IN-SITU SORBENT AMENDMENTS: ITS NOT JUST PIXIE DUST

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USEPA NARPM Meeting

Contaminated Sediments: New Tools And Approaches For In-Situ Remediation Using Amendments

May 27, 2010

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AN HONORS UNIVERSITY IN MARYLAND

MANAGING EXPOSURE FROM HISTORIC DEPOSITS OF 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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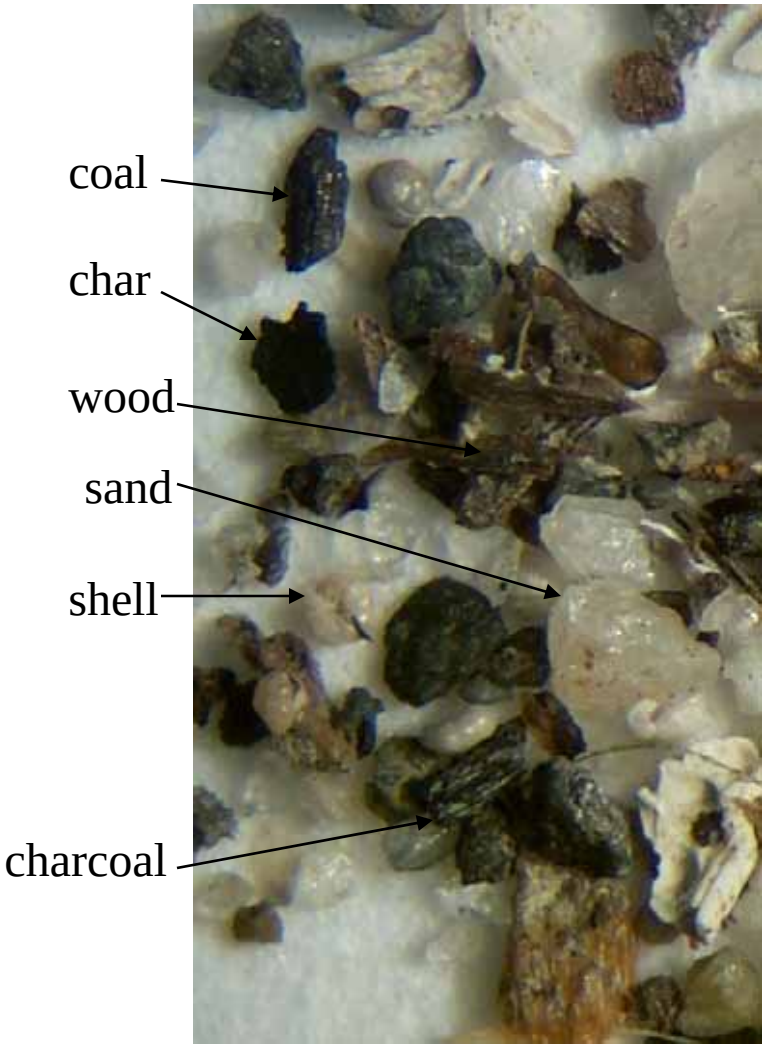
NATURE OF SEDIMENT PARTICLES



Hunters Point Sed (63-250 μm)

- Sediment contains sand, silt, clays, charcoal, wood, char, coal, & shells
- Coal petrography analyses identify carbonaceous particles
- PCBs/PAHs bound to carbonaceous particles less bioavailable

Petrography images

coal charcoal coke

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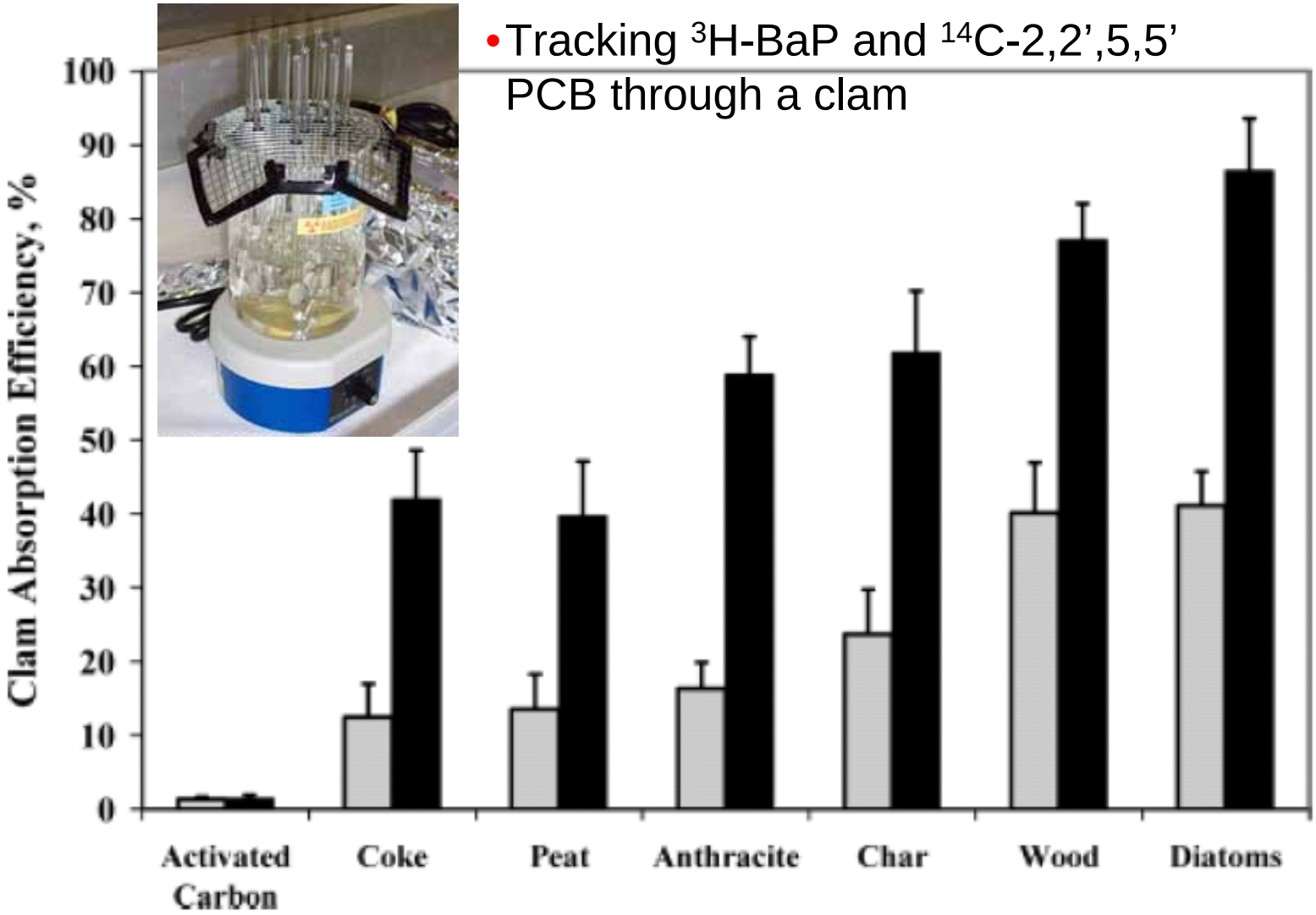
PCB ABSORPTION EFFICIENCY IN CLAM GUT

