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**INNOVATIVE IN-SITU REMEDIATION OF CONTAMINATED
SEDIMENTS FOR SIMULTANEOUS CONTROL OF
CONTAMINATION AND EROSION**

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EXECUTIVE SUMMARY

Current technologies for remediating contaminated sediments offer only temporary solutions, do not address mixtures of organic and inorganic contaminants, and may not be effective in both marine and freshwater environments. New technologies are needed that neutralize contaminant toxicity and control physical transport mechanisms that mobilize sediment contaminants. The last 12 months of this comprehensive project investigated the use of combinations of sequestering agents to develop in situ active sediment caps that stabilize mixtures of contaminants and act as a barrier to mechanical disturbance under a broad range of environmental conditions. Efforts focused on the selection of effective sequestering agents for use in active caps, the composition of active caps, and the effects of active cap components on contaminant bioavailability and retention.

Results from this project showed that phosphate amendments, some organoclays, and the biopolymer, chitosan, were very effective at removing metals from both fresh and salt water. These amendments also exhibited high retention (80% or more) of most metals indicating reduced potential for remobilization to the water column. Experiments on metal speciation and retention in contaminated sediment showed that apatite and organoclay can immobilize a broad range of metals under both reduced and oxidized conditions. These studies were followed by sequential extractions to evaluate the bioavailability and retention of metals in treated sediments. Metal fractions recovered in early extraction steps are more likely to be bioavailable and were termed the Potentially Mobile Fraction (PMF). Less bioavailable fractions collected in later extraction steps were termed the Recalcitrant Factor (RF). Apatite and organoclay reduced the PMF and increased the RF for several elements, especially Pb, Zn, Ni, Cr, and Cd.

Empirically determined partitioning coefficients and modeling studies were used to assess the retention of organic contaminants on selected sequestering agents. Organoclays exhibited exceptionally high sorption of polycyclic aromatic hydrocarbons as indicated by a comparison of K_d values among 12 amendments. These results suggested that organoclays have high potential for controlling organic contaminants. Measured partitioning coefficients were used to model the time required for a contaminant to penetrate sediment caps composed of organoclay. The results showed that a thin layer of highly sorptive organoclay can lead to very long migration times, perhaps longer than the expected lifetime of the contaminant in the sediment environment.

A one-dimensional numerical model was used to examine the diffusion of metals through several cap material based on measured and assumed material and transport properties. These studies showed that active caps composed of apatite or organoclay have the potential to delay contaminant breakthrough due to diffusion by hundreds of years or more compared with passive caps composed of sand. Advectively dominated column experiments are currently underway to define effective sorption related retardation factors in promising amendments for various hydrophobic organic compounds. Upon completion of these experiments, advection transient models will be

used to estimate the time required for the breakthrough of various contaminants in caps composed of different experimental materials.

Biopolymer products for inclusion in active caps were evaluated on the basis of resistance to biodegradation, sorption capacity for organic and inorganic contaminants, and potential for erosion control. More than 20 biopolymer products were evaluated resulting in the selection of chitosan/guar gum cross-linked with borax and xanthan/chitosan cross-linked with calcium chloride for inclusion in active caps to produce a barrier that resists mechanical disturbance. A process was developed for coating sand with cross-linked biopolymers to provide a means for delivery to the sediment surface. Properties of biopolymer coated sand such as carbon fraction (indicating biopolymer coverage), porosity, bulk density, and biodegradability have been evaluated, and experiments are currently underway to assess the resistance of biopolymer coated sand to erosion.

Although the ability of active cap materials to remediate contaminants has been emphasized in this study, it is also important to ensure that these materials do not have deleterious effects on the environment. Therefore, promising amendments were evaluated for toxicity using 10 day sediment toxicity tests, the standardized Toxicity Characteristic Leaching Procedure (TCLP), and measurement of metal concentrations in aqueous extracts from the amendments. Metal concentrations were below TCLP limits, EPA ambient water quality criteria, and other ecological screening values. These results showed that apatite, organoclay, and biopolymer coated sand do not release metals. The sediment toxicity tests indicated that apatite and biopolymer coated sand are unlikely to adversely affect benthic organisms, even when used in high concentrations. Future work will include additional laboratory studies as well as biological surveys of the organisms that colonize pilot-scale sediment caps composed of promising amendments.

During the past 12 months this project has determined the best active cap materials, active cap composition, and the effects of active cap components on metal bioavailability, retention, and toxicity. Apatite, organoclay, and cross linked biopolymers have high potential for the design of an environmentally benign, multiple-amendment active cap that is resistant to erosion and effective for the remediation of organic and inorganic contaminants in fresh and salt water.

PROJECT BACKGROUND

Current technologies for remediating contaminated sediments include removal followed by treatment and disposal; in situ isolation of the sediments from the environment by covering the sediment with a sand or gravel cap (i.e., passive capping); and monitored natural recovery, which involves monitoring processes that isolate, degrade, transform, and immobilize contaminated sediments under natural conditions. However, these remedial alternatives offer only temporary solutions, do not address a wide variety of organic and inorganic contaminants, may not be suitable for both marine and freshwater sediments, and may be destructive to the benthic environment. New technologies are needed that neutralize contaminant toxicity and control physical transport mechanisms that mobilize sediment contaminants.

OBJECTIVES

The primary objective to be accomplished over the life of this project is to identify and evaluate promising sequestering materials for the construction of active caps that stabilize inorganic and organic sediment contaminants and are resistant to physical disturbance. Specific objectives of this research are to:

- 1) evaluate the ability of sequestering materials to stabilize a broad range of contaminants in different types of sediments (e.g. marine, fresh water, oxic, anoxic) under controlled laboratory conditions,
- 2) determine the best combination of amendments for construction of active sediment caps,
- 3) evaluate the resistance of different active caps to physical disturbance,
- 4) develop conceptual and mathematical models for contaminant attenuation in active caps, and
- 5) evaluate the effects of the proposed active caps on contaminant mobility, bioavailability, retention, and toxicity under field conditions.

In the past year work continued on tasks 1, 2 and task 3 was initiated. The primary objectives of the tasks included in this report were to:

- 1) evaluate sequestering agents for the removal, retention, and bioavailability of inorganic and organic contaminants in the laboratory (Task 1, Subtask 1.1, Subtask 1.2),
- 2) evaluate the mechanical properties of biopolymers, develop procedures for making cross-linked biopolymers, and conduct preliminary work on the development of methods to deliver biopolymers to underwater sediments (Task 2, Subtask 2.1)
- 3) evaluate diffusive transport of contaminants through active caps composed of promising sequestering agents (Task 2, Subtask 2.2.),
- 4) evaluate advective transport of contaminants through active caps composed of promising sequestering agents (Task2, Subtask 2.3),
- 5) evaluate potential toxicity of amendments (Task 2, Subtask 2.4 – this subtask was added to the project to determine if promising sediment amendments have the potential to harm benthic organisms),

- 6) evaluate the ability of biopolymer coated sand to reduce erosion in active sediment caps (Task 3).

TECHNICAL APPROACH

The proposed active capping technology consists of the in situ application of phosphate materials, organoclays, biopolymer products, and possibly zeolite. The amendments were tested individually and together in different proportions to determine the best composition for an active capping layer to be applied over contaminated sediments. The treatment is based on the proven ability of phosphate-based materials to stabilize metals and radionuclides, of organoclays to bind nonpolar pollutants such as PCBs and PAHs, and of biopolymers and their cross-link networks to act as plugging agents that bind and stabilize metals, radionuclides, and other contaminants (e.g., PAHs) in porous media, while being stable to biodegradation. Phosphate amendments, organoclays, and the cross-link products of one or more biopolymer products complement each other to stabilize a wider range of organic and inorganic compounds than any could individually. This research integrates development of an active capping system for sediment remediation, its placement for optimal environmental protection, and evaluation of the ecological effects of the capping system. Success is being measured using various short term and long term geochemical and biological approaches.

The study consists of five tasks. The first task consisted of two subtasks. In the first subtask, sorption and desorption laboratory experiments were conducted to evaluate the ability of the amendments to sequester and retain organic and inorganic contaminants. The second subtask concerned the effects of the amendments on contaminant mobility and bioavailability. The bioavailability and retention of inorganic contaminants in treated sediments was evaluated by sequential extraction techniques. The second task consists of four subtasks. Studies under task 2 identified the best combination of amendments for various contaminants and application methods that produce the best cap. The following experiments were conducted in this task: diffusive transport, advective transport, evaluation of contaminant attenuation, mechanical tests, and toxicity and extraction tests. The third task consists of shaker studies that are evaluating the resistance of the caps to physical disturbance. The fourth task consists of analysis and integration of laboratory results with the objective of developing conceptual and mathematical models for effective deployment of the capping amendments under field conditions. The fifth task consists of small-scale field deployment and evaluation of the capping technology at a contaminated site. Task 5 will provide a realistic evaluation of the ability of the innovative capping technologies to control the mobility, bioavailability, and environmental toxicity of contaminants commonly found at DoD sites. Taken together, the results of these five tasks will provide a firm basis for transitioning the proposed technology from the laboratory to field deployment.

PROJECT ACCOMPLISHMENTS

INTRODUCTION

Current remediation/risk management options for contaminated sediments include no action, monitored natural recovery, institutional controls (land use restrictions, etc.), in situ treatment and management, and ex situ treatment and management. Monitored natural recovery (MNR) is the reliance on natural processes to achieve remedial objectives. Natural attenuation processes include physical, chemical, or biological processes that act without human intervention to reduce the mass, toxicity, mobility, or concentration of contaminants (USEPA-ORD 1999). MNR is viable where the short-term risks posed by the contaminants are acceptable, the sediments are fairly stable, and the overall cost/benefit of MNR is desirable. The weaknesses of natural recovery are risk of changes in the site's natural processes, risk of contaminant dispersion due to natural or anthropogenic events, and risks posed by existing sediment concentrations until acceptable levels are achieved.

Traditional efforts to manage contaminated sediments often focus on removal and ex-situ management including dredging or dry excavation followed by off-site management (including treatment) of the removed sediments. Most dredging has been limited to small sites (<50,000 cubic yards). The limitations of dredging include releases during implementation, risks to workers during construction and transportation, community impacts (accidents, noise, odor, air emissions), disruption of use and enjoyment of the resource, disruption of benthic ecology, impacts on fish and wildlife, impacts of contaminated residuals (inside and outside of the remedial area), and risk of releases at the final disposal location.

In-situ management of contaminated sediments is potentially less expensive and risky than ex-situ management, but there are relatively few alternatives for in-situ treatment, and some are still under development. Bioremediation, active capping, and passive capping are among the more promising alternatives for in-situ remediation of sediments. Bioremediation is the use of biological systems to remove or detoxify chemical pollutants in the environment. The goal of bioremediation is to degrade organic pollutants to concentrations that are either undetectable or, if detectable, to concentrations below the limits established as acceptable by regulatory agencies. The complexity of sediment-water ecosystems often limits the effectiveness of in situ bioremediation, which is generally most successful when environmental conditions can be carefully controlled and adjusted as the biotransformation processes progress with time. However, such control is difficult to maintain under natural conditions.

Passive (inactive) capping is defined as the installation of a subaqueous covering or cap of clean, inert material over contaminated sediment, thus isolating it from the surrounding environment and reducing contaminant migration in the water phase. This alternative can be an effective approach for remediation of contaminated sediment under

certain conditions and is relatively economical. However, the inert materials (sand, gravel, or similar nonreactive materials) used in passive caps do not immobilize contaminants and are subject to mechanical disturbance that can release toxic contaminants.

In contrast to passive capping, active or reactive capping, which is targeted by the current study, involves the use of capping materials that react with sediment contaminants to reduce their toxicity or bioavailability. Active capping is a less mature technology that holds great potential for a more permanent solution that avoids residual risks resulting from contaminant migration through the cap or breaching of the cap. Active caps, although directly reducing the bioavailability and toxicity of sediment contaminants (rather than simply making them less accessible), often require additional protection, such as a layer of armoring material to protect them from physical disturbance in dynamic aquatic environments.

Apart from types of amendments potentially useful in active capping, little is known regarding amendment application techniques, application rates, and amendment combinations that will maximize immobilization of contaminants. The current research is designed to extend the range of potential active cap technologies to address a variety of contaminants more effectively. Of the technologies under consideration, only apatite has been evaluated for active capping, but surprisingly little is known about the limitations of apatite, especially for metals other than lead. In addition to furthering our understanding of apatite, the current study will investigate other amendments for sequestration of contaminants and the control of erosion and other physical processes that transport contaminants. These results will provide a basis for combining amendments to produce a multipurpose cap capable of treating an assortment of organic and inorganic contaminants under a range of environmental conditions.

MATERIALS AND METHODS

TASK 1. EFFECT OF AMENDMENTS ON CONTAMINANT MOBILITY AND BIOAVAILABILITY – LABORATORY STUDY

SUBTASK 1.1. SORPTION AND DESORPTION OF CONTAMINANTS BY SEQUESTERING AGENTS

Sorption of organic contaminants by sequestering agents

Twelve amendments were evaluated to determine their sorption capacity for the three polycyclic aromatic hydrocarbons (PAHs): phenanthrene, pyrene, and benzo[a]pyrene. The amendments included organoclays (PM-199 from CETCO, IL and Clayfloc™ 200, 202 and 750 from Biomin Inc, MI), zeolites (clinoptilolite - powder; clinoptilolite TSM 140, -4 mesh; clinoptilolite TSM, 8x14 mesh; and phillipsite TSM 180), apatite/rock phosphate (apatite from North Carolina and washed phosphate ore from Tennessee), PIMS biological apatite (ground fish bones), and calcium phytate. The

sorption capacity of these amendments was compared with the sorption capacity of untreated sediments from the Anacostia River, Washington.

Partitioning coefficient measurements were carried out in 50 mL centrifuge tubes (VWR, PA). A piece of aluminum foil was attached to the inside of each tube cap to minimize sorption loss. Twenty mg of each sorbent was weighed and transferred to individual tubes. Three to five replicates were prepared for each sorbent. Fifty mL of pre-made contaminated solution was then added to each tube, and the tubes were tumbled for 48 hours. After tumbling the tubes were centrifuged for 30 minutes at 3000 rpm, and 1 mL of supernatant from each tube was transferred to 2mL HPLC vials. The concentrations of PAHs remaining in the supernatant were determined immediately by high performance liquid chromatography (HPLC) In addition, 15 mL of supernatant from each tube was transferred to a 15 mL vial containing a one cm polydimethylsiloxane (PDMS)-coated fiber. The vials were then shaken on a shaker table for two hours. The fibers were quickly removed after the shaking and put into small inserts of the 2mL HPLC vials. One hundred μ L of acetonitrile was added to the inserts to desorb contaminants on the fiber. The acetonitrile solution was analyzed with HPLC, and the concentrations were compared with external standards. External standards were prepared by serial dilutions of pre-made stock solution with known concentrations. The standards were treated exactly the same as the samples.

For highly sorptive materials such as Clayfloc 750 and CETCO-199, benzo(a)pyrene in the supernatant was lower than the detection limits for both direct injection and solid phase microextraction (SPME). In this case, the experiment was repeated as described above except that solvent extraction was utilized in the final stage to analyze contaminants in the supernatant. After centrifugation, 40 mL of liquid was transferred to 100 mL tubes and 10 mL of hexane was used to extract the contaminants. The mixture was allowed to shake on a shaker table for approximately 12 hours. The extraction rate of hexane was determined to be over 95%. Following the extraction, as much hexane as possible was taken out with a pipette and blown down with a RAPIDVAP N2-evaporator (Labcono, MO) to about 0.2 mL. Exact volume of hexane was recorded. Acetonitrile was then added to bring the volume back to 2 mL and re-blown down to approximately 0.1 mL. The concentrations were then determined by HPLC. Due to the effect of dissolved organic carbon (DOC), the concentrations of PAHs were higher than measured from direct injection or SPME. To remove the effect of DOCs, the dissolved water concentrations were determined with the following equation:

$$C_w = \frac{C_{WM}}{1 + C_{DOC}K_{DOC}}$$

Where C_{WM} is the water concentration measured via extraction (mg/L), C_w is the free or truly dissolved water concentration (mg/L), C_{DOC} is the DOC content in water and K_{DOC} is the DOC water partition coefficient determined from the following correlation:

$$\log K_{DOC} = \log K_{ow} - 0.58$$

This DOC was then used to correct the partitioning coefficient of benzo(a)pyrene of these materials obtained from solvent extraction. The concentrations of phenanthrene and pyrene obtained by solvent extraction were compared with those obtained by direct injection and SPME, which were similar.

Sorption of organic contaminants on sand coated with cross-linked biopolymers

In the first year of the study, coating sand grains with cross-linked biopolymers was identified as a useful method of delivering biopolymers to the sediment surface (see Task 2, Subtask 2.1). In this experiment the sorption capacities of five coated sand samples (three with chitosan/guar gum cross-linked with borax (CGB, CGB2, and CGB3), one with guar gum cross-linked with borax (GB2), and one with xanthan/chitosan cross-linked with calcium chloride (XCc) were evaluated for organic contaminants. We examined PAHs purchased from a commercial supplier (Sigma Aldrich, MO) including 5000 mg L⁻¹ phenanthrene in methanol, 1000 mg L⁻¹ pyrene in methanol, and 200 mg L⁻¹ benzo(a)pyrene in methylene chloride. These solutions were diluted in electrolyte solutions (0.01M NaCl, 0.01M CaCl₂·2H₂O) to prepare a mixture of 20ppb phenanthrene and 100ppb pyrene. Exact concentrations of these compounds were determined with a high performance liquid chromatograph (HPLC, Waters, MA), affiliated with a Waters 2475 Multi λ Fluorescence Detector and Waters 996 Photodiode Array Detector. Sodium azide (0.05M) was added to the electrolyte solution to inhibit bacterial degradation of the PAHs.

Sorption of metals on biopolymer coated sand

Five biopolymer coated sand products were selected for evaluation of metal sorption: two with chitosan/guar gum cross-linked with borax (CGB1 and CGB3), two with guar gum cross-linked with borax (GB2 and GB3), and one with xanthan/chitosan cross-linked with calcium chloride (XCC). The experiments were conducted in 50 mL centrifuge tubes for one week. Each treatment had three replicates, two for metal analysis by ICP-MS and a third for measurement of pH. The spike solution used in the experiment was obtained from Inorganic Ventures, Lakewood, NJ. The metal concentrations in the spike solution were 1 mg L⁻¹ of As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn. Suspensions composed of 0.2 gram of solid (biopolymer coated sand or a control sand without biopolymers) and 15 mL of spike solution were shaken for one week, phase separated by centrifugation, and then analyzed for metals by ICP-MS.

SUBTASK 1. 2. EFFECT OF SEQUESTERING AGENTS ON THE MOBILITY, BIOAVAILABILITY, AND RETENTION OF CONTAMINANTS IN CONTAMINATED SEDIMENTS

Kinetic studies on retention of organic contaminants

Sorption and desorption are both time sensitive processes. A kinetic study was conducted to ensure that equilibrium was reached before samples were taken for the

measurement of sorption and desorption coefficients. Three materials were tested, with one from each of the three groups of amendments under investigation: apatite, organoclay and zeolite. Specifically, the three materials tested were Clinoptilolite TSM 140 (8x14 mesh), PIMS biological apatite (ground fish bones) and Clay 750 (Biomim). The kinetic studies were performed in 50mL centrifuge tubes. Sorbents (20 mg to 1g) were weighed into the centrifuge tubes followed by 50 mL of electrolyte solutions artificially contaminated with phenanthrene and pyrene. The tubes were then tumbled in a tumbler, and water samples were collected at 6 hrs, 24hrs, 48 hrs, and 96 hrs. The tubes were centrifuged for sample collection and 1mL of liquid was taken for contaminant analysis by HPLC

Effect of sequestering agents on availability and retention of metals

Under this subtask experiments were conducted to determine the effects of potential amendments on metal speciation and retention in contaminated sediment. Sediment samples were treated with North Carolina apatite, zeolite (clinoptilolite), a mixture of North Carolina apatite with chitosan, a mixture of North Carolina apatite with organoclay (OCB-750), and a mixture of North Carolina apatite, chitosan and organoclay (OCB-750). The experiment was conducted under oxidized and reduced conditions. For the reduced treatments, 40g of Anacostia River sediment, 2g of amendment or amendment mixture, and 25-mL of pore water from the Anacostia River sediment was added to 50-mL tubes. The tubes were on a platform shaker for eight weeks before separating the solids and liquids for chemical characterization.

Disposable filtration units were used for the oxidized treatments. These 115-mL plexiglass containers consisted of two chambers separated by a 0.45- μ m filter membrane. Forty g of the Anacostia River sediment, 2 g of amendment or amendment mixture, and 25-mL of pore water from the Anacostia River sediment were added to the treated sediment. The units were open to provide oxygen exchange with the atmosphere. After eight weeks the remaining water was suction vacuumed through the filter and measured for pH, Eh (a measure of the redox status), dissolved O₂, DOC, and electrical conductivity (EC) (a measure of the total concentration of ions in solution). The collected water solutions were analyzed for metals by inductively coupled plasma – mass spectrometry (ICP-MS).

A sequential extraction scheme based on modified methods of Tessier et al. (1979) was used to evaluate the distribution of metals in sediments from the Anacostia River, DC and The Elizabeth River, VA that were untreated and treated with amendments (Table 1). The Anacostia sediment was amended with North Carolina apatite (NCA) at 2.5% of the sediment wet weight, and with a mixture of 50% NCA and 50% organoclay (OCB-750), also at 2.5% of the wet sediment weight. The Elizabeth River sediment was amended with NCA at three rates (2.5%, 5%, and 10%), with OCB-750 (2.5%), and with a mixture of 50% NCA and 50% OCB-750 (2.5 % of the sediment wet weight). The following fractions were extracted: 1) exchangeable, 2) carbonate, 3) amorphous Fe and Mn oxides, 4) crystalline Fe and Mn oxides, 5) organic, 6) sulfides, and 7) residual (Table 1). All extractions, except the final digestion, were conducted in 50-mL

polypropylene centrifuge vials to minimize losses of solid material. Separation of extracts from sediments was achieved by centrifuging at 2400 rpm for 20 min between each successive extraction. The supernatant was removed with a pipette, filtered through a 0.45- μm filter, and stored for analysis. The residue was washed with 10 mL of nanopure water (resistivity greater than 18.0 $\text{M}\Omega\text{-cm}$, conductivity less than $0.055\mu\text{s cm}^{-1}$), centrifuged, and the supernatant was added to the sample extract. The nanopure water was obtained from a water purification system EASY II LF (model D738, Barnstead International, Dubuque, IA). The residual and total concentrations of elements were determined by a total microwave digestion of 1 g of sediment with aqua regia (mixture of concentrated acids HCL and HNO_3). The extract solutions from all fractions were analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Table 1. Sequential extraction procedure employed for the geochemical fractionation of the untreated sediments and sediments treated with amendments.

Step	Operationally defined fraction	Reagents	Extraction time
1	exchangeable	1.0 M MgCl_2	1 h
2	carbonates	1.0 M CH_3COOHNa	6 h
3	amorphous oxides	0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 0.25 M HCl	2 h
4	crystalline oxides	1.0 M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% CH_3COOH	3 h
5	organic	0.1 M $\text{Na}_4\text{P}_2\text{O}_7$	24 h
6	sulfide	4.0N HNO_3	30 min
7	residual	HNO_3 /HCl (agua regia)	

The results of the solid phase sequential extractions were analyzed using the Potentially Mobile Fraction (PMF) and Recalcitrant Factor (RF) concepts (Knox et al, 2006a). Early extraction steps (water soluble, exchangeable, amorphous Mn and Fe oxides, and organic fractions) tend to recover metal fractions that are less strongly bound than the fractions collected in the later extraction steps (crystalline oxides, sulfides, and residue fractions). These less strongly bound potentially bioavailable fractions can be termed the PMF because they constitute the contaminant fraction that has the potential to enter into the mobile aqueous phase under changeable environmental conditions, such as pH, Eh, temperature, etc. Generally, only water and exchangeable fractions are very easily mobile and bioavailable. The PMF will be estimated using the equation shown below:

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

$\text{F}_{\text{Cry. oxides}}$ = crystalline Fe oxide sequential extraction fraction (wt-%),
 $\text{F}_{\text{sulfides}}$ = sulfide sequential extraction (wt-%),
 $\text{F}_{\text{Residual}}$ = residual sequential extraction fraction (wt-%).

The strongly bound fractions collected in the later extraction steps are likely to include metals that will be retained by the treated sediment. Fractions of the contaminant

pool that are very strongly bound by the sediment include crystalline oxides, sulfides or silicates, and aluminosilicates. These strongly bound fractions can be used to calculate the RF (Knox et al., 2006a). The RF is the ratio of strongly bound fractions to the total concentration of the element (i.e., sum of all fractions) in the sediment. The meaning of the RF is opposite to the PMF; i.e., the RF indicates the virtually irreversible retention of metals by the solid phase. The RF will be calculated using the equation shown below:

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

where C represents concentration, and the subscripts *exch*, *org*, *oxide*, *cry oxides*, *S*, and *residual*, represent exchangeable, organic, oxide, crystalline oxide, sulfides, and residual fractions. This construct provides an estimate of the percentage of a contaminant in the sediment that is resistant to remobilization and not bioavailable (Knox et al. 2006a).

Effects of sequestering agents on availability and retention of Uranium

A series of laboratory experiments were conducted to evaluate the influence of four types of phosphate apatites (Florida rock phosphate, North Carolina rock phosphate, biological phosphate [ground fish bones], and calcium phytate) on U availability. In these experiments two sediments were evaluated, one from Tims Branch (a second order stream on the Department of Energy's Savannah River Site – SRS near Aiken, South Carolina) and the other from Hanford (a major Department of Energy facility in Washington state). Tims Branch was contaminated with U and other metals (e.g., Ni, Al, Cr, Cu, Cd) produced during fuel fabrication. Approximately 45 000 kg of depleted U were released into Tims Branch from 1954 to 1985, with approximately 70% still remaining in the sediments, primary as U(VI) (Evans et al., 1992; Bertsch et al., 1994). Hanford sediment was collected from Trench 8. Because U concentrations were low in this sediment, 110 grams of Hanford sediment was spiked with 22 mL of 5 ppm U (Inorganic Ventures, Lakewood, NJ). The initial pH of the Hanford sediment was 8.94 but after spiking went down to about 7.13 and stayed fairly constant during two weeks of equilibration with the spike solution. The spiked, homogenized Hanford sediment was used to evaluate U bioavailability after mixing with amendments. In addition, a portion of this sediment was sterilized to determine if microbial activity affected U bioavailability. Three grams of sediment were mixed individually with 0.150 grams (i.e., 5% by dry weight) of the following amendments: North Carolina apatite (NCA), calcium phytate (CaP), biological apatite (BA), sterilized NCA, sterilized CaP, and sterilized BA. Two replicates were analyzed for U and metals by ICP-MS, and the third replicate was used to measure pH values. The samples were extracted with water for one week, after which they were extracted with 12 mL of 1 M MgCl₂ and analyzed for U and metals by ICP-MS. Evaluation of the effects of the amendments on the bioavailability of U and other metals in Tims Branch sediment was conducted in the same manner as for the spiked Hanford sediment; however, the sterilization step was omitted.

TASK 2. STUDIES FOR DETERMINATION OF THE BEST COMBINATION OF AMENDMENTS FOR PLACEMENT AND CONSTRUCTION OF ACTIVE SEDIMENT CAPS

SUBTASK 2.1. EVALUATION OF MECHANICAL PROPERTIES

Development of biopolymer coated sand

Work continued on the development of cross-linked biopolymers for active capping under Task 2, Subtask 2.1 (Evaluation of the Mechanical Properties) during the past year. This work involved the development of procedures for making promising cross-linked biopolymers and coating sand grains with biopolymer as a means of delivering biopolymer to the sediments. To coat sand with biopolymer, sand was mixed with different combinations of biopolymers such that the biopolymer sand ratio equaled either 0.025:1 or 0.05:1 by weight. A cross linking agent (borax or calcium chloride) and 5% HCL was added to the mixture of sand and biopolymers followed by tap water. Liquid was added slowly while mixing. The mixtures were then put on a shaker table for 12 hours, neutralized with 1N NaOH to pH 6.5-8.0, washed with DI water, and filtered through a sieve (#120). The filtered samples were dried in an oven and then washed with DI water before drying again. Only the six most promising products (from 23 total), which had high carbon fractions (indicating greater coverage of biopolymer) and high viscosity, were evaluated further for metal and organic sorption, for biodegradability, and for resistance to erosion.

Physical Properties of biopolymer coated sand and other amendments

Organic Carbon content of coated sand

The organic carbon content of biopolymer/sand products was measured as an indication of the amount of biopolymer transferred to the sand by the coating process. The organic carbon content was measured by heating samples to 375°C overnight and comparing the combusted samples with the unburned samples to obtain the carbon fraction. Time of exposure to the atmosphere was minimized during this process to minimize moisture uptake.

Porosity and bulk density

Porosity was measured using the water saturation method. Five mL of water was added to graduated cylinders followed by 2 mL of sorbent, which was slowly introduced over three hours to allow saturation. Free water was removed from the top of the graduated cylinder and measured. Pore space was the difference between the total volume of water (5 mL) and the decanted water. Porosity was then calculated as the ratio between unsaturated water and total volume of sorbent and water (approximately 2 mL). For materials that swelled such as ClayFloc, the swollen volume was used as the total volume.

Permeability

Permeability was assessed by measuring the drop in head as water passed through treated sand. Tap water was supplied with a 6-channel syringe pump through a 50 mL syringe (Cole Parmer, IL). The tested samples (organoclays and coated sand) were packed into a threaded 15x2.5cm (LxD) chromaflex column (Kimble/Kontes, NJ). The column was held vertically to allow upward water flow. A low pressure and low vacuum gauge was placed between the pump and the column to measure the water pressure drop due to the resistance of the materials. The pressure in the gauge was read and the height of the water head in the column was recorded at different times throughout the experiment. Permeability was determined with the following equation:

$$q = -\frac{k}{\mu} \frac{dp}{dx} A$$

Where

q is the rate of flow in units of cm³/s,

k is the permeability in the unit of “darcies”,

μ is the viscosity of the fluid (tap water) in units of centipoises,

p is the pressure read from the gauge in the units of atmospheres,

x is the position along the path of water flow in the units of cm,

and A is the cross-sectional area of the column in units of cm².

Biodegradability of biopolymer coated sand

The selected biopolymer/sand products were evaluated for biodegradability by measuring CO₂ release by a Hewlett Packard 5890 series 2 GC with a mass spectrometer. A 250 μl sample of the headspace gas was injected into the GC using a gas tight syringe with a side-hole needle. A carrier gas of He was used to move the sample through the column into the mass spec. An internal standard of Argon was used to calculate CO₂ production in the samples. Uncoated sand was used as a control for comparison with the biopolymer coated sand. The release of CO₂ from the biopolymer coated sands was conducted for ten weeks.

