In Situ Activated Carbon Amendment for Sediment and Soil Mercury Remediation

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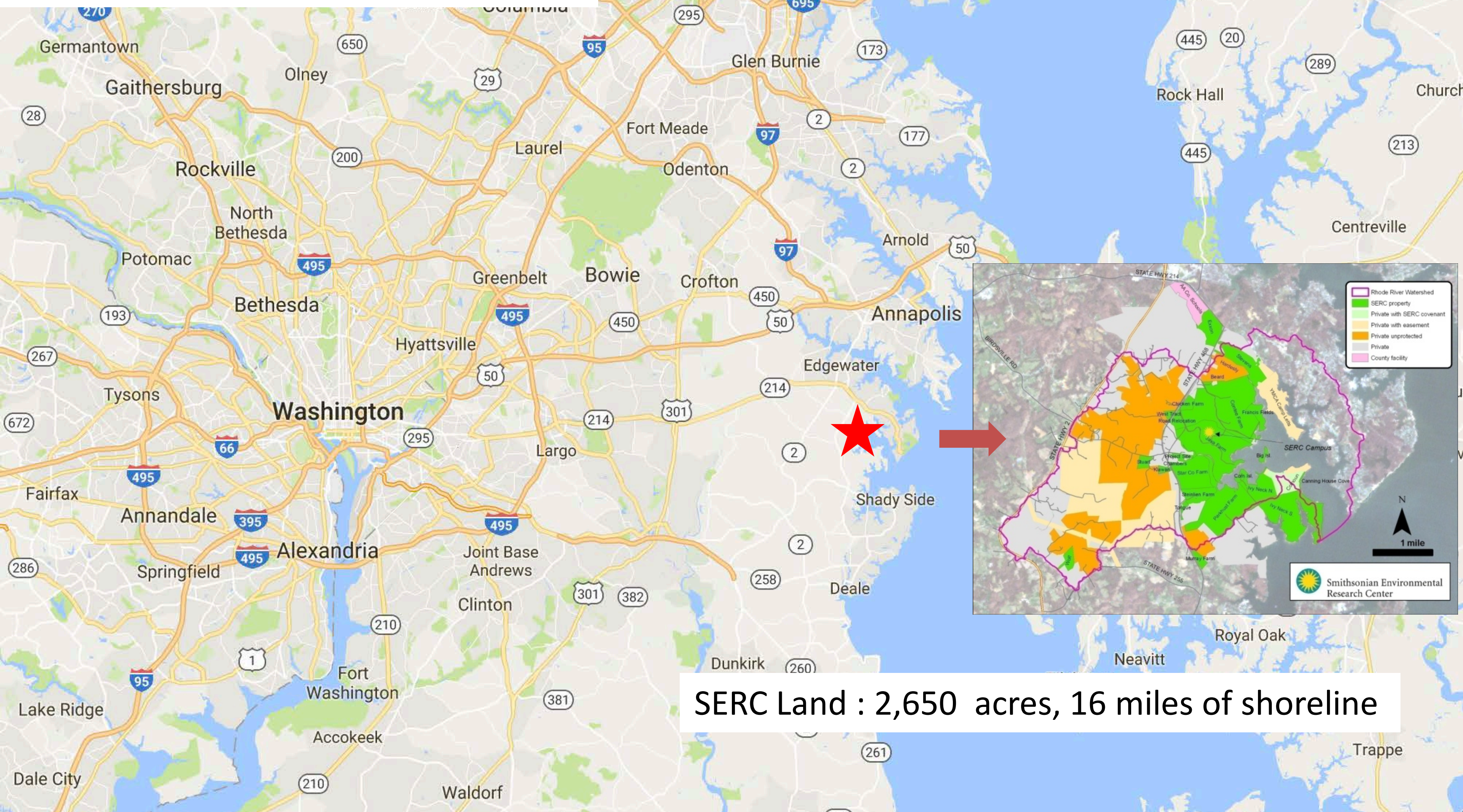

SERC Land : 2,650 acres, 16 miles of shoreline

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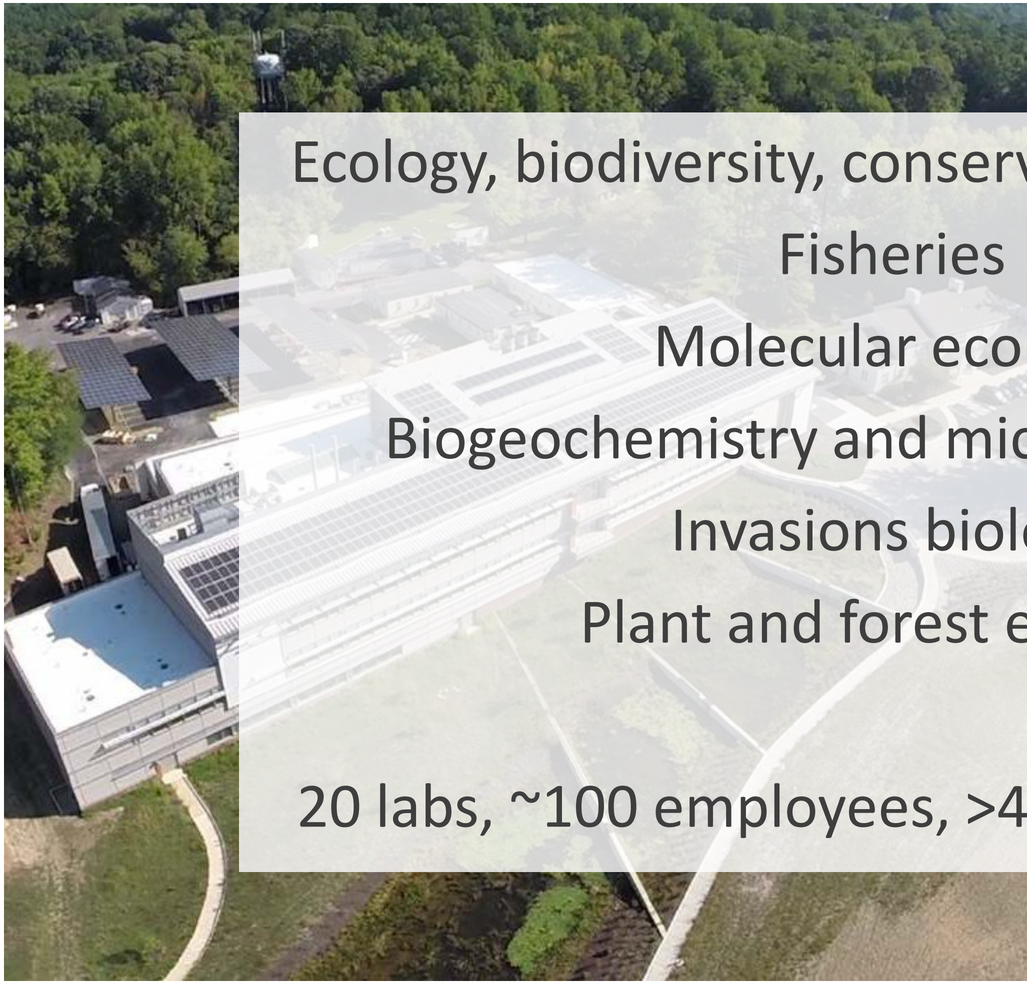