- Tracking ^{3}H-BaP and ^{14}C-2,2',5,5' PCB through a clam



From: McLeod et al. Environ. Sci. Technol. 2004

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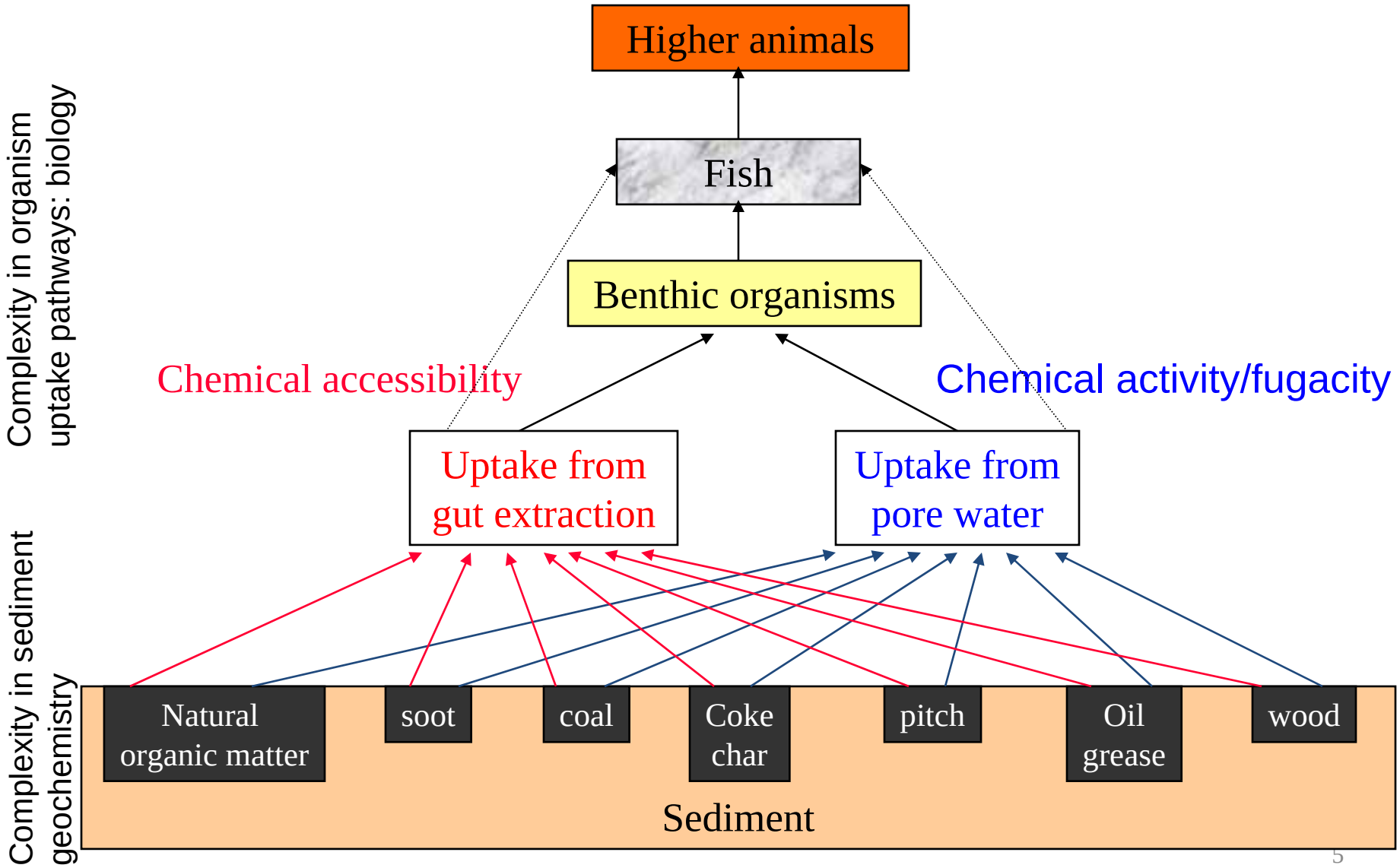
EMERGING UNDERSTANDING OF BIOAVAILABILITY



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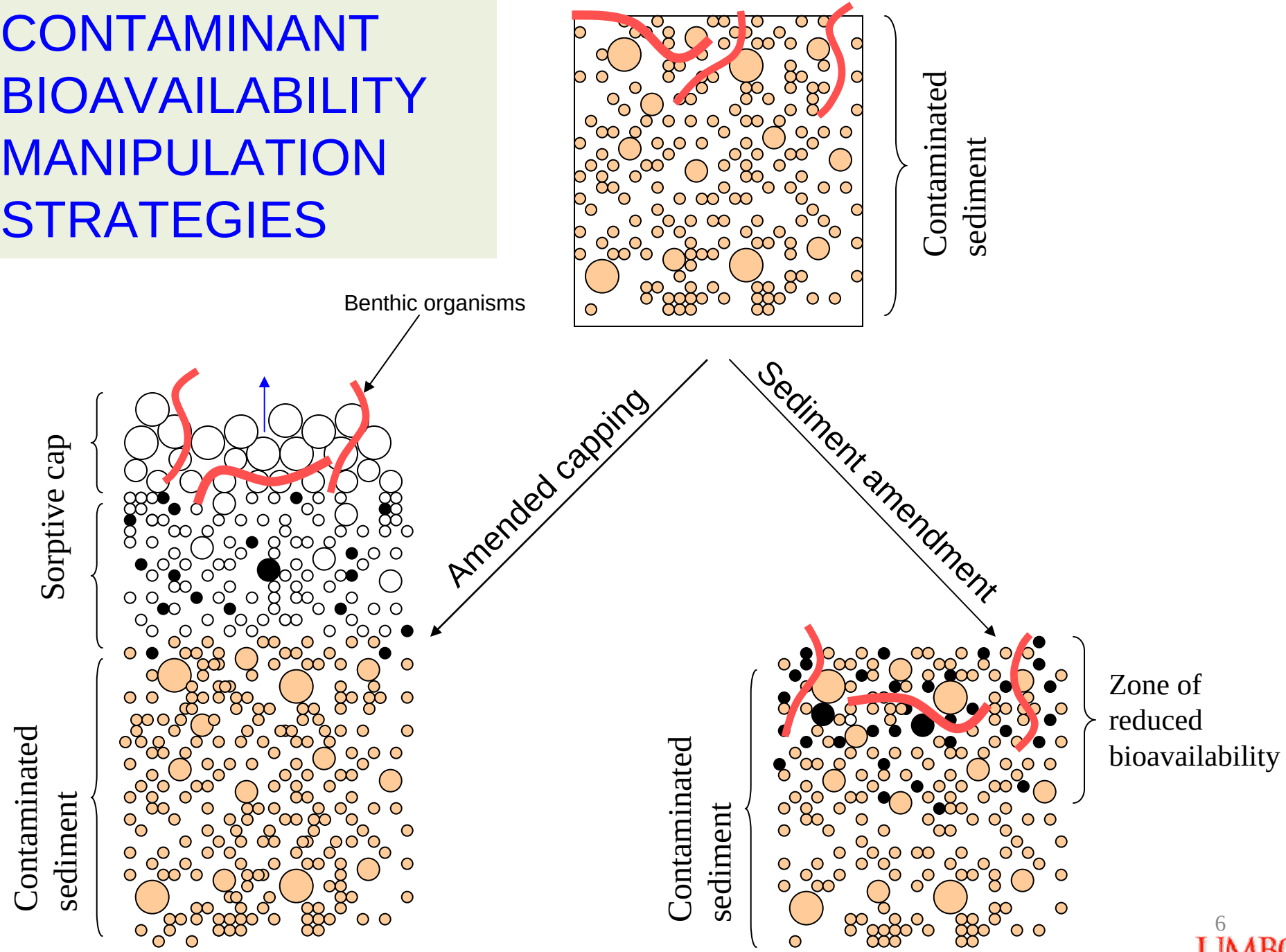
CONTAMINANT BIOAVAILABILITY MANIPULATION STRATEGIES



