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LABILITY OF MERCURY AND METHYLMERCURY IN SEDIMENTS AND NEW APPROACHES FOR REMEDIATION

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Workshop on

Remediation of sites contaminated by mercury in Mantova, Italy

Oct 28, 2014

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GING EXPOSURE FROM HISTORIC DEPOSITS CONTAMINATED SEDIMENTS

- Contaminated sediment sites are large
- Current technologies are expensive and disruptive
- Need for innovative techniques that reduce risks
- How do you clean up an ecologically sensitive site without destroying it?

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PROACHES FOR MANAGEMENT OF CONTAMINATED SEDIMENTS

- Institutional controls
- Monitored natural attenuation
- Dredging/excavation followed by landfiling
- In-situ capping

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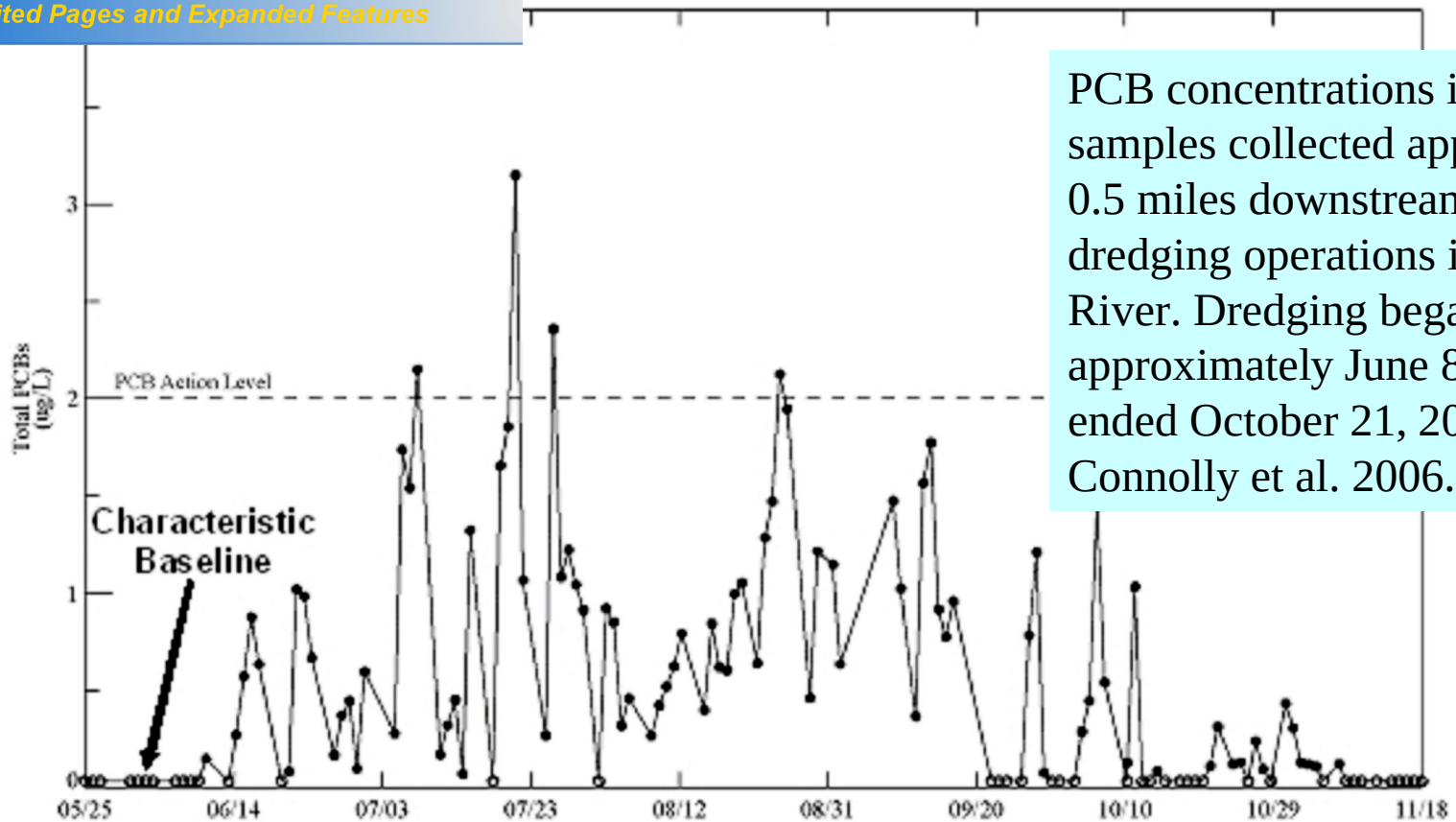
ON EFFECTIVENESS OF DREDGING



PCB concentrations in water samples collected approximately 0.5 miles downstream of the dredging operations in the Grasse River. Dredging began approximately June 8, 2005 and ended October 21, 2005. Source: Connolly et al. 2006.

Of the 20 megasites evaluated by the NRC committee:

- Å25% achieved goals
- Å50% did not achieve goals or were not monitored well
- Å25% not enough time has elapsed to form judgment

(National Research Council June 2007)

The report urges EPA to step up its monitoring activities before, during, and after dredging efforts at all sediment megasites

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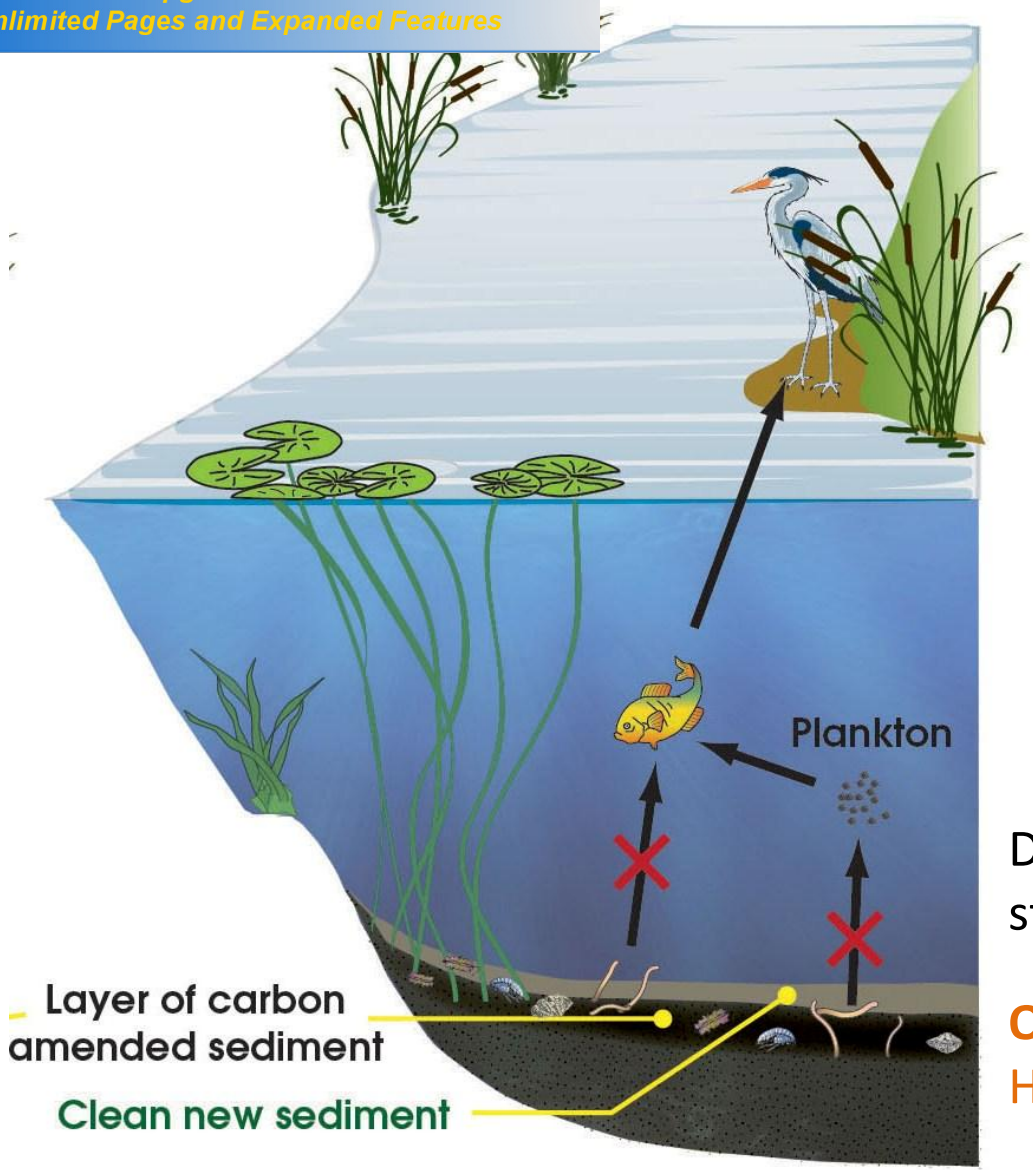
SEARCH BACKGROUND



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.

