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Removal of low levels of Cu from ongoing sources in the presence of other elements – implications for remediated contaminated sediments

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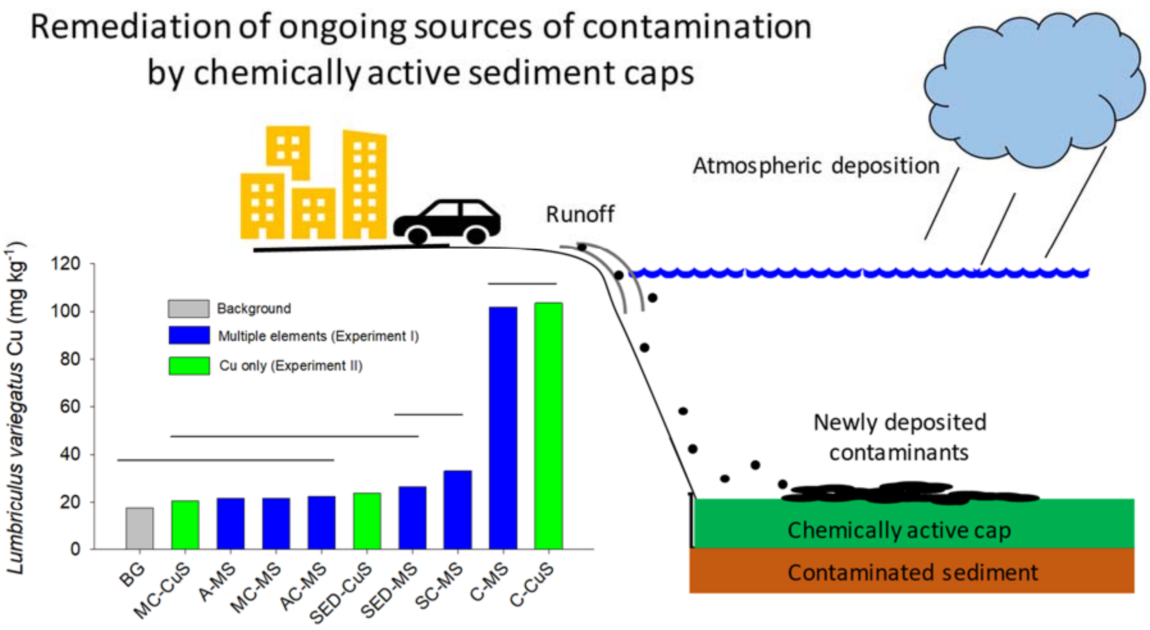
HIGHLIGHTS

- Materials in chemically active caps remediate contaminants from ongoing sources
- Active caps reduced element bioaccumulation by *Lumbriculus variegatus*
- A mixture of elements with Cu was more toxic than Cu alone in uncapped sediment
- Control of Cu by active caps was not affected by the presence of other elements

GRAPHICAL ABSTRACT



Chemically active sediment caps remediate existing sediment contamination and contaminant influxes from ongoing sources. Active cap effectiveness for Cu is not diminished by interactions with other contaminants.

ABSTRACT

Mesocosms were used to investigate the effects of Cu influx, alone and in the presence of other elements, on sediments remediated by active caps, passive caps, and *in situ* treatment. Competitive interactions between Cu and other elements were investigated because contaminants often co-occur. Elements in surface water remained at significantly lower concentrations in mesocosms with apatite and mixed amendment caps than in mesocosms with passive sand caps or uncapped sediment. Element concentrations in *Lumbriculus variegatus* were significantly higher in untreated sediment than in active caps and significantly related to element concentrations in sediment measured by DGT probes. The cumulative toxicity of Cu mixed with other elements was greater than the toxicity of Cu alone in treatments without active caps, but the ability of active caps to control Cu was not affected by the presence of other elements. Active caps can protect remediated sediments by reducing bioavailable elements in ongoing contamination.

KEYWORDS

Copper; element interaction; passive caps; active caps; remediated sediment; re-contamination

1. Introduction

The conventional approach for managing contaminated sediments involves removal by dredging. However, newer remediation techniques are less energy-intensive, expensive, and disruptive to the benthic environment than dredging (Palermo et al., 1998; NRC, 2001). Such methods include passive capping, which involves the physical isolation of contaminated sediments from the water column by a layer of clean inert material such as sand, soil, or sediment; active capping, which involves the application of a discrete layer of chemically reactive amendments over contaminated sediment to bind organic and inorganic contaminants thereby reducing pore water contaminant concentrations and bioavailability; and *in situ* treatment, which involves mixing reactive amendments directly into surficial sediments (Knox et al., 2008; Paller and Knox, 2010; Ghosh et al., 2011; Dixon and Knox, 2012; Knox et al., 2012 and 2014). Regardless of the method used, the recontamination of previously remediated contaminated sediments by the continued influx of contaminants from uncontrolled sources has the potential to negate expensive remedial actions by producing a polluted habitat zone that overlies remediated sediments.

Recontamination 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 in areas previously remediated by dredging or conventional capping with inert materials can degrade the benthic environment as contaminants progressively accumulate. However, remedial effectiveness may persist in areas remediated by active capping because the sequestering agents in active caps interact with incoming contaminants to reduce their bioavailability and toxicity (Knox et al., 2016). In addition, contamination often involves the exposure of aquatic organisms to a mixture of contaminants rather than a single contaminant (Yong et al., 2006; Komjarova and Blust, 2009; Mulligan et al., 2010; Van Ginneken et al., 2015) with unpredictable effects on the maintenance of remedial effectiveness.

Copper (Cu) is an element commonly occurring in the polluted sediments of rivers, bays, estuaries, and other aquatic environments (Kabata-Pendias, 2011). The main anthropogenic sources of Cu in the environment are mining, non-ferrous metal production, iron and steel production, industrial applications, coal combustion, oil combustion, wood combustion, waste incineration, and fertilizer production (Adriano, 2001). Natural sources include minerals in soils and weathered rocks that form sediments, suspended inorganic particles in water, both living and dead organic matter, and hydrothermal systems such as volcanoes and thermal vents. Most Cu compounds settle to the bottom of aquatic ecosystems and bind to sediment particles, inorganic complexes, and organic matter. Copper is present in both soluble and particulate forms in aquatic environments, but soluble Cu compounds form the largest threat to human and ecological health (U.S EPA, 1993; Horne and Dunson, 1995). Water-soluble Cu compounds often occur in the environment after release through application in agriculture. Bioavailability of Cu in aerobic environments is largely controlled by the presence of inorganic ligands (e.g., Fe and Mn oxyhydroxides) as well as dissolved organic ligands (Mulligan et al., 2010; Knox and Paller, 2016; Paller and Knox, 2016). The role of sulfides predominates in anaerobic systems (Adriano, 2001). Although anthropogenic sources of Cu to the aquatic environment have been substantially reduced in the last few decades, it is unlikely that all contaminant sources will be eliminated completely. World Cu production is still rising, and Cu remains a major contaminant in aquatic environments.

In this research, we provide results that address the knowledge gap related to the effects of ongoing sources of contamination on the efficacy of different technologies for the remediation of contaminated sediments. Our objective was to assess the effects of low levels of continued Cu influxes, alone and in the presence of other contaminants, on sediments remediated by different methods. Competitive interactions between Cu and other elements were investigated to better understand conditions occurring at actual contaminated sediment sites where Cu is often present with co-contaminants. We hypothesized that the biouptake of Cu will be reduced in the presence of amendments, and the addition of other elements, especially Cd and Zn will not affect the remedial effectiveness of active caps. This research complements previous work concerning the development of active caps for contaminated sediments (Knox et al., 2008, 2012, 2014) and the effects of recontamination on remediated sediments (Knox et al., 2016).

2. Materials and Methods

2.1. Experimental mesocosms

The experimental setup included flow-through mesocosms designed to test the effects of Cu and other element influxes on selected cap materials. Each mesocosm consisted of a 20 cm wide, 41 cm long, 43 cm high custom built acrylic aquarium with an acrylic lid. Homogenized, dry, clean sediment was placed on the bottom of each mesocosm to produce a 12.5 cm layer, which was equilibrated for two months at approximately 21ºC with soft, synthetic water. The sediment was field-collected from a small creek in South Carolina, dried at ambient temperature, and ground in a porcelain mortar to pass through a No. 10 sieve (opening 2.00 mm). The mesocosms represented different passive and active cap compositions, *in situ* treatment, and uncapped sediment. The passive cap material in the mesocosms was sand; active cap materials included apatite (North Carolina rock phosphate), a mixture of amendments [apatite, organoclay (MRM from CETCO), and activated carbon (bone char)]; and *in situ* treatment with activated carbon (bone char). The activated carbon in the *in situ* treatment was mixed within the upper 2.5 cm of sediment while the other amendments were applied as a discrete layer (i.e., cap) over the sediments.

There were two parallel experiments: Experiment I with multiple elements and Experiment II with only Cu. Experiment II was included to address the possibility of competitive interactions between Cu and the multiple elements employed in Experiment I. Experiment I had 6 treatments: 1) control consisting of multiple element spike solution only (C-MS); 2) uncapped sediment (SED-MS); 3) 2.5 cm sand cap (SC-MS); 4) 2.5 cm apatite cap (A-MS); 5) *in situ* application of 5% by dry weight activated carbon (AC-MS); and 6) 2.5 cm cap composed of a mixture of 75% apatite, 5% activated carbon, and 20% MRM organoclay (MC-MS). Experiment II had 3 treatments: 1) control consisting of Cu spike solution only (C-CuS); 2) uncapped sediment (SED-CuS); and 3) sediment capped with a 2.5 cm cap composed of 75% apatite, 5% activated carbon, and 20% MRM organoclay (MC-CuS). Some treatments were excluded from Experiment II because it was intended to investigate element interactions rather than test treatments. Each treatment in both experiments was represented by three replicates, with treatments randomly allocated among mesocosms. A single reservoir supplied all mesocosms of Experiment I with a continuous inflow (0.5 ml minute^{-1}) of spike solution with multiple elements (referred to as MS), and a different single reservoir supplied all mesocosms of Experiment II with a continuous inflow (0.5 ml minute^{-1}) of spike solution with Cu only (referred to as CuS).

The soft synthetic water was prepared according to EPA methods (EPA, 2002) and was used to equilibrate the mesocosm tanks and prepare spike solutions for both experiments. Using synthetic fresh water helped to accurately maintain target element concentrations and provided consistent physical and chemical properties.

Uniform delivery of the solution was achieved in each experiment by a single multi-channel peristaltic pump that withdrew solution from a reservoir and supplied all mesocosms. All mesocosms were equilibrated with spike solution for two weeks after addition of the amendments, and synthetic spike solution was subsequently pumped in both experiments for a total of 2880 h. Two weeks were sufficient to reach equilibrium as indicated by previous research (Knox et al., 2008 and Knox et al., 2016). All mesocosms were kept at approximately 21°C during both experiments. The tested elements in Experiment I were As, Cd, Cu, Pb, and Zn, and their target concentrations in the synthetic spike water were 150, 15, 30, 65, and 120 $\mu g\ L^{-1}$, respectively. The target Cu concentration in the synthetic spike water used in Experiment II was 30 $\mu g\ L^{-1}$.

