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Sediment Copper Concentrations, In Situ Benthic Invertebrate Abundance, and Sediment Toxicity: Comparison of Treated and Untreated Coves in a Southern Reservoir

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Abstract Copper-based algaecides are used to control algae that compromise uses of lakes and reservoirs. However, there are concerns regarding potential adverse effects to benthic macroinvertebrates following long-term, repeated applications. Multiple lines-of-evidence are useful for evaluating potential ecological risks. These lines-of-evidence are encompassed in the sediment quality triad (SQT) and include sediment copper concentrations, in situ benthic invertebrate abundance, and sediment toxicity testing. The objective of this study was to measure potential ecological risks associated with long-term applications of copper algaecides in coves in Lay Lake, Alabama. Sediments from three coves treated for 7, 10, and 20 years were compared to sediments from three untreated coves in terms of copper concentrations, in situ benthic macroinvertebrate total abundance, and survival of *Hyalella azteca* and *Chironomus dilutus* in laboratory sediment toxicity tests. Sediment copper concentrations were not different between treated and untreated coves, with the exception of one treated cove (PC-1S) that contained elevated sediment copper concentrations compared to all other coves. However, the copper was not bioavailable to organisms based on in situ macroinvertebrate abundance and laboratory toxicity tests. In situ benthic invertebrate abundance was not different between treated and untreated coves. In all sediments tested, there were no measurable adverse effects to *H. azteca* and there were no significant differences in survival of *C. dilutus* between treated and untreated coves. Based on the weight-of-evidence approach utilized in this study, long-term copper use in three Lay Lake coves has not resulted in adverse effects to benthic invertebrates compared to untreated coves.

Keywords Copper-based algaecides · Sediment quality triad · Non-target species · Bioavailability · *Lyngbya*

1 Introduction

Copper-based algaecides are frequently used to control nuisance algae that compromise the uses of lakes and reservoirs. Copper-based algaecides can decrease algal populations by disrupting metabolic and photosynthetic processes, binding to proteins, and producing reactive oxygen species (Stevenson et al. 2013). Following algal exposures in the water column, copper has a lithic biogeochemical cycle and is typically transferred to sediments within days to weeks of an algaecide application (Murray-Gulde et al. 2002). Due to the association of copper with sediments, concerns are often expressed regarding the fate of copper in sediments and its bioavailability and potential adverse effects to non-target organisms (Hullebusch et al. 2008; Prepas and Murphy 1988). These concerns may be heightened in water resources where numerous copper treatments have been applied over time.

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Copper-based algaecides have been used for decades to manage *Lyngbya wollei* in Lay Lake, a 4900 ha reservoir in Alabama. *L. wollei* is a prokaryotic cyanobacterium that produces dense, bi-phasic mats (Speziale and Dyck 1992), taste-and-odor compounds (Brown and Boyd 1982), and dermatotoxins and neurotoxins (Carmichael et al. 1997; Foss et al. 2012; Lajeunesse et al. 2012). *Lyngbya* also may decrease densities of beneficial zooplankton, cause avoidance responses in fish (Mastin et al. 2002), and alter predator–prey relationships, feeding behavior, and fish community structure (Hudon et al. 2012; Hudon et al. 2014). Lay Lake is managed for contact recreation, drinking water, food processing, fishing, industrial and agricultural uses, propagation of fish and wildlife, and homeowner aesthetic value. To control nuisance *L. wollei* in coves of Lay Lake, copper algaecides have been applied for one to more than 20 years, with applications occurring approximately five times a year primarily during the summer months. Due to these long-term and well-documented treatments, as well as the presence of untreated coves in the same water body, Lay Lake is a useful study site to measure copper residues in sediments, resulting from decades of algaecide applications, and the effects on non-target, benthic organisms.

