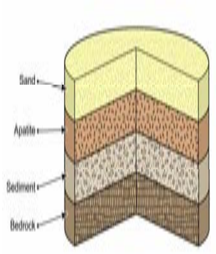
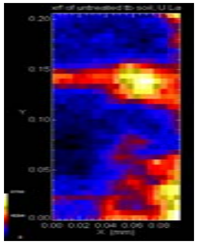
Active Caps for the Remediation of Mixtures of Contaminants and Resistance to Erosion





We Put Science To Work

Anna Knox
Savannah River National Laboratory

FRTR, Arlington, VA

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Problem Statement

Ten percent (1.2 billion yd^3) of the sediment in U.S. waters is contaminated (PAHs, PCBs, metals, metalloids, and others)

Current technologies for contaminated sediments

- **Removal followed by treatment and disposal**
- **In situ isolation of the sediments (passive capping)**
- **Monitored natural recovery**

Problems with current technologies

- **Are not a permanent solution (passive capping)**
- **May cause significant environmental impact**
- **Cannot adequately treat the complex mixtures of organic and inorganic contaminants found at many sites**
- **May be ineffective in dynamic aquatic environments**

Technical Objective

Combine chemical and biological amendments to develop an innovative capping technology that reduces contaminant toxicity while simultaneously creating an erosion resistant barrier

Specific objectives:

- Evaluate innovative chemical and biological sequestering materials to stabilize a broad range of contaminants in different types of sediments
- Evaluate the resistance of different active caps to physical disturbance
- Determine the best combination and deployment of amendments for constructing active sediment caps
- Develop conceptual and mathematical models for contaminant attenuation in active caps
- Evaluate the effects of the proposed active caps on contaminant mobility, retention, toxicity, and bioavailability under field conditions

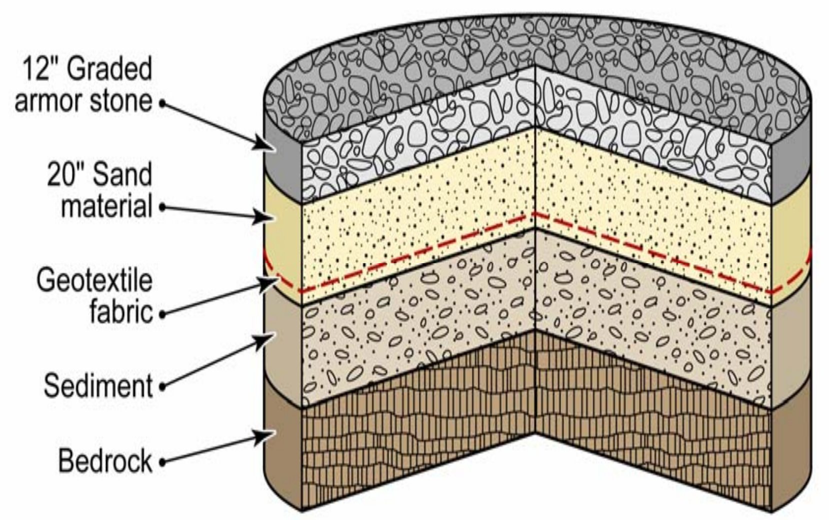
Technical Approach

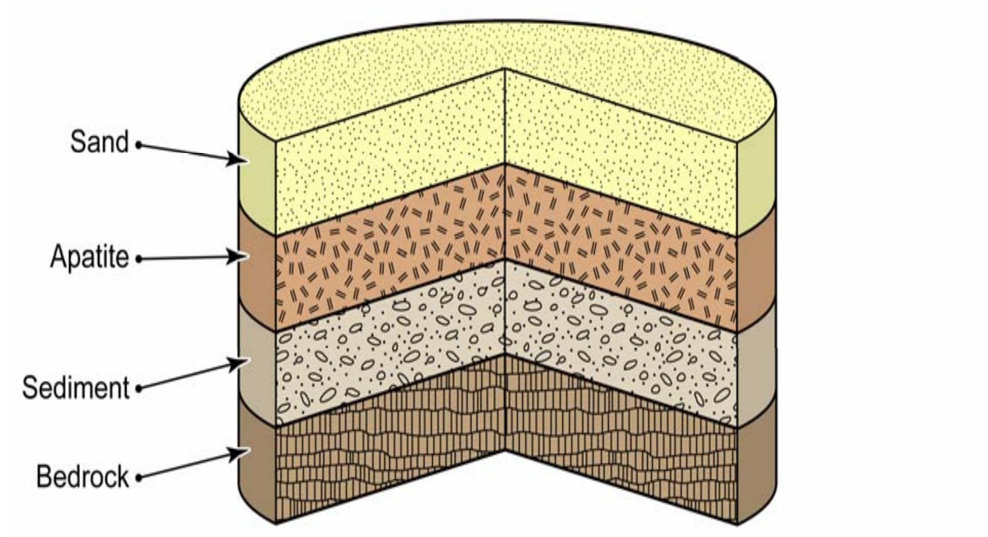
Passive Cap

Layer of inert material that isolates contaminated sediment from the surrounding environment

Active Cap

Reactive material that neutralizes or stabilizes contaminants in situ





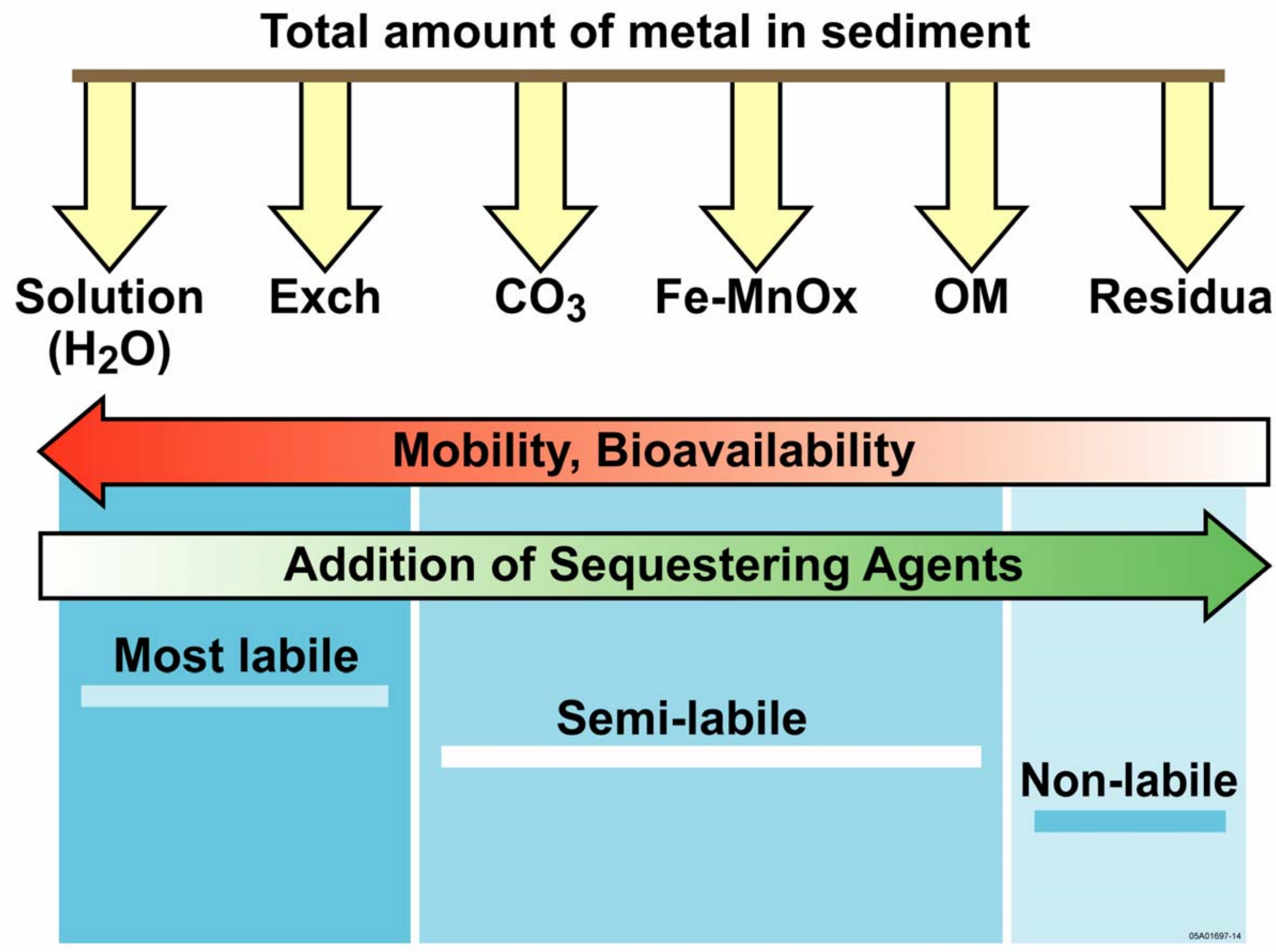
Problems:

- **Subject to transport of contaminants**
- **Not a permanent solution**

Problems:

- **Subject to disruption by physical disturbance**
- **Less mature technology**

Technical Approach



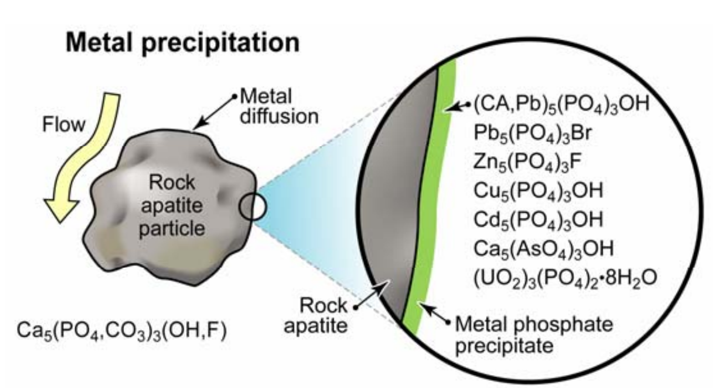
Sequestering Agents

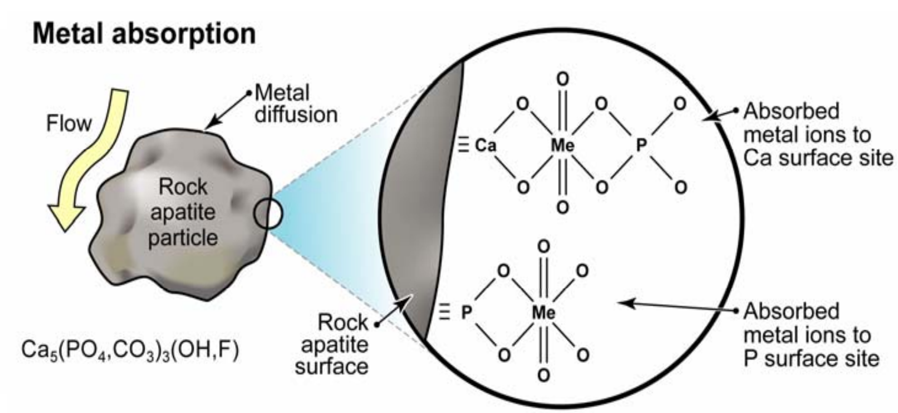
Apatite

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

Phytic acid

- A sugar derivative (6-phosphate ester of inositol) that precipitates contaminant metals in the same manner as apatite
- Naturally occurring metal ions like Ca^{2+} improve metal immobilization processes.
- Can be applied in a soluble form

