

Ecotoxicological assessment of the efficacy of capping materials
in reducing zinc bioavailability in pit lake sediment

by

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Dedication

To my parents; for instilling in me the value of hard work and for working tirelessly to ensure I had the opportunities they never had.

To Sean; for being my life partner and biggest fan.

To my friends, family, and mentors; your love and support made all this possible.

To Burton lab members; your guidance, patience, and, above all else, friendship helped me retain my sanity.

To Allen; for never letting me take the easy way out, and for reminding me that curiosity only ripens with age.

In loving memory of
Jeanine R. Musgrove

Abstract

The contamination of sediments in aquatic ecosystems is a widespread environmental issue. Sediment serves as a reservoir for contaminants and is therefore a potential sink and source of toxicants. Remediation techniques separate, destroy, stabilize, or convert contaminants to less toxic forms and include ex-situ and in-situ physical, chemical, or biological treatments. One such technique is capping, which is intended to isolate sediment-associated contaminants from surface water and benthic community interactions.

Although capping shows promise in bench-scale studies, there is a need for more pilot-scale studies that incorporate multiple lines of evidence, coupled laboratory and field studies, and test organisms that can demonstrate effects through various exposure pathways. The objective of my research is to fill this gap with a weight-of-evidence approach to evaluating the performance of various capping materials in remediating zinc-contaminated sediment at East Wilson Pond (Hot Springs, Arkansas).

The study consisted of both field and laboratory ecotoxicological tests using *Hyaella azteca*, *Daphnia magna*, and *Chironomus dilutus*. Field experiments assessed acute toxicity and water chemistry in test plots covered with three capping materials: Aquablok, limestone, and limestone-bone char. The laboratory tests involved a series of acute toxicity tests and water chemistry sampling conducted in core microcosms created from site-collected sediment. Capping materials assessed in the laboratory tests included two from the field tests (Aquablok, limestone) and two selected per literature review and site geotechnical surveys (zeolite, apatite). Overall, there were no differences in biological endpoints between treatments in both the field and laboratory tests, likely due to below-threshold dissolved zinc concentrations in the surface water. Zeolite was the most effective mitigator of zinc release, but also caused adverse organism effects. This indicates that all treatments successfully prevented zinc release from the sediment, although some may be less effective under certain hydrologic conditions. Final remedy selection will ultimately depend on results from the field and laboratory studies, as well as site conditions, cost, future uses, and ecological considerations.

Table of Contents

1. Introduction.....	1
2. Materials and Methods.....	5
2.1 Site description.....	5
2.2 Test organisms.....	7
2.3 Field investigation.....	7
2.3.1 Temperature Acclimation Containment System (TACs).....	8
2.3.2 Sediment capping materials.....	9
2.3.3 Experimental setup.....	9
2.3.4 Pre-deployment preparation.....	10
2.3.5 Field deployment.....	11
2.3.6 pH adjustment.....	12
2.3.7 Water quality.....	12
2.3.8 Water sample collection.....	12
2.3.9 Control organisms.....	13
2.3.10 Organism retrieval.....	13
2.3.11 Ex-situ experiments.....	13
2.4 Laboratory investigation.....	14
2.4.1 Sediment capping materials.....	15
2.4.2 EWP sediment coring and transfer to laboratory.....	16
2.4.3 Experimental setup.....	16
2.4.4 Acute toxicity tests.....	17
2.4.5 Water quality monitoring and water sample collection.....	17
2.4.6 Sediment sample collection.....	18
2.4.7 Control organisms.....	18

2.5 Sample analyses	18
2.5.1 Surface water and porewater	18
2.5.2 Sediment	18
2.5.3 <i>H. azteca</i> growth and tissue metal residue	19
2.6 Statistical analyses.....	19
3. Results	20
3.1 Field investigation.....	20
3.1.1 Water quality	20
3.1.2 In-situ test surface water zinc	21
3.1.3 In-situ test survival	22
3.1.4 Ex-situ test survival	24
3.2 Laboratory investigation	26
3.2.1 Water quality	26
3.2.2 Sediment [SEM-AVS].....	26
3.2.3 Surface water zinc	27
3.2.4 Porewater zinc	28
3.2.5 Survival.....	28
3.2.6 <i>D. magna</i> reproduction.....	29
3.2.7 <i>H. azteca</i> individual growth rate.....	29
3.2.8 <i>H. azteca</i> tissue metal residue.....	30
3.2.9 Relationship between biological endpoints and surface water zinc and pH.....	30
4. Discussion.....	30
4.1 Field investigation	30
4.2 Laboratory investigation	32
5. Conclusion	34

Appendix A	35
Appendix B	44
Appendix C	54
Literature Cited	55

1. Introduction

Sediment is any matter that can be transported by fluid flow and eventually deposited as a layer of solid particles on the bottom of a body of water. It serves as a reservoir for contaminants and is a potential source of toxins to aquatic ecosystems. Contaminants comprise of both organics (e.g. polychlorinated biphenyls (PCB), dioxins) and inorganics (e.g. metals), and can arise from multiple sources, including municipal and industrial discharge, urban and agricultural runoff, and atmospheric deposition. These pollutants are ubiquitous; currently all U.S. waterways contain contaminated sediments. These sites represent over one-third of the hazardous waste sites on the U.S. Environmental Protection Agency's (USEPA) National Priorities list (USEPA 2008).

Many contaminants persist for years because they do not readily degrade in the aquatic environment. One of the largest Superfund sites – a 200-mile stretch of the Hudson River – is estimated to be polluted with over 1.3 million pounds of PCBs. The site was placed on the USEPA's National Priorities List in 1984, and despite over 33 years of remedial activities, ongoing evaluations of water and sediment quality by USEPA and New York determined that PCBs in the river sediment continue to pose serious threats to ecological and human health (USEPA 2017). The cleanup and restoration of these sites serve as top priority for many other entities – with an estimated liability for the United States Department of Defense (US DoD) surpassing \$2 billion (US DoD 2016), for instance.

The ability of sediments to serve as a sink for these contaminants is a serious source of concern. For instance, while some organic pollutants can be naturally degraded in the sediment, a fraction of these contaminants can bioaccumulate and biomagnify up the food chain (Figure 1) (Burton 1992). Other contaminants, such as heavy metals, cannot be removed by natural processes of decomposition (Namieśnik and Rabajczyk 2010). Instead, their total concentrations are fixed either as freely dissolved ions or various metal-ligand complexes, most commonly to organic matter, carbonate, phosphate, iron and manganese oxyhydroxides, chloride, and reduced sulfur (Cantwell *et al.* 2002, Sprague 1995). When complexed to ligands, metals are not available for biotic uptake. However, as freely dissolved ions, metals become bioavailable and at high enough concentrations, can be directly toxic to aquatic biota when ingested as food, sediment, or water (Muyssen and Janssen 2001).

The speciation and bioavailability of metals is determined by the concentration of binding ligands, which is directly dependent on variable environmental conditions such as pH and dissolved oxygen (DO). Acidic conditions lead to increased competition between H⁺ ions and dissolved metals for ligands, which generally results in the increased solubility and resultant bioavailability of metals (Peng *et al.* 2009). In some cases, even a very small decrease in pH can result in a total flux of metals from the sediment into the overlying water (Gunderson and Steinnes 2003). Reduction-oxidation (redox) conditions also influence the fate and transport of metals. For instance, most cationic metals are sequestered to sulfides under reducing conditions but can become soluble when the water column becomes oxygenated (Simpson *et al.* 1998). This effect can be seasonal in lakes during turnover events, when DO from the epilimnion is delivered to the hypolimnion (Cover and Wilhm 1982).

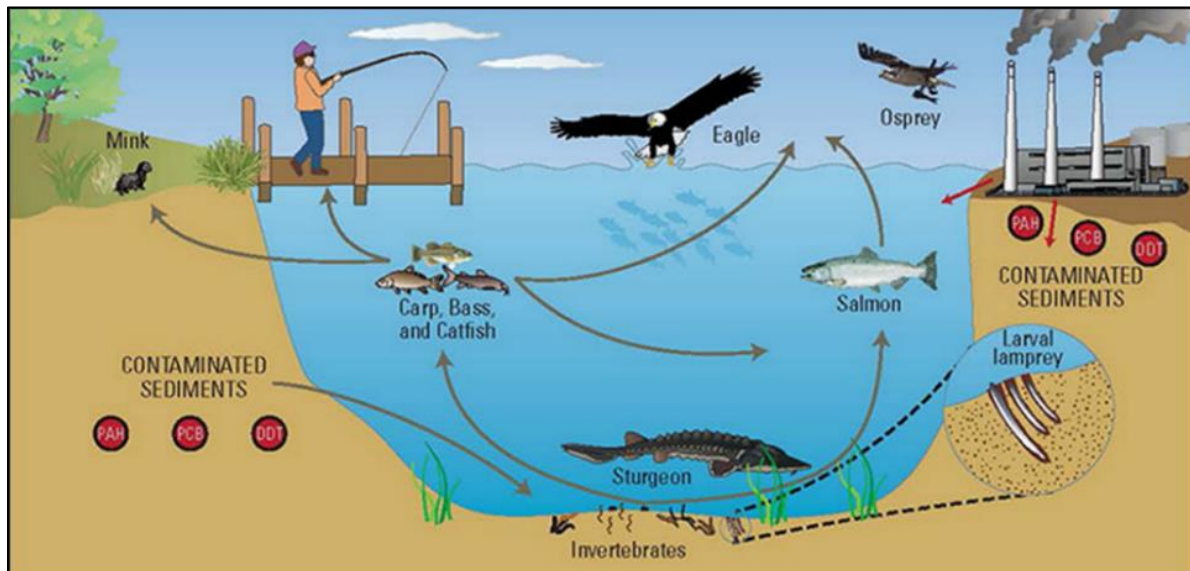


Figure 1: Contaminant pathways through trophic levels (Reible *et al.* 2014).

Contaminated sediments pose difficult cleanup and management problems. Remediation techniques either separate, destroy, stabilize, or convert the pollutants to less toxic and/or bioavailable forms and include ex-situ and in-situ physical, chemical, or biological treatments. Although conventional methods of dredging followed by confined disposal can be effective under certain conditions, it has many limitations. Among these are high costs, resuspension of contaminants into the water column, destruction of benthic ecosystems, worker safety, community impacts (e.g. noise, air emissions), adverse impacts to fish and wildlife, and incompatible site conditions (National Research Council 2007). Additionally, the disposal of

dredged sediment upland in landfills or in water has its own associated costs, leaching risks, and ecological and environmental justice issues.

The limitations of dredging have led to the development of in-situ technologies, such as capping. Capping isolates contaminated sediment from the water column by acting as a physical barrier, and is designed to achieve one or more of the following objectives:

1. Minimize contaminant release and migration due to resuspension, groundwater upwelling, and other physical processes,
2. Separate benthic community from interacting with underlying sediments, and
3. Chemically bind contaminants to reduce bioavailability, migration, and release (Reible *et al.* 2014).

Capping has been shown to be less expensive than traditional methods and is a viable option when site-specific conditions are unfavorable for dredging, such as in ecologically sensitive areas like wetlands and around piers (Luthy *et al.* 2009, Fredette 2006). Two types exist: passive caps made of clean sediment, sand, or gravel; and active caps consisting of various amendments (e.g. activated carbon, zeolite, organoclays, apatite) that reduce exposure by altering sediment geochemistry or promoting contaminant binding. The latter is especially promising, as the chemically-reactive amendments are designed to both treat and contain the contaminants by strengthening the adsorption and degradation capacity.

Although the active capping technology shows promise as a remediation technique in bench-scale studies, there is a need for more pilot-scale studies demonstrating its effectiveness. Several challenges exist with pilot-scale evaluations, including a myriad of environmental conditions, spatial and temporal heterogeneity, sediment deposition, and impacts from contaminated overlying water that can serve as confounding variables (Ghosh *et al.* 2011). Some of these issues can be alleviated with study designs that incorporate multiple lines of evidence (e.g. chemical, biological, physical), coupled laboratory and field studies, and various test organisms that can demonstrate effects through several different exposure pathways.

East Wilson Pond (EWP - Hot Springs, Arkansas) is the site of a former pit mine, where vanadium mining operations took place from the mid-1960s to 1986. Mining activities and associated wastes has negatively affected water quality and contaminated sediment with heavy metals. Zinc (Zn) is the main contaminant of concern within this lake and is suspected to be released from the sediment into the surface water via acid-base reactions at the hypolimnion

and by its known adsorption properties (i.e. complexation) to amorphous iron hydroxide. Sediment and surface water concentrations range from 143-417 mg/kg and 4.85-160 µg/L, respectively. The current USEPA national recommended water quality criteria for aquatic life for acute and chronic Zn toxicity is 120 µg/L (USEPA 1995), although acute toxicity has been demonstrated with as low as 90 µg/L Zn (Rabe and Sappington 1970).

The broader focus of this research is to identify and describe the uncertainties associated with Zn dynamics and to evaluate the effectiveness of sediment capping treatments. More specific objectives include:

1. Assess the performance of capping materials as a potential sediment metal remediation option through metal binding capacity and biological effects,
2. Determine whether sediment-sourced metals are bioavailable and cause negative effects to aquatic macroinvertebrates, and
3. Evaluate the effects of varying water quality conditions (e.g. pH, DO) on the bioavailability and toxicity of metals.

The study is split up into three tasks – with the first two tasks taking place in the field and the third task taking place in the laboratory. The first task evaluated the effectiveness of capping treatments at reducing bioavailability of sediment-sourced metals at the study site. Specifically, in-situ toxicity tests using benthic (*Hyalella azteca* and *Chironomus dilutus*) and pelagic (*Daphnia magna*) macroinvertebrates and associated water quality measurements and surface water sampling were conducted within limnocorrals positioned on each of the capping treatments. This first task addresses objectives 1 and 2.

The second task assessed the effects of pH dynamics on Zn speciation and bioavailability. Water within the limnocorrals was manipulated to reflect the lower pH of the hypolimnion. In-situ toxicity tests were coupled with ex-situ tests using sediment cores collected within each of the limnocorrals. The second task addresses objectives 1, 2, and 3.

The third task complemented the field investigations with a laboratory study examining the efficacy of various sediment capping treatments at decreasing Zn bioavailability. Sediment cores collected from EWP were shipped back to the laboratory, where they were processed and set up for toxicity tests. Ultimately, results from both laboratory and field-based studies will lead to remedy selection for the site and will contribute to the growing knowledge base of the most useful metrics for measuring the success of a treatment technology in field pilot studies.

2. Materials and Methods

2.1 Site description

East Wilson Pond (EWP), Hot Springs, Arkansas, USA (34° 28' N, 92° 56' W) is the site of the former Umetco Minerals Corporation (hereafter referred to as 'Umetco') Wilson Mine site, where vanadium mining operations took place from the 1960 to 1986 (Umetco 2018). The Umetco site spans approximately 375 acres, with Indian Spring Creek feeding into it, and Wilson Creek running through it (Figure 2). Both creeks are tributaries of Lake Catherine and are connected to the larger Ouachita River watershed. EWP is one of two open pit lakes at the site. It retains water year-round and receives runoff, precipitation, and discharge from an adjacent neutralization plant and Wilson Creek.

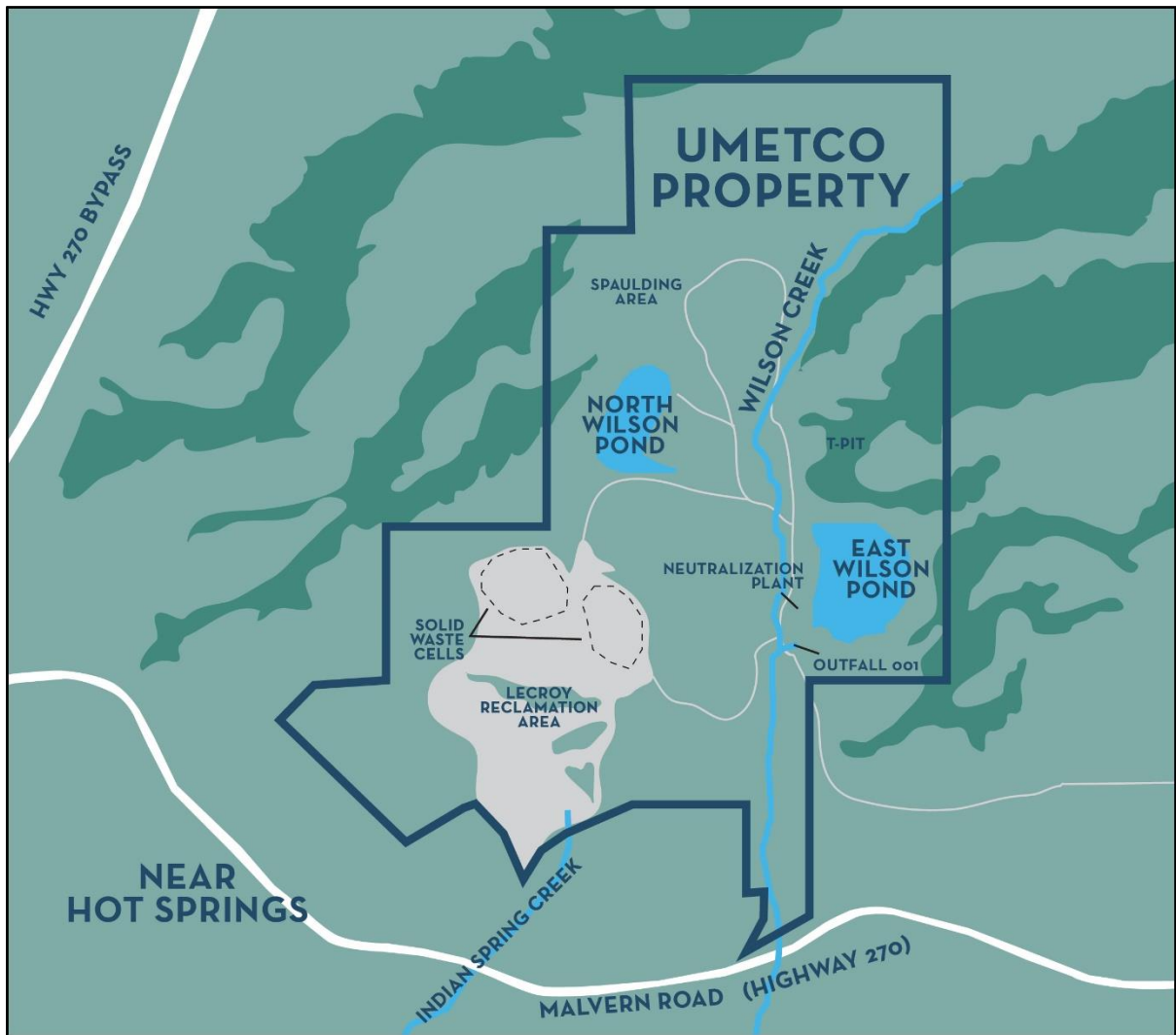


Figure 2: Umetco property map (Umetco 2018); EWP is located in the southeastern area.

