Understanding the relationships among low level metal influx, remediated sediments, and biological receptors

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SERDP DOD • EPA • DOE

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Technical Objective

The main objective of the proposed research is to evaluate the effectiveness of in situ remediation technologies (including single amendment active caps [ACs], multiple amendment active caps [MAACs], and passive caps) influenced by continued low level metal influx and to improve our understanding of relationships among:

- surface sediment recontamination
- remediated contaminated sediments
- biological receptors

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Technical Approach

Task 1. Linkages between contaminant loading and recontamination of remediated sediments - flow through mesocosms with continuous metal influx

Task 2. Understanding how active caps, passive caps, and uncapped sediment are affected by recontamination with contaminated sediment – development of a zone-of-influence

- Experiment 1 A: Mesocosm study – without bioturbation
- Experiment 1 B: Mesocosm study– with bioturbation
- Experiment 2. Field study

Task 3. Prediction of long-term relationships among the low level of influx of contaminants, biological receptors, and remediated sediments

★ Go/No go decision

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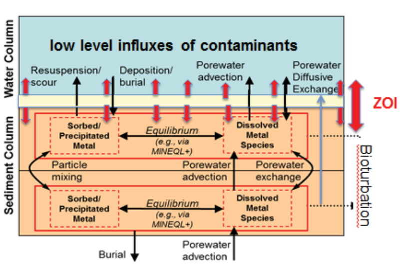
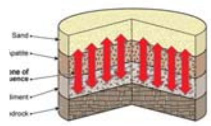
Technical Approach

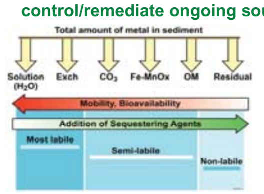
Hypotheses:

1) A Zone of Influence (ZOI) will form in contaminated sediment that is deposited over active caps resulting in chemical changes to the contaminants that will reduce their environmental impact
2) The amendments in active caps will sequester contaminants associated with the continued influx of contaminants





Active caps remediate existing contaminants in sediments and control/remediate ongoing sources



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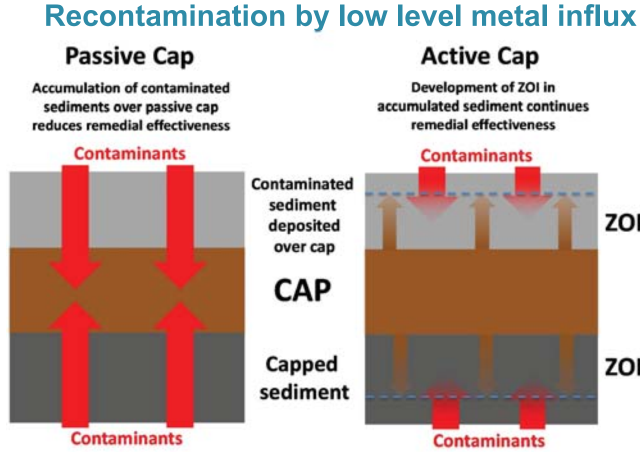
Technical Approach

Recontamination by low level metal influx



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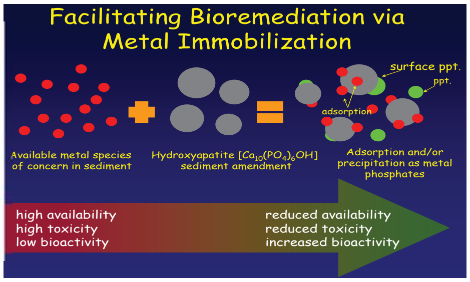
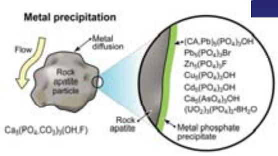
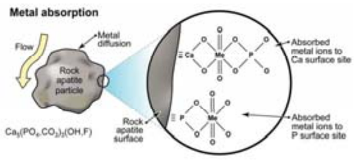
Technical Approach – Sequestering Amendments

