

Welcome to the CLU-IN Internet Seminar

Contaminated Sediments: New Tools and Approaches for in-situ Remediation - Session III

Sponsored by: National Institute of Environmental Health Sciences, Superfund Research Program

January 19, 2011, 2:00 PM - 4:00 PM, EST (19:00-21:00 GMT)

Instructors:

Dr. Richard G. Luthy, Silas H. Palmer Professor, Department of Civil and Environmental Engineering, Stanford University (luthy@stanford.edu)

Dr. Charles A. Menzie, Principal Scientist & Practice Director, Exponent (camenzie@exponent.com)

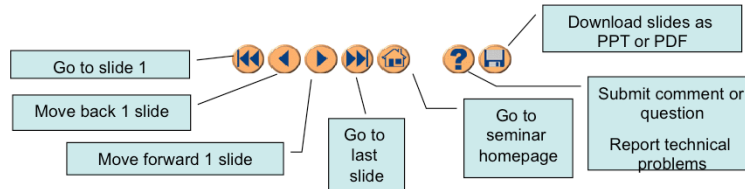
Moderator:

Linda Fiedler, Environmental Engineer, U.S. EPA Office of Superfund Remediation and Technology Innovation (fiedler.linda@epa.gov)

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Housekeeping

- Please mute your phone lines, Do NOT put this call on hold
- Q&A
- Turn off any pop-up blockers
- Move through slides using # links on left or buttons



- This event is being recorded
- Archives accessed for free <http://clu.in.org/live/archive/>

□

In-place Management of Sediment Contaminants: Advances in Modeling Performance, Assessing Bio-uptake, and Designing New Sorbents

Richard G. Luthy

Yeo-Myoung Cho, Elisabeth M.-L. Janssen, Eun-Ah Kim

Stanford University

SRP Web Seminar
January 19, 2011

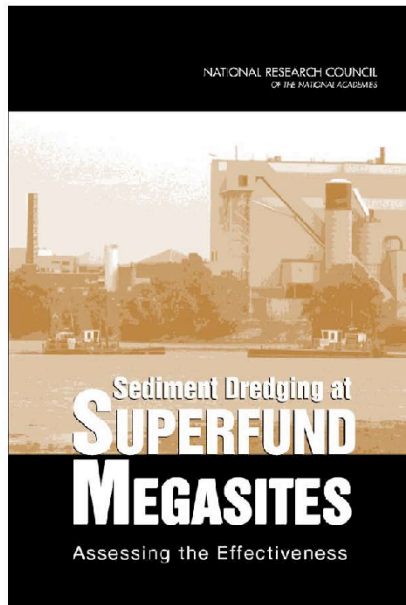


OVERVIEW

- Background
- HOC Mass Transfer Modeling Framework
- Biological Assessment
- Designing New Sorbent
- Conclusion & Acknowledgements



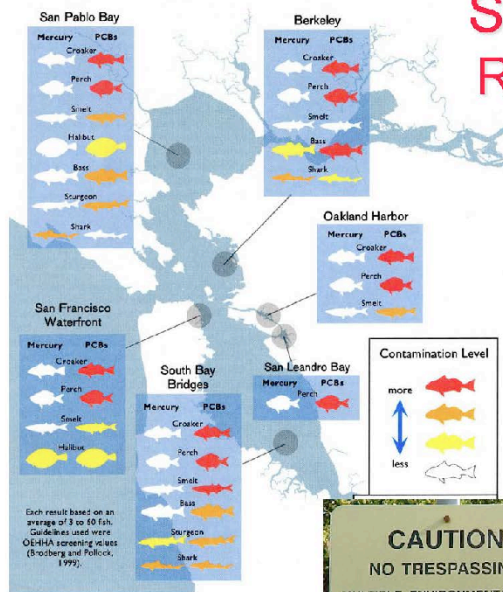
NRC Report on Sediment Dredging



- National Research Council report on sediment dredging
- Greater awareness of factors limiting success
- 26 case studies
- Need for new approaches

National Academies Press, 2007

Fish Contamination 2000—PCBs and Mercury



Superfund process:
RAO→RG→CUL→OG



San Francisco Estuary Inst.

Shoal Point Bayou,
 Panama City, FL
 6



Case studies:

- Bayou Bonfouca, LA
- Black River, OH
- Commencement Bay [Hylebos & Sitcum], WA
- Christina River, DE
- Cumberland Bay, NY
- Duwamish Diagonal, WA
- Fox River [three sites], WI
- GM, St. Lawrence River, NY
- Grand Calumet River, IN
- Grasse River, NY
- Harbor Island [Todd & Lockhead], WA
- Ketchikan [Ward Cove], AK
- Lake Jarnson, Sweden
- Lavaca Bay, TX
- Manistique Harbor, MI

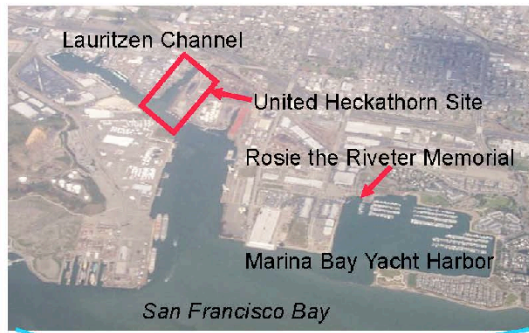


- Marathon Battery, Hud. R., NY
- New Bedford Harbor, MA
- Newport Naval Complex, RI
- Waukegan Harbor, IL
- Puget Sound Nav. Shyd., WA
- Reynolds, St. Law. R., NY
- Lauritzen Chnl., Richmond, CA

Commencement Bay, Tacoma, WA

Hylebos - 'industrial upland' channel cut into delta, closed waterway, 167 acres, three miles, varied industries. Ideal conditions for dredging success.



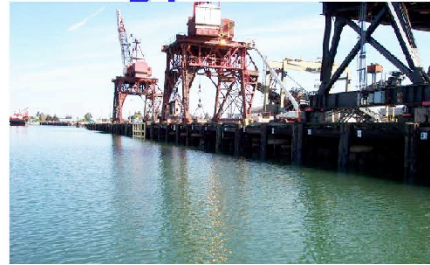


Tomaszewski, Werner & Luthy,
Env. Tox. Chem., p.2143, 2007

Lauritzen Channel

... inadequate
conceptual site
model

... lack of agreement
among parties



Post-dredging water: 100 ng/L

Goal: 0.59 ng/L

Sediment: 0.1-1000 mg/kg

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Sediment Dredging at Superfund Megsites: Assessing the Effectiveness

Dredging is one of the few options available to attempt to clean up contaminated sediments in rivers, harbors and lakes. However, based on available evidence, dredging's ability to decrease environmental and health risks is still an open question. Technical constraints, like underwater obstacles, can prevent dredging equipment from accessing sediments and dredging can uncover and re-suspend buried contaminants, exposing wildlife and people to toxicants. Evaluating the potential long-term benefits of dredging will require that the U.S. Environmental Protection Agency step up monitoring activities before, during and after individual cleanups to determine whether it is working there and what combinations of techniques are most effective.

Some of the nation's estuaries, lakes and other water bodies contain contaminated sediments that adversely affect fish and wildlife, which may then find their way into people's diets and carry negative health impacts. At least 14 states contain large contaminated sediment megasites, which are expected to cost over \$50 million to clean up, that are particularly challenging to remediate. Private companies are responsible for the cleanup at some sites and the U.S. Environmental Protection Agency (EPA) takes the lead in managing remediation at others.

At the request of Congress, EPA asked the National Research Council (NRC) to address the

technical challenges posed by the need to reduce risks at sediment megasites by forming a committee to evaluate dredging as a cleanup technique.