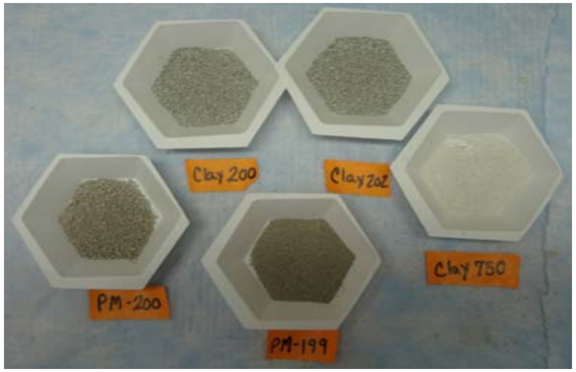




Sequestering Agents

Organoclays

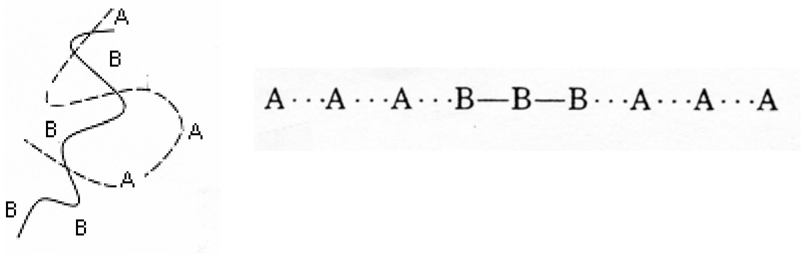
- Consist of modified bentonite
- Effective at removing organics (e.g. PCBs, and PAHs)
- Small positive charge permits removal of some anions
- Retained cation exchange capacity immobilizes metals
- Significant swelling and permeability reduction



Organoclay produced
by Biomin Inc. and CETCO®

Biopolymers

- Natural materials
- Can bind metals and organics
- Resist biodegradation in cross-linked forms
- Plugging effect - increases shear strength of porous media to resist erosion
- Can be injected into sediments
- Economical, non-toxic



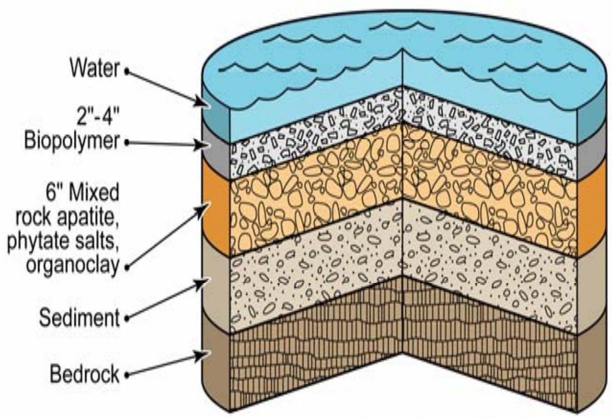
Interpenetrating polymer network

SERDP Strategic Environmental Research and Development Program

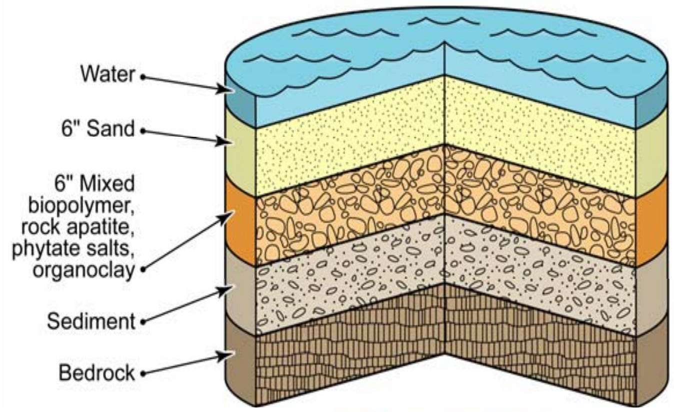
Technical Approach

SRNL

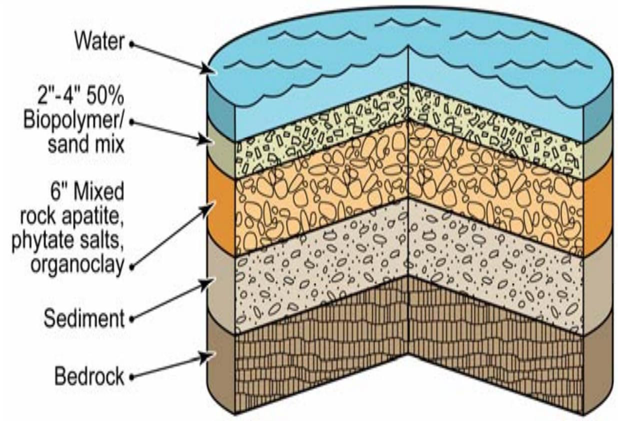
Proposed novel caps



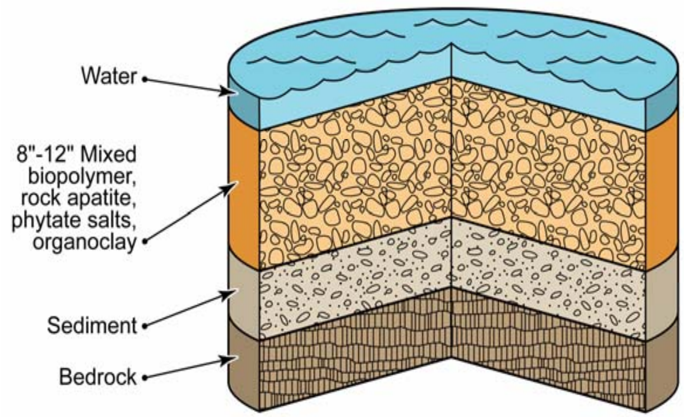
Cap # 1



Cap # 2



Cap # 3



Cap # 4

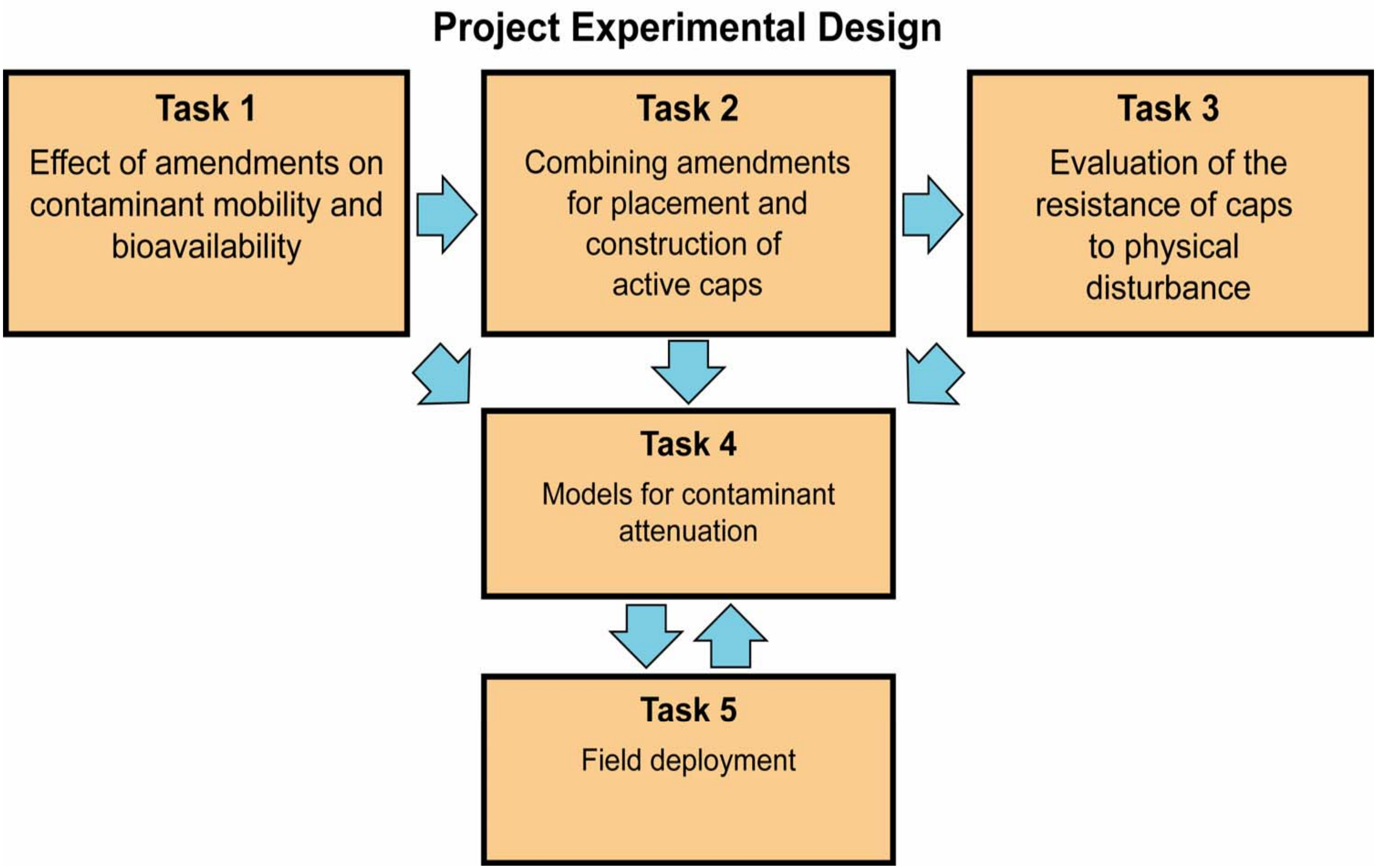
The challenge of active capping

To develop an in situ technology that economically remediates complex mixtures of organic and inorganic contaminants within a dynamic physical environment

Proposed solution

To select and combine amendments that will control organic and inorganic contaminants while providing resistance to erosion

Technical Approach



Experimental Methods

Effect of Amendments on Contaminant Mobility and Bioavailability

Sorption and desorption tests

Contaminants:

Metals: As, Cd, Cr, Co, Cu, Ni, Pb, Se, Zn, and U

Organics: (PAHs and PCBs)

