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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)

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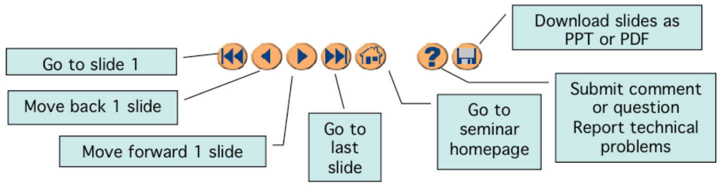

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Reactive Amendments for Remediation of Metal and Metalloid Contaminants in Soils and Sediments

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. Papadopulos & Associates, Portland OR)

Stanford Synchrotron Radiation Lightsource (U.S. DOE)

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Outline

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

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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

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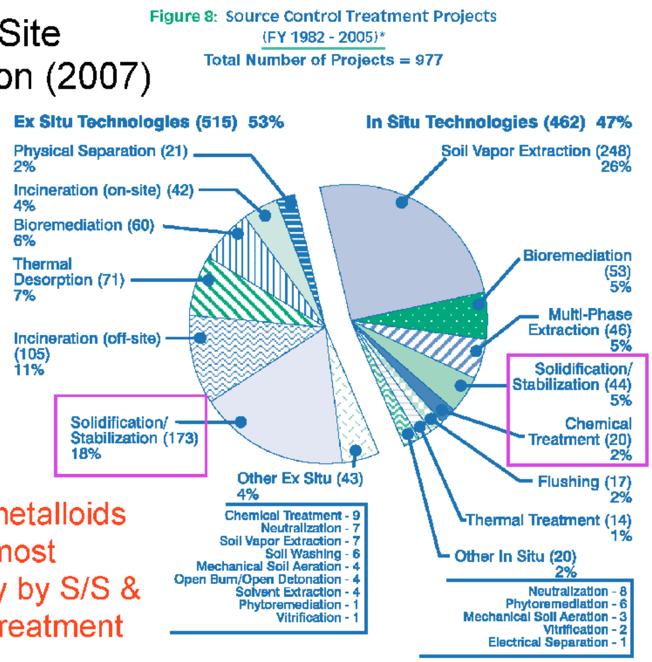
NPL Site Remediation (2007)



- Metals & metalloids treated almost exclusively by S/S & chemical treatment

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

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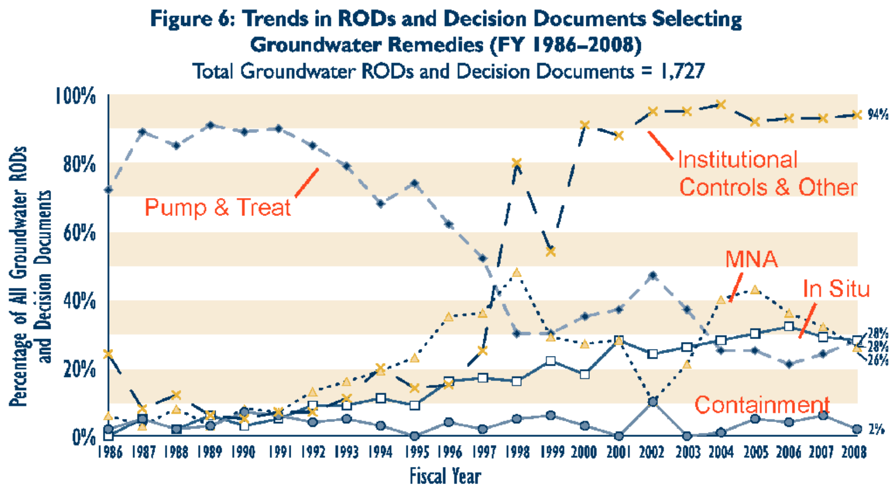

- *In situ* treatments: Bioremediation most common, followed by chemical treatment (chemical oxidation, nano-ZVI), air sparging, ozone sparging; multiple treatments often used.
- Most *in situ* groundwater treatments aimed at organic contaminants.

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

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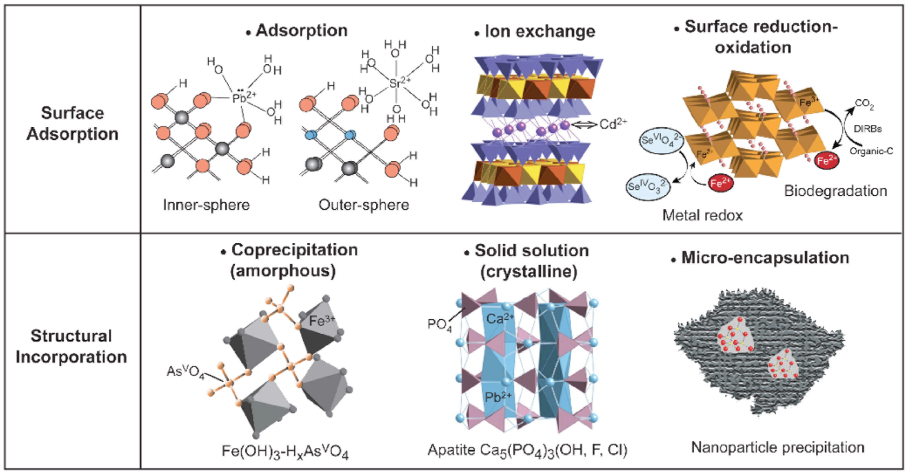
Molecular-Scale Contaminant Sequestration Mechanisms



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

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

Immobilization by Reactive Amendment Treatments

Traditional Applications:

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

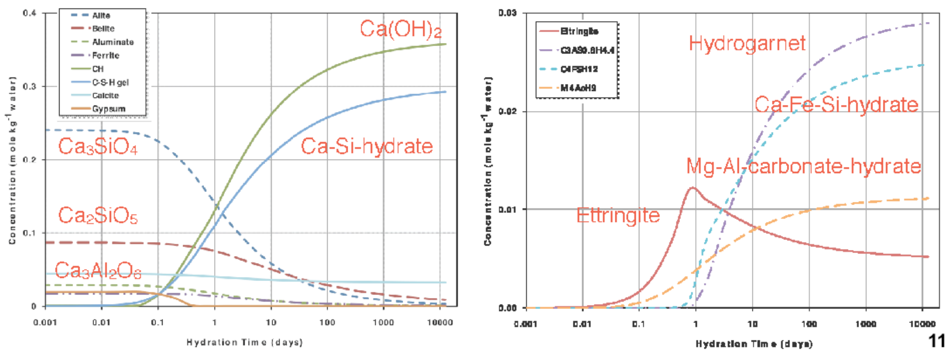
Other types of amendments treatments:

- Apatite-type phosphates, Portland-type cements ± sulfate, Al-Si caustic amendments, carbonates, Fe°, 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 (± sulfate)

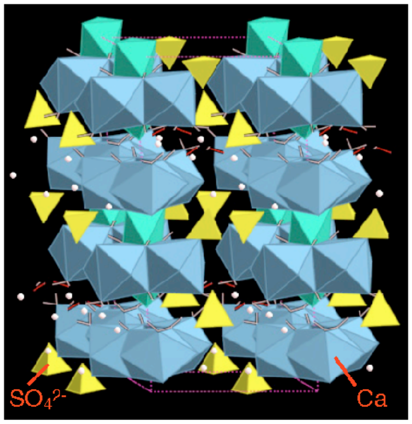
- CaO - Al_2O_3 - SiO_2 - $CaSO_4$ - $CaCO_3$ - H_2O (+ MgO - Fe_2O_3)
- Hydration of Ca-Al-silicates, dissolution of sulfate, carbonate
- Products: Mixtures of aluminosilicates, sulfates, carbonates
- Multiple possibilities for contaminant substitution
- Thermodynamics and kinetics important for predicting product phases (LLNL, Empa databases)

Predicted phases during hydration

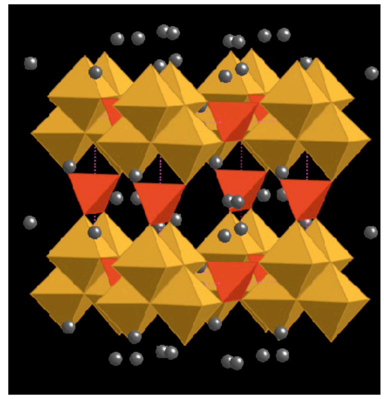


Portland-type Cements + $FeSO_4$: Reaction Products

- Component system: $CaSO_4$ - Al_2O_3 - SiO_2 - Fe_2O_3 - H_2O (+MgO)
- Commonly substituted -- opportunities for contaminant uptake
- Structural analogs in arsenate, borate, other oxyanion systems



Ca-Fe Ettringite:
$Ca_6[Al_{1-x}Fe_x(OH)_6]_2(SO_4)_3 \cdot 26H_2O$



Pharmacosiderite
$(K,Na)(Fe,Al)_4(AsO_4)_3(OH) \cdot 6\text{-}7H_2O$

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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 (± other reactive layers)
- Layers in reactive caps (± 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

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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% $FeSO_4.7H_2O$
- Amended and capped

Illera et al. (in prep.) 14

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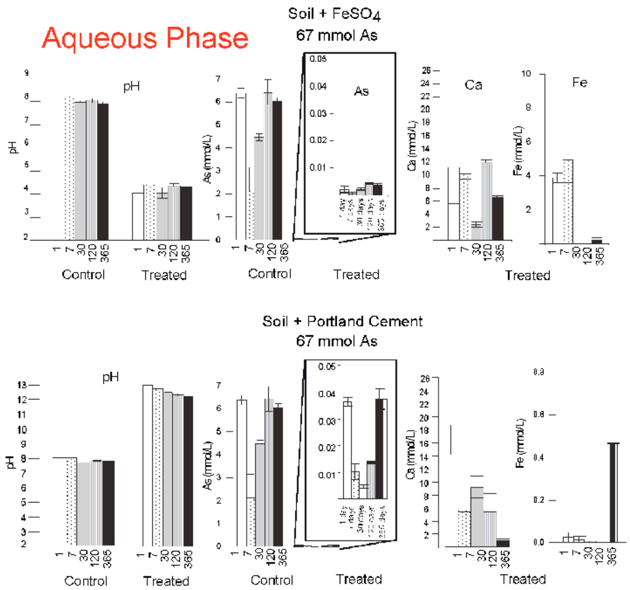
Fe-Sulfate-Portland Cement Treatments: Arsenic Laboratory Analog Samples



- Unamended soil (~20-200 mg kg^{-1} As)
- $FeSO_4$ 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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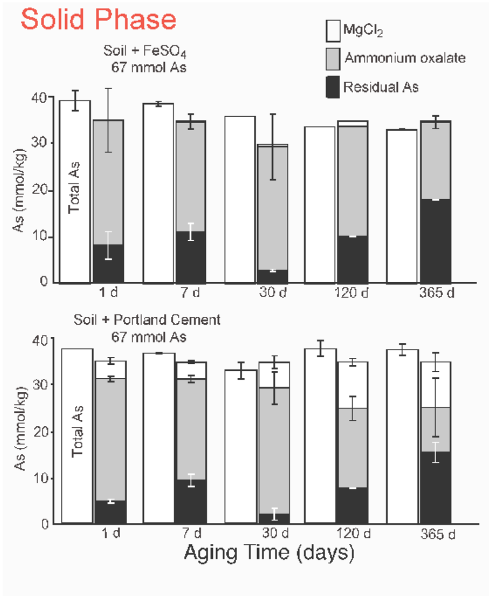
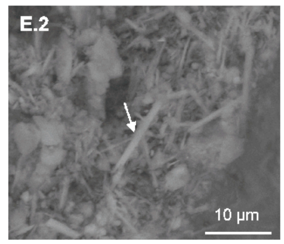
Fe-Sulfate-Portland Cement Treatments: Arsenic Laboratory Analog Samples



- > 90% uptake of As from solution
- Stepwise sequential extractions with $MgCl_2$ and Ammonium oxalate
- Conversion into more recalcitrant fractions with aging to 1 year



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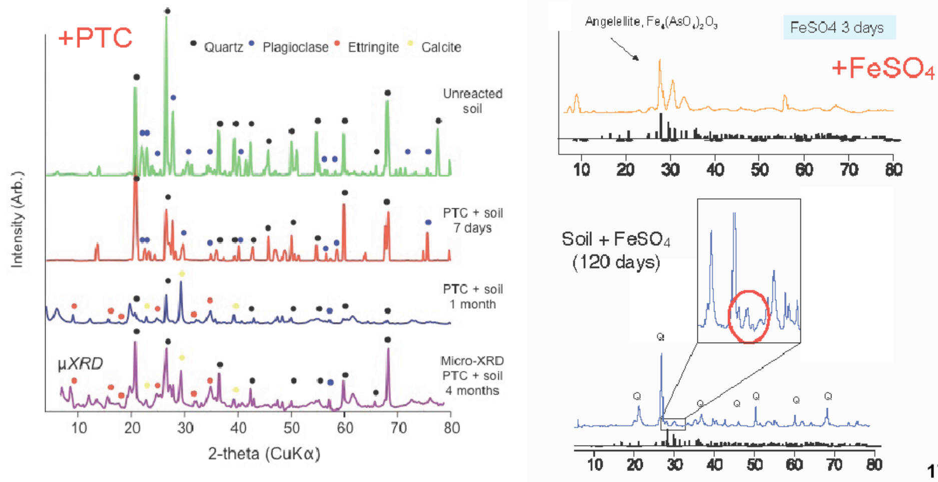
Fe-Sulfate-Portland Cement Treatments: Arsenic

