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

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

Delivered: November 17, 2010, 2:00 PM - 4:00 PM, EST (19:00-21:00 GMT)

Instructors:

*Dr. Peggy O'Day, School of Natural Sciences, University of California, Merced
(poday@ucmerced.edu)*

*Dr. Tom Sheahan, Department of Civil and Environmental Engineering at Northeastern University
(tsheahan@coe.neu.edu)*

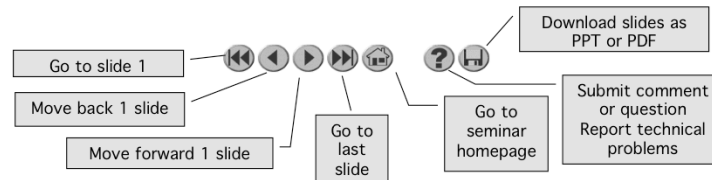
Moderator:

Karl Gustavson, Army Engineer Research and Development Center (gustavson.karl@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/>



Reactive Amendments for Remediation of Metal and Metalloid Contaminants in Soils and Sediments

Peggy O'Day, University of California, Merced

Acknowledgments:

Susana Serrano, Virginia Illera, Tom Stilson, Adam Mazzotti,
Rachel Schlick (UC Merced)

Dimitri Vlassopoulos (Anchor QEA, Portland OR)
Brad Bessinger (S.S. Papadopoulos & Associates, Portland OR)

Stanford Synchrotron Radiation Lightsource (U.S. DOE)

Outline

- Motivation and Background
- Types of Amendments, Sequestration Mechanisms, and Delivery Systems
- Research Highlights
- Future Opportunities and Challenges

In Situ Reactive Amendments:
Motivation for New Technologies & Applications

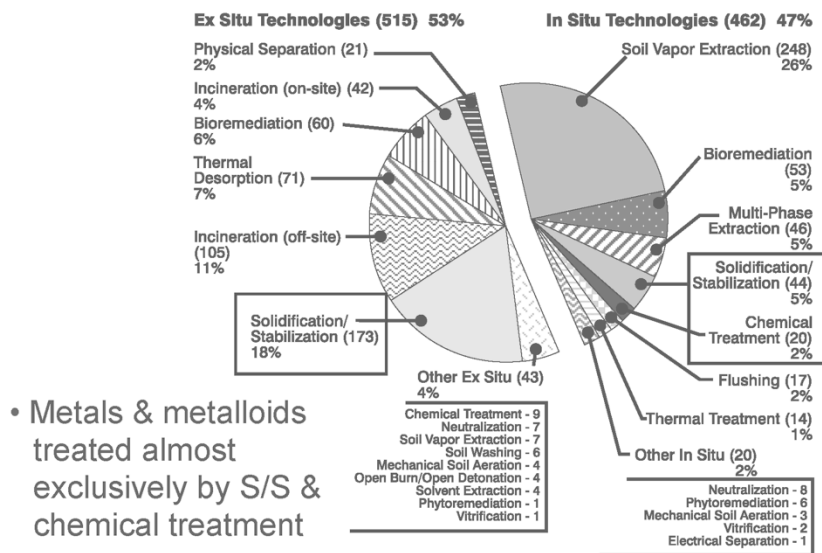
Problematic metal/metalloid contaminants:

As, Hg, U, Cr, Se, Pb, Cd, Ni, Cu, Zn

- Pose persistent hazard at low concentrations; not biodegradable
- Widely dispersed in subaqueous or subsurface environments
- Non-conservative chemical behavior; synergistic/antagonistic behavior not well known
- Toxicity, chemical behavior, bioavailability element-specific
- Limited number of remediation options for subsurface and sub-aqueous sediments

NPL Site Remediation (2007)

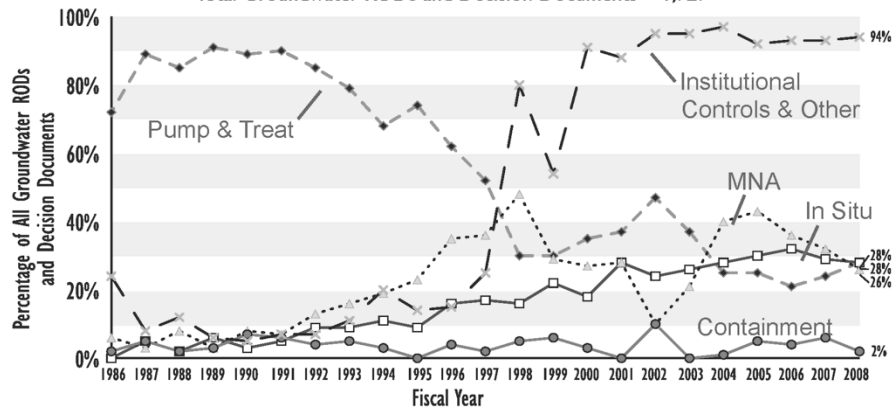
Figure 8: Source Control Treatment Projects
(FY 1982 - 2005)*
Total Number of Projects = 977



USEPA (2007), Treatment Technologies for Site Cleanup, Annual Status Report, 12th Ed.

Figure 6: Trends in RODs and Decision Documents Selecting Groundwater Remedies (FY 1986–2008)

Total Groundwater RODs and Decision Documents = 1,727



- *In situ* treatments: Bioremediation most common, followed by chemical treatment (chemical oxidation, nano-ZVI), air sparging, ozone sparging; multiple treatments often used.
- Most *in situ* groundwater treatments aimed at organic contaminants.

USEPA (2010) Superfund Remedy Report, 13th Ed. 7

In Situ Reactive Amendments for Metals

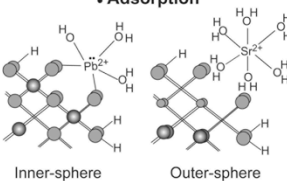
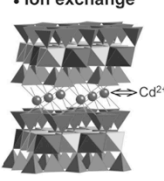
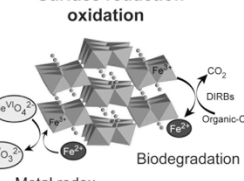
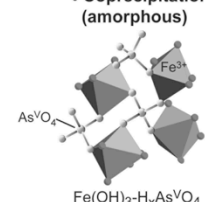
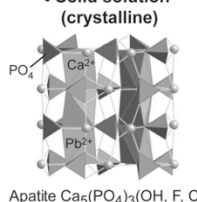
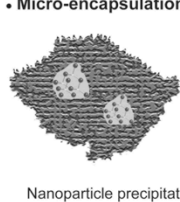
Criteria for effectiveness of *in situ* stabilization:

- Sufficient reduction in bioaccessibility/bioavailability and potential for re-mobilization
- Treatments must have no adverse effects on re-establishment of biota or ecosystems
- Resistant to bioturbation, microbiological alteration/degradation
- Stable under geochemical or hydrologic changes
- Stable for long periods of time

Barriers to adoption:

- Regulatory acceptance and potential liability associated with leaving contaminants in place
- Cost compared with “proven” technologies
- Reluctance to adopt “unproven” technologies, particularly for long-term stabilization
- Effective and cost-effective delivery systems
- Effective and cost-effective post-emplacement monitoring