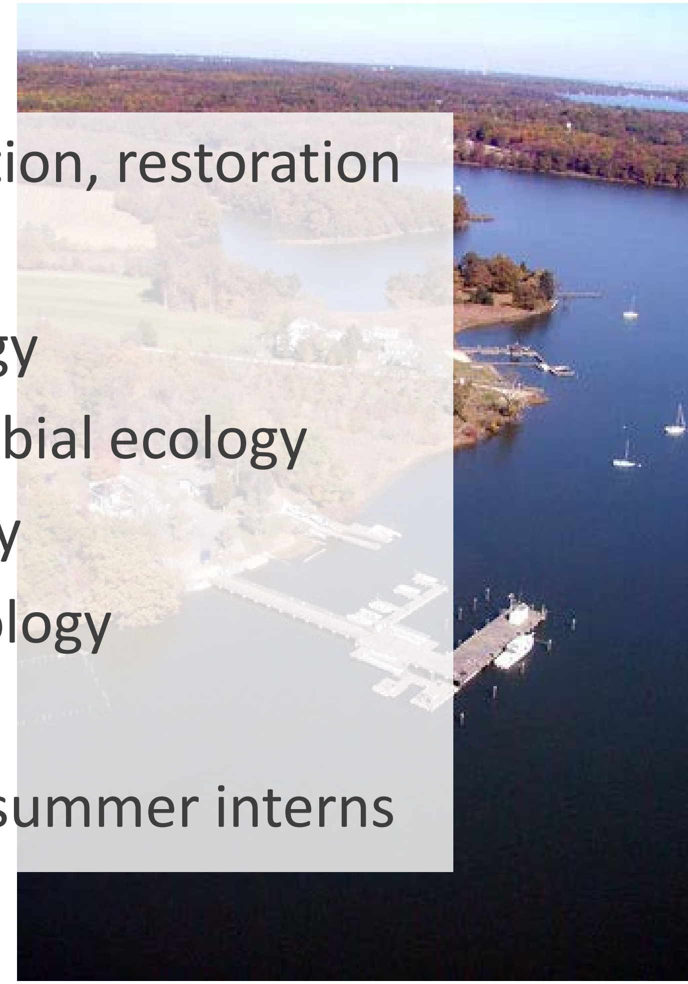

Ecology, biodiversity, conservation, restoration

Fisheries

Molecular ecology

Biogeochemistry and microbial ecology

Invasions biology

Plant and forest ecology

20 labs, ~100 employees, >40 summer interns

Environmental Science & Technology

FEATURE

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

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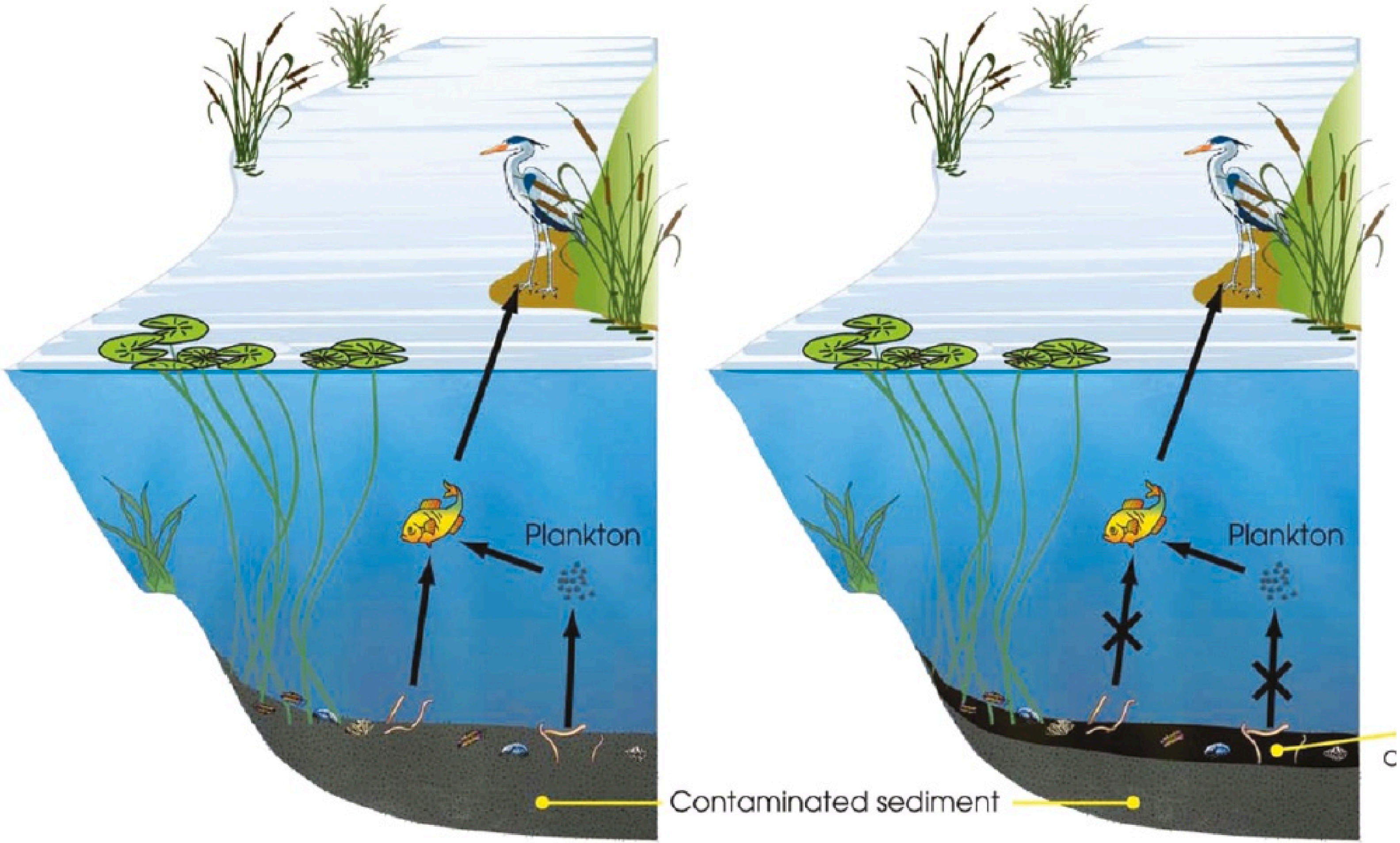
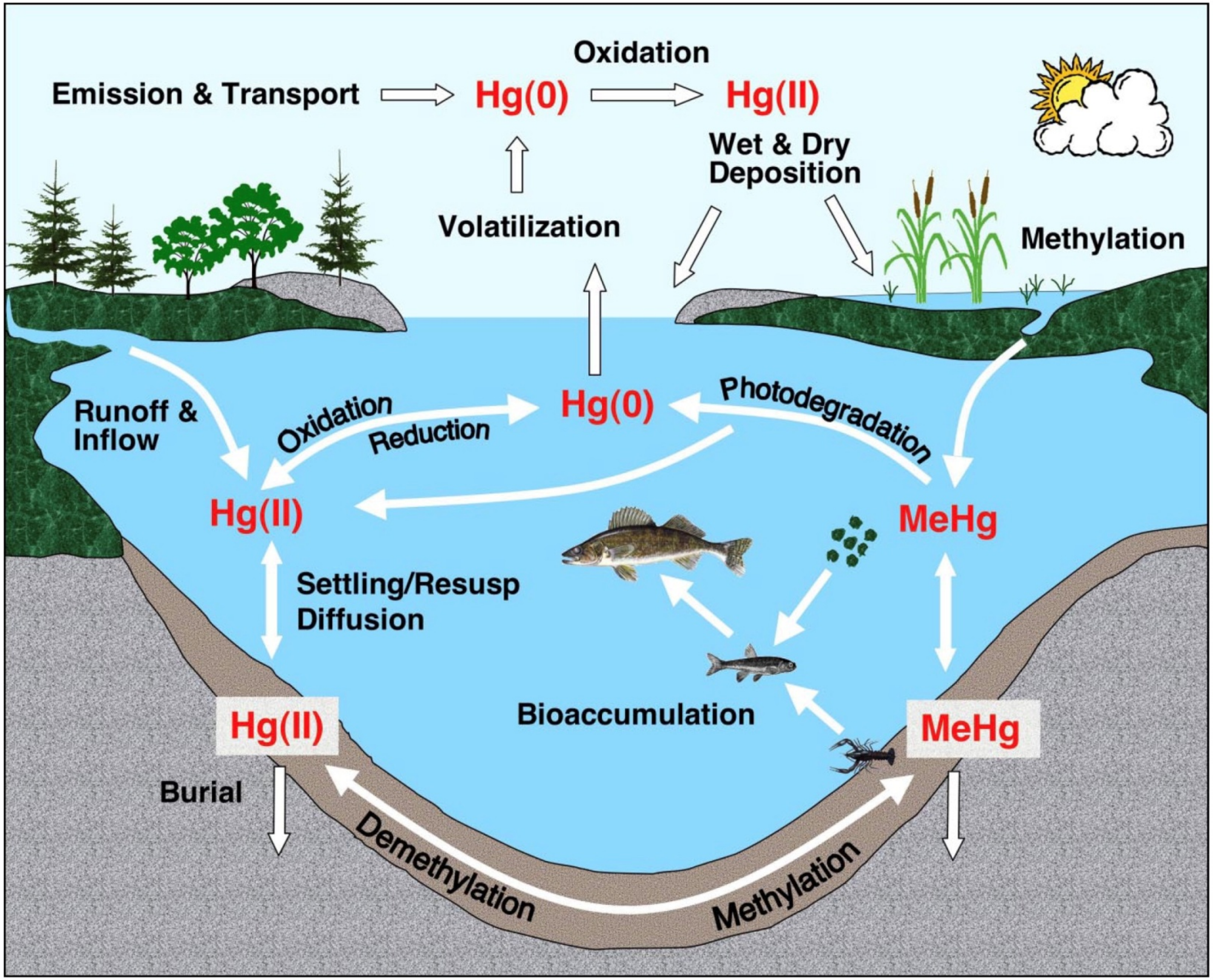


Legacy contaminants in exposed sediment contaminate the food chain through bioaccumulation in benthic organisms, flux into the water column, and uptake in the pelagic food web.

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

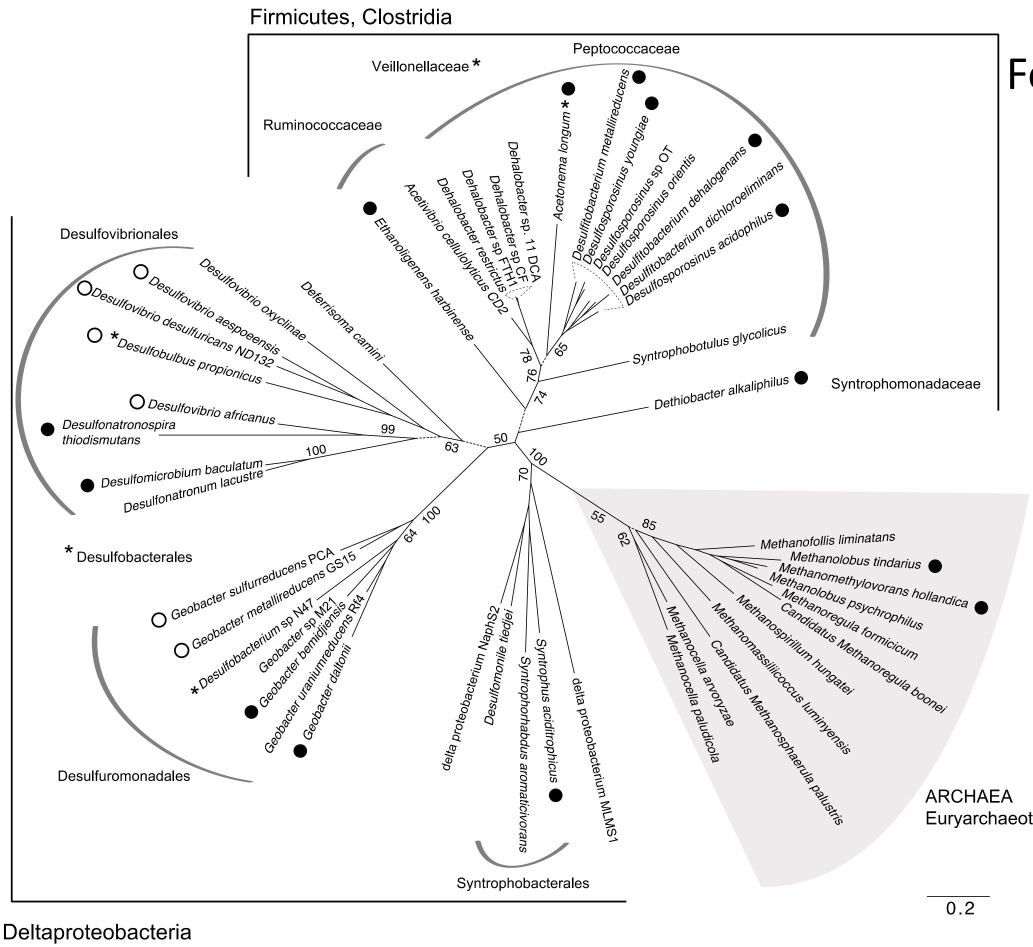
Fermenters

Sulfate-reducers

Syntrophs

Methanogens

Iron-reducers



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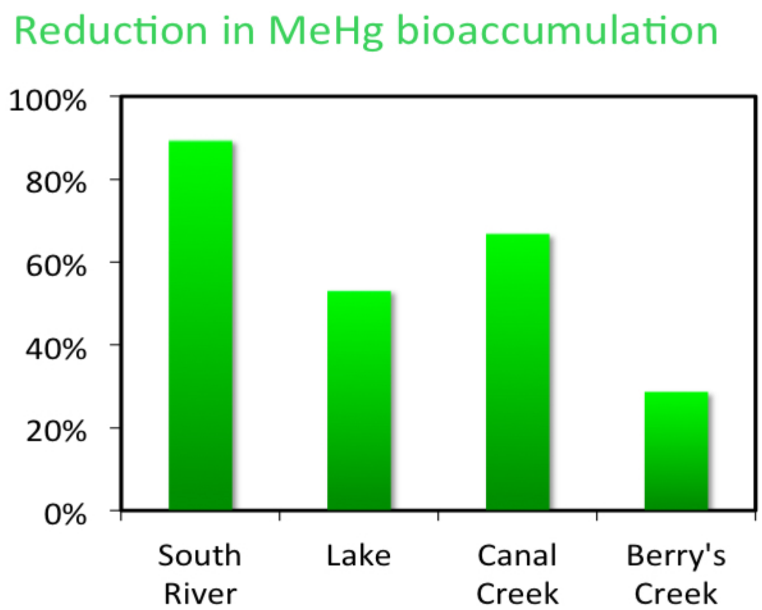
OAK RIDGE National Laboratory

