FINAL REPORT-PART II

Innovative In-Situ Remediation of Contaminated Sediments for Simultaneous Control of Contamination and Erosion

SERDP Project ER-1501

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LIST OF ACRONYMS

A – apatite

ANOVA – one-way analysis of variance

ASSET – adjustable shear stress erosion transport

BTC – break-through curve

C – chitosan, biopolymer

G – guar gum, biopolymer

HPLC- high performance liquid chromatography

K_d – partition coefficient

K_{ow}- octanol water partition coefficient

ICP-MS – inductively coupled plasma – mass spectrometry

MAAC – multiple-amendment active cap

NCA – North Carolina apatite

OCB-750 - ClayflocTM 750, an organocaly-based flocculent (modified bentonite from Biomin Inc. Ferndale, MI)

PAHs – polycyclic aromatic hydrocarbons

PM-199 - an organoclay, i.e., modified bentonite with surfactant dimethyl ammonium chloride

S – sand

SNL – Sandia National Laboratories

SRNL – Savannah River National Laboratory

X – xanthan biopolymer

ZC – clinoptilolite zeolite

ZP – phillipsite zeolite

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EXECUTIVE SUMMARY

Multiple amendment active caps (MAACs) developed under this project for the remediation of contaminated sediments consist of a mixture of chemically active amendments combined with sand or other neutral materials such as clay or clean soil/sediment. The objectives of SERDP project (ER-1501) part II were 1) the development and evaluation of MAAC technology for sorption and desorption of contaminants, 2) prediction of contaminant release over time from MAAC formulations by numerical modeling, 3) evaluation of MAAC resistance to erosion, and 4) assessment of MAAC toxicity to aquatic organisms.

Laboratory evaluations of sorption and desorption capacities and calculation of partition coefficient (K_d) values showed that mixing of apatite with organoclay reduced the sorption capacity and effective retardation factor for organics compared to pure organoclay, but the reductions were small. However, for metals the results from the sorption and desorption studies showed that mixtures were more effective than individual amendments for several tested elements including As, Cd, Co, Ni, and Zn.

Addition of 20% or less bentonite to MAACs is potentially beneficial to the performance of active caps without being harmful to aquatic organisms. The addition of 20% or less bentonite to MAACs can improve metal sorption and also is sufficient to significantly reduce the erosion of MAAC caps.

A numerical model was used to evaluate the long-term effectiveness of various amendments and amendment mixtures. The model, which used desorption K_d values, was used to develop breakthrough curves for numerous metals. These curves were then used to develop nomographs for estimating the amendment thickness needed to delay contaminant breakthrough for a given period of time. The modeling results showed that an amendment mixture containing apatite, organoclay, and chitosan was more effective at retarding metals than apatite alone.

Toxicity tests showed that clinoptilolite and mixtures of clinoptilolite, apatite, and organoclay were nontoxic to *Hyalella azteca,* thus suggesting that these materials can be used for remediation of contaminated sediments with minimal likelihood of collateral effects on aquatic organisms.

Bentonite was toxic to *Hyalella azteca* as were mixtures of bentonite and sand containing as little as 10% bentonite. In contrast, the addition of 10% bentonite to an amendment mixture containing apatite, organoclay, and zeolite did not affect *Hyalella azteca* survival and greater additions of bentonite had only limited effects on survival. These results suggest that the addition of limited amounts of bentonite to amendment mixtures is not harmful to aquatic organisms and more generally indicate the potential environmental benefits of mixtures of amendments (i.e., MAACs) compared with single amendment formulations.

Bentonite is a clay material primarily composed of montmorillonite, a member of the smectite family of clay minerals. Bentonite is the most cohesive of the common clays, and has the greatest effect on erosion rates because of this. In our study small additions of bentonite to a mixture of cap amendments resulted in decreased erosion. The largest reduction in erosion occurred with

additions of small amounts (5%) of bentonite. The addition of larger amounts of bentonite (15 and 20%) to amendment mixtures caused further decreases in erosion rates, but the rate of decrease diminished as the amount of bentonite increased.

In summary, this project showed that MAACs can incorporate different active sequestering agents such as phosphate materials (rock phosphate), organoclays, zeolite, and clay. The results showed that phosphate, zeolite, bentonite, and organoclays individually or mixed with another active or neutral materials can stabilize metals and nonpolar pollutants (e.g., PAHs). Addition of a small amount of bentonite (e.g., 10%) to MAACs can improve erosion resistance and metal sequestration capacity. Based on our results we assume that MAACs can be deployed in any type of benthic habitat considered for conventional capping as well as higher energy environments (if bentonite is included) that might be unsuitable for caps with less erosion resistance. MAACs also present potential advantages in terms of acceptability to aquatic organisms, ease of construction, and economy compared with other active capping technologies.

TECHNICAL APPOACH

Contaminated sediments affect nearly 10% of the nation's waterways with potential remediation costs in the billions of dollars. The treatment of contaminated sediments is complicated by the co-occurrence of organic and inorganic contaminants with differing chemical and physical properties and by the heterogeneous nature of the sediments. Contaminated sediment has traditionally been managed by dredging or dry excavation followed by off-site treatment or disposal (Mohan et al., 2000; Nayar et al., 2004). However, this method is expensive and can remobilize contaminants and degrade the benthic environment. Conventional passive capping is an alternative strategy consisting of the installation of a relatively thick covering or cap of clean, inert material over contaminated sediment, thus isolating it from the water and reducing contaminant migration. However, passive caps are subject to contaminant release as a result of mechanical disturbance and advective transport by upwelling water. Active capping is a more recent alternative that involves the application of reactive material to the sediment to physically or chemically reduce contaminant mobility and/or bioavailability (Jacobs and Forstner, 1999; Berg et al., 2004; Jacobs and Waite, 2004; Reible et al., 2006; Knox et al., 2006, 2007, 2008 a and b, and 2010). Studies have shown that the application of relatively small amounts of reactive amendments such as apatite, zeolite, organoclay, and activated carbon can sequester a variety of contaminants and retard their transport (Reible et al, 2006; Knox et al., 2007, Knox et al., 2008 a and b; Knox et al., 2010).

The main objective of this study was the development of a multiple-amendment active cap (MAAC) composed of a mixture of active amendments and inert materials applied as a single layer in one step. A MAAC consists of a mixture of amendments combined with sand or other neutral materials such as clay or clean soil/sediment. MAAC technology has potential advantages over other technologies due to its low cost, simplicity, potential to remediate a broad range of contaminants, easy adaptation to site requirements, and lack of harmful environmental impacts. MAACs are economical because they contain relatively small amounts of reactive materials and can be constructed using conventional equipment.

MAACs developed under this project were evaluated for sorption and desorption of contaminants, contaminant release over time as predicted by numerical modeling, toxicity to aquatic organisms, and resistance to erosion.

MATERIALS AND METHODS

TASK 1. SORPTION EVALUATION FOR MAAC DEVELOPMENT

Sorption of Organic Contaminants

Sorption of Organic Contaminants on MAAC Formulations with Apatite and Organoclay

In support of the use of amendment mixtures for the construction of MAACs that simultaneously control organic and metal species, batch sorption tests for organic contaminants (polycyclic aromatic hydrocarbons, PAHs) were conducted on a mixture of 75% apatite and 25% organoclay. The general approach was to provide a spiked solution at a known concentration to a mixture of active cap amendments (100 mg) in a 250 mL vessel. The cap material/water mixture was then allowed to equilibrate for 7 days and the water concentration was measured. The change in concentration from the spike concentration defined sorption onto the solid phase (active cap mixture). The sorption experiments for active cap mixtures were conducted in the same way as for the individual amendments. A detailed description of these experiments was presented in the 2007 and 2008 annual reports (Knox et al., 2007 and 2008 b).

Sorption of Organic Contaminants on MAAC Formulations with Zeolite

A sorption study was performed to quantitatively assess the effective sorption of organic contaminants by mixtures of amendments that included zeolite. The mixtures tested in this experiment included organoclay, apatite, zeolite (clinoptilolite), and sand. Sorption isotherm parameters were obtained for sorption of naphthalene, phenanthrene, and pyrene on the following mixtures in water:

- Mixture 1: 25% (w/w) organoclay (CETCO PM-199), 25% (w/w) zeolite (Clinoptilotilte), 25% (w/w) NC apatite, and 25% (w/w) acid-washed sand
- Mixture 2: 25% (w/w) organoclay (CETCO PM-199), 50% (w/w) zeolite (Clinoptilotilte), and 25% (w/w) acid-washed sand
- Mixture 3: 25% (w/w) organoclay (CETCO PM-199) and 75% (w/w) zeolite (Clinoptilotilte)
- Mixture 4: 50% (w/w) organoclay (CETCO PM-199) and 50% (w/w) zeolite (Clinoptilotilte)

Isotherm experiments were designed to yield initial concentrations below half-solubility and final concentrations above the conservative High-Performance Liquid Chromatography (HPLC) minimum detection limits for the compounds of interest. Initial solutions were prepared by dissolving 1.3 grams of NaN_3 in 2 liters of deionized water to yield 0.01 M NaN_3. The resulting solution was placed on a magnetic stir plate and spiked with appropriate volumes of naphthalene, phenanthrene, and pyrene stock solutions under continuous stirring to obtain the desired target initial concentrations. The solutions were allowed to continue stirring for 3-4 hours until all

PAHs were dissolved. The volume of the spike solutions added was increased slightly to account for the increased volume of solution prepared to minimize head space in the flask (Table 1).

For each batch test, approximately 70 milligrams total mass of sorbate materials were weighed out and placed in each of three 250 milliliter amber glass bottles, while no sorbate materials were added to an additional three bottles, which were designated as blanks. Teflon tape was used around the threads of the vessels to assure that there were no leaks. The vessels were then carefully filled to zero head space with the initial sample solution prepared previously, capped with mininert valves equipped with unused septa, and allowed to tumble for 7 days. Samples of the initial solution were taken from the 2 liter volumetric flask before and after filling the bottles and analyzed via HPLC. Following tumbling, samples were taken from the tumbler and allowed to sit for 30 minutes prior to being sampled. Following settling, samples were taken from the supernatant of each bottle and analyzed via HPLC.

Sorption of Inorganic Contaminants

Sorption of Metals on MAAC Formulations with Apatite, Organoclays, and Biopolymers

Materials tested for potential MAAC formulations are presented in Table 2. Sorption of As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn were evaluated for potential MAAC formulations in 50 mL centrifuge tubes for one week. Each treatment had three replicates. The spike solution used in the experiment contained 5 mg L^{-1} of As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn. Suspensions composed of 0.2 g of solid (the amendment mixture) and 15 mL of spike solution were shaken for one week. The liquid phase was separated by centrifugation and analyzed for metal content by inductively coupled plasma – mass spectroscopy (ICP-MS) and pH.

Table 1. Preparation of initial solutions presenting target concentrations for phenanthrene and pyrene, along with the amount of spike solutions used

Batch Test ID	Mix No.	Batch Test No.	Volume 8,000 ppm Naph in 99.9% (w/v) ACN (μL)	Volume 5,000 ppm Phen in 99.9% (w/v) ACN (μL)	Volume 1,000 ppm Pyrene in 99.9% (w/v) ACN (μL)	Initial Concentrations (ppb)		
						Naphthalene	Phenanthrene	Pyrene
BT1M1	1	1	6.4	12	55	21.2	25.3	28.2
BT2M1	1	2	14	23	78	57.1	64.7	40.0
BT3M1	1	3	28	44	99	97.9	103	51.0
BT4M1	1	4	55	88	121	191	212	61.0
BT1M2	2	1	6.4	12	55	21.6	31.4	16.9
BT2M2	2	2	14	23	78	54.9	59.9	32.1
BT3M2	2	3	28	44	99	110	116	46.2
BT4M2	2	4	55	88	121	203	243	66.1
BT1M3	3	1	6.4	12	55	17.5	30.4	27.5
BT2M3	3	2	14	23	78	47.3	65.0	36.6
BT3M3	3	3	28	44	99	112	121	41.5
BT4M3	3	4	55	88	121	`99	201	67.3
BT1M4	4	1	6.4	12	55	20.2	38.0	33.6
BT2M4	4	2	14	23	78	45.0	61.7	35.6
BT3M4	4	3	28	44	99	89.7	107.1	37.7
BT4M4	4	4	55	88	121	205	196	55.6

The metal concentration data obtained in this experiment were used to calculate percent sorption and partition coefficient (K_d) values, defined as the ratio of the concentration of solute sorbed to the solid divided by its concentration in solution. The K_d values (mL g^{-1}) were calculated using the following equation:

$$K_d = [V_{spike} \; x \; (C_{spike} - C_{final})/(C_{final} \; x \; M_{Mineral})]$$

where C_{spike} is the metal concentration in the spike solution before the addition of the amendment mixture (mg L^{-1}), C_{final} is the metal concentration in the solution after contact with the amendment mixture (mg L^{-1}), $M_{mineral}$ is the amendment mixture mass (g), and V_{spike} is the volume of the spike solution (mL). Differences in K_d values among amendments and amendment mixtures were statistically tested using analysis of variance (ANOVA) followed by Holm-Sidak multiple comparison tests for individual differences among means. Data were log transformed before analysis to better meet the assumptions of ANOVA, and test results were therefore expressed as differences among geometric means ($P<0.05$).

Table 2. Amendments and amendments mixtures tested for metal sorption

Amendment of mixture	Acronym	Composition [%]
North Carolina Apatite	A	100
Xanthan/Guar Gum	XG	100
Chitosan	C	100
Organoclay (OCB-750)	O or OCB-750	100
Apatite/OCB-750/chitosan	AOC	75/20/5
Apatite/OCB-750/xanthan/guar gum	AOXG	75/20/5
Apatite/OCB-750*	AO	75/25
Apatite/PM-199**	APM	75/25

* OCB-750 is ClayflocTM 750, an organocaly-based flocculent (modified bentonite from Biomin Inc. Ferndale, MI.
** PM-199 is an organoclay, i.e., modified bentonite with surfactant dimethyl ammonium chloride.

Sorption of Metals on MAAC Formulations with Bentonite

A sorption study was conducted to quantitatively assess the effective sorption of contaminants by various mixtures of amendments including sand and bentonite. Four experiments were conducted to evaluate metal sorption by different mixtures (Tables 3, 4, 5, and 6). The experiments were conducted in 50 mL centrifuge tubes for a period of one week. Each treatment had three replicates. The spike solution that was used in the experiment was obtained from Inorganic Ventures, Lakewood, NJ. The metal concentration in the spike solution was 5 mg L^{-1} of As, Cd, Cr, Cu, Mo, Pb, Ni, Se, and Zn. Suspensions composed of 0.2 g of solid (the sequestering agent) and 15 mL of spike solution were shaken for one week, phase separated by centrifugation, and analyzed for metal content by ICP-MS and pH.

Table 3. Mixtures of sand and bentonite tested for metal sorption.

Mixtures	Sand (%)	Bentonite (%)
B0	100	0
B05	95	5
B10	90	10
B15	85	15
B20	80	20
B25	75	25
B50	50	50
B75	25	75
B100	0	100

Table 4. Mixtures of sand, apatite, organoclay (PM-199), and bentonite tested for metal sorption.

Mixtures	Apatite (NCA) %	Organoclay (PM-199) %	Sand %	Bentonite %
B0	25	25	50	0
B10	25	25	40	10
B20	25	25	30	20
B30	25	25	20	30
B100	0	0	0	100

Table 5. Mixtures of sand, apatite, zeolite (clinoptilolite), and bentonite tested for metal sorption.

Mixtures	Apatite (NCA) %	Zeolite (Clinoptilolite) %	Sand %	Bentonite %
B0	25	25	50	0
B10	25	25	40	10
B20	25	25	30	20
B30	25	25	20	30
B100	0	0	0	100

Table 6. Mixtures of sand, apatite, organoclay (PM-199), zeolite (clinoptilolite), and bentonite tested for metal sorption.

Mixtures	Apatite (NCA) %	Organoclay (PM-199) %	Zeolite (Clinoptilolite) %	Sand %	Bentonite %
B0	25	25	25	25	0
B05	25	25	25	20	5
B10	25	25	25	15	10
B15	25	25	25	10	15
B20	25	25	25	5	20
B25	25	25	25	0	25

TASK 2. PREDICTING THE RELEASE OF CONTAMINANTS OVER TIME FROM MAAC FORMULATIONS BY NUMERICAL MODELING

Laboratory Column Experiments

Laboratory column experiments were conducted to evaluate the effectiveness of amendment mixtures in sequestering inorganic contaminants and provide a basis for the transport modeling described in the next section of this report. Amendments selected for the column experiments include rock phosphate (North Carolina apatite), organoclay (OCB -750), and the biopolymer, chitosan (described in Knox et al., 2010). Three columns were tested: column A (North Carolina apatite), column AO (A - apatite and O - organoclay), and column AOC (A - apatite, O-organoclay, and C- chitosan). Column A was comprised entirely of apatite. Column AO included a mixture of apatite (75%) and organoclay (25%), and column AOC included a mixture of apatite (75%), organoclay (20%), and chitosan (5%).

The dry bulk density of the amendment mixtures used in the NCA, AO, and AOC columns was determined by carefully placing oven dried material (105°C) in a cylinder of known mass and volume and lightly tapping the cylinder to settle the material. Excess material was removed from the filled cylinder using a straightedge. The cylinder was then weighed to determine the dry mass of amendment contained within the cylinder. The dry bulk density was determined by dividing the dry mass of amendment by the cylinder volume. This process was repeated 5 times for each amendment mixture, and the results were averaged to yield the dry bulk density.

A bromide (NaBr) tracer test was completed on each column to estimate porosity and pore volume. The flow rate of the influent spike solution was maintained at 0.5 ml/min with flow upwards through each column. Samples of the column effluent were collected using a fraction collector, and subsets of these samples were analyzed with an ion-selective electrode to yield the bromide break-through time. Once the tracer tests were completed, the columns were purged with DI water to eliminate the bromide from the amendments.

At the conclusion of the tracer tests, a spike solution containing 2 ppm of As, Cd, Co, Ni, Zn, and U was pumped through each column via peristalsis at a flow rate of 0.5 ml/min. The flow rate of the influent spike solution was maintained at 0.5 ml/min with flow upwards through the columns. Samples were collected for metals analysis.

1-D Metal Transport Modeling for Apatite, Organoclay, and Chitosan

A one-dimensional numerical model was used to qualitatively assess the advection of selected metals through various amendments and mixtures of amendments to evaluate their effectiveness in sediment remediation applications. The amendments modeled for this task included North Carolina Apatite (NCA), a mixture of NCA and Organoclay (OCB-750) (AO), and a mixture of NCA, OCB-750, and chitosan (AOC).

Simulations were conducted on a column of material 10 cm in length at a flux of 4.11E-04 cm/sec (which equates to a flow rate of 0.5 ml/min for a column 5 cm in diameter). Advection was considered the primary mechanism for contaminant transport and molecular diffusion a minor component. Specific material dispersion and diffusion data were unavailable for the simulated amendments and amendment mixtures. To account for dispersion and molecular diffusion, a one dimensional analytical model was fitted to the cobalt breakthrough curve (BTC) from a previous column experiment using NCA. The retardation factor was fixed based on the laboratory measured K_d value, and the dispersion coefficient was varied to obtain the optimum fit. The dispersion coefficient determined from the cobalt BTC was used in all subsequent numerical simulations.

Material properties used in the simulations are provided in Table 7. The dry bulk density of each material was determined using standard methods. For NCA and AOC, the porosity was determined based on laboratory data from previous column experiments using the BTC of a conservative tracer (Br$^-$). A porosity of 0.4 was assumed for AO because no porosity data were available for this mixture. The saturated hydraulic conductivity of each material was determined using a falling head method (Mariotte tube). Material specific desorption partitioning coefficients (K_d) were measured for each material and used in the simulations. These values are presented in Table 8.

Table 7. Material properties used in transport modeling.