Molecular-Scale Contaminant Sequestration Mechanisms

Surface Adsorption	<div> <div> • Adsorption  <p>Inner-sphere Outer-sphere</p> </div> <div> • Ion exchange  <p>Cd^{2+}</p> </div> <div> • Surface reduction-oxidation  <p>Metal redox Biodegradation CO_2 DIRBs Organic-C</p> </div> </div>
Structural Incorporation	<div> <div> • Coprecipitation (amorphous)  <p>$\text{As}^{\text{V}}\text{O}_4$ $\text{Fe}(\text{OH})_3\text{-H}_x\text{As}^{\text{V}}\text{O}_4$</p> </div> <div> • Solid solution (crystalline)  <p>PO_4 Ca^{2+} Pb^{2+} Apatite $\text{Ca}_5(\text{PO}_4)_3(\text{OH, F, Cl})$</p> </div> <div> • Micro-encapsulation  <p>Nanoparticle precipitation</p> </div> </div>

- Mechanisms of contaminant uptake and long-term stability not well known for many systems-- opportunities for optimization

O'Day & Vlassopoulos (2010) *Elements*, in press 9

Immobilization by Reactive Amendment Treatments

Traditional Applications:

- Remediation of degraded agricultural soils with lime (CaO or $\text{Ca}(\text{OH})_2$) \pm biosolids
- *Ex situ* waste stabilization and hazardous waste encapsulation (cements, vitrification)
- Contaminant adsorbents: Activated carbon, clay minerals (montmorillonite, vermiculite), zeolites, Al-oxides, Fe

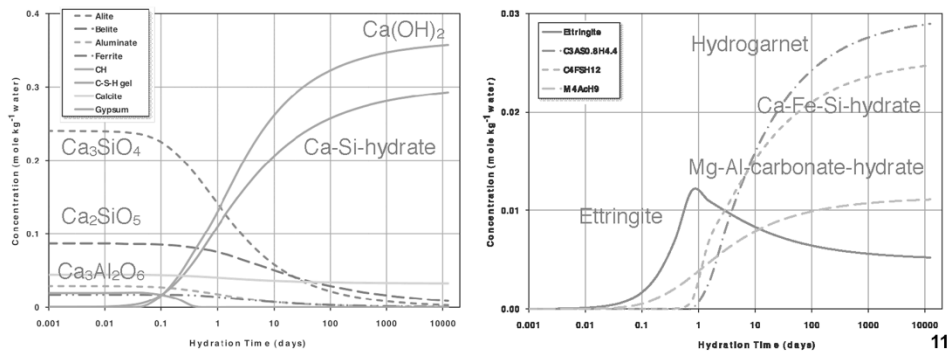
Other types of amendments treatments:

- Apatite-type phosphates, Portland-type cements \pm sulfate, Al-Si caustic amendments, carbonates, Fe^0 , Fe-oxides
- Potential for material recycling (fly ash, industrial residuals, mining residuals)
- May be combined with other remediation approaches, including source removal, capping, barriers, natural attenuation

Portland-type Cements (\pm sulfate)

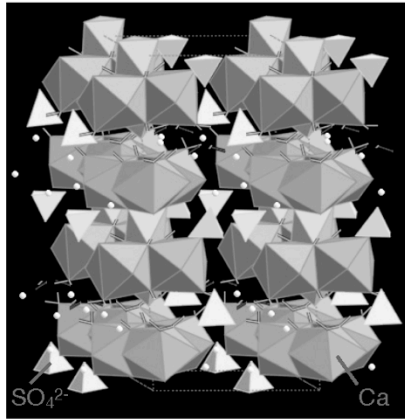
- $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{CaSO}_4 - \text{CaCO}_3 - \text{H}_2\text{O}$ (+ $\text{MgO} - \text{Fe}_2\text{O}_3$)
- Hydration of Ca-Al-silicates, dissolution of sulfate, carbonate
- Products: Mixtures of aluminosilicates, sulfates, carbonates
- Multiple possibilities for contaminant substitution
- Thermodynamics and kinetics important for predicting product phases (LLNL, Empa databases)

Predicted phases during hydration

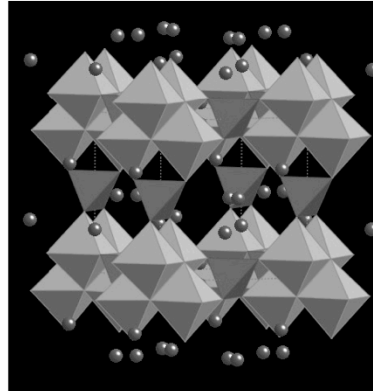


Portland-type Cements + FeSO₄: Reaction Products

- Component system: CaSO₄ - Al₂O₃ - SiO₂ - Fe₂O₃ - H₂O (+MgO)
- Commonly substituted -- opportunities for contaminant uptake
- Structural analogs in arsenate, borate, other oxyanion systems



Ca-Fe Ettringite:
 $\text{Ca}_6[\text{Al}_{1-x}\text{Fe}_x(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$



Pharmacosiderite
 $(\text{K}, \text{Na})(\text{Fe}, \text{Al})_4(\text{AsO}_4)_3(\text{OH}) \cdot 6-7\text{H}_2\text{O}$

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Delivery Systems

- Direct mixing with surface soils/sediments
- Subsurface injection of slurries (phosphate, caustic Si-Al)
- Layers in permeable reactive barriers (\pm other reactive layers)
- Layers in reactive caps (\pm other reactive layers)

Emplacement

- Surface: Auger mixing
- Subsurface: Direct injection
- Subsurface with barrier emplacement
- Subaqueous: Direct broadcast with sand cover
- Subaqueous: Incorporation into polymer/textile mats with sand cover



Field & Lab Amendment Study:
Portland Cement-Sulfate Treatment for
Arsenic Immobilization



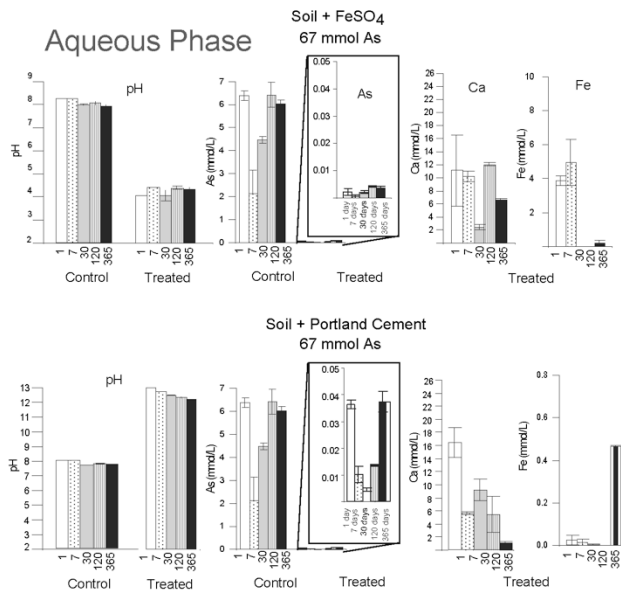
- Source soil As > 5000 mg kg⁻¹ removed
- Treatments in 1992 and 1996



- Soil As 1400 - 1700 mg kg⁻¹
- 10% w/w Type V Portland Cement + 3% FeSO₄·7H₂O
- Amended and capped

