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Laboratory and field-based assessment of the effects of sediment capping materials on zinc flux, bioavailability, and toxicity

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Abstract: A former mining site has been the subject of extensive remediation and restoration, with a significant focus on disconnecting mine spoils from groundwater and managing the quantity and quality of runoff. A remaining task is ensuring concentrations of zinc (Zn) in the stream outflow of a pit lake are reduced below water quality standards. The efficacy of multiple capping materials for decreasing Zn dissolution from sediments was conducted under natural and reasonable worst-case conditions (pH = 5.5). Capping materials included AquaBlok™, limestone, and limestone + bone char. Field exposures were conducted in limnocorrals which isolated overlying water columns above the sediment and capping treatments. Simultaneous *in-situ* and *ex-situ* toxicity tests were conducted using *Daphnia magna*, *Hyalella azteca*, and *Chironomus dilutus*. *In-situ* caged organisms were protected from temperature shock (warm epilimnetic waters) by deploying within a Toxicity Assessment Container System (TACS). Organisms were exposed to surficial sediments, caps and hypolimnetic overlying waters for 4 days. *Ex-situ* testing was conducted in core tube mesocosms containing sediments and caps at similar temperatures (15 - 19 $^{\circ}$C). Results demonstrated the usefulness of TACS deployment in stratified lake systems. There were no differences in responses between treatments involving sediment capping materials in both *in-situ* and *ex-situ* tests. The lack of differences was likely due dissolved Zn in surface water being below the hardness-adjusted threshold effects levels (164 μg L^{-1}). This field and lab-based weight-of-evidence study provided site-specific data to support the selection of an effective remedy, with reduced uncertainty compared to laboratory and chemistry-only approaches.

Keywords: Sediment remediation; Sediment restoration; Capping effectiveness; *In-situ* remediation; Zinc aquatic toxicity.

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INTRODUCTION

Bedded contaminated sediments are recognized as sinks for toxic and bioaccumulative substances (USEPA 2013) and can be reservoirs for chemicals that may be transferred to benthic organisms (Burton 1992). Current remediation options for contaminated sediments include no action, monitored natural recovery, institutional controls (i.e. land use restrictions), *in-situ* and *ex-situ* treatment, and removal (dredging and disposal) (Libralato et al. 2018). Remedial decisions for contaminated sediments should be made based on ecological and human health risks (USEPA 2002) and, as discussed in the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA or Superfund) and National Contingency Plan (NCP), with consideration to cost-effectiveness (USEPA 2005). Although the aforementioned approaches will continue to be an integral part of sediment cleanup remedies, new remediation technologies are needed to supplement or provide alternatives to existing methods (Patmont et al. 2014). Capping is one of the most commonly used alternatives for *in-situ* remediation of contaminated sediments. This involves leaving the contaminated sediment in place and covering it in order to isolate it from overlying waters and benthic organisms, thus reducing pollutant bioavailability and the potential for resuspension into the water column (USEPA 2013). Capping is distinguished from *in-situ* treatment (i.e., with activated carbon) which reduces contaminant bioavailability (and risk) through sorptive or other chemical processes.

Demonstrating risk reduction that is convincing to stakeholders using isolation capping approaches has been somewhat challenging (NRC 2007; Bridges et al. 2010). Although capping has shown promise in bench-scale studies, there is a need for more field-based pilot studies that incorporate multiple lines-of-evidence, coupled laboratory and field experiments, and the use of test organisms to increase confidence that exposure pathways have been eliminated (Ghosh et al. 2011).

A former mining site near Hot Springs, Arkansas (USA) has undergone extensive reclamation over several years, with significant focus on preventing mine spoils from leaching into groundwater and managing the quantity and quality of runoff. While site improvements were indeed highly successful, a remaining task was to evaluate remedial options to ensure that concentrations of Zn in a 16-acre pit lake, which drains into a stream, were reduced below water quality standards at the point of discharge. Prior to the experiments described in this study, Zn concentrations in pit lake sediments were 143 to 417 mg kg^{-1} and dissolved Zn concentrations in hypolimnetic water ranged from 4.85 to 160 μg L^{-1} (CH2M 2016). Initial laboratory experiments were conducted, and geochemical models were developed to evaluate potential benefits of various capping materials on Zn flux. Here we report results from field-based pilot studies and *in-situ* and *ex-situ* toxicity tests which were completed to directly assess the effectiveness of capping materials for reducing Zn flux, bioavailability, and toxicity.

MATERIAL AND METHODS

Study design

The study design consisted of three experiments with the first two taking place in the field and the third taking place in the laboratory (Table 1). The first experiment involved *in-situ* toxicity testing to evaluate the effectiveness of capping treatments at reducing bioavailability of Zn in pit lake sediments under ambient lake (AL) conditions where the pH of hypolimnetic waters was ~7.0. Specifically, *in-situ* acute toxicity tests were conducted using benthic (*Hyalella azteca* and *Chironomus dilutus*) and pelagic (*Daphnia magna*) macroinvertebrates, and associated water quality parameters were measured.

The second experiment employed *in-situ* testing to assess the effects of changes in overlying water pH on Zn flux from the sediments under reasonable worst-case conditions (RWC) where hypolimnetic waters were maintained at pH 5.5. Simultaneous with *in-situ* testing, *ex-situ* acute and short-term chronic toxicity tests were conducted in a field-based laboratory located close to the study site. *Ex-situ* testing included two assays

designed to assess Zn toxicity in water-only exposures, and a third test to evaluate organism (*D. magna* and *H. azteca*) response to a pH-adjusted water and sediment exposure using sediment cores collected from the pit lake.

The third experiment complemented field investigations with a detailed 28-day laboratory study examining the efficacy of various sediment capping treatments at decreasing Zn bioavailability. Sediment cores and waters collected from the pit lake were shipped back to the University of Michigan, and 7-day short-term chronic laboratory toxicity tests were done with *Daphnia magna* and *Hyalella azteca*.

