The Toxicology of Saratoga's Drinking Water:
Herbicides impact aquatic animals

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Abstract

Copper sulfate, an algicide often applied to drinking water reservoirs, controls algal blooms by inhibiting nitrogen fixation by those organisms. Once added, the reactive form of copper released by the algicidal compound accumulates in the

Introduction

The city of Saratoga Springs has been adding the commonly-used algicide, copper sulf 50 0 0 (ddi) 0.250.2 (i) the cellular level are seen through varying degrees of impaired function (the extreme being death) at the level of the whole organism. Although copper is necessary for organisms to thrive, elevated concentrations have been shown to negatively impact the biotic community of lakes.

Lethal effects on organisms are often observed when copper concentrations are high. Past research has documented lethal effects of elevated concentrations on dragonfly larvae, daphnia, freshwater mussels, pond snails, and fish species including rainbow trout and fathead minnows (Tollett *et al.* 2008, Brown *et al.* 1974, Pagenkopf *et al.* 1974, White & Stoner 2008, Cyrino de Olivera-Filho et al. 2004, Sherba et al. 2000, Gupta et al. 1981, Keller & Zam 1991). In two studies involving crayfish (*Orconectes rusticus* and *Cherax destructor),* copper sensitivity was greater in juveniles (Hubschman 1967, Khan & Nugeogda 2007). However, copper tolerance was documented in mayfly larvae, which possess exoskeletons that have been shown to accumulate high levels of copper and other toxic metals (Eisler 1998, Tollet *et al.* 2009). These studies illustrate the differences in locations within the organism. Copper challenges organisms when it interferes with the functioning of the organism. Two explanations for copper toxicity have been identified: at low concentrations, it was hypothesized that copper interferes with cell maintenance and repair, while at high concentrations, copper interferes with the respiratory system by inhibiting enzymes (Hubschman 1967). This direct impact on respiration was also seen in zebra mussels; mussels exposed to higher concentrations of copper experienced decreased respiration (Prasada Rao & Khan 2000). Investigating the precise impacts of copper on these biochemica invertebrates), and freshwater pond snails (gastropod, mollusk, and scrapers of plant material and detritus). These organisms represent three distinct families of aquatic organisms and therefore could provide a scope of possible implications for ecosystem function. Each set of organisms will be exposed to one of four treatments: three copper sulfate treatments (below the EPA limit of 1300 g/L copper sulfate) and a control treatment.. Over a fourteen day period, each individual organism's metabolism will be measured in terms of their respiration (determined through oxygen consumption). Mortality will also be recorded during this time.

Methods

Organisms

The three species of test organisms—pond snails, dragonfly nymphs, and leeches—were obtained from Carolina Biological. The pond snails are protected by a hard shell but also have a permeable foot that protrudes from that shell. They ranged in mass from 0.0401 to 0.7708 g. The within-tank location of the snails once introduced to their tanks varied: some tended to reside on walls of their tank, while others remained on the sand at the bottom of their tank. Overall, the snails were the least active of the three. The dragonfly nymphs were concentration, and an aerating bubbler. Three to five individuals of each test species were placed in each tank. The first 14-day trial began on 2-11-12 and ended on 2-26-12; it included both the pond snails and the first group of dragonfly nymphs. The second trial, which focused on leeches, began on 3-7-12, metabolic readings were only taken on days zero and twelve, but deaths were monitored through day 18, on 3-25-12. The leech trial consisted of two treatments: a control and a copper tank. The initial concentration in the copper tank was 325 g/L copper sulfate. On day 1, a supplementary dose of copper was added, bringing the total concentration to 975 g/L. After the leech trial, we returned to the initial experimental set-up to complete a second dragonfly nymph trial, which began on 3-26-12 and ended on 4-10-12.