To accurately assess potential risks of sediment associated copper, it is critical to implement a weight-of-evidence approach that involves multiple parameters. The sediment quality triad (SQT) approach uses analytical methods to determine copper concentration, biological methods to determine bioavailability and toxicity, and in situ parameters to measure the benthic community structure of organisms present (Chapman et al. 2002). Risks to non-target organisms associated with copper toxicity in sediments are not solely due to copper concentrations, but the bioavailability of the copper that is present (Chapman et al. 1999). Sediment characteristics such as percent organic matter (Besser et al. 2003; Milani et al. 2003), acid volatile sulfides (AVS) (Allen et al. 1993), cation exchange capacity (CEC) (Chapman et al. 1998), and particle size distribution (Hoss et al. 1997) influence the bioavailability of sediment associated copper. Sediment associated copper is typically measured following a rigorous (acid) digestion and the total measured concentration of extracted copper may not be representative of copper that is bioavailable within the sediments. Therefore, it is important to pair organism responses with analytical copper measurements to accurately measure toxicity.

Copper can adversely affect organisms externally through competition for binding sites on the organism or internally through uptake and absorption by the organism (Campbell et al. 2002). In situ organism observations and laboratory toxicity tests using naïve cultured organisms provide different information, and are therefore both necessary in the SQT process (Chapman et al. 2002; McPherson et al. 2008). In situ measures provide information regarding resident benthic assemblages present at the time of sampling while laboratory toxicity assays provide a standardized measure of responses of naïve, cultured organisms that have not previously been exposed to the specific sediments or constituent of concern. *Hyalella azteca* and *Chironomus dilutus* are commonly used for sediment toxicity assays and are recommended by the EPA (US EPA 1993). *H. azteca* and *C. dilutus* spend a significant portion of their lives in sediments, can tolerate a range of sediment types, and are therefore suitable organisms for sediment toxicity analysis (Deaver and Rodgers 1996; Suedel et al. 1996). By implementing the SQT approach and utilizing these three lines of evidence (analytical/chemical, in situ biological measures, and laboratory toxicity analysis), potential risks and the magnitude of the risks associated with sediments and/or a particular constituent of concern in sediments can be assessed (Chapman et al. 2002).

The overall objective of this study was to use the SQT approach to obtain multiple lines of evidence to measure potential ecological risks associated with long-term (i.e., years to decades) applications of copper-based algaecides in coves in Lay Lake, Alabama. To support the overall objective, specific objectives were to: (1) measure and compare sediment copper concentrations in treated and untreated coves; (2) measure and compare the benthic invertebrate assemblages in terms of abundance in treated and untreated coves; (3) measure and compare responses of naïve cultured *H. azteca* and *C. dilutus* in terms of survival in sediments from treated and untreated coves; (4) integrate the information obtained from the SQT to conclude effects, or lack of effects, on benthic invertebrates due to copper treatments; and (5) calculate a mass balance for copper in sediment from known copper algaecide applications and compare with measured values in treated and untreated sediments.

2 Methods

2.1 Site Description

Lay Lake is a 4900 ha reservoir centrally located in Alabama (33.15°,-86.48°). Within the lake, three coves that have been repeatedly treated with copper-based algaecides were sampled along with three untreated coves (Fig. 1, Table 1). Treated coves have records of algaecide treatments ranging from seven to greater than 20 years with applications occurring ~5 times per year primarily during the summer months. At the time of sampling (August 12, 2014), the treated coves had received four applications of algaecides to date in 2014, in April, June, July, and August of 2014 (Table 1).

2.2 Sediment and Water Collection

Sediment samples (0–15 cm sediment depth) were collected from treated and untreated coves using an Ekman Dredge (EPA SOP #2016). Three sediment samples were collected from each cove (three treated and three untreated) for a total of 18 samples, at an average water depth of 2 m. Samples were placed on ice in sealed bags for transport. Composite samples of approximately 20 L of site water were collected from treated and untreated sites. The sediment and water samples were transported to the laboratory on ice where analyses were conducted.