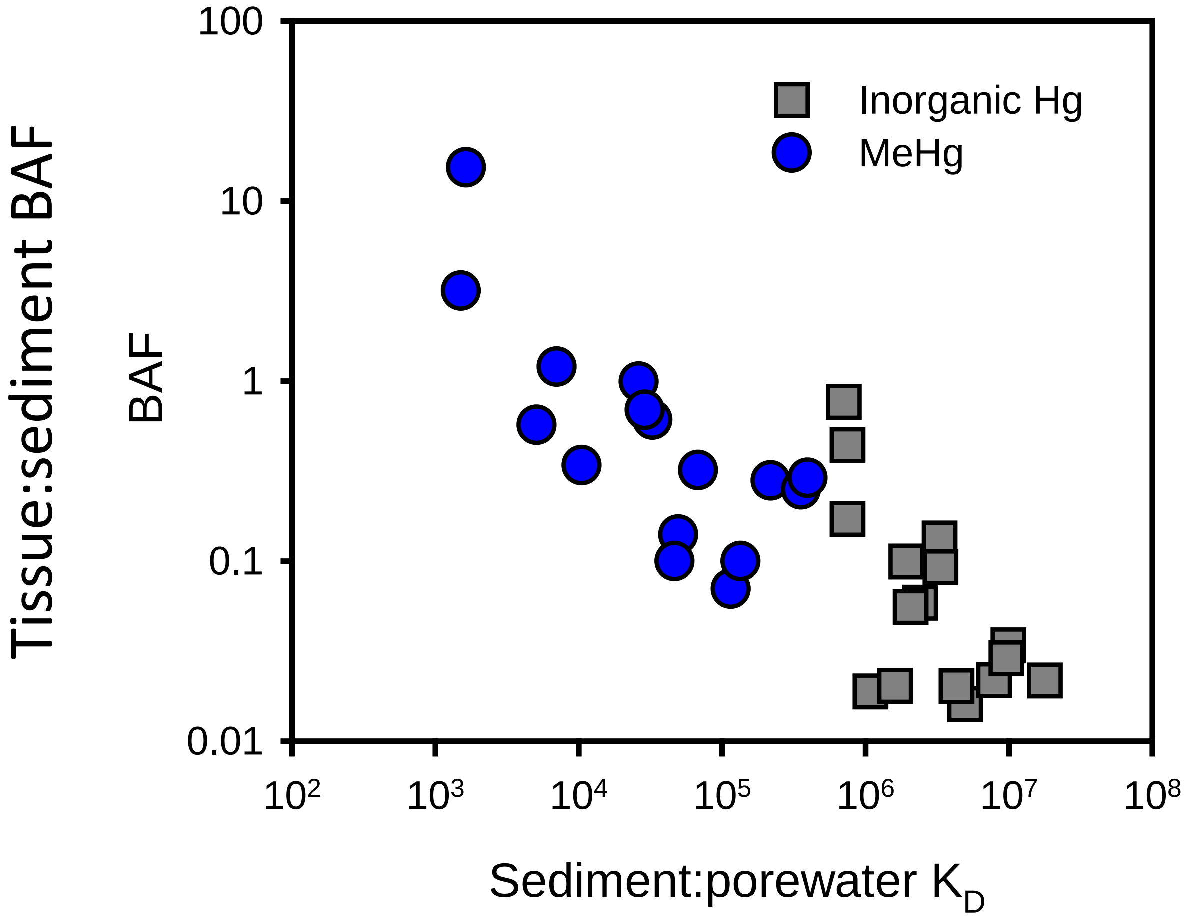
Gilmour et al. 2013 ES&T *Mercury Methylation by Novel Microorganisms from New Environments*

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



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

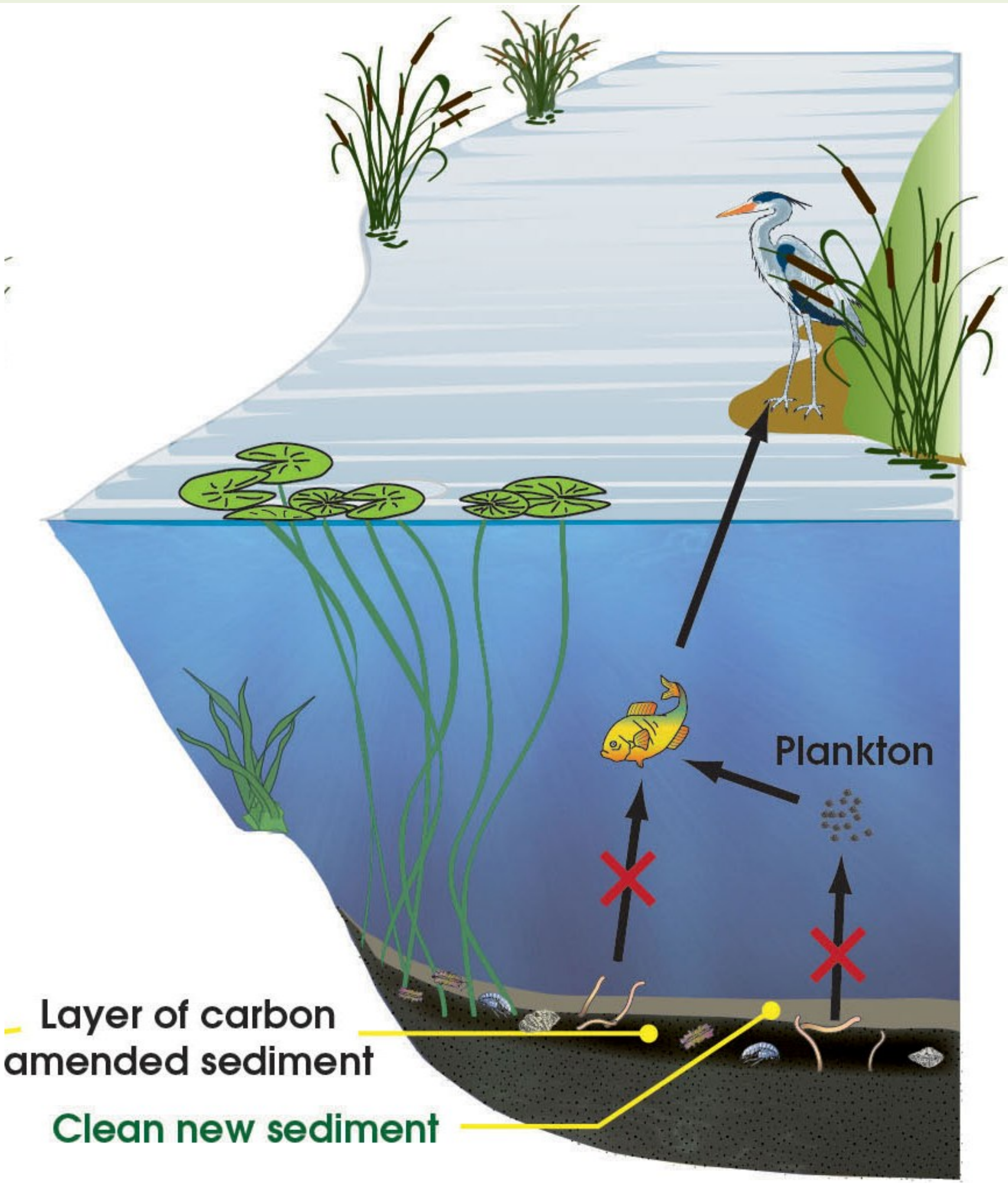
DEVELOPMENT OF *IN-SITU* MERCURY REMEDIATION APPROACHES BASED ON METHYLMERCURY BIOAVAILABILITY

Upal Ghosh and James Sanders
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**

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

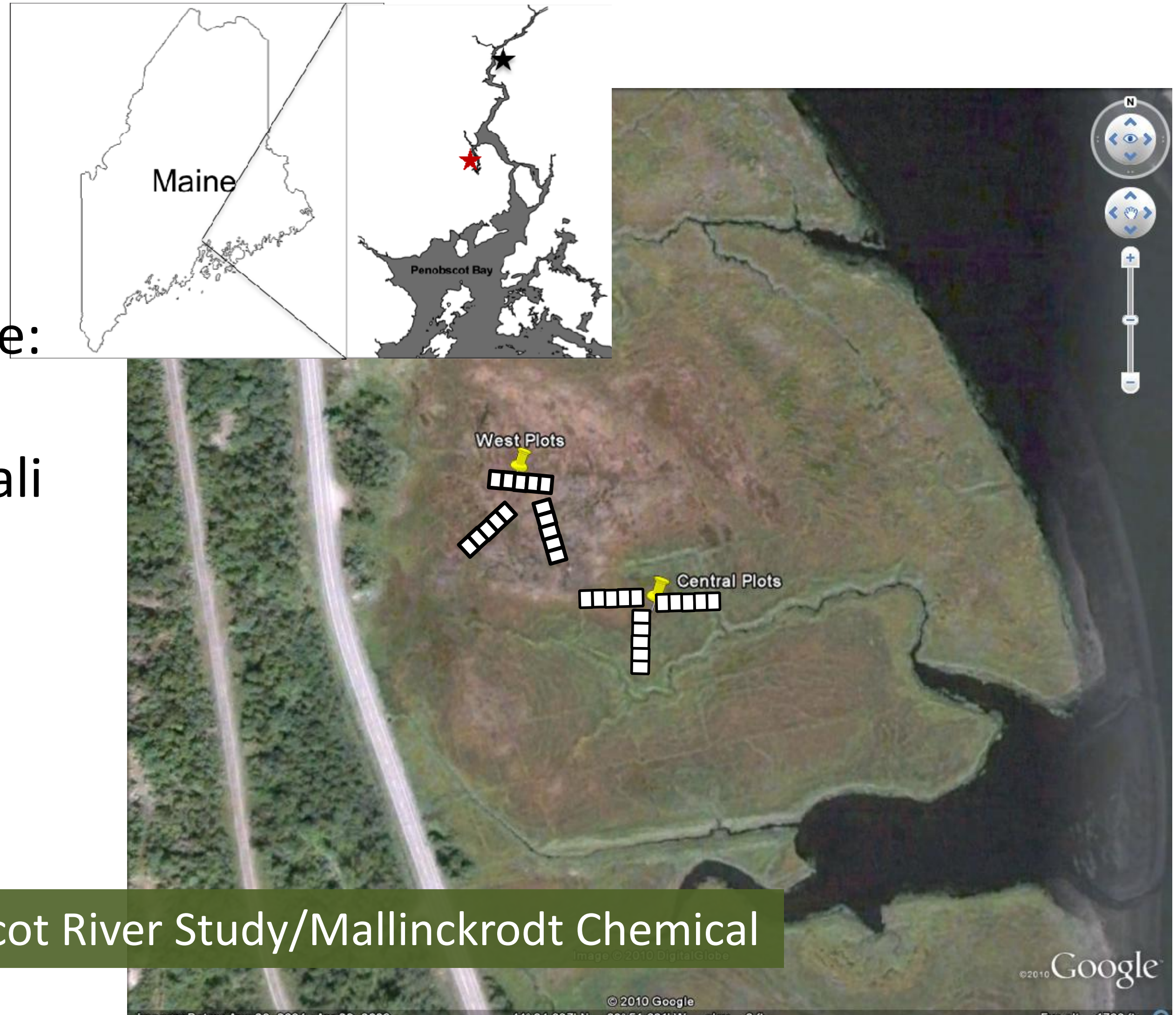
Approach to evaluating AC as a tools for Hg risk remediation in sediments and soils