During the first and last trials, we sampled both the water column and the sediment of all 8 tanks on days 1, 7, and 15 to monitor the movement of copper between the two. Copper was extracted from the sediment using a 1:10 sediment to 0.1 M HCl solution over 16 hours, during which the extractions were agitated on a rocker. After the 16 hours, the extractions were centrifuged at 4,000 rpm for 20 minutes and then filtered through 0.45 m cellulose membrane filters. The water column samples were acidified in a 1:10 ratio of water to 0.1 M HCl and then filtered through 0.45 m cellulose membrane filters. The resulting filtered samples were analyzed with a copper flame method on an Atomic Absorption spectrophotometer.

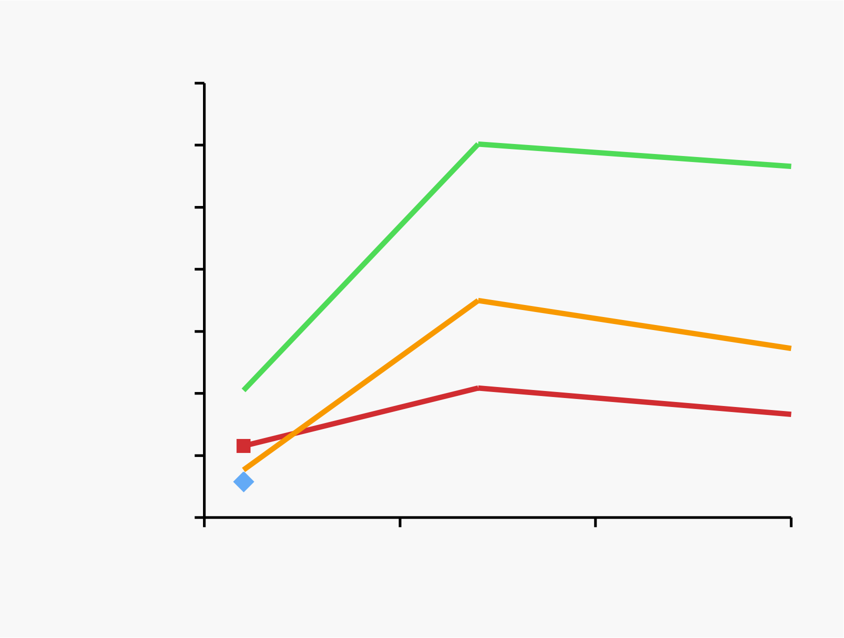
Measurements of metabolism

All organisms were given at least one day to recover from their shipping trip before initial masses and respiration readings were recorded, and they were introduced to their treatment tanks. Respiration was measured individually by placing an organism in a 30 or 60 mL glass chamber with a stopper containing either dionized water (for initial measurements) or water from their respective tank (for all subsequent measurements). For the dragonflies and leeches, the dissolved oxygen (DO) of the water was measured with a DO meter every 30 minutes over an hour; the DO in snail chambers was measured every hour for two hours. For each reading, the chamber was agitated for 20 seconds and then the DO value was recorded 20 seconds after agitation ceased. We standardized the respiration in the larger chambers to match those in the smaller chambers by doubling