Illera et al. (in prep.) 14

Fe-Sulfate-Portland Cement Treatments: Arsenic Laboratory Analog Samples

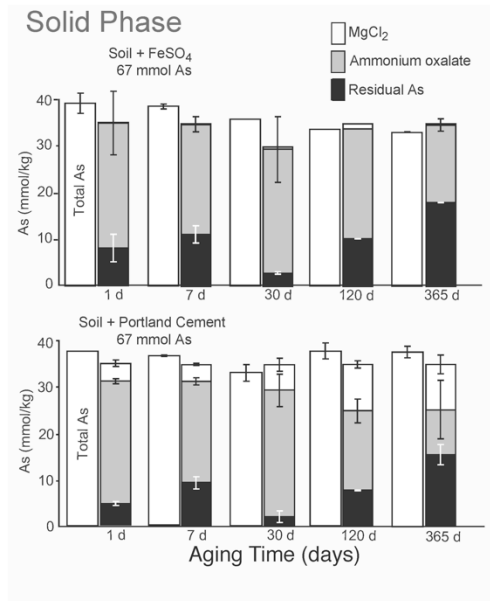


- Unamended soil (~20-200 mg kg⁻¹ As)
- FeSO₄ and/or Portland cement
- Excess As(V) = 50, 2000, 5000 mg kg⁻¹ (6.7, 27, & 67 mM)
- Low pH and high pH
- Aging 1-365 d

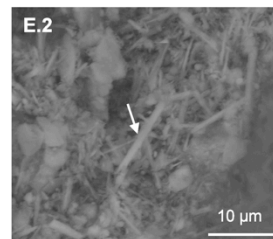
- As(V) uptake rapid (within days)
- Aqueous As < 0.04 mM
- Aqueous Ca, Fe controlled by solubility of precipitated phases

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Fe-Sulfate-Portland Cement Treatments: Arsenic Laboratory Analog Samples



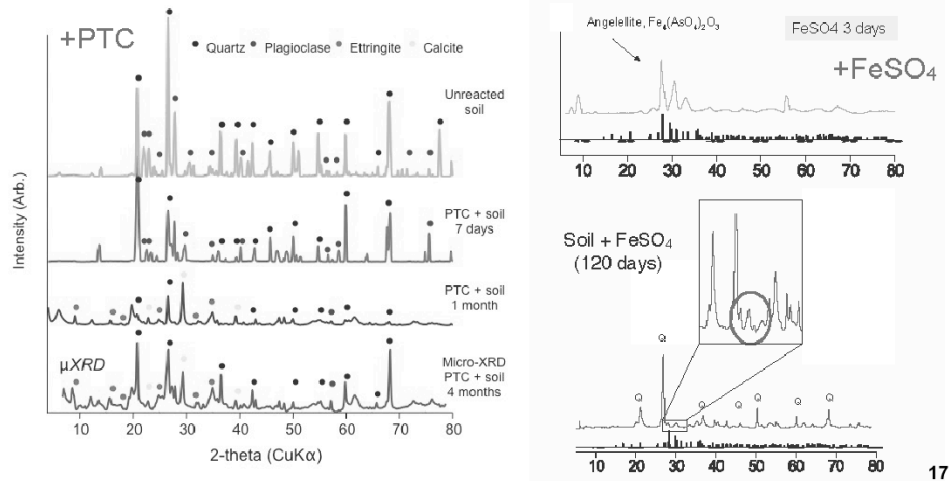
- > 90% uptake of As from solution
- Stepwise sequential extractions with MgCl₂ and Ammonium oxalate
- Conversion into more recalcitrant fractions with aging to 1 year



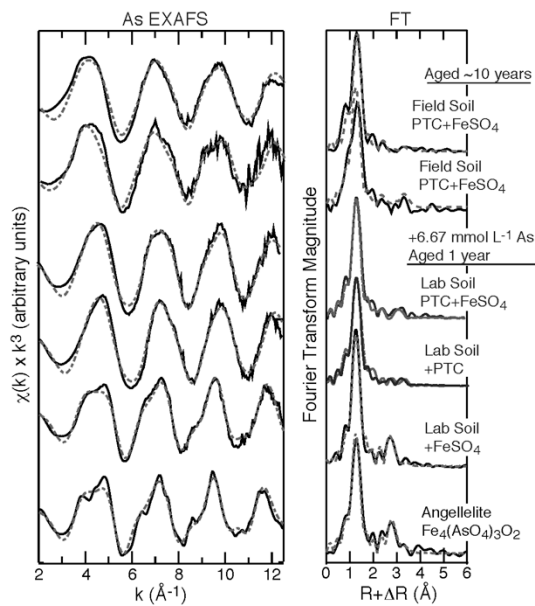
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Fe-Sulfate-Portland Cement Treatments: Arsenic

- PTC \pm FeSO₄: Formation of Ca (\pm Fe)-sulfate-arsenate (ettringite-type) phases within 1 month
- FeSO₄-only: Formation of Fe^{III}-Arsenate phases (angellelite) or Fe^{III}-Arsenate-Sulfate (zykaite) within days



Fe-Sulfate-Portland Cement Treatments: Arsenic



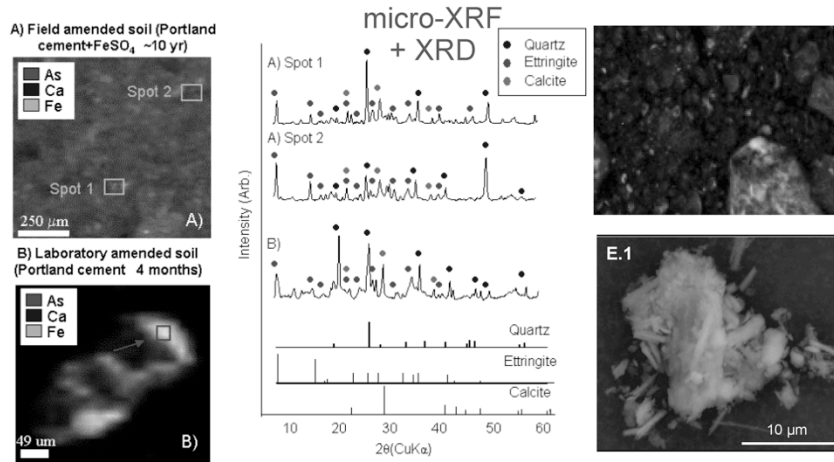
- Field Samples:
As(V) only -- no reduction
Similar to lab PTC
samples

- PTC \pm FeSO₄:
As incorporated into
Ca-sulfate-arsenate
phases

- FeSO₄-only:
As incorporated into
Fe^{III}-arsenate-sulfate
phases

Portland Cement + Fe-Sulfate Treatments: Field data

- Field-amended samples (>10 years) indicate strong sequestration of As(V) and formation of ettringite-type phases
- Bulk EXAFS suggests Ca-Arsenate-rich domains rather than $\text{AsO}_4\text{-SO}_4$ solid solution



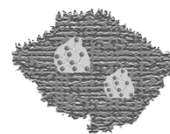
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Summary