- PTC ± $FeSO_4$: Formation of Ca (±Fe)-sulfate-arsenate (ettringite-type) phases within 1 month
- $FeSO_4$-only: Formation of Fe^{III}-Arsenate phases (angellelite) or Fe^{III}-Arsenate-Sulfate (zykaite) within days



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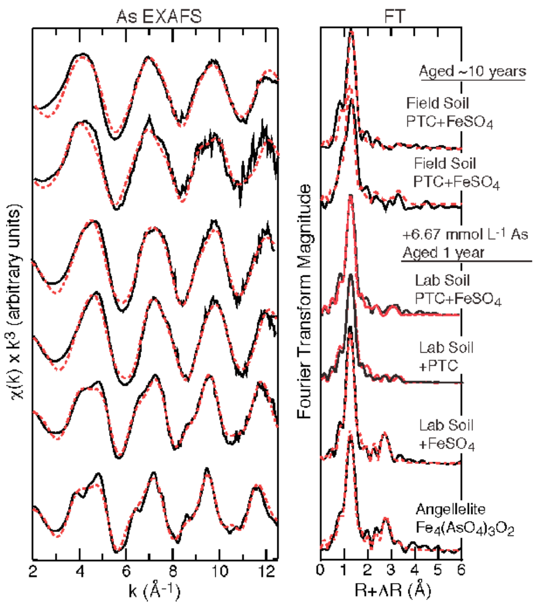
Fe-Sulfate-Portland Cement Treatments: Arsenic



- Field Samples:
  As(V) only -- no reduction
  Similar to lab PTC samples
- PTC ± $FeSO_4$:
  As incorporated into Ca-sulfate-arsenate phases
- $FeSO_4$-only:
  As incorporated into Fe^{III}-arsenate-sulfate phases

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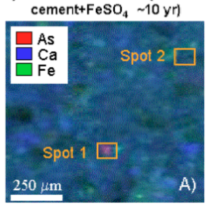
Portland Cement + Fe-Sulfate Treatments: Field data

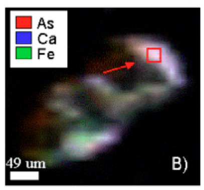
- Field-amended samples (>10 years) indicate strong sequestration of As(V) and formation of ettringite-type phases
- Bulk EXAFS suggests Ca-Arsenate-rich domains rather than AsO_4-SO_4 solid solution

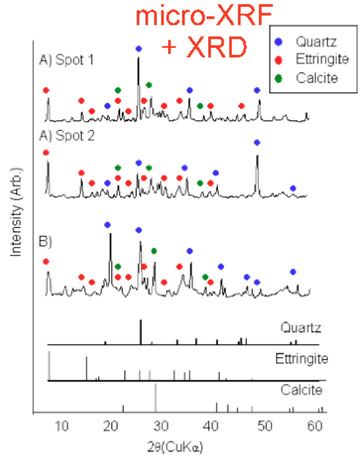
micro-XRF + XRD

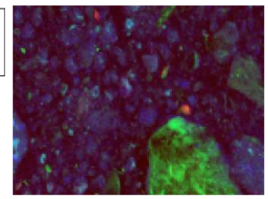
A) Field amended soil (Portland cement+$FeSO_4$ ~10 yr)

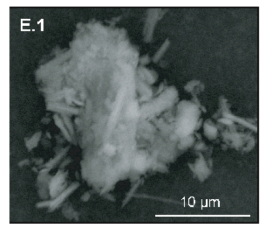


B) Laboratory amended soil (Portland cement 4 months)









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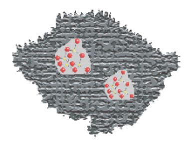
Summary
Arsenic-Contaminated Soil Amendments

- Arsenic stabilization in Ca-sulfate-arsenate phase with PTC ± $FeSO_4$ 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

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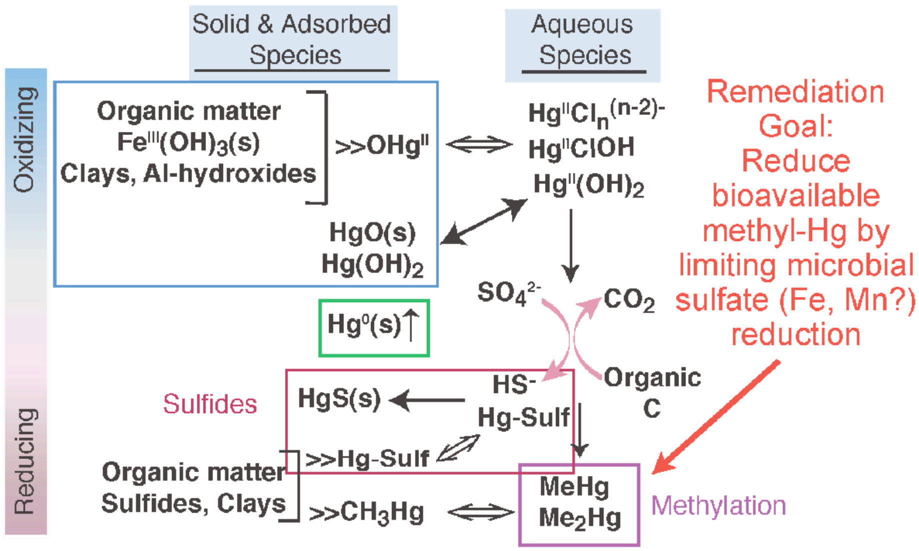
Conceptual Model for Solid/Aqueous Partitioning: Mercury



