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Sequestering Agents for Active Caps – Remediation of Metals and Organics

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1 **ABSTRACT**

2 This research evaluated organoclays, zeolites, phosphates, and a biopolymer as

3 sequestering agents for inorganic and organic contaminants. Batch experiments were

4 conducted to identify amendments and mixtures of amendments for metal and organic

5 contaminants removal and retention. Contaminant removal was evaluated by calculating

6 partitioning coefficients. Metal retention was evaluated by desorption studies in which

7 residue from the removal studies was extracted with 1 M MgCl$_2$ solution. The results

8 indicated that phosphate amendments, some organoclays, and the biopolymer, chitosan,

9 were very effective sequestering agents for metals in fresh and salt water. Organoclays

10 were very effective sorbents for phenanthrene, pyrene, and benzo(a)pyrene. Partitioning

11 coefficients for the organoclays were 3000-3500 ml g^{-1} for benzo(a)pyrene, 400-450 ml

12 g^{-1} for pyrene, and 50-70 ml g^{-1} for phenanthrene. Remediation of sites with a mixture of

13 contaminants is more difficult than sites with a single contaminant because metals and

14 organic contaminants have different fate and transport mechanisms in sediment and water.

15 Mixtures of amendments (e.g., organoclay and rock phosphate) have high potential for

16 remediating both organic and inorganic contaminants under a broad range of

17 environmental conditions, and have promise as components in active caps for sediment

18 remediation.

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20 **Key words:** rock phosphate, zeolite, organoclay, biopolymer, active caps, contaminants

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1 **Introduction**

2 Uncontrolled hazardous wastes can result in chemical exposures that directly and

3 indirectly lead to disease. A pervasive source of such wastes is contaminated sediments,

4 which release recalcitrant chemicals into aquatic food chains contributing to thousands of

5 fish consumption advisories nationwide. It is estimated that contaminated sediments

6 affect nearly 10% of the nation's waterways with potential remediation costs in the

7 billions of dollars. The treatment of contaminated sediments is complicated by the

8 common occurrence of mixtures of organic and inorganic contaminants with differing

9 chemical and physical properties and by the heterogeneous nature of the sediments

10 themselves.

11   Traditional efforts to manage contaminated sediments often focus on removal and

12 ex-situ management consisting of dredging or dry excavation followed by off-site

13 treatment/disposal of the removed sediments (Mohan et al., 2000; Nayar et al., 2004).

14 Significant shortcomings of dredging include the potential for release of contaminants

15 during dredging resulting in human exposure and environmental degradation (Mulligan et

16 al., 2001; Nayar et al., 2004), risks to workers during construction and transportation,

17 disruption of resource use and enjoyment, impacts on fish and wildlife, and the risk of

18 releases at off-site disposal locations. Most dredging has been limited to small sites

19 (<50,000 cubic yards) because of expense.

20   In-situ management of contaminated sediments is potentially less expensive and

21 less risky than ex-situ management. Current alternatives for in-situ treatment are largely

22 limited to monitored natural recovery and passive capping, although bioremediation has

23 recently received some attention. Monitored natural recovery is an in situ management

method that relies on natural physical, chemical, and biological processes that act without

human intervention to reduce the mass, toxicity, mobility, or concentration of

contaminants (USEPA-ORD, 1999). Monitored natural recovery 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 MNR include the

risk of changes in the site's natural processes and the risk of contaminant dispersion due

to unforeseen natural or anthropogenic events.

Bioremediation is the use of biological systems to remove or detoxify pollutants

in the environment. The goal of bioremediation is to degrade organic pollutants to

concentrations that are either undetectable or below the limits acceptable to 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 in nature.

Passive (inactive) capping is defined as the installation of a covering or cap of

clean, inert material over contaminated sediment, thus isolating it from the overlying

water column and reducing contaminant migration. This alternative can be an effective

approach for the remediation of contaminated sediment under certain conditions and is

relatively economical. However, the inert materials (sand, gravel, or similar non-reactive

materials) used in passive caps do not provide permanent stabilization since they are

subject to leaching and mechanical disturbance that can release toxic contaminants.

Furthermore, the required thickness of passive caps to achieve extended waste isolation

can disrupt and alter benthic ecology.

1   In contrast to passive capping, active or reactive capping involves the use of

2   capping materials that react with sediment contaminants to reduce their toxicity or

3   bioavailability (Berg et al., 2004; Jacobs and Forstner, 1999; Jacobs and Waite, 2004;

4   Reible et al., 2006). Active capping is a less mature technology that holds great potential

5   for a relatively cost effective, permanent solution that avoids residual risks resulting from

6   contaminant migration through the cap or breaching of the cap because reactive caps

7   directly reduce the bioavailability of sediment contaminants rather than just isolating

8   them physically.