Layer	Particle Density (g/cm^3)	Dry Bulk Density (g/cm^3)	Total Porosity (fraction)	Saturated Hydraulic Conductivity (cm/sec)
Apatite	2.57	1.89	0.27	2.89E-04
Apatite Organoclay	2.32	1.39	0.40	1.28E-04
Apatite Organoclay Chitosan	2.43	1.46	0.28	2.61E-05

1-D Metal Transport Modeling for Zeolites

In addition to the above mentioned amendment mixtures, zeolites were evaluated as potential replacements for apatite in MAAC formulations. Application of large concentrations of apatite to wetlands or other stagnant bodies of water may be undesirable due to the release of phosphate. In stagnant anoxic, hypolimnetic, and non-bioturbated sediments, molecular diffusion is considered to be the main mechanism for P release. A large release of P could contribute to eutrophication. Generally, eutrophication is an ecosystem response to human activities that fertilize water bodies with nitrogen (N) and P, often leading to changes in animal and plant populations and degradation of water and habitat quality.

Table 8. Partitioning coefficients used in transport modeling.

Metal	Apatite (ml/g)	Apatite Organoclay (ml/g)	Apatite Organoclay Chitosan (ml/g)
As	6.535E+01	6.369E+03	9.570E+03
Cd	4.050E+03	1.070E+04	1.804E+04
Co	1.766E+02	9.339E+03	1.474E+04
Ni	9.027E+01	8.431E+03	1.387E+04
Zn	5.009E+03	1.127E+04	1.654E+04
U	1.212E+03	1.641E+03	5.783E+02
Se	8.566E+01	7.572E+01	1.072E+02
Pb	1.094E+04	2.808E+03	4.407E+03
Tracer[1] (Br⁻)	0.000E+00	0.000E+00	0.000E+00

[1]Nonadsorbed tracer.

Zeolites are naturally occurring crystalline aluminosilicates consisting of a framework of tetrahedral molecules. Their structural properties give them the ability to act as molecular sieves; e.g., taking up ammonium and heavy metal ions from waters. Clinoptilolite is the most abundant zeolite in nature and is readily available.

The amendments modeled for this task included clinoptilolite zeolite (ZC) and phillipsite zeolite (ZP). Simulations were conducted on a column of material 10 cm in length at a flux of 4.11E-04 cm/sec (which equates to a flow rate of 0.5 ml/min for a column 5 cm in diameter). Advection was considered the primary mechanism for contaminant transport and molecular diffusion a minor component. Material specific diffusion data were unavailable for the amendments and amendment mixtures. Therefore, a generic effective diffusion coefficient (3.5E-03 cm^2/sec) was used for this simulation, which included the effects of molecular diffusion and material tortuosity. The generic effective diffusion coefficient was previously estimated from laboratory column experiments where an analytical model was applied to actual breakthrough data for several contaminants of interest (Knox et al., 2010).

Material properties for clinoptilolite and phillipsite include dry bulk density and porosity (Table 9). Particle density was inferred from these data using standard soil physics equations. Material specific desorption partitioning coefficients were measured for each material and used in the simulations. These values are presented in Table 10.

Table 9. Material properties used in transport modeling.

Layer	Particle Density (g/cm³)	Dry Bulk Density (g/cm³)	Total Porosity (fraction)
Clinoptilolite zeolite (ZC)	1.35	0.65	0.52
Phillipsite zeolite (ZP).	1.71	0.78	0.54

Table 10. Partitioning coefficients used in transport modeling.

Metal	Clinoptilolite Zeolite (ml/g)	Phillipsite Zeolite (ml/g)
As	1.100E+01	0.000E+00
Cd	3.127E+03	1.184E+03
Co	1.303E+03	8.990E+02
Ni	1.012E+03	8.100E+02
Zn	4.770E+02	4.150E+02
Se	1.000E+00	0.000E+00
Pb	1.436E+03	2.529E+03
Tracer[1] (Br⁻)	0.000E+00	0.000E+00

[1]Nonadsorbed tracer.

TASK 3. TOXICITY EVALUATION

Laboratory studies were conducted to determine the potential toxicity of mixtures of apatite, organoclay, sand, chitosan, xanthan gum, and guar gum to benthic organisms. Previous laboratory bioassay studies under this project emphasized the toxicity of individual amendments (Knox et al., 2007 and 2008 b). Tests on amendment mixtures consisted of static sediment bioassays with *Hyalella azteca* conducted in glass containers, each with 100 g of a MAAC formulation plus 100 ml of water from Steel Creek (Savannah River Site, Aiken, SC). Sixteen formulations were evaluated plus control groups consisting of sediment from Steel Creek or commercial playground sand (Table 11). Each MAAC formulation and control group was represented by four replicates. Ten *Hyalella azteca* were placed in each container following the addition of MAAC formulations and water. The organisms were acclimated to Steel Creek water before testing, which continued for 10 days. Test water was not replaced during the test period, although intermittent aeration was provided. The tests were conducted at room temperature.

A second series of static sediment bioassays with *Hyalella azteca* was conducted to evaluate the toxicity of the zeolites, clinoptilolite, and phillipsite, to aquatic organisms. The bioassays were conducted in 500 ml beakers, each containing 100 ml of substrate and 200 ml of overlying water from Steel Creek. The substrates consisted of 0%, 5%, 10%, 25%, 50%, 75%, and 100% (by volume) zeolite mixed with commercial grade playground sand. The 0% zeolite (i.e., 100% sand) treatments served as controls. All treatments had four replicates. The test organisms were periodically fed small amounts of ground commercial fish food during the tests, and the water in the beakers was aerated intermittently to increase dissolved oxygen levels. The duration of all tests was 10 days. Water hardness, alkalinity, and pH were measured during the test period.

Table 11. Composition of MAAC formulations and controls used in 10 day static sediment bioassays.

MAAC Formulation *	Steel Creek sand (g)	Apatite (g)	Organo-Clay OCB-750 (g)	Organo-Clay PM-199 (g)	Play ground Sand (g)	Chitosan (g)	Xanthan gum (g)	Guar Gum (g)
SAO-30	0	35	35	0	30	0	0	0
SAPM-30	0	35	0	35	30	0	0	0
SAO-50	0	25	25	0	50	0	0	0
SAOC-45	0	25	25	0	45	5	0	0
SAOXG-45	0	25	25	0	45	0	2.5	2.5
APM-0	0	50	0	50	0	0	0	0
SAPMC-45	0	25	0	25	45	5	0	0
SAPMXG-45	0	25	0	25	45	0	2.5	2.5
SAOC-65	0	15	15	0	65	5	0	0
SAPMC-65	0	15	0	15	65	5	0	0
SAOXG-65	0	15	15	0	65	0	2.5	2.5
SAPMXG-65	0	15	0	15	65	0	2.5	2.5
SAOC-75	0	15	5	0	75	5	0	0
SAPMC-75	0	15	0	5	75	5	0	0
SAOXG-75	0	15	5	0	75	0	2.5	2.5
SAPMXG-75	0	15	0	5	75	0	2.5	2.5
Playground sand (control)	0	0	0	0	100	0	0	0
Steel Creek sand (control)	100	0	0	0	0	0	0	0

* S - sand, A – apatite from North Carolina, O – organoclay OCB - 750, PM – organoclay PM-199, C – chitosan, X – xanthan, G – guar gum

A third series of bioassays using *Hyalella azteca* was conducted to assess the toxicity of clinoptilolite and mixtures of clinoptilolite, apatite and organoclay (Table 12). Controls consisted of sand collected from Steel Creek and playground sand from a local commercial supplier. A final series of experiments was conducted to evaluate the toxicity of bentonite to benthic organisms. These experiments consisted of static bioassays of bentonite and mixtures of bentonite, sand, and amendments using *Hyalella azteca* as the test organism. The amendments and amendment mixtures evaluated in these bioassays are shown in Tables 3 and 5. Laboratory protocols used for these tests were the same as those used for the previously described zeolite bioassays.

The significance of differences among treatments were evaluated by either one-way analysis of variance (ANOVA) or Kruskal-Wallis one way analysis of variance on ranks, depending upon the distributions of the survival data. These tests were followed by Holm-Sidak tests to investigate individual treatment effects.

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Table 12. Mixtures of apatite, clinoptilolite, organoclay, and sand tested for toxicity to *Hyalella azteca*.

Treatment[a]	Average pH	Apatite	Clinopti-lolite	Organo-Clay	Steel Creek Sand	Play-ground sand
a0z100	8.60		100			
a25z75	8.62	25	75			
a50z50	8.92	50	50			
a75z25	8.74	75	25			
a100z0	7.87	100				
a25z25o25s25	7.88	25	25	25		25
a50z25o25	7.95	50	25	25		
a25z50o25	8.12	25	50	25		
a25z25o50	7.65	25	25	50		
scs	7.30				100	
s	7.35					100

[a] a = apatite, z = clinoptilolite, o = organoclay (PM – 199), sc = Steel Creek sand, and s = playground sand; numbers = percentages based on volume

TASK 4. EROSION EVALUATION

In this study, 5 sediment cores were tested for sediment erosion behavior in an adjustable shear stress erosion transport (ASSET) flume (Roberts et al., 2003). The cores were created in the laboratory and consisted of varying amounts of sand, apatite, organoclay, and bentonite. Table 13 shows the percentage of each constituent for each core. In essence the amount of organoclay and apatite were held at 25% while the amount of sand and bentonite were varied such that the overall core contained 0, 5, 10, 15, or 20% bentonite.

Table 13. Percentage of constituents for each of the five erosion cores.

	Apatite (NCA) %	Organoclay (PM-199) %	Sand (Playground) %	Bentonite %
B0	25	25	50	0
B05	25	25	45	5
B10	25	25	40	10
B15	25	25	35	15
B20	25	25	30	20

The erosion cores were created individually by carefully weighing each constituent (dry) and mixing in a 4 liter container. Then water was added to the dry mixture and further mixed until the sediment water mixture was homogeneous. The amount of water added was enough to make the mixture fluid, but care was taken to keep the mixture thick so that stratification of the sediment due to differential settling of the particles did not occur. This means that water content was slightly increased as bentonite content was increased to account for its swelling property. The sediment mixtures were then poured into coring tubes to a depth of ~15 cm. These cores were allowed to consolidate for 5 days.

Each core was tested within the ASSET flume to yield erosion rate as a function of the applied hydrodynamic shear stress and depth within the core as well as the critical shear stress for the initiation of erosion as a function of depth. The non-linear relationship between erosion rate and bed shear stress can make it difficult to quantify variability in erosion within a core and between cores. Therefore, the data were also presented as an erosion rate ratio that produced a single value that accounts for this non-linearity. The erosion rate ratio was used to make comparisons between erodibility within a single core (i.e., changes with depth), and between cores to aid in the identification of the most erosion resistant cap material.

Each core was sub-sampled into 4 separate depth intervals. The erosion rate for each depth interval can be approximated by a power law function of sediment density and applied shear stress (Roberts et al., 1998). Non-cohesive sediments do not show variation of erosion rate with density, therefore the density term is dropped. For each depth interval, the measured erosion rates and applied shear stress were used to develop the following equation:

$$E = A\tau^n$$

where E is the erosion rate (cm/s), and τ is shear stress (Pa). The A parameter and exponent n were determined using log-linear regression. An average erosion rate for the entire core was determined, and the erosion rate at each depth interval was compared to this average. The result was an erosion rate ratio that estimated the erodibility of each depth interval relative to the core average. An average erosion rate of similar cores and for all cores was also determined. The erosion rate for each depth interval within a core as well as each core's average erosion rate was compared to the average, and a graph of the erosion rate ratios for all of the cores was created.

RESULTS AND DISCUSSION

TASK 1. SORPTION EVALUATION FOR MAAC DEVELOPMENT

Organic Contaminants

Batch sorption tests for organic contaminants (PAHs) were conducted on a MAAC formulation consisting of 75% apatite and 25% organoclay (PM – 199). A comparison of the sorbed solid concentration at the measured water concentration provided an effective solid-water partition coefficient for the organoclay. A summary of the measured cap material concentration versus water concentration is shown in Figure 1 for two PAH contaminants.

The measured cap material/water partition coefficients were 172,000 L/kg for pyrene and 45,800 L/kg for phenanthrene. These can be compared to previously measured partition coefficients for these compounds in 100% organoclay material (Table 14). Approximate retardation factors (product of bulk density and partition coefficient) are also presented in Table 14
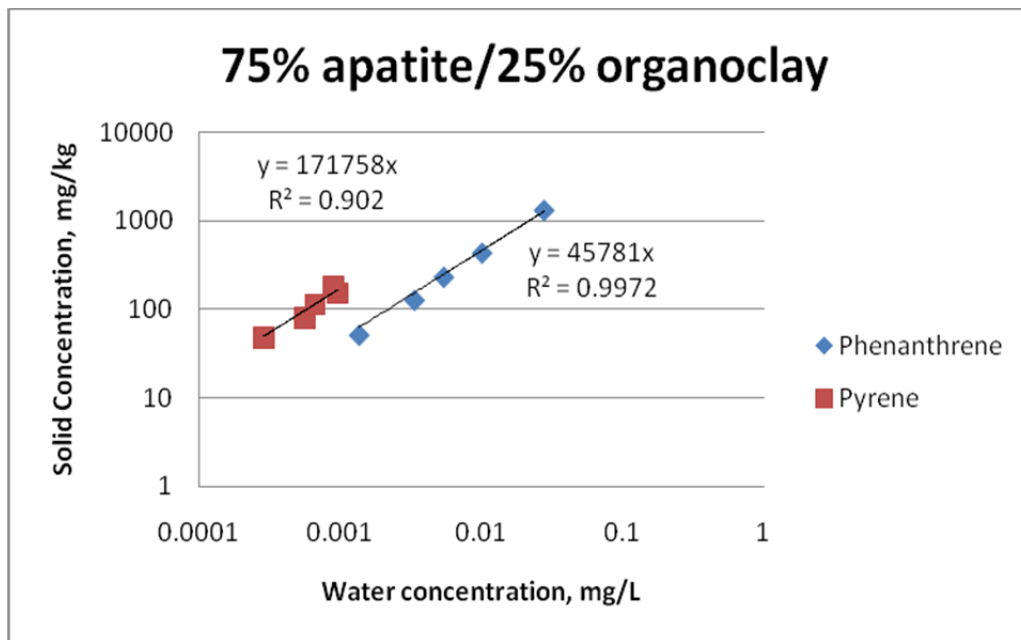
Figure 1.   A summary of the measured cap material concentration versus water concentration for two PAH contaminants; cap composition: 75% apatite and 25% of organoclay (PM-199).

Table 14. Comparison of 75%/25% apatite/organoclay and 100% organoclay partition coefficients and retardation factors.

Cap Material [%]	Bulk Density (g/cm^3)	Phenanthrene (l/kg)	Pyrene (l/kg)
75/25 Mixture	1.29	45,800	172,000
		Rf=59,100	Rf=222,000
100% Organoclay	0.76	68,000-117,000	286,000-454,000
		Rf=51,800-89,200	Rf=217,000-346,000

The results of the experiments on the sorption of organic contaminants on mixtures of amendments including zeolites are summarized in Table 15. The three PAHs were sorbed almost In summary, the mixing of apatite with organoclay reduced the sorption capacity and effective retardation factor compared to pure organoclay, but the reductions were small.
entirely to the organoclay fraction of the mixture. The organoclay normalized partition coefficients were remarkably similar in all four mixtures, indicating that the other mixture constituents were not significant factors in the organic contaminant sorption. Organoclay normalized partition coefficients were approximately equal to the octanol water partition coefficient (K_{ow}) of the three compounds in all mixtures. This is consistent with previous work that also showed that the organoclay, which is nominally 30-35% organic carbon, behaves as though it is 100-200% organic carbon in terms of measured sorption coefficient. As observed in previous studies (Knox et al., 2009), lower molecular weight PAHs are sorbed less strongly than higher molecular weight PAHs relative to the compounds K_{ow}. That is, pyrene and phenanthrene partition coefficients were approximately 0.1 log units greater than their respective K_{ow}s while naphthalene was approximately 0.35 log units lower than K_{ow}.

The results of these studies showed that the sorption capacity for organic contaminants in MAACs containing organoclay was slightly diminished compared with 100% organoclay but high enough for effective remediation.

Inorganic Contaminants

Evaluation of MAAC Formulations with apatite, organoclays and biopolymers

In this study individual amendments and amendment mixtures were tested for As, Cd, Cr, Co, Cu, Pb, Ni, Se, and Zn sorption (removal) in fresh water. The sorption results were used to calculate partition coefficient (K_d) values. The K_d values were highly variable among mixtures, differing by an order of magnitude, but useful in identifying effective amendments and amendments mixtures (Table 16). Statistical tests showed that apatite, organoclay, and mixtures of these materials with or without the biopolymer chitosan produced higher K_d values than other amendments and amendment mixtures (Table 17). The mixture of apatite, 20% organoclay OCB-750, and 5% chitosan produced the highest K_d values for most elements (Tables 16 and 17). These results show the potential ability of MAAC formulations to effectively sorb a variety of metals.

Table 15. Results of experiments on the sorption of organic contaminants on amendment mixtures.

Mixture No.	Fraction Organoclay (w/w)	Fraction Zeolite (w/w)	Fraction Apatite (w/w)	Fraction Sand (w/w)	log K_D			Log(K_D/Organoclay fraction)		
					Naphthalene LogKow=3.37	Phenanthrene LogKow=4.57	Pyrene LogKow=5.18	Naphthalene LogKow=3.37	Phenanthrene LogKow=4.57	Pyrene LogKow=5.18
1	0.25	0.25	0.25	0.25	2.42	4.10	4.72	3.02	4.71	5.33
2	0.25	0.5	0	0.25	2.40	4.09	4.71	3.00	4.69	5.31
3	0.25	0.75	0	0	2.42	4.10	4.72	3.02	4.70	5.32
4	0.5	0.5	0	0	2.79	4.39	4.89	3.09	4.69	5.20
					Average (OC normalized)			3.03	4.69	5.29
					Standard Deviation (OC normalized)			0.04	0.01	0.06

Table 16. Comparison of average K_d (mL g^{-1}) values for nine elements for individual amendments and amendment mixtures: A – North Carolina apatite, XG – xanthan/guar gum, C – chitosan, O – organoclay OCB-750, PM – organoclay PM-199.

Amendments/ Mixtures	Composition %	As	Cd	Cr	Co	Cu	Ni	Pb	Se	Zn
		AVG	AVG	AVG	AVG	AVG	AVG	AVG	AVG	AVG
A	100	65	4050	21010	177	10482	90	10935	86	5009
XG	100	49	72	66	70	66	67	89	67	67
C	100	660	49	2211	8	6366	89	731	171	19
AOC	75/20/5	9570	18038	3113	14735	9535	13873	4407	107	16536
AOXG	75/20/5	643	915	877	1037	220	390	848	81	951
AO	75/25	6369	10701	3110	9339	9121	8431	2808	76	11275
APM	75/25	63	2452	12252	135	8502	71	6411	75	3532
		STDEV	STDEV	STDEV	STDEV	STDEV	STDEV	STDEV	STDEV	STDEV
A	100	5	98	553	3	433	1	3019	7	290
XG	100	17	10	3	7	4	8	9	41	7
C	100	23	1	99	0	140	1	19	17	1
AOC	75/20/5	2216	2979	1211	2452	2724	2495	1167	10	3925
AOXG	75/20/5	94	224	104	202	46	77	147	4	204
AO	75/25	1661	3673	340	2772	1748	2348	58	1	3587
APM	75/25	9	142	1813	13	938	7	1377	14	275

Table 17. Statistical comparisons (analysis of variance of log transformed data followed by Holm-Sidak multiple comparison tests) of Kd values for selected metals and amendment mixtures. Geometric means connected by the same letters are not significantly different (P<0.05).