2.2. Surface water and sediment sampling

Surface water samples (10 ml each) were collected daily for the first 5 days and weekly thereafter for a total of 2880 h (21 samplings). One set of surface water samples was filtered using a 0.45 μm pore diameter membrane filter for determination of dissolved elements. A second set of samples for the determination of total recoverable elements was not filtered. Each sample was acidified to 2% (v/v) with trace metal grade HNO_3 (pH<2) to be consistent with standard practices for water sampling and analysis.

Element concentrations in filtered and unfiltered samples were analyzed by inductively coupled plasma-mass spectrometry (ICP-MS) using a NexION 300 (Perkin Elmer, Inc.) according to the QA/QC protocols outlined in EPA Method 6020B (USEPA, 2014). Dissolved oxygen, temperature, electrical conductivity, pH, turbidity, hardness, and dissolved organic carbon (selected samples) were measured in surface waters. Calcium hardness was measured by ethylenediaminetetraacetic acid (EDTA) titration (Hach, 2013).

Sediment core samples for measurement of sediment pH were collected from each mesocosm at 2880 h with a push-tube coring device. The cores from sediment only and activated carbon treatments were split into three layers: A: 0.0-2.5 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: 0.0-2.5 cm, B: 2.5-5.0 cm, and C: below 5.0 cm). The pH was determined from a 1:1 solid/water equilibrium solution.

2.3. Effect of amendments on toxicity and bioaccumulation of Cu and other elements

California blackworms *Lumbriculus variegatus*, a common freshwater benthic oligochaete found throughout North America and Europe, were used to assess sediment/cap toxicity and metal bioaccumulation in each treatment. The blackworms were obtained from a commercial supplier and placed in 12 cm long, 2 cm inner diameter screened (0.1 mm mesh), plastic cages for deployment in the 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 sediment-water interface and about 5 grams of blackworms. The blackworms were drained of excess water and weighed in aggregate to the nearest hundredth of a gram before deployment in the cages.

The cages were partly (50%) buried in a horizontal position within the mesocosms at hour 1176 of the experiment for a subsequent exposure period of 10 days at about 21ºC. The blackworms were not fed during this period except for organic matter naturally present in the sediment. Upon retrieval, the blackworms were removed from the cages by pouring the contents into a plastic pan and agitating the pan to separate the lighter worms from the heavier substrate. Living individuals were removed, placed on a plastic screen to drain, and weighed in aggregate to determine percent recovery (initial weight/final weight x 100). Changes in aggregate weight between the beginning and end of the tests were used to estimate mortality rather than changes in number because blackworms can reproduce by fragmentation.

Blackworms that remained alive after toxicity testing were analyzed for whole-body element concentrations. They were rinsed, depurated in clean water for six h, drained of excess water, and frozen before processing. Element analyses were conducted on 50 mg samples of freeze-dried tissue that were digested with 1 mL of H_2O_2 (30%) and 3 mL of $HN0_3$ at 85°C. After digestion, the samples were analyzed using the ICP-MS methodology described above. Element levels in blackworms removed from the experimental mesocosms were compared with background element levels measured in six blackworm samples not exposed in the experimental mesocosms.

2.4. Diffusive gradients in thin films (DGT) probes for assessing bioavailability of Cu and other elements

Diffusive gradients in thin films (DGT) is a passive, diffusion-based sampling technology that uses a collection gel or resin layer that selectively binds contaminants (such as metals) and a diffusion gel layer that selectively admits contaminants to quantify the contaminant concentration in water or sediment at the device surface (Davison and Zhang, 1994; Davison and Zhang, 2012). There is evidence that DGT may remove metals from water or sediment in a way that mimics uptake by biota, thus providing a surrogate measure of contaminant bioavailability (Louis et al., 2004; Li et al., 2018; Philipps et al., 2018; Jin et al., 2019; Ren et al., 2019).

DGT probes (purchased from DGT Research Ltd, Lancaster, UK) for water and sediment were used to determine the effects of the cap materials on the bioavailable pool of Cu and other elements. One DGT water probe was placed in each tank for 24 h one day before retrieving the California blackworms used in the 10-day toxicity/bioaccumulation test (1392 h). Each water DGT probe consisted of a plastic piston with a 2 cm window loaded with a filter paper backed by a polyacrylamide diffusive gel and a Chelex 100 ion-exchange resin gel. Fishing line was used to suspend the probes in the water with the open side facing downward. The water temperature was recorded at the time of the deployment and 24 h later when the probes were retrieved. Upon retrieval, the probes were rinsed with deionized water, the resin-gel was removed and extracted with 1 ml of 1 M HNO_3 for 24 h, and the diluted extract (1:4) was analyzed for elements by ICP-MS. DGT element concentrations in water were calculated as described in DGT research Ltd. specifications (Zhang, 2003).

DGT sediment probes were composed of the same materials as the water probes but were rectangular to facilitate vertical insertion in the sediments. They were deoxygenated before deployment in an anaerobic glove bag (Coy, Grass Lake, MI, USA) with ~0.5% H_2 and N_2

circulated over reduced palladium catalysts for trace O_2 removal. The DGT probes were in 0.01 M NaCl solution to remove any trace elements during deoxygenation.

One sediment DGT probe was deployed within each mesocosm by inserting it vertically into the sediment to measure element levels in cap and sediment layers A (0.0-2.5 cm), B (2.5-5.0 cm), and C (5.0-7.5 cm). The units were rinsed upon retrieval, and the resin-gel layer from each probe was removed and divided into sections representing each previously described layer prior to analysis by ICP-MS. The resin-gel sections were extracted with 1 ml of 1 M HNO_3 for 24 h, and the diluted extract (1:4) was analyzed for elements by ICP-MS. The DGT concentrations of elements in the sediment (C_{DGT}) were calculated as shown in Zhang and Davison (1995), Zhang et al. (2001), and Zhang (2003). Blank water and sediment DGT probes were analyzed to determine background metal levels unrelated to experimental treatments.

2.5. Statistical analysis

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

3. Results and Discussion

3.1. Surface water properties

The hardness of the spiked synthetic soft water used in both experiments was about 20 mg L^{-1} before entering the mesocosms. Some amendments increased the water hardness significantly: apatite increased hardness to above 180 mg L^{-1} and the amendments in the mixed amendment (MC) caps increased hardness to about 250 mg L^{-1} in Experiment I (Figure 1). A similar trend was observed in Experiment II with the MC cap amendments increasing surface water hardness to about 270 mg L^{-1}. The hardness for each treatment did not change with time through the 2880 h experiment. Because the acute toxicity of Cu and other elements depends on water hardness (EPA, 2016), these results indicate that the beneficial effects of some amendments may be at least partly related to their ability to influence this important property (Knox et al., 2016).

Surface water pH was affected by the pH of the spike solution and by the cap materials. However, patterns were similar between Experiments I and II. The highest pH values were in treatments with activated carbon (AC) followed by MC and apatite caps (Figure 2). Average pHs in the mesocosms with apatite caps, MC caps, and activated carbon treatment were higher than in the mesocosms with sand caps and untreated sediment.

Surface water turbidity in Experiment I was highest in the mesocosms with sediment and activated carbon mixed with sediment (Figure 2). Turbidity levels were also high in the mesocosms with sediment in Experiment II. Turbidity levels were high in these treatments because of the relatively small size of the sediment particles, which facilitated their suspension.

Sediment was not in direct contact with the surface water in the treatment with caps, and the relatively large particle size of the cap materials prevented their suspension in the water column.

Surface water dissolved oxygen concentrations were consistent during the 2880 h test period and generally similar among treatments (Figure 2). Electrical conductivity (EC) trends were also consistent over time and highest in mesocosms with MC caps followed by mesocosms with apatite caps (Figure 2).

3.2. Effect of amendments on elements and element interactions in surface water

The target total concentrations of As, Cd, Cu, Pb, and Zn in the synthetic spike water for Experiment I were 150, 15, 30, 65, and 120 µg L^{-1}, respectively. The concentrations of As, Cd, Cu, and Zn in the control, C-MS, approximated the target levels near the middle of the experiment (864 -1200 h), thereby verifying the achievement of target concentrations in the spike solution (C-MS) (Tables 1 and 2). Similarly, Cu concentrations in the C-CuS mesocosms near the middle of Experiment II (~1200 h) were near the target concentration of about 30 µg L^{-1} (Table 1). The largest deviation between target and actual concentrations was shown by Pb, which was present at slightly lower levels in the supply element spike solution and C-MS control than the target levels (Table 2). This was due to the low solubility of Pb at pH > 5, which was the case with the synthetic soft water in our experiment (pH > 7) (Figure 2) (Kabata-Pendias and Mukherjee, 2007). Also, Vignati (2004) classified Pb into terrigenous metals because Pb associates mainly with the particulate phase; often more than 90% of total.

The behavior of Cu was similar in Experiments I and II; i.e., total Cu concentrations were highest in control and sediment treatments and lowest in MC cap and apatite cap treatments

(Tables 1 and 2 and Figure 3). However, Cu concentrations in surface water with MC treatments were slightly higher in Experiment II than Experiment I. In the controls of both experiments (C-MS and C-CuS), Cu dominated in dissolved form from time 0 to about 360 h (Figure 3). With additional time, the particulate form of Cu increased slightly but remained below 5 μg L^{-1} throughout the experiments (2880 h). The opposite occurred in uncapped sediment where most of the Cu in surface water was in the particulate form in both experiments and very little (less than 5 μg L^{-1}) was in the dissolved form (Figure 3). On the other hand, MC caps in both experiments reduced both dissolved and particulate Cu, with the average total Cu concentrations in surface water being 3.7 and 5.2 μg L^{-1} in Experiment I and II, respectively (Figure 3 and Table 1). The relationships among Cu in particulate, colloid, and dissolved phases depend on master environmental variables including oxides, organic matter content, and pH (Kabata-Pendias, 2011).

Slightly lower concentrations of Cu in Experiment I than Experiment II were visible after 528 h in treatments with mixed amendment caps (Table 1). This difference was likely related to increasing concentrations of Cd and Zn in Experiment I, which caused precipitation of Cu and lowering of the average total Cu concentration in the surface water (Tables 1 and 2; Figure 3). Other researchers have also reported that Cu-Zn and Cu-Cd interactions are common (Weltje, 1998, Komjarova and Blust, 2009; Kabata-Pendias, 2011; Van Ginneken et. Al., 2015). In fact, substitution of essential metals like Cu and Zn is one of the underlying mechanisms of Cd and Pb toxicity (Weltje, 1998; Komjarova and Blust, 2009). Weltje (1998) showed displacement of Cu and Zn by Cd and to a lesser extent of Cu by Pb in earthworm tissue. Similarly, a decrease in Zn tissue concentrations after Cd exposure was observed in oribatid mites and sea stars (Van Straalen et al., 1989; Den Besten et al., 1991).

Total arsenic in surface waters increased over time in all treatments but increased least in the mesocosms with apatite and MC caps (Table 2). The total target concentration of As of about 150 μg L^{-1} in the control treatment was achieved by about 864 h and remained at this level until the end of experiment (2880 h) (Table 2). The average arsenic concentration in uncapped sediment treatment was 32.8% lower than the target As concentration at 2880 h (Table 2). At 2880 h, the lowest total As concentrations were in mesocosms with apatite and mixed caps: 38.2 l and 41.3 μg L^{-1}, respectively (Table 2).