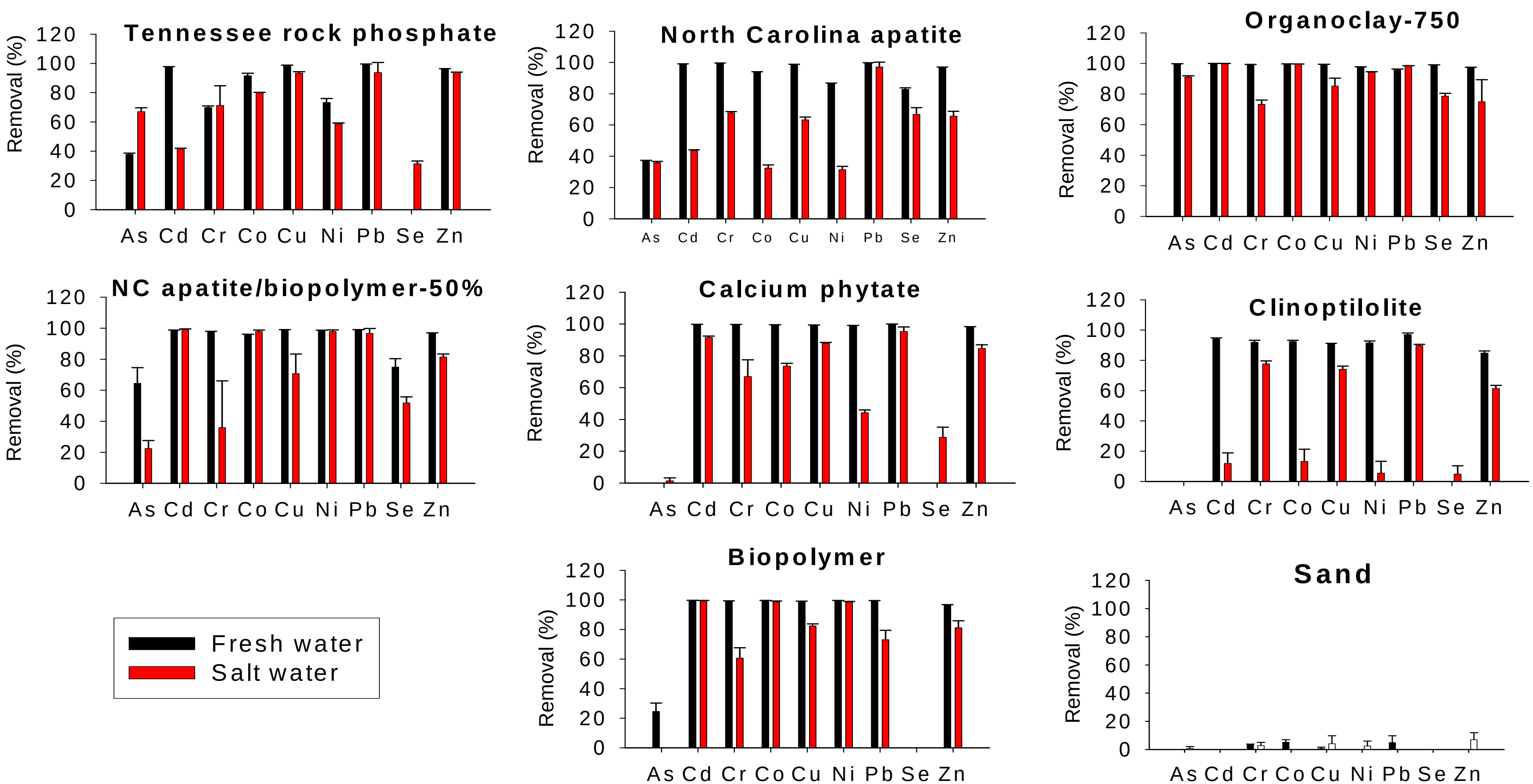
Amendments:

Apatite, calcium phytate, biological apatite, organoclays, zeolite, and biopolymers (e.g., xanthan, chitosan)

Deliverables:

Distribution coefficient (Kd), % removal, and % retention

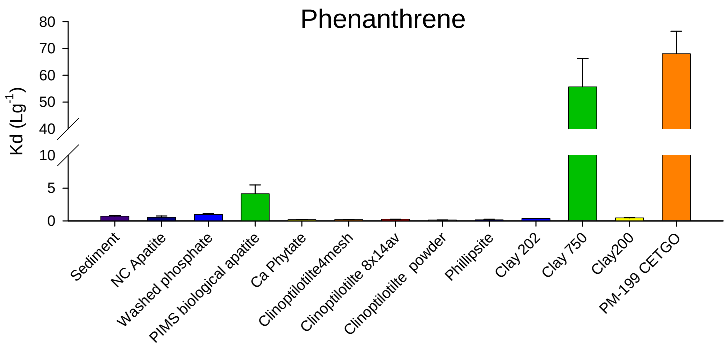
Sorption and Desorption of Metals

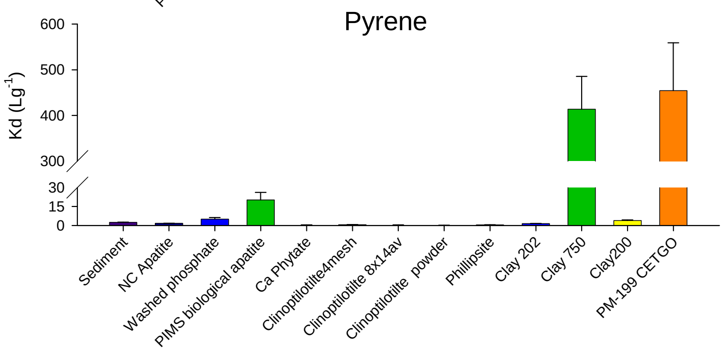


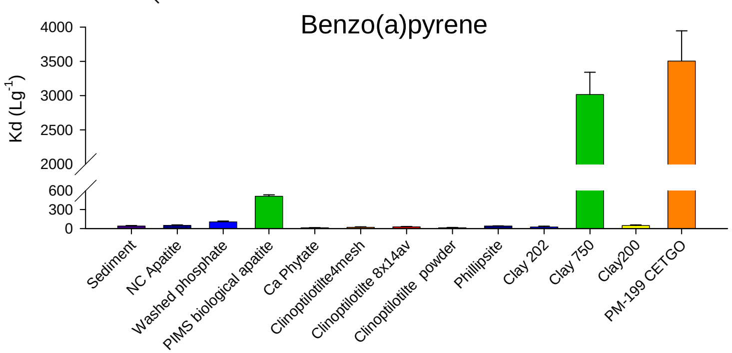
Comparison of metal removal by amendments in fresh and salt water

Sorption of Organic Contaminants

Removal of organic contaminants by amendments. Higher Kds indicate greater potential for removal.





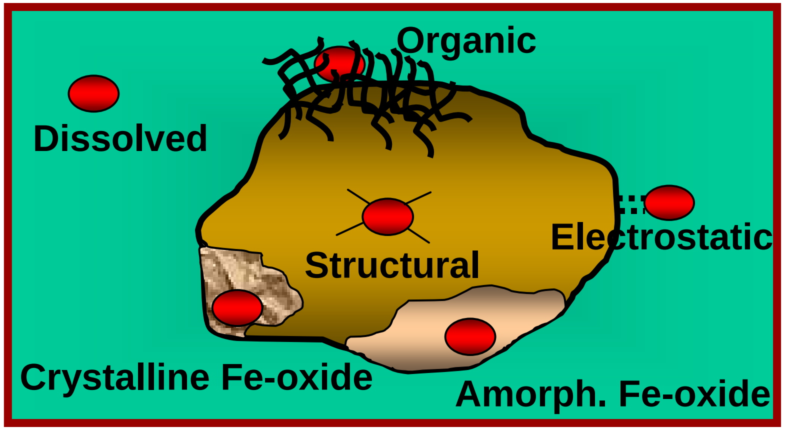


Experimental Methods

Effects of amendments on contaminant mobility/bioavailability

Sequential extractions

Step	Operationally defined fraction	Reagents	Extraction time
1	exchangeable	1.0 M $MgCl_2$	1 h
2	carbonates	1.0 M CH_3COONa	6 h
3	amorphous Fe oxides	0.25 M $NH_2OH{\cdot}HCl$ in 0.25 M HCl	2 h
4	crystalline Fe oxides	1.0 M $NH_2OH{\cdot}HCl$ in 25% CH_3COOH	3 h
5	organic	0.1 M $Na_4P_2O_7$	24 h
6	sulfide	4.0N HNO_3	30 min
7	residual	Agua regia (HCL/HNO_3)	



Tested sediments:

Anacostia River, DC
Elizabeth River, VA

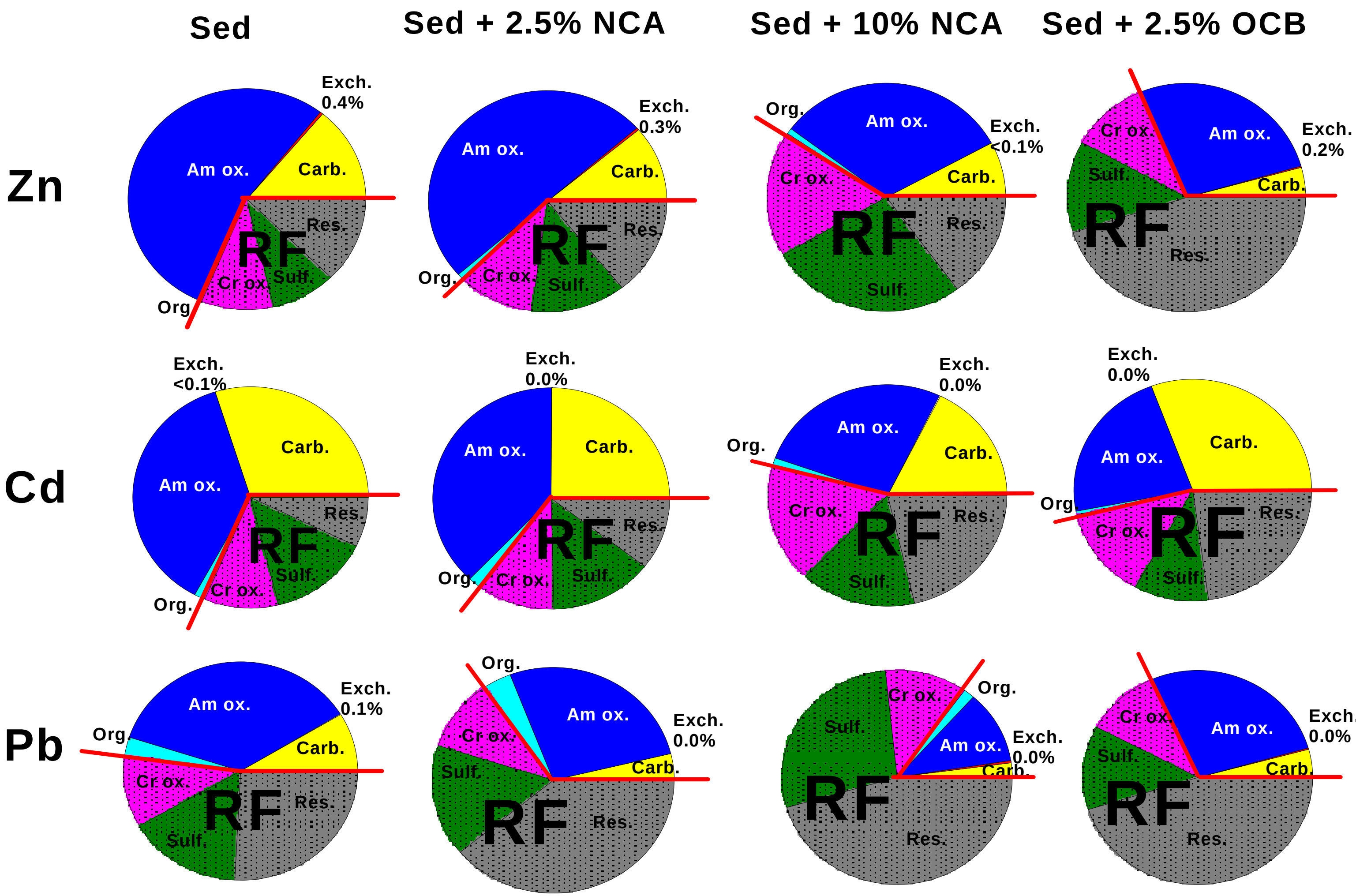
Treatments for Anacostia River sediment:

North Carolina apatite (NCA)
Mixture of 50% NCA and 50% organoclay (OCB-750)

Treatments for Elizabeth River sediment:

NCA at three rates of 2.5%, 5%, and 10%
Organoclay (OCB-750)
Mixture of 50% NCA and 50% organoclay (OCB-750)

Effects of amendments on contaminant mobility/bioavailability



Effect of NCA and OCB on the partitioning of metals in untreated and treated Elizabeth River Sediment. The RF is the fraction that is unlikely to be bioavailable.

Experimental Methods

Effects of amendments on contaminant mobility/bioavailability

Deliverables:

Potentially Mobile Fraction (PMF): the contaminant fraction that has the potential to enter into the mobile aqueous phase under changeable environmental conditions, such as pH, Eh, temperature and others. The PMF includes the water, exchangeable, acid soluble, organic, and amorphous Mn and Fe oxide fractions.

$$\text{PMF} = 100 - (\text{F}\ \textit{Cry. oxides} + \text{F}\ \textit{Residual})$$

F *Cry. Oxides* -crystalline Fe oxide sequential extraction fraction (wt-%)
F*Residual* - residual sequential extraction fraction (wt-%)

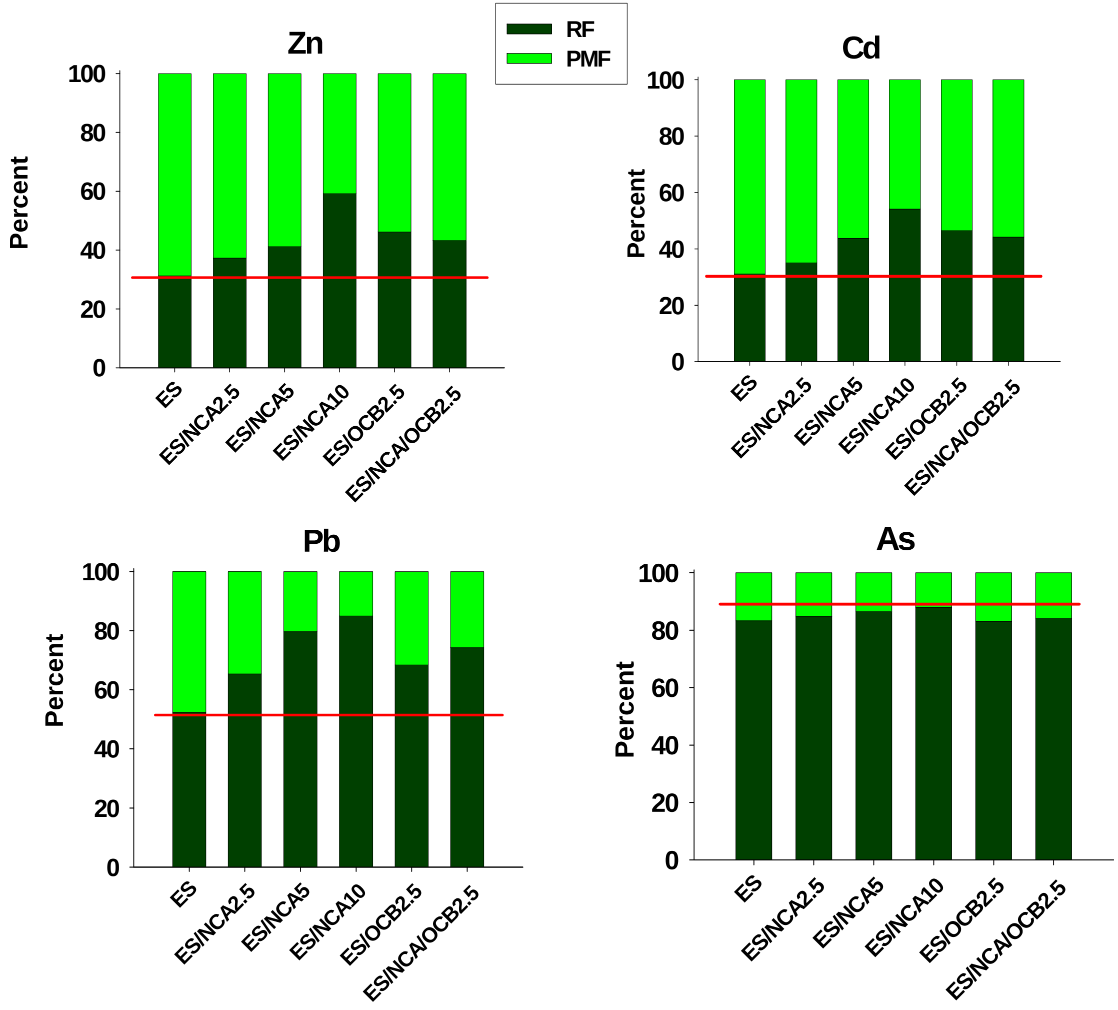
Recalcitrant Factor (RF): the ratio of strongly bound fractions to the total concentration of the element (i.e., sum of all fractions) in the sediment. The RF represents metal fractions that are irreversibly retained by the solid phase.

$$\text{RF} = \left[\frac{C_{\text{cry.oxides}} + C_{\text{residual}}}{C_{\text{exch}} + C_{\text{AS}} + C_{\text{org}} + C_{\text{oxides}} + C_{\text{residual}}}\right] \times 100$$

Effects of amendments on contaminant mobility/bioavailability

Effect of Apatite and Organoclay on PMF and RF

Addition of 10% NCA to the sediment resulted in about a 40% reduction in the PMF values of Cd, Pb, and Zn. Organoclay and a mixture of organoclay with apatite produced similar results; i.e., lower PMF and higher RF.

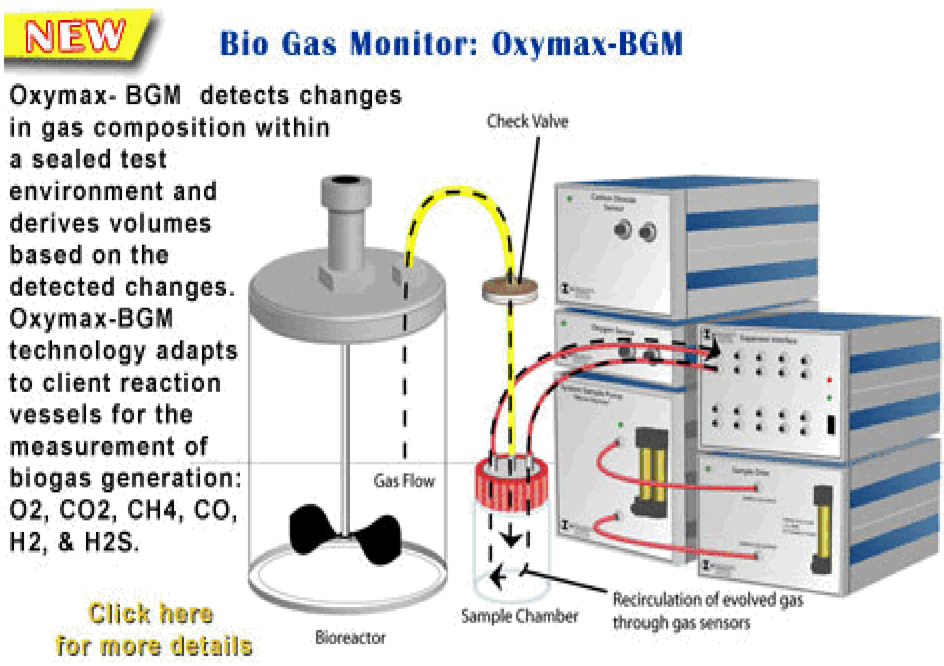


Experimental Methods

Development of cross-linked biopolymer products to provide erosion resistance for active caps and organic carbon for sorption of contaminants

Biopolymer products were tested for:

- Retention of organic carbon
- Sorption
- Biodegradability
- Erosion control



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Preparation of deliverable forms of biopolymers by coating on sand particles

Several cross-linked products were tested using two coating procedures:

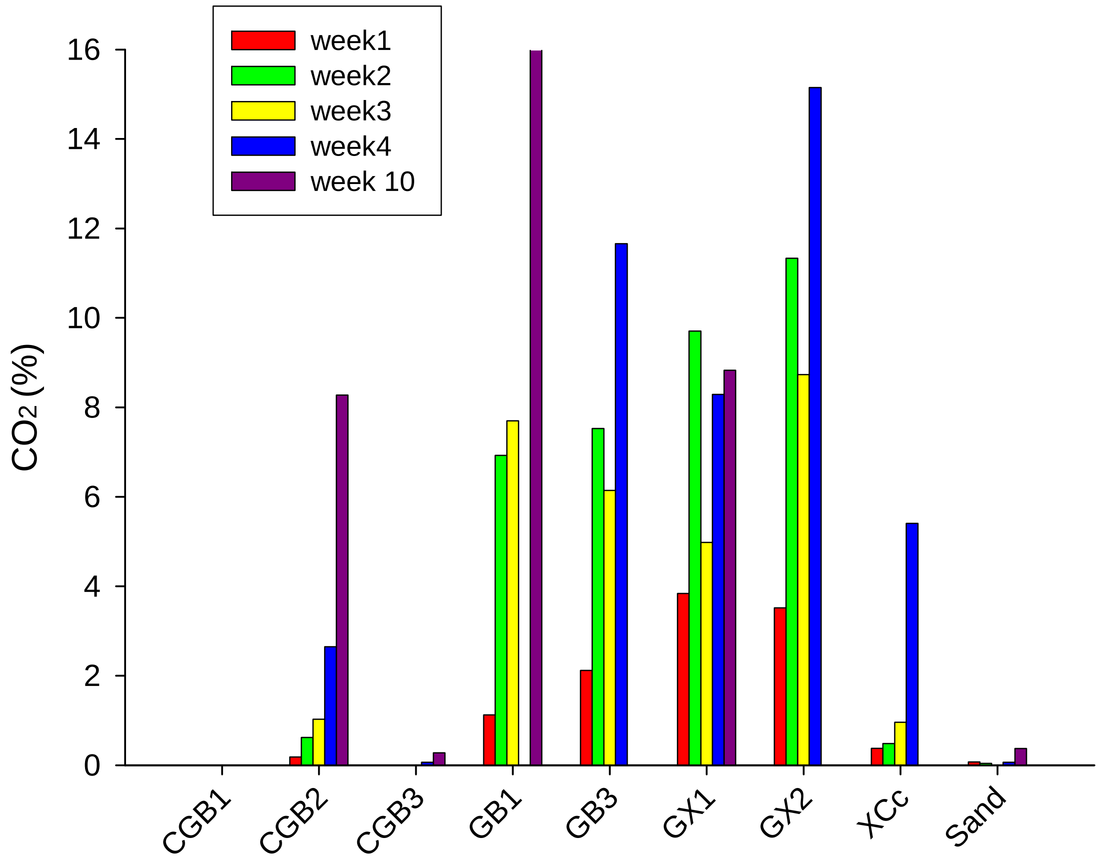
Liquid –treatment of sand with liquid or gel biopolymers

Solid –treatment of sand with a mixture of biopolymer and cross-linker in solid phases.

Adhesive product of sand coated with guar crossed with borax

Coated sand products before (left) and after drying (right)

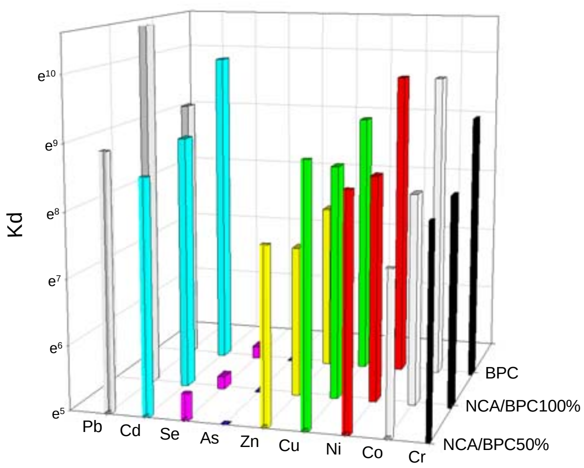
Biodegradability of coated sands

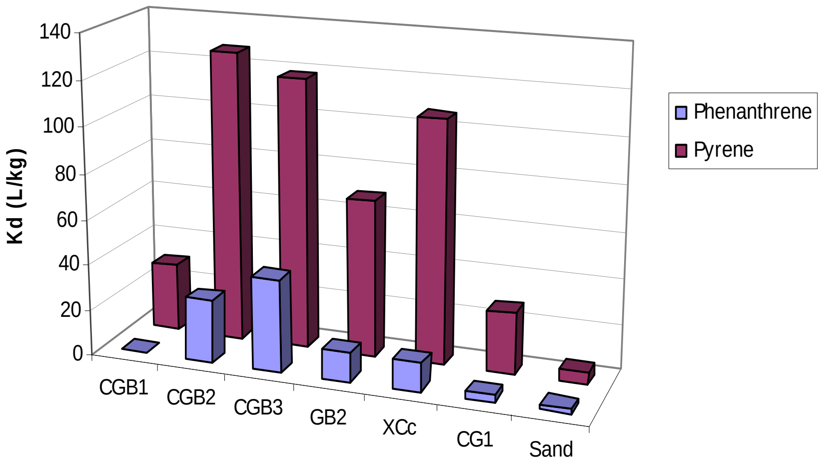


Sand coated with several biopolymers was evaluated for biodegradability in a respirometer (Bio Gas Monitor) where CO_2 was measured for 10 weeks; B - borax, C - chitosan, G - guar gum, X - xanthan, c - calcium chloride, 1 - without glutaraldehyde, 2 - with glutaraldehyde, 3 - without glutaraldehyde but with NaOH

Sorption of metals and organics on biopolymers

Partition coefficients (Kd) (mL g-1) for As, Cd, Cr, Co, Cu, Ni, Pb, Se, and Zn in fresh water for the biopolymer chitosan (BPC) and for mixtures of BPC with North Carolina apatite (NCA).





Partition coefficients (Kds) were measured for each biopolymer coated sand. Sorption studies reveal the potential containment capacities of the coatings as an active cap. Kd values varied, narrowing the spectrum of potential active capping agents.

Experimental Methods

Erosion Evaluation of Biopolymer Products

Standard shaker test (Tsai and Lick, 1986)

Tested materials:

Sand

Organoclay

Dried biopolymer coated sands – XCc, CGB

Slurries of biopolymer coated sands – XCc, CGB, XG

Slurries – biopolymer coated sand XG with apatite and/ or organoclay

Shaker for simulating erosion

Erosion evaluation – shaker tests

Plain sand was easily resuspended at very low speed (3.7 m/s) and exhibited marked erosion at higher speed (11 m/s)

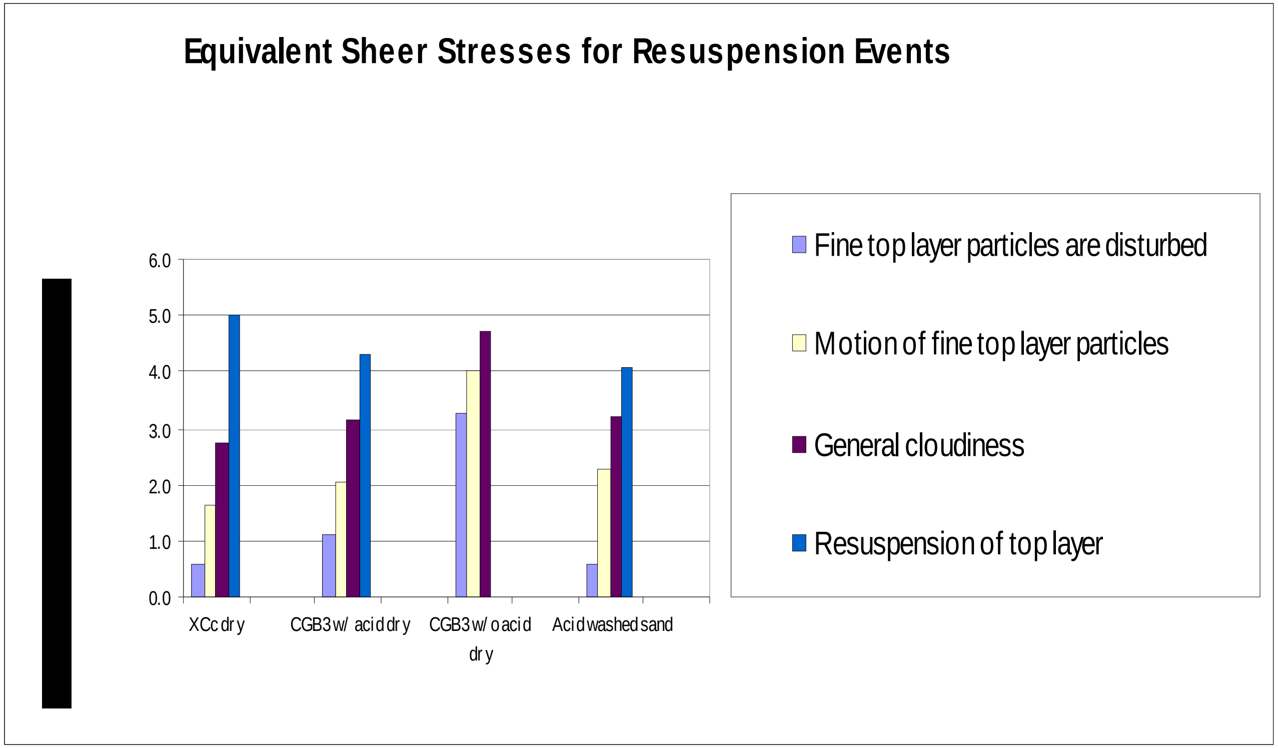
Coated sand with xanthan and guar gum did not exhibit erosion at speeds of 3.7 m/s or 11m/s

Erosion evaluation – shaker tests

Sand and organoclay (PM-199) mixed with the biopolymers xanthan and guar gum did not show erosion at speeds of 3.7m/s or 11m/s

Resuspension of organoclay (PM-199) leading to cloudiness and surface erosion at speeds of 3.7m/s and 11m/s

Erosion evaluation – shaker tests



Effects of equivalent sheer stresses on resuspension of sand and three types of dry and rewetted biopolymer coated sand

