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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)

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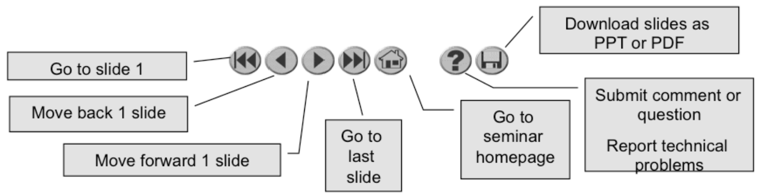
- Q&A
- Turn off any pop-up blockers
- Move through slides using # links on left or buttons



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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

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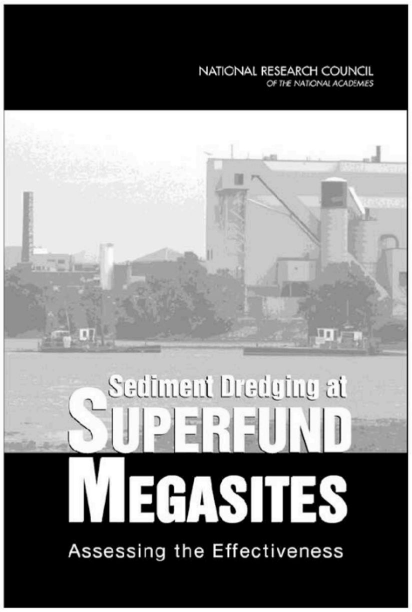
OVERVIEW

- 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

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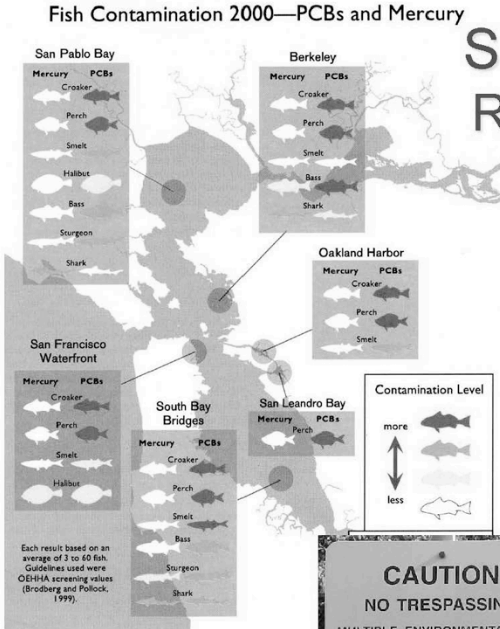
Superfund process:
RAO→RG→CUL→OG



San Francisco Estuary Inst.

Shoal Point Bayou,
Panama City, FL

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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

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Commencement Bay, Tacoma, WA

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

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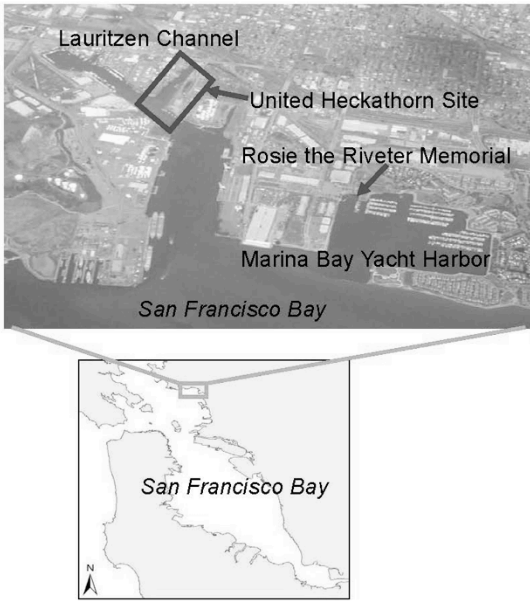

Lauritzen Channel

... 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

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

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THE NATIONAL ACADEMIES

REPORT IN BRIEF

June 2007

Sediment Dredging at Superfund Megasites: 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

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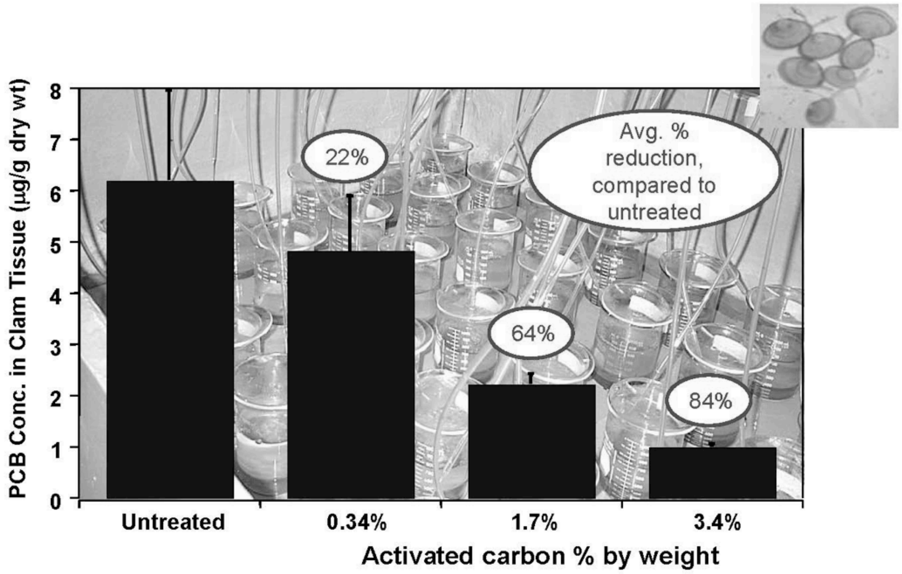
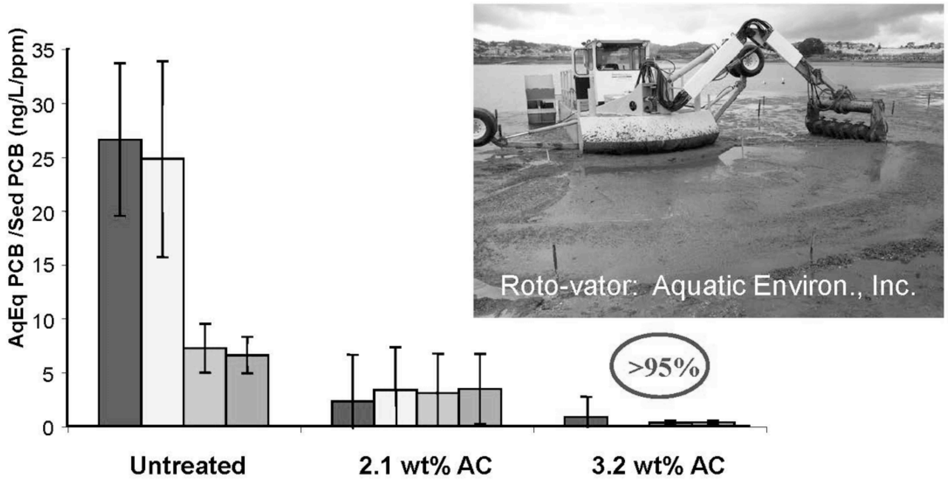
Proof of Concept: Lab Biouptake



