# *In Situ* Activated Carbon Amendment for Sediment and Soil Mercury Remediation

**Presented at: FRTR Semi-Annual General Meeting**
**NRC Headquarters, Rockville, MD**
**Nov. 8, 2017**


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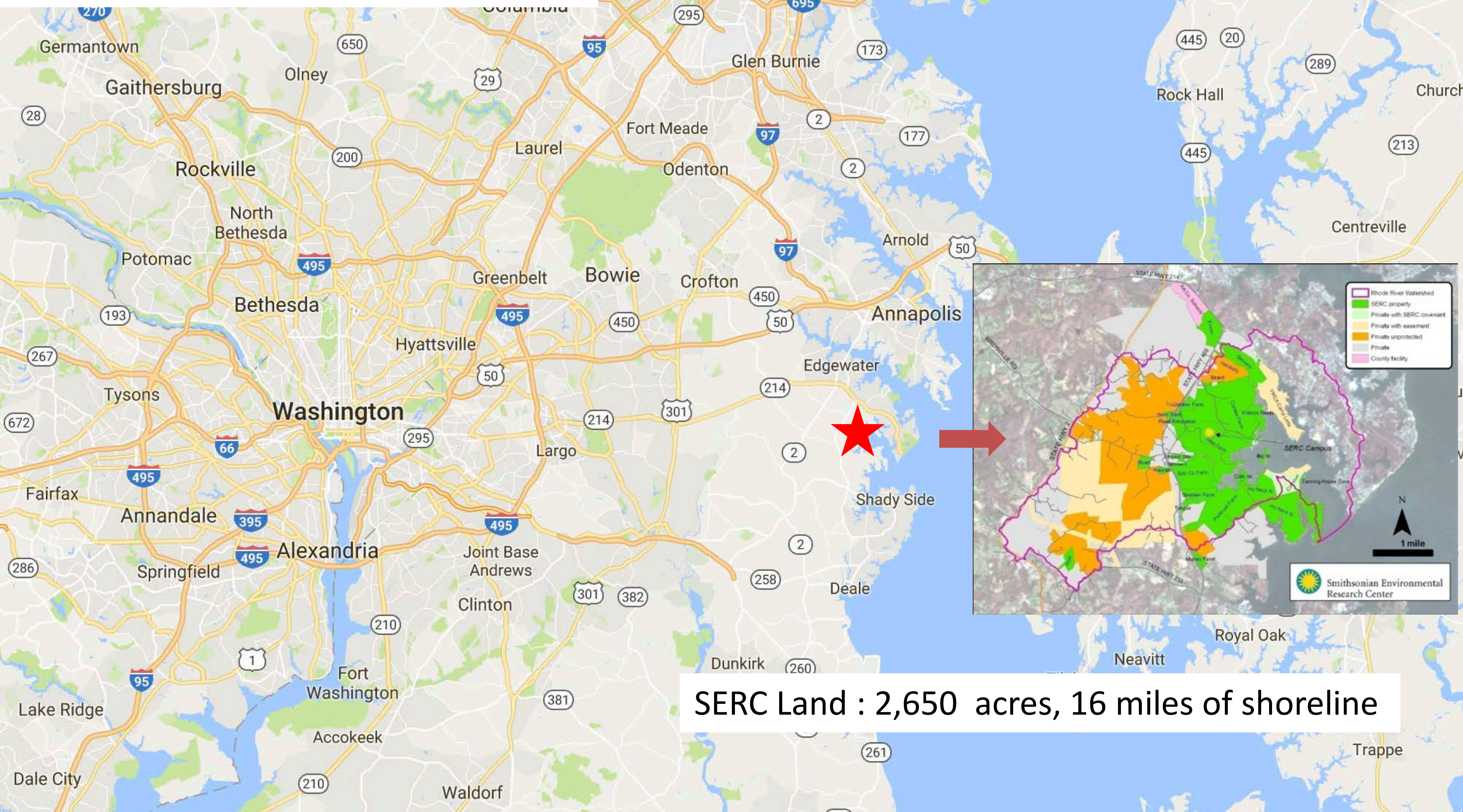
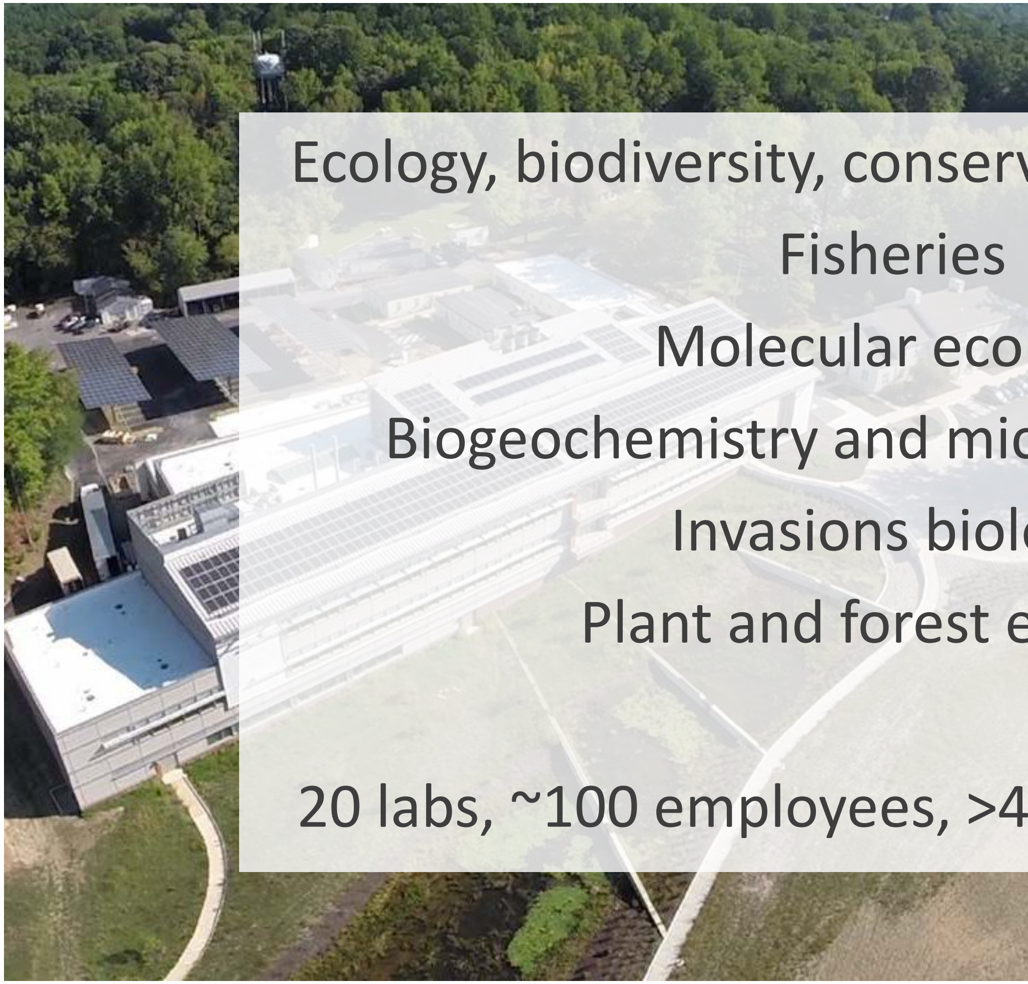
Smithsonian Environmental Research Center

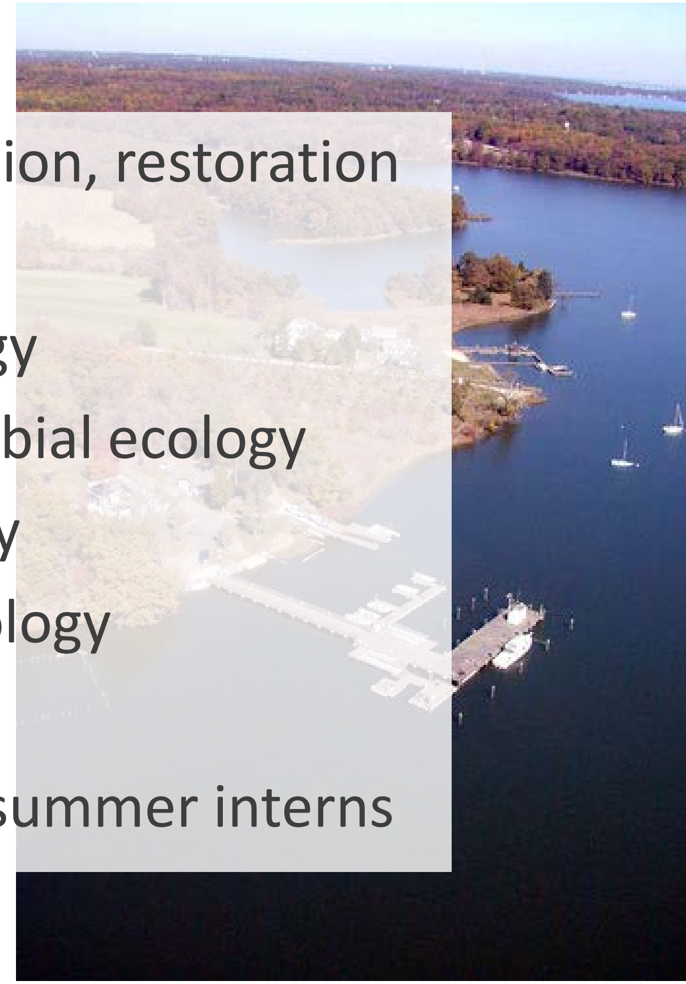
# Smithsonian Environmental Research Center