Sediment capping treatment plots

An initial series of laboratory studies were conducted to establish alternatives for sediment capping with different pH buffering, Zn-adsorptive media. This involved a series of bench-scale physical and settling studies (jar tests), isotherm analyses, geochemical modelling, and a literature review (unpublished data). Based on preliminary results, three sediment capping treatment plots (Aquablok™, limestone, and limestone-bone char mix) were installed in the pit lake using a truck-mounted telescopic belt conveyor. A fourth test plot remained untreated as a non-capped reference (i.e., native pit lake sediments). The surface area of each cover plot was approximately 75 - 95 m^2 (approximately 0.3% of the total water surface area), with each plot positioned in water depths of approximately 12 to 18 meters below the surface (Supplemental Data, Figure S1).

Field-based ambient lake conditions

Limnocorrals (LC, Curry Industries™) were secured on top of each of the sediment capping treatments plots (Aquablok™, limestone, limestone-bone char, and non-capped sediment). Each LC was suspended from a floating collar attached to a cylindrical curtain (90 cm i.d.) made of clear high-density polyethylene that extended 12 - 18 meters to the bottom of the pit lake.

Within the LCs, *in-situ* acute toxicity tests were conducted to evaluate the effects of sediment cap materials on Zn flux and bioavailability (Table 1). *In-situ* tests were conducted using *Daphnia magna* (4 d old), *Hyalella azteca (*8 d old*),* and *Chironomus dilutus* (second larval instar) which were shipped from Aquatic Biosystems® (Colorado, USA). Test organisms were slowly acclimated overnight to site water at hypolimnetic temperatures. On the morning of deployment, 10 individuals of each species were added to exposure cages in triplicate, as described in Burton et al. (2005). A chiller was used to ensure test organisms were maintained at site temperatures throughout the deployment process.

Triplicate cages were secured to a plastic covered rack to allow for exposures to surficial sediments through a nylon mesh (pore size of 250 nm), and triplicate cages were also placed on top of the rack for exposure to near bottom waters only. The rack of cages was then placed into a Toxicity Assessment Container System (TACS) (Figure 1). The TACS were fabricated from aluminum, with the bottom covered with grated stainless steel to allow depositional sediment to contact the organism cages. The TACS were deployed inverted to allow the acclimated cold deployment water to safely pass through the warm epilimnion, thereby preventing temperature shock to the organisms. Once it passed into the hypolimnion the TACS was inverted to allow for sediment contact (Supplemental Data, Figure S2).

Field-based reasonable worst-case scenario

Reasonable worst-case conditions were created to match lowest pH conditions (pH 5.5) observed during late summer in the hypolimnion. To simulate RWC conditions, a 30% hydrochloric acid (HCl) solution was used for acidification with 10% sodium hydroxide (NaOH) solution to buffer any pH overshoot. Acid was pumped into the bottom of each LC through tygon tubing attached to a peristaltic pump, and mixing was facilitated by deploying a second tube with an air stone attached to an air compressor. The pH and dissolved oxygen (DO) of hypolimnetic water in LCs were monitored approximately 0.25 m above the bottom, and acid addition/mixing was considered complete after pH was stablized at 0.25 - 1 m above the sediment surface.

Water samples were collected within the LC by using tygon tubing (1/8" i.d.) secured at three depths: surface (8 cm), mid-depth, and near bottom (approximately 30 cm above lake bottom). Water samples were also collected external to the LC for comparison.

Field-based ex-situ testing

The *ex-situ* water-only exposures (experiments AL_3 and RWC_2) were conducted using near bottom water (approximately 30 cm above lake bottom) collected from each LC using a Van Dorn sampler. Water was placed into a container and transported to the field laboratory for *ex-situ* toxicity tests. Within the container, ten individuals of *Daphnia magna* (4 d old), *Hyalella azteca (*8 d old*)*, and *Chironomus dilutus* (second larval instar) were added to exposure cages in triplicate. A chiller was used to ensure test organisms were acclimated to *in-situ* hypolimnetic temperatures (Supplemental Data, Figure S3).

Organisms from water-only exposures were retrieved following the *in-situ* TACS procedures to determine survival. Surviving *H. azteca* were placed into 100 mL of 50 µM ethylenediaminetetraacetic acid (EDTA) to depurate overnight, then subsequently dried and placed into centrifuge tubes for tissue Zn residue analysis. Two 10 mL water samples were collected from each exposure container using pre-rinsed syringes and analyzed for dissolved and particulate Zn.

For experiment RWC_1, *ex-situ* toxicity tests were conducted in sediment-water microcosms. Microcosms were acrylic core tubes (5 cm in diameter x 90 cm long) collected in triplicate from each test plot outside of and adjacent to the respective LCs. Surface sediments were collected, capped, and maintained in a vertical position to minimize resuspension, then transported to the field laboratory for *ex-situ* toxicity tests. *Ex-situ* tests were initiated within 24 h of core collection.

Microcosms were placed into a container with water chilled to hypolimnetic temperature and the overlying water was pH-adjusted as it was for *in-situ* tests. Again, the acid addition process was considered complete when the pH was stabilized at approximately 5.5. At this point, 10 *H. azteca* caged in small exposure cages (see Figure

1E) and 10 non-caged *D. magna* and 10 *C. dilutus* were added to each of the cores. After 48 h, organisms in each core were retrieved in polypropylene trays 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 µM EDTA solution with Tetramin® to depurate overnight, then subsequently dried and placed into centrifuge tubes for tissue Zn residue analysis.

Laboratory microcosm testing

Laboratory investigations involved a series of 7-day short-term chronic toxicity tests and water chemistry characterizations conducted over four consecutive weeks in sediment-water microcosms (Figure 2). Surface sediments were collected from the northern end of the pit lake, away from the sediment capping pilot plots. These sediments were added to each of 15 microcosms (acrylic core tubes 5 cm in diameter x 50 cm long). The core tubes were cut at the sediment line (no overlying water) with a pipe cutter, capped, and secured with duct tape to minimize vertical gradient alterations. All cores were tightly packed into a cooler for overnight shipment to the University of Michigan laboratory. Cores were placed at 4 °C upon receipt.

In the laboratory, each core tube was cut so that there was approximately 35 cm of sediment in each microcosm. Then, the bottom was capped and secured with electrical tape, and the microcosm was placed upright in a plastic holder. Approximately 200 mL of overlying pit lake water was added immediately to minimize surficial sediment oxygenation. Resuspended sediment particles were allowed to settle and about 10 cm of each capping material was added to the cores. In addition to Aquablok™ and limestone

which were used in the pit lake sediment capping field pilot study, apatite and zeolite were also tested as potential capping materials, and the limestone-bone char material was not used in the laboratory studies (i.e., 4 treatments + a non-capped control). 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).