Since operations at the site ceased, Umetco has been working with the Arkansas Department of Environmental Quality (ADEQ) and various environmental consulting companies to reclaim the site. Major sitewide efforts include topographic alterations, storm water runoff redirection, phytoremediation, wetland mitigation, and infiltration reductions. Currently, an active lime treatment plant (denoted as Neutralization Plant in Figure 2) treats and discharges mining-influenced water from EWP to Wilson Creek to comply with National Pollutant Discharge Elimination System (NPDES) standards (NPDES Permit no. AR0048950). Ongoing monitoring and maintenance activities include weekly water quality measurements, flow measurements, lime treatment plant upkeep, sediment removal, mowing, and seeding (Umetco 2018). The ultimate goal of this pilot study is to terminate the NPDES permit, shut down the lime plant, and convert the site to a publicly-usable recreational space by demonstrating that EWP sediment is geochemically stable in the long run, and will not present an environmental or human health risk.

Site investigations in April 2016 by the principal remediation contractor, CH2MHill Engineers, Inc. (hereafter CH2M, now Jacobs Engineering, Inc.) characterized the site and provided baseline water quality and sediment data (CH2M 2017). Zinc concentrations in sediment samples ranged from 143-417 milligrams per kilograms (mg/kg) and were preferentially adsorbed to amorphous iron hydroxide. Zinc concentrations in surface water samples ranged from 4.85-160 $\mu\text{g/L}$, while in porewater ranged from 5.4-64.7 $\mu\text{g/L}$, indicating relative stability in the sediment given alkaline surface water conditions. Shallow sediment porewater pH range from 7.90-9.40, with higher pH observed near the lime plant discharge and lower pH values observed further away from the lime plant. Longitudinally, pH was observed to drop significantly below the thermocline, indicating lake stratification was isolating the hypolimnion from lime plant discharge influences and promoting anoxic metabolic processes. Accordingly, surface water Zn was lower in the epilimnion than hypolimnion, presumably due to effluent from the lime plant. Measurable DO levels were observed throughout the lake.

EWP is comprised of up to several feet of low density, floc-like sediments that are non-uniformly distributed throughout the bottom of the lake. This is likely a result of steep walled slopes, which are not conducive to sediment deposition. Higher sediment thickness (6+ feet)

was observed in the northwestern portion of the lake, presumably due to proximity to the lime treatment plant and Wilson Creek.

2.2 Test organisms

Organisms used in the field and laboratory studies include *Hyalella azteca*, *Daphnia magna*, and *Chironomus dilutus*. These organisms are ideal for sediment toxicity testing, given their well-documented sensitivities to common contaminants, interaction with sediment, ease of culturing, short generation time, and high tolerance to other physicochemical properties that vary with sediment and surface water that could act as confounding variables (USEPA 2000). *H. azteca* is a benthic freshwater amphipod commonly found in North and South America. Because it exhibits burrowing behavior and obtains food from ingesting sediment and grazing on algae and macrophytes (Wang *et al.* 2004), *H. azteca* serves as a useful proxy for benthic organisms exposed to contaminated sediment. *D. magna* is a freshwater zooplankton that filter feeds on suspended particles and thus serve as important indicators of water column contamination. It will also feed on sediment surfaces when confined in beakers and mesocosms. *C. dilutus* is a freshwater midge adapted to brief anoxic conditions and replaced *H. azteca* in the field tests, as the amphipod appeared to be adversely affected by deep water atmospheric pressure.

2.3 Field investigation

A series of field-deployed toxicity tests (Tasks 1 and 2) were conducted during Fall 2017 to assess Zn toxicity in the water and sediment of EWP. The field tests were split up into two tasks that evaluated sediment cap performance and assessed Zn bioavailability under ambient lake conditions (experiments 1a, 1b, and 1c) and reasonable worst-case scenario conditions (experiments 2a and 2b), respectively (Table 1).

Table 1: Tasks 1 and 2 Timeline; including experiment number, date range of each experiment, organisms used, and additional details.

Experiment	Date(s)	Organisms	Details
1a	August 28-30	<i>D. magna</i> <i>H. azteca</i>	48-hr in-situ exposure
1b	September 18-22	<i>D. magna</i> <i>H. azteca</i>	96-hr in-situ exposure
1c	October 9-11	<i>D. magna</i> <i>C. dilutus</i>	48-hr in-situ exposure 48-hr EWP-water exposure
2a	October 17-19	<i>D. magna</i> <i>C. dilutus</i>	48-hr in-situ exposure 48-hr EWP sediment core exposure
2b	October 31-November 1	<i>D. magna</i> <i>C. dilutus</i>	48-hr in-situ exposure 48-hr EWP-water exposure

2.3.1 Temperature Acclimation Containment System (TACs)

An in-situ deployment system was developed to protect test organisms against stressful temperature exposure changes occurring during deployment through the epilimnion to the hypolimnion (Figures 3 and B-5). Five 12” x 8” x 8” TACs were fabricated from aluminum, with the bottom covered with grated sheet metal (stainless steel) to allow for contact with sediment. Five stainless steel eyebolts were secured onto the top of each TACS, four for rope attachment to a buoy and one to open the hatch for organism addition. The TACs are designed to hold up to six organism chambers (Figure 3B) arranged in two rows of three chambers to reflect two different types of exposure. The three chambers on the bottom row serve as sediment exposures, while the three chambers on the top row serve as water column exposures.

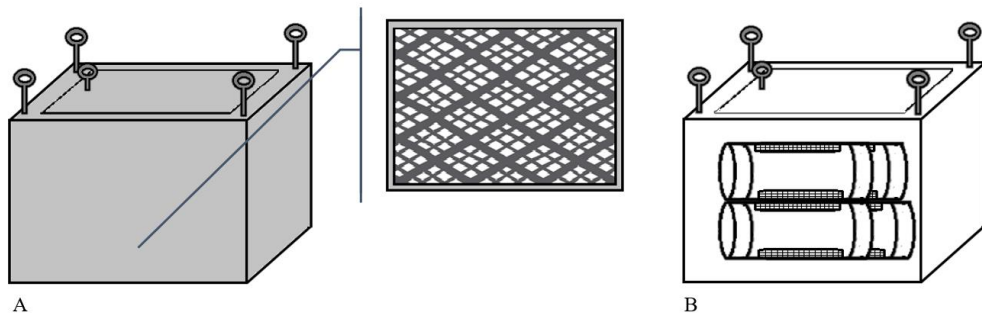


Figure 3: Conceptual model depicting A) TACs with bottom open grate and B) TACs setup with organism chambers.

2.3.2 Sediment capping materials

In field tests, three different types of sediment capping materials were tested: Aquablok™ (hereafter Aquablok), limestone, and limestone-bone char mix. These materials were chosen for the field treatability studies after preliminary research by CH2M, which included bench-scale physical and settling studies, isotherm analyses, geochemical modelling, and a literature review. Aquablok is a bentonite clay and polymer composite that, once hydrated, swells to create a continuous and highly impermeable isolation barrier (Reible *et al.* 2006, Knox *et al.* 2006). Limestone is a calcium carbonate mineral that is widely used in remediation as an acid-neutralization agent, typically in mine drainage system applications (Johnson and Hallberg 2005, IRTC 2010). By creating more alkaline conditions, metals are largely sequestered and unavailable for biotic uptake. In some instances, limestone is blended with organic solids such as bone char, which serve as a source of hydroxyapatite for enhanced metals sorption (Lin *et al.* 2007, Siebers and Leinweber 2013). Summary information for all three capping materials used in the field studies can be found in the Appendix (Table A-1).

2.3.3 Experimental setup

In July 2017, CH2M installed sediment capping materials using a truck-mounted telescopic belt conveyor. A figure depicting the test plot location can be found in Appendix B (Figure B-1). The specific pilot study location within EWP was determined after extensive feasibility considerations. Final cover placement observations, including total material thickness, area, and material mass can be found in Appendix A (Table A-2).

Approximately two weeks after cap placement, four Limnocorrals™ (hereafter limnocorrals) equipped with lake divider curtains (Figure B-4), were installed on each of the four capping plots. Limnocorrals were constructed with flotation devices fabricated from plastic, with a thick, curtain-like high-density polyethylene (HDPE) sheeting attached. The limnocorrals extend down to the sediment surface and are anchored and sealed to prevent seepage (Curry Industries 2016). In EWP, the limnocorrals were anchored on each plot a minimum of 20-feet apart, with the top open to the atmosphere and the bottom open to the sediment, but otherwise sealed to prevent water column exchange. Each limnocorral was 3-feet in diameter and designed with an accordion-style attachment allowing for column depth to vary between 36-54 feet. The first of four limnocorrals were installed on the control (no

capping material) plot, followed by limestone, limestone-bone char, then Aquablok. Figures and photographs depicting the limnocorral placement within the test plot are in Appendix B (Figures B-2 and B-3).

In order to collect water quality data throughout the water column, plastic tubing with small weights were secured within each limnocorrals at three different depths: surface (8 centimeter [cm]), mid-depth, and near bottom (approximately 1-foot above lake bottom). A conceptual model depicting the experimental setup can be seen below in Figure 4.

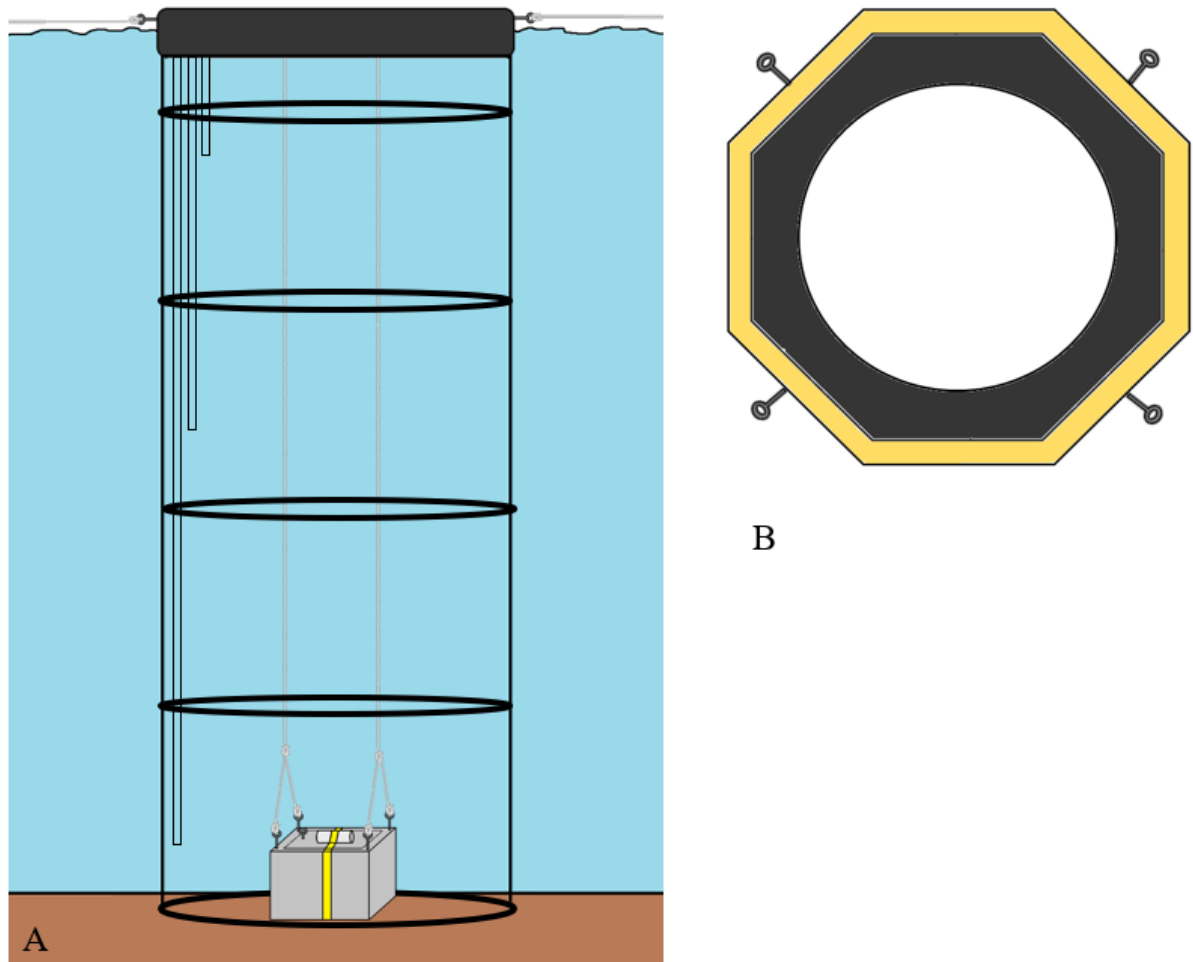


Figure 4: Conceptual model depicting A) TACs deployed within a limnocorral (flip rope not shown) and B) Bird's eye view of a limnocorral.

2.3.4 Pre-deployment preparation

The night before each deployment, organism acclimation and TACs setup were conducted off-site. Test organisms were assessed for survival and appearance and counted and checked for

quality assurance/quality control (QA/QC). One TACS was placed into a transport container (26.5-l volume) with a plastic-coated metal rack and one organism chamber (Figure B-5). Ten organisms of each species (*D. magna* and *H. azteca* (experiments 1a and 1b) or *C. dilutus* (experiments 1c, 2a, and 2b) were added to each chamber with a small amount of food (0.5-gram ground Tetramin and 1-milliliter (ml) Sel-Cero, a mixture of *Raphidocelis subcapitata* (green algae) and Cerophyl (1.0×10^7 algal cells/ml)). The organism chamber was then capped, submerged in water, air bubbles removed, and zip-tied to the plastic-coated metal rack. This process was repeated for the remaining five organism chambers. Once all six organism chambers were then secured so that their mesh windows were horizontal to the bottom, ensuring their exposures would be of water near the sediment surface. An 8" PVC pipe was placed on top of the TACS and fastened by tightly wrapping a ratchet strap around the unit. Then, a "flip rope" was tied onto two diagonally-positioned eyebolts. At this point, the TACS was transferred to one of the transport coolers and placed grate side up. Finally, a lowering rope marked with meter (m) depths was attached onto the bottom grate.

Water chillers with aquarium pumps controlled the temperature of the coolers by chilling a 14-gallon plastic bucket reservoir of surface water from Lake Catherine. Lake Catherine is a 1,940-acre lake located about two miles southwest of the Umetco mining property and has been used as a recent reference site (Nedrich *et al.* 2018). The ambient water temperature of the test organism transport containers was lowered at a rate of 2 degrees per hour until the water temperature at the deployment depth was achieved. Pictures of the pre-deployment process are in Appendix B (Figure B-6).

2.3.5 Field deployment

The TACS coolers were transported to a staging area adjacent to EWP and maintained at the correct temperature until deployment. TACS were deployed at each limnocorral using a pulley-and-cleat system. The TACS was lowered with the grate side up, to maintain the chilled water during the descent through the epilimnion. Once it was in the hypolimnion, the TACS flip rope was pulled to correctly position the TACS bottom grate for sediment contact. It was then slowly lowered to the bottom, as in Figure 4.

2.3.6 pH adjustment

For Task 2 experiments, the pH of the EWP water within each limnocorral was adjusted down to approximately 5.5 to evaluate Zn dynamics under a reasonable worst-case scenario observed previously in EWP. A 30% hydrochloric acid (HCl) solution was used for acidification with 10% sodium hydroxide (NaOH) solution to counteract any pH overshoot. Acid was pumped into the bottom of each limnocorral through tygon tubing attached to a peristaltic pump. The pH and DO were monitored at a depth near the bottom (approximately 0.25 m above the bottom). Another tygon tube was lowered to the same depth with an air stone for air compressor aeration to facilitate acid mixing and increase the DO in the limnocorral. Acid addition was considered complete after the pH was stable at 0.25 to 1 m above the sediment surface. It was assumed water density differences and the lack of currents would reduce acid dilution and pH increase.

2.3.7 Water quality

As a part of ongoing weekly monitoring efforts, water quality was measured at several different locations and depths within EWP. In-situ profile measurements were collected at each sampling point by lowering a YSI and an underwater camera. Data on temperature, pH, and DO were recorded every meter, as indicated by live feed from the underwater camera.

2.3.8 Water sample collection

At various time periods (depending on the experiment) two 10-ml water samples were collected in clean, unused centrifuge tubes from the three depths within each limnocorral using a handpump. Samples were both filtered and unfiltered and preserved with 714 microliters (μl) of 30% nitric acid. Tubing was purged six times prior to sampling. Filtered and unfiltered samples were analyzed for dissolved and particulate metals, respectively. Additionally, two 250-ml grab samples were collected in HPDE bottles for hardness and alkalinity analyses, and one 45-ml grab sample was collected in a glass amber vial for dissolved organic carbon analysis at 0 and 48 hours.

2.3.9 Control organisms

To confirm the viability of organisms used in the toxicity tests, controls consisted of 5 sets each of 10 *D. magna*, 10 *H. azteca*, and 10 *C. dilutus* in laboratory culture water and Lake Catherine water. Additionally, there were three sets of inter-mixed organism controls consisting of 10 *D. magna*, 10 *H. azteca*, and 10 *C. dilutus*. The control organisms were only fed at time 0 to be consistent with the field-deployed organisms. The organisms were maintained at the same temperature as in-situ deployment.

2.3.10 Organism retrieval

At test termination, TACS were quickly raised through the epilimnion in an inverted position (as deployed) to reduce the temperature change and placed in chilled water for transport. Organisms were counted within 30 minutes of collection to determine survival rates. Any surviving *H. azteca* were placed into 100-ml of a 50 micromolar (μM) ethylenediaminetetraacetic acid (EDTA) solution with a small amount of ground Tetramin and allowed to depurate overnight. The next morning, they were dried and placed into centrifuge tubes for tissue metal residue analysis. Measured organism endpoints included survival and tissue metal residue.