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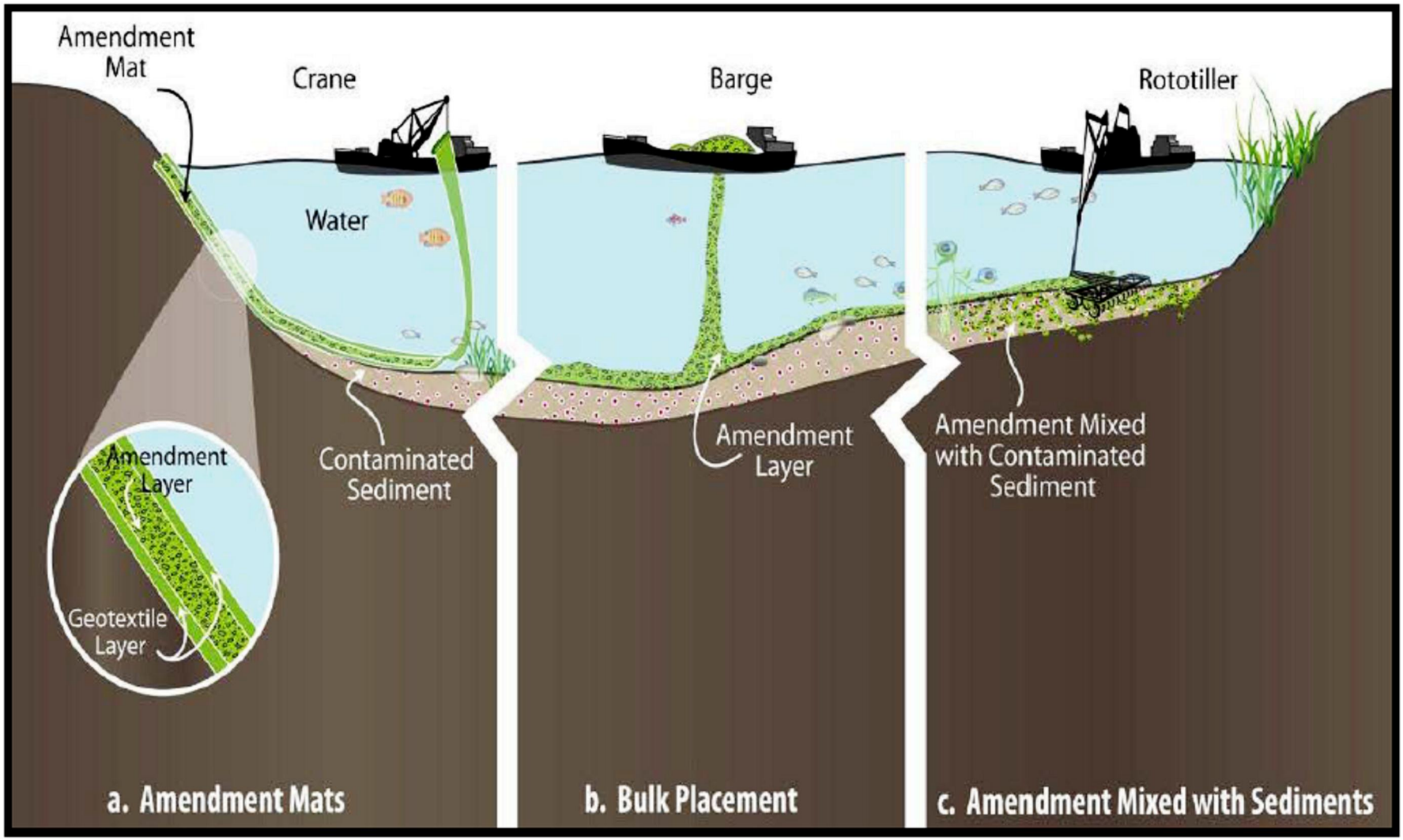
MENTS FOR IN-SITU REMEDIATION OF ERFUND SEDIMENT SITES

USEPA Directive 9200.2-128FS; April 2013



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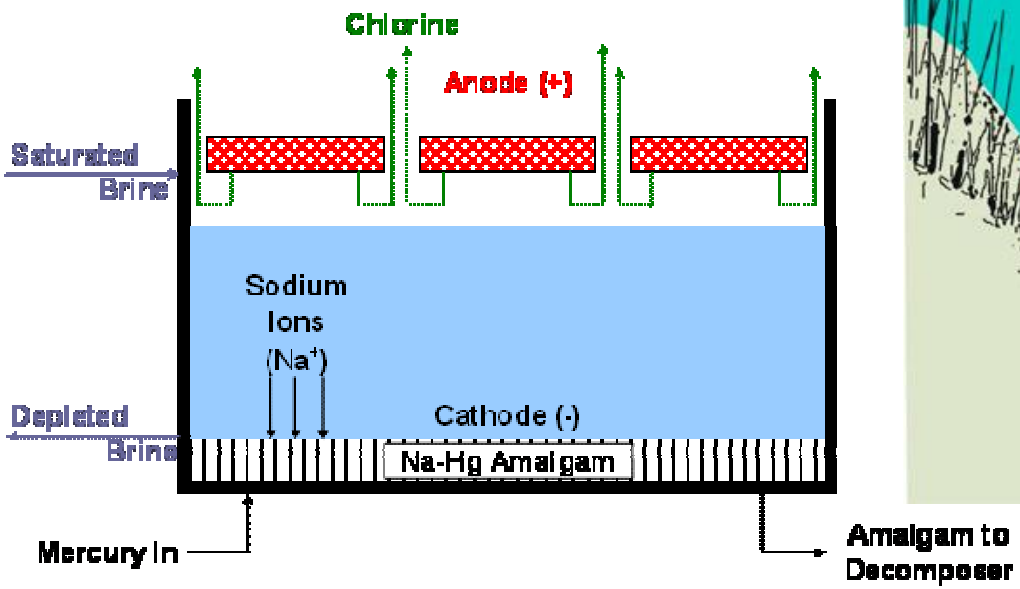
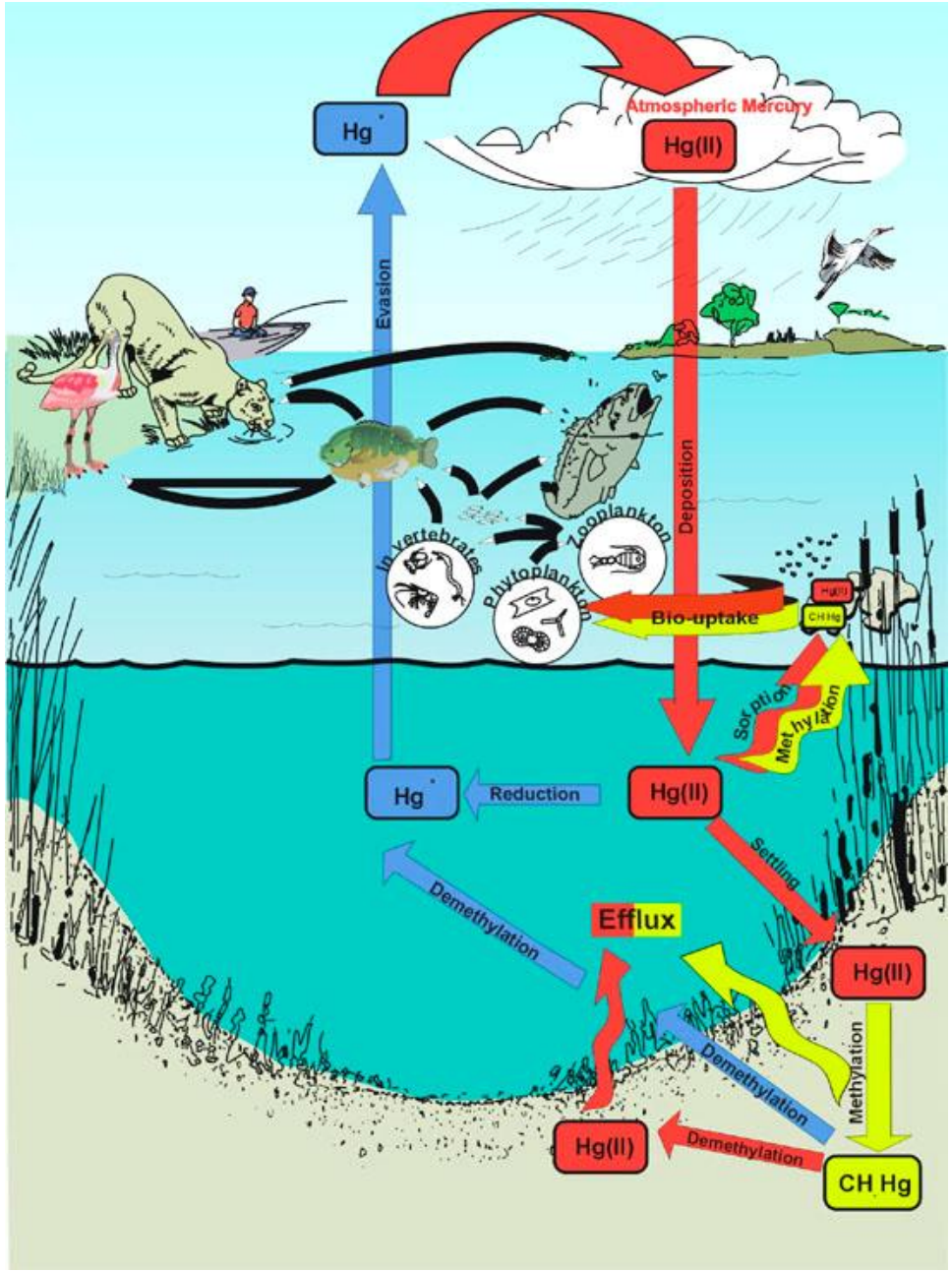
Used extensively in chlorine production (chlor-alkali process) and gold refining. Hg is also released from coal-fired power plants.