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**

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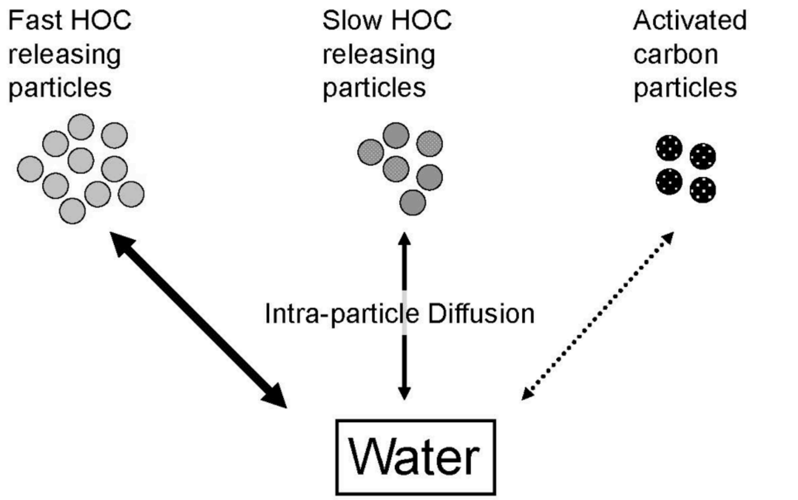
Geochemical HOC Mass Transfer



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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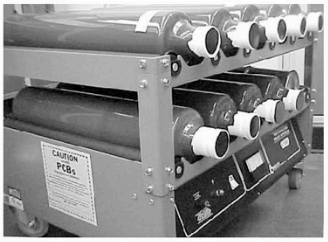
Slow Mass Transfer in the Field



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

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

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

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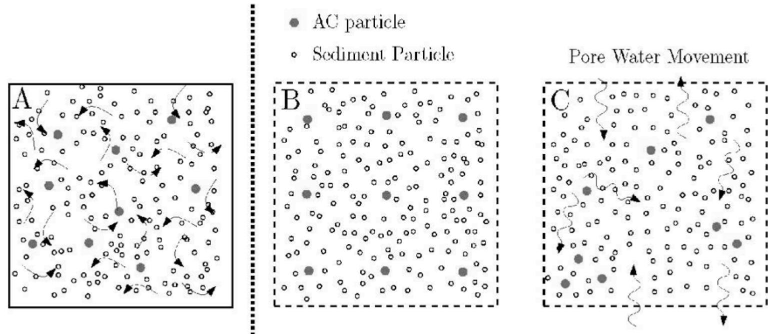
Lab vs. Field Conditions



(A) Complete & Continuous Mixing

Laboratory

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

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

Field

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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^3g^{-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_{aq} (cm^2s^{-1})	L
bulk dry sediment density	d_s (gcm^{-3})	M, S
sediment-water partitioning coeff.	K_d (cm^3g^{-1})	M, S
advective pore water flow	υ (cms^{-1})	M, E, S
AC fouling factor	$K_{AC\ apparent}/K_{AC\ clean}$	M, S
AC micro-scale particle distribution	-	E, S

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

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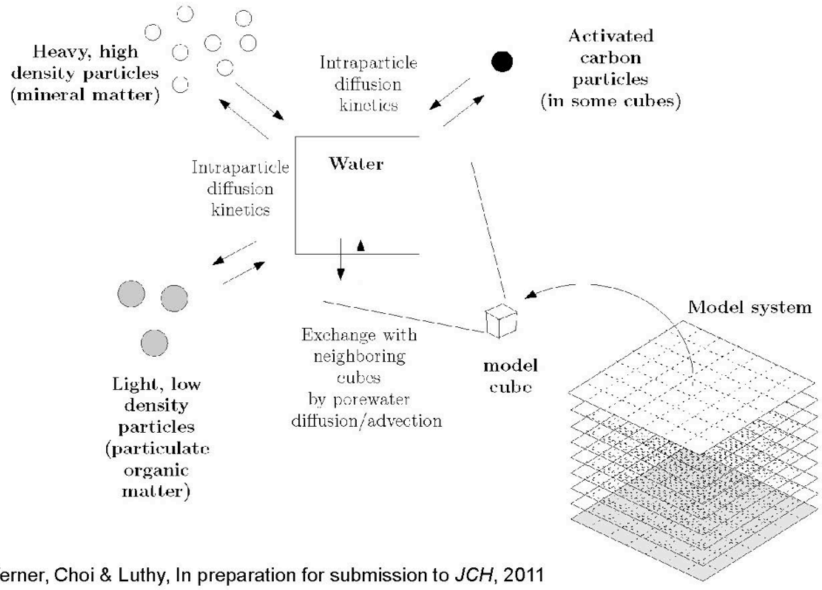
Model System



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

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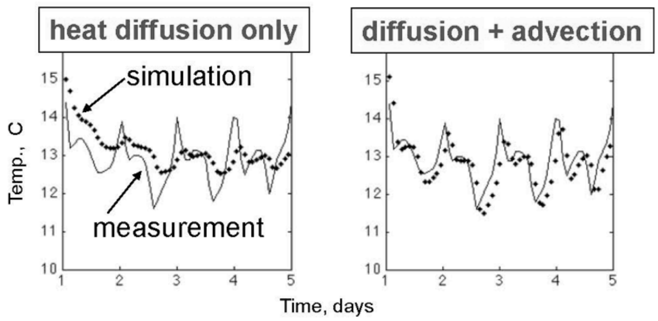
Quantification of Pore Water Movement



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

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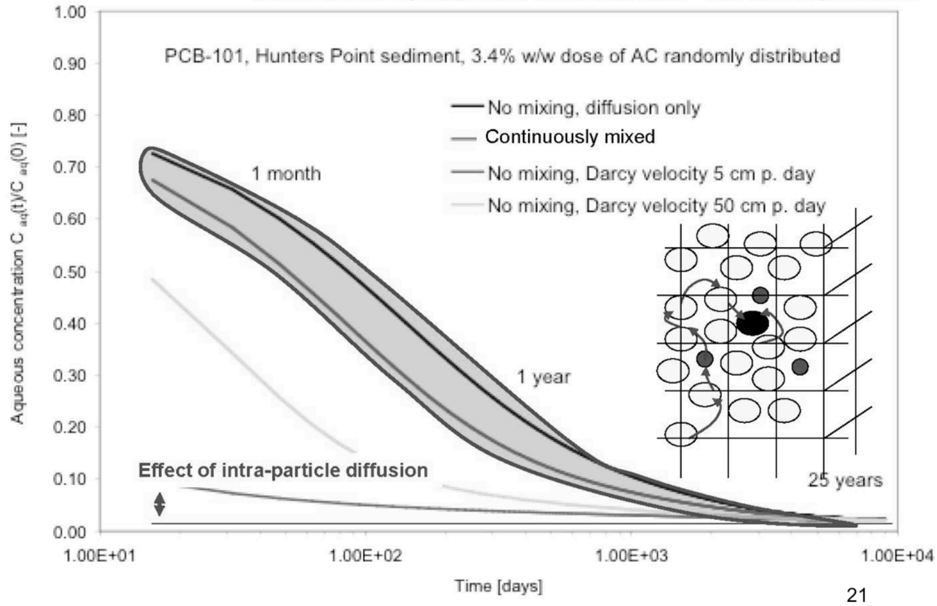
Effect of Advective Pore Water Movement