Remediation via Apatite

Apatite
- Stable end-products
- Can be placed by existing technology
- Does not affect sediment physical properties
- Can be mixed with other additives
- Low cost, readily available, non-toxic







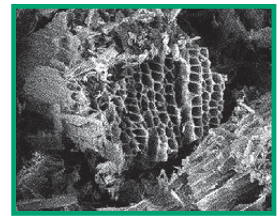
Technical Approach – Sequestering Amendments

Remediation via Activated Carbon

Activated carbon (AC) is particles of carbon that have been treated to increase their surface area and increase their ability to adsorb a wide range of contaminants

AC is a highly porous material
- It has an extremely high surface area for contaminant adsorption
- The equivalent surface area of 1 pound of AC ranges from 60 to 150 acres (over 3 football fields)

The adsorption on AC depends on the following factors:
- Physical properties of the AC, such as pore size distribution and surface area
- Chemical nature of the carbon source, or the amount of oxygen and hydrogen associated with it
- Chemical composition and concentration of the contaminant
- Temperature and pH of the water
- Flow rate or time exposure of water to AC

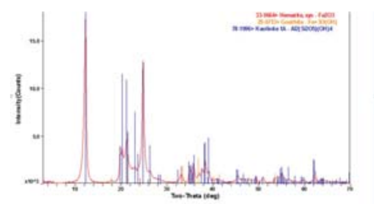


In this study we used Brimac Carbon which contains both carbon surface area and hydroxyapatite lattice surface area

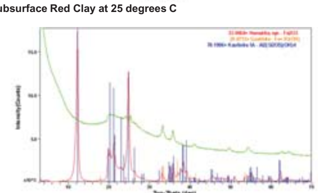
Technical Approach – Sequestering Amendments

Remediation via Silty Clay

Properties	Subsurface Red Clay Sediment
% sand (>53 μm)	57.9
% silt (53 – 2 μm)	40.6
% clay (<2 μm)	1.6
Textural classification	Silty clay
pH	5.55
% OM	1.21
CEC (cmol/kg)	1.09 ± 0.31
AEC (cmol/kg)	1.58 ± 0.61
BET surface area (m²/g)	15.31
Single point surface area (m²/g)	15.07
CDB extractable Fe (mg/g)	15.26
Al (ppm)	63.59
Na (ppm)	42.91
Mg (ppm)	144.05
Ca (ppm)	64.41
K (ppm)	182.87
Mineralogy	Kao > goeth > Hem (no qtz or 14 A)



Subsurface Red Clay at 25 degrees C



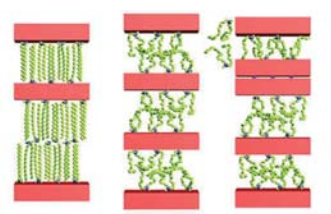
Subsurface Clay at 550 degrees C for 1 hr

Technical Approach – Sequestering Amendments

Remediation via Organoclay MRM

Organoclay® MRM is a sulfur-impregnated organophilic clay granular filtration media that adsorbs non-aqueous phase liquids (NAPL) and dissolved low-solubility organics. It also sequesters mercury and arsenic from water.

What is an Organoclay?
- Modified bentonite clay
- Bentonite clay is primarily composed of montmorillonite



Results – Experimental Setup

Task 1. Linkages between contaminant loading and recontamination of remediated sediments

Objective: To study the effect of contaminant loading on remediated sediments and benthic organisms - The experimental setup included flow-through mesocosms designed to assess the effects of a continuous influx of metals on selected cap materials in different thicknesses and on untreated sediment

Sediment Properties	
% sand (>53 μm)	87.9
% silt (53 – 2 μm)	11.3
% clay (<2 μm)	0.8
Textural classification	Sandy
pH	6.55
% OM	1.16
% C	0.14
CEC (cmol/kg)	0.79 ± 0.31
AEC (cmol/kg)	0.58 ± 0.61
Bulk Density (g/ml)	1.2631
As (ppm)	1.013
Cd (ppm)	0.014
Co (ppm)	2.316
Cr (ppm)	5.652
Cu (ppm)	17.629
Ni (ppm)	2.688
Pb (ppm)	3.015
Se (ppm)	0.067
Zn (ppm)	20.62

The mesocosms were constructed using 10 gallon aquaria. About 1000 lbs of clean sediment was collected and homogenized. A 5 inch layer (12.7 kg of sediment) was placed in the bottom.