9   There are a number of materials that may be useful for controlling contaminants

10   in active caps. Apatite (calcium phosphate derived from rock phosphate) is a common

11   surface and subsurface amendment that effectively and economically immobilizes Pb and

12   other constituents (e.g., Cd, Ni, Zn, and U) in contaminated soils/sediments (Knox et al.,

13   2003 and 2006; Ma et al., 1997). Calcium phytate removes contaminants in the same

14   manner as apatite minerals. Recent studies suggest that phytate (IP6) can be applied in a

15   soluble form for delivery to remote contaminated sediments, where it undergoes various

16   reactions that eventually result in the precipitation of the contaminant metals (Nash et al.,

17   1998).

18   Organoclays consist of bentonite that is modified with quaternary amines.

19   Organoclays are particularly effective at removing non-polar pollutants such as oil,

20   polychlorinated biphenols, chlorinated solvents, and polycyclic aromatic hydrocarbons

21   (Alther 2002, Xu et al., 1997). Organoclays may be used in combination with phytate or

22   other amendments to stabilize both organic and inorganic contaminants.

1   The zeolites are framework silicates consisting of interlocking tetrahedrons of

2   SiO_4 and AlO_4. Zeolites have large vacant spaces or cages in their structures that allow

3   space for cations and even relatively large molecules and cation groups such as water,

4   ammonia, carbonate ions and nitrate ions. Zeolites have many useful purposes - ion

5   exchange, filtering, odor removal, and chemical sieve. Many researchers have reported

6   effective metal removal by zeolite. For example, Leppert (1990) reported that zeolite,

7   especially clinoptilolite, has strong affinities for Pb, Cr, and Cd.

8   Biopolymers are high-molecular weight compounds with repeated sequences that

9   may become multiple reactive sites with high opportunity for chemical interaction with

10   other compounds. Depending on their functional groups, biopolymers can bind metals or

11   soil particles, and can form interpenetrating cross-linking networks with other polymers

12   (Berkeley, 1979; Yang and Zall, 1984).

13   The objective of this study was to evaluate phosphates, organoclays, zeolites, and

14   biopolymers for possible incorporation into active caps for the remediation of

15   contaminated sediments. This evaluation was based on the ability of these materials

16   (alone and in combinations) to remove and retain a broad range of inorganic (As, Cd, Cr,

17   Co, Cu, Pb, Ni, Se, and Zn) and organic (polycyclic aromatic hydrocarbons)

18   contaminants under fresh and salt water conditions within the laboratory.

19

20   **Materials and Methods**

21

22   ***Removal and Retention of Metals by Sequestering Agents***

1   Removal and retention of As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn in fresh water was

2   evaluated for the following amendments: rock phosphates (from Tennessee [RPT]

3   and North Carolina [NCA]), biological apatite (ground fish bones from PIMS NW,

4   Inc. Richland, WA [BA]), calcium phytate (from Dong Li Phytate Ltd., China [CaP]),

5   organoclays (from Biomin, Inc., Ferndale, MI [OCB-200, OCB-202, and OCB-750],

6   two types of zeolite (from Steelhead Specialty Minerals, Spokane, WA - phyllipsite

7   [ZP] and clinoptilolite [ZC]), and a biopolymer (from AIDP, Inc., City of Industry,

8   CA, chitosan [BPC]). Sand, collected at the Savannah River Site (Aiken, SC),

9   containing 0.6% of organic matter was used as a control. Acronyms for all

10   amendments and combinations of amendments are listed in Table 1.

11   A sorption study to evaluate the removal of metals by the amendments was

12   conducted for one week in 50 mL centrifuge tubes containing amendments (or

13   amendment mixtures) and a metal spike solution. The spike solution, which was from

14   Inorganic Ventures (Lakewood, NJ), contained 1 mg L^{-1} of As, Cd, Cr, Co, Cu, Pb,

15   Ni, Se, and Zn. The amendments or mixtures of amendments were tested in three

16   replicates: two for metal analysis by inductively coupled plasma-mass spectrometry

17   (ICP-MS) and the third for pH measurements. Suspensions composed of 0.2 g of

18   solid (the sequestering agent) and 15 mL of spike solution were shaken for one week,

19   phase separated by centrifugation, and analyzed.

20   The retention study was run on the residue from the sorption study. The

21   residue was washed twice with deionized water and extracted with 15 mL of 1 M

22   MgCl$_2$ to determine the readily available pool of sorbed metals. The samples were

1 centrifuged and the supernatant decanted after one hour. The extract was analyzed for

2 metals by ICP-MS.

3   The removal and retention experiments in salt water were conducted as

4 described for fresh water, except the spike solution was made from artificial ocean

5 water (salinity 3.5%), and there were fewer treatments. The following amendments

6 were evaluated: sand (as a control), RPT, NCA, CaP, OCB-750, ZC, BPC, and a

7 mixture of NCA and BPC.