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



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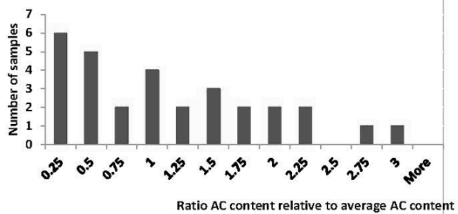
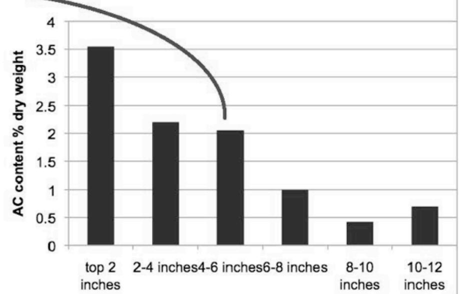
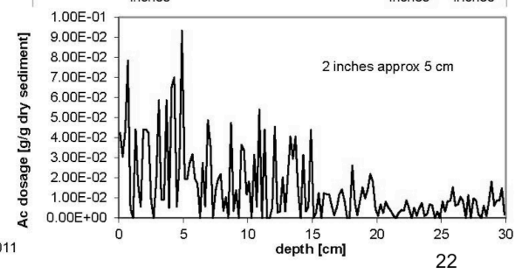
Estimation of AC Distribution

Micro-scale AC distribution histogram







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

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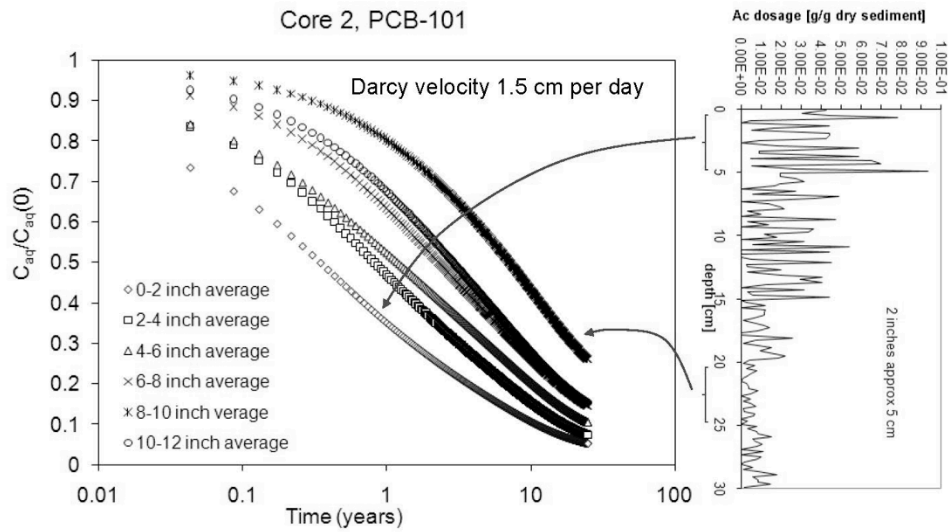
Effect of Heterogeneous AC Distribution



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

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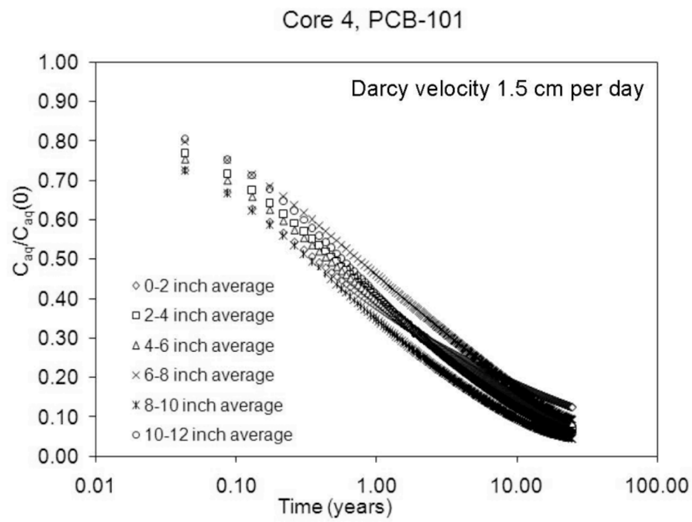
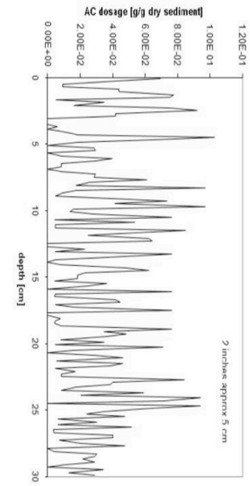
AC Distribution: more homogeneous case





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

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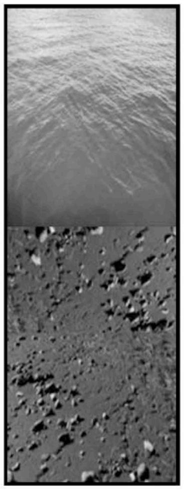
Biological Assessments: Functional Feeding Traits

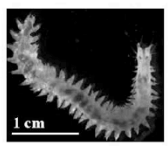


Meyer & Möbius, 1872

Filter feeder
Mytilus edulis, mussel

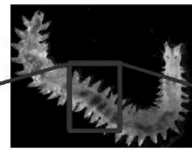
http://users.hartwick.edu

Surface + filter feeder
Macoma balthica, clam



Deposit feeder
Neanthes arenaceodentata, polychaete

Biodynamic modeling



uptake from water

$$\frac{d\,C_{org}}{d\,t} = IR \cdot C_{sed} \cdot AE + C_w \cdot k_w - C_{org,\,t} \cdot (k_e + k_g)$$

uptake from sediment — elimination + growth dilution

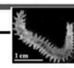
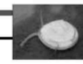
IR = Ingestion rate
C_{sed} = Concentration in sediment
AE = Assimilation efficiency

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

Physiological Parameters

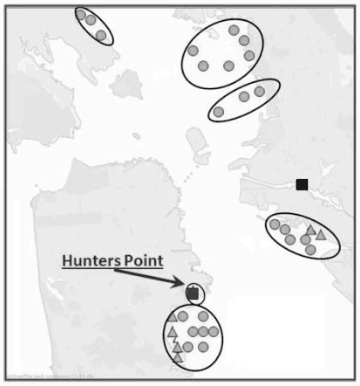




Parameter, symbol and unit	*N. arenaceodentata*	*M. balthica*	*M. edulis*
Filtration rate, FR, L water/ g dry wt / d		2[c]	45[d]
Aqueous assimilation efficiency, AE_{aq}, %		50[c]	20[e]
Aqueous uptake rate constant, k_w, L water / g dry wt / d, = FR x AE_{aq}	0.5[a]	1	9
Ingestion rate, IR, g sediment / g dry wt / d	3.5[b]	0.25[c]	0.02[h]
Sediment assimilation efficiency, AE_s, %	7[b]	20[c]	10[i]
Elimination rate constant, k_e, 1 / d	0.04[a]	0.05[c]	0.144[e]
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), [h]Supporting Data (Details on filter feeder), [i](Björk and Gilek 1999),