2.3.11 Ex-situ experiments

In addition to the field experiments, a series of off-site toxicity tests were conducted in conjunction with experiments 1c, 2a, and 2b (Table 1). Two tests were designed to assess Zn toxicity from EWP water only exposures (experiments 1c and 2b). The third test evaluated organism survival and reproduction (*D. magna* only) from pH-adjusted water and sediment exposure using sediment cores collected from EWP (experiment 2a). Measured endpoints for the ex-situ toxicity tests included survival, reproduction, and tissue metal residue analysis.

The EWP water only exposures were set up using water collected from within each limnocorral. In order to better simulate field exposures, organisms were also acclimated to in-situ hypolimnetic temperatures. Two 10-ml samples were collected for dissolved and particulate metals analyses, and one 500-ml bulk sample was collected for alkalinity, total dissolved solids, and hardness analyses. Organisms from these exposures were counted following the in-situ TACS retrieval to determine survival. Surviving *H. azteca* were placed

into 100-ml of 50 μ M EDTA to depurate overnight, then subsequently dried and placed into centrifuge tubes for tissue metal residue analysis.

For experiment 2a, three sediment cores were collected from each test plot directly adjacent to the limnocorrals. A total of twelve cores were collected in plastic core tubes (5-cm diameter). The sediment cores were collected, capped, and maintained in a vertical position to minimize sediment resuspension, then transported to the field laboratory for ex-situ toxicity tests. The toxicity tests were initiated within 24 hours of core collection.

Off-site, each core tube was measured and marked denoting the point where there was approximately 4" water overlying the surficial sediment. A pipe cutter was used to cut the core tubes to the appropriate length. The modified core tubes were placed into a container with water chilled to hypolimnetic temperature and pH adjusted as in the field. Acid addition process was considered complete when the pH was approximately 5.5. At this point, 10 *H. azteca* caged in small organism chambers (Figure B-5) and 10 non-caged *D. magna* and 10 *C. dilutus* were added to each of the twelve cores. After 48 hours, organisms in each core were retrieved and counted to determine survival. Surviving *D. magna* and *H. azteca* were placed into small plastic cups with approximately 200-ml of culture water for an additional one-week post-exposure short-term chronic toxicity study. The *D. magna* and *H. azteca* were fed twice during the one-week post-exposure period, with *D. magna* fed as under normal culture conditions to promote reproduction. One week after the ex-situ study, test organisms from the short-term chronic test were collected and counted to determine survival and reproduction (*D. magna* neonates). *H. azteca* were placed into 100-ml of 50 μ M EDTA solution with Tetramin to depurate overnight, then subsequently dried and placed into centrifuge tubes for tissue metal residue analysis. Pictures of the ex-situ experiment can be found in Appendix B (Figure B-7).

2.4 Laboratory investigation

A series of laboratory toxicity tests (Task 3) were carried out during Fall 2017 to better understand how overlying water quality is affected by EWP sediments and how various capping treatments influence Zn toxicity. These laboratory tests were conducted using sediment cores and surface water collected from EWP and were split up into a four 7-day acute toxicity tests (Table 2).

Table 2: Task 3 Timeline; including exposure number, date range of each exposure, organisms used, and additional details.

Exposure #	Date(s)	Organisms	Details
1	November 9-16	<i>D. magna</i> <i>H. azteca</i>	7-day exposure
2	November 16-23	<i>D. magna</i> <i>H. azteca</i>	7-day exposure
3	November 23-30	<i>D. magna</i> <i>H. azteca</i>	7-day exposure
4	November 30-December 7	<i>D. magna</i> <i>H. azteca</i>	7-day exposure

2.4.1 Sediment capping materials

In addition to the two capping materials used in the field (Aquablok, limestone), two other materials were selected after an extensive review of literature and site-specific geotechnical reports, and preliminary tests. The limestone-bone char material was unable to be obtained for use in the laboratory studies.

Two preliminary tests assessed 1) zinc removal between different types of zeolite and 2) zinc removal between apatite and iron sulfide powder. For the first preliminary test, six different types of zeolites (SIR-300, SIR-600, Deep Blue Ammonia Reducer Lab Grade Zeolite, API Ammochips, 0.3 nm molecular sieve zeolite beads, 0.4 nm molecular sieve zeolite beads) were added to 200-ml of 250 µg/l zinc-spiked deionized water. Water samples were collected and analyzed for dissolved zinc concentration. The 0.4 nm molecular sieve zeolite was chosen for the study due to its optimal zinc removal in the preliminary test. The second preliminary test assessed zinc removal between apatite and iron sulfide powder using the same methods. Out of these two materials, apatite was most effective at removing surface water dissolved zinc and was therefore chosen to use in the lab studies.

Apatite is comprised of mined phosphate rock with a characteristically high cation exchange capacity and has the capability to preferentially adsorb select metals (Singh *et al.* 2001, Cao *et al.* 2004). Zeolites are crystalline, hydrated aluminosilicates of alkali and alkaline earth elements (Jacobs and Forstner 1999). Its inherent tetrahedron structure comprised of SiO₄ and AlO₄ results in a net negative charge, which is counterbalanced by exchange with cations

such as divalent metals (Wingenfelder *et al.* 2005). Summary information for all four capping materials used in the laboratory studies can be found in Appendix A (Table A-1).

2.4.2 EWP sediment coring and transfer to laboratory

Sixteen sediment cores and surface water were collected from EWP in October 2017. Cores were collected adjacent to the field study plots. Offsite, the core tubes were cut at the sediment line (no overlying water) with a pipe cutter, capped, secured with duct tape to minimize vertical gradient alterations. All sixteen cores were tightly packed into a cooler for overnight shipment to the UM laboratory. Cores were placed at 4°C upon receipt.

2.4.3 Experimental setup

After marking up each tube so that there were approximately 14” of sediment in each core post-processing, the tube was cut using a pipe cutter. This process required two UM researchers, one to manage the pipe cutter and one to maintain suction within the core tube to allow for a controlled release of sediment from the bottom. This was done by slightly piercing the top cap with a box cutter and positioning the thumb directly on the cut. As soon as the plastic was pierced, a large paint scraper was slid in place, and slowly slid out of the way to remove any excess sediment. As soon as there was 14” of sediment left in the tube, the bottom was capped, secured with electrical tape, and placed upright into a modified shelf. Approximately 200-ml of overlying EWP water was added immediately after to minimize surficial sediment oxygenation. After resuspended sediment particles were observed to have settled, about 4” of each capping material were added to twelve of the cores, for a total of twelve capped treatments and three non-capped treatments (Figure 5).

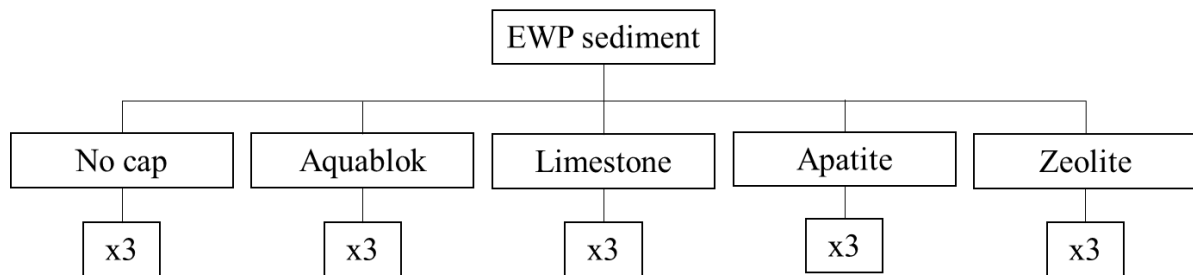


Figure 5: Task 3 experimental design consisting of three replicates each of non-capped sediment, and Aquablok, limestone, apatite, and zeolite-capped sediment.

To sample porewater, holes were drilled at the capping layer (~14.5 cm from the top), cap-sediment mixing layer (~18.5-cm from the top), and sediment layer (21-cm from the top). For uncapped treatments, holes were drilled at 1, 2 and 3 cm below the sediment surface. Immediately after the core hole was drilled, electrical tape was placed over the hole. Rhizon samplers (Rhizosphere Research Products Item no. 19.21.23) were inserted into the holes, then sealed and reinforced with nontoxic, waterproof, silicone sealant. Dissolved oxygen, temperature and pH were monitored and once they stabilized, test organisms were added, and the first exposure initiated. Pictures of the experimental setup are in Figure B-8.

2.4.4 Acute toxicity tests

Testing was initiated using 4-day-old *D. magna* and 8-day-old *H. azteca* from laboratory stock cultures. Ten sets of 8-10 *H. azteca* were placed on aluminum tins and dried as a reference for growth and tissue metal residue analysis. Ten *H. azteca* were caged in small chambers (Figure B-5) and 10 non-caged *D. magna* were added to each of the fifteen cores. The *D. magna* were fed Sel-Cero three times during the exposure. The *H. azteca* were not fed to promote sediment grazing. At the end of the 7-day exposure period, *D. magna* and *H. azteca* assessed for survival. Surviving *H. azteca* were placed into 100-ml of 50 μ M EDTA solution with a small amount of ground Tetramin to deplete overnight, then subsequently dried and placed into centrifuge tubes for growth and tissue metal residue analysis.

2.4.5 Water quality monitoring and water sample collection

Dissolved oxygen, temperature, and pH were measured in surface and porewater three times a week prior to overlying water exchanges at days 1, 4, and 6. Two 10-ml surface water samples were collected using pre-rinsed syringes as filtered and unfiltered, and preserved with 714- μ l of 30% nitric acid. Filtered and unfiltered samples were analyzed for dissolved metals and particulate metals, respectively. Three 10-ml porewater samples were collected from the cap material, mixed material, and sediment in the capped treatments, and at 1-cm, 2-cm, and 3-cm in the non-capped treatments. Porewater sampling consisted of a large needle (20 gauge by 1.5") in the rhizon hole and immediately inserting a vacutainer. Because the rhizons have a built-in filter, water samples were not filtered, but instead collected and immediately preserved with 714- μ l of 30% nitric acid. After all water samples were collected, the remaining surface

water in each core was siphoned until about 1” above the sediment or capping layer. Fresh EWP water was carefully added back into each core.

2.4.6 *Sediment sample collection*

Sediment samples were collected pre- and post-test for sediment characterization and to assess any changes in sediment-associated metals and sulfides. A modified plastic micro-corer was used.

2.4.7 *Control organisms*

To confirm the viability of organisms used in the laboratory toxicity tests, controls were set up and maintained for the duration of each test. Controls consisted of three sets of 10 *D. magna*, three sets of 10 *H. azteca* in 200-ml of EWP water, and three sets of 10 *D. magna* and 10 *H. azteca* in 200-ml of ion-enriched water (IEW). The *D. magna* were fed Sel-Cero at the same intervals as the test organisms. The *H. azteca* were not fed, but instead provided with approximately 5-grams of reference sediment at the beginning of each 7-day test to graze on.

2.5 Sample analyses

2.5.1 *Surface water and porewater*

All surface water collected for dissolved metals analyses were syringe-filtered with a 25 mm 0.45 µm Isopore™ polycarbonate membrane filter (EMD Millipore Corporation, Billerica, MA). All water samples were acidified with 30% trace metal grade nitric acid (Fisher Scientific) and analyzed by inductively-coupled plasma-optical emission spectroscopy (ICP-OES) using USEPA method 6010B for Zn.

2.5.2 *Sediment*

Sediment samples collected pre- and post-laboratory studies were analyzed for acid-volatile sulfides (AVS) and simultaneously-extracted metals (SEM) using methods developed by the USEPA (USEPA 1991b). AVS was determined by mixing the sediment with deionized water, acidifying the slurry with 1 M hydrochloric acid, and trapping the resulting hydrogen sulfide in a sodium hydroxide solution, which would subsequently be analyzed for sulfide content

colorimetrically. The remaining sediment-water slurry was vacuum-filtered into a 250-ml volumetric flask and acidified with 0.5 M HCl, diluted, and analyzed for SEM content by ICP-OES.

2.5.3 *H. azteca* growth and tissue metal residue

Metal body burden was determined on surviving *H. azteca* collected from each experiment. After a 24-hour depuration period, the *H. azteca* were placed on aluminum tins, transferred to a desiccator for 48-72 hours, and then weighed to the nearest 0.001 milligrams (mg). This final weight was averaged for each treatment replicate and subtracted from the average weight of the *H. azteca* initially set aside to calculate individual growth rate (IGR), calculated as follows:

$$IGR = \frac{\left[\frac{\sum(mass_{org})_{final}}{n_{org}} - \frac{\sum(mass_{org})_{initial}}{n_{org}} \right]}{time}$$

Where $mass_{org}$ is in μg , n is the number of *H. azteca* in each organism chamber, and $time$ is in days.

After *H. azteca* were weighed, they were placed into separate plastic tubes and for tissue metal residue analysis. This was done by digesting the organisms for six days in nitric acid, followed by a 24-hour digestion in hydrogen peroxide (ACS grade, Fisher Scientific). Following the digestion period, the organisms were diluted and analyzed by inductively-coupled plasma mass spectroscopy (ICP-MS).

2.6 Statistical analyses

All statistical analyses were conducted using R Studio 1.1.383 (R Development Core Team). Prior to significance testing, the Shapiro-Wilk test for normality was applied to determine whether a given dataset was normally or non-normally distributed. Levene's test was used to determine whether variances were equal among treatments. The Kruskal-Wallis test was used for multivariate comparisons of non-parametric variable. When warranted, the Posthoc Kruskal-Nemenyi test (R package PMCMR) was used for further post-hoc testing between treatment types, with any apparent ties in data broken assuming averages. For survival data, binomial generalized linear models were also used as an additional point of comparison. Otherwise, equivalent one- or two-way analysis of variances (ANOVA) were used for

multivariate comparisons of normally-distributed variables, followed up with Tukey's Honest Significant Difference post-hoc test when warranted. Welch's t-test was used to compare differences in Zn between Tasks 1 and 2 experiments.

Pearson correlations between survival, *H. azteca* growth, *H. azteca* tissue metal residue and surface water dissolved Zn and pH were used when assumptions were met (normality, linear relationship, homoscedasticity). Otherwise, Spearman rank tests were used to estimate correlation for non-parametric data.

3. Results

Because sample analyses from the field investigations is still ongoing, for the purposes of this thesis, only the organism survival and reproduction and dissolved and particulate surface water Zn results from the in-situ field experiments will be discussed. All analyses for the laboratory experiments were completed and will be discussed.

3.1 Field investigation

3.1.1 Water quality

Water quality results from sampling point EWL-23 along transect EWL-2 are being used for the following discussions (Figure B-1). This sampling point is the deepest part of EWP (47-m). The TACS, however, were deployed at approximately 15-m close to the lake bank due to logistical limitations (Figure B-1). Overall, lower pH was observed in the hypolimnion, averaging 5.88 ± 0.24 . pH gradually increases closer to the epilimnion, averaging 7.45 ± 0.17 . Dissolved oxygen followed the same trend, with lower levels detected closer to the hypolimnion (0.56 ± 0.26 milligrams per liter (mg/l)), and higher levels detected near the epilimnion (8.76 ± 0.49 mg/l). The entire water column contained dissolved oxygen (0.01-11.68 mg/l), indicating oxidizing conditions throughout the surface water albeit low near the bottom of EWP. This low to high vertical water column profile was maintained throughout the series of field experiments for both pH and dissolved oxygen. Conversely, temperature profiles indicate initially, there was lake stratification (experiments 1a-1c) with lower temperatures observed in the hypolimnion ($9.8 \pm 0.08^{\circ}\text{C}$) and progressively higher temperatures observed closer to the epilimnion ($25.4 \pm 1.69^{\circ}\text{C}$). This temperature gradient becomes less apparent

during experiment 2a, and virtually disappears in the top 15-m during experiment 2b. This suggests that, between experiments 2a and 2b, EWP experienced seasonal turnover (Table A-3).

3.1.2 *In-situ test surface water zinc*

Although Zn concentrations were higher at the bottom compared to mid-depth and surface, both dissolved and particulate Zn concentrations were similar between plots for each depth during experiments 1a-1c ($p > 0.097$) (Tables A-4 and A-5; Figures 6, B-9, and B-10). In experiments 2a and 2b, there was higher dissolved Zn in surface waters of the limestone-bone char plot compared to Aquablok ($p = 0.047$). Particulate Zn was higher in surface and mid-depths of the limestone-bone char plot compared to limestone ($p < 0.02$) and Aquablok ($p < 0.02$), respectively. Otherwise, there were no other differences in dissolved or particulate Zn between capped and non-capped plots. However, both dissolved and particulate Zn concentrations were higher across all treatments for Task 1 experiments as compared to Task 2 experiments ($p = 5.69e-8$ and $p = 0.0004$, respectively). The pH adjustment either had no effect or a contradictory effect on Zn release from the sediment.

