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**Original Article**

## Environmental Toxicology

# Fate and effects to the benthic community of a copper treatment to eradicate invasive mussels in a large western river, USA

Austin K. Baldwin[1,*], Erin M. Murray[1], Lauren M. Zinsser[1], Tyler V. King[1], Scott D. Ducar[1], India Southern[2], Theresa A. Thom[3], and Christopher A. Mebane[1]

[1]U.S. Geological Survey, Boise, ID, United States
[2]Idaho Department of Environmental Quality, Boise, ID, United States
[3]U.S. Fish and Wildlife Service, Portland, OR, United States

*Corresponding author: Austin K. Baldwin. Email: akbaldwi@usgs.gov

## Abstract

Copper-based chemical treatments are commonly used to eradicate invasive mussels in small ponds and lakes, but their use in large rivers has been limited. In 2023, in response to a detection of invasive quagga mussels, a 10-km reach of the Snake River (Idaho, USA), was treated with an unprecedented 19,300 kg of chelated copper molluscicide to a target concentration of 1,000 μg/L for 10 days. We assessed the transport and fate of the copper and its exposure and effects on the nontarget benthic community downstream. Water samples were collected at seven locations throughout the treatment period, and sediment, periphyton, and benthic macroinvertebrates were collected pre- and posttreatment. Nearly half of the original mass of copper was removed from the water column via sedimentation, sorption to algae, or biological uptake within the 10-km treatment reach and the first 15 km downstream. Even so, dissolved copper concentrations exceeded the acute toxicity threshold at least as far as 28 km downstream for more than 2 weeks. Sediment copper increased by up to 8.3-fold, exceeding the consensus-based sediment quality threshold effect concentration at several sites. Effects on benthic macroinvertebrates varied by taxa. From 0–28 km downstream, invertebrate abundances decreased 52%–94%, with gastropods among the most affected. Of the unique taxa present at these sites pretreatment, 52%–64% were not found posttreatment but were replaced by other taxa, indicating a reorganization of the base of the food web. Additionally, from 0–15 km downstream, the percentage of individuals from tolerant taxa increased two to15-fold. Findings from this study can help watershed managers plan future invasive mussel responses while protecting culturally, economically, and ecologically important nontarget species in large rivers.

**Keywords:** quagga mussels, dreissenid mussels, Snake River, macroinvertebrates, biotic ligand model

## Introduction

Dreissenid mussels, such as zebra and quagga mussels (*Dreissena polymorpha* and *Dreissena rostriformis bugensis*, respectively), are invasive aquatic species that disrupt freshwater ecosystems and cause major economic and social damage (Connelly et al., 2007; Higgins & Zanden, 2010). In the United States, Dreissenid mussels were first introduced in the Great Lakes around 1988 (May & Marsden, 1992). The subsequent decades have seen the spread of dreissenids to lakes and rivers throughout the eastern and central United States, causing dramatic shifts in food webs, collapsed fisheries, altered biogeochemistry, decreased dissolved oxygen levels, increased algal blooms, and, from 1989 through 2004, an estimated $267 million in mitigation costs to water treatment and electrical plants alone (Connelly et al., 2007; Ram & Palazzolo, 2008; Strayer, 2009). However, to date, much of the western United States remains uninfested (Brown et al., 2020). Compared with the central and eastern United States, the western United States is much more reliant on hydroelectric facilities for energy and water supply and distribution infrastructures for agriculture, industry, fish passage, and municipal uses (Bossenbroek et al., 2009; Counihan et al., 2023). The cost of mitigating for dreissenid mussels in western basins is therefore expected to be far greater than elsewhere in the United States. For example, it was previously estimated that a widespread dreissenid mussel infestation of the Snake River would cost hundreds of millions of dollars annually and have untold impacts on native species and habitats (Independent Economic Analysis Board, 2010).