SUBTASK 2.2. EVALUATION OF DIFFUSIVE TRANSPORT

Diffusion of metals through active caps – Laboratory Experiment

The following amendments were tested in the diffusion experiment: sand (playground sand), washed rock phosphate from NC, organoclay (OCB 750), sand coated with biopolymer XCC, sand coated with biopolymer CGB-3, and acid washed sand. A 10 cm layer (421 grams) of dry sediment was placed at the bottom of clear plastic tubes (total 18 tubes). The sediment was taken from Tims Branch, a stream located on the Savannah River Site near Aiken, SC. The tube bottoms were secured with tape. The sediment was subsequently spiked with 8 ppm of the following metals: Cd, Cr, Co, As, Ni, Se, Zn, and Pb. The sediment was saturated with 50 mL of DI water and permitted to equilibrate for two weeks. After two weeks a cap (5 cm layer) composed of an individual dry amendment or a mixture of dry amendments was added to each tube. Then 500 mL of

DI water was added gently to each tube, which raised the water level about 25 cm. All tubes were covered with a plastic cap to avoid evaporation. The first set of water samples was collected after two days. The samples were collected from the center of the water column (about 10 cm from the surface), and one sample was collected from each tube. Another set of samples was collected after one month. Both sets of water samples were analyzed for pH and metals by ICP-MS. The experiment will be continued for another 2 or 3 months. Water samples will be collected every month and analyzed for metal concentration. At the conclusion of the experiment, the water column will be separated from the cap and sediment and analyzed for metal concentrations. The cap material and sediment will be sliced into 1 cm slices, and each slice will be analyzed for total metal content and metal speciation. Additionally, mineral phases on some treatments will be analyzed to determine changes in mineralogical composition in the cap material. Mineralogy of cap materials will be characterized using X-ray powder diffractometry (XRD) and scanning electron microscopy (SEM).

Diffusion of metals through active caps – modeling

A one-dimensional numerical model was used to qualitatively assess the diffusion of selected metals through the various cap materials as tested in the laboratory column diffusion experiments. The modeling exercise was not intended to exactly predict concentration as function of time for each element and cap material. Rather, it was intended to provide general insight into the diffusive behavior of the metals for each cap material based on measured and assumed material and transport properties.

A total of four cases were modeled: three cases with cap materials and one case with no cap. The cases simulated were:

1. Contaminated sediment and water only (no cap)
2. Contaminated sediment, apatite (NCA) cap, and water
3. Contaminated sediment, sand cap, and water
4. Contaminated sediment, organoclay (OCB750) cap, and water.

The numerical simulations conducted for this analysis were performed using the PC-based PORFLOW code (ACRI, 2004). The PORFLOW code is capable of solving problems involving transient and steady-state fluid flow, heat and mass transport in multi-phase, variably saturated, porous or fractured media with dynamic phase change.

A 1-dimensional diffusive transport model was created to represent the laboratory column experiments. The 1-dimensional governing equation for mass transport of species *k* in the fluid phase is given by:

$$\frac{\partial C_k}{\partial t} + \frac{\partial}{\partial x} \left(\frac{V}{R_f} C_k \right) = \frac{\partial}{\partial x} \left(\frac{D_m}{R_f} \frac{\partial C_k}{\partial x} \right) \quad (1)$$

Where:

- C_k concentration of species *k*, ppm
- V fluid velocity in the *i*th direction, m/yr

D_m	molecular diffusion coefficient for the species, cm ² /yr
R_f	retardation factor
t	time, yr
x	distance coordinate, cm

For this analysis, the advection term was disabled within PORFLOW and only the diffusive term was evaluated. For this analysis, the molecular diffusion coefficient of each element in open water was used for the water layer. As such, Equation 1 may be simplified as follows:

$$\frac{\partial C_k}{\partial t} = \frac{D_m}{R_f} \frac{\partial^2 C_k}{\partial x^2} \quad (2)$$

For the remaining material layers, an effective diffusion coefficient was used which takes into account the tortuosity of the material. For this case, Equation 1 may be simplified as follows.

$$\frac{\partial C_k}{\partial t} = \frac{D_e}{R_f} \frac{\partial^2 C_k}{\partial x^2} \quad (3)$$

Equations 2 and 3 were solved within PORFLOW to evaluate the transient diffusive transport of metals from the contaminated sediments through the cap material and into the overlying column of water.

The boundary conditions imposed on the entire model domain included:

- No-flux specified for all metals along sides, top, and bottom
($\partial C/\partial X = 0$ at $x=0$, $x=1$ and $\partial C/\partial Y = 0$ at $y=0$, $y=y_{\max}$)

The initial condition imposed on the domain, except for the waste zone, included:

- Species concentration set to 0 at time = 0
($C=0$ for $0 \leq x \leq 1$ at $t=0$ and $C=0$ for $0 \leq y \leq y_{\max}$ at $t=0$)

The initial conditions for the model assumed a concentration of 1 ppm of each metal uniformly spread through the pore water of the sediment layer. Simulations were conducted in transient mode for diffusive transport with results being obtained over 10,000 years.

The numerical grid for the diffusion model was constructed as a node mesh 3 nodes wide by 202 nodes high. This mesh creates a vertical stack of 200 model elements totaling 40 cm in length with each element having a uniform width of 0.2 cm. Three material layers were used in the model which included the sediment layer, the cap layer, and the water layer. The sediment layer consisted of 50 elements and totaled 10 cm in length. The cap layer consisted of 25 elements and totaled 5 cm in length. The water layer consisted of 125 elements and totaled 25 cm in length. A set of consistent units was

employed in the simulations for length, mass and time, these being centimeters, grams and years, respectively.

SUBTASK 2.3. EVALUATION OF ADVECTIVE TRANSPORT

Advection transient models can calculate the time required for the breakthrough of various contaminants in caps composed of different experimental materials (Choy and Reible, 1998). A key parameter in such models is the sorption related retardation factor, R_f . Advectively dominated column experiments are being used in this study to define effective sorption related retardation factors, R_f , in organoclays and biopolymer coated sand for various hydrophobic organic compounds. Point (single concentration) partition coefficient measurements suggested solid-water concentration ratios in the order of 10^5 L/kg for phenanthrene and 10^6 L/kg for pyrene (previously reported). With a dry bulk density in the order of 1 kg/L, this implies a retardation factor of 10^5 or 10^6 for phenanthrene and pyrene, respectively. Less hydrophobic organics, such as naphthalene, would exhibit smaller retardation factors and more hydrophobic organics, such as benzo(a)pyrene and most PCBs would exhibit larger retardation factors. Although these estimates of the retardation factor are based upon single concentration partitioning, they represent a good starting point for the design of experiments to better define effective retardation in column experiments.

This magnitude of these sorption-related retardation factors suggests that diffusion measurements for hydrophobic organic compounds would not be productive in the organoclay caps. The time required for significant diffusion is given by:

$$\text{Diffusion Time} \sim 0.1 L^2 * R_f / (D_w \varepsilon / \tau)$$

Where the molecular diffusivity in water, D_w , is $\sim 5 * 10^{-5}$ cm²/s, and the ratio of porosity, ε , to tortuosity, τ , is typically around 0.2. If R_f is of the order of 10^5 , then the time required to diffuse through a 1 cm layer is 10^9 s or decades.

Although advection is also retarded by sorption, the velocity in a column experiment can be adjusted to allow measurements of effective retardation within a reasonable time frame without using unrealistic velocities. The time required for significant advection is given by:

$$\text{Advection Time} \sim 0.1 L R_f / U$$

If $R_f \sim 10^5$ and U is of the order of 100 cm/day ($\sim 10^{-3}$ cm/s), then the time required to migrate at measurable levels through a column 1 cm in length is of the order of 10^7 seconds or a few months. It is this basic design that is being employed in the column experiments for organic contaminants in organoclay and biopolymer caps.

To achieve a 1 cm cap layer thickness, a conventional 15 cm long, 1 inch diameter column will be filled with glass beads except for the last 1 cm length, which will be filled with organoclay. A superficial (Darcy) velocity of 100 cm/day will be passed through the column. Due to the high flow rates required (100 cm/day with a 1 inch

diameter column corresponds to 500 cm³/day of feed solution), the column will be operated in a closed loop with the effluent recycled back to the influent. A feed reservoir will supply the influent and collect the effluent. To maintain a constant concentration in the feed reservoir, solid samples of the feed organic constituents will be introduced to the feed reservoir, maintaining saturated water conditions in the column influent. Since the test organic compounds (naphthalene, phenanthrene, chosen to minimize required column operation time) can be detected at concentrations far below saturation, only the earliest phases of the breakthrough time in the column will be measured. Naphthalene is expected to be detectable in the effluent from the column within 30-60 days of initiation and the effective retardation factor will be estimated from the observed breakthrough curve and compared to the single concentration partition coefficient measurement.

Column experiments will also be used to estimate the effective retardation factor of hydrophobic organics in the biopolymer coated sand capping material. Only two types of biopolymer coated sand will be used; sand coated with xanthan and chitosan and cross-linked with calcium chloride (XCC) and sand coated with chitosan and guar gum cross-linked with borax (CGB3). These two cross-linked biopolymer coated showed the lowest released of CO₂ as reported previously. Because preliminary single concentration partition coefficient measurements indicated a far smaller partition coefficient for these materials, the column design can be relaxed significantly. For the biopolymer coated sand column experiments, the 15 cm column will be filled with the media and flow rates as low as 1 cm/day may be used. Again, the contaminant breakthrough curve for specific organic contaminants will be monitored and used to estimate an effective retardation factor applicable to the capping material.

In both sets of experiments, a bromide tracer will be used to evaluate the residence time distribution in the columns prior to initiation of the contaminant migration experiments. The bromide breakthrough curve will provide an estimate of dispersion in the columns, which is needed to evaluate the effective retardation factor of the organic contaminants in the subsequent experiments.

SUBTASK 2.4. EVALUATION OF POTENTIAL AMENDMENT TOXICITY

Analysis of extracts

Extracts from the amendments were analyzed to determine if they contained impurities that could affect aquatic organisms. Elements were extracted using water extractions and the EPA TCLP leaching procedure. The water extraction procedure was conducted by mixing 0.15 g of each amendment (rock phosphate, organoclay, and biopolymer coated sand) with 30 ml of distilled water in 50 ml centrifuge tubes. The tubes were placed on a shaker for 24 hrs hours, after which the supernatant was decanted, acidified, and analyzed for metals by ICP-MS. Concentrations of metals in the water extracts were compared with EPA ambient water quality criteria, EPA final chronic values, ORNL lowest chronic values (Suter and Tsao, 1996), and CCME water quality guidelines (1998).

The toxicity characteristic leaching procedure (TCLP) is a regulatory test widely used to classify materials as hazardous or nonhazardous (U.S. EPA, 1992). Rock phosphate (NCA and TRP), organoclay (OCB750 and PM-199), biopolymer coated sand (with xanthan and chitosan and cross-linked with calcium chloride) (CS), and playground sand (PS) were extracted using the TCLP. The TCLP leaching solution was comprised of 0.1M glacial acetic acid and 0.0643 M NaOH, with a final pH of 4.93. Forty milliliters of leaching solution was added to 2 g of tested material; the mixture was agitated on a shaker for 18h at 25°C, and then centrifuged. After centrifugation, the supernatants were filtered through 0.22µm pore-size polycarbonate filters, acidified to 1% HNO₃, and analyzed for metals with ICP-MS for 20 elements.

Sediment Toxicity Tests for Fresh and Salt Water

Sediment toxicity tests were used to determine if the amendments have the potential to harm aquatic organisms. Both freshwater and brackish water (estuarine) sediment toxicity tests were conducted because the amendments may be used in both environments. The tests followed standard EPA protocols and involved the exposure of laboratory cultured known-age *Hyallorella* (freshwater) and *Leptocheirus* (brackish water) to sediments composed entirely of North Carolina apatite or biopolymer coated sand (with xanthan and chitosan and cross-linked with calcium chloride). All tests were conducted for 10 days under controlled temperature and light conditions. Freshwater tests employed eight chambers with amendments and eight chambers with control sediments; each contained 10 organisms. Brackish water tests employed four chambers with amendments and four chambers with control sediments; each contained 20 organisms. Freshwater test chambers consisted of 500 ml beakers filled with 100 ml of sediment and 175 ml of overlying water, and brackish water test chambers consisted of 1000 ml beakers, each with 175 ml of sediment and 800 ml of overlying water. Control sediments for the freshwater tests were from an uncontaminated natural environment (Middle Tyger River at Jones Gap, SC) and control sediments for the brackish water tests were purchased from Aquatic Biosystems (Fort Collins, CO). Measured amounts of a standardized food supply were added to each chamber to prevent starvation, and the overlying water was renewed at consistent intervals to maintain water quality. Conductivity, hardness, pH, alkalinity, and ammonia were measured at the beginning and end of each test, and dissolved oxygen was measured daily. Because the survival data were generally characterized by non-normal distributions and heterogeneous variances, Wilcoxon rank sum tests were used to determine the significance of differences in survival between chambers with control sediments and chambers with amendments.

In addition to the previously described standard sediment toxicity tests, studies were conducted on the oligochaete worm *Ilyodrilus templetoni* to obtain information on survival, growth, and contaminant uptake in sediment mixed with organoclay. In these studies organoclay was mixed at rates of 15% and 50% with Anacostia River sediment containing the PAHs phenanthrene, chrysene, and benzo[a]pyrene. Uncontaminated sediment was used as a control. The experiment was conducted in 50 ml tubes, each with 20 organisms. There were seven replicates per treatment. The worms were analyzed for survival, growth, lipid content, and PAH concentration at the end of 28 days.

TASK 3. EVALUATION OF THE RESISTANCE OF CAPS TO PHYSICAL DISTURBANCE

Erosion test

Principle

In order to accurately assess the erosion susceptibility of the biopolymer coated sand a portable shaker device developed by Tsai and Lick (1986) will be used. The device was initially developed to quantitatively predict sediment transport. In our case this device will measure the re-suspension of sand particles in the overlying water column.

Experimental device

The device consists of a cylindrical chamber outfitted with an oscillating perforated disk slightly smaller in diameter than the chamber (Figure 1). Sediment will be placed in the bottom of the chamber and then covered with water (5 inches in depth). The oscillating grid is suspended in the water column above the sediment and is mechanically controlled by a permanent magnet DC motor. The turbulence created by the grid re-suspends some fraction of the underlying sediment. This re-suspension is then compared to that caused by equivalent sheer stresses as experienced by sediment in a calibrated laboratory flume. A detailed description of the shaker mechanism and operation is given in the paper of Tsai and Lick (1986).

Analysis

The sediment concentration (mg sediment/L water) will be measured using a sampling port located 5 inches from the bottom of the cylinder. The total duration of each test will be 20 minutes, with sampling occurring every 5 minutes.

Products to be Tested

Selected products to be tested (each in triplicate) by the shaker test include: uncoated sand; XCc, XCc produced without acid addition, CGB3, 50% best biopolymer coated sand (evaluated from combinations described before) + 25% apatite + 25% organoclay, organoclay, apatite. These materials will be tested in a slurry phase (mixed with water). The dry product will be mixed with water in each case. Depending on other available data, for those materials that show promising application as a slurry (without being first dried), the slurry will be tested. This will be determined at a later stage after the completion of the shaker tests suggested before.

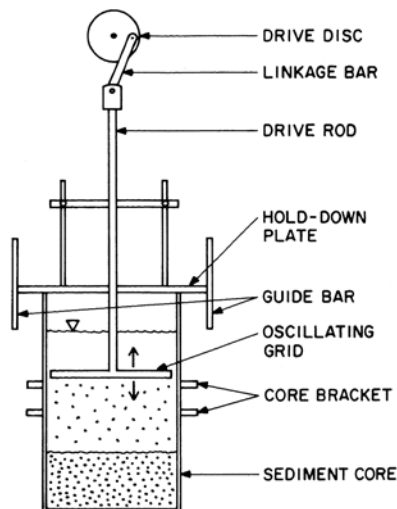


FIG. 1. A schematic of the shaker.

Figure 1. Shaker test experimental design (after Tsai and Lick, 1986)

RESULTS AND DISCUSSION

TASK 1. EFFECT OF AMENDMENTS ON CONTAMINANT MOBILITY AND BIOAVAILABILITY – LABORATORY STUDY

SUBTASK 1.1. SORPTION AND DESORPTION OF CONTAMINANTS BY SEQUESTERING AGENTS

Sorption of organic contaminants by sequestering agents

Two organoclays, Clayfloc 750 and PM-199, exhibited relatively high sorption capacities for phenanthrene, pyrene, and benzo(a)pyrene as indicated by a comparison of K_d values among the 12 amendments under study. Partitioning coefficients for these two organoclays ranged from about 3000-3500 ml/g for benzo(a)pyrene, 400-450 ml/g for pyrene, and 50-70 ml/g for phenanthrene (Table 2). Biological apatite followed the organoclays with K_d s of about 500 ml/g for benzo(a)pyrene, 20 ml/g for pyrene, and 4 ml/g for phenanthrene (Table 2). The sorption capacities of the other amendments were substantially lower; usually under 100 for benzo(a)pyrene, five ml/g for pyrene, and one ml/g for phenanthrene. These results suggest the potential utility of some organoclays and, to a lesser extent, biological apatite for controlling organic contaminants.

Table 2. Partitioning coefficients (L/g) for sorption of organic compounds on various amendments

Solid phase	Phenanthrene	Pyrene	Benzo(a)pyrene
Sediment	0.7116* (0.1186 ^o)	2.52 (-)	38.75 (-)
Clay200	0.459 (0.0186)	3.828 (0.6162)	48.12 (9.336)
Clay 202	0.356 (0.0267)	1.380 (0.1814)	24.24 (11.42)
Clay 750	55.63 (10.68)	413.5 (71.97)	3016 (324.1)
PM-199, CETGO	68.02 (8.423)	454.2 (104.9)	3505 (441.9)
Clinoptilolite Zeolite powder	0.1303 (0.0088)	0.1577 (0.0153)	12.25 (5.386)
Clinoptilolite zeolite - 4mesh	0.1865 (0.0320)	0.5152 (0.1113)	19.34 (6.405)
Clinoptilolite zeolite 8x14	0.2606 (0.0065)	0.3111 (0.03)	27.15 (4.838)
Phili Zeolite	0.1775 (0.0828)	0.4656 (0.1017)	38.67 (3.2617)
Apatite NC	0.5567 (0.1893)	1.658 (0.0062)	50.39 (7.489)
PIMS biological apatite	4.151 (1.326)	20.19 (6.012)	512.3 (20.69)
Washed phosphate Ore, Tennessee	0.986 (0.1203)	5.038 (1.243)	105.5 (10.66)
Calcium Phytate	0.1937 (0.0587)	0.3215 (0.0197)	12.84 (2.152)

* The average of three to four replicates
^o Standard deviation

Sorption of organic contaminants on biopolymer coated sand

The sorption capacities of the coated sand samples are presented in Table 3. Coated sand showed more sorption capacity than sand (Table 3), but less than organoclays (Table 2).

Table 3. Sorption coefficients of selected sand products coated by biopolymers (standard deviation among replicates in parentheses); B - borax, C – chitosan, G - guar gum, X - xanthan, c – calcium chloride.

	Phenanthrene L/kg	Pyrene L/kg
Sand	3.19 (1.87)	27.01 (5.34)
CGB1	0.4 (-)	29.54 (4.19)
CGB2	27.72 (3.07)	127.1 (23.26)
CGB3	40.64 (24.32)	118.3 (17.15)
GB2	13.18 (2.32)	68.82 (14.4)
XCc	12.8 (3.42)	106.7 (15.08)

Sorption of metals on biopolymer coated sand

Five biopolymer coated sand products were selected for evaluation of metal sorption: two with chitosan/guar gum cross-linked with borax (CGB1 and CGB3), two with guar gum cross-linked with borax (GB2 and GB3), and one with xanthan/chitosan cross-linked with calcium chloride (XCc). The results are presented in Figure 2. Most of the biopolymer coated sand products showed little removal of metal from the spike solution. However, sand coated with chitosan and guar gum cross-linked with borax showed some removal of As, Cd, and Ni (Figure 2), and sand coated with xanthan and chitosan cross-linked with calcium chloride showed substantial removal of Se from the spike solution. The Se concentration in the spike solution was 1066 $\mu\text{g L}^{-1}$ compared with 246 $\mu\text{g L}^{-1}$ in the solution in contact with sand coated with xanthan and chitosan cross-linked with calcium chloride (Figure 2).

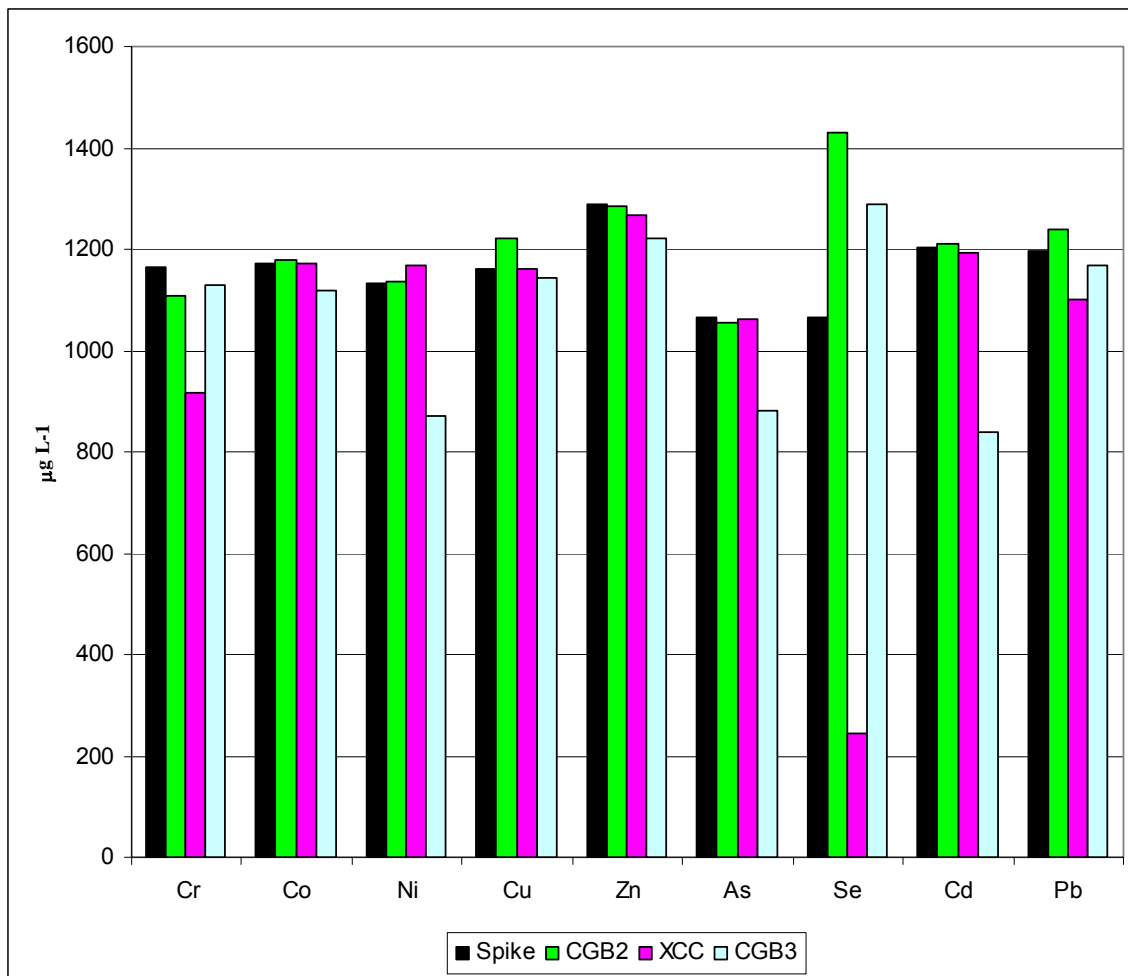


Figure 2. Sorption of elements on sand coated with cross-linked biopolymers; metal concentration in the spike solution was about 1000 $\mu\text{g}\cdot\text{L}^{-1}$, CGB2 – chitosan and guar gum cross-linked with borax with glutaraldehyde addition, CGB3 - chitosan and guar gum cross-linked with borax without glutaraldehyde, and XCC – xanthan and chitosan cross-linked with calcium chloride with glutaraldehyde addition.

SUBTASK 1. 2. EFFECT OF SEQUESTERING AGENTS ON THE MOBILITY, BIOAVAILABILITY, AND RETENTION OF CONTAMINANTS IN SEDIMENT

Retention of organic contaminants

Kinetic study and sorption/ desorption of organic contaminants by selected amendments

Sorption and desorption are both time sensitive processes. A kinetic study was conducted to ensure that equilibrium was reached before samples were taken for the measurement of sorption and desorption coefficients. Three materials were tested, with one from each of three groups of amendments: apatite, organoclay and zeolite. Specifically, the three materials were Clinoptilolite TSM 140 (8x14 mesh), PIMS biological apatite (ground fish bones) and Clay 750 (Biomin).

Equilibrium for sorption was reached after 24 to 48 hours (Figures 3 through 5). Therefore, 48 hours was used as the equilibrium time, and all sorption coefficients were measured at 48 hours. The measured sorption coefficients differed significantly among materials; the most sorptive materials for PAHs were CETCO-199, CETCO-200, and Clay 750 (Table 4).

The desorption kinetics studies indicated that desorption reached equilibrium within 48 hours for all four materials chosen as potential capping amendments. The desorption kinetics for NC apatite and organoclay materials are shown in Figures 6, 7, and 8. PM199 and PM 200 were the same organoclays but with different particle sizes; therefore, only results for PM 200 are shown (Figure 8).

Based on the kinetic studies, all desorption coefficients were measured after 48 hours of tumbling. The measured desorption coefficients are listed in Table 4. In general, the desorption coefficients were several times higher than the sorption coefficients, meaning that some of the phenanthrene and pyrene adsorbed to the sorbents will not be released at the same environmental conditions. This is advantageous because only contaminants dissolved in porewater are available to benthic organisms (Lu et al.; 2006).

The partition coefficients in Table 4 were used to estimate model-generated penetration times through a cap using an analytical advection-diffusion model. The penetration time is the time until concentrations at the top of the active cap layer are 50% of what they would be under steady state conditions (or 50% of the concentration at the bottom of the active cap layer). This time is given by

$$\tau_{adv/diff} \approx \left(\frac{1}{1/\tau_{diff} + 1/\tau_{adv}} \right) \approx \left(\frac{1}{D_1 / (\epsilon R_f h_{eff}^2) + U / (\epsilon R_f h_{eff})} \right) \approx \frac{\epsilon R_f h_{eff}^2}{D_1 + U h_{eff}}$$

Where D_1 is an effective diffusion/dispersion coefficient, h_{eff} is the effective cap thickness, U is the Darcy upwelling velocity, ϵ is the active cap layer porosity, and R_f is the effective sorption-related retardation factor in the cap.

Assuming a velocity of 100 cm/yr as an upper bound for upwelling (which typically causes diffusion and dispersion to be negligible), Table 5 contains estimates of the penetration time in years. Clearly, the active cap amendments can be extremely effective for the containment of the contaminants.

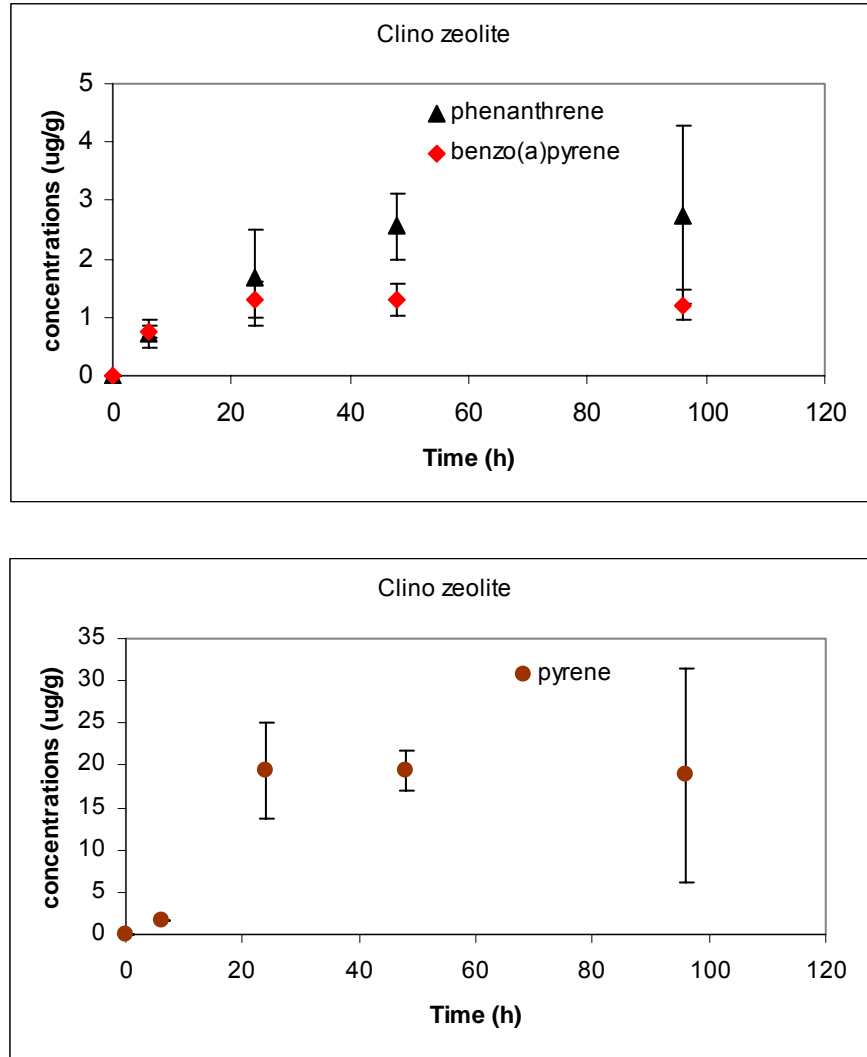


Figure 3. Sorption of three PAHs to Clino Zeolite (8x14) with time.