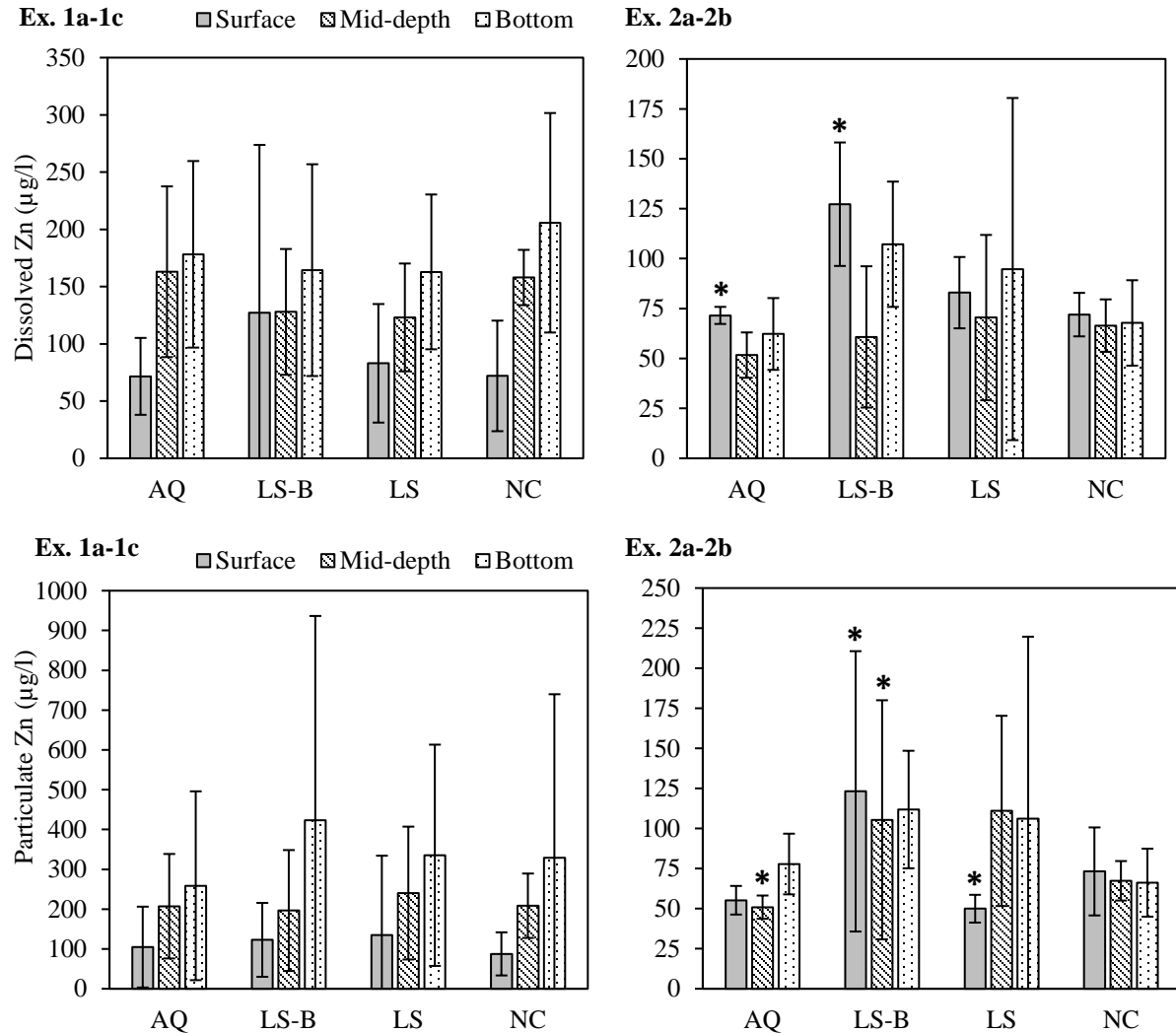


Figure 6: In-situ field experiments dissolved and particulate Zn concentrations (\pm standard deviation). Statistical significance is denoted with an asterisk. Treatments have been abbreviated as follows: AQ = Aquablok, LS-B = Limestone-bone char, LS = Limestone, and NC = No cap.

3.1.3 In-situ test survival

Overall, there were no differences between non-capped and capped plots on survival of *D. magna* or *C. dilutus* ($p > 0.1$, Figure 7). In cases where average control survival was low ($< 80\%$ for *D. magna* and *H. azteca*; $< 70\%$ for *C. dilutus*), test results were disregarded due to violating the QA/QC threshold (USEPA 1991a). These included *H. azteca* in 1a, *C. dilutus* in 2a, and *D. magna* in 2b.

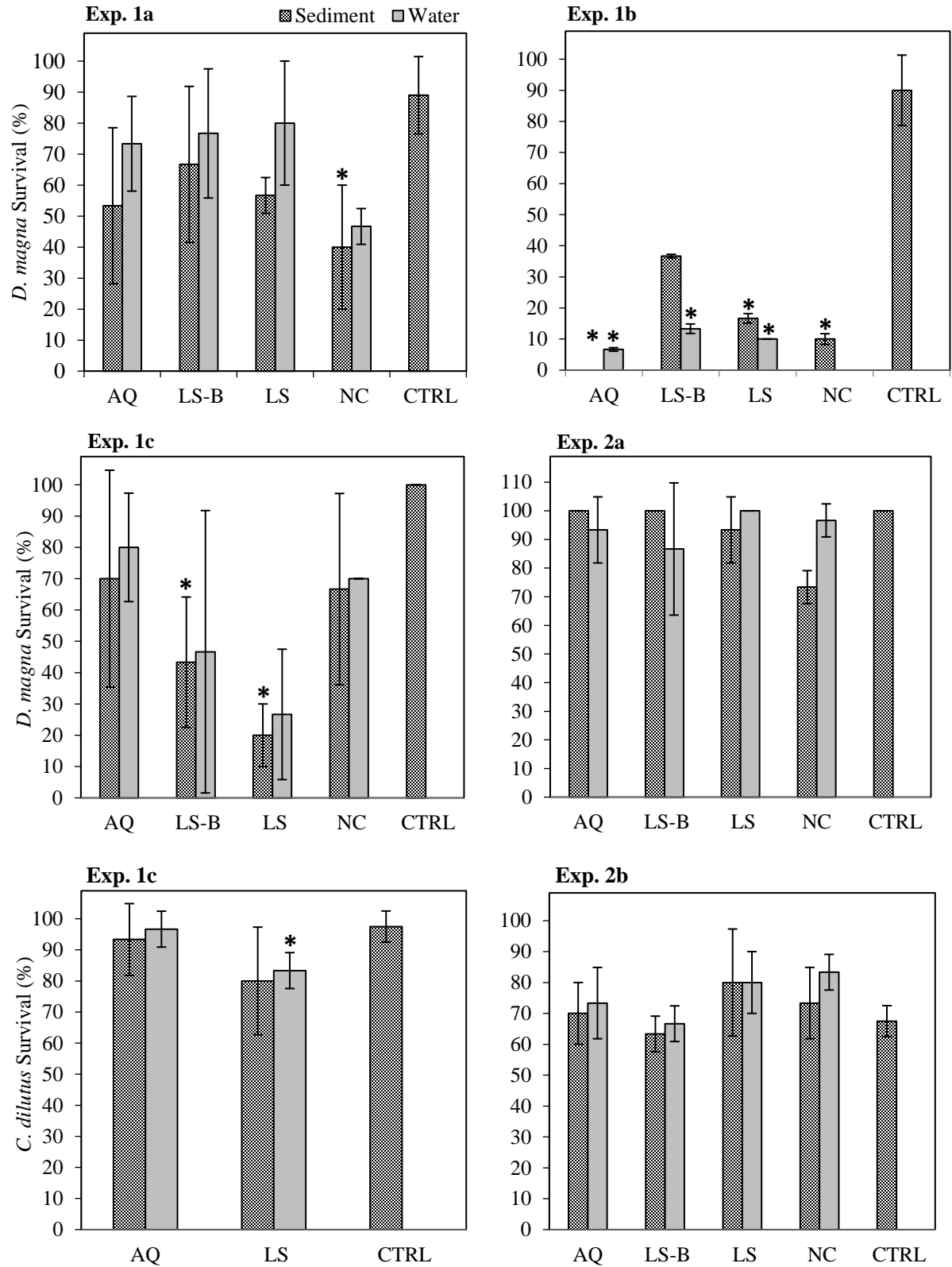
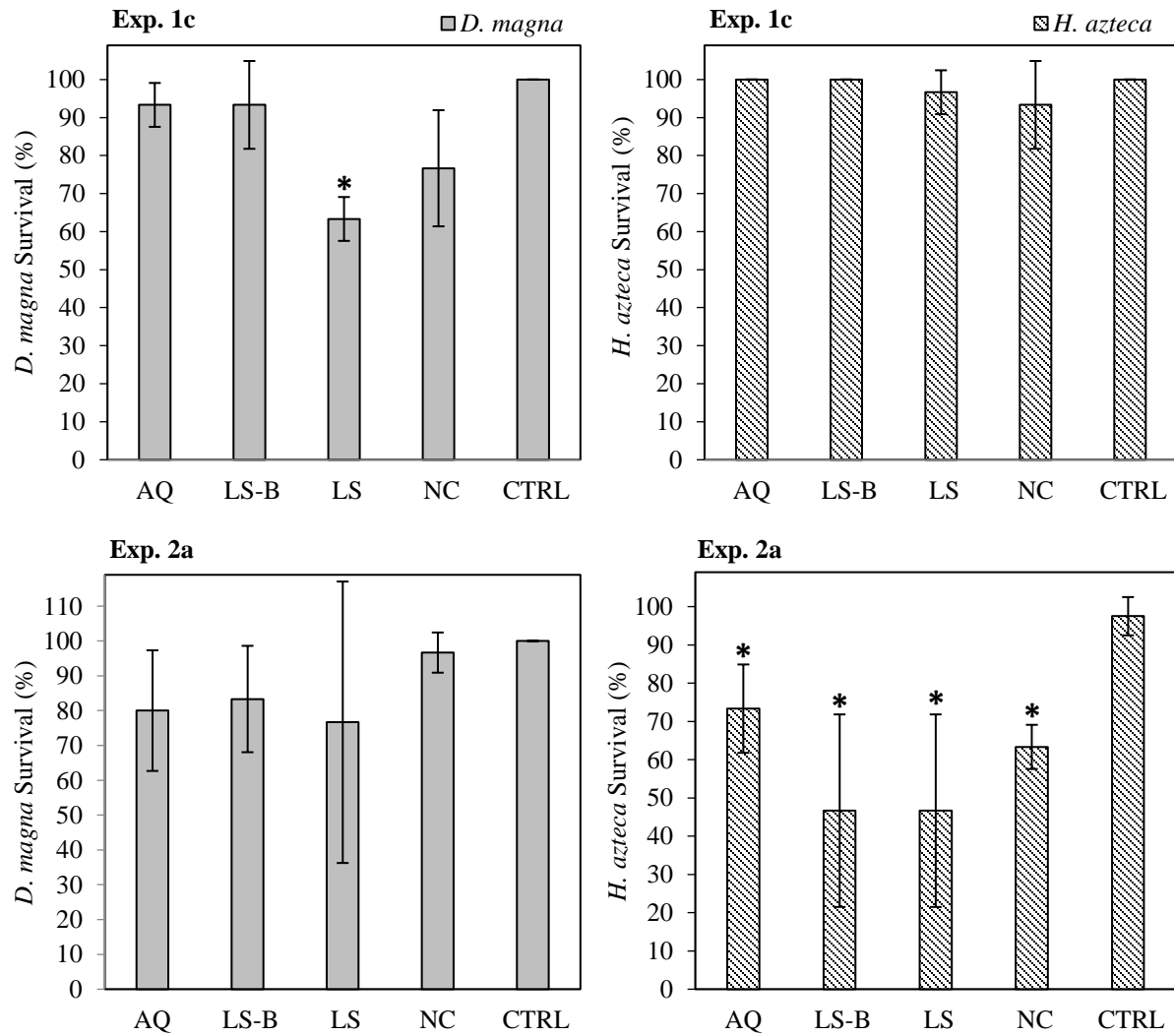


Figure 7: In-situ field experiments organism survival (\pm standard deviation). The same control is used for both sediment and water exposures. Statistical significance is denoted as difference

from control with an asterisk. Treatments have been abbreviated as follows: AQ = Aquablok, LS-B = Limestone-bone char, LS = Limestone, NC = No cap, and CTRL = control.

3.1.4 *Ex-situ* test survival

Poor control survival resulted in the removal of results from *C. dilutus* in experiment 2b. Apart from two experiments, there were no observed differences in survival ($p > 0.1$). In experiment 1c, *D. magna* had lower survival than the control ($p < 0.055$), but otherwise survival was similar in both non-capped and capped treatments. Low survival was also observed in *H. azteca* in experiment 2a for non-capped and capped treatments compared to the control ($p < 0.02$). Overall, it appears effects from water-only exposures were limited (Figure 8).



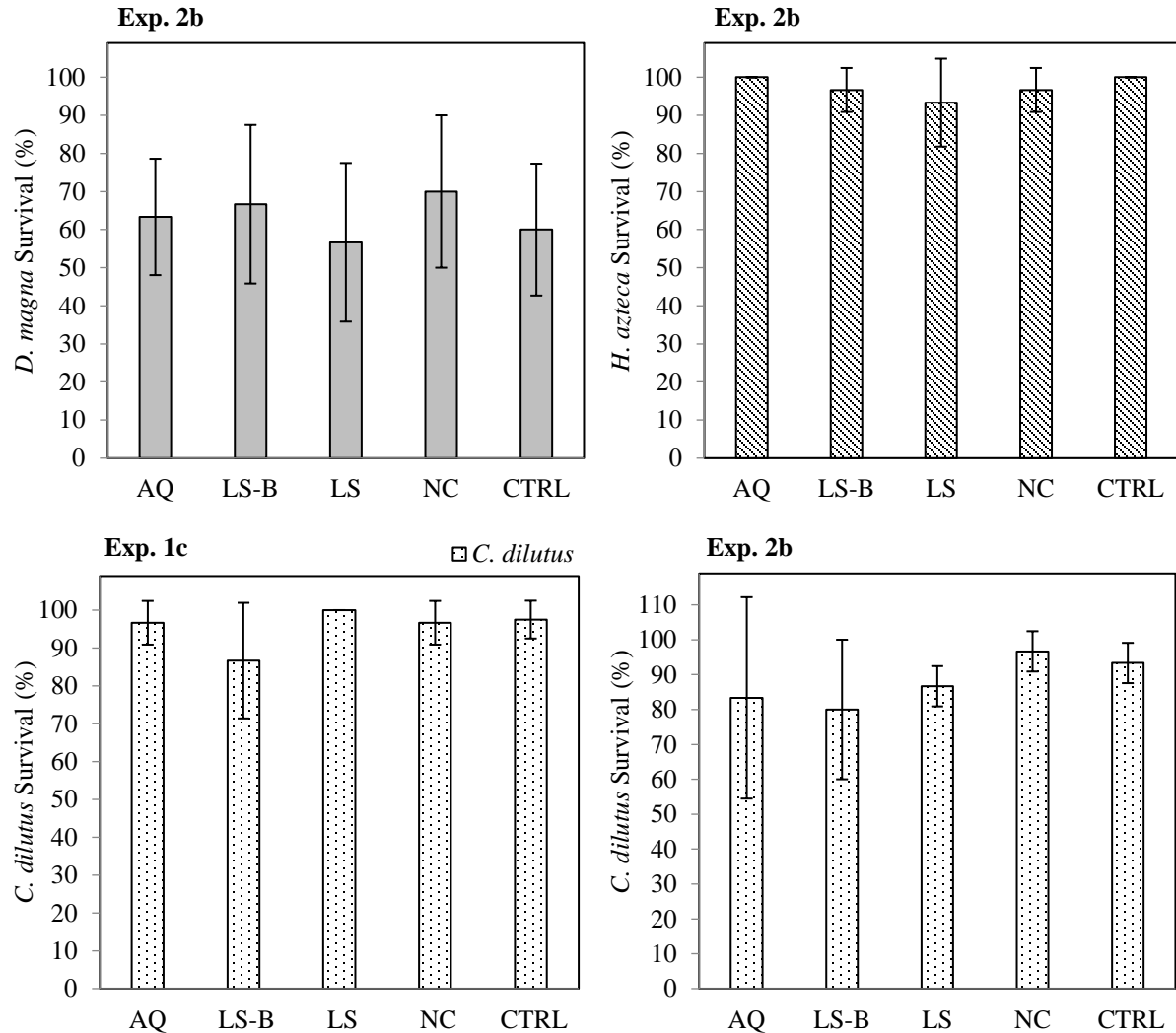


Figure 8: Ex-situ field experiments organism survival (\pm standard deviation). The same control is used for both sediment and water exposures. Statistical significance is denoted as difference from control with an asterisk. Lower *D. magna* survival in experiment 1c limestone compared to controls. Lower *H. azteca* survival in 2a across all treatments compared to controls.

For the post-exposure chronic toxicity test (experiment 2a) there were no differences between non-capped and capped treatments. Overall, the survival for *D. magna* one-week post-exposure was high (~80%). Reproduction was high showing no short-term chronic toxicity. On the other hand, *H. azteca* survival was low in both the non-capped and capped treatments ($p < 0.06$) (Figure 9).

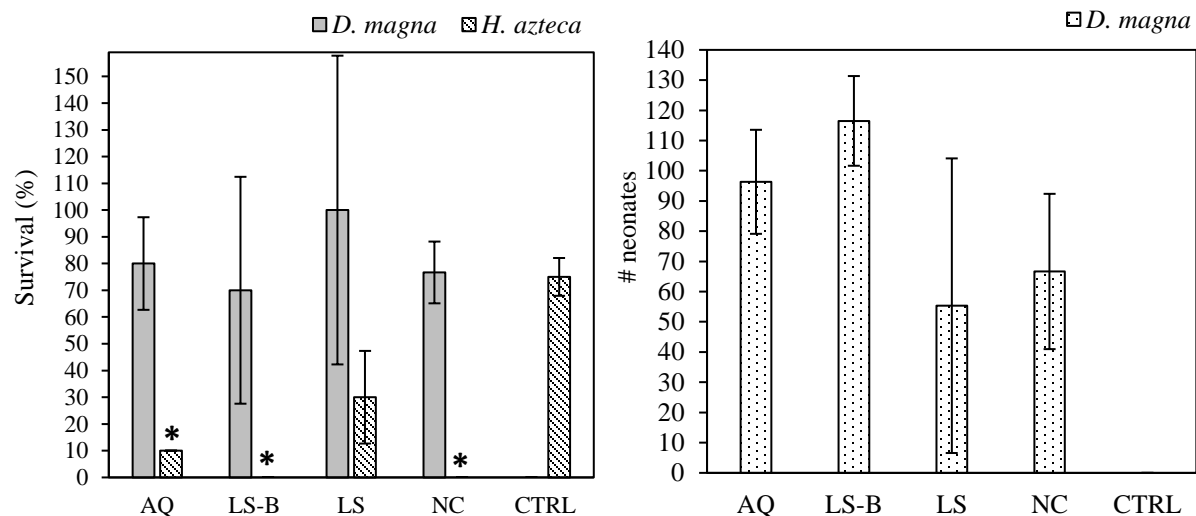


Figure 9: Experiment 2a post exposure *D. magna* and *H. azteca* survival (left) and *D. magna* reproduction (right) (\pm standard deviation). The same control is used for both sediment and water exposures. Statistical significance is denoted as difference from control with an asterisk.

3.2 Laboratory investigation

3.2.1 Water quality

Over the course of the laboratory tests, dissolved oxygen averaged $5.33 \text{ mg/l} \pm 0.71$, temperature ranged from $18.4\text{-}22.6^\circ\text{C}$ and averaged $21.1 \pm 0.8^\circ\text{C}$, and pH averaged 7.53 ± 0.45 units. Significantly higher pH was observed in the zeolite treatment compared to the other treatments ($p < 0.001$), while dissolved oxygen levels and temperature were similar across all treatments ($p > 0.14$) (Table A-6).