Hg cycles in the environment and can transport long distances through the atmosphere.

Microbial processes can produce methyl-Hg in sediments which is highly toxic and bioaccumulates





From : US Geological Survey

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MERCURY FROM COAL FIRED POWER PLANTS

2.6 GW plant in Ohio; coal combustion: 2500 t/day

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SPECIATION IN SEDIMENTS

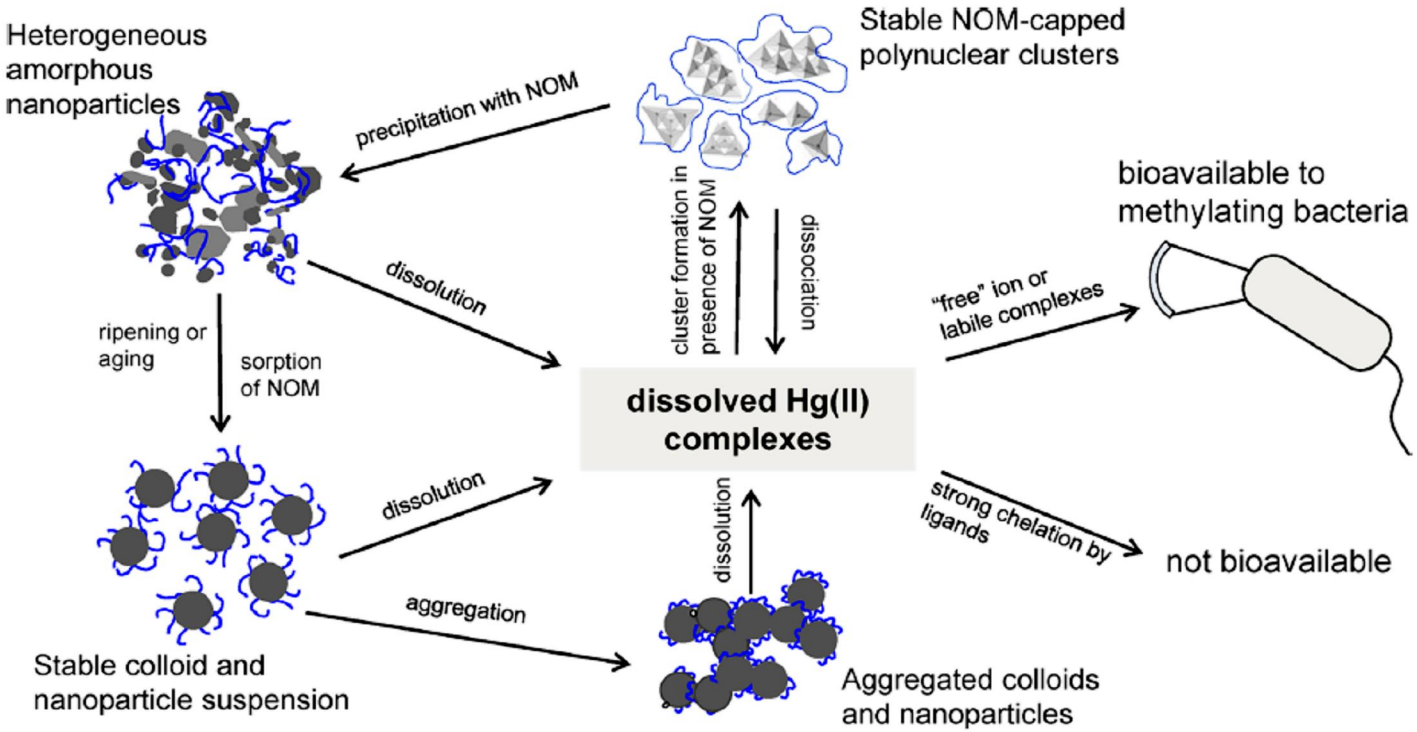

Figure 4. The transformations of mercuric sulfides in anoxic settings involve a diverse collection of species, many of which are intermediates of metal–ligand complexation reactions and precipitation and dissolution of $HgS_{(s)}$. Natural organic matter (NOM) is expected to play an important role in modifying reaction rates and the composition of metastable intermediates. If uptake of Hg(II) involves a facilitated mechanism (e.g., via metal transporter), then bioavailability will be governed by the propensity of Hg(II) to bind to a receptor site. Nanoscale phases could also cross membrane boundaries, but these would presumably need to dissolve or dissociate inside the organism prior to methylation. Modified from Aiken et al.[80].

Hsu-Kim et al. Review Article, Environ Sci. Technol. 2013

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URY METHYLATION IN SEDIMENTS