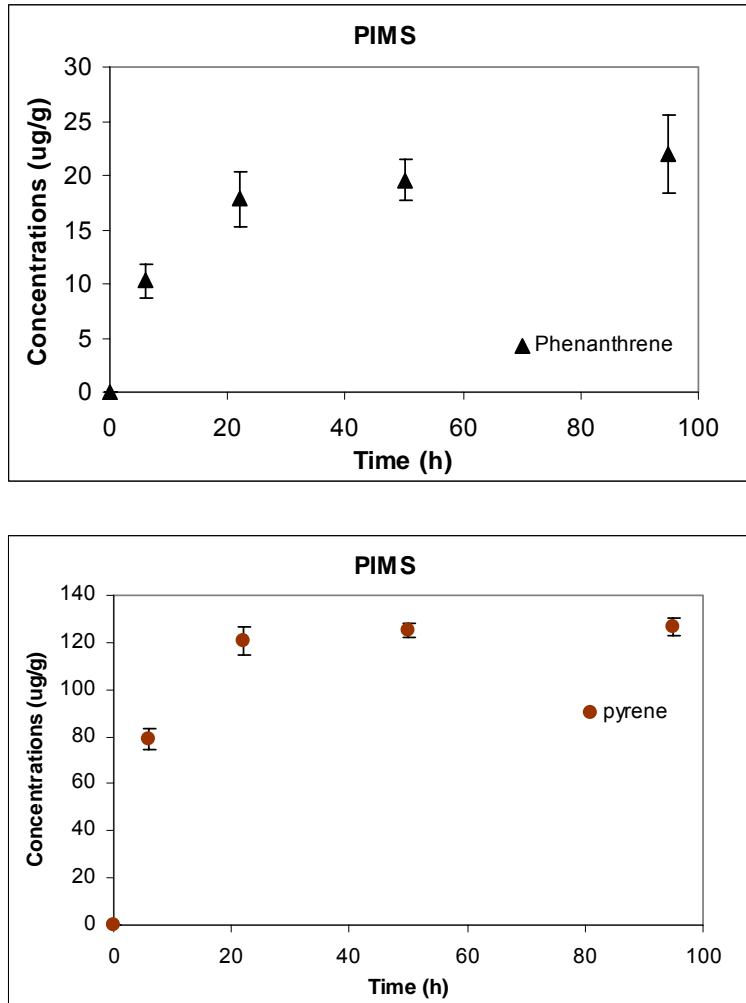


Figure 4. Sorption of three PAHs to PIMS with time.

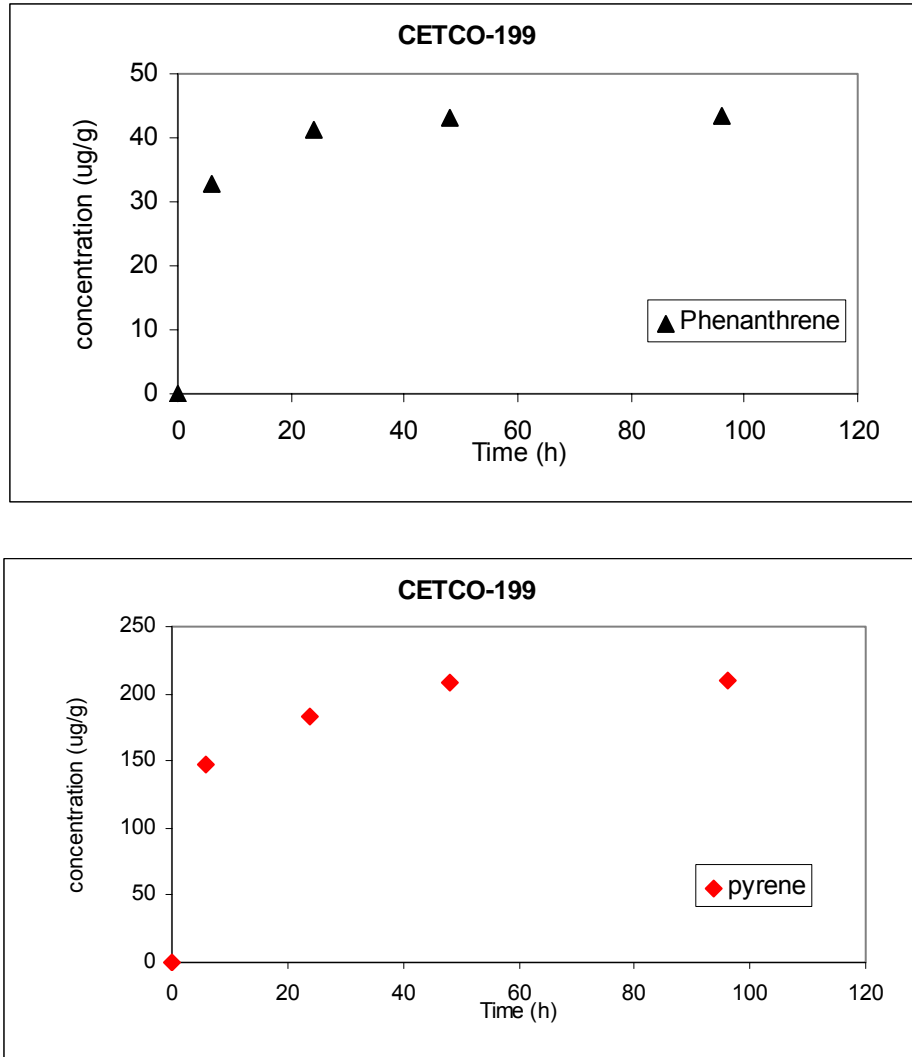


Figure 5. Sorption of phenanthrene and pyrene to CETCO-199 with time.

Table 4. Sorption and desorption coefficients for selected amendments (L/Kg)

	Sorption (std dev)		Desorption (std dev)	
	Phenanthrene	Pyrene	Phenanthrene	Pyrene
Clay 750	55600 (10700)	414000 (72000)	95300 (25600)	304000 (88800)
PM-199	68000 (8400)	454000 (105000)	126000 (22300)	-
PM-200	36500 (5800)	98700 (31000)	94400 (15100)	377000 (50100)
NC Apatite	220 (8.9)	695 (131)	428 (127)	1060 (319)

Table 5 – Estimation of cap penetration time (in years) for 15 and 2.5 cm thick active layers subject to a 100 cm/yr groundwater upwelling velocity.

	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

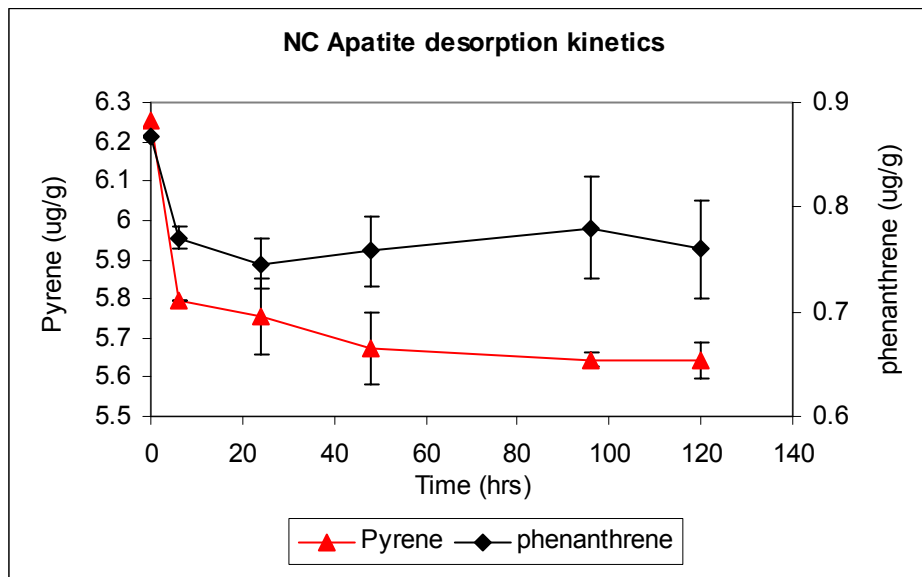


Figure 6. North Carolina apatite desorption kinetics. Reported data were the average of three replicates. The error bars are standard deviations.

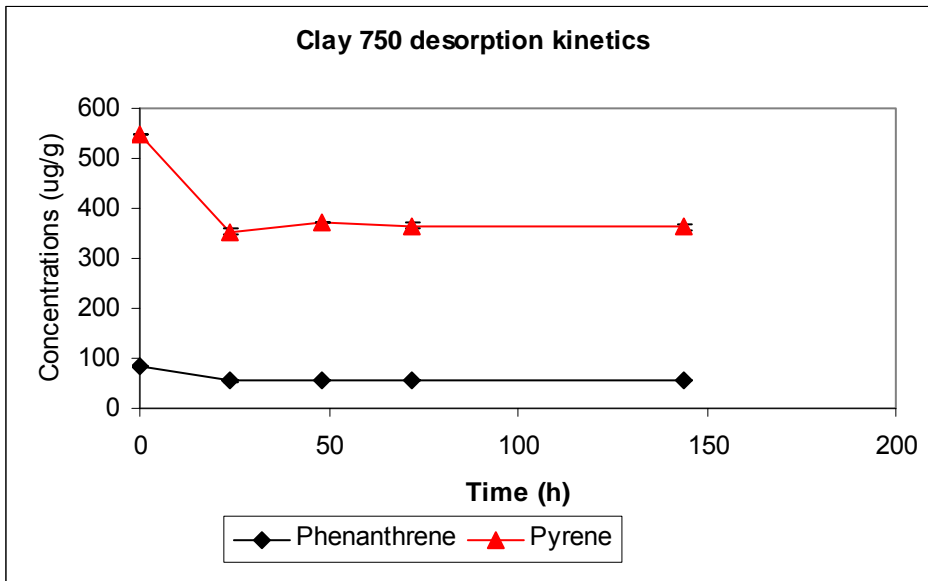


Figure 7. Organoclay (OCB750) desorption kinetics. Reported data were the average of three replicates. The error bars are standard deviations.

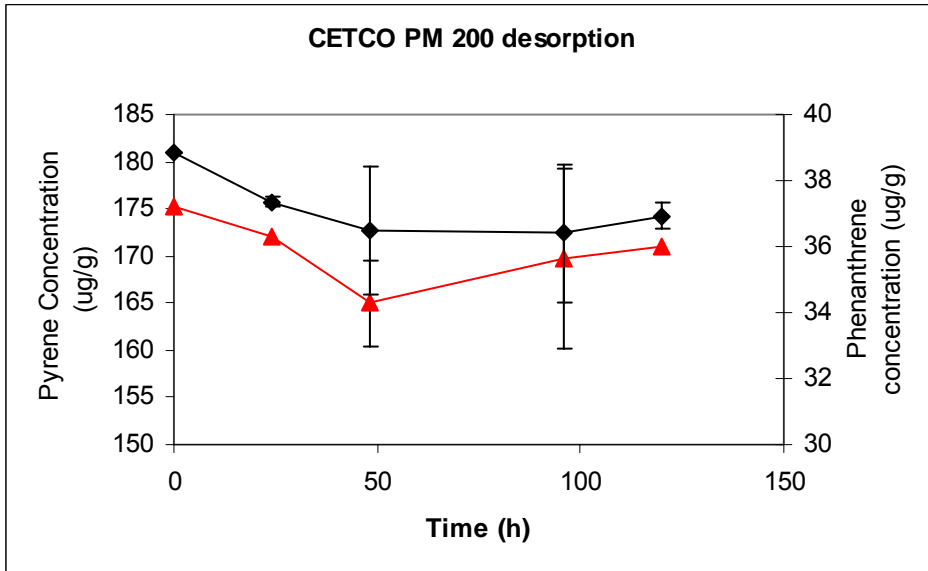


Figure 8. Organoclay (CETCO PM 200) desorption kinetics. Reported data were the average of three replicates. The error bars are standard deviations.

Cap effectiveness for organics

Measured partitioning coefficients were used to indicate the effectiveness of a one inch (2.54 cm) layer of the material as a sediment cap by estimating the time required for a contaminant to penetrate the cap. The time was estimated assuming that the underlying concentration remained constant and that no degradation or transformation processes were operative. The time was estimated by the methods recommended by the standard EPA guidance on capping.

A one inch layer of active capping material simulates the placement of the material in thin layers. Such a placement might be considered for high value materials that might be cost-prohibitive if placed in bulk. If placed in bulk, an alternative placement might be six inches (15 cm) of active sorbent. If the time to penetrate a six inch active capping layer is required, the times in Table 6 should simply be multiplied by six. The active layer would likely be overlain by biopolymer coated sand or a similar inert material. For purposes of the current estimates, the sand cover is conservatively assumed to provide no additional contribution to the time required for contaminants to migrate through the cap. Two scenarios were considered:

- A cap layer in which migration is dominated by upwelling at an average rate of 1 cm/day.
- A cap layer in which migration is dominated by molecular diffusion.

Table 6 summarizes the time, in years, before a significant flux might be observed at the top of the one inch active cap layer. As indicated previously, the time required for penetration of a six inch layer is simply six times these values

An examination of the predicted times before the measurement of a flux through the cap shows that the highly sorptive cap materials can lead to very long migration times perhaps longer than the expected lifetime of the contaminant in the sediment environment. If the predicted time is longer than the expected lifetime of the contaminant it should be expected that no significant flux will ever be detected.

Table 6. Cap effectiveness for organics.

Active Media 1 inch layer	Breakthrough Time, yr Phenanthrene	Breakthrough Time, yr Pyrene	Breakthrough Time, yr Benzo[a]pyrene	Transport Condition
Sediment	19	66	1011	Upwelling dominated
	8	29	442	Diffusion dominated
Clay200	12	100	1256	Upwelling dominated
	5	44	548	Diffusion dominated
Clay 202	9	36	633	Upwelling dominated
	4	16	276	Diffusion dominated
Clay 750	1452	10791	78705	Upwelling dominated
	634	4711	34363	Diffusion dominated
PM-199, CETCO	1775	11853	91466	Upwelling dominated
	775	5175	39935	Diffusion dominated
Clinoptilolite zeolite powder	3	4	320	Upwelling dominated
	1	2	140	Diffusion dominated
Clinoptilolite zeolite -4mesh	5	13	505	Upwelling dominated
	2	6	220	Diffusion dominated
Clinoptilolite zeolite 8x14	7	8	709	Upwelling dominated
	3	4	309	Diffusion dominated
Phili Zeolite	5	12	1009	Upwelling dominated
	2	5	441	Diffusion dominated
Apatite NC	15	43	1315	Upwelling dominated
	6	19	574	Diffusion dominated
PIMS biological apatite	108	527	13369	Upwelling dominated
	47	230	5837	Diffusion dominated
Washed phosphate Ore, Tennessee	26	131	2753	Upwelling dominated
	11	57	1202	Diffusion dominated
Calcium phytate	5	8	335	Upwelling dominated
	2	4	146	Diffusion dominated

Effect of selected sequestering agents on mobility and retention of metals

Water extraction under reduced and oxidized conditions

The chemistry of water extracts from the oxidized and reduced treatments differed significantly (Figure 9). The redox potential was about -200mV in the reduced treatments and about -15mV in the oxidized treatments. Dissolved oxygen concentrations were about 1 mg L⁻¹ or less in the reduced treatments and about 7 mg L⁻¹ in the oxidized treatments. Differences in pH and EC between treatments were smaller but still substantial (Figure 9). Generally, addition of apatite and biopolymer or their mixture to the Anacostia River sediment did not significantly influence EC values, especially in reduced treatments. However, addition of zeolite and organoclay significantly increased EC values in both oxidized and reduced treatments (Figure 9).

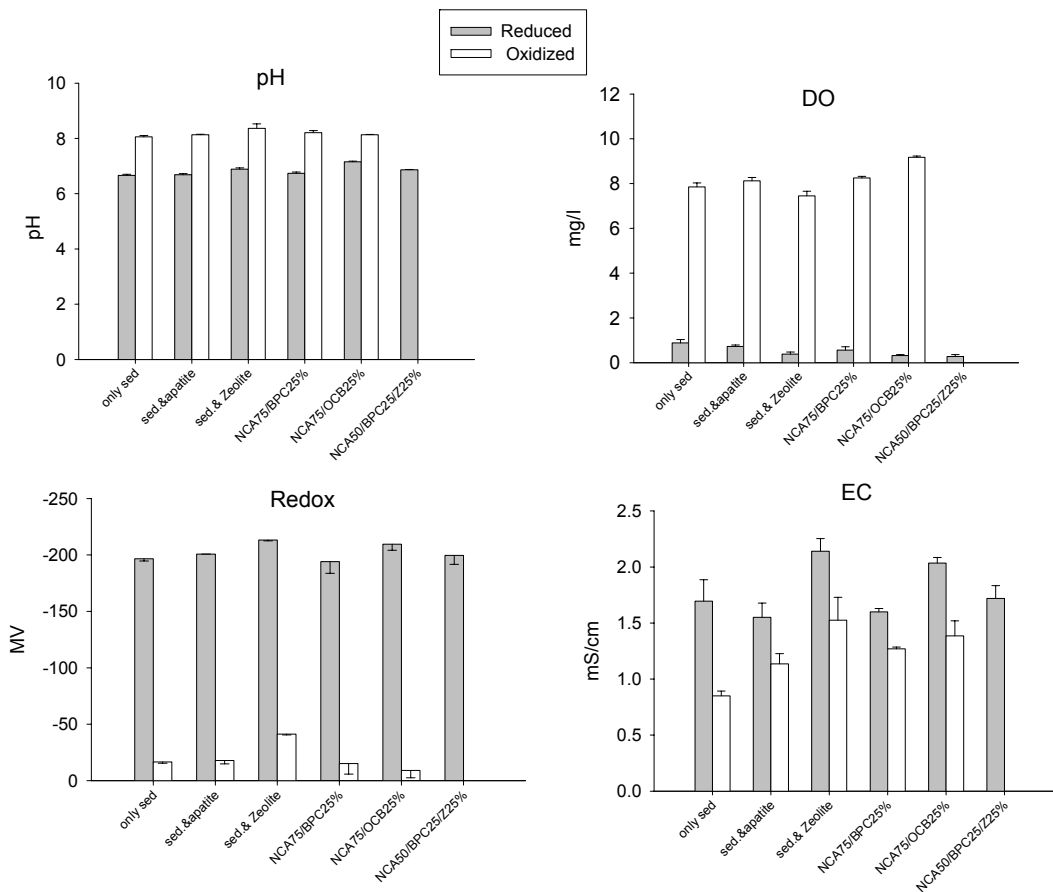


Figure 9. Effect of amendments on the Anacostia River sediment properties under oxidized and reduced conditions; NCA – North Carolina apatite, OCB – organoclay 750 from Biomin, Inc., BPC – biopolymer chitosan, Z- zeolite.

Metal concentrations were generally higher under reduced conditions than under oxidized conditions (Table 7). The addition of 2% (dry weight) of apatite, zeolite, biopolymer, and organoclay, by itself or as a mixture influenced concentrations of elements in water extracts from both reduced and oxidized treatments (Table 7, Figure 10 and 11). Generally, all amendments reduced Fe and Mn concentration under reduced condition (Table 8). However, addition of North Carolina apatite increased P concentration from 2.5 to 3.3 mg L⁻¹ and from 0.8 to 1.4 mg L⁻¹; under reduced and oxidized conditions, respectively. Addition of NCA increased the Ca concentration under oxidized conditions (Table 8). Addition of other amendments generally reduced Ca concentration under oxidized condition.

The concentrations of most metals in water extracts from both reduced and oxidized Anacostia River sediments were lower than typical of contaminated sediments and often below drinking water standards (Table 7). The concentrations of some elements, especially under oxidized conditions, approached method detection limits making it difficult to accurately assess treatment effects. Therefore, only a few elements are presented for oxidized treatments in this report. In the reduced sediments North Carolina apatite (NCA), a mixture of NCA with chitosan (biopolymer) and zeolite (clinoptilolite), and a mixture of NCA with organocly (OCB 750 from Biomin Inc.) substantially reduced Cr, Co, Ni, and Pb (Figure 10). Other elements such as As, Cd, and Se showed some reduction (e.g., in case of NCA); however, effects were not consistent for all amendments. Also, standard deviations were relatively high for these elements reflecting the variability of the sediments and suggesting a need for more replicates (Figure 10). In the oxidized treatments, element concentrations were very low and often near the detection limit for ICP-MS; therefore, we only present data for Pb and Cd in this report. The addition of 2 % NCA, zeolite or a mixture of NCA with biopolymer, zeolite, or organoclays reduced Cd concentrations in the water extracts from the oxidized treatments (Figure 11). Lead concentrations were significantly reduced by all tested amendments or mixtures of amendments under oxidized conditions (Figure 11).

Table 7. Comparison of element concentration in water extracts from the Anacostia River sediment under reduced and oxidized conditions.

Elements	Units	Reduced		Oxidized	
		Avg	Stdev	Avg	Stdev
Cr	$\mu\text{g L}^{-1}$	77.0	5.2	28.4	1.4
Co	$\mu\text{g L}^{-1}$	16.9	1.2	3.6	0.2
Ni	$\mu\text{g L}^{-1}$	56.9	0.9	11.3	0.6
Cu	$\mu\text{g L}^{-1}$	33.1	15.5	25.7	0.4
Zn	$\mu\text{g L}^{-1}$	137.5	10.6	85.1	6.5
As	$\mu\text{g L}^{-1}$	23.1	2.8	3.3	0.2
Se	$\mu\text{g L}^{-1}$	7.1	0.2	2.0	0.1
Cd	$\mu\text{g L}^{-1}$	0.40	0.08	0.12	0.05
Pb	$\mu\text{g L}^{-1}$	22.8	0.4	4.6	0.4
Ca	mg L^{-1}	310.8	8.3	126.0	8.3
Fe	mg L^{-1}	88.3	3.0	0.4	0.1
Mn	mg L^{-1}	12.0	0.2	3.4	0.3
P	mg L^{-1}	2.5	0.1	0.8	0.1

Table 8. Effect of amendments on Ca, Fe, Mn, and P concentration in water extracts from reduced and oxidized treatments of the Anacostia River sediment.

Treatments		Unit	Reduced				Oxidized			
			Ca	Fe	Mn	P	Ca	Fe	Mn	P
Ctrl	Avg	Mg L ⁻¹	310.8	88.3	12.0	2.5	126	0.37	3.39	0.76
NCA	Avg	Mg L ⁻¹	265.5	68.0	8.6	2.5	215.4	0.39	4.83	1.40
ZC	Avg	Mg L ⁻¹	137.8	36.8	5.4	3.3	61.4	0.71	1.81	0.80
NCA/BPC	Avg	Mg L ⁻¹	236.9	48.8	6.8	1.5	181.3	0.22	4.24	0.80
NCA/OCB	Avg	Mg L ⁻¹	385.9	8.2	2.6	2.0	225.7	0.29	2.56	1.56
NCA/BPC/Z	Avg	Mg L ⁻¹	195.5	39.3	5.8	1.6	111.3	0.19	3.33	0.52
Ctrl	Stdev		8.3	3.0	0.2	0.1	22.1	0.05	0.29	0.11
NCA	Stdev		30.6	5.8	1.1	0.1	47.5	0.27	1.81	0.35
ZC	Stdev		3.0	0.6	0.1	0.1	17.7	0.30	0.54	0.68
NCA/BPC	Stdev		8.6	5.0	0.4	0.1	28.8	0.03	0.25	0.04
NCA/OCB	Stdev		50.6	0.8	0.1	0.2	7.7	0.01	0.10	0.74
NCA/BPC/Z	Stdev		8.5	0.6	0.2	0.2	89.4	0.08	4.42	0.09

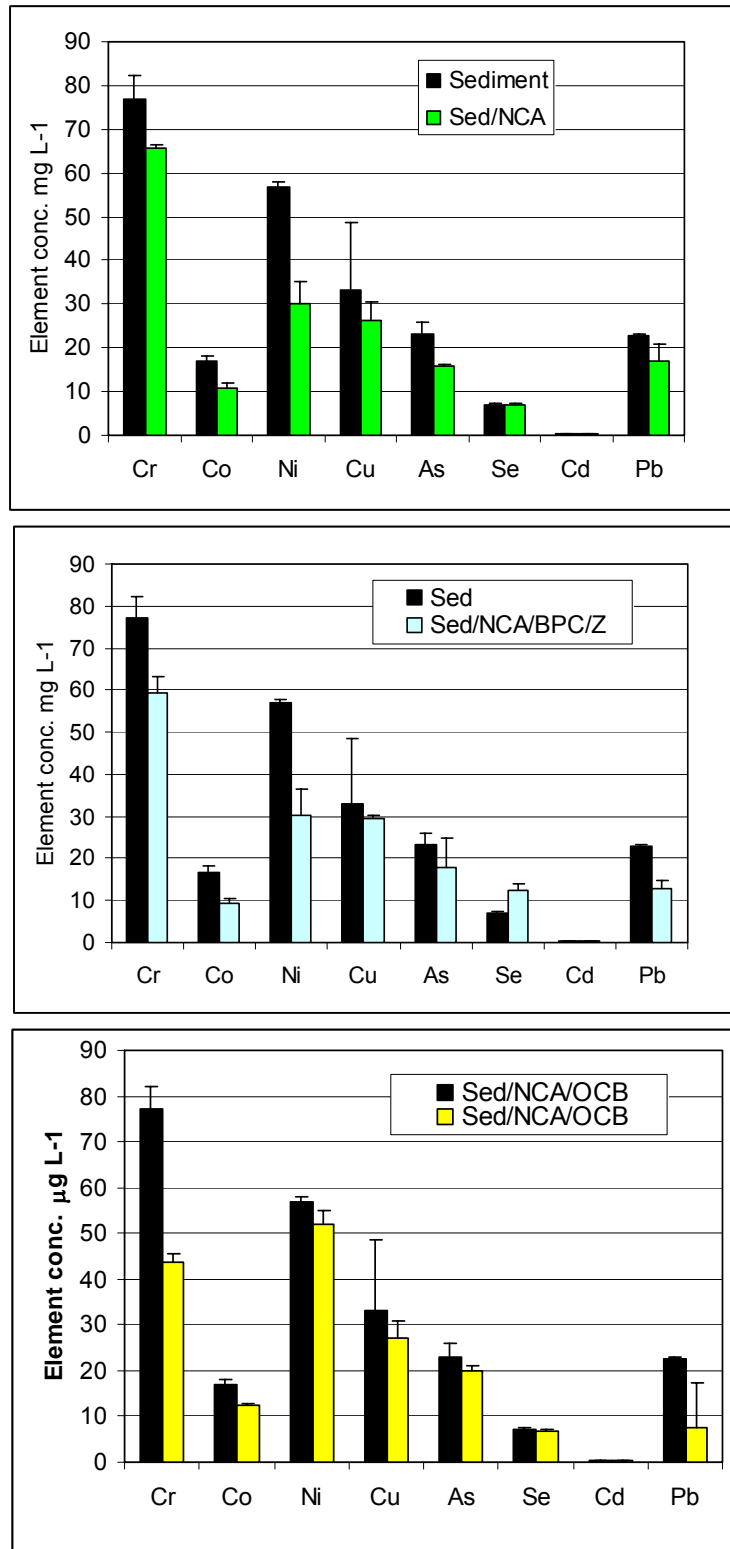


Figure 10. Effect of amendments on metal concentrations in the water extracted from the Anacostia sediment after eight weeks of contact with amendments under reduced conditions (~200mV); the amount of added amendments - 2 % by dry weight.

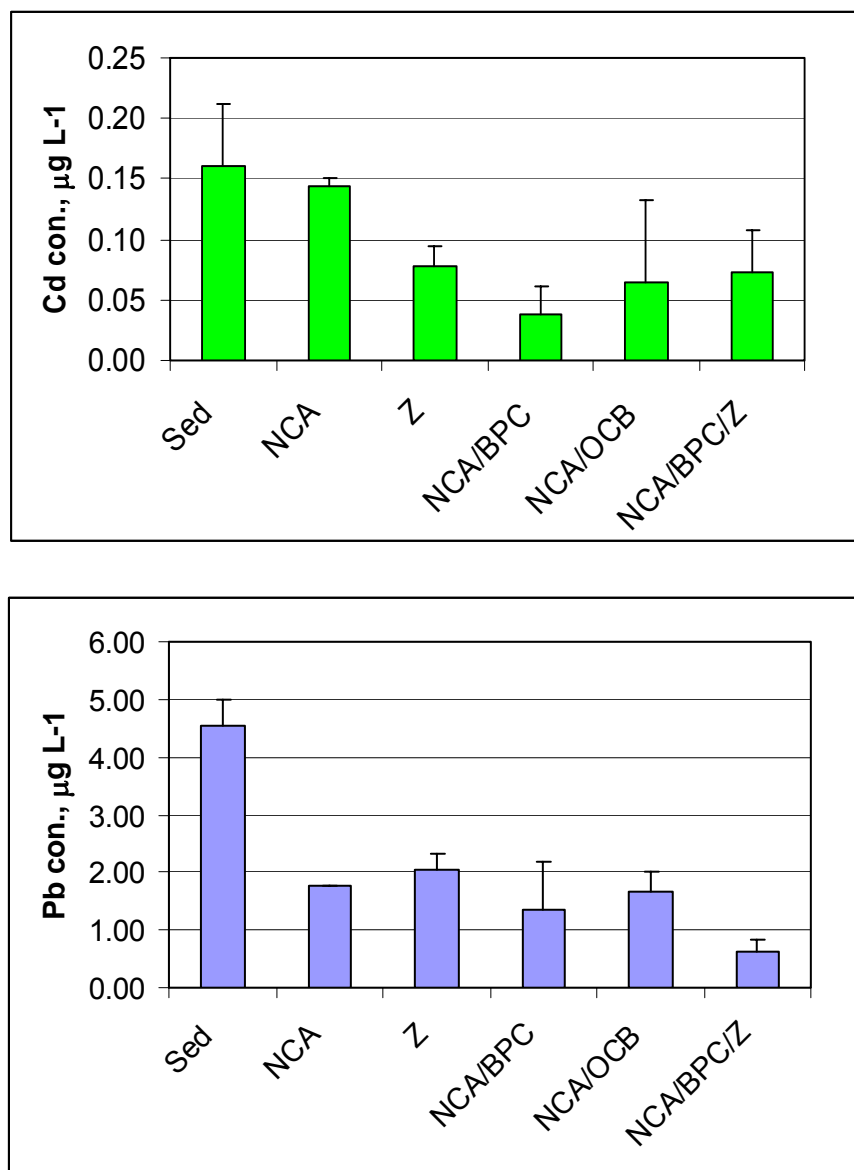


Figure 11. Effect of amendments on metal concentrations in the water extracted from the Anacostia sediment after eight weeks of contact with amendments under oxidized conditions; the amount of added amendments - 2 % by dry weight.