2.3 Sediment Characteristics

For measurement of copper concentrations (mg Cu/kg), sediments were digested with HNO_3 and H_2O_2 (EPA method 3050B, USEPA 1996a, b). Extracted copper per gram of sediment was quantified using a flame atomic absorption (AA) spectrophotometer (Perkin-Elmer 5100 PC -Waltham, MA) using a matrix-matched calibration curve from serial dilution of a 1000 mg/L copper standard (Fisher Scientific, Inc.; APHA 2005). Quality assurance and control for analytical methods included comparisons to standard curves and replicate analyses. Acid volatile sulfides (AVS) were determined following the modified diffusion method (Leonard et al. 1996). The sulfide ions were measured using an ion-selective electrode (ISE; Fisher Accumet 950 pH/ion meter) to determine the molar concentration of AVS. A summary of methods used for obtaining explanatory water and sediment characteristics is presented in Table 2.

2.4 Macroinvertebrate Survey

Benthic macroinvertebrates were enumerated within 24 h of sediment collection. Approximately 100 mL (0.0004 m^3) of sediment was subsampled from each cove. The subsamples were washed through stainless steel sieves with 500 μm openings and benthic macroinvertebrates were preserved in 20 mL scintillation vials containing 70 % ethanol (EtOH; Sigma-Aldrich). All organisms collected were sorted, counted, and identified to the order level using a dissecting microscope.

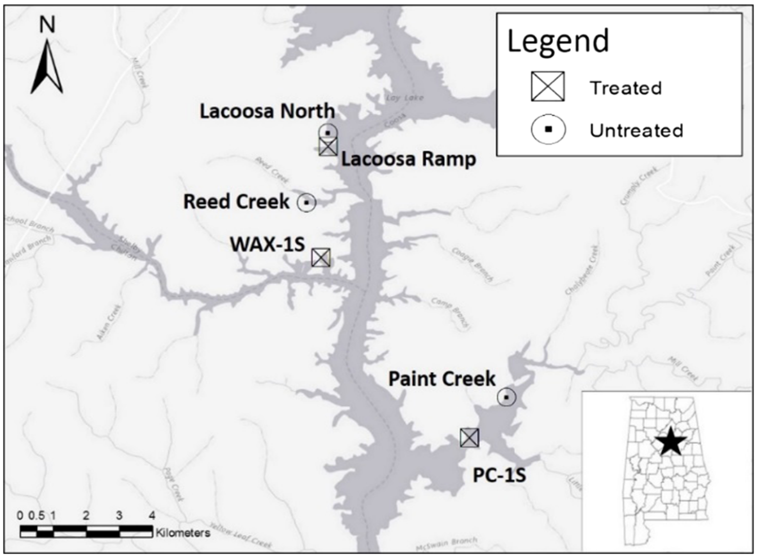

Fig. 1 Location of treated and untreated coves in Lay Lake, Alabama

Table 1 Site (cove) description

Cove name	Type	Coordinates latitude, longitude	Years of treatments (≈approximately)	2014 treatment dates
Lacoosa Ramp	Treated	N33° 03.284′ W86° 31.573′	≈7	4/29, 6/9, 7/21, 8/11
PC-1S	Treated	N32° 59.171′ W86° 29.916′	>20	4/29, 6/10, 7/23, 8/12
WAX-1S	Treated	N33° 01.713′ W86° 31.674′	≈10	4/28, 6/9, 7/21, 8/13
Paint Creek	Untreated	N32° 59.741′ W86° 29.056′	0	Untreated
Reed Creek	Untreated	N33° 02.491′ W86° 31.883′	0	Untreated
Lacoosa North	Untreated	N33° 03.468′ W86° 31.583′	0	Untreated

Abundance (i.e., total number of individuals present) was extrapolated and estimated per square meter (Resh et al. 1988; Merritt et al. 2008) and the total number of organisms per order present was recorded for samples from each cove. Significant differences in total abundance between treated and untreated coves were determined with non-parametric rank comparisons (Median Test) (JMP v.11).