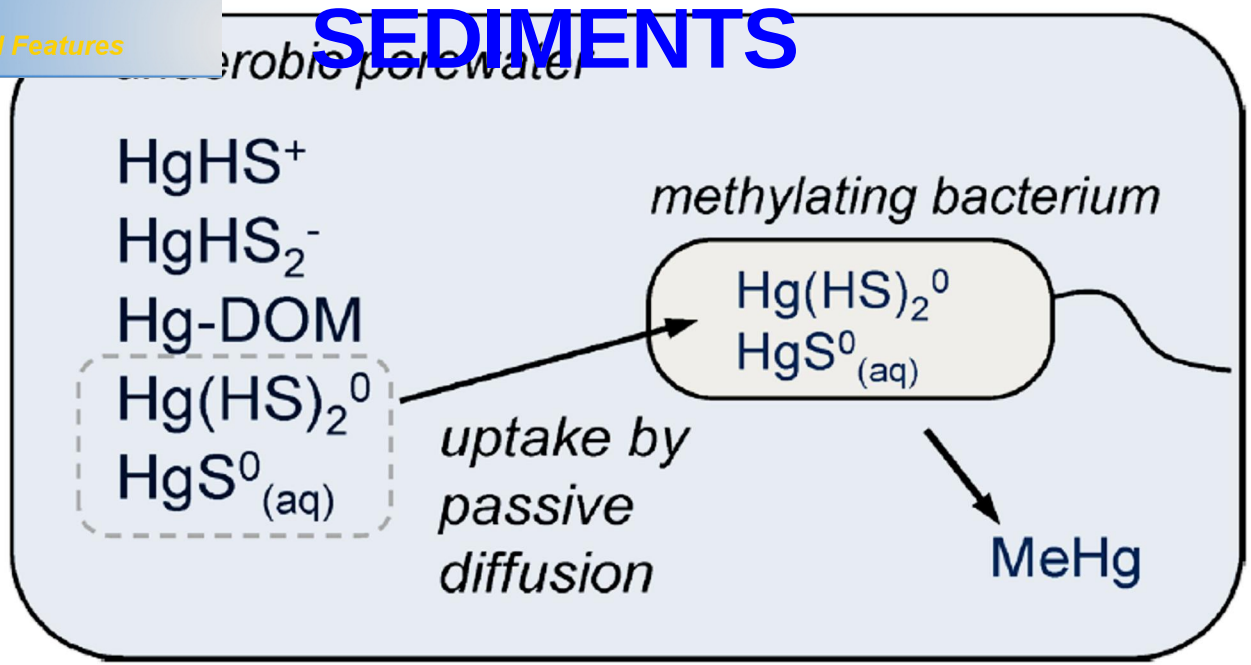

Figure 2. Neutral mercury-sulfide bioavailability model postulates that only the neutrally charged forms of Hg(II) are able to passively diffuse into methylating bacteria. The model also presumes that the speciation of dissolved inorganic mercury in porewater has reached chemical equilibrium. From this basis, equilibrium chemistry predicts that aqueous mercury-sulfide complexes are the predominant form of dissolved mercury in porewater, and the net production of methylmercury (MeHg) is related to the concentration of neutrally charged Hg–sulfide complexes. (Originally postulated by Benoit et al.[61])

Hsu-Kim et al. Review Article, Environ Sci. Technol. 2013

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BONS INVESTIGATED

Carbon Type	C (%)[a]	Surface area (m^2/g)[b]	Skeletal density (g/cm^3)[d]
Bituminous coal based AC	80.9	1116	1.61
Coconut shell based AC	90.8	1305	1.45
Lignite coal based AC	72.8	968[c]	1.52
Regenerated AC	73.3	1150[c]	1.81
Chemically activated pine dust biochar	71.0	2266	1.16
Chemically activated phragmites biochar	64.6	1579	1.14
Steam activated turkey litter biochar	26.8	300	1.79
Steam activated chicken litter biochar	26.9	270	1.97
Pine dust biochar	77.9	542	0.97
Phragmites biochar	69.6	464	1.06
Peanut hull biochar	31.9	107	1.28
Acai pit biochar	77.2	198	1.23
Hardwood lump charcoal	70.8	224	1.29

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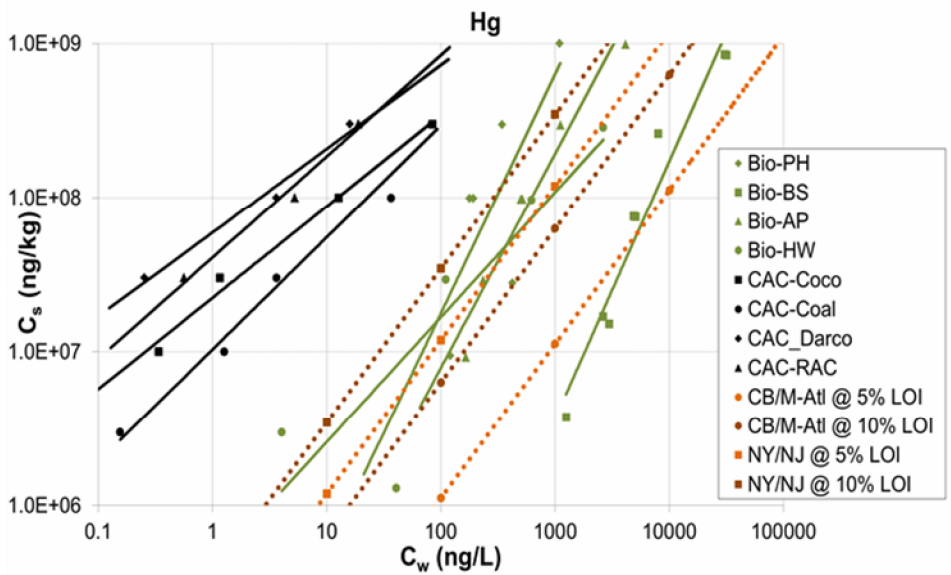
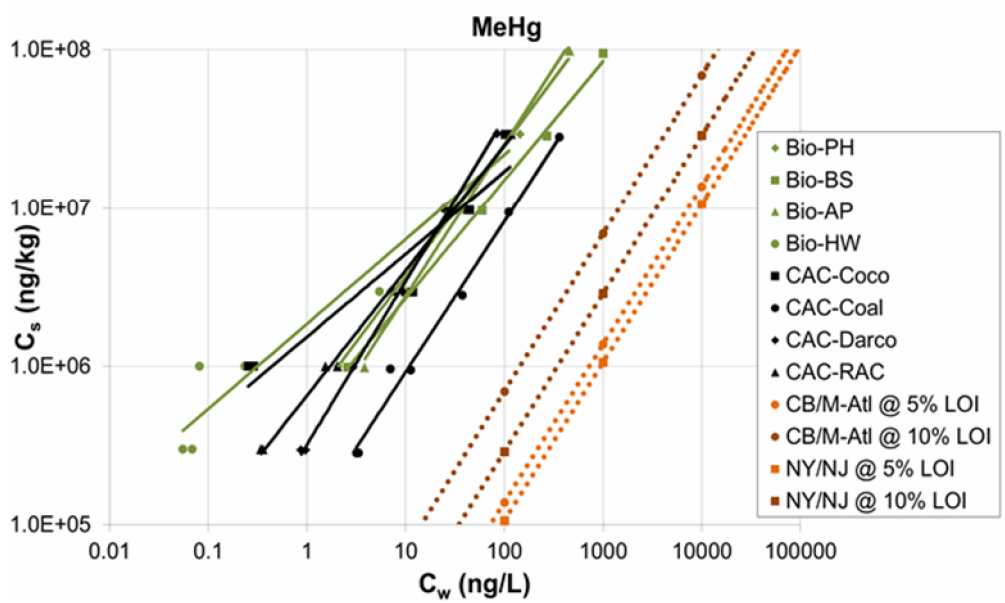
OTHERM STUDIES FOR SELECTED S AND ACTIVATED CARBONS





- ACs 2-3 orders of magnitude stronger sorbents for Hg and MeHg compared to natural sediments
- ACs stronger sorbent of Hg compared to biochars
- ACs and biochars equally effective for MeHg

Gomez-Eyles et al. ES&T 2013

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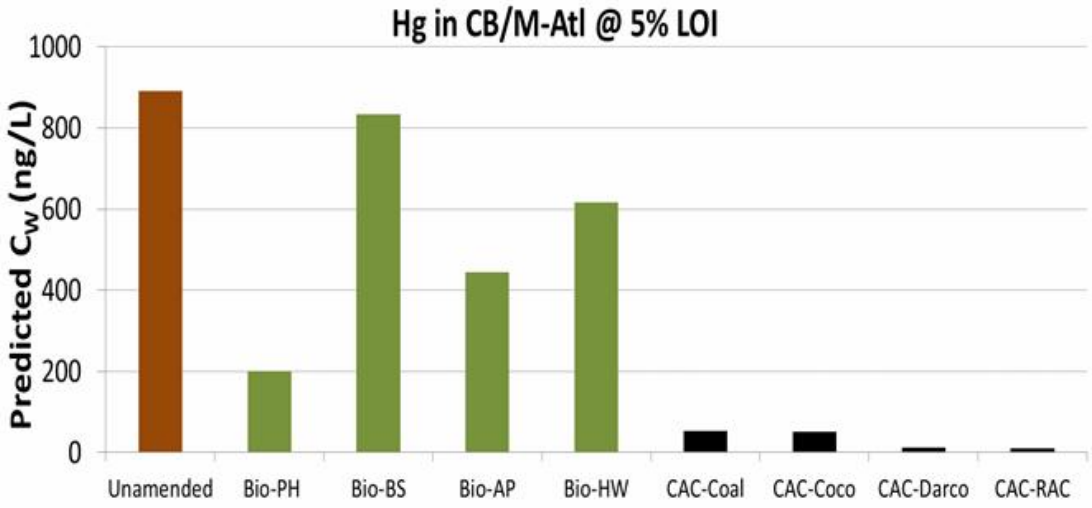
RBON EFFECTIVENESS FOR Hg AND MeHg POREWATER