- 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

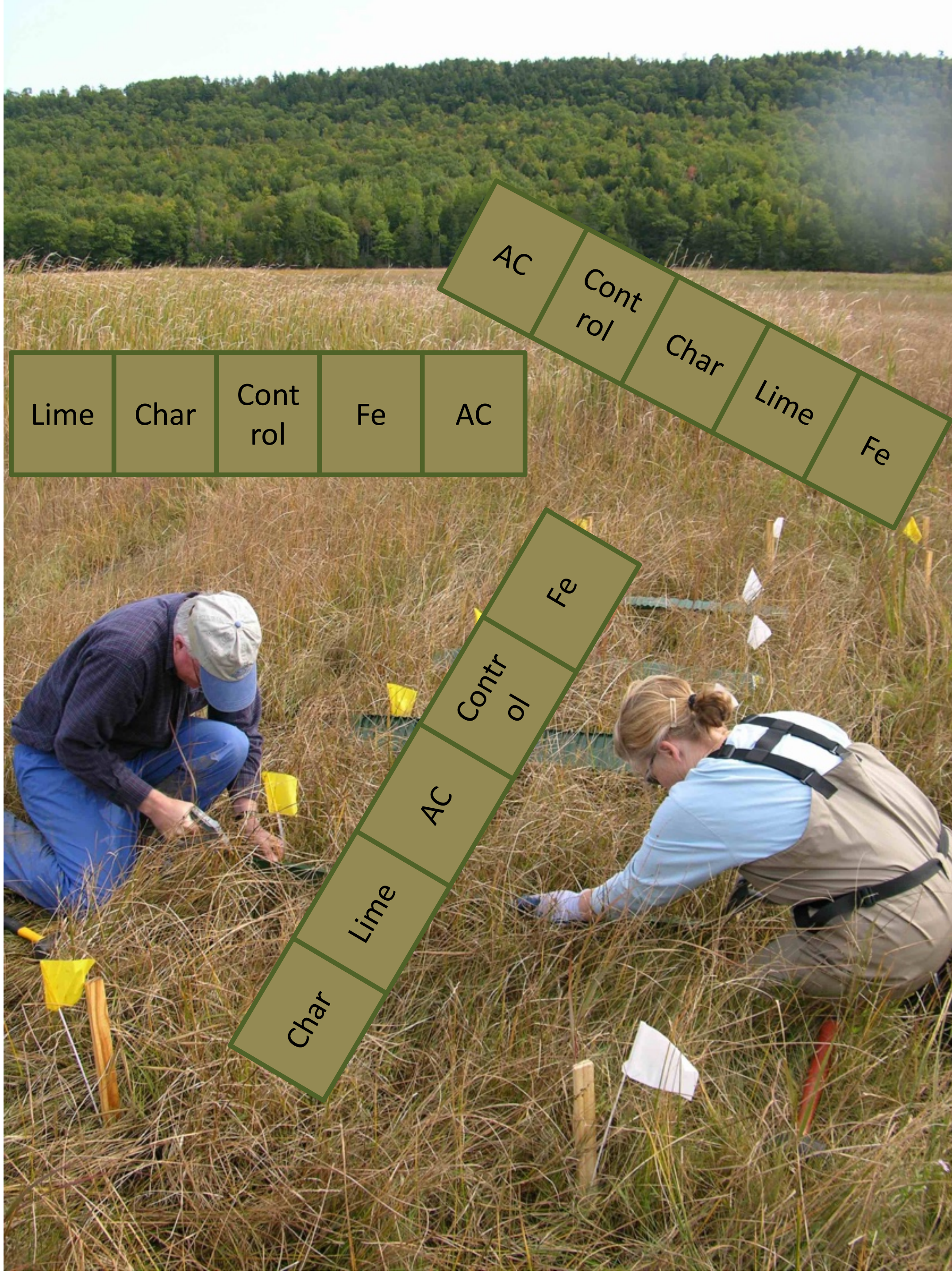


Supported by: Penobscot River Study/Mallinckrodt Chemical

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

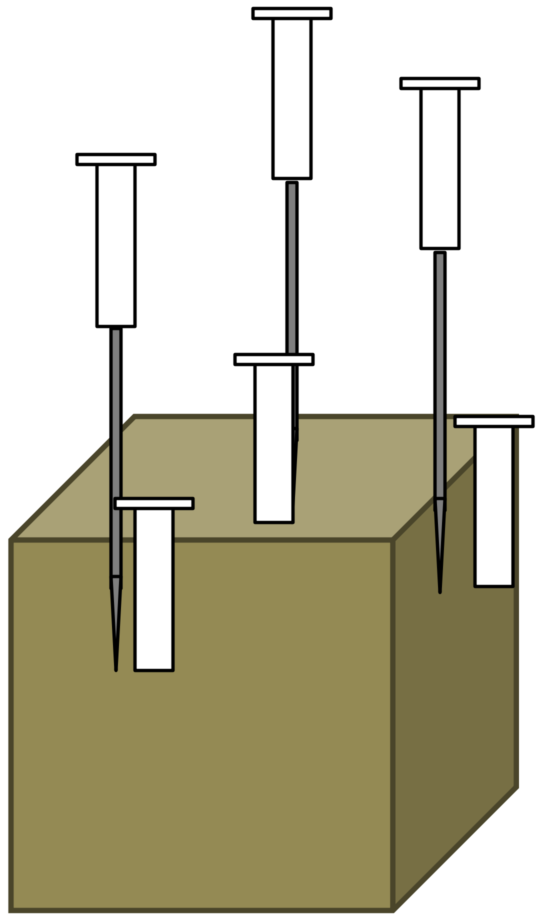
Amendment retention

- Black carbon in sediment

Efficacy and longevity

- Pore water [MeHg]
- Not evaluated: bioaccumulation

Impacts on soil biogeochemistry

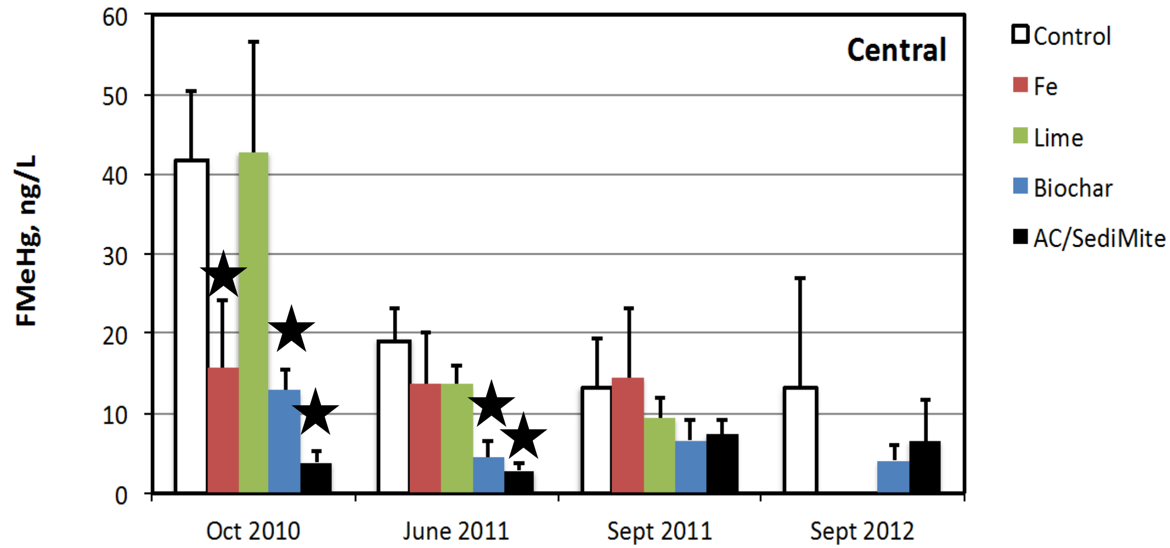


Soil and pore water sampling over time

Pore water MeHg

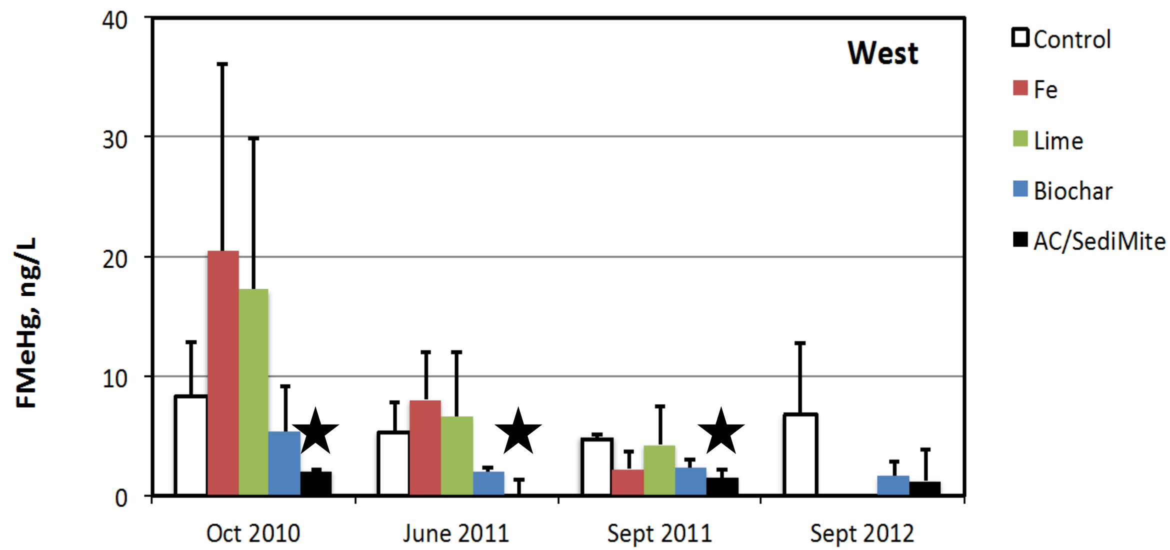
Central: Drier, moderately sulfidic

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



West: Standing pools, highly sulfidic

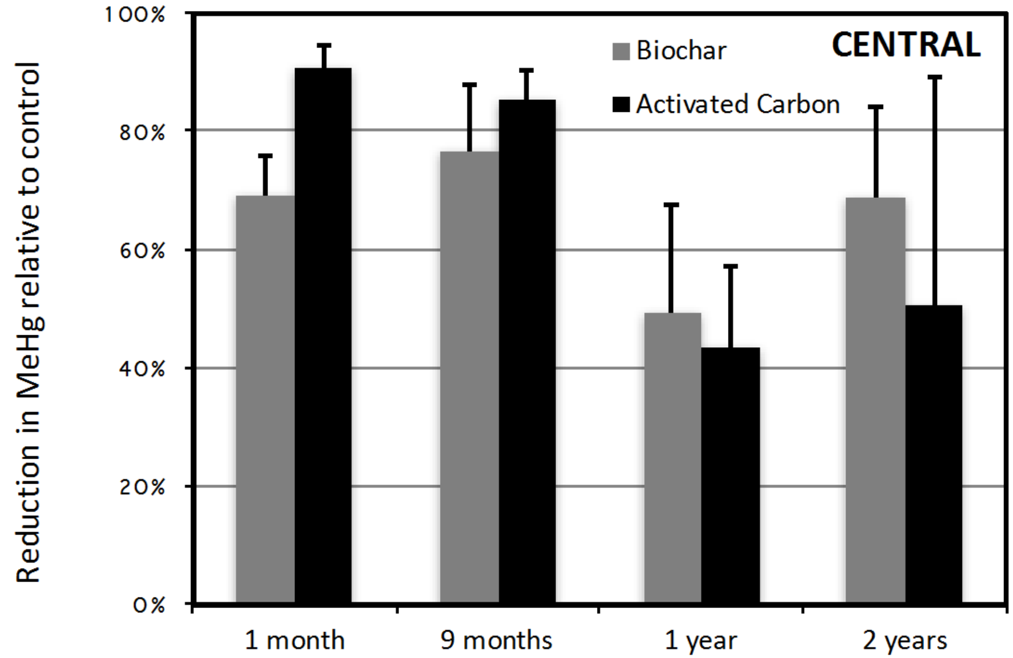
Spartina patens (salt marsh hay),
Agrostis stolonifera (creeping bentgrass), Eleocharis uniglumis (spike rush)