SERC Land : 2,650 acres, 16 miles of shoreline

# Smithsonian Environmental Research Center





Ecology, biodiversity, conservation, restoration

Fisheries

Molecular ecology

Biogeochemistry and microbial ecology

Invasions biology

Plant and forest ecology

20 labs, ~100 employees, >40 summer interns

Environmental Science & Technology

FEATURE

pubs.acs.org/est

# In-situ Sorbent Amendments: A New Direction in Contaminated Sediment Management†

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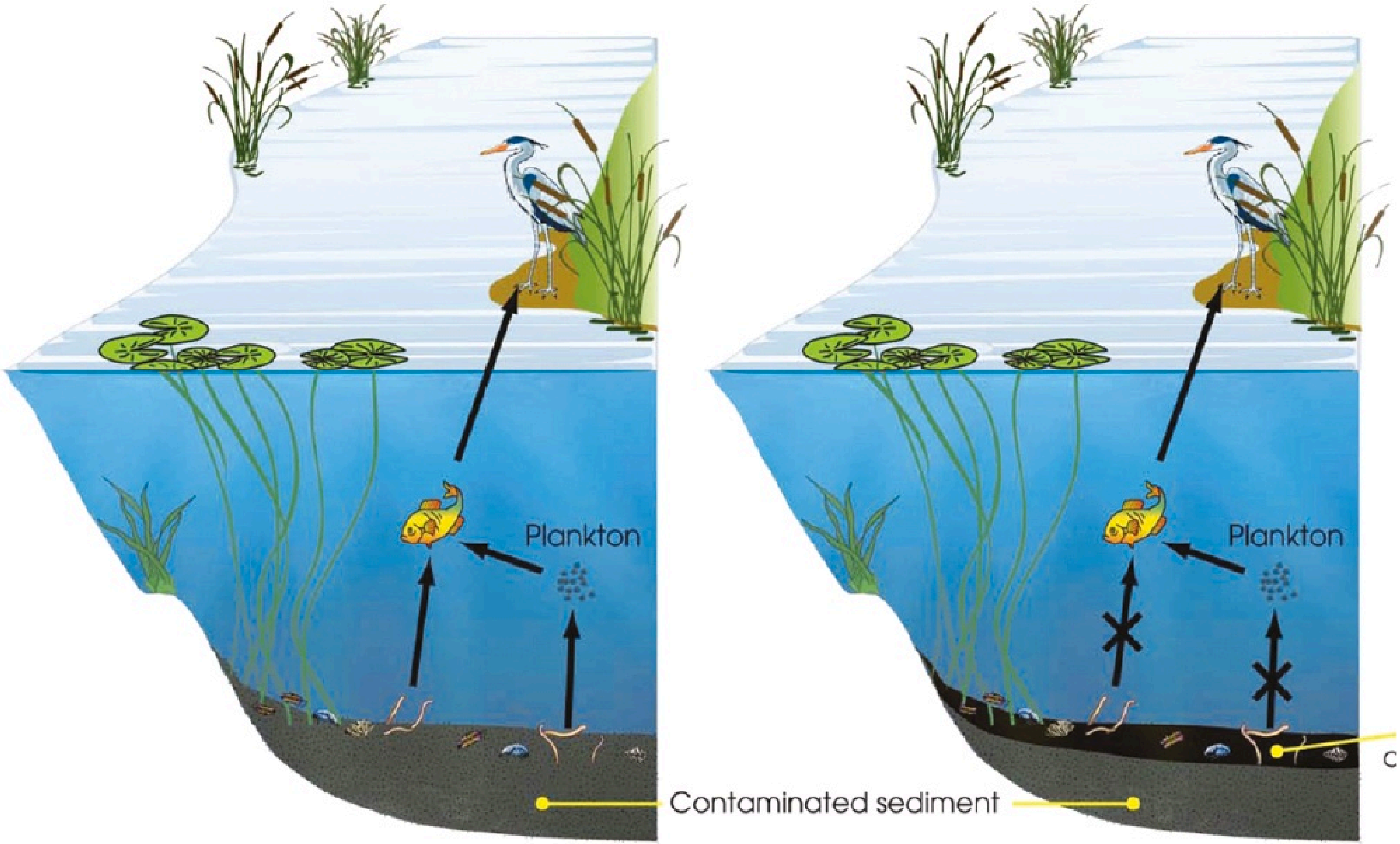
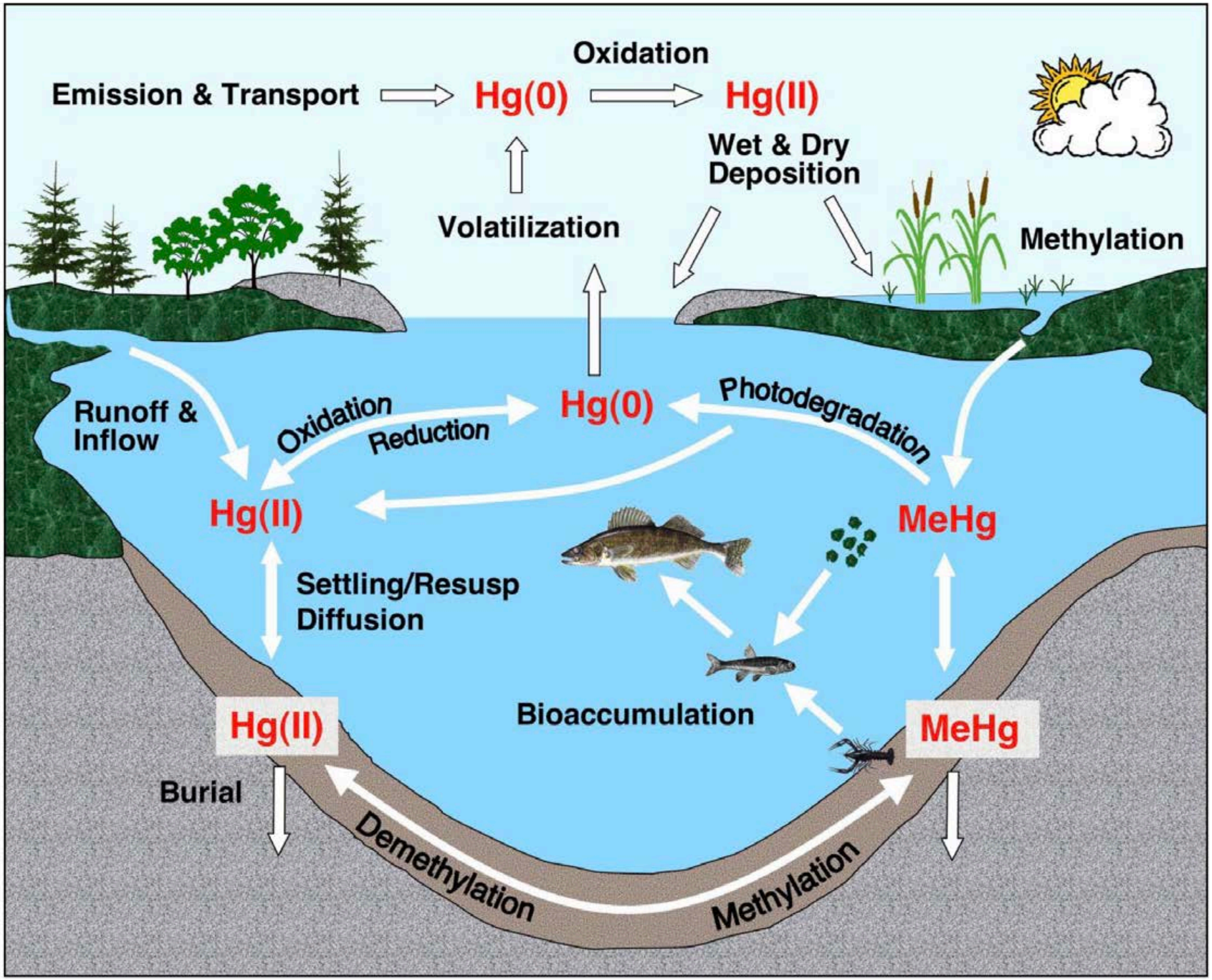



Legacy contaminants in exposed sediment contaminate the food chain through bioaccumulation in benthic organisms, flux into the water column, and uptake in the pelagic food web.

Activated carbon amended to surficial bioactive sediments reduces contaminant exposure to food chain through reduced bioaccumulation in benthic organisms and reduced flux into water column and uptake in the pelagic food web.

Ghosh et al. ES&T 2011

# The Aquatic Mercury Cycle




From Engstrom PNAS 2007

# Discovery of *hgcAB* led to identification of new types of Hg-methylators

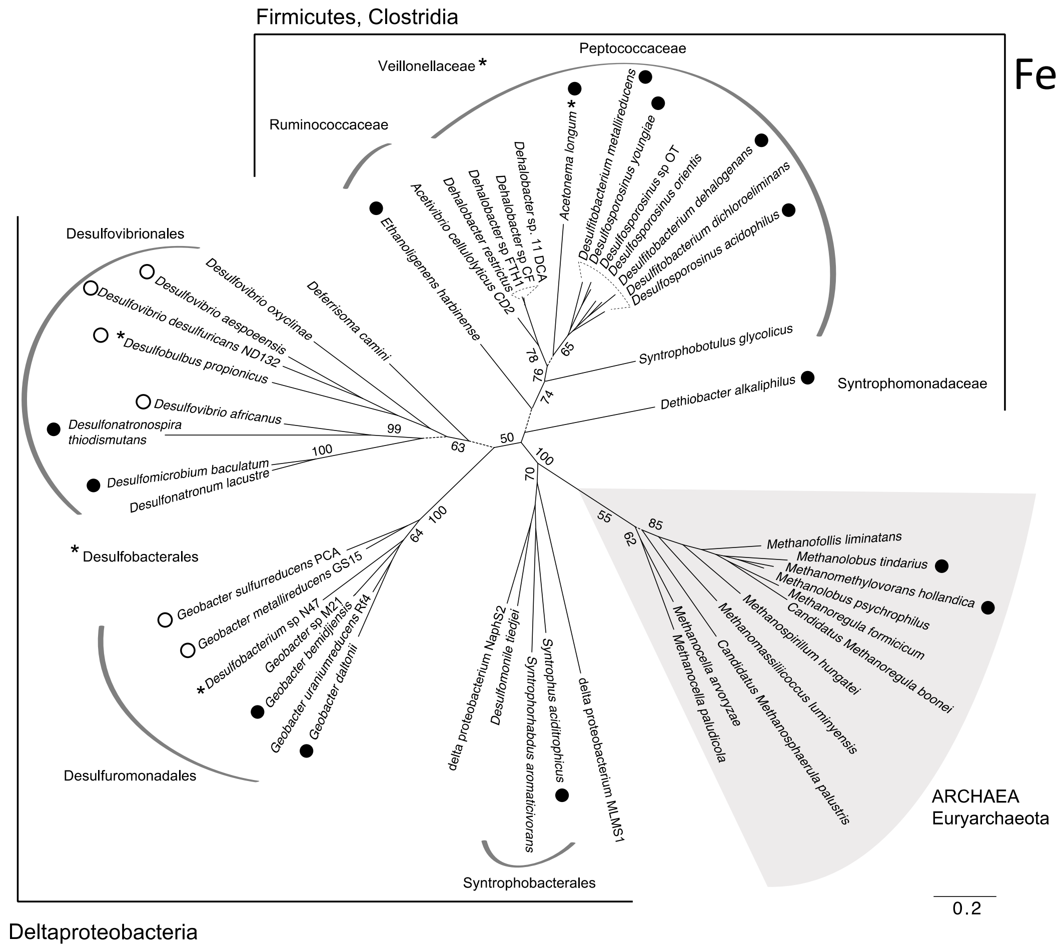
Fermenters

Sulfate-reducers

Syntrophs

Methanogens

Iron-reducers

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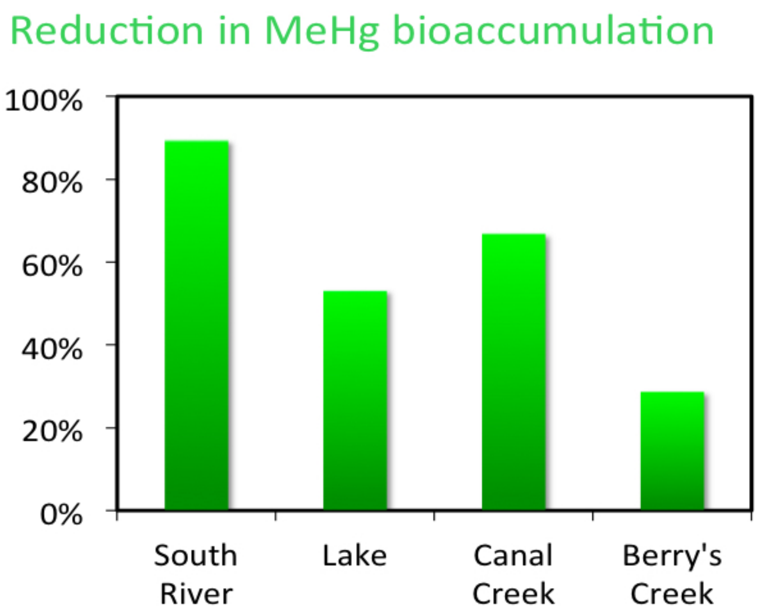
OAK RIDGE National Laboratory