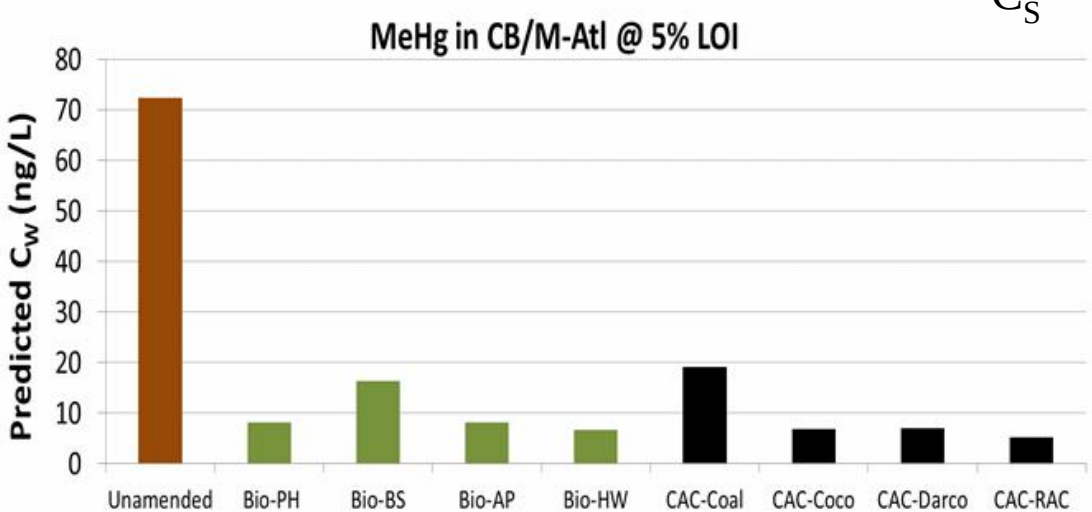
Reductions were modeled for a typical Hg impacted sediment

Hg : 10 mg/kg Hg

MeHg : 0.1 mg/kg

Reductions after amendment were predicted using the following linear model:

$$C_S = (f_{sed} \times K_{d\text{-}sed} \times C_W) + (f_{BC} \times K_{d\text{-}BC} \times C_W)$$



94-98% reduction in porewater Hg predicted after 5% AC amendment

73-92% reduction in porewater MeHg predicted after 5% AC amendment

Lower reductions for higher sediment native K_d

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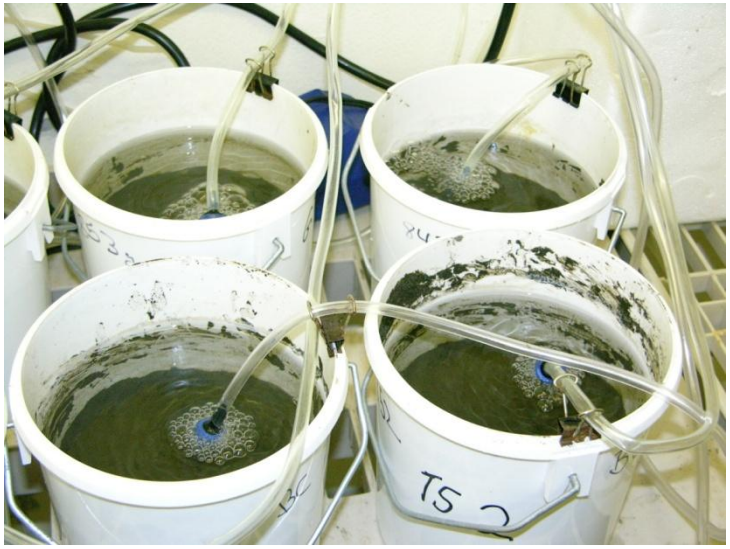
TUDIES WITH Hg CONTAMINATED SEDIMENTS

Microcosm Study Design

- Å Exposure studies with freshwater oligochaetes
- Å 300 or 750 cc sediment and 200 or 500 cc of overlying water
- Å Amendments 5 % by sediment dry wt
- Å Treatments: Thiol SAMMS, GAC, MRM, HGR + Control (5 replicates)
- Å Incubated at 20~25^0 C, 12 h light; 12 h dark
- Å Examine contaminant concentrations in worr tissue and partitioning, and sediment geochemistry



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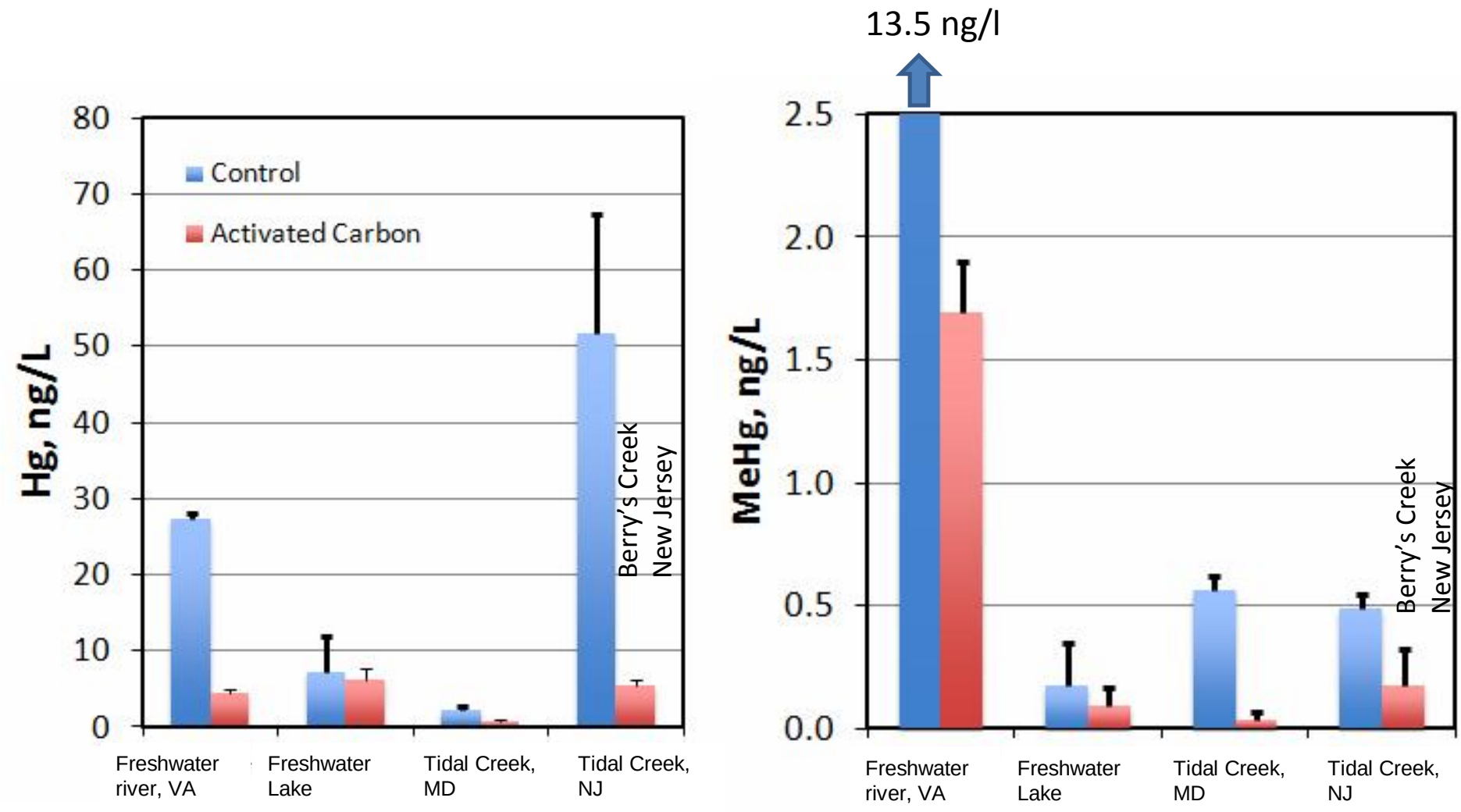
eHg IN POREWATER AFTER AC
NT TO A RANGE OF SEDIMENTS