8

9 ***Sorption of Organic Contaminants***

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11 Organoclays (PM-199 from CETCO, IL and OCB-200, OCB-202, and OCB-750),

12 zeolites (ZC-powder, ZC-4 mesh, and ZP), rock phosphate (NCA and RPT), BA, and

13 CaP were evaluated for their ability to sorb three polycyclic aromatic hydrocarbons

14 (PAHs). The PAHs were purchased from a commercial supplier (Sigma Aldrich, MO)

15 and included 5000 mg L^{-1} phenanthrene in methanol, 1000 mg L^{-1} pyrene in methanol,

16 and 200 mg L^{-1} benzo(a)pyrene in methylene chloride. The sorption capacity of these

17 amendments was compared with the sorption capacity of untreated sediments from the

18 Anacostia River, Washington, DC.

19   The PAHs were diluted in electrolyte solutions (0.01M NaCl, 0.01M CaCL$_2$.2H$_2$O)

20 to prepare 20 μg L^{-1} phenanthrene, 100 μg L$^-$ pyrene, and 3 μg L$^-$ benzo(a)pyrene. Exact

21 concentrations were determined with a high performance liquid chromatograph (HPLC;

22 Waters, MA) coupled with a Waters 2475 Multi λ Fluorescence Detector and Waters 996

1 Photodiode Array Detector. Sodium azide (0.05 M) was added to the electrolyte solution

2 to inhibit bacterial degradation of the PAHs.

3   Water sorbent partitioning coefficient measurements were carried out in 50 mL

4 centrifuge tubes with a piece of aluminum foil attached to the inside of each tube cap to

5 minimize sorption loss. Twenty mg of each sorbent and 50 mL of PAH solution were

6 added to each of the tubes, which were then tumbled for 48 hours and centrifuged for 30

7 minutes (3000 rpm) after tumbling. One mL of supernatant from each tube was analyzed

8 for PAHs by HPLC. In addition, 15 mL of supernatant from each tube was transferred to

9 a vial containing a one cm polydimethylsiloxane (PDMS)-coated fiber for solid phase

10 microextraction (SPME). The vials were shaken for two hours, after which the fibers

11 were removed and put into 2mL HPLC vials with 100 μL of acetonitrile to desorb

12 contaminants on the fiber. The acetonitrile solution was analyzed by HPLC, and the

13 concentrations were compared with external standards prepared by serial dilutions of pre-

14 made stock solution with known concentrations. The standards were treated exactly as

15 the samples. There were three to five replicates for each sorbent.

16   For highly sorptive materials such as OCB-750 and PM-199, benzo(a)pyrene in

17 the supernatant was lower than the detection limits for both direct injection and SPME. In

18 this case, the experiment was repeated as described above except that solvent extraction

19 was utilized in the final stage to analyze contaminants in the supernatant. After

20 centrifugation, 40 mL of liquid was transferred to 100 mL tubes and 10 mL of hexane

21 was used to extract the contaminants. The mixture was shaken for approximately 12

22 hours. The extraction rate of hexane was determined to be over 95%. Following

23 extraction, as much hexane as possible was taken out with a pipette and blown down to

1   about 0.2 mL. Acetonitrile was then added to bring the volume back to 2 mL and re-

2   blown down to approximately 0.1 mL. The concentrations were then determined by

3   HPLC. Because of dissolved organic carbon (DOC), the concentrations of PAHs were

4   higher than measured by direct injection or SPME. To account for DOCs, the dissolved

5   water concentrations were determined with the following equation:

6    $$C_W = \frac{C_{WM}}{1 + C_{DOC} K_{DOC}} \qquad (1)$$

7   where C_{wm} is the water concentration measured via extraction (mg L^{-1}), C_w is the free or

8   truly dissolved water concentration (mg L^{-1}), C_{DOC} is the DOC content in water, and

9   K_{DOC} is the DOC water partition coefficient determined from the following correlation:

10   $$\log K_{DOC} = \log K_{OW} - 0.58 \qquad (2)$$

11   This value was then used to correct the partitioning coefficient of benzo(a)pyrene for the

12   materials obtained from solvent extraction. The concentrations of phenanthrene and

13   pyrene obtained by solvent extraction were compared with those obtained by direct

14   injection and SPME, which were similar.

15

16   ***Data Analysis***

17

18   Data from the studies on metal contaminants were used to calculate percent removal

19   (sorption) and partition coefficient (K_d) values, defined as the ratio of the

20   concentration of solute sorbed to the solid divided by its concentration in solution.

21   Presenting the sorption data as percent removal instead of concentrations (mg L^{-1})

22   facilitated comparisons among amendments. The K_d (mL g^{-1}) was calculated using

23   equation 3 (American Society for Testing and Materials, 1993):

1 $$K_d = V_{spike}\,(C_{spike} - C_{final})/(C_{final} \times M_{Mineral})\qquad\qquad(3)$$

2 where C_{spike} is the metal concentration in the spike solution before the addition of the

3 amendment (mg L^{-1}), C_{final} is the metal concentration in the solution after contact with

4 the amendment (mg L^{-1}), $M_{mineral}$ is the amendment mass (g), and V_{spike} is the volume

5 of the spike solution (mL).