Clean Up Options at Superfund Megasites

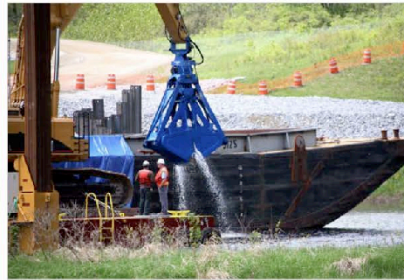
The EPA Superfund program was established more than 25 years ago to address sites contaminated with hazardous chemicals. The program relies on surveys and scientific sampling of sediments under

water bodies to assess the extent of the contamination and to explore ways of cleaning it up.

Cleanup techniques range from removing the sediments by using a dredge or large under-



Acushnet River, 2010



Hudson River, 2009 10



More tools in the tool box ...

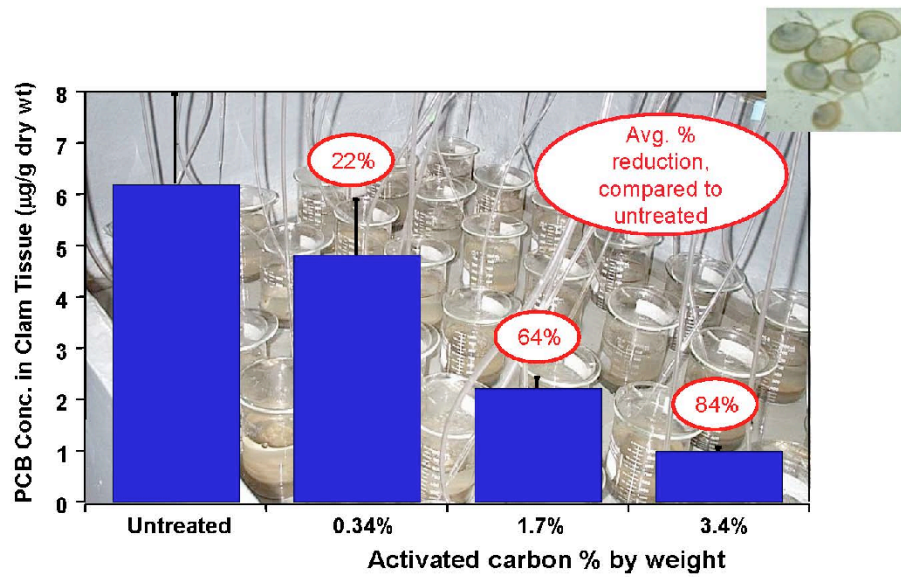


If: on-going sources are eliminated & freshly deposited sediments are clean,

Then: AC amendment can reduce exposures to water and biota from contaminants within the sediment



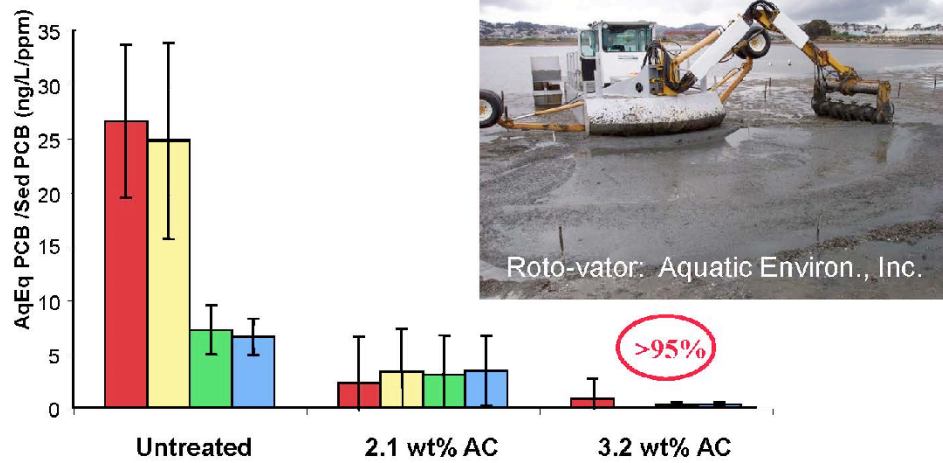
Proof of Concept: Lab Biouptake



McLeod et al., *Environ. Tox. Chem.*, 26:980, 2007 12



Proof of Concept: Field Trial



Aqueous equilibrium shows a dose-response relation
– the sorption capacity of the AC is retained over 18 months

Cho et al., *Env. Sci. & Technol.* 43:3815, 2009 ¹³



Predictive Models

- **Sediment and amendment stability** Zimmerman et al., *Water Research* 42:4135, 2008
- **Biouptake**



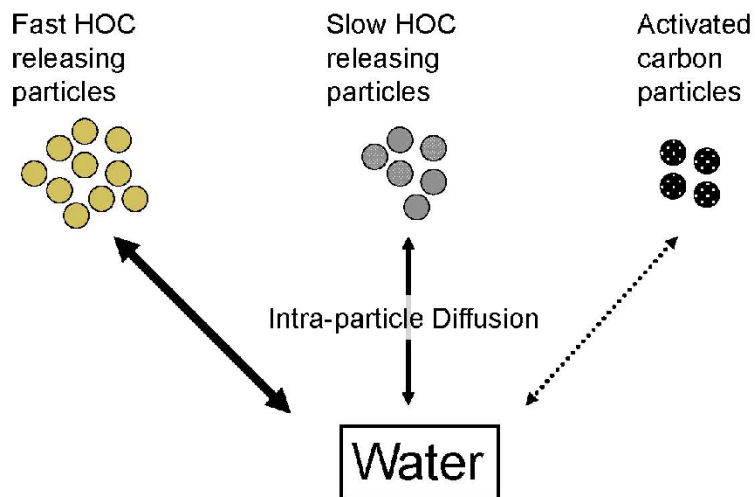
Janssen et al., *Environ. Sci. & Technol.* 44:2857, 2010



- **Geochemical HOC mass transfer**



Geochemical HOC Mass Transfer

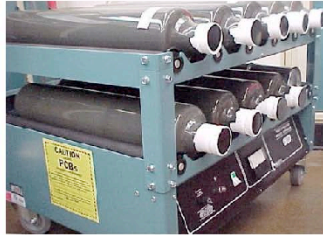


Release from sediment particles into sediment pore water is slow.
Also, up-take by AC is slow for highly hydrophobic compounds.

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Slow Mass Transfer in the Field



Laboratory:
continuous AC-sediment mixing
on a roller for 1 month

Werner, Ghosh & Luthy, *ES&T*, 2006
Hale, Tomaszewski, Luthy, Werner, *Water Res.*, 2009
Hale & Werner, *ES&T*, 2010.

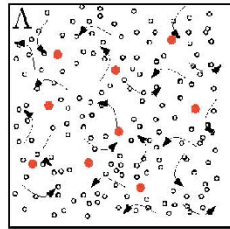


**Field: one time mixing event
less than 30 min
large mixing devices**





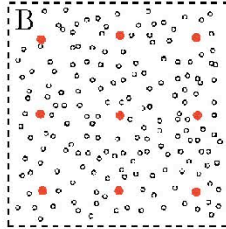
Lab vs. Field Conditions



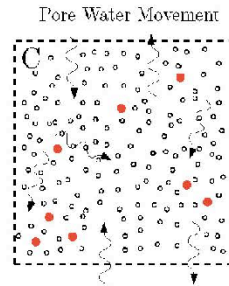
(A) Complete &
Continuous Mixing

Laboratory

- AC particle
- Sediment Particle



(B) Un-mixed
1) Molecular
diffusion only
2) Homogeneous
AC Distribution



(C) Un-mixed
**1) Advective pore water
movement**
**2) Heterogeneous AC
Distribution**