Sediment porewater Hg and MeHg both reduced after AC amendment

Gilmour et al. ES&T 2013

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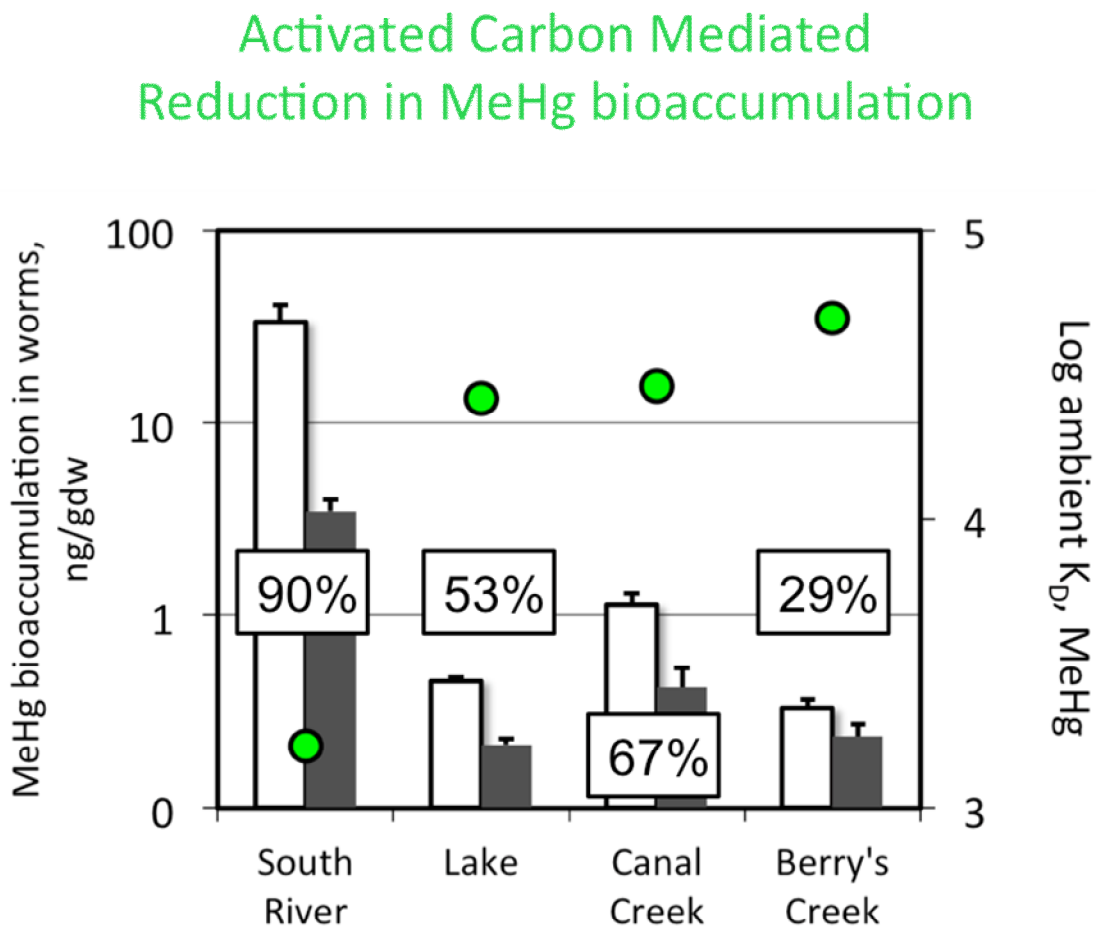
BIOACCUMULATION IN ORGANISMS



Gilmour et al. ES&T 2013

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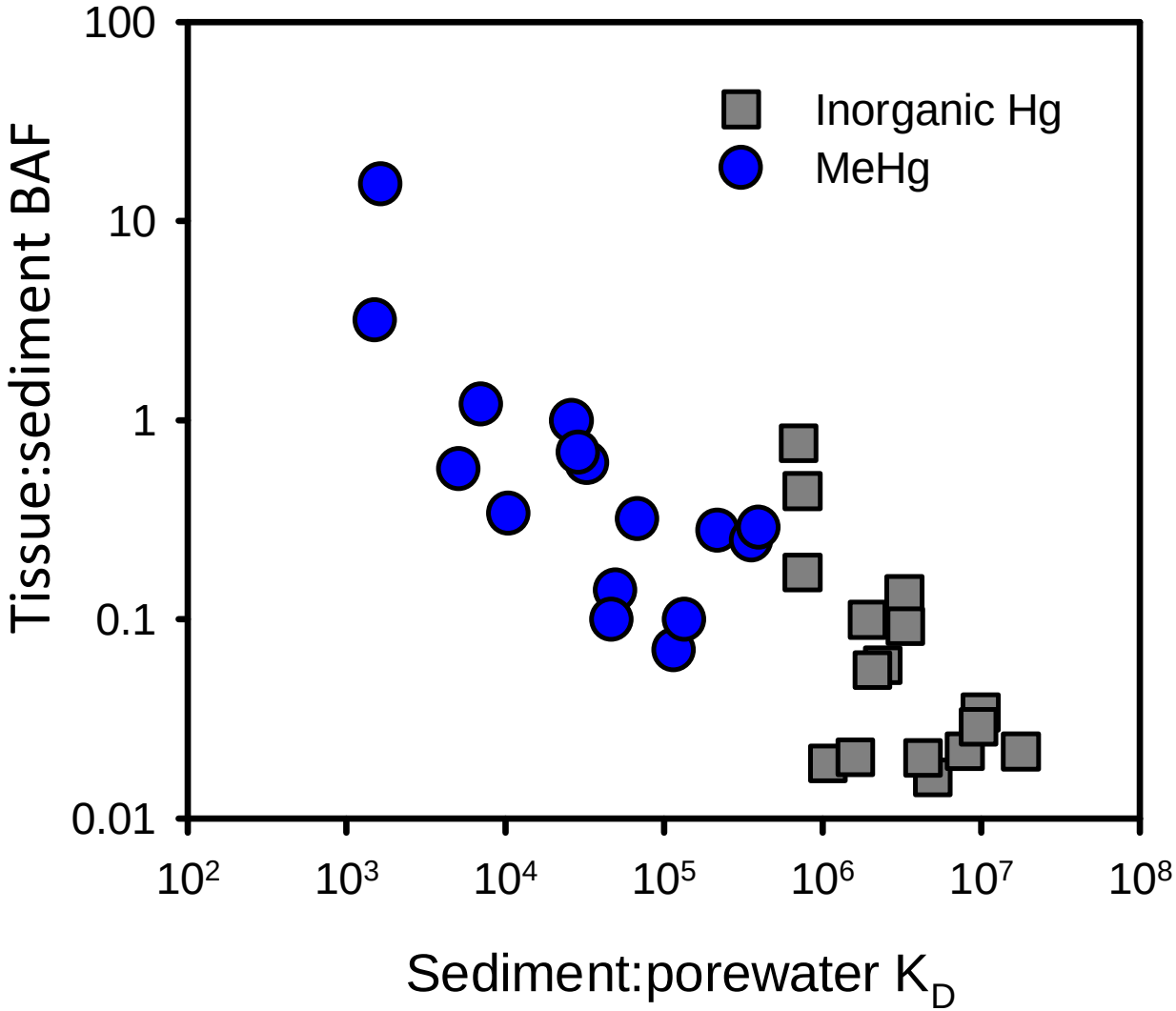
R Hg AND MeHg, ALL TREATMENTS