6   The desorption and soption data were used to calculate percentage retention

7 on each amendment using equation 4:

8 % retention = $[(C_{adsorbed} - C_{desorbed})/C_{spike}] \times 100$ (4)

9 where $C_{adsorbed}$ is the concentration of metal adsorbed at the end of the adsorption

10 experiment, $C_{desorbed}$ is the concentration of metal desorbed at the end of the

11 desorption experiment, and C_{spike} is the concentration of metal in the spike solution.

12   Principal components analysis (PCA), a statistical method for revealing the

13 basic structure of complex data sets, was used to summarize the metal removal data

14 from the fresh water experiments, which included a large number of amendments and

15 amendment mixtures. The PCA was based on the Pearson correlations among the

16 percent removal values for the metals by each amendment or mixture of amendments.

17 The percent removal data were arcsine transformed prior to analysis to normalize

18 variances. Scores from the first three principal components were plotted to show

19 relationships among amendments as indicated by their relative positions in three-

20 dimensional space.

21   Data from the studies on organic contaminants were used to calculate partitioning

22 coefficients. These coefficients were used to model the effectiveness of a 2.54 cm thick

23 layer of each amendment as a sediment cap by estimating the time required for a

1   contaminant to penetrate the cap. The time was estimated by the methods recommended

2   by the standard EPA guidance on capping (Palermo et al., 1996) assuming that the

3   underlying concentration remained constant and that no degradation or transformation

4   processes were operative.

5

6   **Results and Discussion**

7

8   *Effect of Sequestering Agents on pH*

9

10   Changes in pH resulting from the application of amendments can be important because of

11   the potential effects of pH on aquatic organisms. Most freshwater lakes, streams, and

12   ponds have a natural pH in the range of 6 to 8, and extreme pH can harm invertebrates

13   and fish. When the pH of freshwater becomes highly alkaline (e.g., 9.6), fish may suffer

14   death, damage to outer surfaces like gills, eyes, and skin, and an inability to dispose of

15   metabolic wastes. High pH may also increase the toxicity of other substances (e.g., the

16   toxicity of ammonia is ten times more severe at pH 8 than at pH 7, USEPA 1985), and

17   the mobility of potentially toxic metals including As, Mo, Se, and Cr increases in soils or

18   sediments with elevated pH (Adriano, 2001). Harmful effects can also occur when the pH

19   falls below 6 and especially below 5. As the pH nears 5, non-desirable species of

20   plankton may begin to predominate in some aquatic systems and populations of desirable

21   fish may diminish (Fryer 1980, Findlay 2003). Calcium levels in female fish may decline

22   to the point that egg production fails or eggs and/or larvae develop abnormally. Acidity

23   can also result in the release of aluminum ions (Al^{3+}) attached to minerals in sediment,

1   resulting in damage to gill tissues, excessive mucous formation, and ionic imbalances

2   (Jagoe and Haines, 1997). Identification of amendments or combinations of amendments

3   that avoid large and/or rapid changes in pH may be an important factor in the

4   development of an active capping system that results in minimal environmental impact.

5   Figure 1 shows the effect of the sequestering agents on the spike solution pH in

6   fresh water. The pH measurements were taken after one hour (initial pH) and after one

7   week of contact of the spike solution with the amendments (final pH). The addition of

8   some amendments to the fresh water spike solution resulted in large changes in pH.

9   Organoclays increased the pH of the spike solution the most; for example, OCB-750

10   increased the pH of the spike solution (control) from 3.09 to 11.9 (Figure 1-A). In some

11   cases, mixtures of amendments were associated with smaller pH shifts than were

12   individual amendments (Figure 1 - B). Amendments such as RPT, NCA, CaP, ZC, and

13   ZP did not result in large pH changes in the salt water spike solution, which had an initial

14   pH of 7.2 (Figure 1-C). The greatest change was observed for OCB-750, which raised the

15   pH from 7.2 to 7.6 (Figure 1-C). The pH changes for fresh water solutions were greater

16   than for salt water solutions. It is important to note that the fresh water spike solutions

17   were made from deionized water with little buffering capacity. Natural waters with

18   greater alkalinity would likely be subject to smaller pH shifts.

19

20   ***Removal of Metals***

21

22   The K_d values were determined from sorption experiments for nine elements that are

23   typical in contaminated sediments (As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn). It is

1   important to recognize that the results from laboratory batch sorption tests generally

2   allow no distinction to be made on how the sorbate (i.e., contaminant) is associated with

3   the sorbent (i.e., sediment or sequestering agent). The sorbate may be adsorbed by ion

4   exchange, chemisorption, bound to complexes that are themselves sorbed on the solid,

5   and /or precipitated.

6   The K_d values in fresh water were highly variable, differing by an order of

7   magnitude (Table 1), but were useful in identifying effective amendments. Phosphates

8   (especially NCA and CaP), organoclay (OCB-750), and biopolymer (BPC) had relatively

9   high K_d values for Cd, Cr, Cu, Pb, Ni, and Zn (Table 1). However, only OCB-750 and the

10   mixture of NCA and OCB-750 produced relatively high K_d values for As and Se.

