Environmental impact of ongoing sources of metal contamination on remediated sediments

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ABSTRACT

A challenge to all remedial approaches for contaminated sediments is the continued influx of contaminants from uncontrolled sources following remediation. We investigated the effects of ongoing contamination in mesocosms employing sediments remediated by different types of active and passive caps and in-situ treatment. Our hypothesis was that the sequestering agents used in active caps and in situ treatment will bind elements (arsenic, chromium, cadmium, cobalt, copper, nickel, lead, selenium, and zinc) from ongoing sources thereby reducing their bioavailability and protecting underlying remediated sediments from recontamination. Most element concentrations in surface water remained significantly lower in mesocosms with apatite and mixed amendment caps than in mesocosms with passive caps (sand), uncapped sediment, and spike solution throughout the 2520 hour experiment. Element concentrations were significantly higher in *Lumbriculus variegatus* from untreated sediment than in *Lumbriculus* from most active caps. Pearson correlations between element concentrations in *Lumbriculus* and metal concentrations in the top 2.5 cm of sediment or cap measured by diffusive gradient in thin films (DGT) sediment probes were generally strong (as high as 0.98) and significant ($p<0.05$) for almost all tested elements. Metal concentrations in both *Lumbriculus* and sediment/cap were lowest in apatite, mixed amendment, and activated carbon treatments. These findings show that some active caps can protect remediated sediments by reducing the bioavailable pool of metals/metalloids in ongoing sources of contamination.

KEYWORDS

Metals; passive caps; active caps; remediated sediment; bioavailability; re-contamination

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1. Introduction

Rapid industrialization and urbanization has led to the contamination of sediments with heavy metals and organic contaminants and created a pervasive problem worldwide. Major sources of contamination include agricultural and urban lands, industrial activities, spills, and accidents. Arsenic (As), cadmium (Cd), cobalt (Co), copper (Cu), mercury (Hg), nickel (Ni), lead (Pb), and zinc (Zn) are often found in harbor sediments and other areas affected by anthropogenic activities. Sediments containing these contaminants act as secondary sources of contamination, posing significant direct and indirect environmental risks through bioaccumulation in aquatic organisms and incorporation into aquatic food webs that may lead to human exposure (NRC, 2003). Episodic physical redistribution of contaminated sediments within dynamic waterways over time can disperse such risks, potentially affecting biological and water quality conditions far from the original sediment source over long periods (Admiralet al., 2000; Beachler et al., 2003).

The remediation of contaminated sediment requires lowering chemical risks to ecological receptors and human health via the removal, elimination, or reduction of contaminant release and uptake (U.S. EPA, 2005). The most commonly used methods to remediate metal contaminated sediments are environmental dredging, followed by monitored natural recovery, passive and active capping, and in situ remediation techniques. Environmental dredging involves the removal of contaminated sediment from freshwater or marine water bodies to reduce risks to human health and the environment. Removal is particularly effective for source control (mass removal of hot spots) but potentially less effective for overall risk reduction because of resuspension and residual contamination (ITRC, 2014).

Capping and related in situ remediation techniques are usually less energy-intensive, less expensive, and less disruptive to the benthic environment than environmental dredging (Palermo et al., 1998; NRC, 2001, ITRC, 2014). Conventional or passive capping is a remediation technique in which contaminated sediment is covered with a layer (cap) of clean, inert material such as sand, soil, or sediment to physically isolate the contaminants and prevent them from being released to the water column and accumulated by biota. The cap increases the path length that contaminants have to travel to be released to the water, decreases the resuspension of contaminated particles, and provides a cleaner habitat for benthic fauna. An example of successful remediation with a passive cap is Bellinghan Bay, WA, a shallow intertidal lagoon contaminated with Hg (ITRC, 2014). In contrast, active capping and in situ treatment involve the application of chemically reactive amendments to the sediment surface that bind organic and inorganic contaminants, thereby reducing pore water contaminant concentrations and contaminant bioavailability (Knox et al., 2008; Paller and Knox, 2010; Ghosh et al., 2011; Dixon and Knox, 2012; Knox et al., 2012 and 2014). In active capping these amendments are applied as a discrete layer on the sediment surface; whereas in in situ treatment they are broadcast over the sediment surface or mixed into the surficial layer of sediment. Amendments used in active capping include activated carbon, phosphate materials (e.g., apatite), zeolite, organoclays, bentonite, and others based on the proven ability of these materials to sequester metals, or organic contaminants (Ghosh et al., 2011; Knox et al., 2012).

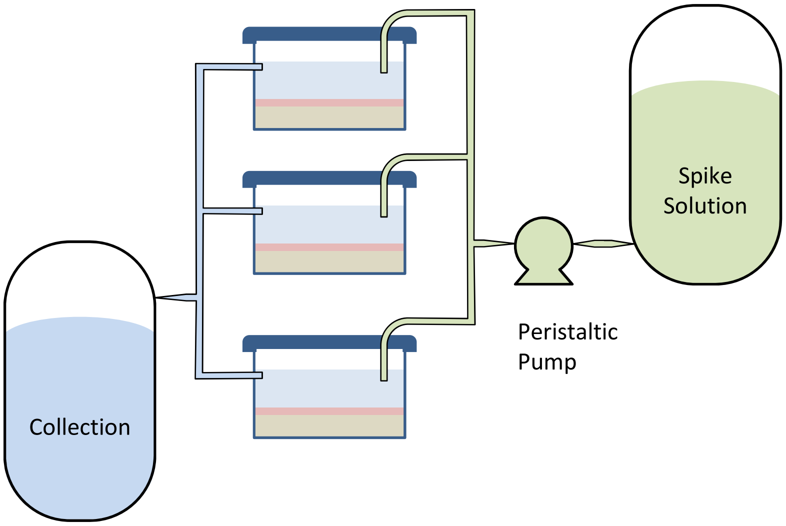
Although substantially reduced in the last few decades, it is unlikely that all contaminant sources will be completely eliminated from aquatic environments. As a result, remediated sediments may be exposed to continued inputs from permitted discharges, upstream contaminated sites, or stormwater discharge resulting in recontamination that can slow or reverse recovery associated with sediment remediation efforts. This is of concern to environmental regulators in the U.S. EPA and U.S. Department of Defense (DoD), who have expressed the need for a better understanding of how releases from ongoing sources relate to recontamination of the sediment bed (SERDP and ESTCP, 2012). This knowledge will contribute to more rigorous risk management that incorporates the resilience of remedies in the face of ongoing contamination into the criteria for remedy selection. The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) sediment cleanup actions, and Clean Water Act (CWA)-related Total Maximum Daily Loads (TMDL) actions provide legal context for dealing with the environmental challenges posed by sediment recontamination (SERDP and ESTCP, 2012).

The recontamination of previously remediated contaminated sediments has the potential to negate expensive remedial actions by producing a polluted habitat zone that overlies remediated sediments. This is a challenge to all remedial approaches, but the severity of the problem may be affected by the type of remediation that has been undertaken. Influxes of contaminants can be expected to degrade the benthic environment as contaminants progressively accumulate in areas previously remediated by environmental dredging or conventional capping with inert materials. However, we hypothesize that the sequestering agents used in active caps or in in situ treatment will interact with incoming contaminants, thereby reducing their bioavailability and toxicity. In this paper, we provide novel results that address the research gap related to the effects of ongoing sources of contamination on different technologies for the remediation of contaminated sediments. This paper complements previous work on the development of active caps for contaminated sediments (Knox et al., 2008, 2012, and 2014). However, neither active caps nor other remediation technologies have been evaluated for their effectiveness and environmental impact when confronted with ongoing contamination.