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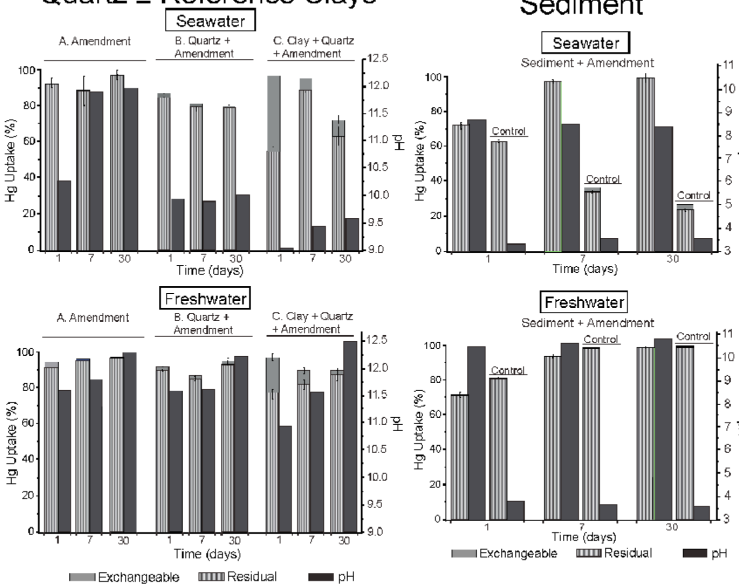
Fe-Sulfate-Portland Cement Treatments: Extractable Mercury

Quartz ± Reference Clays

Sediment



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

- 70-100% Hg uptake
- Small exchange-able Hg fraction

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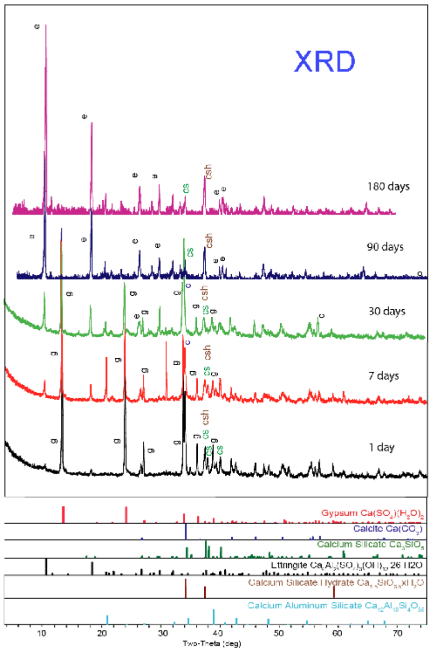
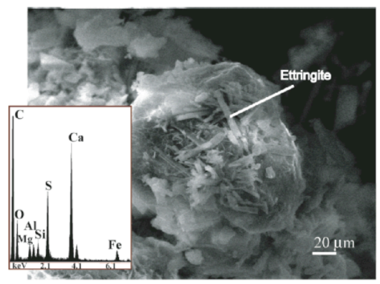
Serrano et al. (in prep.)

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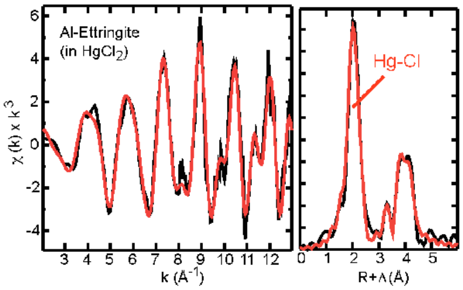
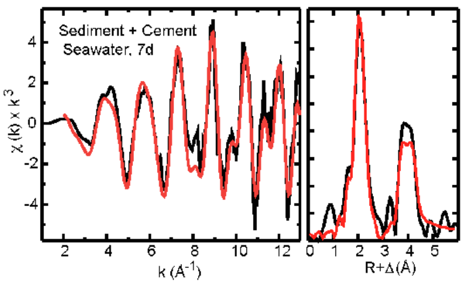
Fe-Sulfate-Portland Cement Treatments: Mercury L_{III} EXAFS



- Al-Ettringite synthesis
  - -- CaO + $Al_2(SO_4)_3$
  - -- 25 ppm Hg(II)
  - -- adjusted to pH 12 (NaOH)

Ca-Al-Ettringite:

$Ca_6Al_2[(OH)_4(SO_4)]_3 \cdot 26H_2O$



- 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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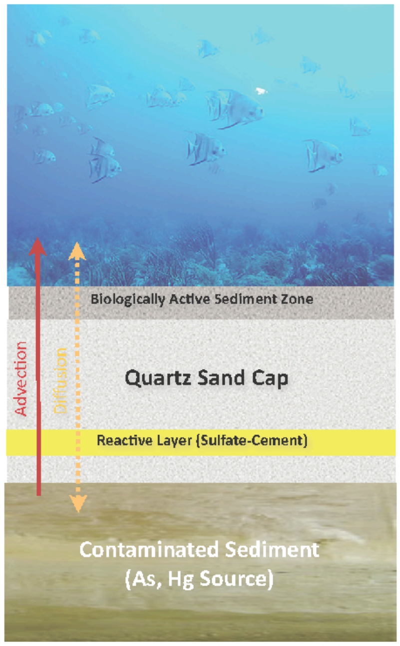
Reactive Caps



-- 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 (± inert filler)
- Contaminant source sediment

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Mercury Reactive Transport Model

- Coupled thermodynamic-kinetic (bio)geochemical processes:
  - -- Equilibrium homogeneous and heterogenous 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

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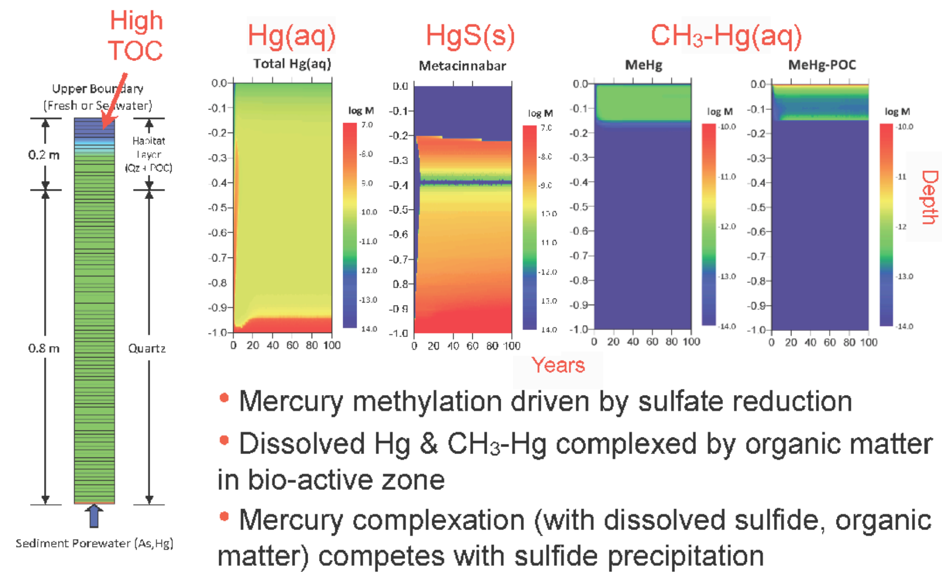
Mercury Sediment Cap Modeling:
100 years, seawater scenario, advection + diffusion