Janssen et al., submitted to *ETC*, 2011

Different Levels of PCB Exposure



Location	*PCB concentration in sediment [ppb]*
■ **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

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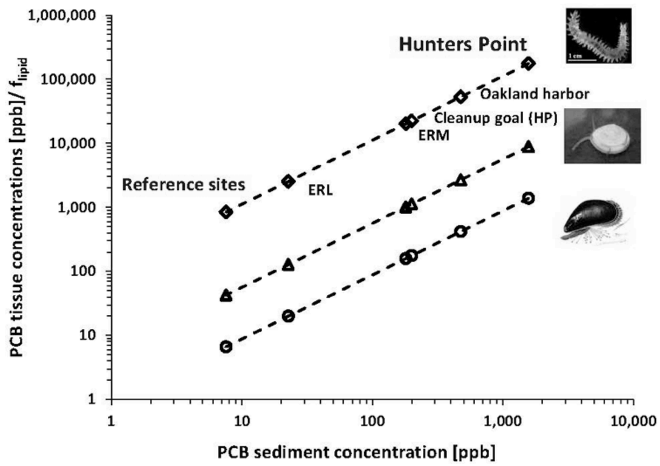
PCB Bioaccumulation



Janssen et al., submitted to *ETC*, 2011

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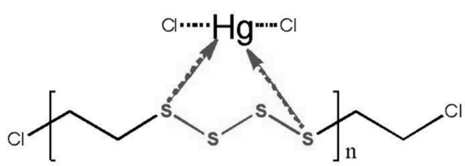
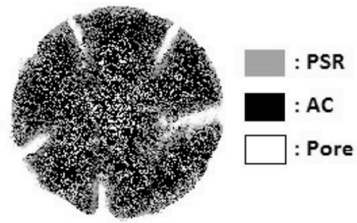
Polysulfide-rubber-coated Activated Carbon



Polysulfide-rubber polymer

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



Polysulfide-rubber-coated activated carbon

Inherit AC properties:
- Large surface area
- Porous structure
- Good adsorbent for PCBs

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

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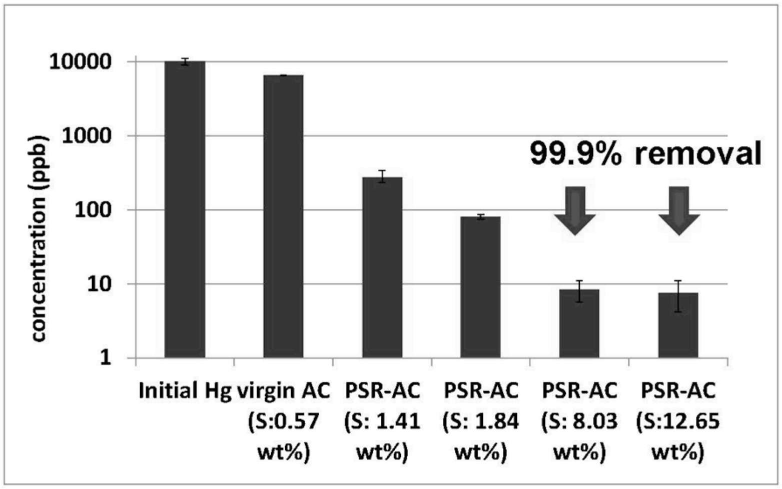
PSR Loading Effect on Hg Removal



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

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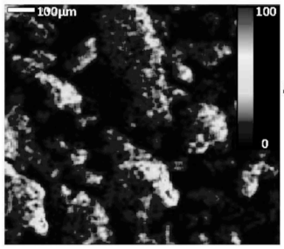
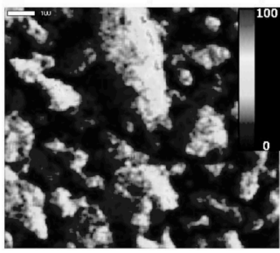
Micro-x-ray fluorescence imaging of PSR-AC

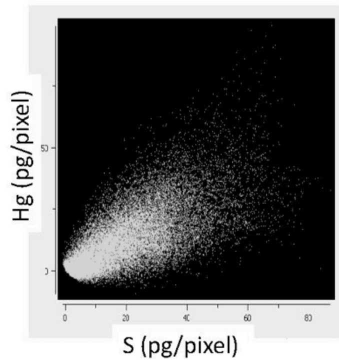
Hg on PSR-AC



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

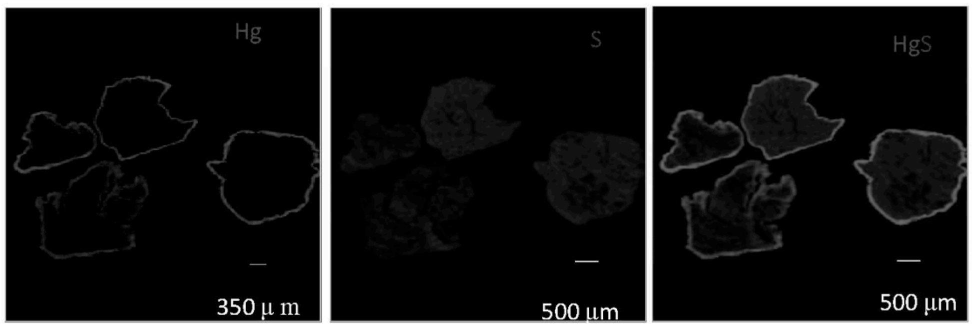


Correlation between Hg and S on PSR-AC



Scale bar unit: picogram/pixel
1 pixel: 5µmX5µm

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



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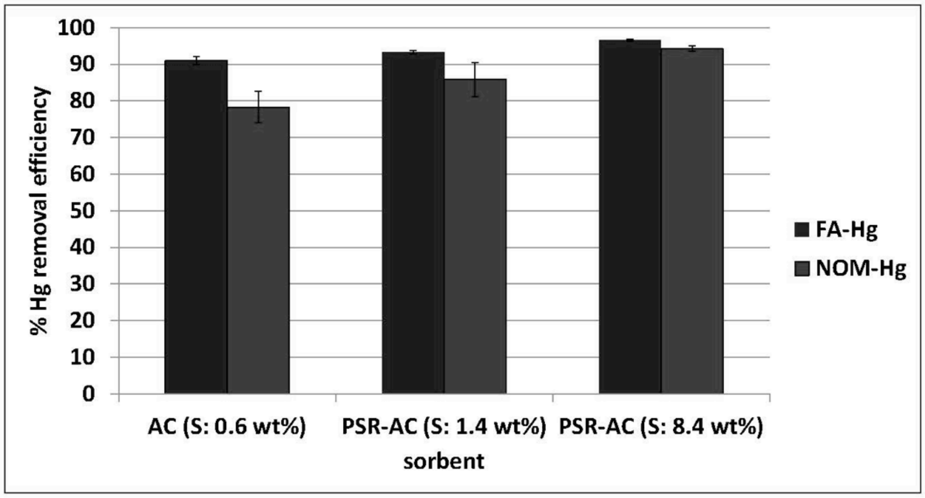
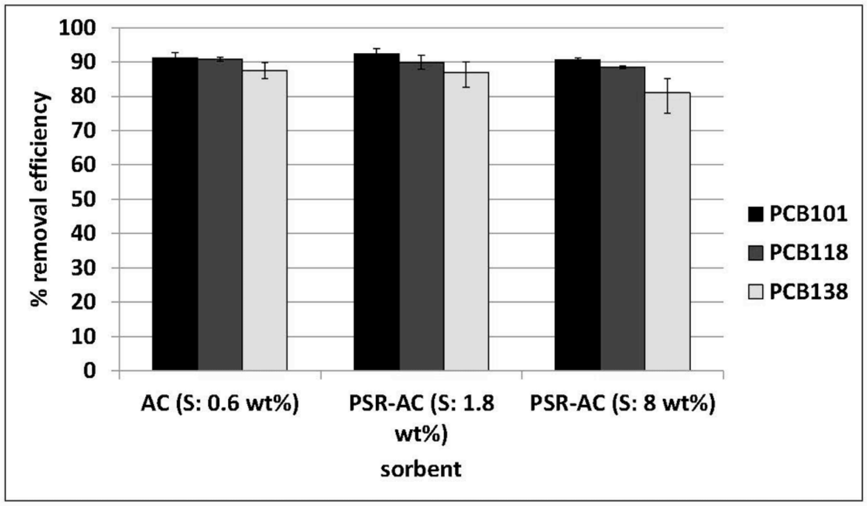
Removal of DOM-Hg with AC or PSR-AC