2. Materials and methods

2.1. Experimental setup

The experimental setup included 30 flow-through mesocosms designed to test the effects of dissolved and particulate metal influxes on selected cap materials present in different thicknesses (Figure 1). Each mesocosm consisted of a 20 cm wide, 41 cm long, 43 cm high custom built acrylic aquarium with an acrylic lid. Homogenized clean sediment was placed in the bottom of 27 of the mesocosms to produce a 12.5 cm layer.



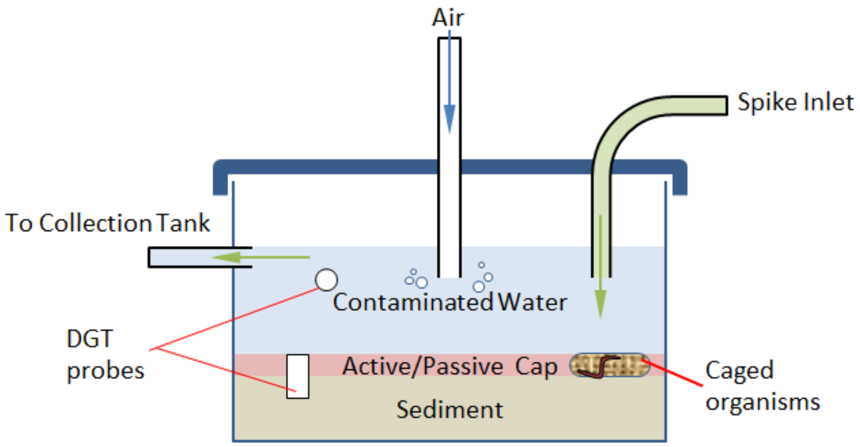


Figure 1. Mesocosm experimental design.

The mesocosms represented different cap compositions, cap thicknesses, controls with sediment but without caps, and controls without sediment or caps (spike solution only). Passive caps consisted of sand; materials used in active caps included apatite (North Carolina rock phosphate), organoclay (MRM from CETCO), activated carbon, and locally collected, subsurface red clay sediment. Apatite had a pH of 7.8 (1:1 solid to H_2O), cation exchange capacity (CEC) of 218 g kg^{-1}, Ca content of 15.2 %, and was composed mostly of hydroxyapatite (X-ray diffraction analyses of apatite are presented in Chlopecka and Adriano (1996) and Knox et al. (2003). Organoclay (MRM) is a sulfur-impregnated organophilic clay granular filtration medium that adsorbs non-aqueous phase liquids (NAPL) and dissolved low-solubility organics (CETCO, 2012). It also sequesters mercury and arsenic from water. Activated carbon was bone char from Norit America, Inc., which is produced from animal bones. It differs from plant derived activated carbon in containing both carbon surface area and hydroxyapatite lattice surface area, which makes bone char very effective for metal removal. Clay sediment had a pH of 5.5, a surface area of 15.07m^2 g^{-1}, and included minerals rich in Fe (goethite and hematite) that could effectively sorb some metals.

There were 10 treatments: a control consisting of spike solution only (C); uncapped sediment (SED); 2.5 cm sand cap (S-1); 5.0 cm sand cap (S-2); 2.5 cm silty clay cap (SC); 2.5 cm apatite cap (A-1); 5.0 cm apatite cap (A-2); activated carbon treatment (AC, 5% by dry weight broadcasted on the sediment surface); 2.5 cm organoclay cap (MRM); and a 2.5 cm cap composed of a mixture of 60 % apatite, 5 % activated carbon, and 35% organoclay MRM (MC). Each treatment was represented by three replicates, with treatments randomly allocated among mesocosms. Sediments were permitted to equilibrate for two weeks, and the cap materials were placed on top of the sediment. The treated and untreated sediments were then saturated and the tanks were filled with deionized water and equilibrated for four weeks prior to receiving spike solution consisting of deionized water with dissolved metals. A single 50 liter reservoir supplied the mesocosms with a continuous inflow (0.3 ml $minute^{-1}$) of spike solution that contained 0.5 mg L^{-1} each of arsenic (As), chromium (Cr), cadmium (Cd), cobalt (Co), copper (Cu), nickel (Ni), lead (Pb), selenium (Se), and zinc (Zn). A single multi-channel peristaltic pump that withdrew water from the reservoir uniformly delivered the spike solution to all mesocoms during the 2520 hour experiment.

An airstone diffuser was placed in each mesocosm to suspend particulate matter, thereby simulating field conditions in which particle-bound metals are a significant source of recontamination (Figure 1).

2.2. Surface water sampling

Surface water samples (10 ml each) were collected daily for the first 10 days and weekly thereafter. Samples for dissolved metals were filtered using a 0.45μm pore diameter membrane filter; samples for total recoverable metals were not filtered. All samples were acidified with nitric acid to pH<2. Metal concentrations in filtered and unfiltered samples were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) using a NexION 300X mass spectrometer (Perkin Elmer, Inc.) in accordance with the quality assurance and quality control protocols of EPA method 6020A (U.S. EPA, 2007). Surface water in all tanks was monitored for dissolved oxygen, temperature, electrical conductivity, pH, and turbidity. Calcium hardness was measured by ethylenediaminetetraacetic acid (EDTA) titration (Hach, 2013).

2.3.Toxicity and bioaccumulation testing

The California blackworm *Lumbriculus variegatus* is a common freshwater benthic oligochaete that burrows in shallow sediments. Blackworms were obtained from a commercial supplier (California Blackworm Co.). Three grams of blackworms were drained of excess water, and placed in each of thirty 12 cm long, 2 cm inner diameter screened cages for deployment into the experimental mesocosms. Each mesocosm received one cage, which was filled to 40-50% of maximum volume with cap material or sediment taken from just below the solid-water interface. The cages were partly (50%) buried in a horizontal position for 10 days and retrieved at hour 2040 of the 2520 hour experiment. Living blackworms were removed from the cages and weighed in aggregate to determine percent recovery (initial weight/final weight x 100), which was used as an estimate of survival.

Blackworms that remained alive were analyzed in aggregate for whole-body metal concentrations. They were rinsed, depurated in clean water for six hours, drained of excess water, and quick frozen prior to lyophilization. Metal analyses were conducted on 50 mg samples of freeze-dried tissue digested with 1 mL of H_2O_2 (30%) and 3 mL of trace metal grade nitric acid at 85 °C. After digestion, the samples were analyzed by ICP-MS using the protocols listed above (U.S. EPA, 2007).

2.4. Assessment of cap effectiveness by diffusive gradients in thin films (DGT) probes

Diffusive gradient in thin films (DGT) is a passive sampling technology that consists of a collection gel-layer with a medium that selectively binds to the contaminant of interest and a diffusion gel-layer that selectively admits analyte molecules (Davison and Zhang, 1994). Chelex 100 sediment DGT probes (purchased from DGT Research Ltd, Lancaster, UK) were deoxygenated before deployment. One probe was deployed for 24 hours within each mesocosm at 2016 hours by inserting it vertically to measure metal levels in the cap and underlying sediment layers, which were divided into A (0-2.5 cm), B (2.5 – 5.0 cm), and C (5 - 7.5 cm). The probes were rinsed upon retrieval, and the resin-gel layer from each probe was removed and divided into sections representing each layer. Each section was immersed in 1 ml of 1 M HNO_3 for 24 hours, which was diluted with deionized water prior to analysis by ICP-MS. The masses of metal accumulated on the resin gel layers and the DGT concentrations of metals in the sediment (C_{DGT}) were calculated as shown in Zhang and Davison (1995) and Zhang et al. (2001).