Among the preferred tools for dreissenid mussel suppression and eradication are copper-based molluscicides and algaecides, which have been used primarily in small water bodies such as ponds and small lakes (Dahlberg et al., 2023; Hammond & Ferris, 2019; Lund et al., 2018). Yet the indiscriminate toxicity of copper (Brix et al., 2021) in these products presents a potential risk to nontarget organisms as well. Evaluation of the effects of copper-based algaecides and molluscicides on nontarget species has been largely limited to laboratory settings (Bishop et al., 2014; Johnson et al., 2008; Kang et al., 2022; Mastin & Rodgers, 2000;

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Murray-Gulde et al., 2002). In the natural environment, copper exposure, bioavailability, and toxicity are affected by a complex combination of biogeochemical factors such as pH and dissolved organic carbon (DOC) content, biological factors such as life stage development, and hydrologic factors such as travel time and exposure duration, which vary over space and time and complicate our ability to predict adverse biological effects (Bishop et al., 2018; Mebane, 2023). Bioavailability is also affected by the copper formulation. Several laboratory studies have shown that, compared with copper sulfate, some chelated copper formulations are more toxic to algal species (Calomeni et al., 2014; Masuda & Boyd, 1993; Stauber & Florence, 1987) but less toxic to some fish and aquatic invertebrates (Bishop et al., 2018; Murray-Gulde et al., 2002; Wagner et al., 2017). The relative lack of field studies on the effects of copper-based molluscicides and algaecides on nontarget species is a critical knowledge gap that hinders decision-making during rapid responses to invasive mussel outbreaks.

Additionally, little is known about the transport and fate of copper-based algaecides and molluscicides in large natural rivers, as their use in flowing waters has largely been limited to irrigation canals for the removal of nuisance algae (Willis et al., 2018). This represents another critical knowledge gap for watershed managers responsible for determining concentrations of copper treatments to be effective against the target species yet protective of priority species downstream. The downstream transport and fate of copper-based molluscicides and algaecides are affected by several factors, including the copper formulation; its ability to bind with dissolved organic matter, aquatic plants, algae, and sediments; and its uptake by biota (Bishop et al., 2018; Rader et al., 2019; Willis et al., 2018). For example, compared with copper sulfate, some chelated copper formulations are expected to remain in the water column for a longer period, thereby increasing exposure duration and downstream transport (Masuda & Boyd, 1993). Ultimately, copper-based molluscicides and algaecides will accumulate in sediments (Rader et al., 2019) where they may pose a toxicity risk to benthic organisms (Chen et al., 2024), but the relative partitioning to sediment versus aquatic plants/algae over space and time is not clear.

In late September 2023, the State of Idaho found larval and adult quagga mussels in the Snake River near Twin Falls (Idaho, USA) – the first known occurrence in the Columbia River Basin. To prevent the spread of quagga mussels throughout the basin, the state implemented an eradication plan to treat an approximately 10-km reach of the river with a chelated copper molluscicide (SePRO Natrix) to a target concentration of 1,000 μg/L dissolved copper (the maximum allowable concentration per the product label) for a duration of 10 days. This molluscicide contains 28.2% copper ethanolamine and 9.1% metallic copper. In total, 176,000 L of molluscicide was used in the treatment (Jeremey Varley, Idaho Department of Agriculture, personal communication, December 15, 2023), equating to 19,300 kg of copper. Because previous uses of copper-based molluscicides and algaecides had focused on ponds, small lakes, and canals, the scale of this effort—in a river flowing at 15 $m^3$/s—was unprecedented. Effects to nontarget species downstream of the treatment reach were expected, but the extent of the effects and to what downstream distance were unclear.

