Active capping technology - new approaches for in situ remediation of contaminated sediments

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ABSTRACT

This study evaluated pilot-scale active caps composed of apatite, organoclay, biopolymers, and sand for the remediation of metal-contaminated sediments. The active caps were constructed in Steel Creek, at the Savannah River Site near Aiken, South Carolina. Monitoring was conducted for 12 months. Effectiveness of the caps was based on an evaluation of contaminant bioavailability, resistance to erosion, and impacts on benthic organisms.

Active caps lowered metal bioavailability in the sediment during the one-year test period. Biopolymers reduced sediment suspension during cap construction, increased the pool of carbon, and lowered the release of metals. This field validation showed that active caps can effectively treat contaminants by changing their speciation, and that caps can be constructed to include more than one type of amendment to achieve multiple goals.

INTRODUCTION

Contaminated sediments affect nearly 10 percent of the nation’s waterways with potential remediation costs in the billions of dollars (USEPA, 2005). 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 sediments.

Contaminated sediment has traditionally been managed by dredging or dry excavation followed by off-site treatment or disposal (Mohan, Brown, & Barnes, 2000; Nayar, Goh, & Chou, 2004). However, this method is expensive and can remobilize contaminants and degrade the benthic environment. Current remediation/risk management options for contaminated sediments also include no action, monitored natural recovery, in-situ treatment, and ex-situ treatment. In-situ treatment of contaminated sediments is potentially less expensive than ex-situ treatment, but there are relatively few proven in-situ methods. Capping is the most commonly used alternative for the in-situ remediation of sediments.

Passive (inactive) capping is the installation of a subaqueous covering or cap of clean, neutral material over contaminated sediment, thus, producing a physical barrier that isolates contaminated sediment from the surrounding environment and reduces contaminant migration into the water column. Passive capping commonly employs clean dredged material that contains sand, silt, clay, and organic carbon. This alternative can be an effective approach for the remediation of contaminated sediment and is relatively economical. However, passive caps can release toxic contaminants and, because of their thickness, are not suitable in shallow areas, under existing marine structures (e.g., docks, piers), and in sensitive habitats, such as marshes.

In contrast to passive capping, active or reactive capping involves the use of capping materials that react with sediment contaminants to reduce their mobility, toxicity, and bioavailability. Active capping is a more recent alternative that has been the subject of several studies (Berg, Neumann, Donnert, Nuesch, & Stuben, 2004; Jacobs & Forstner, 1999; Jacobs & Waite, 2004; Knox, Kaplan, & Paller, 2006; Knox, Paller, Reible, Ma, & Petrisor, 2008; Knox et al., 2010a; Knox, Paller, Dixon, Reible, & Roberts, 2010b; Reible, Lampert, Constant, Mutch, & Zhu, 2006). The application of relatively small amounts of reactive amendments, such as apatite, zeolite, organoclay, and activated carbon, can sequester a variety of contaminants and control their transport (Ghosh, Luthy, Cornelissen, Werner, & Menzie, 2011; Knox et al., 2010a and 2010b ; Reible et al, 2006).

Although a less mature technology, active capping holds great potential for a relatively permanent solution that avoids residual risks resulting from contaminant migration through the cap, and active caps can be applied in areas where more traditional thick passive caps cannot. However, apart from the types of amendments potentially useful in active capping, comparatively little is known regarding amendment application techniques, application rates, and amendment combinations that will maximize the immobilization of a broad range of contaminants and produce caps that retain their physical integrity in aquatic environments. Current active capping technologies typically produce caps with limited physical stability that are suitable primarily for low-energy, depositional aquatic environments. However, depositional environments can become erosive as a result of unpredictable natural events, such as storms, as well as anthropogenic actions including boating and construction activities. Caps can be compromised under such conditions resulting in the mobilization of contaminated sediments.

This research consisted of a small-scale field deployment and evaluation of capping technologies initially researched in the laboratory (Knox et al., 2008). The laboratory studies showed that apatite, organoclay, and biopolymers have high potential for the development of active caps that can remediate a variety of contaminants and resist ersosion. Apatite can immobilize Pb and other metals in contaminated soils/sediments (Knox, Kaplan, Adriano, & Hinton, 2003; Ma, Logan, & Traina, 1995; Ma & Rao, 1997; Singh, Ma, & Harris, 2001), thus, offering an economical, simple, and environmentally benign alternative for treating contaminated environments. Organoclays consist of bentonite that is modified with quaternary amines, which become attached to the surface of the clay platelets through cation exchange. Organoclays are effective at remediating non-polar pollutants, such as oil, polychlorinated biphenols, chlorinated solvents, and polycyclic aromatic hydrocarbons (Alther, 2002; Xu, Sheng, & Boyd, 1997). Biopolymers are high-molecular weight compounds with repeated sequences that may chemically interact with other compounds. Depending on their functional groups, biopolymers can bind metals or soil particles and form interpenetrating cross-linking networks with other polymers (Schmuhl, Krieg, & Keizer, 2001; Yen, 2001).

The objective of this study was to evaluate pilot-scale active caps composed of apatite, organoclay, and biopolymers. The capped sediments were contaminated with metals, which are a common contaminant in many marine and fresh water environments as a result of industry, mining, and other activities. The mobile, soluble forms of metals are generally considered toxic to aquatic organisms. Induced chemical precipitation can shift metals from the aqueous phase to a solid, precipitated phase which is often less bioavailable. This can be achieved through application of sequestering agents in active caps. The active caps were constructed in Steel Creek near Aiken, South Carolina. Monitoring was conducted for 12 months. Effectiveness of the caps was based on an evaluation of contaminant immobilization, resistance to erosion, and impacts on benthic organisms.

MATERIAL AND METHODS

Selection and Pre-Cap Characterization of the Study Site

Sediment contaminant levels have been measured at numerous locations on the 800 km^2 Savannah River Site (SRS), a Department of Energy (DOE) reservation established in 1951 near Aiken, South Carolina for nuclear materials production. Steel Creek, a stream on the SRS, was chosen for the field deployment because metals were present in the creek sediments and because its width and depth were sufficient for the experimental plots (Exhibit 1). Steel Creek is a third order stream averaging about 6 to 8 m wide and 30 to 40 cm deep during low flow conditions. The bottom substrate was primarily sand in high energy areas and silt in depositional areas. Limited gravel was also present. Concentrations of several metals in Steel Creek sediments as a result of past discharges from industrial facilities located in the headwaters substantially exceed those in Tinker Creek, a nearby uncontaminated stream (Exhibit 2). Samples of surface water, pore water, and sediment were collected from each plot before cap construction to characterize the study site as described below.

Surface Water

The following variables in surface water were measured in situ with a portable environmental sampler (Model 7518-02, Cole-Parmer Instrument Company) before cap construction: temperature, electrical conductivity (EC), dissolved oxygen (DO), pH, and redox potential (ORP). Total carbon (TC), total organic carbon (TOC), and total inorganic carbon (TIC) were measured in replicated water samples (n=2) with an OI Analytical Combustion TOC Analyzer, Model 1020A. The stream water velocity was recorded using a portable water flow meter (Marsh-McBirney, Inc., Model 201).

Pore Water

Pore water samplers consisted of stainless steel wire mesh screen connected to nylon tubing. Two pore water samplers were buried in the stream sediment beneath each cap to a depth of about 5 cm, and two were buried within each cap to a depth of about 5 cm (Exhibit 1). Additionally, two pore water samplers were located downstream of each plot (1.8 m apart) to help determine if cap materials were transported downstream (P concentrations served as an indicator of apatite transport, and C concentrations served as an indicator of biopolymer transport) (Exhibit 1). Pore water samples were analyzed for metal concentrations, TC, TOC, and TIC. TC, TIC, and TOC were analyzed as previously described. Pore water metal concentrations were analyzed by inductively coupled plasma – mass spectrometry (ICP-MS) following the methods described below. Pore water samples were collected with a portable peristaltic pump operated at low speed to avoid entraining surface water. Sample temperature, EC, DO, pH, and ORP were measured with a portable environmental sampler (described above).

Sediment

Two sediment core samples were collected from each plot with a push-tube coring device. The first sediment core was split into two parts: 0 to 5 cm and 5 to 10 cm. The 5 to 10 cm interval was analyzed for acid volatile sulfide (AVS) and simultaneously extracted metals (SEM) (Allen, Gongmin, Boothman, DiToro, & Mahony, 1991). The second sediment core from each plot was split into three parts: 0 to 5 cm, 5 to 10 cm, and below 10 cm. All three parts were analyzed for metal concentrations, pH, Eh, organic content in the solid phase, and metal speciation (using double acid extraction methods described below). A solid TOC Analyzer manufactured by OI Analytical was used to measure TC and TOC in the sediment samples.

Cap Construction

The field deployment in Steel Creek included eight plots with four treatments: two control treatments consisting of uncapped sediments; two caps composed of a single 15 cm layer of 50 percent apatite and 50 percent sand (A/S); two caps composed of two layers including a 5 cm layer of biopolymer/sand slurry over a 10 cm layer of 50 percent apatite and 50 percent sand (B/A/S); and two caps composed of three layers including a 5 cm top layer of biopolymer/sand slurry, a 5 cm middle layer of 50 percent apatite and 50 percent sand, and a 5 cm bottom layer of 25 percent organoclay and 75 percent sand (A/B/O/S) (Exhibits 1 and 3). The control plots were located at the front and end of the 150 m long study area (Exhibit 1). The two replicates for each of the three caps (each 1.8 m wide, 1.8 m long, and 15 cm thick) were split between two locations: an erosive area with the an average flow rate of 27 cm/s (plots 1, 2, 6, and 7) and a depositional area with a lower average flow rate of 12 cm/s (plots 3, 4, 8, and 5). The leading edge of each cap was preceded by a sloped transition zone rising from the sediment to the top of the cap to prevent undercutting (Exhibit 1). The transition zone was composed of sand in A/S plots or biopolymer/sand slurry in plots with a top layer of biopolymer/sand slurry (xanthan crossed linked with guar gum). The cap corners were permanently marked with 1.2 m long PVC pipes to ensure accurate sample collection during the study and to provide a basis for assessing possible changes in cap dimensions as a result of erosion.

An aluminum frame was used during the construction of each cap to deflect downstream flow, stabilize the working area, reduce turbulence, and avoid loss of amendments. The frame was removed when construction was completed and all cap materials had settled. Cap layers that contained low density materials, such as biopolymers, were applied as a slurry to prevent material separation and differential settling. Sediment cores (five per plot) were collected after cap placement to confirm and characterize cap-layer thickness.

Post–Cap Monitoring

Monitoring of the plots was conducted for 12 months. Cap effectiveness was based on an evaluation of metal mobility/bioavailability, cap resistance to erosion, and amendment impact on benthic organisms (toxicity tests). Impacts on benthic organisms are discussed in Paller and Knox (2010). The effect of the active caps on metal mobility/bioavailability was evaluated by measuring metal concentrations in surface and pore water, acid volatile sulfide (AVS), simultaneously extracted metals (SEM), the SEM/AVS ratio, and by diffusive gradients in thin films (DGT) probes. The erosion evaluation was based on visual observations, sediment core characterization for integrity of the cap layers, and measurements of erosion rates and critical shear stresses by an adjustable shear stress and erosion transport (ASSET) flume. Details are provided below.

Surface and Pore Water

Temperature, EC, DO, pH, and ORP were measured in situ in the surface water within each plot with a portable environmental sampler (Model 7518-02, Cole-Parmer Instrument Company) every month for the first two months and every three months thereafter. Other variables included TC, TOC, TIC (OI Analytical Combustion TOC Analyzer), and current velocity (Marsh-McBirney Inc., Model 201 water flow meter).

Pore water samples were collected with a peristaltic pump monthly for the first two months after cap construction and every three months thereafter. Pore water temperature, EC, DO, pH, and ORP were measured in the field with a portable environmental sampler. TC, TIC, TOC, and metals were measured in the laboratory using previously described methods.