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: 25µg 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.

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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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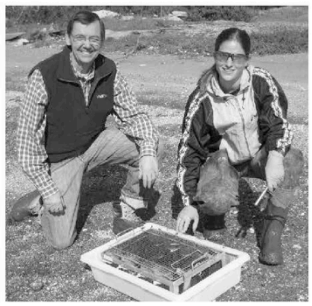
Acknowledgement

- **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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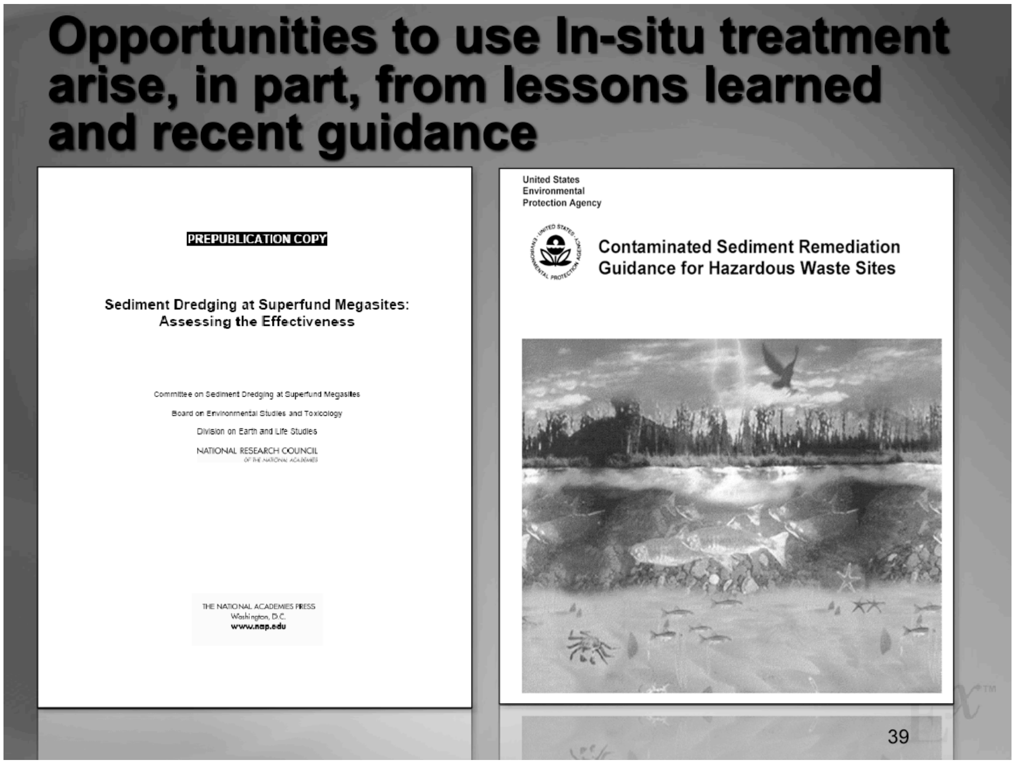
Opportunities to use In-situ treatment arise, in part, from lessons learned and recent guidance
PREPUBLICATION COPY
Sediment Dredging at Superfund Megasites:
Assessing the Effectiveness
Committee on Sediment Dredging at Superfund Megasites
Board on Environmental Studies and Toxicology
Division on Earth and Life Studies
NATIONAL RESEARCH COUNCIL
THE NATIONAL ACADEMIES PRESS
Washington, D.C.
www.nap.edu
United States
Environmental
Protection Agency
Contaminated Sediment Remediation
Guidance for Hazardous Waste Sites
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The USEPA guidance offers insights into how to compare alternative remedial measures

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

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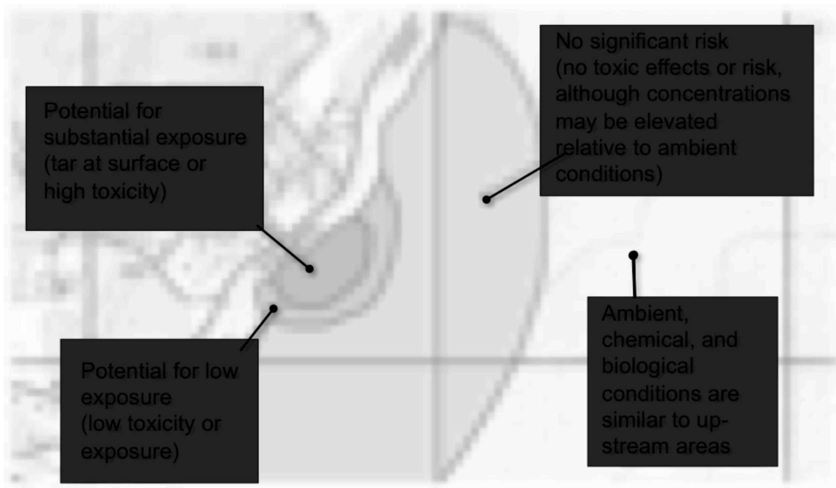
Considerations used to judge which remedy is more appropriate