This rare use of a copper-based molluscicide presented an opportunity to address critical knowledge gaps related to the downstream transport and fate of copper and its exposure and effects on nontarget organisms in a large river environment. We hypothesized that copper exposure and effects on nontarget organisms would decrease with distance downstream of the treatment, as copper in the water column was diluted and sorbed to sediment and plant material. We present (a) water column copper concentrations before, during, and after the treatment at seven locations upstream, within, and as far as 28 km downstream of the treatment; (b) daily and cumulative water column copper loads at 15 km downstream of the treatment; and (c) pre- and post-treatment sediment copper concentrations; periphyton biomass, chlorophyll *a*, and pheophytin *a* concentrations; and benthic macroinvertebrate community composition, abundance, and taxa richness at seven locations as far as 104 km downstream of the treatment. The observed effects of the copper treatment on benthic macroinvertebrates are discussed in the context of toxicity estimates based on the biotic ligand model (Di Toro et al., 2001; Santore et al., 2001), median lethal doses (LC50s), and consensus-based sediment quality guidelines (MacDonald et al., 2000). We propose that effects on nontarget benthic macroinvertebrates, and especially nontarget bivalves, may be used as a proxy for effects on quagga mussels, which remain rare in the study area. This multifaceted evaluation of the transport, exposure, and biological effects of a copper molluscicide in a large, natural river will help future invasive mussel rapid responses to mitigate impacts to nontarget species in the western United States and elsewhere.

## Materials and methods

### Site selection

Sites were selected to evaluate the downstream transport, fate, exposure, and biological effects of the copper treatment. Eight sites spanned from within the treatment reach (Pillar Falls) and its downstream boundary (Km-0) to 104 km downstream of the treatment reach (Km-104; Figure 1A; Table 1). Additionally, control samples were collected upstream of the treatment at Murtaugh (sediment, periphyton, and benthic invertebrates) and Above Twin Falls (water). The Murtaugh location is 21 km upstream of the treatment reach but was the nearest accessible upstream riverine location (the river is impounded immediately upstream of the treatment reach). Detailed site information is available in Murray et al. (2025).

Different sites and media were sampled by different agencies, and not all media types were collected at every site due to limitations related to habitat, access, resources, and agency priorities (Table 1). All sediment, periphyton, and benthic macroinvertebrate samples, as well as high-frequency water samples at Km-15, were collected by the U. S. Geological Survey (USGS). Water samples at all other sites were collected by the Idaho Department of Environmental Quality (IDEQ). In some cases, USGS and IDEQ sites were separated by a short distance but have been combined to facilitate analysis. For example, water samples were collected at Clear Lakes, 2.8 km downstream of where sediment, periphyton, and benthic macroinvertebrates were collected at Buhl. Because the impact of this distance on water column copper concentrations was expected to be minor, these two sites have been combined as Km-28 Buhl/Clear Lakes for this analysis. Similarly, the upstream control is treated as a single site despite water samples having been collected at Above Twin Falls and sediment, periphyton, and the benthic macroinvertebrates collected at Murtaugh (Figure 1A). Water was not collected at the two farthest downstream sites (Km-62 and Km-104) because of resource limitations.