Arsenic			Cadmium			Lead			Zinc		
Amendment mixture*	Geo Mean		Amendment mixture*	Geo Mean		Amendment mixture*	Geo Mean		Amendment mixture*	Geo Mean	
AOC	9441	A	O	24378	A	A	10715	A	AOC	16293	A
O	6637	A B	AOC	17906	A B	APM	6339	A B	BA	13964	A
AO	6266	A B	BA	13305	A B C	BA/O/C	5998	A B	O	13614	A
BAO	3034	A B	AO	10375	A B C	BA	5754	A B	AO	10990	A
BA/O/C	2972	B	BA/O/C	7079	A B C D	BAO	4966	A B	A	5000	A B
C	659	C	BAO	5309	B C D	AOC	4325	A B	BA/O/C	4083	A B
AOXG	640	C	A	4046	C D	AO	2805	B	APM	3524	A B
BAOXG	492	C	APM	2449	D E	AOXG	841	C	BAO	2489	A B
A	65	D	AOXG	902	E	C	731	C	AOXG	940	B C
APM	63	D	BAOXG	753	E	BAOXG	671	C	BAOXG	214	C D
XG	48	D	XG	71	F	O	641	C	XG	67	D
BA	41	D	C	49	F	XG	89	C	C	19	D

* A=apatite, O=organoclay OCB-750, C=chitosan, BA=biological apatite, XG=xanthan and guar gum, PM=organoclay PM-199

Evaluation of MAAC Formulations with Bentonite

An additional sorption study was conducted to quantitatively assess the effective sorption of contaminants by various mixtures of amendments including sand and bentonite. Four experiments were conducted to evaluate metal sorption by different mixtures. We decided to test Na- bentonite (Boroid Technology, Inc; Wyoming Bentonite) due to its high erosion resistance. Since biopolymers are biodegradable and might have adverse effects on benthic communities (Paller and Knox, 2010), we wanted to replace biopolymers with a material that can prevent erosion and help to significantly prolong the life of active caps. Bentonite is an absorbent aluminum phyllosilicate, generally impure clay consisting mostly of montmorillonite. There are different types of bentonites and their names depend on the dominant elements, such as potassium (K), sodium (Na), calcium (Ca), and aluminum (Al). Bentonite usually forms from weathering of volcanic ash, most often in the presence of water. For industrial purposes, mainly two classes of bentonite are used: sodium and calcium bentonite. Sodium bentonite expands when wet, possibly absorbing several times its dry mass in water. Because of its excellent colloidal properties it is often used in environmental investigations. The property of swelling also makes sodium bentonite useful as a sealant, especially for the sealing of subsurface disposal systems for spent nuclear fuel and for quarantining metal pollutants of groundwater. Similar uses include making slurry walls, waterproofing of below-grade walls and forming other impermeable barriers; e.g., to seal off the annulus of a water well, to plug old wells, or as a liner in the base of landfills to prevent migration of leachate. It is also known to be useful for erosion control, but its considerable potential for remediation of contaminants in sediments has not been exploited.

Addition of up to 25% bentonite to sand increased sorption of Cr and Pb. However, addition of more than 25% bentonite reduced the sorption capacity of bentonite/sand mixtures (Figure 2, Table 18). Sorption of Cd and Zn slightly increased with increasing amounts of bentonite in bentonite/sand mixtures (Figure 3, Table 18). A similar pattern was observed for Co and Ni (Figure 4, Table 18). Only As and Se were not sorbed by bentonite in the bentonite/sand mixture. At additions of bentonite exceeding 50%, higher concentrations of both elements were observed than in the spike solution, indicating release of As and Se from the mineral structure of bentonite (Figure 5, Table 18).

The following amendment mixtures were evaluated for best metal sorption capacity with addition of 0 to 30% bentonite:
1) apatite, organoclay (PM-199), and sand
2) apatite, zeolite (clinoptilolite), and sand
3) apatite, organoclay (PM – 199), zeolite (clinoptilolite), and sand.
One hundred percent bentonite was also used for comparison. The metal sorption results for the amendment mixtures with bentonite are presented in Figures 6 – 11, Tables 19 - 21. Differences between mixtures containing up to 30% bentonite were not significant indicating that the addition of bentonite did not decrease the sorptive capacity of the other amendments. Mixtures of amendments containing bentonite exhibited greater sorption of metals than 100% bentonite in all cases (Figures 6 – 11, Table 19 - 21).

Table 18. Effect of bentonite on As, Cd, Cr, Co, Cu, Ni, Se, Zn, and Pb sorption. Treatments are described in Table 3.

Treatments	Replicates	Cr	Co	Ni	Cu	Zn	As	Se	Cd	Pb
Control	1	5015	5163	5356	5270	5173	4990	4540	5054	5230
	2	4998	5143	5287	5235	5200	4996	4566	5029	5212
	3	5032	5183	5452	5305	5146	4984	4514	5079	5248
	AVG	5015	5163	5365	5270	5173	4990	4540	5054	5230
	STDEV	17	20	83	35	27	6	26	25	18
S100/B0	1	4592	5267	5520	5203	5305	5034	4337	5362	4007
	2	4761	5172	5387	5104	5193	5143	4546	5007	5054
	3	5023	5167	5456	5200	5345	5154	4566	5079	5213
	AVG	4792	5202	5454	5169	5281	5110	4483	5149	4758
	STDEV	217	56	67	56	79	66	127	188	655
S95/B5	1	1587	4926	5148	4777	4980	5157	4751	4831	4316
	2	842.9	4731	4936	4621	4786	5103	4538	4630	4647
	3	1230	4879	4987	4657	4789	5100	4537	4769	4435
	AVG	1220	4845	5024	4685	4852	5120	4609	4743	4466
	STDEV	372	102	111	82	111	32	123	103	168
S90/B10	1	485	4283	4465	4152	4337	5067	4677	4224	3115
	2	596	4434	4624	4296	4485	5061	4827	4328	3730
	3	512	4356	4567	4168	4327	5061	4769	4274	3457
	AVG	531	4358	4552	4205	4383	5063	4758	4275	3434
	STDEV	58	76	81	79	88	3	76	52	308
S85/B15	1	278.7	3592	3749	3558	3662	5117	4768	3584	3118
	2	420.5	4096	4255	3964	4158	5102	4899	4021	2981
		320	3678	3980	3789	3789	5100	4800	3678	3000
	AVG	340	3789	3995	3770	3870	5106	4822	3761	3033
	STDEV	73	270	253	204	258	9	68	230	74
S80/B20	1	137.5	2862	2971	2837	2950	4774	4315	2984	1100
	2	182.2	3111	3250	3115	3212	4833	4442	3238	1759
	3	145	2980	3012	2980	2950	4770	4312	2976	1309
	AVG	155	2984	3078	2977	3037	4792	4356	3066	1389
	STDEV	24	125	151	139	151	35	74	149	337
S75/B25	1	198	3195	3340	3256	2962	4453	4306	2632	1456
	2	236.6	3366	3497	3535	3542	4859	4662	3676	1648
	3	172	3293	3308	3317	3465	4756	4576	3546	1343
	AVG	202	3285	3382	3369	3323	4689	4515	3285	1482
	STDEV	33	86	101	147	315	211	186	569	154
S50/B50	1	1943	2932	3056	2924	3138	7350	5560	3054	2490
	2	1653	3235	4435	4238	3535	6790	6813	3319	2260
	3	1549	3213	3823	3873	2925	6387	4831	2927	2233
	AVG	1715	3127	3771	3678	3199	6842	5735	3100	2328
	STDEV	204	169	691	678	310	484	1002	200	141
S25/B75	1	1846	2439	2521	1858	2452	7103	5601	2176	2804
	2	1855	2398	2533	1830	2496	6860	5796	2279	2831
	3	1836	2239	2451	1868	2462	7203	5801	2176	2824
	AVG	1846	2359	2502	1852	2470	7055	5733	2210	2820
	STDEV	10	106	44	20	23	176	114	59	14
S0/B100	1	1581	2006	2105	1644	2212	8158	6240	1903	2949
	2	1608	1957	2080	1734	2213	8225	6260	1933	2842
	3	1552	1923	2022	1729	2221	8270	6133	1876	2946
	AVG	1580	1962	2069	1702	2215	8218	6211	1904	2912
	STDEV	28	42	43	51	5	56	68	29	61

Table 19. Effect of bentonite addition to an amendment mixture (apatite, organoclay, and sand) on As, Cd, Cr, Co, Cu, Ni, Se, Zn, and Pb sorption. Treatments are described in Table 4.

Treatments	Replicate	Cr	Co	Ni	Cu	Zn	As	Se	Cd	Pb
Control	1	5015	5163	5356	5270	5173	4990	4540	5054	5230
	2	4998	5143	5287	5235	5200	4996	4566	5029	5212
	3	5032	5183	5452	5305	5146	4984	4514	5079	5248
	AVG	**5015**	**5163**	**5365**	**5270**	**5173**	**4990**	**4540**	**5054**	**5230**
	STDEV	**17**	**20**	**83**	**35**	**27**	**6**	**26**	**25**	**18**
A25/O25/S50/B0	1	103.3	3291	3756	139	421	2759	3558	625	164
	2	63	4007	4382	102.8	976	2699	3795	1286	107
	3	102	3700	4200	124	769	2698	3566	879	125
	AVG	**89**	**3666**	**4113**	**122**	**722**	**2719**	**3640**	**930**	**132**
	STDEV	**23**	**359**	**322**	**18**	**281**	**35**	**135**	**333**	**29**
A25/O25/S40/B10	1	75.6	3548	3810	619	1100	2920	3730	1476	123
	2	103.3	4223	4511	585	836	2790	3577	1123	138
	3	78	3698	3987	596	861	2792	3600	1145	129
	AVG	**86**	**3823**	**4103**	**600**	**932**	**2834**	**3636**	**1248**	**130**
	STDEV	**15**	**354**	**365**	**17**	**146**	**74**	**83**	**198**	**7**
A25/O25/S30/B20	1	90.9	3366	3623	305	2071	3216	4200	2110	138
	2	5	3259	3378	202	1765	3115	4114	1750	132
	3	2	3312	3416	126	1648	3102	3988	1709	102
	AVG	**33**	**3312**	**3472**	**211**	**1828**	**3144**	**4101**	**1856**	**124**
	STDEV	**50**	**54**	**132**	**90**	**218**	**62**	**107**	**221**	**19**
A25/O25/S20/B30	1	88	2509	2705	124	733.3	2972	3964	1130	138
	2	95	2393	2614	124	597.2	3058	3799	1018	172
	AVG	**92**	**2451**	**2660**	**124**	**665**	**3015**	**3882**	**1074**	**155**
	STDEV	**5**	**82**	**64**	**0**	**96**	**61**	**117**	**79**	**24**
A0/O0/S0/B100	1	1670	2096	2140	1871	2376	8759	6588	2035	3192
	2	1552	1923	2022	1729	2221	8270	6133	1876	2946
	3	1592	1872	1909	1765	2143	8183	6258	1828	3025
	AVG	**1605**	**1964**	**2024**	**1788**	**2247**	**8404**	**6326**	**1913**	**3054**
	STDEV	**60**	**117**	**116**	**74**	**119**	**311**	**235**	**108**	**126**

Table 20. Effect of bentonite addition to an amendment mixture (sand, apatite, and zeolite - clinoptilolite) on As, Cd, Cr, Co, Cu, Ni, Se, Zn, and Pb sorption. Treatments are described in Table 5.

Treatments	Replicates	Cr	Co	Ni	Cu	Zn	As	Se	Cd	Pb
Control	1	5015	5163	5356	5270	5173	4990	4540	5054	5230
	2	4998	5143	5287	5235	5200	4996	4566	5029	5212
	3	5032	5183	5452	5305	5146	4984	4514	5079	5248
	AVG	**5015**	**5163**	**5365**	**5270**	**5173**	**4990**	**4540**	**5054**	**5230**
	STDEV	**17**	**20**	**83**	**35**	**27**	**6**	**26**	**25**	**18**
A25/Z25/S50/B0	1	2	2386	3160	57	328	3183	3994	577	174
	2	0	2384	3406	48	333	3196	3489	561	172
	3	0	2384	3150	48	330	3173	3458	569	172
	AVG	**1**	**2385**	**3239**	**51**	**330**	**3184**	**3647**	**569**	**173**
	STDEV	**1**	**1**	**145**	**5**	**3**	**12**	**301**	**8**	**1**
A25/Z25/S40/B10	1	0	1380	1777	18.08	135.5	3168	3253	348.7	148.6
	2	0	1742	2216	21.81	178.6	3339	3727	430.2	150.2
	3	0	1430	1890	21	156	3256	3268	367	148
	AVG	**0**	**1517**	**1961**	**20**	**157**	**3254**	**3416**	**382**	**149**
	STDEV	**0**	**196**	**228**	**2**	**22**	**86**	**269**	**43**	**1**
A25/Z25/S30/B20	1	0	1480	1884	14.2	185	3428	3781	427	150
	2	0	1977	2583	49.0	435	3564	3818	683	194
	AVG	**0**	**1729**	**2234**	**32**	**310**	**3496**	**3800**	**555**	**172**
	STDEV	**0**	**351**	**494**	**25**	**177**	**96**	**26**	**181**	**31**
A25/Z25/S20/B30	1	0	1369	1710	21.47	245	3481	3936	532.4	150.2
	2	5	1047	1313	58.05	226.8	3505	4167	425.2	106
	AVG	**3**	**1208**	**1512**	**40**	**236**	**3493**	**4052**	**479**	**128**
	STDEV	**4**	**228**	**281**	**26**	**13**	**17**	**163**	**76**	**31**
A0/Z0/S0/B100	1	1592	1984	2150	1560	2065	8383	6284	1834	3051
	2	1609	2071	2208	1577	2243	8307	6281	1963	3051
	3	1552	1923	2022	1729	2221	8270	6133	1876	2946
	AVG	**1584**	**1993**	**2127**	**1622**	**2176**	**8320**	**6233**	**1891**	**3016**
	STDEV	**29**	**74**	**95**	**93**	**97**	**58**	**86**	**66**	**61**

Table 21. Effect of bentonite addition to an amendment mixture (sand, apatite, organocly – PM-199, and zeolite - clinoptilolite) on As, Cd, Cr, Co, Cu, Ni, Se, Zn, and Pb sorption. Treatments are described in Table 5.