2.5 Sediment Toxicity Testing

The potential bioavailability of copper from sediments was determined using *H. azteca* and *C. dilutus*. Test organisms were cultured at Clemson University following USEPA methods (US EPA 1993, 1994) for *H. azteca* and *C. dilutus*. Two to three week old amphipods (Deaver and Rodgers 1996) and second instar *C. dilutus* were collected for sediment toxicity experiments. Tests were initiated by adding ten *H. azteca* and ten *C. dilutus* separately to 250 mL borosilicate glass beakers containing 40 mL of wet sediment and 150 mL of site water in 10-day toxicity experiments, three replicate beakers were used per sediment sample (Deaver and Rodgers 1996). Three 7 mm diameter leached maple leaf disks and 0.1 mL Tetramin slurry were added to each beaker at the start of the experiment as a food

Table 2 Analytical methods of testing parameters

Parameter	Method	Method detection limit
pH[a, b]	Direct instrumentation: Orion Model 420A (Standard Methods 4500-H^+ B) (APHA 2005)	0.01 SU
Temperature[a]	Direct Instrumentation: Orion Model 420A	0.01 °C
Dissolved oxygen[a]	Direct Instrumentation: YSI Model 52	0.1 mg/L
Conductivity[a]	Direct Instrumentation: YSI 30 (Standard Method 2510 B) (APHA 2005)	0.1 μS/cm
Alkalinity[a]	Standard Methods: 2320 B (APHA 2005)	2 mg/L as CaCO3
Hardness[a]	Standard Methods: 2340 B (APHA 2005)	2 mg/L as CaCO3
Particle size[b]	Hydrometer method (Gee and Bauder 1986)	2 %
Organic carbon content[b]	Loss-on-ignition at 450 °C (Nelson and Sommers 1996)	0.0001 g
AVS and SEM[b]	Modified diffusion method (Leonard et al. 1996)	0.01 μmol sulfide/ mL
Copper[c]	Extraction (USEPA 3050b) measured with flame atomic adsorption spectrometer (Perkin-Elmer 5100 PC; APHA 2005)	6 mg Cu/kg

[a] Site water measurement

[b] Sediment measurement

[c] USEPA 1996a, b; Willis et al. 2013

source for *H. azteca* and *C. dilutus*, respectively (Deaver and Rodgers 1996). Test chambers were aerated to maintain dissolved oxygen concentrations above 4 mg O_2/L. Significant differences in organism responses to sediments were determined using ANOVA and Tukey's pairwise comparison test (JMP v.11).

3 Results and Discussion

3.1 Sediment Copper Concentrations, Sediment, and Water Characteristics

Water characteristics were similar in treated and untreated coves (Table 3). Sediment copper concentrations ranged widely in sediments (20–403 mg Cu/kg) and overall were not significantly different between treated and untreated coves ($p=0.77$, $\alpha=0.05$; treated $n=27$, mean = 51.6 mg Cu/kg; untreated $n=27$, mean = 151.3 mg Cu/kg) (Fig. 2), with the exception of treated cove PC-1S which had a significantly higher sediment copper concentration compared to all other treated and untreated coves measured in this study ($p=0.007$, $\alpha=0.05$, mean = 334 mg Cu/kg). The elevated copper concentration in PC-1S may have been due to a copper algaecide application that occurred on the day that the sediment was collected prior to sampling. Sediment copper concentrations within the measured coves were generally within the ranges of background values found in the USA (<1–300 mg Cu/kg) (Suedel and Rodgers 1991; Forstner and Wittmann 1979), with the exception of recently treated site PC-1S (201–400 mg Cu/kg) where sediment copper concentrations were relatively high.

Measured AVS concentrations from Lay Lake coves ranged from 0.3 to 10.1 μmol/g and organic carbon ranged from 4 to 23 %. Particle size of collected sediments was primarily sand (43–70 %), followed by silt (23–50 %), and clay (5–10 %) (Table 4). Measured AVS concentrations from Lay Lake coves ranged from 0.3 to 10.1 μmol/g which are within reported ranges of AVS in freshwater systems (0.03–75.3 μmol/g) (Besser et al. 1996; Leonard et al. 1999). Organic carbon ranged from 4 to 23 % with an average of 17 % in the six sites. This is greater than what is typically seen in freshwater sediments across the continental USA (0.03–12 %) (Suedel and Rodgers 1991). The relatively high organic carbon percentage in sediments is likely due to *L. wollei* which was a major component in nearly all collected sediment samples. The *L. wollei* was present either as live algae or was decomposing in sediments.