Within each microcosm, Rhizon® samplers were inserted at three locations: within the capping layer (~1.5 cm below the cap-water interface), at the interface of the capping layer and pit lake sediment (mixing layer), and within the pit lake sediment layer (~1.5 cm below the cap-pit lake sediment interface). Rhizon® samplers allow for the collection of overlying water and sediment porewater, drawing it through a 0.22 μm built-in filter and immediately into a BD vacutainer®. For the non-capped (i.e., control) microcosms, Rhizons® were inserted at 1, 2, and 3 cm below the sediment surface (Supplemental Data, Figure S4).

Surface water samples were collected from microcosms using pre-rinsed syringes and analyzed for dissolved and particulate Zn. All surface water samples collected for dissolved Zn analysis were syringe-filtered with a 0.45 μm Isopore™ polycarbonate membrane filter (EMD Millipore Corporation, MA, USA). After all water samples were collected (at days 1, 4, and 6), the remaining surface water in each core was siphoned until about 3 cm above the sediment or capping layer. Fresh pit lake water was carefully added back into each microcosm. 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.

Dissolved oxygen, temperature, and pH were measured in surface and porewater three times a week prior to overlying water exchanges. Sediment/porewater and overlying water toxicity were assessed with *H. azteca* (10 individuals, 8 d old) and *D. magna* (10 individuals, 4 d old), respectively. *H. azteca* were caged in small exposure cages and non-

caged *D. magna* were added to the overlying water of each of the microcosms. *D. magna* were fed Sel-Cero three times during the exposure. At the end of the 7-day exposure period, *D. magna* were assessed for survival.

Sediment/porewater toxicity tests with the amphipod *H. azteca* were conducted to assess possible effects on survival and growth, and to determine Zn body concentration (Borgmann and Norwood 1995). Exposure cages were placed vertically with a 250 nm mesh opening ~0.5 cm deep into sediment. This method exposes *H. azteca* to surficial sediments while enabling organism recovery. *H. azteca* were not fed to promote sediment grazing. After the 7-d exposure period, organisms were counted, depurated, weighed, and digested.

A 24 h depuration in 50 mM EDTA solution adequately removed undigested gut material so metal content reflected true tissue concentrations (Neumann et al. 1999). Organisms were desiccated for several days and weighed for growth. Ten sets of representative groups (8 - 10 organisms each) were collected from stock cultures to estimate initial mass. Individual growth rate (IGR) was calculated according to Nedrich and Burton Jr. (2017) as follows:

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

where mass is in µg, *n* is the number of organisms per replicate, and time is days.

Body tissue was digested with trace metal grade HNO_3 and measured on an ICP-MS for Zn (Norwood et al. 2006). Final body concentration (BC_{Zn}) was calculated by subtracting sediment exposed organism tissue concentrations by culture water exposed control organisms (i.e. BC_{SED} e BC_{CNTL}).

Quality assurance/quality control (QA/QC)

Analytical data quality was guaranteed through the implementation of laboratory QA/QC protocols, including the use of standard curves, reagent blanks, percent

recoveries and analysis of triplicates. All reagents used were analytical grade (certified purity >99.9%). All plastic and glassware used during the experiments were new or soaked in 12% (v/v) hydrochloric acid for at least 24 h followed by two rinses with deionized water (prepared using a Milli-Q 18 mΩ cm).

To confirm the viability of organisms used in the laboratory toxicity tests, laboratory controls were set up and maintained for the duration of each test. Low-metal reference sediment was collected from River Raisin in Manchester, Michigan, USA and used as a sediment control for toxicity tests. Controls consisted of three sets of 10 *D. magna* and three sets of *10 H. azteca* in 200 mL of pit lake water, plus three sets of 10 *D. magna* and 10 *H. azteca* in 200 mL of ion-enriched water (IEW). *D. magna* controls were fed Sel-Cero at the same intervals as the test organisms. *H. azteca* were not fed, but instead provided with approximately 5 grams of River Raisin sediment at the beginning of each 7 days test to graze on.

Statistical analysis

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. All tests for significant differences were at $p < 0.05$. The Kruskal-Wallis test was used for multivariate comparisons of non-parametric variables. When warranted, the Post-hoc 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 variance (ANOVA) was 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 ambient lake and reasonable worst-case conditions.

RESULTS

Field-based investigation

Water temperature profiles indicated stratification within the pit lake, with lower temperatures in the hypolimnion (17.3 + 1.73 $^{\circ}$C) and progressively higher temperatures in the epilimnion (23.3 + 2.98 $^{\circ}$C). Lower pH was observed in the hypolimnion (7.09 + 0.81 at depth of 12 – 18 meters) and pH gradually increased in the epilimnion (7.46 + 0.17). Dissolved oxygen ranged from 8.79 + 0.48 mg L^{-1} in the epilimnion to 10.06 + 0.71 mg L^{-1} in the hypolimnion.

Dissolved and particulate Zn concentrations measured in the LCs during *in-situ* experiments are shown in Figure 3. Under ambient lake (AL) conditions, dissolved and particulate Zn concentrations were consistently higher near the bottom (150 – 200 μg L^{-1} for dissolved Zn and 250 – 375 μg L^{-1} for particulate Zn) compared to mid-depth and near the surface. However, Zn concentrations were variable, and these differences were not statistically significant. Under reasonable worst-case conditions (pH = 5.5), differences in Zn concentrations based on depth were not observed.

In-situ acute toxicity tests (Figure 4) showed variable responses which impeded detection of treatment differences in survival of *D. magna* and *C. dilutus*. Toxicity was not observed in any of the capped sediments compared to non-capped LC, indicating that none of the capping materials appeared to cause toxicity. Also, results from the first round of toxicity tests with *D. magna* conducted under ambient lake conditions (AL_1) indicated that all of the sediment capping treatments reduced toxicity vs. the non-capped control, indicating that some form of sediment cap is beneficial. Observed low survival in the experiments with limestone in AL_3 appeared to result from substantial accumulation of sediment and iron oxide particulates on top of the cap, which increased suspended solids when the cages were deployed. This iron oxide accumulation was due to pit lake bank sloughing onto the treatment plot after the sediment cap material was added. Poor survival which was observed in tests associated with AL_2 is believed to have resulted from the attempt to extend the test duration/exposure time from 48 to 96 h.