Sequential extractions

The mobility and retention of metals in sediments strongly depends on their specific chemical and mineralogical forms and their binding characteristics. This implies that these forms and characteristics should be studied in addition to total metal concentrations. Since the early 1980s, single and sequential extraction schemes have been designed for the speciation of metals in soils and sediments (Tessier et al., 1979; Quevauviller et al., 1997). The technique developed by Tessier et al (1979) is one of the most frequently employed sequential extraction schemes. However, to obtain a greater understanding of potential metal mobility and retention in sediments, the method was modified. The original single extraction targeting Fe and Mn oxides as described by Tessier et al (1979) was replaced with two separate extractions (Amacher, 1996). Additionally, the sulfide fraction was included as an individual step to address the effect of reduced conditions that are typical for sediments.

The data presented below are only for the Elizabeth River sediment.

Sequential extraction of arsenic (As)

Many arsenic compound sorb strongly to hydrous oxides and sulfides in sediments and therefore are not very mobile. Rather a small portion of the As is detected in the exchangeable and carbonate fractions. Exchangeable and carbonate fractions include metals weakly sorbed via specific adsorption and precipitation reactions as well as those sorbed via outer-sphere reactions (Tessier et al., 1979) that are readily exchanged with other cations.

The partitioning of As in treated sediment was similar to the control sediment (untreated); however, more mobile fractions such as exchangeable and carbonates were higher in the untreated sediment than in the sediment treated with NCA or OCB-750 (Figure 12). In the sediment with the highest addition of NCA (10%), sulfide and residual fractions increased substantially compared with the control sediment (Figure 12).

Sequential extraction of cadmium (Cd)

In soils and sediments, Cd may be adsorbed by clay minerals (e.g., illite), carbonates or hydrous oxides of iron and manganese or it may be precipitated as Cd carbonate, hydroxide, or phosphate phase. Dudley et al. (1988 and 1991) suggested that adsorption mechanisms may be dominant for the deposition of Cd in soil and sediment. In the sequential extraction of sediments contaminated with Cd, the greatest proportion of the total Cd is typically associated with the exchangeable fraction (Hickey and Kittrick, 1984). Under strongly reducing conditions, precipitation as CdS controls the mobility of Cd (Smith et al., 1995).

Apatite is known to effectively remove soluble Cd (Wright 1995, Ma et al, 1994). From results for short-term contact studies with the use of fossil apatite mineral, Ma et al. (1997) concluded that minor octavite (CdCO₃) precipitation does occur, but that sorption mechanisms (such as surface complexation, ion exchange, or the formation of amorphous

solids) are primarily responsible for the removal of soluble Cd. Cadmium phosphate, if formed, should be more stable than otavite under acidic conditions (Bodek et al., 1988; Chen et al., 1997).

The partitioning of Cd within the various fractions of the untreated and treated Elizabeth River sediment is illustrated in Figure 13. The distribution patterns are similar for the sediment with and without amendments, except that the proportion of Cd in exchangeable, carbonate, and amorphous oxides is substantially greater in the untreated sediments (Figure 13). The greatest increase in the Cd sulfide fraction was observed for the addition of 10% NCA. The residual fraction increased proportionally to the increased dose of NCA, with the highest values for the 10% addition of NCA (Figure 13). Similar patterns of Cd distribution among the fractions were observed for the addition of OCB and the mixture of OCB and NCA (Figure 13).

Sequential extraction of cobalt (Co)

Various investigators have found that Co accumulates in hydrous oxides of Fe and Mn in soils and sediments (Adriano, 2001). However, the sorption mechanism of Co by crystalline Fe and Mn oxides apparently differs at different pH values and generally is based on the interchange of Co^{2+} with Mn^{2+} and on the formation of the hydroxyl species, $\text{Co}(\text{OH})_2$, precipitated at the oxide surface. Different redox mechanisms have been proposed for Co sorption by Mn oxides (Kabata-Pendias, 2001). These include: (1) oxidation of Co^{2+} to Co^{3+} at the oxide interface, (2) reduction of Mn^{4+} to Mn^{3+} in the oxide crystal lattice, and (3) replacement of Mn^{3+} or Mn^{4+} by Co^{3+} . Generally, the sorption of Co by Mn oxides increases greatly with pH, however, mobility of Co in sediments is influenced by Mn oxides and by Eh-pH sediment intensities. Also, sediment organic matter and clay content are important factors that govern Co distribution and behavior (Kabata-Pendias, 2001). Under very reducing conditions in the presence of dissolved sulfide, Co(II) bisulfide species, such as $\text{Co}(\text{HS})_2$ likely dominate (Krupka and Serne, 2002).

Figure 14 illustrates the effect of apatite and organoclay on Co distribution in the Elizabeth River sediment. In the untreated sediment Co mainly associated with the amorphous Fe, Mn oxide, and sulfide fractions. The carbonate and crystalline oxide fractions were the second most predominant fractions. The exchangeable pool of Co in the untreated sediment was even higher than the residual Co pool; i.e., 1.3 mg kg^{-1} and 0.4 mg kg^{-1} , respectively (Figure 14). Addition of 2.5, 5.0, and 10% by weight of NCA reduced substantially the exchangeable fraction of Co, and increased the residual fraction. A similar pattern was observed for the addition of organoclay and the mixture of NCA with organoclay (Figure 14).

Sequential extraction of chromium (Cr)

Chromium sorbs to many sediment mineral phases, such as clays and oxides of Fe and Mn, but this is pH dependent and is competitive with common anions such as sulfate, sulfide, and carbonate (Zachara et al., 1987). Thus, chromate generally remains relatively mobile. Reduced Cr^{3+} is readily hydrolyzed to form $\text{Cr}(\text{OH})_3$ hydrates, which also may form

a solid intermixed with Fe oxyhydroxide. The solubility and mobility of reduced Cr is typically very low. The existence of minerals such as embreyite (hydrated lead chromate phosphate) suggests that it is possible for Cr⁶⁺ (as chromate) to be co-precipitated into crystalline structures along with phosphate phases.

Data summarized in Figure 15 indicate that there was substantial interaction between the highest dose of NCA (10%) and Cr in the Elizabeth River sediment, which resulted in a substantial increase of Cr in the residual fraction (Figure 15). Also, a 2.5% dose of organoclay and organoclay mixed with NCA provided similar results, i.e., reduced the exchangeable pool of Cr and increased the residual pool of Cr (Figure 15).

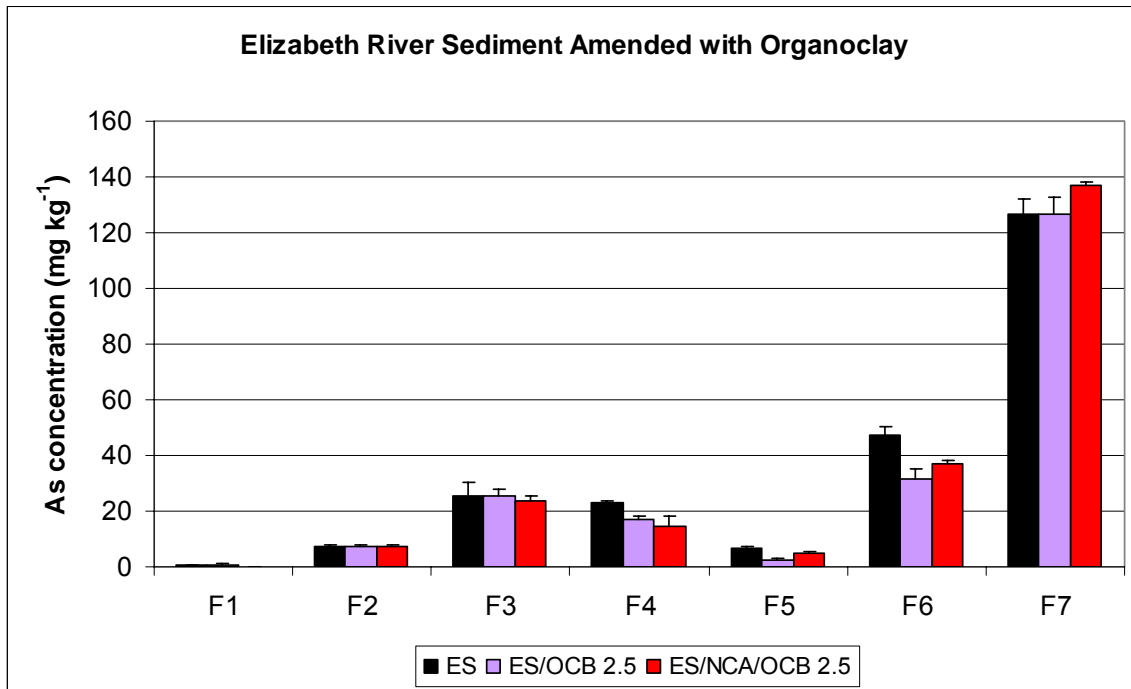
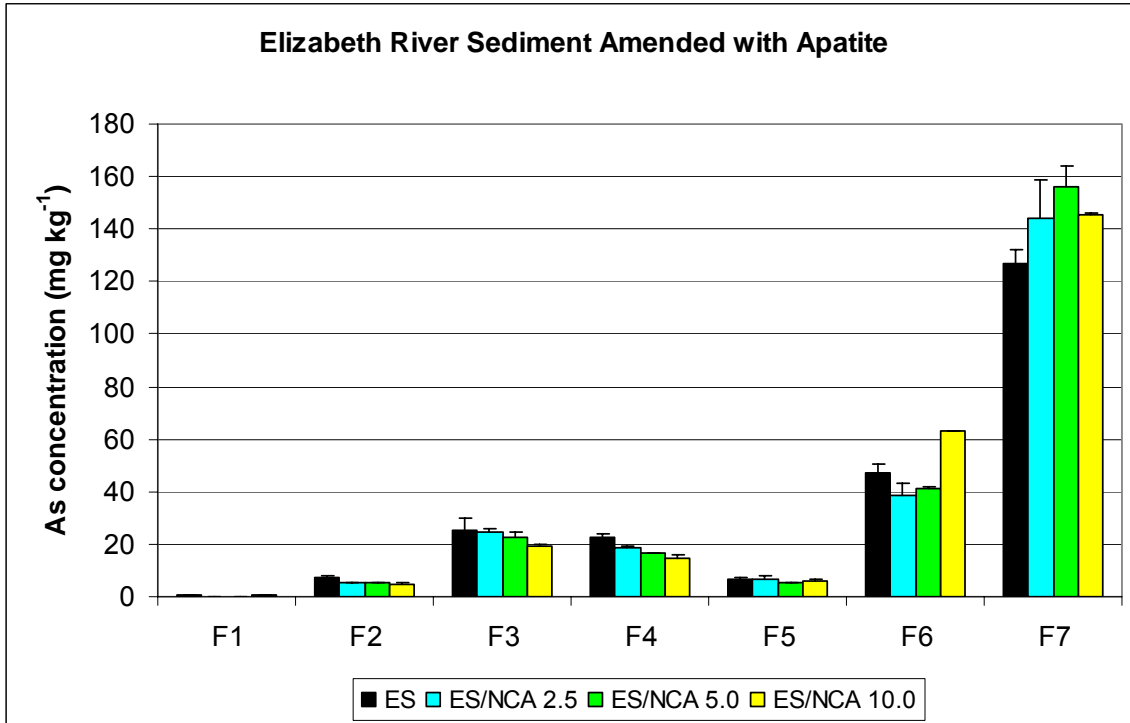


Figure 12. Effect of North Carolina apatite (NCA) and organoclay (OCB) on the partitioning of As in the Elizabeth River sediment (ES); F1 - exchangeable fraction, F2 - carbonate fraction, F3 - amorphous fraction, F4 - crystalline oxide, F5 - organic, F6 - sulfide, and F7 - residual; doses of amendments in % by dry weight: 2.5, 5, and 10.

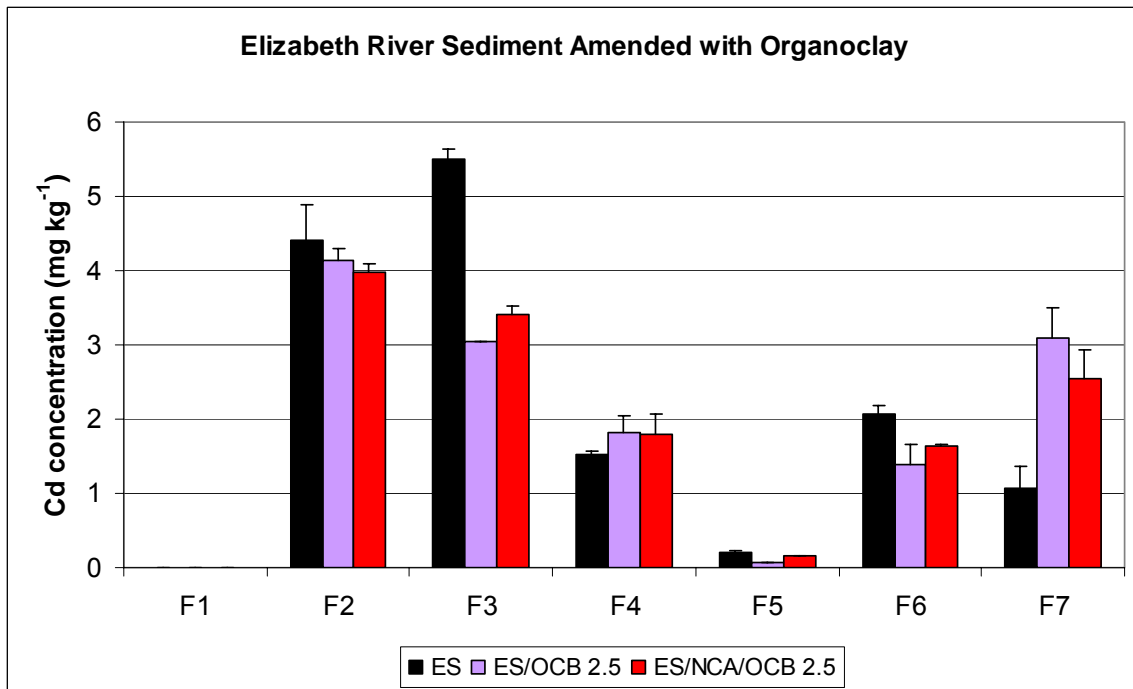
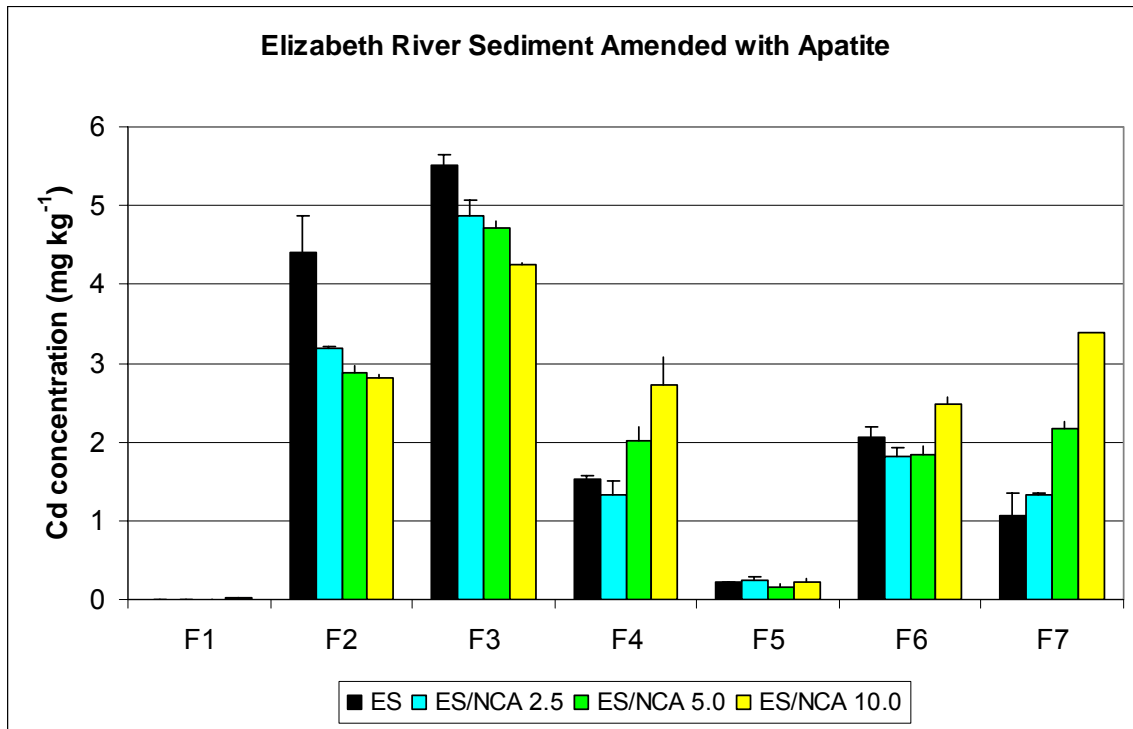


Figure 13. Effect of NCA and OCB on the partitioning of Cd in the Elizabeth River sediment; F1 - exchangeable fraction, F2 - carbonate fraction, F3 - amorphous fraction, F4 - crystalline oxide, F5 - organic, F6 - sulfide, and F7 - residual.

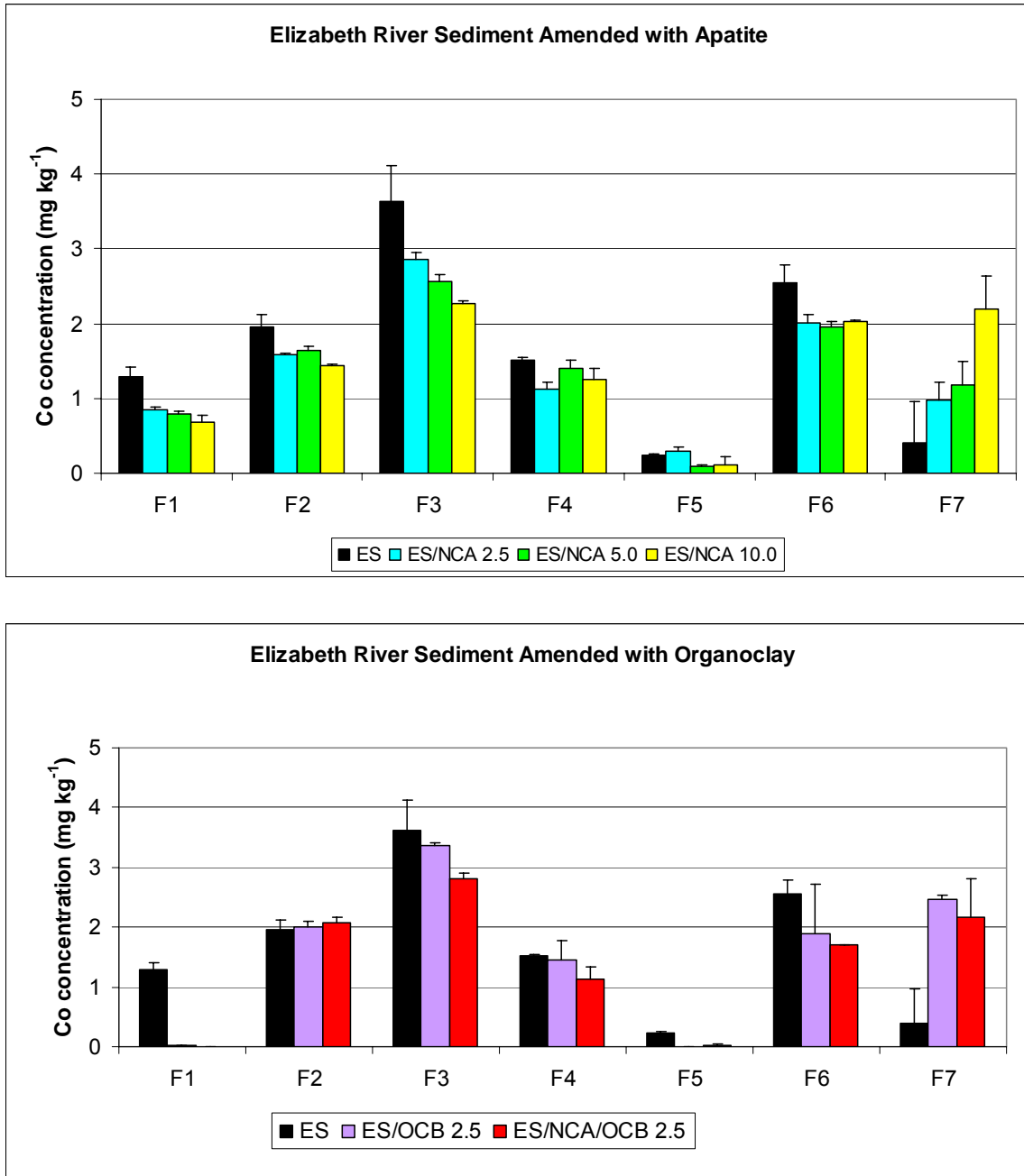


Figure 14. Effect of NCA and OCB on the partitioning of Co in the Elizabeth River sediment; F1 - exchangeable fraction, F2 - carbonate fraction, F3 - amorphous fraction, F4 - crystalline oxide, F5 - organic, F6 - sulfide, and F7 - residual.

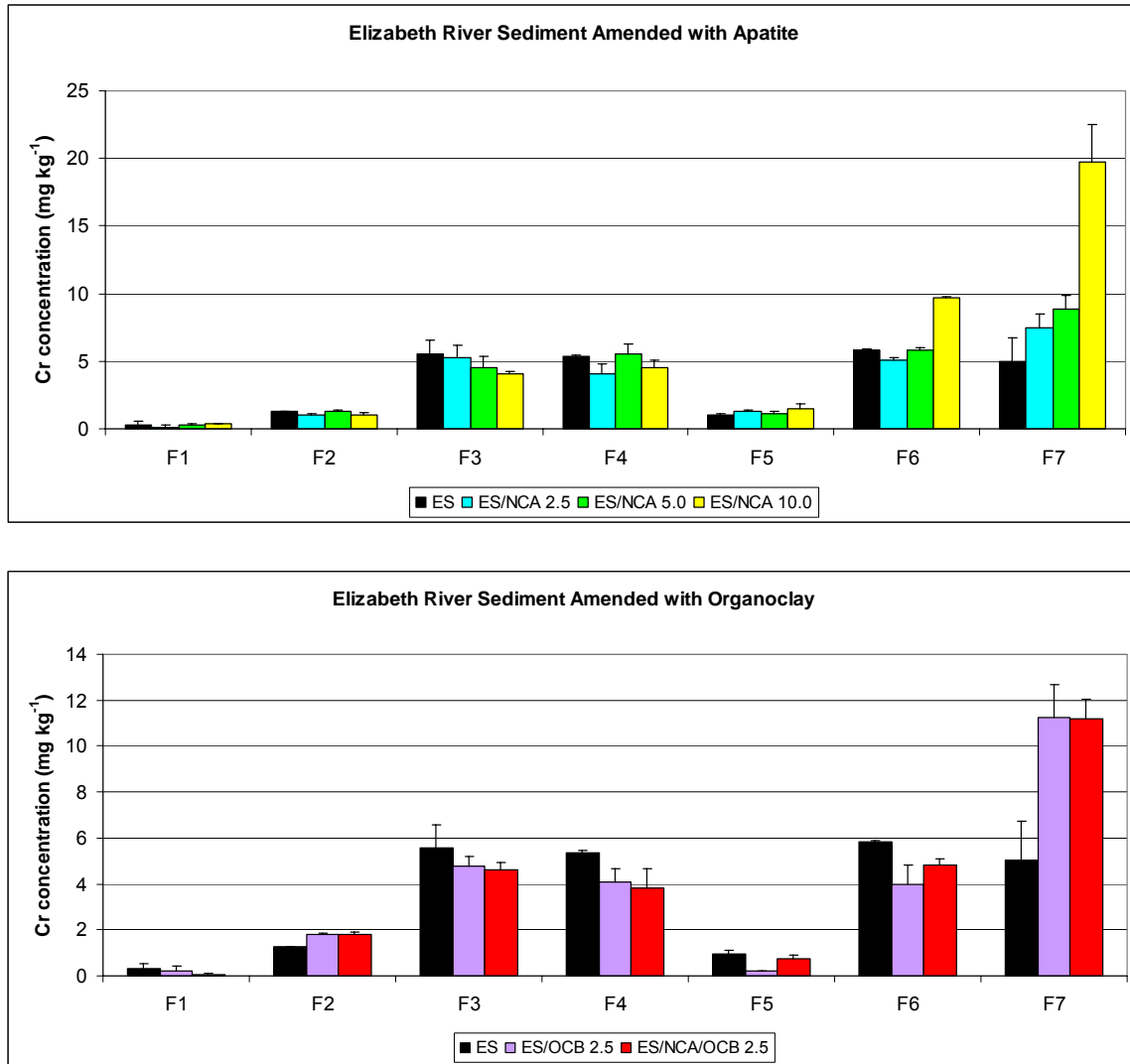


Figure 15. Effect of NCA and OCB on the partitioning of Cr in the Elizabeth River sediment; F1 - exchangeable fraction, F2 - carbonate fraction, F3 - amorphous fraction, F4 – crystalline oxide, F5 – organic, F6 – sulfide, and F7 – residual.

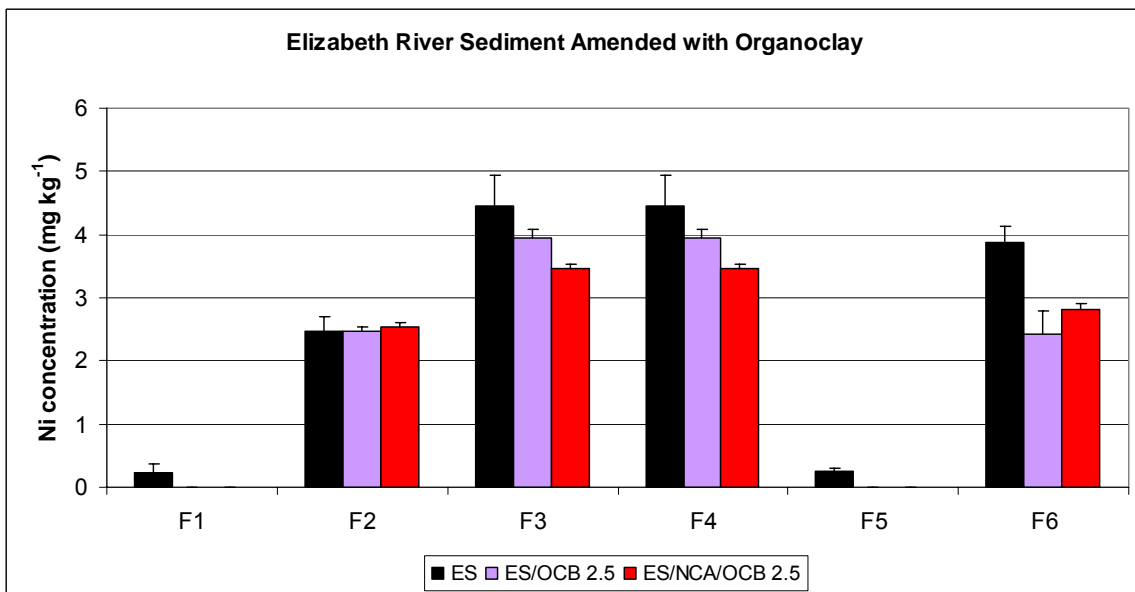
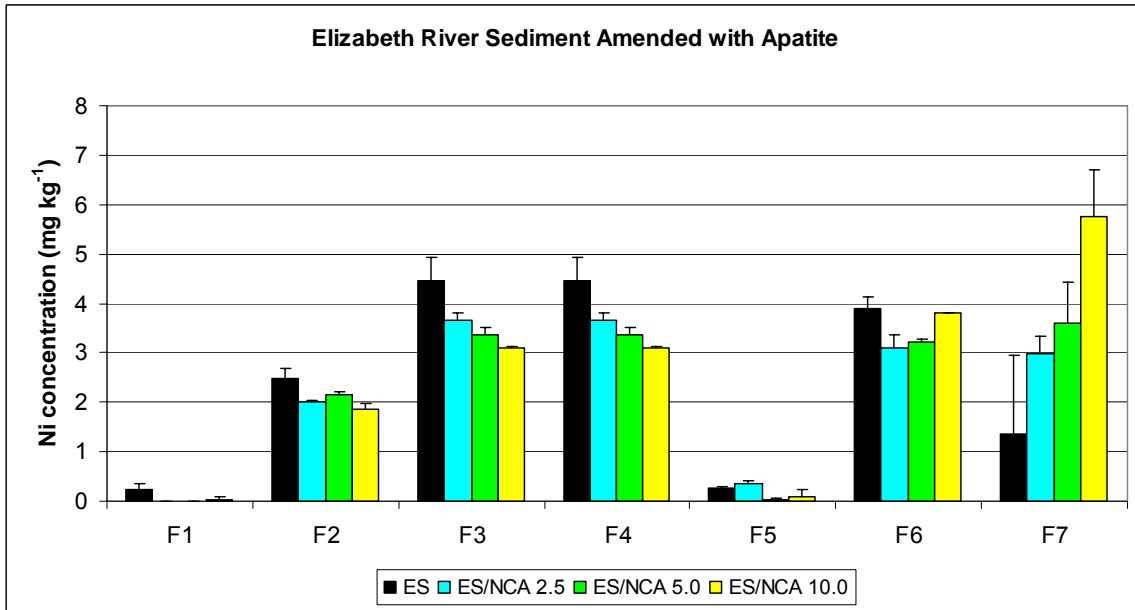


Figure 16. Effect of NCA and OCB on the partitioning of Ni in the Elizabeth River sediment; F1 - exchangeable fraction, F2 - carbonate fraction, F3 - amorphous fraction, F4 – crystalline oxide, F5 – organic, F6 – sulfide, and F7 – residual.