Gilmour et al. 2013 ES&T *Mercury Methylation by Novel Microorganisms from New Environments*

# Preliminary lab studies with AC

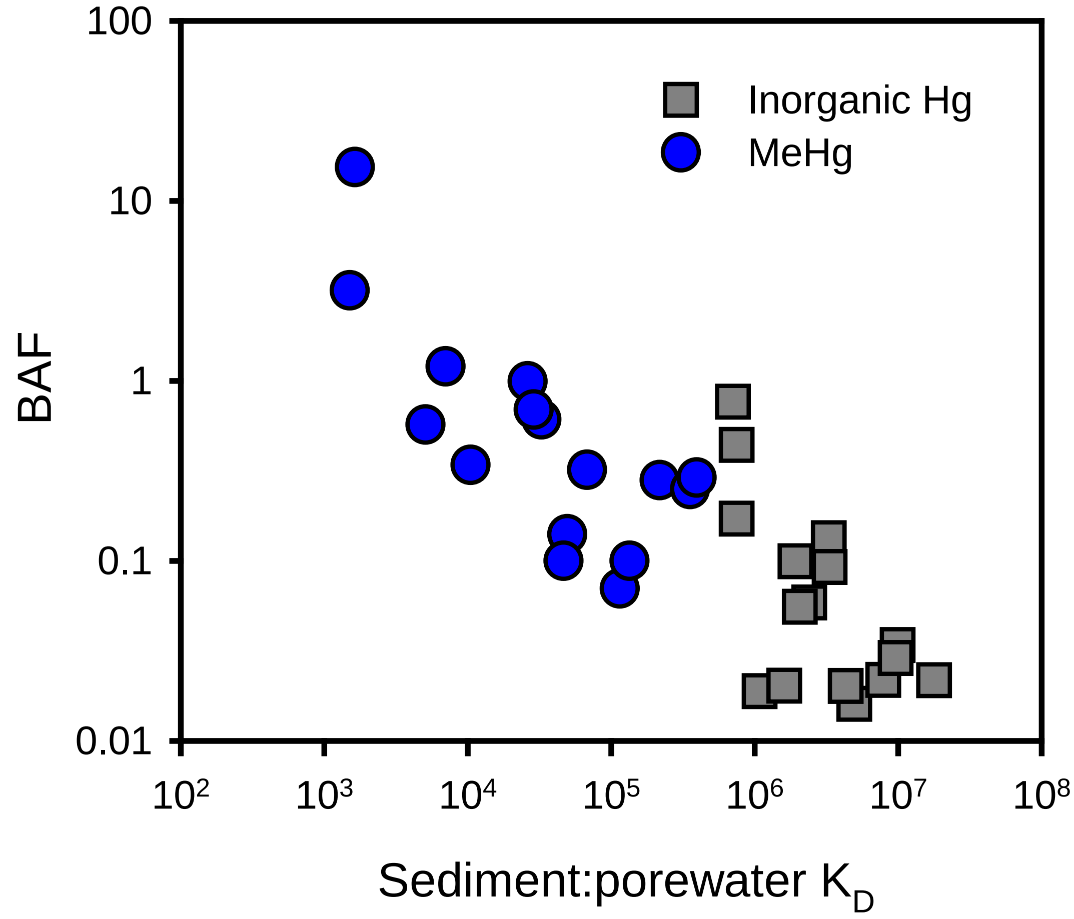




Gilmour, C.C., G.S. Riedel, G. Riedel, S. Kwon and U. Ghosh. 2013. Activated carbon mitigates mercury and methylmercury bioavailability in contaminated sediments. Environ. Sci. Technol. 47:13001-13010.

# $K_D$ as surrogate for Hg and MeHg bioavailability

Tissue:sediment BAF




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

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

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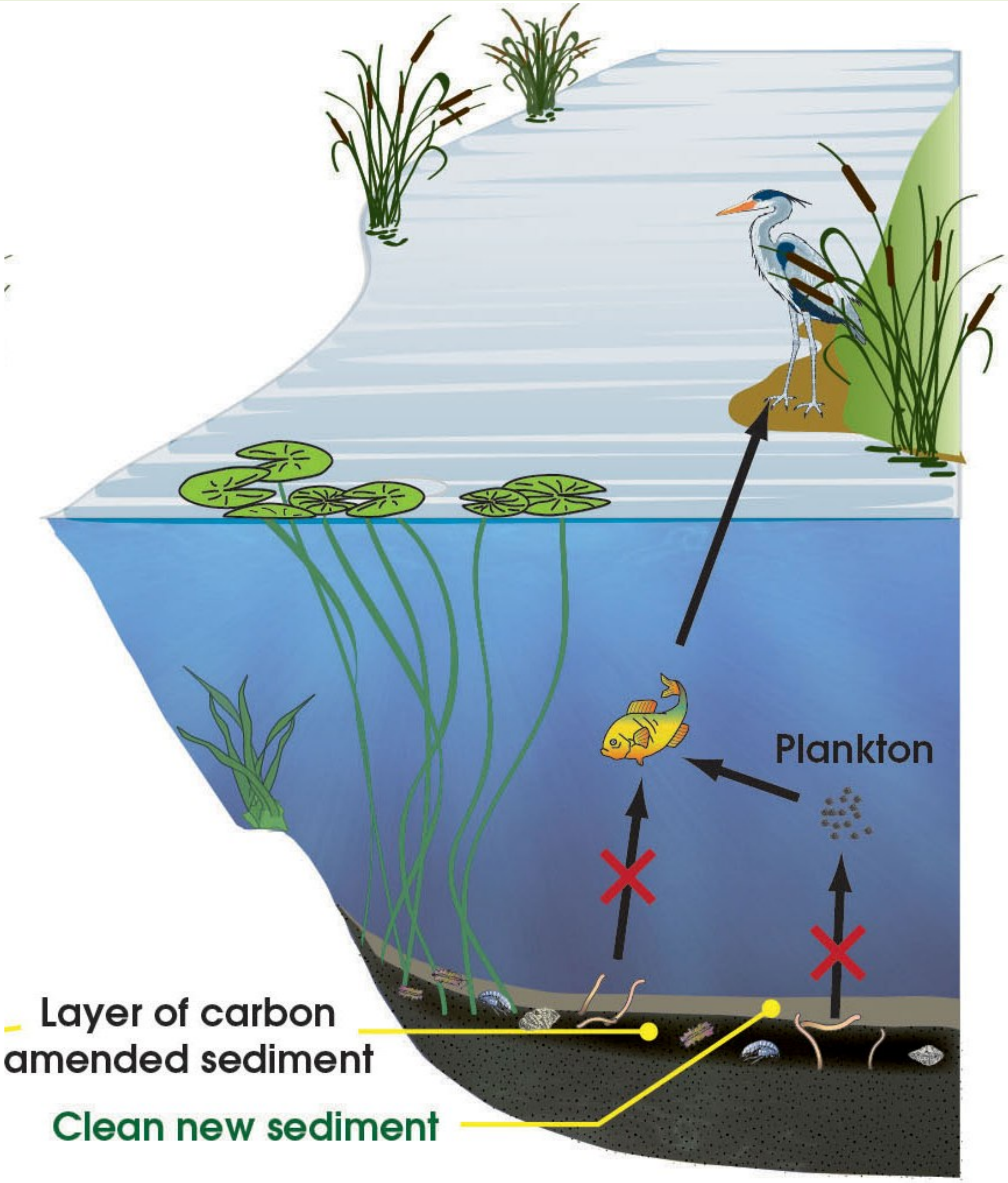
Department of Chemical, Biochemical, and Environmental Engineering, UMBC
**Cynthia Gilmour**
Smithsonian Environmental Research Center
**Dwayne Elias**
University of Tennessee/ Oak Ridge National Laboratory

**Specific Aim 1**: Develop *in situ* remediation tools for Hg and MeHg impacted sediments
**Specific Aim 2**: Fill key knowledge gaps needed to develop a **biogeochemical model for MeHg production and degradation in contaminated sediments and soils**

NIH National Institute of Environmental Health Sciences

# ACTIVTED CARBON REMEDIATON MODEL




Activated carbon acts as a sorbents, to reduce:

1) Hg bioavailability for methylation
2) MeHg bioavailability for uptake by benthos
3) MeHg flux to overlying water

TEST SITES TO DATE:

Lab trials:
South River, VA
Berry's Creek, NJ
Pompton Lake, NJ
Rhode River, MD

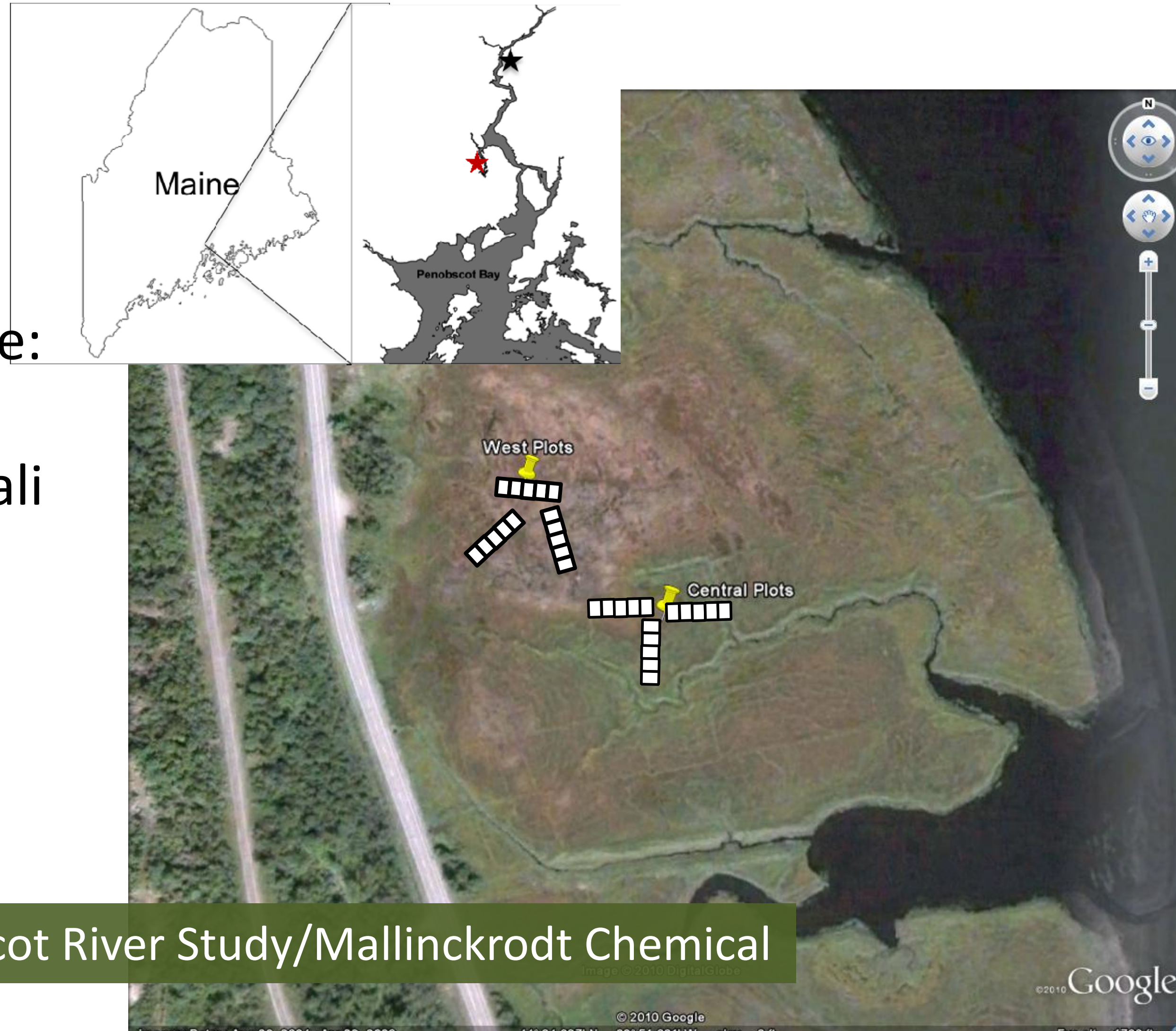
Field Trials:
Canal Creek, MD
Penobscot River, ME
Berry's Creek, NJ