Results – Experimental Setup

The experiment consisted of 30 aquaria, representing different cap compositions, cap thicknesses, controls without caps, and controls without caps and sediment

Tested materials:
- **Control** – no cap
- **Active materials**

NCA – North Carolina apatite
AC – activated carbon
MRM – organoclay from CETCO
- **Passive material**

S- sand
CL – silty clay

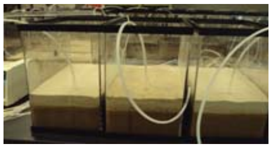
Passive Materials	Active Materials	Cap thickness 0 cm	2.5 cm	5 cm
No	No	3*		
No	No	3		
No	NCA		3	3
No	AC		3	
No	MRM		3	
No	NCA/MRM /AC		3	
CL	No		3	
S	No		3	3

* Control – no sediment, no cap

Results – Experimental Setup

Placement of cap materials over saturated sediment

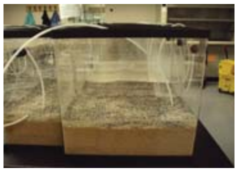
Passive materials



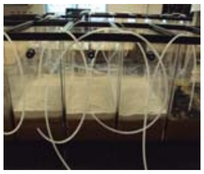
Sand

Silty clay

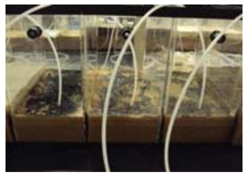
Active materials



North Carolina Apatite



Organoclay MRM



Activated carbon

Results – Experimental Setup

A single 32 channel peristaltic pump ensured uniform delivery of DI water followed by spike solution to all mesocosms from a single reservoir

The concentration of each element in the spike solution was ~0.500 mg/L, flow rate of the system was 0.3 mL/min

Results – Experimental Setup

An airstone diffuser was placed in in each mesocosm to suspend particulate matter, thereby simulating field conditions in which particle-bound metals are a significant source of recontamination

Suspension of particulates was monitored by measuring turbidity within the mesocosms with a turbidity meter.

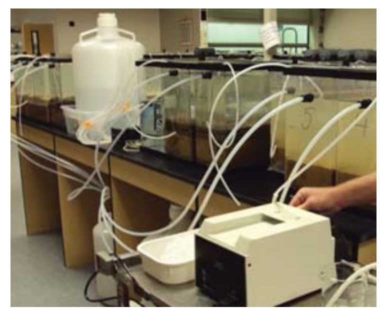
Results – Pore Water

Collection of Pore Water Samples

Pore water samples were collected before addition of the spike solution; i.e., 4 weeks after addition of cap materials.

Measurements:

- Metal concentrations
- Temperature
- Electric conductivity (EC)
- Dissolved oxygen (DO)
- pH
- ORP



Results – Surface Water

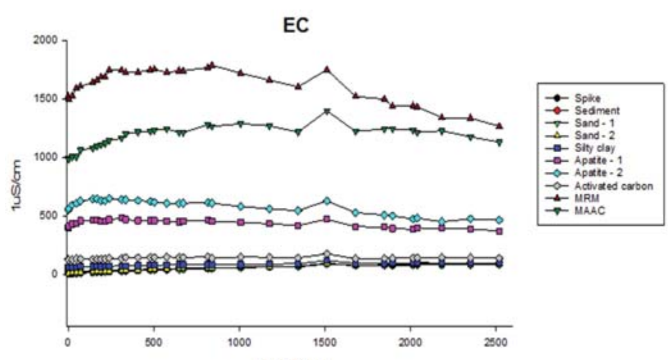
Collection of Surface Water Samples

Surface water samples were collected for 2520 hrs. One set of samples for dissolved metals was filtered using a 0.45mm pore diameter membrane filter. A second set of samples for total recoverable metals was not filtered.