Zinc is very soluble, easily available to organisms over a wide range of pHs (Adriano, 2001), and has relatively low electronegativity (1.65) (McBride, 1994); therefore, Zn concentrations in the control treatments were comparable to those in the spike solution despite differences in pH (Table 2). Total Zn in the surface waters of the control mesocosms (C-MS) increased over the 2880 h experiment from about 31.8 to 123.0 μg L^{-1} due to the continuous addition of spike solution (Table 2). In the sand cap treatment (one-inch sand cap), total Zn increased from 29.9 μg L^{-1} to about 81.9 μg L^{-1} (Table 2). However, in treatments with apatite and MC caps, the concentration of total Zn did not change and remained near concentrations typical of uncontaminated waters (Adriano, 2001) (Table 2). At 2880 h dissolved Zn concentrations were highest in control treatment (C-MS), sand cap, and uncapped sediment treatments (Figure 4).

Cadmium is soluble over a wide range of pHs (Kabata-Pendias, 2011). Like Zn, Cd concentrations in the control treatment were similar to Cd concentrations in the spike solution (Table 2). 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 (McBride, 1994). Therefore, dissolved Cd dominated in the control treatment (C-MS) during Experiment I

(Figure 4). Particle bound Cd was a small fraction of total Cd in most treatments but was the highest fraction in uncapped sediment treatments (Figure 4). At 2880 h, total Cd concentrations in surface water were lowest in the mesocosms with apatite caps, which reduced the Cd concentration by 88.5% (Table 2). The next most effective treatments were the amendment mixture and the *in situ* application of activated carbon; Cd concentrations in surface water in both treatments were reduced by 76.3%. Total Cd concentration in the sand cap treatment remained high, near control treatment levels, throughout the experiment (i.e., 2880 h).

Total concentrations of Pb in the control treatments were lower than concentrations in the spike solution (Table 2) suggesting the possibility of 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. Total Pb in the control mesocosms (C-MS) increased from 0.1 to 39.7 μg L^{-1} (Table 2), and most of the Pb was in the particulate fraction (23.6 μg L^{-1} at 2880 h) (Figure 4). The multiple element spike solution also had high concentrations of Pb in the particulate fraction (Figure 4). Lead is usually insoluble when the pH of the solution is above 5 (Dragun, 1998). The pH of the multiple element spike solution was generally below 7, but all other treatments had a pH above 7, consistent with the observation that most Pb was in the particulate fraction. Total Pb increased in all treatment types with time (Table 2), but like the other elements, the lowest increase was in treatments with apatite and MC caps (Table 2).

The amendment that resulted in the most effective reduction of element concentrations in surface waters was apatite. In this study, apatite reduced element concentrations in the surface waters of Experiment I in the following order: Pb<Cu<Cd<As<Zn (at 2880 h) (i.e., by 96, 90, 89, 76, and 63%, respectively (Table 2). In contrast, the passive sand cap reduced element

concentrations in the surface waters by less than 20-30% at time 2880 h; e.g., Cd and As (Table 2). These results support earlier findings that apatite effectively immobilizes metals in contaminated soils/sediments and reduces their toxicity and bioavailability (Ma et al., 1995; Knox et al., 2000 a and b, 2003, and 2006; Singh et al., 1998). Apatite in commercial phosphate rocks is usually in the form of carbonate apatite with isomorphic substitution of carbonate for phosphate, F for hydroxyl anion, and minor substitution of Ca^{2+} by Na^{+} and Mg^{2+} atoms. Apatite can immobilize Pb, Mn, Co, Cu, Cd, Zn, Mg, Ba, U, and Th in contaminated media (Ma et al., 1995; Knox et al., 2000 a and b, 2003, and 2006). Ma et al. (1995) reported that the interaction between apatite and metals in solution is controlled by apatite dissolution and results in the precipitation of various phosphate phases. Phosphate-metal precipitates are typically very stable over a wide range of environmental conditions (Wright et al., 1995).

In this study, activated carbon effectively removed Cd, Cu, and Zn: concentrations of these elements in surface water at time 2880 h were reduced by 76.3, 53.8, and 45%, respectively (Tables 1 and 2). Activated carbon, also called activated charcoal or activated coal, is carbon that has been processed to make it extremely porous and thus have a very large surface area for adsorption and chemical reactions. Numerous commercially available activated carbons have been tested for organic contaminant and metal sorption (Reed, 2001). Metal removal varies widely among carbon sources and metal types; however, removal is pH dependent for all carbon-metal combinations. For cationic metals, removal increases with increasing pH, and for anionic metals the opposite behavior occurs. Activated carbons can also be impregnated with various materials to impart unique sorption properties. For example, activated carbon impregnated with sulfur is a mature technology used for mercury removal from flue gases and water (Kwon and Vidic, 2000; Kwon et al., 2010). Bone char, which was used in this study, is activated carbon that is produced from animal bones. It differs from plant derived activated carbon by containing both carbon surface area and hydroxyapatite lattice surface area, which makes bone char very effective for metal removal.

3.3. Toxicity and bioaccumulation assessment

A toxicity test corresponding to ten days of exposure to elements in the mesocosms was conducted with California blackworms. In Experiment I, average percent mortality (based on changes in aggregate weight before and after placement in the mesocosms) for the ten-day test was 30, 51.2, 29.3, 11.6, and 12.9% for control, sediment only, sand, apatite, and MC caps, respectively (Figure 5). In Experiment II, the lowest mortality was observed in treatments with an MC cap; an average of 12.5% for 10 days of exposure. These results demonstrate that the active caps provided more protection from the continued influx of dissolved and particulate elements than the sand caps or uncapped sediment.

For uncapped sediment treatments, there were significant ($p<0.05$) differences in mortality between Experiment I and Experiment II: 51.2 and 34.7% mortality in SED-MS and SED-CuS, respectively (Figure 5). These results indicate that cumulative toxicity of the mixture of elements was greater than the toxicity of Cu alone (Figure 5). Treatments with lower mortality (i.e., apatite and MC caps) had lower concentrations of the tested elements, and the water had higher pH and hardness (Figures 1, 2, and 5). The toxicity of dissolved elements is related to element concentration and speciation, which depends on the water composition. For instance, the concentration and type of dissolved organic carbon (DOC) have been shown to modify the bioaccumulation of Cu via chemical complexation (Lores et al., 1999; Luis et al., 2004; Zhong et al., 2012). Furthermore, some studies have shown that speciation alone is insufficient for predicting accumulation and toxicity because of competition with cations. For instance, the presence of competing cations such as Ca^{2+}, Mg^{2+}, H^{+}, Na^{+} or K^{+} reduces the bioavailability of Cu (De Schamphelaere and Janssen, 2002; Ferreira et al., 2009).

California blackworms that survived exposure in the mesocosms were analyzed for whole-body element concentrations (Figure 6). The concentrations of most elements in *Lumbriculus* (10-day evaluation) were significantly higher in the spike solution, sand cap, and uncapped sediment than in the apatite or MC caps, even though uncapped sediment removed significant amounts of the spiked elements (e.g., Cd and Pb) from the surface water (Table 2). This likely occurred because water hardness was significantly higher in treatments with apatite and mixed amendment caps (Figure 1). Analysis of variance of differences in *Lumbriculus variegatus* Cu concentrations (whole body, 10-day exposure) among treatments in Experiment I (multi-element) and Experiment II (Cu only) showed that the ability of the mixed amendment cap to influence the bioaccumulation of Cu was not affected by the presence of other elements (Figure 6).

Cadmium and Zn can suppress the uptake rates of other elements (e.g., Cu) under some conditions (Hopkin and Hames, 1994; Donker et al., 1996; Weltje, 1998; Norwood et al., 2003; Rainbow and Black, 2005; Komjarova and Blust, 2009; Abboud et al., 2013; Van Ginneken et al., 2015). This effect is observed even at low Cd and Cu concentrations and reaches a maximum at higher concentrations (Komjarova, 2009; Komjarova and Blust, 2008; Komjarova and Blust, 2009). Comparing results for Cu between Experiment I (Cu mixed with Cd, As, Pb, and Zn) and Experiment II (Cu only) provided insights concerning competitive interactions among multiple elements and their potential effects on treatment effectiveness. This study showed that a mixture of elements that included Cu was more toxic than Cu alone (at the same concentration as in the mixture) in uncapped sediment, likely because of additive toxicity contributed by the other elements (SED-MS versus SED-CuS in Figure 5). However, the effectiveness of the mixed amendment caps in both experiments was similar showing that Cu uptake, as indicated by toxicity and bioaccumulation, was not affected by the presence of other elements in Experiment I (MC-MS versus MC-CuS in Figures 5 and 7). These results suggest that the effectiveness of the amendments used in active caps and *in situ* treatments may be unaffected by element interactions that can influence bioaccumulation in aquatic organisms.

3.4. Bioavailability assessment by diffusive gradients in thin films (DGT) probes

Results from the DGT water probes showed that concentrations of potentially bioavailable Cu, Cd and Pb in the water column were significantly lower ($p<0.05$) in the apatite, activated carbon, and MC treatments than in the control and passive sand cap treatments (Figure 8). Also, there were no significant differences between Cu concentrations measured by water DGT probes in Experiments I and II for MC treatments indicating that the presence of other elements in Experiment I did not affect the potential bioavailability of Cu (as indicated by DGT measurements) and that the MC treatment was effective for Cu in presence of other elements such as Cd, Pb, and Zn (Figure 8).

Lower bioavailable pools of Cu and other elements measured by water DGT probes in apatite and MC treatments may be related to the higher pH and hardness of surface water in these treatments (Figures 1 and 2). Other researchers have reported that water hardness can reduce the concentrations of Cu ions and the amount of Cu measured by DGT (Philipps et al., 2018). The lower toxicity of Cu in hard water compared to soft water is due to the protective effects of Ca^{2+} on and in living cells. Countries such as Canada have outlined Water Quality Standards for the protection of aquatic life that are stricter for soft water than hard water (Bradl, 2005; Wright and Welbourn, 2002).

DGT sediment probes showed that DGT element concentrations, especially Cd, Cu, and Pb in the apatite and MC cap layers, were very low compared with DGT element concentrations in the passive sand cap layer (Table 3). Lower sediment element levels in apatite and MC treatments persisted deeper within the sediment profile, especially compared with the uncapped sediment, which exhibited relatively higher Cu and Cd levels to a depth of 5.0 cm in the sediment column (Table 3). Although these differences in element concentration are likely amendment related, they could have been influenced by vertical differences in sediment pH among mesocosms (Figure 9). These results show that potentially bioavailable element species were lower in the sediments of treatments with apatite, activated carbon, and MC active caps than in uncapped sediments or sediments with passive caps. Differences were especially pronounced in the surface sediment/cap layers, which constitute the habitat for most benthic organisms. Linear regressions showing the relationship between element concentrations in *Lumbriculus* and potentially bioavailable element concentrations in the top 2.5 cm of sediment or cap materials (measured by DGT sediment probes) were strong ($R^2 = 0.63$-0.76) and significant ($p<0.05$) for Cd, Cu, and Pb (Figure 10). These results suggest a causative relationship and indicate the potential for active caps to control the bioaccumulation of elements by reducing concentrations of bioavailable elements in sediment porewater. In contrast to the previous elements, the relationship between DGT measurements of Zn and Zn concentrations in *Lumbriculus* were comparatively weak ($R^2 = 0.22$) and only marginally significant ($p<0.036$).

