Assessment and Treatment of Contaminated Sediments

October 29, 2015
Welcome and Introductions

Rula Deeb, Ph.D.
Webinar Coordinator
Agenda

- **Webinar Logistics**  
  Dr. Rula A. Deeb  
  Geosyntec Consultants  
  (5 minutes)

- **Overview of SERDP and ESTCP**  
  Dr. Andrea Leeson  
  SERDP and ESTCP  
  (5 minutes)

- **The Roles of Biology, Chemistry and Exposure in the Development of Resilient Remedies**  
  Dr. Todd Bridges  
  Army Engineer Research and Development Center  
  (25 minutes + Q&A)

- **In Situ Treatment of Polychlorinated Biphenyl Impacted Sediments by Microbial Bioaugmentation**  
  Dr. Kevin Sowers  
  University of Maryland  
  (25 minutes + Q&A)

- **Final Q&A session**
How to Ask Questions

Type and send questions at any time using the Q&A panel.
In Case of Technical Difficulties

- Delays in the broadcast audio
  - Click the mute/connect button
  - Wait 3-5 seconds
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  - If delays continue, call into the conference line
    - U.S./Canada: 1-877-776-3503
    - International: 330-871-6014
    - Required conference ID: 14263238

- Submit a question using the chat box
SERDP and ESTCP Overview

Andrea Leeson, Ph.D.
Environmental Restoration Program Manager
SERDP

- Strategic Environmental Research and Development Program
- Established by Congress in FY 1991
  - DoD, DOE and EPA partnership
- SERDP is a requirements driven program which identifies high-priority environmental science and technology investment opportunities that address DoD requirements
  - Advanced technology development to address near term needs
  - Fundamental research to impact real world environmental management
ESTCP

- Environmental Security Technology Certification Program
- Demonstrate innovative cost-effective environmental and energy technologies
  - Capitalize on past investments
  - Transition technology out of the lab
- Promote implementation
  - Facilitate regulatory acceptance
Program Areas

1. Energy and Water
2. Environmental Restoration
3. Munitions Response
4. Resource Conservation and Climate Change
5. Weapons Systems and Platforms
Environmental Restoration

- Major focus areas
  - Contaminated groundwater
  - Contaminants on ranges
  - Contaminated sediments
  - Wastewater treatment
  - Risk assessment
<table>
<thead>
<tr>
<th>DATE</th>
<th>Topics</th>
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<tr>
<td>November 12, 2015</td>
<td>Munitions Response: Land Based Program Closeout</td>
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<tr>
<td>December 3, 2015</td>
<td>Emerging Contaminants: DoD Overview and State of Knowledge on Fluorochemicals and 1,4-Dioxane</td>
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<tr>
<td>December 17, 2015</td>
<td>Watershed and Stormwater Management</td>
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The Roles of Biology, Chemistry and Exposure in the Development of Resilient Remedies

Todd Bridges, Ph.D.
U.S. Army Engineer Research and Development Center
Agenda

- The problem with contaminated sediments
- Technology advancement
- Results highlighting the role of biology and chemistry in exposure
- Next steps toward resilient remedies
- Conclusions
General Problem

- Contaminated sediments are a widespread, national problem
  - >1 billion cubic yards of sediment pose environmental risks
  - U.S. Navy has 200 sediment sites
  - The costs for sediment cleanup are high, $10’s - $100’s millions per site

- Uncertainties regarding contaminant exposure processes are driving cleanup decisions and costs
  - Bioavailability is poorly characterized
  - Risk estimates are biased high, resulting in low cleanup levels
  - Uncertainties regarding long-term remedy performance affects remedy selection
Specific Problem: Exposure Processes

- Improve exposure characterizations
  - Resolve the role of functional ecology in exposure processes
    - How interactions with sediment particles, porewater and overlying water determine exposure
  - Incorporate functional ecology into exposure models for more credible risk assessments and remedy performance predictions

![Diagram of sediment layers, water column, and contaminant flux (CF).](image)
Specific Problem: Remedy Resilience

- Contaminated sediment sites occur in urban environments, complicating the following:
  - Risk assessment
  - Identifying causes (e.g., allocation)
  - Developing resilience remedies

- Urban sites will require a dynamic, contrasted with the current static, approach to contaminated sediment remediation

- Need a comprehensive approach to monitoring exposure processes in relation to remedy performance
Technology Advancement: Passive Sampling

- A variety of approaches developed for sampling water, sediment and porewater
  - Semi-permeable membrane devices (SPMD)
  - Polyethylene devices (PEDs)
  - Polyoxymethylene (POM)
  - Solid-phase micro-extraction (SPME)