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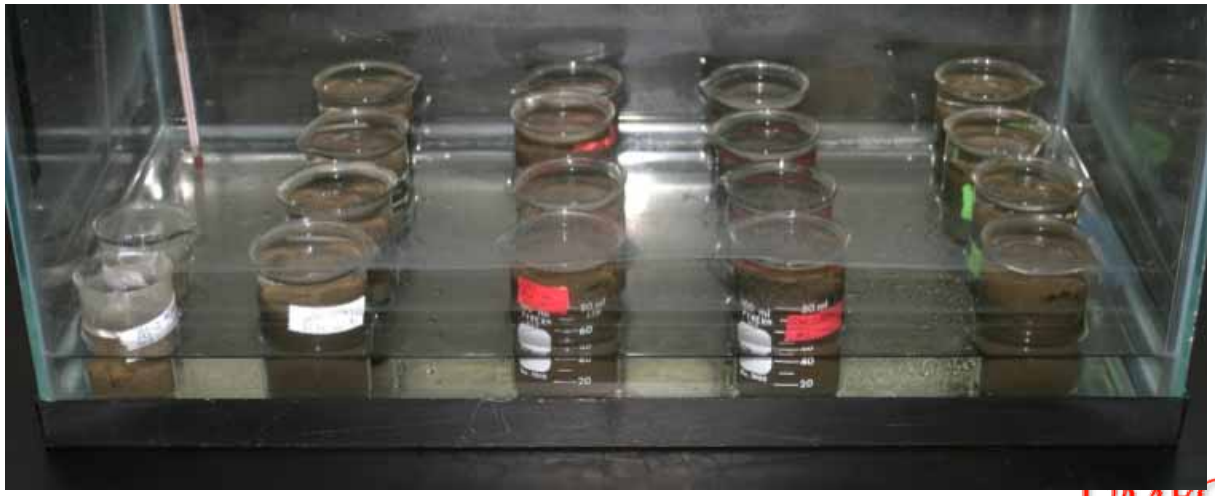
DIFFERENT MODES OF CARBON ADDITION:

- Our previous work mixed GAC into sediment for 1-6 months
- Field application will typically involve little mechanical mixing
- Need to evaluate short-term or no mixing of GAC

Different GAC application modes:

Control	:no GAC added
Mixed 2.6%	:50×200 mesh GAC ; 2 min
Layered 2.6%	:50×200 mesh GAC; no mixing
Mixed 2.6%	:80×325 mesh GAC; 2 min.
Mixed 2.6%	:50×200 mesh GAC; 1 month.

Bioaccumulation testing based on USEPA 2000 using *Lumbriculus variegatus*



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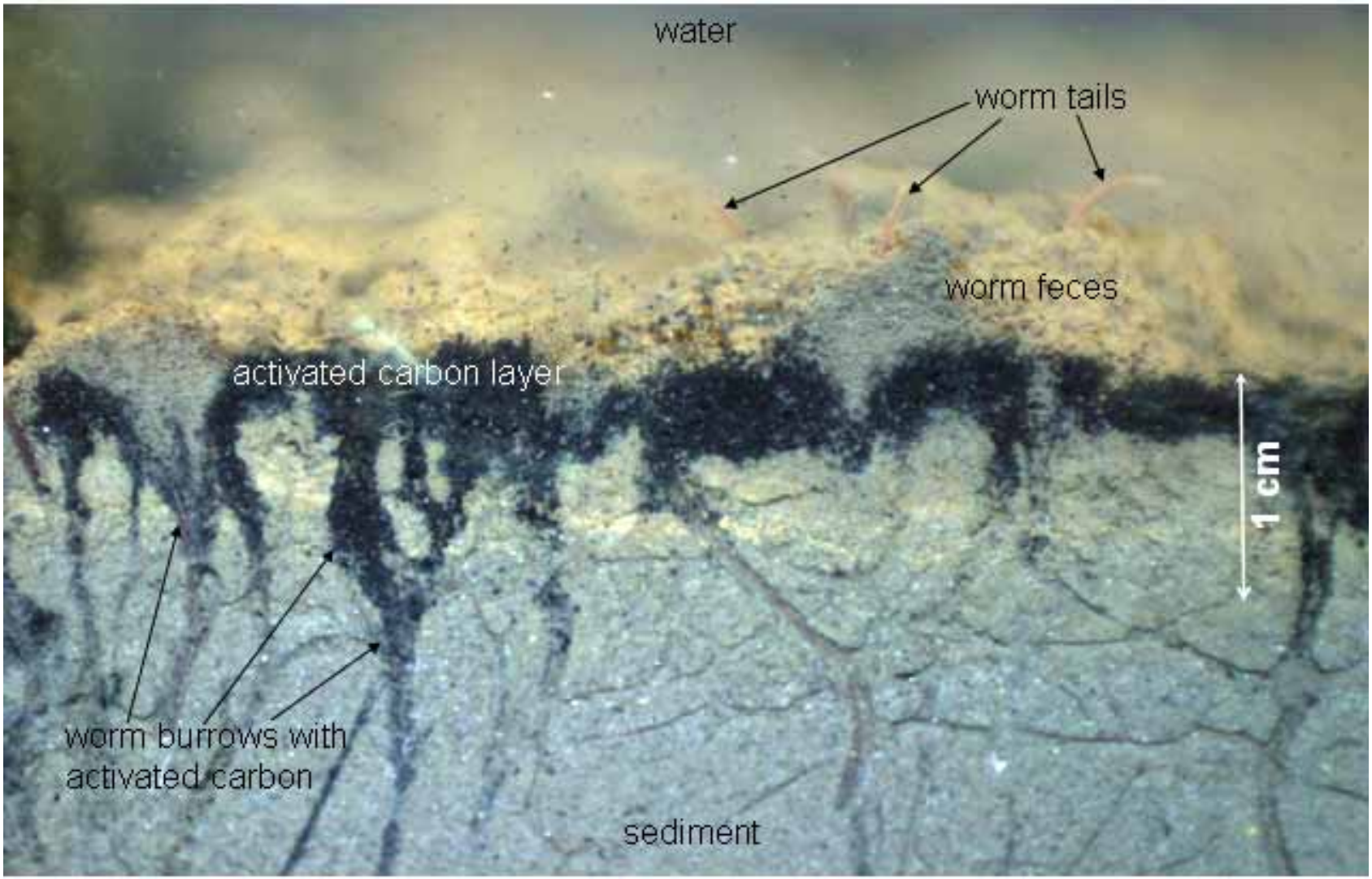
MIXING OF AC LAYER BY BIOTURBATION