3.2.2 Sediment [SEM-AVS]

Due to the small volume of sediment collected in micro-cores, only one sample per treatment pre- and post-test was available to analyze. As a result, statistical differences could not be determined for [SEM-AVS]. However, it is important to note all sediments had a positive average [SEM-AVS] when normalized to organic carbon (USEPA 2005), indicating the potential for Zn toxicity (Figure 10), with an observed increased toxicity potential in the Aquablok, limestone, and zeolite treatments, and a decreased potential in apatite and the non-capped treatment.

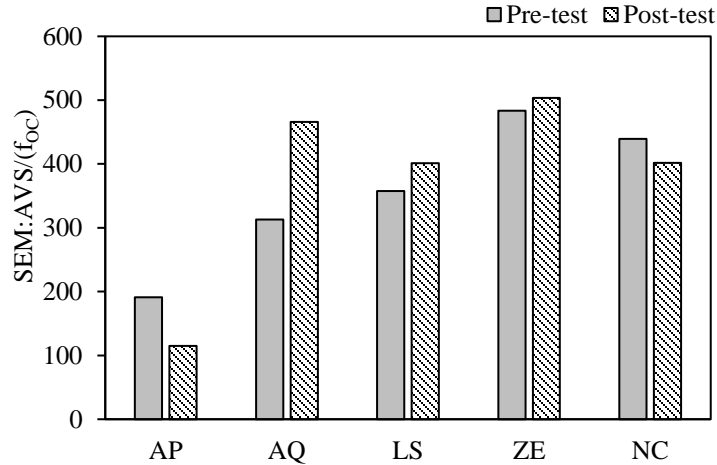


Figure 10: SEM-AVS normalized to organic carbon content (f_{oc}) for sediment samples collected before and after the laboratory test. All treatments exhibited a positive SEM-AVS ratio, indicating potential Zn toxicity. Treatments have been denoted as follows: AP = Apatite, AQ = Aquablok, LS = Limestone, ZE = Zeolite, and NC = no cap.

3.2.3 Surface water zinc

There were statistically lower concentrations of dissolved Zn in the surface water of the zeolite treatment compared to the other capped treatments and non-capped treatment ($p < 0.01$) (Figures 11 and B-11; Table A-7). Particulate Zn concentrations were similar across capped and non-capped treatments ($p > 0.25$) (Figures 11 and B-11; Table A-7).

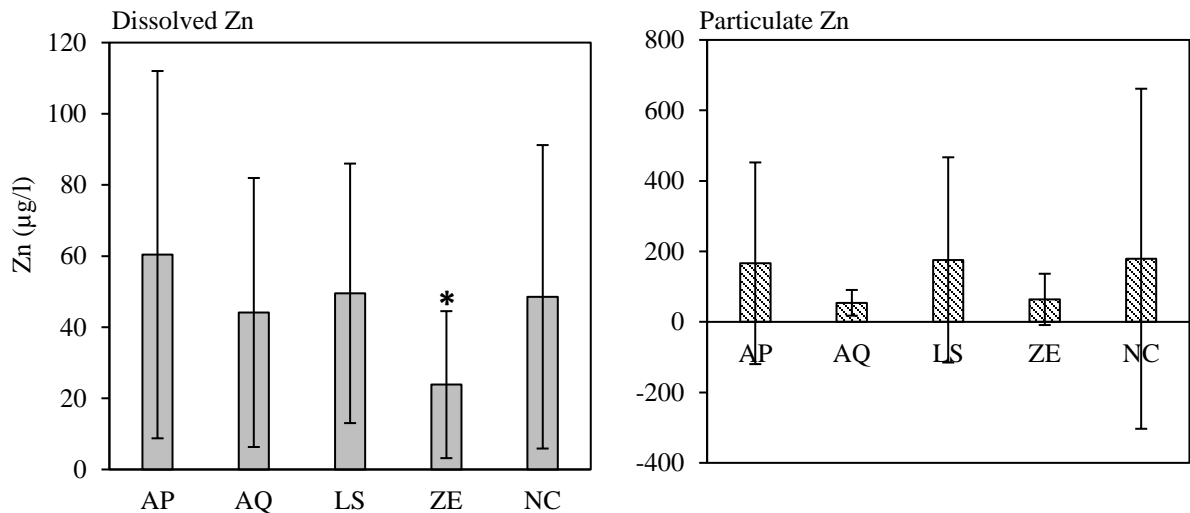


Figure 11: Laboratory experiment surface water dissolved and particulate Zn concentrations (\pm standard deviation). Statistical significance is denoted as difference between treatments with an asterisk. Zeolite exhibited lowest dissolved zinc concentrations compared to all other treatments.

3.2.4 Porewater zinc

In the capping layer, there were lower concentrations of dissolved porewater Zn in the zeolite treatment compared to Aquablok, limestone, and non-capped treatments ($p < 0.04$) (Figure 12). In the mixed cap-sediment layer, there were lower concentrations of dissolved porewater Zn in apatite compared to the non-capped treatment ($p < 0.04$). In the sediment layer, there were lower concentrations of dissolved porewater Zn in zeolite compared to apatite and Aquablok treatments ($p < 0.02$); and, sediment underlying the limestone had lower concentrations of dissolved porewater Zn compared to Aquablok ($p < 0.05$) (Table A-8, Figure B-12).

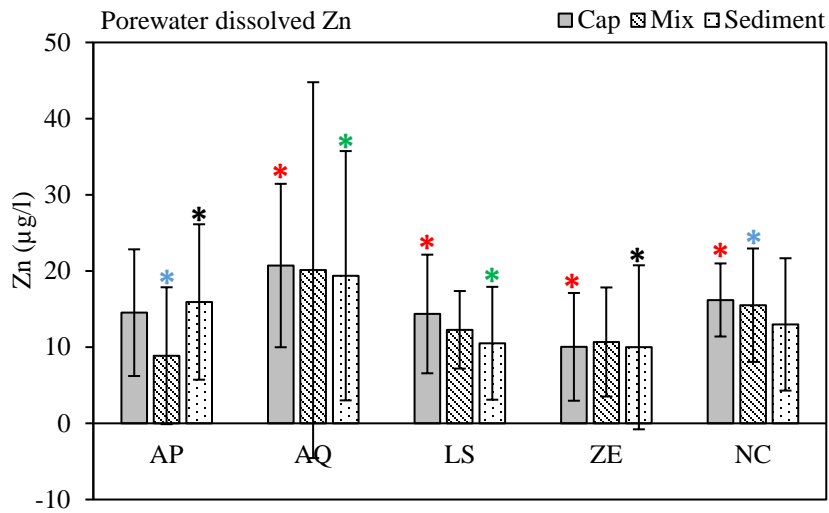


Figure 12: Laboratory experiment porewater dissolved Zn concentrations (\pm standard deviation). Statistical significance is denoted as difference between treatments with corresponding colored asterisks. Differences detected across multiple layers across all treatments.

3.2.5 Survival

Overall, there were no survival differences between the non-capped and capped treatments (Figure 13), apart from *H. azteca* having lower survival in zeolite treatment compared to the non-capped treatment ($p < 0.02$). *D. magna* survival in both the capped and non-capped treatments was below controls ($p < 0.0001$), with lowest survival in the non-capped and zeolite treatments ($p < 0.05$).

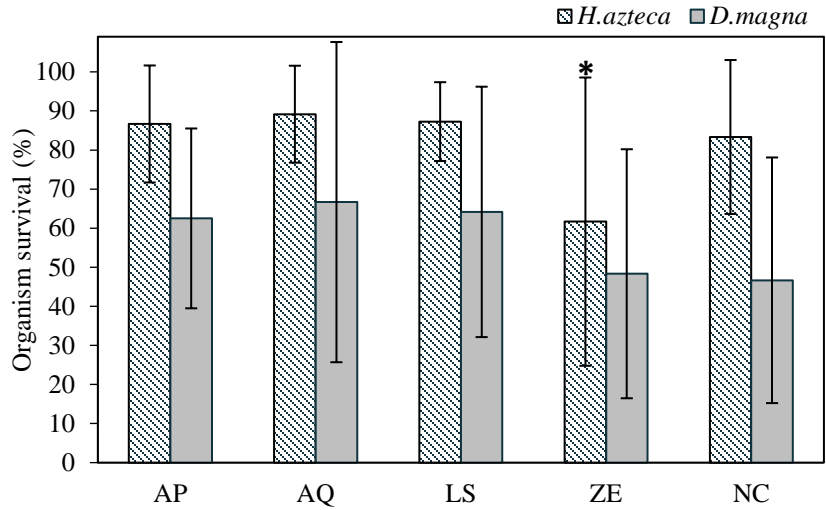


Figure 13: Laboratory experiment test organism survival (\pm standard deviation). Statistical significance is denoted as difference from the non-capped treatment with an asterisk. *H. azteca* had lowest survival in zeolite treatment compared to other treatments.

3.2.6 *D. magna* reproduction

There were no neonates observed over the course of the laboratory test.

3.2.7 *H. azteca* individual growth rate

Overall, *H. azteca* IGR was similar between capped and non-capped treatments ($p > 0.86$, Figure 14), although all capped treatments had higher IGR compared to the EWP water-only control ($p < 0.05$). Note the large variances prevented any detection of significance.

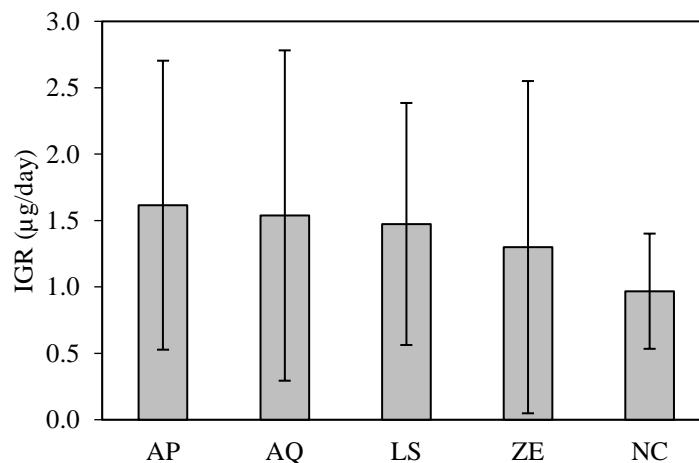


Figure 14: Laboratory experiment *H. azteca* IGR (\pm standard deviation). IGR in all treatments were similar.

3.2.8 *H. azteca* tissue metal residue

H. azteca tissue Zn residue was similar between treatments ($p = 0.28$, Figure 15). Note the large variances prevented any detection of significance.

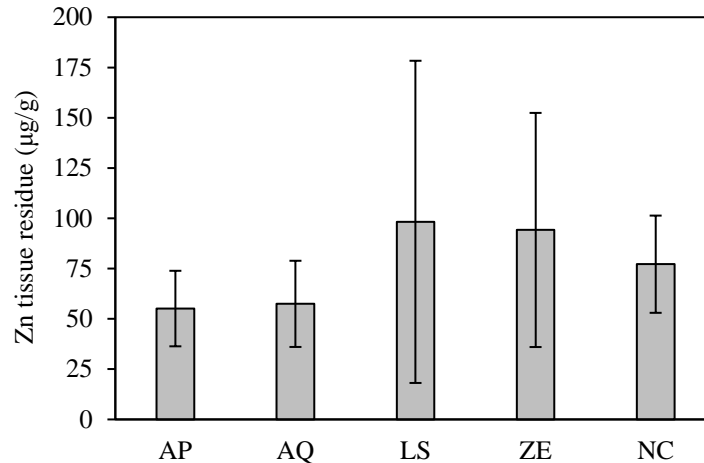


Figure 15: Laboratory experiment *H. azteca* tissue Zn residue (\pm standard deviation). Zn tissue residue in all treatments were similar.

3.2.9 Relationship between biological endpoints and surface water zinc and pH

D. magna and *H. azteca* survival were not correlated with the core mesocosm surface water dissolved Zn concentrations ($p > 0.12$ and $p > 0.06$, respectively). *H. azteca* growth and Zn tissue metal residue was not associated with surface water dissolved Zn concentrations ($p > 0.3$ and 0.2 , respectively). Although further statistical testing suggested a slight negative correlation between pH and survival, it was not significant ($p > 0.20$).

4. Discussion

4.1 Field investigation

Overall, the only observed differences in in-situ survivals were between the culture water control and deployed organisms. This could be due to non-lethal levels of dissolved Zn in the bottom depths of the test plots, where organisms were deployed. Zn concentrations across all treatments and experiments averaged $143 \pm 86 \mu\text{g/l}$ (Table A-4), which is below the hardness-adjusted USEPA threshold for acute toxicity to freshwater organisms ($164 \mu\text{g/l}$; USEPA 2016a). Out of the three capped plots, it appears Aquablok performed most similar to control

survival, apart from *D. magna* in 1b. This lower survival is likely a result of the extended exposure period of 96 hours (not a standard protocol) as opposed to 48 hours. These organisms were not fed and likely suffered from starvation.

Similar to the in-situ toxicity tests, few adverse biological effects were observed in the ex-situ and chronic field studies. An exception was low survival in the experiment 1c limestone core, where there was an accumulation of sediment and iron oxide particulates on top of the cap, which increased suspended solids when organisms were initially added. Turbidity has been linked to adverse effects on motility, fecundity, growth, and survival (Chen *et al.* 2012, Robinson *et al.* 2010).

During experiments 1a-1c, both dissolved and particulate Zn had a common trend across treatments. Higher Zn occurred at the bottom of the hypolimnion, gradually decreasing near the epilimnion (Figure 6). This shift in Zn distribution is further substantiated by the time series plots, in which both dissolved and particulate Zn follow a stratified distribution during 1a-1c (Figure B-9). This stratification starts to become less apparent during experiment 2a, and almost disappears in experiment 2b (Figure B-10). This Zn response is likely due to the destratification occurring between Task 1 and 2. EWP was thermally stratified during the Task 1 experiments, resulting in a predictable lateral distribution of Zn. During experiment 2a, EWP started to mix, then became more uniform in temperature in the top 15-m by experiment 2b (Table A-3). At this point, Zn levels no longer followed the same predictable distribution. This is consistent with other studies showing lake turnover and related changes in metal concentrations (Cover and Wilhm 1982). The timing of the turnover event is consistent with previous site investigations, which have noted EWP (and other Arkansas reservoirs) mixing between October and November (CH2M 2016, ADEQ 1999).

Mixing and stratification in EWP is important because it likely alters Zn dilution (i.e., mixing of the entire waterbody) and solubility via shifts in reducing and oxidizing conditions (Mortimer 1942, Geller *et al.* 1998, Cantwell *et al.* 2002, Atkinson *et al.* 2007). Oxygenation of the water column increases the precipitation of manganese and iron oxyhydroxides, both of which are important ligands for Zn (Terzano *et al.* 2007, Sprague 1995). This could explain why there were, on average, significantly lower levels of dissolved Zn in Task 2 versus Task 1. This could also explain why Zn was concentrated in anoxic hypolimnetic waters during the experiments occurring during stratification.

Second, it further demonstrates the suitability of capping as a remediation solution. Seasonal changes in physical lake conditions have implications for metal toxicity to aquatic organisms (Zhuang *et al.* 1994, Cover and Wilhm 1982). This is partially because partitioning of Zn to sediment is dependent on the concentration and speciation of ligands, which is dependent on water column characteristics, such as pH and redox potential (Tessier *et al.* 1989, Calmano *et al.* 1993, Atkinson *et al.* 2007, Huang *et al.* 2017). In order to prevent Zn release, the underlying sediment must be isolated from influences from these overlying physical processes.

In general, organism toxicity appeared to be unaffected by the presence of a cap. This is especially promising given organisms were deployed at the bottom of EWP, where water quality conditions (low dissolved oxygen and pH) favor Zn release, and therefore represent a worst-case exposure scenario. This suggests capping layers are successfully preventing Zn release into the water column. This hypothesis can be tested when Zn water chemistry results are available. Of the three capping materials tested in the field studies, Aquablok appeared to perform most like the control, albeit only marginally.

4.2 Laboratory investigation

Generally, there were no adverse impacts to organism survival, growth, or metal tissue residue levels, nor were there differences between capping treatments, as found in the field studies. One possible explanation for the lack of effects is that surface water dissolved Zn concentrations never exceeded 164 µg/l, the hardness-adjusted USEPA threshold for acute toxicity to freshwater organisms (USEPA 2016a). Additionally, although the model for sediment toxicity (SEM-AVS) predicted a potential for adverse effects to benthic organisms (USEPA 2005), our previous research field studies of benthic colonization suggests chronic toxicity effects are more likely to occur if the (SEM-AVS)/fOC values exceed approximately 583 µmol/g (or a SEM/AVS ratio of 2 to 8) (Burton *et al.* 2005). All test sediments were below these threshold values. Further statistical analysis confirmed survival, growth, and Zn tissue residue were not correlated with surface water dissolved Zn concentrations.

Lower concentrations of dissolved Zn in the surface and porewater indicate that zeolite was the most effective mitigator of Zn release from underlying sediments (Figures 11 and 12). This is not surprising, as zeolites are well-known for their exceptionally high cation exchange

capacity and are consequently widely used as a chelating agent in industrial, wastewater treatment, and agricultural processes (Reyes *et al.* 1997, Babel and Kurniawan 2003, Wang and Peng 2010). Nevertheless, it is a concern that organism survival was lowest in zeolite treatments (Figure 13). This may not be due to zeolite directly, but rather the resulting increase in pH it causes (Table A-6). This pH effect may be diluted in actual field scenarios, due to the water-sediment ratio difference. Both *D. magna* and *H. azteca* are sensitive to sudden changes in pH (Lewis and Weber 1985, France and Stokes 1987, Pilgrim and Burt 1993). Because zeolites are amphoteric in nature, they quickly neutralize solutions when placed in initially acidic or basic surface waters (Barthomeuf 1991, Filippidis *et al.* 1996). Although zeolites may be an effective capping material for the containment of metals, it has yet to be used for sediment remediation; and thus, it has unknown ecological effects.

Over the course of the 28-day study, porewater dissolved Zn was similar across treatments, apart from Aquablok (Figure B-12). Although it followed a similar trend as the other treatments (e.g. it spikes and dips in a manner similar to the other treatments), effects were notably more exaggerated, particularly in the cap and mixed layers. Increased Zn availability in the laboratory mesocosm may result from a lack of sequestering ligands in Aquablok, as compared to the other caps (Aquablok Ltd. 2006, USEPA 2007). This suggests any perturbations to this “impervious” layer, such as currents, upwellings, gas ebullition, and bioturbation (porewater sampling, in the case of the laboratory study) may mobilize porewater Zn. This suggests a potential for reduced long-term containment and effectiveness, as demonstrated by previous studies (Liu *et al.* 2001, Reible *et al.* 2006, Barth *et al.* 2008).