- Mercury methylation driven by sulfate reduction
- Dissolved Hg & CH_3-Hg complexed by organic matter in bio-active zone
- Mercury complexation (with dissolved sulfide, organic matter) competes with sulfide precipitation

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

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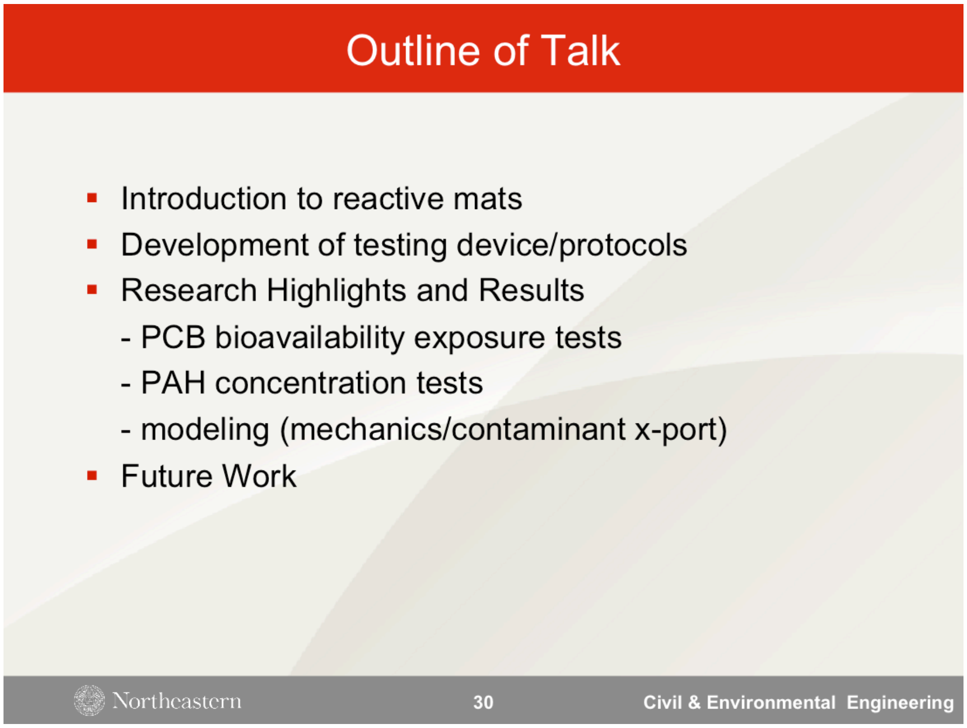
Reactive Geocomposite Sediment Mats: Adaptable Remediation Tools

Thomas C. Sheahan

Northeastern University

NIEHS National Institute of Environmental Health Sciences

November 17, 2010


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
Northeastern
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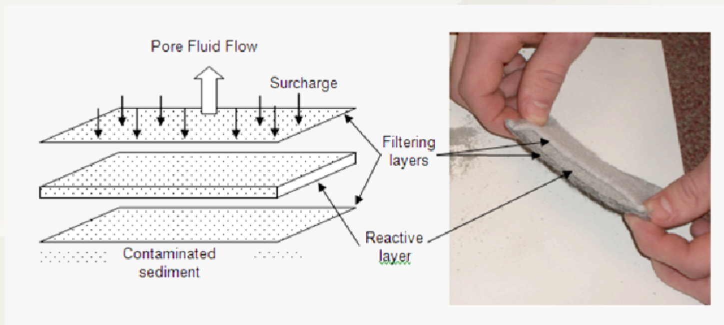
Civil & Environmental Engineering