Arsenic-Contaminated Soil Amendments

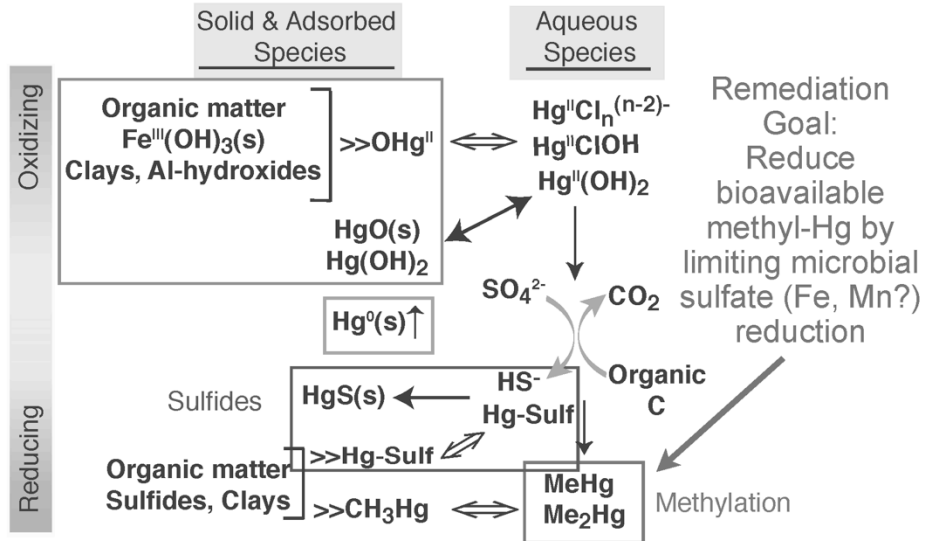
- Arsenic stabilization in Ca-sulfate-arsenate phase with PTC \pm FeSO_4 treatment
- Fast As uptake from solution; formation of neophases within days and aging to stable phase within 1-3 months
- Formation of Fe-arsenate-sulfate phases with FeSO_4 treatment
- Field-amended samples stable as As(V) incorporated into ettringite-type/Ca-arsenate phases for > 10 years (capped, dry); possible microencapsulation
- Stability in reduced aqueous conditions under investigation

• Micro-encapsulation



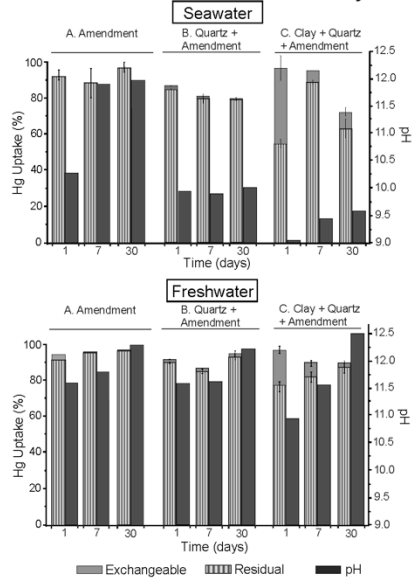
Nanoparticle precipitation

Conceptual Model for Solid/Aqueous Partitioning: Mercury

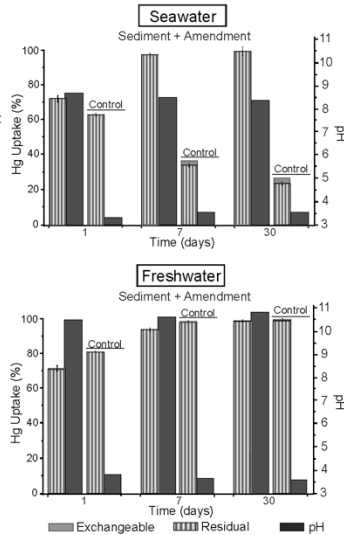


Fe-Sulfate-Portland Cement Treatments: Extractable Mercury

Quartz ± Reference Clays



Sediment



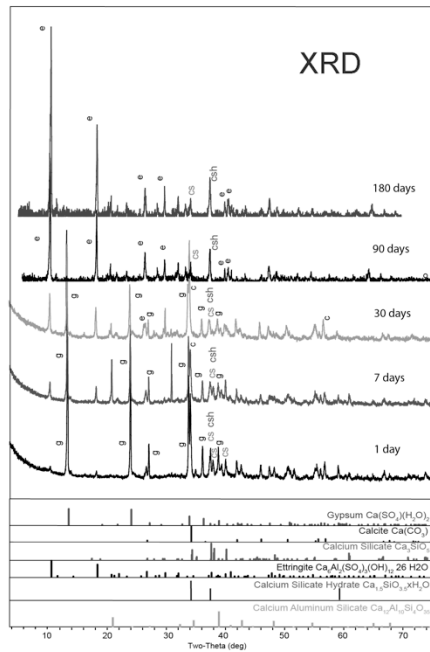
- Hg(II) added (1 or 2 ppm)
- Two-step sequential extraction
- Control: No sediment

- 70-100% Hg uptake
- Small exchangeable Hg fraction

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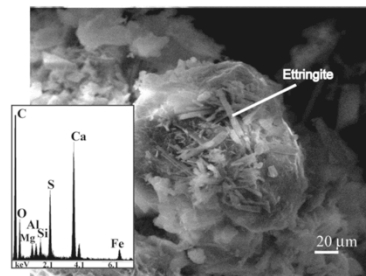
Serrano et al. (in prep.)

Sulfate-Portland Cement Treatments: Mercury



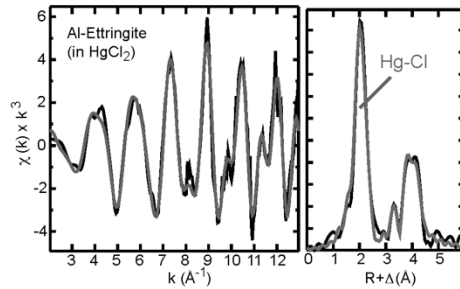
Sediment-free controls:

- ~82-95% of Hg in recalcitrant residual
- Formation of gypsum, Ca-Fe-ettringite, calcite, Ca-Si hydrates
- After 356 days, crystalline solids dominated by ettringite with residual Ca-silicate



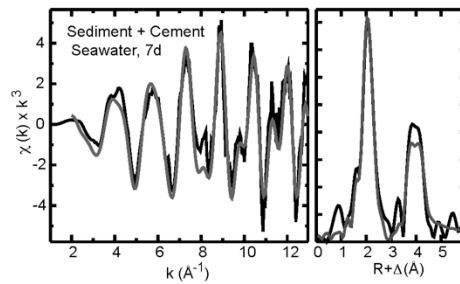
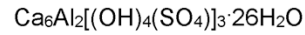
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Fe-Sulfate-Portland Cement Treatments: Mercury L_{III} EXAFS



- Al-Ettringite synthesis
 - $\text{CaO} + \text{Al}_2(\text{SO}_4)_3$
 - 25 ppm Hg(II)
 - adjusted to pH 12 (NaOH)

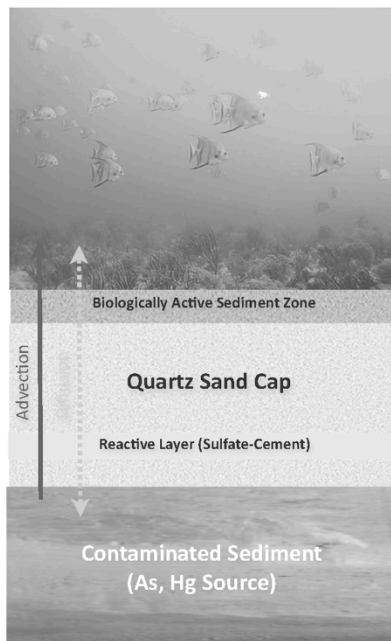
Ca-Al-Ettringite:



- Sediment + Seawater
 - EXAFS not consistent with substitution of Hg for Ca in ettringite
 - Local Hg structure more consistent with Hg-Cl bonding
 - Microencapsulation in ettringite?