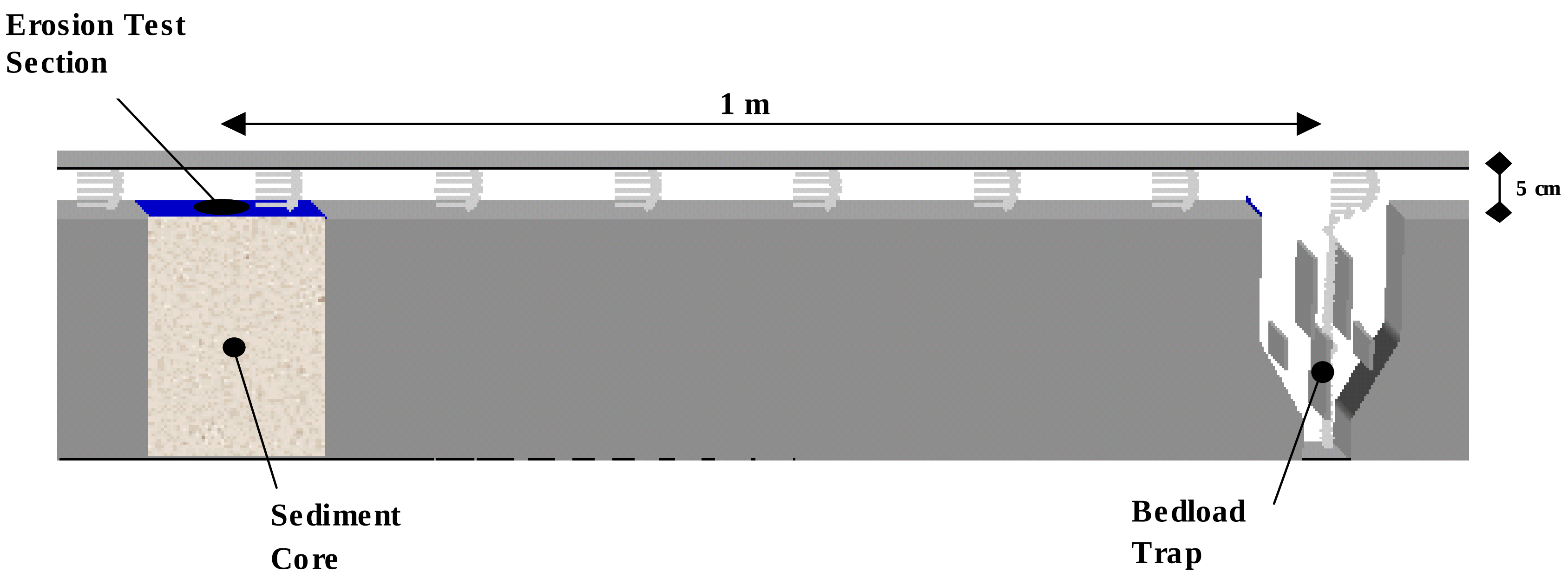
Experimental Methods

Erosion Evaluation of Biopolymer Products

Adjustable Shear Stress Erosion and Transport (ASSET) Flume Test

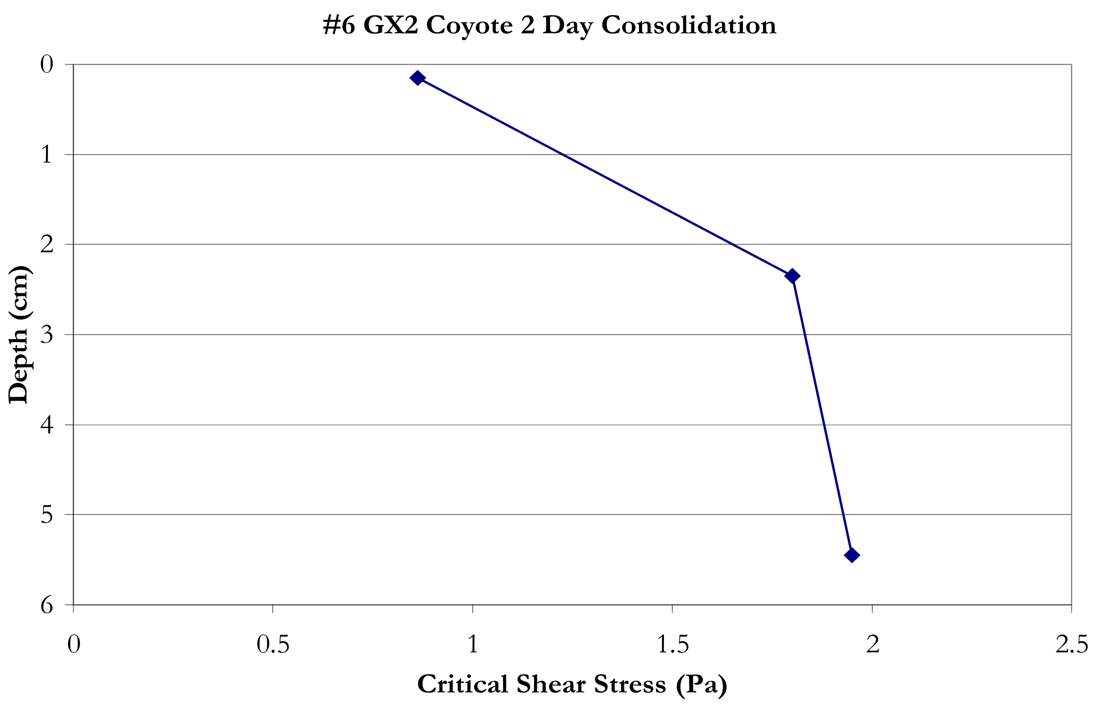
Tested materials:

Sand, slurries of biopolymer coated sands (XCc, CGB, XG) and slurries of biopolymer coated sand (XG), apatite, and/or organoclay



Schematic of the ASSET flume

Adjustable Shear Stress Erosion and Transport (ASSET) flume test



Erosion rates and critical shear stress vs. depth for an active cap composed of coated sand with guar gum/xanthan (GX). This active cap appeared very cohesive.

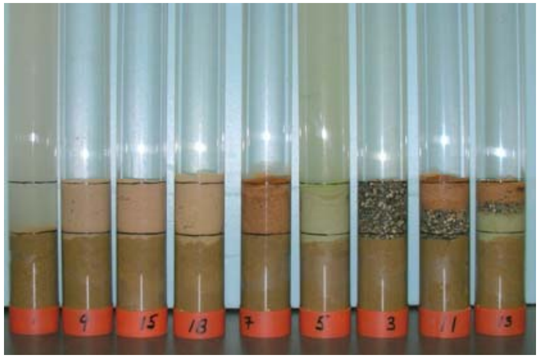
Experimental Methods

Evaluation of diffusive & advective transport of metals and organic contaminants

Column studies

❑Measurement of diffusive transport

Cap composition: 1- no cap (control - only sediment), 9- playground sand, 15 – acid washed sand, 18 – biopolymer coated sand (CGB), 7 - biopolymer coated sand (XCc), 5 – organoclay 750 from Biomin Inc., 3 – NC apatite, 11- biopolymer coated sand (XCc) with NC apatite (50% of each), 13 - biopolymer coated sand (XCc) with NC apatite, and organoclay 750 (33.3% of each)
Deliverables: metal release, carbon release, microbial activity



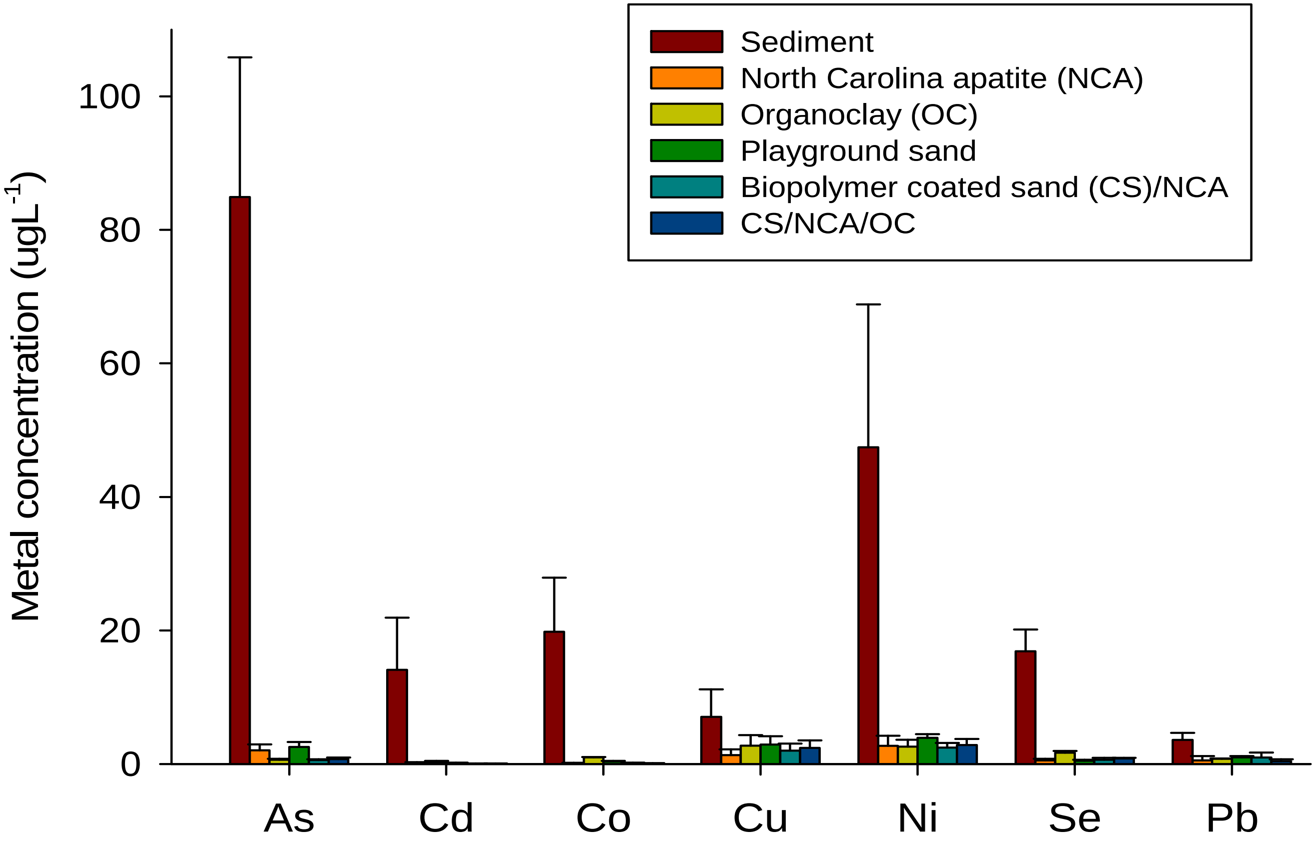
Columns for diffusive transport of metals through cap materials

❑ Measurement of advective transport

Cap composition for metals: playground sand, apatite, and organoclay
Cap composition for organics: organoclay, XCc, and CGB
Bromide tracer: to establish initial breakthrough of the advective front
Deliverables: metal release

Experiment on advective transport of metals through cap materials

Diffusive transport of metals



Metal release in the diffusion experiment after six months; average of five samplings

Experimental Methods

Evaluation of diffusive & advective transport of metals and organic contaminants

Modeling of diffusive and advective transport

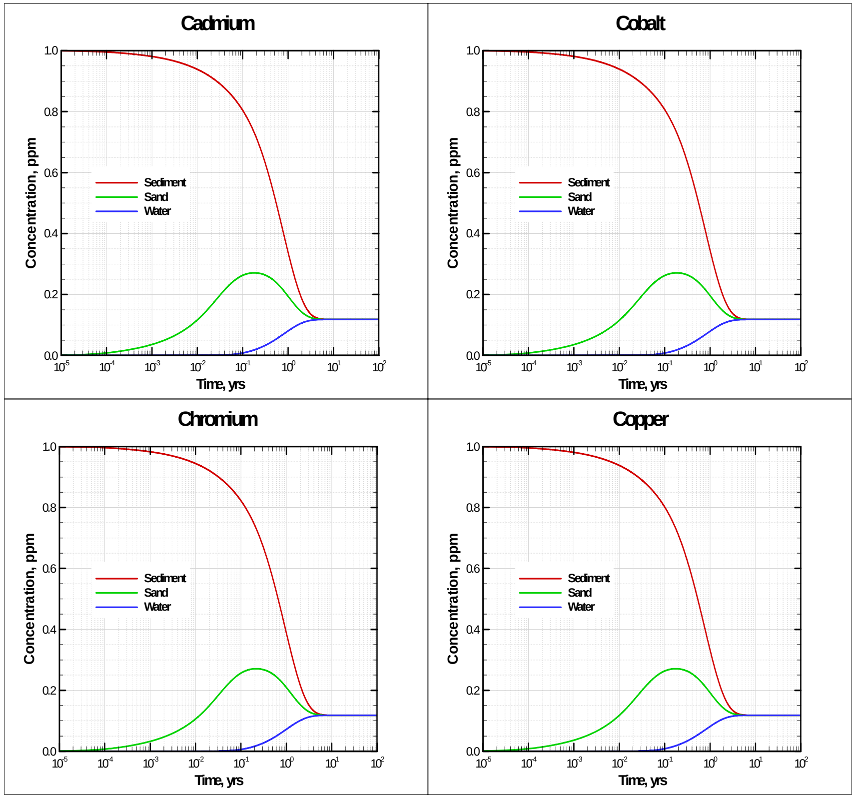
For metals a one-dimensional diffusive transport model was created to represent the laboratory column experiments. The one-dimensional governing equation for mass transport of species ***k*** in the fluid phase is given by:

