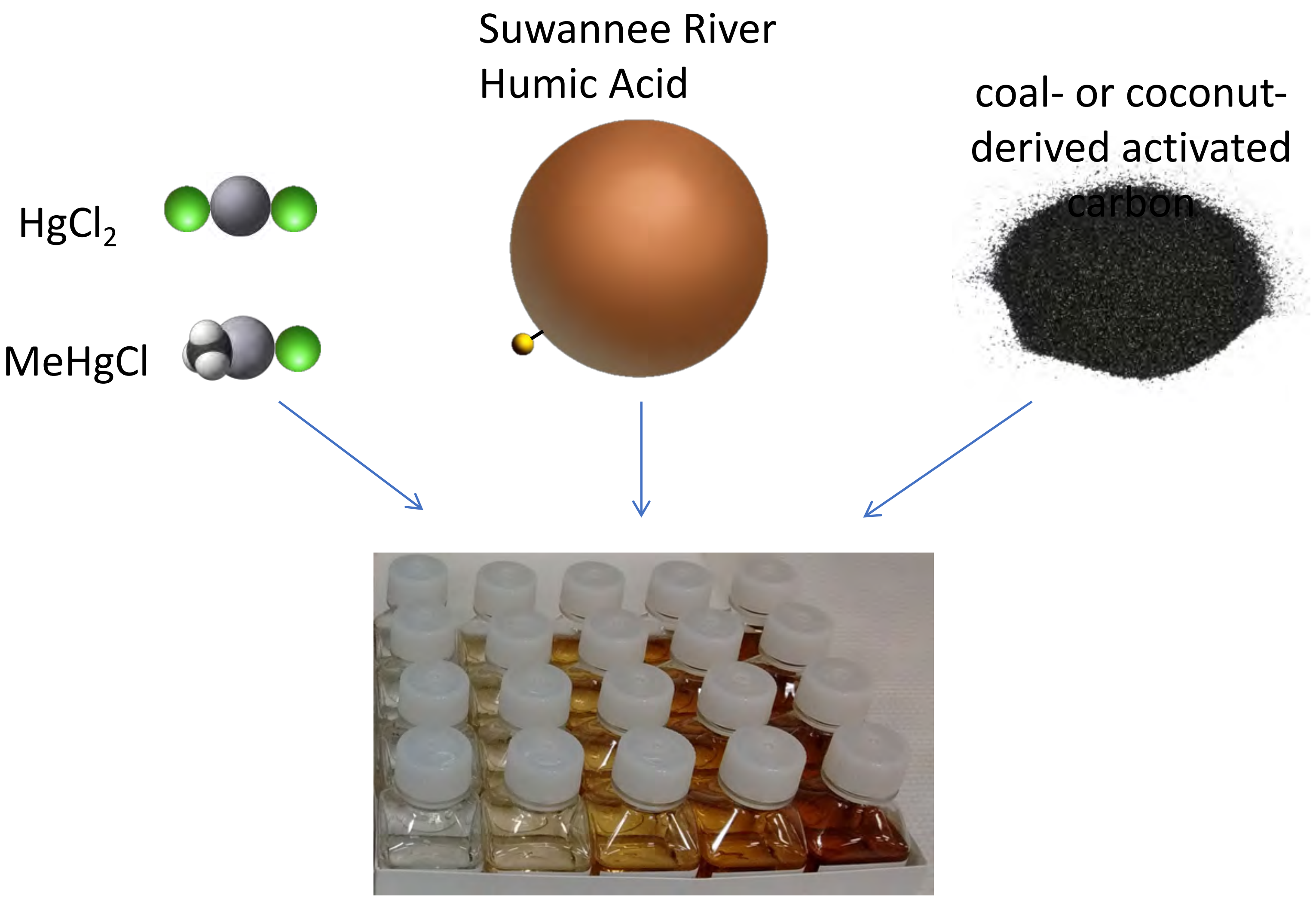
biochar



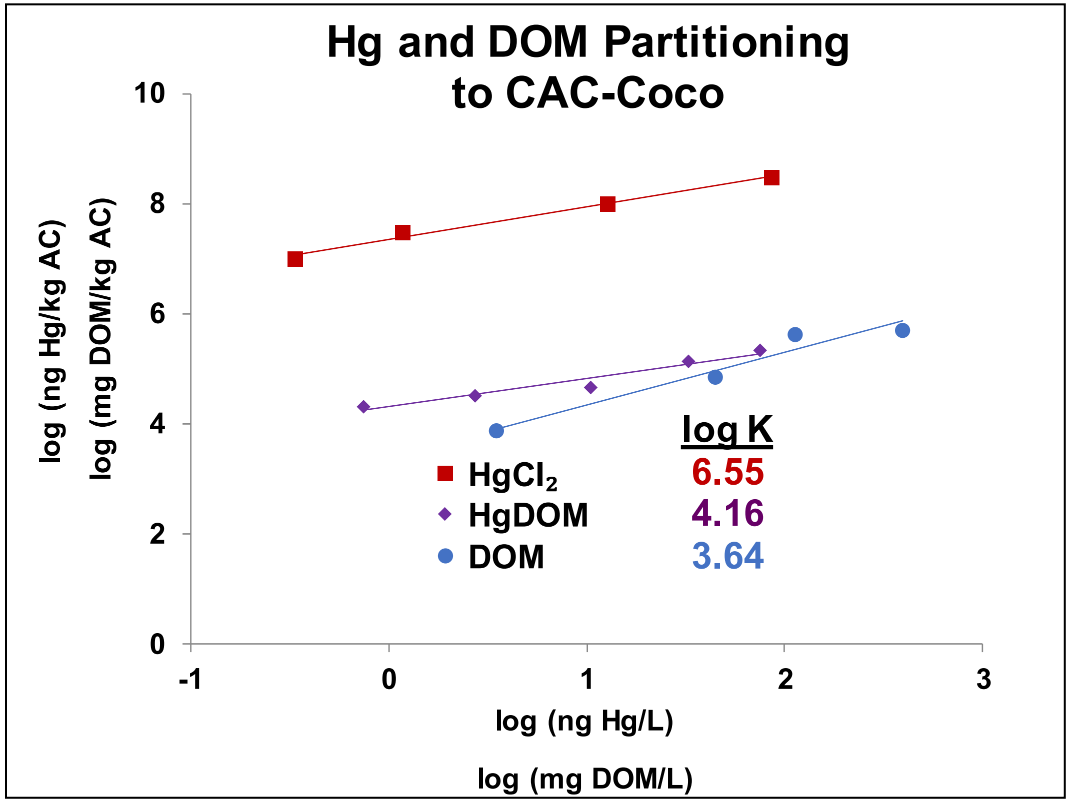
- ACs 2-3 orders of magnitude stronger sorbents than natural sediments
- ACs stronger sorbent of Hg compared to biochars
- ACs and biochars equally effective for MeHg
- Predicted reductions in sediment with 5% AC:
  - 94-98% for porewater Hg
  - 73-92% for porewater MeHg