Field-based ex-situ testing

Results from *ex-situ* acute toxicity testing showed that, with two exceptions, there were no treatment-based (i.e., capped vs. non-capped) differences in test organism survival (Supplemental Data, Figure S5). In AL_3, *D. magna* survival was significantly lower, and low survival was also observed in *H. azteca* in RWC_1 for non-capped and capped treatments compared to laboratory control ($p < 0.02$).

For the post-exposure chronic toxicity test (RWC_1) there were no differences in test organism performance between the capped treatments and non-capped control. Survival of *D. magna* one-week post-exposure was high (~80%) and reproduction was also high showing no chronic toxicity (Supplemental Data, Figure S6). On the other hand, *H. azteca* survival in the post-exposure chronic toxicity test was low in both the non-capped and capped treatments.

Laboratory investigation

For the laboratory tests in sediment microcosms, temperature ranged from 18.4 - 22.6 °C (average 21.1 + 0.8 °C), pH averaged 7.53 + 0.45, and DO averaged 5.33 + 0.71 mg L^{-1}. DO and temperature were similar across treatments. Not surprisingly, significantly higher pH was observed in the overlying water in the zeolite treatment compared to other treatments ($p < 0.001$).

Dissolved Zn concentrations in the overlying water of laboratory microcosms ranged from 25 to 60 μg L^{-1} (Figure 5). Dissolved Zn concentrations in the overlying water of microcosms treated with zeolite were lower than levels in other treatments and the non-capped control ($p < 0.01$).

Over the course of the 28-day laboratory study, with one exception, dissolved Zn concentrations in porewater remained relatively low (< 30 μg L^{-1}) in both capped and non-capped microcosms (Figure 6). The exception was that microcosms treated with AquaBlok™ exhibited sediment porewater with levels of dissolved Zn that were

somewhat elevated. Only the zeolite treatment exhibited levels of dissolved Zn that were lower than the non-capped control ($p < 0.04$).

There were no significant differences in organism survival between the non-capped control and capped treatments during the 7-d laboratory exposures (Figure 7), apart from the fact that *H. azteca* exhibited lower survival in microcosms containing zeolite compared to the non-capped control ($p < 0.02$).

Results for *Hyalella azteca* individual growth rate (IGR) and Zn tissue concentrations are shown in Figure 8. IGR was highly variable within treatments and, while mean IGRs were higher for capped treatments vs. non-capped controls, no statistically significant differences were observed. Zn tissue concentrations in *H. azteca* were also comparatively similar among treatments.

DISCUSSION

Field investigation

In-situ studies using limnocorrals were started during summer when the pit lake was thermally stratified and initial exposures were done under ambient lake (AL) conditions involving no pH manipulation. These studies showed that dissolved and particulate Zn concentrations were higher near the pit lake bottom (hypolimnion) and declined near the surface. This pattern was evident in both capped and non-capped limnocorrals, and so, at least under ambient conditions, Zn concentrations in the overlying water of limnocorrals treated with capping materials were not different from levels in the non-capped control.

In-situ experiments in limnocorrals simulating reasonable worst-case conditions (RWC) where pH was adjusted to 5.5 began in early Fall at roughly the same time the pit lake started to thermally mix (lake turnover). Under these conditions of low pH and mixing/destratification, Zn concentrations in overlying water of some of the capped limnocorrals differed significantly from levels observed in the non-capped control (although ratios of dissolved and particulate Zn were similar). These results suggest that

Zn flux from pit lake sediments may be influenced by changes in pH (or other water quality variables related to destratification), and that sediment cap materials can mitigate these effects.

Mixing and stratification in the pit lake is important because it likely dilutes and disperses Zn (i.e., mixing of the entire waterbody) and also alters bioavailability via shifts in reducing to oxidizing conditions (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). This could explain why there were, on average, significantly lower levels of dissolved Zn in RWC versus AL conditions, as the limnocorrals prevented water column mixing and turnover. This could also explain why Zn was concentrated in hypolimnetic waters during system stratification.

These results are similar to those from other studies showing relationships between lake turnover and changes in metal concentrations in the water column (Cover and Wilhm 1982). The timing of fall turnover observed in the present study (October-November) is consistent with results from previous investigations of the pit lake and with observations from other Arkansas reservoirs (ADEQ 1999). Such seasonal changes in physical lake conditions have implications for water quality and potential metal toxicity to aquatic organisms (Zhuang et al. 1994). Partitioning of Zn to sediment depends on the availability (concentration) and speciation of ligands (e.g., Fe oxyhydroxides, organic matter), and on water column characteristics such as pH and redox potential (Atkinson et al. 2007, Huang et al. 2017).

Across all *in-situ* treatments and experiments (capped and non-capped, AL and RWC), dissolved Zn concentrations in surface water were below the hardness-adjusted USEPA water quality criteria threshold for acute and chronic toxicity to freshwater organisms (164 $\mu g\ L^{-1}$) (USEPA 2016a). It is not surprising, therefore, that differences in responses were generally not observed in *in-situ* acute tests conducted in limnocorrals where sediments were either capped or non-capped.

Similar to results from *in-situ* toxicity tests, few adverse biological effects were observed in *ex-situ* tests. Low survival was observed in both experiments involving the addition of limestone in AL_3 and this was likely due to accumulation of sediment and iron oxide particulates on top of the cap, leading to high turbidity in the exposure cages. Turbidity has been linked to adverse effects on motility, fecundity, growth, and survival (Chen et al. 2012, Robinson et al. 2010). Bottom cameras confirmed that loose sediments sloughed off the sides of the pit lake and settled on the bottom when the limestone capping material was deployed. These sediments contained high levels of iron oxides.