If perturbations are not likely for the Aquablok cap, it appears to be the most promising remedy, albeit only marginally. Out of the four capping materials tested, it performed most similarly to the culture water control in terms of *H. azteca* survival – although the difference is only slightly higher than apatite and limestone and is not statistically significant. This is consistent with the results from the field studies, where Aquablok also performed most similarly to the control, apart from experiment 1b *D. magna*.

Further studies are needed to determine if zeolite toxicity would be an issue in-situ. If so, then limestone and apatite are good choices, as the two materials also performed similarly with good *H. azteca* survival and bottom perturbations of the cap are less of an issue than for Aquablok. Limestone is desirable because it can enhance cover performance by acting as pH

buffering agent, and thus can maintain interstitial water at a sufficient pH to halt sediment Zn leaching (RowCowdhury *et al.* 2015). Apatite is desirable because it can act as a medium for ion-exchange and adsorption. These materials also have the added benefit of resilience to shifts in physical conditions, such as from seasonal turnover events. Apatite can potentially mitigate the effects of this seasonality, as metal phosphates have low solubility and are stable at a wide range of Eh-pH conditions (Sheddon *et al.* 2006). Additionally, semi-permeable, chemically reactive capping materials have had demonstrated success in reducing contaminant breakthrough over the long-run (Reible *et al.* 2006, USEPA 2016b).

5. Conclusion

In general, there were no differences between capping materials in terms of biological endpoints in both field and laboratory investigations. Aside from the zeolite treatment in the laboratory study, there were no differences between surface water dissolved concentrations between capping materials. Aquablok performed marginally better in terms of biological endpoints in both field and laboratory studies, but porewater Zn data suggest that factors like gas ebullition and groundwater upwelling could compromise cap integrity over time. Zeolite was most successful in mitigating Zn release from the sediment but caused adverse biological effects due to indirect pH effects. Ultimately, final remedy selection will depend on a multitude of other factors, including site conditions and the cost-benefit ratio.

The viability of capping as a remediation option for contaminated sediment is dependent on remedial objectives, contaminant characteristics, appropriate site conditions, compatible current and intended future uses, and ecological function. Ultimately, this research highlights the need for a weight of evidence approach to remedy selection. For instance, without assessing for biological effects, zeolite could have potentially been selected as a remedy option – which could have had unintended adverse ecological impacts. It also adds to the growing knowledge base of capping as a remediation option.

Appendix A

Table A-1: Test capping materials; including amendment type, mechanism for contaminant control, chemical composition, and manufacturer (when known).

Amendment	Mechanism	Composition	Manufacturer
Aquablok ¹	Permeability control	Bentonite clay Polymer composite	Aquablok, Ltd.
Limestone ²	Acid neutralization	Calcium carbonate	
Limestone-bone char ³	Adsorption Acid neutralization Precipitation	Calcium carbonate Bone char (hydroxyapatite, calcium carbonate, calcium sulfate)	
Apatite ⁴	Adsorption Ion exchange Precipitation	Calcium phosphate	Potash Corporation
Zeolite ⁵	Adsorption Ion exchange Acid neutralization	Aluminosilicates	EMD Millipore Corporation

1) Aquablok 2016, 2) RowCowdhury *et al.* 2015, 3) LeGeros 1994, 4) Zhang *et al.* 2016, and 5) Yuna 2016.

Table A-2: Cover placement for field studies; with amendment type, capping layer thickness, total area of cap placement, and total mass.

	Plot 1	Plot 2	Plot 3
Amendment	Aquablok	Limestone-bone char	Limestone
Thickness (in)	3.5	1.65	9.1
Area (ft ²)	800	800	1040
Mass (tons)	12.4	5.25	39.4

Table A-3: Tasks 1 and 2 water quality by depth; including pH, DO, and temperature^{1,2,3}.

Depth (mbs)	pH					Dissolved oxygen (mg/l)					Temperature (°C)				
	Ex. 1a-1c			Ex. 2a-2b		Ex. 1a-1c			Ex. 2a-2b		Ex. 1a-1c			Ex. 2a-2b	
	8/29	9/18	10/10	10/17	10/31	8/29	9/18	10/10	10/17	10/31	8/29	9/18	10/10	10/17	10/31
0.5	7.32	--	7.74	7.55	7.27	8.11	--	9.06	9.15	9.27	27.1	--	23.6	22.1	18.7
1	7.35	7.29	7.76	7.53	7.30	8.12	8.30	9.07	9.13	9.24	27.2	24.8	23.5	22.1	18.7
2	7.44	7.31	--	7.51	--	8.12	8.40	--	9.13	--	27.2	24.6	--	22.0	--
3	7.50	--	7.77	7.48	7.27	8.11	--	9.07	9.12	9.26	27.2	--	23.4	22.0	18.7
4	7.54	7.32	--	7.47	--	8.11	8.46	--	9.11	--	27.2	24.1	--	22.0	--
5	7.55	7.33	7.89	7.46	7.28	8.11	8.45	9.28	9.11	9.25	26.9	23.8	23.1	21.9	18.7
6	7.33	--	--	7.49	--	7.96	--	--	9.09	--	26.1	--	--	21.9	--
7	7.01	7.21	7.74	7.47	7.28	8.06	8.64	9.32	9.08	9.23	22.8	22.8	22.8	21.9	18.7
8	6.72	7.03	7.85	7.49	--	7.92	9.24	9.59	9.07	--	21.5	21	22.2	21.9	
9	6.54	6.75	7.72	7.50	7.27	8.56	9.32	9.70	9.08	9.26	19.9	20.1	22.1	21.8	18.7
10	6.45	--	--	7.49	--	8.67	--	--	9.22	--	18.8	--	--	21.6	--
11	6.35	6.78	7.48	7.41	7.29	8.58	9.68	9.68	9.26	9.26	17.8	18.8	20.6	21.3	18.8
12	6.32	--	7.65	7.23	--	9.36	--	10.00	9.59	--	16.9	--	19.9	20.3	--
13	6.31	6.53	7.98	7.09	--	9.38	9.78	10.42	9.78	--	16.3	17.3	19.3	19.8	--
14	6.30	6.36	7.00	7.07	--	9.77	9.02	9.89	10.01	--	14.8	16.6	18.9	18.8	--
15	6.33	6.87	8.86	8.21	7.29	10.16	10.75	11.33	11.23	9.26	14.4	15.6	17.5	17.3	18.7
16	6.35	6.95	8.81	8.78	7.30	10.28	10.79	11.68	11.61	9.31	14.2	15.4	16.9	17.1	18.7
17	6.32	--	--	8.73	7.34	10.29	--	--	11.63	9.65	14.1	--	--	17.0	18.4
18	--	6.99	8.65	--	7.79	--	10.78	11.66	--	11.48	--	15.3	16.8	--	17.2

19	--	--	--	--	7.97	--	--	--	--	11.44	--	--	--	--	17.1
20	6.32	7.02	8.54	8.66	8.08	10.23	10.76	11.59	11.61	11.57	14	15.2	16.6	16.8	17
22	--	--	--	--	--	--	--	--	--	--	--	15.1	16.5	--	16.8
23	--	7.05	8.49	--	8.09	--	10.76	11.55	--	11.19	13.9	--	--	16.7	--
24	6.32	--	--	8.58		10.02	--	--	11.47	--	13.8	15	16.4	16.6	16.6
25	6.28	7.04	8.44	8.53	8.10	9.99	10.58	11.50	11.41	11.24	--	14.9	--	--	--
26	--	7.04	--	--	--	--	10.47	--	--	--	13.7	--	--	16.5	--
27	6.25	--	--	8.42	--	9.81	--	--	11.29	--	--	--	16.2		16.4
28	--	--	8.28	--	7.94	--	--	11.38	--	10.71	--	14.6	--	--	--
29	--	6.94	--	--	--	--	10.29	--	--	--	13.6	--	--	16.2	--
30	6.23	--	--	8.10	--	9.61	--	--	11.12	--	--	14.4	15.9	--	16.1
31	--	6.70	7.79	--	7.78	--	10.17	11.21	--	10.54	--	14.3	15.7	--	15.9
32	--	6.58	7.64	--	7.68	--	10.04	11.08	--	10.40	13.1	14.2	15.6	15.8	15.6
33	6.19	6.50	7.56	7.77	7.60	8.70	9.96	11.00	10.92	10.11	12.9	13.8	13.2	14.2	14.3
34	6.16	6.33	6.49	7.30	7.45	8.66	9.45	7.13	9.36	8.46	11.5	12	12.1	12.3	12.9
35	6.03	5.81	6.32	6.76	7.19	4.71	2.82	3.81	3.18	3.77	10.5	11.3	--	10.9	11
36	5.93	5.78	--	6.56	7.03	2.56	2.09	--	2.30	1.60	9.9	10.1	10.2	10.5	10.5
37	5.82	5.75	6.22	6.37	6.92	2.20	1.89	2.05	1.91	1.11	9.8	9.8		10.1	10.2
38	5.79	5.72	--	6.16	6.83	1.95	1.69	--	1.50	0.84	--	--	9.8	--	--
39	--	--	6.00	--	--	--	--	1.31	--	--	--	9.7	--	--	--
40	--	5.70	--	--	--	--	1.32	--	--	--	9.7	--	9.7	9.9	9.9
41	5.76	--	5.88	6.02	6.66	1.54	--	1.17	1.25	0.59	--	9.7	9.7	--	
43	--	5.67	5.83	--	--	--	1.15	1.15	--	--	9.6	--	--	9.7	9.9
44	--	--	--	--	--	--	--	--	--	--	9.6	9.7	9.7	9.7	--

45	5.73	--	--	5.94	6.49	1.22	--	--	1.18	0.51	9.7	--	--	9.7	9.9
46	5.71	5.66	5.82	5.90		1.08	0.80	1.13	1.16	--	9.7	9.8	9.7	9.7	9.9
47	5.71	--	--	5.87	6.43	0.80	--	--	1.04	0.31	9.7	9.8	9.8	9.8	--

- 1) Note that water quality data was collected at sampling point EWL-23 along transect EWL-2.
- 2) -- denotes lack of data point
- 3) mbs = meters below water surface
- 4) Blue-shaded cells represent data points of interest.

Table A-4: Tasks 1 + 2 dissolved surface water zinc; including plot name, depth of water sample collection, range and average of dissolved Zn concentrations with standard deviation (SD).

Plot	Depth	Dissolved Zn ($\mu\text{g/l}$)	Average \pm SD ($\mu\text{g/l}$)
Experiments 1a-1c			
Aquablok	Surface	45 - 145	72 \pm 34
	Mid-depth	104 - 320	163 \pm 75
	Bottom	101 - 295	178 \pm 81
Limestone-Bone char	Surface	46 - 443	127 \pm 146
	Mid-depth	59 - 256	128 \pm 55
	Bottom	70 - 379	164 \pm 92
Limestone	Surface	30 - 209	83 \pm 52
	Mid-depth	42 - 188	123 \pm 47
	Bottom	86 - 331	163 \pm 68
No cap	Surface	36 - 195	72 \pm 48
	Mid-depth	115 - 196	158 \pm 24
	Bottom	89 - 370	206 \pm 96
Experiments 2a-2b			
Aquablok	Surface	44 - 55	48 \pm 4
	Mid-depth	41 - 67	52 \pm 11
	Bottom	45 - 92	62 \pm 18
Limestone-Bone Char	Surface	51 - 131	78 \pm 31
	Mid-depth	0 - 104	61 \pm 35
	Bottom	75 - 139	107 \pm 31
Limestone	Surface	37 - 87	53 \pm 18
	Mid-depth	48 - 154	70 \pm 41
	Bottom	49 - 267	95 \pm 86
No cap	Surface	50 - 79	60 \pm 11
	Mid-depth	54 - 86	66 \pm 13
	Bottom	50 - 110	68 \pm 21

Table A-5: Tasks 1 + 2 particulate surface water zinc; Tasks 1 + 2 dissolved surface water zinc; including plot name, depth of water sample collection, range and average particulate Zn concentrations with SD.

Plot	Depth	Particulate Zn (µg/l)	Average ± SD (µg/l)
Experiments 1a-1c			
Aquablok	Surface	44 - 382	105 ± 102
	Mid-depth	95 - 436	207 ± 131
	Bottom	98 - 735	259 ± 237
Limestone-Bone char	Surface	51 - 366	123 ± 93
	Mid-depth	56 - 501	197 ± 152
	Bottom	70 - 1809	424 ± 513
Limestone	Surface	44 - 696	135 ± 199
	Mid-depth	88 - 608	240 ± 167
	Bottom	120 - 951	335 ± 278
No cap	Surface	35 - 187	88 ± 54
	Mid-depth	118 - 340	209 ± 81
	Bottom	95 - 1456	329 ± 411
Experiments 2a-2b			
Aquablok	Surface	46 - 69	55 + 9
	Mid-depth	42 - 59	51 + 7
	Bottom	55 - 102	78 + 19
Limestone-Bone Char	Surface	50 - 282	123 + 87
	Mid-depth	48 - 253	105 + 75
	Bottom	82 - 174	112 + 37
Limestone	Surface	43 - 67	50 + 9
	Mid-depth	48 - 253	111 + 59
	Bottom	48 - 337	106 + 114
No cap	Surface	58 - 128	73 + 27
	Mid-depth	54 - 86	67 + 12
	Bottom	52 - 108	66 + 21

Table A-6: Task 3 water quality; including range and average pH, DO, and temperature with SD.

Treatment	pH	Average \pm SD	Dissolved oxygen (mg/l)	Average \pm SD	Temperature (°C)	Average \pm SD
Exposure #1						
Apatite	7.35 - 8.27	7.72 \pm 0.34	5.19 - 6.95	6.20 \pm 0.52	20.8 - 21.9	21.3 \pm 0.4
Aquablok	6.31 - 8.12	7.63 \pm 0.51	5.42 - 6.85	5.87 \pm 0.44	20.8 - 22.1	21.4 \pm 0.4
Limestone	7.15 - 8.41	7.64 \pm 0.36	5.12 - 6.69	5.88 \pm 0.53	20.6 - 22.2	21.4 \pm 0.5
Zeolite	7.65 - 9.40	8.48 \pm 0.64	5.59 - 6.83	5.96 \pm 0.36	20.4 - 22.0	21.3 \pm 0.6
No cap	7.07 - 7.95	7.66 \pm 0.27	5.80 - 6.94	6.30 \pm 0.37	20.4 - 22.1	21.2 \pm 0.6
Exposure #2						
Apatite	6.89 - 7.73	7.41 \pm 0.32	4.82 - 6.11	5.49 \pm 0.38	20.6 - 21.9	21.2 \pm 0.4
Aquablok	6.90 - 7.92	7.43 \pm 0.32	5.38 - 6.03	5.74 \pm 0.20	20.4 - 22.3	21.3 \pm 0.5
Limestone	6.47 - 7.79	7.31 \pm 0.39	5.19 - 5.80	5.44 \pm 0.18	20.5 - 22.3	21.3 \pm 0.6
Zeolite	7.05 - 9.29	8.08 \pm 0.63	4.77 - 6.22	5.67 \pm 0.40	20.4 - 22.4	21.1 \pm 0.6
No cap	6.91 - 7.85	7.45 \pm 0.31	4.31 - 5.91	5.39 \pm 0.42	20.4 - 22.2	21.2 \pm 0.6
Exposure #3						
Apatite	6.89 - 7.69	7.28 \pm 0.24	3.52 - 5.20	4.50 \pm 0.51	20.1 - 21.9	21.1 \pm 0.6
Aquablok	6.90 - 7.57	7.36 \pm 0.19	3.93 - 5.83	5.06 \pm 0.53	20.0 - 21.8	21.0 \pm 0.6
Limestone	6.47 - 7.69	7.24 \pm 0.34	3.85 - 5.31	4.78 \pm 0.48	20.0 - 22.1	21.1 \pm 0.6
Zeolite	7.05 - 8.02	7.64 \pm 0.25	4.44 - 6.72	5.30 \pm 0.66	20.0 - 22.0	20.9 \pm 0.6
No cap	6.91 - 7.62	7.37 \pm 0.20	4.15 - 5.54	4.77 \pm 0.47	20.2 - 21.8	21.0 \pm 0.6
Exposure #4						
Apatite	6.94-7.69	7.31 \pm 0.20	3.52 - 5.60	4.59 \pm 0.75	18.8 - 22.2	20.8 \pm 1.2
Aquablok	7.00-7.72	7.38 \pm 0.21	3.81 - 5.47	4.79 \pm 0.53	18.6 - 22.3	20.8 \pm 1.2

Limestone	6.98-7.69	7.30 ± 0.17	3.85 - 5.43	4.71 ± 0.50	18.4 - 22.6	20.9 ± 1.4
Zeolite	7.40-8.02	7.67 ± 0.20	4.10 - 5.56	5.06 ± 0.49	18.6 - 22.3	20.6 ± 1.2
No cap	5.80-7.72	7.26 ± 0.48	4.15 - 5.80	5.03 ± 0.58	18.6 - 22.2	20.8 ± 1.2

Table A-7: Task 3 dissolved and particulate surface water zinc; including treatment type, range and average of dissolved and particulate Zn concentrations with SD.

Treatment	Dissolved Zn (µg/l)	Average ± SD (µg/l)	Particulate Zn (µg/l)	Average ± SD (µg/l)
Apatite	0 - 208	60 ± 52	0 - 1344	166 ± 286
Aquablok	0 - 217	44 ± 38	0 - 217	54 ± 37
Limestone	0 - 183	50 ± 36	0 - 1217	176 ± 291
Zeolite	0 - 78	24 ± 21	0 - 364	64 ± 73
No cap	0 - 205	49 ± 43	0 - 2949	179 ± 482

Table A-8: Task 3 dissolved porewater zinc; including treatment type, layer of water sample collection, range and average of dissolved Zn concentrations with SD.