Sediment

Four sediment cores were collected from each plot with a push-tube coring device 6 and 12 months after cap construction. The sediment beneath the caps was split into three layers: 0 to 2.5 cm, 2.5 to 5 cm, and 5 to 10 cm. Each portion was analyzed for pH, TC, and TOC, and the lowermost layer was analyzed for AVS and SEM. Quality control for samples analyzed by SEM/AVS and double acid methods (described below) included replicate analysis, blanks, matrix spike recovery, and blank spike recovery.

Zone of Influence (ZOI)

Additional sediment cores were collected 6 and 12 months after cap placement to determine the effects of the caps on metal concentrations in the sediment beneath the caps and the depth of these effects (i.e., the ZOI of the caps). Two replicate cores were collected from control plot #5, A/S plot #3, B/A/S plot #4, and B/A/O/S plot #8. The cores were divided into three layers: cap material, upper sediment (0 to 2.5 cm), and lower sediment (2.5 to 5 cm). Sub-samples (5 g) from each layer were extracted with double acids (0.05 n HCl and 0.25 n H_2S0_4) for evaluation of available phophorous and metals. Each sediment sample was placed into a 50 ml centrifuge tube with 40 ml of the double acid extracting solution (0.05 n HCl and 0.25 n H_2SO_4). The tubes were shaken for 30 minutes and centrifuged for 10 minutes. The supernatant was filtered through Whatman filters (#41) into plastic bottles. Metals were analyzed by ICP-MS.

Diffusive Gradients in Thin Films (DGT) Probes

Sediment DGT probes were used for evaluation of metal bioavailability. The probes were placed in-situ in untreated sediment and in the A/S cap (plot #3). Additionally, sediment and cap samples were brought to the laboratory where DGT performance was evaluated under laboratory conditions. Comparison of DGT performance between the laboratory and field is important because the use of DGT probes is generally limited to shallow sediments. Metal concentrations in deep sediment cores could be measured ex-situ in the laboratory using DGT providing that laboratory and field measurements are in agreement. Successful results could expand the usefulness of DGT methods to deeper sediments located below active caps.

Preparation of the DGT probes prior to field deployment and their subsequent analysis in the laboratory is described in Knox et al. (2010a). The probes were deployed by inserting them vertically into the sediment. Upon removal from the sediment, they were rinsed with deionized water, sealed in a plastic bag, and stored in a refrigerator until analysis.

The DGT results were analyzed using two Analysis of Variance (ANOVA) models. The first ANOVA included only DGT data and assessed the significance of three factors: treatment (A/S cap vs. control plot), location (i.e., location of the sediment samples during the 24-hour exposure period – laboratory vs. field), and metal concentrations (Cd, Co, Cr, Cu, and Ni), plus all interactions. The second ANOVA compared DGT data with sediment pore water data collected using sippers. It included three factors: treatment (A/S cap vs. control plot), method (DGT vs. pore water collected with sippers), and metal (Cd, Co, Cr, Cu, and Ni), plus all interactions. The dependent variable in both ANOVAs was the measured metal concentration (mg kg^{-1}), which was $\log_{10}$ transformed to better meet the assumptions of ANOVA.

Cap Erosion

Sediment cores were collected weekly for the first month and monthly thereafter to visually characterize the integrity of the cap layers. Also, the stream bottom was visually examined downstream from the tests plots for cap materials displaced by erosion. In addition, sediment cores were collected for analysis in an ASSET flume (Roberts and Jepsen, 2001; Roberts et al., 2003). Eight sediment cores were collected (three from the apatite cap plot #3, three from the biopolymer/apatite/organoclay cap plot #8, and two from the untreated control area plot #5) by pushing thin-walled, polycarbonate core tubes (approximately10 cm in diameter) into the sediment. The sediment strata and density profiles remained intact during this process. Cores varied in length from 13.1 to 16.2 cm.

Each core was sub-sampled into depth intervals. The erosion rate for each depth interval was approximated by a power law function of sediment density and applied shear stress. The measured erosion rates and applied shear stresses were calculated for each depth interval using methods described in Knox et al. (2010a). An average erosion rate for the entire core was also determined, and this erosion rate was compared to the average for all cores.

RESULTS AND DISCUSSION

Surface and Pore Water before Cap Placement

The average surface water pH was 7.0 in all plots (Exhibit 4). The average dissolved oxygen for all eight plots was 7.0 mg/L, and the average electrical conductivity was 62.2 μS/cm. The average dissolved oxygen concentration in the pore water from the eight plots was 3.3 mg/L; much lower than for surface water. ORP values were also lower in the pore water than the surface water; average values were 147.5 and 287.9mV, respectively, for pore and surface water.

Effects of Caps on Surface Water and Pore Water

The average surface water pH before cap placement was 7.0 (Exhibit 4). The pH increased slightly to 7.3 one month after cap placement, returned to pH 7 after two months and again increased to 7.8 after nine months (Exhibit 4). The highest EC of the surface water was observed one month after cap placement (80.9 μS/cm). The EC values of the surface water 12 months after cap placement were similar to the EC values before cap placement (Exhibit 4).

The addition of cap materials influenced pore water chemistry, especially pH, EC, and the ORP (Exhibits 5, 6, 7, and 8). The pH of pore water collected from and beneath all caps remained elevated during the 12-month sample period compared with the control plots and the measurements before cap placement (Exhibit 5). The highest EC values in pore water were beneath and within the three layer cap with organoclay (Exhibit 6). The EC in pore water beneath this cap increased from 68 μS/cm before cap placement to 703 μS/cm one month after cap placement. However, by 12 months after cap placement, the EC was only slightly elevated compared with pore water collected before cap placement and pore water outside the plots

(Exhibit 6). Generally, the ORP values beneath the caps were substantially lower than before cap placement and lower than in the control plots (Exhibit 7).

Average TC concentrations in surface water from the test area changed little during the 12-month evaluation (Exhibit 8). The slight changes that occurred were likely due to seasonal factors, such as changes in floodplain run-off of organic detritus. In contrast, TC concentrations in pore water changed because of the active cap materials. The highest concentrations were beneath the three layer B/A/O/S cap. TC in the pore water collected beneath this cap increased to 42 mg/L one month after cap placement compared with 9.9 mg/L in the control plots (Exhibit 9). It later declined to about 25 mg/L and continued to decrease for another 10 months to TC values comparable to those before cap placement or outside the plots (Exhibit 9).

Concentrations of some metals; e.g., Cr, Ni, Pb, Se, and V, in surface water were lower during the 12 months after cap placement than before cap placement (Exhibit 10). The concentrations of elements, such as Ca, P, and Mg, did not change after cap placement. In contrast, the concentration of Na in surface water increased somewhat after cap placement, possibly due to the addition of organoclay (Exhibit 10).

Concentrations of As, Cd, Cr, Mo, Pb, and Zn clearly declined after cap placement in pore water collected from sediment beneath the A/S cap (Exhibit 11). Reduction of metal concentrations in pore water was less clear for the B/A/S and B/A/O/S caps (Exhibit 11). Reduction of metal concentrations in pore water beneath the A/S cap was related to the sequestering agents and to changes in pore water chemistry resulting from the caps. Parameters modified by cap placement included redox potential and pH (Exhibits 5 and 7). These parameters have major effects on metal speciation in pore water.

Although metal concentrations in pore water generally decreased during the 12 months after cap placement, concentrations of Ca, K, Na, and P increased, especially P concentrations within the A/S cap and Na within the B/A/O/S cap (Exhibit 12). The use of apatite in active caps raises questions about the release of P, since P can cause eutrophication. Cap placement did not increase the P concentration in surface water, but P concentrations increased in pore water collected within the caps especially in the first month after cap placement. After three months, the P concentrations in pore water collected outside the caps were similar to P concentrations in the control plots (Exhibit 12).

Effects of Caps on Sediment pH and Total Carbon

The pH in the one layer A/S caps and two layer B/A/S caps was higher than in the control plots six months after cap placement due to the apatite in these caps, but the difference diminished with time (Exhibit 13). The pH of sediment beneath the three layer B/A/O/S caps remained almost the same as in the control plots (i.e., 4.5 and 4.6) six months after cap placement but later increased to about 6.4 (Exhibit 13).

Total carbon content remained relatively constant in the sediment beneath the A/S caps, but increased substantially in the sediment beneath the B/A/S and B/A/O/S caps (Exhibit 14). Higher concentrations of carbon beneath the caps with biopolymer suggest that the biopolymers were biodegrading with time and releasing carbon to the sediment. Similar results were obtained in the laboratory (Knox et al., 2008). The relationship between carbon, especially dissolved organic carbon, and metal ions or organic contaminants is important because it affects the retention and mobility of these contaminants in sediments and waters (Adriano, 2001).

Effect of Caps on Simultaneously Extracted Metals/Acid Volatile Sulfide (SEM/AVS)

The ratio of simultaneously extracted metals (SEM) to acid-volatile sulfide (AVS) largely dictates metal bioavailability and, thus, toxicity in anoxic sediment (Berry et al., 1996; Di Toro et al., 1990). It is theorized that bioavailability is controlled primarily by the dissolved metal concentration in the sediment pore water. Therefore, using SEM/AVS molar ratios to estimate Cd, Cu, Hg, Ni, Pb, and Zn (generally present as divalent species) availability in pore water provides a better indicator of sediment toxicity than total mass concentrations (Allen et al., 1991; DeWitt, Swartz, Hansen, McGovern, & Berry, 1996; Di Toro, Mahoney, Hansen, & Scott, 1992; Hansen et al., 1996). AVS is usually the dominant-binding phase for divalent metals in sediment. Metal sulfide precipitates are typically very insoluble, and this limits the amount of dissolved metal in pore water. When AVS exceeds SEM on a molar basis for a particular metal (i.e., the SEM/AVS ratio is below 1), the metal concentration in the pore water will be low because of the limited solubility of the metal sulfide. Other factors may also affect metal bioavailability and toxicity (Ingersoll, Haverland, & Brunson, 1996; MacDonald, Carr, Calder, Long, & Ingersoll, 1996); e.g., dietary factors (i.e., sediment ingestion) can be an important pathway to biotic uptake (Lee et al., 2000). Some researchers have reported that, although metal concentrations in sediment pore water may be controlled by geochemical equilibration with metal sulfide, metal exposure and subsequent toxicity is influenced by sediment ingestion (Lee et al.; Long, MacDonald, Cubbage, & Ingersoll, 1998).

In this study, AVS, SEM, SEM/AVS, and other measures of sediment chemistry were evaluated to assess their potential applicability for evaluating sediment remediation by active caps. The AVS pool from the control plot and the A/S cap plot increased over the 12-month study (Exhibit 15). The AVS pool in the plot with the B/A/O/S cap initially increased and then declined slightly (Exhibit 15). The SEM/AVS ratio decreased over time to low levels in all plots but the decrease was greater in the plot with the apatite cap than in the control plot (Exhibit 15). SEM/AVS concentrations measured over time were used to compute rates of SEM/AVS change for each treatment. The rate of decrease in SEM/AVS in sediment beneath the A/S cap was significantly faster than in sediment in the control plot as indicated by a comparison of the regression slopes between the two trend lines ($t=3.00$, $df=12$, $P \leq 0.05$) (Exhibit 16).

The differences in the SEM/AVS ratio before and 12 months after cap placement were statistically significant ($P \leq 0.05$) for both the A/S and B/A/O/S plots ($t=287.6$ [df=4] and $t=6.78$ [df=4], respectively, for A/S and B/A/O/S plots). To some extent these changes could be related to seasonal factors (Grabowski, Houpis, Woods, & Johnson, 2001). Seasonal changes in redox conditions can control Fe-S-P concentrations in the sediments, pore waters, and overlying water and, therefore, the AVS concentrations in sediments (Grabowski et al.). However, the significantly more rapid decrease in SEM/AVS that occurred beneath the A/S cap than in the control plot indicates a treatment effect associated with capping that resulted in decreased metal bioavailability.