In general, organism responses in *in-situ* and *ex-situ* toxicity tests appeared to either benefit from or be unaffected by the presence of a cap. However, a further laboratory investigation was conducted at the pit lake (Cervi et al. 2019, unpublished manuscript) to evaluate the need and efficacy of multiple capping materials for decreasing Zn flux. The tests were conducted in sediment-water microcosms at reasonable worst-case conditions (pH = 5.5) over 28 days. Results showed that dissolved Zn was maintained below 40 µg L^{-1} in the OW of all capped microcosms. Zinc release sharply increased between days 7 and 21 in the OW of the control, but still remained below the USEPA Water Quality Criterion for acute and chronic effects in freshwater organisms (120 µg L^{-1}). Zn concentrations in porewaters within the capping materials also remained low (< 30 µg L^{-1}).

Laboratory investigation

As was found in the field studies, results from investigations conducted in laboratory microcosms indicated no effects of sediment capping materials on growth and survival of *D. magna* and *H. azteca*, and no effects on Zn biouptake in *H. azteca*. *H. azteca* growth was reduced and tissue Zn concentrations were higher in exposures to non-capped sediments, but these differences were not significant. These laboratory studies also showed there were no differences among capping treatments. Again, as was observed *in-situ* exposures, dissolved Zn concentrations in overlying water of laboratory microcosms never exceeded 164 µg L^{-1}, the hardness-adjusted USEPA threshold for acute and chronic toxicity to freshwater organisms (USEPA 2016a).

Lower concentrations of dissolved Zn were observed in overlying water and porewater collected from microcosms treated with zeolite, suggesting it was effective at reducing Zn release from underlying sediments. However, *H. azteca* exhibited lower survival in microcosms containing zeolite. Zeolite exhibits exceptionally high cation exchange capacity and is widely used as a chelating agent in industrial, wastewater treatment and agricultural processes (Babel and Kurniawan 2003, Wang and Peng 2010). Observed reductions in test organism survival may be due to increases in pH in laboratory microcosms caused by zeolite addition, as both *H. azteca* and *D. magna* are sensitive to sudden changes in pH (Pilgrim and Burt 1993). These effects in laboratory microcosms may be ameliorated in field scenarios where the influence of pH increase is mitigated by mixing and dilution. Although zeolites may be an effective capping material for the containment of metals, the potential ecological effects of using zeolites in sediment remediation (capping) are essentially unknown (Xiong et al. 2018).

Results indicated that capping sediments with AquaBlok™ provided no unique benefits beyond other capping materials for addressing Zn flux. In fact, AquaBlok™-treated sediments exhibited increased concentrations of dissolved Zn in the porewater of laboratory microcosms, which may have resulted from a lack of sequestering ligands in Aquablok™ compared to the other cap materials (USEPA 2006). This suggests that perturbations to an Aquablok™ cap, such as currents, upwellings, gas ebullition, and bioturbation could mobilize porewater Zn and reduce long-term containment and effectiveness, as demonstrated by previous studies (Liu et al. 2001, Reible et al. 2006).

In contrast, laboratory microcosms treated with limestone and apatite (clay) exhibited no increase in dissolved Zn levels in porewater or overlying water and resulted in high survival and growth of *H. azteca*. Limestone can enhance cover performance by acting as a pH buffering agent to reduce sediment Zn leaching (RowChowdhury et al. 2015). Apatite acts as a medium for ion-exchange and adsorption, and can mitigate the effects of seasonality, as metal phosphates have low solubility and are stable at a wide range of E_H-pH conditions (Sneddon 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).

CONCLUSIONS

There were no differences in organism responses between treatments involving sediment capping materials and the non-capped control in both *in-situ* and *ex-situ* tests. The lack of adverse effects was likely due to dissolved Zn in surface water being below threshold effects levels. Differences in particulate and dissolved Zn concentrations under AL and RWC conditions were due to mixing and stratification in the pit lake. This study demonstrated the usefulness of the TACS acclimation system for use in stratified lakes and reservoirs, where temperatures vary dramatically between the epilimnion and hypolimnion. Both field and laboratory-based weight-of-evidence studies provided site-specific data to support decisions on optimal remedies, with reduced uncertainty compared to traditional approaches.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.xxxx.

Disclaimer— The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data accessibility— Please contact the corresponding author (burtonal@umich.edu) for any requests for access to data.

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FIGURES

Figure 1. Diagram and photographs showing (A) the Toxicity Assessment Container System (TACS) deployed within the limnocorrals, (B) TACS, (C) open TACS with bottom grate depicted, (D) open TACS with exposure cages, and (E) larger exposure cage (240 mL) 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.

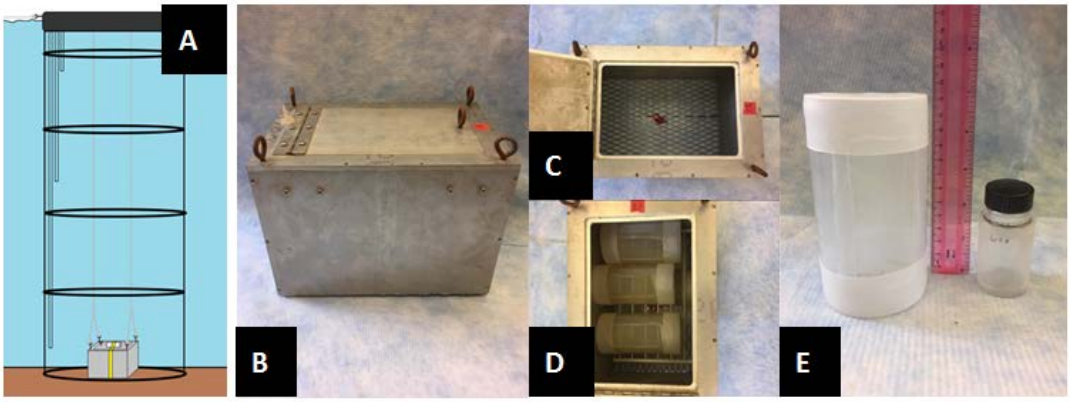


Figure 2. Laboratory microcosms were used to conduct 7-day short-term chronic toxicity tests two species over four consecutive weeks.