- Work by organic contaminant partitioning directly from dissolved phase into an organic phase.
Concentrations for PCB101 at the site of a pilot cap (a) on the Palos Verdes Shelf Superfund site in California, and (b) a nearby site with no cap

Use of Activated Carbon

- AC has a lot of surface area
- Strongly sorbs organic contaminants
- Effectively reduces bioavailability/exposure to organic contaminants like PCBs

Developing Resilient Remedies

Passive sampler

Water column

Amended Cap

Benthic organisms

Contaminated sediment
The Role of Biology in Bioaccumulation Kinetics

Uptake Kinetics in New Bedford Harbor (NBH) Sediment

Species

<table>
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<tr>
<th>Species</th>
<th>Steady state</th>
<th>BSAF</th>
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</thead>
<tbody>
<tr>
<td>Leptocheirus</td>
<td>2 days</td>
<td>5.4</td>
</tr>
<tr>
<td>Eohaustorius</td>
<td>4 days</td>
<td>2.4</td>
</tr>
<tr>
<td>Neanthes</td>
<td>3 days</td>
<td>2.0</td>
</tr>
<tr>
<td>Mercenaria</td>
<td>7 days</td>
<td>0.3</td>
</tr>
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</table>

Time to steady state (based on ASTM method) and biota-to-sediment accumulation factors (BSAFs)

\[
C_{tissue} = \left( \frac{k_1 \ast Cp}{k_2} \right)(1 - e^{-k_2 \ast t})
\]
Experimental Design

- Fine sand added to porewater and overlying water Pathway Isolation Chambers (PICs)
- 3 month system equilibration
- Exposure system re-circulates and passively dose congeners 24, 104 (SPMD)
- Each PIC chamber contains organisms, PEs (in sediment and overlying water)
Pathway Experiments

**PE Derived Results (New Bedford Harbor)**

- PEs indicated much higher porewater concentrations in whole sediment PICs
- PEs detected PCB24 in overlying water and within PICs
- Similar results for Bremerton exposure
Pathway Experiments

Bioaccumulation of Overlying Water PCBs (Bedford)

- Bulk tissue: amphipods bioaccumulated highest concentrations and were more exposed in overlying water and porewater PICs
- Lipid normalized: importance for *Mercenaria* in all PICs becomes more clear
- Low PCB24 in *Neanthes*; low importance of overlying water exposure
- Similar results for PC104 and the Bremerton exposure
Pathway Experiments

Bioaccumulation of Sediment PCBs (Bedford)

- Significant differences in bulk tissue between organisms and PIC exposures
- Lipid normalization reduced differences, although *Leptocheirus* still bioaccumulated significantly higher concentrations from all PICs
Pathway Experiments

Bioaccumulation of PCBs (Bremerton)

- PCBs more bioavailable than in New Bedford Harbor sediment
- Bioaccumulation of overlying water PCBs higher
  - Sandier sediment allowed exposure
  - However, *Eohaustorius* adapted to sandy sediment and burrowed deeper resulting in less exposure to overlying water PCBs
Whole Sediment Bioaccumulation

- BAFs significantly different between organisms
- BSAsFs reduced differences, *Mercenaria* still significantly lower for Bremerton (grain size)
- *Leptocheirus* bioaccumulated more high log $K_{ow}$ congeners than other organisms
Remediation Experimental Methods

- **Treatments**
  - Unamended sediment (Bremerton)
  - Granular activated carbon (GAC); 2% dry mass
    - 10 min mixing, 7 day contact
    - Added to top 2 cm sediment
  - Sand cap (top 2 cm)
Remediation Experiment

PE-derived Concentrations

Sediment associated PCBs

Overlying water (PCB24)

- Porewater concentrations reduced in sand cap but not in GAC amendment at 1 cm depth
- Overlying water PCB24 penetrated the sand cap; concentrations much lower at 3 cm depth
Remediation Experiment

Bioaccumulation of PCBs

Sediment-associated PCBs (no 24,104)

- Concentrations of sediment-associated PCBs significantly reduced by sand cap but not GAC
  - No impact on *Mercenaria* which is exposed to overlying water
- Sediment amendments led to higher overlying PCB water exposure
- Overlying water exposure less important for deep burrowing *Eohaustorius*, *Neanthes*