Bioaccumulation strongly correlated with sediment K_d

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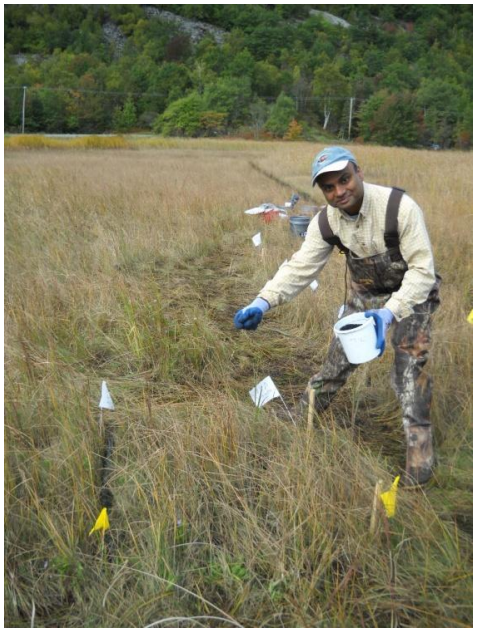
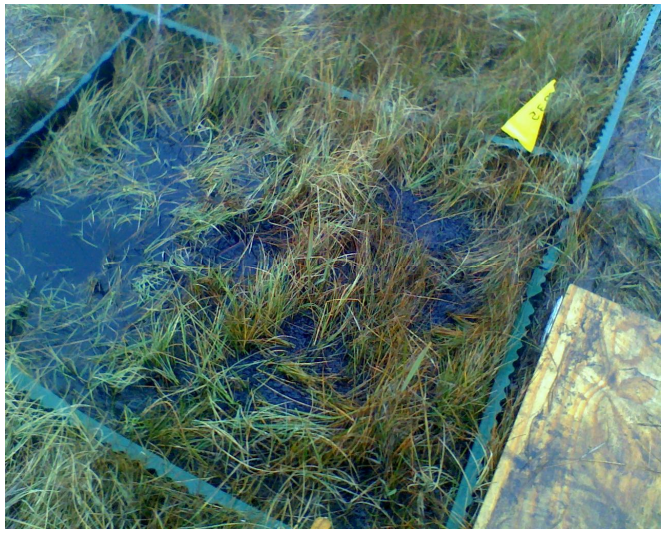
G: TIDAL MARSH IN NEW ENGLAND

- Å 3’ X 3’ plots in two parts of the marsh
- Å set up in 3 rows of 5 plots
- Å Treatments are randomized within each row
- Å 3 replicate plots per treatment

Treatments	Loading (kg/plot)	Hg (ng/gdw)
Control		
FeCl2	2.3	
Lime	0.5	<1
Biochar	1	<1
SediMite (Activated C)	2.3	4.4
Sand	2” cap	<1
Clay	2” cap	7



1 day after AC application



2 years after AC application

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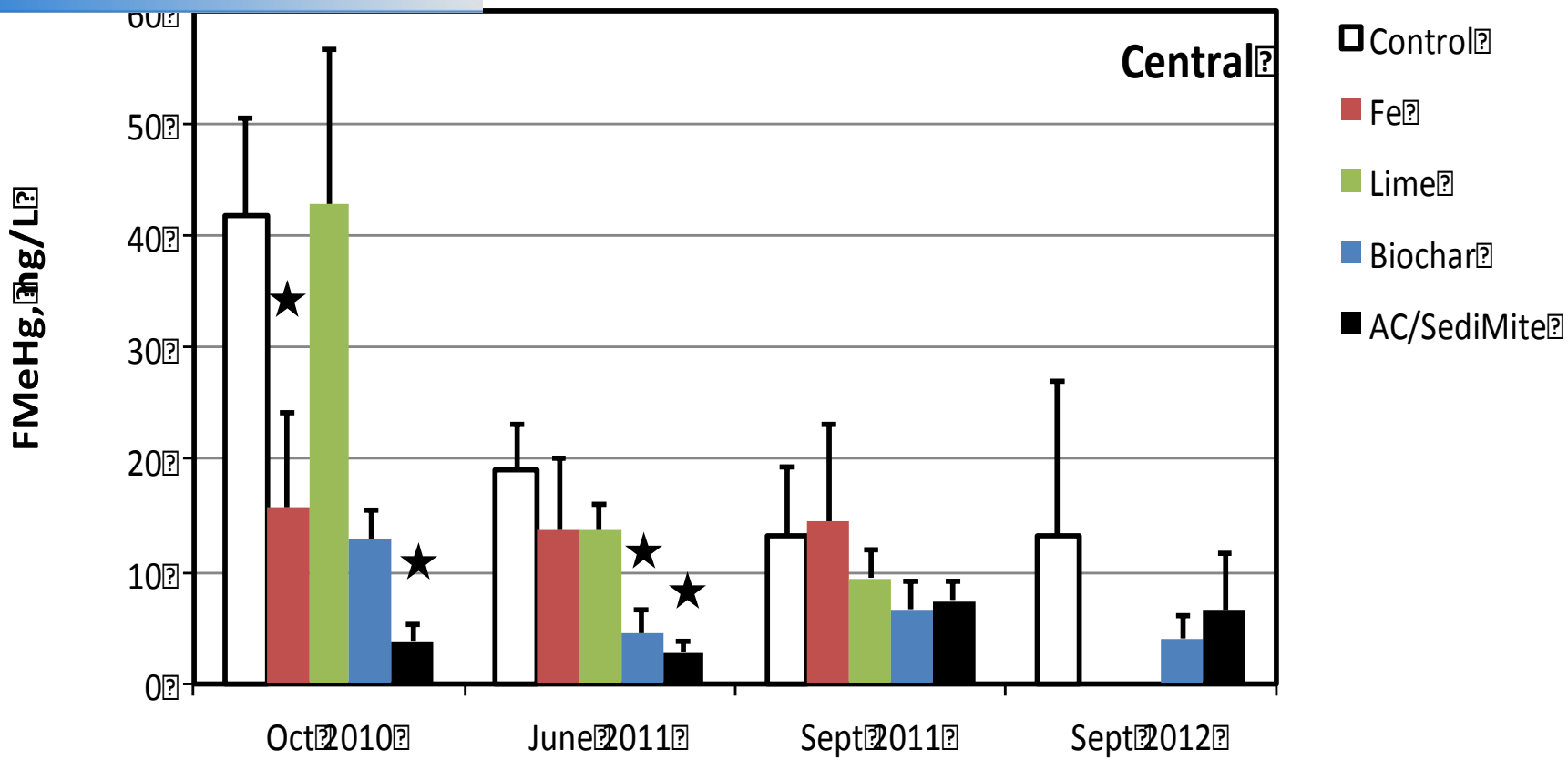
OM NEW ENGLAND TIDAL MARSH



Pore water MeHg concentrations in surface soils (0-5 cm) of amendment plots over time.

Bars are the averages ± standard deviation of values from triplicate plots for each treatment.

★

Treatments significantly different than control plots

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N IN A CONTAMINATED WETLAND IN LETIZED FORM: SEDIMITE™

Vortex Granular Systems, LLC TR Aquatic Spreader

August, 2009

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STING: PHRAGMITES MARSH

performed in Fall 2012 with ongoing monitoring

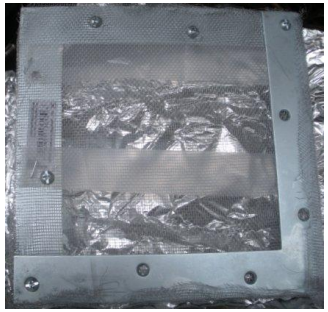
Coarse AC, Coarse AC with thin sand layer, Fine AC as SediMite pellets,

Monitoring methods

Native Orchestia

Caged Leptocheirus

Passive samplers for porewater PCBs



Sippers for porewater Hg

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PLICATION IN A PHARAGMITES MARSH