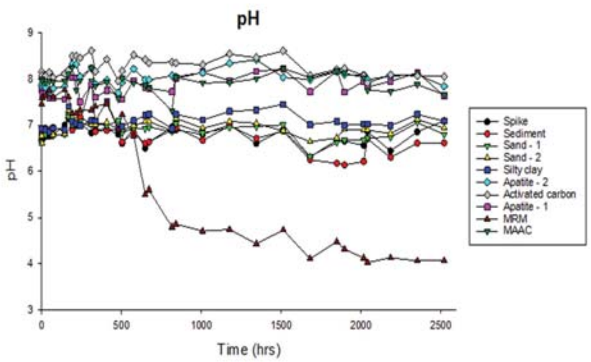
Measurements:

- Metal concentrations by ICP-MS
- Turbidity
- Temperature
- Electric conductivity (EC)
- Dissolved oxygen (DO)
- pH
- Hardness
- ORP

Results – Surface Water Properties (2520 Hrs)



Results – Surface Water Properties (2520 Hrs)



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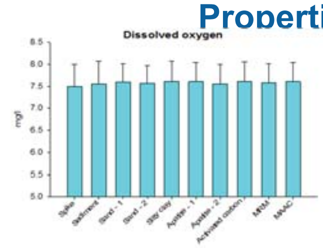
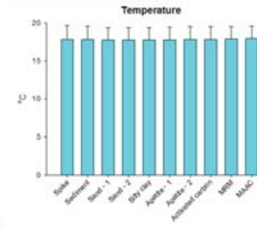
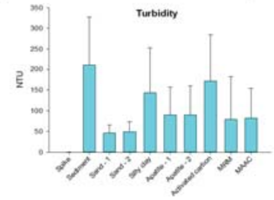
Results – Surface Water Properties (2520 Hrs)







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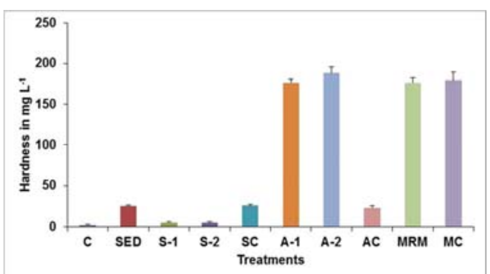
Results – Surface Water Properties (2520 Hrs)

Hardness of surface water (mg L^{-1}) for each treatment at 2520 hours; only spike solution only (C), uncapped sediment (SED), sediment with passive sand caps (S-1: 2.5 cm, S-2: 5 cm), and sediment with several types of active caps (SC: 2.5 cm silty clay, A-1: 2.5 cm apatite , A-2: 5.0 cm apatite, AC: activated carbon – no cap, MRM: 2.5 cm organoclay, and MC: 2.5 cm mixture of active amendments)



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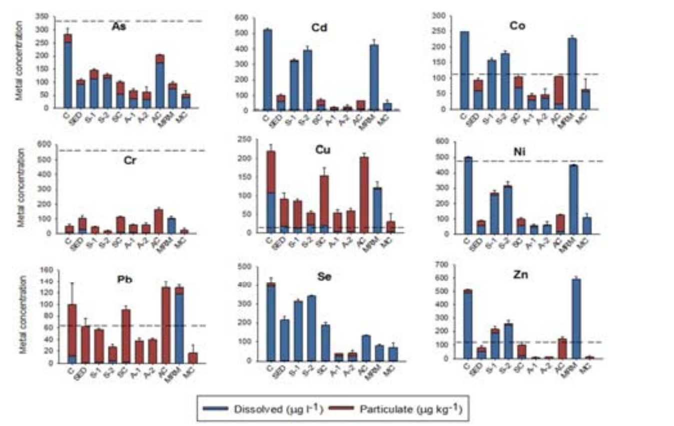
Results – Surface Water

Average surface water concentration of metals in mesocosms, 2520 hours. The dashed lines represent EPA acute toxicity levels for dissolved metals at hardness 100 mg/L.