Effect of Caps on Metal Bioavailability – Comparison of DGT Probes and Pore Water

DGT actively removes metals from water, pore water, and sediments while providing quantitative measurements of mean concentrations of metals in the pore water at the surface of the device. The labile species measured by DGT correspond more closely than bulk phase measurements to bioavailable metal fractions (Zhang & Davison, 1995; Zhang & Davison, 2001).

ANOVA of the DGT data indicated that DGT measurements generated in the field did not differ significantly (i.e., $P>0.05$) from DGT measurements generated in the laboratory, thus, confirming the comparability of in-situ and ex-situ DGT data (Exhibit 17). These preliminary results suggest that DGT methods can be used successfully on ex-situ sediment cores including deep cores collected from below sediment caps. Not surprisingly, the main effect of metal was significant ($P<0.001$) indicating that concentrations differed among metals. Of greater interest was a significant ($P<0.001$) interaction between metal and treatment, indicating that the A/S cap lowered sediment pore water concentrations measured by DGT for some metals but not others. Specifically, concentrations of Co, Cu, Zn, and Pb were lower in the sediments beneath the A/S cap than in the untreated sediments; whereas concentrations of other metals did not differ between treatments (Exhibit 17).

The ANOVA of the DGT results and results from analysis of pore water samples collected with sippers indicated that the main effects of treatment (apatite cap vs. control plot), sample type (DGT vs. pore water samples), and metal were all significant ($P=0.012$ or less). There were also significant two-way interactions between treatment and sample type ($P=0.023$) and between sample type and metal ($P<0.001$). These results show that the DGT measurements differed from the pore water measurements, but that these differences were inconsistent among metals and between treatments. Specifically, metal concentrations in pore water samples were somewhat higher than metal concentrations measured by DGT with the exceptions of Pb and Zn (Exhibit 17). Additionally, pore water measurements tended to indicate greater differences between treatments than did DGT measurements.

Evaluation of Cap Erosion

Visual examination of the stream bottom in and around the test plots was conducted every week, for four weeks and every month thereafter to see if cap materials were displaced downstream. Generally, caps in areas of high flow (27 to 37 cm/s) showed substantial erosion within the first month following storms during which stream flow exceeded 91 cm/s near the caps. The A/S cap eroded the fastest, and material from this cap was transported up to 6 m downstream within one month (Exhibit 18). However, caps with a mixture of sand and biopolymer as the top layer showed no movement of the lower layers composed of apatite or organoclay/sand during this period. The caps located in depositional areas with flow rates under 12 cm/s showed little evidence of erosion (Exhibit 18).

After two months, caps with a top layer of biopolymer/sand started to degrade in both high and low flow (depositional) areas. These data are consistent with the laboratory evaluation of biopolymer xanthan/guar gum by the ASSET flume (below), which showed biopolymer degradation after two months (Knox et al., 2010a). Although the top biopolymer layer eroded, the cores showed that it prevented movement of the underlying cap material. This was also suggested by P concentrations in pore water collected outside of the B/A/S cap, which were lower than the P concentrations in the pore water outside of the A/S cap (Exhibit 12). This difference suggested faster erosion of apatite when it was not protected by a biopolymer layer.

Cap Erosion – Evaluation by Adjustable Shear Stress Erosion Transport (ASSET) Flume

Erosion rate data were collected for eight core samples: two from control plots, three from the B/A/O/S cap, and three from the A/S cap. Exhibit 19 compares the average erosion rate of the three different material types with the average for all materials. There was comparatively little difference between the average erosion rates of the cores; all cores and material types had an average erosion rate that differed from the overall mean by a factor of two or less. The results from the erosion tests in the field are consistent with the laboratory evaluation of biopolymers (Knox et al., 2010a). Both showed that guar gum cross-linked with xanthan (Kelzan) became less erosion resistant after two months. Therefore, the application of xanthan/guar gum in the field as the top layer of an active cap imparts erosion resistance for only a short time. However, biopolymers reduced sediment suspension and facilitated the settling of other amendments that were placed below the biopolymer layer during construction, increased the pool of carbon in the sediment beneath the caps, and lowered the release of metals and other elements, especially P, in comparison with apatite only. However, more research is needed on the type of biopolymer to apply to caps and the best way to deliver biopolymers to caps. A three layered cap composed of biopolymer on the top, apatite in middle, and organoclay on the bottom is not ideal for biopolymer interaction with other amendments, which could serve as cross-link reagents. A very important aspect of biopolymer application in remedial work is the biodegradability of biopolymers, especially under extreme conditions (e.g., high summer temperatures).

CONCLUSIONS

Acknowledgement of the limitations of dredging and passive capping have led to various approaches that employ chemical sequestering agents to alter the speciation of contaminants and reduce their bioavailability. These can range from mixing amendments into the sediments to the addition of amendments to conventional passive caps for improved effectiveness. Potential concerns with these approaches are the ability to treat co-occurring mixtures of contaminants with different properties and the dispersion of sequestering agents under extreme hydrological conditions. The depositional areas in which contaminated sediments generally accumulate can become erosive during storms or floods or when disturbed by anthropogenic activities. The active caps employed in this study represent an effort to overcome some of these problems through the use of multiple amendments, including biopolymers, which were intended to impart erosion resistance by making cap materials more cohesive. In general, there has been limited effort to validate different active capping technologies in the field. The results of this field validation show that active caps can effectively treat metal contaminants in the field by changing their speciation and that caps can be constructed to include more than one type of amendment (e.g., apatite, biopolymers, and organoclay) to achieve multiple goals. Specific conclusions include the following:

- Metal concentrations in pore water within and beneath the caps in depositional areas one year after cap placement were lower than metal concentrations in pore water collected before cap placement or outside the caps.
- Active caps lowered SEM/AVS in the sediment beneath the caps resulting in substantially lower metal bioavailability during the one-year test period.
- Double acid extract data show that downward migration of the amendments used in active caps can neutralize contaminants located deeper in the sediment profile (i.e., in the zone of influence).
- The mobile pool of metals in remediated contaminated sediments can be successfully evaluated using SEM/AVS ratios, DGT sediment probes, and by measuring metal concentrations in pore water.
- Biopolymers increased cap resistance to erosion for a short period. However, field studies showed that biopolymers were not physically stable after 6 months.
- Addition of biopolymers reduced sediment suspension during cap construction and facilitated the rapid settling of other amendments that were placed below the biopolymer layer. Biopolymers also increased the pool of carbon in the sediment beneath the cap and lowered the release of some elements, especially P, in comparison with apatite only.

ACKNOWLEDGMENTS

This work was sponsored by the DoD Strategic Environmental Research and Development Program (SERDP) under project ER 1501 and the Savannah River National Laboratory (SRNL) Mini-Sabbatical Program. The SRNL is operated by Savannah River Nuclear Solutions, LLC for the U.S. Department of Energy under Contract DE-AC09-798861048.

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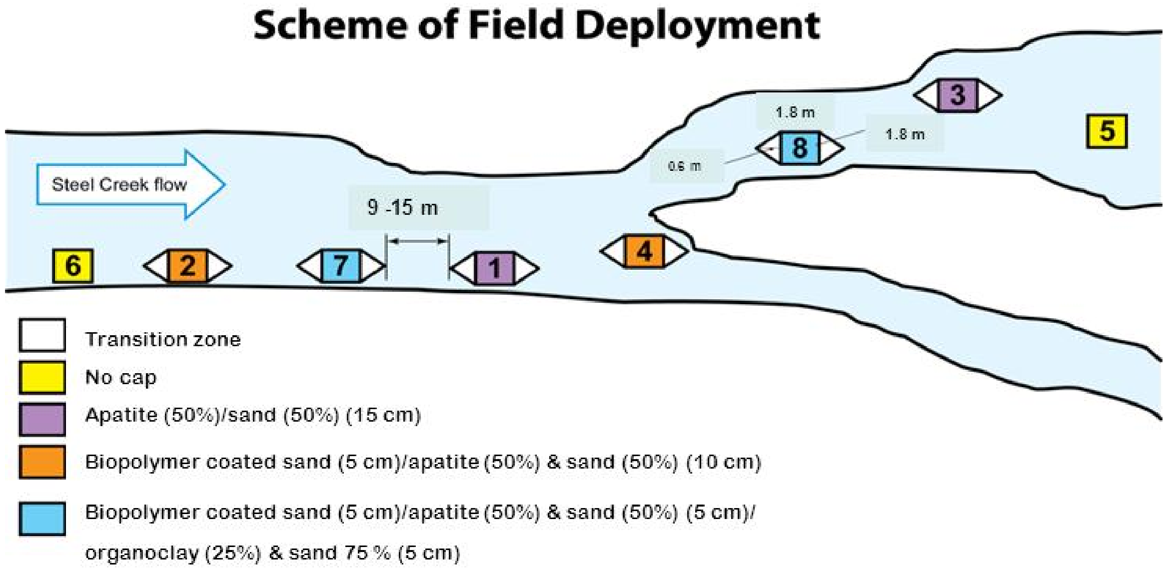

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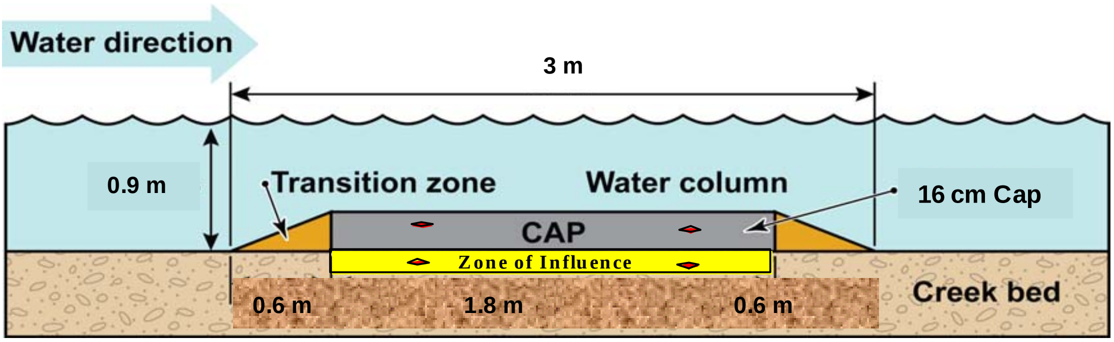

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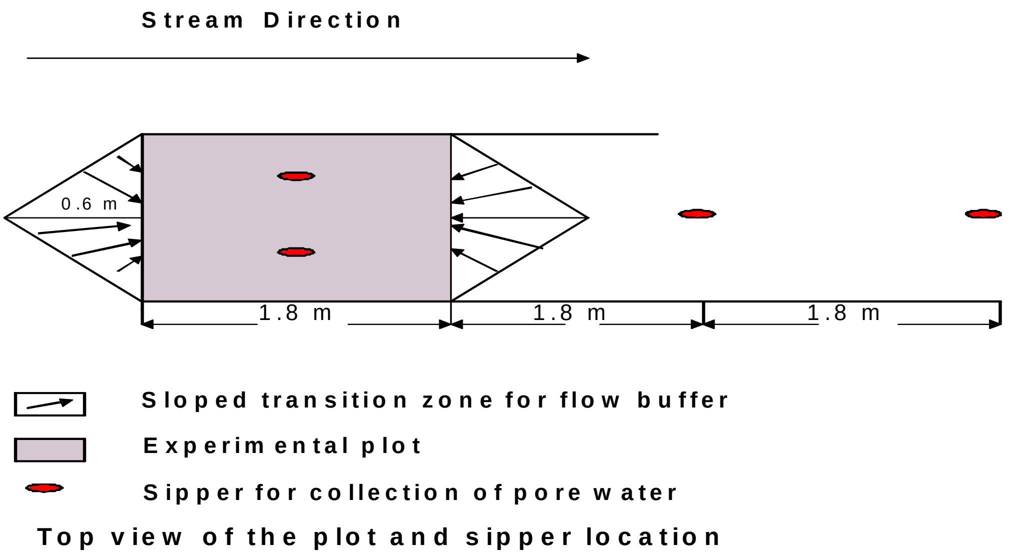


Exhibit 1. Deployment of pilot-scale active caps and control sites in Steel Creek (A). cross-section, and top views of a cap with pore water sippers (B and C).