Field



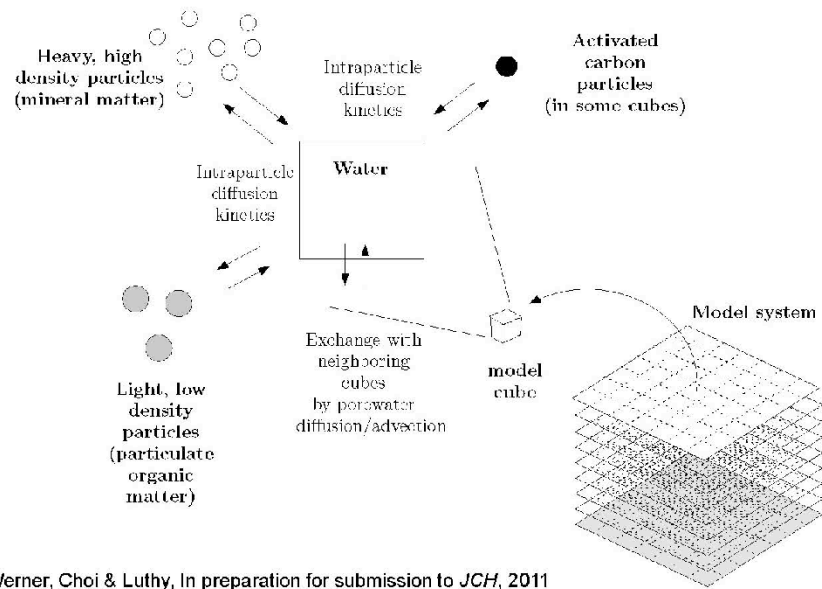
Input Parameters

PARAMETER	ANNOTATION	SOURCE
AC related parameters: particle radius, density, porosity, partitioning coeff., dose, contaminant uptake rate by AC	r_{ac} (cm), d_{ac} (gcm ⁻³), p_{ac} (-), K_{AC} (cm ² g ⁻¹), dose (gg ⁻¹), $rate_{AC}$ (s ⁻¹)	C, M, L
fast release rate from sediment	$rate_{fast}$ (s ⁻¹)	M, S
slow release rate from sediment	$rate_{slow}$ (s ⁻¹)	M, S
mass fraction of sediment with $rate_{fast}$	f_{fast} (-)	M, S
sediment pore water tortuosity	τ (-)	M, S
water-phase diffusion coeff.	D_{ac} (cm ² s ⁻¹)	L
bulk dry sediment density	d_s (gcm ⁻³)	M, S
sediment-water partitioning coeff.	K_d (cm ³ g ⁻¹)	M, S
advective pore water flow	v (cms ⁻¹)	M, E, S
AC fouling factor	$K_{AC \text{ apparent}}/K_{AC \text{ clean}}$	M, S
AC micro-scale particle distribution	-	E, S

- C (controlled/experimental variable), M (measurement), E (estimation), L (literature), S (site-specific parameters)



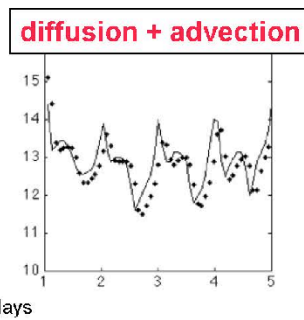
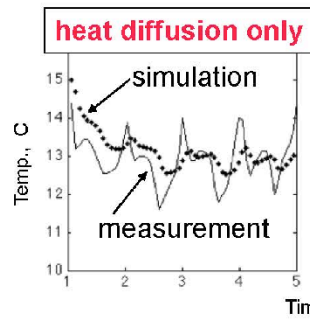
Model System



Cho, Werner, Choi & Luthy, In preparation for submission to *JCH*, 2011



Quantification of Pore Water Movement



Hunters Point, CA

Use heat as a tracer of pore water movement

Average pore water velocity: **5 cm per day**

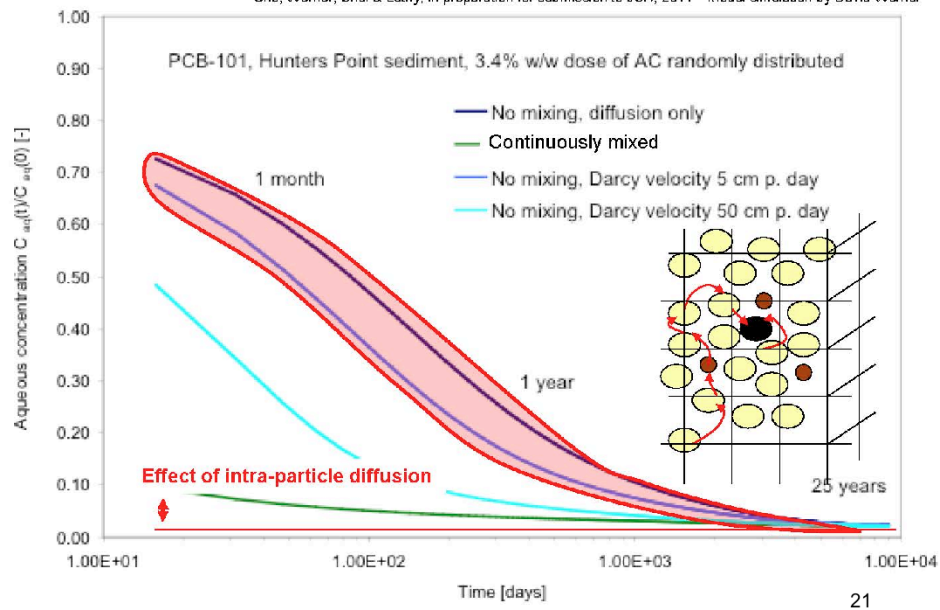
Plausible range: 0 - 10 cm per day

Cho, Werner, Moffett & Luthy, *ES&T*, 44:5842, 2010
20



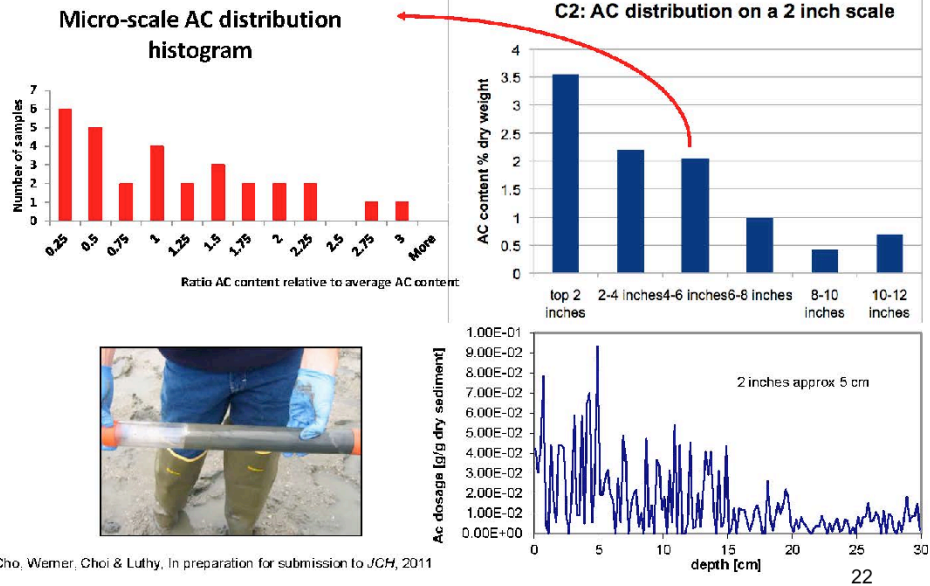
Effect of Advective Pore Water Movement

Cho, Werner, Choi & Luthy, In preparation for submission to JCH, 2011 Model simulation by David Werner