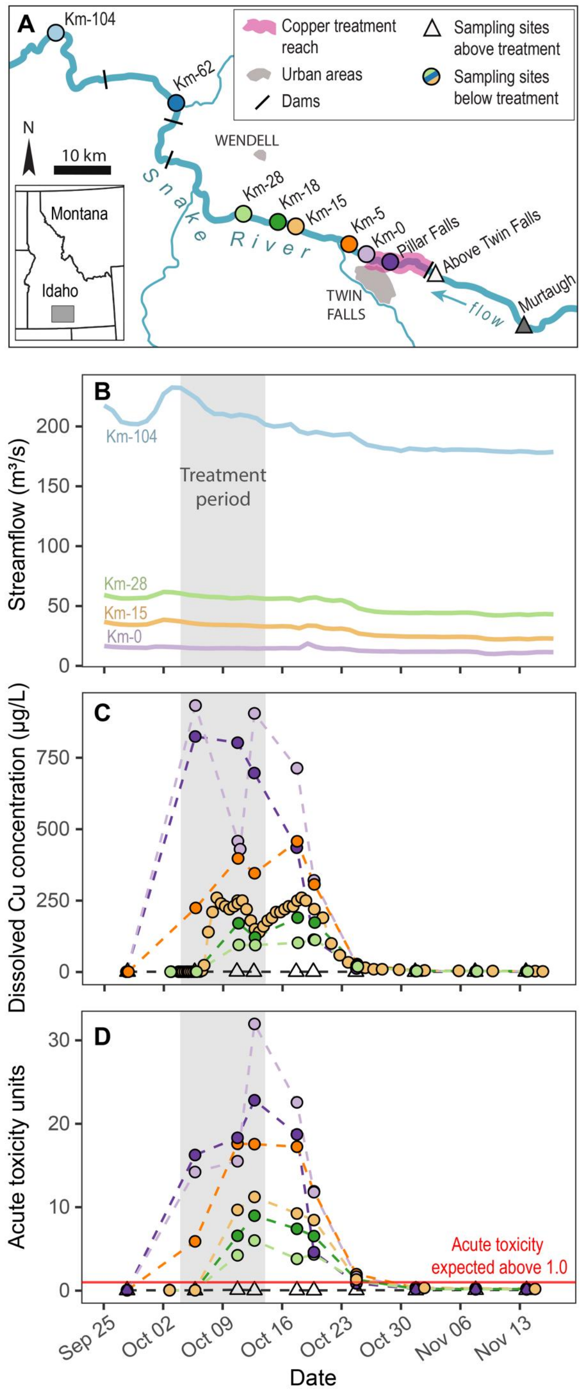


**Figure 1.** Snake River sampling locations (A) and time series of streamflow (B), water column dissolved copper concentrations (C; $n = 126$), and associated acute toxicity estimated from the biotic ligand model (D) during and after the 2023 copper treatment. Grey area represents the copper treatment period.

## Sample collection and analysis

Murray et al. (2025) provide detailed descriptions of sample collection and analytical methods as well as results for all samples associated with our study. Sample collection and analyses are described briefly below.

### Water samples

To evaluate the spatial and temporal aspects of the downstream transport of the copper plume, water samples were collected at low frequency at six sites and at high frequency at one site (Table 1). Pretreatment water samples were collected at each site in the week leading up to the treatment (September 27–October 3, 2023). At low-frequency sites, water samples were collected by IDEQ every 3 days, on average, during the first 3 weeks after the start of the treatment and then weekly through November 21, 2023, 6 weeks posttreatment. In total, 11 water samples were collected at each of the low-frequency water sampling sites. Low-frequency water samples were collected using the grab method at a depth of approximately 15 cm below the water surface in well-mixed portions of the river, where the water depths were ≥ 0.5 m. These samples were accompanied by measurements of water temperature, pH, and dissolved oxygen.

High-frequency water samples were collected at Km-15 to provide better resolution of the copper plume and enable estimation of daily copper loads 15 km downstream of the treatment. These samples were collected by USGS using an ISCO automated sampler (intake 2–3 m from bank at ∼1 m below surface; total depth at intake ∼1.3 m) and occasional grab sampling (Murray et al., 2025). The sampling frequency was every 6 hr at the start of the treatment and gradually tapered to every few days through November 15, 2023, 5 weeks posttreatment. In total, 57 water samples were collected at Km-15.

Water samples were analyzed for different constituents at different sites based on the monitoring questions. Aliquots of all water samples were filtered through a 0.7-μm glass fiber filter, preserved with nitric acid, and analyzed for dissolved copper concentrations by the Idaho State Bureau of Laboratories (Boise, ID) using U. S. Environmental Protection Agency (USEPA) Method 200.8 (U.S. Environmental Protection Agency, 1994). Half of the water samples from Km-15 ($n = 32$) were also analyzed for total copper concentrations using the same laboratory and method. Water samples from the low-frequency sites were analyzed for additional constituents required by the biotic ligand model (Di Toro et al., 2001; U.S. Environmental Protection Agency, 2007) to estimate site and sample-specific thresholds for acute toxicity of copper, including DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity. Laboratory and analytical method information for these constituents are described in Murray et al. (2025).