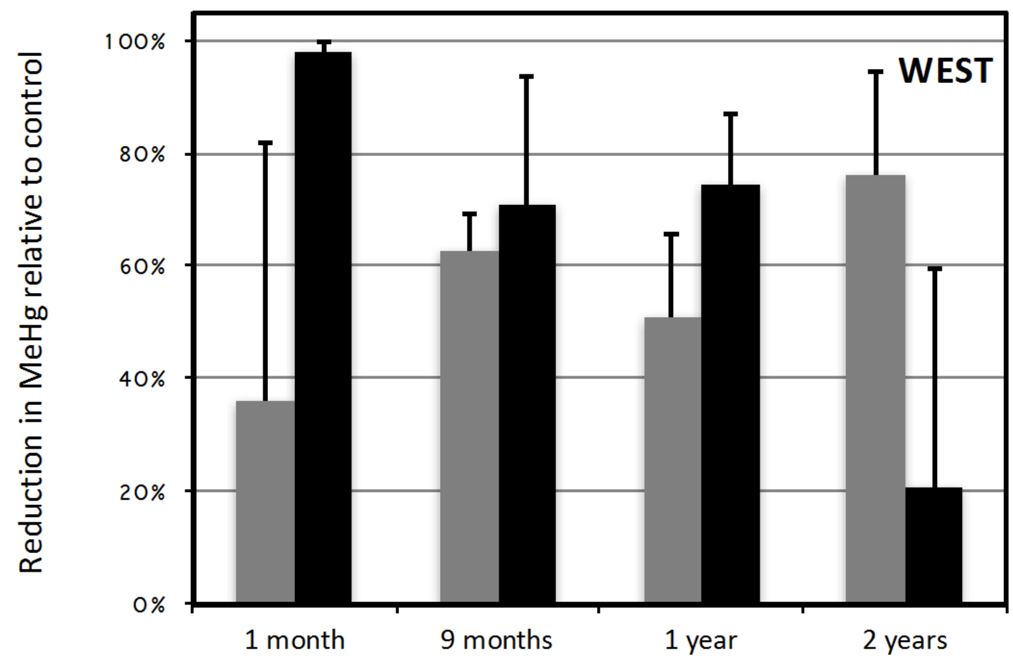


- Each bar is the average ± std of triplicate plots.
- Samples for each plot are composites of 3 samples.

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

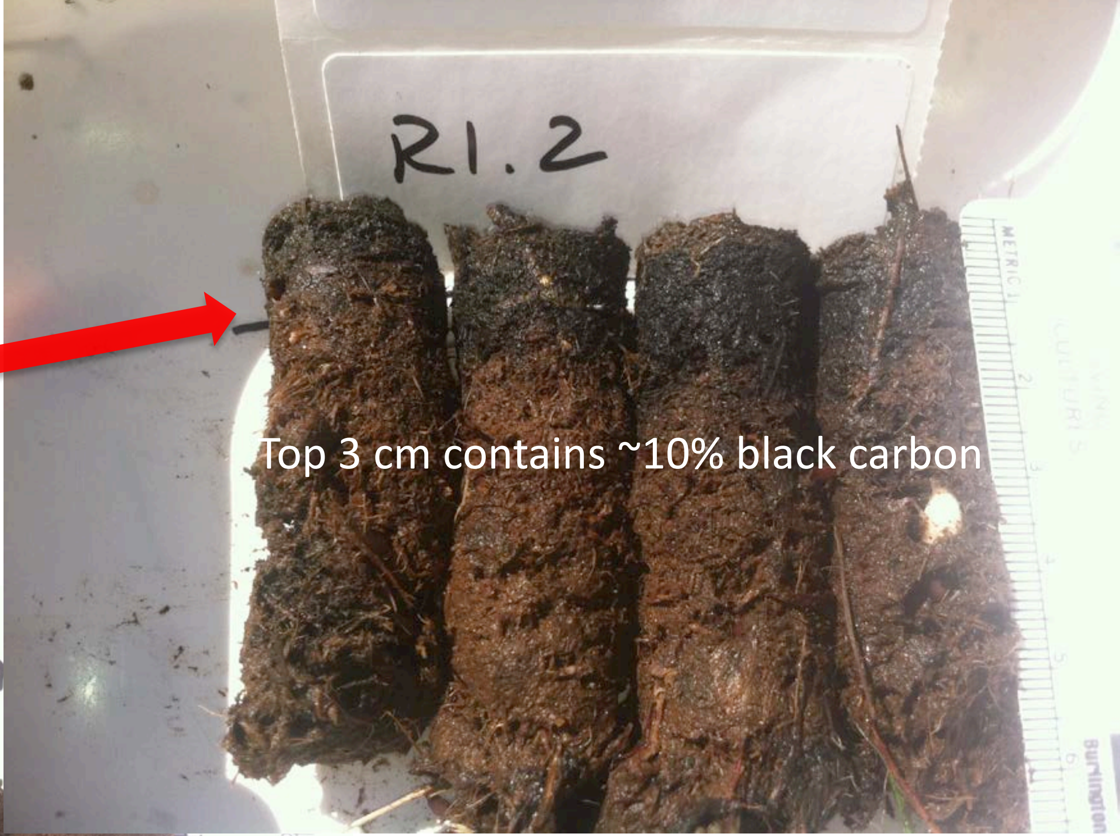
Pore water MeHg reductions





Penetration of AC into marsh surface

~2 cm in 2 years



Untreated control plot

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
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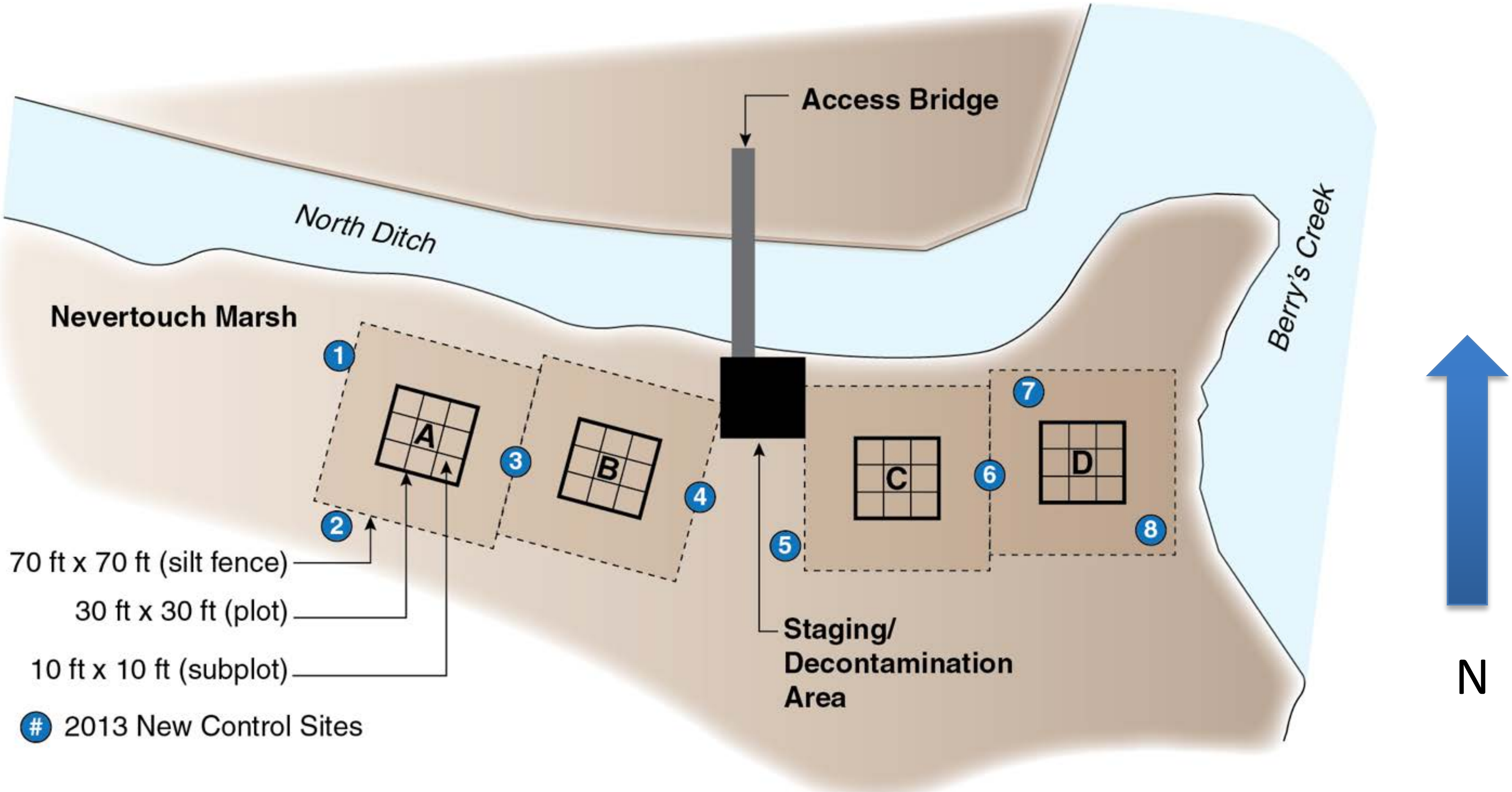
Upal Ghosh, James Sanders
University of Maryland Baltimore County
Susan Kane Driscoll, Charlie Menzie, and Ben Amos, Exponent
Betsy Henry, Anchor QEA
Steve Brown, The Dow Chemical Company