Exhibit 2. Metal concentrations in sediments from Steel Creek and Tinker Creek.

	Steel Creek		**Tinker Creek**	
Metal	**Concentration (mg/kg)**	**Number Samples**	**Concentration (mg/kg)**	**Number samples**
Ag	4.5	77	2.0	21
Al	3,780	64	2,435	24
As	9.7	92	1.2	22
Ba	23.8	95	16.7	23
Be	0.16	62	0.29	20
Cd	1.32	84	0.70	21
Cr	16.3	99	4.0	32
Cu	7.2	93	3.5	24
Hg	0.11	93	0.04	22
Mn	950	78	4.7	15
Ni	4.1	95	2.5	23
Pb	58.9	95	4.4	24
Sb	5.2	81	5.0	21
Se	7.1	84	0.94	20
Sn	135	31	5.06	10
V	12.0	52	4.8	24
Zn	38.5	93	5.4	24

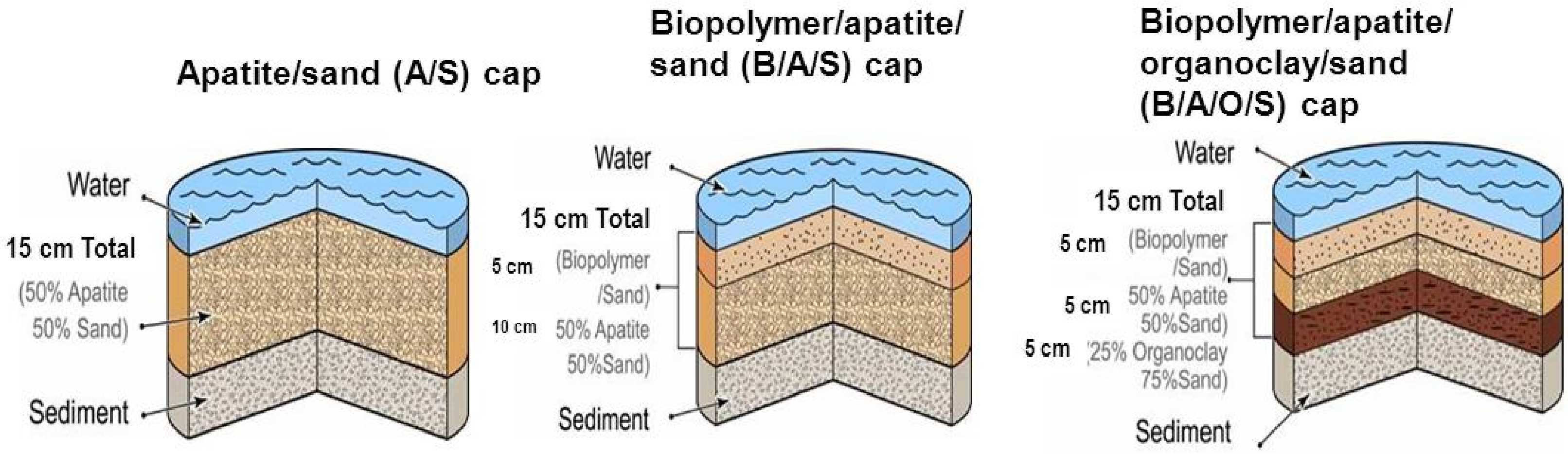


Exhibit 3. Three types of caps were tested in the field.

Exibit 4. Properties of surface water in eight plots before and after cap placement.

Parameters	**Unit**	**Plots**								**AVG**	**STDEV**
		1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**n = 8**	**n = 8**
Before Cap Placement											
EC	µS/cm	62	62.3	62	63	62	63	61	62	62.2	0.6
DO	mg/L	7.0	7.0	6.9	7.2	7.0	7.0	7.0	7.1	7.0	0.1
pH		7.0	6.9	7.0	7.2	7.0	7.0	7.1	6.9	7.0	0.1
ORP	mV	281	283	275	316	285	275	303	285	287.9	14.3
After One Month											
EC	µS/cm	81	81	81	81	81	80	81	81	80.9	0.4
DO	mg/L	6.8	6.9	7.2	6.9	7.2	6.8	6.9	7.0	7.0	0.2
pH		7.4	7.4	7.3	7.0	7.2	7.4	7.4	7.4	7.3	0.1
ORP	mV	89.4	96.5	63.4	82.3	45.7	104	95	76	81.5	19.3
After Two Months											
EC	µS/cm	53	52	52	52	53	52	53	52	52.4	0.5
DO	mg/L	12.2	11.8	10.0	10.4	9.5	10.9	11.4	10.4	10.8	0.9
pH		7.3	6.8	7.0	7.0	7.0	6.8	6.8	7.1	7.0	0.2
ORP	mV	63.5	104.2	70.3	82.4	79	109	94.2	75	84.7	16.3
After Five Months											
EC	µS/cm	65	65	66	65	66	65	65	66	65.4	0.5
DO	mg/L	6.7	6.9	7.3	7	6.8	7	6.8	7.6	7.0	0.3
pH		7.2	7.4	7.2	7.4	7.4	7.5	7.3	7.3	7.3	0.1
ORP	mV	115	103.7	102	104	69	122	112	94.7	102.8	16.1
After Nine Months											
EC	µS/cm	64	64	65	64	64	64	64	64	64.1	0.4
DO	mg/L	3.7	3.3	3.6	3.7	3.6	3.6	3.7	3.5	3.6	0.1
pH		7.8	7.9	7.7	7.8	7.7	8.1	7.8	7.7	7.8	0.1
ORP	mV	75	63	64	76	69	68	76	76	70.9	5.6
After Twelve Months											
EC	µS/cm	69	65	65	69	64	69	64	70	66.9	2.6
DO	mg/L	6.7	7.2	10.9	10.0	8.7	9.9	3.7	7.1	8.0	2.3
pH		7.8	7.9	6.9	6.8	7.7	7.1	6.9	7.3	7.3	0.4
ORP	mV	75	63	110	60	69	81	96	128	85.3	24.1

Notes:
EC – electrical conductivity, DO – dissolved oxygen, ORP – oxidation/reduction potential.

Exhibit 5. Average pH of pore water before and after capping.

Time	Location	A/S Avg	B/A/S Avg	B/A/O/S Avg	Control Avg	A/S Stdev	B/A/S Stdev	B/A/O/S Stdev	Control Stdev
Before capping	S	6.92	6.80	6.78	7.01	0.33	0.07	0.09	0.12
After one month	C	7.65	7.60	7.36		0.09	0.24	0.17	
	B	7.51	7.36	7.21	7.13	0.24	0.17	0.06	0.05
	O	7.51	7.39	7.48		0.25	0.03	0.24	
After two months	C	7.29	7.35	7.32		0.44	0.00	0.28	
	B	7.05	6.96	7.41	6.86	0.23	0.37	0.39	0.08
	O	7.25	6.74	7.20		0.36	0.17	0.22	
After five months	C	7.08	7.20	7.08		0.08	0.10	0.11	
	B	7.07	7.40	7.19	6.92	0.02	0.09	0.13	0.04
	O	7.05	6.97	7.13		0.07	0.13	0.04	
After nine months	C	7.88	7.65	7.80		0.06	0.09	0.09	
	B	7.88	7.58	7.95	7.64	0.06	0.09	0.28	0.09
	O	7.83	7.65	7.69		0.01	0.04	0.20	
After one year	C	8.11	7.31	7.65		0.09	0.03	0.07	
	B	7.93	7.58	7.74	6.71	0.12	0.03	0.06	0.07
	O	7.86	7.26	7.51		0.06	0.04	0.07	

Notes:

S – uncapped sediment, C- within cap, B – sediment beneath cap, O – sediment outside cap.

Exhibit 6. Average EC (electrical conductivity) of pore water before and after capping.

Time	Location	A/S Avg	B/A/S Avg	B/A/O/S Avg	Control Avg	A/S Stdev	B/A/S Stdev	B/A/O/S Stdev	Control Stdev
Before capping	S	85.33	77.50	68.50	75.00	5.86	11.33	3.42	4.69
After one month	C	145.00	129.75	297.50		64.31	23.64	249.89	
	B	170.75	171.25	702.67	90.50	78.18	84.22	540.98	9.95
	O	90.33	99.75	103.75		5.69	30.61	4.35	
After two months	C	106.00	93.67	103.33		41.50	13.65	35.81	
	B	146.00	98.00	177.50	77.75	74.01	25.06	159.86	26.13
	O	58.00	85.00	69.67		0.00	14.76	15.31	
After five months	C	83.00	125.33	226.67		16.46	26.73	96.10	
	B	133.67	124.00	126.00	86.00	43.25	48.07	21.93	9.54
	O	77.50	75.67	106.00		16.26	9.45	5.29	
After nine months	C	101.50	129.67	160.00		16.26	13.65	21.21	
	B	98.50	118.00	130.50	95.50	20.51	10.15	33.23	13.96
	O	103.00	92.33	116.33		0.00	10.12	21.36	
After one year	C	119.50	69.00	112.50		3.54	1.41	4.95	
	B	110.50	109.00	193.50	79.00	24.75	5.66	2.12	10.80
	O	92.50	70.00	90.00		12.02	2.83	5.66	

Notes:

S – uncapped sediment, C- within cap, B – sediment beneath cap, O – sediment outside cap.

Exhibit 7. Average ORP (redox potential) of pore water after capping.

Time	Location	A/S Avg	B/A/S Avg	B/A/O/S Avg	Control Avg	A/S Stdev	B/A/S Stdev	B/A/O/S Stdev	Control Stdev
After one month	C	-108	-91	-105	-19	2	5	5	14
	B	-168	-153	-179		0	11	1	
	O	-43	-18	-90		19	23	40	5
After two months	C	-84	-25	-57	-16	35	7	47	
	B	-109	-63	-106		1	16	9	
	O	-39	-11	-70			26	14	
After five months	C	-95	-49	-89	-31	17	22	5	14
	B	-148	-104	-155		50	31	30	
	O	-32	-45	-64		12	22	26	
After nine months	C	-82	-113	-128	-36	17	42	42	19
	B	-67	-127	-160		7	23	3	
	O	-45	-59	-108		33	6	5	
After one year	C	-70	-27	-96	-26	6	1	18	4
	B	-99	-107	-110		0	21	4	
	O	-58	-27	-28		14	6	12	

Notes:

S – uncapped sediment, C- within cap, B – sediment beneath cap, O – sediment outside cap.