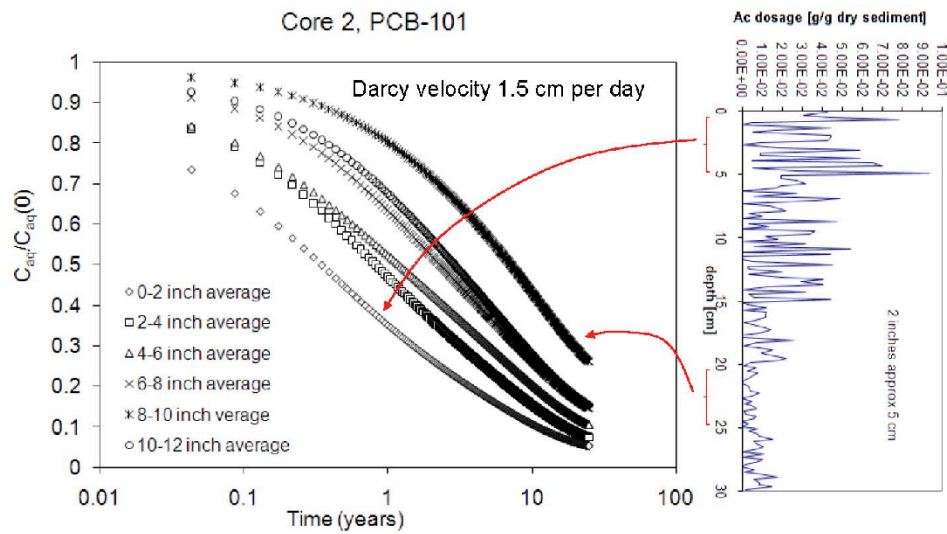


Estimation of AC Distribution





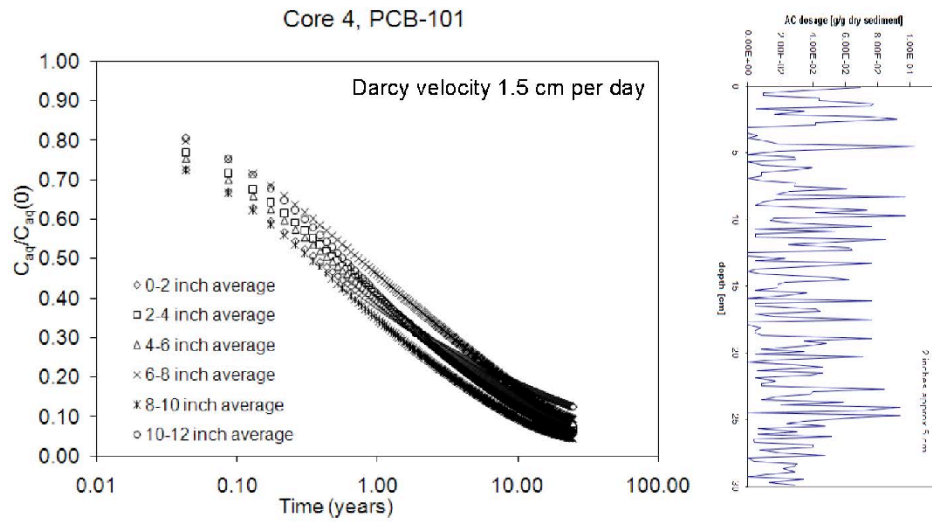
Effect of Heterogeneous AC Distribution



Cho, Werner, Choi & Luthy, In preparation for submission to JCH, 2011 Model simulation by David Werner



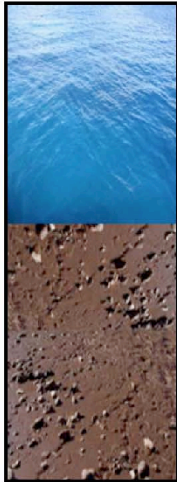
AC Distribution: more homogeneous case



Cho, Werner, Choi & Luthy, In preparation for submission to *JCH*, 2011 Model simulation by David Werner



Biological Assessments: Functional Feeding Traits



Meyer & Möbius, 1872

Filter feeder

Mytilus edulis, mussel



<http://users.hartwick.edu>

Surface + filter feeder

Macoma balthica, clam

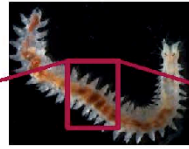


Deposit feeder

Neanthes arenaceodentata, polychaete



Biodynamic modeling



$$\frac{dC_{org}}{dt} = \underbrace{IR \cdot C_{sed} \cdot AE}_{\text{uptake from sediment}} + \underbrace{C_w \cdot k_w}_{\text{uptake from water}} - \underbrace{C_{org,t} \cdot (k_e + k_g)}_{\text{elimination + growth dilution}}$$

IR = Ingestion rate
 C_{sed} = Concentration in sediment
AE = Assimilation efficiency

C_w = Concentration in water
 k_w = Aqueous uptake rate constant

k_e = Elimination rate constant
 k_g = Growth rate constant

Luoma & Rainbow, *ES&T*, 2005

McLeod et al., *ES&T*, 2008




Janssen et al., *Environ. Sci. & Technol.* 44:2857, 2010

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Physiological Parameters

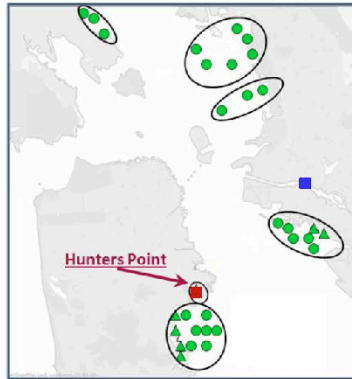
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Parameter, symbol and unit	 <i>N. arenaceodentata</i>	 <i>M. balthica</i>	 <i>M. edulis</i>
Filtration rate, FR, L water/ g dry wt / d		2 ^e	45 ^d
Aqueous assimilation efficiency, AE_{aq}, %		50 ^e	20 ^e
Aqueous uptake rate constant, k_w, L water / g dry wt / d, = FR x AE _{aq}	0.5 ^a	1	9
Ingestion rate, IR, g sediment / g dry wt / d	3.5 ^b	0.25 ^c	0.02 ^h
Sediment assimilation efficiency, AE_s, %	7 ^b	20 ^e	10 ⁱ
Elimination rate constant, k_e, 1 / d	0.04 ^a	0.05 ^c	0.144 ^c
Growth rate constant, k_g, 1 / d	0 ^b	0	0.002 ^f
lipid content of dry weight, %	5 ^{a,b}	18 ^g	10 ^f

^a(Janssen, Croteau et al. 2010), ^b(Janssen, Oen et al. 2010), ^c(McLeod, Luoma et al. 2008), ^d(Tomaszewski, McLeod et al. 2008), ^e(Björk and Gilek 1997), ^f(Gilek, Björk et al. 1996), ^g(Wenne and Polak 1989), ^hSupporting Data (Details on filter feeder), ⁱ(Björk and Gilek 1999), Janssen et al., submitted to *ETC*, 2011



Different Levels of PCB Exposure

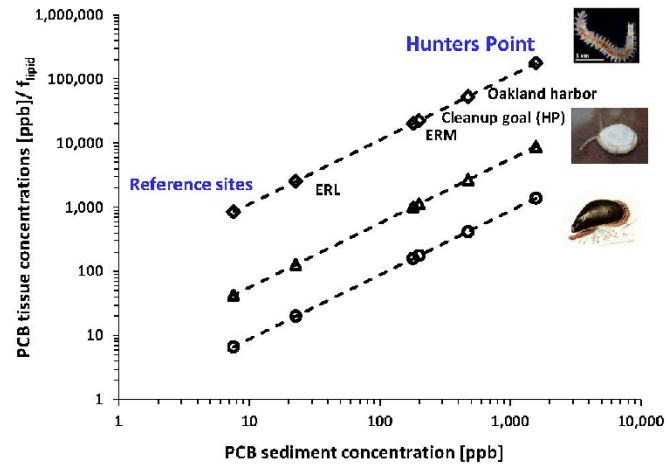


<i>Location</i>	<i>PCB concentration in sediment [ppb]</i>
■ Hunters Point	1570
■ Oakland Harbor (hot spot)	476
Cleanup goal (HP)	200
ERM for PCBs	180
ERL for PCBs	23
● Reference sites ▲ Central SF Bay	9