Funding from Dow, DuPont, Mallinckrodt, SERDP

# Approach to evaluating AC as a tools for Hg risk remediation in sediments and soils

- Lab studies to evaluate efficacy across soil types
- Small-scale field trials
  - Penobscot River, ME
  - Berry’s Creek, NJ
- Lab work to examine mechanisms and parameterize models

# Mendell Marsh, Penobscot River, ME




Contamination source:

HoltraChem chloralkali facility

Supported by: Penobscot River Study/Mallinckrodt Chemical

# Design

- 15 plots per site; 5 treatments,
- 3 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 |

# Study Time Line

Plots sited, edging installed

Amendments applied 9/23/2010

9/2010

10/2010
1 month

6/2011
9 months

9/2011
1 year

9/2012
2 years

# Key Endpoints/Metrics

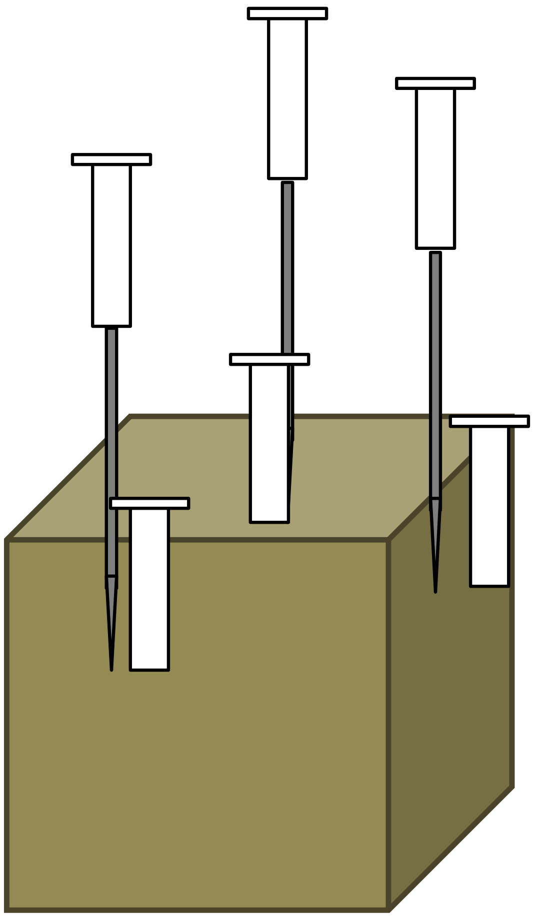
**Amendment retention**

- Black carbon in sediment

**Efficacy and longevity**

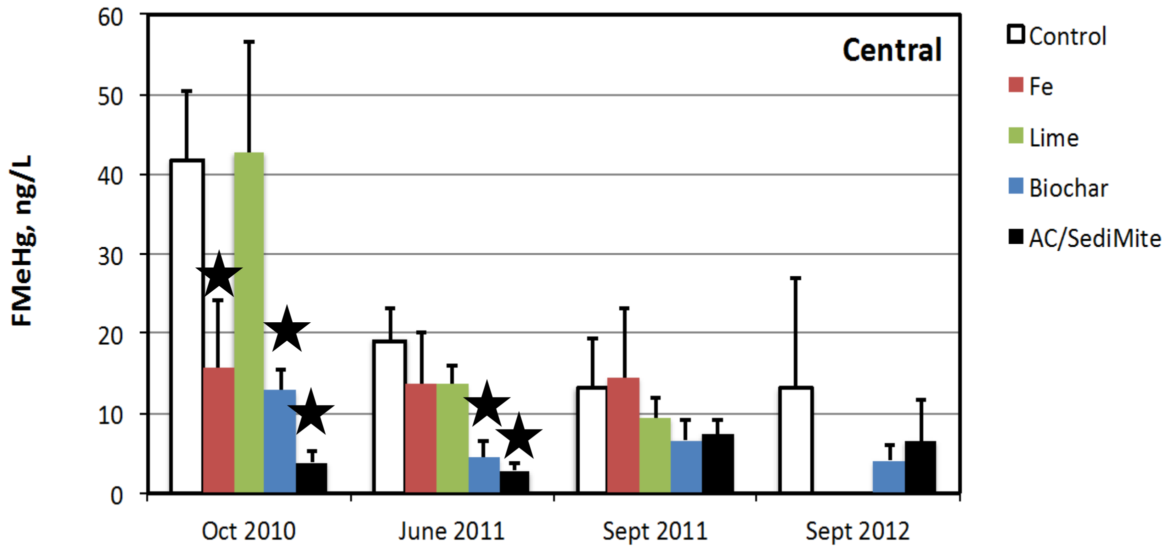
- Pore water [MeHg]
- Not evaluated: bioaccumulation

**Impacts on soil biogeochemistry**



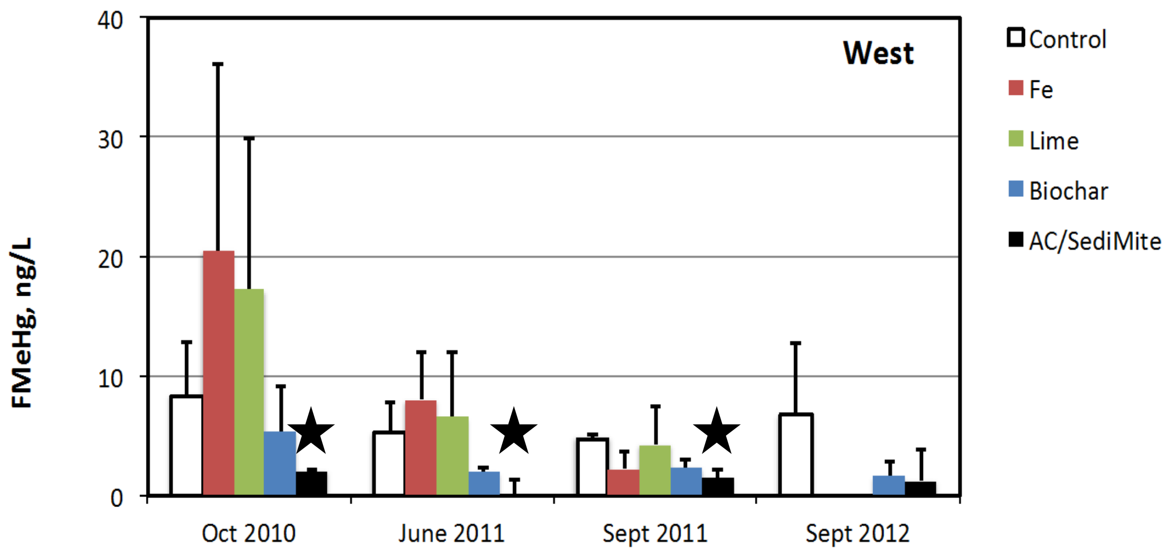
Soil and pore water sampling over time

# Pore water MeHg




Central: Drier, moderately sulfidic

*Schoenoplectus pungens (three square)*
*Juncus gerardii (saltmarsh rush),*
*Agrostis stolonifera (creeping bentgrass),*



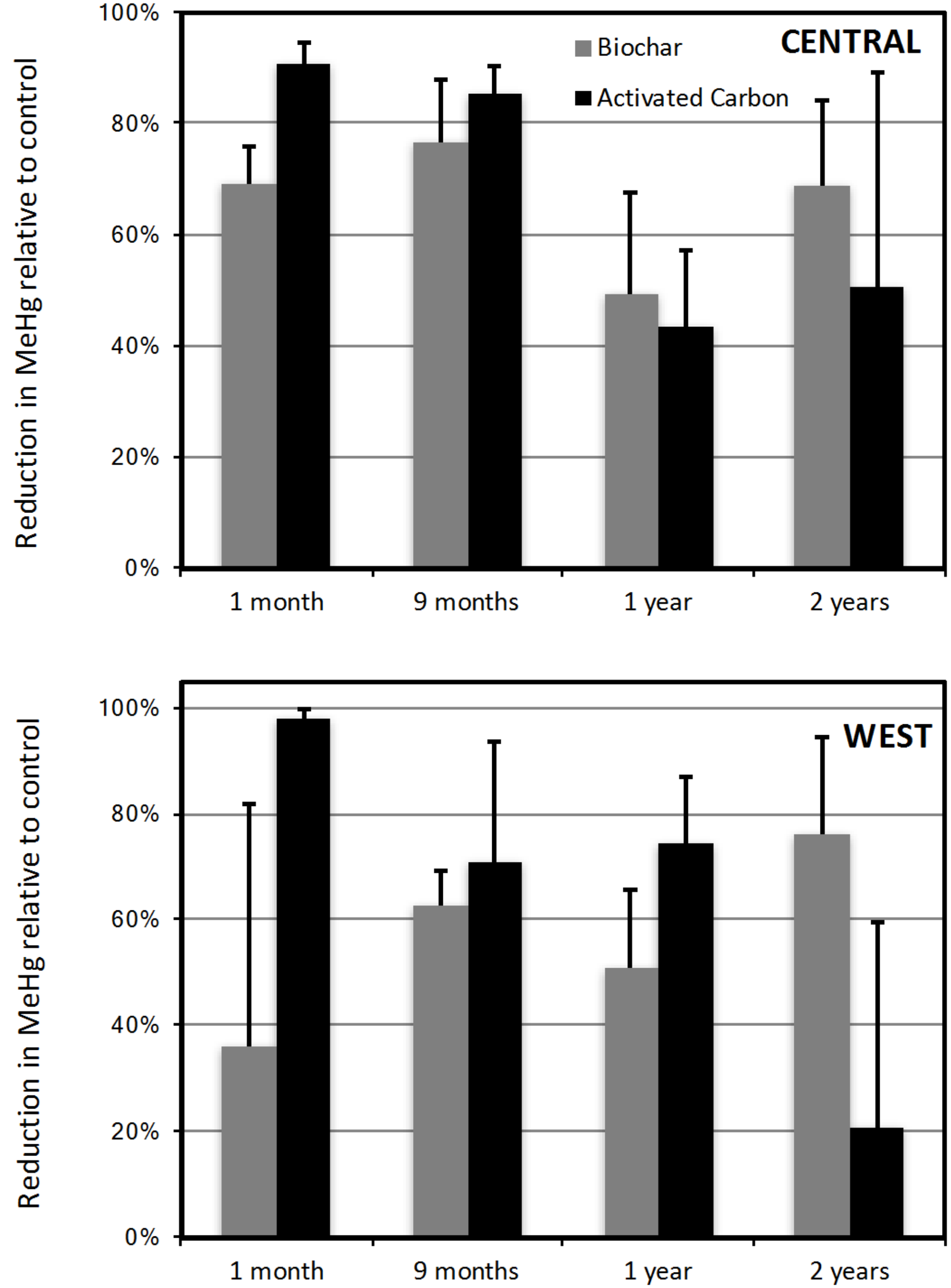

West: Standing pools, highly sulfidic

*Spartina patens (salt marsh hay),*
*Agrostis stolonifera (creeping bentgrass), Eleocharis uniglumis (spike rush)*

- Each bar is the average ± std of triplicate plots.
- Samples for each plot are composites of 3 samples.