Plot A, April 2013

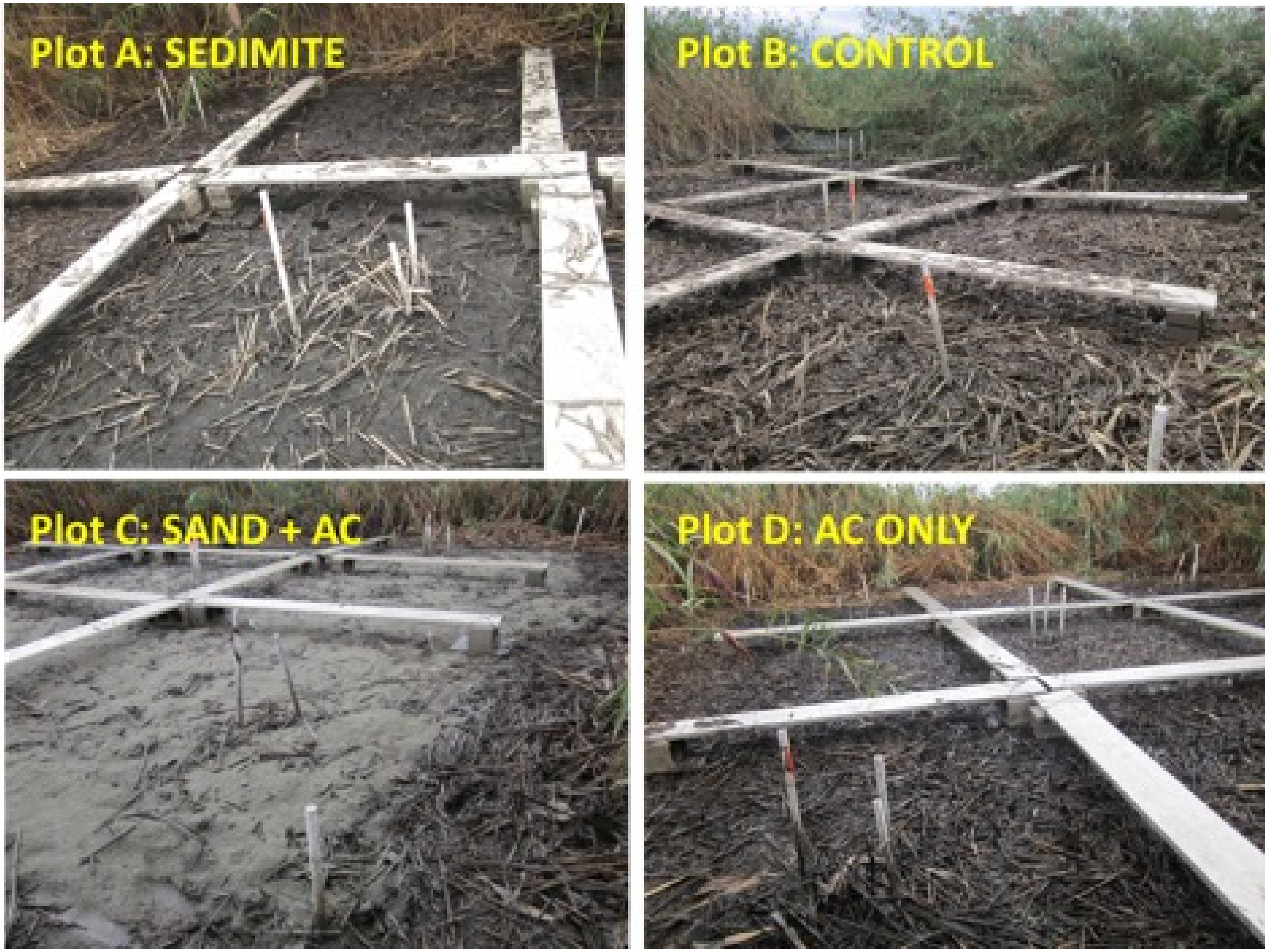
Plot Design – thin layer surface placements

Plot A	Plot B	Plot C	Plot D
SediMite	Control	AC+Sand	AC
(formulated with regenerated PAC)		(Calgon GAC + ~2 cm sand)	(Calgon GAC)



Design

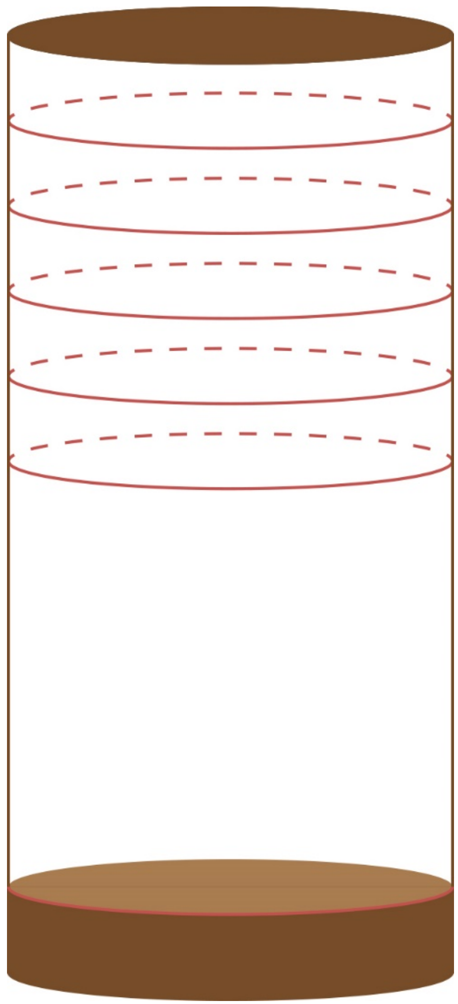
- Application by vortex sprayer
- 2 year study
- Soil sampling design similar to Penobscot – cores and sippers, composites and replicates, focus on top 5 cm
- Also included caged and wild amphipod exposure

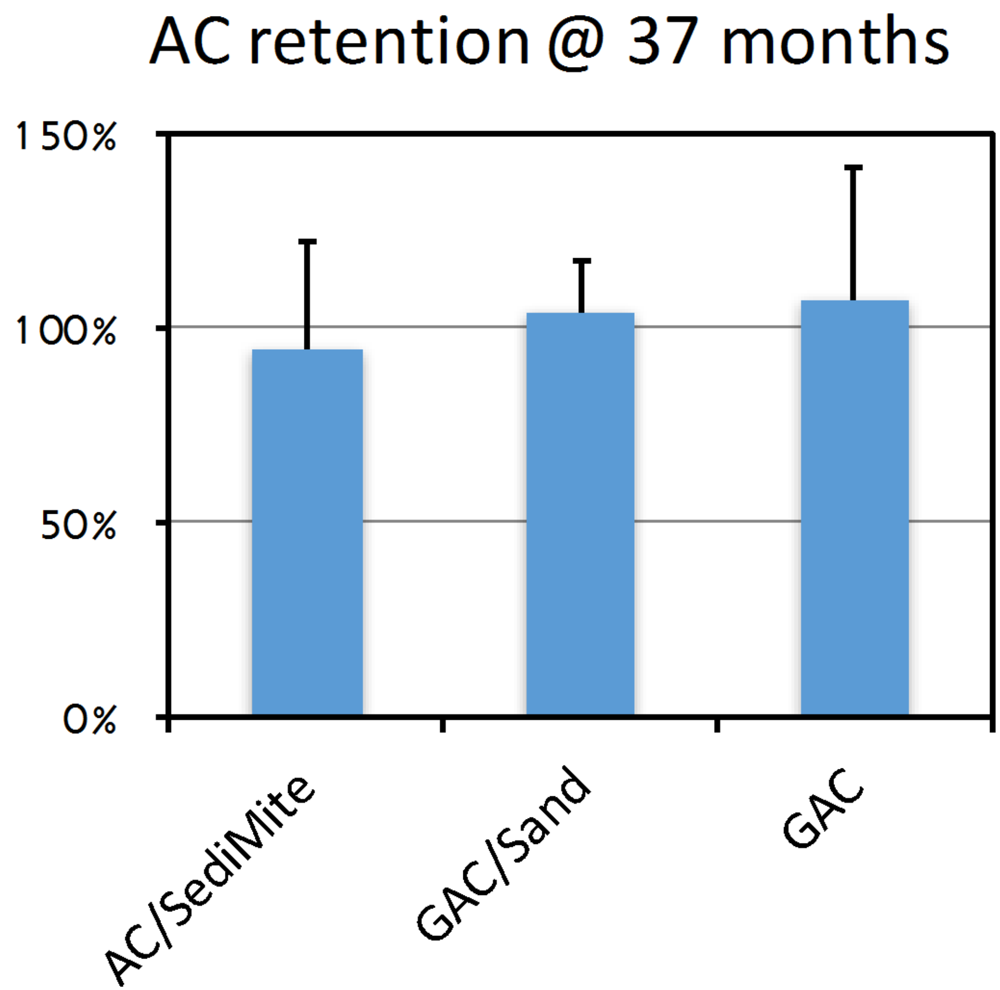


Appearance of the experimental plots two months after amendment application.