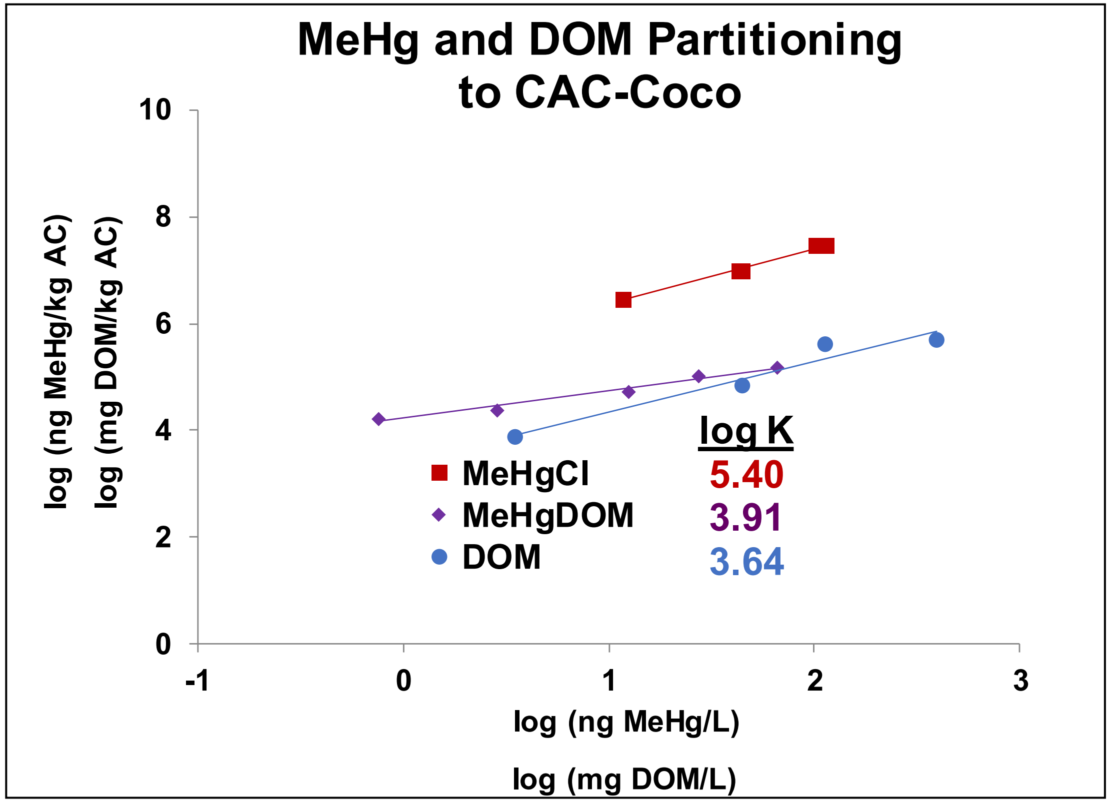
Gomez-Eyles et al. ES&T 2013

Mercury/DOM/AC Isotherms



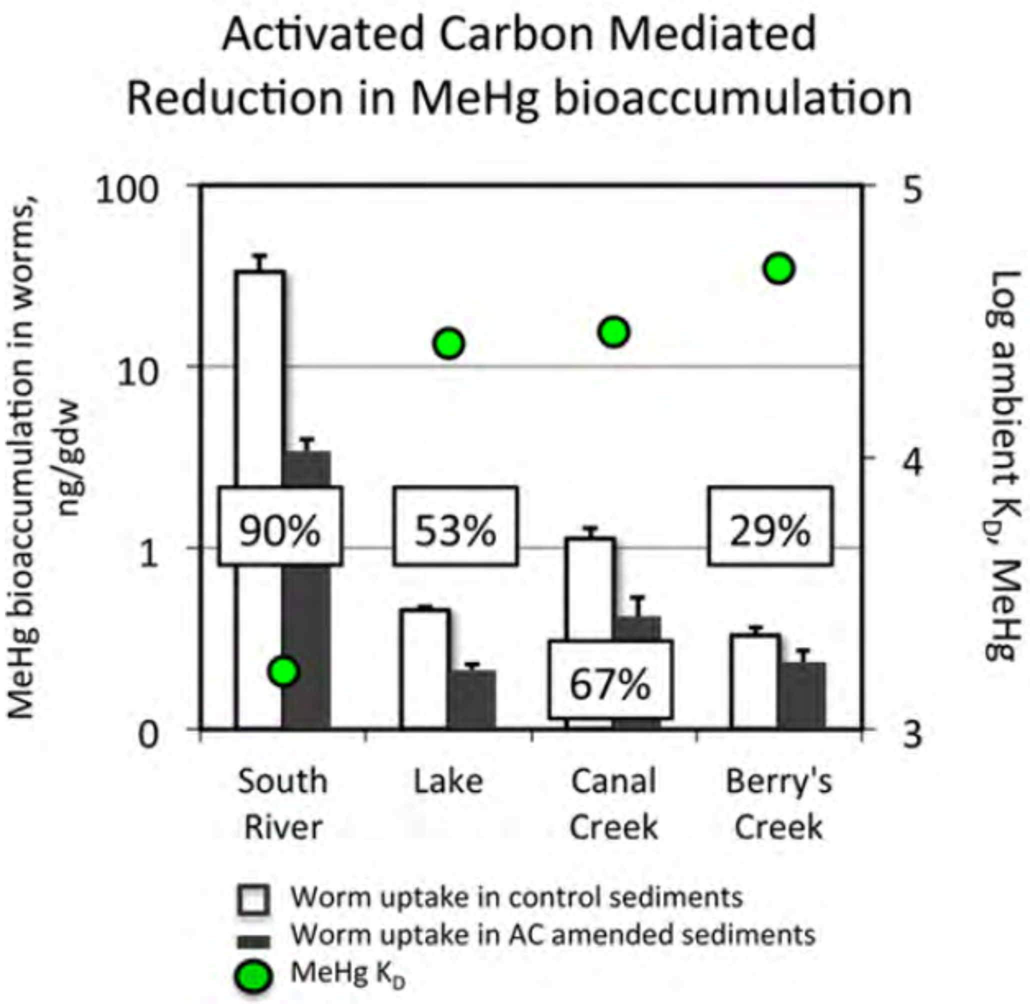
MERCURY ISOTHERM STUDIES WITH DOM





- One to three orders of magnitude difference in AC partitioning for Hg, MeHg complexed to DOM vs. Cl^-
- Sorption behavior closely resembles, and is likely controlled by, DOM
- Potentially critical implications for remedy dose calculations
- Highlights importance of understanding aqueous chemistry for fate and transport

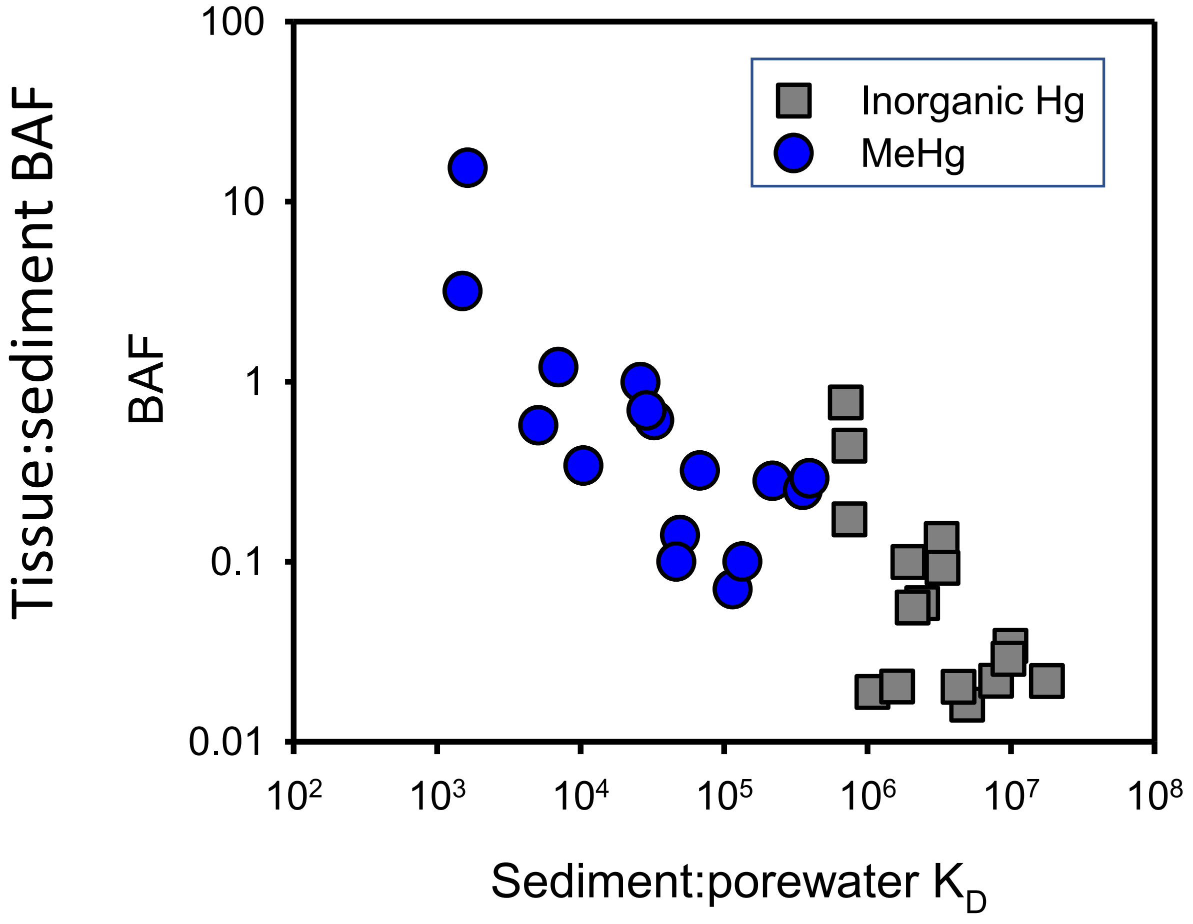
PRELIMINARY LAB STUDIES WITH AC



- Field sediments used to set up laboratory mesocosms
- Freshwater and estuarine sites
- Large range of native Hg concentrations
- 5% AC amendment
- Bioaccumulation in *L. variegatus*

Gilmour, C.C., G.S. Riedel, G. Riedel, S. Kwon and U. Ghosh. 2013. Activated carbon mitigates mercury and methylmercury bioavailability in contaminated sediments. Environ. Sci. Technol. 47:13001-13010.

K_D : SURROGATE FOR HG AND MEHG BIOAVAILABILITY

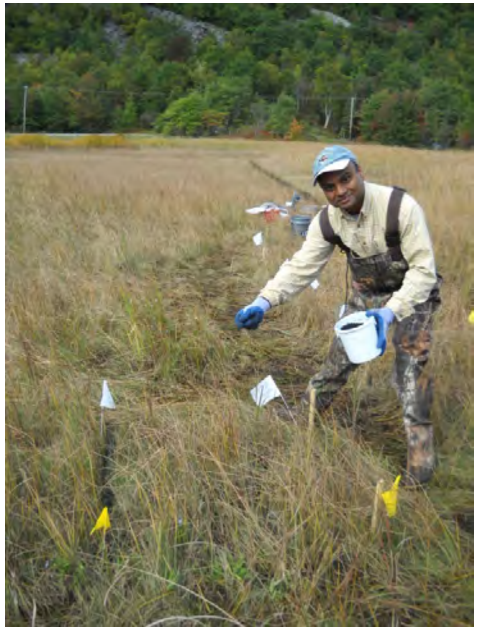


Lumbriculus BAFs vs. K_D for Hg and MeHg, all treatments

PILOT TESTING: TIDAL MARSH IN NEW ENGLAND
Mendell Marsh, Penobscot River, ME

Design

- 3’ X 3’ plots in two parts of the marsh
- Set up in 3 rows of 5 plots
- Treatments are randomized within each row
- 3 replicate plots per treatment
- Loading: 5% by dry weight of soil, based on top 10 cm of soil