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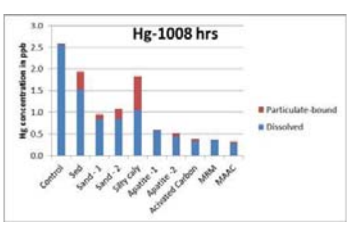
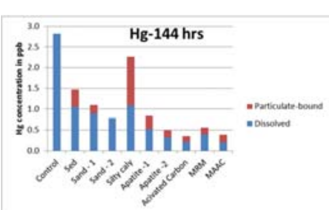
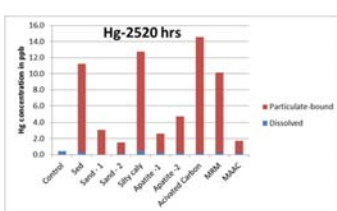
Results – Surface Water

Average surface water concentration of mercury in mesocosms with no sediment (Control), uncapped sediment (Sed), sediment with passive sand caps, and sediment with several types of active caps after 144, 1008, and 2520 hours







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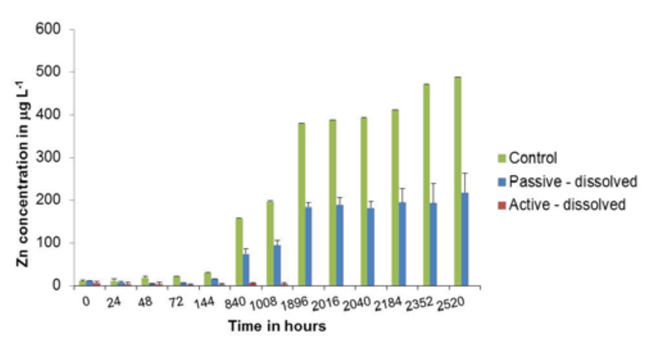
Results – Surface Water

Average surface water concentrations of particle-bound and dissolved zinc (Zn) in mesocosms with passive caps (S), active caps (A, AC, MAAC), and without caps or sediment (control)



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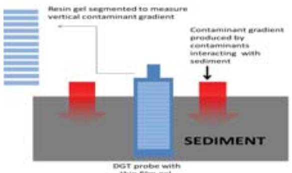
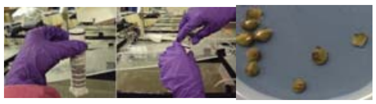
Evaluation of bioavailable pool of metals

- The bioavailable pool of metals in the water and sediment/cap was measured by diffusive gradients in thin films (DGT) probes (water and sediment)
- DGT measurements were compared with metal uptake by caged organisms (*Lumbriculus variegatus and Corbicula Fluminea*) and other methods of bioavailability analysis

The bioavailable pool of metals in the water and sediment (capped and untreated) was measured by two types of diffusive gradients in thin films (DGT) probes

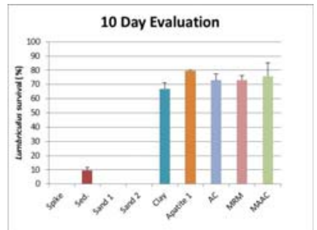


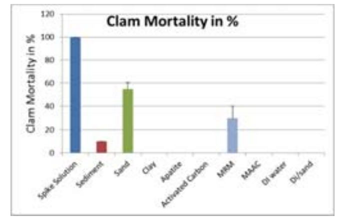


Placement and retrieval of California black worms and clams

Evaluation of bioavailable pool of metals

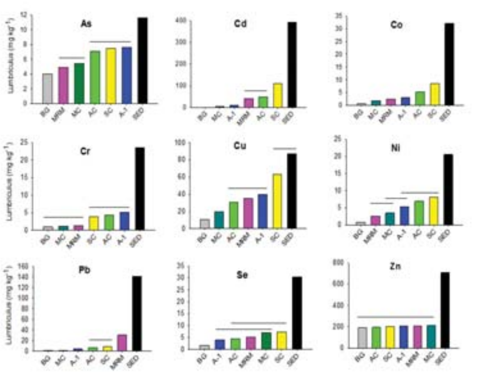
Lumbriculus variegatus were observed for toxicity. Sand caps and spike solution resulted in 100% mortality after 24 hours. Active caps and clay cap showed minimal toxicity after one, six, and ten days