-Side view of a lab microcosm 2 days after placing a layer of AC on sediment
-AC is slowly worked into the sediment through bioturbation

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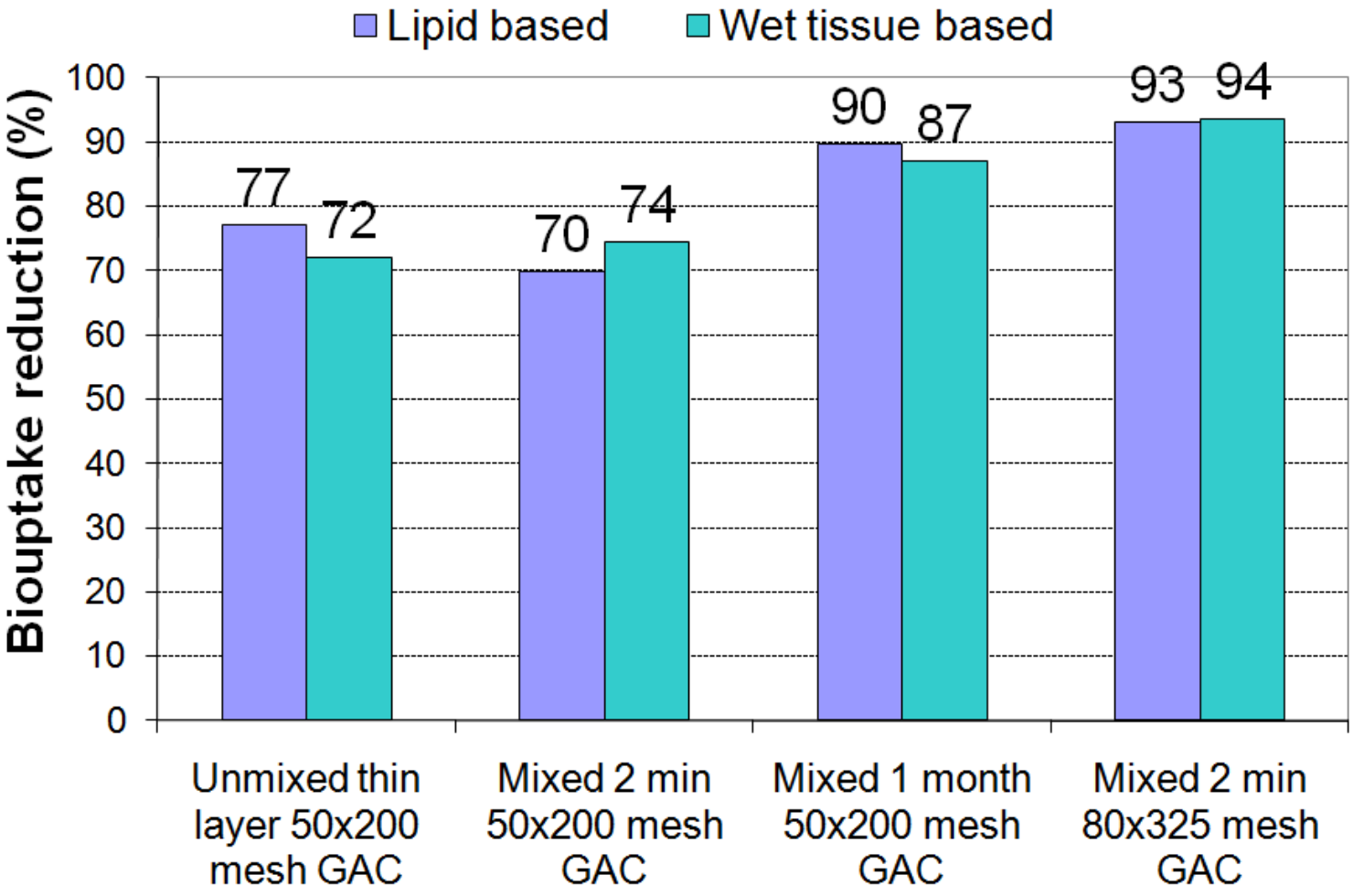
REDUCTION IN TOTAL PCB BIOUPTAKE:



- > 70% reduction in PCB biouptake after brief or no mixing of AC
- PCB biouptake reduction enhanced with AC contact time
- Finer AC works better

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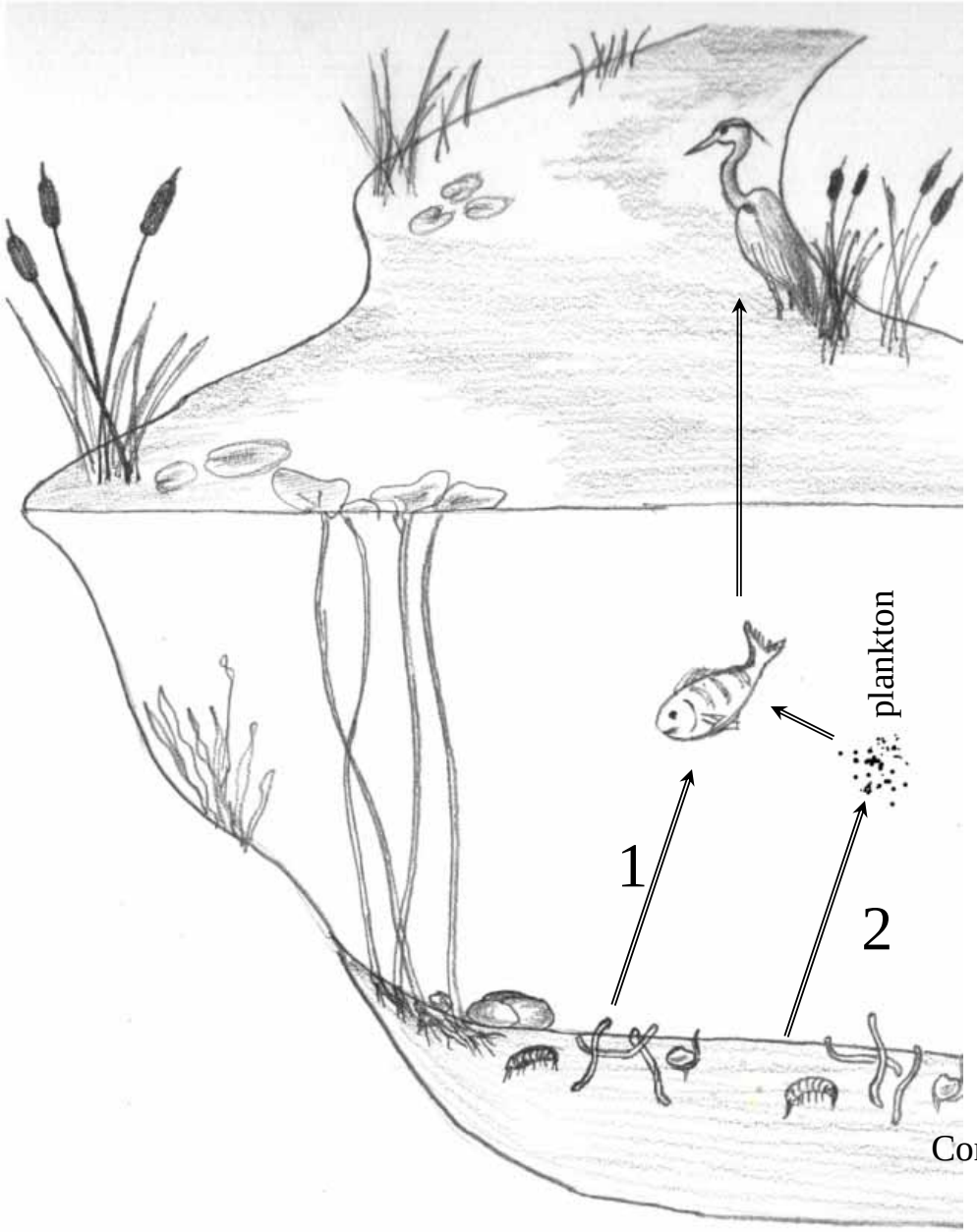
CONCEPTUAL MODEL: BEFORE TREATMENT