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



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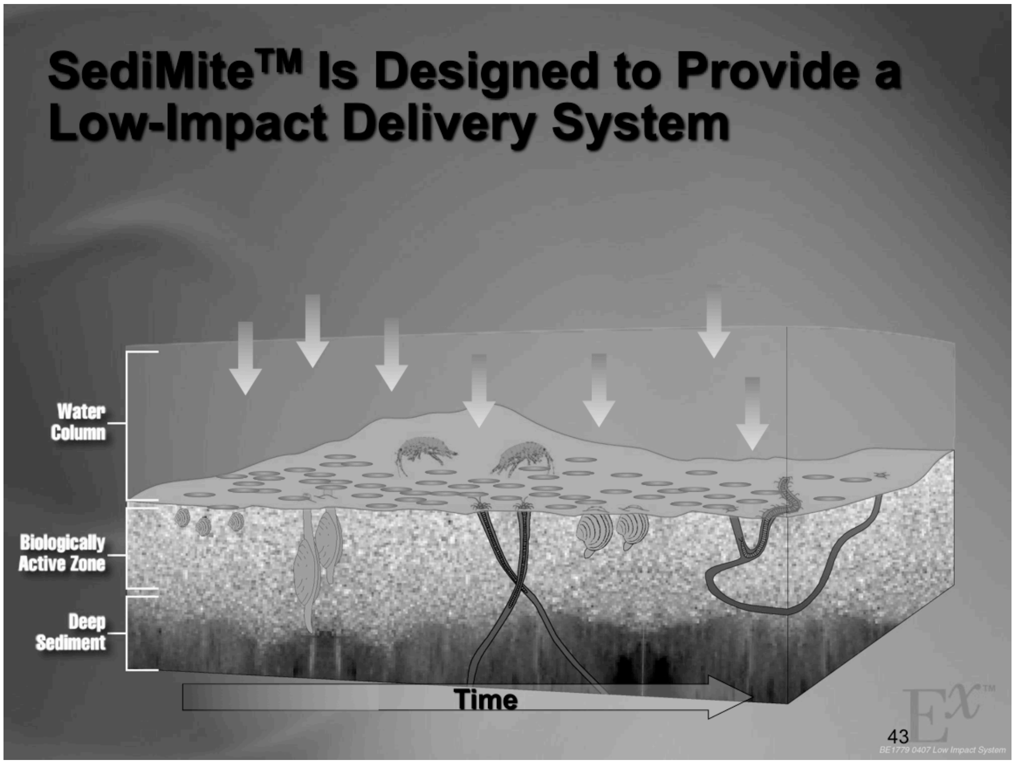
Idea = get concept of zones accress

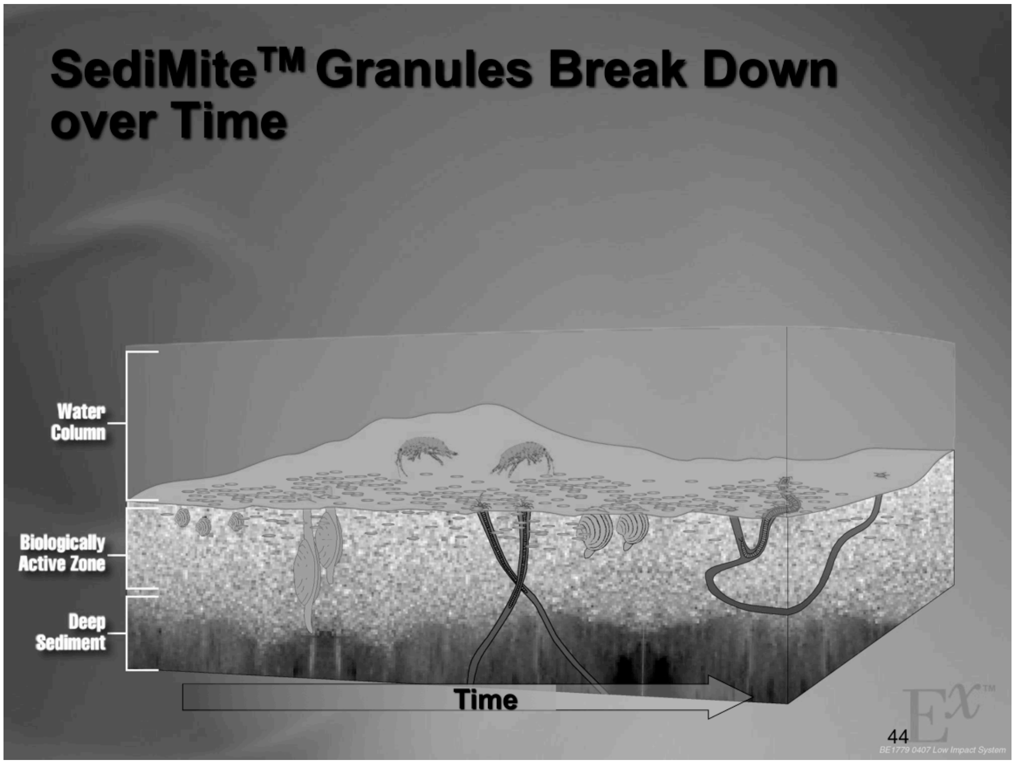
This example is

Surgery might be best for zones of high exposure/risk

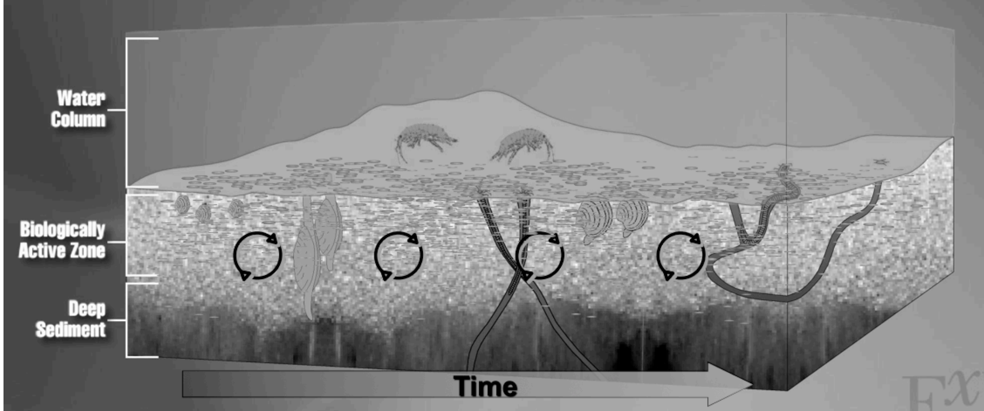
MNR is better for zones of lower exposure/risk

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


SediMite™ Is Designed to Provide a Low-Impact Delivery System
Water Column
Biologically Active Zone
Deep Sediment
Time
43
BE1779 0407 Low Impact System