Sediment core samples were collected from each mesocosm at 2520 hours with a push-tube coring device to measure sediment pH. The cores from sediment only and activated carbon treatments were split into three layers: A: 0-2.5 cm, B: 2.5-5.0 cm, and C: below 5.0 cm. The cores from treatments with caps were split into a cap layer and three layers of sediment beneath the cap (A: 0-2.5 cm, B: 2.5-5 cm, and C: below 5.0 - 7.5 cm). The pH was determined from a 1:1 solid/water equilibrium solution.

2.5.Statistical analysis

The significance ($p<0.05$) of differences in metal concentrations in blackworm tissues among treatments was assessed with one-way analysis of variance (ANOVA) followed by pair-wise Holm-Sidak tests. Data were $\log_{10}(X+1)$ transformed to better approximate the assumptions of normality and homoscedasticity. Test results are presented as geometric means calculated by back-transformation. Pearson correlations were calculated between metal concentrations in blackworm tissues and metal concentrations in sediment measured by DGT probes.

3. Results and discussion

The treatments were evaluated based on the following criteria: 1) surface water properties, 2) dissolved and particulate metal concentrations in surface water, 3) toxicity to *Lumbriculus*, 4) *b*ioaccumulation of metals by *Lumbriculus*, and 5) metal concentrations measured by diffusive gradients in thin films (DGT) probes.

3.1 Surface water properties

Electrical conductivity (EC) was consistent throughout the 2520 hour experiment and was highest in the mesocosms with MRM caps followed by the mesocosms with mixed amendments (Figure 2). Turbidity was highest in the mesocosms with uncapped sediments, activated carbon treatments, and silty clay caps because these mesocosms contained easily suspended fine particles (Figure 2). Surface water pH was affected by the pH of the spike solution and the cap materials. The highest average pH was in treatments with activated carbon followed by apatite and MC caps. Only the mesocosm with organoclay MRM caps showed significant changes over time, with pH decreasing from about 6.6 to 4.0 (Figure 2). Dissolved oxygen concentrations and temperatures (average of about $18^{o}C$) were similar among treatments and stable throughout the experiment. Some amendments (e.g., apatite and MRM) increased the water calcium carbonate hardness from less than 5 (control and sand cap treatments) to about 180 mg L^{-1} (Figure 3).

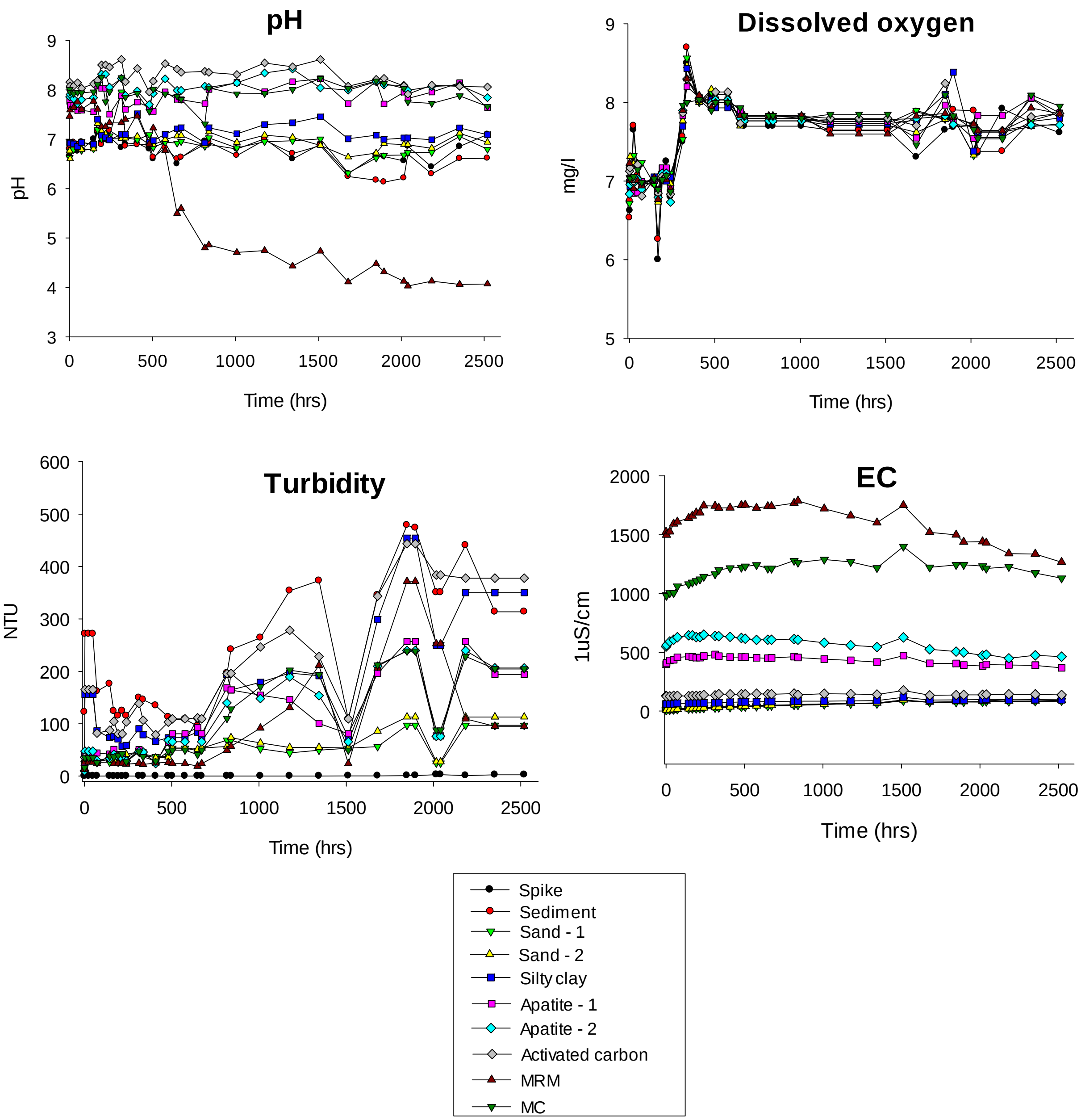


Figure 2. Water quality over time for each treatment; average results for pH, dissolved oxygen turbidity, and electrical conductivity (EC) (n=3).