Legacy contaminants in exposed sediment contaminates the food chain through:

1)bioaccumulation in benthic organisms

2)flux into the water column, and uptake in the pelagic food web.

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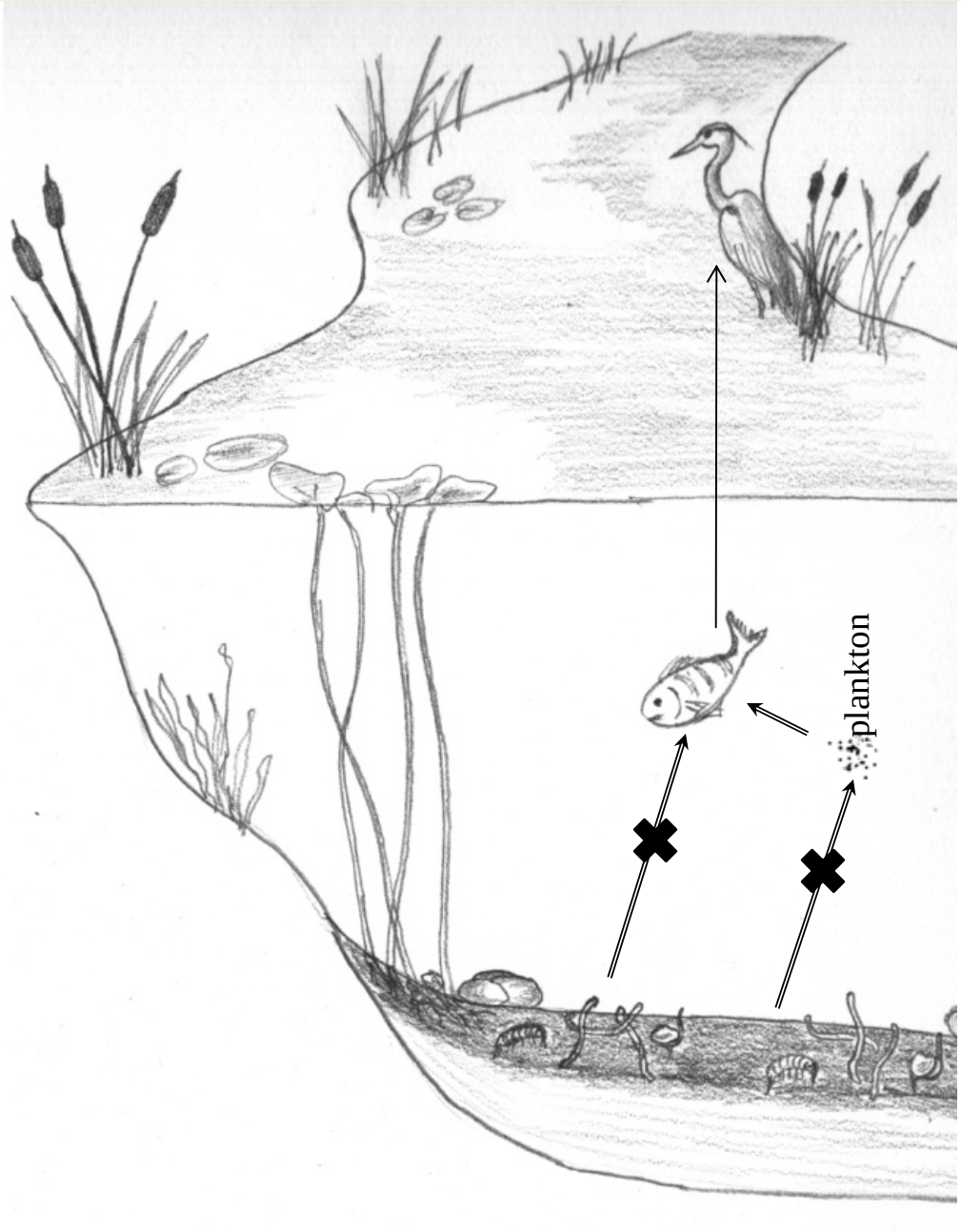
CONCEPTUAL MODEL: AFTER TREATMENT



Activated carbon amended to surficial sediments reduces contaminant exposure to food chain through:

1)Reduced bioaccumulation in benthic organisms

2)Reduced flux into water column and uptake in the pelagic food web.

1)In the long-term, the carbon amended layer is covered with clean sediment.

Layer of carbon amended sediment

Contaminated sediment

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ONGOING AC DEMONSTRATION PROJECTS

SITE LOCATION	Type of application	Funding	Application date	Contaminants	Contact
Hunters Point, CA tidal mudflat (2 trials)	AC-mixed	NAVFAC DoD-ESTCP	Aug 2004 Jan 2006	PCBs	luthy@stanford.edu
Grasse River, NY: River sediments	AC-mixed/ unmixed	Alcoa, EPA, DoD	Sep, 2006	PCBs	ughosh@umbc.edu
Trondheim Harbor, Norway: Ocean harbor	AC-slurry unmixed	Norwegian Res. Council	May, 2007	PCBs, PAHs, PBDEs, DDT	Gerard.Cornelissen@ngi.no
Aberdeen Proving Ground, MD: Tidal creek & marsh	AC as SediMite	DoD-ESTCP	June 2010	Hg, Me-Hg, PCBs, DDT	camenzie@exponent.com
US Army Installation in VA: Tidal creek & marsh	AC as SediMite	SBRP, NIH	Aug 4-5, 2009	PCBs	ughosh@umbc.edu
Frierfjord, Norway: Ocean harbor	AC-unmixed	Norwegian Res. Council	2009	Chlorobenzenes and dioxins	Gerard.Cornelissen@ngi.no

PILOT DEMONSTRATION IN GRASSE RIVER

(Participants: Alcoa, EPA, UMBC, Stanford University, Anchor Env., Brennan, Tetra Tech, Arcadis-BB&L, QEA)

Mixed Tiller (75’ x 100’)

Unmixed (50’ x 50’)

Tine Sled (50’ x 60’)