11   Although numerous studies have focused on the sorption of nonionic organic compounds

12   to organoclays, this study and Tillman et al. (2005) show that organoclays also remove

13   heavy metals.

14   The removal (sorption) of Cd, Co, Cr, Cu, Pb, and Zn from spike solutions in

15   fresh water was very high for most tested amendments (Figure 2), but removal of As and

16   Se was only effective for OCB-750, and mixtures of NCA with OCB-750 or BPC. These

17   results were graphically summarized by PCA, which ordinated the amendments and

18   mixtures of amendments based on their metal removal capacity. The first principal

19   component was inversely correlated with the removal of Cu, Zn, Cd, Cr, Co, and Pb; the

20   second principal component was positively correlated with the removal of Se, and As;

21   and the third principal component was inversely correlated with the removal of Ni (Table

22   2). The ordination showed that OCB-750 and mixtures of OCB-750 with NCA exhibited

23   the best overall ability to remove the entire suite of metals under this study (Figure 3).

1   Other amendments such as CaP effectively removed most metals except As and Se, while

2   others such as RPT exhibited relatively poor removal for Ni.

3   Removal in salt water (3.5% salinity, room temperature, alkaline pH) was very

4   high for most metals, especially Cr, Cu, Pb, and Zn (Figure 2). However, the removal of

5   Cd, Co, Ni, and some other elements by phosphates in salt water was lower than in fresh

6   water (Figure 2). Zeolite (ZC) effectively removed only Cr, Cu, Pb, and Zn in both fresh

7   and salt water (Figure 2). A study by Leppert (1990) similarly reported that zeolite,

8   especially clinoptilolite, demonstrates strong affinity for Pb, Cr and Cd. Other researchers

9   have reported that sorption by clinoptilolite is not affected by increased Ca^{2+}, Na^+, and K^+

10   in solution (Ponizovsky and Tsadilas, 2003); however, in this study sorption by

11   clinoptilolite was substantially lower in salt water than in fresh water (Figure 2).

12   Organoclay (OCB-750) removed the tested metals about equally from metal

13   spiked fresh and salt water (Figure 2), with lower performance only for Se in fresh water.

14   Chitosan was very promising as a stand-alone amendment and when mixed with

15   phosphate amendments (Figure 2). Chitosan can be produced chemically from chitin and

16   is found naturally in some fungal cell walls. It is inexpensive and abundant and is a

17   strong adsorbent for heavy metals (Berkeley, 1979; Yang and Zall, 1984). Our results

18   showed that chitosan was very effective in fresh and salt water at sorbing Cd, Co, Cu, Ni,

19   Pb, and Zn (Figure 2). Mixing it with North Carolina apatite increased its effectiveness

20   for As and Se (Figure 2). Other researchers have reported high adsorption capacities of

21   chitosan for Cd, Cr, Hg, and Pb (Yang and Zall, 1984).

22   A sand treatment served as a control treatment in all experiments. Sorption of all

23   metals on the sand was near zero in fresh and salt water (Figure 2). The slight sorption

1   observed for some metals may have been due to the presence of small amounts of organic

2   matter in the sand.

3

4   ***Retention of Removed Metals on the Sequestering Agents***

5

6   The retention studies determined how strongly metals were bound to the amendments in

7   fresh and salt water. Scientific understanding of binding strength and the irreversibility of

8   reactions is essential to obtain regulator approval of in-situ immobilization as an

9   acceptable remediation strategy because these variables have a direct effect on

10   bioavailability and mobility. Although amendments remove contaminants from water

11   very efficiently, subsequent contaminant remobilization from the amendments can release

12   contaminants back to the water or treated sediments. Choosing the most appropriate

13   treatment requires an understanding of how amendments bind contaminants and the

14   conditions under which they could release the removed metals back into the water

15   column.

16   Tables 3 and 4 show retention of metals in fresh and salt water. Almost all tested

17   amendments showed high retention (80% or more) for Cr, Cu, Pb, and Zn (Tables 3 and

18   4). The best Cd retention was by organoclay (OCB-750), biopolymer (BPC), and the

19   mixture of NCA and BPC (Table 3). The highest retention (80% or more) of As was by

20   organoclay (OCB-750) (Table 3). In fresh water only NCA and the mixture of NCA and

21   BPC had Se retention higher than 50% (Table 3). Retention in fresh and salt water was

22   similar for Cu, Cr, Ni, Pb, and Zn, mostly 80% or higher (Tables 3 and 4).

23

1 *Sorption of Organic Contaminants by Sequestering Agents*

2

3 Organoclays are produced by the exchange of organic quaternary ammonium cations

4 (QACs) for inorganic cations (e.g., Ca^{+2}, Na^+) that naturally occur on the internal and

5 external mineral surface of the clay. Compared to natural clays, organoclays are

6 organophilic and have increased sorption capacity for relatively nonpolar organic solutes

7 (Smith et al., 1990). In our study two organoclays, OCB-750 and PM-199, exhibited

8 relatively high sorption capacities for phenanthrene, pyrene, and benzo(a)pyrene.