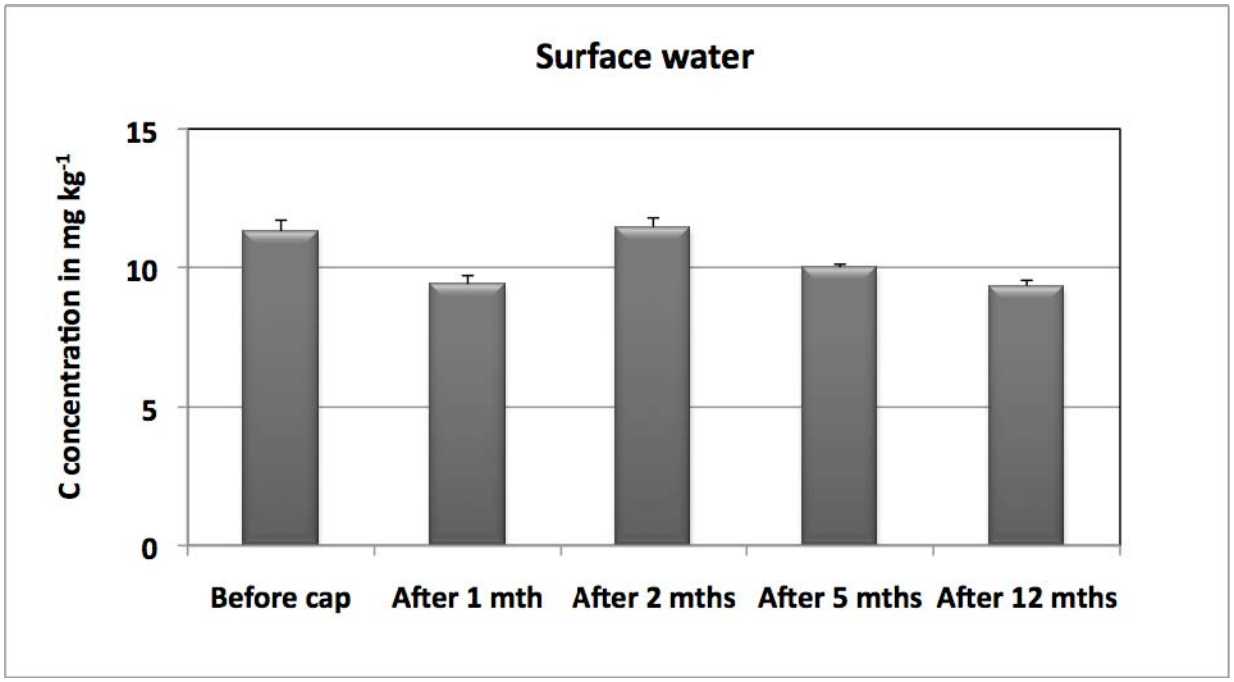
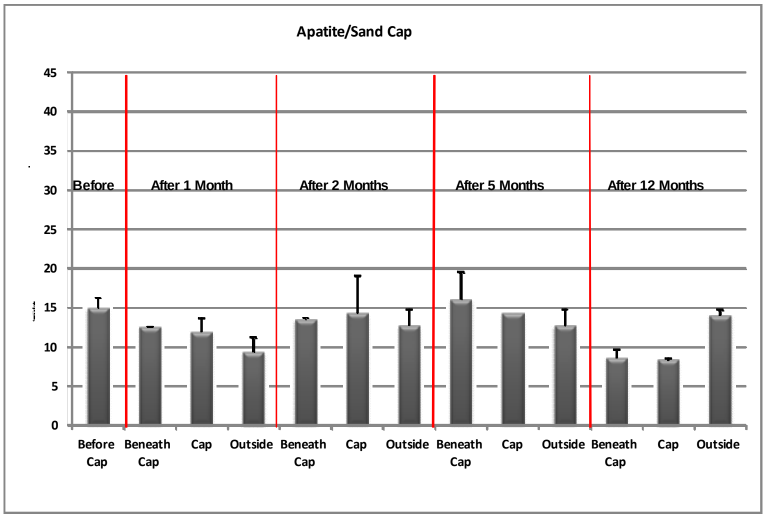
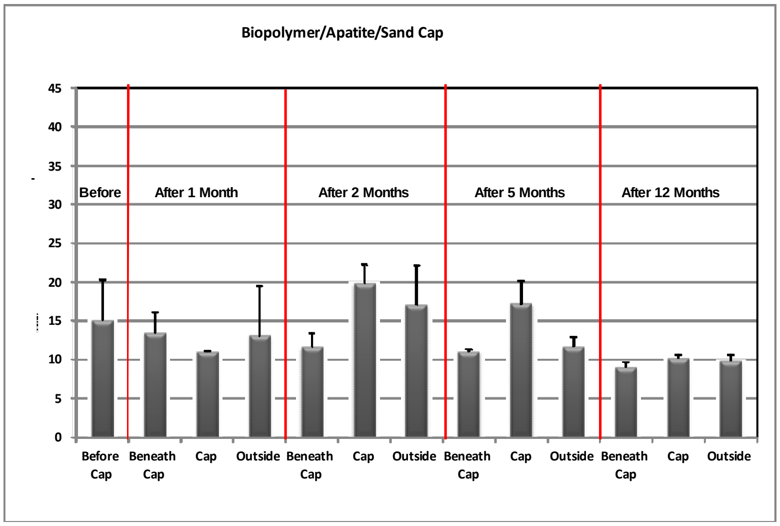


Exhibit 8. Total carbon in surface water collected before cap placement and one, two, five, and 12 months after cap placement.





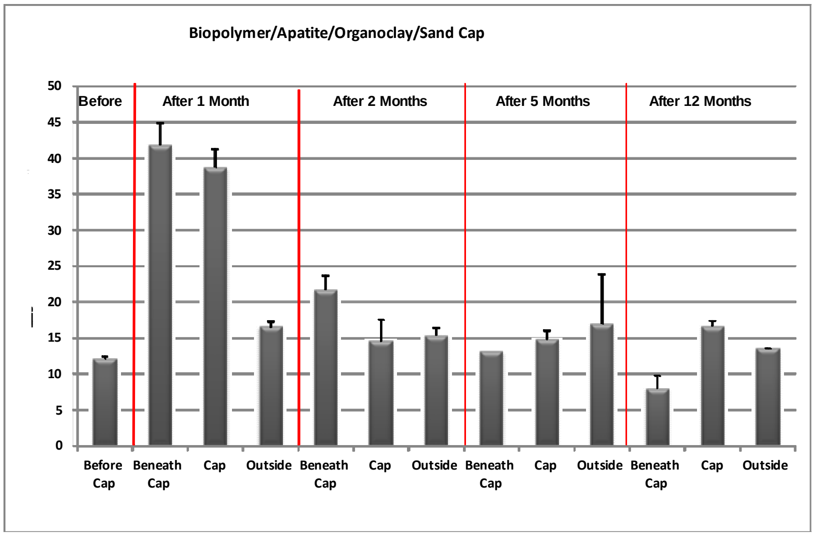
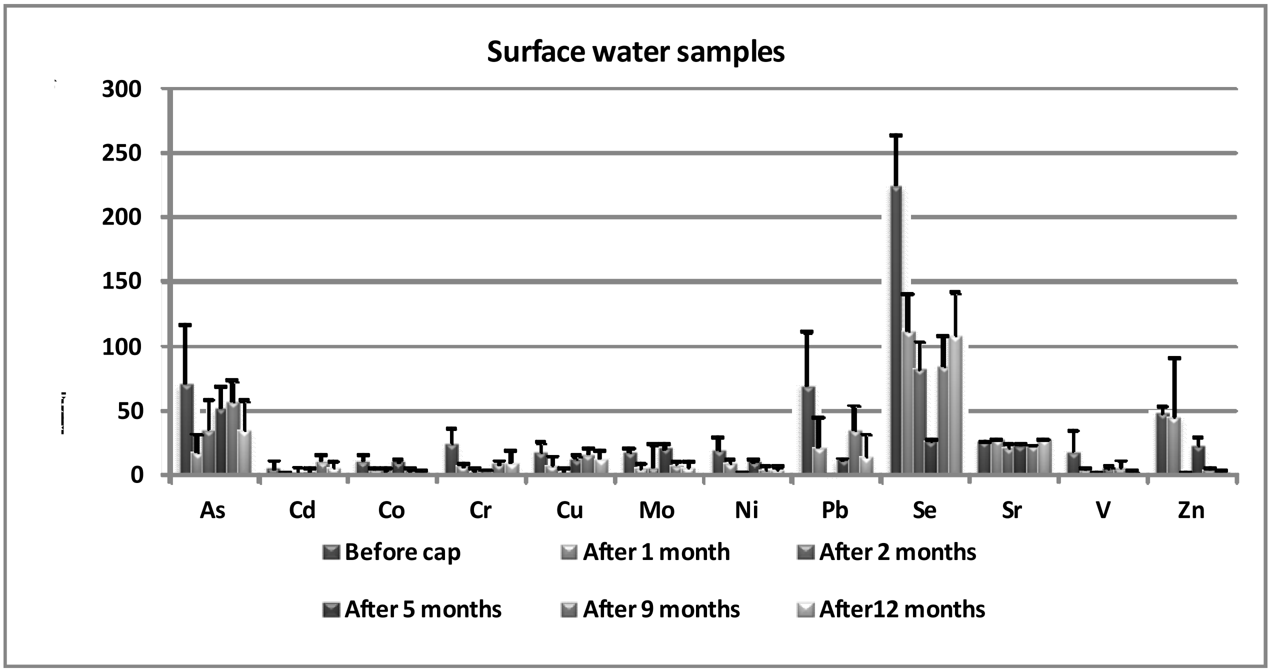


Exhibit 9. **Average (stdev) total carbon concentrations in pore water samples collected from each type of cap before and after cap placement.**