Overlying water PCB24
Next Steps

- **ER-2431: Quantitative Thermodynamic Exposure Assessment (Q-TEA) Supporting Resilient Contaminated Sediment Site Restoration**
  - Develop capability for evaluating the effect of contaminant influx on the performance of in situ remedies
  - Assess exposure processes using equilibrium and non-equilibrium passive sampling
  - Develop Q-TEA to guide and monitor in situ remediation using passive sampling, tissue analysis and modeling
  - Reveal how activated carbon amendments can be applied to enhance the resilience of in situ sediment remedies challenged by ongoing inputs of contamination
Experimental Design for ER-2431

EXP 1: No Inputs
EXP 2: Ongoing PCB Inputs
EXP 3: AC sed
EXP 4: Cap
EXP 5: AC Cap
EXP 6: Mob AC

SERDP & ESTCP Webinar Series (#21)
ER-2431 Experimental System

Mercenaria mercenaria
Nereis virens
Conclusions

- Developing evidence about the complex interaction of biology, chemistry and exposure will produce more useful risk assessments
- Passive sampling can provide significant insight
  - Should be integrated into RI/FS’s now
- In situ remedies are vulnerable to threats from below and above
- Project objectives should include designing and implementing resilient remedies
For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-1750

Speaker Contact Information
todd.s.bridges@usace.army.mil; 601-634-3626
In Situ Treatment of Polychlorinated Biphenyl Impacted Sediments by Microbial Bioaugmentation

Kevin Sowers, Ph.D.
University of Maryland
Project Team

- Kevin R. Sowers  
  University of Maryland, Institute of Marine and Environmental Technology

- Upal Ghosh  
  Sediment Solutions, LLC

- Harold D. May  
  Medical University of Southern Carolina, Marine Biomedicine and Environmental Science Center
Agenda

- Background
- Technology description
- Treatability studies
- Site demonstration
- Summary
PCBs: An Environmental Legacy

- 209 congeners
- Very stable
- Bioaccumulate
- Toxicity concern
- Sediments = global sinks
Problem Statement

- Many sediment sites across the country impacted with PCBs
- Current technologies are destructive to environmentally sensitive areas and may not sufficiently reduce the risk
- In situ treatment with Bioamended Activated Carbon
  - Cost-effective
  - Both sequesters and degrades PCBs
  - Rapidly deployed and minimally invasive
  - Reduces health risks associated with sediment disruption
  - Reduces overall energy use
  - Negates requirement for extensive waste management and habitat restoration
  - Potentially applicable to other contaminants
How PCB Bioaugmentation Works

Aroclor 1260

Anaerobic Dechlorination

Aerobic Degradation

\[ \text{CO}_2 + \text{H}_2\text{O} \]
Technology/Methodology Description

- Treatability assessed in lab microcosms
- Anaerobic/aerobic biocatalysts scaled-up in pilot facility
- Deployment of bioamended SediMite using Air Horn
- Biocatalysts are dispersed into sediments by benthic activity
- Fate of bioamendments and PCBs monitored after treatment
Abraham’s Creek, Quantico, VA

- Eight-acre watershed outflow to Chopawamsic Creek
- PCB concentration = 3 - 5 mg kg\(^{-1}\), possibly from pesticides
- Water depth = 100 - 250 cm
- TOC = 28,000 mg kg\(^{-1}\)
- Road access
Treatability Study - Mesocosms

- Sediment samples from site were homogenized
- Treatability tested in 2 L sediment recirculating mesocosms
- Treatments = different numbers/types of microorganisms
- PCBs monitored for 120 days
Effect of Treatments on PCB Homologs

- Untreated or abiotic = no degradation in 120 d
- SediMite with bioamendment = 72% degradation in 120 d
- Decrease observed for all homologs
Effect of Cell Numbers on PCBs

- $10^3$ cells/gram sediment = no significant degradation in 120 d
- $10^4$ cells/gram sediment = 50% degradation in 120 d
- $10^5$ cells/gram sediment = 72% degradation in 120 d
Effect of Treatments with Depth

- Decrease in PCBs observed throughout benthic zone
- Indicates mixing from benthic activity
Microbial Scale-Up and Storage

- $10^5$ cells/cm$^3$ in 0.25 acre = $10^{12}$ cells
- $10^{12}$ anaerobic halorespirers generated in 200 L bioreactor
- $10^{13}$ aerobic degraders generated in 20 L bioreactor
Microbial Scale-Up and Storage

- 10^9 cells/mL transferred to 20 L SS Cornelius flasks
- Concentrated cultures stored at room temperature (20 - 22°C)
- Sufficient viability of anaerobe and aerobe maintained <30 days
SediMite as a Delivery System

- SediMite is an agglomerate of activated carbon, a weighting agent and an inert binder.
- Demonstrated that activated carbon is an effective carrier for PCB transforming bacteria.
- Concurrently reduces bioavailability to benthic organisms and provides a solid substrate for biofilm formation.
- SediMite licensed to Sediment Solutions and currently being transitioned to the field.