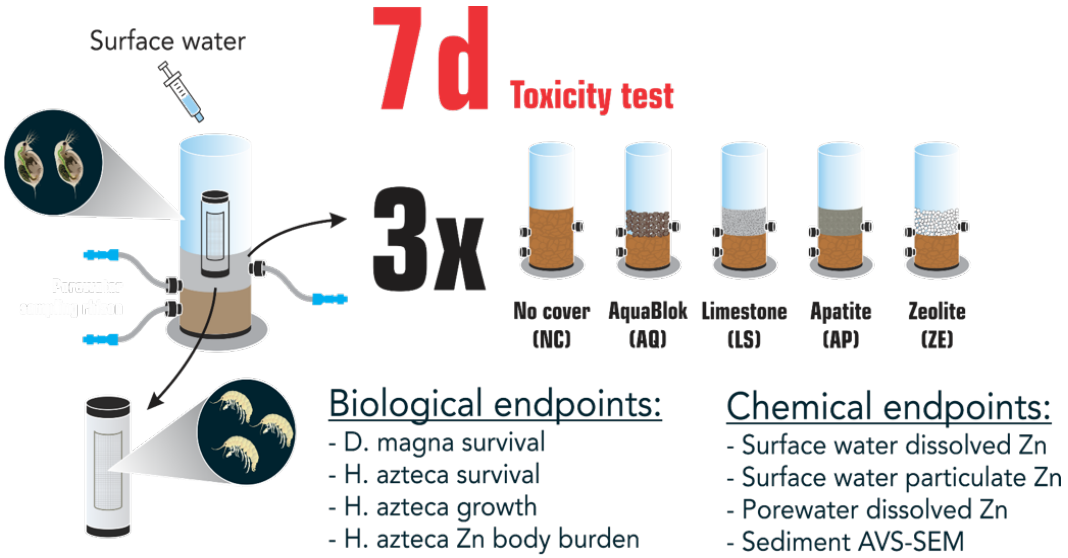


Figure 3. Dissolved and particulate Zn concentrations for multiple capping materials at near-bottom, mid-depth, and surface water of the pit lake (+ SD). Statistically significant ($p < 0.05$) differences between capping treatments and non-capped control are denoted with an asterisk. AQ = AquaBlok™, LS-B = Limestone-bone char, LS = Limestone, and NC = Non-capped.

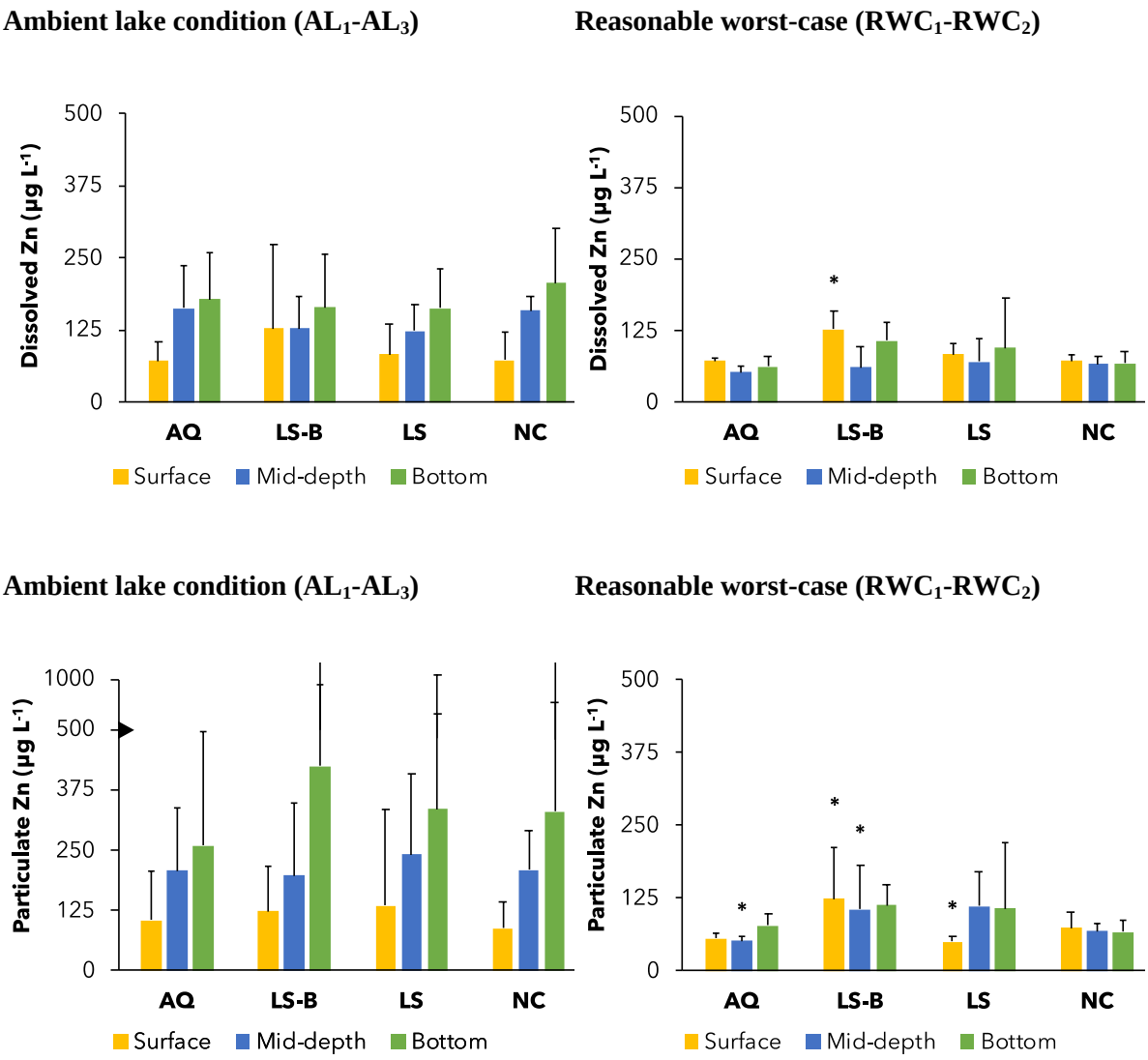
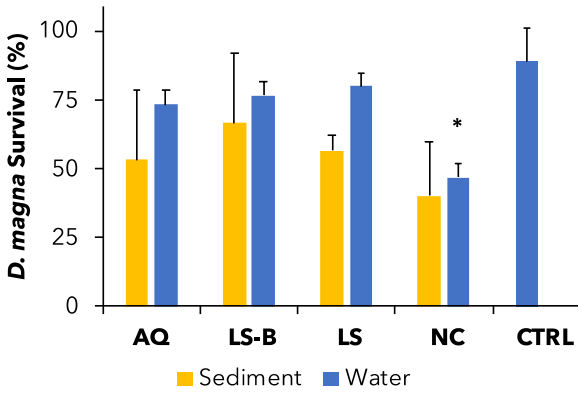
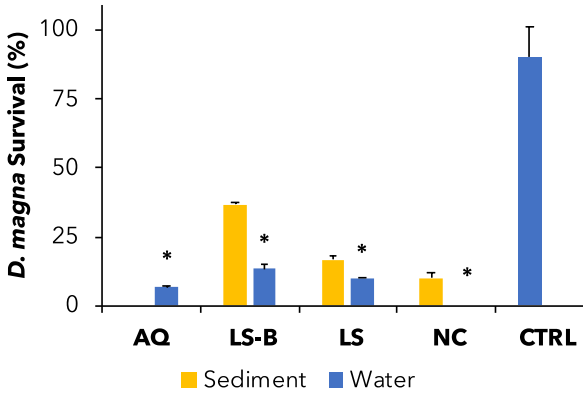