| Treatments	Replicates	Cr	Co	Ni	Cu	Zn	As	Se	Cd	Pb
Control	1	5015	5163	5356	5270	5173	4990	4540	5054	5230
	2	4998	5143	5287	5235	5200	4996	4566	5029	5212
	3	5032	5183	5452	5305	5146	4984	4514	5079	5248
	AVG	5015	5163	5365	5270	5173	4990	4540	5054	5230
	STDEV	17	20	83	35	27	6	26	25	18
A25/O25/Z25/S25/B0	1	89.6	2431	3294	73	449.3	3138	3815	848	170
	2	78	2490	3348	52	531.8	3273	4043	1044	165
	3	79	2457	3269	58	489	3260	3845	876	170
	AVG	82	2459	3304	61	490	3224	3901	923	168
	STDEV	6	30	40	10	41	74	124	106	3
A25/O25/Z25/S20/B5	1	108	2088	2710	12	351	3049	3968	804	156
	2	82	2354	3151	47	527	3289	3892	1003	170
	3	82	2100	2790	23	430	3279	3890	809	160
	AVG	90	2181	2884	27	436	3206	3917	872	162
	STDEV	15	150	235	18	88	136	44	113	7
A25/O25/Z25/S15/B10	1	110	2617	3414	312.4	1287	3695	4543	1795	183
	2	100	2129	2830	166.6	498.8	3310	3823	956	183
	AVG	105	2373	3122	240	893	3503	4183	1375	183
	STDEV	7	345	413	103	557	272	509	593	0
A25/O25/Z25/S10/B15	1	0	2092	2790	204.2	754.6	3522	3871	1120	131.7
	2	0	2043	2769	185.4	629.9	3606	3954	929.7	181.1
	AVG	0	2068	2780	195	692	3564	3913	1025	156
	STDEV	0	35	15	13	88	59	59	135	35
A25/O25/Z25/S5/B20	1	81	1572	1998	131	297	3477	4149	680	183
	2	97	1895	2456	174	500	3497	3773	827	180
	AVG	89	1734	2227	152	398	3487	3961	754	181
	STDEV	11	228	324	30	143	14	266	104	2
A25/O25/Z25/S0/B25	1	50	1292	1651	38	145	3090	3624	365	103
	2	23	1952	2525	174	716	3556	3804	928	175
	3	45	1872	2394	167	778	3407	3852	988	102
	AVG	39	1705	2190	126	546	3351	3760	760	127
	STDEV	14	360	471	77	349	238	120	344	42
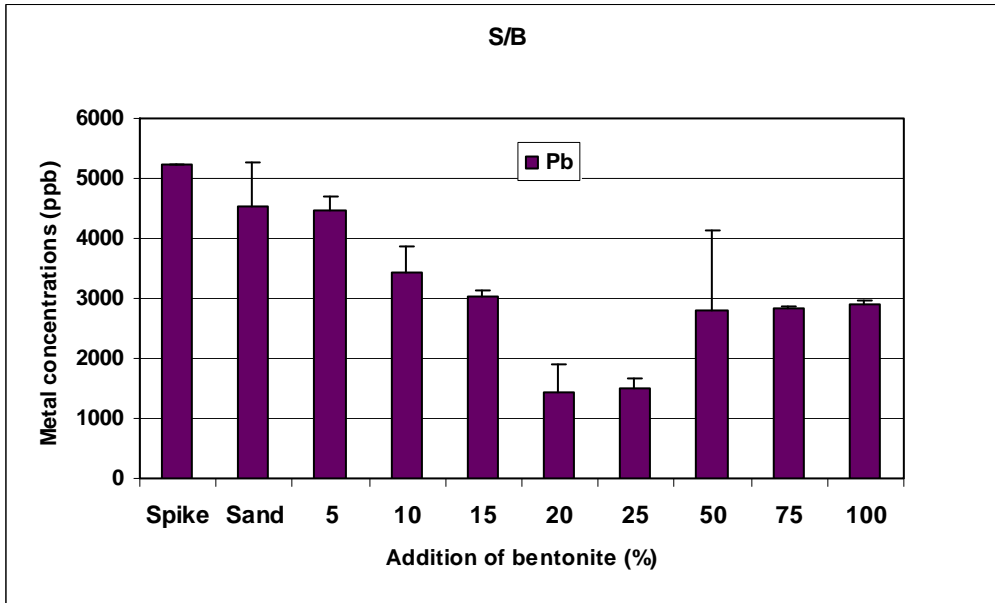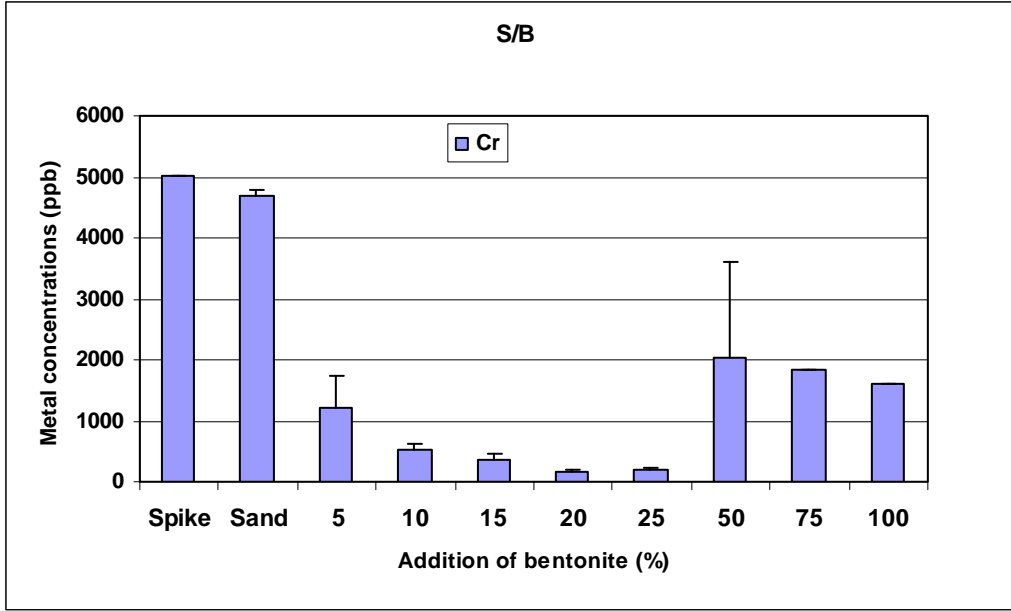
Figure 2. Effect of bentonite addition to sand on Cr and Pb sorption. Treatments are described in Table 3.
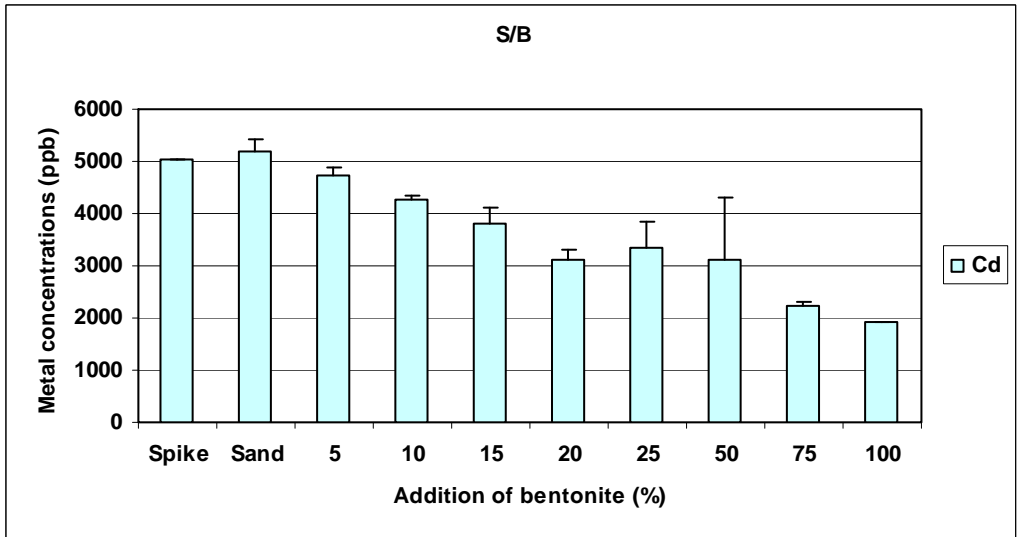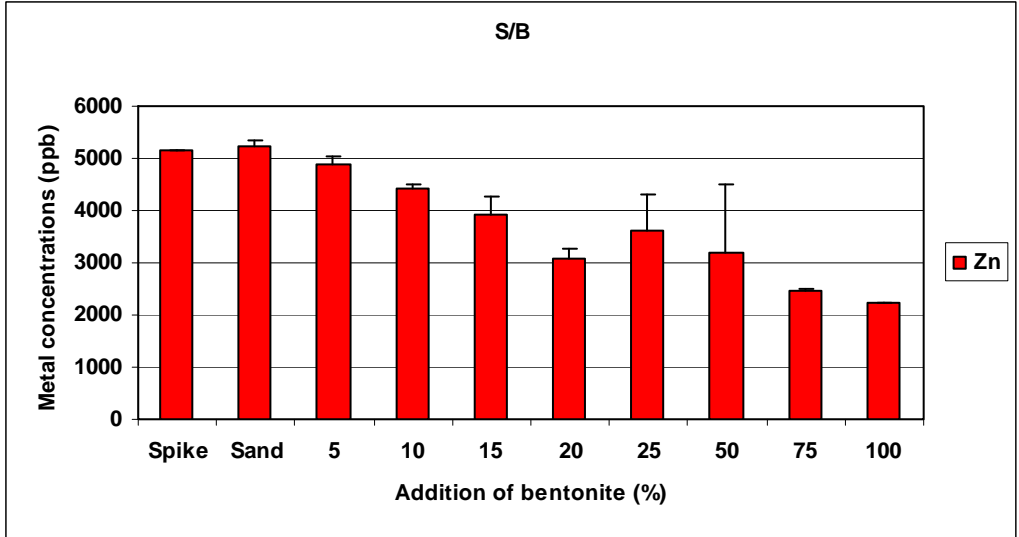
Figure 3. Effect of bentonite addition to sand on Cd and Zn sorption. Treatments are described in Table 3.
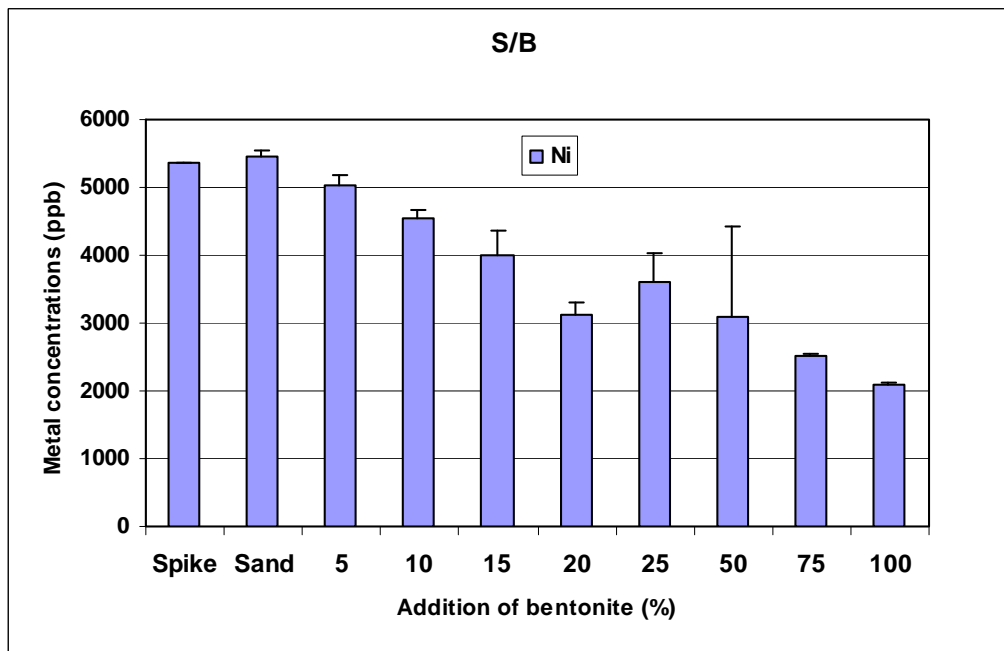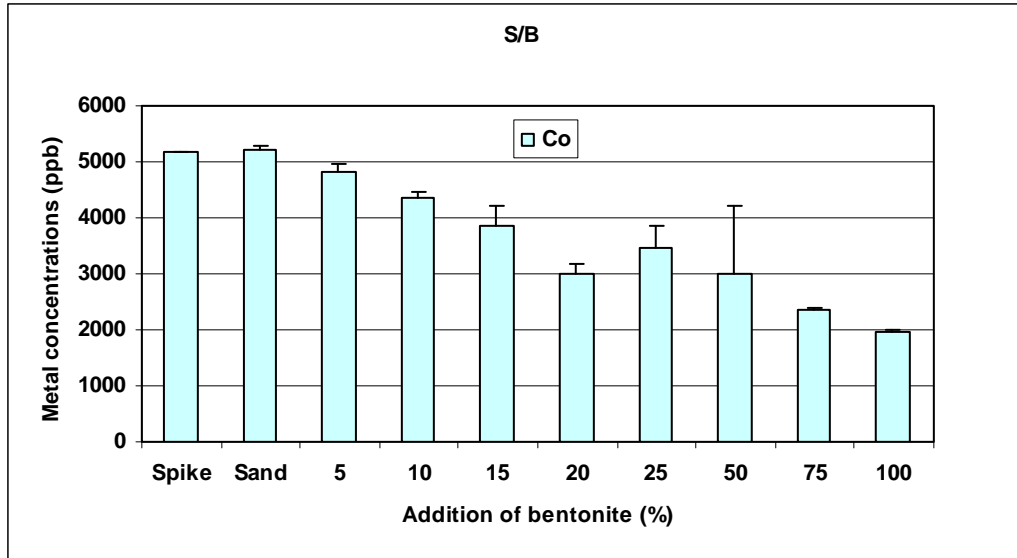
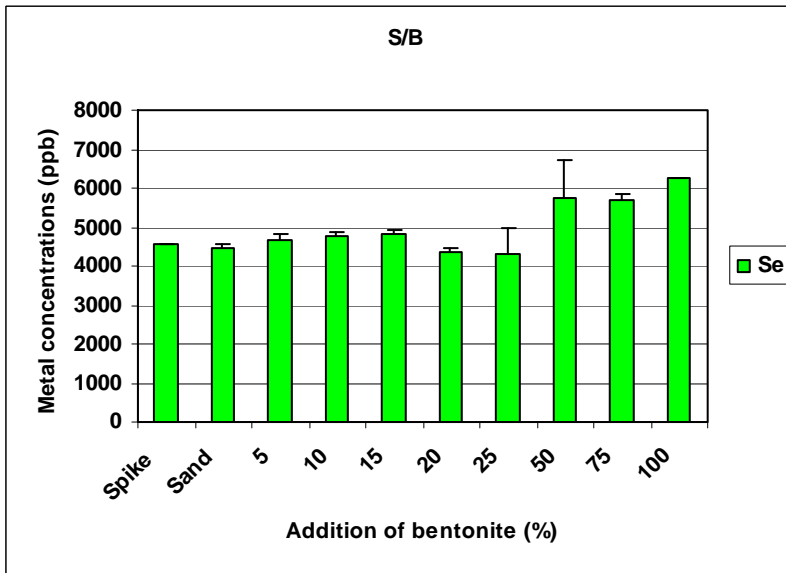**Figure 4. Effect of bentonite addition to sand on Co and Ni sorption. Treatments are described in Table 3.**
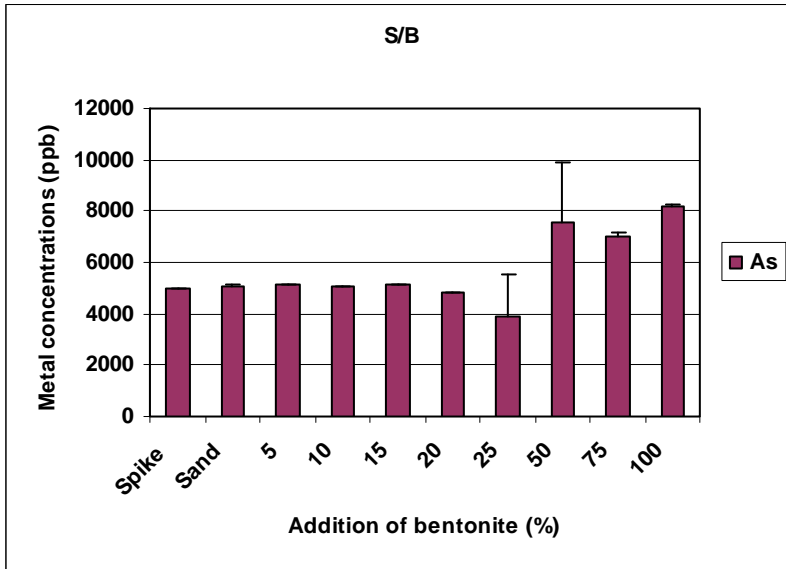
Figure 5. Effect of bentonite addition to sand on As and Se sorption. Treatments are described in Table 3.
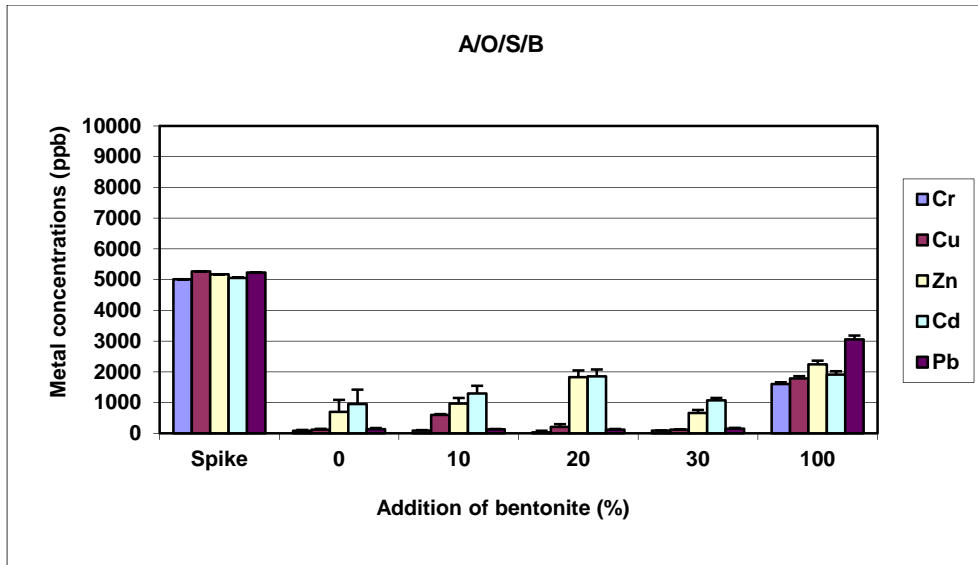
Figure 6. Effect of bentonite addition to an amendment mixture (apatite, organoclay, and sand) on Cd, Cr, Cu, Zn, and Pb sorption. Treatments are described in Table 4.
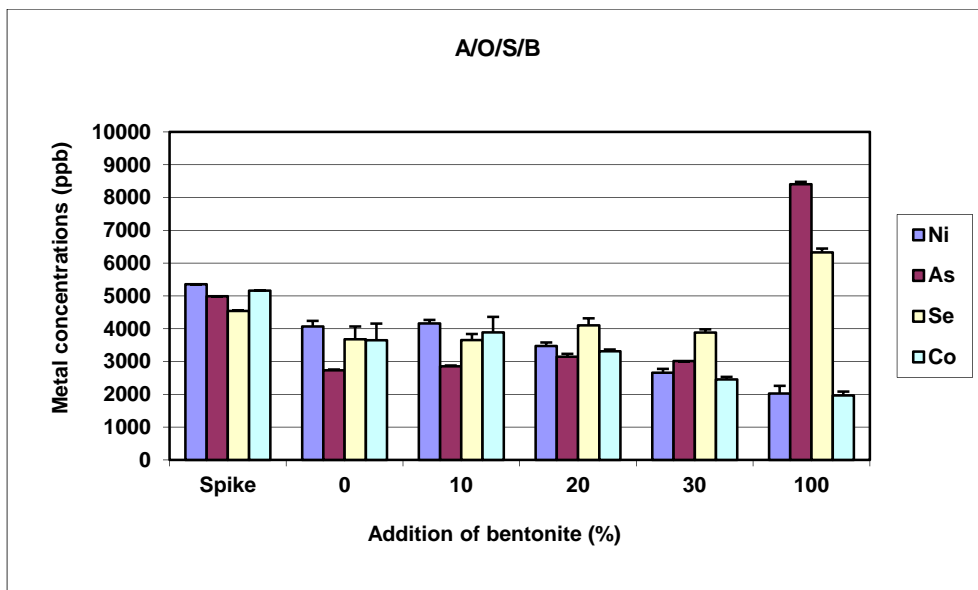

Figure 7. Effect of bentonite addition to an amendment mixture (apatite, organoclay, and sand) on As, Co, Ni, and Se sorption. Treatments are described in Table 4.
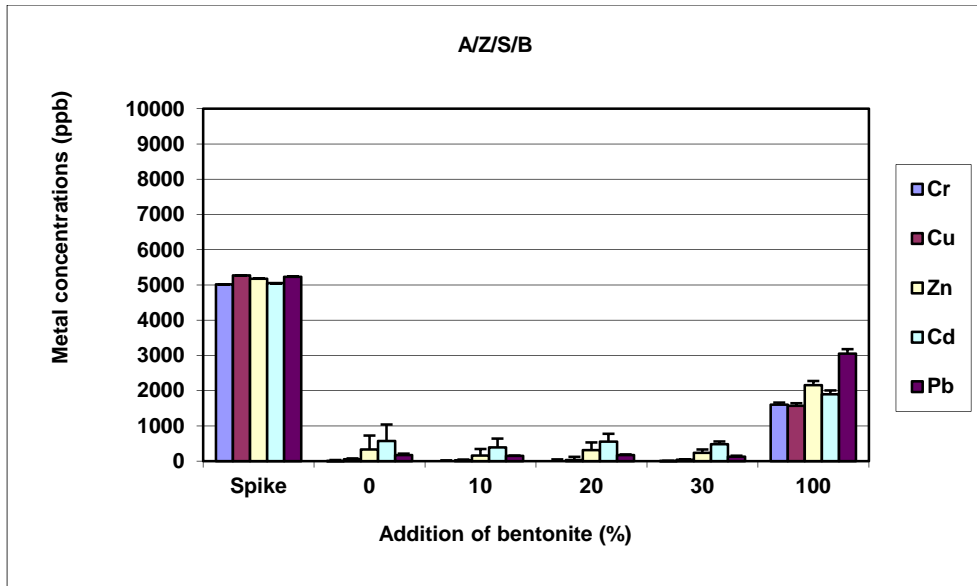
Figure 8. Effect of bentonite addition to an amendment mixture (apatite, zeolite – clinoptilolite, and sand) on Cd, Cr, Cu, Zn, and Pb sorption. Treatments are described in Table 5.
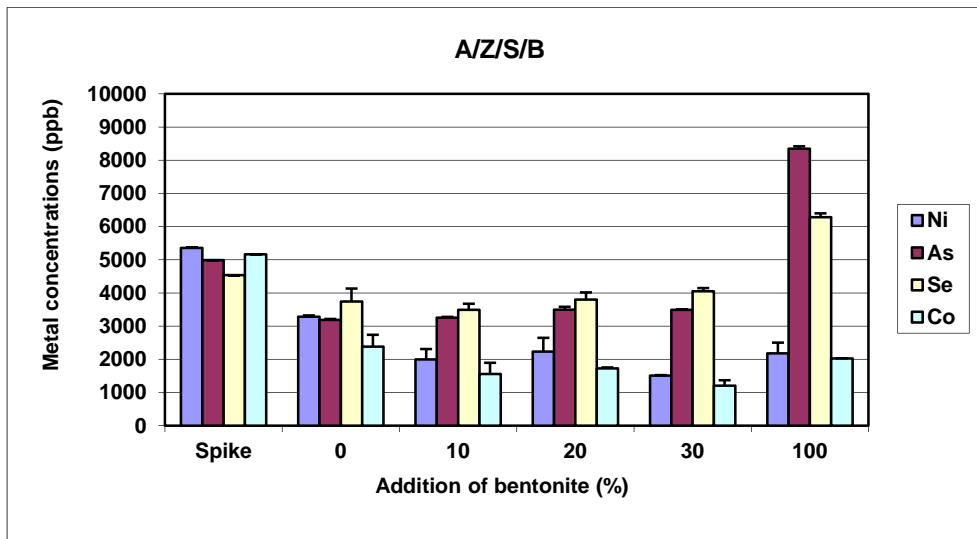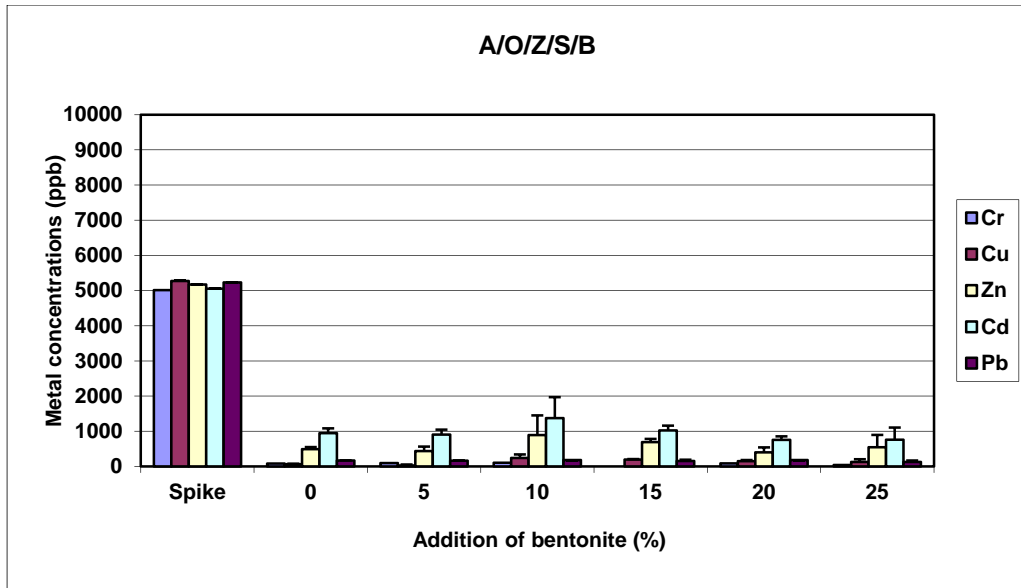

Figure 9. Effect of bentonite addition to an amendment mixture (apatite, zeolite – clinoptilolite, and sand) on As, Co, Ni, and Se sorption. Treatments are described in Table 5.