(U.S. Patent No. 7,824,129 and 8,945,906)
Delivery Efficiency Through Water

- Inoculated SediMite passed through water column
- No significant loss of cells or viability

<table>
<thead>
<tr>
<th>Bacterial Strain</th>
<th>Cells/g SediMite before water column</th>
<th>Cells/g SediMite after water column</th>
<th>N</th>
<th>Significant difference (P &lt; 0.05)</th>
</tr>
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<tbody>
<tr>
<td>LB400 Total</td>
<td>3.0 ± 2.3×10^{-7}</td>
<td>2.6 ± 0.5×10^{-7}</td>
<td>3</td>
<td>No</td>
</tr>
<tr>
<td>Viable</td>
<td>2.0 ± 0.6×10^{-7}</td>
<td>1.5 ± 0.8×10^{-7}</td>
<td>8</td>
<td>No</td>
</tr>
<tr>
<td>DF1 Total</td>
<td>0.7 ± 0.2×10^{-7}</td>
<td>0.9 ± 0.2×10^{-7}</td>
<td>3</td>
<td>No</td>
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<tr>
<td>Viable</td>
<td>1.0 ± 0.5×10^{-7}</td>
<td>2.4 ± 0.9×10^{-7}</td>
<td>3</td>
<td>No</td>
</tr>
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</table>
Site Demonstration Test Design

- Four 10 x 40 m plots
- Plots sampled on -1, 4 and 12 months relative to treatments
- Plots randomly sampled at five locations/time point
- Measured depths of 0 - 7.5, 7.5 - 15 and 15 - 30 cm
Deployment of Bioamended SediMite

Abraham’s Creek, Quantico, VA; April 27, 2015

6000 lbs SediMite transported to site

Microorganisms inoculated onto SediMite

Bioamended SediMite moved to shoreline

...and loaded onto boat
Deployment of Bioamended SediMite

- Bioamended SediMite deployed with air horn
- Each plot covered with 1 cm depth of amendment
Deployment of Passive Samplers

Float

PE membrane in water column

PE membrane in Sediment
Sampling 140 Days After Treatment

- Twenty cores collected
- 24 passive samplers deployed and collected after 30 days
- Analysis of samples pending
Initial Results Top 7.5 cm

<table>
<thead>
<tr>
<th>Plot</th>
<th>Day 0</th>
<th>Day 140</th>
<th>% Reduction</th>
</tr>
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<tbody>
<tr>
<td>Plot 1</td>
<td>3</td>
<td>3.5</td>
<td>0</td>
</tr>
<tr>
<td>Plot 2</td>
<td>2.5</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Plot 3</td>
<td>2.5</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>Plot 4</td>
<td>2.5</td>
<td>2</td>
<td>36</td>
</tr>
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Summary

- PCB levels reduced by 72% in mesocosms after 120 days
- Methods developed for scale-up and deployment of bioamendments into sediments
- Bioamended SediMite successfully deployed in Abraham’s Creek in May 2015
- PCB levels reduced 24 to 36% in the field after 140 days
- Next step: Reassess site after 365 days and identify parameters necessary for effective full-scale treatment
## Benefits of Bioremediation

<table>
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<tr>
<th></th>
<th>Bioamended SediMite</th>
<th>Dredging</th>
<th>Capping</th>
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<tbody>
<tr>
<td><strong>Cost</strong></td>
<td>~$150K/acre</td>
<td>~$1000K/acre</td>
<td>~$170K/acre</td>
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<tr>
<td><strong>Health Risks</strong></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
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<tr>
<td><strong>Environmental Disruption</strong></td>
<td>Low</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td><strong>Energy Use</strong></td>
<td>Low</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Long-Term Waste Management</strong></td>
<td>None</td>
<td>Long-term storage</td>
<td>20-year life</td>
</tr>
<tr>
<td><strong>Habitat Restoration Cost</strong></td>
<td>None</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td><strong>Wetland Environments</strong></td>
<td>Well-suited</td>
<td>Not suitable</td>
<td>Not suitable</td>
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</table>
For additional information, please visit
https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-201215

Speaker Contact Information
sowers@umbc.edu; 410-234-8878
Q&A Session 2
The next webinar is on November 12, 2015

“Munitions Response: Land Based Program Closeout”
Survey Reminder

Please take a moment to complete the survey that will pop up on your screen when the webinar ends.