Sediments contaminated with mercury and PCBs

Pelletized AC on the marsh surface immediately after application

Phragmites grew back in the plots after 1 year

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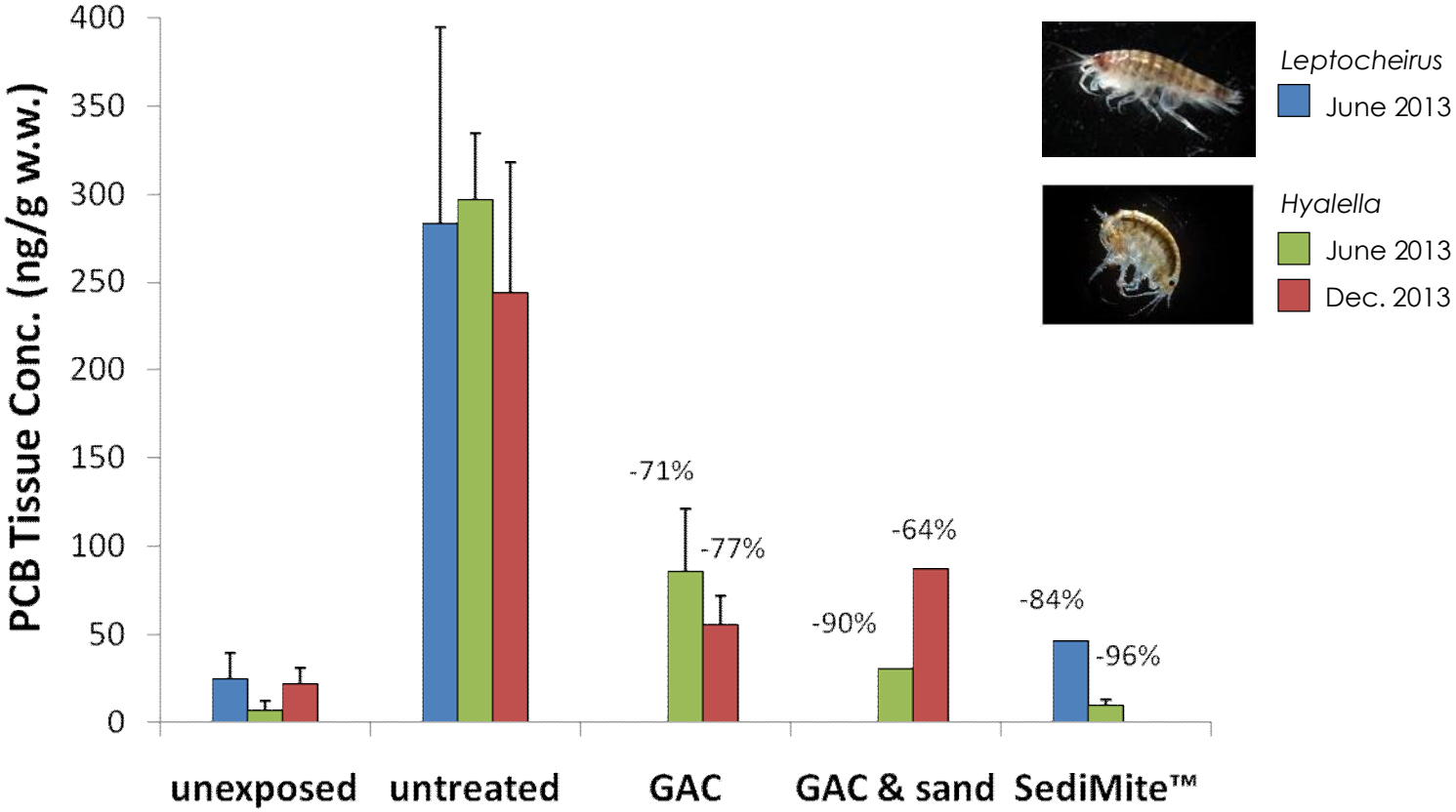
TISSUE PCBs

Bioaccumulation studies with benthic organisms



- Tissue PCB concentrations reduced after treatment
- Uptake in each plot was comparable between species and across multiple sampling events.

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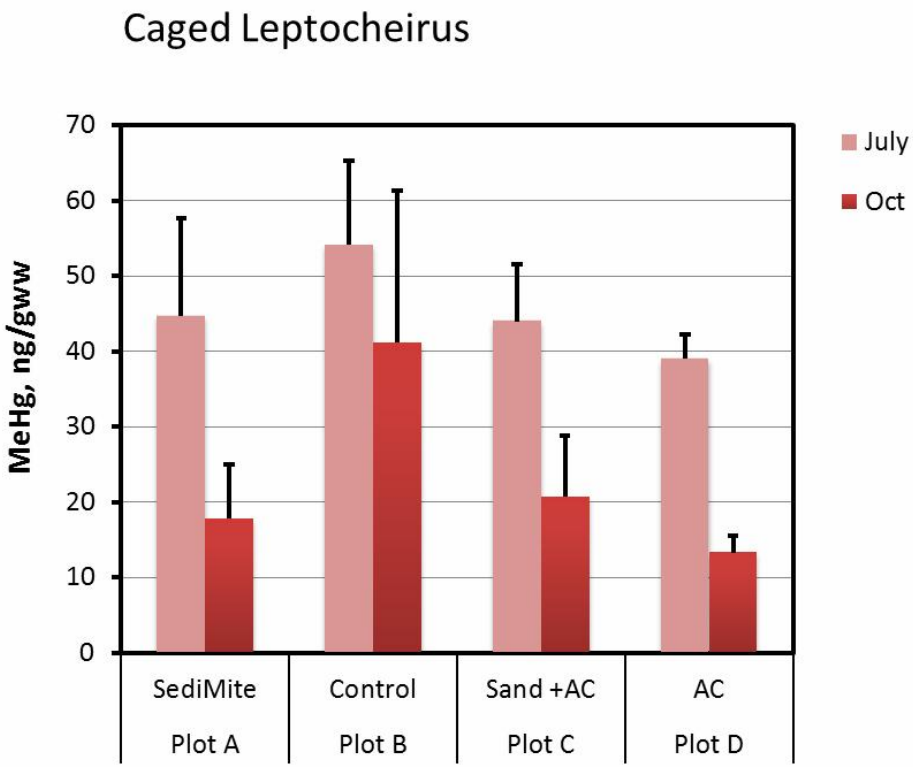
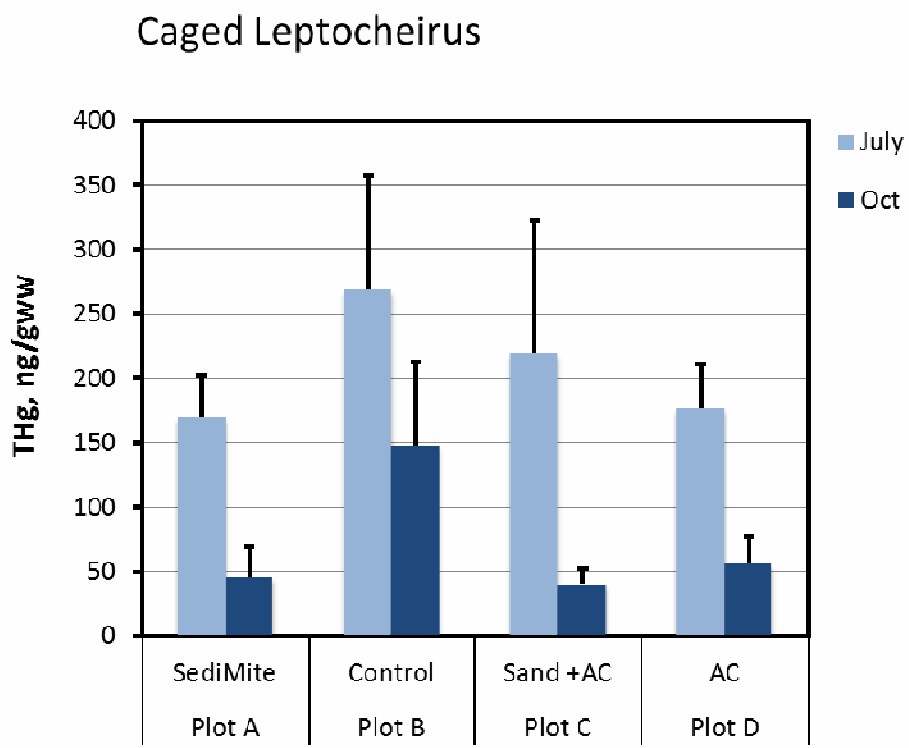
EPTOCHEIRUS MeHg/THg





- **MeHg and THg concentrations were lower in treatments than control in October**

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LICATION IN A LAKE WITH A TELE-BELT
Nov 2013

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KEY MESSAGES

- First report of Hg/MeHg isotherms at environmentally relevant ultra low concentrations for a range of ACs and biochars
- Activated carbons 2-3 orders of magnitude superior in Hg sorption compared to native sediment
- While MeHg sorption is similar for AC and biochars, the stronger binding of Hg and other organics makes ACs more suitable for most sites
- Bioaccumulation in benthic invertebrates strongly correlated with porewater Hg and MeHg
- Sediments with low native sediment:water MeHg partition coefficients were most effectively treated

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US Dept of Defense, The Dow Chemical Company, DuPont, NIH

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.