3.2 In Situ Macroinvertebrate Assemblage

Benthic macroinvertebrate abundance was generally greater in treated coves than untreated coves although differences were not statistically significant ($p=0.4919$, $\alpha=0.05$; treated $n=9$, mean = 130,000 organisms/m^3; untreated $n=9$, mean = 57,000 organisms/m^3) (Fig. 3). Untreated coves were dominated by oligocheates and amphipods with the exception of La Coosa North which was dominated by *Diptera*. Treated coves PC-1S and WAX-1 were dominated by *Diptera* while treated cove La Coosa Ramp primarily contained amphipods. Although organisms were sorted to the order level taxonomically, differences in organism order were not statistically analyzed between coves. In situ information typically used in the SQT method includes numerical dominance, number of taxa, and/or total abundance (Chapman et al. 2002). In this study, total abundance per cove was statistically analyzed. No significant differences in total abundance of in situ benthic invertebrates were measured between treated and untreated coves.

3.3 Responses of Naïve *C. dilutus* and *H. azteca* to Site Sediments

Percent survival of *H. azteca* in untreated sediments ranged from 87–88 % and 87–98 % in treated sediments (Fig. 4). There was a statistical difference in *H. azteca* survival measured between treated and untreated coves following exposure to site sediments ($p=0.02$, $\alpha=0.05$; treated $n=27$, mean = 93 %; untreated $n=27$, mean = 86 %). Although there was a statistical

Table 3 Water characteristics

Site	pH	Dissolved O_2 (mg/L)	Conductivity (μs/cm)	Alkalinity (mg $CaCO^3$)	Hardness (mg $CaCO^3$)
Untreated	7.58	8.11	338.4	68	72
Treated	7.85	8.36	202.8	60	72

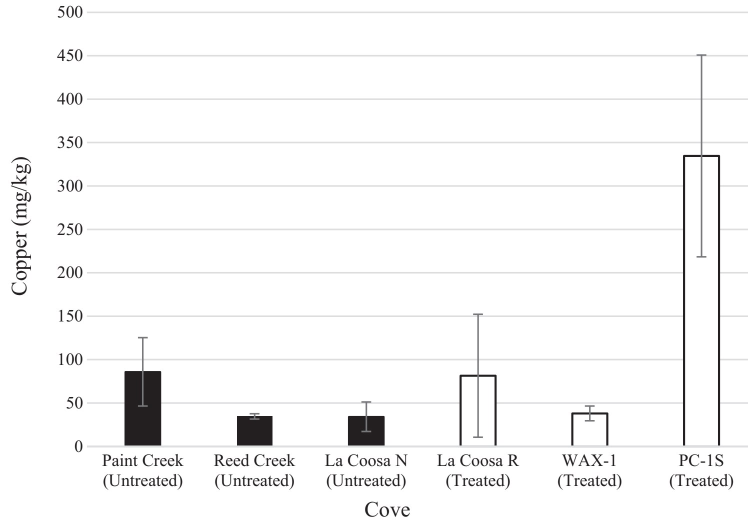

Fig. 2 Measured sediment copper concentrations in treated and untreated coves

difference in percent survival of *H. azteca* between treated and untreated coves in this study, this likely is not environmentally relevant (93 versus 86 % survival). Percent survival greater than 80 % in sediment toxicity analyses using *H. azteca* and *C. dilutus* is acceptable to conclude no measureable adverse effects (US EPA 1996a, b).