Janssen et al., submitted to ETC, 2011
28



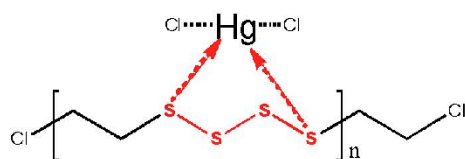
PCB Bioaccumulation



Janssen et al., submitted to *ETC*, 2011₂₉

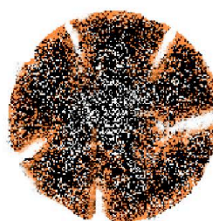


Polysulfide-rubber-coated Activated Carbon



Polysulfide-rubber polymer

- Sulfur-rich compound
- Adhesive
- Water proof material (used in marine sealants)
- Low risk in oxidative decomposition



■ : PSR
■ : AC
□ : Pore

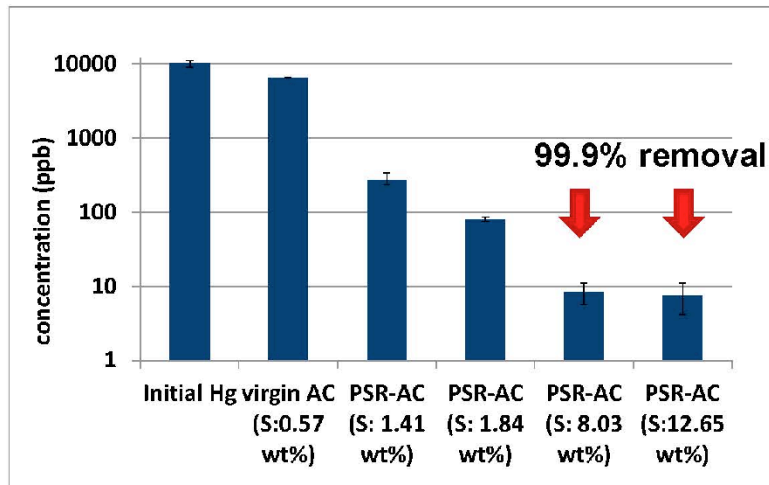
Polysulfide-rubber-coated activated carbon

Inherit AC properties:

- Large surface area
- Porous structure
- Good adsorbent for PCBs



PSR Loading Effect on Hg Removal



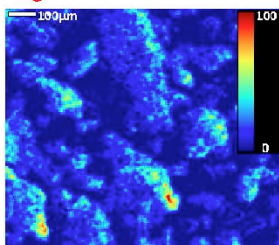
Kim et al., *Water Research*, 45:453, 2011

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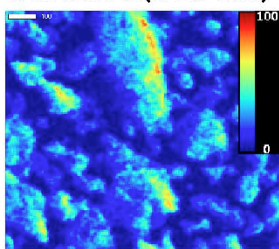


Micro-x-ray fluorescence imaging of PSR-AC

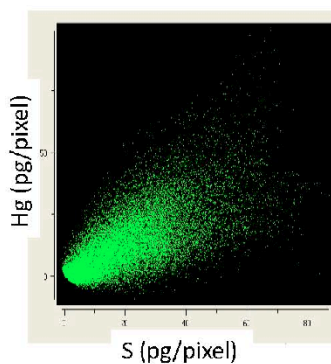
Hg on PSR-AC



S on PSR-AC (S: 8.0 wt%)



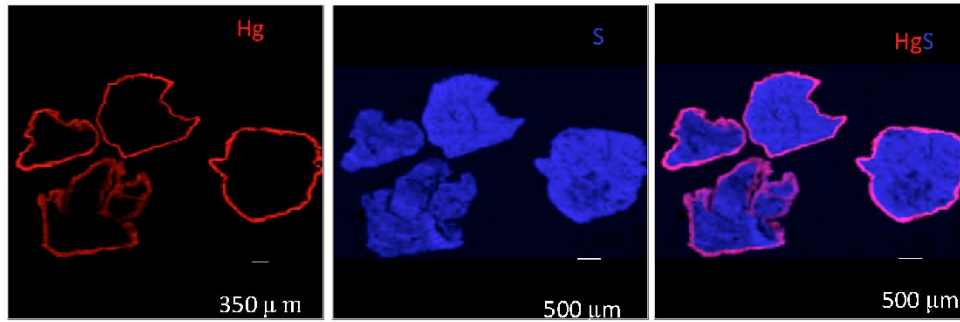
Correlation between Hg and S on PSR-AC



Scale bar unit: picogram/pixel
1 pixel: 5 μmX5 μm

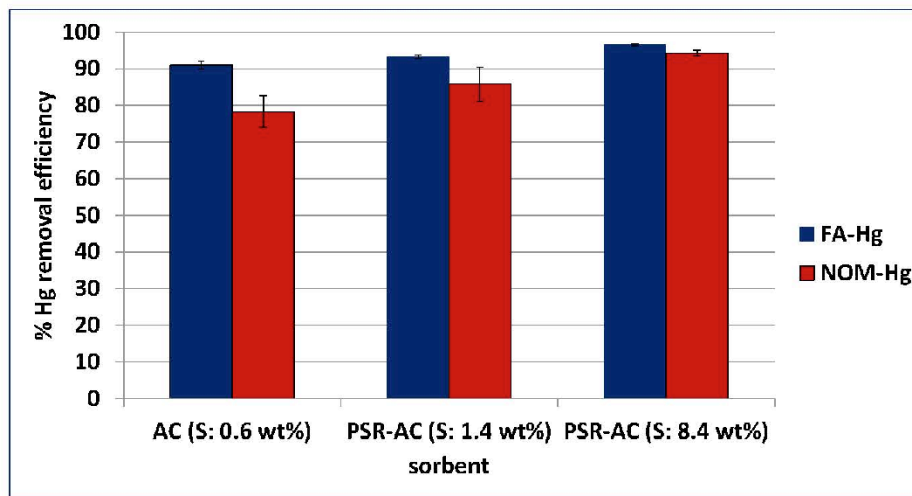


X-ray fluorescence imaging of PSR-AC cross-section





Removal of DOM-Hg with AC or PSR-AC



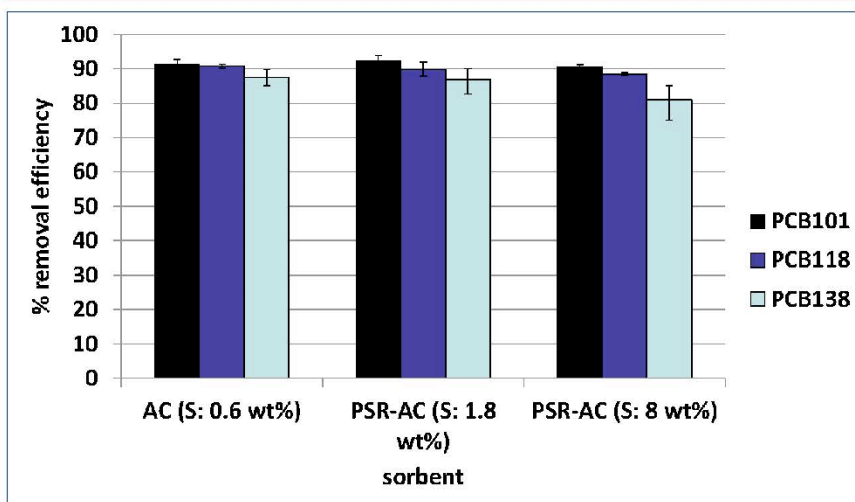
FA: Suwannee River fulvic acid (10 mg/L)

NOM: Suwannee River natural organic matter (10 mg/L)

Initial Hg concentration: 5 ppb



Removal efficiencies of PSR-AC for PCBs



Initial input amount of Aroclor 1254: $25\mu\text{g L}^{-1}$, HgCl_2 : 10 mg Hg L^{-1}

PCBs were partitioned between 10 mg AC/PSR-AC, 75 ± 2.5 mg polyethylene strip, and 40 mL water.