Figure 10. Effect of bentonite addition to an amendment mixture (apatite, organoclay, zeolite – clinoptilolite, and sand) on Cd, Cr, Cu, Zn, and Pb sorption. Treatments are described in Table 6.
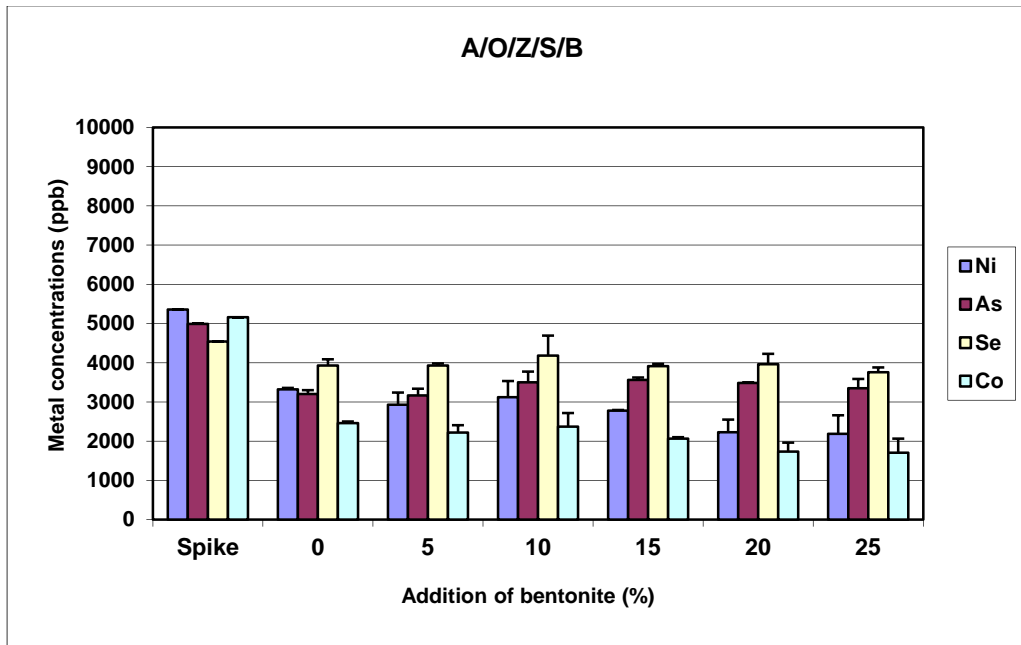

Figure 11. Effect of bentonite addition to an amendment mixture (apatite, organoclay, zeolite – clinoptilolite, and sand) on As, Co, Ni, and Se sorption. Treatments are described in Table 6.

TASK 2. PREDICTING THE RELEASE OF CONTAMINANTS OVER TIME FROM MAAC FORMULATIONS BY NUMERICAL MODELING

Inorganic Contaminants

Laboratory column experiments were conducted to evaluate the effectiveness of amendments and amendment mixtures in sequestering inorganic contaminants. The average dry bulk densities of the amendments and amendment mixtures in the apatite (NCA), apatite/organoclay (AO). and apatite/organoclay/chitosan (AOC) columns were determined to be 1.89, 1.39, and 1.46 g/cm^3, respectively. The porosity of the NCA and AOC column was calculated from the bromide BTC, and the results are presented in Table 7. The total volume of each column was estimated to be 203 cm^3. The saturated hydraulic conductivity of each amendment mixture was estimated using a constant head method (Mariotte tube) and the results are presented in Table 7. The bromide breakthrough curve (BTC) for the AOC column is presented in Figure 12.
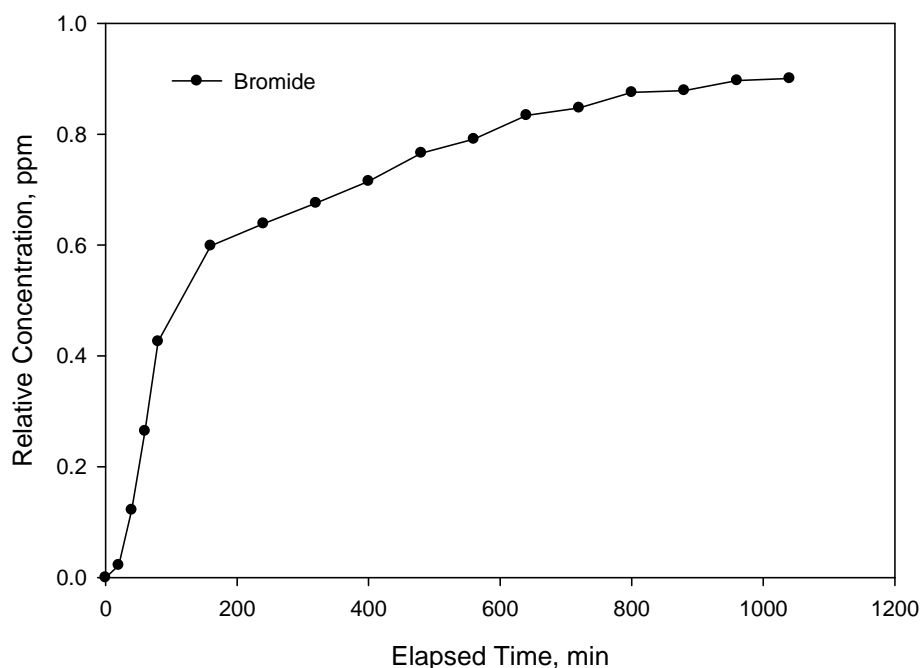
Figure 12. Bromide breakthrough curve for the AOC column containing 75% apatite, 20% organoclay (OCB -750), and 5% chitosan.

In addition to the laboratory column experiments, a 1-dimensional numerical transport model was created using the PORFLOW code to further evaluate the effectiveness of each mixture (ACRI, 2004). The same general model framework was used for each mixture with material properties being the only difference. Three cases were simulated using the 1-dimensional model: 1) apatite, 2) apatite-organoclay mixture (AO), and 3) apatite-organoclay-chitosan mixture (AOC). The results of the modeling are shown in Figures 13 through 15. Each figure shows the

breakthrough curve for selected metals and a conservative tracer as well as nomographs for determining the required amendment thickness to delay contaminant breakthrough for a given time period. For the breakthrough analysis, a steady state advective flux of 4.11E-04 cm/sec (Darcy velocity) was used with a thickness of 10 cm. The nomographs were then scaled from the breakthrough curves. Flow rates indicated on the nomographs are per unit area of material available for flow (cm^2).

Nomographs are presented for As, Co, and Ni. These graphs provide a comparison of the effectiveness of each amendment or amendment mixture for retarding the movement of these metals. When compared to the amendment mixtures AO and AOC, apatite appeared less effective in sequestering As, Co, and Ni. The breakthrough curves show that the amendment mixtures effectively sequestered more metals compared with only apatite. U and Pb are examples where apatite was more effective than the amendment mixtures. The performance of the amendment mixtures could likely be improved for some metals by increasing the percentage of apatite relative to the other amendments.

Two cases were simulated using the 1-dimensional model for clinoptilolite zeolite (ZC) and phillipsite zeolite (ZP). The results of the modeling are shown in Figures 16 and 17. Each figure shows the breakthrough curve for selected metals and a conservative tracer. Nomographs were created for determining the required amendment thickness to delay contaminant breakthrough for a given time period (Figures 18 and 19). For the breakthrough analysis, a steady state advective flux of 4.11E-04 cm/sec (Darcy velocity) was used with a thickness of 10 cm. The nomographs were then scaled from the breakthrough curves. Flow rates indicated on the nomographs are per unit area of material available for flow (cm^2).

Figures 16 and 17 show that arsenic (As) and selenium (Se) were not significantly sorbed by either of the zeolites. However, cadmium (Cd), cobalt (Co), nickel (Ni), zinc (Zn) and lead (Pb) were sorbed by both materials. Similar sorption characteristics were noted between clinoptilolite and phillipsite for Zn, Ni, and Co. Clinoptilolite appeared to better sequester Pb, whereas phillipsite better sequestered Cd. Nomographs are presented for Pb, Cd, and Ni (Figures 18 and 19). These graphs provide a comparison of the effectiveness of each amendment for retarding the movement of these metals.
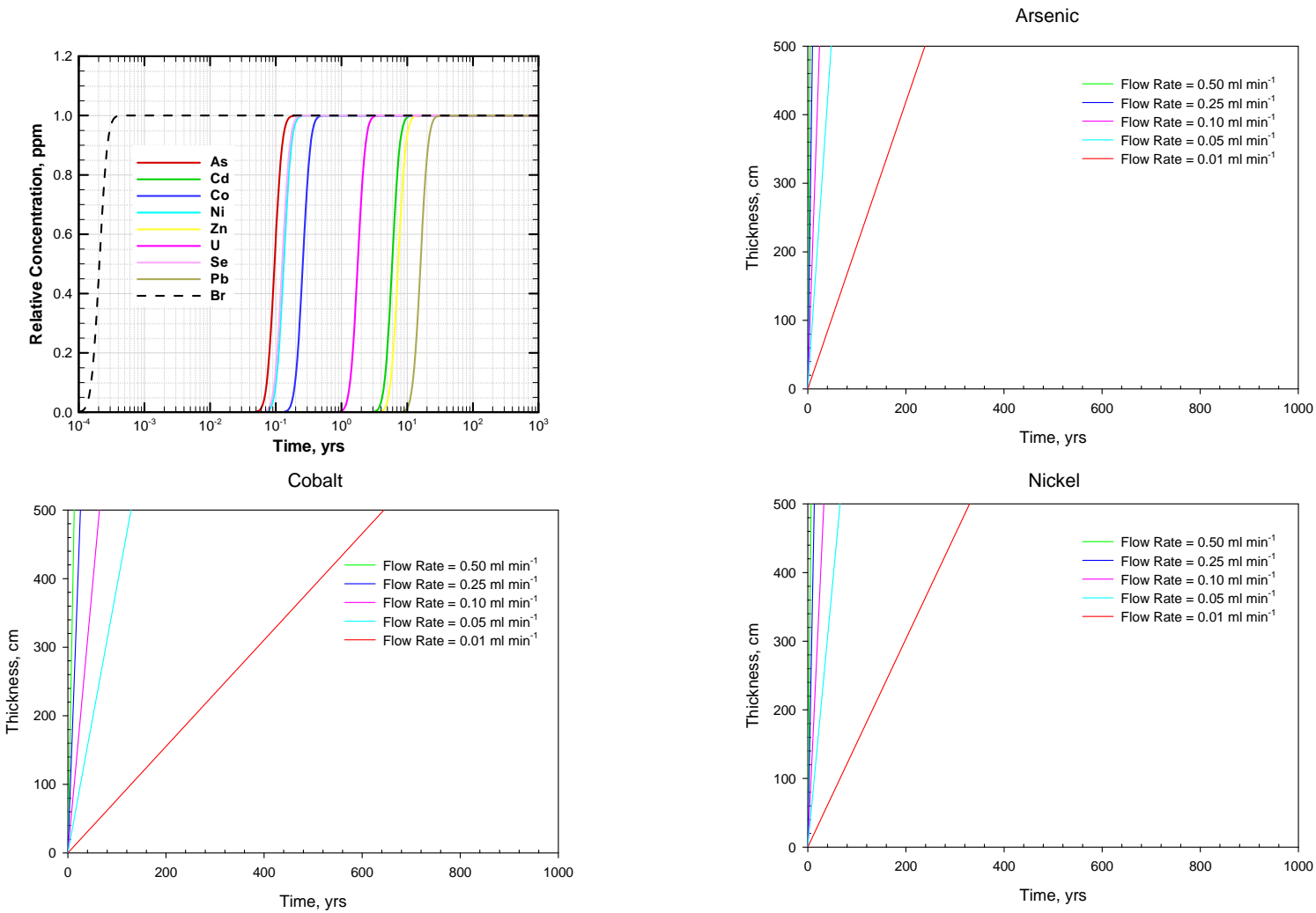
Figure 13. Breakthrough curve (Darcy velocity = 4.11E-04 cm/sec, thickness 10 cm) and material thickness nomographs for apatite.

Figure 14. Breakthrough curve (Darcy velocity = 4.11E-04 cm/sec, thickness 10 cm) and material thickness nomographs for AO mixture (apatite-organoclay).
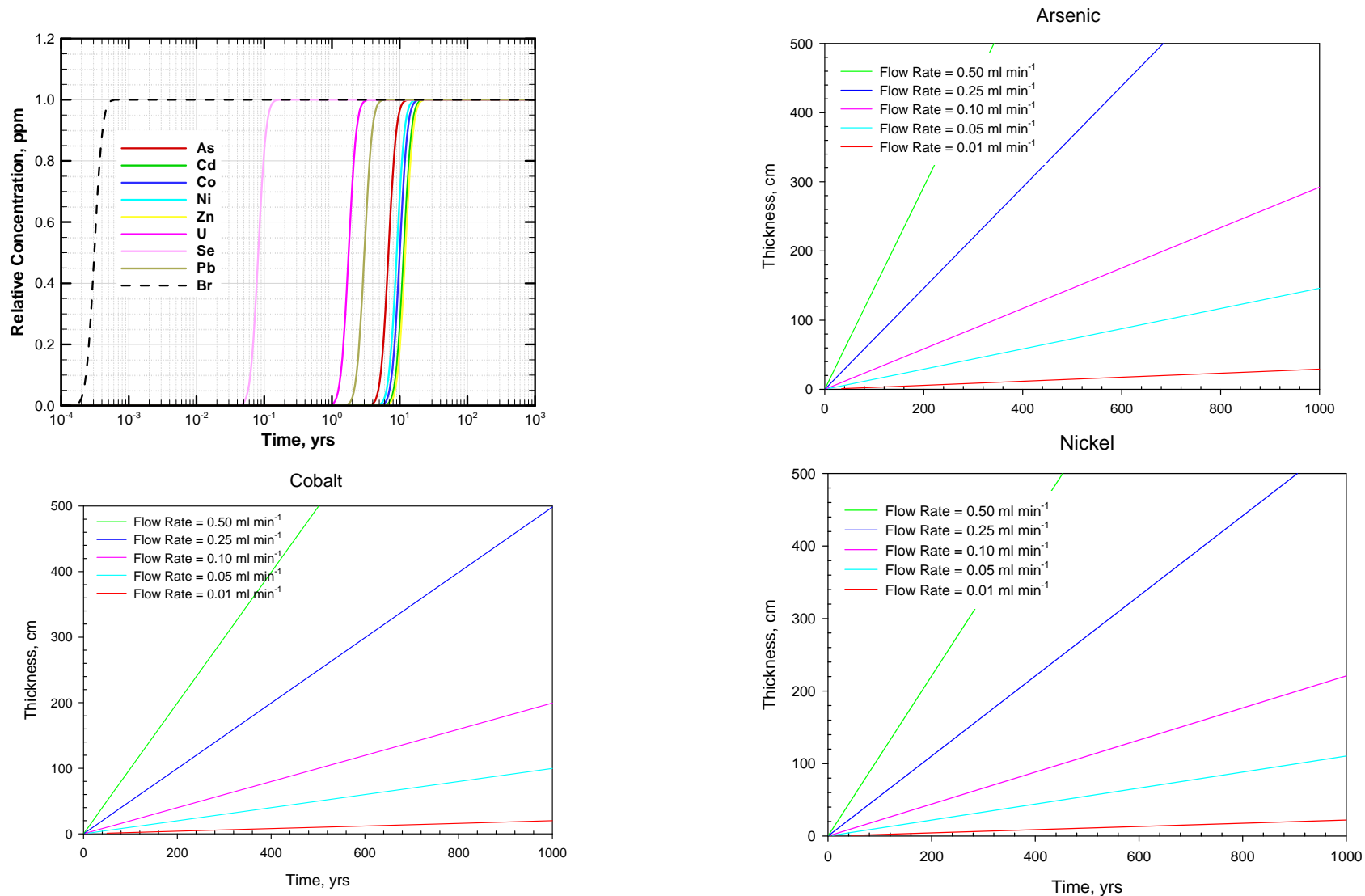
Figure 15. Breakthrough curve (Darcy velocity = 4.11E-04 cm/sec, thickness 10 cm) and material thickness nomographs for AOC mixture (apatite-organoclay-chitosan).

Figure 16. Breakthrough curves for metals in zeolite – phillipsite.

Figure 17. Breakthrough curves for metals in zeolite – clinoptilolite.

Figure 18. Breakthrough curve (Darcy velocity = 4.11E-04 cm/sec, thickness 10 cm) and material thickness nomographs for clinoptilolite zeolite.