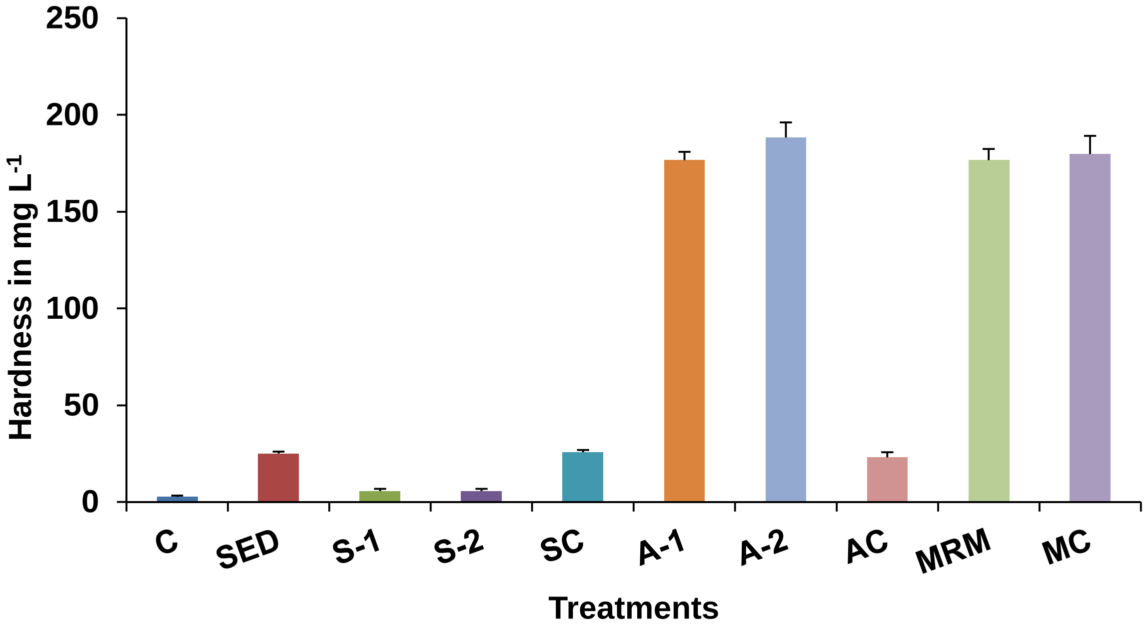


Figure 3. Hardness of surface water (mg L^{-1}) for each treatment at 2520 hours; spike solution only (C), uncapped sediment (SED), sediment with passive sand caps (S-1: 2.5 cm, S-2: 5 cm), and sediment with several types of active caps (SC: 2.5 cm silty clay, A-1: 2.5 cm apatite , A-2: 5.0 cm apatite, AC: activated carbon treatment, MRM: 2.5 cm organoclay, and MC: 2.5 cm mixture of active amendments).

3.2 Effect of ongoing contaminant influx on metal concentrations in surface water

The concentration of each metal in the spike solution was about 0.5 mg L^{-1} as indicated by ICP-MS. Maintaining these concentrations required keeping the pH of the spike below 7.0 to prevent metals from precipitating. The effects of the treatments on metal concentrations in surface water are shown in Figures 4 and 5. Electrons neutralize protons (i.e., H^+) in many naturally-occurring reactions (Dragun, 1998), so the fixation of elements in sediment and cap materials was dependent upon Eh and pH. Because the Eh of the water column was stable for all treatments and above 0.0, dissolved and particulate metal concentrations in the water column were mostly dependent on pH. Other factors that likely affected the chemisorption of metals in this experiment included electronegativity, electrostatic forces between metal ions and sediment/cap material surfaces, surface complexation reactions, charge-to-radius ratios, and hydrolysis constants (McBride, 1994; Shi et al., 2009).

At 2520 hours, the average dissolved arsenic concentration in the mesocosms with active caps was about 70 $\mu g\ L^{-1}$ compared with 250 $\mu g\ L^{-1}$ in the control mesocosms (spike solution only) and 114 $\mu g\ L^{-1}$ in the mesocosms with passive caps (Figure 4). Dissolved As concentrations in mesocosms with active caps (especially MC and A) were lower than in mesocosms with passive caps and control mesocosms (Figure 4). Arsenic concentrations were about 50% lower in the control treatment than in the spike solution, likely due to As precipitation as As_2O_3. Dragun (1998) reported that particle bound As predominates under Ehs above 0.0 and at pH 7.

Dissolved Cd increased over time in all treatments, but the increases were much greater in the control mesocosms and mesocosms with passive caps (Figure 5). At 2520 hours, average Cd concentrations in surface water were less than 100 $\mu g\ L^{-1}$ in the mesocosms with active caps (except MRM) compared with more than 300 $\mu g\ L^{-1}$in the mesocosms with passive caps and 500 $\mu g\ L^{-1}$ in the control mesocosms (Figures 4 and 5). Total Cd concentrations were relatively high in the mesocoms with MRM caps due to low pH (Figure 2). Particle bound Cd was a small fraction of total Cd in all treatments (Figure 4). Cadmium is soluble over a wide range of pHs (Adriano, 2001), so Cd concentrations in the control treatment were similar to Cd concentrations in the spike solution (Figure 4). Also, the relatively low metal electronegativity of Cd (1.69) tended to reduce the specific adsorption of this ion resulting in a relatively high proportion of Cd being dissolved.

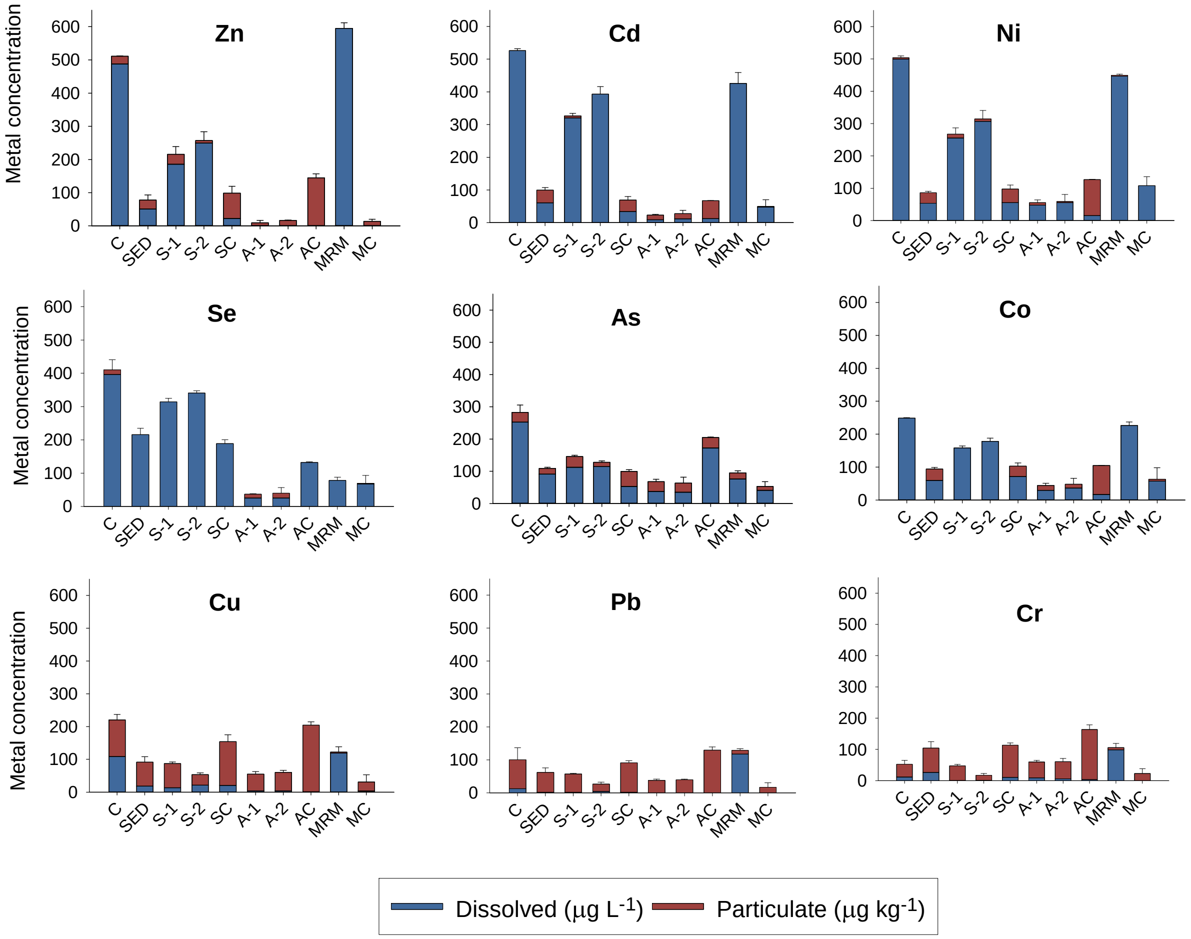
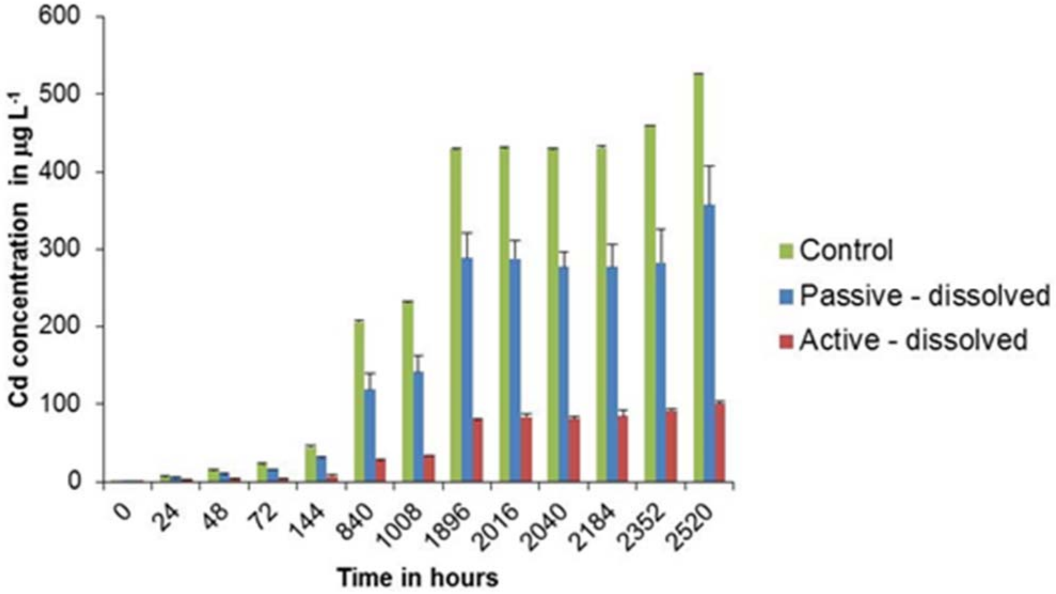