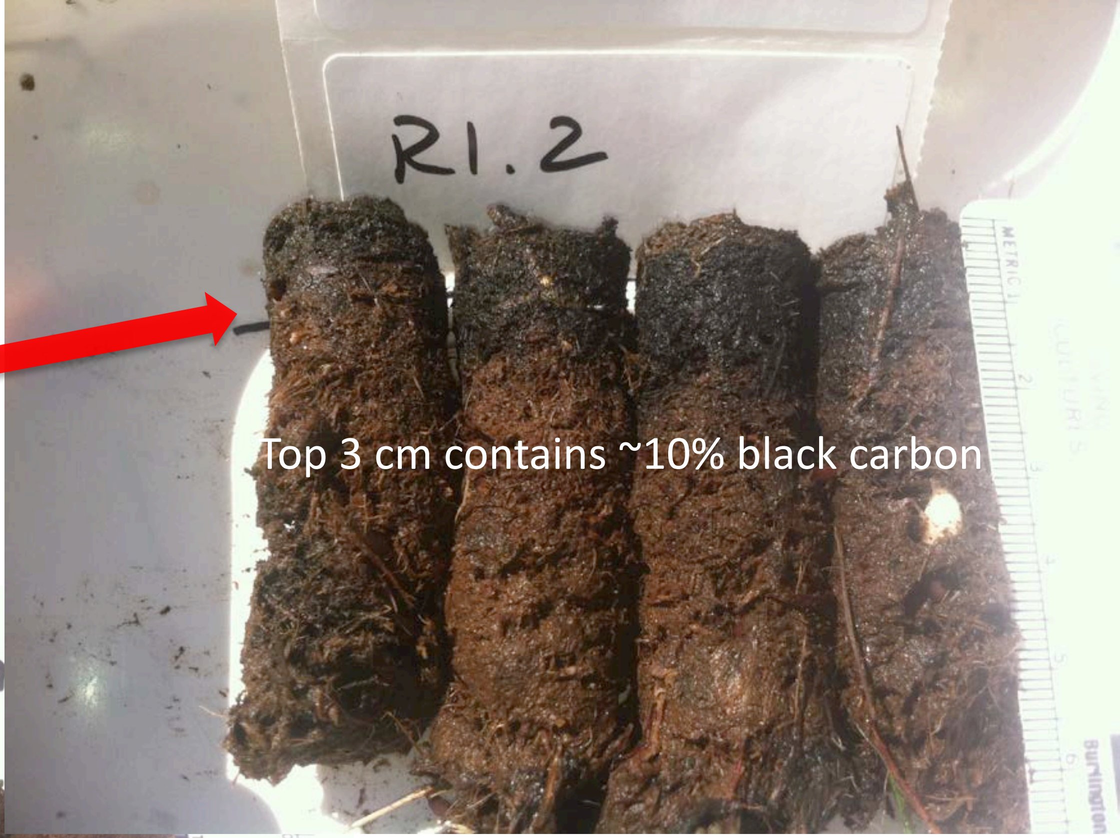
★ Treatments significantly different from control on each date ($p<0.05$ by pairwise Student's t-test)

# Pore water MeHg reductions



# Penetration of AC into marsh surface

~2 cm in 2 years





1 year retention:

| | |
|---|---|
| AC/SediMite | 55 ± 20% |
| Biochar | 28 ± 35% |

# Depth of Carbon layer, Sept. 2017




# Field Trial: Berry's Creek, NJ Phragmites marsh


Cindy Gilmour, Tyler Bell, Alyssa McBurney, Nise Butera, Ally Bullock
Smithsonian Environmental Research Center
Upal Ghosh, James Sanders
University of Maryland Baltimore County
Susan Kane Driscoll, Charlie Menzie, and Ben Amos, Exponent
Betsy Henry, Anchor QEA
Steve Brown, The Dow Chemical Company


Plot A, April 2013

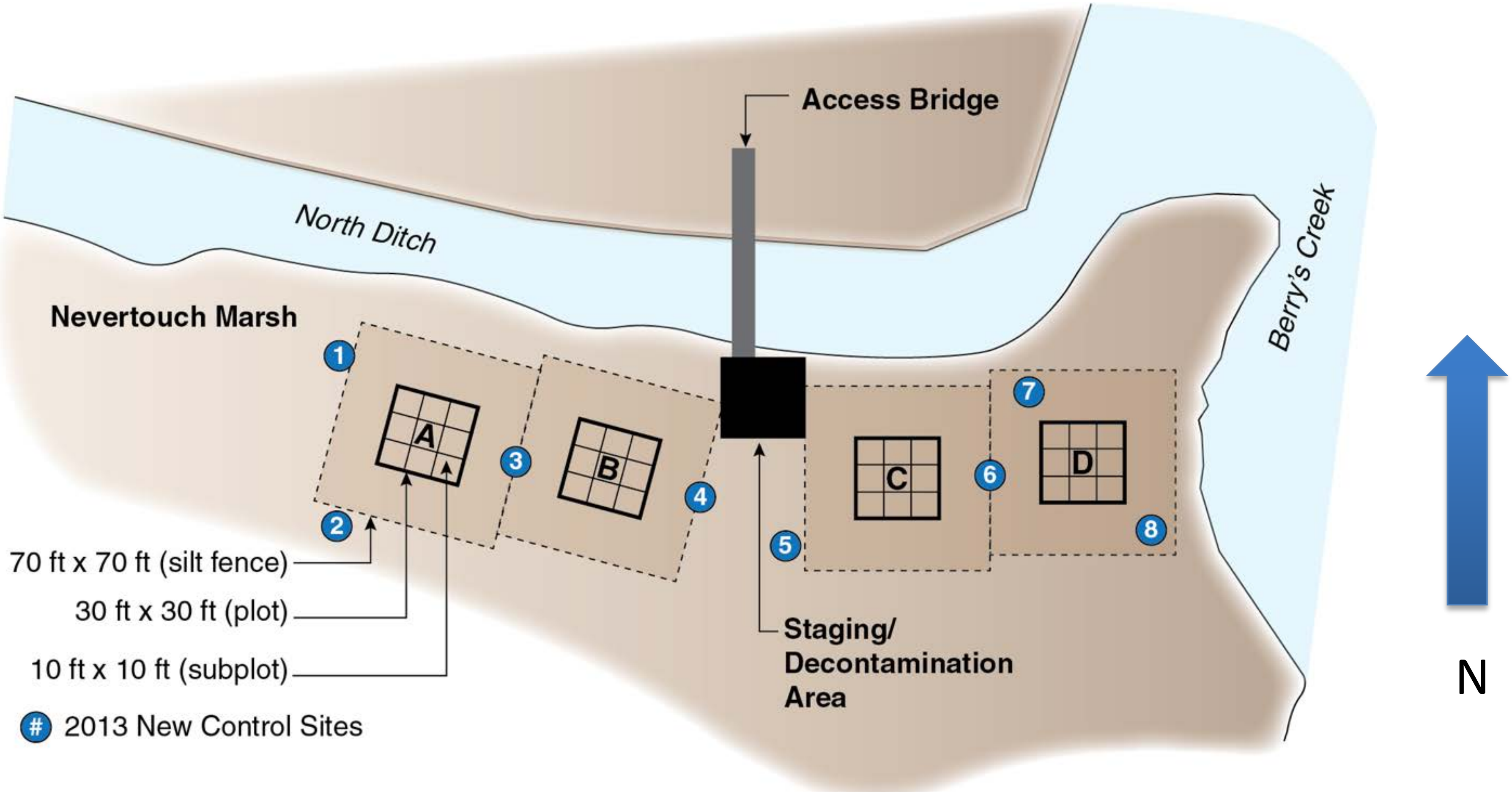
# Plot Design – thin layer surface placements

Plot A
SediMite
(formulated with
regenerated PAC)

Plot B
Control

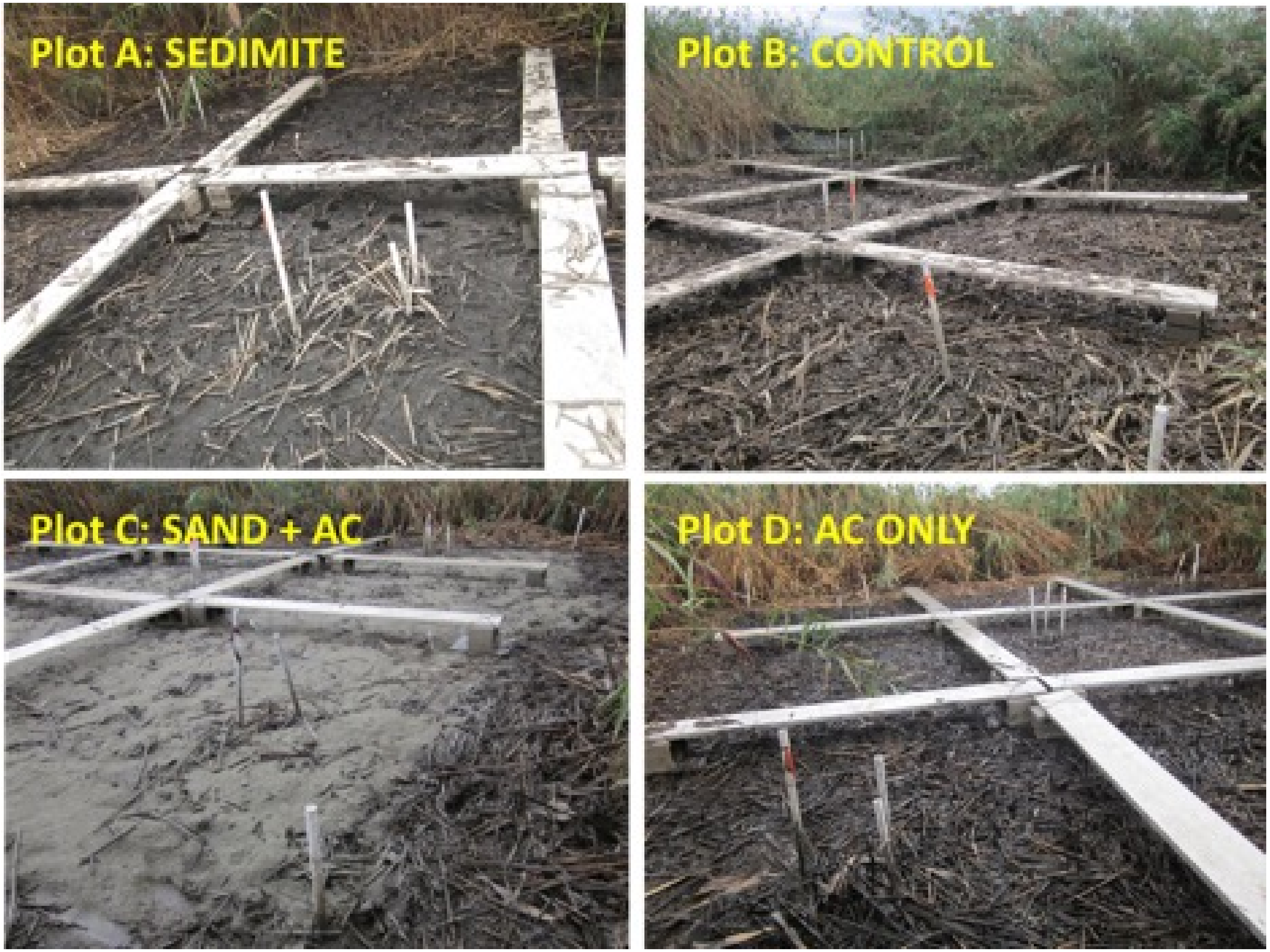
Plot C
AC+Sand
(Calgon GAC
+ ~2 cm sand )