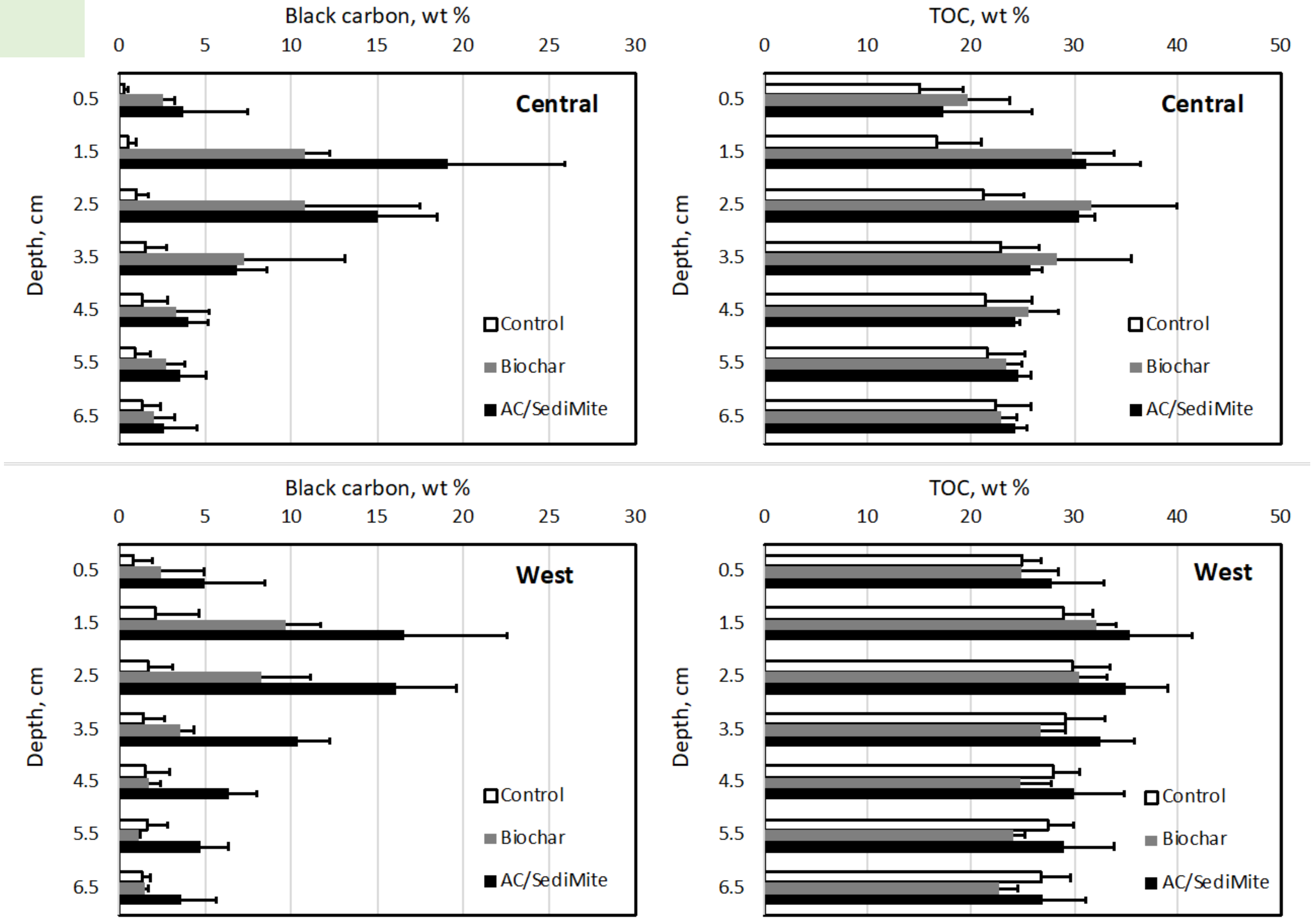


Treatment	Loading (kg/m2)
Control	None
$FeCl_2 . 4H_20$	2.3
Lime	0.5
Biochar – Pine Dust	1
SediMite (coconut shell PAC 50%)	2.3

Supported by: Penobscot River Study/Mallinckrodt Chemical

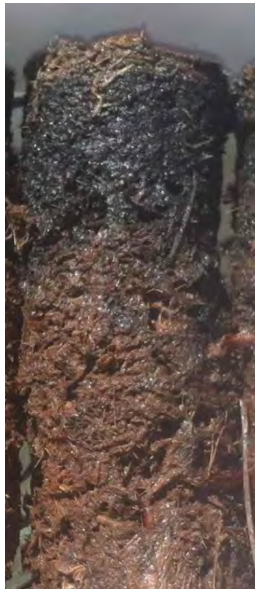
KEY RESULTS FROM PILOT STUDY

Black carbon depth profiles, 2017 to 7 cm



Retention and depth of black carbon in Mendall Marsh soils

1 year after AC application

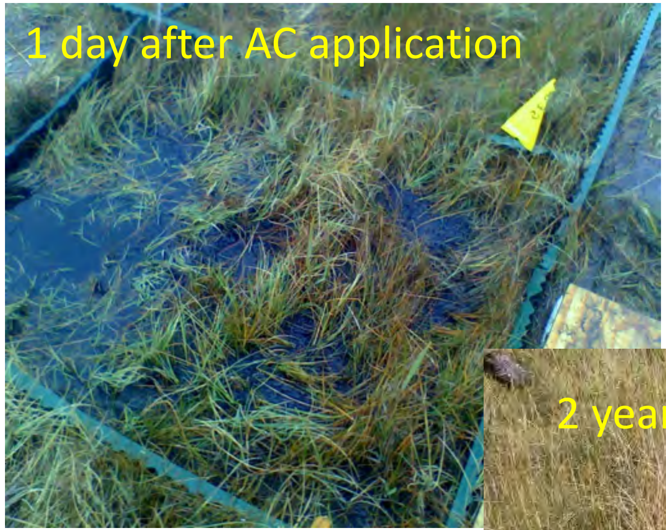


7 years after AC application

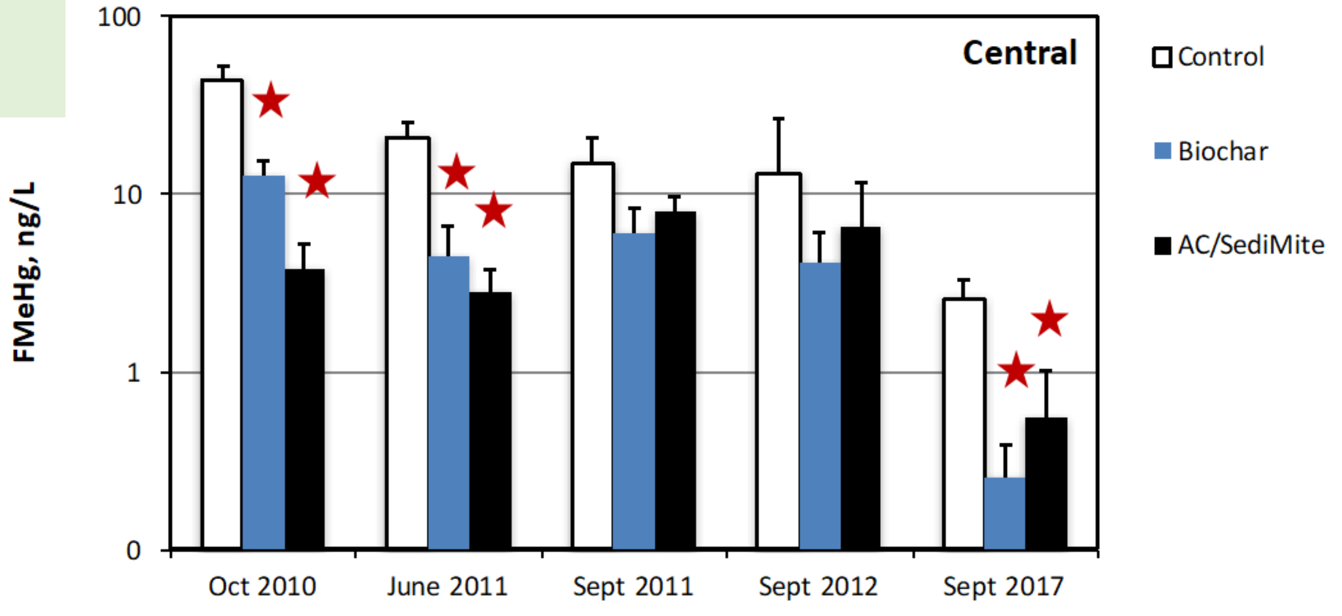
Retention after 7 years: AC 108 ± 46 %; Biochar 46 ± 26 %