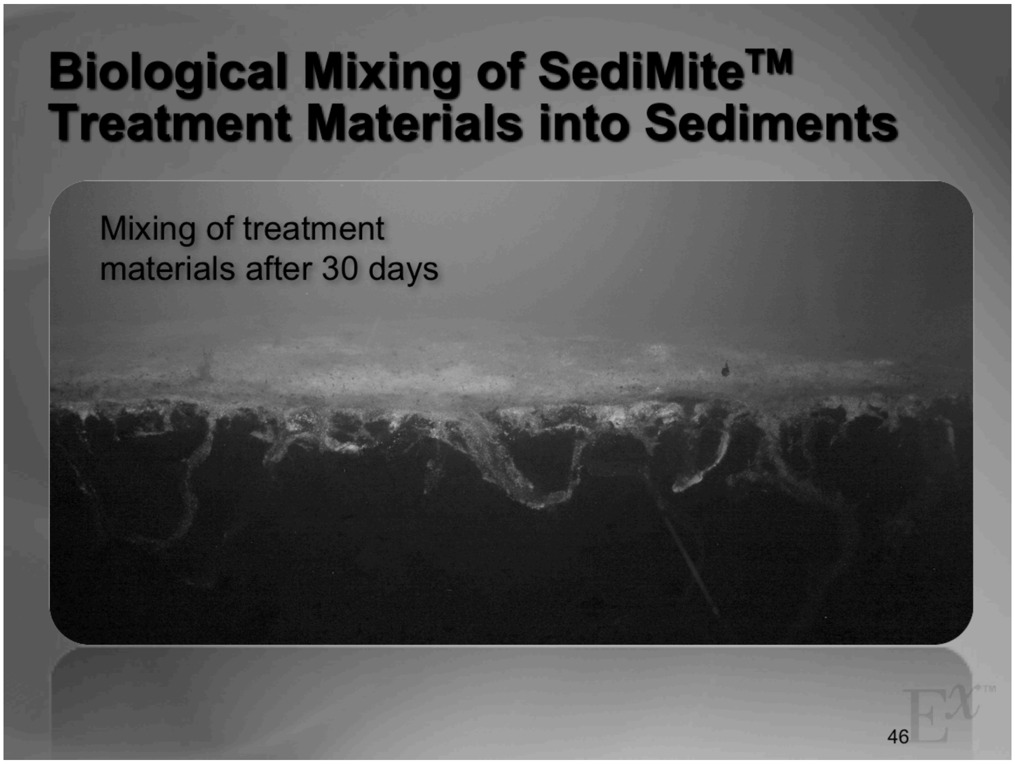

SediMite™ Granules Break Down over Time
Water Column
Biologically Active Zone
Deep Sediment
Time
44
BE1779 0407 Low Impact System

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

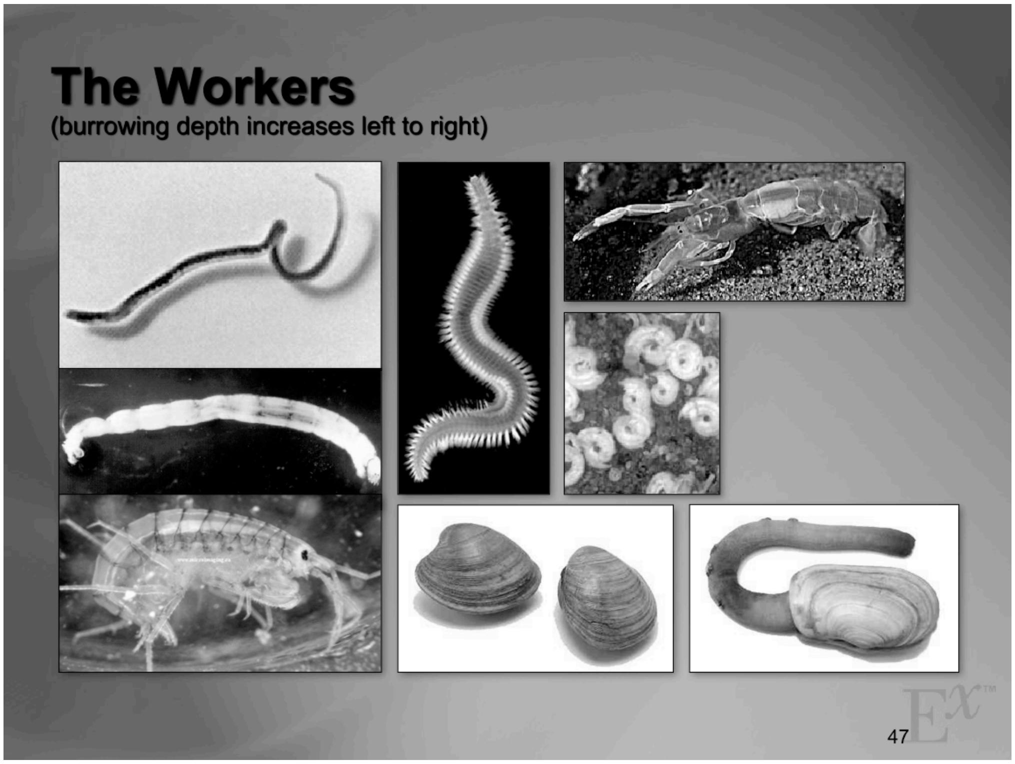


45

BE1779 0407 Low Impact System

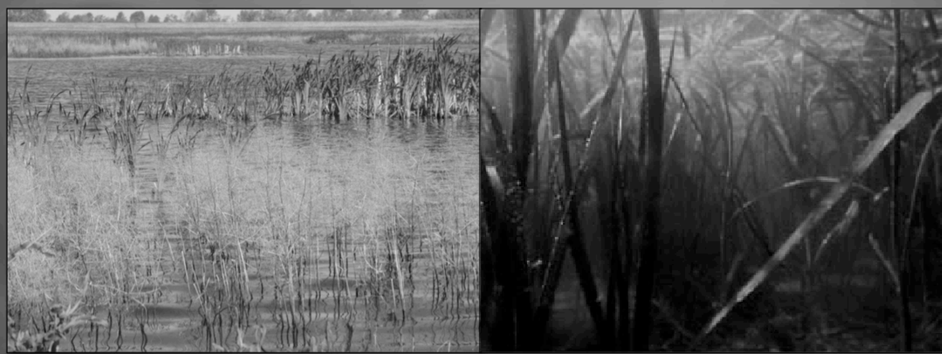


Microcosm study. Tagged sediment with fluoresent particles



Far left = typical freshwater organism (oligos, chironomid, hyalella)
Gooey 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

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

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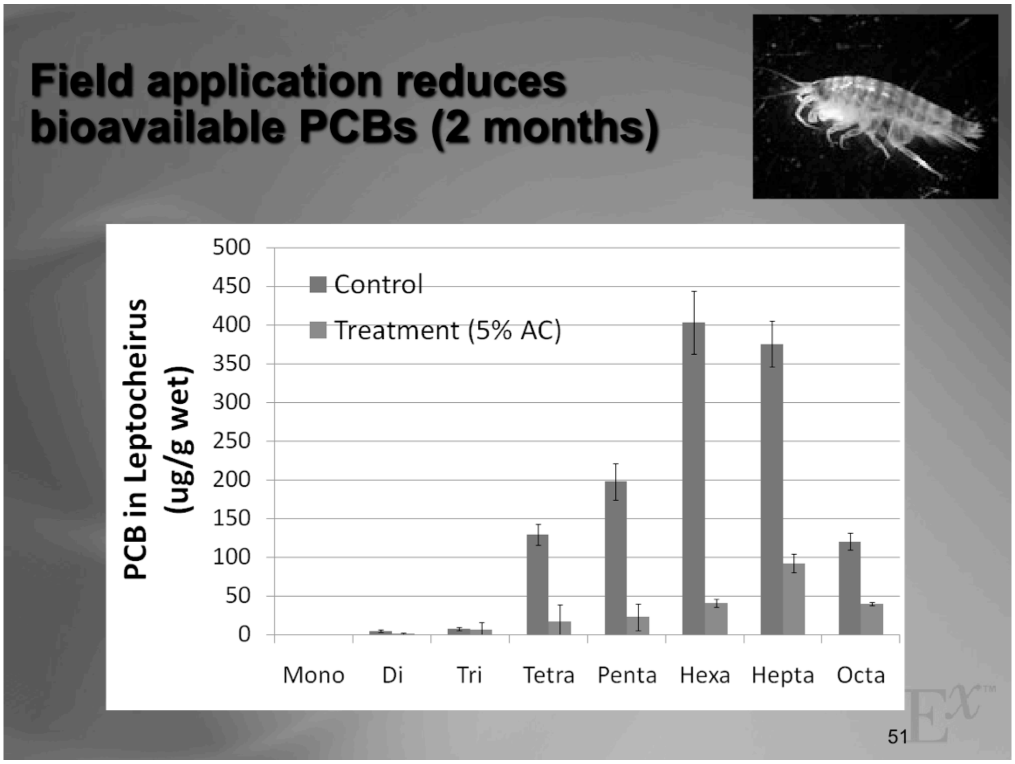
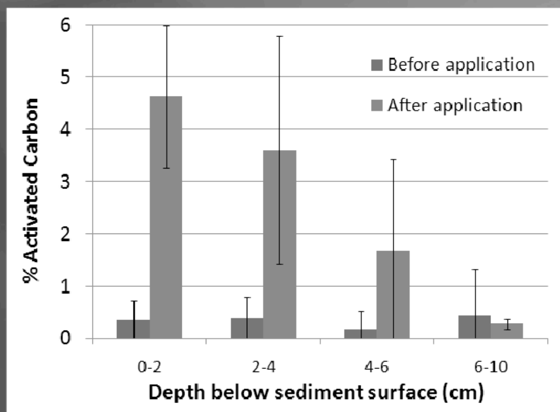
Case 1: Fort Eustis - SEDIMITE™ application in a tidal creek and wetland contaminated with PCBs