Initial testing area (50’ x 100’)

- L-shaped silt screen to minimize suspended particle transport
- Equipment mobilized on barges
- Target dose of activated carbon = 0.5x TOC in surficial sediments (+50% safety factor)
- No measurable change in water-column PCBs downstream
- Post-treatment monitoring for 2-3 years

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DELIVERY DEVICES USED AT GRASSE RIVER, NY

Tine injection system
Designed and built by Brennan with inputs from collaborators

Injection and mixing in an enclosed rototiller
Designed and built by Brennan with inputs from collaborators

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GRASSE RIVER ACTIVATED CARBON PILOT BASELINE AND LONG-TERM MONITORING

Parameter	Baseline (Aug/Sep '06)	After Placement (Oct '06)	Year 1 (Fall '07)	Year 2 (Fall '08)	Year 3 (Fall '09)
Black carbon in sediment cores	√	√	√	√	√
Field PCB biouptake	√		√	√	√
Lab PCB biouptake	√		√	√	√
Equilibrium	√		√	√	√
Desorption	√		√	√	
Benthic community	√		√	√	√
Erosion potential	√		√	√	
Impact of AC on aquatic plant growth					√

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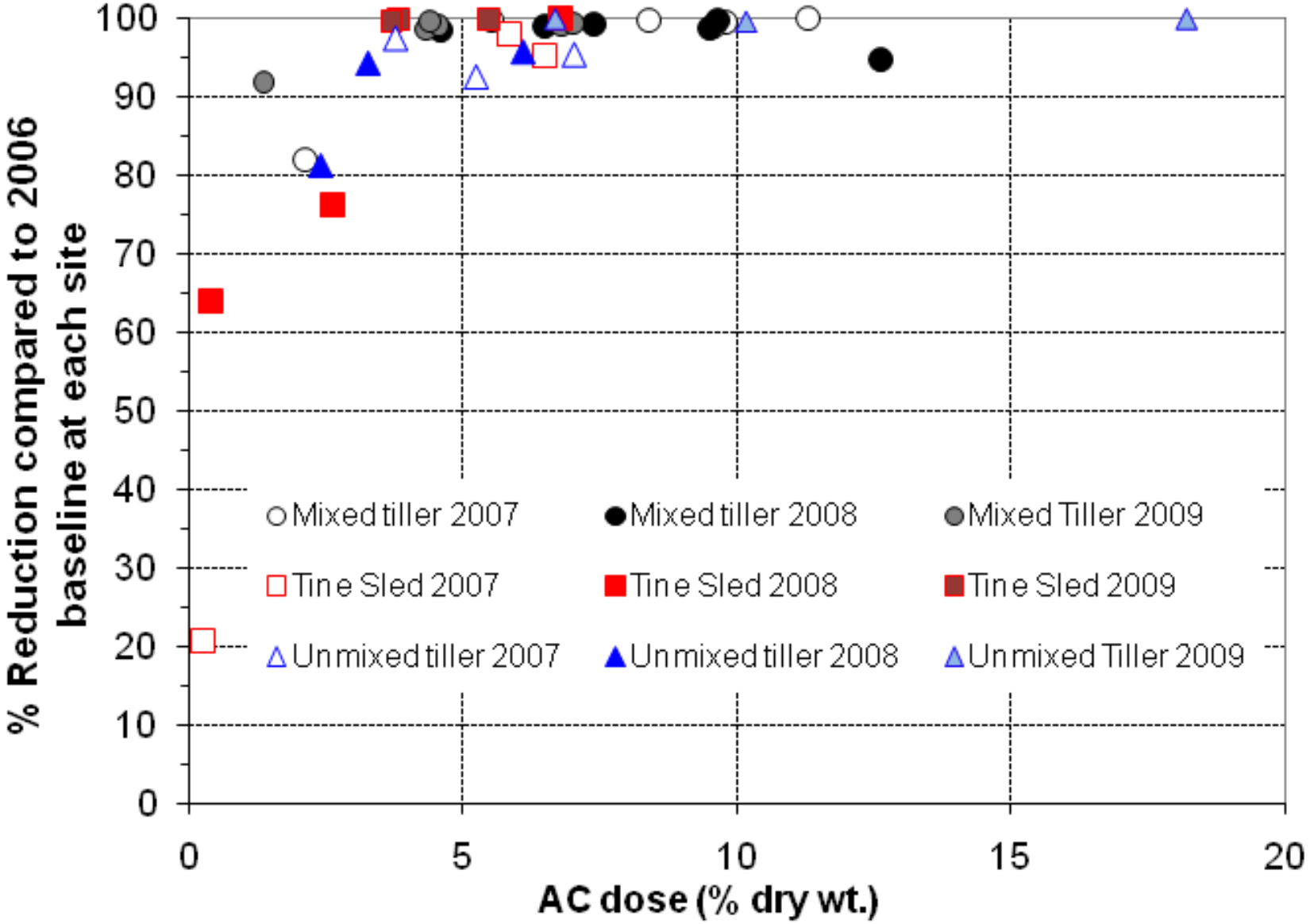
AQUEOUS EQUILIBRIUM REDUCTION VS. AC DOSE



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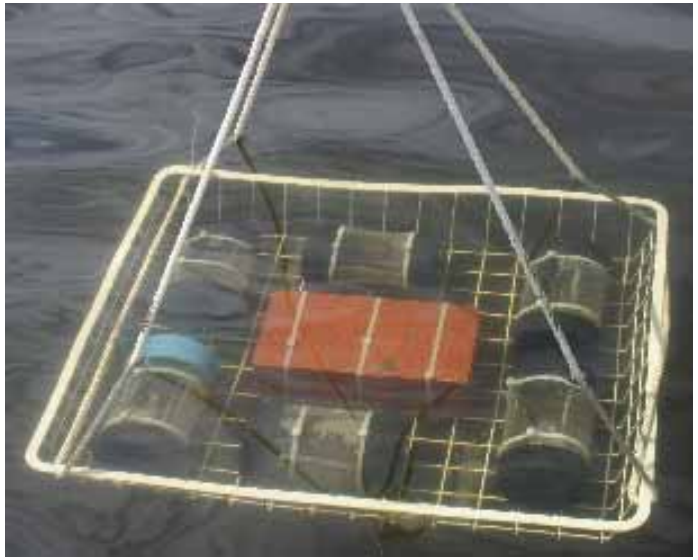
IN-SITU PCB MONITORING STUDIES



In-river deployment of field exposure cages with *L. variegatus* for baseline study using a modified ASTM draft method (Burton et al. 2005)