KEY RESULTS FROM PILOT STUDY

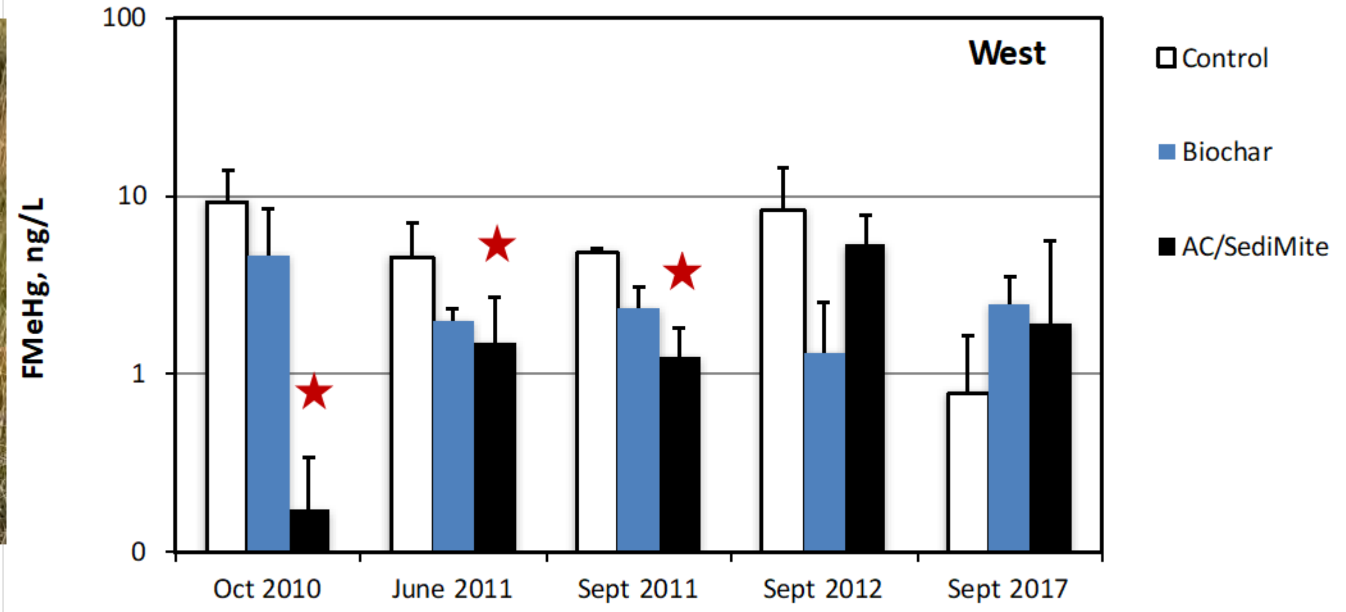
AC and Biochar impacts on porewater MeHg (top 5 cm) over time



91% 86% 78%



99% 66% 74% % Reduction by AC/SediMite



PENOBSCOT SUMMARY

Both AC/SediMite and Pine Dust biochar were visually retained in marsh soils

- retained in a discrete layer below the soil surface
- marsh soils have accreted/grown up around surface amendments
- Roughly 100% retention of AC, 50% retention of biochar

Black carbon remained effective in reducing pw Hg and MeHg to some degree even after 7 years.

PILOT TESTING: MARSH MESOCOSMS, SERC

Focussed study to evaluate impacts of:

- marsh elevation (redox condition)
- Effectiveness of MnO_2 amendment

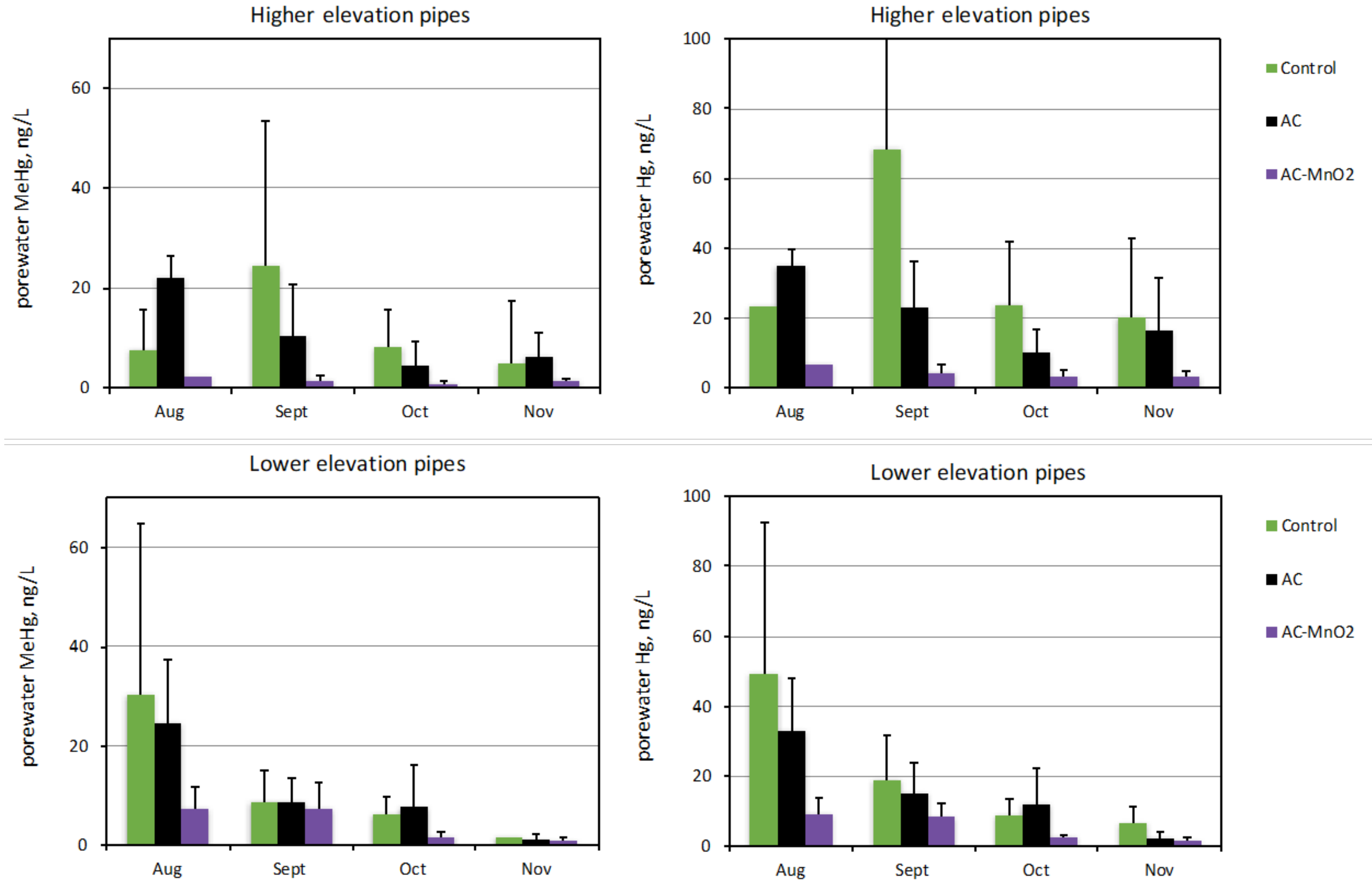
Treatment	Elevation	
	+ 5 cm	- 10 cm
Control	6	6
AC 5%	6	6
AC 9% + MnO_2 12%	3	3

Schwartz, Gilmour, Brown, Vlassopoulos et al. in prep. Quantifying the effects of activated carbon amendment and tidal inundation on mercury and methylmercury partitioning in Phragmites marsh mesocosms.

KEY RESULTS FROM MARSH ORGAN PILOT STUDY

- AC/MnO_2 significantly decreased MeHg at both pipe elevations
  - Control = AC > AC/MnO_2
- Variability among pipes was high
- Amendment effects varied with pipe elevation and soil depth (not shown)
- Porewater MeHg generally declined over time

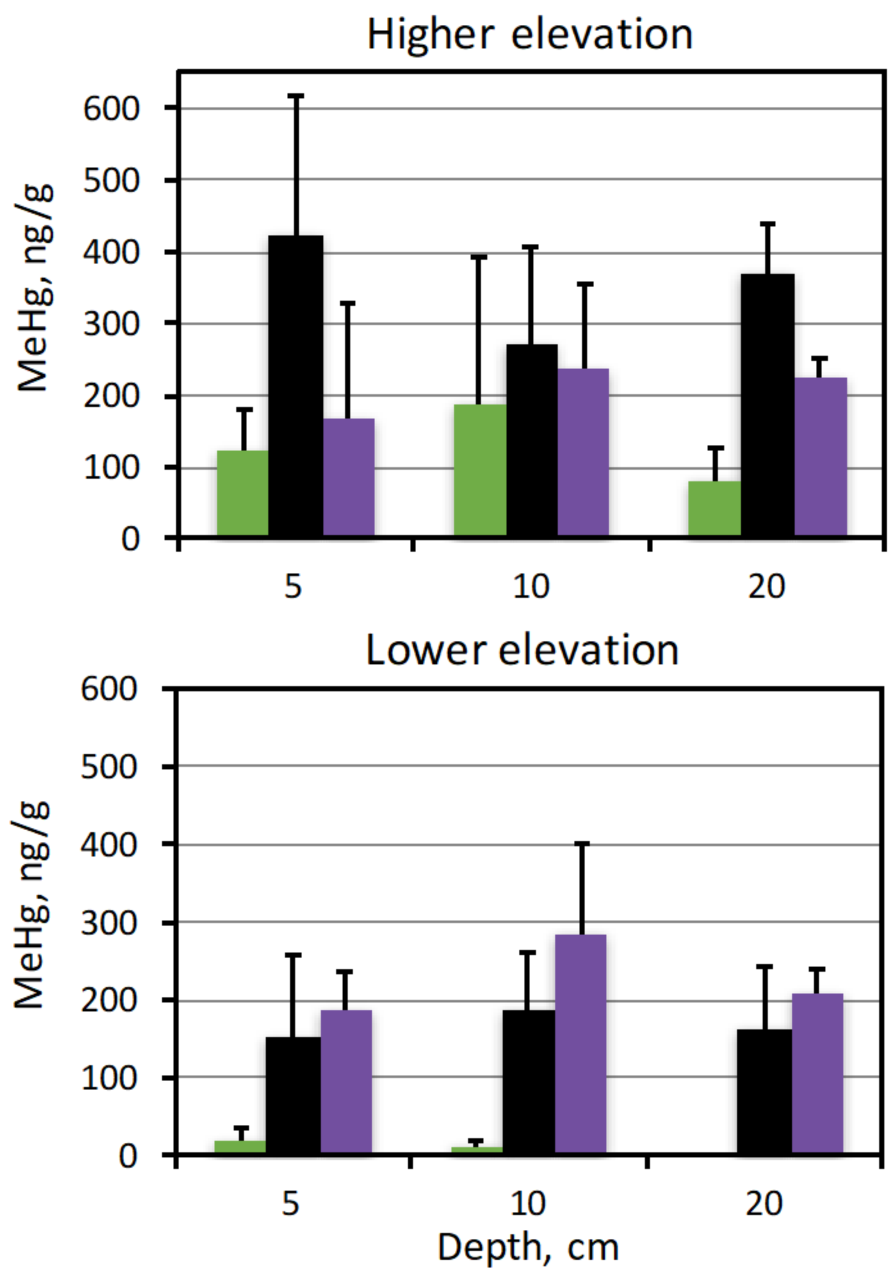
Porewater MeHg (0-10 cm) over time



KEY RESULTS FROM MARSH ORGAN PILOT STUDY

- Both AC and AC/MnO_2 increased soil MeHg.
  - MnO_2 did not mitigate MeHg accumulation