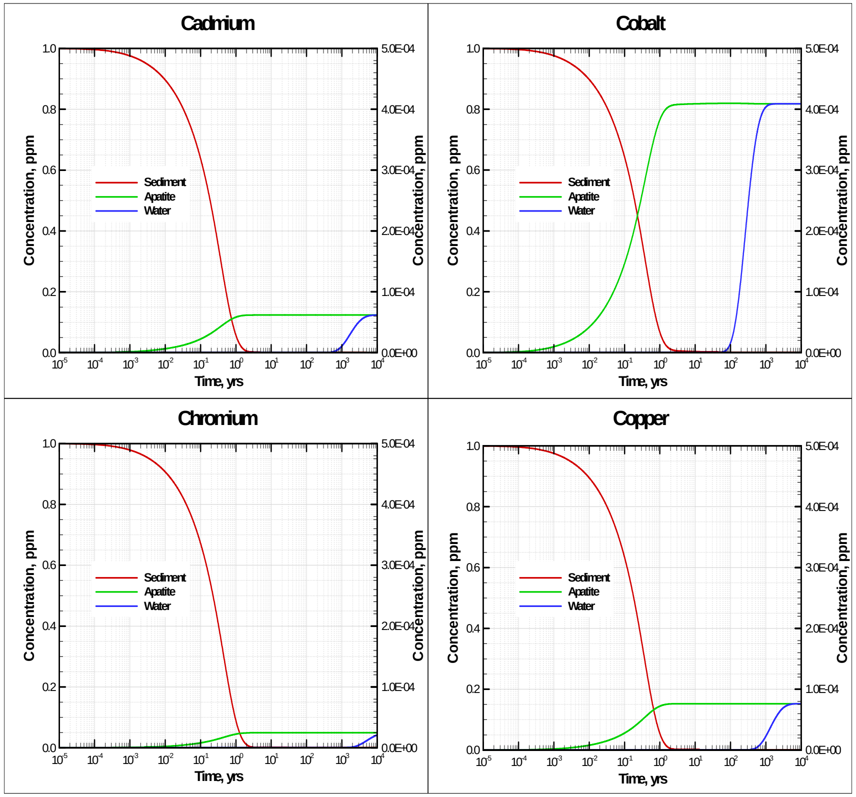
$$\frac{\partial C_k}{\partial t} + \frac{\partial}{\partial x}\left(\frac{V}{R_f} C_k\right) = \frac{\partial}{\partial x}\left(\frac{D_m}{R_f}\frac{\partial C_k}{\partial x}\right)$$

For organic contaminants a diffusion advection transient model was used for modeling the breakthrough time curve for active cap components

$$C_{pw}(z,t) = \frac{C_o}{2}\left[erfc\left(\frac{R_f z - Ut}{2\sqrt{R_f Dt}}\right) + \exp\left(\frac{Uz}{D}\right) erfc\left(\frac{R_f z + Ut}{2\sqrt{R_f Dt}}\right)\right]$$

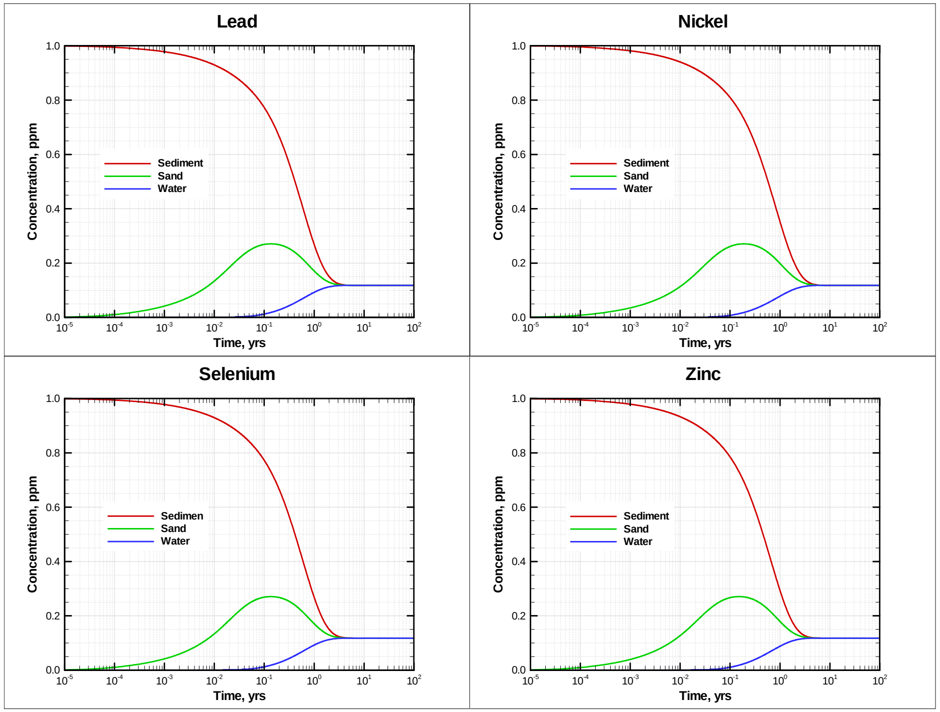
Modeling of diffusive transport of metals

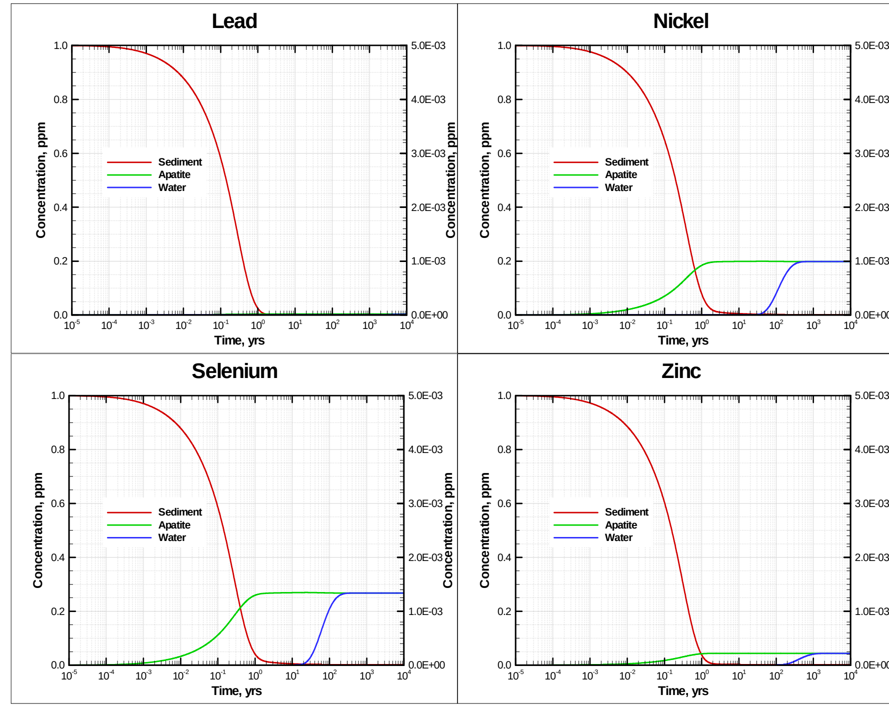




Breakthrough curves for Cd, Co, Cr, and Cu for the sand and apatite cap case

Modeling of diffusive transport of metals





Breakthrough curves for Pb, Ni, Se, and Zn for the sand and apatite cap case

Predicted times for breakthrough of organic contaminants in active caps composed of organoclay and apatite (NCA)

	K_d	τ 15 cm	τ 2.5 cm	K_d	τ 15 cm	τ 2.5 cm
	Phenanthrene			Pyrene		
Clay 750	55600	11000	1800	414000	79000	13000
PM-199	68000	13000	2200	454000	87000	15000
PM-200	36500	7100	1200	98700	19000	3200
NC Apatite	220	43	7.1	695	140	22

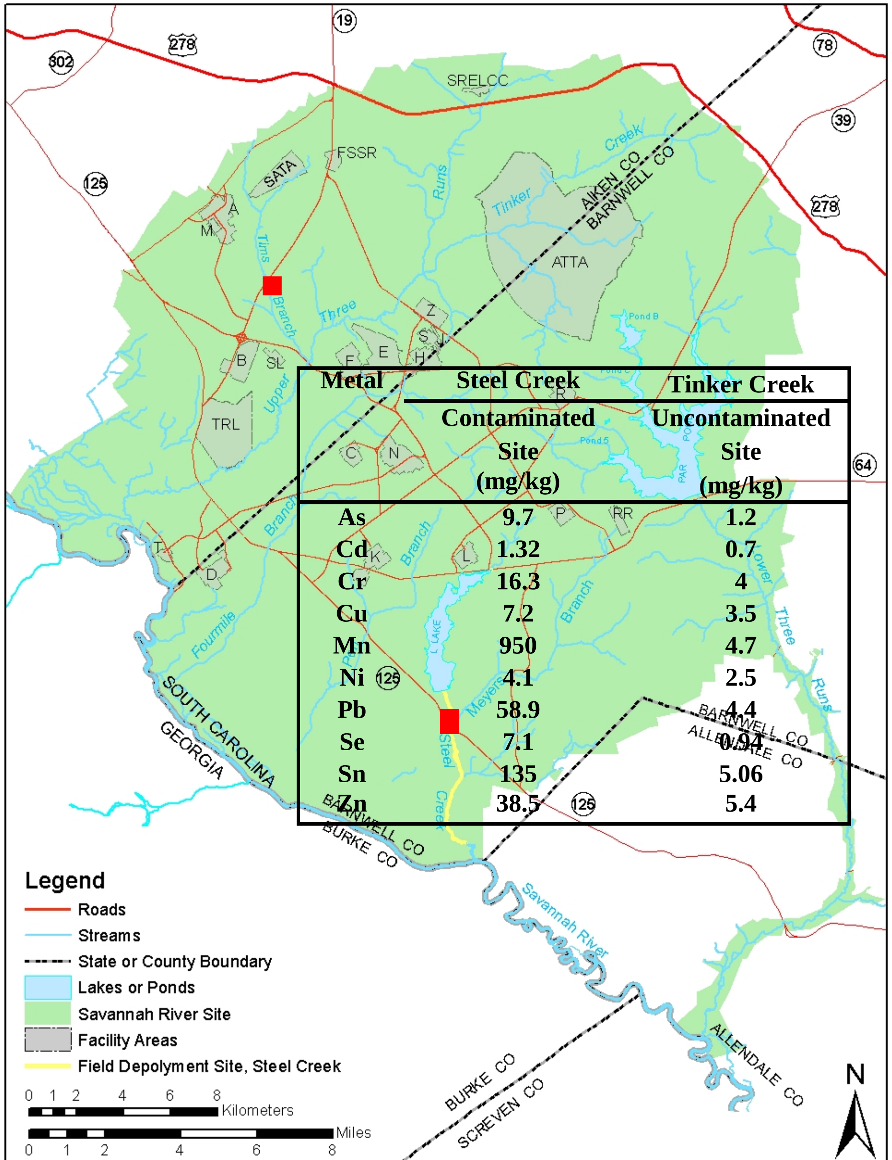
Estimation of cap penetration time (in years) for 15 and 2.5 cm thick active layers; Organoclays – clay 750, PM-199, PM-200, NC Apatite – rock phosphate from NC.