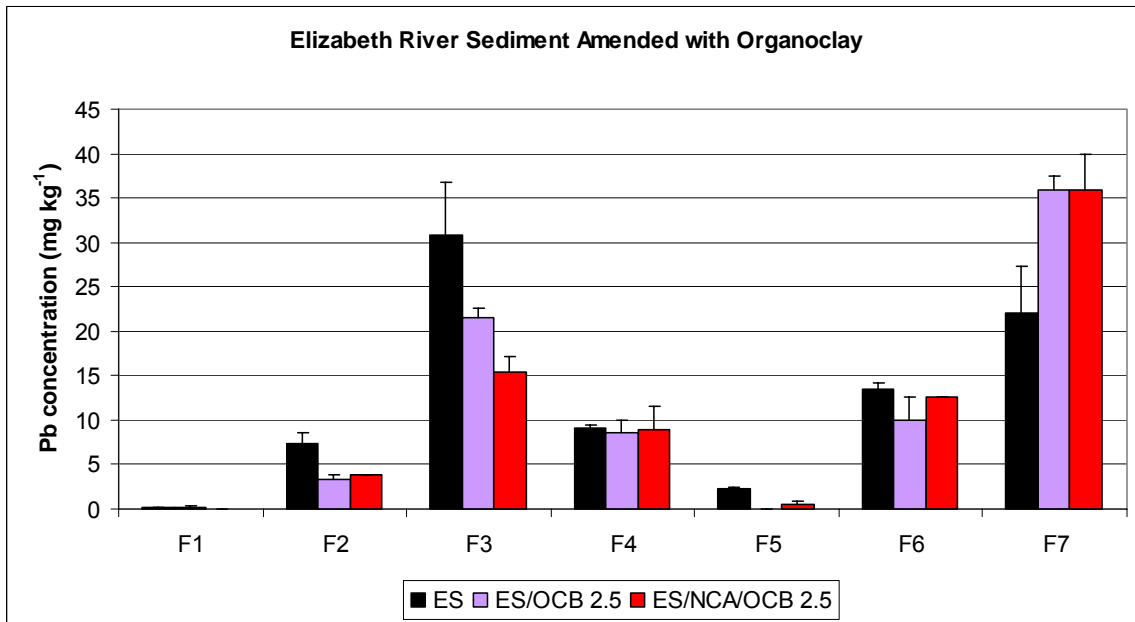
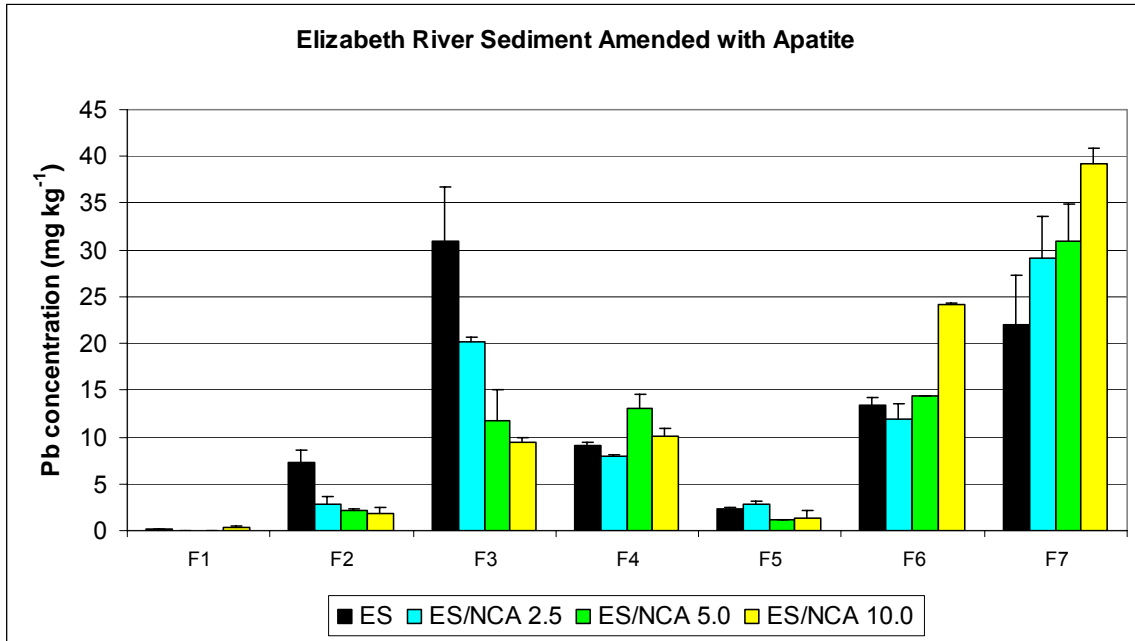


Figure 17. Effect of NCA and OCB on the partitioning of Pb in the Elizabeth River sediment; F1 - exchangeable fraction, F2 - carbonate fraction, F3 - amorphous fraction, F4 – crystalline oxide, F5 – organic, F6 – sulfide, and F7 – residual.

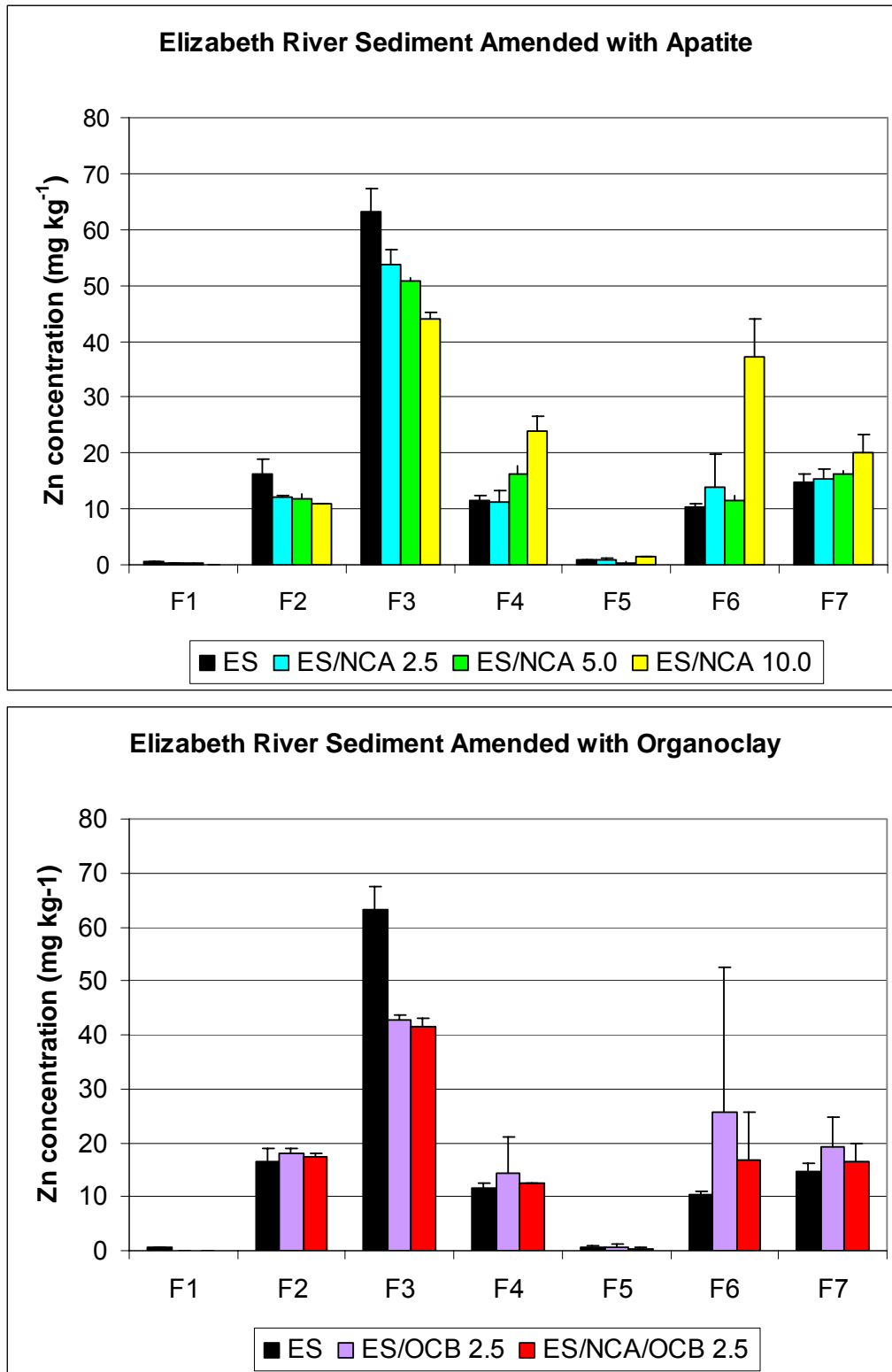


Figure 18. Effect of NCA and OCB on the partitioning of Zn in the Elizabeth River sediment; F1 - exchangeable fraction, F2 - carbonate fraction, F3 - amorphous fraction, F4 - crystalline oxide, F5 - organic, F6 - sulfide, and F7 - residual.

Sequential extraction of nickel (Ni)

Suzuki et al. (1981) studied the removal of selected metals from solutions passed through columns packed with synthetic hydroxyapatite; very limited data suggests that appreciable Ni (II) could be removed. The authors assumed a cation exchange mechanism, and ranking in terms of the amount exchangeable was Cd(II), Zn(II)>Ni(II),Ba(II), Mg(II). Sowder et al. (1999) also suggested that hydroxyapatite may be effective for reducing Ni availability in sediment. Nickel forms an insoluble phosphate salt ($\text{Ni}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$) and should be amenable to precipitation by the phosphate released by the dissolving apatite phase. In addition, the existence of mixed nickel-containing phosphate minerals (e.g., cassidyite, hydrated calcium nickel magnesium phosphate) suggests that synergistic co-precipitation may occur (Bostick et al., 2003).

The data on the effect of apatite and organoclay on Ni distribution among mineral phases extracted from the Elizabeth River sediment are presented in Figure 6. Addition of NCA or OCB, or OCB/NCA resulted in a reduction of the exchangeable pool of Ni and an increase in the residual pool of Ni in the sediment (Figure 16).

Sequential extraction of lead (Pb)

Most Pb salts (e.g., phosphates, sulfates, sulfides, carbonates, hydroxides) are either sparingly soluble or almost completely insoluble. Lead interacts strongly with clay minerals, oxides of Fe and Mn, and with organic matter such as humic acids (Bodek, 1988, McLean and Bledsoe, 1992). As a result, Pb solubility and mobility is low in most subsurface systems. In natural waters at $\text{pH} > 7$, Pb is either adsorbed on clay surfaces or forms Pb-carbonate precipitate. Lead has a strong affinity for organic ligands, and the formation of such complexes may greatly increase Pb mobility in sediments. The long-term stability of Pb-compounds in the sediments depends upon differences in the nearly insoluble phases, e.g., pyromorphite-type phosphate minerals versus carbonate or hydroxide phases. Lead phosphates, especially pyromorphite minerals, demonstrate minimal solubility and bioassessibility (Ruby, 1994, Chen 1997, and Zhang 1998).

The partitioning of Pb within the various fractions of the Elizabeth River sediment with and without amendments is illustrated in Figure 17. For the untreated Elizabeth sediment, the Pb was predominantly associated with the amorphous Fe and Me oxide fraction, presumably by sorption to these oxides (Barnett et al, 2002). The next most abundant fractions were the residual and sulfite fractions, with the exchangeable fraction being the least abundant (Figure 17). As expected, the additions of NCA (2.5%, 5.0%, and 10% by weight) shifted Pb from amorphous oxide, carbonate, and exchangeable fractions to the sulfide and residual fractions. The largest shift was observed with the addition of 10% NCA (Figure 17).

Sequential extraction of zinc (Zn)

Zinc in dilute solution hydrolyzes negligibly below pH 6, but at pH values >7.5, the neutral species $Zn(OH)_2$ typically becomes the predominant soluble species in aqueous systems (Bodek et al, 1988). As its species formed with common ligands in surface waters are soluble in neutral and acidic solution, zinc is readily transported in most natural waters and is one of the most mobile heavy metals (Bodek et al., 1988).

Zinc may be sequestered by reaction with apatite, as demonstrated by Wright et al., (1995), Moody and Wright (1995), and Chen et al. (1997). Chen et al. (1997) reported that sorptive removal of Zn(II) by apatite is significantly pH dependent, with a sharp increase in the removal of soluble Zn when the final solution pH value is >6.5. Chen et al. (1997) also reported that hopeite [$Zn_3(PO_4)_2 \cdot 4H_2O$] is the principal mineral phase formed by interaction of Zn(II) and apatite at near-neutral pH values.

The partitioning of Zn within the various fractions of the untreated and treated Elizabeth River sediment is illustrated in Figure 18. For the untreated sediment, the Zn was predominantly associated with the amorphous oxide and carbonate fractions, which are relatively mobile fractions (Figure 18). Oxyhydroxide (oxide) minerals, along with organic matter, have been recognized as the predominant metal sorbents in aquatic systems. In comparison with carbonate minerals, amorphous oxide minerals have a surface site density that is three to four orders of magnitude greater and a larger surface area (oxides up to $300 \text{ m}^2 \text{ g}^{-1}$, organic matter up to $1900 \text{ m}^2 \text{ g}^{-1}$, and carbonates usually $<1 \text{ m}^2 \text{ g}^{-1}$) (Forstner and Wittmann, 1979; Benjamin and Leckie, 1981; Bilinski et al., 1991). The addition of only 2.5% (by dry weight) of NCA or OCB reduced by 90% the exchangeable pool of zinc. Also, carbonate and amorphous oxide fractions were substantially reduced in the Elizabeth River sediment when treated with NCA or OCB (Figure 18). The reduction of relatively mobile fractions such as the exchangeable, carbonate, and amorphous resulted in new mineral phases associated with the crystalline, sulfide, and residual fractions (Figure 18).

Potentially mobile fraction and recalcitrant factor

Sequential extraction results can be summarized using the concepts of the Potentially Mobile Fraction (PMF) and Recalcitrant Factor (RF) (Knox et al., 2006). Early extraction steps (exchangeable, carbonate, amorphous oxides, and organic fractions) tend to recover metal fractions that are less strongly bound than the fractions collected in the later extraction steps (crystalline oxides, sulfides, and residue fractions). The less strongly bound fractions can be termed the PMF because they constitute the contaminant fraction that has the potential to enter into the mobile aqueous phase in response to changing environmental conditions, such as pH, Eh, temperature, etc. The PMF for the untreated and treated Elizabeth River sediment was calculated using equation shown below:

$$\text{Potentially Mobile Fraction} = 100 - (F_{\text{Cry. oxides}} + F_{\text{Sulfide}} + F_{\text{Residual}})$$

where $F_{\text{Cry. oxides}}$ represents the crystalline Fe oxide fraction (wt-%), F_{Sulfide} the sulfide fraction (wt-%), and F_{Residual} the residual fraction (wt-%).

Fractions of the contaminant pool that are very strongly bound by the sediment include crystalline oxides, sulfides or silicates, and aluminosilicates. These strongly bound fractions were used to calculate the RF. The RF is the ratio of strongly bound fractions to the total concentration of the element (i.e., sum of all fractions) in the sediment. The meaning of the RF is opposite to the PMF; i.e., the RF indicates the virtually irreversible retention of metals by the solid phase. For this study the RF was calculated using equation shown below:

$$\text{Recalcitrant Factor} = \left[\frac{C_{\text{cry.oxides}} + C_s + C_{\text{residual}}}{C_{\text{exch}} + C_c + C_{\text{org}} + C_{\text{oxides}} + C_s + C_{\text{residual}}} \right] \times 100$$

where C represents concentration, and the subscripts *crystalline oxides* (*cry. oxides*), *sulfides* (*s*) and *residual*, represent the three final fractions of the sequential extractions. The subscripts *exch*, *c*, *org*, and *oxides* stand for water soluble and exchangeable metals, carbonates, organically bound metals, and metals bound to amorphous and crystalline oxides, respectively. This construct provides an estimate of the percentage of a contaminant in the sediment that is resistant to remobilization; i.e., retention of contaminants in sediments.

Results for the untreated and treated Elizabeth sediment are presented in Figure 19. Of the seven tested elements, Cd, Zn, Co, and Pb showed the highest PMF values in the untreated sediment, more than 50% (Figure 19). Addition of amendments such as apatite or organoclay to the sediment reduced substantially the PMF values of all tested elements, with the greatest reductions for the most mobile elements; i.e., Pb, Zn, Cd, and Co (Figure 19). For example, the addition of 10% NCA to the sediment resulted in about a 40% reduction in the PMF values for Co, Cd, Pb, and Zn (Figure 19). Of all tested elements, As had the highest RF value in the untreated sediment: 84 % (Figure 19). When the mobile fraction is very limited, like for As, the addition of amendments reduces the PMF and increases the RF less substantially (Figure 19).

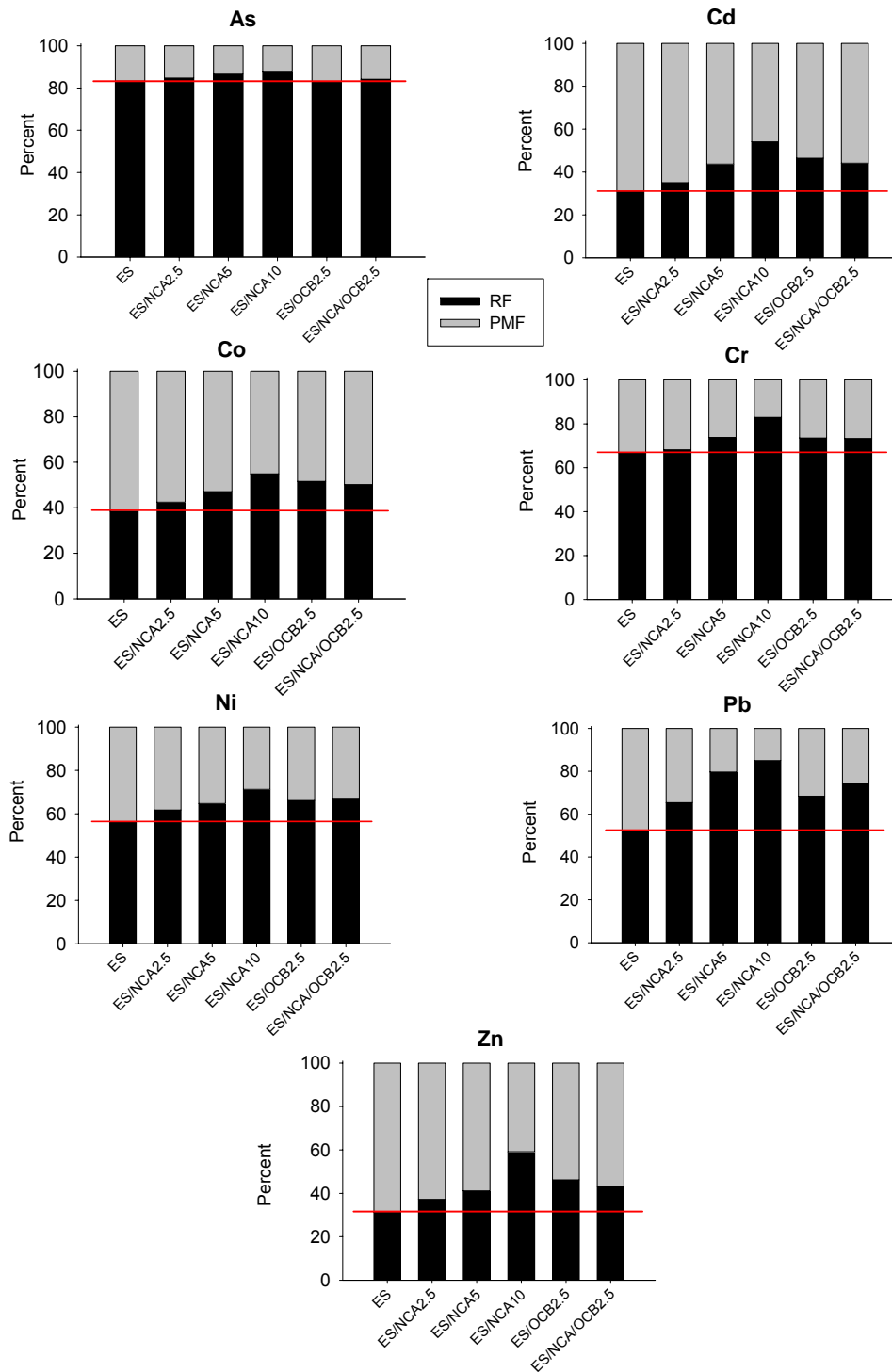


Figure 19. Average potentially mobile fraction (PMF) and recalcitrant factor (RF) for As, Cd, Co, Cr, Ni, Pb, and Zn in the untreated and treated Elizabeth River sediment. The red line represents the partitioning of untreated sediment.

Effects of sequestering agents on availability and retention of Uranium

Two phosphate amendments, North Carolina apatite and calcium phytate significantly reduced water extractable U from Tims Branch sediment (Figure 20). However, it was observed that calcium phytate also contributed to substantial release of Fe from Tims Branch sediment (Figure 21). The release of Fe could reduce the ability of phosphate amendments to immobilize U and other metals due to the strong affinity of Fe oxides for these elements. Increased release of Fe or Mn was related very likely to higher native microbial population in calcium phytate (Figure 22). Therefore, the contribution of microorganisms to U removal was examined by testing P amendments with their natural populations and autoclaved amendments that were sterilized to remove microbial populations. The effects of sterilization of amendments on U mobility were evaluated by water extraction and 1 M MgCl₂ extraction.

The phosphate amendments alone were observed to contain some microorganisms including bacteria and fungi in addition to natural microbial populations found in the sediment. Sterilization of amendments had a significant effect on U mobility (Figure 23 and 24). The U concentration in 1 M MgCl₂ extract from the U spiked Hanford sediment was 437 µg/kg, but in the same sediment without microbes (autoclaved), the U concentration was only 103 µg/kg (Figure 24). In spiked Hanford sediment that was sterilized by autoclaving and treated with sterilized biological apatite, U concentration in the 1 M MgCl₂ extract was zero suggesting that microbes may enhance U mobility (Figure 24).

Uranium is a significant inorganic contaminant on the Savannah River Site (SRS) and at many other locations. Radionuclides that contaminate sediments cannot be destroyed, but their toxicity can be diminished through alteration of their chemical speciation. Ideally, such chemical alterations (e.g., reduction or precipitation) will convert toxic and mobile species to nontoxic and immobile species. The use of sequestering agents to remediate contaminated sediments offers considerable potential for long-term environmental cleanup; however, their effectiveness may be improved by additional steps, such as sterilization. The potential effects of microbial organisms on amendment effectiveness require further investigation.

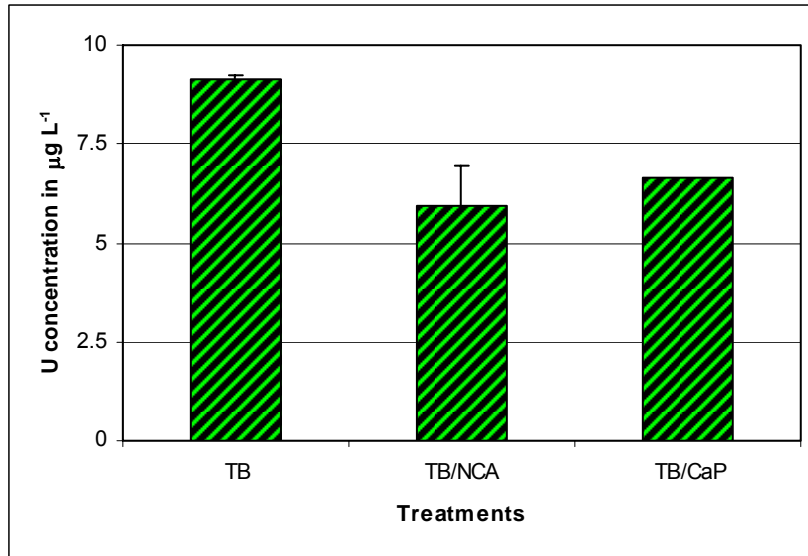


Figure 20. Effect of North Carolina apatite (NCA) and calcium phytate (CaP) on water extracted U from Tims Branch sediment (TB).

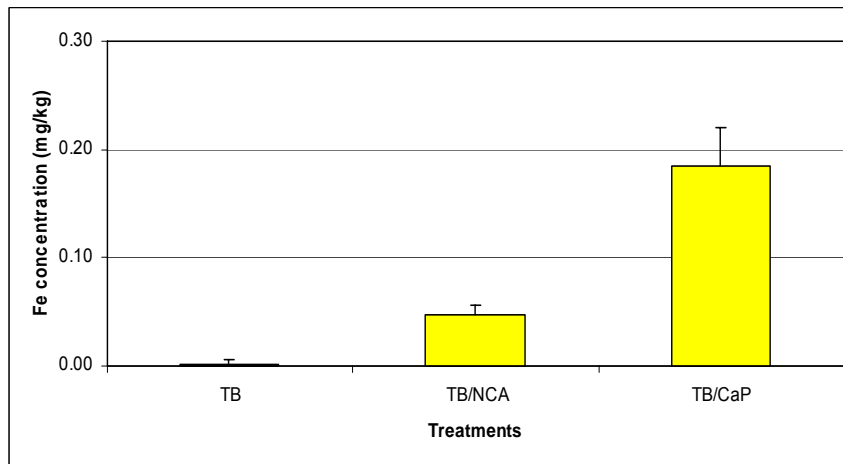
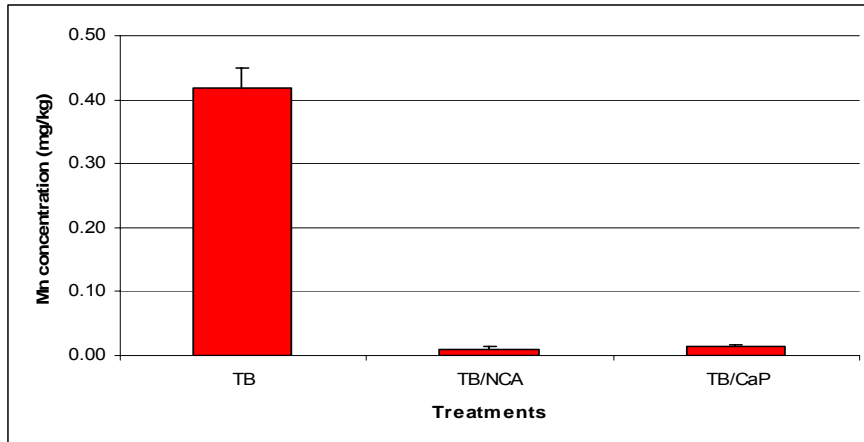


Figure 21. Effect of phosphate amendments on Mn and Fe concentration in water extracts, TB – Tims Branch sediment, NCA – North Carolina apatite, CaP – calcium phytate.

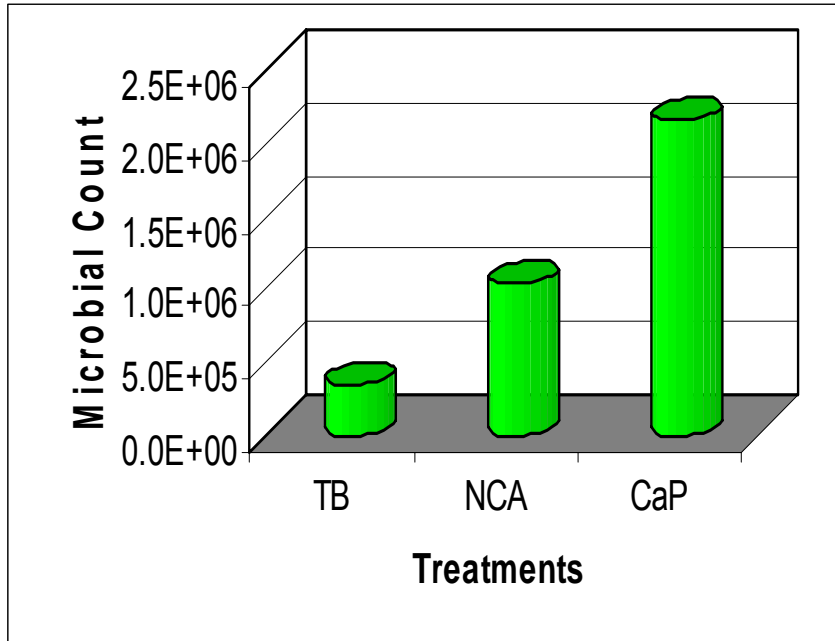


Figure 22. Microbial activity in Tims Branch sediment and in the phosphate amendments.

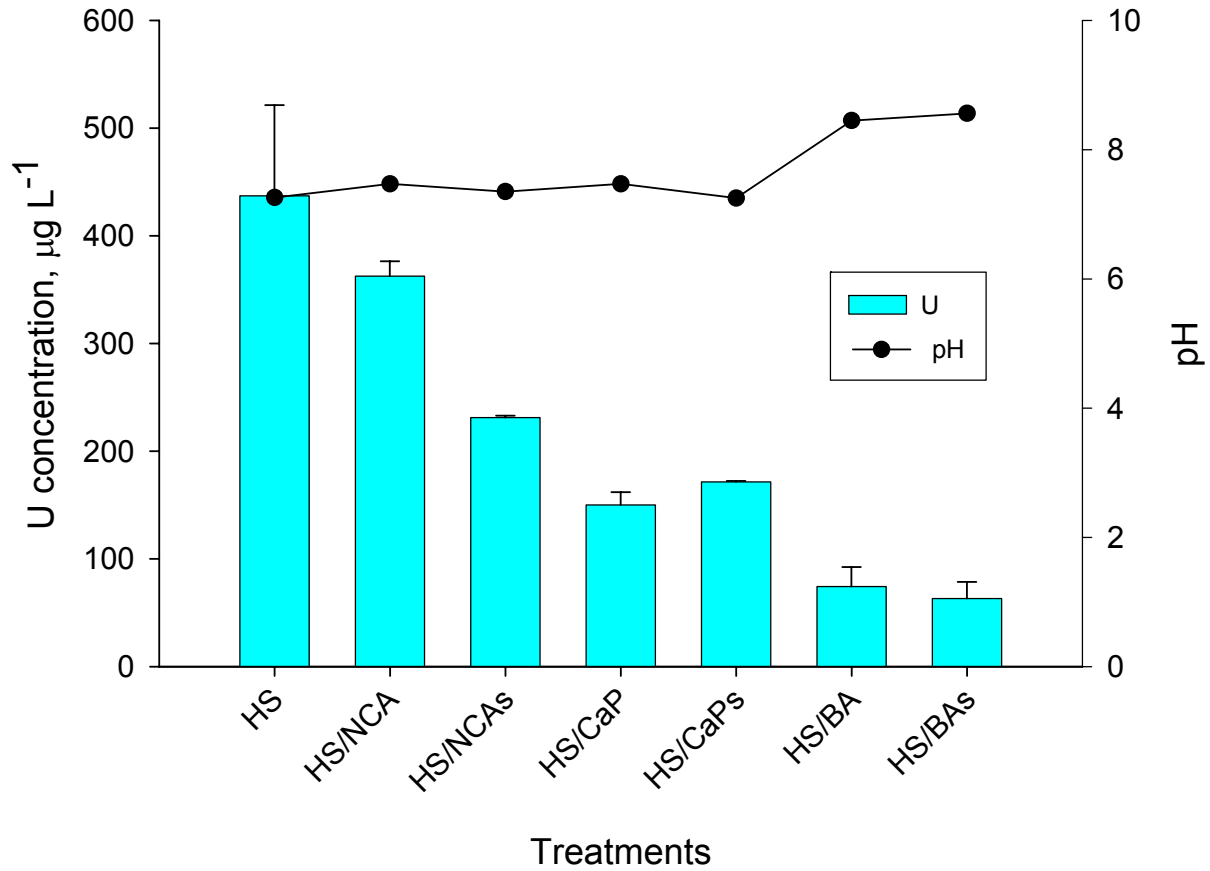


Figure 23. Effect of phosphate amendments and sterilization of amendments on U mobility; 1 M MgCl₂ extraction, the following acronyms stand for: HS - U spiked Hanford sediment, NCA – North Carolina Apatite, NCAs – sterilized North Carolina Apatite, CaP – calcium phytate, CaPs –sterilized calcium phytate, BA – biological apatite (ground fish bones), Bas – sterilized biological apatite, soil/amendment/liquid ratio: 3g/0.15g/20 mL

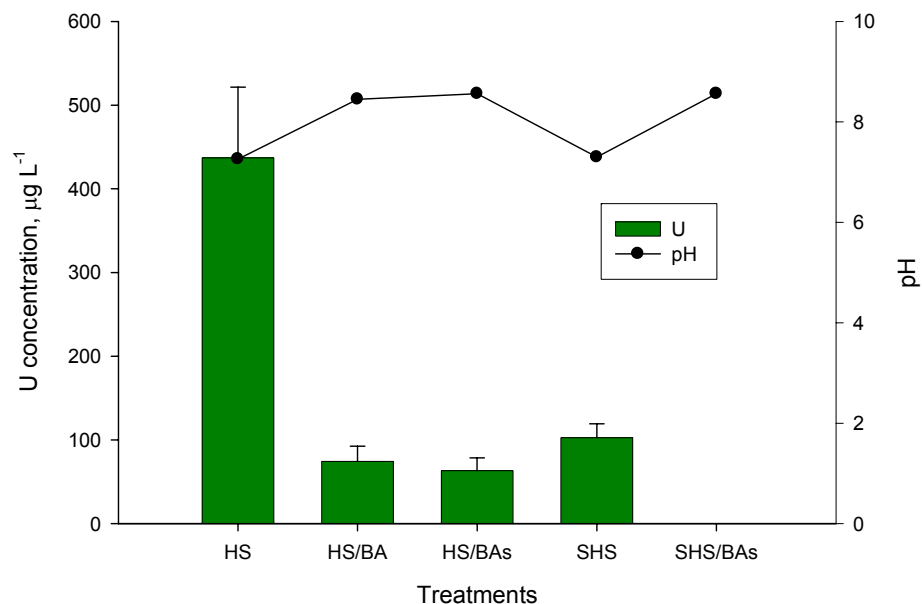


Figure 24. Effect of sterilization of soil and biological apatite on U mobility following 1 M MgCl₂ extraction; HS – U spike Hanford soil, SHS – sterilized U spiked Hanford soil, BA – biological apatite (ground fish bones), BAs – sterilized biological apatite, soil/amendment/liquid ratio: 3g/0.15g/20 mL.