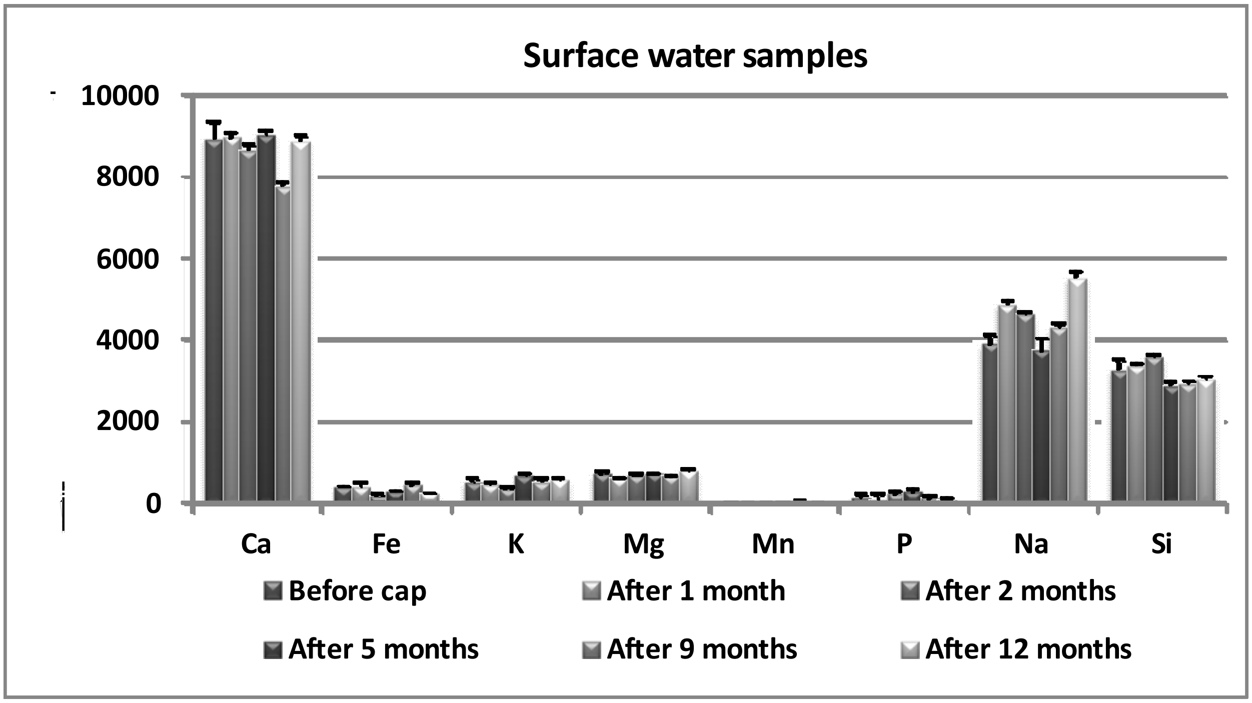
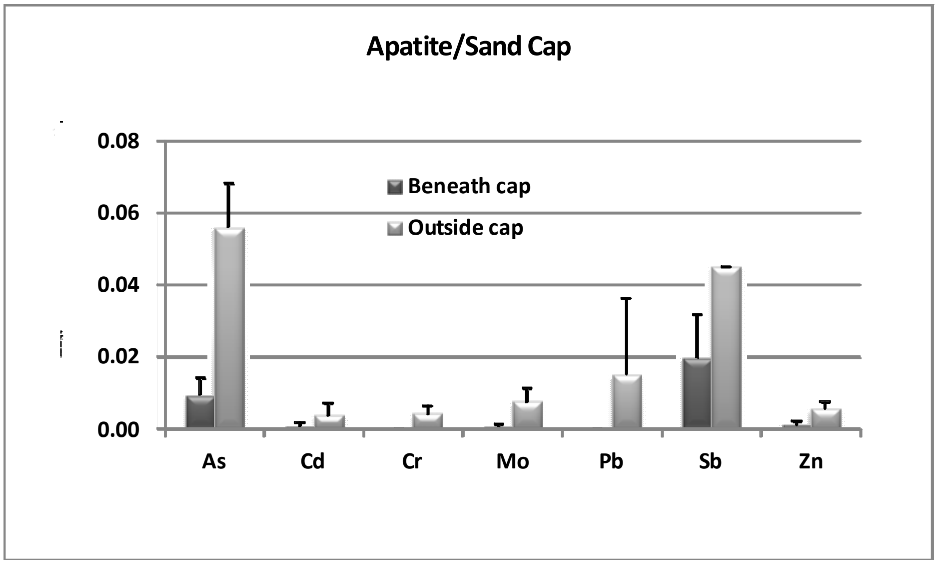
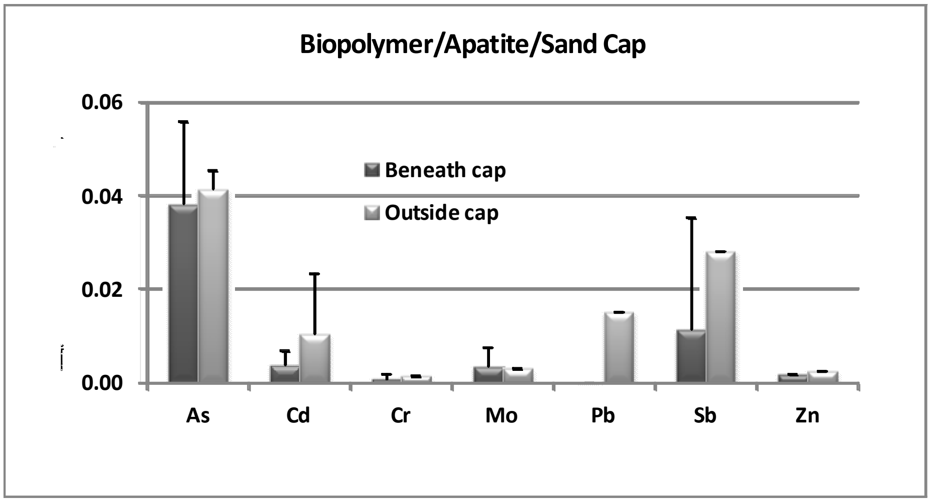


Exhibit 10. Average (stdev) element concentrations in surface water before and after cap placement.


Apatite/Sand Cap


Biopolymer/Apatite/Sand Cap

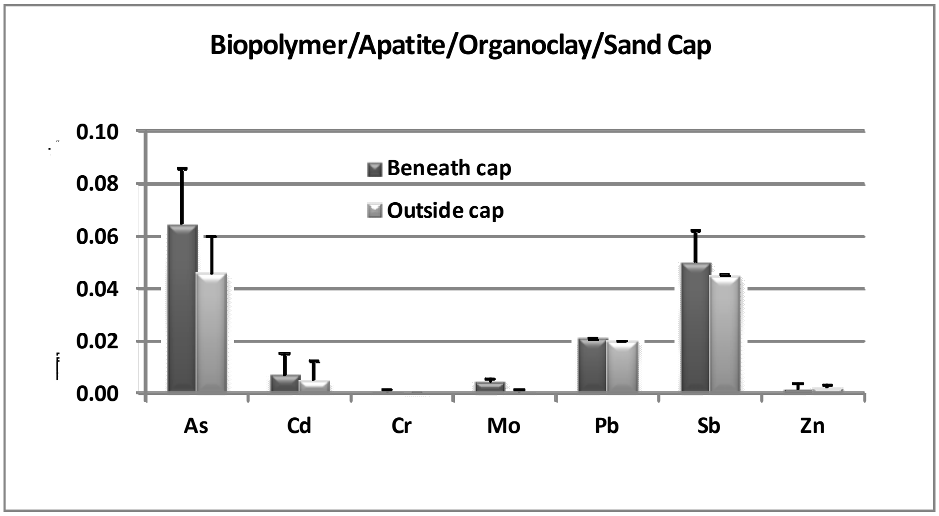

Biopolymer/Apatite/Organoclay/Sand Cap

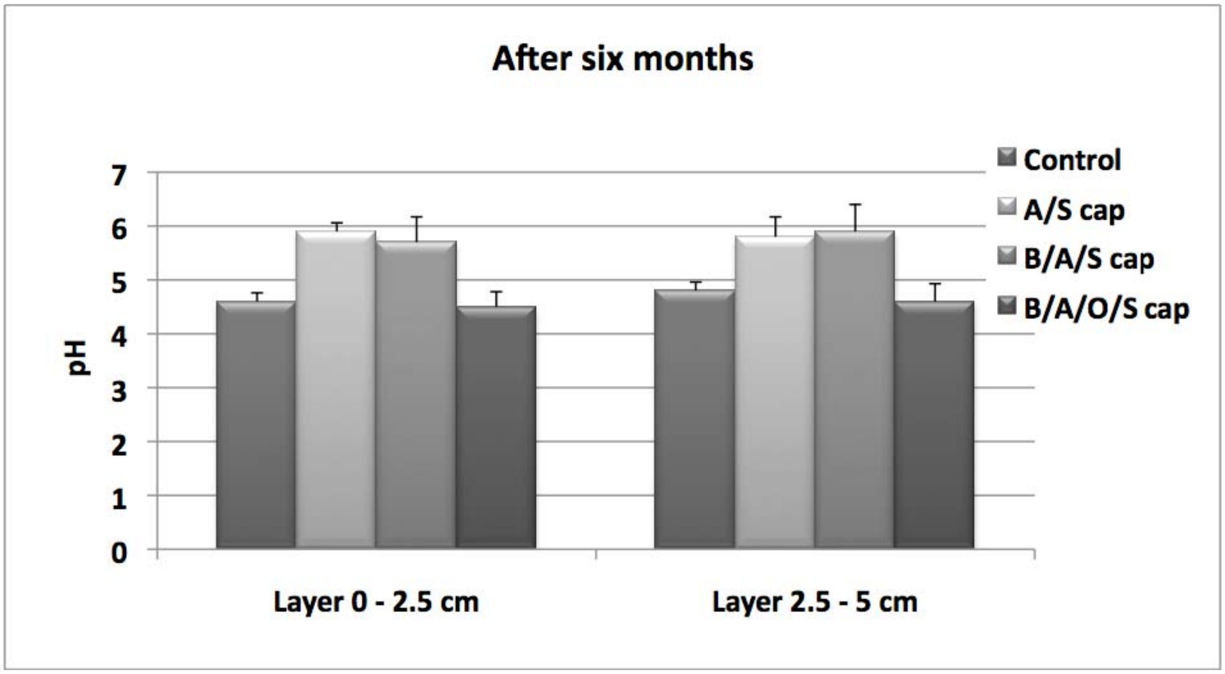
Exhibit 11. Average (stdev) metal concentrations in pore water beneath and outside the active caps 12 months after cap placement.

Exhibit 12. Average P concentrations (ppm) in pore water collected 1, 2, 5, and 12 months after cap placement.

Treatment	Control	A/S cap			B/A/S cap			B/A/O/S cap		
Location	S	C	B	O	C	B	O	C	B	O
					One month					
Avg	0.11	0.55	0.39	0.27	0.38	0.25	0.21	0.41	0.21	0.17
Stdev	0.05	0.74	0.14	0.11	0.16	0.16	0.07	0.04	0.11	0.06
					Two months					
Avg	0.2	0.3	0.23	0.15	0.25	0.21	0.04	0.3	0.2	0.09
Stdev	0.18	0.12	0.11	0.07	0.24	0.10	0.04	0.15	0.12	0.12
					Three months					
Avg	0.09	0.25	0.13	0.09	0.21	0.88	0.09	0.17	0.10	0.07
Stdev	0.05	0.16	0.11	0.01	0.10	0.05	0.16	0.12	0.08	0.01
					12 months					
Avg	0.16	0.46	0.23	0.21	0.37	0.11	0.07	0.35	0.06	0.09
Stdev	0.03	0.09	0.03	0.15	0.02	0.12	0.06	0.02	0.01	0.07

Notes:

S – uncapped sediment, C- within cap, B – sediment beneath cap, O – sediment outside cap.



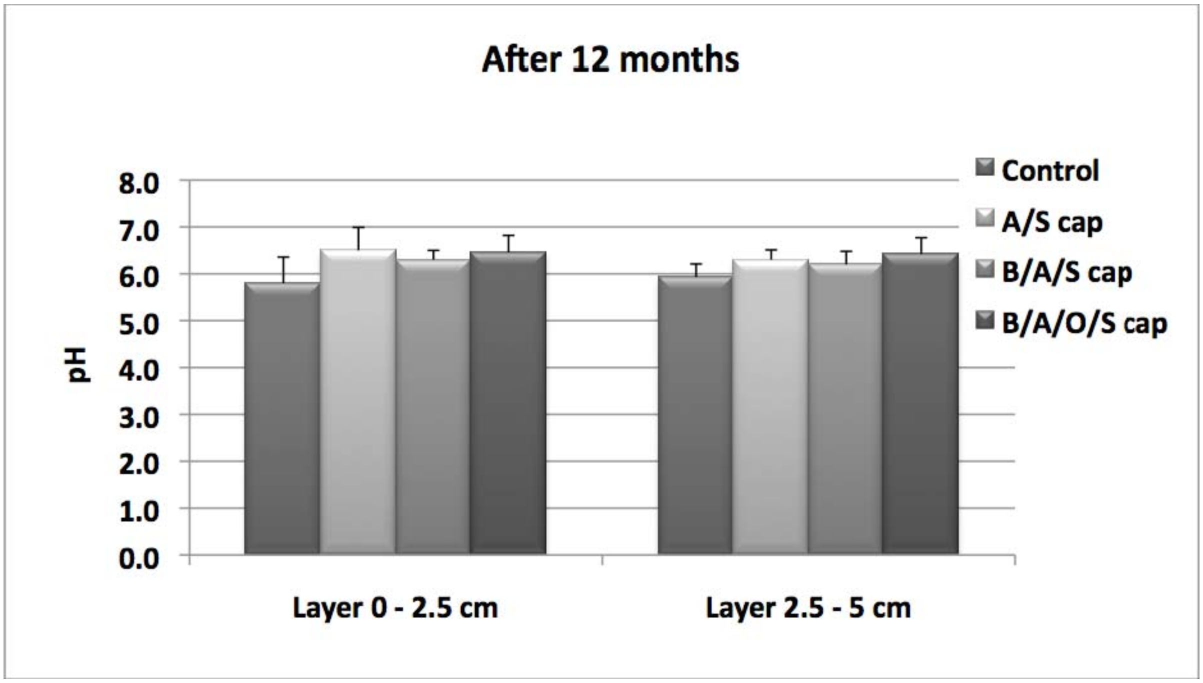


Exhibit 13. Average (stdev) pH in sediment samples collected 6 and 12 months after cap placement.