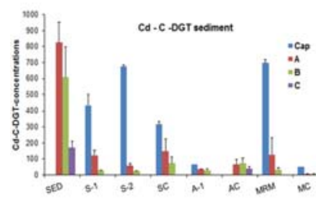
Average mortality of Asian clams after 10 day toxicity tests conducted in mesocosms receiving water spiked with dissolved metals. Mesocosm treatments included spike solution only, uncapped sediment, sediment with passive caps (sand), and sediment with active caps [clay; apatite; activated carbon (AC); organoclay (MRM); and a mixture of activated carbon, apatite, and MRM]. Error bars are standard deviations (n=3).

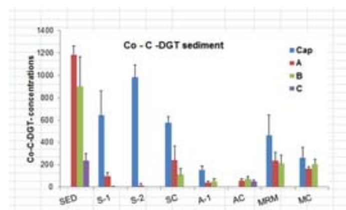
Evaluation of bioavailable pool of metals



Analysis of variance of differences in *Lumbriculus variegatus* metal concentrations (whole body, 10 day exposure) among sediment treatments (BG =background, AC: activated carbon, SC: silty clay cap, A: apatite cap (2.5 cm), MRM: organoclay MRM cap, MC: mixture of active amendments, SED: untreated sediment). Geometric means connected by the same line are not significantly different at $p<0.05$.

Evaluation of bioavailable pool of metals

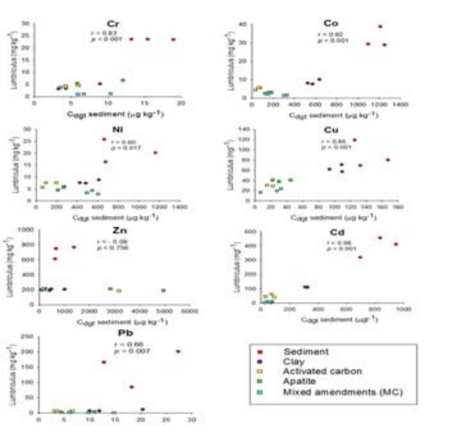




Cd and Co concentrations (mg kg^{-1}) measured by sediment DGT probes (C_{DGT}) in cap materials and individual layers of sediment (layer A: 0-2.5 cm, layer B: 2.5 – 5.0 cm, and layer C: 5 - 7.5 cm) at 2040 hours.

Sediment DGT probes showed that ongoing contamination increased the bioavailable pool of metals in the top layer of uncapped sediment or cap layer composed of sand or organoclay MRM but not in cap or sediment with apatite or activated carbon.

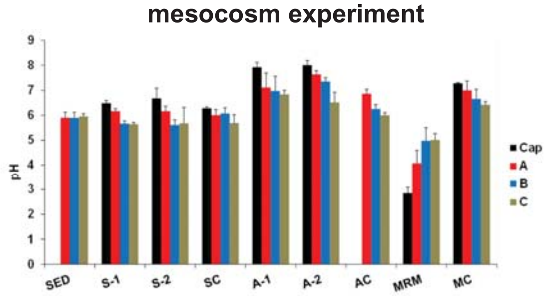
Evaluation of bioavailable pool of metals



Pearson correlations between metal concentrations in Lumbriculus (ten day test) and metal concentrations in the top 2.5 cm of sediment or cap measured by diffusive gradient in thin films (DGT) sediment probes were generally strong (as high as 0.98) and significant ($p<0.05$) for almost all tested metals. Metal concentrations in both Lumbriculus and sediment/cap were lowest in apatite, mixed amendment, and activated carbon treatments.