Summary

- **Heterogeneous AC distribution** at the micro-scale retards the approach to equilibrium.
- **Advection/dispersion** in the sediment pore water assists pollutant mass transfer somewhat.
- **AC dose, small particle size & thorough mixing** are most important factors to achieve rapid response.
- Biodynamic modelling shows that accumulation of contaminants by benthic organisms highly depends on their **physiological parameters** such as feeding strategy.
- Polymer-sulfur coated AC shows **enhanced removal efficiency for Hg**.

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Acknowledgement

- **Collaborator:**
David Werner, Newcastle University, UK
- **Researchers:**
Yeo-Myoung Cho, Elisabeth Janssen, Eun-Ah Kim
- **Funding:** ESTCP, SERDP, Chevron, NIH



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Low-impact delivery system for in-situ treatment of sediments contaminated with PCBs and methylmercury

Presentation through NIEHSA
January 19, 2011

Charles Menzie, Ph.D., Exponent
camenzie@exponent.com
571-214-3648

Exponent[®]

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Opportunities to use In-situ treatment arise, in part, from lessons learned and recent guidance

PREPUBLICATION COPY

Sediment Dredging at Superfund Megsites: Assessing the Effectiveness

Committee on Sediment Dredging at Superfund Megsites
Board on Environmental Studies and Toxicology
Division on Earth and Life Studies
NATIONAL RESEARCH COUNCIL
OF THE NATIONAL ACADEMIES

THE NATIONAL ACADEMIES PRESS
Washington, D.C.
www.nap.edu

United States
Environmental
Protection Agency



Contaminated Sediment Remediation Guidance for Hazardous Waste Sites

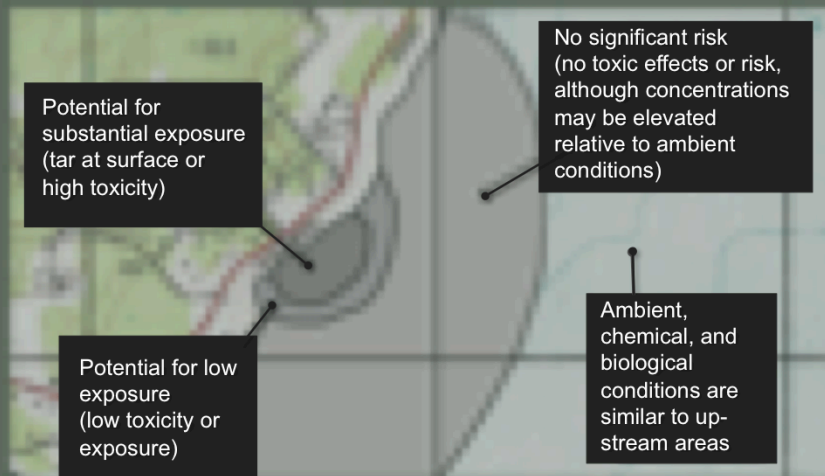


The USEPA guidance offers insights into how to compare alternative remedial measures

Monitored Natural Recovery	In-situ Capping	Dredging/Excavation
<p>Expected human exposure is low and/or reasonably controlled by ICs</p> <p>Site includes sensitive, unique environments that could be irreversibly damaged by capping or dredging</p>	<p>Expected human exposure is substantial and not well-controlled by ICs</p> <p>Long-term risk reduction outweighs habitat disruption, and/or habitat improvements are provided by the cap</p>	<p>Expected human exposure is substantial and not well-controlled by ICs</p> <p>Long-term risk reduction of sediment removal outweighs sediment disturbance and habitat disruption</p>

Considerations used to judge which remedy is more appropriate

The exposure zone concept helps guide selection of remedial approaches including MNR and in-situ



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Idea = get concept of zones across