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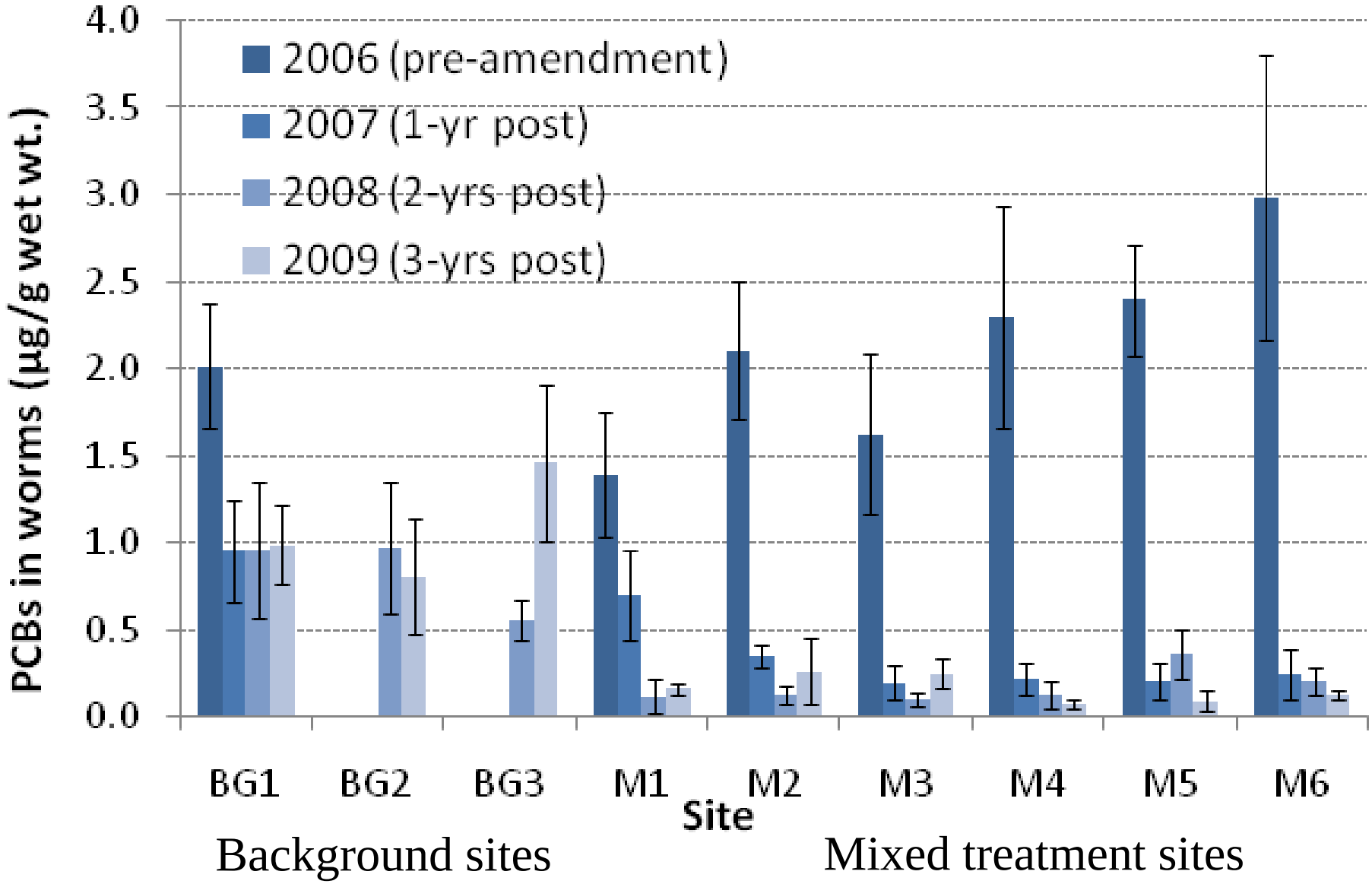
PCB BIOUPTAKE IN-SITU



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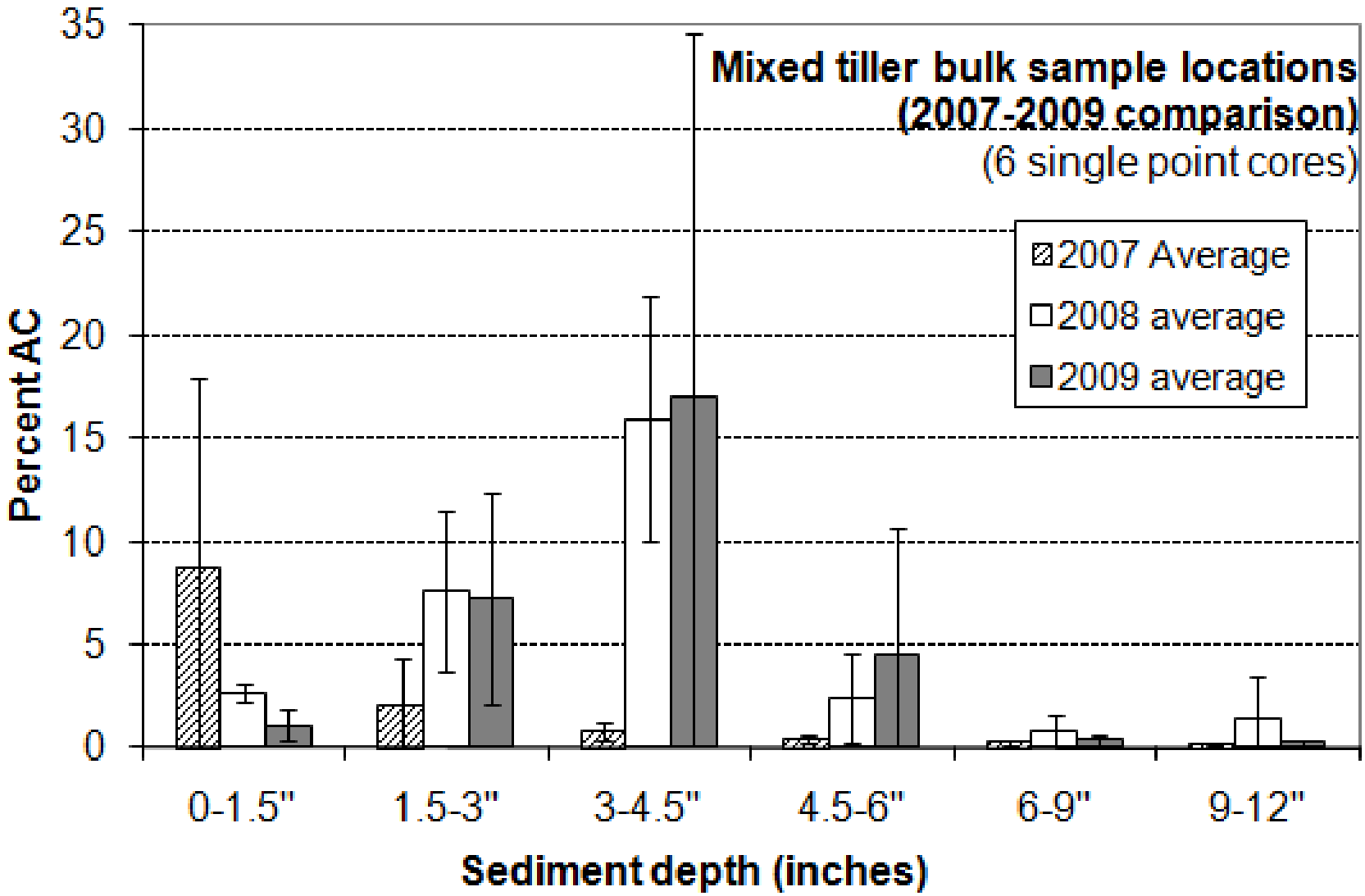
CARBON PROFILE WITH TIME