- Contrast: Did not observe increased MeHg in solids in the Penobscot or Berry's Creek field studies

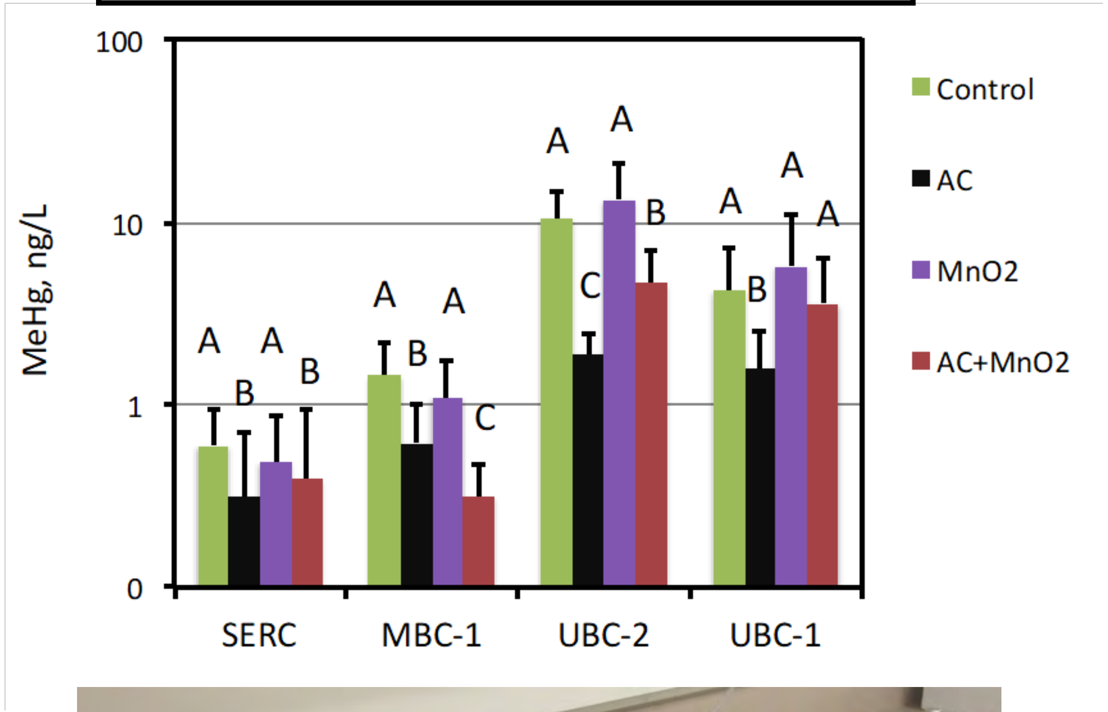


IMPACTS OF AC ON Hg METHYLATION, DEMETHYLATION IN MARSH SOILS

Slurry experiment with Berry's Creek marsh soils

- Anaerobic, 10 mM SO4, 5 ppt salinity
- 28 day time course w/ weekly destructive sampling
- 4 sites – 3 sites in Berry's Creek, + SERC
- Treatments:
  - Control
  - AC (5% of dry weight soil)
  - MnO_2 (~6% MnO_2)
  - AC + MnO_2 (sum of single amendments)

Porewater MeHg averages over 28 days



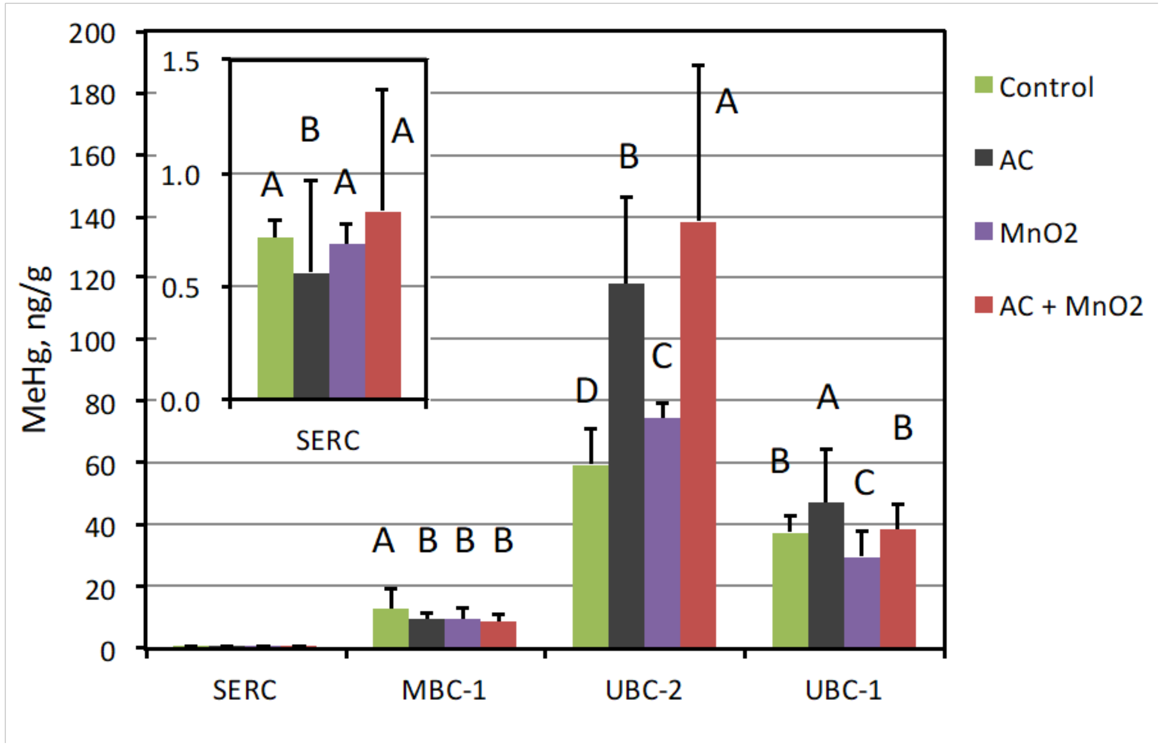
AC efficacy results:

- 5% AC significantly reduced porewater MeHg
- Effectiveness vary between 20 and 80% depending on site chemistry.

EFFECTS OF AC ON METHYLATION AND DEMETHYLATION

AC resulted in significantly higher solid MeHg than controls in two of four sites

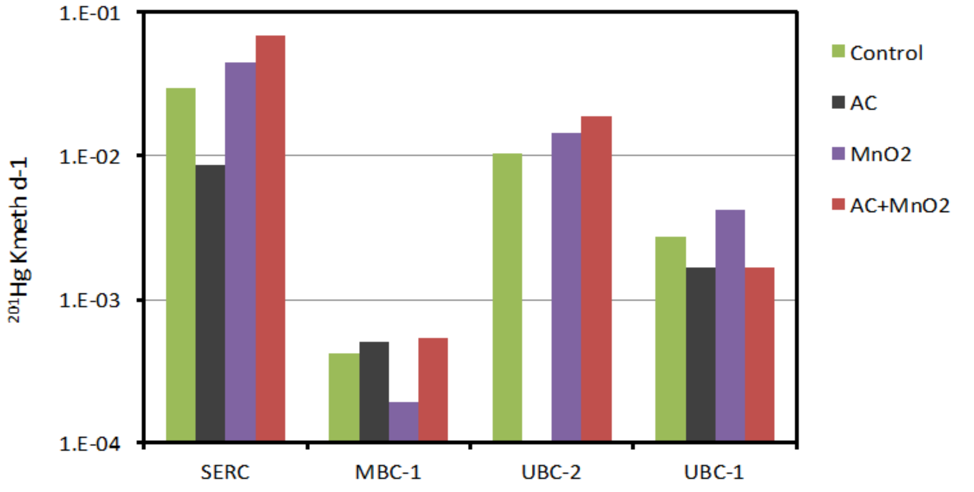
Native MeHg in solids



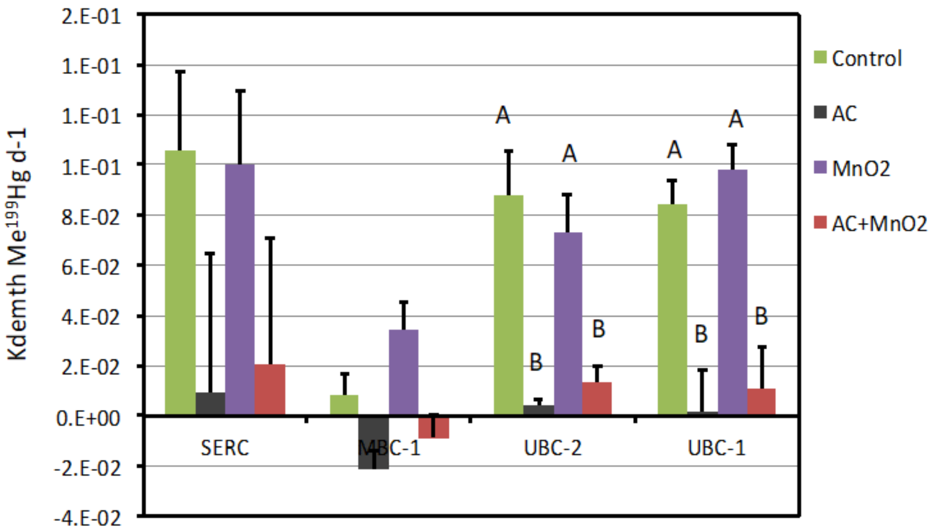
Methylation and demethylation assays with enriched stable isotopes each week