Some elements such as As, Cd, and Pb have no essential metabolic functions, are toxic at low concentrations, and tend to bioaccumulate (Rainbow, 1997, 2002). Other elements, such Cu and Zn, play an important role in cellular metabolism and their internal concentrations are regulated by organisms. Essential and non-essential elements may; however, share common uptake routes and interact with each other affecting mobility, uptake, bioaccumulation, and toxicity. These element interactions are highly variable since they depend on element concentrations, exposure scenarios, organism-specific differences, and examined organs (Norwood et al., 2003). For example, Pb at a concentration 0.25 uM increased Cu uptake in the water flea *Daphnia magna* showing that element interactions are significant and occur at environmentally realistic concentrations (Komjarova and Blust, 2008 and 2009). In our experiments, we observed significantly higher Cu uptake by *Lumbriculus* in uncapped sediment in Experiment I (Cu in presence of Pb and other elements) but lower Cu uptake in uncapped sediment in Experiment II (where Cu was tested alone) (Figure 7).

4. Conclusions

We used mesocosms to investigate the effects of low levels of continuing Cu influx, alone and in the presence of other elements, over uncapped sediment and sediments remediated by different types of active and passive caps and *in situ* treatment with activated carbon. Our hypothesis was that the sequestering agents used in active caps and *in situ* treatments will bind elements introduced from uncontrolled sources of ongoing contamination, thereby reducing their bioavailability and protecting underlying, previously remediated sediments from recontamination. Competitive interactions between Cu and other elements were investigated to better understand conditions occurring at actual contaminated sediment sites where several contaminants often co-occur. Tested elements in surface water remained at significantly lower concentrations in mesocosms with apatite and mixed amendment caps than in mesocosms with passive caps (sand), uncapped sediment, and spike solution throughout the 2880 h experiment. Element concentrations were significantly higher in *Lumbriculus variegatus* from untreated sediment than in *Lumbriculus variegatus* from the active caps, and regressions of element concentrations in *Lumbriculus* on element concentrations in the top 2.5 cm of sediment or cap measured by DGT were strong and significant ($p<0.05$) for most tested elements. Comparing results for Cu between Experiment I (Cu mixed with As, Cd, Pb, and Zn) and Experiment II (Cu only) showed that the ability of a mixed amendment active cap to control Cu was not affected by the presence of other elements. Our findings showed that some types of active caps can protect remediated sediments by reducing the bioavailable pool of elements from ongoing sources of contamination and that the ability of mixed amendment caps to control the bioaccumulation of Cu was not affected by the presence of other elements. 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.

Conflict of interest

The author declares no conflict of interest.

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List of Tables

Table 1. Average (Avg) and standard deviation (Stdev) of total Cu concentrations (n = 3) in surface water in Experiments I and II from time 0 to 2880 h. Each value is an average of three samples. Experiment I (multiple element spike solution): control with no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): control with no sediment (C-CuS), uncapped sediment (SED-CuS), and sediment with mixed amendment active caps (MC-CuS).

Table 2. Average and standard deviation of total As, Cd, Pb, and Zn concentrations (n = 3) in surface water in mesocosms with multiple element spike solution (Experiment I): control with no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS) from time 0 to 2880 h.

Table 3. Metal concentrations (μg kg^{-1}) measured by sediment DGT probes (C_{DGT}) in cap materials and individual layers of sediment (layer A: 0.0-2.5 cm, layer B: 2.5-5.0 cm, and layer C: 5.0-7.5 cm). Each value is an average of three samples. Experiment I (multiple element spike solution): uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): uncapped sediment (SED-CuS), and sediment with mixed amendment active caps (MC-CuS).

Table 1.

Time (h)	0	192	360	528	864	1200	1872	2880
Experiment I (multiple element spike solution)								
C-MS	0.4 ± 0.4	7.0 ± 1.4	11.1 ± 0.9	19.0 ± 1.4	24.6 ± 0.7	27.9 ± 0.9	24.7 ± 1.7	27.3 ±6.3
SED-MS	0.6 ± 0.1	5.8 ± 2.6	6.2 ± 0.0	13.6 ± 0.6	21.0 ± 3.5	23.4 ± 1.9	21.1 ± 0.7	20.1 ± 1.9
SC-MS	0.6 ± 0.2	4.7 ± 0.7	3.9 ± 0.5	14.9 ± 1.8	15.5 ± 1.0	21.9 ± 3.3	21.1 ± 1.9	18.7 ± 0.5
A-MS	0.8 ± 0.1	1.5 ± 0.4	1.5 ± 0.1	2.4 ± 0.4	3.3 ± 0.7	4.1 ± 0.7	3.4 ± 0.4	2.7 ± 0.4
AC-MS	0.5 ±0.5	4.8 ± 1.3	6.0 ± 0.3	11.6 ± 4.4	18.1 ± 1.4	17.1 ± 2.8	15.0 ± 0.8	12.6 ± 1.7
MS-MS	0.6 ± 0.1	2.0 ± 0.8	2.7 ± 0.1	3.3 ± 1.2	3.6 ± 0.8	3.7 ± 0.5	3.7 ± 0.5	3.7 ± 0.5
Experiment II (Cu spike solution)								
C-CuS	0.0 ± 0.0	5.9 ± 0.6	10.4 ± 1.9	17.2 ± 2.5	23.4 ± 0.3	27.4 ± 1.1	29.0 ± 1.1	29.5 ± 0.7
SED-CuS	0.7 ± 0.0	3.6 ± 0.5	5.4 ± 2.2	12.9 ± 2.3	21.2 ± 2.9	19.4 ± 0.7	19.2 ± 0.7	16.2 ± 0.2
MS-CuS	0.6 ± 0.2	2.3 ± 1.5	2.4 ± 0.7	5.2 ± 0.6	5.5 ± 0.6	5.5 ± 1.2	5.0 ± 1.2	5.2 ± 0.2

Table 2.

Time (h)	0	192	360	528	864	1200	1872	2880
				As				
C-MS	1.6 ± 0.3	66.5 ± 2.6	112.6 ± 2.3	120.0 ± 2.3	161.3 ± 1.4	159.8 ± 5.9	181.4 ± 0.6	157.8 ±7.3
SED-MS	1.0 ± 0.4	29.7 ± 6.0	53.0 ± 14.4	75.0 ± 3.0	89.4 ± 7.1	84.8 ± 8.5	95.2 ± 11.5	106.0 ± 7.7
SC-MS	1.1 ± 0.2	50.0 ± 0.4	83.1 ± 7.7	91.1 ± 12.8	107.3 ± 3.0	126.8 ± 14	145.9 ± 8.0	128.6 ± 2.7
A-MS	2.2 ± 0.4	9.0 ± 3.0	11.8 ± 1.4	13.8 ± 1.3	18.7 ± 1.3	44.1 ± 1.5	43.3 ± 0.4	38.2 ± 1.3
AC-MS	0.7 ±0.2	32.1 ± 2.5	55.0 ± 0.5	69.4 ± 3.3	81.8 ± 1.7	85.8 ± 2.2	89.2 ± 6.6	91.6 ± 6.9
MC-MS	2.6 ± 0.4	16.1 ± 3.9	18.6 ± 2.5	25.3 ± 2.5	25.6 ± 1.4	49.4 ± 2.9	55.7 ± 1.6	41.3 ±4.0
				Cd				
C-MS	0.4 ± 0.1	7.2 ± 0.4	9.9 ± 0.8	13.7 ± 1.0	16.4 ± 0.3	15.1 ± 0.2	15.9 ± 1.0	13.1 ± 0.9
SED-MS	0.6 ± 0.1	3.4 ± 0.7	3.7 ± 1.0	6.6 ± 0.9	7.3 ± 1.2	4.8 ±0.6	7.0 ± 1.7	11.5 ± 1.5
SC-MS	0.6 ± 0.2	4.4 ± 0.4	5.8 ± 0.3	7.4 ± 0.8	7.4 ± 0.8	9.2 ± 0.6	9.5 ± 0.3	9.2 ± 0.9
A-MS	0.8 ± 0.1	1.4 ± 0.2	0.8 ± 0.1	1.6 ± 0.2	1.8 ± 0.3	2.6 ± 1.3	1.4 ± 0.2	1.5 ± 0.1
AC-MS	0.5 ± 0.1	2.4 ± 0.4	2.0 ± 0.7	3.4 ± 0.4	5.3 ± 0.4	3.3 ± 0.8	3.7 ± 0.6	3.1 ± 0.4
MC-MS	0.6 ± 0.1	1.7 ± 0.2	1.2 ± 0.5	1.6 ± 0.4	2.1 ± 0.2	3.4 ± 0.5	3.4 ± 0.3	3.1 ± 0.5
				Pb				
C-MS	0.1 ± 0.0	8.2 ± 0.5	13.2 ± 1.4	16.9 ± 1.0	26.9 ± 1.1	27.9 ± 1.0	34.2 ± 1.3	39.7 ± 1.2
SED-MS	0.3 ± 0.1	9.8 ± 0.3	8.2 ± 1.5	16.0 ± 0.9	19.7 ± 1.3	17.3 ± 1.1	18.7± 0.8	22.2 ± 1.3
SC-MS	0.2 ± 0.0	8.8 ± 0.5	5.6 ± 0.4	8.7 ± 0.8	13.4 ± 1.1	13.7 ± 1.0	14.8 ± 3.0	16.8 ± 1.5
A-MS	0.1 ± 0.1	1.5 ± 0.7	1.1 ± 0.4	1.8 ± 0.2	2.4 ± 0.3	2.8 ± 0.5	1.8 ± 0.6	1.6 ± 0.1
AC-MS	0.2 ± 0.0	6.2 ± 0.6	9.3 ± 0.6	11.1 ± 0.4	11.7 ± 0.3	15.1 ± 0.3	13.6 ± 2.1	14.3 ± 2.5
MC-MS	0.4 ± 0.1	2.8 ± 1.0	2.9 ± 1.5	3.5 ± 0.4	2.5 ± 0.6	3.8 ± 0.7	4.1 ± 0.3	4.9 ± 0.5
				Zn				
C-MS	31.8 ± 6.3	62.3 ± 1.5	96.8 ± 10.6	108.6 ± 6.6	122.7 ± 5.7	132.8 ± 8.1	122.1 ± 5.0	123.0 ± 2.7
SED-MS	34.0 ± 7.3	44.7 ± 0.4	60.2 ± 5.0	66.8 ± 3.9	62.7 ± 9.6	80.1 ± 8.7	76.4 ± 5.4	82.3 ± 8.1
SC-MS	29.9 ± 5.2	63.7 ± 3.4	76.6 ± 1.5	80.0 ± 8.7	88.9 ± 2.9	86.1 ± 10.4	83.6 ± 3.2	81.9 ± 1.8
A-MS	30.0 ± 1.0	35.0 ± 7.2	34.7 ± 3.8	29.0 ± 8.7	43.6 ± 0.5	34.8 ± 4.4	27.5 ± 4.6	45.5 ± 5.3
AC-MS	26.3 ± 8.0	34.3 ± 4.3	58.3 ± 2.7	59.3 ± 5.7	61.0 ± 7.1	73.6 ± 1.2	49.1 ± 7.1	55.8 ± 3.7
MC-MS	34.8 ± 1.9	36.7 ±4.4	42.6 ± 2.9	33.9 ± 2.7	47.5 ± 4.8	44.2 ± 4.3	44.1 ± 3.7	48.6 ± 6.4

Table 3.