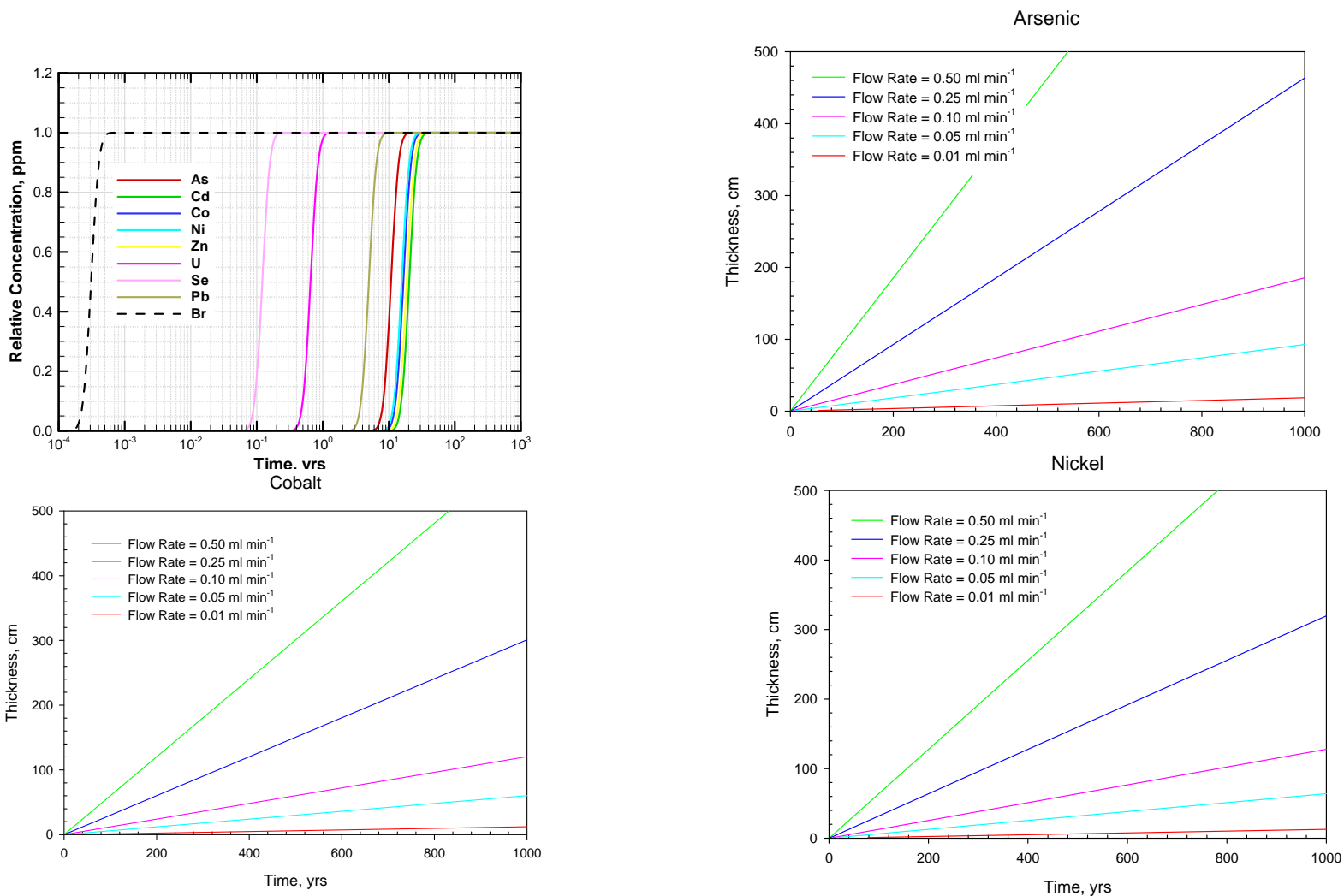**Figure 19. Breakthrough curve (Darcy velocity = 4.11E-04 cm/sec, thickness 10 cm) and material thickness nomographs for phillipsite zeolite.**

TASK 3. TOXICITY EVALUATION
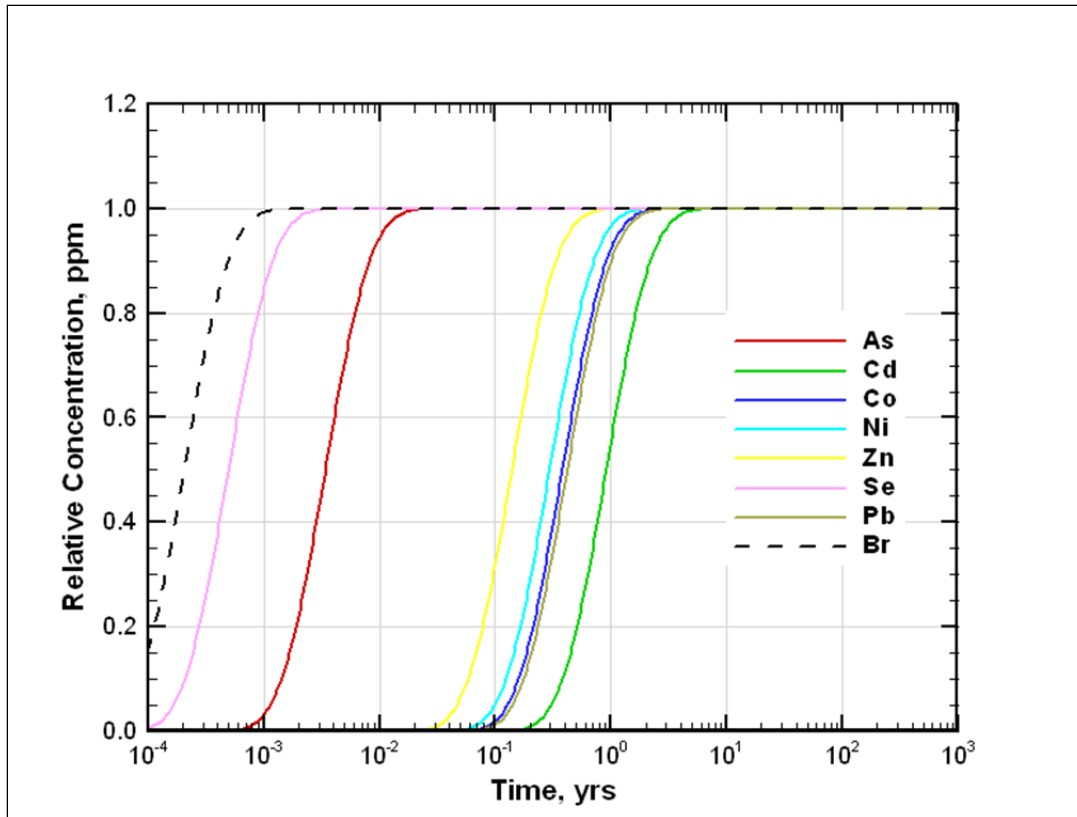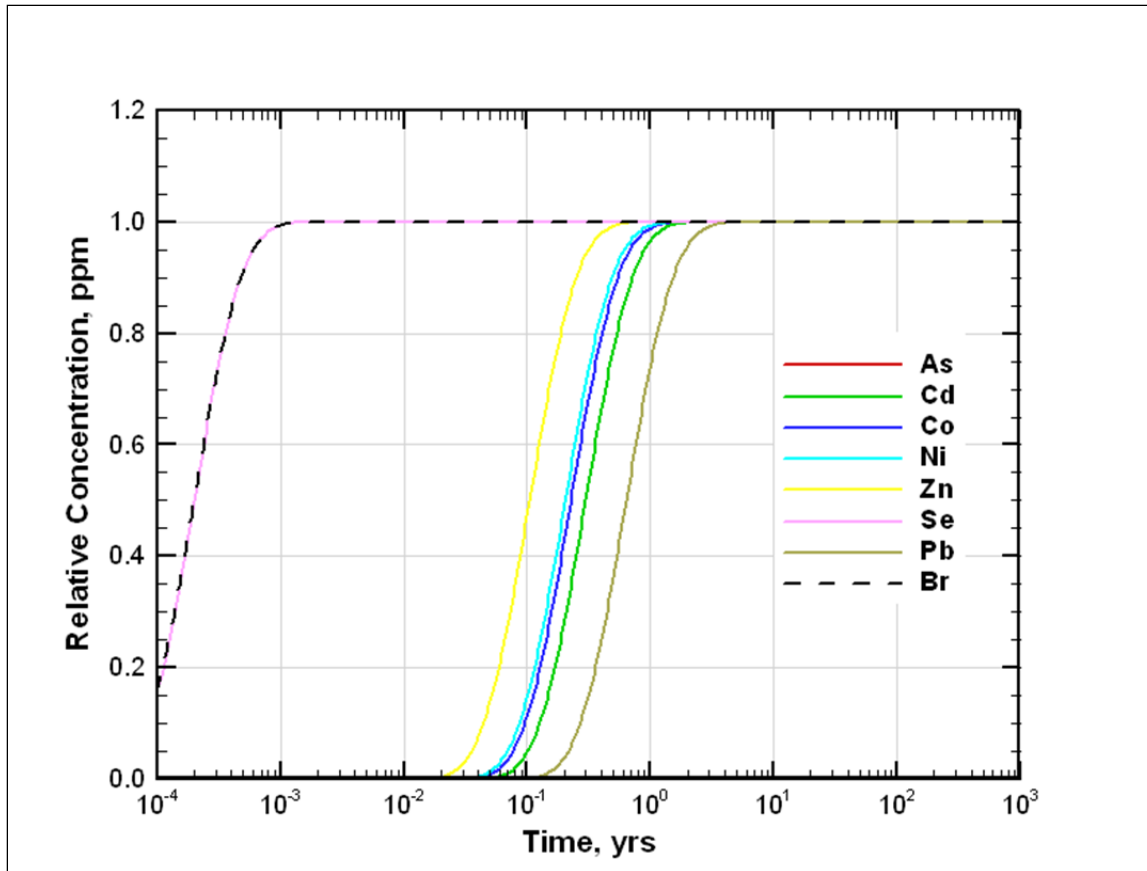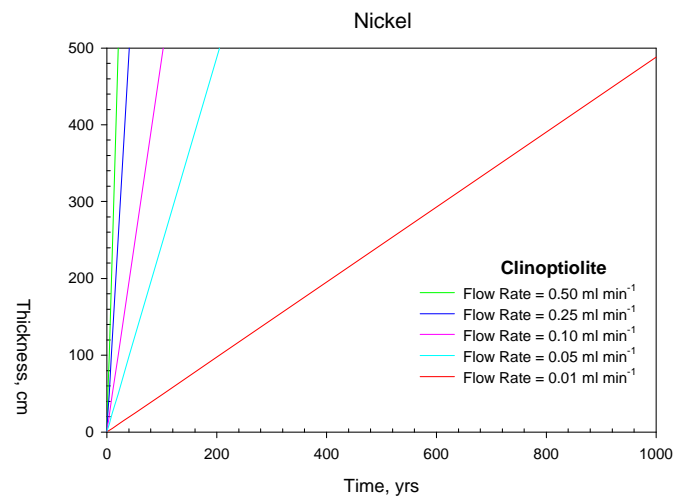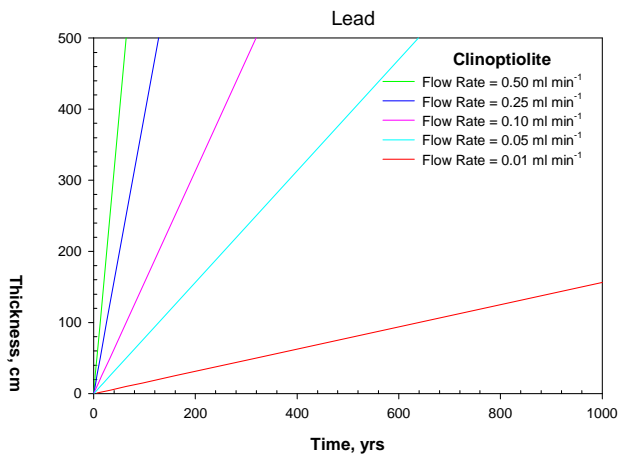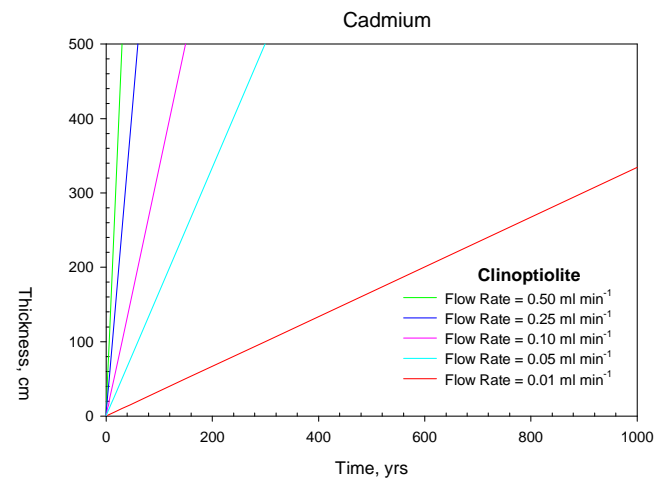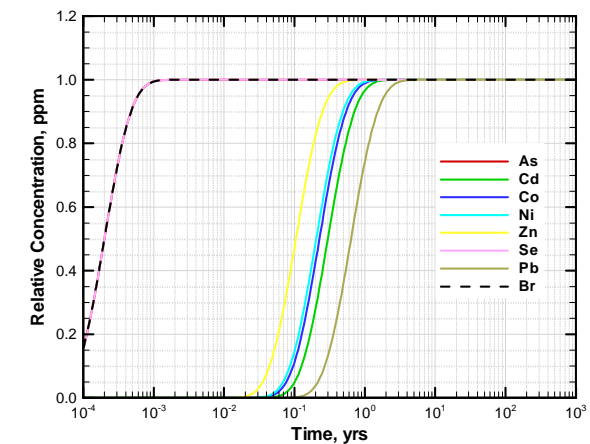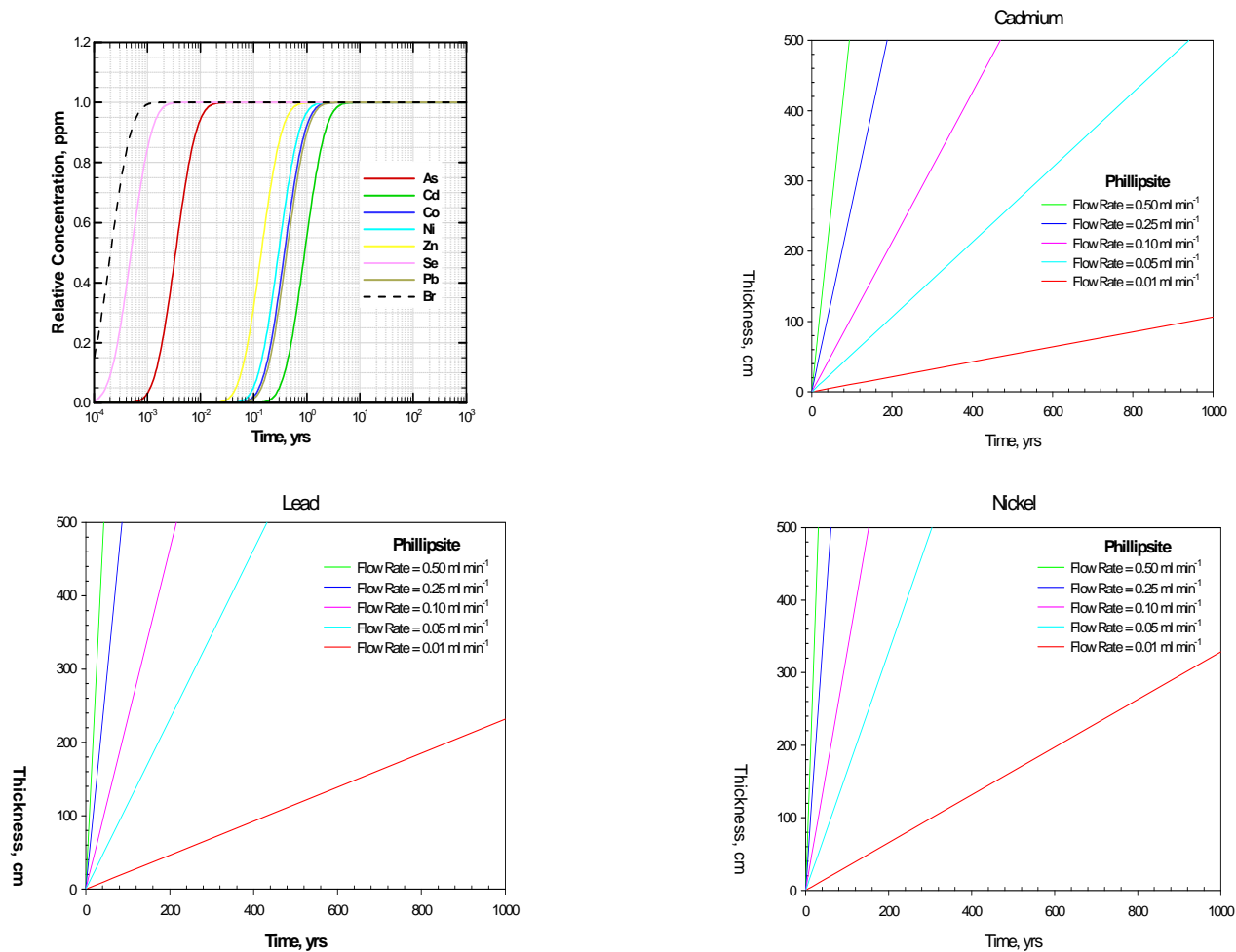
Laboratory acute toxicity tests employing *Hyalella azteca* were used to assess the possible toxicity of different MAAC formulation to aquatic organisms. *Hyalella azteca* was selected over other benthic organisms (such as annelids) for these tests because of its comparatively greater sensitivity to the toxicity of some amendments (Knox et al. 2010). The survival of *Hyalella azteca* was greatest in Steel Creek sand (68%) followed by the MAAC formulations consisting of apatite and organoclay PM-199 (APM-0, 55%) and sand, apatite, and organoclay PM-199 (SAPM-30, 37.5%) (Figure 20, Table 22). Survival in commercial playground sand averaged 35%, and survival in all other MAAC formulations was very low or zero. Test organisms in contact with all MAACs containing organoclay OCB-750 died within 30 minutes as a result of pHs that reached 11 to 12 or greater. Similarly, organisms in contact with MAACs containing biopolymers (xanthan gum cross-linked with guar gum and chitosan) died as a result of entrapment within the viscous biopolymer matrix formed by biopolymers and/or oxygen depletion of the test water due to biodegradation of the biopolymers.

In summary, these test results indicate that xanthan gum crossed linked with guar gum can harm benthic organisms by physical entrapment and/or suffocation. Organoclay toxicity varies with different types of organoclay and, in the case of OCB-750, is probably caused by pH elevations. However, survival in mixtures of apatite, organoclay PM-199, and sand was comparable to survival in the control sediments showing that some MAAC formulations are acceptable to sensitive benthic organisms such as *Hyalella azteca*. These results largely corroborated previous in situ field bioassays with caged organisms, which showed that mixtures of 25% organoclay PM-199, apatite, and sand were nontoxic to a variety of benthic organisms including *Hyalella azteca*, the oligocheate worm, *Lumbriculus variegatus*, and the Asian clam, *Corbicula fluminea* (Knox et al., 2008 b and 2009, Paller and Knox, 2010).

Clinoptilolite and phillipsite differed in their effects on *Hyalella azteca* (Figure 21, Table 23). Clinoptilolite exhibited no evidence of toxicity. Exposure to substrates consisting of 100% clinoptilolite resulted in a mean survival of 95% compared with 97.5% in the control beakers. Nor was their evidence of depressed survival at any of the intermediate concentrations of clinoptilolite. This was confirmed by ANOVA, which indicated that statistically significant ($P<0.05$) differences among clinoptilolite treatments were lacking. Phillipsite, in contrast, was highly toxic to *Hyalella asteca* at higher concentrations. Mean survival of *Hyalella azteca* in 100% phillipsite was 7.5% compared with 97.5% in sand without phillipsite (i.e. control), and survival was only 40% at a phillipsite concentrations of 25% (Figure 21, Table 23). ANOVA followed by Holm-Sidak tests indicated that differences among phillipsite treatments were significant ($P<0.05$) and that survival was significantly depressed by as little as 25% phillipsite.

Figure 22 and Table 24 shows the survival of *Hyalella* in different potential MAAC formulations. The survival of *Hyalella azteca* was 97.5% in substrates composed of 100% clinoptilolite indicating that this amendment was nontoxic. The survival of *Hyalella* in 100% apatite was somewhat lower, 77.5%. Survival in the various mixtures
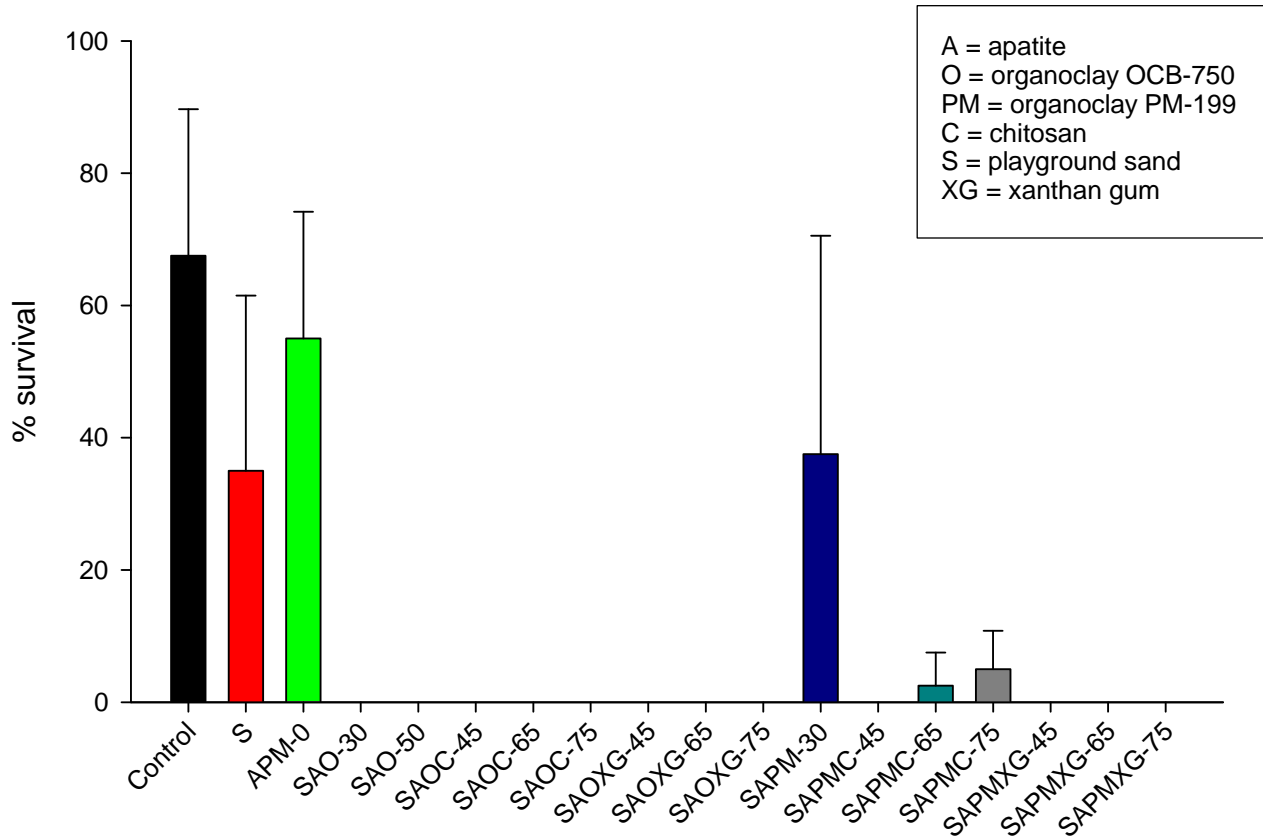
Figure 20. Percent survival of *Hyalella azteca* in static 10 day sediment toxicity tests employing different MAAC formulations. The control consisted of sediment from Steel Creek. Numbers following MAAC abbreviations indicate percentage of playground sand.