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



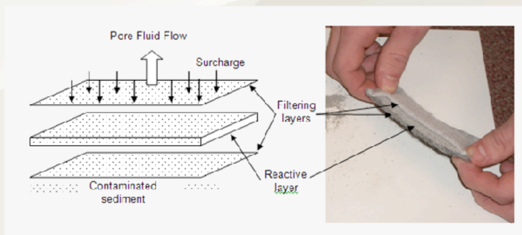
Reactive Core Mat – Field Placement

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

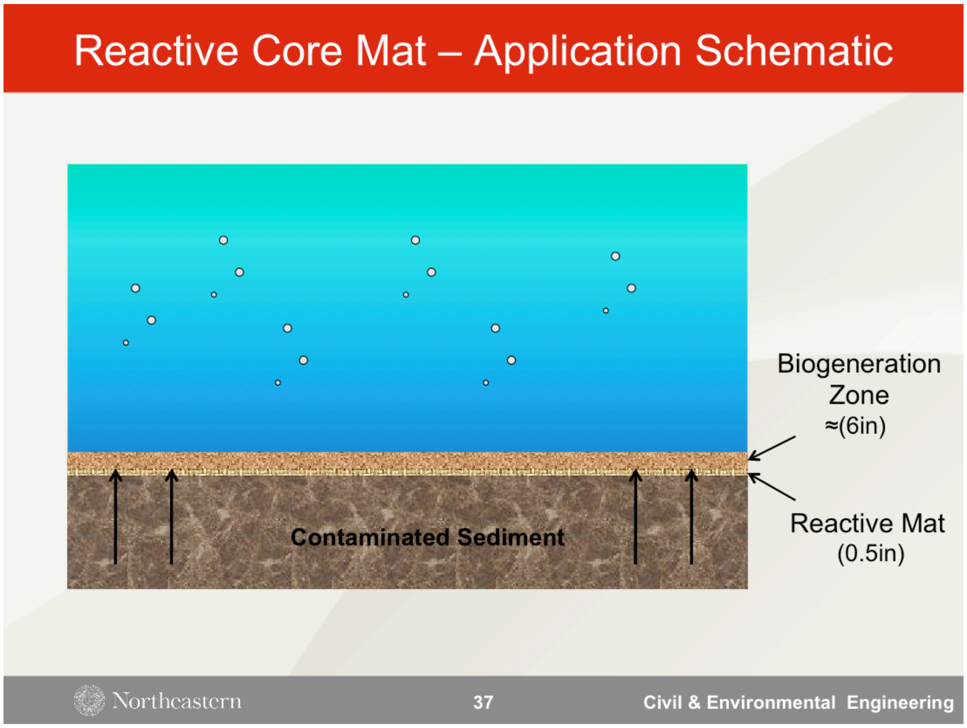
However…

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

…are not well understood

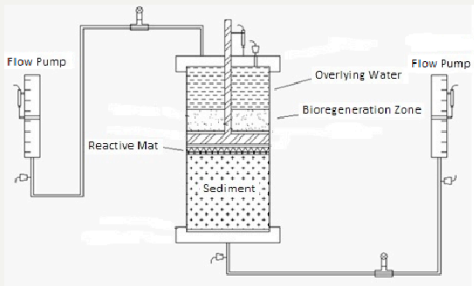
Research Approach

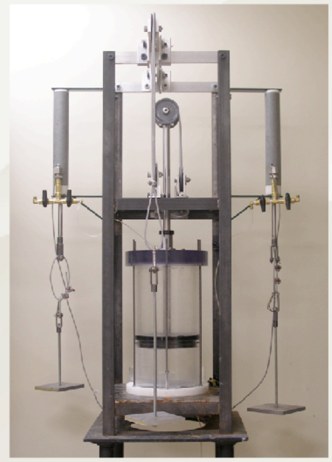
- Develop benchtop device, testing protocols
- Test efficiency of reactive mat
  - Isolation of contaminants
  - Remediation of contaminated sediment
  - Bioavailability in overlying sediment biogeneration zone
- Measure RCM reactive capacity
- Analytically model process for field scalability

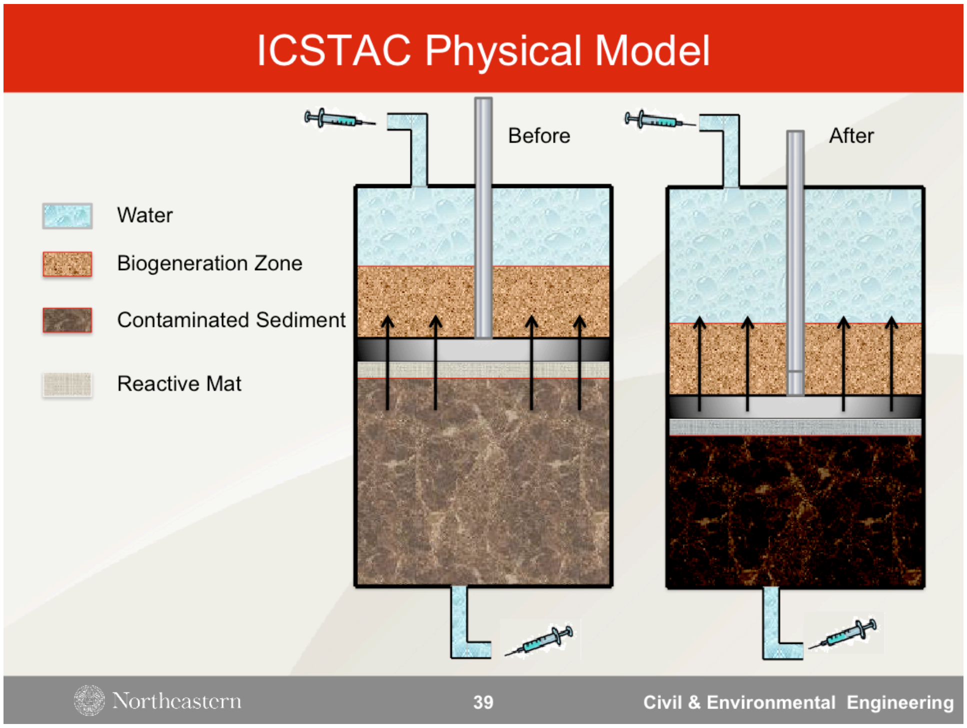


Thick, can include reactive materials, subject to erosion

New Testing Device - ICSTAC






ICSTAC Physical Model
Before
After
Water
Biogeneration Zone
Contaminated Sediment
Reactive Mat
Northeastern
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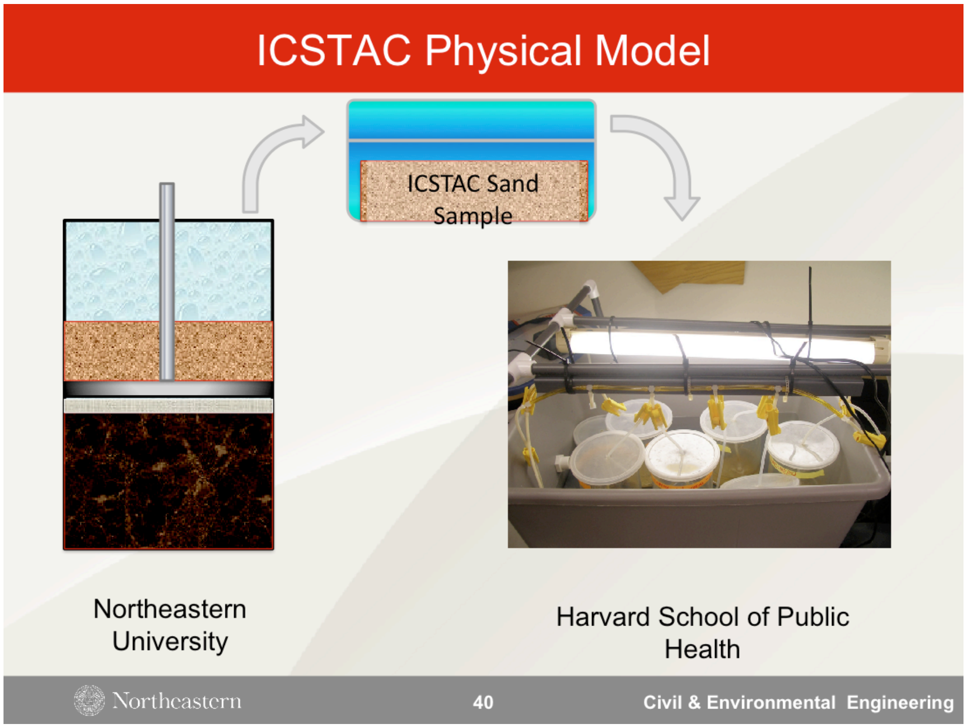
Civil & Environmental Engineering


ICSTAC Physical Model
ICSTAC Sand Sample
Northeastern University
Harvard School of Public Health
Northeastern
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Civil & Environmental Engineering