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Reactive Caps



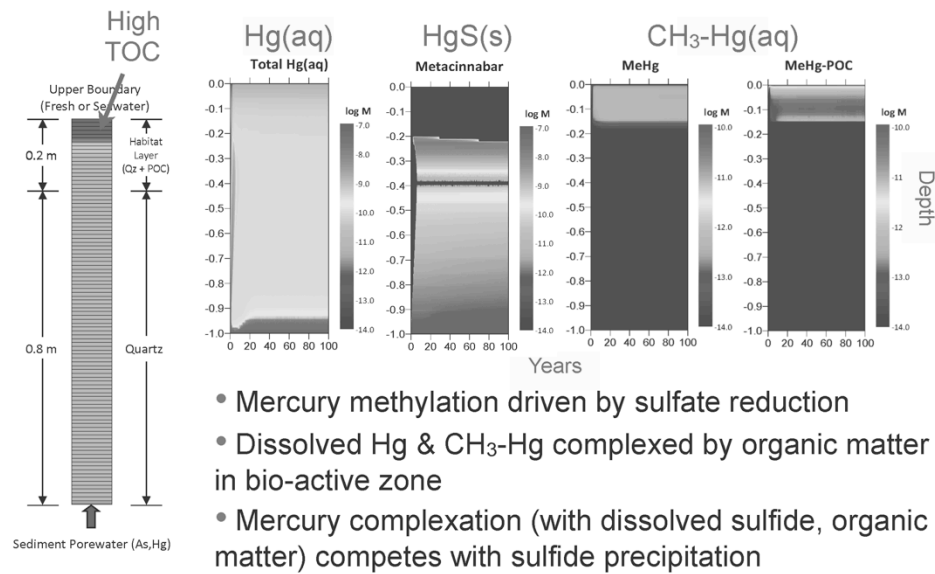
-- Promising technology for subaqueous sediment remediation
-- Opportunities for optimizing contaminant attenuation both chemically and hydrologically

- Habitat layer: Sediment + Sediment/water interface
- Isolation layer:
 - Porewater advection + diffusion
 - May include geosynthetic barrier
- Amendment layer: Reactive or adsorbent material (\pm inert filler)
- Contaminant source sediment

Mercury Reactive Transport Model

- Coupled thermodynamic-kinetic (bio)geochemical processes:
 - Equilibrium homogeneous and heterogeneous speciation
 - Kinetic models for microbial organic carbon (OC) oxidation, denitrification, Fe^{III} reduction, sulfate reduction
- Mercury:
 - Methylation rate tied to sulfate reduction rate (Gilmour et al., 2008); composite de-methylation rate
 - Equilibrium Hg complexation with OC, sulfide
 - Equilibrium Hg adsorption to POC
- Transport: 1-dimensional
 - Diffusion-only; Advection + Diffusion
 - Sediment cap only; no reactive amendment layer
- Code: PHREEQC (USGS) with modified LLNL database

Mercury Sediment Cap Modeling: 100 years, seawater scenario, advection + diffusion



Bessinger et al. (in review)

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Summary: Opportunities

- Site-specific design of treatments tailored for particular contaminants and biogeochemical compatibility
- Cements, aluminosilicates, and other phases offer possibilities for solid-solution or encapsulation of contaminants
- Combination and optimization of treatment methods: amendments, permeable barriers, reactive caps, natural attenuation
- Must be cost-competitive with existing technologies!

Needs and Knowledge Gaps

- Long-term stability and bioavailability reduction under variable conditions must be verified
- Improvements in delivery systems for site-specific conditions
- Improvements in monitoring and assessment of risk reduction
- Regulatory, industry, and stakeholder acceptance and willingness to employ novel treatments

Reactive Geocomposite Sediment Mats: Adaptable Remediation Tools

Thomas C. Sheahan

Northeastern University



November 17, 2010



Northeastern

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Civil & Environmental Engineering

Outline of Talk

- Introduction to reactive mats
- Development of testing device/protocols
- Research Highlights and Results
 - PCB bioavailability exposure tests
 - PAH concentration tests
 - modeling (mechanics/contaminant x-port)
- Future Work



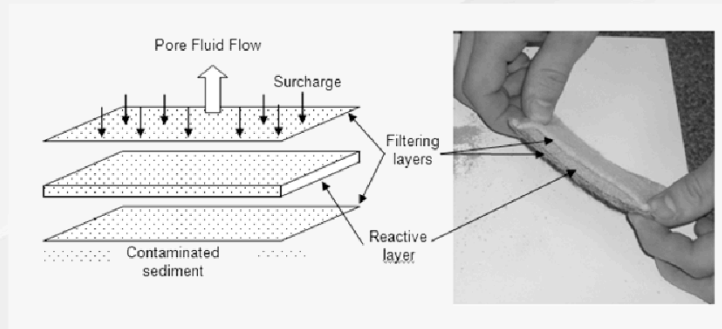
Conventional Aquatic Sediment Treatment

- Environmental Dredging
 - significant re-suspension potential
 - leakage
 - sediment disturbance
 - large disposal volume
- Geomaterial capping
 - erosion potential
 - navigation hazard
- Natural Attenuation
 - no action taken
 - long duration
 - requires favorable environmental conditions

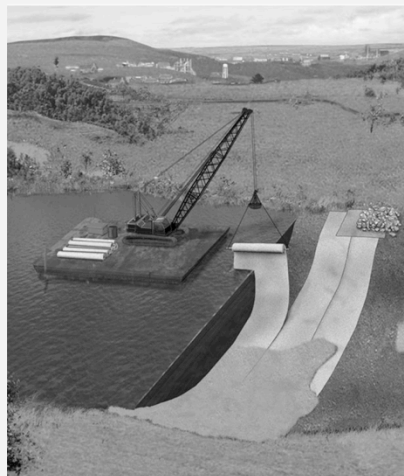


Introduction to Reactive Core Mats

- Reactive/adsorptive matl. with filtering geotextiles
- Placed on top of contaminated sediment
- Advection/diffusion draws pore fluid through RCM



Reactive Core Mat – Field Placement



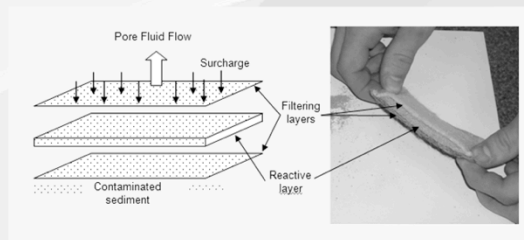
Placement on Subaqueous Sediment (courtesy of CETCO®)



Advantages of Reactive Core Mats

RCM Advantages over traditional caps:

- can neutralize/adsorb/isolate contaminants
- prevent migration of fines
- foundation for new, overlying sediment
- “designer” reactive core for diff. contaminants



State of RCM Knowledge & Use

- Use is becoming more common

However...

- Remediation/isolation efficacy ...
- Long-term capacity...
- Contaminants for which RCMs appropriate ...
- Modeling of processes and scalability...