August, 2009
50


Field application reduces bioavailable PCBs (2 months)
PCB in Leptocheirus (ug/g wet)
500
450
400
350
300
250
200
150
100
50
0
Control
Treatment (5% AC)
Mono
Di
Tri
Tetra
Penta
Hexa
Hepta
Octa
51

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



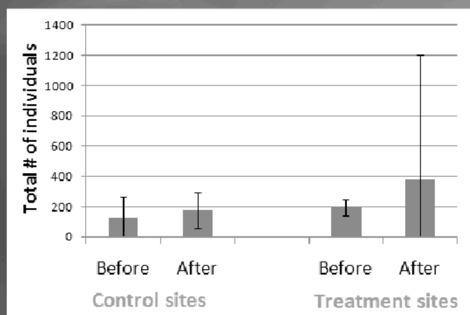
2-4 cm core section

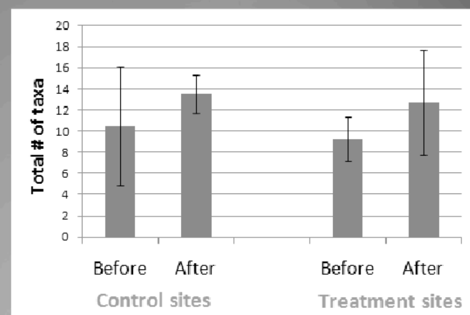
Error bars indicate ±95% CI

52

Effects on Benthic Community

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





Error bars indicate ±95% CI

Data courtesy of Dr. Upal Ghosh, UMBC

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

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

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Site Description

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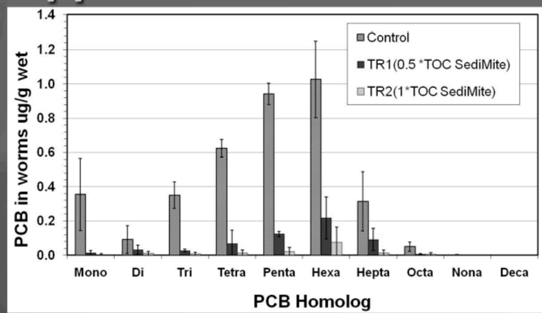
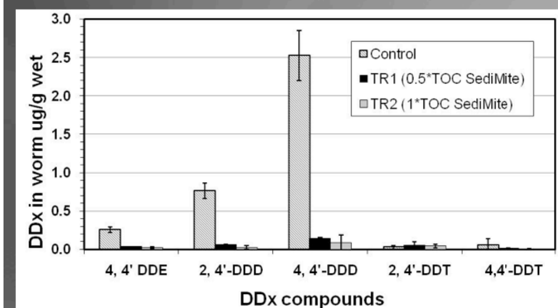
Treatability results for PCBs and DDxin upper Canal Creek sediments

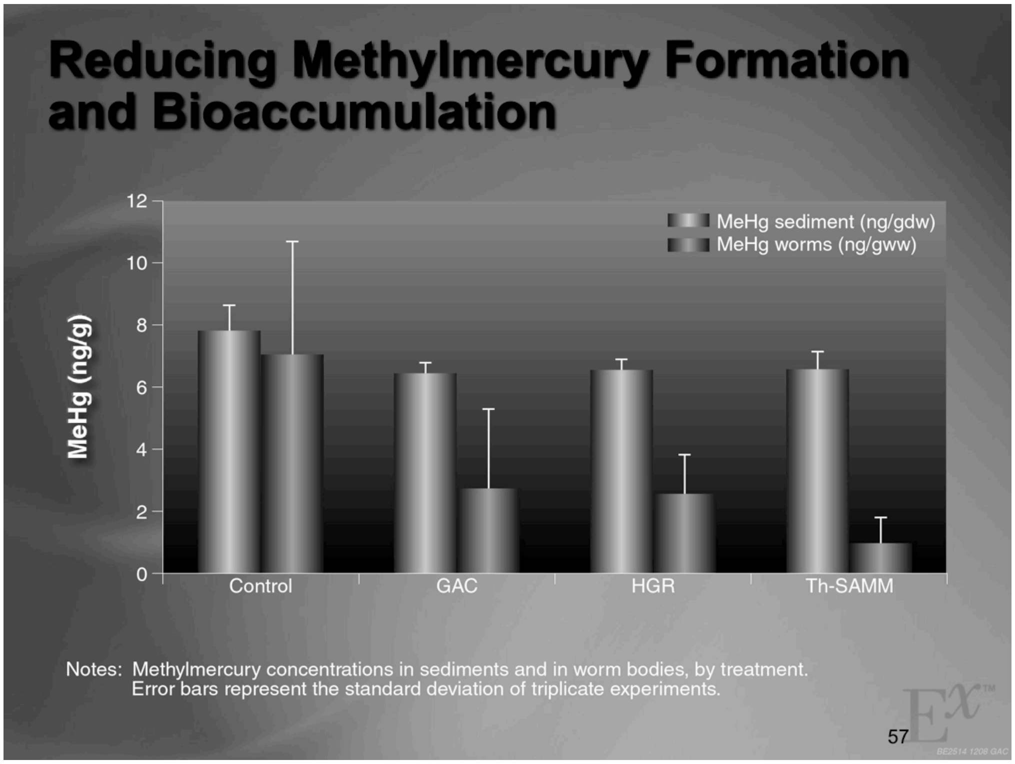




14-day bioaccumulation studies with *L. variegatus*

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%



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 Pore water	MeHg Pore water	Sediment MeHg	Worms Hg	Worms 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 Pore water	MeHg Pore water	Sediment MeHg	Worms Hg	Worms 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

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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

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Application to a wetland

walkways

plots

61

Sediment Colonization Study

And other studies of effects

62

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

63

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

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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 evalauting 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	(dark grey)
Moderate	(light grey)
Low to Moderate	(medium grey)
Not Compatible	(darkest grey)

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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

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