Experimental Methods

Field Deployment

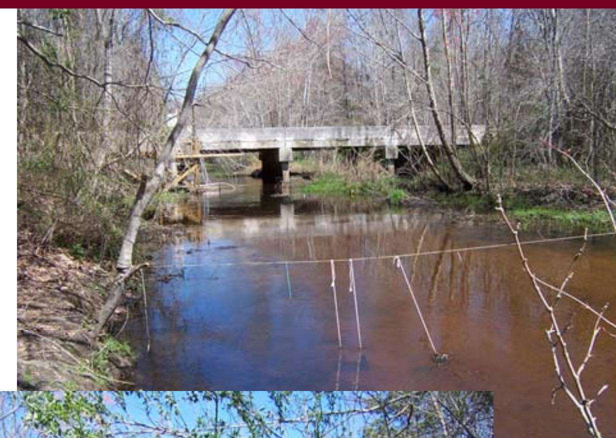
- Determine if the selected amendments pose an environmental hazard (toxicity tests and metal extraction tests)
- Identify a suitable site for the field study based on historical contaminant data
- Collect sediment cores and analyze for metal content
- Determine cap structure and composition
- Determine a method of deployment
- Obtain the required permits from Savannah River Site and state regulators

Task 5. Field Deployment



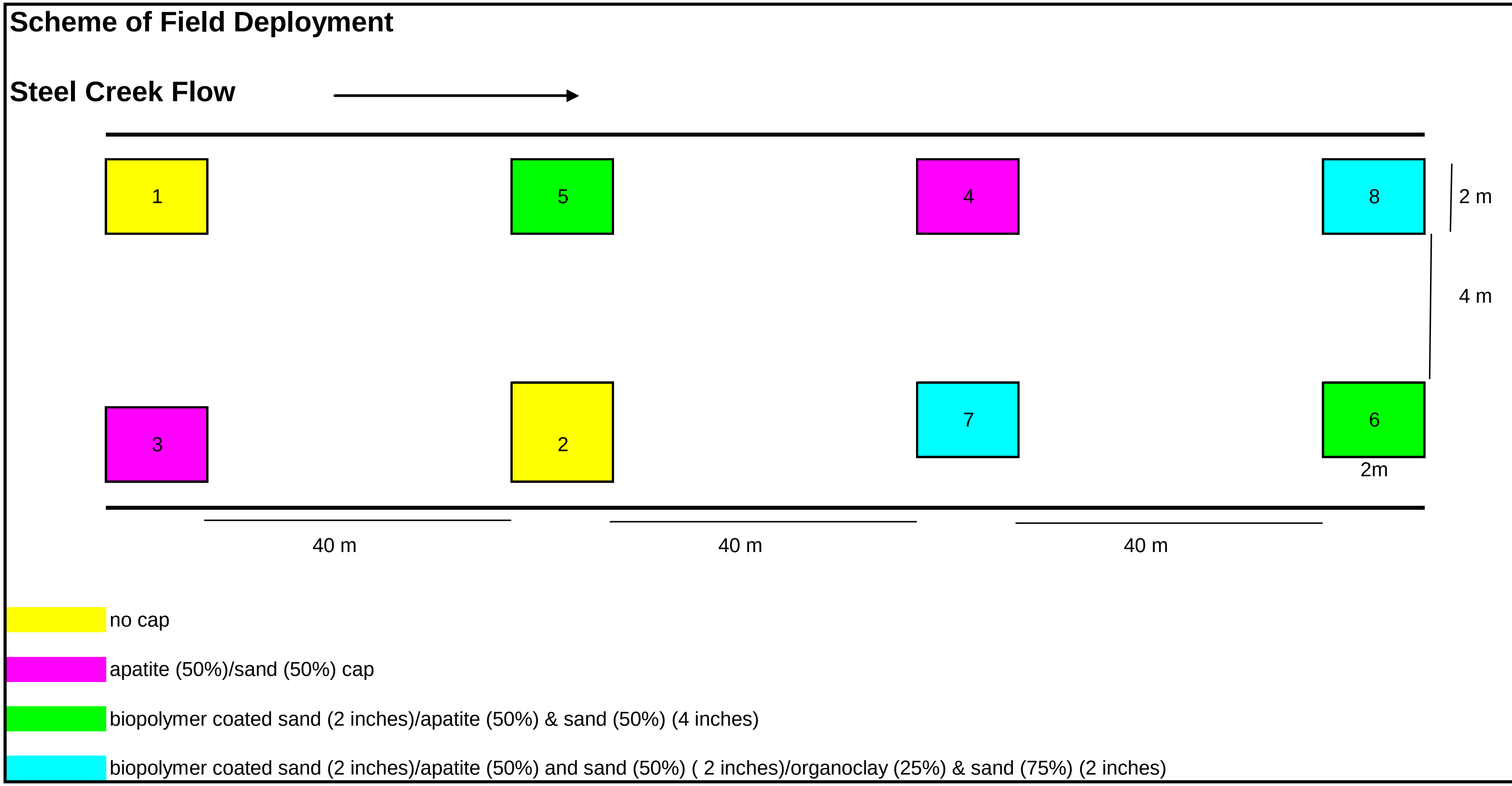
Metal	Steel Creek Contaminated Site (mg/kg)	Tinker Creek Uncontaminated Site (mg/kg)
As	9.7	1.2
Cd	1.32	0.7
Cr	16.3	4
Cu	7.2	3.5
Mn	950	4.7
Ni	4.1	2.5
Pb	58.9	4.4
Se	7.1	0.94
Sn	135	5.06
Zn	38.5	5.4

Site Selection - Map of the Savannah River Site showing potential field study locations on Steel Creek and Tims Branch (red squares)



Views of Steel Creek in the proposed study area

Task 5. Field Deployment



Preliminary schematic drawing of experimental field plots (not drawn to scale)

Metal concentrations in aqueous extracts from amendments

Metal concentrations remained below EPA ambient water quality criteria and other ecological screening values (ESVs)

Element	North Carolina apatite	Organoclay	Biopolymer coated sand	Sand	ESV
Al	30	43	0	<1	**87**
As	0.9	0.1	0	0.4	**2.2**
B	7.4	7.0	7.8	1.1	**750**
Cd	0.2	<0.1	<0.1	0.0	**0.7**
Co	<0.1	<0.1	<0.1	0.0	**3**
Cr	<0.1	0.0	0.2	0	**11**
Cu	1.3	0.4	1.4	0.0	**6.5**
K	337	980	406	104	**53000**
Mn	0.2	46.3	3.7	0.5	**80**
Mo	4.0	0.8	0.2	0.3	**240**
Na	515	48690	21495	<1	**680000**
Ni	<0.1	1	2	<0.1	**88**
Pb	1.2	0.1	0.0	0.2	**1.3**
Sb	0.1	<0.1	<0.1	<0.1	**160**
Se	0.8	1.2	0	0.8	**5**
Zn	2.3	0.5	1.9	1.5	**59**

Evaluation of toxicity

Results of the Toxicity Characteristic Leaching Procedure

Amendments	As (ppm)	Ba (ppm)	Cd (ppm)	Cr (ppm)	Ni (ppm)	Sb (ppm)	Se (ppm)	Pb (ppm)
North Carolina Apatite (NCA)	0.24	0.48	0.02	0.43	0.58	0.02	0.04	0.02
Tennessee brown Rock (TRP)	0.05	1.07	0.00	0.29	0.06	0.00	0.00	0.02
Organoclay (PM-199)	0.03	2.59	0.07	0.26	0.84	0.02	0.08	0.46
Organoclay 750, Biomin	0.03	3.01	0.00	0.36	0.79	0.00	0.01	0.09
Coated sand (CS)	0.01	2.34	0.01	0.39	0.09	0.00	0.02	0.06
Playground sand (PS)	0.01	0.17	0.00	0.29	0.04	0.01	0.01	0.18
TCLP Limit	**5.00**	**100.00**	**1.00**	**5.00**	**70.00**	**1.00**	**1.00**	**5.00**

Leachates from all amendments were well below the TCLP limits.

Sediment toxicity test results

Survival of *Hyalella azteca* was not reduced in sediment composed of North Carolina apatite or biopolymer coated sand

Amendments for use in active caps	Control sediment mean % survival	Amendment mean % survival	Rank sum test of differences
North Carolina apatite	81.3	72.5	Not significant
Biopolymer coated sand (XCc)	88.8	78.8	Not significant

SUMMARY

- Amendments that sequester and retain mixtures of contaminants under a broad range of environmental conditions were identified. Apatite, organoclays, and the biopolymer, chitosan were identified as the best amendments for removing metals from both fresh and salt water. They also exhibited high retention (80% or more) of most tested metals indicating reduced potential for remobilization to the water column.
- Organoclays were identified as the best amendment for containing organic contaminants
- Modeling studies demonstrated that active caps composed of apatite or organoclay can delay contaminant breakthrough due to diffusion by hundreds of years or more compared with passive caps composed of sand
- The EPA TCLP procedure showed that the amendments do not leach hazardous metals
- North Carolina apatite and biopolymer coated sand do not adversely affect benthic organisms, even when used in high concentrations

SUMMARY

- More than 20 biopolymer products were compared resulting in the selection of chitosan/guar gum cross-linked with borax and xanthan/chitosan cross-linked with calcium chloride and xanthan/guar gum for inclusion in active caps to produce a barrier that resists mechanical disturbance

- Slurries of selected biopolymer coated sand particles show high erosion resistance

- A field deployment will be conducted in Steel Creek, at the Savannah River Site, Aiken, SC

- The overall accomplishment of this project is determination of the best active cap materials, the effects of active cap components on metal bioavailability and retention, and the identification of biopolymer products that provide erosion resistance to active caps

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