Figure 4. *In-situ* toxicity to *D. magna* and *C. dilutus* in overlying water and sediment for non-capped and capped pit lake sediments (+ SD). Laboratory culture water (CTRL) and non-capped treatment were used as reference control for overlying water and sediment, respectively. Statistical significance ($p < 0.05$) is denoted with an asterisk. AQ = AquaBlok™, LS-B = Limestone-bone char, LS = Limestone, and NC = Non-capped.

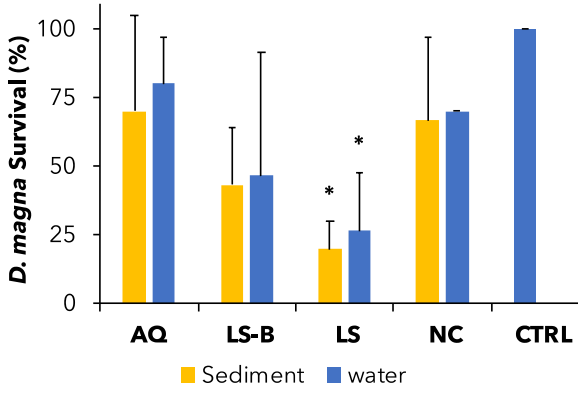
Ambient lake condition (AL_1)



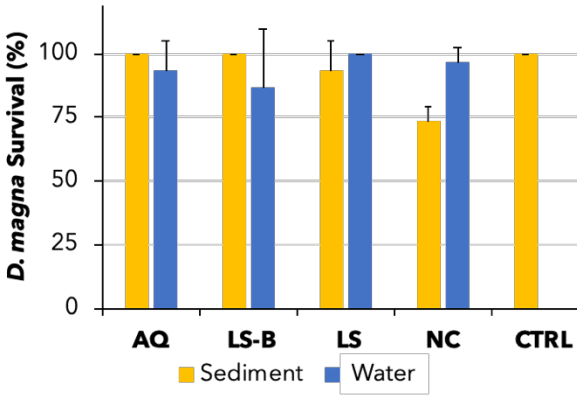
Ambient lake condition (AL_2)



Ambient lake condition (AL_3)



Reasonable worst-case (RWC_1)



Ambient lake condition (AL_3)

Reasonable worst-case (RWC_2)

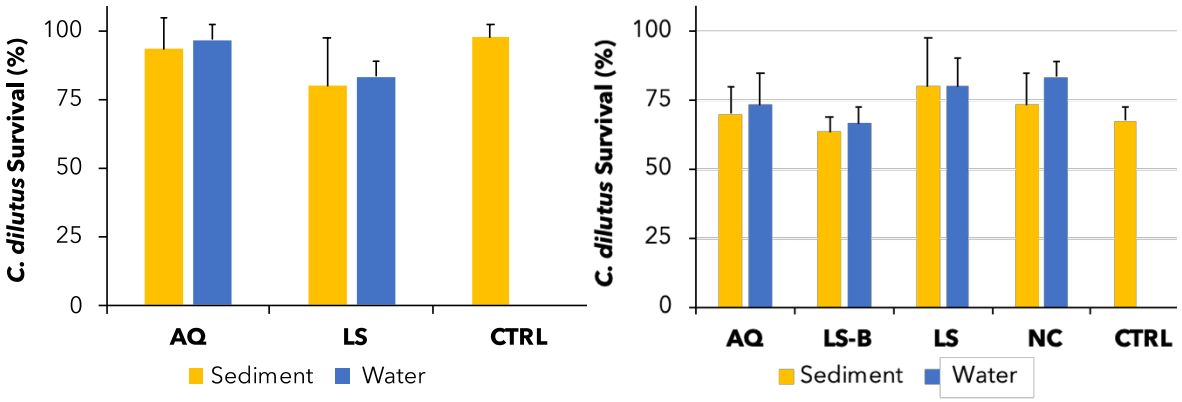


Figure 5. Dissolved Zn concentrations (+ SD) in overlying water of pit lake microcosms treated with different capping materials (AP = Apatite, AQ = AquaBlok™, LS = Limestone, ZE = Zeolite, and NC = Non-capped). Statistical significance ($p < 0.05$) is denoted with an asterisk.

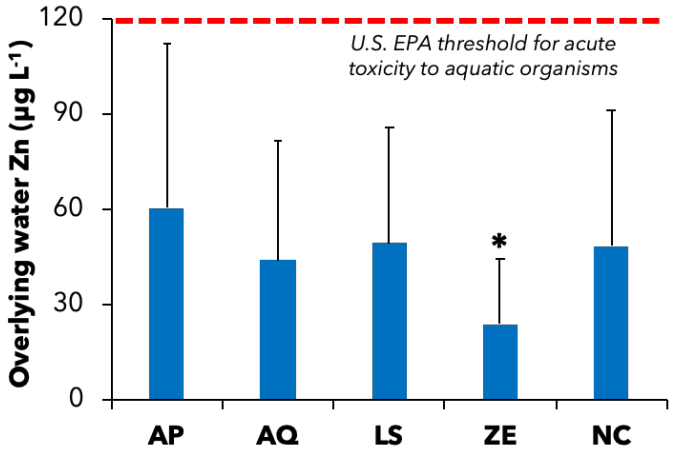


Figure 6. Dissolved Zn in porewater of pit lake microcosms with multiple capping materials (+ SD). Statistical significance ($p < 0.05$) is denoted as difference between treatments with corresponding colored asterisk. AP = Apatite, AQ = AquaBlok™, LS = Limestone, ZE = Zeolite, and NC = Non-capped.