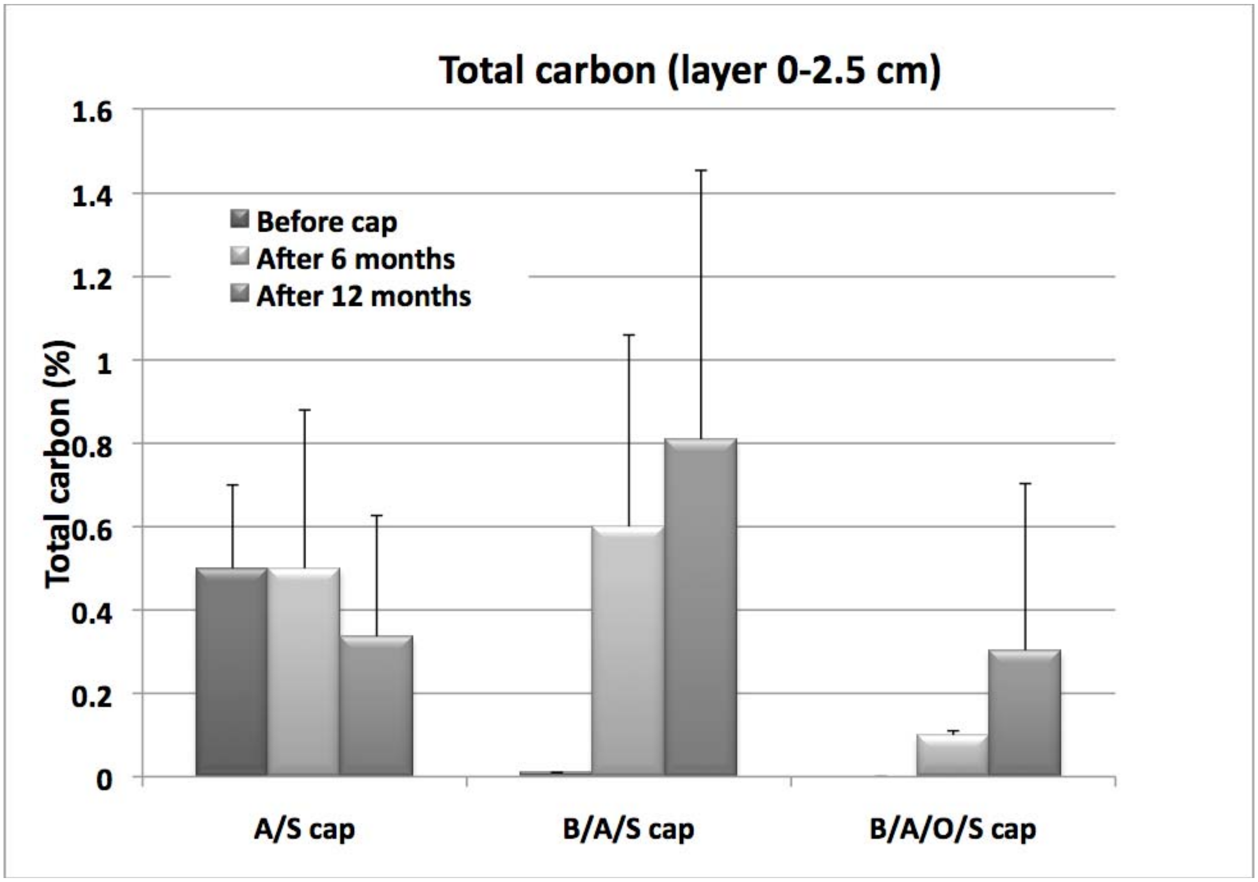
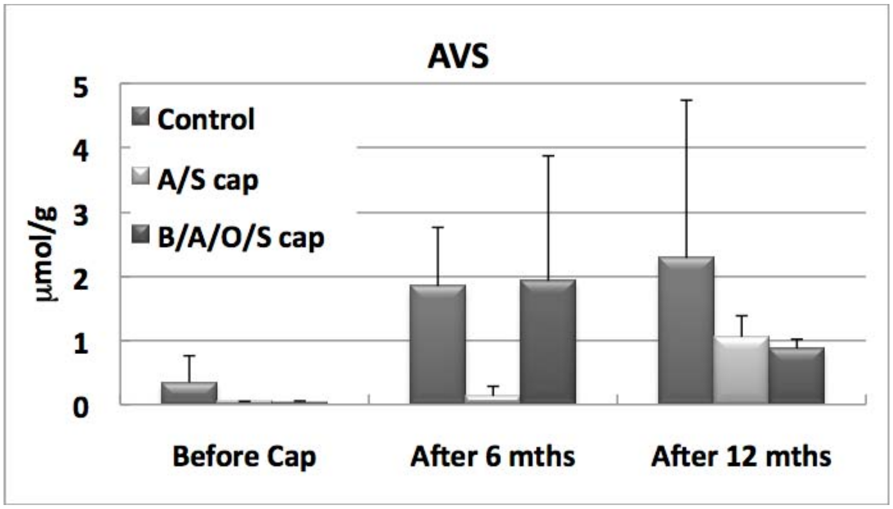
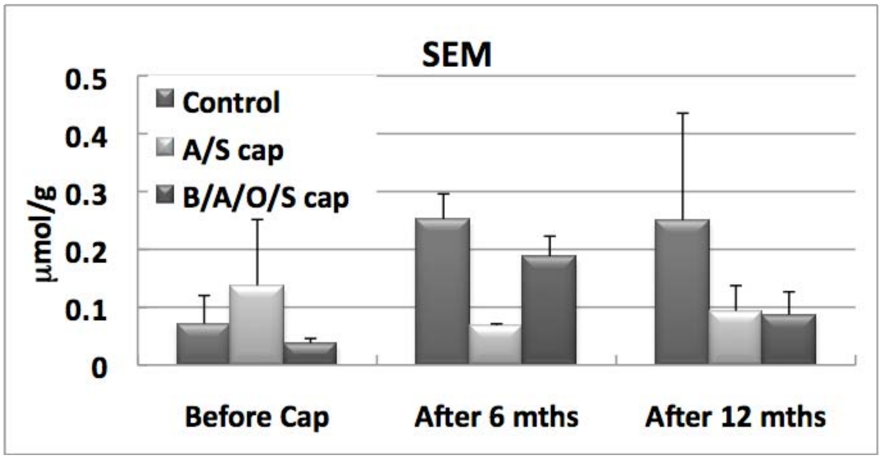


Exhibit 14. Average (stdev) total carbon content in sediment before capping and 6 and 12 months after cap placement.


AVS
µmol/g
5
4
3
2
1
0
Control
A/S cap
B/A/O/S cap
Before Cap
After 6 mths
After 12 mths


SEM
µmol/g
0.5
0.4
0.3
0.2
0.1
0
Control
A/S cap
B/A/O/S cap
Before Cap
After 6 mths
After 12 mths

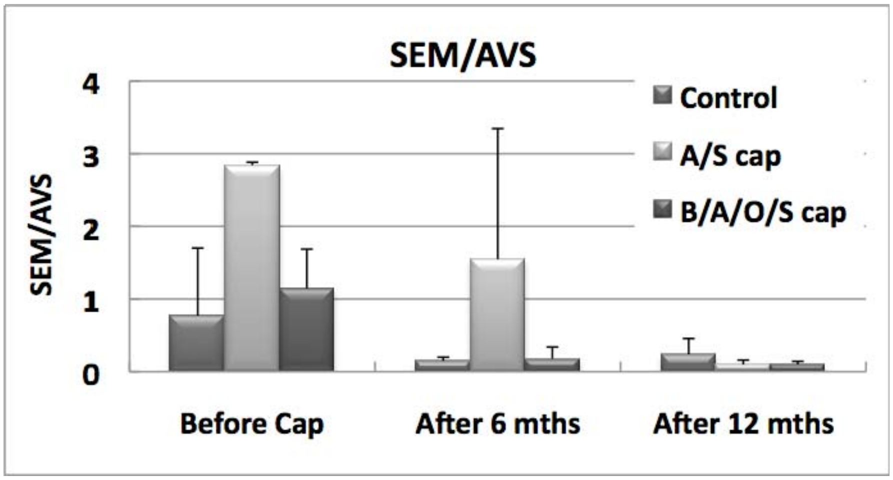

SEM/AVS
SEM/AVS
4
3
2
1
0
Control
A/S cap
B/A/O/S cap
Before Cap
After 6 mths
After 12 mths

Exhibit 15. Average (stdev) AVS, SEM, and SEM/AVS in sediment before and after cap placement.

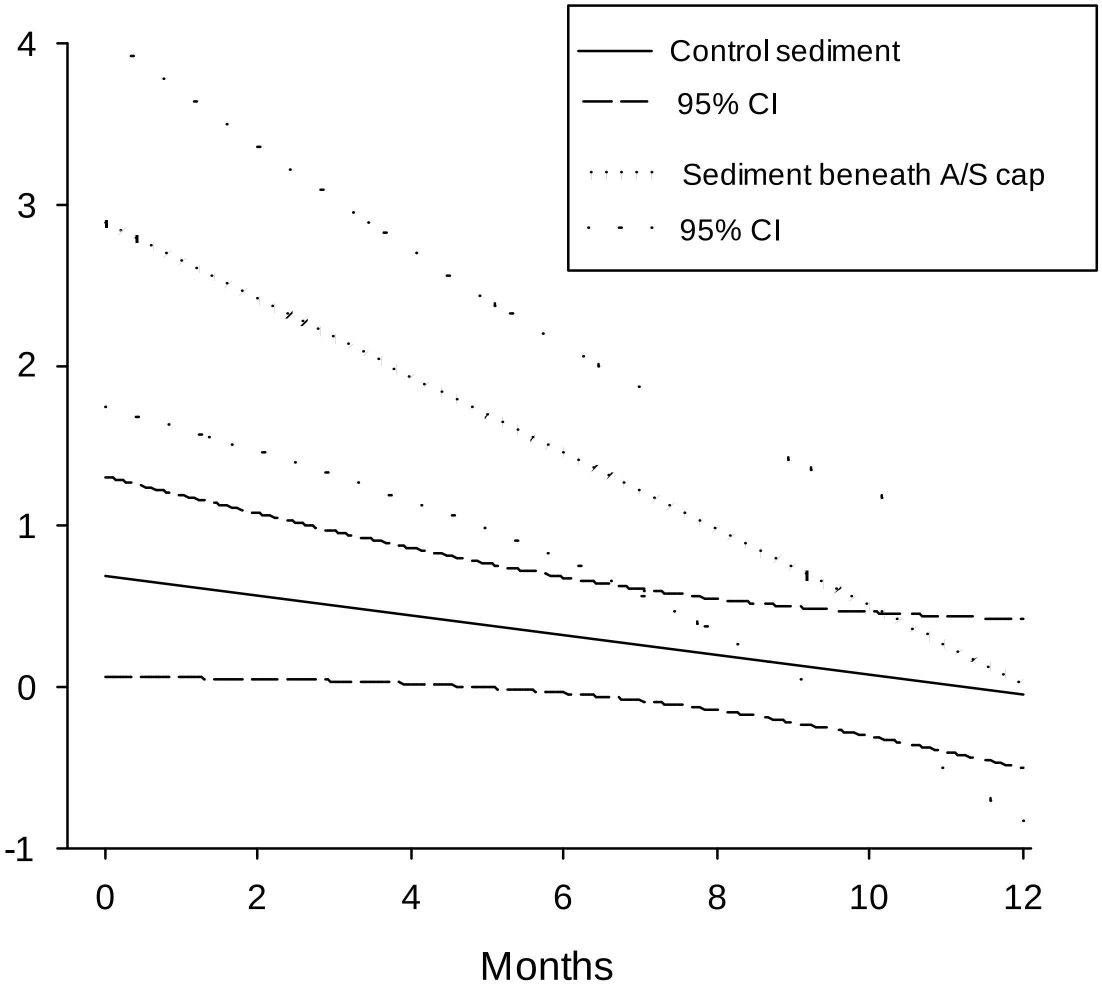


Exhibit 16. Regression lines and 95% confidence intervals (CIs) describing changes in SEM/AVS over time.