9 Partitioning coefficients for these two organoclays ranged from about 3000-3500 ml g^{-1}

10 for benzo(a)pyrene, 400-450 ml g^{-1} for pyrene, and 50-70 ml g^{-1} for phenanthrene (Figure

11 4). The phosphate (BA) followed the organoclays with K_{ds} of about 500 ml g^{-1} for

12 benzo(a)pyrene, 20 ml g^{-1} for pyrene, and 4 ml g^{-1} for phenanthrene (Figure 4). The

13 sortpion capacities of the other amendments were substantially lower; usually under 100

14 ml g^{-1} for benzo(a)pyrene, five ml g^{-1} for pyrene, and one ml g^{-1} for phenanthrene. These

15 results suggest the potential utility of some organoclays and, to a lesser extent, BA for

16 controlling organic contaminants.

17   Organoclay removes organic and inorganic contaminants by itself or when mixed

18 with other amendments. For example, a mixture of OCB-750 and NCA lowered As, Cd,

19 Co, and Mn concentrations by more than 80 to 90% in the water extractable fraction of a

20 contaminated river sediment (Knox et al., 2007). Mixtures of organoclay and rock

21 phosphates (e.g., NCA) have high potential for remediating both organic and inorganic

22 contaminants in sediments. Sediment amendments that include sorbents of various types

23 constitute a potentially important strategy for environmental remediation, restoration, and

1   stabilization. Selection and/or design of composite amendments is the key to realization

2   of this potential. Composites of rock phosphates and organoclays provide an attractive

3   alternative to relatively inert and costly sorbents such as activated carbons and adsorptive

4   synthetic resin (Jonker et al., 2004; Rust et al., 2004; Zimmerman et al., 2004).

5

6   *Cap Effectiveness for Organics*

7

8   The time required for organic contaminants to penetrate a simulated active cap was based

9   on a 2.5 cm layer of active capping material (Table 5). Such a placement might be

10   feasible for high value materials that are cost-prohibitive if placed in bulk. An alternative

11   placement might be 15 cm of active sorbent for materials placed in bulk. The penetration

12   times for a 2.5 cm layer (Table 5) can be multiplied by six to determine the time to

13   penetrate a 15 cm active capping layer. The active layer would likely be overlain by sand

14   or a similar inert material. For purposes of the current estimates, the sand cover is

15   conservatively assumed to provide no additional contribution to the time required for

16   contaminants to migrate through the cap. Two scenarios were considered: i) a cap layer in

17   which migration was dominated by upwelling at an average rate of 1 cm day^{-1}, and ii) a

18   cap layer in which migration was dominated by molecular diffusion.

19   An examination of the predicted times before the measurement of a flux through

20   the cap shows that the highly sorptive cap materials can lead to very long migration times

21   perhaps longer than the expected lifetime of the contaminant in the sediment environment

22   (Table 5). Significant flux will not occur if the predicted migration time is longer than the

23   expected lifetime of the contaminant.

1

2 **Conclusions**

3

4 Laboratory batch studies showed that phosphates amendments, some organoclays, and

5 the biopolymer, chitosan, are very effective in removing metals from both fresh and salt

6 water. They also showed that all amendments exhibited high retention (80% or more) of

7 Cr, Cu, Pb, and Zn in fresh and salt water suggesting reduced potential for remobilization

8 of these metals. In addition to metals, we evaluated the sorption capacity of the

9 amendments for three polycyclic aromatic hydrocarbons (PAHs). The most sorptive

10 materials for these organic compounds were the organoclays, PM-199, and OBC-750.

11 Phosphates (e.g., BA) sorbed less than the organoclays but showed greater sorption than

12 the original sediments. Additionally, an examination of the predicted times before the

13 measurement of a flux through simulated sediment caps shows that highly sorptive cap

14 materials can lead to very long migration times, perhaps longer than the expected lifetime

15 of the contaminant in the sediment environment.

16   Mixtures of amendments, for example organoclays and rock phosphates, have

17 high potential for remediating both organic and inorganic contaminants in sediments.

18 Combinations of metals and organic pollutants ranked fifth (based on frequency of

19 occurrence) among the 51 pairs of compounds found in soil and sediments at

20 contaminated Department of Energy sites (Riley et al., 1992). Remediation of sites

21 contaminated with waste mixtures is generally more difficult than sites contaminated

22 with a single contaminant, since metals and organic contaminants have different fate and

23 transport mechanisms in sediment and water. Organoclay, by itself or with other

1   amendments (e.g., rock phosphates) can effectively remediate sites with mixed-waste,

2   and has high promise for use in active caps.

3

11

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Table 1. Average K_d values (standard deviations) for metal removal by amendments proposed for sediment active capping.