TASK 2. STUDIES FOR DETERMINATION OF THE BEST COMBINATION OF AMENDMENTS FOR PLACEMENT AND CONSTRUCTION OF ACTIVE SEDIMENT CAPS

SUBTASK 2.1. EVALUATION OF MECHANICAL PROPERTIES

Development of biopolymer coated sand

The methods for cross-linked biopolymers and the best cross-linked products are presented in Table 9. Only the six most promising products (from 23 total), which had high carbon fractions (indicating greater coverage of biopolymer) and high viscosity, were evaluated further for metal and organic sorption, and for biodegradability.

Table 9. Cross-linked biopolymers products that were used for sand coating.

Major Product Name	Primary Biopolymers	Cross-link Agent	Modified product name	Biopolymer sand ratio	Solid liquid ratio	Additives			
						5%HCl	glutaraldehyde	1N NaOH	water
						mL	mL	mL	mL
CGB	Chitosan & Guar gum	Borax	CGB1	0.05	0.44	475			
			CGB2	0.05	0.41	200	5		300
			CGB3	0.05	0.34	200		20	400
GB	Guar gum	Borax	GB1	0.005	0.35	100			500
			GB2					20	600
			GB3	0.025	0.33		5	20	600
GX	Guar gum	Xanthan	GX1	0.05	0.35	100			500
			GX2	0.05	0.35			20	600
			GX3						
XCc	Xanthan&Chitosan	Calcium chloride	XCC	0.025	0.34	100	5		500
Xc	Xanthan	Calcium chloride	XC	0.025	0.34	100			500
AC	Alginat	Calcium chloride	AC	0.025	0.34	100			500

Physical properties of biopolymer coated sand and other amendments

Organic carbon content was measured as an indicator of the efficiency of the procedure for coating the sand with biopolymers and as an indicator of the potential for the sorption of organic contaminants on the coated sand. The acid washed sand was successfully coated with cross-linked biopolymers as described above. The carbon fraction of the acid washed coated sand was similar to with the carbon fraction of the coated play sand indicating that the coating procedure was equally effective with both types of sand. The measured carbon fractions are listed in Table 10. The carbon fractions of coated sand with one wash, two washes and three washes did not differ substantially from the unwashed sand, indicating that the coated sand was resistant to washing.

Table 10. Carbon fractions of biopolymer coated sand

Samples	Unwashed (%)		Washed (%)	
	Replicate 1	Replicate 2	Replicate 1	Replicate 2
CGB1	9.210	6.009	2.932	3.180
CGB2	7.893	-	5.197	5.964
CGB3	3.938	-	2.366	2.062
GB1	1.482	4.809	2.653	2.615
GB2	3.670	3.828	2.515	2.877
GB3	4.000	2.329	5.919	0.607
GX1	6.072	5.267	3.395	2.618
GX2	4.634	3.941	2.97	-
GX3	0.385	0.369	0.301	0.306
XCc	3.660	4.282	3.631	3.490
Xc	3.645	1.964	1.361	1.018
Ac	1.207	2.049	0.332	0.277
CGB*	1.050	1.058	0.774	1.042
XCc*	1.297	1.888	0.953	1.352
GX1*	1.197	2.267	0.482	0.966
GX2*	1.781	0.415	0.064	0.174
C*	5.287	5.576	3.336	3.996
C*	1.622	1.322	1.097	1.190

* Sand used in these batch studies is unwashed; C-chitosan; G-cuar gum, B-borax, X-xanthan; c- calcium chloride.

Other properties such as bulk density and porosity of amendments and coated sands are presented in tables 11-14. The coated sands had lower density than regular sand (Table 12). On the other hand, the porosity of the coated sand was higher than the regular sand (Table 14).

Table 11. Bulk density of sequestering agents (g/mL).

Sorbents	Density (g/mL)	Standard deviation
PIMS biological appetite	0.7835	0.0134
Clino zeolite 8x14	0.7646	0.0182
Clino zeolite -4 mesh	0.9335	0.0246
Clino zeolite powder	0.6538	0.0365
Phili Zeolite	0.7779	0.0179
CETCO TM-199	0.7618	0.0272
Washed phosphate	1.2631	0.0133
Clay 750	0.3875	0.0128
Clay 202	1.1303	0.0331
Clay 200	1.1637	0.0185
North Carolina AP	1.5138	0.0294
Calcium phytate	0.4418	0.0243
CETCO TM-200	0.6885	0.0338

Table 12. Bulk density of coated sand (g/mL).

Coated Sand	Density (g/mL)	Standard deviation
CGB1	0.741	0.074
CGB2	0.909	0.024
CGB3	1.061	0.004
GB2	1.287	0.009
XCc	1.182	0.081
GX1*	1.182	0.048
Sand	1.515	0.069

Table 13. Porosity of sorbents.

Sorbents	Porosity	Standard deviation
PIMS biological appetite	0.791	0.013
Clino zeolite 8x14	0.486	0.009
Clino zeolite -4 mesh	0.435	0.050
Clino zeolite powder	0.516	0.022
Phili Zeolite	0.544	0.009
CETCO TM-199	0.557	0.053
Washed phosphate	0.479	0.035
Clay 750	0.857	0.024
Clay 202	0.861	0.076
Clay 200	0.805	0.056
North Carolina AP	0.412	0.068
Calcium phytate	0.567	0.047
CETCO TM-200	0.550	0.001

Table 14. Porosity of coated sand.

Sorbents	Porosity	Standard deviation
CGB1	0.646	0.005
CGB2	0.650	0.008
CGB3	0.629	0.054
GB2	0.561	0.056
XCc	0.546	0.001
GX1*	0.388	0.017
Sand	0.378	0.031

Biodegradability of biopolymer coated sand

The ten week evaluation showed no CO₂ release for chitosan/guar gum cross-linked with borax and slight CO₂ released for xanthan/chitosan cross-linked with calcium chloride (Figure 25) suggesting little or no biodegradation. Other biopolymer/sand products show very rapid release of CO₂ after the first week of the experiment. Future studies will emphasize biopolymer products with little or no CO₂ release since they are likely less susceptible to biodegradation.

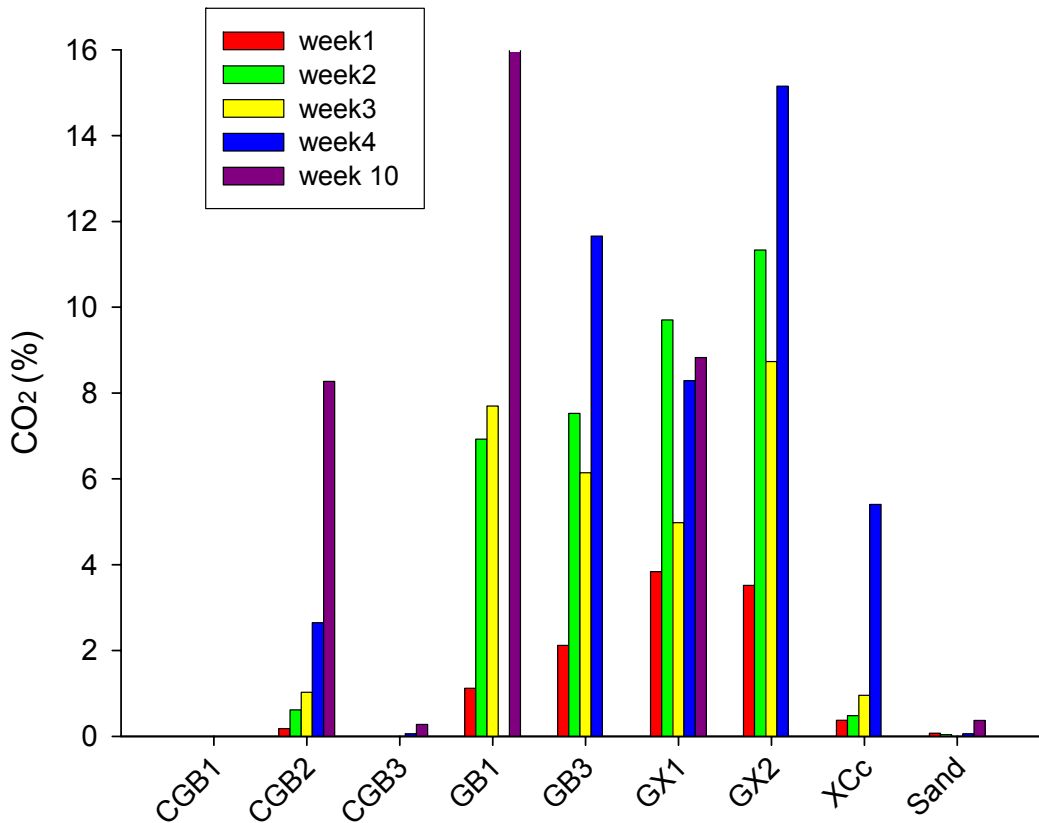


Figure 25. Evaluation of the biodegradability of sand coated with cross-linked biopolymers and uncoated sand (control) as indicated by CO₂ release; B - borax, C - chitosan, G - guar gum, X - xanthan, c - calcium chloride, 1 - without glutaraldehyde, 2 - with glutaraldehyde, 3 - without glutaraldehyde but with NaOH

SUBTASK 2.2. EVALUATION OF DIFFUSIVE TRANSPORT

Diffusion of Metals through Active Caps – Laboratory Experiment

Diffusion is a spontaneous process that results in the movement of a solute. It is caused by the random thermal motion of a solute in solution and is driven by concentration gradients. Solutes move from high concentration areas to low concentration areas. As below equation indicates, the diffusional flux is directly proportional to the concentration gradient: the higher the concentration gradient, the stronger the flux. The flux will continue until the concentration equilibrates (Dragun, 1998).

$$J_c = -D_e \left(\frac{dc}{dx} \right)$$

J_c = diffusion flux of chemical c (moles/cm²sec)

D_e = measured diffusion coefficient (cm²/sec),

dc/dx = concentration gradient of c in the x direction (moles/cm⁴)

D_e is a function of the diffusivity of pure water and the porosity and tortuosity of the medium. It is retarded by sorption onto the medium.

In the diffusion experiment, the first set of water samples was collected 48 hrs after the experiment was initiated. The water samples were analyzed for metal content, and the data are presented in Table 15. The water from the control treatment (i.e., sediment without cap material) showed the highest metal concentrations, especially for metals that were added to the sediment with the spike solution. As was expected, all cap materials prevented desorption of metals from the underlying sediment; therefore, metal concentrations in solution were near zero or close to the background DI water (Table 15) for all treatments employing sediment caps. Rock phosphates released the highest concentration of P, but treatments with organoclay had the highest content of Na. The Mn concentration in the presence of cap materials was reduced drastically in comparison with the control treatment (Table 15).

Pictures 1 and 2 show potentially important observations from the diffusion experiment. Substantial changes occurred over one month in a treatment with biopolymer coated sand (xanthan and chitosan cross-linked with calcium chloride) and NC apatite as cap materials. In the presence of the coated sand NC apatite became very dark in color and individual particles of NC apatite were no longer visible. This change in the NC apatite did not occur in the treatment without biopolymer coated sand (Picture 2). At the end of this experiment, microbial counts and other analyses will be conducted to explain this phenomenon. If microbial growth has increased, it may contribute to phosphate dissolution that could lead to enhance removal of contaminants or vice versa. There are several bacterial species (*Alcaligenes*, *Acinetobacter*, *Arthrobacter*, *Azospirillum*, *Bacillus*, *Pseudomonas*, *Rhizobium*, and others) that are able to solubilize phosphate minerals (Rodriguez et al., 1999) and therefore, could enhance or inhibit the in-situ remediation of metals with phosphate amendments. It is generally accepted that the major mechanism of mineral phosphate solubilization is the action of organic acids synthesized by soil microorganisms.

Table 15. Average (standard deviation) concentrations of elements (in ppb) in water from diffusion experiments; samples were collected 48 hrs after the experiment began.

Cap material*	As	Cd	Co	Cu	Ni	Pb	Se	Na	P	Mn
No cap	55.1 (6.9)	17.4 (16.1)	7.8 (7.4)	4.5 (1.9)	23.9 (21.4)	3.6 (0.6)	30.5 (11.1)	22 (1)	80 (13)	26.1 (26.7)
NCA	0.6 (0.0)	0.2 (0.1)	0.1 (0.1)	2.1 (0.6)	3.0 (1.9)	0.0 (1.7)	0.0 (0.0)	1237 (716)	428 (97)	1.6 (0.0)
OCB750	0.4 (0.1)	0.0 (0.0)	1.2 (0.0)	5.9 (1.5)	22.4 (0.6)	1.2 (0.1)	1.0 (0.1)	63555 (6116)	290 (215)	1.0 (0.2)
XCc	0.3 (0.0)	0.0 (0.0)	0.0 (0.0)	1.5 (0.5)	0.7 (0.1)	0.5 (0.0)	0.4 (0.2)	29335 (7304)	28 (0)	2.9 (0.4)
S	0.2 (0.0)	0.1 (0.0)	0.1 (0.0)	1.8 (0.2)	1.3 (0.2)	0.8 (0.7)	0.2 (0.0)	62 (12)	62 (3)	5.4 (0.7)
XCc/NCA	0.3 (0.0)	0.1 (0.1)	0.0 (0.0)	4.5 (2.1)	2.6 (1.5)	0.4 (0.3)	0.8 (0.0)	4673 (1250)	127 (53)	5.6 (4.5)
XCc/NCA/ OCB750	0.5 (0.0)	0.1 (0.0)	0.0 (0.0)	2.8 (1.3)	1.8 (0.2)	0.5 (0.2)	0.8 (0.0)	111655 (26509)	127 (31)	2.2 (1.3)
AWS	0.3 (0.0)	0.1 (0.1)	0.0 (0.0)	2.5 (1.1)	2.3 (0.5)	0.4 (0.1)	1.3 (0.0)	70 (25)	101 (1)	2.8 (1.1)
CGB3	0.6 (0.0)	0.0 (0.0)	0.1 (0.0)	5.0 (2.7)	4.2 (0.8)	0.5 (0.4)	1.1 (0.1)	161400 (42144)	199 (1)	0.7 (0.0)
DIW	0.2 (0.0)	0.1 (0.1)	0.0 (0.0)	3.0 (0.1)	2.1 (1.3)	0.2 (0.0)	0.5 (0.1)	52 (18)	22 (0)	0.4 (0.2)

* Cap materials: NCA = washed North Carolina Apatite, OCB750 = organoclay 750 from Biomin Inc., XCc = sand coated with xanthan, chitosan and cross-linked with calcium chloride, S = playground sand, AWS = acid washed sand, CGB3 = sand coated with chitosan and guar gum cross-linked with borax, DIW = distilled water



9/28/2007



10/4/2007

Picture 1. Diffusion experiment at the beginning (9/28/07) and after one month (10/4/2007); cap composition: 1- no cap (control - only sediment), 9- playground sand, 15 – acid washed sand, 18 – biopolymer coated sand (chitosan and guar gum cross-linked with borax), 7 - biopolymer coated sand (xanthan and chitosan cross-linked with calcium chloride), 5 – organoclay 750 from Biomin Inc., 3 – NC apatite, 11- biopolymer coated sand (xanthan and chitosan cross-linked with calcium chloride) with NC apatite (50% of each), 13 - biopolymer coated sand (xanthan and chitosan cross-linked with calcium chloride) with NC apatite, and organoclay 750 (33.3% of each).

Diffusion of Metals through Active Caps – Modeling

Material Properties and Other Input Parameters

Material properties utilized within the 1-D numerical model were specified by material layer for each case simulated. Each material zone was assigned values of particle density, total porosity, saturation, and tortuosity. The bulk density and porosity of each material type except the sediment were previously measured. These values were used to calculate particle density. The properties assigned to each material type are given in Table 16.

The sediment used in the diffusion experiment and simulated in the modeling exercise originated from Tim’s Branch at the SRS. The sediments along Tim’s Branch belong to the soil series named Fluvaquents (Rogers, 1990). The Fluvaquents soil series consists of poorly drained, permeable soils which occur along the flood plain of small streams and drainages in the sandy sediments of the Atlantic Coastal Plain. Surficial sediments from this soil series typically grade from sand to loamy sand. Material properties of these sediments were not measured for the diffusion experiment. However, properties for similar sediments at SRS have been previously measured. Thus, average property values for the sediment were determined based on existing data for sediments classified as sand, loamy sand, and sandy loam. These properties are given in Table 16.

An effective diffusion coefficient was used for each metal and material layer (except the water layer). Molecular diffusion coefficients for each metal were taken from Li and Gregory (1974). Effective diffusion coefficients for each metal and material type were calculated using the molecular diffusion coefficient and the material tortuosity. The diffusion coefficients used in the model are given in Table 17.

The partitioning coefficient K_d was determined from earlier sorption studies for each metal and cap material. These values were used in the model to account for partitioning of the metals in the cap materials. Values of K_d were not available for the sediment and K_d was set to zero in this material layer. This should be a conservative assumption for this modeling exercise as it will allow for maximum diffusion into the overlying cap material. The partitioning coefficients assigned to each metal and material type are given in Table 18.

Table 16. Material properties used in diffusion modeling.

Layer	Particle Density (g/cm ³)	Total Porosity (fraction)	Average Saturation (fraction)	Tortuosity (unitless)
Sediment layer	2.66	0.360	1.00	2
Apatite layer	2.57	0.412	1.00	4
Sand layer	2.44	0.378	1.00	2
Organoclay Layer	2.71	0.857	1.00	4

Table 17. Diffusion coefficients used in diffusion modeling.

Metal	Water ¹ (cm ² /yr)	Sediment (cm ² /yr)	Apatite (cm ² /yr)	Sand (cm ² /yr)	Organoclay (cm ² /yr)
Cd	2.261E+02	1.131E+02	5.653E+01	1.131E+02	5.653E+01
Cr	1.873E+02	9.366E+01	4.683E+01	9.366E+01	4.683E+01
Co	2.204E+02	1.102E+02	5.511E+01	1.102E+02	5.511E+01
Cu	2.312E+02	1.156E+02	5.779E+01	1.156E+02	5.779E+01
Pb	2.980E+02	1.490E+02	7.450E+01	1.490E+02	7.450E+01
Ni	2.141E+02	1.071E+02	5.353E+01	1.071E+02	5.353E+01
Se	2.983E+02	1.492E+02	7.458E+01	1.492E+02	7.458E+01
Zn	2.693E+02	1.347E+02	6.733E+01	1.347E+02	6.733E+01

¹From Li and Gregory, 1974

Table 18. Partitioning coefficients used in diffusion modeling.

Metal	Water (cm ² /yr)	Sediment (cm ² /yr)	Apatite (cm ² /yr)	Sand (cm ² /yr)	Organoclay (cm ² /yr)
Cd	0.000E+00	0.000E+00	7.696E+03	0.000E+00	2.073E+05
Cr	0.000E+00	0.000E+00	1.928E+04	0.000E+00	1.135E+04
Co	0.000E+00	0.000E+00	1.161E+03	0.000E+00	2.471E+04
Cu	0.000E+00	0.000E+00	6.237E+03	0.000E+00	1.146E+04
Pb	0.000E+00	0.000E+00	2.494E+04	0.000E+00	1.622E+03
Ni	0.000E+00	0.000E+00	4.760E+02	0.000E+00	3.058E+03
Se	0.000E+00	0.000E+00	3.520E+02	0.000E+00	7.141E+03
Zn	0.000E+00	0.000E+00	2.157E+03	0.000E+00	2.744E+03

Diffusive transport of metals

The results of the modeling are shown in Figures 26 through 33. Each figure shows the sediment pore water concentration and subsequent depletion due to diffusion into the overlying materials. Figures 26 and 27 show the results for Case 1 where there is no cap and, contaminants are allowed to diffuse out of the sediment into the overlying water column. These graphs show that the sediment and water concentration for each metal reach equilibrium in about 2 to 3 years. Slight differences in the time to equilibrium is a function of the effective diffusion coefficient used for each metal. Because there is no sorption processes involved with this simulation, the equilibrium concentration of each metal is identical.

Figures 28 and 29 show the results for Case 2 where there is a sand cap overlying the contaminated sediments. Since there is no sorption in the sand cap, this case is similar to Case 1. The concentration of contaminants in the pore water of the sediment and sand reach equilibrium with the overlying water column in 3 to 5 years. The equilibrium concentration of each metal is identical.

Figures 30 and 31 show the results for Case 3 where there is an apatite cap overlying the contaminated sediments. Compared to Case 2 (sand cap), these figures clearly show the apatite cap delayed contaminant breakthrough. Except for nickel and selenium, equilibrium is delayed for a minimum of 1000 years. Therefore, due primarily to sorption processes, the apatite cap appears to be an effective barrier against diffusive transport of the contaminants to the overlying water column.

Figures 32 and 33 show the results for Case 4 where there is an organoclay cap overlying the contaminated sediments. These figures show the organoclay cap delayed contaminant breakthrough. Contaminant equilibrium was reached between 100 and 1000 years for each contaminant except cadmium and cobalt which were delayed past 1000 years. As with the apatite cap, due primarily to sorption processes, the organoclay cap appears to be an effective barrier against diffusive transport of the contaminants to the overlying water column.

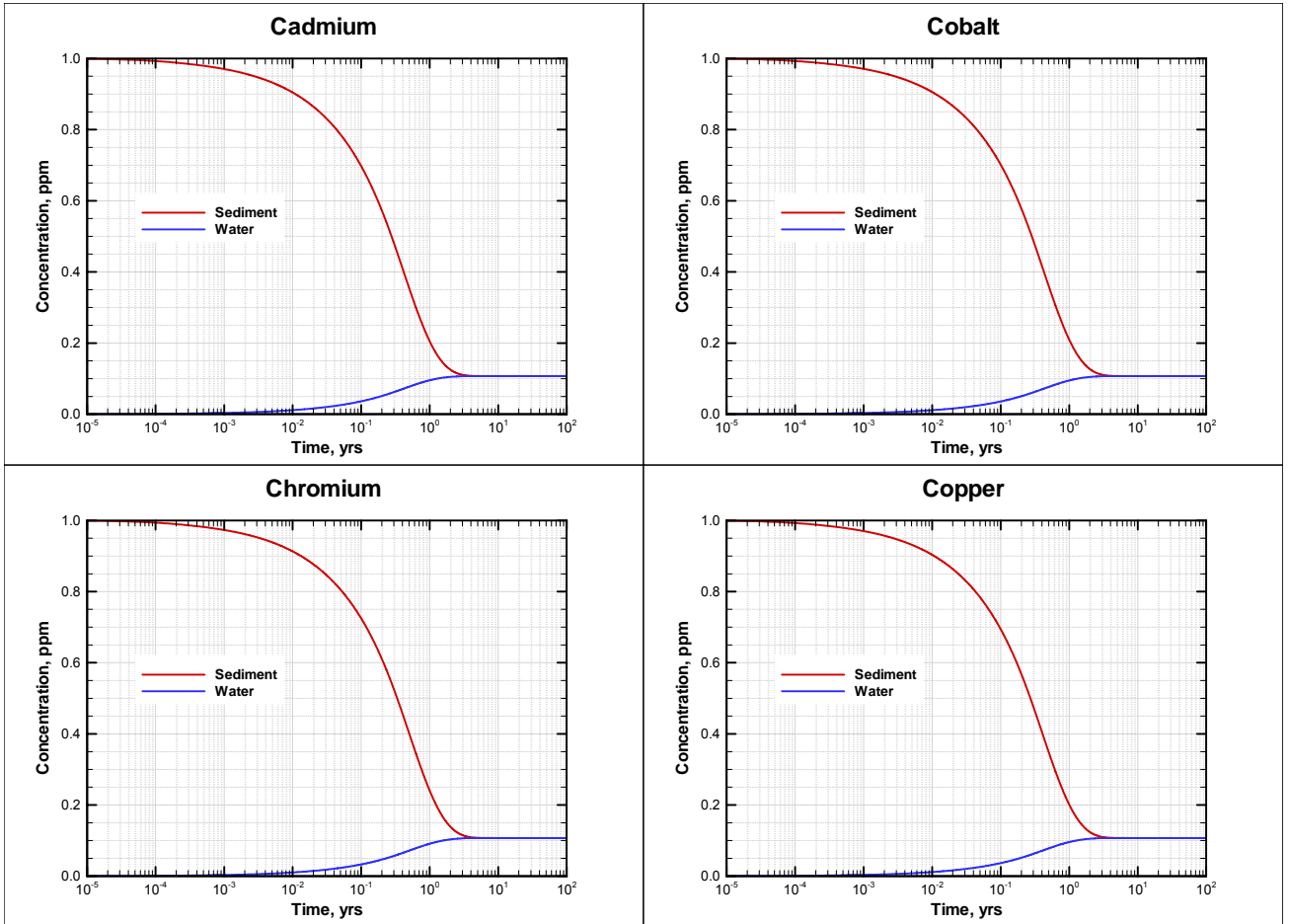


Figure 26. Breakthrough curves for Cd, Co, Cr, and Cu for the no cap case.

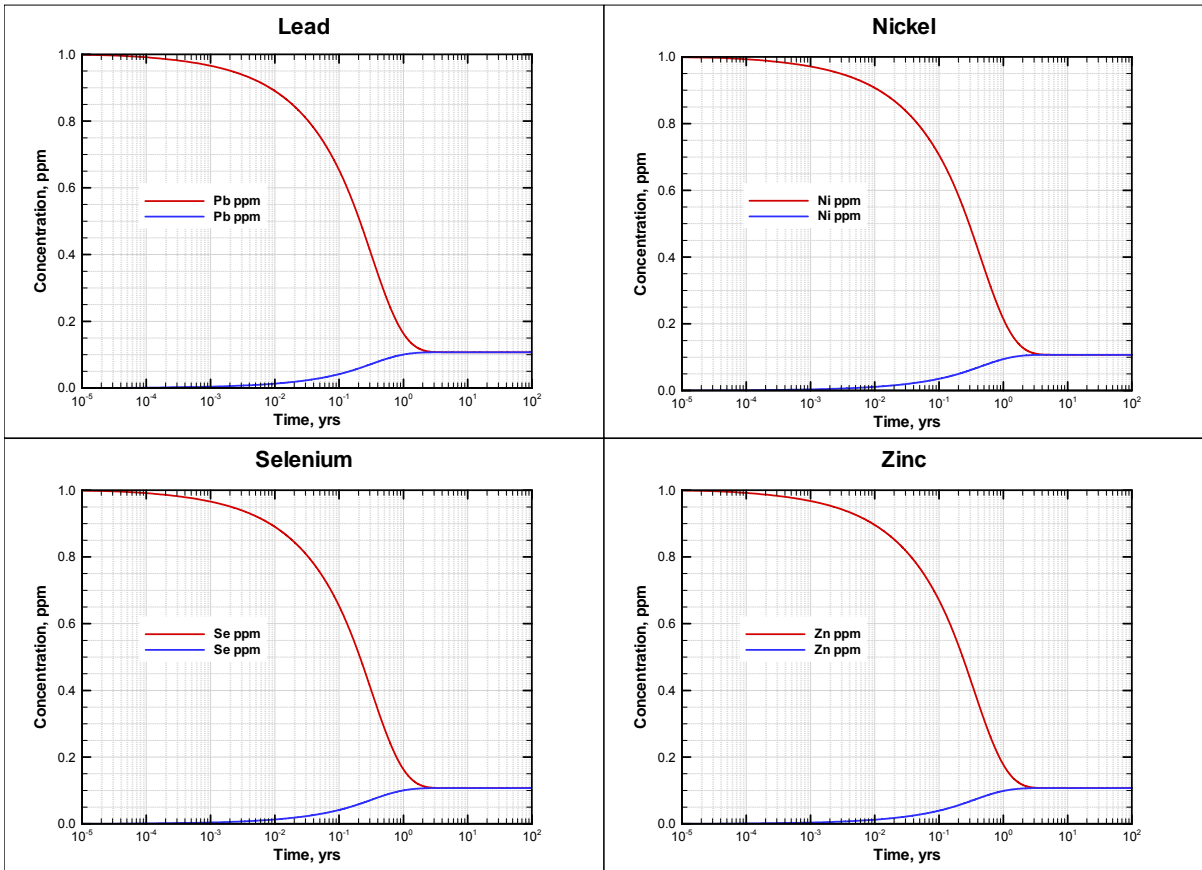


Figure 27. Breakthrough curves for Pb, Ni, Se, and Zn for the no cap case.