AC reduced methylation, but effectively blocked demethylation

Methylation rate constants from ^{201}Hg

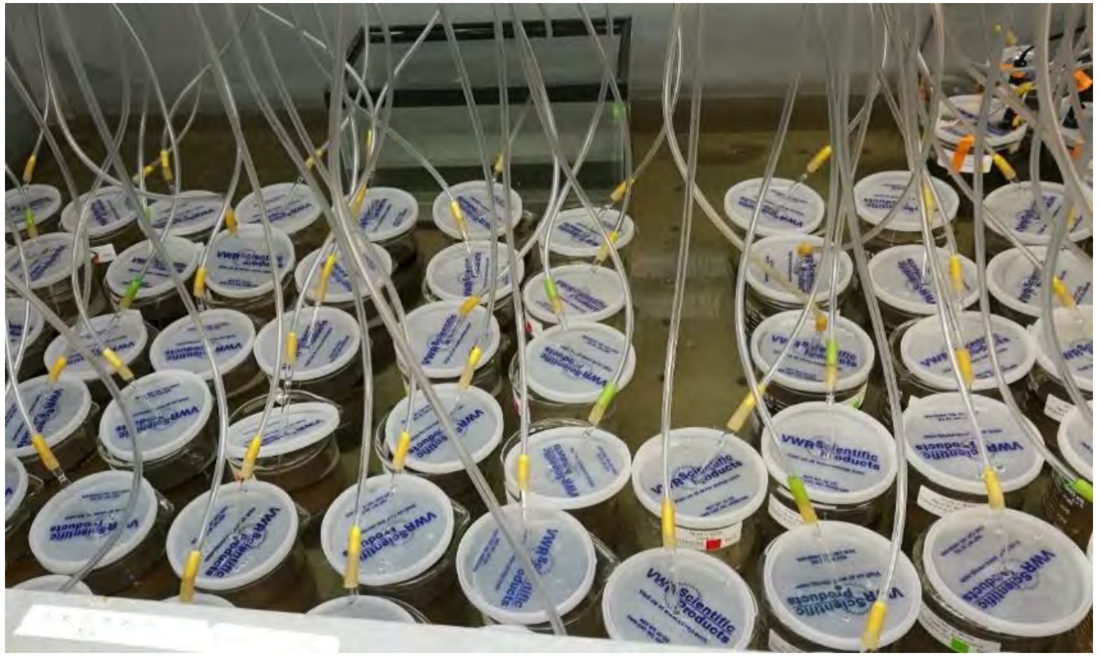


Demethylation rate constants from $Me^{199}Hg$



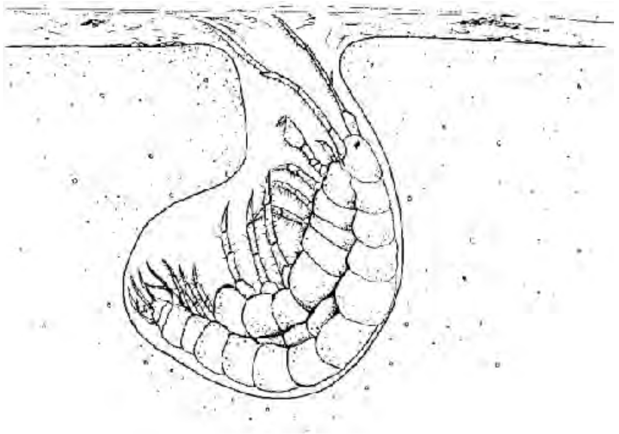
AC IMPACTS ON MeHg UPTAKE BY BENTHIC ANIMALS

Uptake studies done at ERDC in collaboration with Daniel Farrar and James Biedenbach; and Steve Brown (Dow) and Sue Driscoll (Exponent)



GOAL: Develop a method to test MeHg uptake by *L. plumulosus*

- Modify standard protocols to maintain and monitor MeHg in beaker sediments
- Evaluate AC effects on MeHg uptake, in comparison with MeHg in soils and porewaters, and sediment chemistry
- Evaluate the ability of equilibrium passive samplers to predict MeHg in porewater (Cw) and in animals

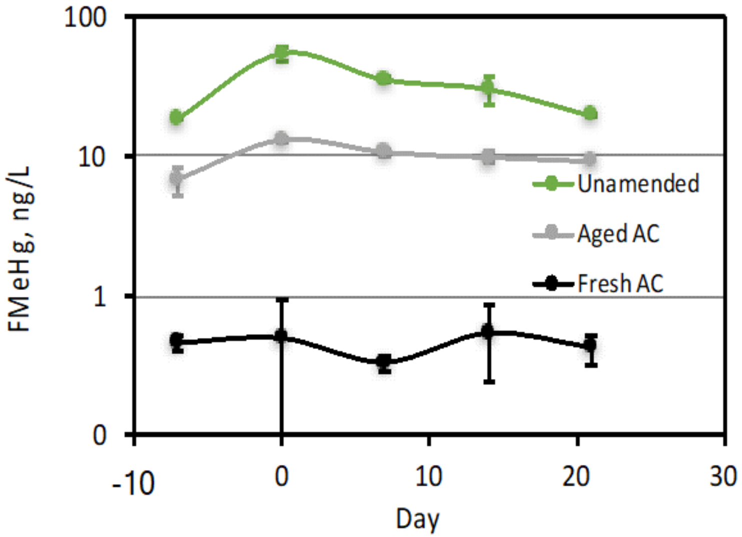


IMPACT OF AC AMENDMENTS ON UPTAKE BY *LEPTOCHEIRUS*

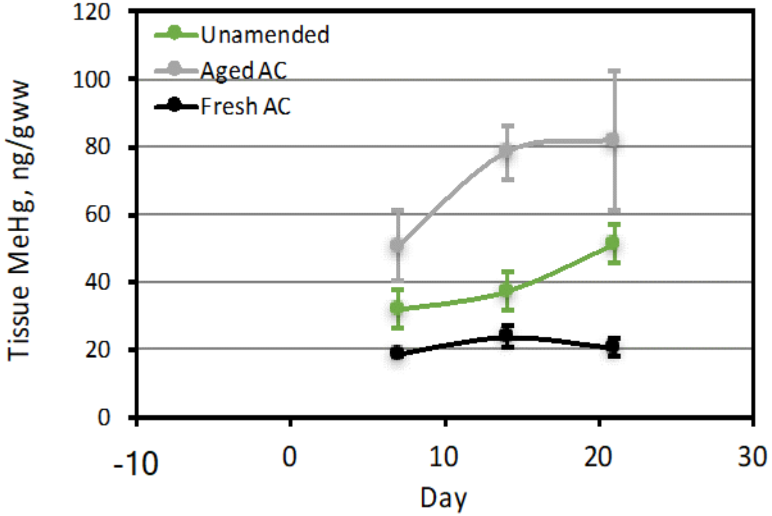
Beaker study of fresh and aged AC effects, using soils from *Phragmites* mesocosm study

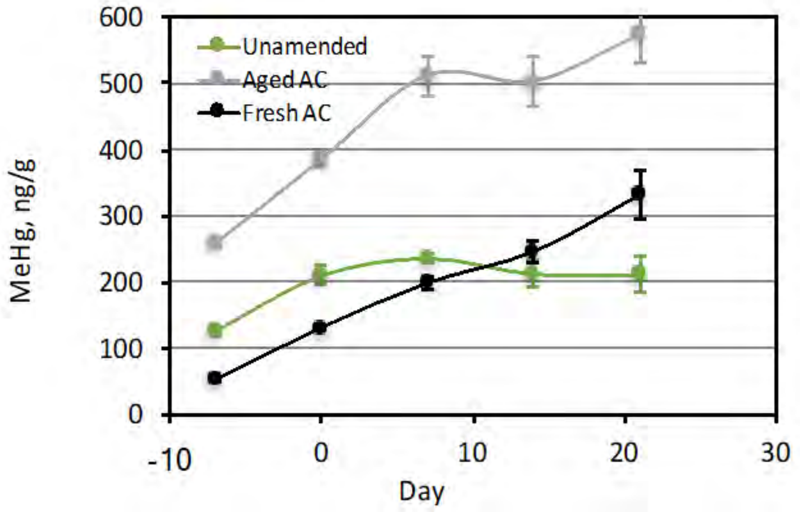
- Aged (1.5 years) and fresh AC reduced porewater Hg and MeHg relative to unamended control
- MeHg accumulated in the solid phase in aged AC samples above controls
- Fresh AC reduced uptake by amphipods
- MeHg bound to AC is less available than MeHg bound to untreated soils