Plot D
AC
(Calgon GAC)



# Design

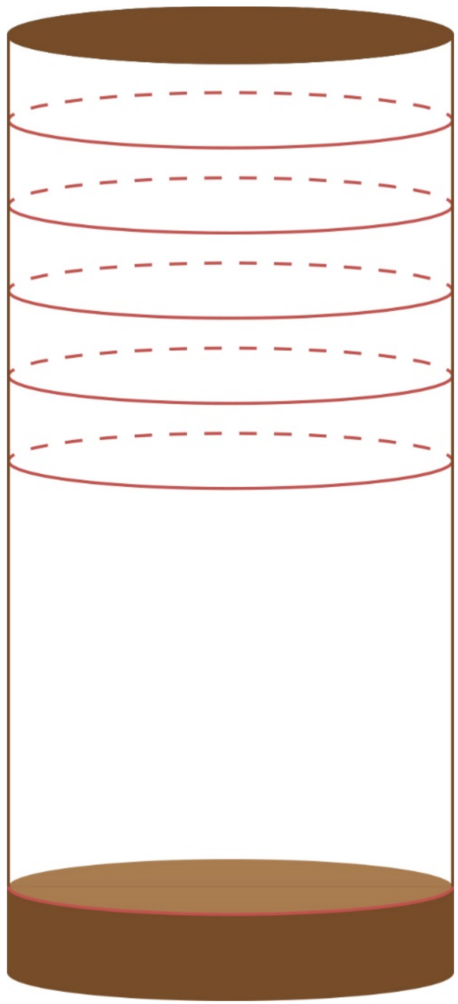
- Application by vortex sprayer
- 2 year study
- Soil sampling design similar to Penobscot – cores and sippers, composites and replicates, focus on top 5 cm
- Also included caged and wild amphipod exposure

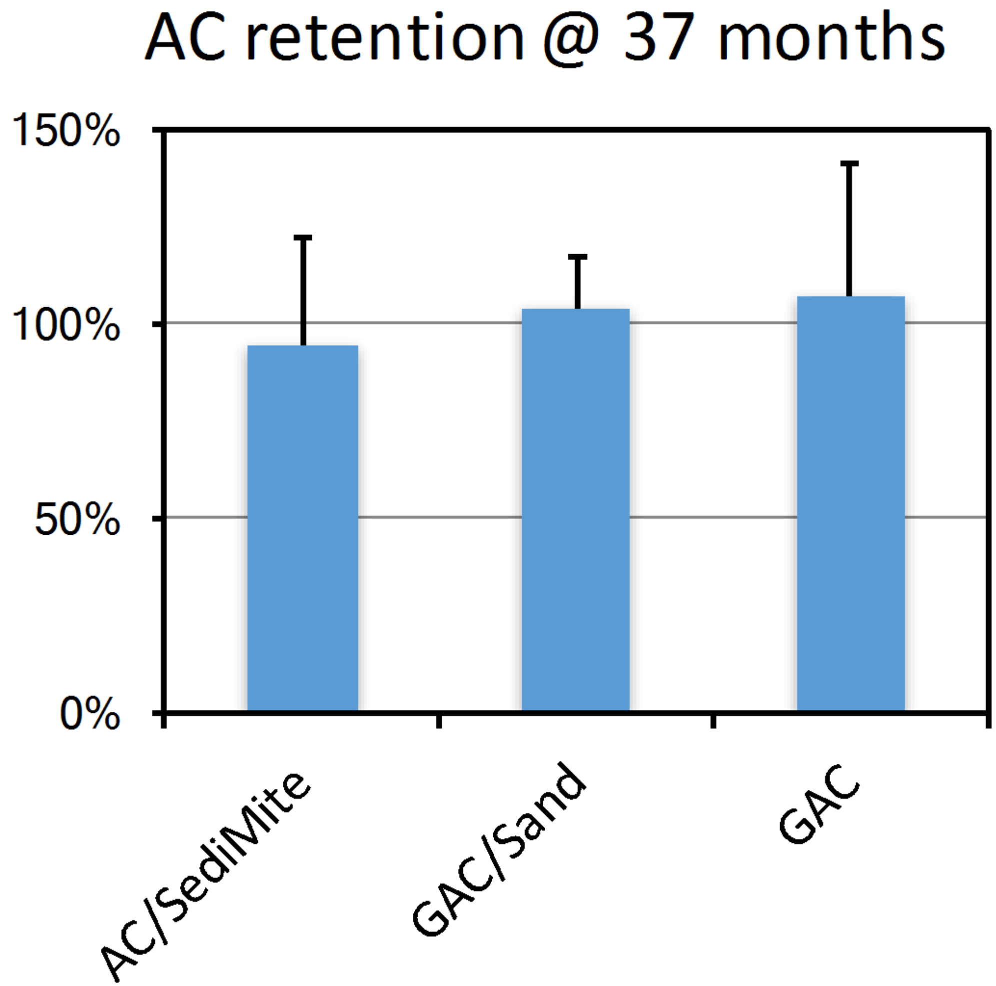



Appearance of the experimental plots two months after amendment application.

# Activated Carbon Retention in Berry's Creek

Sediment cores from SediMite™ plot were sectioned in 1-cm intervals.