Activated Carbon Retention in Berry's Creek

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

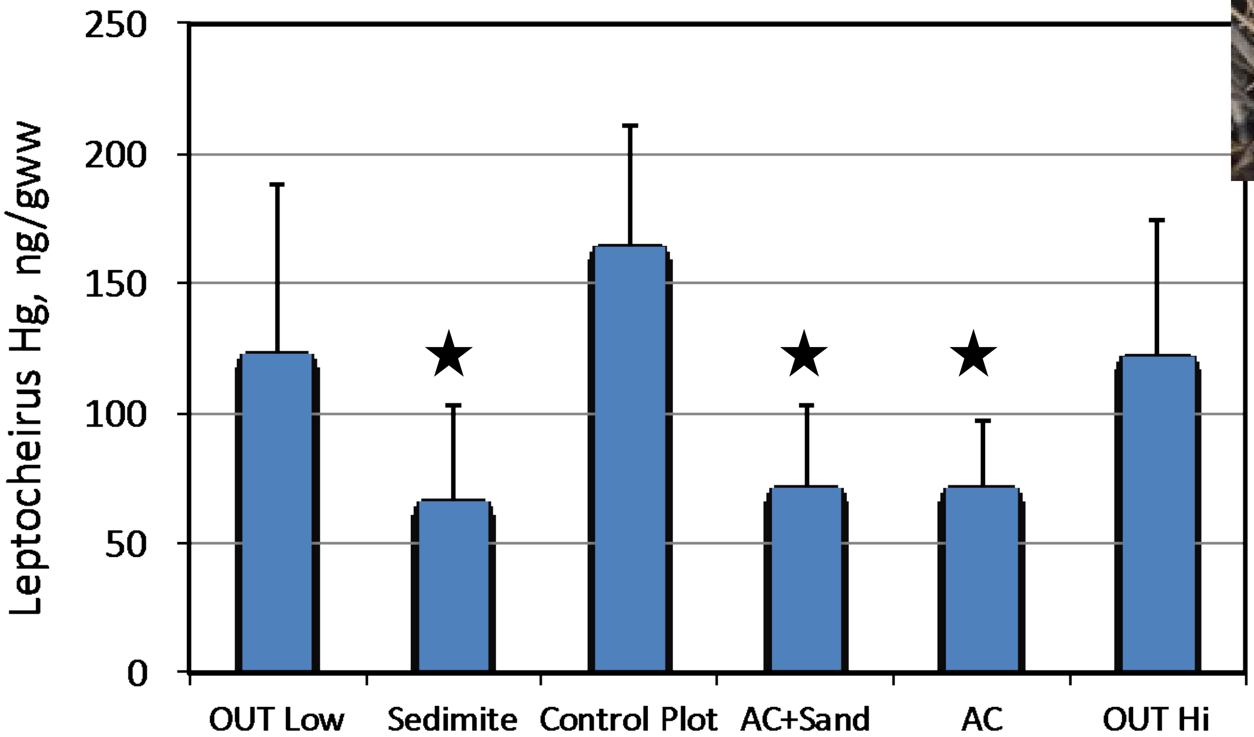




Site heavily impacted by Hurricane Sandy, but AC persisted in marsh sediments

UMBC
AN HONORS UNIVERSITY IN MARYLAND

Total Hg uptake by *Leptocheirus*



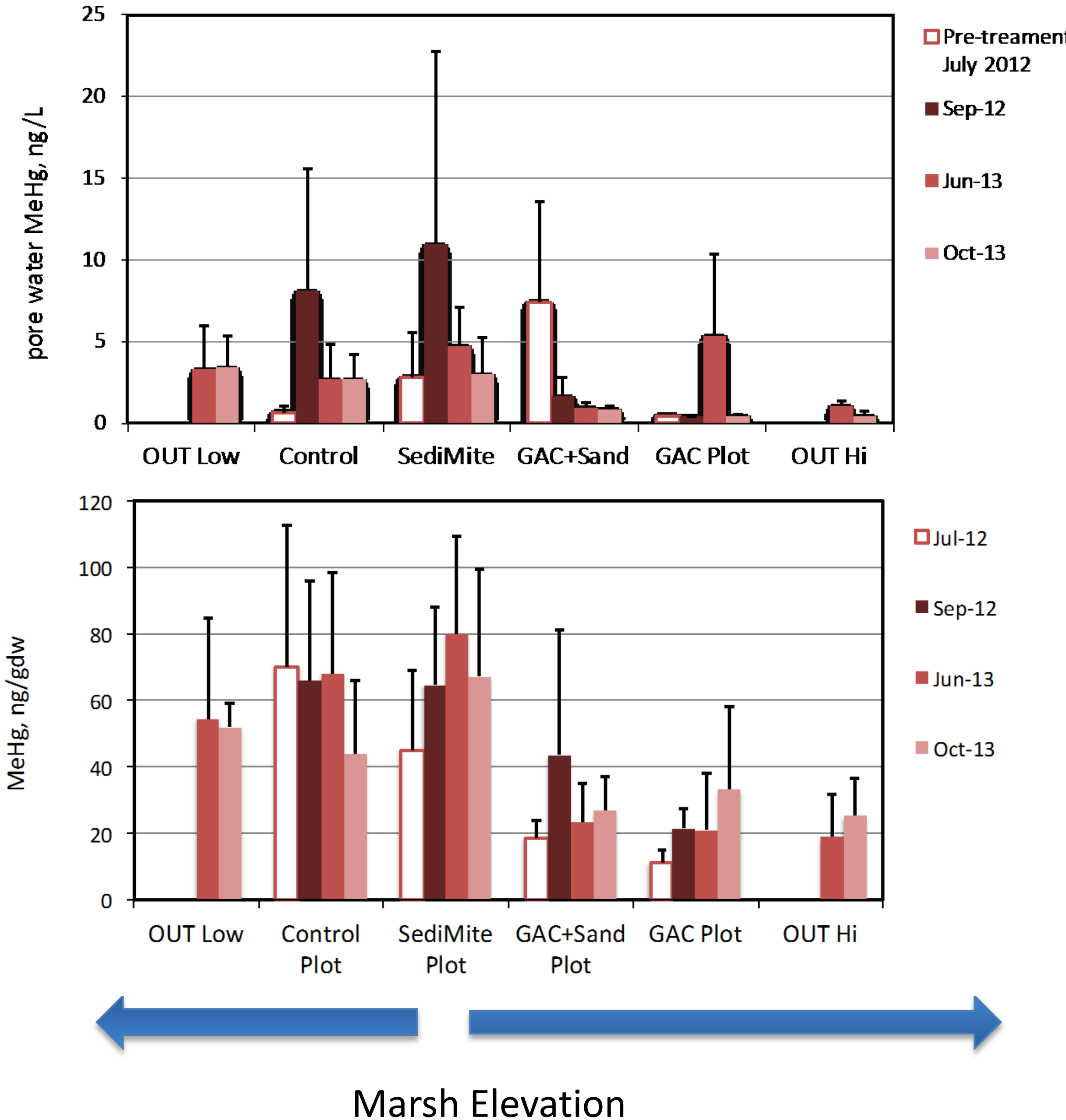
Exposure chamber design by Bennett Amos

- 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

A cautionary tale: Elevation differences among plots

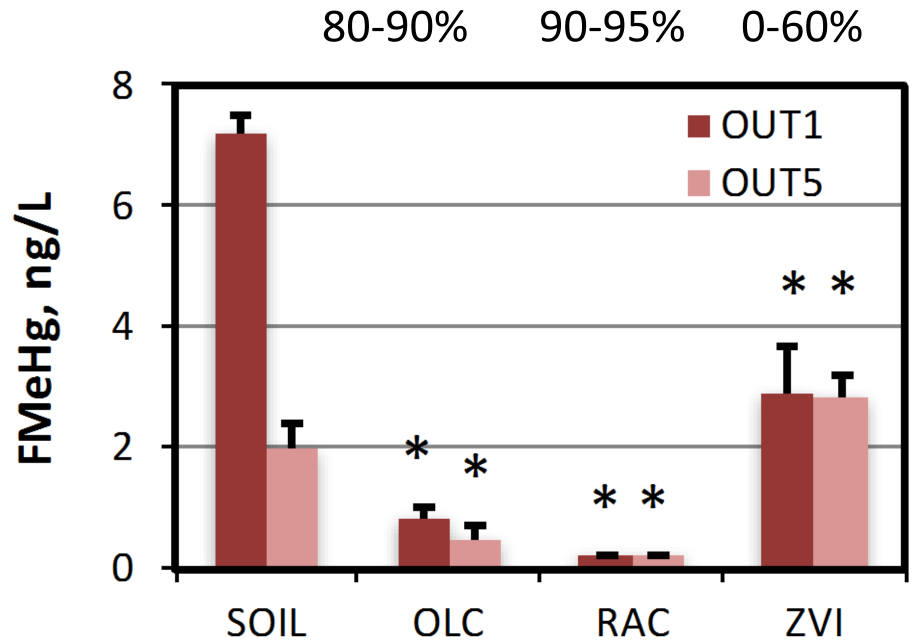
Ex-situ evaluation of AC on MeHg in Berry's Creek Marsh soils

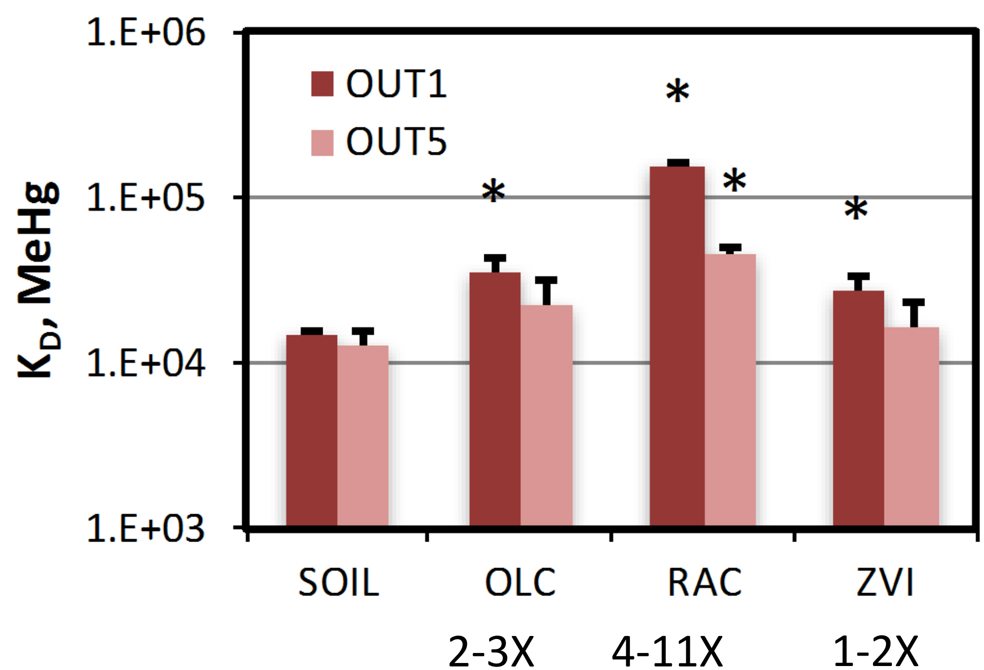
Effect of amendments mixed into anaerobic soil slurries (2:1 soil:water)
1 week incubation

OLC = Calgon OLC GAC

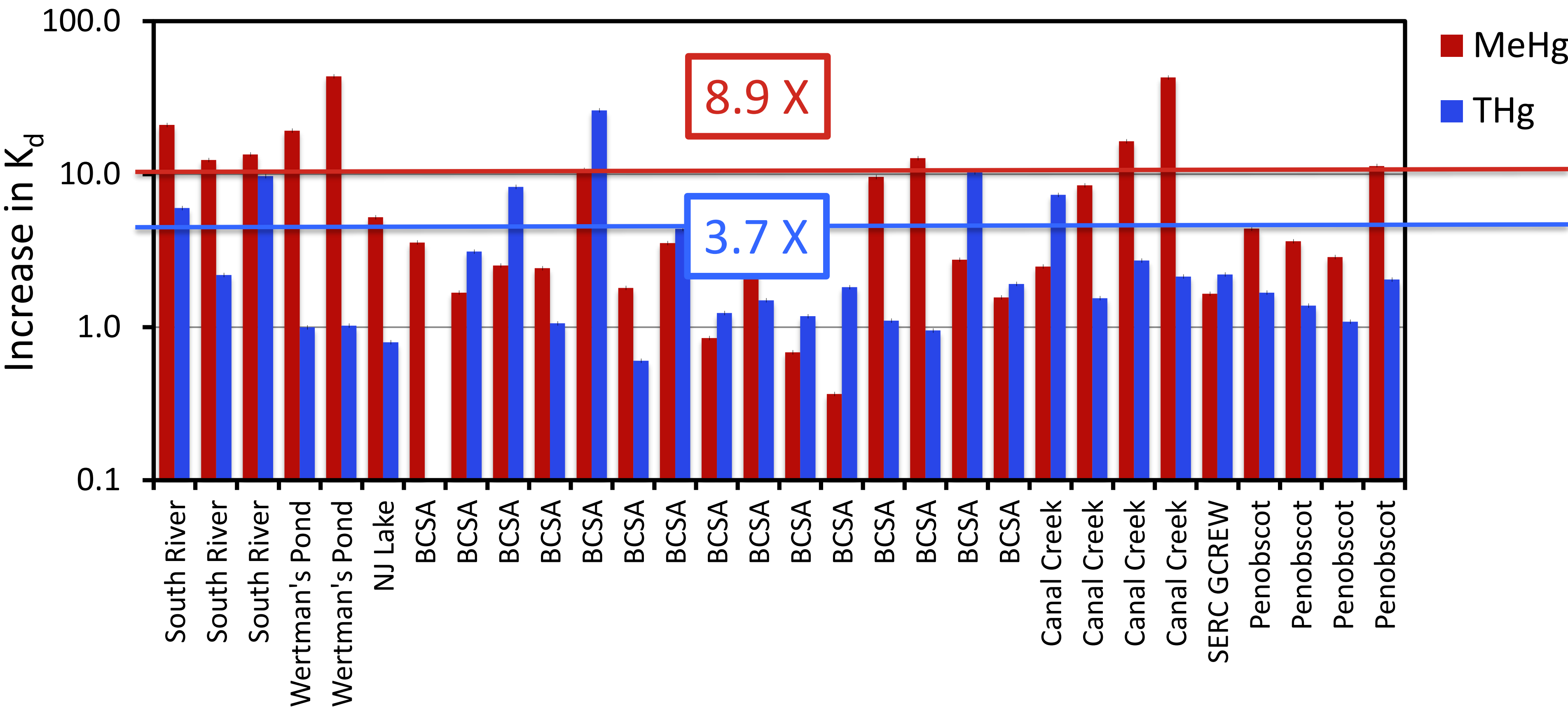
RAC = SediMite formulated with regenerated PAC