Porewater MeHg

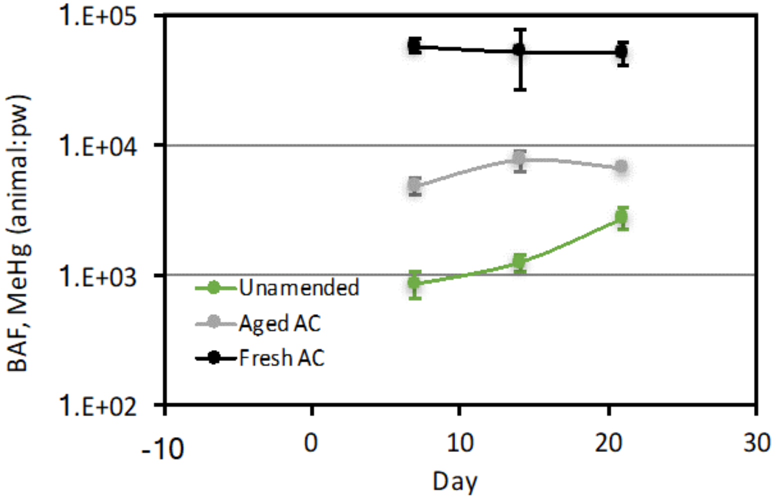


MeHg in *Leptocheirus*

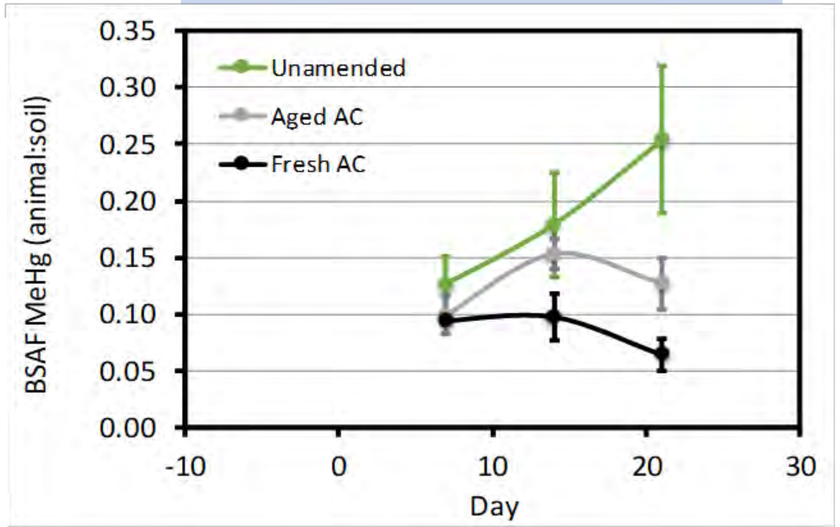




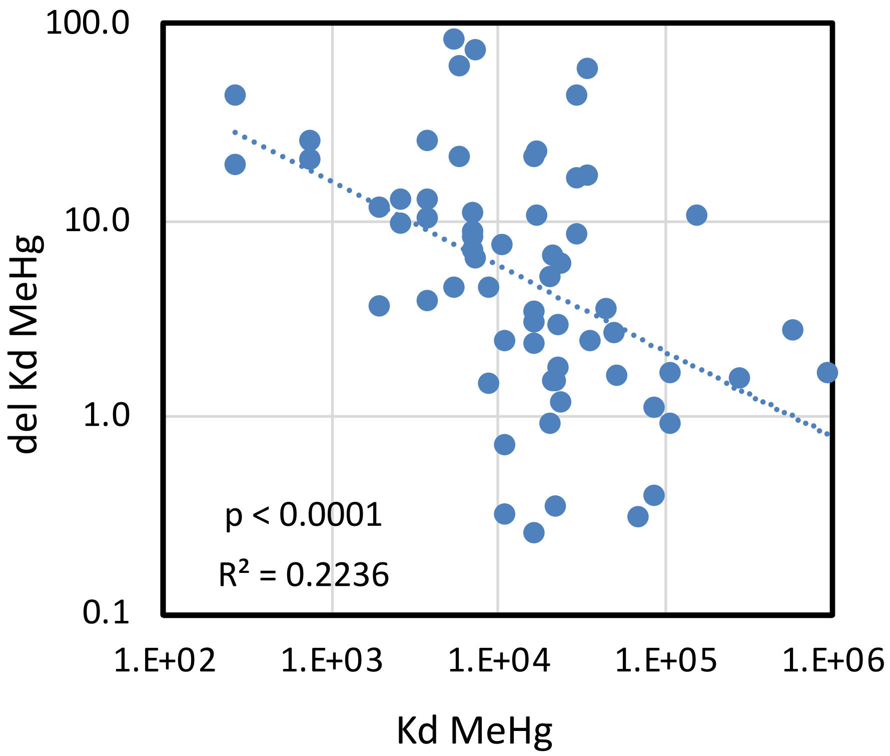
BAF from porewater



BAF from solid phase



Identification of characteristics that make sites suitable for *in situ* remediation



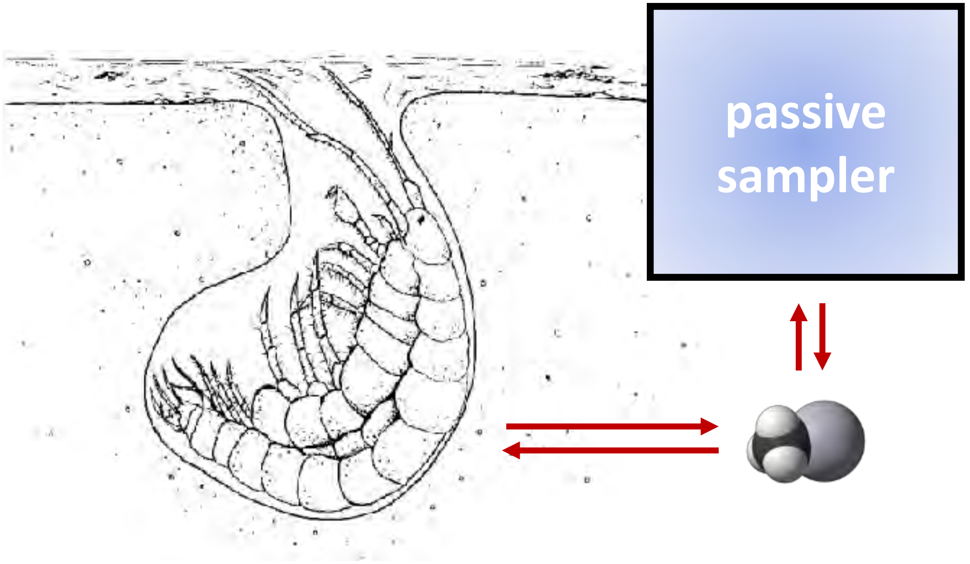
Summary of lab and field experiments
N=66

AC works best in soils and sediments with naturally low K_d

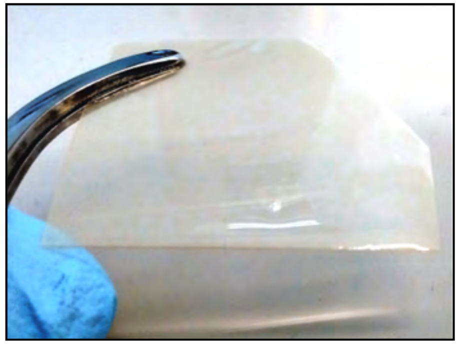
Stepwise model for increase in MeHg K_d:
Incubation time, sediment organic content, DOC, and sediment mineral content account for 50% of variability

ONGOING WORK: DEVELOPMENT OF A NOVEL EQUILIBRIUM PASSIVE SAMPLER FOR MEHG

1. Synthesize polymers with desired affinity for MeHg
2. Attain equilibrium with surroundings
3. Measure MeHg accumulation under increasingly realistic conditions
4. Select one or more polymers based on:
   a) physical stability
   b) strong partitioning of MeHg (log K ≅ 3 to 5)
   c) log-linear partitioning across a realistic range of C_w
5. Investigate kinetics and modes of accumulation
6. Correlate with *L. plumulosus* bioaccumulation



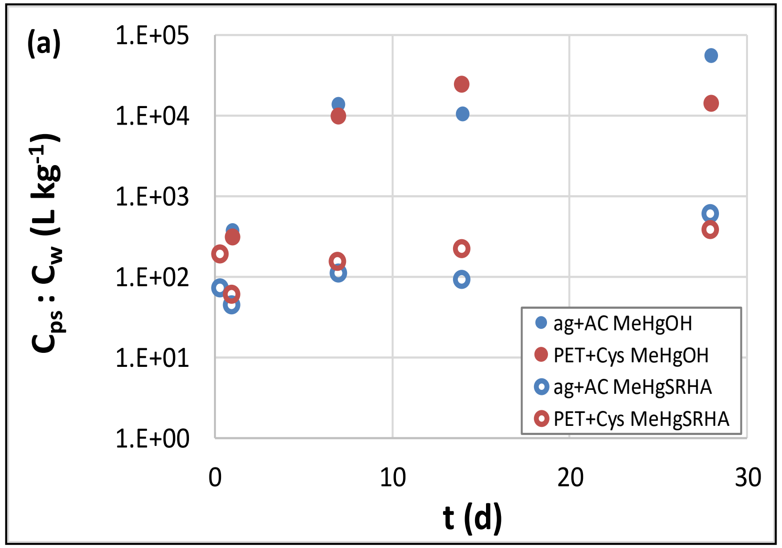
Note: Passive sampling method is being developed through a separate project supported by the DoD SERDP program