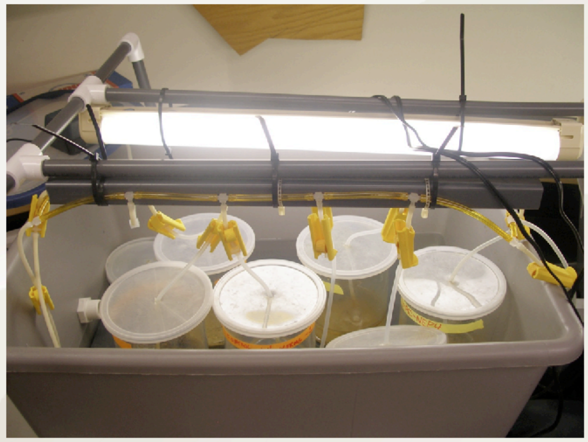
Bioaccumulation Testing

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

Northeastern 41 Civil & Environmental Engineering

Sediment Sampling and Preparation

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

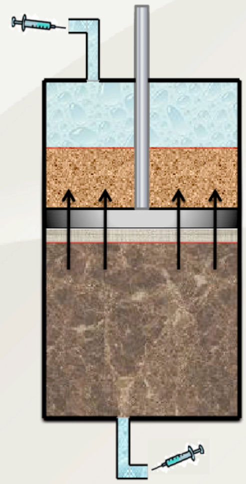
Northeastern 42 Civil & Environmental Engineering

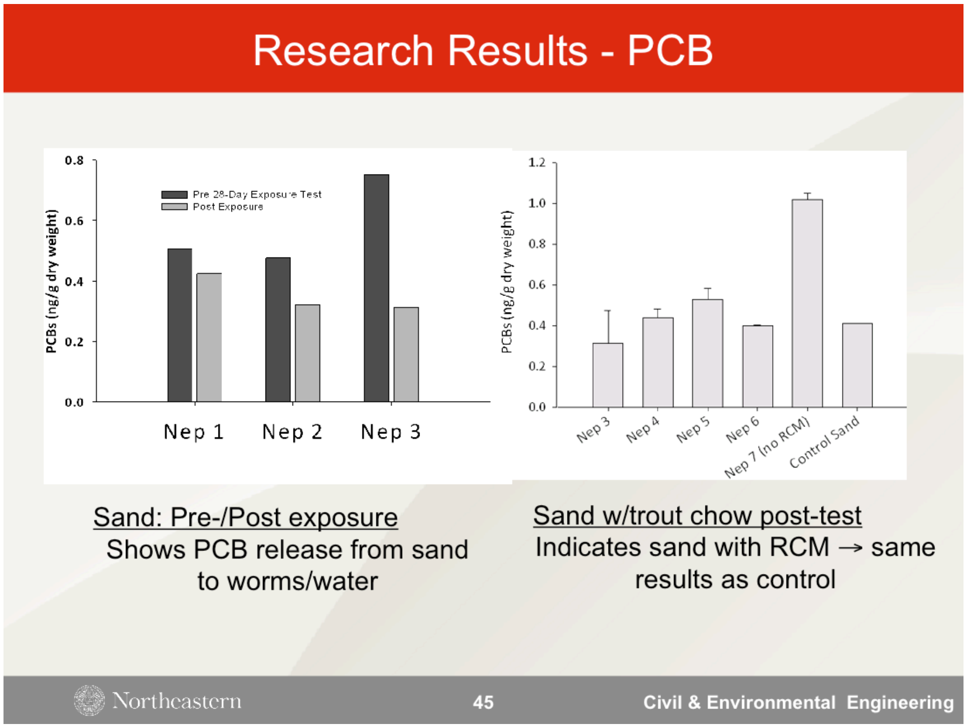
Sediment Sampling and Preparation

- 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
PCBs (ng/g dry weight)
0.0
0.2
0.4
0.6
0.8
Pre 28-Day Exposure Test
Post Exposure
Nep 1
Nep 2
Nep 3
PCBs (ng/g dry weight)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Nep 3
Nep 4
Nep 5
Nep 6
Nep 7 (no RCM)
Control Sand
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
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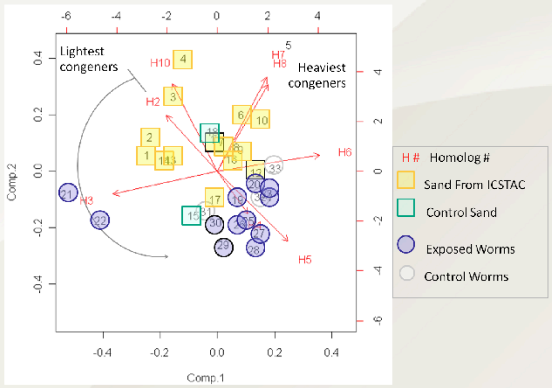
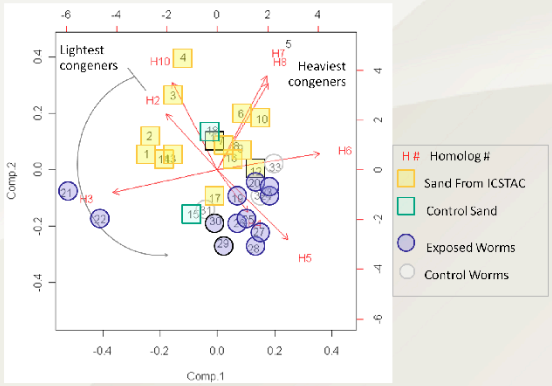
Research Results – PCB – PCA Analysis

- 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



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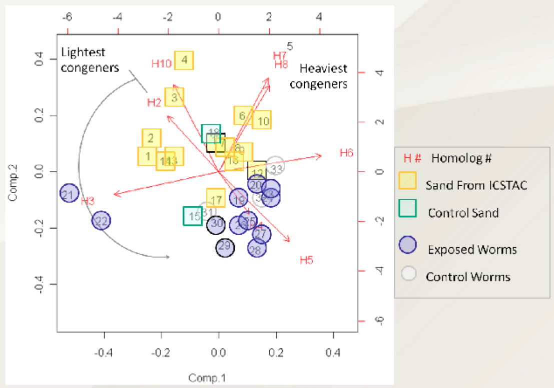
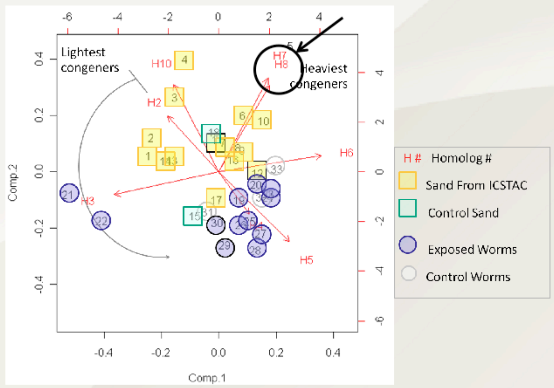
Research Results – PCB – PCA Analysis