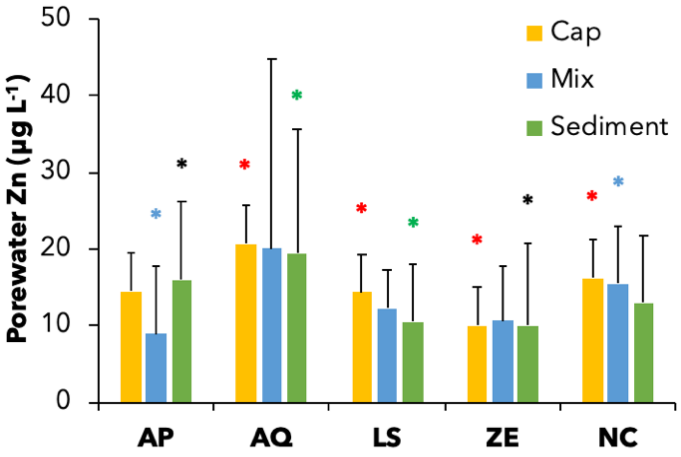


Figure 7. Laboratory toxicity results (mean survival + SD) for *Daphnia magna* and *Hyalella azteca* exposed in microcosms containing capping treatments vs non-capped controls. Statistical significance ($p < 0.05$) is denoted with an asterisk. AP = Apatite, AQ = AquaBlok™, LS = Limestone, ZE = Zeolite, and NC = Non-capped.

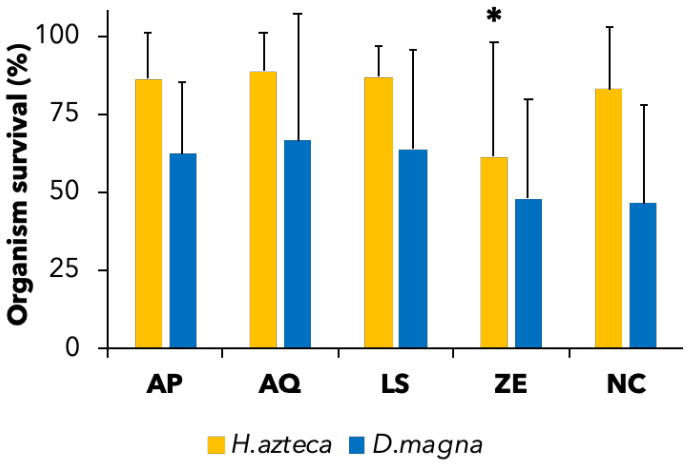


Figure 8. Individual growth rates (IGR) and zinc tissue concentrations for *Hyalella azteca* exposed to pit lake sediment mesocosms with capping treatments vs. non-capped controls (+ SD). IGR and zinc tissue concentration in all treatments were similar. AP = Apatite, AQ = AquaBlok™, LS = Limestone, ZE = Zeolite, and NC = Non-capped.

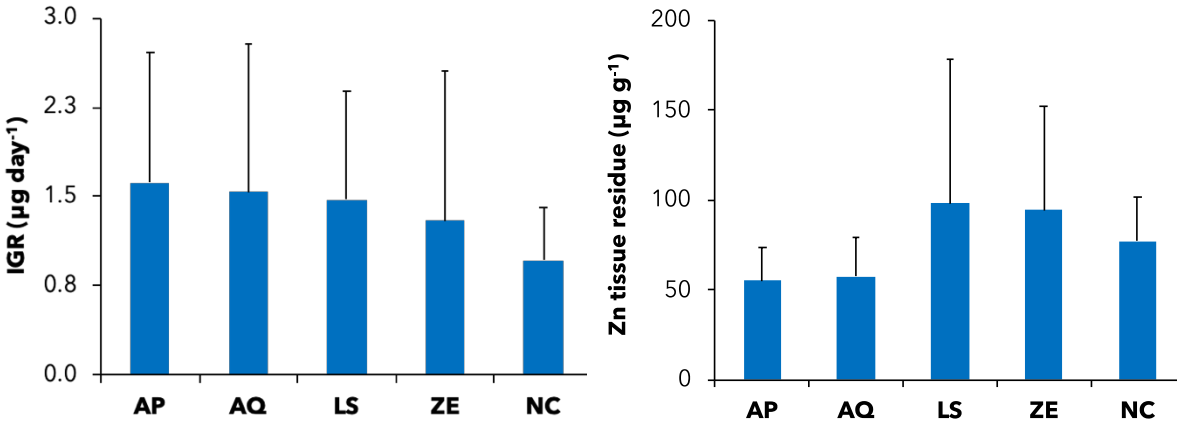


Table 1. Field-based exposures under ambient lake (AL) and reasonable worst-case conditions (RWC), and laboratory microcosms toxicity testing

Experiment	Name	Organisms	Description
Field-based ambient lake conditions (pH = 7.0)	AL_1	*D. magna* *H. azteca*	48 h *in-situ* exposure
	AL_2	*D. magna* *H. azteca*	96 h *in-situ* exposure
	AL_3	*D. magna* *C. dilutus*	48 h *in-situ* exposure 48 h *ex-situ* water exposure

Field-based reasonable worst-case scenario (pH = 5.5)	RWC_1	*D. magna* *H. azteca* *C. dilutus*	48 h *in-situ* exposure 48 h *ex-situ* sediment exposure
	RWC_2	*D. magna* *C. dilutus*	48 h *in-situ* exposure 48 h *ex-situ* water exposure
Laboratory toxicity testing	Microcosms	*D. magna* *H. azteca*	7-d microcosm exposure