Amendments[a]	Cr	Co	Ni	Cu	Zn	As	Se	Cd	Pb
Phosphates									
RPT	172 (10)	827 (166)	205 (25)	6187 (205)	1784 (213)	45 (2)	0 (1)	2787 (470)	13504 (5438)
NCA	19278 (2662)	1161 (12)	476 (3)	6237 (202)	2157 (289)	43 (0)	352 (17)	7696 (667)	24942 (11146)
BA	4333 (551)	3404 (2574)	469 (478)	1717 (494)	2152 (348)	8 (8)	484 (54)	1362 (953)	1980 (1189)
CaP	23722 (2218)	17302 (1074)	7886 (169)	9106 (1559)	4215 (93)	0 (0)	0 (0)	33077 (2163)	35049 (28003)
Organoclays									
OCB-200	492 (95)	1314 (65)	918 (26)	802 (23)	520 (2)	1 (9)	0 (8)	514 (28)	385 (17)
OCB-202	376 (184)	1411 (178)	919 (64)	800 (62)	539 (39)	1 (2)	1 (0)	442 (9)	428 (50)
OCB-750	11348 (28)	24711 (2277)	3058 (140)	11457 (2012)	2744 (132)	33864 (9012)	7141 (1100)	207270 (132054)	1622 (240)
Zeolites									
ZC	855 (157)	899 (114)	810 (132)	711 (53)	415 (43)	0 (0)	0 (4)	1184 (156)	2529 (950)
ZP	509 (90)	1303 (99)	1012 (134)	948 (128)	477 (28)	11 (5)	1 (4)	3127 (461)	1436 (203)
Biopolymer									
BPC	9115 (1250)	16870 (928)	16831 (2460)	8466 (216)	1926 (193)	23 (6)	0 (3)	20829 (3825)	9536 (4361)
Mixtures									
NCA/ZC50%[b]	809 (28)	1455 (13)	1122 (24)	822 (66)	498 (12)	5 (7)	69 (2)	728 (41)	378 (29)
NCA/OCB-750-50%	3937 (1762)	42570 (19491)	5251 (2442)	5628 (432)	1648 (388)	12818 (4835)	3334 (1093)	42205 (16025)	6374 (7483)
NCA/ZC100%	352 (1)	643 (16)	548 (22)	490 (7)	284 (30)	0 (0)	43 (2)	538 (53)	316 (9)
NCA/OCB750-100%	3814 (438)	15866 (5439)	1714 (807)	4597 (325)	1589 (82)	4823 (948)	2847 (325)	27560 (34926)	9400 (11792)
NCA/BPC100%	3691 (1276)	3665 (1000)	4676 (560)	5241 (670)	1482 (309)	62 (18)	180 (11)	7263 (1759)	1220795 (10246)
NCA/BPC50%	3501 (12)	1722 (82)	5026 (540)	7435 (1145)	2165 (174)	138 (61)	221 (65)	5190 (875)	7376 (1143)

[a] Rock phosphate from Tennessee (RPT), rock phosphate from North Carolina (NCA), biological apatite (BA), calcium phytate (CaP), organoclays from Biomin, Inc.: Clayfloc™ 200 (OCB-200), Clayfloc™ 202 (OCB-202), and Clayfloc™ 750 (OCB-750), clinoptilolite (ZC), phillipsite (ZP), chitosan (BP)

[b] 50% indicates 0.1g of each constituent and 100% indicates 0.2 g of each constituent

Table 2. Pearson correlations with the first three axes of the principal components analysis (PCA) of amendments based on their metal removal capacity.

Metal	Axis 1	Axis 2	Axis 3
As	-0.517	0.763	0.122
Cd	-0.924	-0.152	0.098
Co	-0.862	0.034	-0.283
Cr	-0.872	-0.116	-0.242
Cu	-0.943	-0.12	0.233
Ni	-0.603	-0.085	-0.728
Pb	-0.804	-0.416	0.321
Se	-0.578	0.72	0.043
Zn	-0.928	-0.108	0.256

TABLE 3. Evaluation of amendment effectiveness in fresh water based on retention of metals[a] (acronyms as in Table 1).

Amendment	As	Cd	Co	Cr	Cu	Ni	Pb	Se	Zn
RPT	X		XX	XX	XXX	X	XXX		X
NCA	X		XX	XXX	XXX	XX	XXX	XXX	XX
CaP			XX	XXX	XXX	XX	XXX		XXX
OCB-750	XXX	XXX	XXX	XXX	XXX	XXX	XXX		XXX
ZC			X	XXX	XX		XXX		X
BPC		XXX	XXX	XX	XXX	XXX	XXX		XX
NCA/BPC50%	X	XXX	XXX	XXX	XXX	XXX	XXX	XX	XXX

[a] X - retention at 30 - 50%; XX - retention at 50 - 80%; XXX - retention at 80 - 100%

TABLE 4. Evaluation of amendment effectiveness in salt water based on retention of

metals[a] (acronyms as in Table 1).