...are not well understood

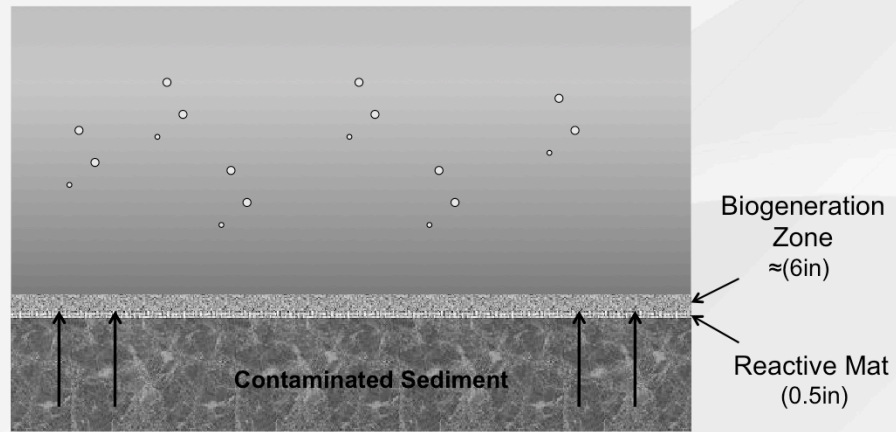


Research Approach

- Develop benchtop device, testing protocols
- Test efficiency of reactive mat
 - Isolation of contaminants
 - Remediation of contaminated sediment
 - Bioavailability in overlying sediment biogeneration zone
- Measure RCM reactive capacity
- Analytically model process for field scalability

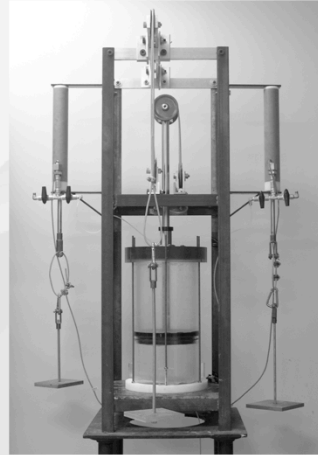
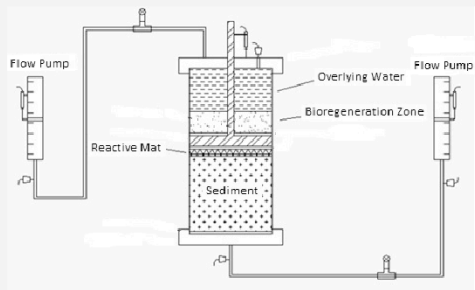


Reactive Core Mat – Application Schematic

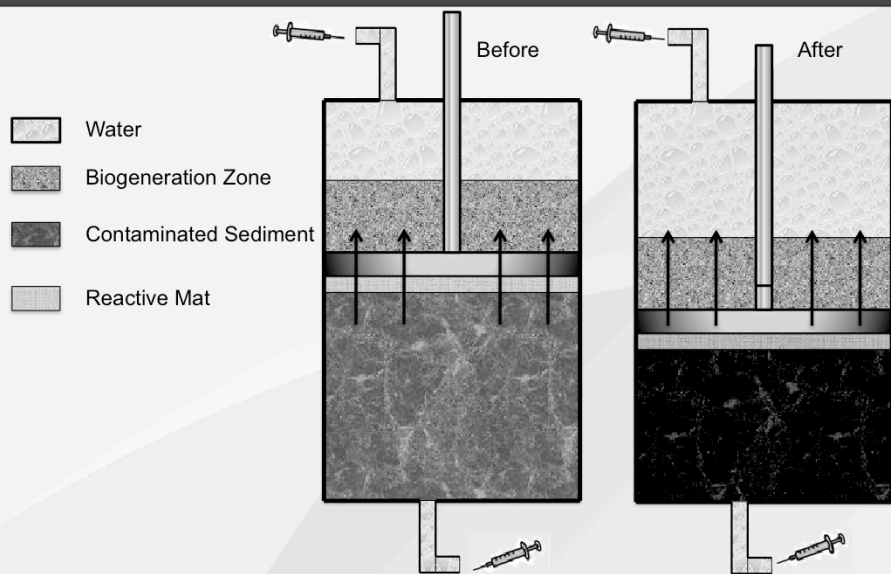


Thick, can include reactive materials, subject to erosion

New Testing Device - ICSTAC



ICSTAC Physical Model




Northeastern


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Civil & Environmental Engineering


ICSTAC Physical Model



Northeastern
University



Harvard School of Public
Health

 Northeastern

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Civil & Environmental Engineering

Bioaccumulation Testing

▪ Process

- Day 1 - Start 14-day incubation period
- Day 15 - Worms added
- Day 43 - Worms frozen and acid digested

Worm Species

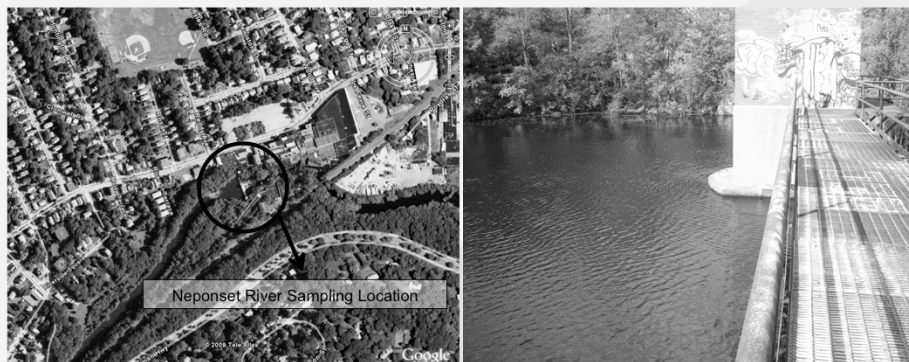
- *Lumbriculus variegatus*
fresh-water
deposit-feeding



Courtesy Harvard School of Public Health



Sediment Sampling and Preparation



Tilestone & Hollingsworth Dam, Neponset River MA DEP Site (PCB)
(5 sets of sampling performed)

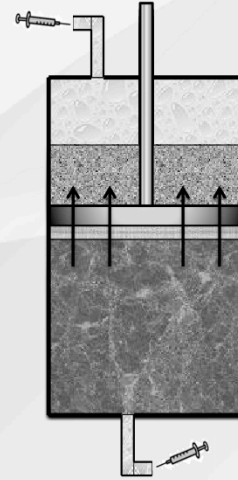
Sediment Sampling and Preparation

- Early tests used natural sediment
≈ 10 ppm PCB
- Then moved to naphthalene spiking
 - higher solubility – better test of RCM
 - (much) lower chemical costs
 - safer to work with in high concentrations
- 14 day rotational mixing

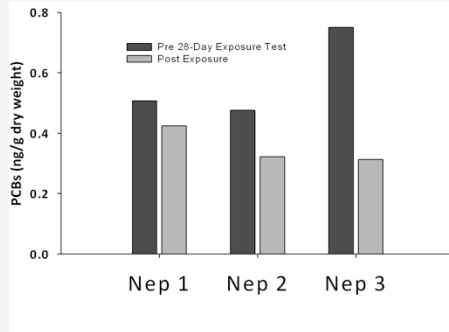


Research Results - PCB

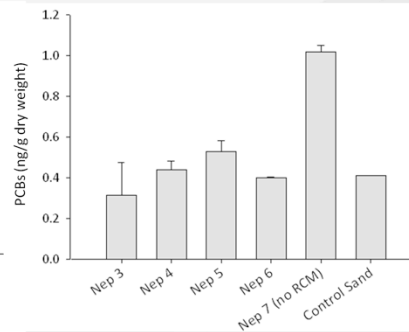
- Bioavailability based on worm exposure tests
- Natural sediment (no spiking)
- Results from
 - original sediment
 - overlying sand, worms pre-/post-treatment
- Data difficult to interpret – low concentrations