### Sediment samples

Sediment samples were collected before and after the copper treatment at seven sites (Table 1) to assess copper accumulation in sediments and exposure to benthic organisms. Pretreatment sediment samples were collected immediately before the treatment began (0–1 days), and posttreatment samples were collected at the same locations 6 weeks later, November 14–15, 2023. Sediment samples targeted fines in depositional areas and were composites of three or more subsamples collected from the top approximately 2 cm of the streambed using a plastic scoop. Sediments were sieved through a 2-mm stainless steel sieve to remove gravels and large organic debris and stored in plastic bags. Sediments were analyzed by SVL Analytical, Inc. (Kellogg, ID), for dry weight copper concentration using USEPA Method 6020B (U.S. Environmental Protection Agency, 2014), and for total organic carbon using ASTM International Method E1915-11 (Advancing Standards Transforming Markets International, 2013). Sediment subsamples were analyzed for grain size (sands versus fines) by the USGS Cascade Volcano Observatory (Vancouver, WA).

**Table 1.** Snake River monitoring site locations relative to the 2023 copper treatment reach.

| Site abbreviation | Site name | Location relative to treatment reach | Samples collected | | |
|---|---|---|---|---|---|
| | | | Water (low frequency) | Water (high frequency) | Sediment, periphyton, invertebrates |
| Upstream | Murtaugh/Above Twin Falls* | Upstream (controls) | X | — | X |
| Pillar | Pillar Falls | Within | X | — | — |
| Km-0 | Centennial Park | 0 km DS | X | — | X |
| Km-5 | Auger Falls | 4.6 km DS | X | — | X |
| Km-15 | Pigeon Cove | 14.5 km DS | — | X | X |
| Km-18 | Cedar Draw | 18.1 km DS | X | — | — |
| Km-28 | Buhl/Clear Lakes* | 24.7-27.5 km DS | X | — | X |
| Km-62 | Malad | 62.1 km DS | — | — | X |
| Km-104 | King Hill | 104 km DS | — | — | X |

*Note.* DS = downstream
* location of water sampling differed from other constituents.

### *Periphyton and benthic macroinvertebrate samples*

Periphyton and benthic macroinvertebrate samples were collected before and after the copper treatment at seven sites (Table 1) to assess potential effects from the treatment. As with sediment samples, pretreatment periphyton and benthic macroinvertebrate samples were collected immediately before the treatment began (0–1 days), and posttreatment samples were collected at the same locations 6 weeks later, November 14–15, 2023. Collection of periphyton and benthic macroinvertebrate samples was in the vicinity of sediment samples and followed USGS protocols described by Moulton II et al. (2002) and Murray et al. (2025). Periphyton was scraped from a known surface area from eleven or more cobbles, homogenized, and filtered. Periphyton filters were analyzed at the Bureau of Reclamation Laboratory (Boise, ID) for periphyton biomass using method B-3520-85 (U.S. Geological Survey, 2006) and for periphyton chlorophyll *a* and pheophytin *a* using method 10200-H (American Public Health Association, 1998).

Benthic macroinvertebrate samples were collected using either semiquantitative or qualitative methods (Moulton II et al., 2002), depending on the available habitats. Semiquantitative benthic macroinvertebrate samples were collected using the disturbance-removal method with a 500-μm mesh Slack sampler and fixed-area template of 0.25 $m^2$. At each semiquantitative sampling site, five locations were sampled and composited, for a total sampled area of 1.25 $m^2$. Samples were collected from riffle habitats with cobble substrates where present and otherwise from shallow runs and bank areas. Qualitative samples were collected at sites where the habitat was not conducive to semiquantitative sampling, often because a riffle was not present or the stream velocity was too slow to transport the disturbed invertebrates into a Slack sampler (i.e., Km-15, Km-104). Qualitative samples were collected over a 1-hr period using a 500-μm mesh D-frame kick net targeting each of the different habitats present within the reach. After collection, the semiquantitative or qualitative benthic macroinvertebrate samples were transferred into 1 L plastic bottles, preserved with 70% ethanol, and submitted to EcoAnalysts (Moscow, ID) for taxonomic identification and organism counts (Murray et al., 2025). Organisms were identified to the genus or species level. For each sample, abundance values were estimated based on a large/rare scan and count of up to 300 organisms, and the percentage of the sample analyzed.