Percent survival of *C. dilutus* in untreated sediments ranged from 62 to 81 % and 73 to 88 % in treated sediments over a 10-day test period. No overall statistical difference in *C. dilutus* survival was measured between treated and untreated coves following exposure to site sediments ($p = 0.47$; treated $n = 27$, mean = 82 %; untreated $n = 27$, mean = 72 %) over a 10-day test period. However, there was a significant difference between two coves specifically ($p = 0.0331$, $\alpha = 0.05$), treated cove La Coosa Ramp (mean = 88 %) and untreated cove Paint Creek (mean = 62 %). Less than 80 % survival was measured in untreated coves Reed and Paint Creek and in treated cove PC-1S (Fig. 5). Although *C. dilutus* survival was less than 80 % in sediments from these three coves, this occurred in both treated and untreated sediments, indicating that any adverse effects were likely not attributable to copper treatments.

3.4 Combined Sediment Quality Triad Information

Combining measured copper concentrations in sediments, in situ benthic macroinvertebrate total abundance, and laboratory toxicity assays using site sediments allows for a weight-of-evidence based conclusion regarding the probability that organisms inhabiting treated sites are adversely affected due to a specific constituent of concern (copper applications) or combination of constituents or factors (Chapman et al. 2002). This is achieved by comparing measurements from treated coves to those from untreated coves.

Table 4 Sediment characteristics measured in treated and untreated coves

Site	mg Cu/kg	AVS (μmol/g)	% Organic Carbon	% Clay	% Silt	% Sand
Paint Creek	86 (42–118)	5.2 (2.6–10.1)	23	7	30	63
Reed Creek	35 (31–36)	1.3 (1.0–1.7)	12	7	50	43
La Coosa North	34 (20–53)	3.3 (0.3–6.2)	23	5	25	70
La Coosa Ramp[a]	81 (24–160)	6.3 (4.0–7.9)	18	7	30	63
WAX-1[a]	38 (29–45)	1.4 (1.1–1.7)	4	7	23	70
PC-1S[a]	334 (200–410)	2.2 (1.3–3.3)	22	10	40	50

Numbers in parentheses represent minimum and maximum measured values

[a] Indicates treated sites

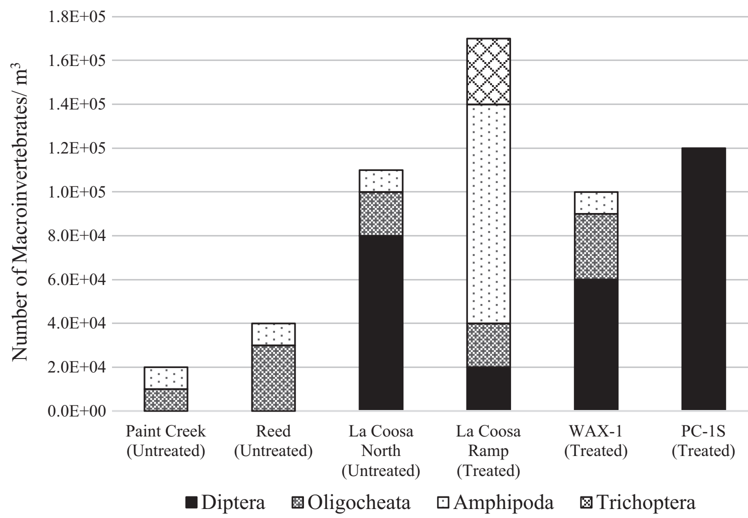

Fig. 3 Benthic macroinvertebrate abundance by cove. Results are presented as the total number of organisms present in three cubic meters of sediment (extrapolated from sub-sample) for each site. Organisms are further divided by the order of the organisms present in each cove and are represented as proportions of the total number of organisms present

Based on the combined results, there were no significant differences between treated and untreated coves in any measurement except sediment copper concentrations of cove PC-1S (Table 5). Lack of significant differences in SQT measurements between untreated coves and the treated coves La Coosa Ramp and WAX-1 provides strong evidence to conclude no evidence of adverse effects on benthic macroinvertebrates due to copper residuals in the sediments in La Coosa Ramp and WAX-1. For cove PC-1S, we can infer that the elevated concentration of sediment copper compared to control sites is not bioavailable because no adverse effects to benthic macroinvertebrates were measured in either laboratory toxicity analyses or in situ abundance measurements.