Results

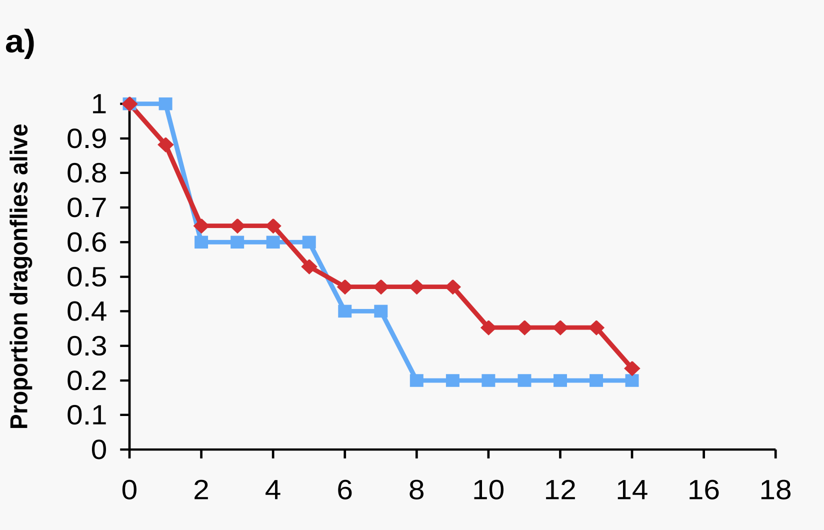
Copper concentrations

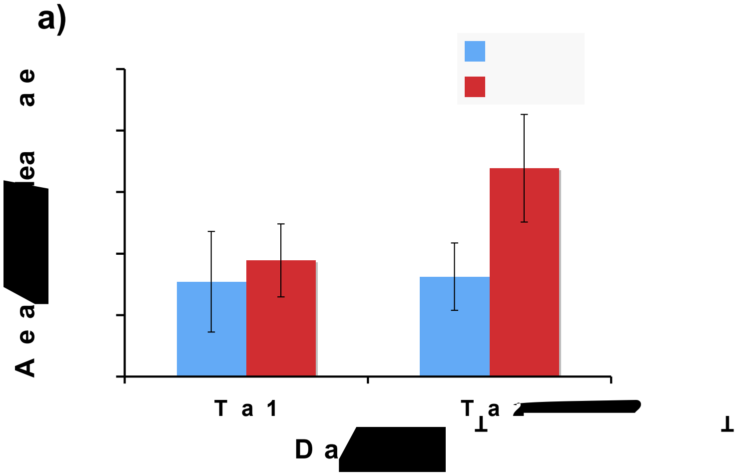
The copper concentrations in the water column decreased over a 15-day span (Figure 1a; table 1). During that same time span, the copper concentrations in the sediment increased (Figure 1b; table 2). In all three copper treatment concentrations, the sediment copper concentration dropped slightly between days 7 and 15.



daily death rates for control and copper exposed snails were 0.05 and 0.12, respectively (Figure 3b).

The control and copper death rates for leeches were similar for the first three days of the trial. Overall, however, the leeches exhibited the greatest and most significant difference between control and copper daily death rates, which were 0.006, and 0.140, respectively (Figure 3c).

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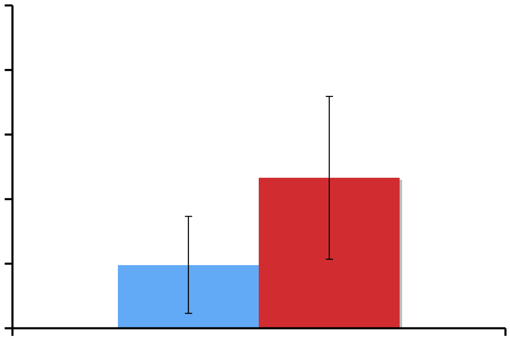

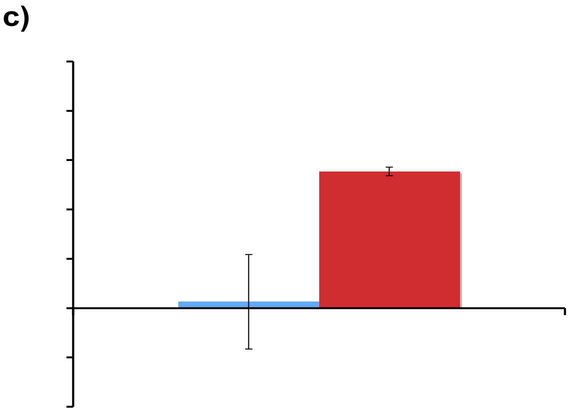
c)