This example is

Surgery might be best for zones of high exposure/risk

MNR is better for zones of lower exposure/risk

□

SediMite™ as a means of delivering in-situ treatment materials



Tens of grams/day
production in the
laboratory



2-5 Million lb/year at a
production facility



30 lb buckets

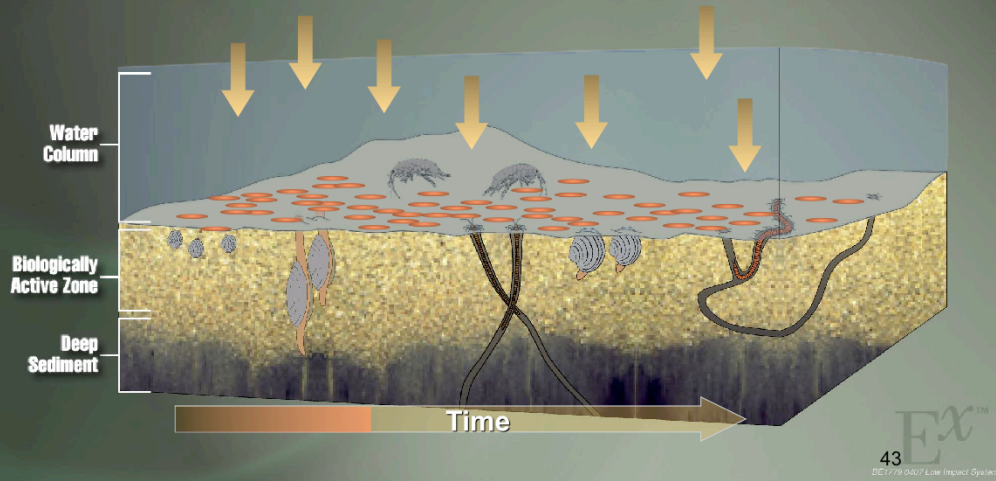


1800 lb bulk bags

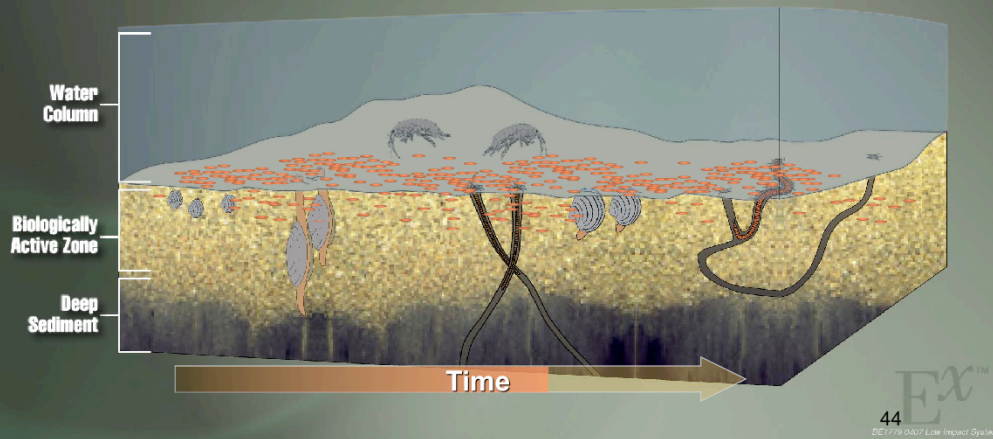
42

However, there is a technology that gets around the need for mechanical mixing

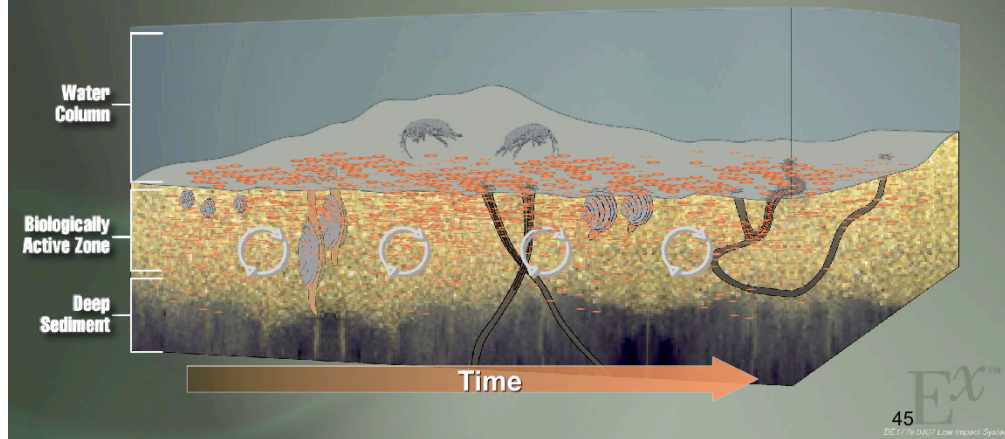
SediMite™ Is Designed to Provide a Low-Impact Delivery System



SediMite™ Granules Break Down over Time

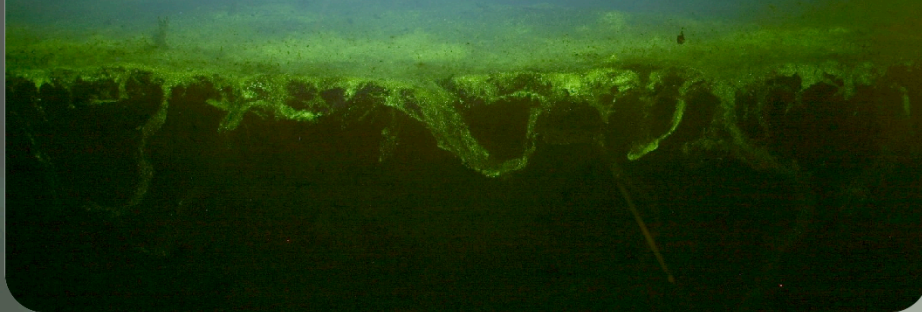


And Are Mixed by Bioturbation, Thus Targeting the Biologically Active Zone



Biological Mixing of SediMite™ Treatment Materials into Sediments

Mixing of treatment
materials after 30 days



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Microcosm study. Tagged sediment with fluorescent particles

The Workers

(burrowing depth increases left to right)

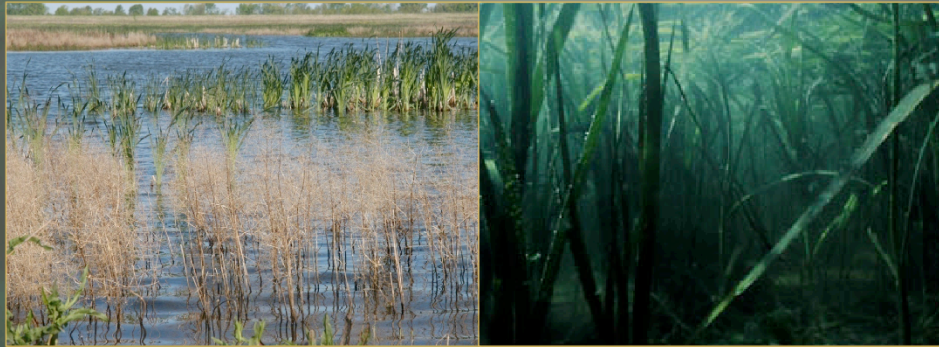


47 Ex™

Far left = typical freshwater organism (oligos, chironomid, hyalella)
Goosey ducks, burrowing shrimp

□

A low-impact in-situ approach is attractive when natural resources may be impacted by more invasive methods (dredging and capping)



Note: these same areas are often the most productive regions of a lake or river and can make a proportionally greater contribution to chemicals in pelagic food webs

□

Potential Applications Include Ways to Treat Contamination in Sediments in and around Structures



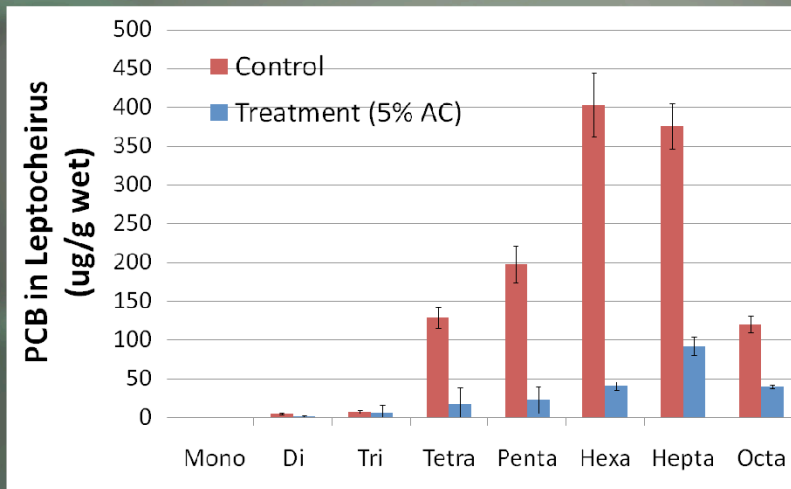
ExTM

49

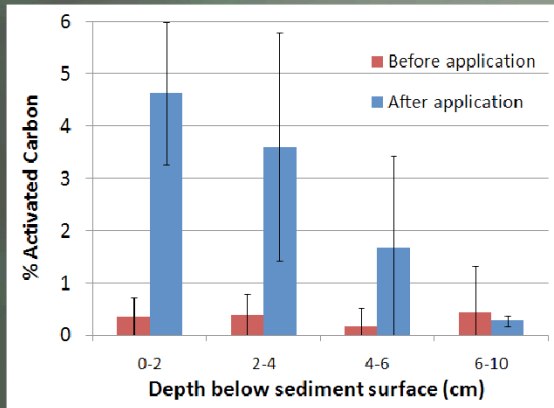
Case 1: Fort Eustis - SEDIMITE™ application in a tidal creek and wetland contaminated with PCBs



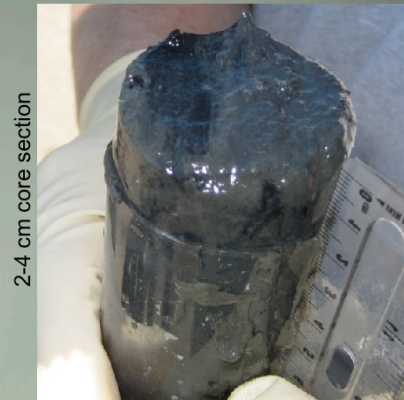
Field application reduces bioavailable PCBs (2 months)



RESULTS FROM FIELD DEMONSTRATION: AC in sediments 2 months after application



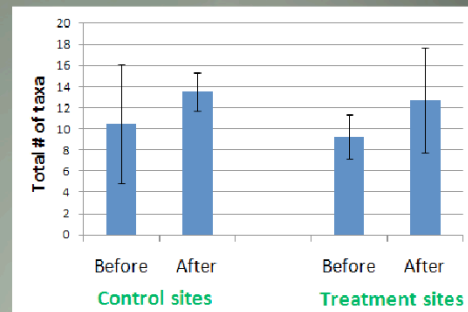
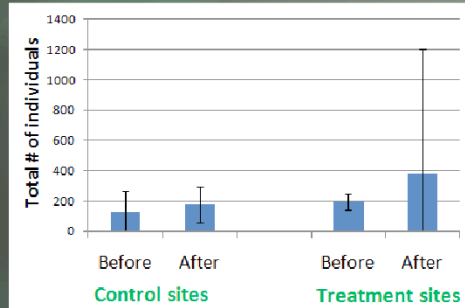
Error bars
indicate $\pm 95\%$ CI