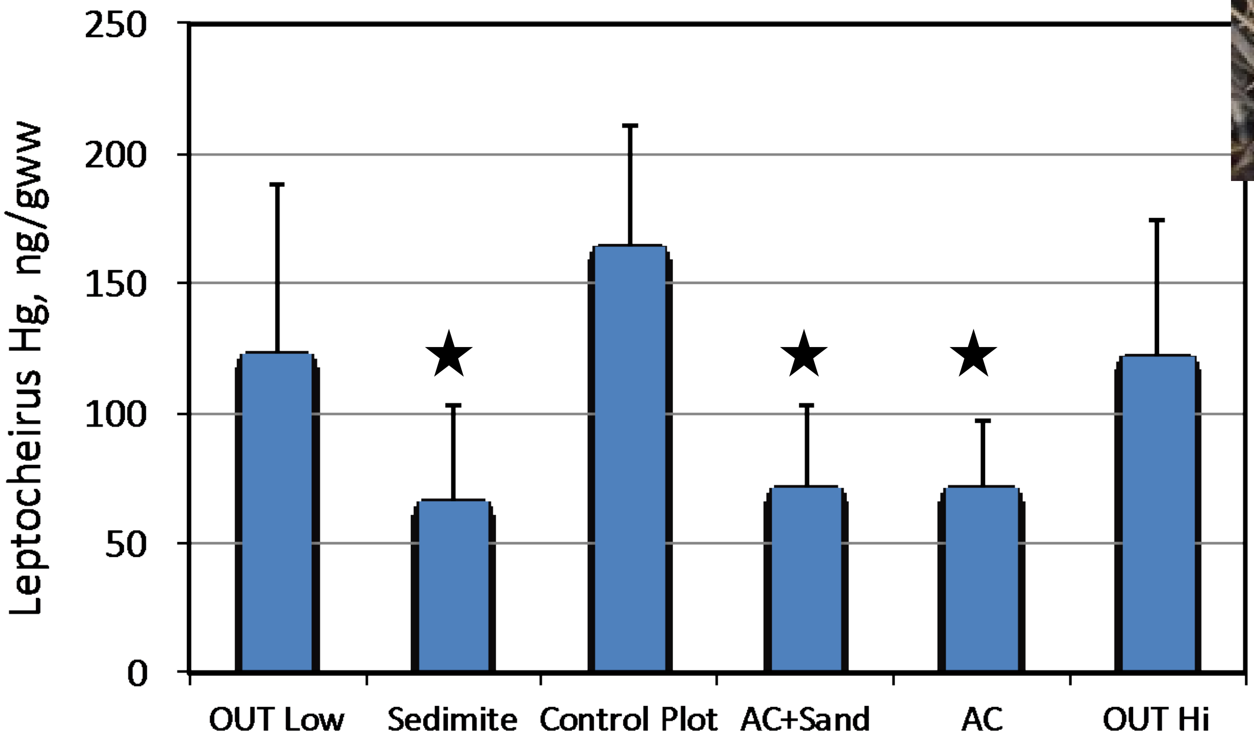





Site heavily impacted by Hurricane Sandy, but AC persisted in marsh sediments

UMBC
AN HONORS UNIVERSITY IN MARYLAND

# Total Hg uptake by *Leptocheirus*



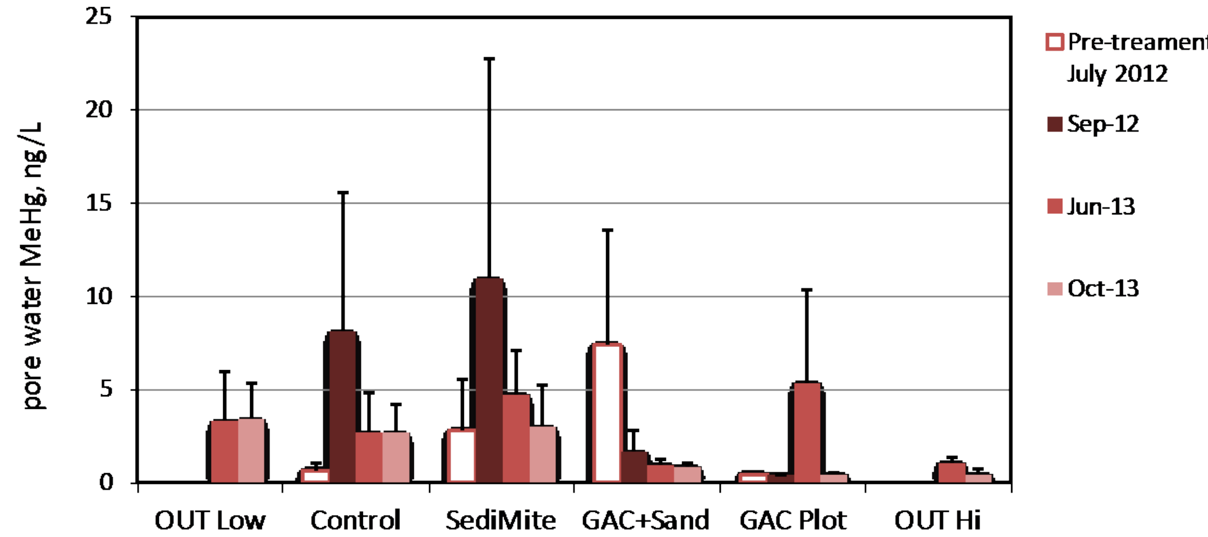

Exposure chamber design by Bennett Amos

- Average uptake across 3 sampling dates, 5 composites per plot per date

★ Treatments significantly different from controls

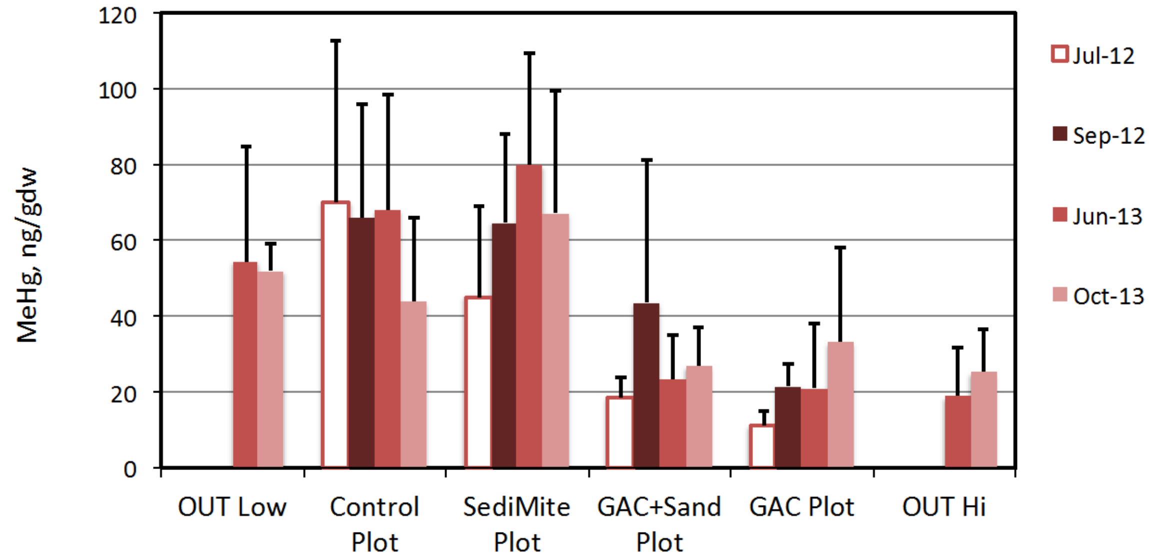
- Modeled with elevation as a co-variate, AC reduced total Hg uptake on average by ~50%

# MeHg in soil and pore waters




- 1-2’ of elevation difference among the plots

- Large redox effect confounded evaluation of AC effects on MeHg




Marsh Elevation

# A cautionary tale: Elevation differences among plots

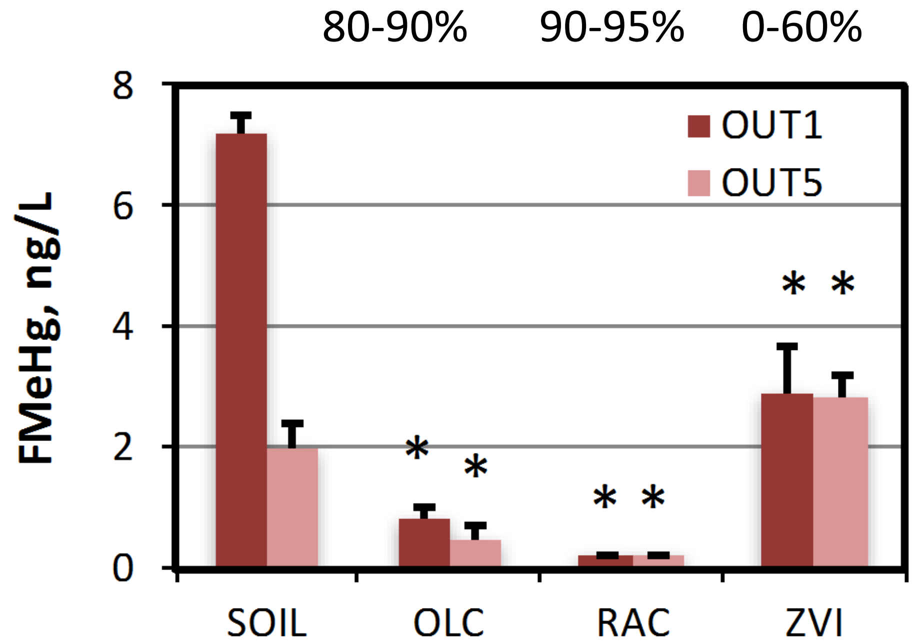
# *Ex-situ* evaluation of AC on MeHg in Berry's Creek Marsh soils

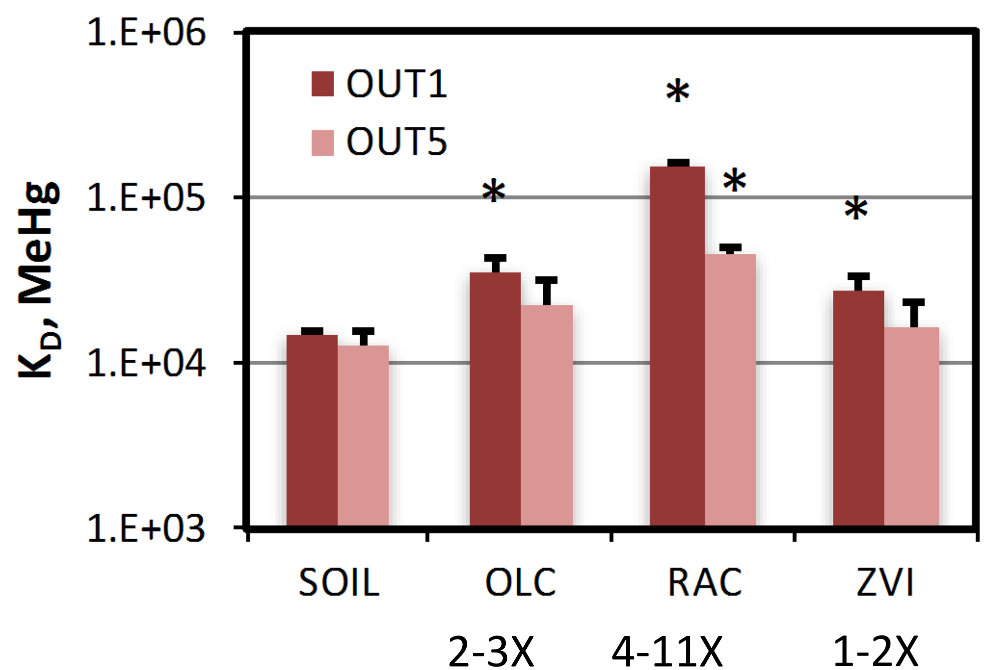
Effect of amendments mixed into anaerobic soil slurries (2:1 soil:water)
1 week incubation

OLC = Calgon OLC GAC

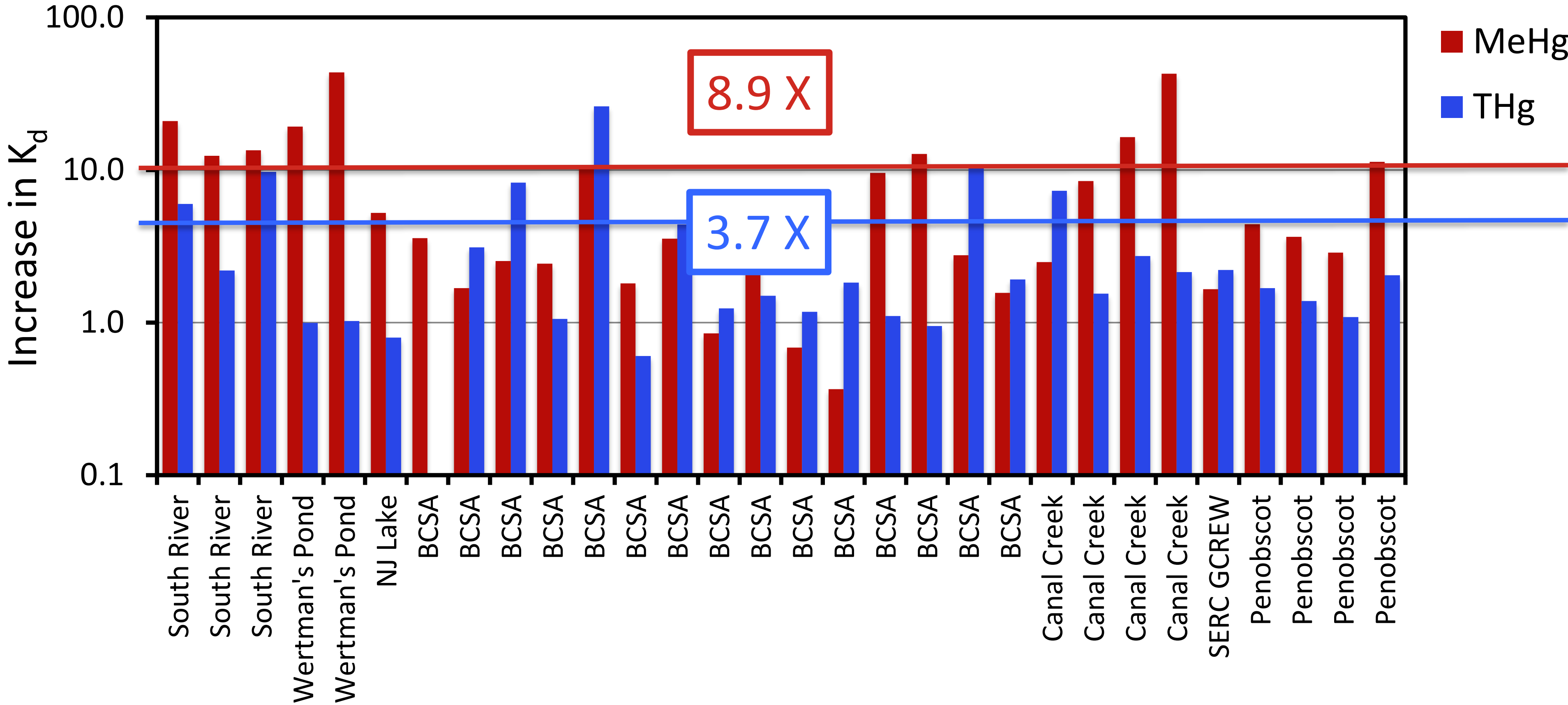
RAC = SediMite formulated with regenerated PAC