Amendment	As	Cd	Cr	Co	Cu	Ni	Pb	Se	Zn
RPT	XX		XX	XX	XXX	XX	XXX		XXX
NCA	X		XX		XX		XXX	XX	XX
CaP		X	XX		XXX		XXX		XXX
OCB-750	XXX	XXX	XX	XXX	XXX	XXX	XXX	XX	XX
ZC			XX		XX		XXX		XX
BPC		XXX		XXX	XXX	XXX	XX		XXX
NCA/BPC50%		XXX		XXX	XX	XXX	XXX	XX	XXX

[a] X - retention at 30 - 50%; XX - retention at 50 - 80%; XXX - retention at 80 - 100%

Table 5. Cap effectiveness for organics as indicated by the predicted time (in years) for three organic contaminants to breakthrough a 2.5 cm thick layer of active media (acronyms as in Table 1).

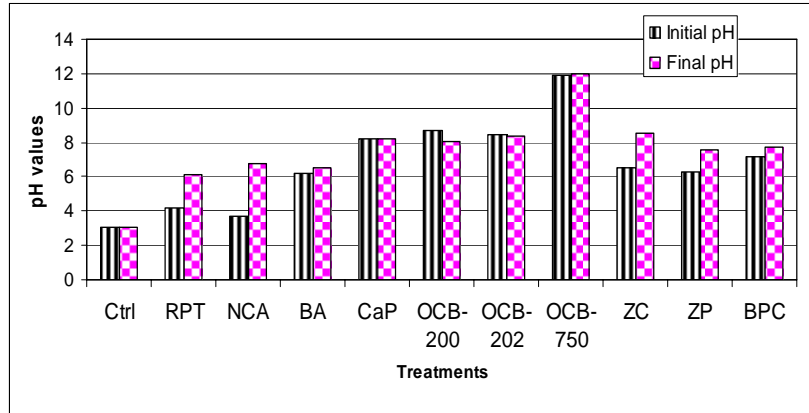| Media	Phenanthrene	Pyrene	Benzo[a]pyrene	Transport Condition
Sediment	19	66	1011	Upwelling
	8	29	442	Diffusion
OCB-200	12	100	1256	Upwelling
	5	44	548	Diffusion
OCB-202	9	36	633	Upwelling
	4	16	276	Diffusion
OCB-750	1452	10791	78705	Upwelling
	634	4711	34363	Diffusion
PM-199	1775	11853	91466	Upwelling
	775	5175	39935	Diffusion
ZC (powder)	3	4	320	Upwelling
	1	2	140	Diffusion
ZC (4 mesh)	5	13	505	Upwelling
	2	6	220	Diffusion
ZC (8x14)	7	8	709	Upwelling
	3	4	309	Diffusion
ZP	5	12	1009	Upwelling
	2	5	441	Diffusion
NCA	15	43	1315	Upwelling
	6	19	574	Diffusion
BA	108	527	13369	Upwelling
	47	230	5837	Diffusion
RPT	26	131	2753	Upwelling
	11	57	1202	Diffusion
CaP	5	8	335	Upwelling
	2	4	146	Diffusion

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Figure 1. Effect of sequestering agents on spike solution pH. Figure A –individual sequestering agents in fresh water; Figure B – mixtures of sequestering agents in fresh water; Figure C – salt water, (abbreviations defined in Table 1).

Figure 2. Removal of metals by amendments in fresh and salt water (concentration of each metal in the spike solution was ~ 1 mg L^{-1}).
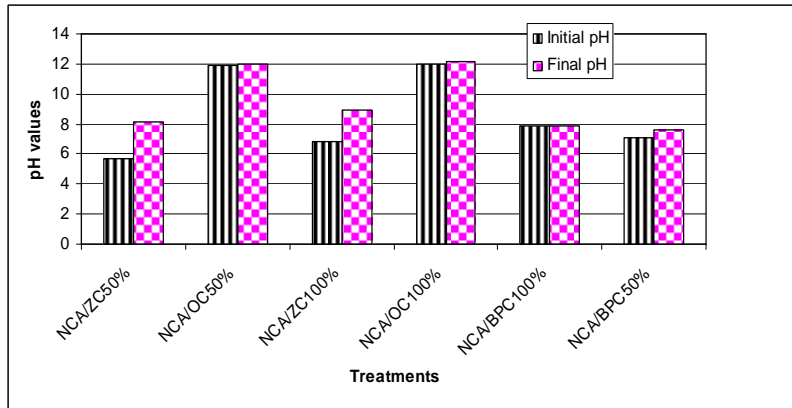
Figure 3. Principal components analysis (PCA) of amendments based on their ability to remove metals from a spike solution (abbreviations defined in Table 1). Percents represent the proportion of variation associated with each PCA axis. Arrows indicate directions of increasing metal removal.

Figure 4. Sorption of organic contaminants by sequestering agents.

A   Fresh water

B   Fresh water

C   Salt water

Phenanthrene

Pyrene

Benzo(a)pyrene