Layers	Cu	Zn	Cd	Pb
SED-MS (Uncapped sediment – multiple element spike)				
A	1.0 ± 0.1	163.5 ± 2.8	0.7 ± 0.0	0.3 ± 0.1
B	1.4 ± 0.4	21.4 ± 0.6	0.7 ± 0.1	0.1 ± 0.0
C	0.9 ± 0.2	19.5 ± 2.5	0.5 ± 0.1	0.1 ± 0.1
SED-CuS (Uncapped sediment – copper spike)				
A	1.3 ± 0.2	23.2 ± 4.7	0.2 ± 0.0	0.1 ±0.0
B	0.7 ± 0.2	21.0 ± 3.5	0.2 ± 0.0	0.1 ± 0.0
C	0.6 ± 0.6	19.1 ± 2.2	0.2 ± 0.2	0.1 ± 0.1
AC-MS (Sediment with activated carbon – multiple element spike)				
A	0.5 ± 0.1	82.4 ± 7.5	0.2 ± 0.0	0.1 ±0.0
B	0.3 ± 0.1	16.1 ± 2.8	0.2 ± 0.0	0.1 ± 0.0
C	0.5 ±0.1	17.8 ± 1.4	0.2 ± 0.0	0.1 ± 0.1
SC-MS (Sand cap and sediment – multiple element spike)				
Cap	1.8 ± 0.2	157.5 ± 11.9	5.7 ± 0.5	1.2 ± 0.3
A	1.1 ± 0.3	127.9 ± 11.2	0.4 ± 0.1	0.3 ± 0.0
B	0.5 ± 0.2	19.2 ± 2.2	0.3 ± 0.1	0.1 ± 0.0
C	0.4 ± 0.1	19.9 ± 0.9	0.2 ± 0.1	0.1 ± 0.0
A-MS (Apatite cap and sediment – multiple element spike)				
Cap	0.4 ± 0.1	90.7 ± 2.3	0.4 ± 0.1	0.1 ± 0.1
A	0.5 ± 0.1	33.4 ± 14.2	0.3 ± 0.0	0.2 ± 0.0
B	0.3 ± 0.0	19.1 ± 1.7	0.3 ± 0.0	0.1 ± 0.0
C	0.3 ± 0.1	19.9 ± 1.2	0.3 ± 0.1	0.1 ± 0.0
MC-MS (MC cap and sediment – multiple element spike)				
Cap	0.3 ±0.1	47.2 ± 9.4	0.3 ± 0.2	0.1 ± 0.0
A	0.4 ± 0.2	23.0 ± 2.2	0.3 ± 0.1	0.1 ± 0.1
B	0.2 ± 0.0	18.2 ± 1.4	0.1 ± 0.1	0.1 ± 0.0
C	0.4 ± 0.0	21.7 ± 3.4	0.1 ± 0.1	0.1 ± 0.0
MC-CuS (MC cap and sediment – copper spike)				
Cap	0.3 ± 0.0	20.8 ± 3.5	0.2 ± 0.0	0.1 ± 0.1
A	0.3 ± 0.3	24.5 ± 7.5	0.2 ± 0.1	0.1 ± 0.2
B	0.2 ± 0.0	23.3 ± 0.7	0.2 ± 0.0	0.1 ± 0.0
C	0.3 ± 0.0	18.1 ± 0.6	0.2 ± 0.0	0.1 ± 0.0

List of Figures

Figure 1. Average hardness of surface water (mg L^{-1}) (n = 21) for each treatment in both experiments. Experiment I (multiple element spike solution): control with no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): control with no sediment (C-CuS), uncapped sediment (SED-CuS), and sediment with mixed amendment active caps (MC-CuS).

Figure 2. Temporal changes in surface water electrical conductivity (EC), pH, dissolved oxygen (DO), and turbidity for each treatment. Each value is an average of three samples. Experiment I (multiple element spike solution): control with no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): control with no sediment (C-CuS), uncapped sediment (SED-CuS), and sediment with mixed amendment active caps (MC-CuS).

Figure 3. Average Cu concentrations in surface water in Experiments I and II from time 0 to 2880 h. Each value is an average of three samples. Experiment I (multiple element spike solution): control with no sediment, uncapped sediment, sediment with multi-amendment caps. Experiment II (Cu spike solution): control with no sediment, uncapped sediment, and sediment with multiple amendment active caps.

Figure 4. Average dissolved and particulate surface water concentrations of As, Cd, Pb, and Zn in Experiment I mesocosms at 2880 h. Each value is an average of three samples; multiple element spike solution (MS), control mesocosms with multiple element spike solution and no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS).

Figure 5. Average mortality of *Lumbriculus variegatus* after ten-day toxicity tests conducted in mesocosms receiving water spiked with metals (MS) and copper only (CuS). Experiment I (multiple element spike solution): control with no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): no sediment (C-CuS), uncapped sediment (SED-CuS), and sediment with mixed amendment active caps (MC-CuS). Groups represented by different letters are significantly different ($p<0.05$, ANOVA followed by Student-Newman-Keuls method for multiple comparison).

Figure 6. Analysis of variance of differences in *Lumbriculus variegatus* element concentrations (whole body, 10-day exposure) among treatments. Geometric means connected by the same line are not significantly different at $\alpha<0.05$. Experiment I: background (BG), mesocosms with multiple element spike solution and no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-

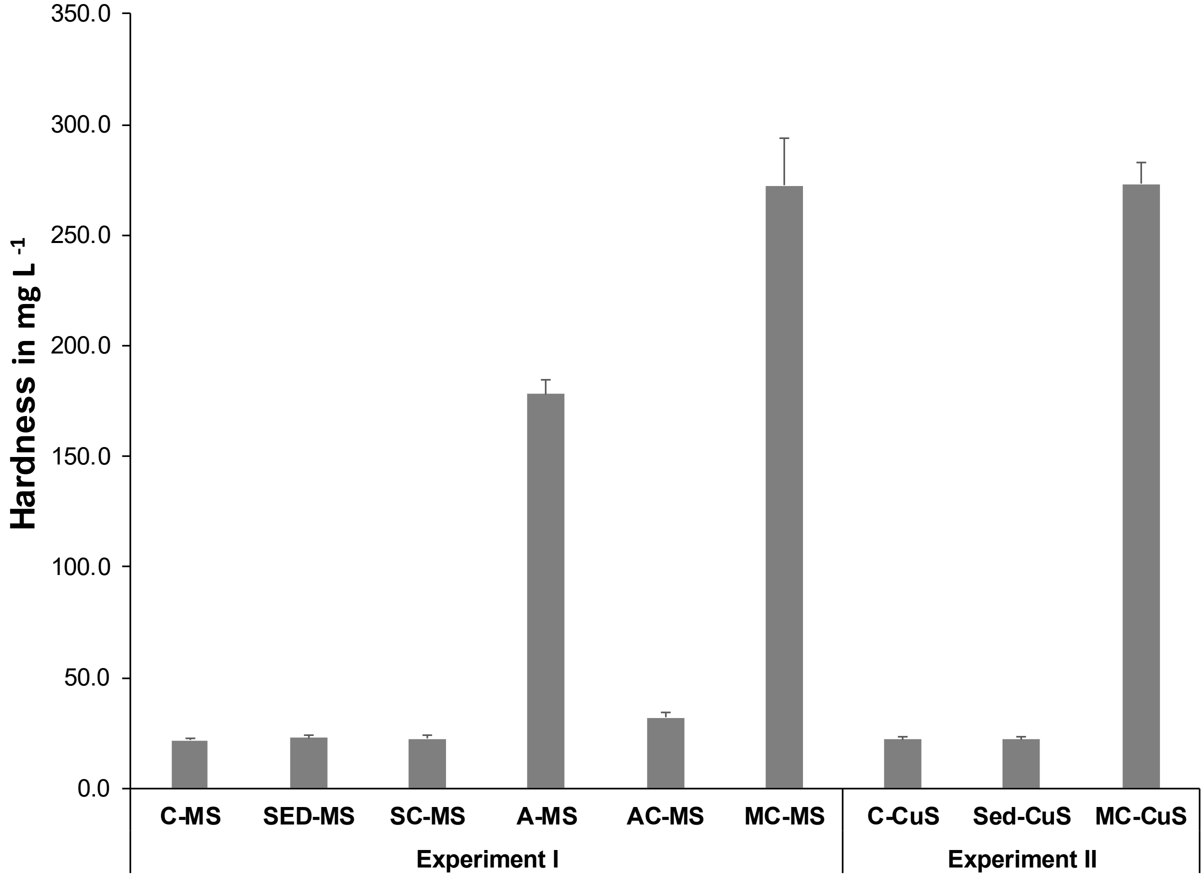
MS). Experiment II: mesocosms with Cu spike solution and no sediment (C-CuS), uncapped sediment (SED-CuS), sediment with mixed amendment active caps (MC-CuS), and background (BG).

Figure 7. Analysis of variance of differences in *Lumbriculus variegatus* Cu concentrations (whole body, 10-day exposure) among treatments in Experiment I and Experiment II. Geometric means connected by the same line are not significantly different at $\alpha<0.05$. Experiment I (multiple element spike solution): control with no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): control with no sediment (C-CuS), uncapped sediment (SED-CuS), sediment with mixed amendment active caps (MC-CuS), and background (BG).

Figure 8. Average Cd, Cu, Pb, and Zn concentrations ($\mu g\ L^{-1}$) measured by water DGT probes. Experiment I (multiple element spike solution): control with no sediment (C-MS), uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): control with no sediment (C-CuS), uncapped sediment (SED-CuS), and sediment with mixed amendment active caps (MC-CuS). Groups represented by different letters are significantly different ($\alpha<0.05$, ANOVA followed by Student-Newman-Keuls method for multiple comparison).

Figure 9. Average pH values (n = 3) in cap materials and individual layers of sediment (layer A: 0.0-2.5 cm, layer B: 2.5-5.0 cm, and layer C: 5.0-7.5 cm) at 2880 h; Experiment I (multiple element spike solution): uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): uncapped sediment (SED-CuS) and sediment with mixed amendment caps (MC-CuS).

Figure 10. Regression of metal concentrations in *Lumbriculus variegatus* (whole body) and metal concentrations in sediment measured by sediment DGT probes (C_{dgt}, depth 0.0-2.5 cm). Experiment I (multiple element spike solution): uncapped sediment (SED-MS), sediment with sand caps (SC-MS), sediment with apatite active caps (A-MS), sediment with mixed amendment active caps (MC-MS), and sediment treated *in situ* with activated carbon (AC-MS). Experiment II (Cu spike solution): uncapped sediment (SED-CuS) and sediment with mixed amendment active caps (MC-CuS).



Hardness in mg L -1
350.0
300.0
250.0
200.0
150.0
100.0
50.0
0.0
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
C-CuS
Sed-CuS
MC-CuS
Experiment I
Experiment II

Figure 1.