Research Results - PCB



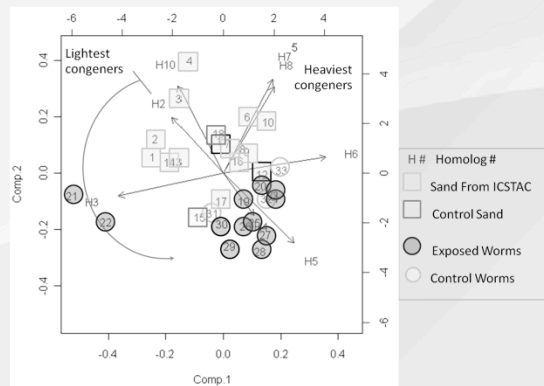
Sand: Pre-/Post exposure
Shows PCB release from sand
to worms/water



Sand w/trout chow post-test
Indicates sand with RCM → same
results as control

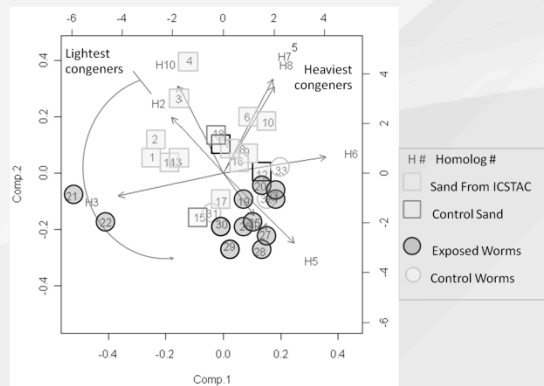
Research Results – PCB – PCA Analysis

- Data analysis in progress:
Principal Component Analysis (PCA)
- Differential partitioning of PCB congeners



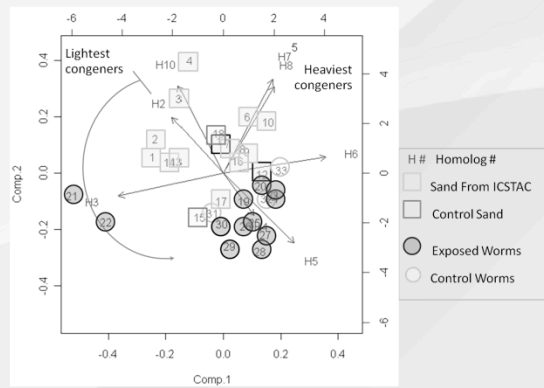
Research Results – PCB – PCA Analysis

- Compresses data without much loss of information
- Presents data in Principle Component space
- Enables visualization of data



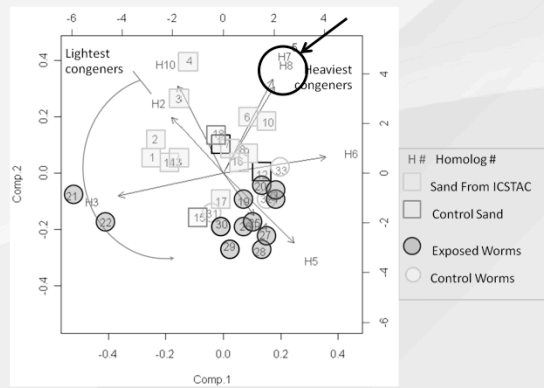
Research Results – PCB – PCA Analysis

- Vectors =
(relative position of homolog groups from all data) vs.
(individual sand & worm data from ICSTAC tests)



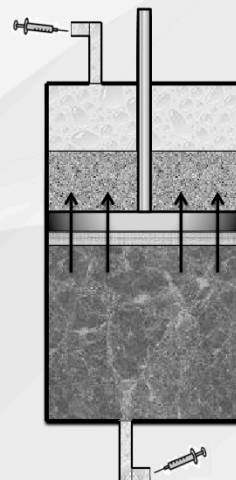
Research Results – PCB – PCA Analysis

- Example: If sample high in homolog group H7 (7 chlorines) → likely to be high in H8 (8)
- Samples 6 and 10 more likely to contain H7 and H8