Figure 4. Average surface water concentrations of metals in mesocosms with no sediment, spike solution only (C), uncapped sediment (SED), sediment with passive sand caps (S-1: 2.5 cm cap, S-2: 5 cm cap), and sediment with several types of active caps (SC: 2.5 cm silty clay cap, A-1: 2.5 cm apatite cap, A-2: 5.0 cm apatite cap, AC: activated carbon treatment, MRM: 2.5 cm organoclay cap, and MC: 2.5 cm mixed amendment cap) at 2520 hours.



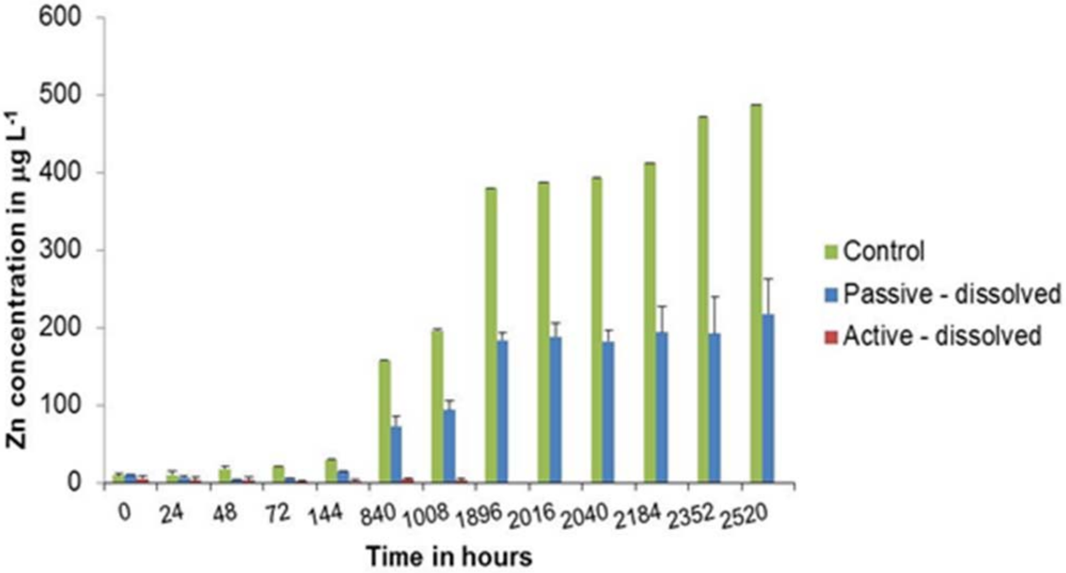


Figure 5. Average surface water concentrations of dissolved Cd and Zn in mesocosms with passive caps (n=6 for 2.5 cm sand cap and 5.0 cm sand cap), active caps (n=12 for the 2.5 cm apatite cap, 5.0 cm apatite cap, activated carbon treatment, and 2.5 cm mixed amendment cap), and without caps or sediment (control) (n=2) over 2520 hours.

Dissolved Se in the control mesocosms was 400 μg L^{-1} at 2520 hours and was also relatively high in the treatments with passive sand caps (Figure 4). Levels were substantially lower in the mesocosms with active caps, especially apatite caps (under 50 μg L^{-1}). At 2520 hours, most Se was dissolved in all treatments (Figure 4). Although relatively ineffective at removing divalent metals such as Zn, Cd, and Ni, MRM caps were about as effective as apatite caps at removing Se and As from the surface water. MRM is specifically designed for the removal of Hg and As rather than other elements (CETCO, 2012).

Like Cd, Zn is very mobile over a wide range of pHs (Adriano, 2001) and has relatively low electronegativity (1.65) (McBride, 1994); therefore, Zn concentrations in the control treatment were comparable to those in the spike solution. Average dissolved Zn increased over time in the control mesocosms and mesocosms with passive caps, reaching 500 μg L^{-1} in the former and nearly 200 μg L^{-1} in the latter (Figure 5). In contrast, average dissolved Zn concentrations remained under 10 μg L^{-1} in most active cap treatments during the experiment (Figure 5). High dissolved Zn concentrations in the MRM treatment were likely the result of low pH (about 4.0; Figure 2) that facilitated metal dissolution. The lowest average total Zn concentrations were in mesocosms with apatite caps (A) and multiple amendment caps (MC). Most of the Zn in these mesocosms was particle-bound, and very little was in the more bioavailable dissolved phase (Figure 4). Ma et al. (1995) and Wright et al. (1995) have reported that the interaction between apatite and metals in solution is controlled by the precipitation of various phosphate phases, soption, and isomorphic substitution.

Nickel behaved similarly to Cd, Co, Zn, and Se (Figure 4). However, Cr, Cu and Pb total concentrations in the control treatment were lower than concentrations in the spike solution (500 μg L^{-1}) suggesting the possibility of co-interference among these elements and solid phase partitioning through sorption and precipitation. This is consistent with other reports; e.g., Dragun (1998) reported that Pb is generally in particulate-bound forms such as $PbCO_3$ and PbO above Eh 0.0 and pH 4.

3.3. Toxicity and bioaccumulation

Average percent survival of *Lumbriculus* for the 10 day test was 0% in the control mesocosms, 0% in the mesocosms with passive (sand) caps, 10% in the mesocosms with uncapped sediment, and 65-80% in the mesocosms with active caps suggesting that the latter can protect benthic organisms from ongoing contamination (Figure 6). High water hardness likely contributed to the relatively low mortality of test organisms in the treatments with apatite, organoclay, and MC (Figure 3). The acute toxicity of many elements (e.g., Cd, Cr, Cu, Ni, Pb, and Zn) depends on water hardness, with toxicity diminishing as hardness increases (U.S. EPA, 2016). In contrast, mortality was high in treatments with low hardness (e.g., sediment only or sand) (Figures 3 and 6). Therefore, evaluation of cap materials should be based not only on their ability to sequester metals but also on their indirect effects on water properties (e.g., hardness) that can influence metal bioavailability and toxicity.