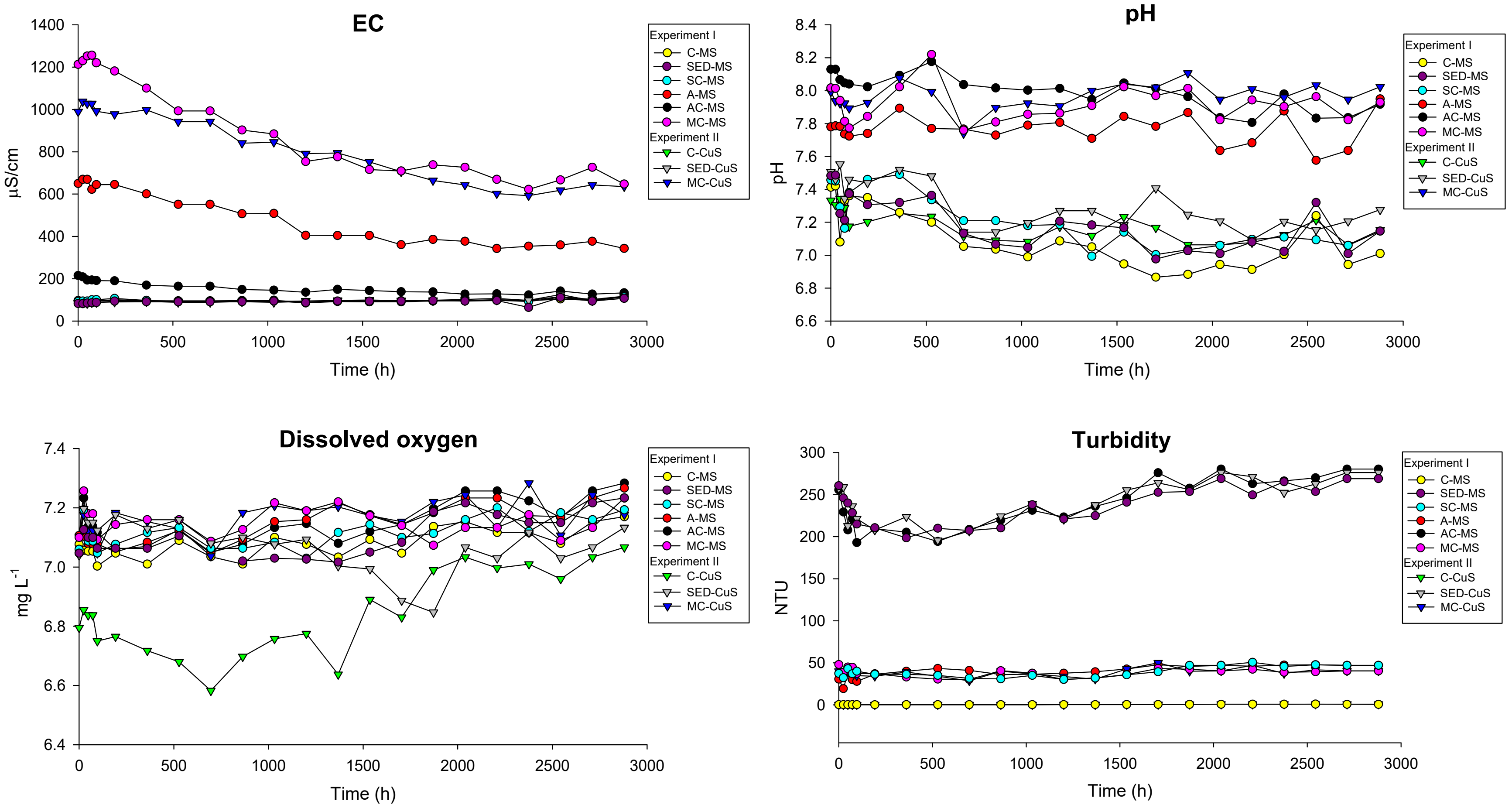

EC
μS/cm
0
200
400
600
800
1000
1200
1400
Time (h)
0
500
1000
1500
2000
2500
3000
Experiment I
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
Experiment II
C-CuS
SED-CuS
MC-CuS
pH
pH
6.6
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
Time (h)
Dissolved oxygen
mg L-1
6.4
6.6
6.8
7.0
7.2
7.4
Time (h)
Turbidity
NTU
0
50
100
150
200
250
300
Time (h)

Figure 2.

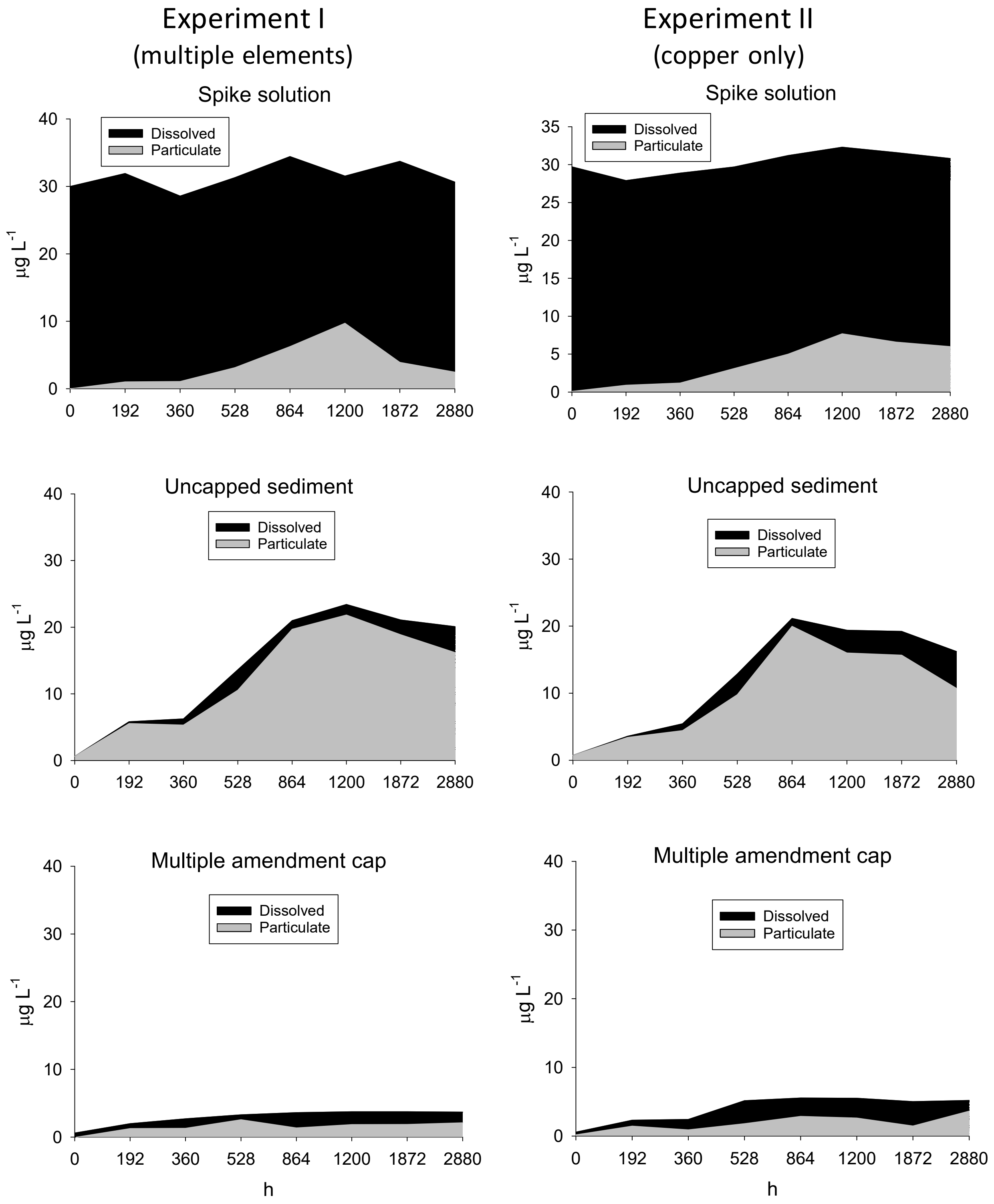

Experiment I
(multiple elements)
Experiment II
(copper only)
Spike solution
Uncapped sediment
Multiple amendment cap
Dissolved
Particulate
µg L^{-1}
0
5
10
15
20
25
30
35
40
0
192
360
528
864
1200
1872
2880
h

Figure 3.

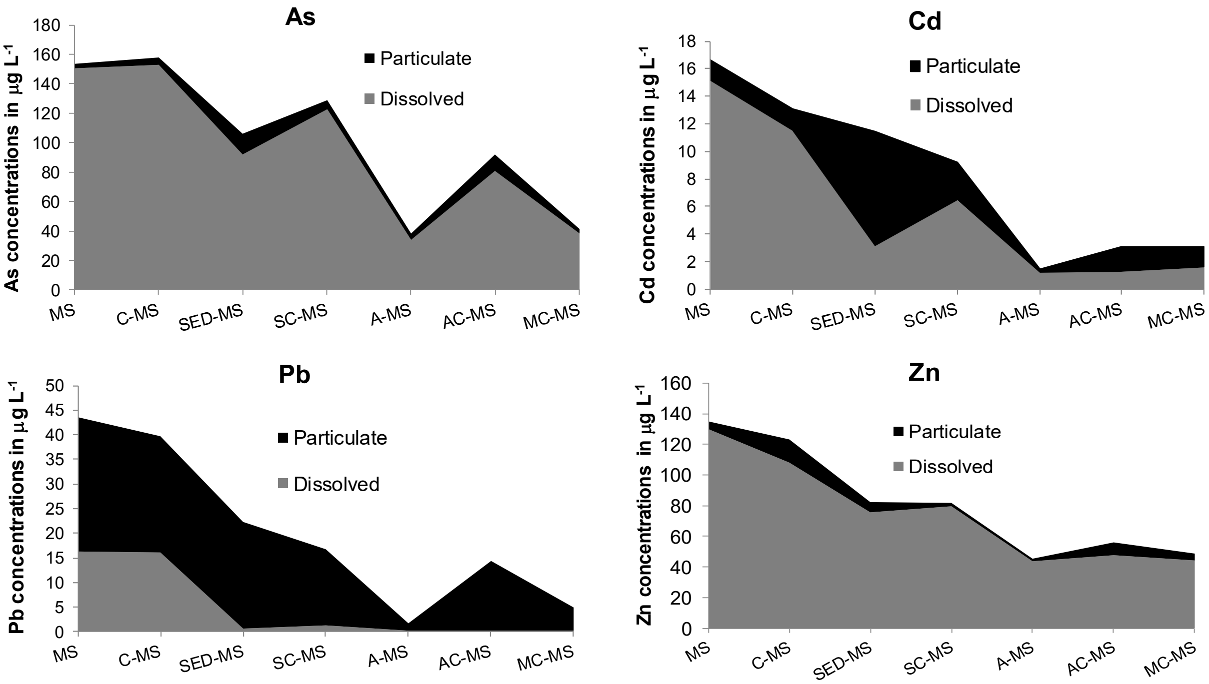
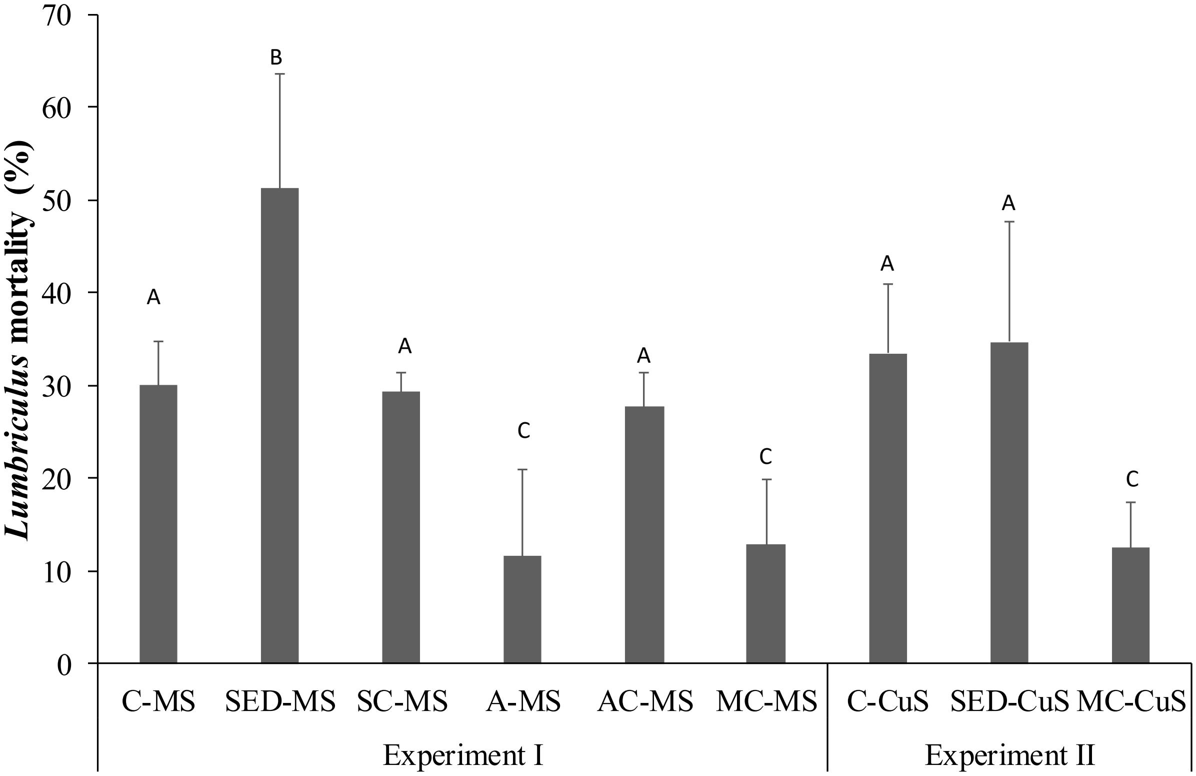