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KEY LEARNINGS FROM PILOT-SCALE STUDIES:

1. AC can be applied to sediment in a large scale
2. AC remains in place 3 years after placement
3. Reductions in porewater PCB levels
4. Reductions in tissue PCB levels
5. Over time, the AC-amended sediment is covered with new sediment deposit

THE BIG PICTURE:

5% AC by dry wt in top 4” = 6 lb/sq. ya. = **30,000 lb/acre**
(equivalent to a mass deposition rate for 2 mm/yr sedimentation)

100 acre site: 3M lb of AC (<1% of US annual production of AC)

Material cost at $1/lb cost of AC = **$30,000/acre**
Application cost will depend on the method utilized

Promising considerations:

•Application of small increments over multiple years to incorporate into annually deposited sediments

•Use of activated biochars from agricultural residue can provide additional opportunity for carbon sequestration

•Low-impact delivery methods

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LIST OF PUBLICATIONS ON IN-SITU AMENDMENTS

1. Bioaccumulation of polychlorinated dibenzo-p-dioxins/dibenzofurans in *E. foetida* from floodplain soils and the effect of activated carbon amendment. Sonja K. Fagervold, Yunzhou Chai, John W. Davis, Michael Wilken, and Upal Ghosh. In press, ***Environ. Sci. Technol***. 2010.
2. Evaluation of sorbent amendments for in situ remediation of metal contaminated sediments. Seokjoon Kwon, Jeff Thomas, Brian E. Reed, Laura Levine, Victor S. Magar, and Upal Ghosh. In press, ***Environ. Toxicol. Chem***., 2010.
3. Quantification of activated carbon contents in soils and sediments using chemothermal and wet oxidation methods. Braendli, Rahel; Bergsli, Anders; Ghosh, Upal; Hartnik, Thomas; Breedveld, Gijsbert; Cornelissen, Gerard. ***Environmental Pollution.*** 157, 3465-3470, 2009.
4. Field application of activated carbon amendment for in-situ stabilization of polychlorinated biphenyls in marine sediment. Cho, Y., Ghosh, U., Kennedy, A. J., Grossman, A., Ray, G.; Tomaszewski, J. E., Smithenry, D., Bridges, T. S., Luthy, R. G. ***Environ. Sci. Technol***. 43, 3815-3823, 2009.
5. Modeling PCB Mass Transfer and Bioaccumulation in a Freshwater Oligochaete before and after Amendment of Sediment with Activated Carbon. Sun, X.; Werner, D.; Ghosh, U. ***Environ. Sci. Technol***., 43, 1115-1121, 2009.
6. Measurement of Activated Carbon and Other Black Carbons in Sediments. Adam Grossman, and Upal Ghosh. ***Chemosphere,*** 75, 469-475, 2009.
7. The effect of activated carbon on partitioning, desorption, and biouptake of native PCBs in four freshwater sediments. X. Sun and U. Ghosh. ***Environ. Toxicol. Chem***. 27, 2287-2295. 2008.
8. The Stability of Marine Sediments at a Tidal Basin in San Francisco Bay Amended with Activated Carbon for the Sequestration of Organic Contaminants. John R. Zimmerman, Philip J. Dacunto, Jeremy D. Bricker, Craig Jones, Robert L. Street, and Richard G. Luthy. ***Water Research***; 42(15) pp 4133-4145; 2008.
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10. PCB Bioavailability Control in *Lumbriculus variegatus* Through Different Modes of Activated Carbon Addition to Sediments. X. Sun and U. Ghosh. ***Environ. Sci. Technol***. 41, 4774-4780, 2007.
11. Activated Carbon Amendment as a Treatment for Residual DDT in Sediment from a Superfund Site in San Francisco Bay, Richmond, California, USA, Jeanne Tomaszewski and Richard G. Luthy, ***Environmental Toxicology & Chemistry***, vol. 26, pp 2143-2150, 2007.
12. Field methods for amending marine sediment with activated carbon and assessing treatment effectiveness. Y-M. Cho, D.W. Smithenry, U. Ghosh, A.J. Kennedy, R.N. Milward, T.S. Bridges, R.G. Luthy. ***Marine Environment Research***. 64, 541–555, 2007.
13. Biological Uptake of Polychlorinated Biphenyls by Macoma balthica from Sediment Amended with Activated Carbon, Pamela B. McLeod, Martine J. van den Heuvel-Greve, Samuel N. Luoma, and Richard G. Luthy, **Environmental Toxicology &** ***Chemistry***, vol. 26, no. 5 pp. 980-987, 2007.
14. Modeling Polychlorinated Biphenyl Mass Transfer after Amendment of Contaminated Sediment with Activated Carbon. D. Werner, U. Ghosh, and R. G. Luthy. ***Environ. Sci. Technol***. 40, 4211-4218. 2006.
15. Addition of Activated Carbon to Sediments to Reduce PCB Bioaccumulation by a Polychaete (Neanthes arenaceodentata) and an Amphipod (Leptocheirus plumulosus). R.N. Millward, T.S. Bridges, U. Ghosh, J.R. Zimmerman, R.G. Luthy. ***Environ Sci. Technol***. 39, 2880-2887, 2005.
16. The Effects of Dose and Particle Size on Activated Carbon Treatment to Sequester Polychlorinated Biphenyls and Polycyclic Aromatic Hydrocarbons in Marine Sediments. J.R. Zimmerman, D. Werner, U. Ghosh, R.N. Millward, T.S. Bridges, R.G. Luthy. ***Environ. Toxicol. Chem***. 24, 1594-1601, 2005.
17. Response to comment on: "Addition of carbon sorbents to reduce PCB and PAH bioavailability in marine sediments. Physicochemical tests. J.R. Zimmerman, U. Ghosh, R.G. Luthy, R.N. Millward, T.S. Bridges. J.R. Zimmerman, U. Ghosh, R.G. Luthy, R.N. Millward, T.S. Bridges. ***Environ Sci. & Technol***, 39, 1199-1200, 2005.
18. The Sequestration of PCBs in Lake Hartwell Sediment with Activated Carbon, David Werner, Christopher P. Higgins, and Richard G. Luthy, ***Water Research***, vol. 39, pp. 2105-2113, 2005.
19. Effects of Particulate Carbonaceous Matter on the Bioavailability of Benzo[a]pyrene and 2,2',5,5' Tetrachlorobiphenyl to the Clam, Macoma balthica. McLeod, P.M., M.J. van den Heuvel-Greve, R.M. Allen-King, S.N. Luoma, and R.G. Luthy,. ***Environ. Sci. & Technol***., vol. 38(17), pp. 4549-4556. 2004
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ACKNOWLEDGEMENTS

UMBC Graduate Students and post docs:

Barbara Beckingham; Adam Grossman; Jennifer Jerschied, Seokjoon Kwon, Xueli Sun

Current and Past Collaborators:

G. Cornelissen, D. Werner; C.A. Menzie; Cindy Gillmour; R.G. Luthy; T.S. Bridges, K. Sowers, J. E. Baker

Sponsors:

National Institutes of Health, Superfund Research Program; DoD SERDP/ESTCP Programs; USEPA GLNPO; Alcoa, USEPA SBIR program;

Ghosh research group at UMBC

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