Surviving *Lumbriculus* were analyzed for whole-body metal concentrations, which were compared with background concentrations measured in *Lumbriculus* received from the supplier. Background concentrations of Co, Cd, Cr, Ni, Pb, and Se were <2.0 mg kg^{-1}, similar to those reported by Piol et al. (2006). Following 10 days of exposure, these metals increased to 20 - 150 mg kg^{-1} in *Lumbriculus* from mesocosms with uncapped sediment but remained under 10 mg

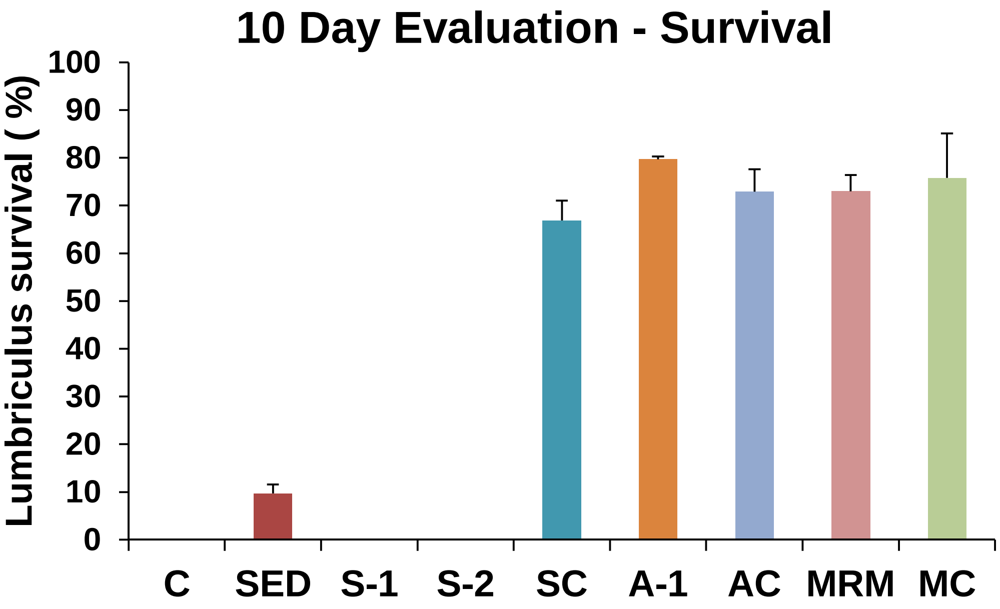


Figure 6. Average survival of *Lumbriculus variegatus* after 10 day toxicity tests conducted in mesocosms receiving water spiked with dissolved metals. Mesocosm treatments included spike solution only (C), uncapped sediment (SED), sediment with sand caps (S-1: 2.5 cm and S-2: 5 cm), and sediment with active caps (SC: 2.5 cm silty clay, A-1: 2.5 cm apatite, AC: activated carbon, MRM: 2.5 cm organoclay, and MC: 2.5 cm mixture of active amendments). Error bars are standard deviations (n=3).

kg^{-1} in *Lumbriculus* from most mesocosms with active caps (Figure 7). Differences between mesocosms with active caps and mesocosms with untreated sediment were statistically significant ($p<0.05$). Although all active caps were effective at reducing metal uptake, there were significant differences among cap types, with the most effective caps varying among metals (Figure 7). Differences in *Lumbriculus* tissue concentrations between active caps and untreated sediment were less prominent for As and Cu than for the previously discussed metals but were statistically significant except for Cu in the silty clay cap (Figure 7). The concentrations of most metals in *Lumbriculus* from the active cap treatments were higher than background concentrations, but these differences were not always statistically significant (Figure 7). Background levels of Zn in *Lumbriculus* (about 200 mg kg^{-1}) were higher than for the other metals. These levels were comparable to those in the mesocosms with active caps and significantly lower than in the mesocosms with uncapped sediment (about 700 mg kg^{-1}) (Figure 7).

Kwon et al. (2010) reported that the sorbent material, Thiol-SAMMS, was able to reduce the uptake of Cd by *Lumbriculus* from beakers of contaminated sediment by up to 98%. These results are comparable to those in our mesocosms with apatite and mixed amendment caps (Figure 7) despite more challenging conditions of exposure involving the continuous influx of contamination via the overlying water column.

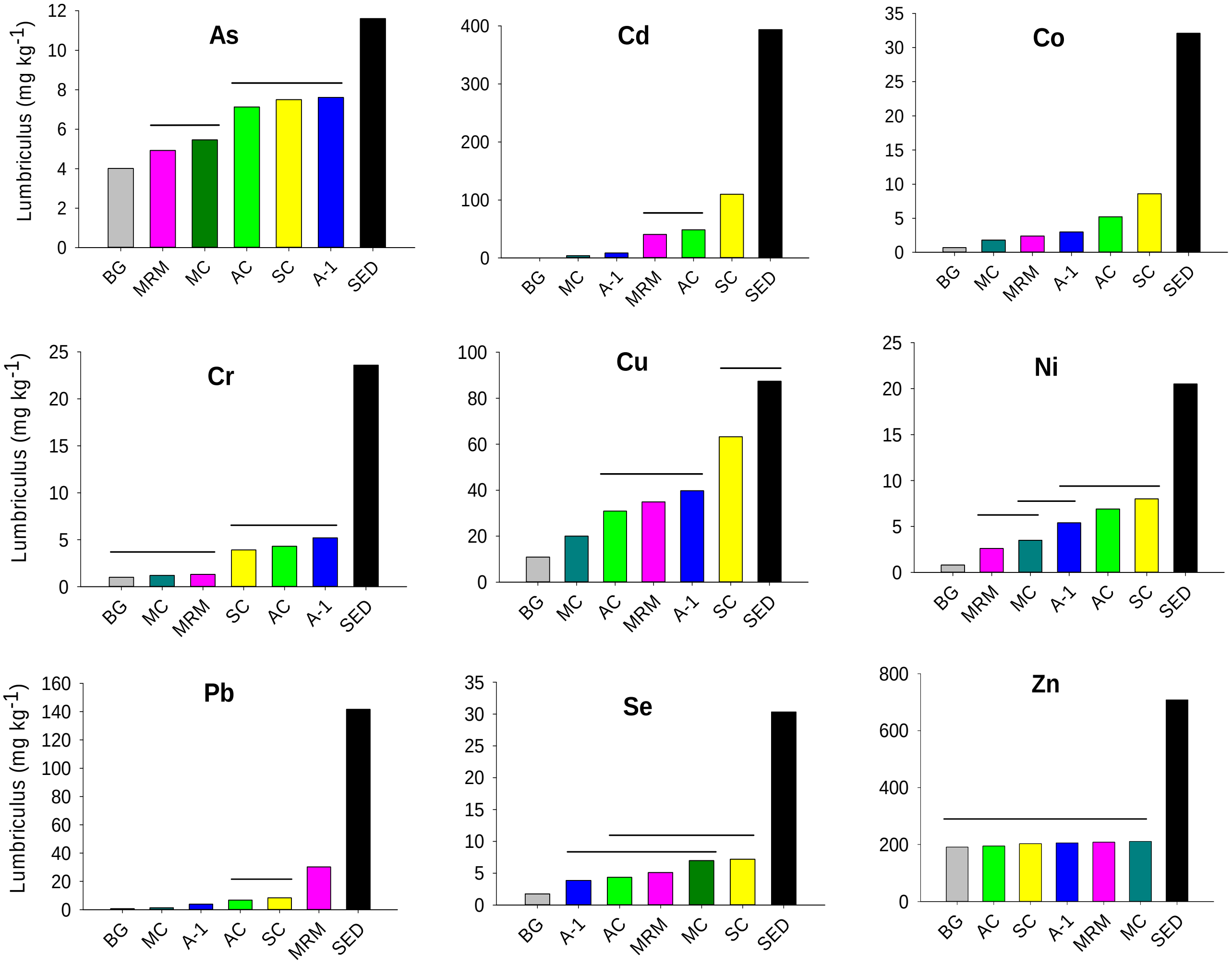


Figure 7. Analysis of variance of differences in *Lumbriculus variegatus* metal concentrations (whole body, 10 day exposure) among sediment treatments (BG =background, AC: activated carbon, SC: silty clay cap, A: apatite cap (2.5 cm thick), MRM: organoclay MRM cap, MC: mixture of active amendments, SED: untreated sediment). Geometric means connected by the same line are not significantly different at $p<0.05$.