Treatment	Layer	Dissolved Zn (µg/l)	Average ± SD (µg/l)
Apatite	Cap	0 - 33	15 ± 8
	Mix	0 - 25	9 ± 9
	Sediment	0 - 37	16 ± 10
Aquablok	Cap	0 - 46	21 ± 11
	Mix	0 - 82	20 ± 25
	Sediment	0 - 70	19 ± 16
Limestone	Cap	0 - 31	14 ± 8
	Mix	0 - 21	12 ± 5
	Sediment	0 - 23	11 ± 7
Zeolite	Cap	0 - 23	10 ± 7
	Mix	0 - 25	11 ± 7
	Sediment	0 - 51	10 ± 11
No cap	1 cm	8 - 28	16 ± 5
	2 cm	0 - 41	16 ± 7
	3 cm	0 - 29	13 ± 9

Appendix B

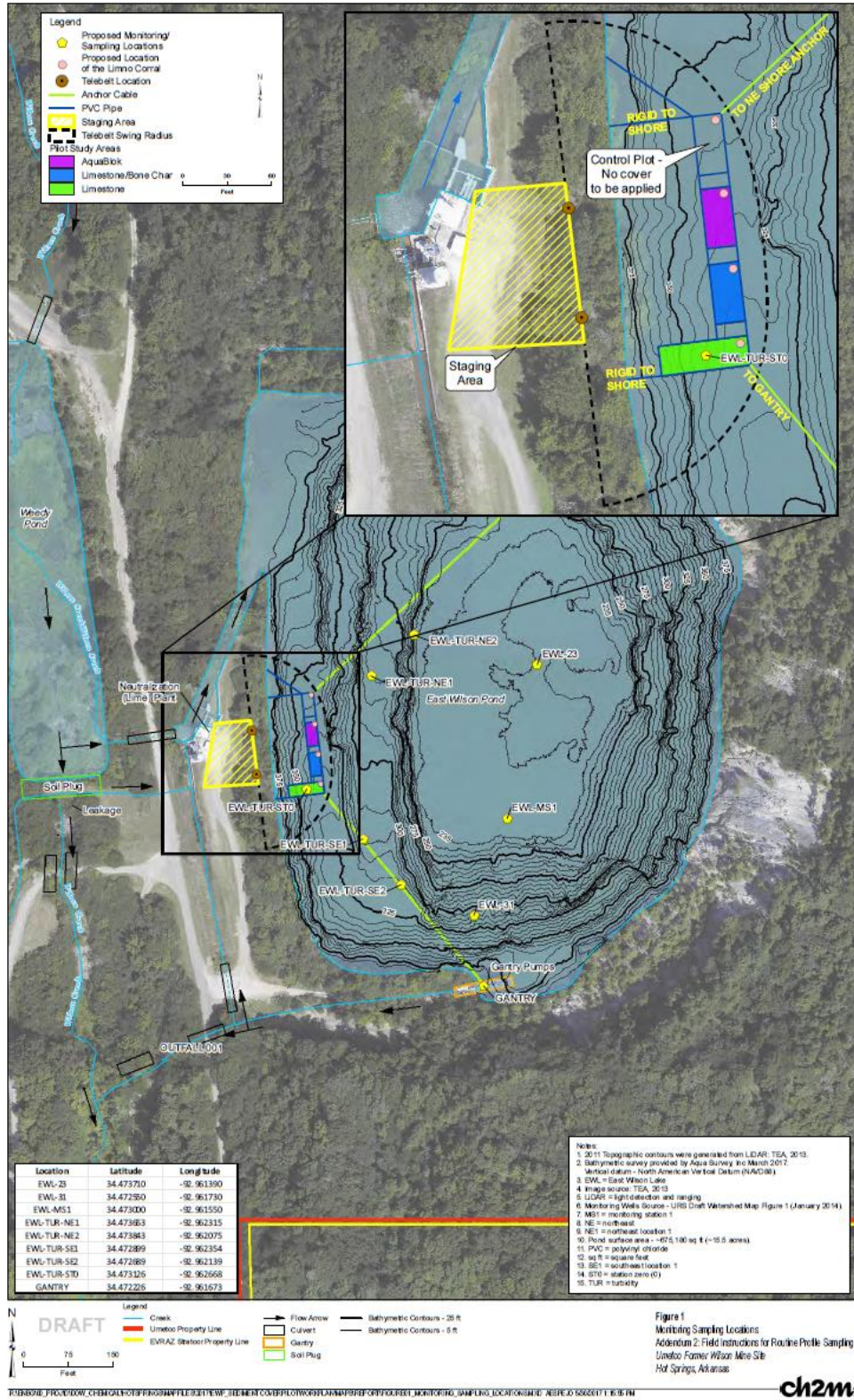


Figure B-1: Test plots location within EWP (CH2M 2017a).

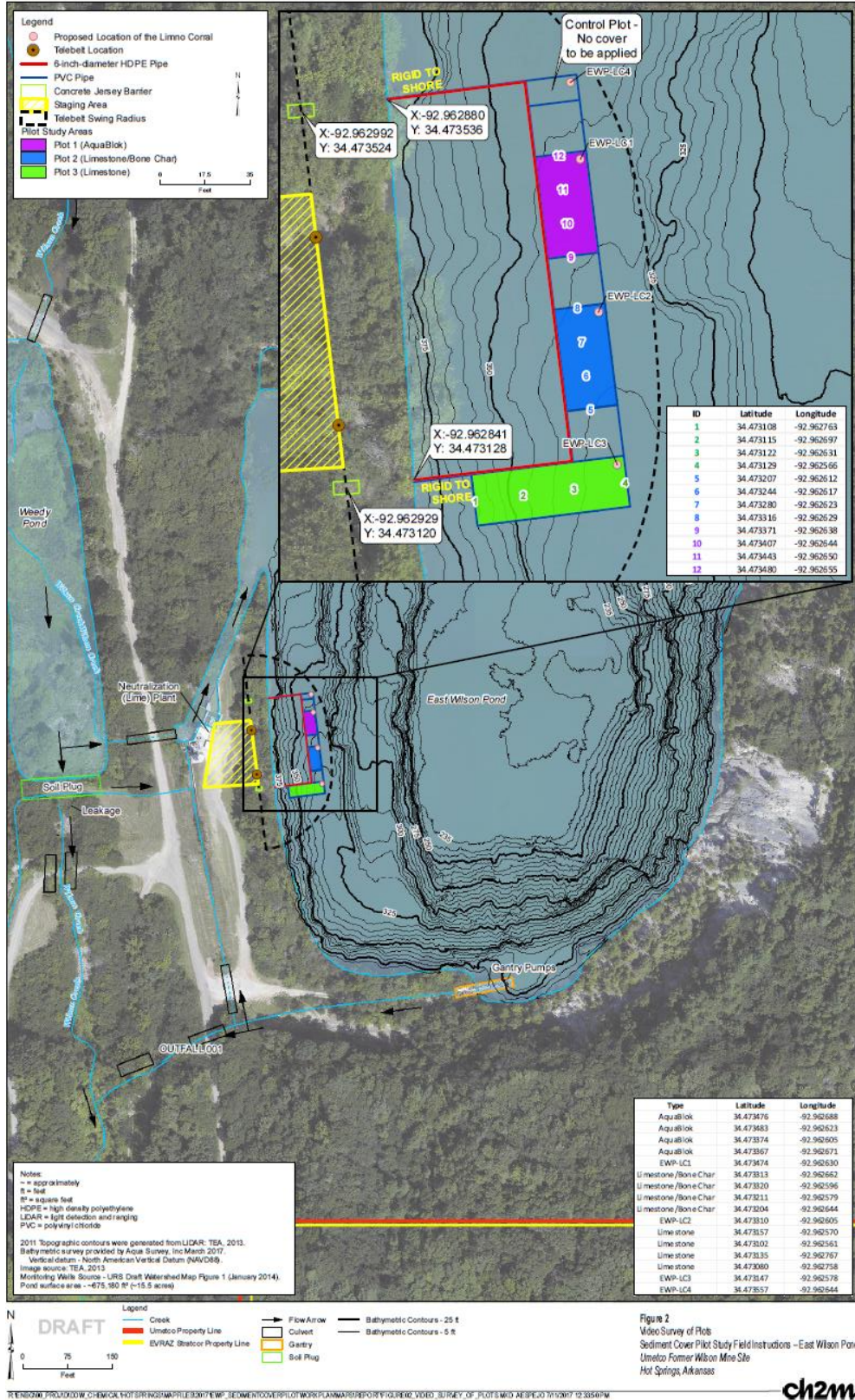


Figure B-2: Limnocorral placement within test plots (CH2M 2017b). From top to bottom: non-capped (control), AquaBlok, limestone-bone char, and limestone.



Figure B-3: Limnocorral placement within each test plot. From left to right: non-capped (control), Aquablok, limestone-bone char, and limestone.



Figure B-4: Limnocorral with lake divider curtains. Poly-pipe rings in belt loop pockets with anchoring skirt provide stability and reduce leakage (Curry Industries 2016).

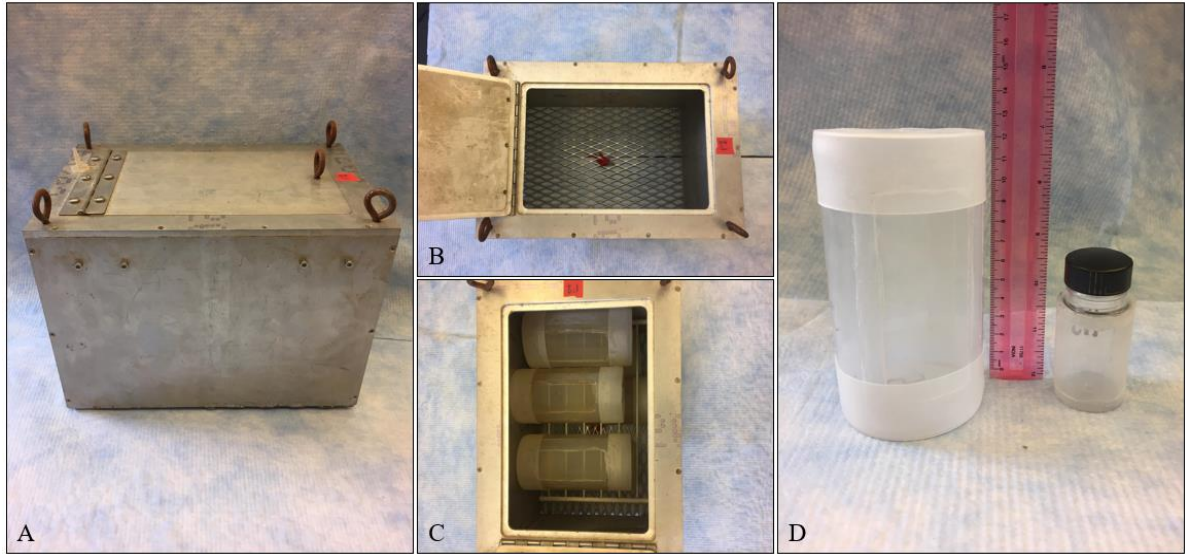


Figure B-5: TACS setup and organism chambers, where A) TACS, B) Open TACS with bottom grate depicted, C) Open TACS with organism chambers, and D) Larger organism chamber (240-ml volume) used in field studies (left) and smaller chamber (40-ml volume) used for ex-situ field and lab studies (right), with a ruler to scale.

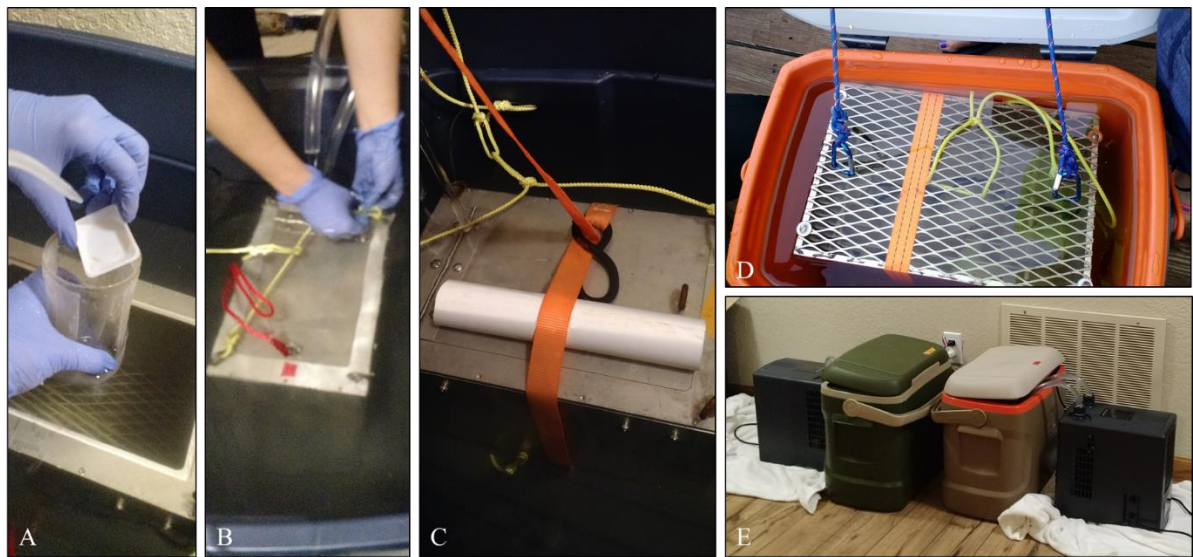


Figure B-6: Pre-deployment preparation process depicted chronologically, where A) Organism addition, B) Attaching the flip rope, C) Securing the PVC pipe with a ratchet strap, D) Attaching the lowering rope, and E) Cooler setup with corresponding chillers.

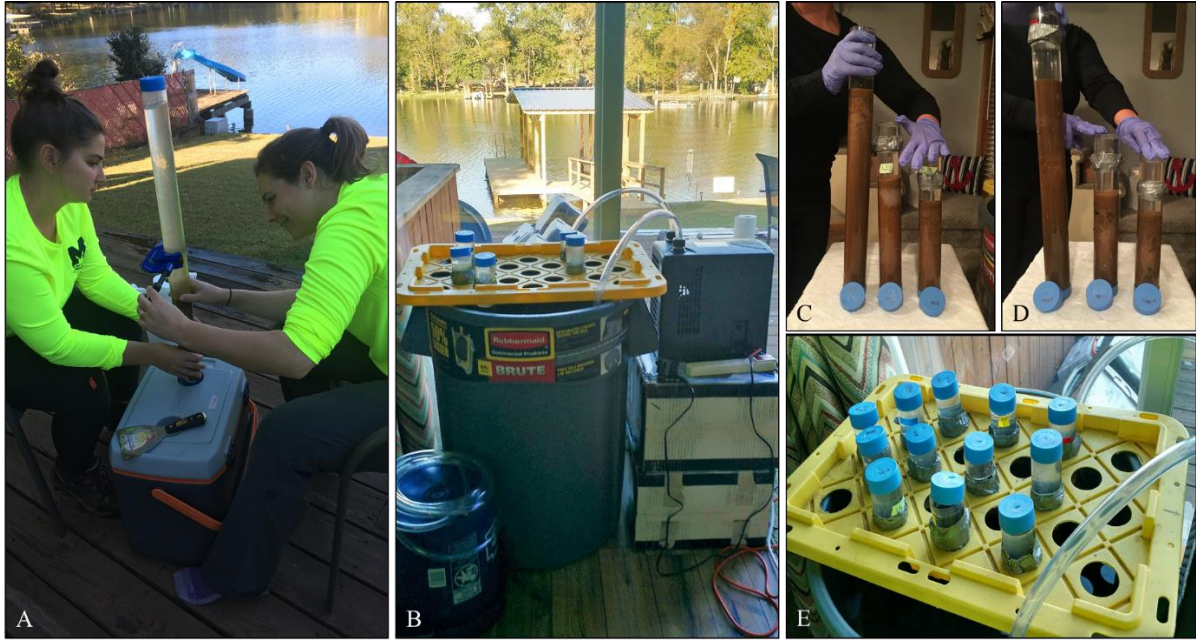
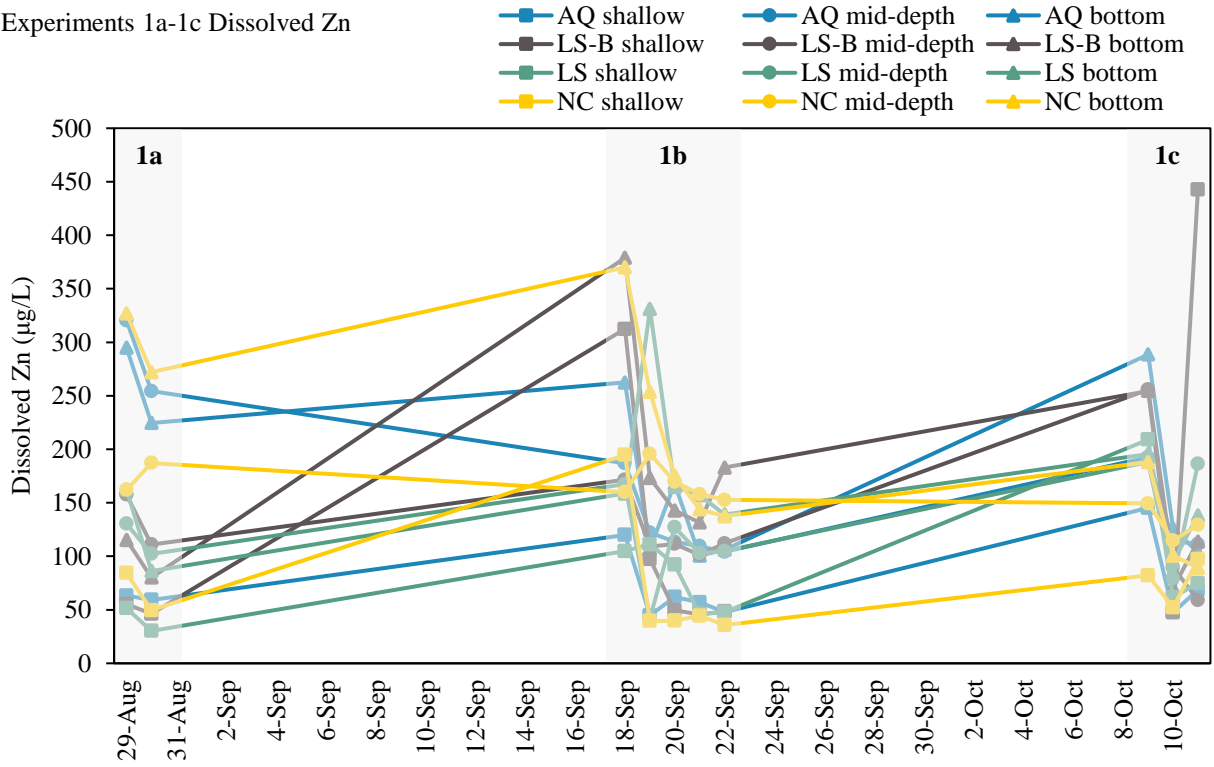


Figure B-7: Ex-situ tests complementing experiment 2a field study, where A) Core processing, B) Ex-situ test setup, C/D) Processed cores, and E) Closer up of ex-situ test setup.