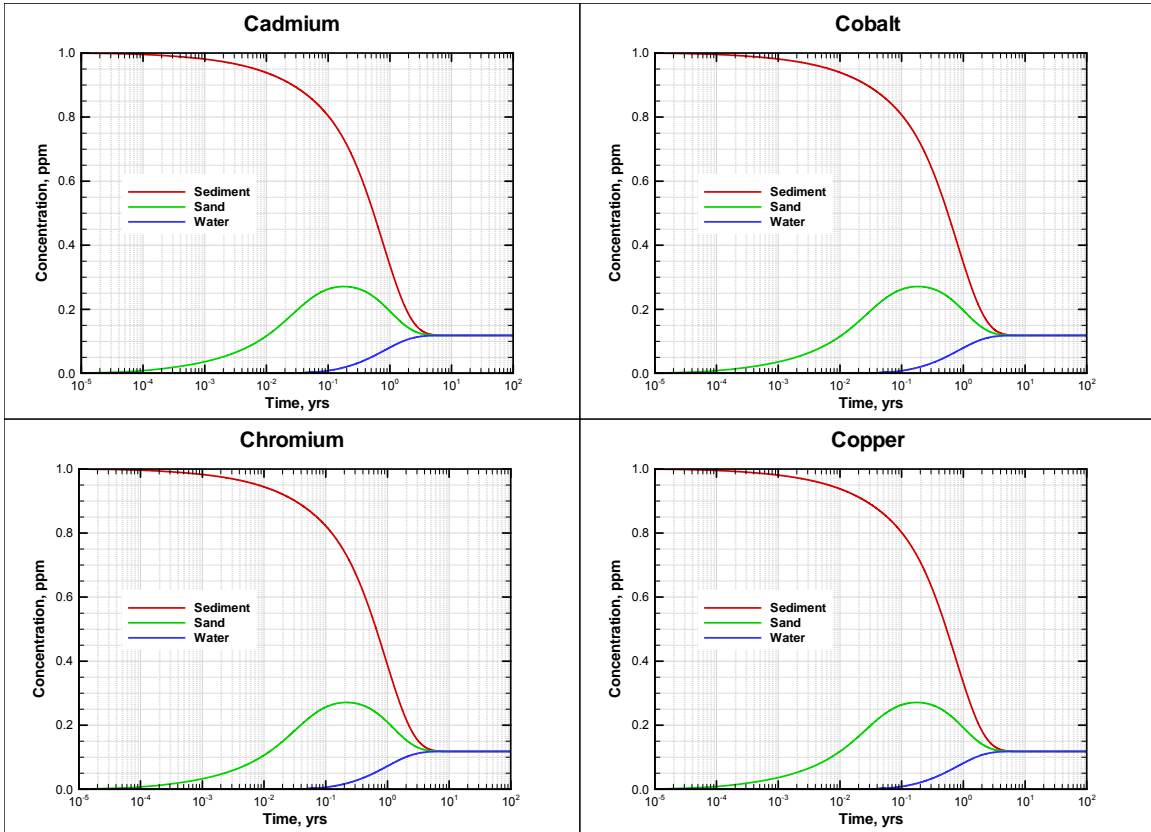


Figure 28. Breakthrough curves for Cd, Co, Cr, and Cu for the sand cap case.

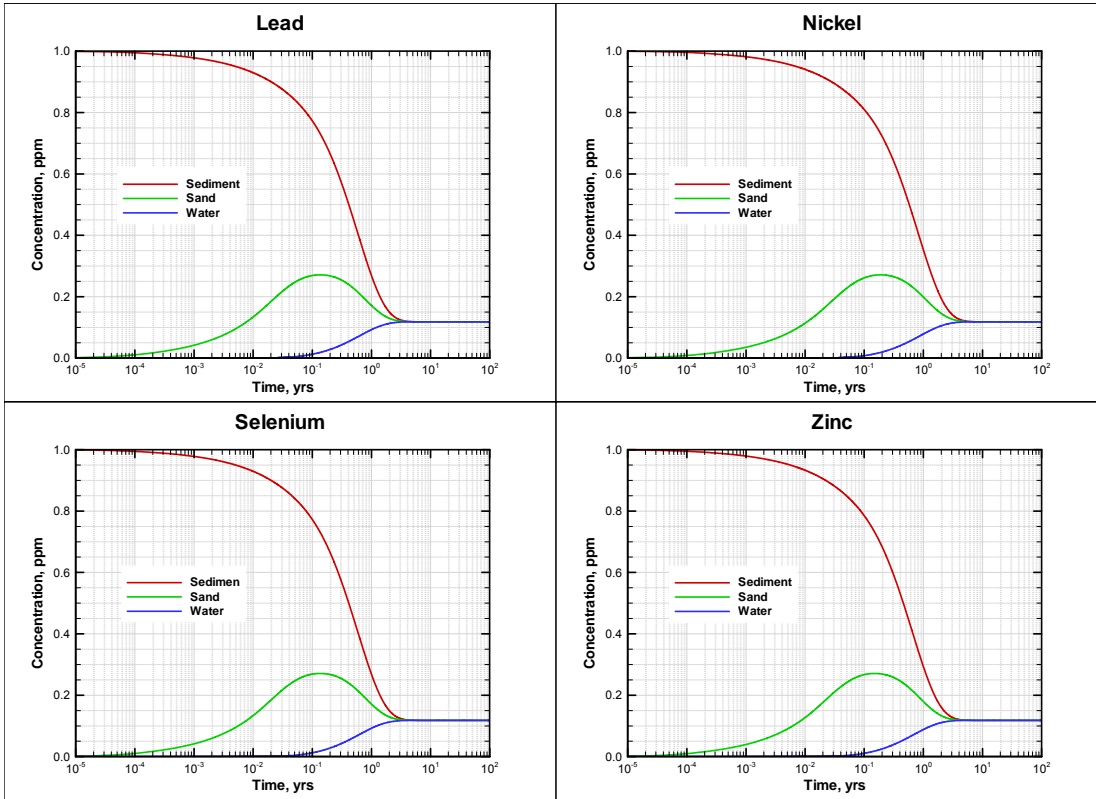


Figure 29. Breakthrough curves for Pb, Ni, Se, and Zn for the sand cap case.

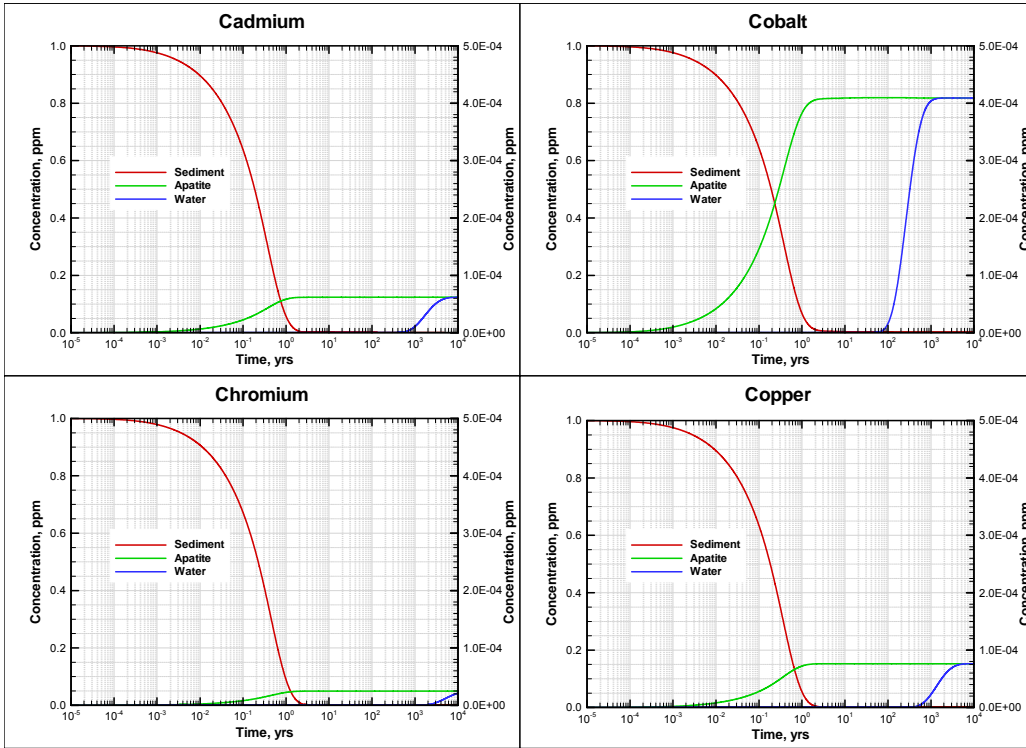


Figure 30. Breakthrough curves for Cd, Co, Cr, and Cu for the apatite (NCA) cap case. The sediment concentration curves are plotted against the left y-axis and all others against the right y-axis.

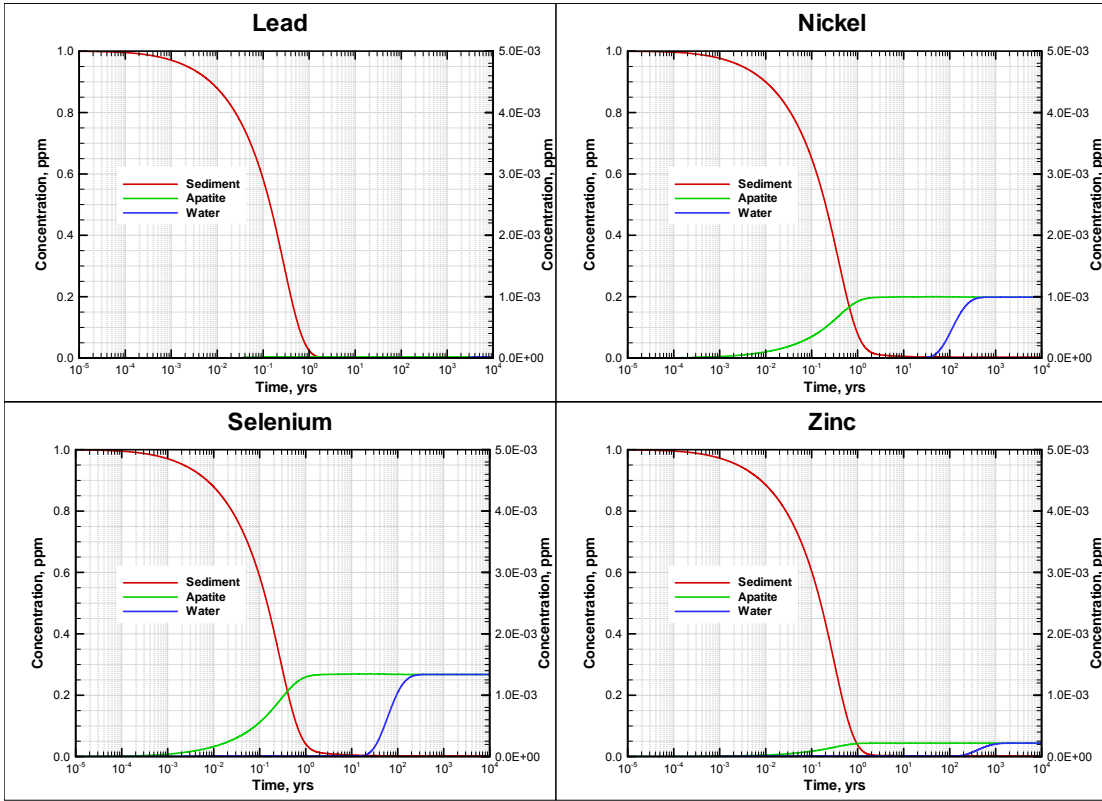


Figure 31. Breakthrough curves for Pb, Ni, Se, and Zn for the apatite (NCA) cap case. The sediment concentration curves are plotted against the left y-axis and all others against the right y-axis.

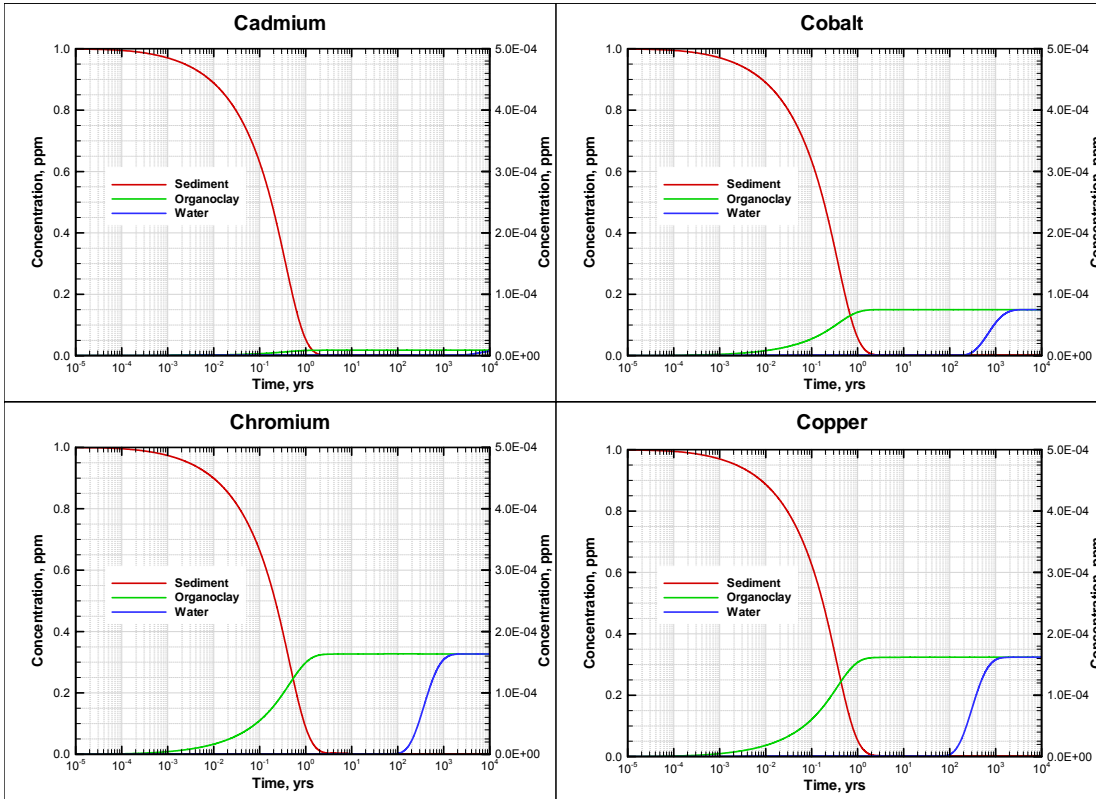


Figure 32. Breakthrough curves for Cd, Co, Cr, and Cu for the organoclay (OCB750) cap case. The sediment concentration curves are plotted against the left y-axis and all others against the right y-axis.

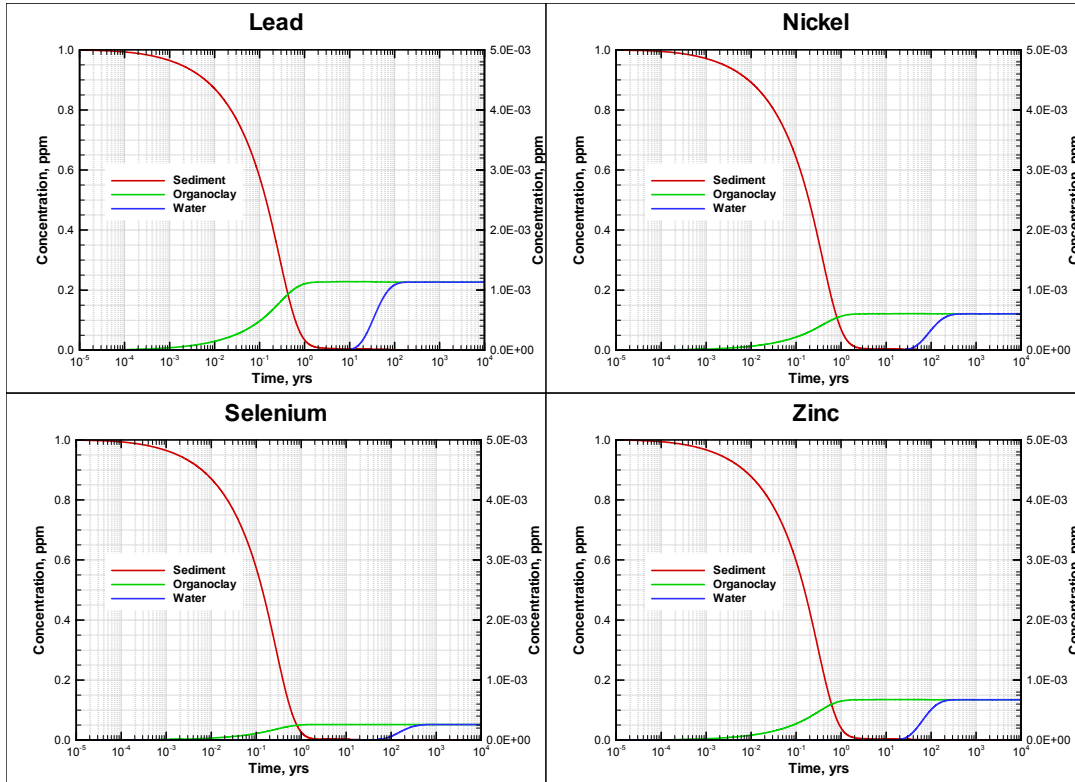


Figure 33. Breakthrough curves for Pb, Ni, Se, and Zn for the organoclay (OCB750) cap case. The sediment concentration curves are plotted against the left y-axis and all others against the right y-axis.

SUBTASK 2.3. EVALUATION OF ADVECTIVE TRANSPORT

Data has been collected to parameterize diffusion advection transient models for two types of cross-linked biopolymer coated sand (one coated with xanthan and chitosan and cross-linked with calcium chloride [XCC] and the other coated with chitosan and guar gum cross-linked with borax [CGB3]) and for organoclay (PM-199) (Tables 19 and 20 and Figures 34 and 35). Preliminary runs of the model suggest that organoclay is successful in retarding organic contaminant breakthrough for long periods (Figure 35). The model has also been used to generate theoretical depth profiles and breakthrough times for naphthalene and phenanthrene in caps composed of biopolymer coated sand (Figure 34). Definitive model predictions will become available after more accurately defined R_f values are generated by the column experiments.

Table 19. Model inputs and parameters for diffusion advection transient models for biopolymer coated sand.

Model Inputs			
Contaminant Pore Water Concentration	C_o (ug/L)	Napthalene	100
		Phenanthrene	40
		Pyrene	60
Organic Carbon Partition Coefficient	$\log K_{oc}$ (log L/kg)	Napthalene	3.0406
		Phenanthrene	4.270865
		Pyrene	4.827
Water Diffusivity	D_w (cm ² /s)		6.00E-06
Porosity	ϵ		0.625
Particle Density	ρ_P (g/cm ³)		2.67
fraction organic carbon	$(foc)_{cap}$	Napthalene	0.001094
		Phenanthrene	0.0023
		Pyrene	0.00158
Cap Depth	h_{cap} (cm)		2.5
Darcy Velocity	U (cm/yr)		1825
Cap Decay Rate	λ_{cap} (s ⁻¹)		3.00E-08
time scale (yr)	τ_{ss}		
Parameters			
Interstitial velocity	v	$v = U/\epsilon$	
Sorption-related retardation factor	R_f	$R_f = 1 + \frac{1-\epsilon}{\epsilon} \rho_P f_{oc} K_{oc}$	
Effective Cap Layer Diffusion Coeff.	D_{diff}	$D_{diff} = D_w * \epsilon^{4/3}$	
Effective Cap Layer Dispersion Coeff.	D_{disp}	$D_{disp} = \alpha * U$	
Dispersivity	α	$\alpha = 0.0169 h_{cap}^{1.53}$	

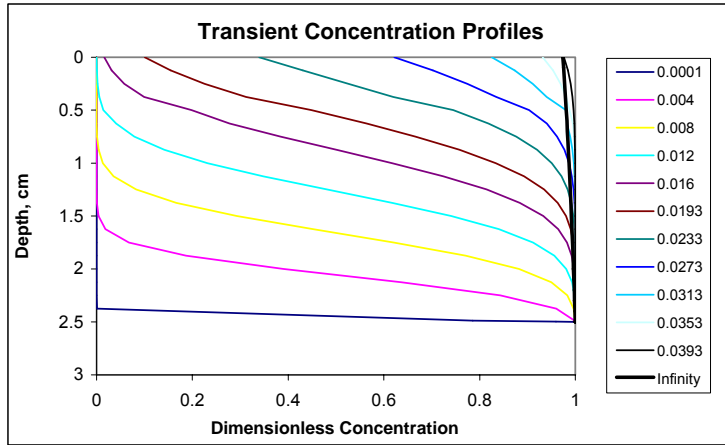
Table 20. Diffusion advection transient model and parameters for modeling the breakthrough time curve for organoclay as an active component of cap.

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

Parameters			
ρ_b	bulk density of cap material (1-n)*pb	1.272	g/cm ³
ϵ	Porosity	0.52	
v	Porewater Velocity (U/ ϵ)	70192.3	cm/yr
U	Darcy Velocity (measured through upwelling work or v* ϵ)	36500.00	cm/yr
C_o	Initial porewater concentration	430.00	$\mu\text{g/L}$
α	dispersivity (1/2 grain size diameter)	0.1000	
D_w	Molecular diffusion coefficient (1*10 ⁻⁵ cm ² /s)	1.00E-05	cm ² /sec
D_{eff}	(=diffusivity of compound* $\epsilon^{4/3}$ +dispersivity*U)	3782.0	cm ² /yr
foc	fraction of organic carbon	365.00%	
Koc	organic carbon partition coeff	18660	mL/g
K_d^{obs}	Mercury (organics=foc*Koc, metals=literature value))	68109	L/kg
z	Chemical Isolation Layer Thickness	2.5	cm
t	time (end of simulation)	100	yr
R_f	Retardation Factor (formula specific to model) $R_f = \epsilon + \rho_b \cdot K_d^{obs}$	86635	

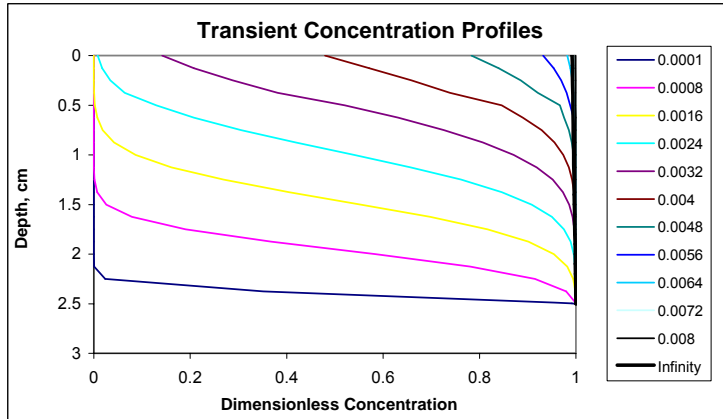
CGB3

Phenanthrene



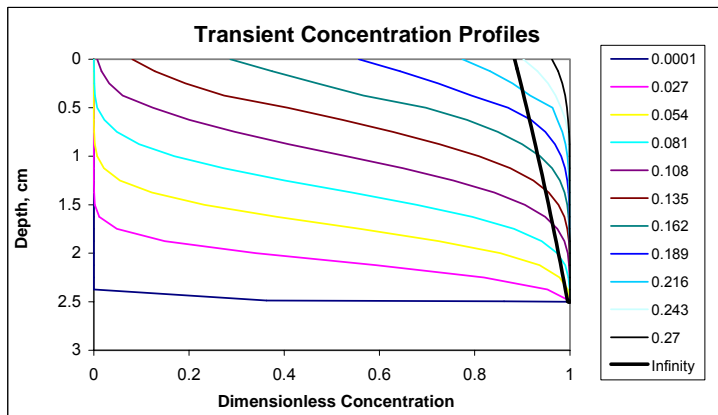
Days	Breakthrough
5.475	1%
7.0445	10%
16.425	99%

Napthalene



Days	Breakthrough
0.876	1%
1.11325	10%
2.555	99%

Pyrene



Days	Breakthrough
39.42	1%
50.005	10%
109.5	99%

Figure 34. Predicted breakthrough curves for biopolymer coated sand (CGB3) for phenanthrene, napthalene, and pyrene.

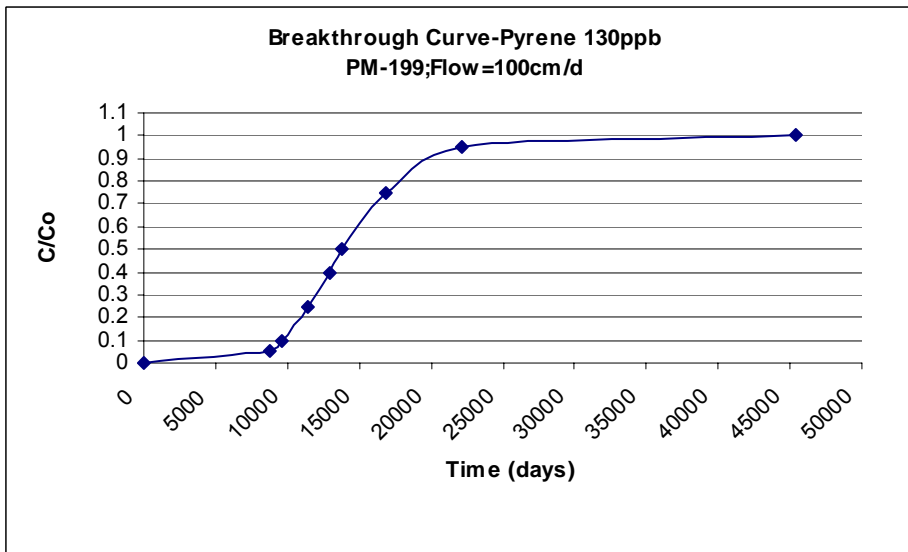
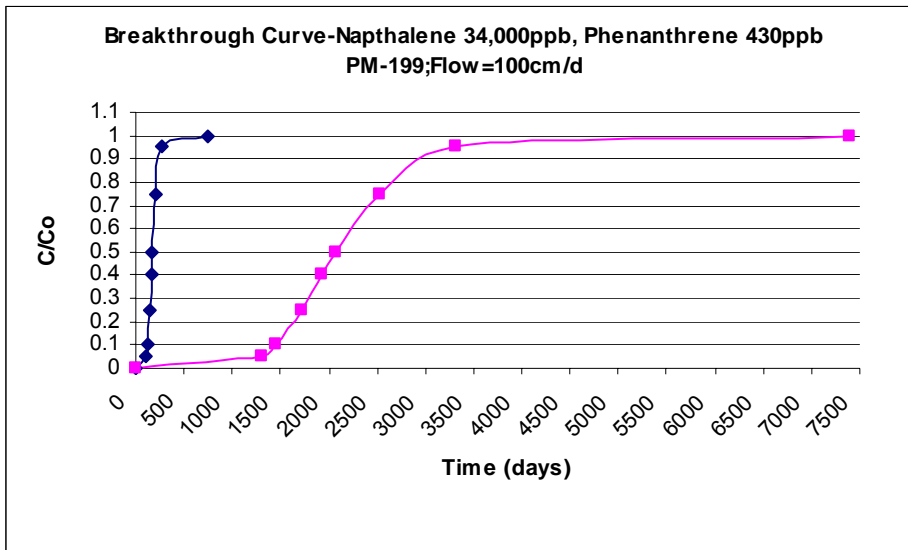


Figure 35. Predicted breakthrough curves for organoclay PM-199 for phenanthrene and naphthalene.

SUBTASK 2.4. EVALUATION OF POTENTIAL AMENDMENT TOXICITY

Analysis of extracts

Metal concentrations in aqueous extracts from the amendments remained well below EPA ambient water quality criteria and other ecological screening values (Table 21). This finding was important because some types of apatite contain heavy metals as a result of natural geological processes. The results of these tests showed that amendment extracts do not contain heavy metals that will not contaminate sediment porewater or enter the water column.

For this project it was important to determine the TCLP concentration since this is one of the regulatory requirement at the Savannah River Site, where we plan to have the next phase (a field deployment) of this project. Comparing the extracts to the regulatory levels indicated that all metal concentrations were well below the regulatory TCLP limits (Figure 36 and Table 22). Organoclays had higher concentrations of Ba, Cr, Ni, and Pb than the other tested amendments; however, these concentrations were still lower than TCLP limits (Table 22). Also, mixtures of amendments such as apatite with organoclay or apatite with coated sand (50% by dry mass) had lower concentrations of metals in the TCLP extracts than individual amendments (100%) (Table 22). These data show that the individual amendments and mixtures of amendments do not pose an environmental hazard due to metal leaching and are acceptable for the upcoming field deployment.

Table 21. Metal concentrations in aqueous extracts from amendments to be used in active caps.

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

Table 22. Evaluation of amendments for Toxicity Characteristic Leaching Procedure (TCLP) (data in ppb).