3.4. Assessment of cap effectiveness by diffusive gradients in thin films (DGT) probes

DGT probes have the theoretical advantage of selectively measuring metal phases that are bioavailable and potentially toxic (Davison and Zhang 1994). DGT gel probe samplers were used to determine the effects of the cap materials on the bioavailable pools of metals in the caps and sediments. Only Cd, Co, Cu, Ni, Pb, and Zn (Figures 8 and 9) could be measured by the chelex 100 sediment DGT probes. Generally, metal concentrations in the apatite and MC cap layers and in the upper layer of sediment treated with activated carbon were very low compared with metal concentrations in the passive sand and silty clay cap layers and much lower than in the surface layer of sediment in the mesocosms without caps (Figures 8 and 9). Lower sediment metal levels in apatite, activated carbon, and MC treatments persisted deeper within the sediment profile, especially compared with uncapped sediment, which exhibited relatively high metals levels to a depth of 5.0 cm (examples are shown for Cd and Co, Figure 8). Metal levels, especially levels of Ni, in treatments with MRM caps were higher than in the treatments with other active caps (Figure 9), probably because of low sediment pH (Figure 10). At 2520 hours the highest pH values were in mesocosms with apatite and MC caps followed by mesocosms with activated carbon (Figure 10). Mesocosms with organoclay MRM caps had the lowest pH values in the cap and the sediment below the cap (Figure 10).

The preceding results show that potentially bioavailable pool of metals was lower in the apatite and MC caps, in the sediments with activated carbon, and in the sediment layers underlying these treatments than in uncapped sediments or passive caps. Pearson correlations between metal concentrations in *Lumbriculus* and metal concentrations in the top 2.5 cm of sediment or cap materials (measured by DGT sediment probes) were generally strong (as high as 0.98) and significant ($p<0.05$) for all metals except zinc (Figure 9). These relationships suggest that metal concentrations in *Lumbriculus* were the result of uptake from the surrounding sediment or cap and possibly the overlying water. Low metal concentrations in *Lumbriculus* from the apatite, MC, and activated carbon treatments may have resulted from metal sequestration by these amendments (Figure 7). Previous reports by Knox et al. (2012), Ghosh et al (2011), and Ma et al. (1995) indicate that active amendments (e.g., apatite and activated carbon) can reduce the bioavailable pool of contaminants in sediments. Dissolved metals that precipitate on the sediment/cap surface or that are immobilized more deeply in the sediment profile are generally biologically unavailable unless the re-enter the dissolved phase, which facilitates transport through respiratory membranes (Campbell, 1995; McGreer et al., 2002). An exception is metals that are ingested by sediment feeding organism, which may be released by interactions with digestive fluids and again become available for biological uptake within the organism (Fan and Wang, 2001).

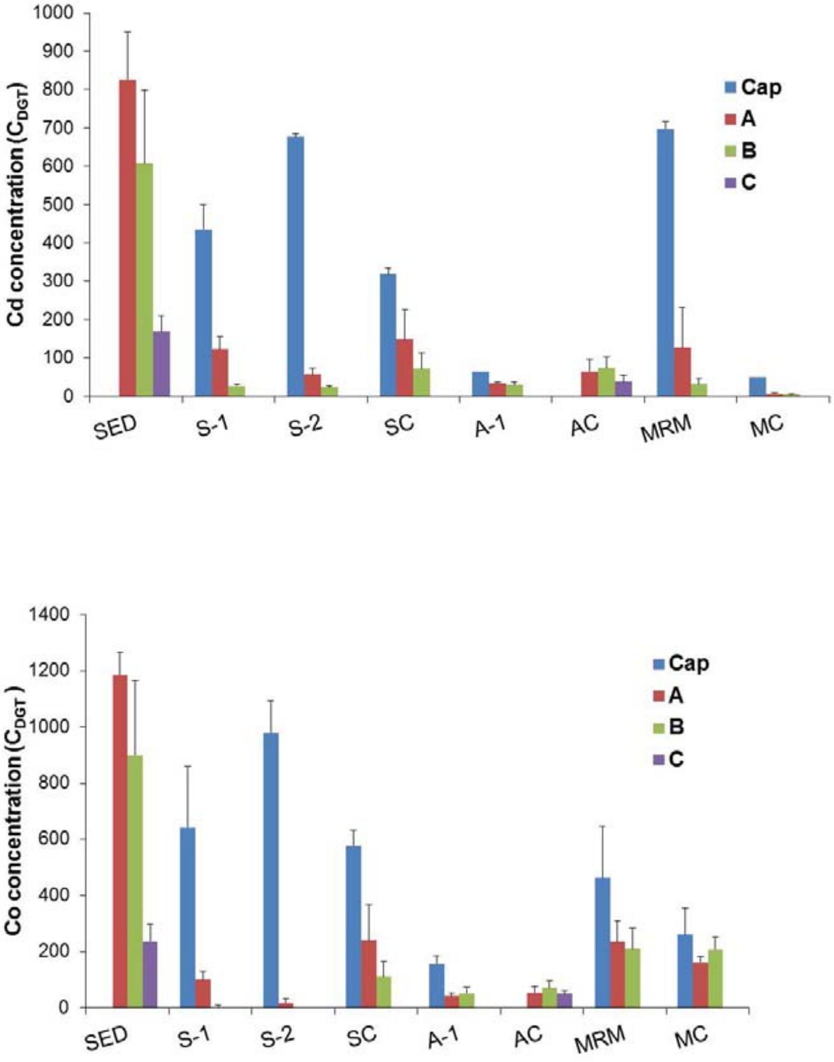


Figure 8. Cadmium (Cd) and cobalt (Co) concentrations (μg kg^{-1}) measured by sediment DGT probes (C_{DGT}) in cap materials and layers of sediment beneath the cap (layer A: 0-2.5 cm, layer B: 2.5 – 5.0 cm, and layer C: 5 - 7.5 cm). Treatments: uncapped sediment (SED), sediment with passive sand caps (S – 1: 2.5 cm thick cap and S – 2: 5 cm thick cap) and sediment with several types of active caps (2.5 cm thick) (apatite A-1; silty clay - SC; activated carbon, no cap - AC; organoclay – MRM:, and mixture of active amendments – MC) at 2040 hours.