Figure B-8: Task 3 laboratory study setup where A) Overall setup, B) Aquablok treatment, C) Non-capped treatment, and D) EWP and IEW controls.

Experiments 1a-1c Dissolved Zn



Experiments 1a-1c Particulate Zn

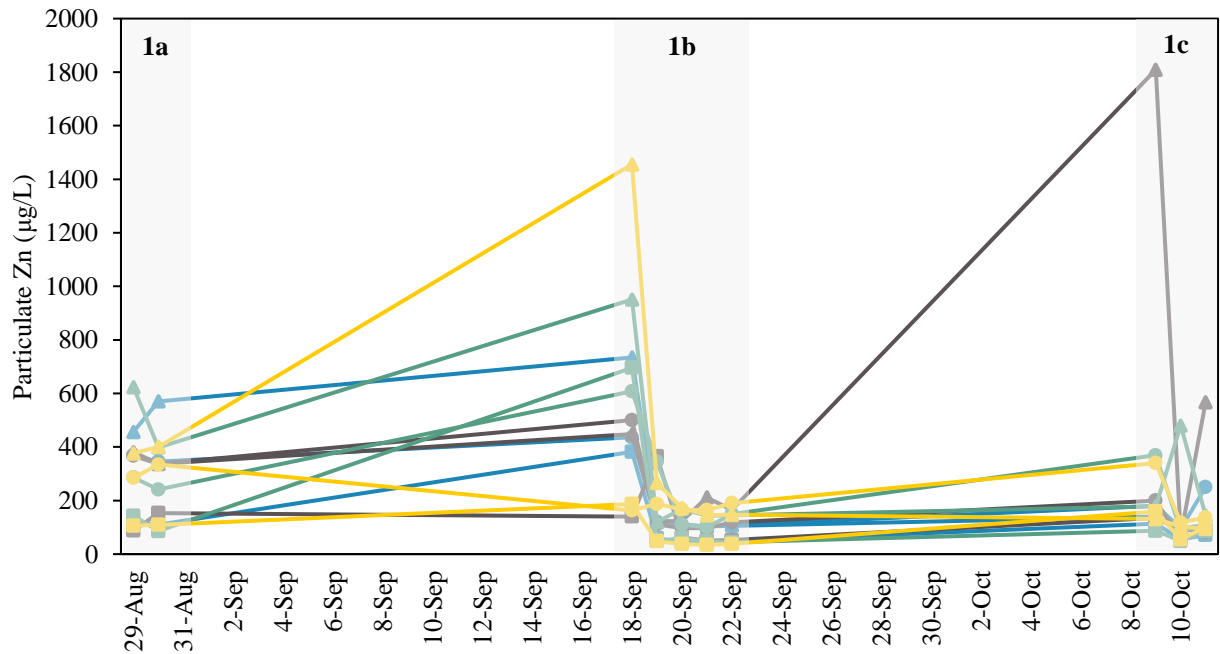
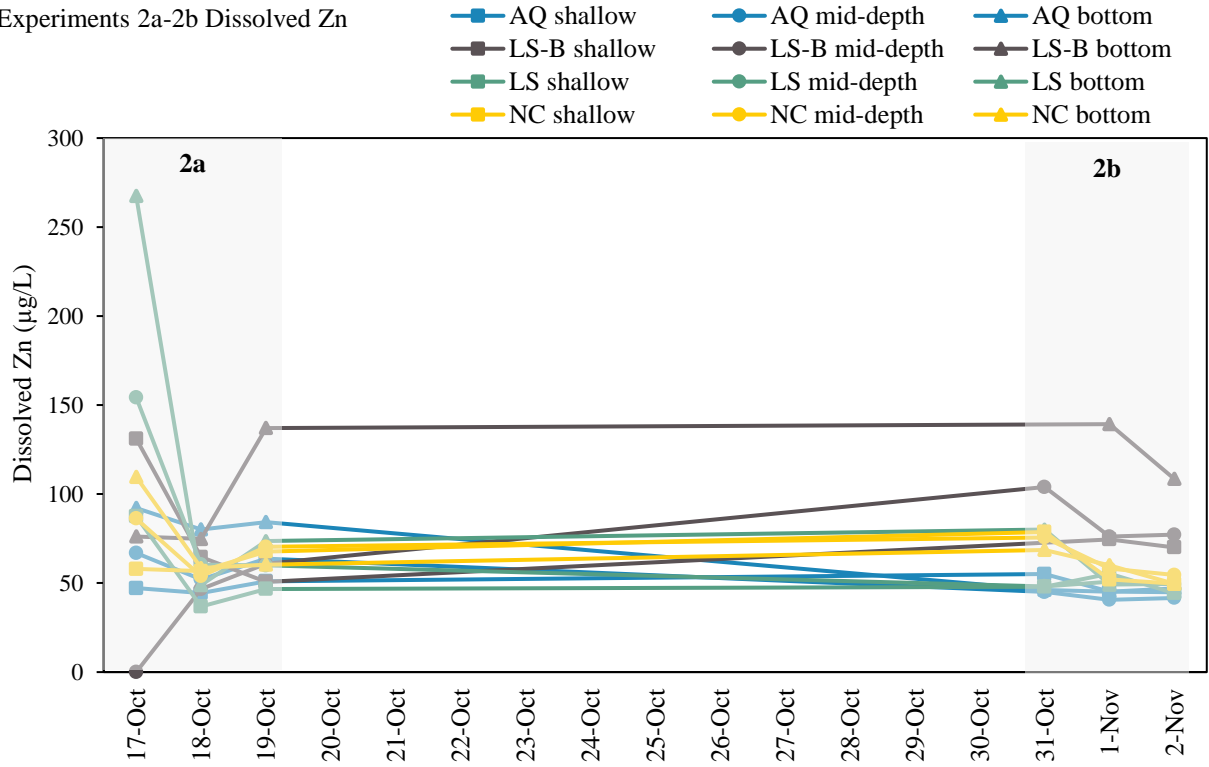


Figure B-9: Surface water dissolved and particulate Zn concentrations for field experiments 1a-1c over time. Each experiment is denoted with experiment name and grey shaded boxes.

Experiments 2a-2b Dissolved Zn



Experiments 2a-2b Particulate Zn

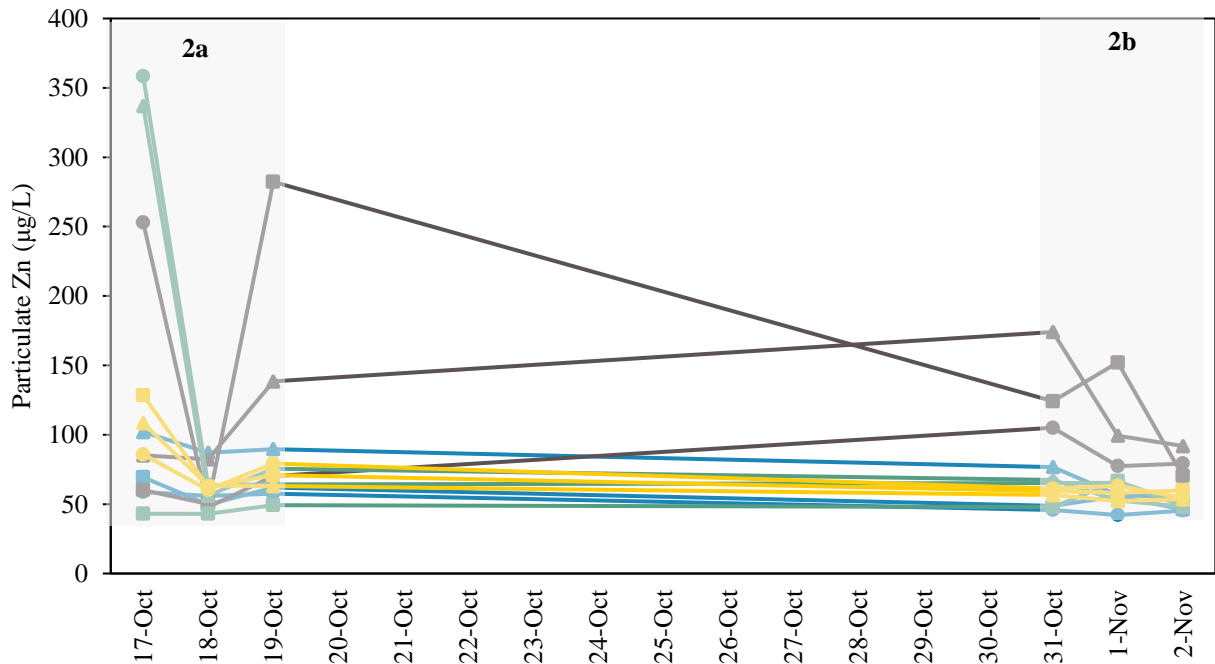


Figure B-10: Surface water dissolved and particulate Zn concentrations for field experiments 2a-2b over time. Each experiment is denoted with experiment name and grey shaded boxes.

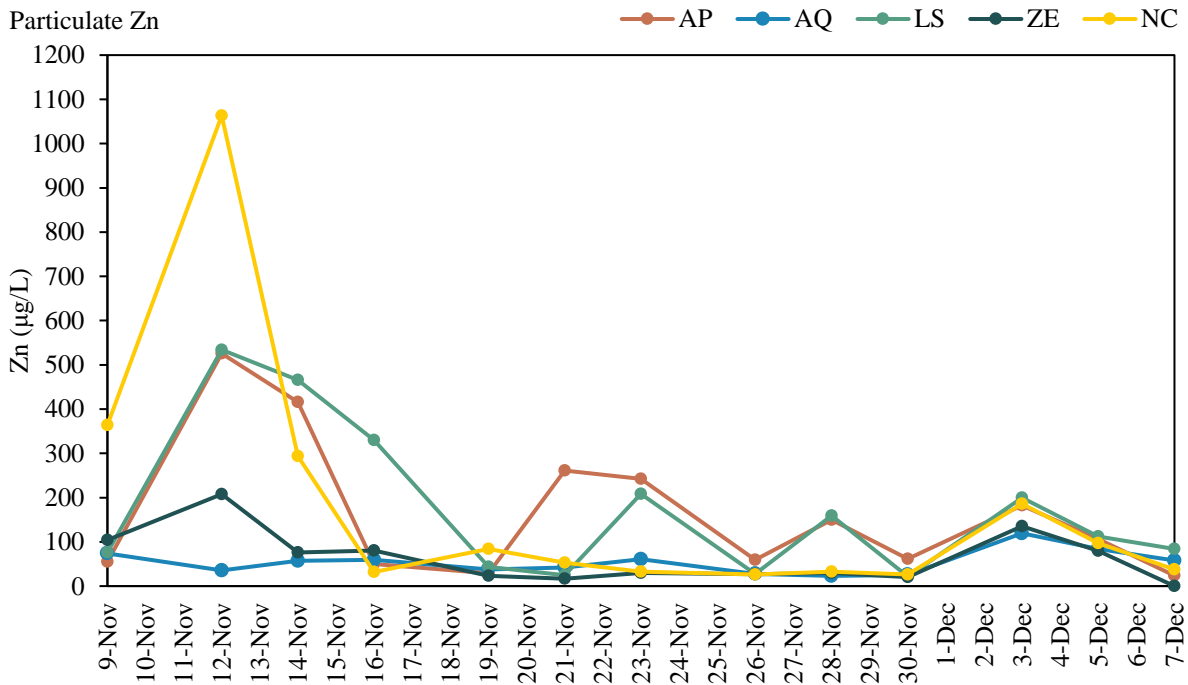
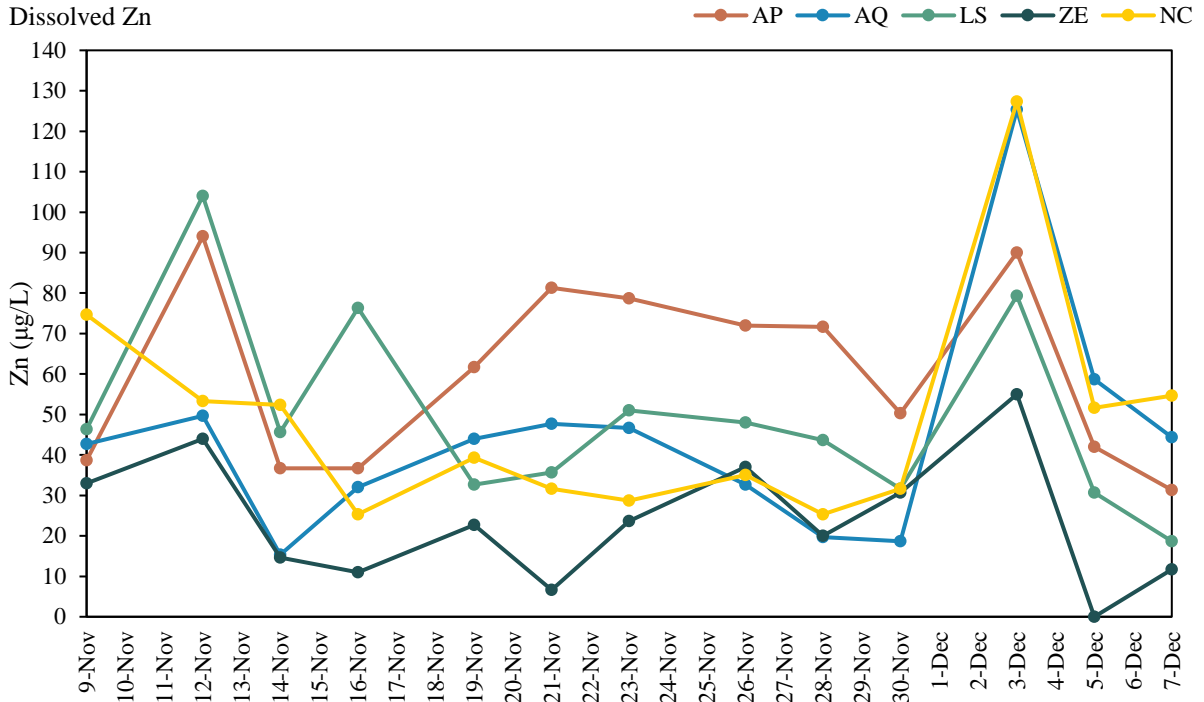


Figure B-11: Surface water dissolved and particulate Zn concentrations over 28-day laboratory study.

Dissolved Zn

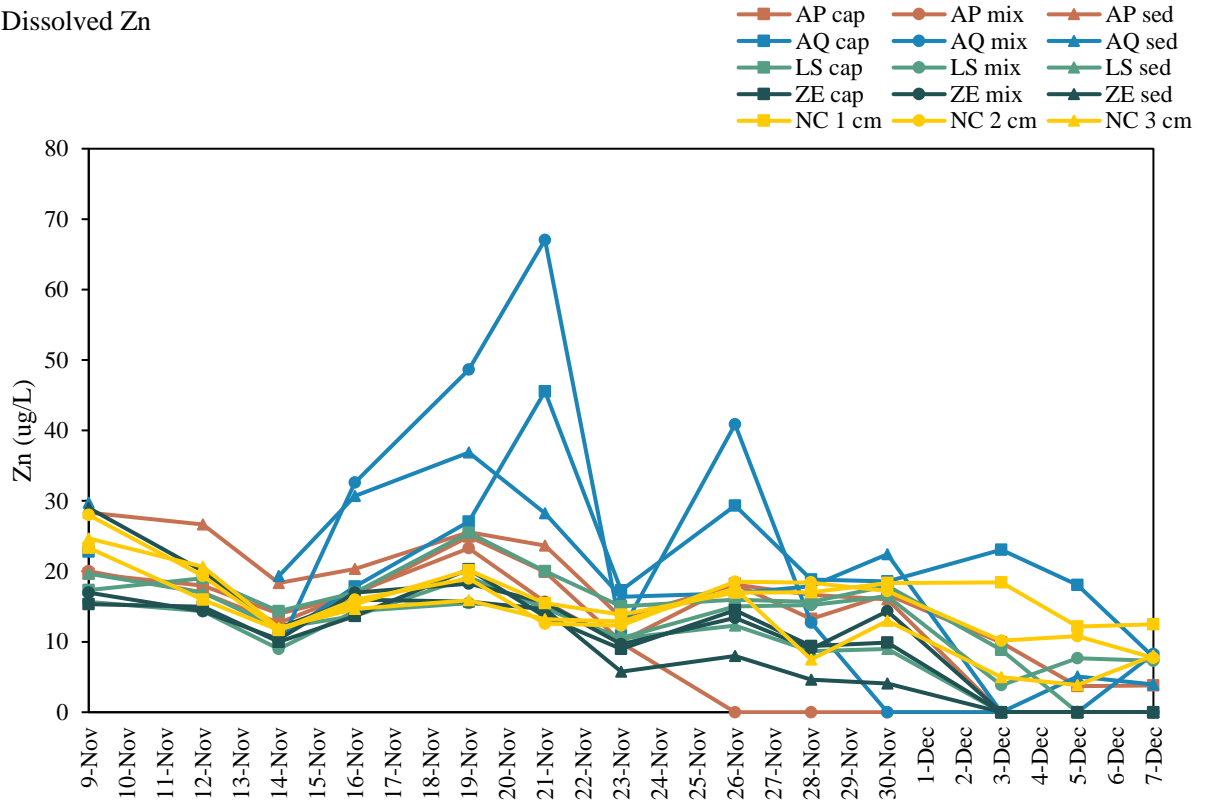


Figure B-12: Porewater dissolved Zn concentrations over 28-day laboratory study.

Appendix C

EWP Study Timeline

July 12-14: Sediment cover installation

July 17-18: Limnocorral installation

August 28-30: Experiment 1a

September 18-22: Experiment 1b

October 9-11: Experiment 1c

October 17-19: Experiment 2a

October 31: Sediment coring for laboratory study

October 31-November 1: Experiment 2b

November 9-16: Task 3 Exposure 1

November 16-23: Task 3 Exposure 2

November 23-30: Task 3 Exposure 3

November 30-December 7: Exposure 4

Literature Cited

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