3.5 Predicted Sediment Copper Concentrations

Questions arise regarding the lack of discernable differences in sediment copper concentrations between treated and untreated coves. A simple, retrospective mass balance calculation (Eq. 1) was applied to provide an estimate of copper concentrations in sediment following algaecide treatments. Based on this conservative equation, and the assumptions that no copper transport or sediment accretion occurred, significantly elevated copper concentrations (compared to background) would be detectable in treated coves after 7 (La Coosa Ramp), 10 (WAX-1), and 20 (PC-1S) years of copper algaecide treatment.

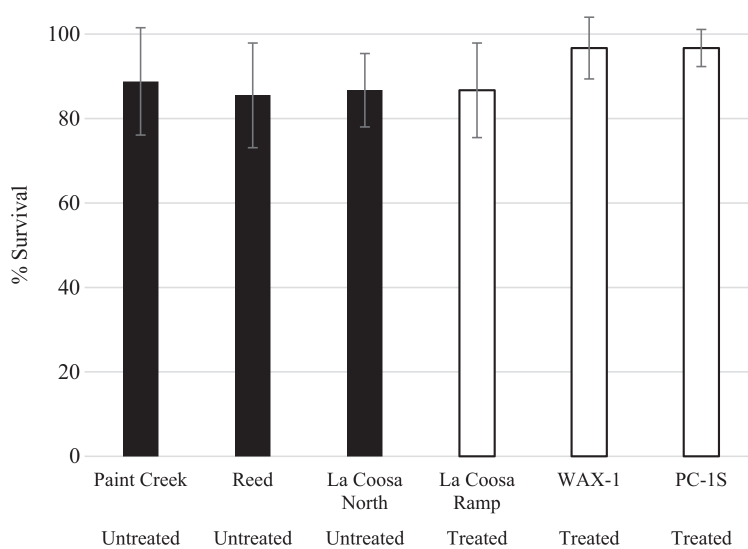

Fig. 4 Responses of naïve, cultured *H. azteca* following 10-day exposures to site sediment from each sampled cove. Results are presented as percent survival

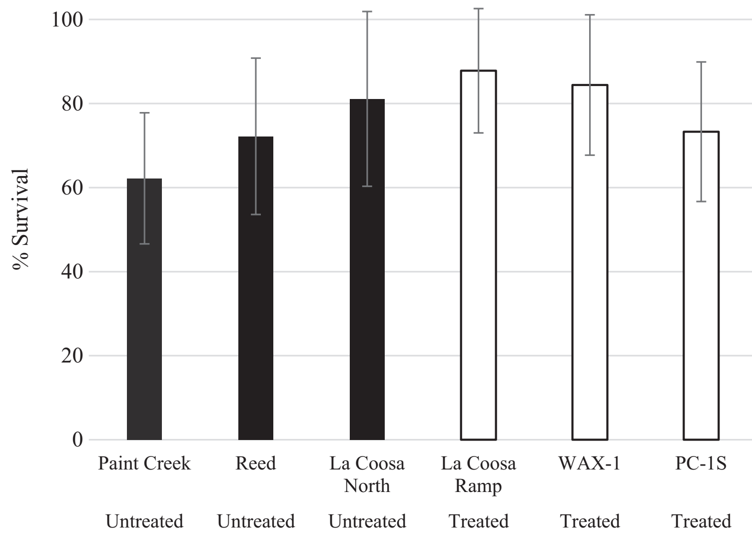

Fig. 5 Responses of naïve, cultured *C. dilutus* following 10-day exposures to site sediment from each sampled cove. Results are presented as percent survival

$$\frac{C\left(mg\ L^{-1}\right)\times V\ (L)}{V_1\ (cm^3)\times D\left(kg\ cm^{3^{-1}}\right)} = \frac{MA\ (mg)}{MS\ (kg)} \qquad (1)$$

Where:

C copper application rate = 1.0 mg Cu L^{-1}

V volume of water (1 acre, 10 ft deep) = 1.23×10^7 L

V_1 volume of sediment (1 acre, 6 in. deep [estimate of depth sampled with Ekman Dredge]) = 6.16×10^8 cm^3

D sediment density = 0.002 kg cm^{3-1}

MA mass of copper = 1.23×10^7 mg

MS mass of sediment = 1.23×10^6 kg

MA/MS mass of copper added to sediments per algaecide application = 10.0 mg Cu kg^{-1}

Based on these assumptions, approximately 10 mg Cu/kg would be deposited in sediments with each algaecide application, and approximately 50 mg Cu/kg per year following five applications. This would yield a measureable increase in sediment copper concentration of 350 mg/ kg in La Coosa Ramp (7 years of treatment), 500 mg/kg in WAX-1 (10 years of treatment), and 1000 mg/kg in PC-1S (20 years of treatment). However, with the exception of cove PC-1S, there were no measurable increases in sediment copper concentrations compared to untreated coves. Based on this comparison, the simple mass balance calculation (mass of copper/ mass of sediment) was not useful for predicting copper concentrations in treated coves.

More specific factors such as sediment accretion and copper transport may provide a more accurate prediction. Average sediment deposition in reservoirs across North America is approximately 200 m^3/km^2, contributing to an average loss of 0.11–0.52 % reservoir water storage capability every year (Sumi and Hirose 2002). A USDA (1936) study specific to Lay Lake Reservoir estimated the loss of storage capacity to be 0.52 % and an annual sedimentation rate of approximately 0.89 acre-feet/mile^2 (424 m^3/km^2) (USDA 1936). *L. wollei*

Table 5 Combined sediment quality triad measures

Copper Treated Cove	Copper concentration (mg/kg)	Toxicity		Alteration (in situ) benthic invertebrate abundance
		H. azteca	*C. dilutus*	
La Coosa Ramp	–	–	–	–
WAX-1	–	–	–	–
PC-1S	+	–	–	–

(+) represents a significant difference in the specified measure in the treated cove as compared to the untreated coves, (−) signifies no significant difference in the specified measure between the treated and untreated sites growths produce significant amounts of biomass and have been measured at densities up to 1–1.5 kg/m^2 (dry biomass), with the greatest densities occurring during the summer months (Beer et al. 1986; Speziale and Dyck 1992). Factoring in literature values of yearly terrestrial sediment mass inputs and mass of *Lyngbya* is also insufficient to account for the lack of differences in sediment copper concentrations between treated and untreated coves. Based on the above literature values, yearly mass inputs of sediment and *Lyngbya* combined would equal approximately 4050 kg of sediment/acre (3.4 kg as sediment, 4046.6 kg as *Lyngbya*). This value does not impact the mass balance equation for copper and sediment (1.23×10^6 kg sediment compared to 1.234×10^6 kg sediment). Aqueous copper transport, dilution and dispersion, as well as sediment density, volume, compressibility, and permeability of existing sediments, incoming sediments, and *Lyngbya* may all be contributing, site specific factors affecting the concentrations of sediment associated copper that were not accounted for in this mass balance.

4 Conclusions

With the exception of cove PC-1S, no significant differences between treated and untreated coves were measured in terms of sediment copper concentrations, in situ total benthic macroinvertebrate abundance, and survival of naive cultured *H. azteca* and *C. dilutus*. Treated cove PC-1S had significantly higher copper concentrations compared to all other treated and untreated coves. Although sediment copper concentrations were elevated in cove PC-1S, the results indicate that copper was not bioavailable to organisms based on in situ benthic abundance data and laboratory toxicity analyses. Simple mass balance calculations for expected copper concentrations due to copper algaecide applications were inaccurate for predicting measured copper concentrations in treated sediments. Based on the weight-of-evidence approach utilized in this study, long-term copper use in three Lay Lake coves has not resulted in adverse effects to benthic invertebrates compared to untreated coves.

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