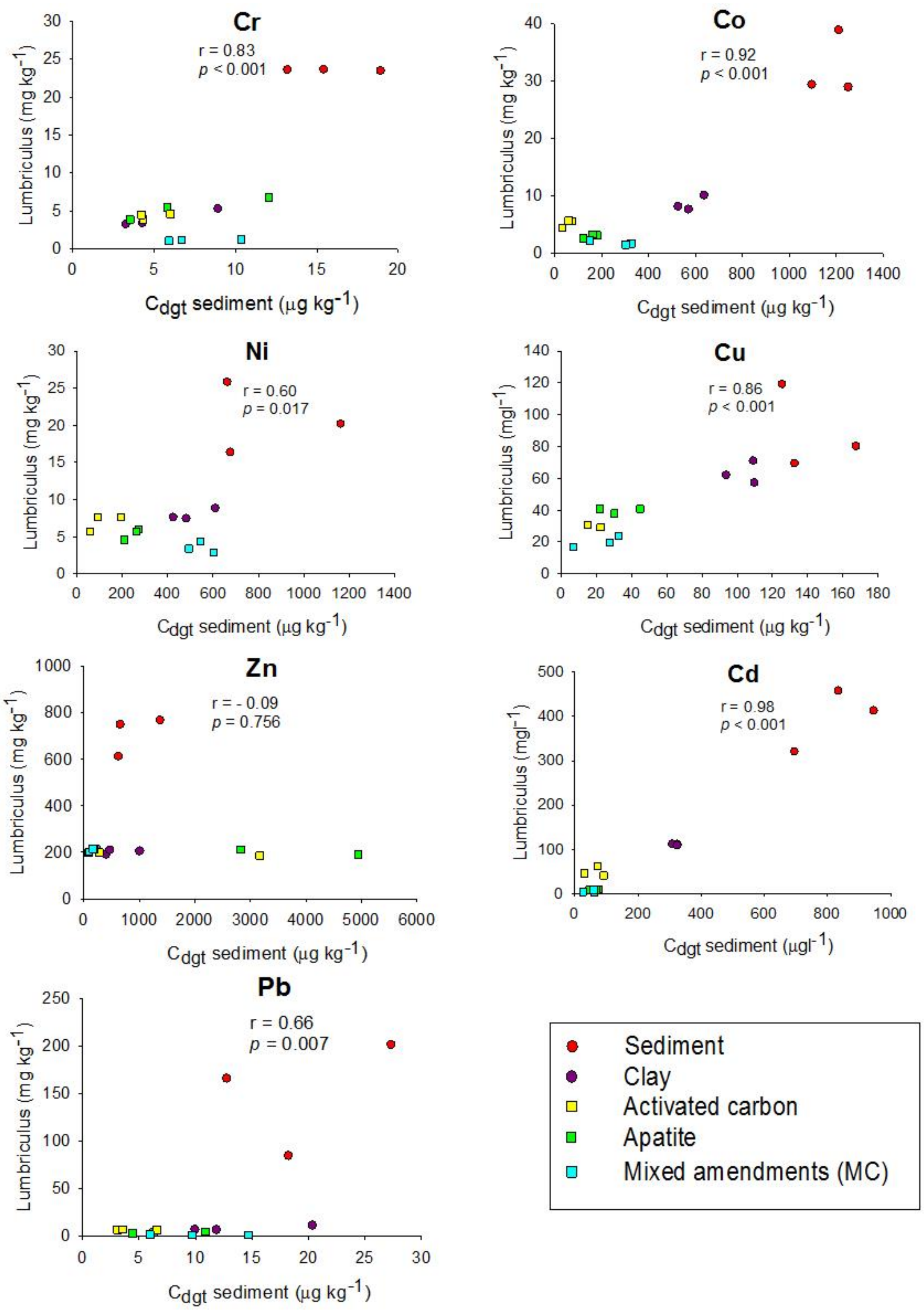


Figure 9. Pearson correlations between metal concentrations in *Lumbriculus variegatus* (whole body, 10 day exposure) and metal concentrations in sediment measured by sediment DGT probes.

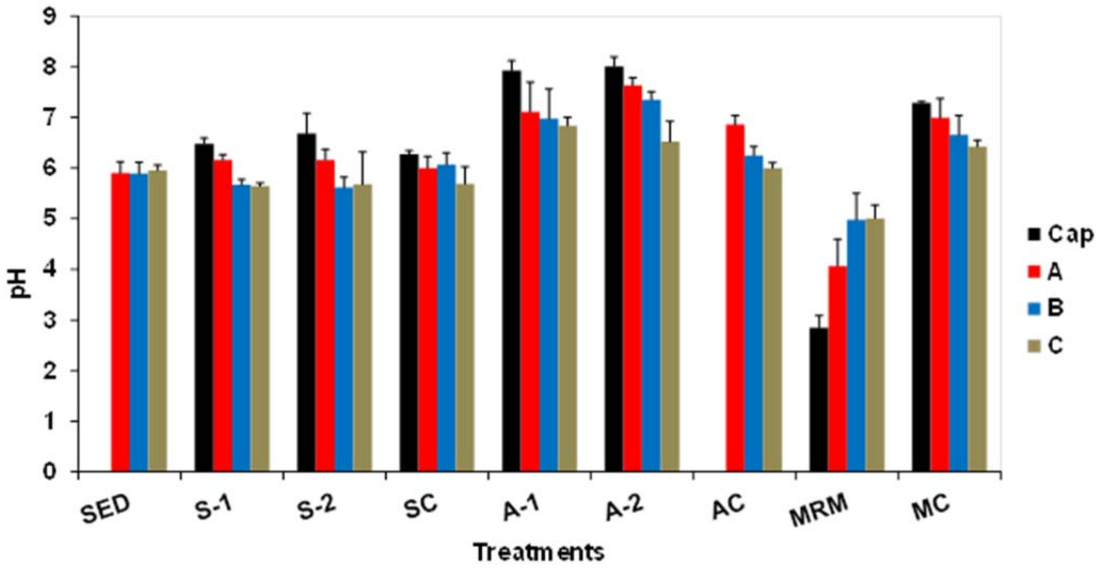


Figure 10. Average pH values (n = 3) in cap materials and individual layers of sediment (layer A: 0-2.5 cm, layer B: 2.5 – 5.0 cm, and layer C: 5 - 7.5 cm) at 2520 hours; uncapped sediment (SED), sediment with passive sand caps (S-1: 2.5 cm, S-2: 5 cm), and sediment with several types of active caps (SC: 2.5 cm silty clay, A-1: 2.5 cm apatite, A-2: 5.0 cm apatite, AC: activated carbon treatment, MRM: 2.5 cm organoclay, and MC: 2.5 cm mixture of active amendments).

4. Conclusions

We hypothesized that some sequestering agents in active caps will bind metals from ongoing sources thereby reducing their bioavailability and protecting underlying remediated sediments from recontamination. In contrast, metals from ongoing sources will contaminate passive caps and uncapped sediment. Our results support this hypothesis:

1. The concentrations of most metals in the surface waters of mesocosms with apatite caps, mixed amendment caps, and activated carbon treatments were significantly lower than in mesocosms with passive caps (sand) and uncapped sediment.

2. Survival was significantly higher for *Lumbriculus variegatus* in mesoscosms with active caps than in mesocosms with passive caps or uncapped sediment, and whole-body concentrations of most metals were lower in *Lumbriculus variegatus* in mesoscosms with active caps.
3. Organoclay MRM was not effective at removing metals from surface waters with the exception of As and Se. However, toxicity and biouptake were lower in this treatment than in the uncapped sediment or sand cap treatments very likely due to increased water hardness associated with MRM.
4. Sediment DGT probes showed that ongoing contamination increased the bioavailable pool of metals in the top layer of uncapped sediment but not in sediment capped or treated with active amendments.

The remediation of contaminated sediments is a very expensive process that can be negated by the continued influx of contaminants from uncontrolled sources. However, our results indicate that some types of active amendments have the potential to protect remediated sediments by reducing the bioavailable pool of metals emanating from ongoing sources of contamination. Future work will extend these findings by quantifying how metal speciation and bioavailability change in incoming contaminated sediment that is deposited over active and passive caps and how these key variables are affected by bioturbating organisms.

Conflict of interest

The author declares no conflict of interest.

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