As
As concentrations in µg L-1
180
160
140
120
100
80
60
40
20
0
■ Particulate
■ Dissolved
MS
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
Cd
Cd concentrations in µg L-1
18
16
14
12
10
8
6
4
2
0
■ Particulate
■ Dissolved
MS
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
Pb
Pb concentrations in µg L-1
50
45
40
35
30
25
20
15
10
5
0
■ Particulate
■ Dissolved
MS
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
Zn
Zn concentrations in µg L-1
160
140
120
100
80
60
40
20
0
■ Particulate
■ Dissolved
MS
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS

Figure 4.



Lumbriculus mortality (%)
70
60
50
40
30
20
10
0
A
B
A
C
A
C
A
A
C
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
C-CuS
SED-CuS
MC-CuS
Experiment I
Experiment II

Figure 5.

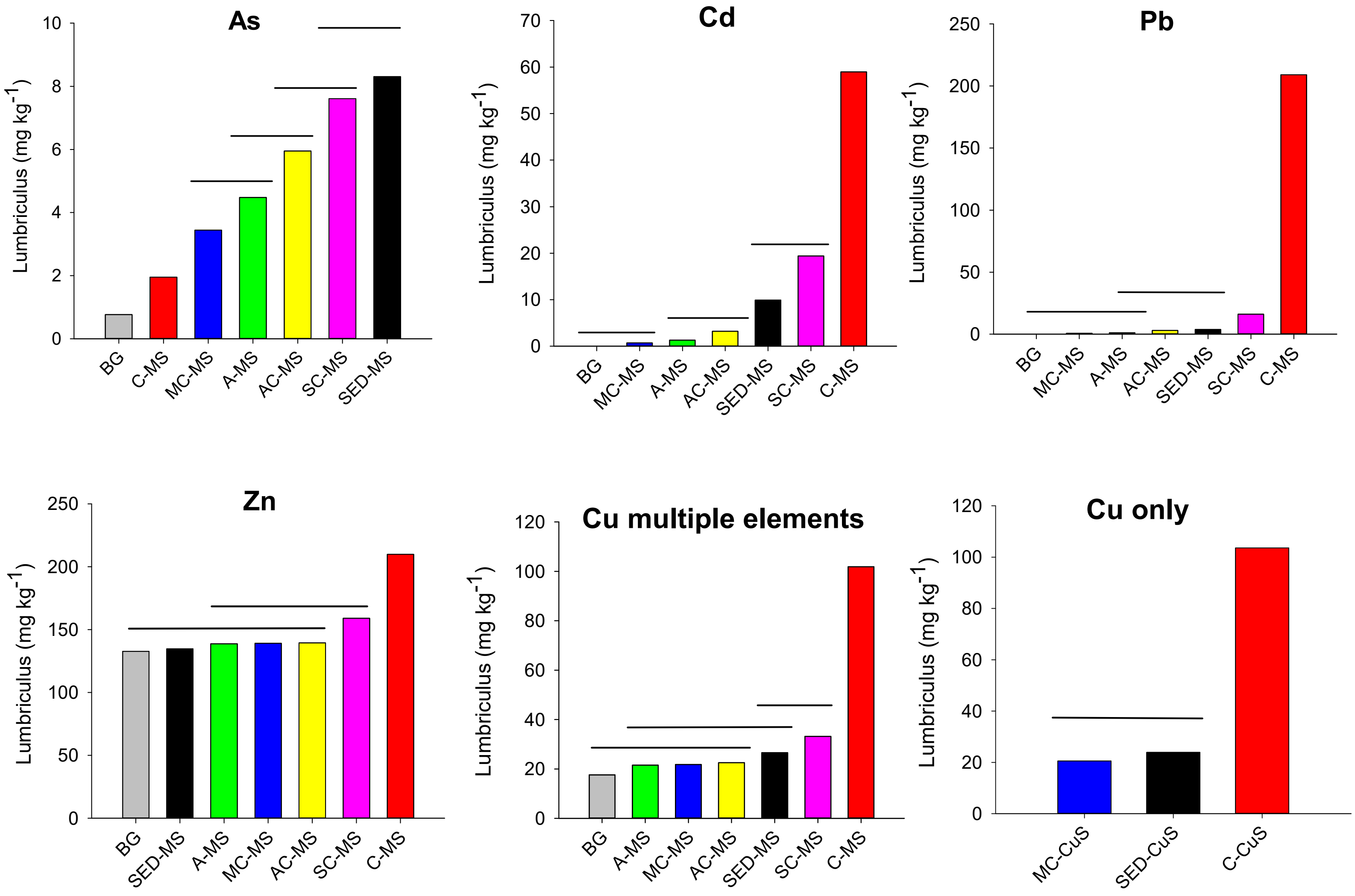
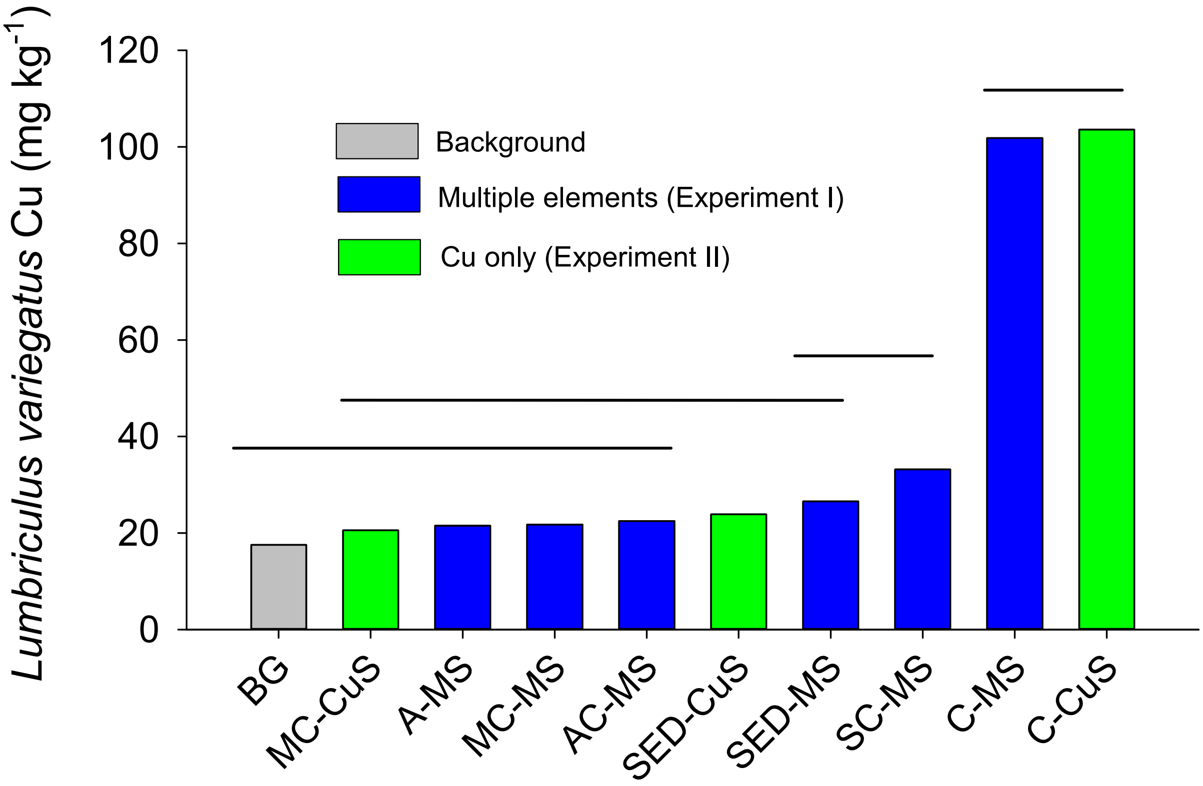

As
Lumbriculus (mg kg^{-1})
0
2
4
6
8
10
BG
C-MS
MC-MS
A-MS
AC-MS
SC-MS
SED-MS
Cd
Lumbriculus (mg kg^{-1})
0
10
20
30
40
50
60
70
BG
MC-MS
A-MS
AC-MS
SED-MS
SC-MS
C-MS
Pb
Lumbriculus (mg kg^{-1})
0
50
100
150
200
250
BG
MC-MS
A-MS
AC-MS
SED-MS
SC-MS
C-MS
Zn
Lumbriculus (mg kg^{-1})
0
50
100
150
200
250
BG
SED-MS
A-MS
MC-MS
AC-MS
SC-MS
C-MS
Cu multiple elements
Lumbriculus (mg kg^{-1})
0
20
40
60
80
100
120
BG
A-MS
MC-MS
AC-MS
SED-MS
SC-MS
C-MS
Cu only
Lumbriculus (mg kg^{-1})
0
20
40
60
80
100
120
MC-CuS
SED-CuS
C-CuS

Figure 6.