Snail metabolism

Baseline respiration readings were taken on day 0, however, oxygen consumption

Snails

Baseline metabolic data (from day 0) could not be included in any of our analyses or data depictions due to evolving methodologies between days 0 and 1. On day 0, over 50% of our snails' metabolic readings were negative (exhibiting an *increase* in dissolved oxygen concentrations within their concentrations) likely because their changes in DO were measured within 60-ml chambers that were too large for the small and relatively sedentary organisms. Additionally, chambers were disrupted for readings at 10-minute intervals and their oxygen consumption was only measured over 1 hour. After extending snail metabolic readings to two hours (with only one measurement in between at 1 hour), oxygen consumption measurements were more consistently positive (exhibiting a decrease in DO) and reliable.

The copper-exposed snails in all three concentrations of copper sulfate exhibited a higher increased metabolic response after 48 hours than those snails in the control

death rate when compared to the dragonfly larvae and snails could be attributed to the leech's lack of an exoskeleton or hard shell that limits copper exposure and absorption.

The Bigger Picture

The sediments of Loughberry Lake range from 2199 to 3819 g/g copper, which is well above the New York State Department of Health's severe effect level (SEL) for metal sediment concentration of 110 g/g (NYSDEC 1999, Eliot *et al.* 2008). At metal concentrations above the SEL, the aquatic biota are at risk. In our study, the highest sediment concentration measured was 6.02 g/g in the 1300 g/L copper sulfate treatment on day seven. The copper accumulation in Loughberry Lake sediments has occurred over decades and the volume of copper sulfate applied was much greater than in our experiment, which would explain why our experimental sediment had much lower concentrations.

On average, the city of Saratoga Springs applies 206 kilograms of copper sulfate to Loughberry Lake four times during the spring and early summer (Alley 2008). Based on this average and the entire volume of the lake, the water column concentration immediately after application would be 215 g/L. While this value is less than our lowest concentration, these applications are concentrated in the north end of the lake where algal blooms primarily occur, and thus the actual water column concentration is probably much higher in this region (Eliot *et al.* 2008). It is more likely that the water column concentration in this region of the lake is closer to the 650 g/L treatment and therefore the organisms that inhabit this area may experience a brief metabolic response after each application. Considering the elevated sediment copper concentration in Loughberry Lake, it is reasonable to assume that the trend of increased mortality in our copper treatments translates to the organisms inhabiting Loughberry, specifically the northern region (Figure 2). Currently no species census of the lake exists, so populations of dragonfly nymphs, snails, and leeches may be minimal or nonexistent.

Loughberry Lake's purpose is to serve as a drinking water reservoir, so one can argue that it does not matter if the functioning of the biotic community is being severely impacted by the application of copper sulfate. However, Loughberry is not a closed

exoskeleton and may experience higher rates of copper uptake due to the increased exposure of permeable surfaces.

Future studies should focus on the effects of repeated pulses of copper sulfate, which may occur if algicide application to lakes occurs multiple times during the spring. The length of the intervals between these applications may impact whether the individuals can recover from the prior application. This information could be used in recommending a minimum period of time between applications to minimize the impact on the aquatic invertebrates. Additionally, more research should be done on the metabolic responses to copper sulfate treatment over multiple life stages, for example sensitive periods in development.

Based on the results presented in this study, there is evidence that the application of copper sulfate does impact both the metabolism and lifespan of the three organisms we studied. These consequences may be magnified in the lake due to the elevated sediment copper concentrations and concentrated applications. While our results do suggest that leeches are very copper sensitive; as an individual species, their absence would not greatly impact the ecosystem functioning. Pond snails also experienced an increased mortality in the copper treatments. Pond snails do provide an important service to the ecosystem as scrapers; they feed on detritus and assist with decomposition within the lake. Since algicide application is localized to the north end of the lake, it is possible that the negative impact of copper is limited to a small enough proportion of the pond snail population that there would be no significant detriment to the ecosystem. Further investigation of these topics will lend more evidence to whether the algicide regime should be altered or halted.

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