Amedments		Cap composition % of dry weight of each amedment	As ppb	Ba ppb	Cd ppb	Cr ppb	Ni ppb	Sb ppb	Se ppb	Pb ppb
North Carolina Apatite (NCA)	Avg	100	237.5	482.4	17.1	431.0	579.7	15.8	41.8	17.7
	Stdev		1.1	53.3	0.5	2.7	1.0	2.0	3.7	1.3
Tennessee brown Rock (TRP)	Avg	100	47.2	1067.2	2.5	292.4	61.5	3.0	0.0	22.6
	Stdev		0.3	69.0	0.0	11.7	2.0	0.3	0.0	0.7
Organoclay (PM-199)	Avg	100	26.8	2590.5	71.4	260.8	839.7	23.2	80.1	461.1
	Stdev		0.3	26.6	0.0	21.2	41.7	3.1	3.1	2.3
Organoclay 750, Biomin	Avg	100	29.1	3012.9	0.7	357.6	793.0	0.5	11.6	90.4
	Stdev		0.3	117.3	0.1	33.6	146.5	0.0	0.8	0.8
Coated sand (CS)	Avg	100	8.8	2335.5	6.2	386.6	94.7	2.6	19.0	57.8
	Stdev		0.8	129.4	0.1	6.8	0.1	0.1	3.1	24.3
Playground sand (PS)	Avg	100	13.2	169.8	0.9	290.6	39.6	5.3	10.6	178.9
	Stdev		0.1	18.7	0.0	1.7	0.4	0.6	0.7	32.9
TRP/sand	Avg	50/50	41.3	942.5	2.6	276.4	82.5	2.9	9.5	16.8
	Stdev		0.3	53.8	0.1	6.9	0.4	0.0	1.4	3.8
TRP/sand	Avg	75/25	37.1	856.2	2.5	253.3	76.1	7.3	10.2	33.2
	Stdev		0.2	36.9	0.0	20.9	2.2	1.3	4.6	46.9
PM-199/sand	Avg	50/50	12.9	2810.9	41.8	280.3	693.6	11.5	35.1	381.9
	Stdev		0.3	154.6	1.1	4.1	5.1	0.4	0.8	8.5
PM-199/sand	Avg	75/25	20.0	2447.2	60.7	291.4	898.4	14.7	60.6	394.4
	Stdev		1.1	3.5	0.3	9.2	1.5	0.3	0.7	8.6
TRP/CS	Avg	50/50	35.3	1084.1	3.6	273.8	85.2	6.2	17.1	0.0
	Stdev		0.8	58.2	0.0	14.1	2.0	0.2	0.7	0.0
TRP/CS	Avg	75/25	36.2	1899.2	5.6	371.6	147.5	4.5	22.9	0.0
	Stdev		7.6	190.5	2.2	70.4	32.5	0.2	3.0	0.0
CS/OCB750	Avg	50/50	25.3	2744.1	0.6	297.0	632.2	9.1	33.9	3.9
	Stdev		nd	nd	nd	nd	nd	nd	nd	nd
CS/TRP/OCB750	Avg	25/33.5/33.5	23.5	1119.4	0.0	276.0	481.3	12.7	25.9	0.0
	Stdev		0.4	98.8	0.0	3.5	0.7	2.8	4.6	0.0
TRP/PM_199	Avg	50/50	39.4	2006.2	18.9	369.7	474.4	8.6	40.1	0.0
	Stdev		7.9	123.8	0.9	14.2	16.8	0.1	7.7	0.0
TRP/PM_199	Avg	25/75	34.9	2449.7	39.5	373.1	799.3	12.7	67.0	1.8
	Stdev		0.8	106.7	0.2	6.0	12.2	0.2	2.5	2.5
TRP/PM_199	Avg	75/25	47.2	1516.4	6.7	249.5	228.0	9.1	31.6	0.0
	Stdev		5.0	90.8	0.1	17.0	1.0	0.9	3.3	0.0
TCLP Limit			5000	100000	1000	5000	70000	1000	1000	5000

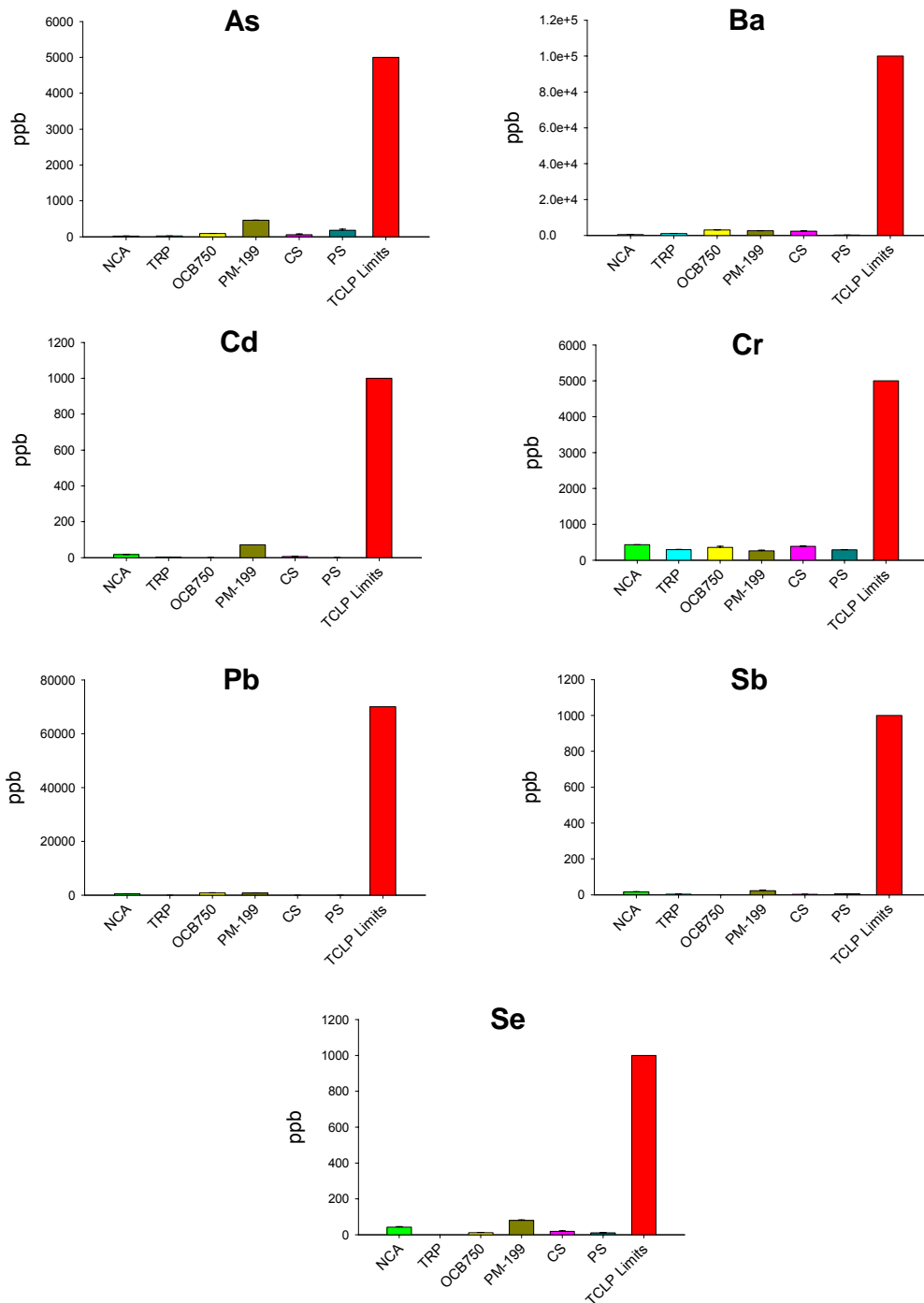


Figure 36. Comparison of the concentrations of As, Ba, Cd, Cr, Pb, Sb, and Se in the TCLP extract solution to TCLP limits (in ppb); NCA = North Carolina Apatite, TRP = rock phosphate from TN, OCB750 = organoclay 750 from Biomin Inc., PM-199 organoclay from CETCO, CS = coated sand with xanthan, chitosan and cross-linked with calcium chloride, PS = playground sand.

Sediment Toxicity Tests for Fresh and Salt Water

Before they are used in aquatic environments, potential sediment amendments must be assessed for possible side-effects that could stem from the presence of impurities or other properties that could directly or indirectly harm aquatic life. The objective of this portion of the project is to determine whether several amendments that hold promise for the construction of active caps have detrimental side-effects; and, if such is the case, to develop strategies for their use that minimize potential problems.

Substrates consisting of 100% apatite or 100% biopolymer coated sand did not or only slightly affected the survival of *Hyalella* in freshwater tests (Table 23). In contrast, *Hyalella* survival was reduced in 100% organoclay and in mixtures of organoclay and reference sediment. The survival of *Hyalella* decreased as the proportion of organoclay increased showing a clear dose-response relationship in the freshwater tests (Figure 36). Unlike *Hyalella*, the survival of *Leptocheirus* in brackish water tests (salinity 20-26 ppt) was not affected by mixtures of organoclay and sediment. Tests employing 100% sand (commercial grades) resulted in mortality of *Hyalella*, possibly as a result of grain size or texture, suggesting that *Hyalella* is highly sensitive to substrate composition.

Relatively high conductivities in some of the freshwater test chambers coupled with previously collected data indicated that organoclay contains high concentrations of chloride. Chloride was removed from organoclay by successive washings to see if this reduced the toxicity of organoclay to *Hyalella*. However, additional bioassays indicated that the toxicity of organoclay to *Hyalella* was not reduced by washing (Figure 36).

Ilyodrilus was less sensitive than *Hyalella* to organoclay. Survival was not affected by up to 50% organoclay in sediment, although growth decreased and behavior was abnormal at this concentration (Figure 37). Bioaccumulation of PAHs (lipid normalized) by *Ilyodrilus* decreased significantly in the presence of 50% organoclay (Figure 38), a not unexpected result considering the ability of organoclay to sequester these contaminants in sediment.

Initial results on NC apatite, organoclay, and biopolymer coated sand support the following conclusions:

- Sediment toxicity tests indicate that NC apatite and biopolymer coated sand are unlikely to adversely affect freshwater benthic organisms, even when used in high concentrations.
- Sediment toxicity tests indicate that organoclay may be harmful to sensitive freshwater benthic organisms, but not necessarily brackish water benthic organisms. Additional testing is required to better understand the effects of organoclay on *Hyalella*. This organism is highly sensitive to substrate composition as indicated by its poor survival on substrates composed of unadulterated sand.
- Amendment extracts do not contain metals that could contaminate sediment porewater or enter the water column.
- Research under SERDP ER 1501 indicates that low doses of amendments (less than 5% addition) can effectively immobilize most contaminants, suggesting that amendments

with detrimental side effects can be strongly diluted by mixing with sediment or nontoxic capping materials such as biopolymer coated sand. Alternatively, amendments such as organoclay may be covered with a surficial layer of clean sediment, non toxic amendments, or other habitat material to improve acceptability to benthic organisms if necessary.

It is important to verify the results of laboratory tests with field studies. Future work will include additional laboratory studies as well as biological surveys of the organisms that colonize pilot-scale sediment caps composed of promising amendments.

Table 23. Sediment toxicity test results

Amendment	Test type	Amendment survival (%)	Control Sediment survival (%)	Significant difference (rank-sum test)	Amendment*			
					pH	DO (mg/l)	Conductivity umhos/cm	NH ₃
Apatite								
North Carolina Apatite (100%)	freshwater	72.5	81.3	marginal	8	8.6	249	2.2
NC Apatite (50%) / sand (50%)	freshwater	76.3	88.8	marginal	7.83	8.22	240	1.9
Organoclay								
Organoclay (100%)	freshwater	0	92.5	yes	6.98	7.8	2420	0.65
Organoclay (50%) / sand (50%)	freshwater	0	87.5	yes	7.07	8.07	4600	0.6
Organoclay (25%) / sediment (75%)	freshwater	32.5	86.3	yes	6.93	8.67	328	0.5
Organoclay (10%) / sediment (90%)	freshwater	67.5	86.3	yes	7.09	9.31	803	0.2
Organoclay (5%) / sediment (95%)	freshwater	73.8	86.3	yes	7.42	9.31	472	0.3
Organoclay (10%) / sediment (90%)	estuarine	87.5	87.5	no	7.77	8.84	37000	0.2
Organoclay (25%) / sediment (75%)	estuarine	78.7	87.5	no	7.77	8.26	37000	0.2
Biopolymer coated sand								
Biopolymer coated sand (100%)	freshwater	78.8	88.8	no	7.04	6.49	895	0.3
Sand								
Sand (commercial paver) (100%)	freshwater	0	86.3	yes	7.80	8.42	57	0.2
Sand (commercial play) (100%)	freshwater	2.5	88.8	yes	7.36	6.74	44	1.1

*Comparable values for the controls were: pH, 7.1- 8.0; DO, 7.7-8.6; Conductivity, 29 – 46; NH₃, <0.1 – 0.2 in freshwater and pH 7.7, DO 8.2, Conductivity 37000, NH₃ 0.2 in brackish water.

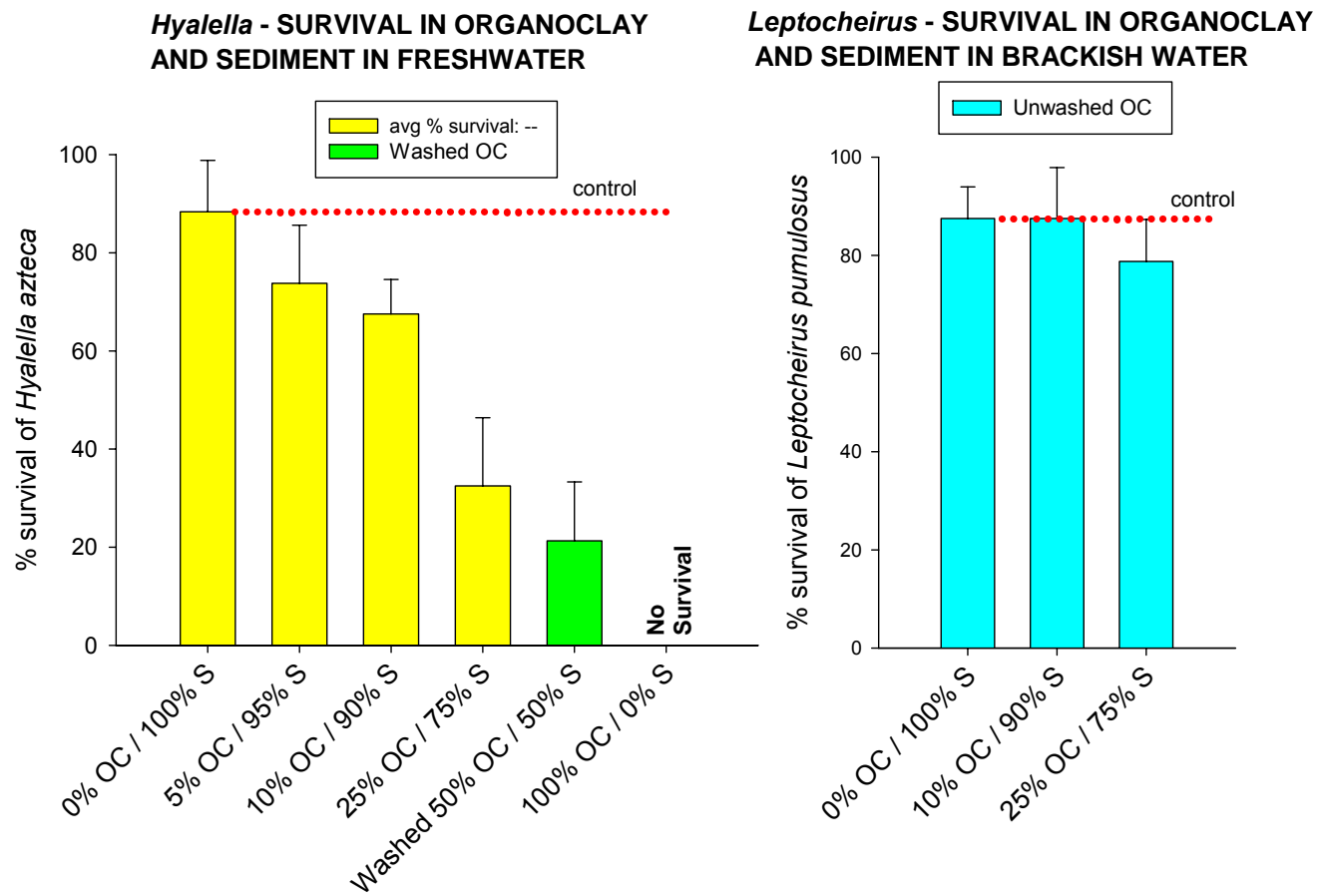


Figure 36. Effects of organoclay on the survival of *Hyalella* and *Leptocheirus*.

Ilyodrilus - SURVIVAL AND GROWTH

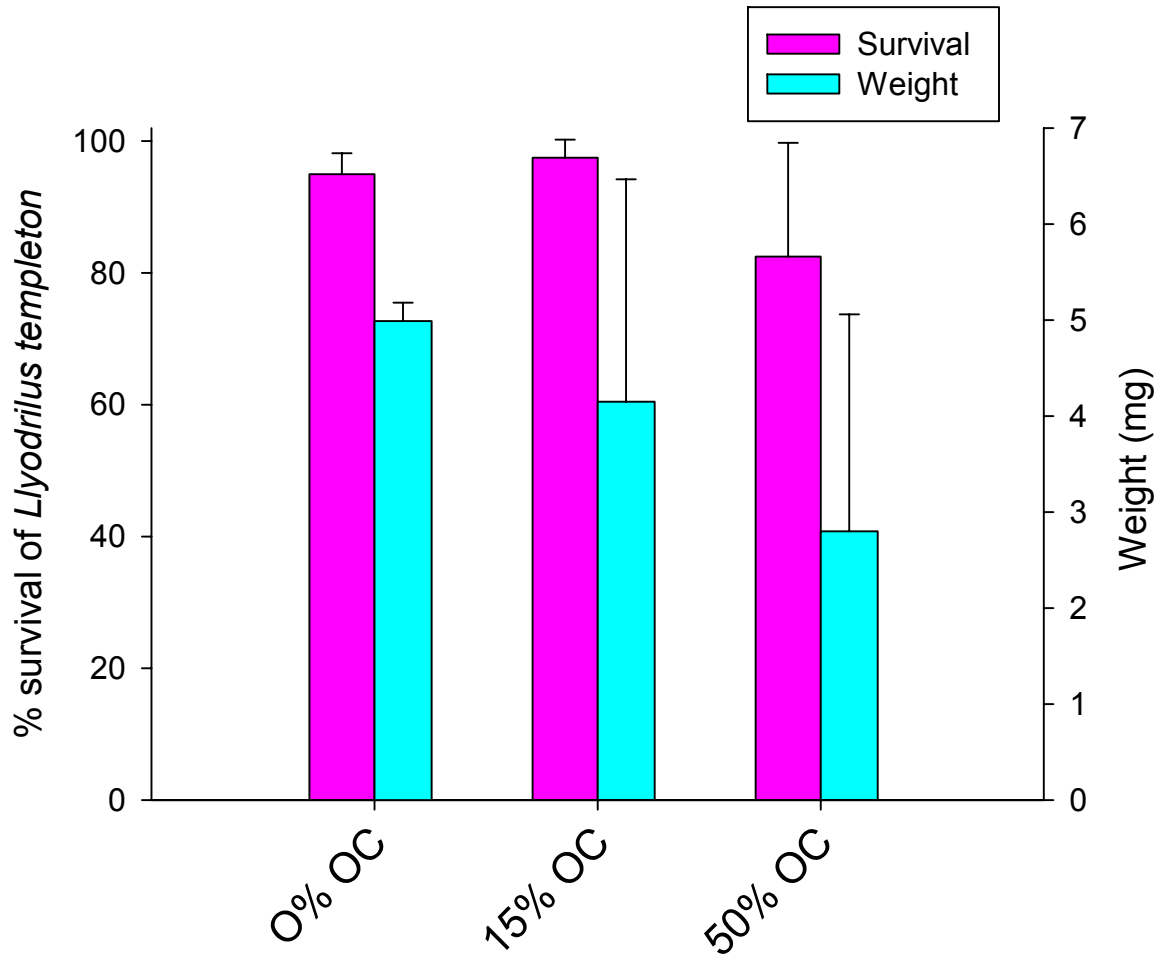


Figure 37. Effects of organoclay on survival and growth of of *Ilyodrilus*.

Ilyodrilus - BIOACCUMULATION OF PAHs

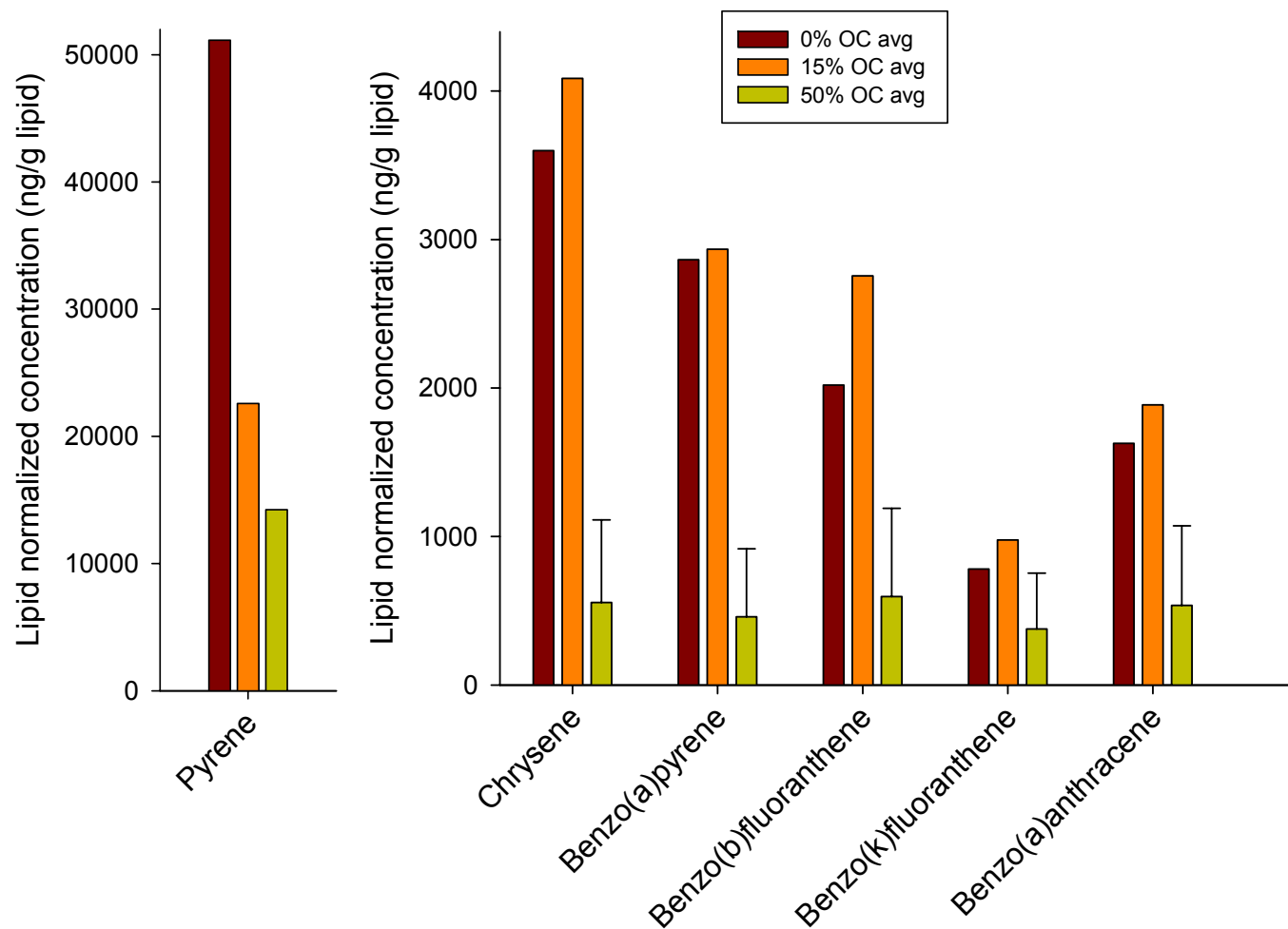


Figure 38. Effect of organoclay on lipid normalized bioaccumulation of PAHs in Ilyodrilus. OC = organoclay.

TASK 3. EVALUATION OF THE RESISTANCE OF CAPS TO PHYSICAL DISTURBANCE

This work is currently being conducted and results will be presented in the next report.

SUMMARY AND CONCLUSIONS

During the past 12 months this project has determined the best active cap materials, active cap composition, and the effects of active cap components on metal bioavailability, retention, and toxicity. Modeling procedures were used and are being further developed to assess diffusive and advective transport through active caps composed of promising amendments. Procedures were developed for making cross-linked biopolymers, and the basic physical properties of several cross-linked biopolymers were assessed and compared. Specific conclusions are:

- Apatite, organoclays, and the biopolymer, chitosan are effective amendments for removing metals from both fresh and salt water. They also exhibit high retention (80% or more) of most metals indicating reduced potential for remobilization to the water column.
- Organoclays are the best amendment for containing organic contaminants. Kinetic studies showed long-term retardation of contaminant migration through organoclay.
- After comparing more than 20 biopolymer products, chitosan/guar gum cross-linked with borax and xanthan/chitosan cross-linked with calcium chloride were identified as having high potential for inclusion in active caps to produce a barrier that resists mechanical disturbance.
- 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.
- Biopolymer coated sand and NC apatite do not harm aquatic organisms, indicating the suitability of these material for aquatic applications. The EPA TCLP procedure showed that the amendments do not leach hazardous metals.

The next year of research under this project will focus on:

- Collection of laboratory data to confirm diffusive and advective transport models for inorganic and organic contaminants through active caps.
- Refinement of active cap composition, structure, and method of construction based on effective contaminant sequestering, cap durability, and effects on aquatic organisms.

- Further evaluation of biopolymer coated sand for erosion control.
- Development of conceptual and mathematical models for contaminant attenuation in active caps composed of multiple amendments.
- Selection of a field site and initiation of the field evaluation of the proposed active caps for contaminant mobility, retention, toxicity, and bioavailability

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Appendix 1

Publication in the past year:

Papers:

1. Knox, A. S., M. H. Paller, D. D. Reible, and I. G. Petrisor. 2007. Sequestering Agents for Metal Immobilization – Application to the Development of Active Caps in Fresh and Salt Water Sediments. In: the Conference Proceedings of the Fourth International Conference on Remediation of Contaminated Sediments, Savannah, Georgia, January 22-25, 2007, Battelle Press: ISBN 978-1-57477-159-6.
2. Knox, A.S., M.H. Paller, D.D. Reible, X. Ma, and I. G. Petrisor. 2007. Sequestering Agents for Active Caps – Immobilization of Metals and Organics. *Journal of Soil and Sediment Contamination* (in press).
3. Knox, A.S., R. Brigmon, D. Kaplan, and M. Paller. 2007. Interactions among phosphate amendments, microbes and uranium mobility in contaminated sediments, *Science of the Total Environment* (in press).

Abstracts:

1. Knox, A.S., M.H. Paller, I.G. Petrisor, and D.D. Reible. 2006. Sequestering Agents for Contaminants in Sediments - Application to the Development of Active Caps, the SERDP/ and ESTCP Partners in Environmental Technology Technical Symposium & Workshop, Washington, D.C., November 28-30, 2006.
2. Knox, A.S., M.H. Paller, I.G. Petrisor, and D.D. Reible. 2006. Sequestering Agents for Inorganic Contaminants in Sediments, the 4th International Conference on Remediation of Contaminated Sediments, January 22-25, 2007, Savannah, GA.
3. Knox, A.S., M.H. Paller, I.G. Petrisor, and D.D. Reible. 2006. Sequestering Agents for Active Caps – Their Effects on Contaminant Mobility, Bioavailability, and Microbial Activity, the 9th International In-situ and On-situ Bioremediation Symposium, May 7-10, 2007, Baltimore, Maryland.
4. Knox, A.S., M.H. Paller, and D.D. Reible. 2007. Effect of Apatite and Organoclay on Metal Bioavailability in Contaminated Sediments, the 3rd International Conference on Environmental Science and Technology, Houston, TX, August 6-9, 2007.
5. Knox, A.S., M.H. Paller, and D.D. Reible. 2007. Sequestering Agents for Metals and Organic Contaminants-Application in Remediation of Contaminated Sediments, the American Society of Agronomy, Soil Science Society of America International Annual Meetings, New Orleans, LA, November 4-8, 2007.
6. Knox, A. S., M. H. Paller, D D. Reible, X. Ma, and I. Petrisor. 2007. In-Situ Remediation of Sites Contaminated with Waste Mixtures, the 5th International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, Niagara Falls, New York, USA, September 24-27, 2007.

7. Knox, A. S., M. H. Paller, D.D. Reible, and I. Petrisor 2007. Effects of Active Cap Components on Contaminant Mobility, Bioavailability, SERDP/ and ESTCP Partners in Environmental Technology Technical Symposium & Workshop, Washington, D.C., December 4-6, 2007.
8. Paller, M.H. and A.S. Knox. 2007. Evaluation of the potential side effect of sequestering agents used for the development of active caps for contaminated sediments, SERDP/ and ESTCP Partners in Environmental Technology Technical Symposium & Workshop, Washington, D.C., December 4-6, 2007.
9. Galjour, J., L. Moretti, S. Ma, X.X. Lu, D.D. Reible, A.S. Knox, and M.H. Paller. 2007. Evaluation of the applicability and effectiveness of organoclay as active capping materials. SERDP/ and ESTCP Partners in Environmental Technology Technical Symposium & Workshop, Washington, D.C., December 4-6, 2007.
10. Forrest, C., S. Ma, D.D. Reible, I. Petrisor, and A.S. Knox. 2007. Evaluation of Biopolymer Coated Sands as Capping Materials. SERDP/ and ESTCP Partners in Environmental Technology Technical Symposium & Workshop, Washington, D.C., December 4-6, 2007.
11. Galjour, J., L. Moretti, S. Ma, X.X. Lu, D.D. Reible, A.S. Knox, and M.H. Paller. 2007. Evaluation of the applicability and effectiveness of organoclay as active capping materials. Pittcon Conference & Expo, New Orleans, LA, March 2-7, 2008.
12. Knox, A.S., D.I. Kaplan, M.H. Paller, and D.D. Reible. Use of apatite for chemical stabilization of contaminants in soils and sediments. Pittcon Conference & Expo, New Orleans, LA, March 2-7, 2008.

Presentations:

1. Anna Sophia Knox and Michael H. Paller, Danny D. Reible, and Ioana G. Petrisor “Sequestering Agents for Contaminants in Sediments - Application to the Development of Active Caps” during the SERDP and ESTCP Partners in Environmental Technology Technical Symposium & Workshop, Washington, D.C., November 28-30, 2006 (poster).
2. Knox, A.S., M.H. Paller, D.D. Reible, and I.G. Petrisor “Sequestering Agents for Inorganic Contaminants in Sediments” during the Fourth International Conference on Remediation of Contaminated Sediments, January 22-25, 2007, Savannah, Georgia (oral).
3. Knox, A.S., M.H. Paller, D.D. Reible “Effect of Apatite and Organoclay on Metal Bioavailability in Contaminated Sediments” presented during the 3rd International Conference on Environmental Science and Technology, Houston, TX, August 6-9, 2007 (oral).
4. Knox, A. S., M. H. Paller, D D. Reible, X. Ma, and I. Petrisor. 2007. In-Situ Remediation of Sites Contaminated with Waste Mixtures, presented during the 5th International Conference on Oxidation and Reduction Technologies for In-Situ Treatment of Soil and Groundwater, Niagara Falls, New York, USA, September 24-27, 2007 (oral).
5. Knox, A.S., M.H. Paller, and D.D. Reible. 2007. Sequestering Agents for Metals and Organic Contaminants-Application in Remediation of Contaminated Sediments, presented during the 100th American Society of Agronomy, Soil

Science Society of America International Annual Meetings, New Orleans, LA,
November 4-8, 2007 (oral).