Lumbriculus variegatus Cu (mg kg-1)
0
20
40
60
80
100
120
Background
Multiple elements (Experiment I)
Cu only (Experiment II)
BG
MC-CuS
A-MS
MC-MS
AC-MS
SED-CuS
SED-MS
SC-MS
C-MS
C-CuS

Figure 7.

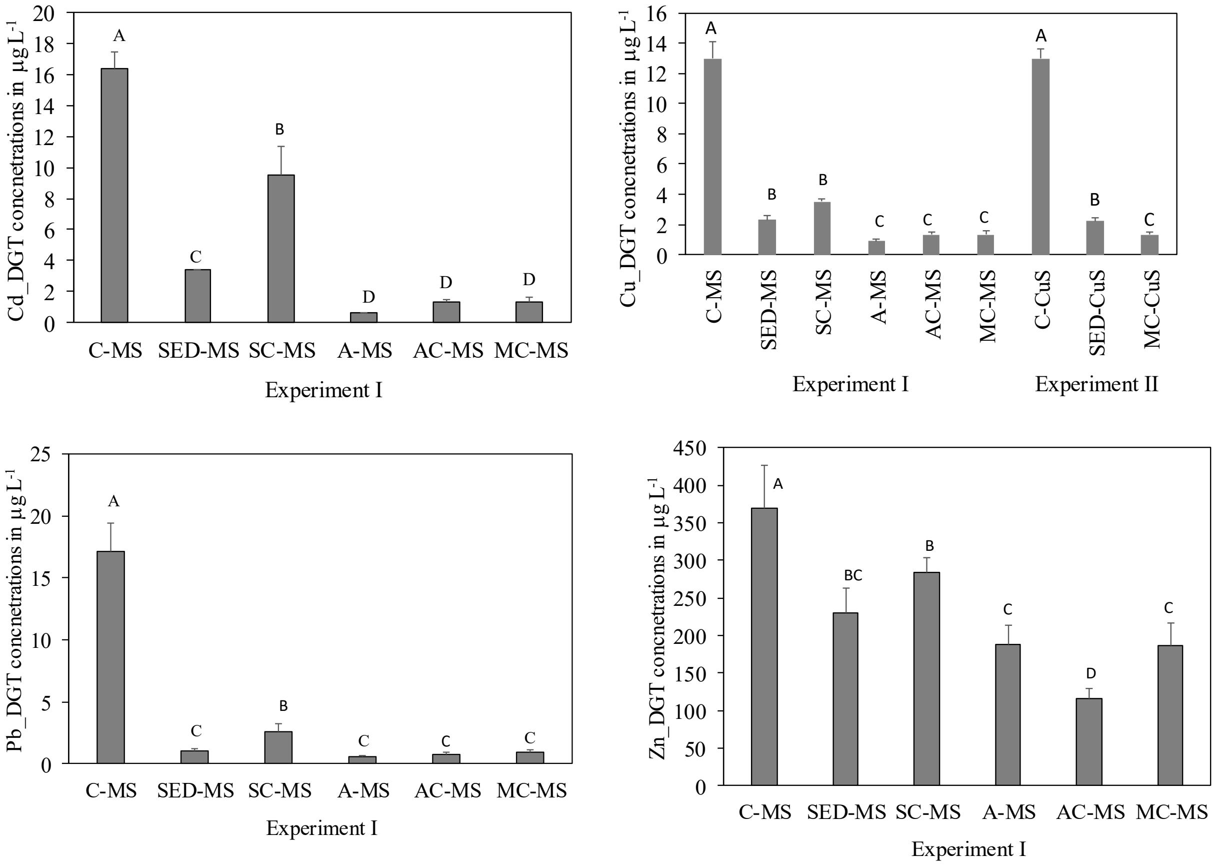

Cd_DGT concnetrations in µg L-1
20
18
16
14
12
10
8
6
4
2
0
A
B
C
D
D
D
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
Experiment I
Cu_DGT concnetrations in µg L-1
16
14
12
10
8
6
4
2
0
A
B
B
C
C
C
A
B
C
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
C-CuS
SED-CuS
MC-CuS
Experiment I
Experiment II
Pb_DGT concnetrations in µg L-1
25
20
15
10
5
0
A
C
B
C
C
C
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
Experiment I
Zn_DGT concnetrations in µg L-1
450
400
350
300
250
200
150
100
50
0
A
BC
B
C
D
C
C-MS
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
Experiment I

Figure 8.

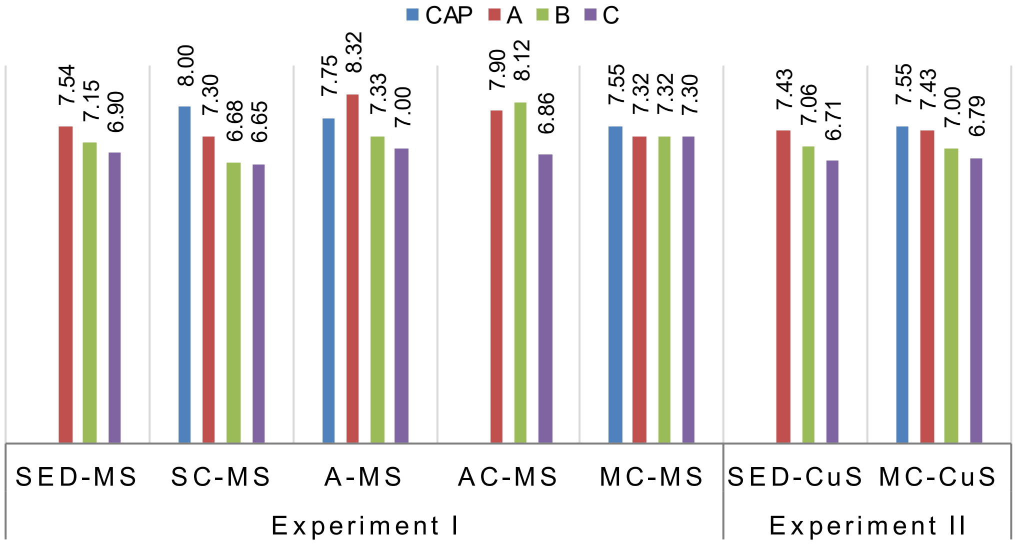

CAP
A
B
C
7.54
7.15
6.90
8.00
7.30
6.68
6.65
7.75
8.32
7.33
7.00
7.90
8.12
6.86
7.55
7.32
7.32
7.30
7.43
7.06
6.71
7.55
7.43
7.00
6.79
SED-MS
SC-MS
A-MS
AC-MS
MC-MS
SED-CuS
MC-CuS
Experiment I
Experiment II

Figure 9.

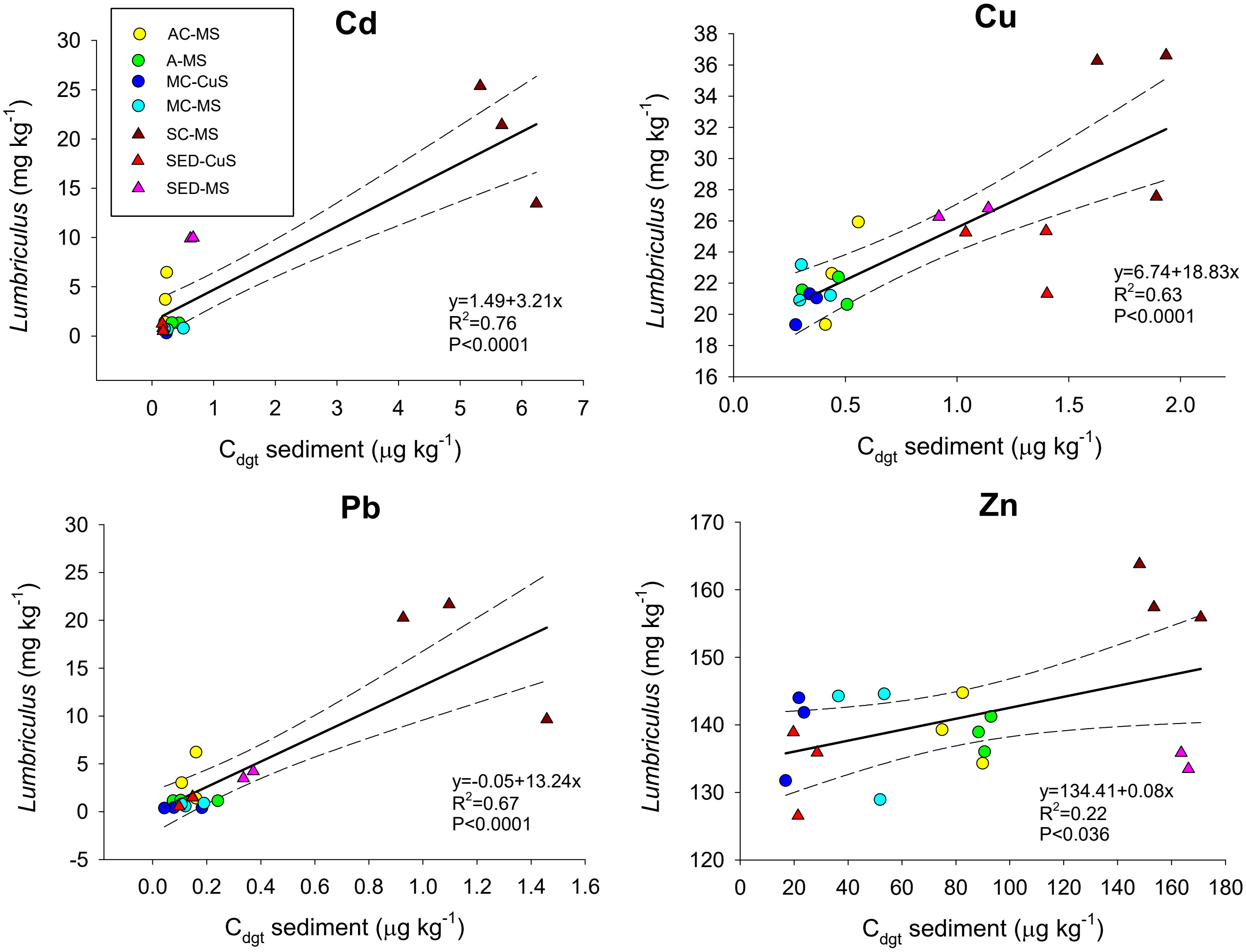

Cd
AC-MS
A-MS
MC-CuS
MC-MS
SC-MS
SED-CuS
SED-MS
y=1.49+3.21x
R2=0.76
P<0.0001
Lumbriculus (mg kg-1)
Cdgt sediment (µg kg-1)
0
5
10
15
20
25
30
0
1
2
3
4
5
6
7
Cu
y=6.74+18.83x
R2=0.63
P<0.0001
Lumbriculus (mg kg-1)
Cdgt sediment (µg kg-1)
16
18
20
22
24
26
28
30
32
34
36
38
0.0
0.5
1.0
1.5
2.0
Pb
y=-0.05+13.24x
R2=0.67
P<0.0001
Lumbriculus (mg kg-1)
Cdgt sediment (µg kg-1)
-5
0
5
10
15
20
25
30
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
Zn
y=134.41+0.08x
R2=0.22
P<0.036
Lumbriculus (mg kg-1)
Cdgt sediment (µg kg-1)
120
130
140
150
160
170
0
20
40
60
80
100
120
140
160
180

Figure 10.