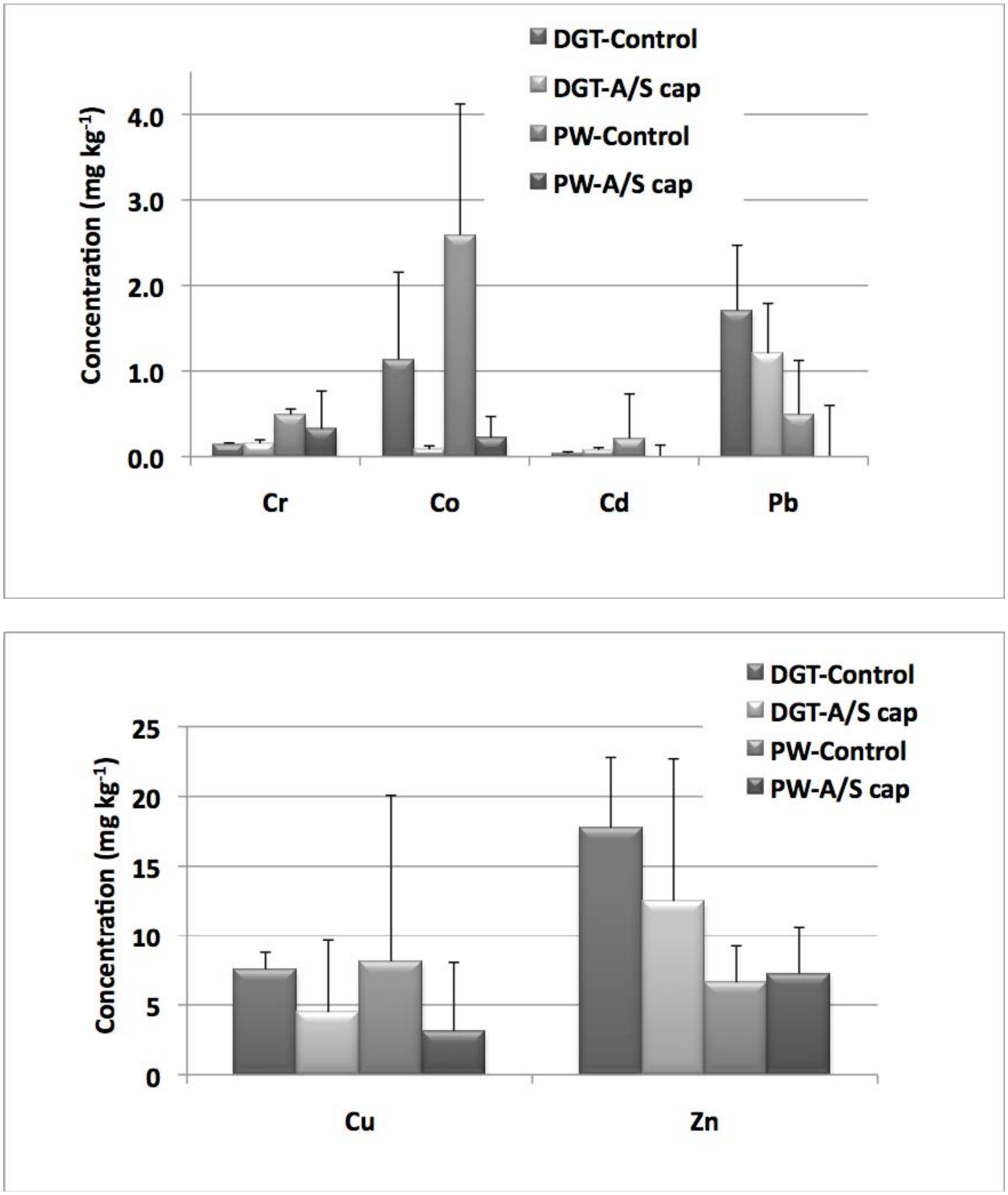


Exhibit 17. Average (stdev) metal concentrations measured by DGT compared with metal concentrations in pore water (PW).

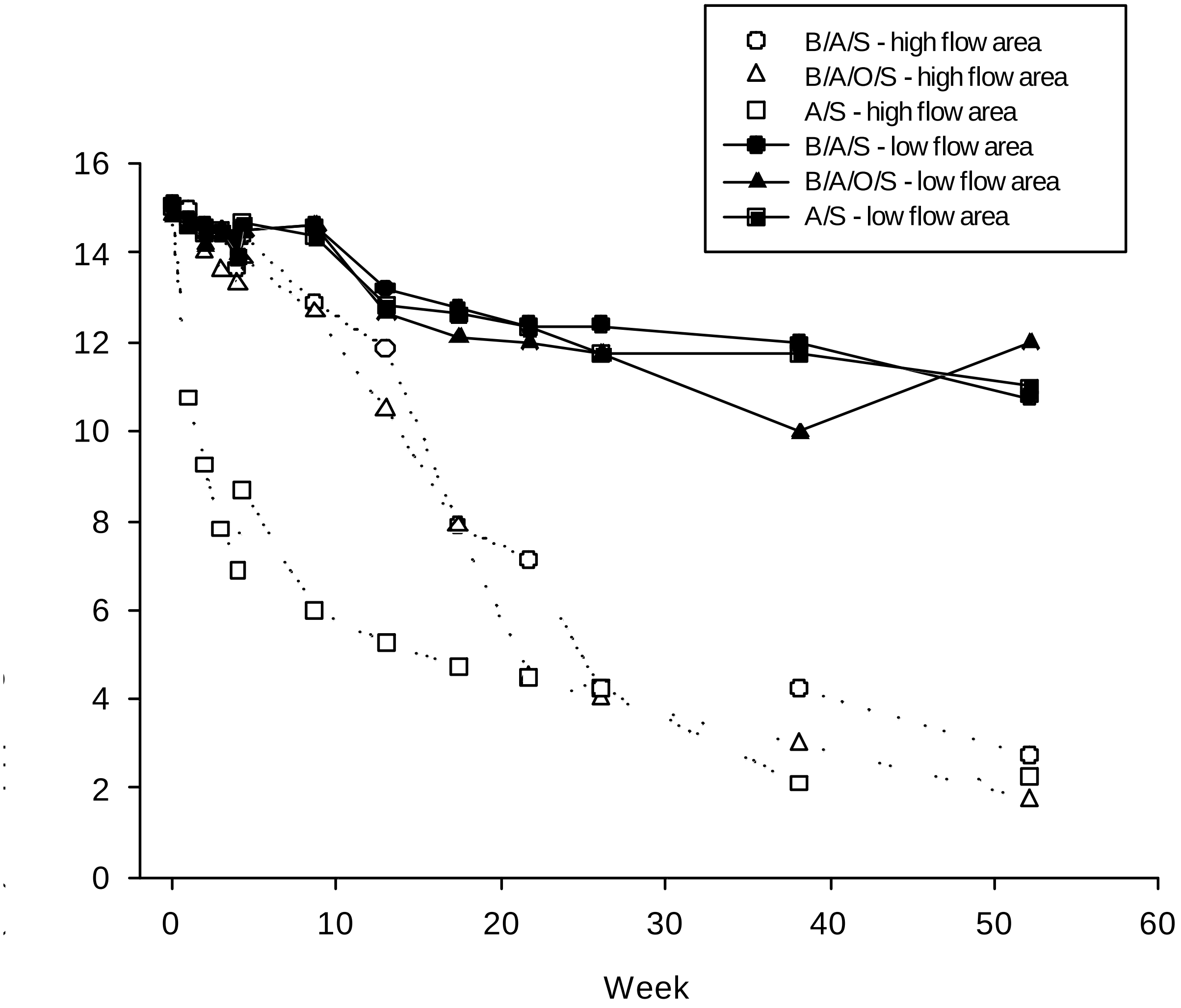


Exhibit 18. Changes in cap thickness over 12 months.

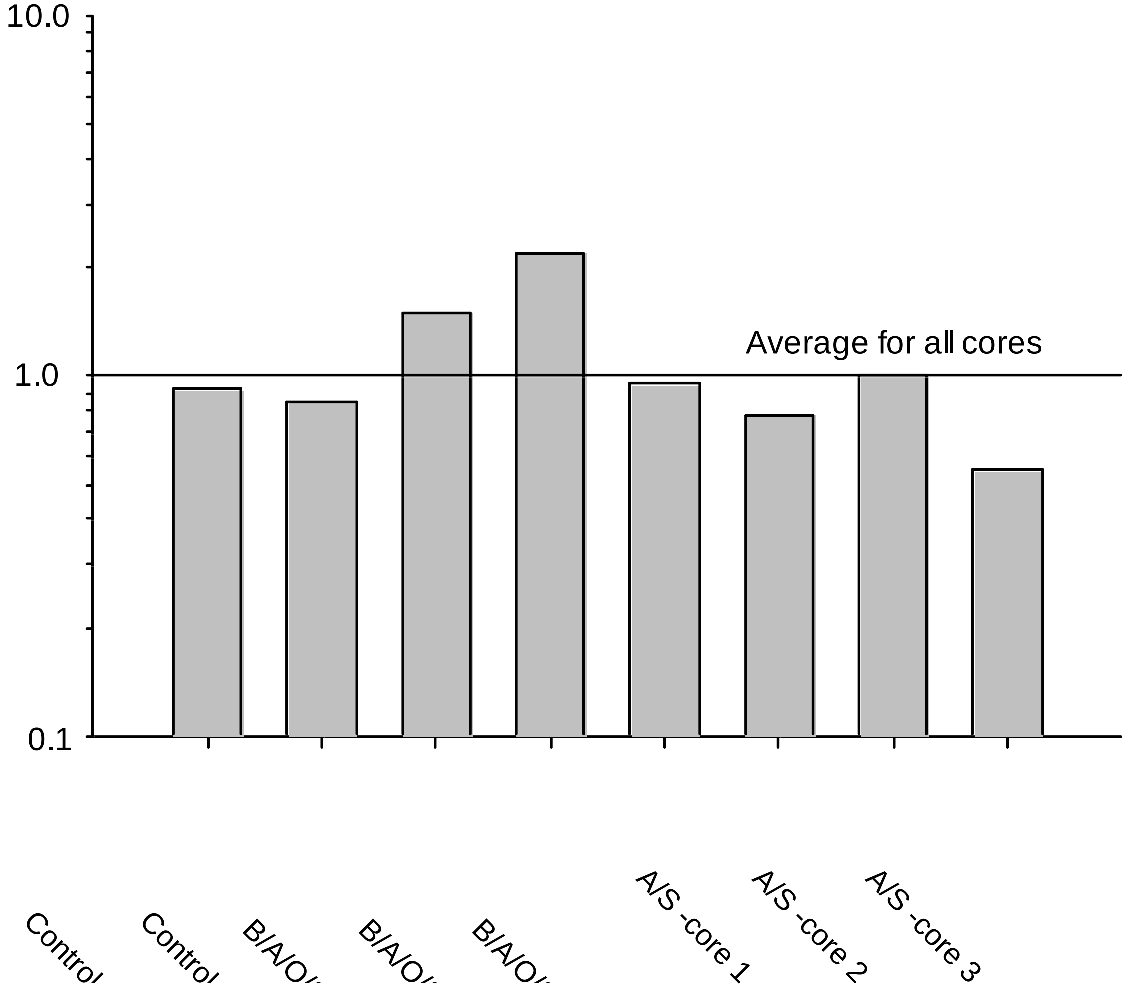


Exhibit 19. Erosion rate ratio for cores from control and capped plots (1, 2, 3 = replicates).