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





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

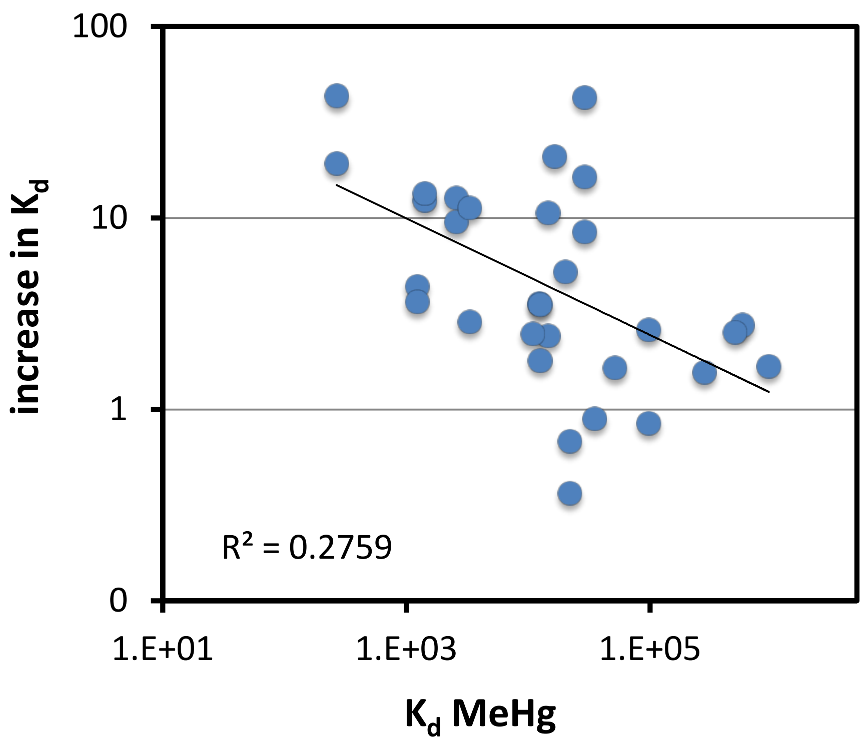


Wide range of reduction in partitioning
AC is more effective in reducing pore water MeHg

Correlates of AC efficacy

AC is more effective in sediments and soils with:

- naturally low K_d

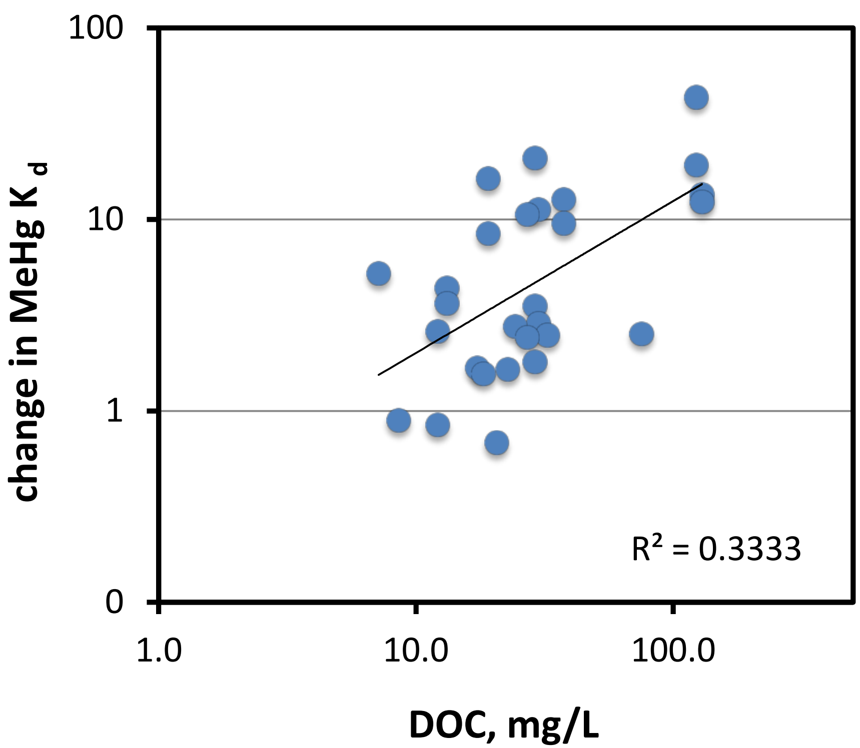


Correlates of AC efficacy

AC is more effective in sediments and soils with:

- naturally low K_d

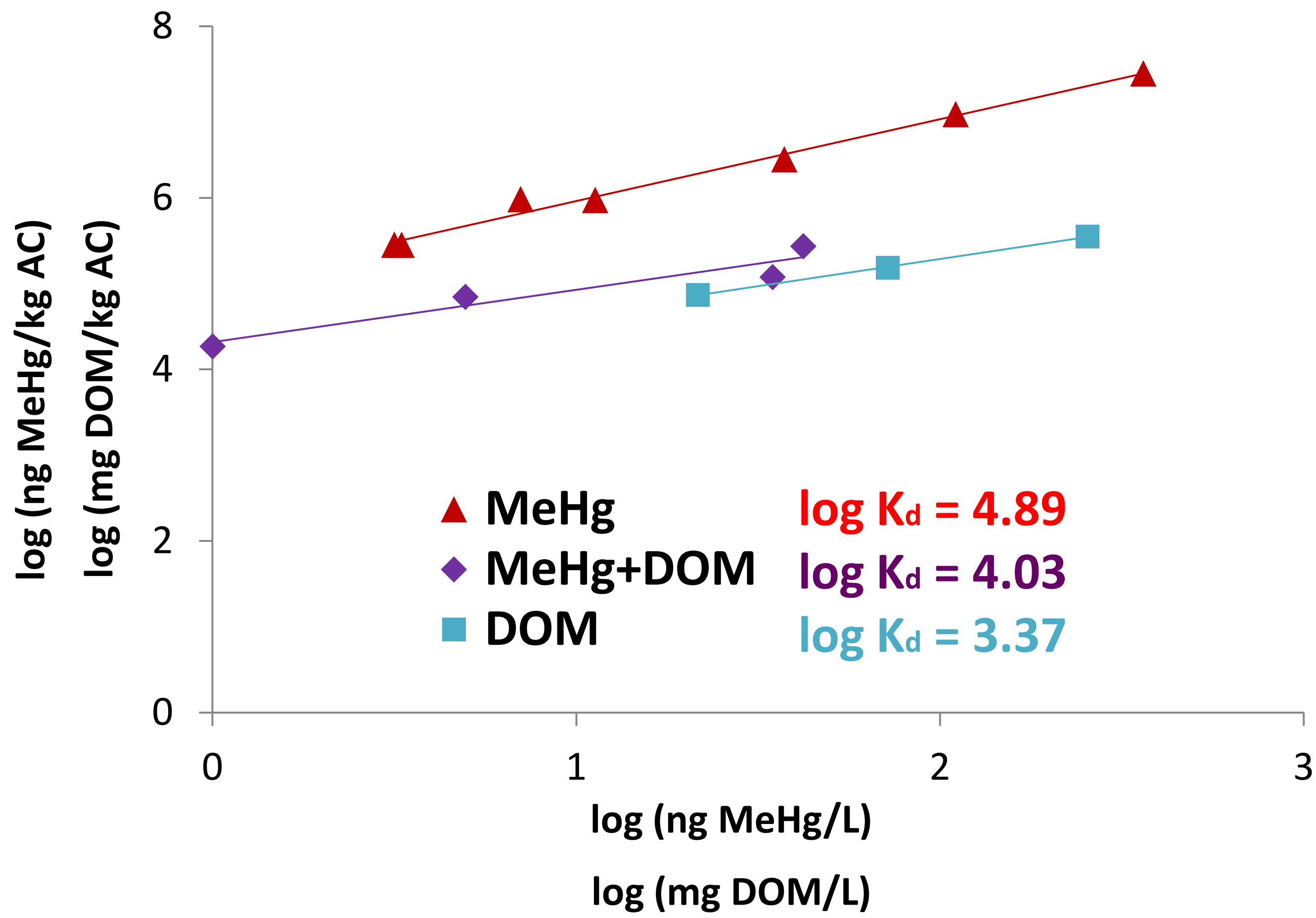
- higher pore water DOC



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

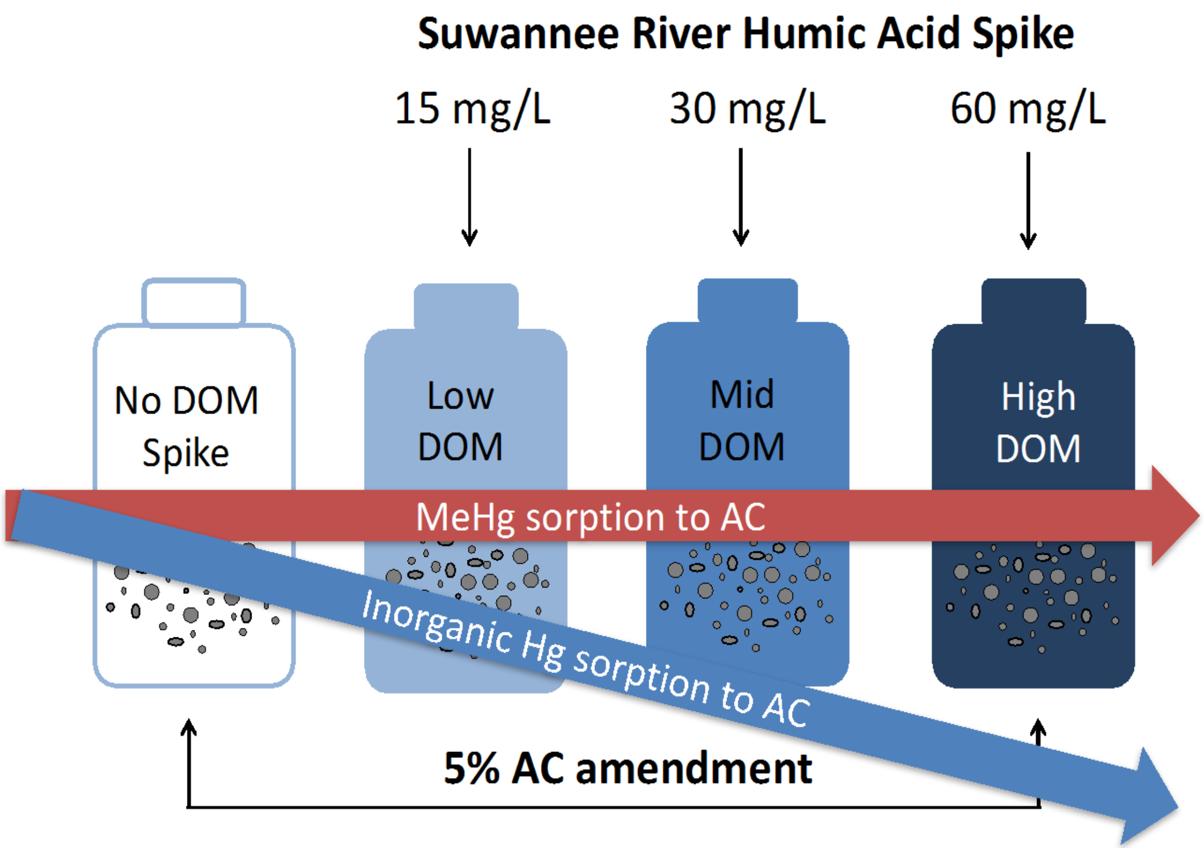
How does DOM Impact MeHg partitioning to Activated Carbon?

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