ZVI – zero-valent iron "ETI CC-1004" from Connelly-GPM



# How does sediment chemistry affect AC performance in reducing MeHg risk?



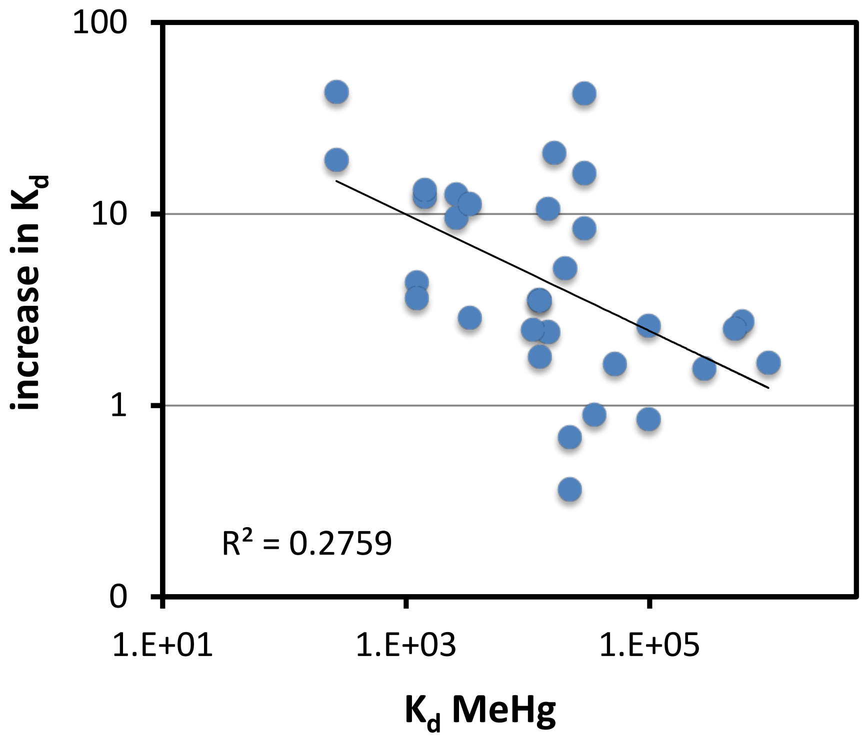

AC is more effective in reducing pore water MeHg

Wide range of reduction in partitioning

# Correlates of AC efficacy

AC is more effective in sediments and soils with:

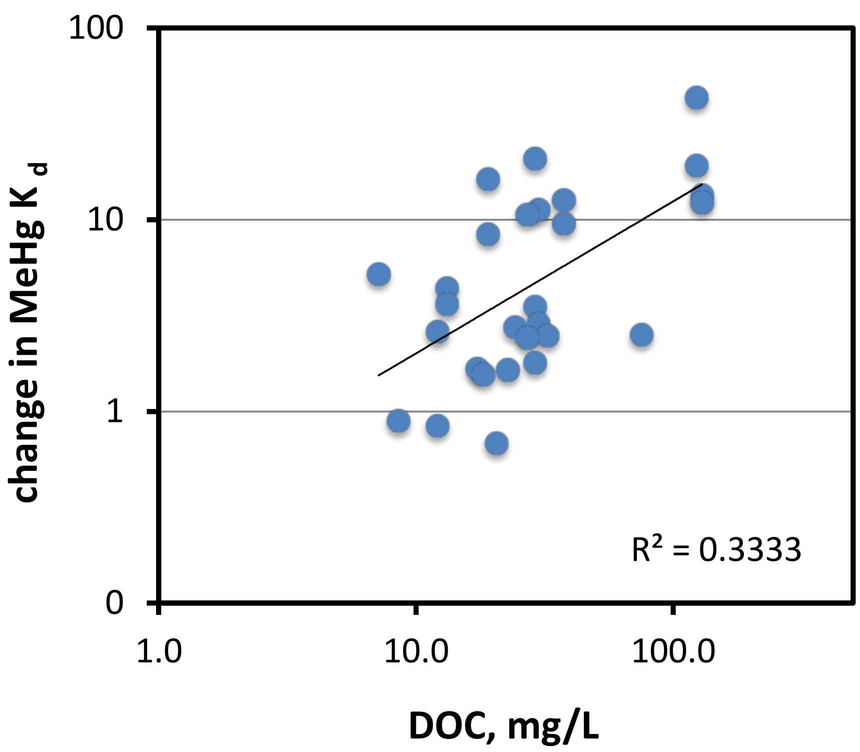
- naturally low $K_d$



# Correlates of AC efficacy

AC is more effective in sediments and soils with:

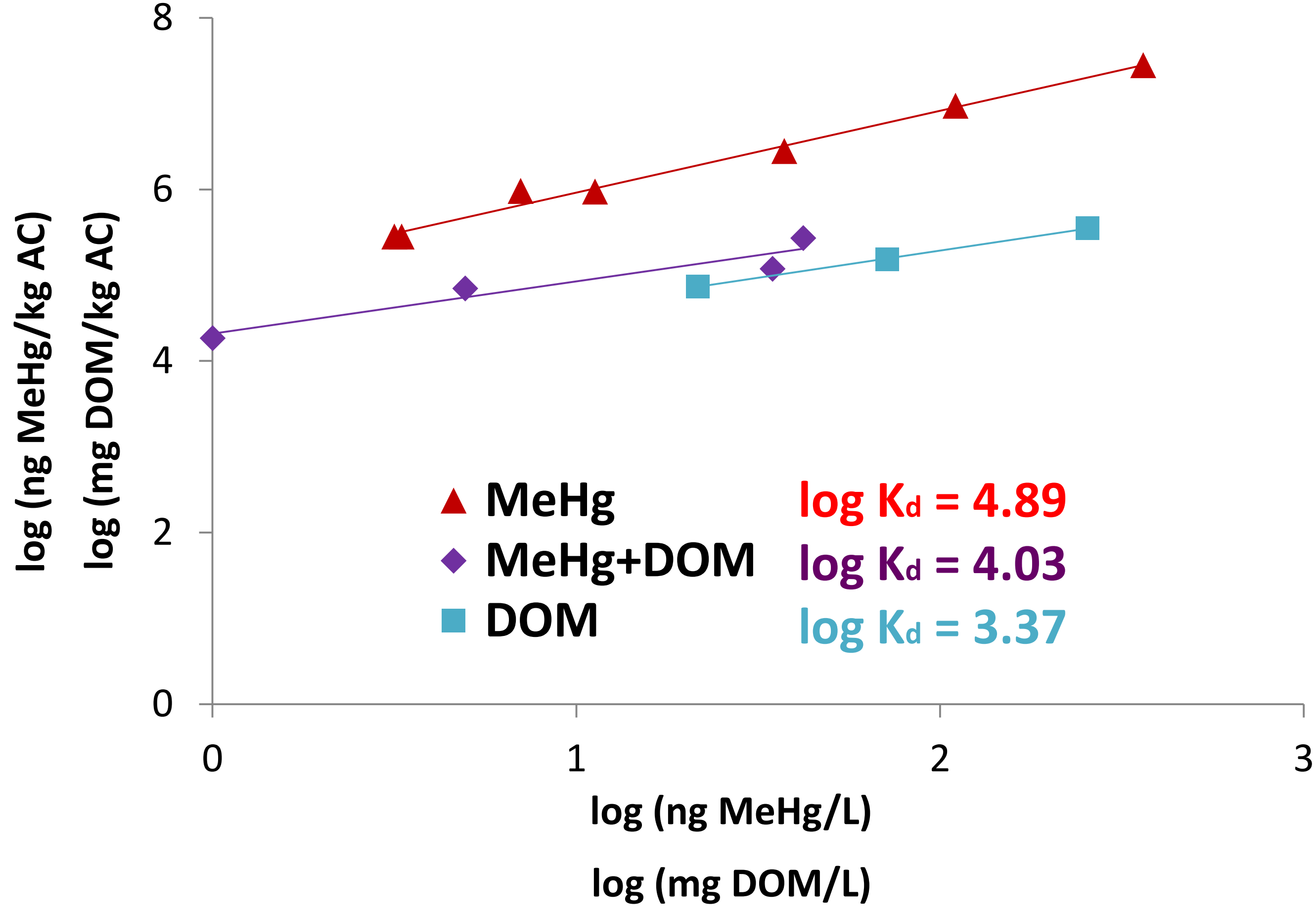
- naturally low $K_d$
- higher pore water DOC




- No relationship with Hg or MeHg concentration in pw or solid

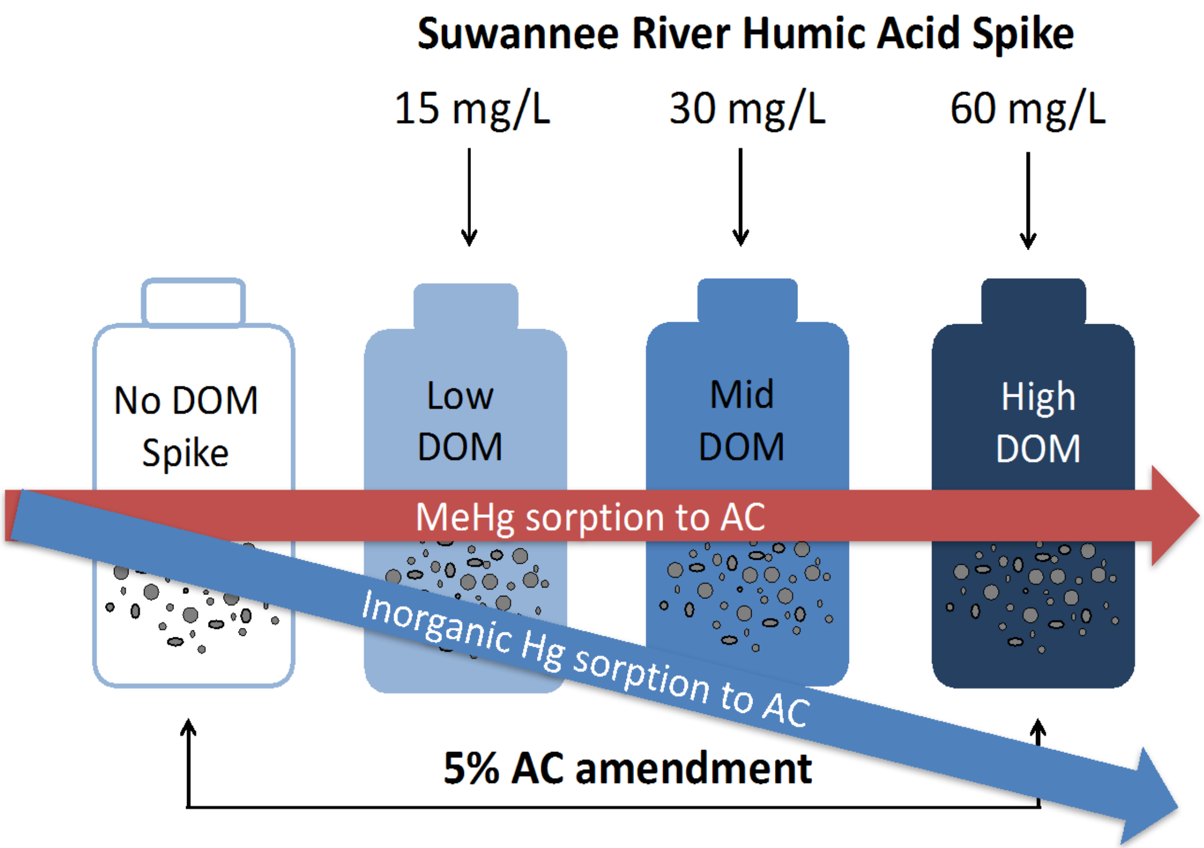
# How does DOM Impact MeHg partitioning to Activated Carbon?

Sorption isotherms for MeHg onto AC in the presence and absence of DOM




Schwartz et al (in prep)

# Impact of DOM on Hg and MeHg sorption to AC in soils



# Summary

- Activated Carbon can be an effective tool in reducing MeHg risk by reducing MeHg in pore waters
- Efficacies range from no impact to 50X increase in $K_d$
  - Avg pore water reduction of ~50% across all studies
- Early days for AC use in sediment/soil Hg remediation

# Summary

- Activated Carbon seems most effective for MeHg in soils with natural low $K_d$ high DOC
- AC was more effective in reducing MeHg than total Hg for most sites
- Goal: develop an empirical model to predict the potential effectiveness of AC amendments for specific sites

# Thank you

**Funding:**
NIEHS
SERDP
The DOW Chemical Company
Penobscot River Study
The Smithsonian Institution