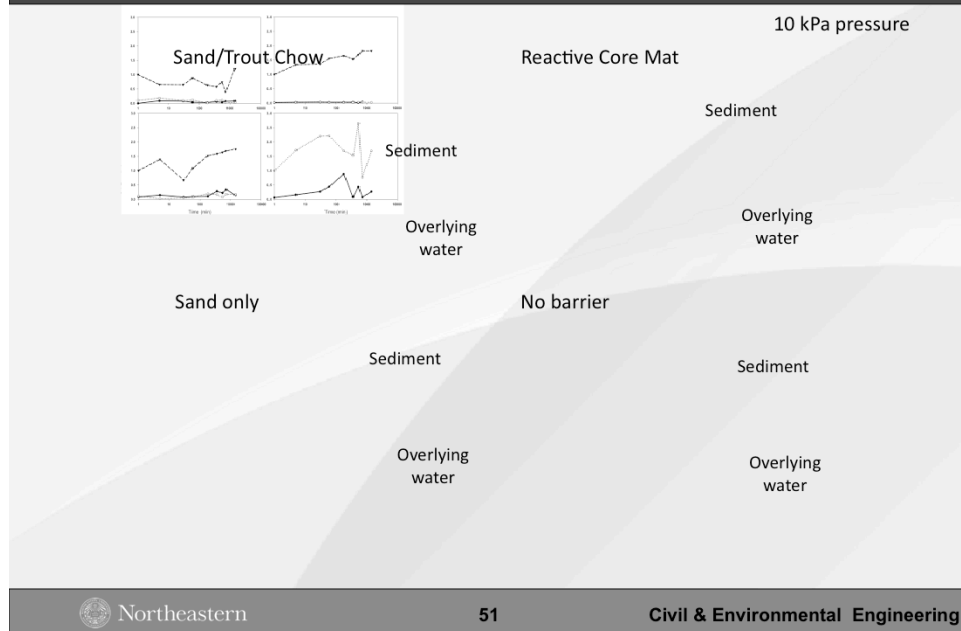


Research Results - PAH

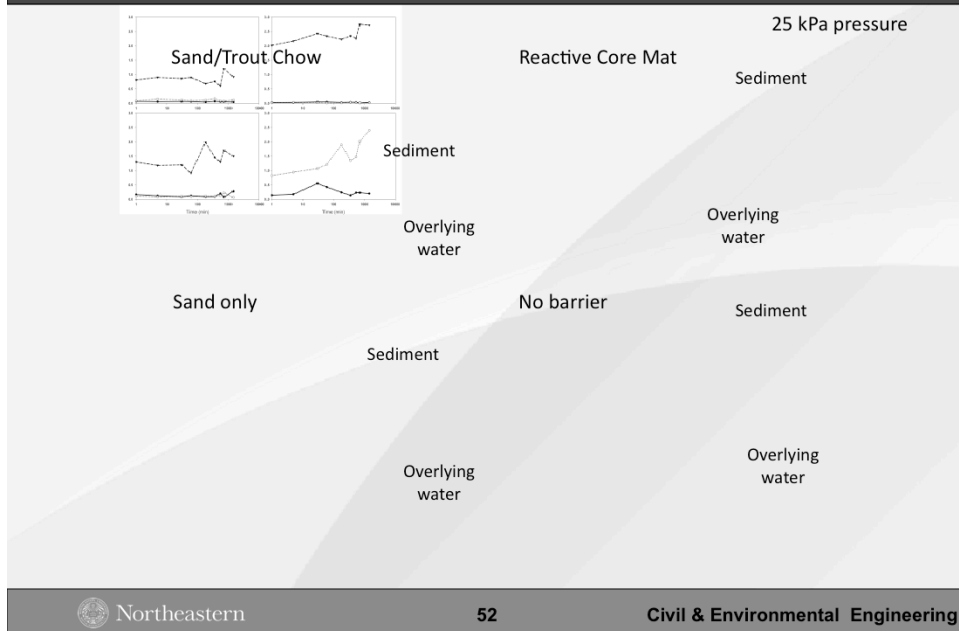
- Spiked natural sediment
- 250 mg naphthalene/kg dry sediment
- Sampled from ICSTAC during testing
- Concentrations analyzed using GC-MS
- Plotted normalized C's



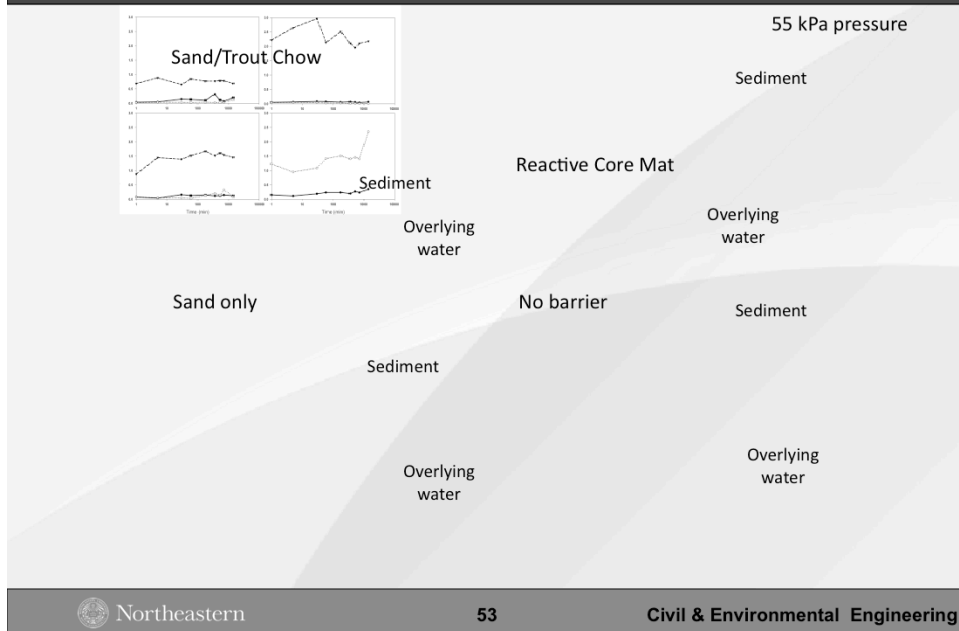
Research Results – PAH Concentrations



Research Results – PAH Concentrations



Research Results – PAH Concentrations



Research Results – Modeling of Process

- Phase 1 (complete)

Small Strain Consolidation

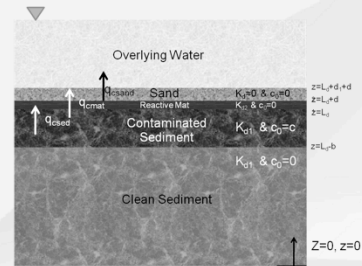
Reactive Mat Layer

Bioturbation effect in sand layer

Advective flux coupled contaminant transport

Builds on work by Alshawabkeh et al. (2005)

Sample results in Meric et al (2010)



Research Results – Modeling of Process

- Phase 2 (in progress)

Large Strain Consolidation

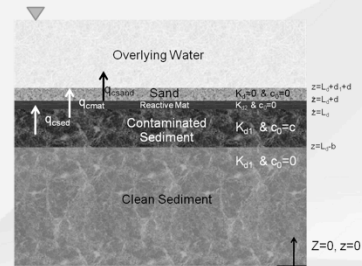
Integrates RCM

Bioturbation effect in sand

Non-linear constitutive relation-based sorption

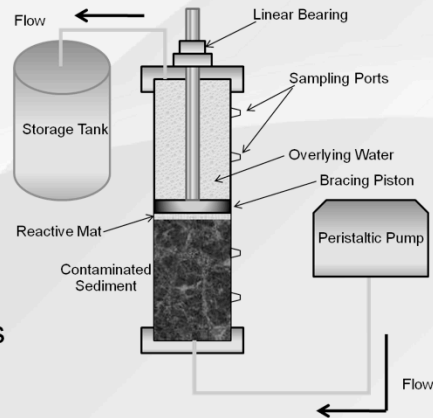
Variable initial contamination profile by depth

Advective flux-coupled contaminant transport



Future Research – Constant Flow Column

- Tests breakthrough, RCM capacity
- 2.5" diameter column
accelerate the process
scale time
measure breakthrough
- 1 mL/min = 1 pore vol./day
- Goals:
reduce sediment/test
characterize RCM capacity
model upflow site conditions



Summary

- New ICSTAC device & protocols developed
- Experimental
 - RCM shows good PAH sequestration
 - Biouptake of PCB may be transformative/selective
- Analysis methods being adapted to understand results
- Mechanics model adapted and validated
- New column device will further test RCM capabilities



Future Research

- Experimental
 - PAH exposure results being analyzed
 - constant flow column tests beginning
- Analysis
 - water concentrations, PCA for PCB biouptake studies
- Modeling
 - more advanced multi-process, multi-layer coupling
 - use for field scaling, long-term performance prediction
- Salt water testing – New Bedford Harbor

Participants and Sponsorship

Participants

Northeastern University: Akram Alshawabkeh, Dogus Meric,
Sara Barbuto, Mansoureh Norouzirad

Harvard School of Public Health: Jim Shine

EPA Region 1: Steve Mangion

CETCO: Chuck Hornaday, Jerry Darlington, Jim Olsta

Disclaimer

The work described in this paper is supported by the National Institute of Environmental Health Sciences under grant number R01ES16205.

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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



The screenshot shows a web form titled "EPA Technology Innovation Program". The header includes the EPA logo and the text "U.S. EPA Technical Support Project Engineering Forum Green Remediation: Opening the Door to Field Use Session C (Green Remediation Tools and Examples) Seminar Feedback Form". A message states: "We would like to receive any feedback you might have that would make this service more valuable. Please take the time to fill out this form before leaving the site." The form contains several input fields: "First Name:" (with "Jan" entered), "Last Name:" (with "Bent" entered), "Daytime Phone Number:" (with "703-603-8924" entered), and "Email Address:" (with "jbent.amr@epa.gov" entered). Below these fields is a checkbox labeled "Please send a copy of my feedback confirmation as a record of my participation to this address." which is currently unchecked. The form also includes a "Date of Seminar:" field with the value "October 15, 2009" and a "Delivery Media:" field.

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