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



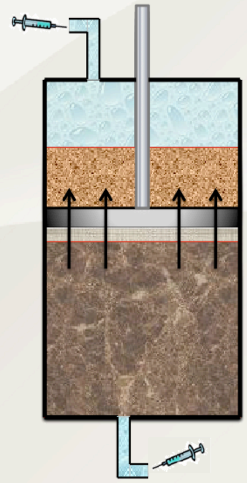
Research Results – PCB – PCA Analysis

- 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



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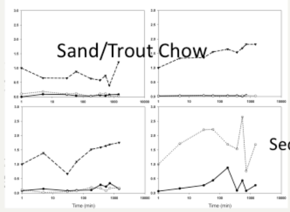
Research Results – PAH Concentrations



Sand/Trout Chow

Reactive Core Mat

10 kPa pressure

Sediment

Overlying water

Sediment

Overlying water

Sand only

No barrier

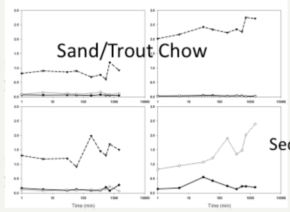
Sediment

Overlying water

Sediment

Overlying water

Research Results – PAH Concentrations



25 kPa pressure

Sand/Trout Chow

Reactive Core Mat

Sediment

Sediment

Overlying water

Overlying water

Sand only

No barrier

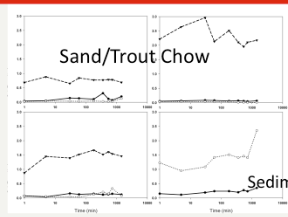
Sediment

Sediment

Overlying water

Overlying water

Research Results – PAH Concentrations



55 kPa pressure

Sand/Trout Chow

Sediment

Reactive Core Mat

Sediment

Overlying water

Overlying water

Sand only

No barrier

Sediment

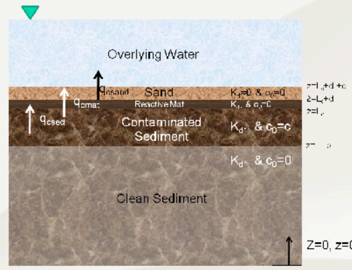
Sediment

Overlying water

Overlying water

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)

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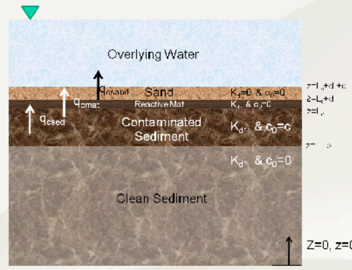
Research Results – Modeling of Process

- 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

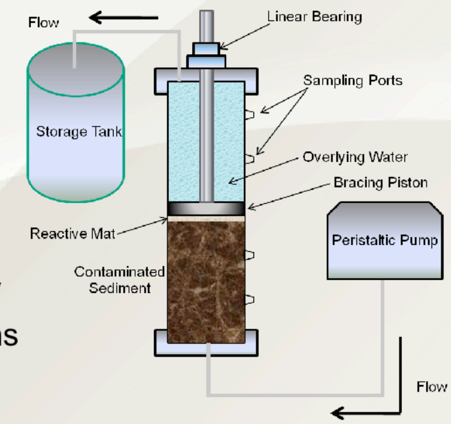
  scale time

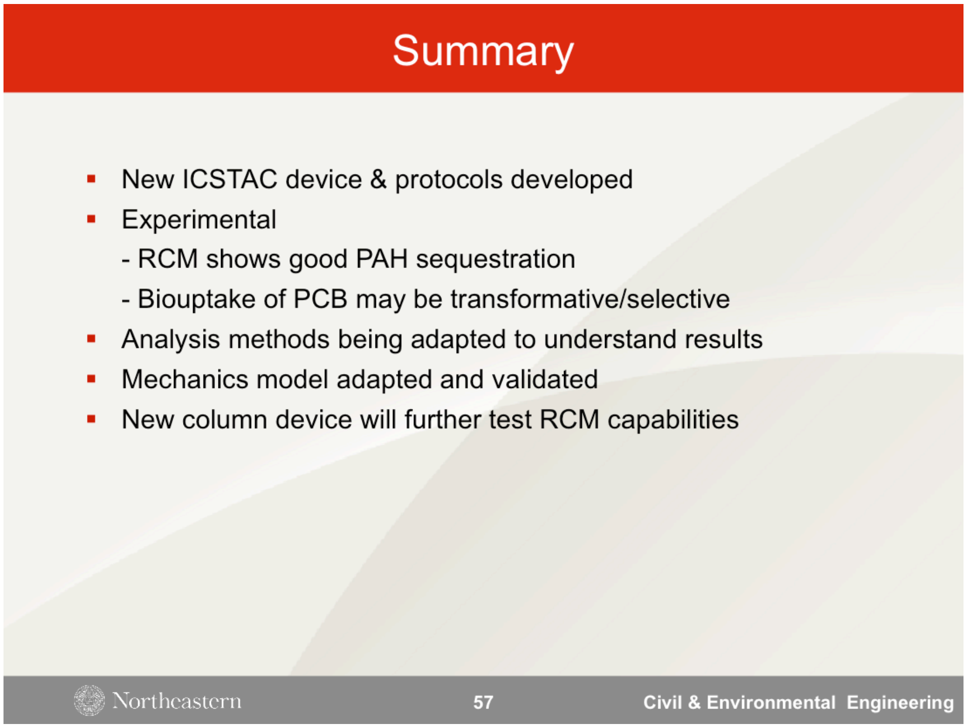
  measure breakthrough
- 1 mL/min = 1 pore vol./day
- Goals:

  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
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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

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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

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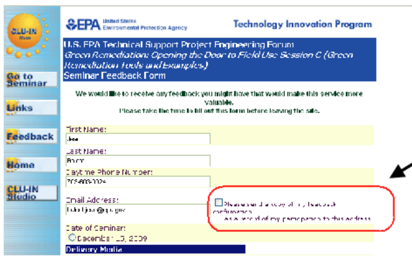
Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NIEHS.

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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