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Effects on Benthic Community

Comparison of pre-treatment and 2-months post-treatment benthic community at a field demonstration site



Error bars indicate $\pm 95\%$ CI
Data courtesy of Dr. Upal Ghosh, UMBC

Case 2: APG - SEDIMITE™ application in a tidal creek contaminated with PCBs and mercury

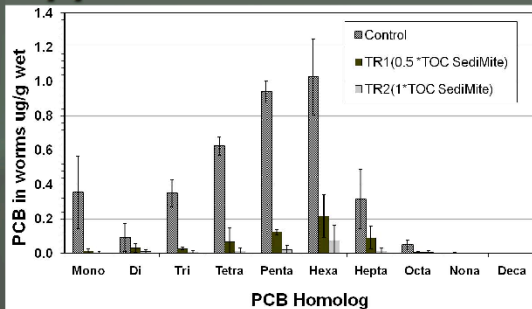
Canal Creek, Edgewood Area of Aberdeen Proving Ground (APG)



Site Description



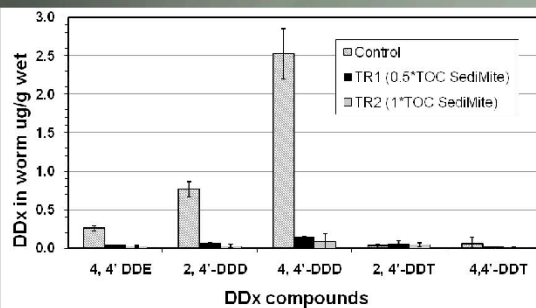
Treatability results for PCBs and DDx in upper Canal Creek sediments



14-day bioaccumulation studies with *L. variegatus*

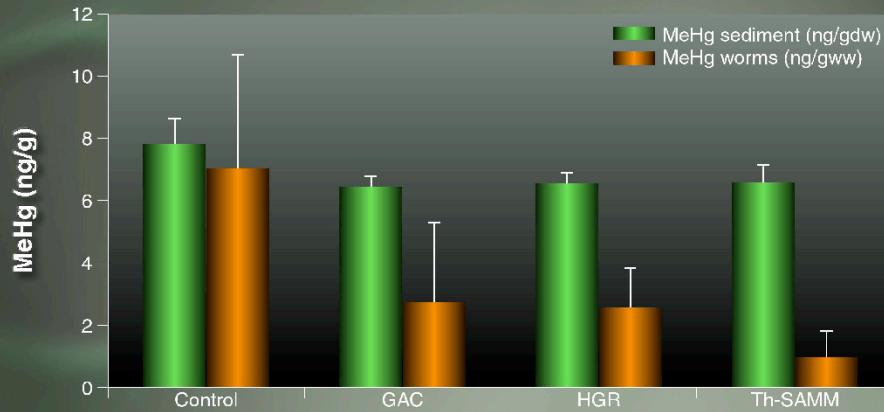
Treatment at the low dose of SediMite (0.5xTOC as carbon) reduced total PCB bioaccumulation by 81% and total DDx bioaccumulation by 87%

At the higher dose of SediMite (1xTOC as carbon), PCB bioaccumulation was reduced by 95% and DDx bioaccumulation by 92%



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Reducing Methylmercury Formation and Bioaccumulation



Notes: Methylmercury concentrations in sediments and in worm bodies, by treatment. Error bars represent the standard deviation of triplicate experiments.

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Could be reducing formation or concentration, don't know yet

Reductions in mercury exposure at two other planned pilot sites (shown as fractions of the control)

A freshwater river

	Hg	MeHg	Sediment	Worms	Worms
	Pore water	Pore water	MeHg	Hg	MeHg
TS	0.7	0.3	0.95	0.23	0.04
MRM	1.3	1.6	1.44	0.58	0.29
PAC	0.2	0.1	2.50	0.16	0.10

A brook

	Hg	MeHg	Sediment	Worms	Worms
	Pore water	Pore water	MeHg	Hg	MeHg
TS	0.8	1.8	1.22	0.56	0.40
MRM	0.6	2.5	1.14	0.88	1.35
PAC	0.9	0.3	1.42	0.51	0.47

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Test Design

- Distribute SediMite™ over test plots and control plots in Upper and Lower Canal Creek
- Monitor efficacy of treatment over 8-10 months (through 2010/2011)
- Compare test plots to control plots
 - Measure changes in sediment mercury and PCBs
 - Measure changes in pore water mercury and PCBs
 - Measure impacts to benthic invertebrate community
 - Measure impacts to wetland plant community

SediMite Application for lower Canal Creek – access via Gunpowder R

- Deployment of SediMite™:
 - Barge-mounted spreader (Millcreek “Turf Tiger”)
 - Thin-layer cap placement barge
 - Deposition rate and position can be controlled
 - Can access shallow areas
 - Field test completed:
 - minimal breakage of pellets
 - 23 kg/min application rate
 - 10 ft. wide application area



Application to a wetland

walkways



plots



Sediment Colonization Study

And other studies of effects



Trays were prepared of native but azoic sediments amended with various levels of activated carbon



Colonization trays are being used to assess long-term effects on benthic communities



Examining the compatibility of site conditions with sediment management alternatives

	MNR	Capping	Dredging	In-Situ	Reactive Caps
Site Characteristics					
Human and Ecological Environment					
Hydrodynamic Conditions					
Sediment Characteristics					
Contaminant Characteristics					
Compatible					
Moderate					
Low to Moderate					
Not Compatible					

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Categories that EPA identified as broad factors to consider in evaluating remedial alternatives

Examining the compatibility of site conditions with sediment management alternatives at a site in Pennsylvania

	MNR	Capping	Dredging	In-Situ	Reactive Caps
Site Characteristics	Compatible	Uncertain	Low to Moderate	Compatible	Uncertain
Human and Ecological Environment	Compatible	Not Compatible	Not Compatible	Compatible	Not Compatible
Hydrodynamic Conditions	Moderate	Moderate	Moderate	Moderate	Moderate
Sediment Characteristics	Moderate	Compatible	Low to Moderate	Moderate	Compatible
Contaminant Characteristics	Moderate	Compatible	Low to Moderate	Moderate	Compatible
Compatible					
Moderate					
Low to Moderate					
Not Compatible					

Key challenges and possible steps

- Need to consider longer timeframes to let nature and/or in-situ accomplish healing
- Need to broaden the dimensions of the project to consider overall goals, consequences, and benefits
- May need additional regulatory guidance along with regional workgroups

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Analogy to medical care for people: spectrum of diseases and treatments, surgery vs. less invasive species, counters impression that you always need to do surgery, surgery is not always the best option

Proposal: states should band together, MA is model for that sort of thing

Resources & Feedback

- To view a complete list of resources for this seminar, please visit the [Additional Resources](#)
- Please complete the [Feedback Form](#) to help ensure events like this are offered in the future

U.S. EPA United States Environmental Protection Agency

Technology Innovation Program

U.S. EPA Technical Support Project Engineering Forum
Guest Representatives Invited to Attend the Session C (Green Remediation Tools and Techniques) Seminar Feedback Form

We would like to receive and feedback you input how that would make this service more valuable.
 Please take the time to fill out this form before leaving this site.

First Name: Jim
 Last Name: Hart
 E-mail Address: jim.hart@epa.gov
 Comments: I would really enjoy all the feedback I can give to help you provide this service

Need confirmation of
your participation today?

Fill out the feedback form
and check box for
confirmation email.