Table 22. Percent survival of *Hyalella azteca* in mixtures of apatite (A), organoclay OCB-750 (O), organoclay PM-199 (PM), chitosan (C), commercial playground sand (S), and xanthan gum (XG) in 10 day sediment toxicity tests.

| Amendment mixture	R1	R2	R3	R4	Mean	StDev
C	100	50	60	60	67.5	22.2
S	70	20	40	10	35.0	26.5
APM-0	40	40	60	80	55.0	19.1
SAO-30	0	0	0	0	0.0	0.0
SAO-50	0	0	0	0	0.0	0.0
SAOC-45	0	0	0	0	0.0	0.0
SAOC-65	0	0	0	0	0.0	0.0
SAOC-75	0	0	0	0	0.0	0.0
SAOXG-45	0	0	0	0	0.0	0.0
SAOXG-65	0	0	0	0	0.0	0.0
SAOXG-75	0	0	0	0	0.0	0.0
SAPM-30	0	30	40	80	37.5	33.0
SAPMC-45	0	0	0	0	0.0	0.0
SAPMC-65	10	0	0	0	2.5	5.0
SAPMC-75	0	10	0	10	5.0	5.8
SAPMXG-45	0	0	0	0	0.0	0.0
SAPMXG-65	0	0	0	0	0.0	0.0
SAPMXG-75	0	0	0	0	0.0	0.0
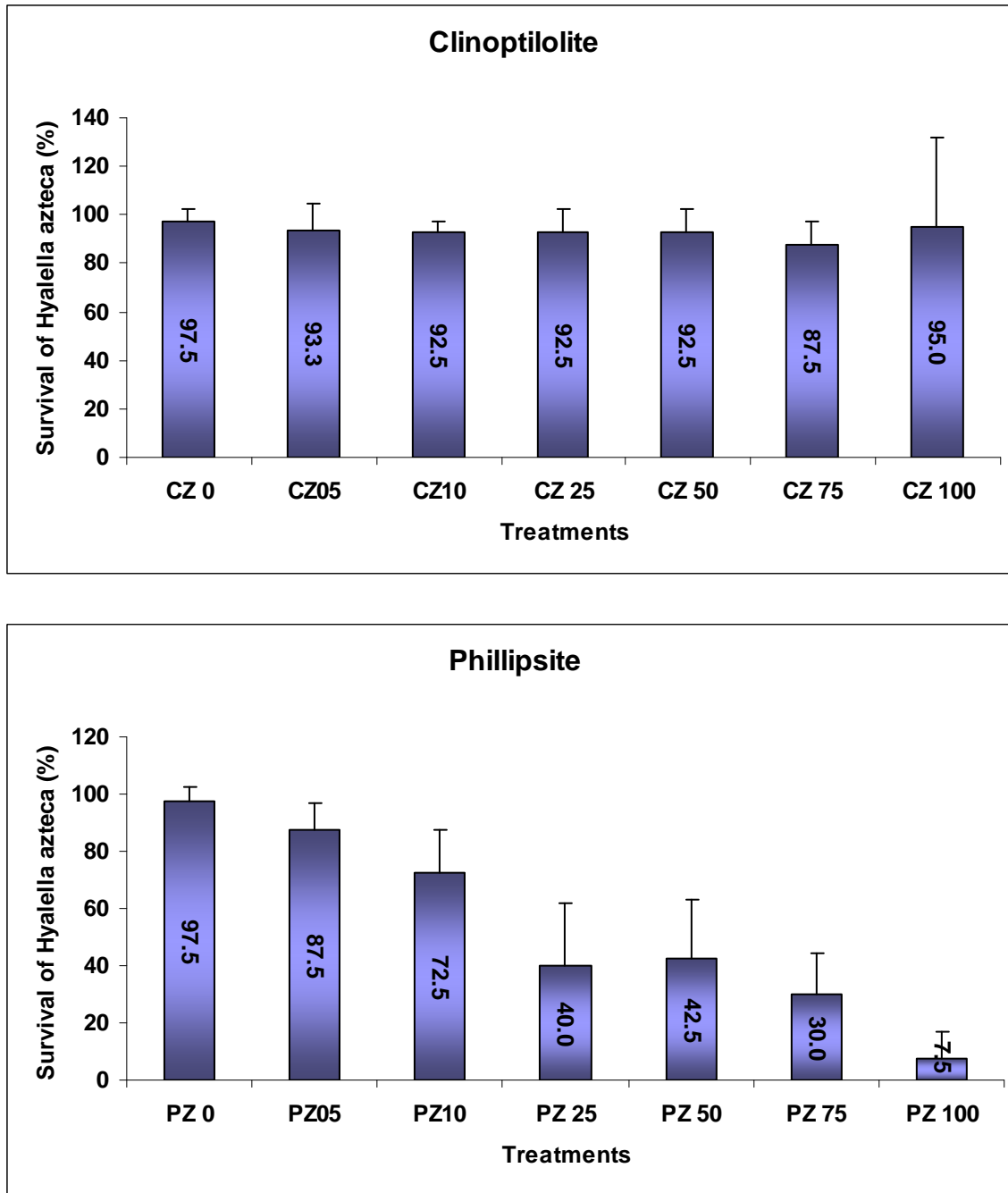
Figure 21. Percent survival of *Hyalella azteca* in static 10 day toxicity tests employing two types of zeolite: clinoptilolite and phillipsite. X-axis labels indicate material type (CZ = clinoptilolite, PZ = phillipsite) and percentage.

Table 23. Percent survival of Hyalella azteca in static 10 day toxicity tests employing two types of zeolite: clinoptilolite and phillipsite. X-axis labels indicate material type (CZ = clinoptilolite, PZ = phillipsite) and percentage.

Percent Zeolite	R1	R2	R3	R4	Mean	StDev
			Clinoptilolite			
0	90	100	100	100	97.5	5.0
5	80	100	100		93.3	11.5
10	90	100	90	90	92.5	5.0
25	100	90	100	80	92.5	9.6
50	100	80	100	90	92.5	9.6
75	90	80	80	100	87.5	9.6
100	80	70	150	80	95.0	37.0
			Phillipsite			
0	90	100	100	100	97.5	5.0
5	90	80	80	100	87.5	9.6
10	60	90	60	80	72.5	15.0
25	10	60	50	40	40.0	21.6
50	60	60	30	20	42.5	20.6
75	50	20	30	20	30.0	14.1
100	0	20	10	0	7.5	9.6
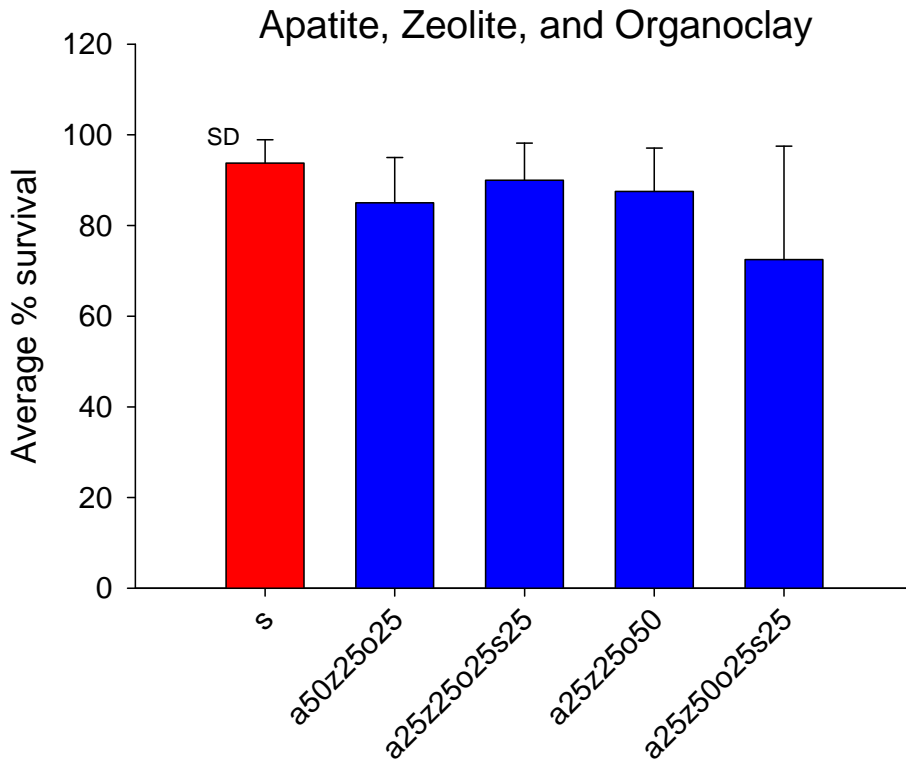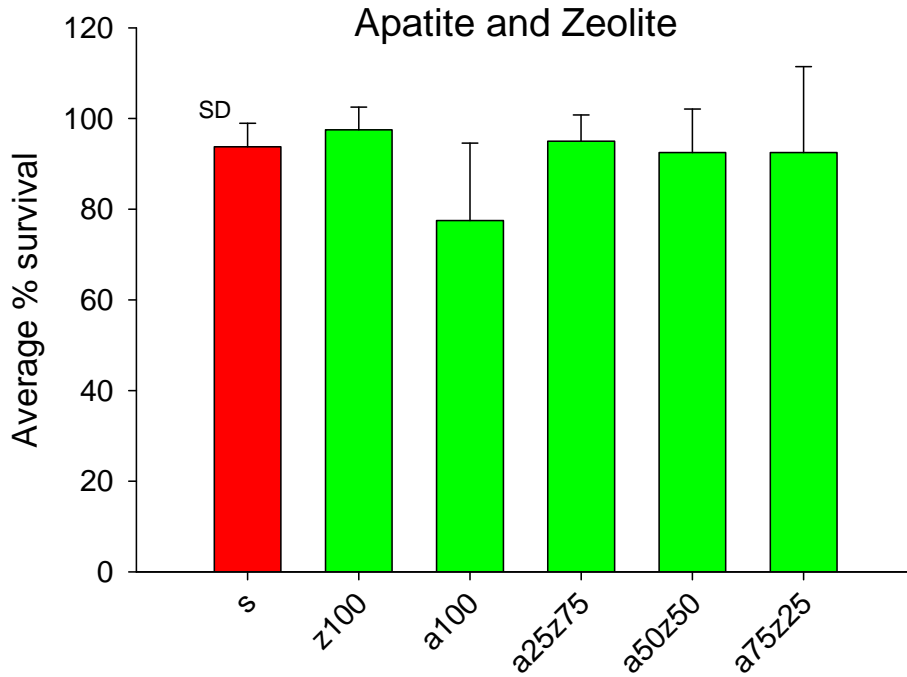
Figure 22. Percent survival of *Hyalella azteca* in mixtures of apatite (a), zeolite (z), organoclay (o), and sand (s) following 10 days of exposure. Numbers in x-axis labels indicate percent composition.

Table 24. Percent survival of Hyalella azteca in mixtures of apatite (A), zeolite (Z), organoclay (O), and sand following 10 days of exposure.

Amendment mixture*	R1	R2	R3	R4	Mean	StDev
Z100	100	90	100	100	97.5	5.0
A25Z75	90	90	100	100	95.0	5.8
A50Z50	80	100	90	100	92.5	9.6
A75Z25	90	80	120	80	92.5	18.9
A100	60	80	100	70	77.5	17.1
A25Z25O25S25	90	90	100	80	90.0	8.2
A50Z25O25	90	90	70	90	85.0	10.0
A25Z50O25	40	100	80	70	72.5	25.0
A25Z25O25	80	90	100	80	87.5	9.6
Steel Creek sand	90	90	90	100	92.5	5.0
Sand (commercial play ground)	100	90	100	90	95.0	5.8

* Numbers indicate percent composition

of apaptite, clinoptilolite, organoclay, and sand ranged from 85% to 95% (Figure 22, Table 24). The Kruskal-Wallis test indicated an absence of significant differences (at $P \leq 0.05$) among any of the treatments. These results show that clinoptilolite and mixtures of clinoptilolite, apatite, and organoclay are nontoxic to *Hyalella,* thus suggesting that these materials can be used for remediation of contaminated sediments with minimal likelihood of collateral effects on aquatic organisms.

Additional experiments were conducted to evaluate the toxicity of bentonite to benthic organisms. These experiments consisted of static bioassays of bentonite and mixtures of bentonite, sand, and amendments using *Hyalella azteca* as the test organism. Bentonite was toxic to *Hyalella* as were mixtures of bentonite and sand containing as little as 10% bentonite (Figure 23, Table 25). It is likely that the organisms suffocated in the slurry produced by bentonite at the substrate surface. In contrast, the addition of 10% bentonite to an amendment mixture containing apatite, organoclay, and zeolite did not affect *Hyalella* survival, and greater additions of bentonite had only limited effects on survival (Figure 24, Table 26). These results suggest that the addition of limited amounts of bentonite to amendment mixtures is not harmful to aquatic organisms and more generally indicate the potential environmental benefits of mixtures of amendments (i.e., MAACs) compared with single amendment formulations.
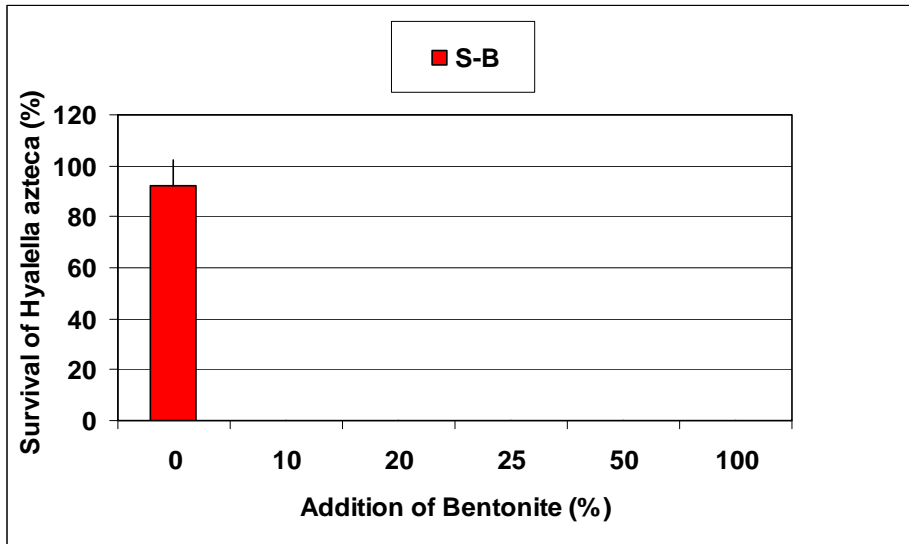
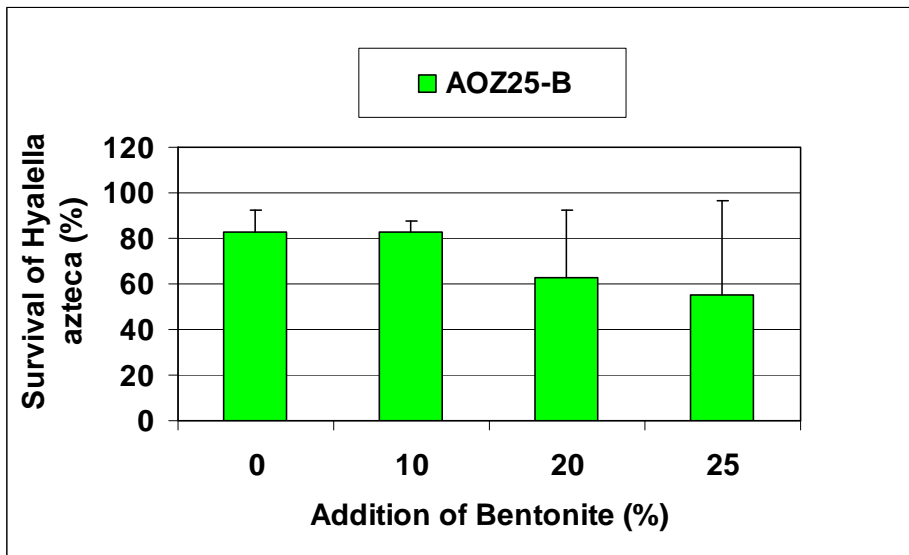**Figure 23. Survival of *Hyalella azteca* in mixtures of bentonite and sand.**

Figure 24. Survival of Hyalella azteca in mixtures of bentonite, sand, apatite, organoclay, and zeolite (AOZ25 = apatite, organoclay, and zeolite – 25% each).

Table 25. Survival of Hyalella azteca in mixtures of bentonite and sand.

Percent bentonite	R1	R2	R3	R4	Mean	StDev
0	80	90	100	100	92.5	9.6
10	0	0	0	0	0.0	0.0
20	0	0	0	0	0.0	0.0
25	0	0	0	0	0.0	0.0
50	0	0	0	0	0.0	0.0
100	0	0	0	0	0.0	0.0

Table 26. Survival of Hyalella azteca in mixtures of bentonite, sand, apatite, organoclay, and zeolite (AOZ25 = apatite, organoclay, and zeolite – 25% each).

Percent bentonite	R1	R2	R3	R4	Mean	StDev
0	90	80	90	70	82.5	9.6
10	80	80	90	80	82.5	5.0
20	70	30	50	100	62.5	29.9
25	80	20	100	20	55.0	41.2

TASK 4. EROSION EVALUATION

Bulk properties that significantly affect erosion rates include bulk density, particle size (both mean and distribution), mineralogy, organic content, volume of gas in the sediments, salinity of the pore waters, oxidation and other chemical reactions, and time after deposition. Some work has been done on the effects of each of these properties, but there is not a quantitative understanding of, nor ability to predict, the effects on erosion rates of most of these properties, especially in combination. In particular, little is known quantitatively about the effects of different minerals. It is qualitatively known that the addition of small amounts of clay minerals can have a significant effect on sediment bulk properties and erosion rates (Mitchner and Torfs 1996). Mitchner (1993) has shown that the order of the effect of the different clay minerals on erosion rates were bentonite>illite>kaolinite>mica, a sequence that is generally followed in quantifying the effects of clay minerals on soil properties.

Bentonite is a clay material primarily composed of montmorillonite, a member of the smectite family of clay minerals. The reason bentonite was selected as the additive is that it is the most cohesive of the common clays and, because of this, should have the most effect on erosion rates (Mitchner, 1993). Previous research on clays added to sand has indicated that even small amounts of clay (2 or 4 percent) will significantly increase the critical shear stress for initiation of erosion (Mitchner and Torfs 1996; Gailani et al., 2001 a and b).