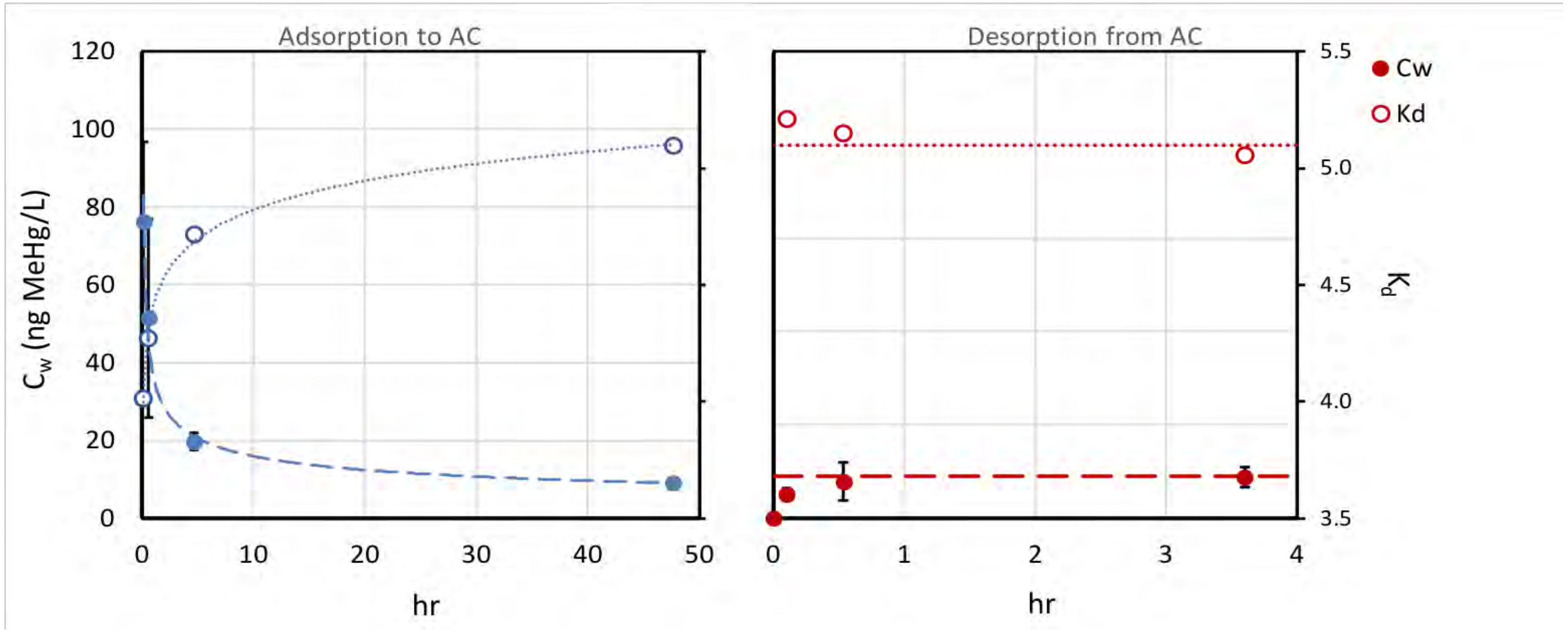


DEVELOPMENT OF AN EQUILIBRIUM PASSIVE SAMPLER FOR MeHg

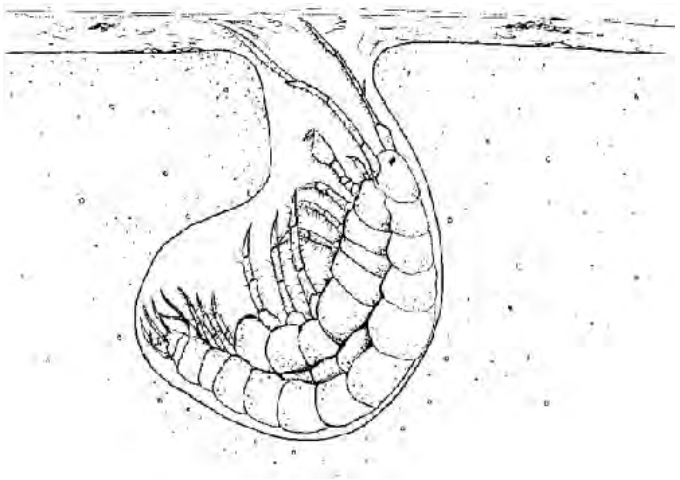
Goals:

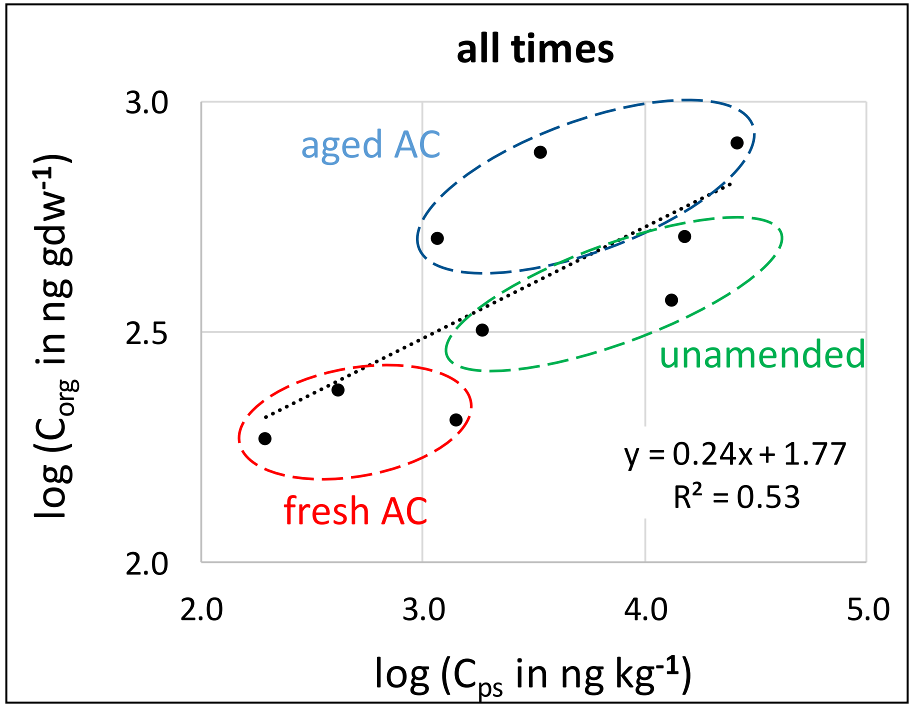
- identify sampler materials that would mimic MeHg partitioning into animals and sediments,
- provide reversible sorption and desorption in a time frame appropriate for *in situ* samplers,
- allow prediction of the concentration of the labile fraction of MeHg in sediment porewaters and uptake into animals

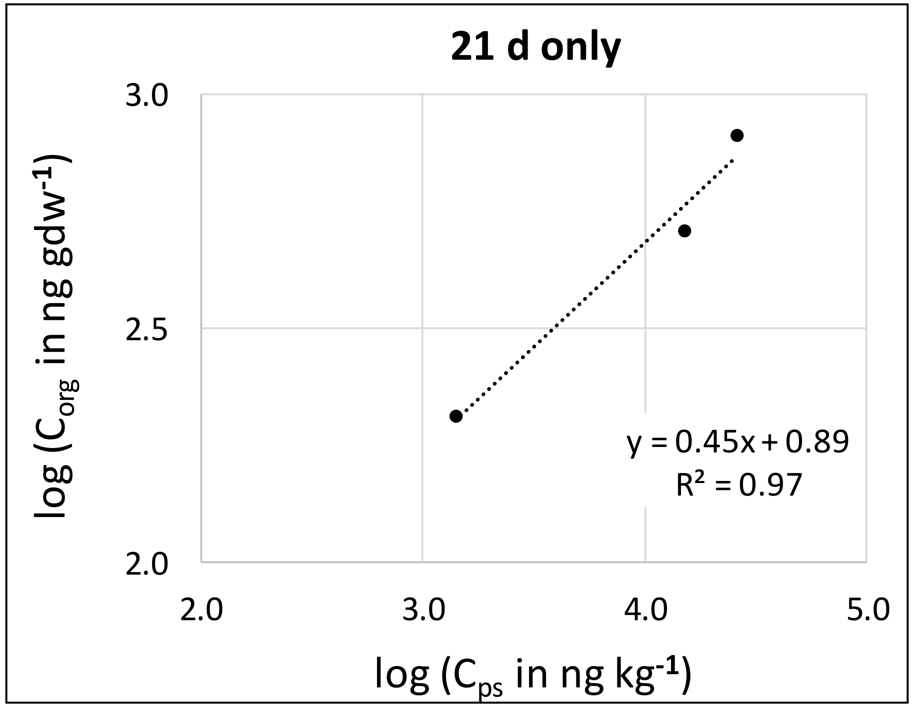




PASSIVE SAMPLING FOR MeHg & COMPARISON WITH BIOUPTAKE







SUMMARY

- Activated Carbon can be an effective tool in reducing MeHg risk by reducing MeHg in pore waters
- AC was more effective in reducing MeHg than total Hg for most sites
- AC efficacy for MeHg ranges from no impact to 50X increase in K_d
    - Avg. pore water reduction of ~50% across all studies
- AC is most effective for MeHg in soils with natural low K_d (high DOC, low FeS in soils)
- Ongoing research developing equilibrium passive sampling for MeHg

ACKNOWLEDGEMENTS

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Dimitri Vlassopoulos (Anchor QEA)
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- DoD SERDP/ESTCP Programs
- The Dow Chemical Company
- Penobscot River Study

Disclosure statement:
Upal Ghosh 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.