Evaluation of bioavailable pool of metals

Sediment pH values after termination of the mesocosm experiment



Treatments: uncapped sediment (SED), sediment with passive sand caps (S – 1: 2.5 cm cap and S – 2: 5 cm cap) and sediment with several types of active caps (2.5 cm) (apatite A-1; silty clay - SC; activated carbon - AC; organoclay – MRM:, and mixture of active amendments – MC)

Key Points

The hypothesis tested in Task 1 is that sequestering agents in active caps may bind metals from ongoing sources thereby reducing the bioavailability of the metals and protecting underlying remediated sediments from recontamination. The preliminary findings support this hypothesis:

- From all tested amendments, apatite was the most effective (70 or 80 % of removal) at removing Cd, Co, Cu, Ni, Zn, As, and Se from the surface water. The least effective amendment at removing metals from surface water was organoclay MRM
- Active caps increased surface water hardness to about 180; therefore, they reduced the toxicity of many tested elements (e.g., Cd, Cu, Ni, Pb, and Zn). This likely contributed to better survival observed with black worms and clams within active caps, even organoclay MRM
- Metal concentrations were significantly higher in Lumbriculus (10 days evaluation) from untreated sediment than in Lumbriculus from active caps and clay, even though the untreated sediment removed significant amounts of the tested elements (e.g., Ni, Zn, and Cd) from the surface water. This likely occurred because the chemistry of the surface water was not affected in the same way by the sediment as by some active caps (e.g., apatite or MAAC).

Key Points

- Pearson correlations between metal concentrations in Lumbriculus (ten day test) and metal concentrations in the top 2.5 cm of sediment or cap measured by diffusive gradient in thin films (DGT) sediment probes were generally strong (as high as 0.98) and significant ($p<0.05$) for almost all tested metals. Metal concentrations in both Lumbriculus and sediment/cap were lowest in apatite, mixed amendment, and activated carbon treatments
- These findings show that some types of active caps can protect remediated sediments by reducing the bioavailable pool of metals in ongoing sources of contamination, thereby supporting our initial hypothesis
- The results of Task 1 should help to better understand the remediation of contaminated sediments subjected to the continued influx of contaminants from uncontrolled sources

BACKUP MATERIAL

Task 3 – Model Evaluation Approach & Methods

- ***General approach (applies to both models):***
  - Configure model layers and constituents to represent mesocosm conditions:
    - Multiple cap configurations (sand, active caps) – use of 0.5" layer thicknesses
    - Multiple metal species (Cd, Ni, As, etc.)
  - Configure model based on mesocosm physical dimensions and observed data
  - Estimate/calibrate rates of deposition, resuspension, and diffusion
  - Compare model results to mesocosm observations (e.g., vertical profiles)
  - Sensitivity analysis for key input parameters
- ***Sediment Flux Model (SFM):***
  - Enhance framework to represent multiple metals, dynamic water column conditions
  - Incorporated distribution coefficient ("Kd") estimates (provided by SRNL)
  - Suspended solids simulated in water column (support deposition/resusp. calculations)
- ***TICKET Model:***
  - Attempt to identify appropriate components/species to include in simulations (e.g., to represent cap materials)
  - Estimate initial concentrations for all species
  - Configure & test various transport processes (settling, resuspension, diffusion)

Task 3: Prediction of long-term relationships among the low level influx of contaminants, biological receptors, and remediated sediments

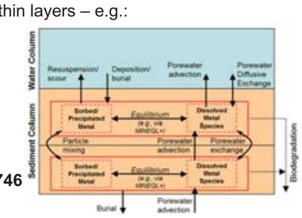
<u>Overall Objective</u>: Conceptualize and implement an approach for configuring and applying a numerical model to predict long-term relationships among the low level influx of contaminants, biological receptors, and remediated sediments.