The results from the ASSET flume clearly demonstrated that erosion rate and critical shear stress were reduced with the addition of higher concentrations of bentonite throughout the range of concentrations studied (Figures 25, 26, 27, 28, 29, 30, 31). Also, Jin et al. (2000) observed that erosion rate decreased rapidly as the amount of bentonite increased (from 0 to 16 percent) in three different sediments (sand, topsoil, and a 50/50 mix of the two). In our study, as more bentonite was added to MAACs the benefits of decreased erosion behavior declined (Figures 32 and 33). The largest reduction in erosion occurred with the addition of 0% - 5% of bentonite (Figures 32 and 33). The addition of larger amounts of bentonite (15 and 20%) to the amendment mixtures caused further decreases in erosion rates, but the rate of decrease diminished as the amount of bentonite increased (Figure 32 and 33). Similarly, Lick and McNeil (2002) observed that for all four tested clays (bentonite, kaolinite, plainman clay – a surrogate for pure illite, and mica) erosion decreased as the percentage of clay increased. The greatest decreases were for bentonite, smaller but still significant reductions occurred for kaolinite and plainman clay; only a small effect was observed for mica. Pure bentonite has a very low density, behaves as a gel, and is very difficult to erode. In the case of pure bentonite and for low applied shear stresses, a small amount of surface erosion occurs by particle-by particle and small chunk erosion. For large stresses, the bentonite fails by fractures (Lick and McNeil, 2002).
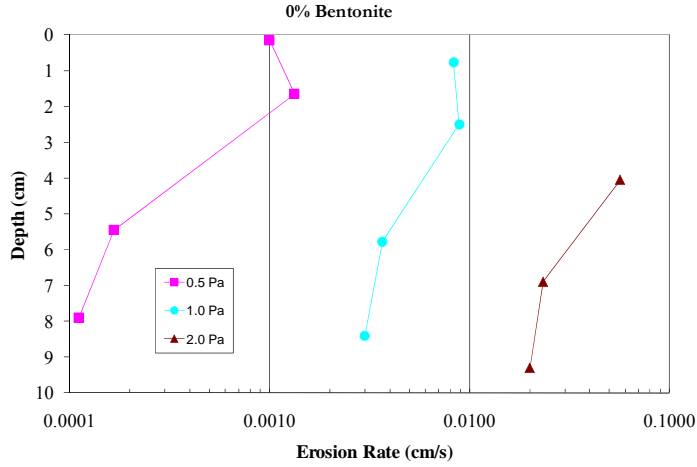
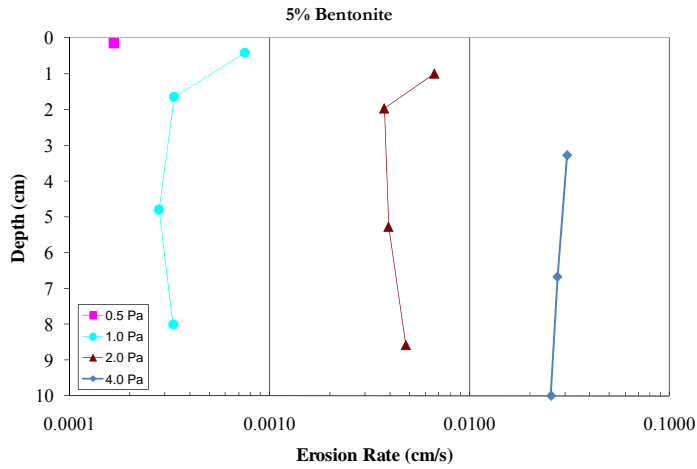**Figure 25. Erosion rate as a function of shear stress and depth; 0% bentonite addition.**
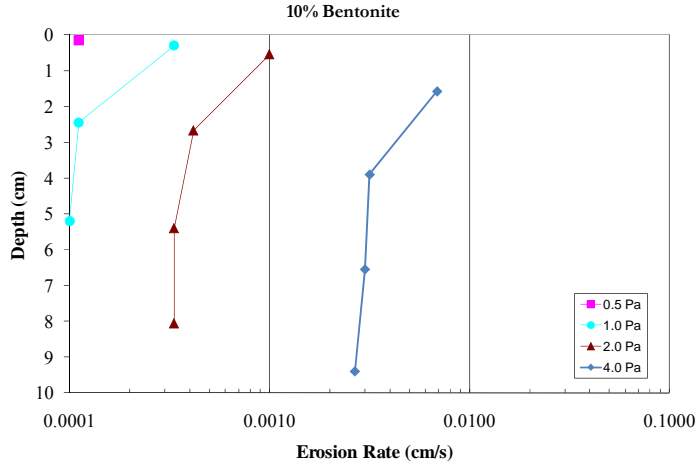
.

Figure 26. Erosion rate as a function of shear stress and depth; 5% bentonite addition.

Figure 27. Erosion rate as a function of shear stress and depth; 10% bentonite addition.
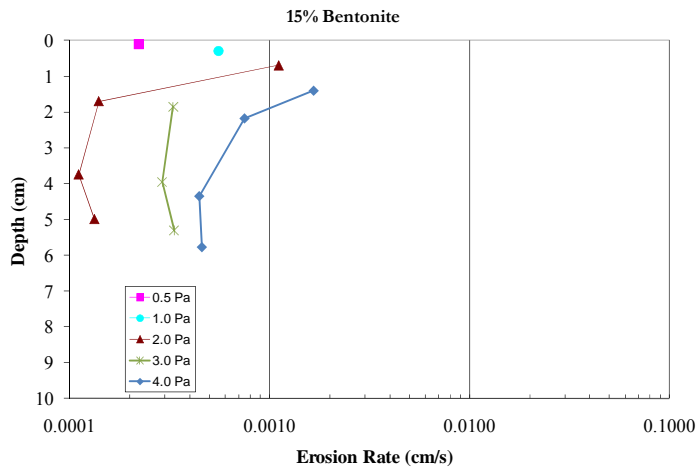

Figure 28. Erosion rate as a function of shear stress and depth; 15% bentonite addition.

Figure 29. Erosion rate as a function of shear stress and depth; 20% bentonite addition.
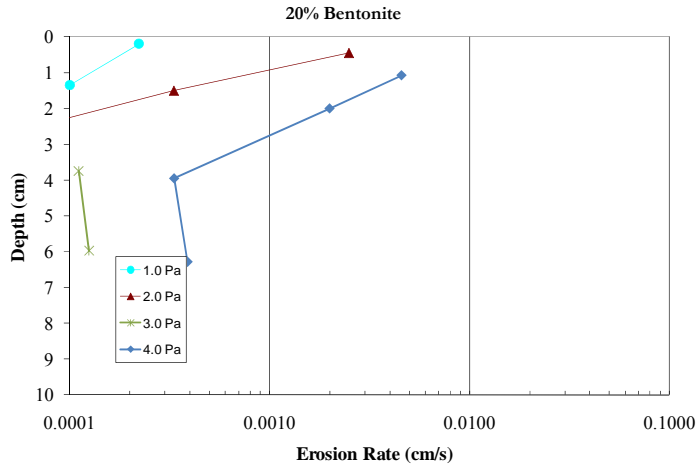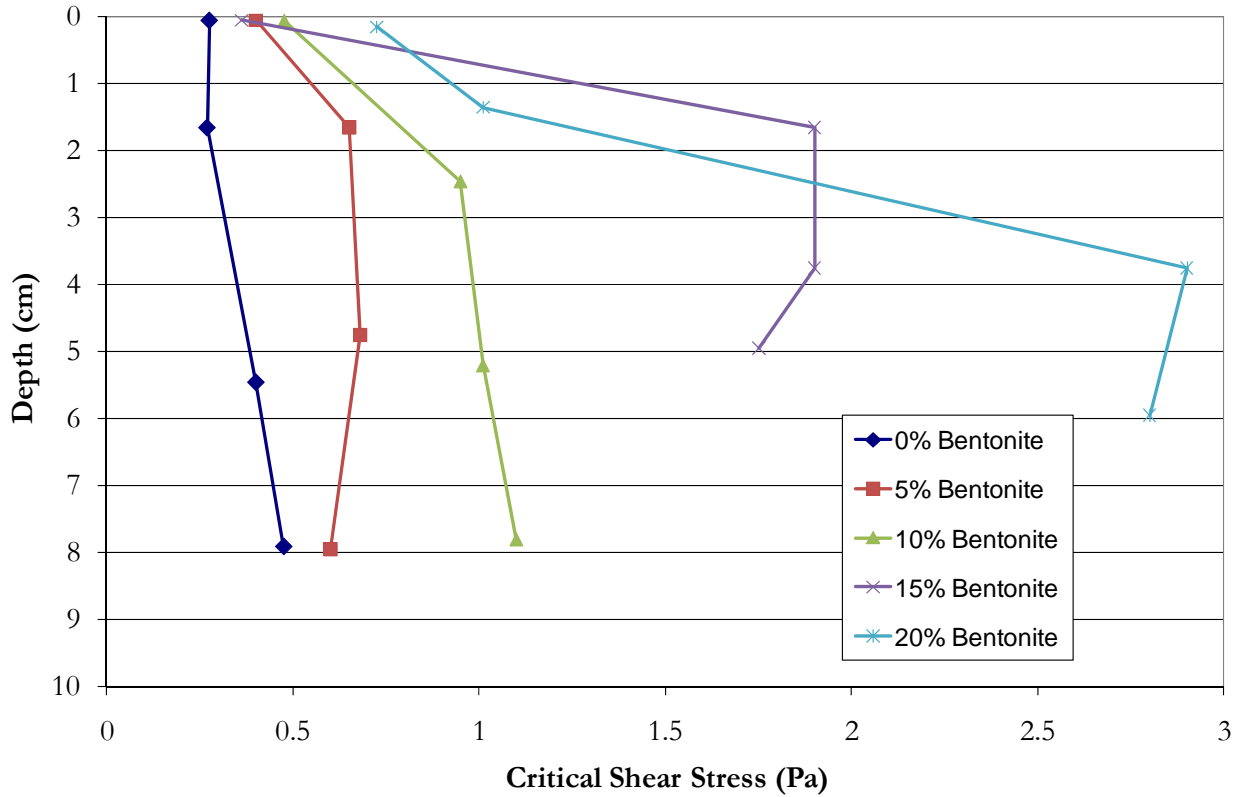

Figure 30. Critical shear stress as a function of depth and bentonite concentration.
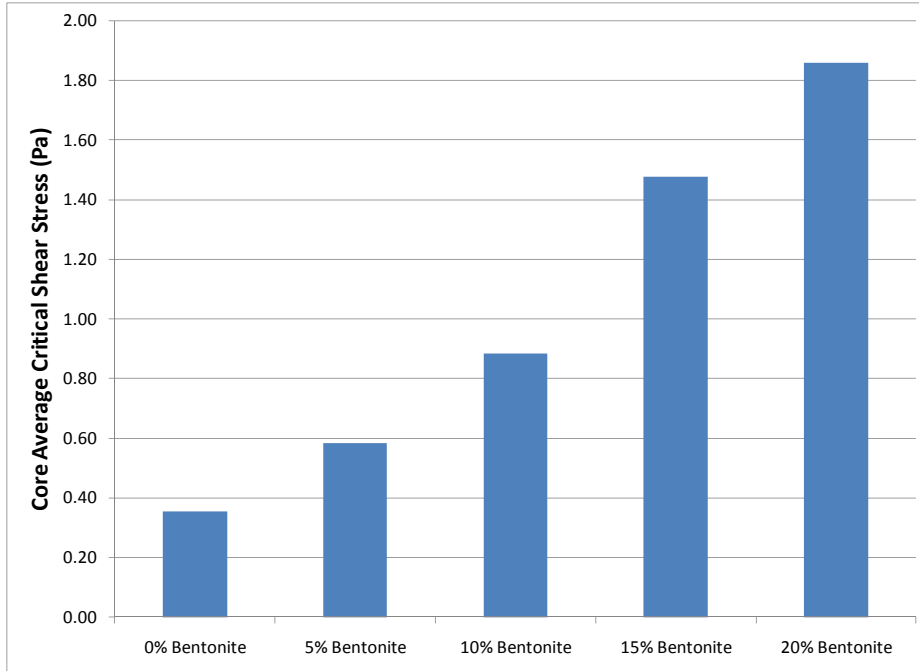
Figure 31. Core average critical shear stress as a function of bentonite concentration.
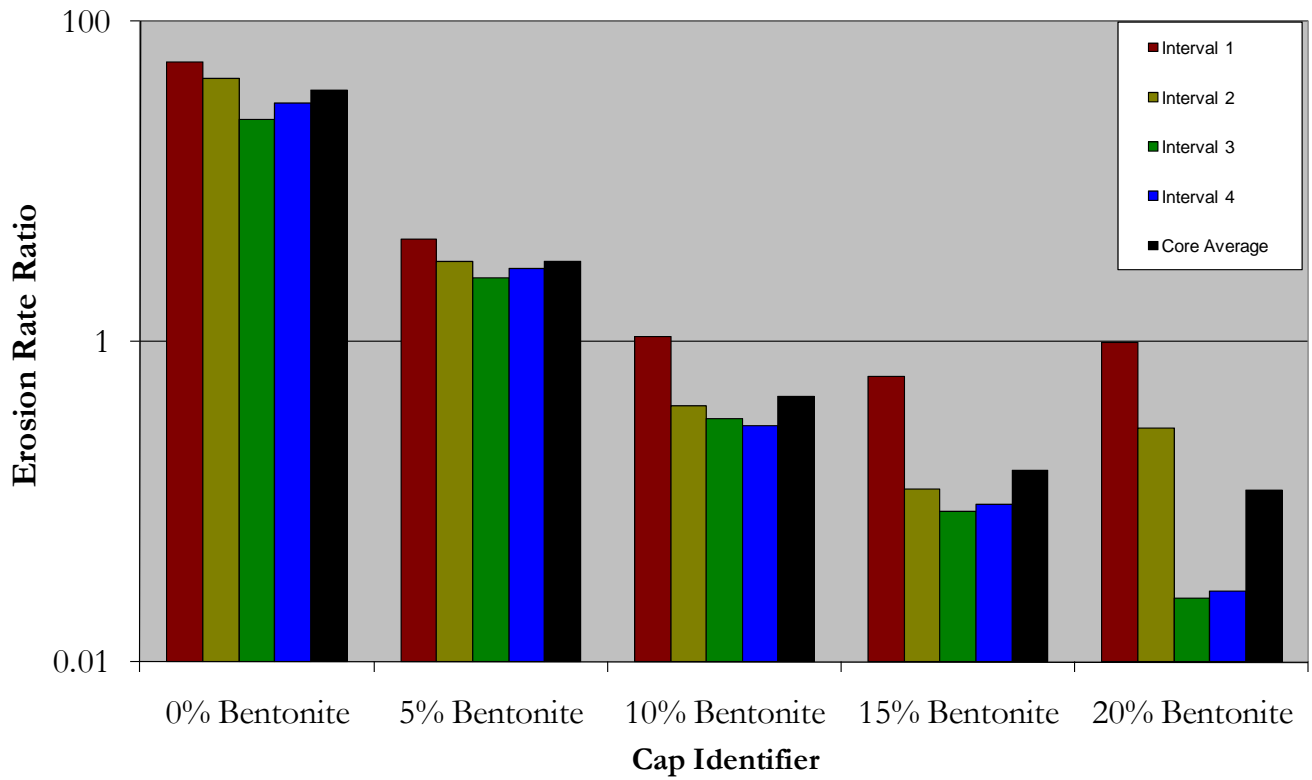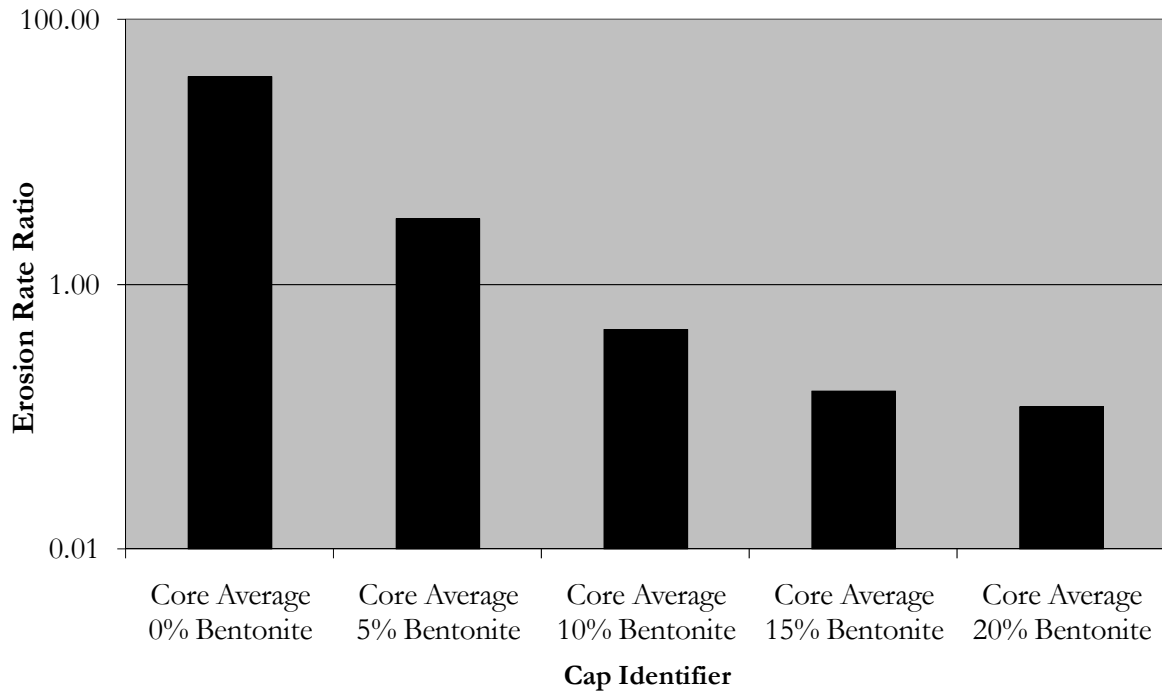
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Figure 32. Erosion rate ratio for all four depth intervals and the core average.

Figure 33. Core average erosion rate ratio for all cores.

SUMMARY

Part II of the final project report for SERDP ER-1501 describes the development and evaluation of a multiple-amendment active cap (MAAC) for the control of sediment contaminants. Specific objectives included 1) evaluation of the sorption and desorption of contaminants by mixtures of amendments, 2) use of numerical models to predict contaminant release over time from MAAC formulations, 3) evaluation of the addition of bentonite to MAACs to improve erosion resistance, and 4) assessment of the toxicity of MAACs to benthic organisms.

A MAAC consists of a mixture of amendments combined with sand or other neutral materials such as clay or clean soil/sediment. MAACs represent a one-step, simple, and versatile technology that permit the rapid construction of active caps. MAACs incorporate chemically active amendments to remediate a variety of inorganic and organic contaminants and can include bentonite to resist erosion. Studies conducted under this project show that mixtures of amendments compare favorably with individual amendments for the control of most sediment contaminants and are, in some cases, superior. Mixtures also exhibit less toxicity to the benthic organism, *Hyalella azteca*, than individual amendments. Potential advantages of MAAC technology are low cost, simplicity, potential to remediate a broad range of contaminants, easy adaptation to site requirements, and lack of harmful environmental impacts. MAACs are acceptable to benthic organisms due to lack of toxicity and the incorporation of natural materials. The advantages of MAACs are summarized below:

1) MAACs can be mixed onsite with a combination of locally available materials (e.g., sand) plus reactive amendments (e.g., apatite) that are usually available from several sources.
2) MAACs can be made in different formulations as needed to remediate different types of contaminants or mixtures of contaminants.
3) MAACs can be applied using conventional equipment and methods. In relatively shallow water, a MAAC can be constructed using an excavator. In deeper water, MAACs can be applied as a slurry through a flexible pipe using a slurry pump.
4) MAACs are relatively economical because they can be constructed using conventional equipment and contain only moderate amounts of reactive materials.
5) MAACs are nontoxic to aquatic organisms because the ratio of chemically active amendments to inert materials is low. High concentrations of some active amendments can harm benthos (Paller and Knox, 2010).

 A MAAC could be deployed in any type of benthic habitat considered for conventional capping as well as in higher energy environments (if bentonite is included) that might be unsuitable for caps with less erosion resistance.

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