<u>Specific Modeling Objectives for Year 1:</u>

- Develop a comparative evaluation of SFM ("Sediment Flux Model") and TICKET model via application of models to mesocosm experiments
- Based on comparative evaluation, recommend a specific modeling approach for use in supporting field experimental work and forecasting long-term sediment conditions (for Years 2-3 of project)

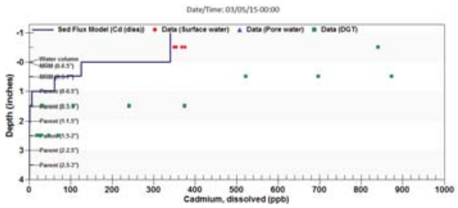
Task 3 – Models Evaluated for Simulation of Capped Conditions

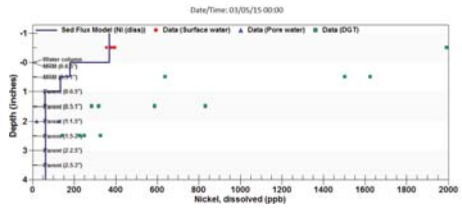
- ***"Sediment Flux Model" (SFM):***
  - Originally developed and field-tested for hydrophobic organic compounds under **ER-1371** (previous cap study)
  - Represents a one-dimensional sediment column with multiple vertical sediment layers at fine scale
  - Defines and tracks discrete sediment "types" within layers – e.g.:
    - Native sediment, newly deposited layer
    - Sand / active cap materials
  - Enhanced for Year 1 applications



- ***TICKET Model:***
  - Developed by Farley et al. partially under **ER-1746**
  - Combines simulation of transport with tableau approach to calculate "dynamic" chemical equilibrium and kinetic exchanges
  - Relies on thermodynamic database
  - Requires considerable input data to represent initial concentration of key species

Example Vertical Profile Results
(SFM Results for Cd, Ni – organoclay cap case)





Task 3 – Key Findings from Model Evaluation

- ***TICKET Model:***
  - Chemistry data limitations contribute significant uncertainty to model application
    - Model requires information for all major cations / anions
    - Initial species concentrations largely unknown (e.g., organic carbon, iron content/speciation)
  - Significant expansion of supporting database would be required to represent key sequestering agents
    - Organic carbon species (e.g., via WHAM V)
    - Active cap materials (e.g., organoclay, apatite)
  - Key transport processes do not function as expected (diffusion, deposition, resusp.)
  - Model stability / convergence and efficiency is a significant concern (especially for long-term simulations)
  - Model documentation is generally lacking
- ***Sediment Flux Model (SFM) – recommended for Tasks 2, 3***
  - Distribution coefficient ("Kd") approach is simplified - but allows for capturing major characteristics of metal vertical profiles
  - Data requirements are better aligned with actual data availability
  - Additional development / testing work required is minimal

Project Number (ER-2427): Understanding the relationships among low level metal influx, remediated sediments, and biological receptors

Performers: ***A. S. Knox, M. Paller, K. Dixon***
Savannah River National Laboratory
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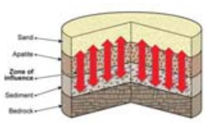
LimnoTech Inc.

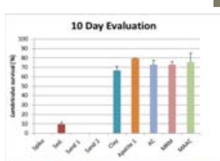
Technology Focus: *The effectiveness of in situ remediation technologies for contaminated sedimen when challenged by the continued influx of new contaminants*

Reseach Objectives: *To understand how active and passive sediment caps and underlying sediments are affected by recontamination. We hypothesize that sequestering agents in active caps will produce a "Zone-of-Influence" that will bind contaminants from ongoing sources.*

Project Progress and Results: *Results show lower concentrations of several metals in surface and benthic organism tissues, and lower toxicity some active caps.*

Technology Transition: *Next steps will assess metal speciation and bioavailability using diffusive gradient in thin films (DGT) and document development of the Zone of Influence (ZOI) in sediment deposited over active caps in laboratory experiments and in the field.*





Sand caps and spike solution resulted in 100% mortality of Lumbriculus after 10 days, but active caps: apatite, activated carbon (AC), clay, organoclay (MRM), and a mixture of amendments (MAAC) did not show toxicity.