## Quality assurance and quality control

Quality assurance and quality control measures included collection of water sample field replicates and blanks, and an evaluation of whether autosampler-collected water samples at Km-15 were representative of concentrations in the thalweg at that location. A total of 14 pairs of field replicates were collected, with a mean relative percentage difference of 3.5% in dissolved copper concentrations. Relative percentage differences in field replicate concentrations of other constituents are summarized in online supplementary material Figure S1. Twelve field blanks were collected for dissolved copper and other constituents using deionized water, including one blank sample collected through the autosampler at Km-15. Dissolved copper concentrations in all 12 field blanks were less than the detection limit of 0.11 μg/L. Field blank concentrations of copper and other constituents relative to environmental concentrations are summarized in online supplementary material Figure S2. At Km-15, we compared copper concentrations and field parameters at the center of the channel to those collected by the automated sampler and collocated sonde, 2–3 m off the northern riverbank. The relative percentage difference in dissolved copper concentrations between the two locations was 4.0%, and water temperature and pH were the same at both locations, indicating that samples collected by the automated sampler were adequately representative.

## Data analysis

Mean daily streamflow (cubic meters per second) data were downloaded from USGS streamgages at Km-0 (USGS 13090500), Km-15 (13093383), Km-28 (13094000), and Km-104 (13154500; U.S. Geological Survey 2024). Daily load (kilograms per day) was computed as the product of instantaneous concentration (micrograms per liter), mean daily streamflow (liters per second) and a combined unit conversion factor of 0.0864 (86,400 s/day × 1,000 L/$m^3$ × 1 kg/1,000,000,000 μg).

Cumulative total copper loads at Km-15 were estimated to understand the downstream fate of the copper injected in the treatment area. Of the 57 samples collected at Km-15, all were analyzed for dissolved copper but only 30 were analyzed for total copper. For the 27 samples with only dissolved copper concentrations, total copper was estimated based on a simple linear regression between total and dissolved copper concentrations in the 30 samples where both were available ($R^2$ of regression = 0.997). The background total copper load, estimated from the daily streamflow and a total copper concentration of 1.5 μg/L (based on average pretreatment concentrations), was subtracted from each daily load. Linear interpolation was used to estimate loads on days without samples. Daily loads were then summed to get the cumulative total copper load associated with the copper treatment.

The dissipation of copper over time and with distance downstream was computed to provide a reference for potential future treatments. For these analyses, concentration or load data were fit using a first order exponential decay formula of $y_i = C_0 * e^{(rate * t)}$, where $y_i$ is the concentration or load at day or km $i$, $C_0$ is the concentration or load, *rate* is the exponential decay rate constant, and $t$ is either time in days or distance downstream in kilometers.

The mass of copper accumulated in streambed sediments was approximated from pre- and posttreatment sediment samples. Accumulated copper (in milligrams per kilogram of dry wt), calculated as the posttreatment concentration minus the pretreatment concentration, was linearly interpolated between sampling locations at 1-km intervals along the river's length using the NHDPlus HR flowline (U.S. Geological Survey, 2022). Within the treatment reach, where no sediment samples were collected, we used the copper accumulation at Km-0. To account for variations in river width, a 5 m by 5 m grid was generated to cover the study reach as defined by the NHDPlus HR river polygon area (U.S. Geological Survey, 2022). An inverse distance weighting scheme between the centerline points was used to assign copper accumulation for each grid cell. A grid cell thickness of 2 cm was assumed to represent the thickness of sampled sediment, for a total per grid cell volume of 500,000 $cm^3$. Grid cell volume was multiplied by an assumed density representative of dry-bulk fine-grained sediments (1.3 $g/cm^3$; Lapham, 1989) to estimate its total dry-weight sediment mass, which was multiplied by its interpolated dry-weight copper accumulation to estimate the mass of copper accumulated in each grid cell. The copper masses of each cell were then summed to represent the total mass of copper accumulation in sediment. The resulting estimate of total copper mass accumulated in the sediments is considered an approximation, because the approach is based on several important assumptions. Namely, it assumes that copper is deposited over the entire streambed area (which is not accurate but estimates of depositional areas are not available); samples are representative of the river cross-section; copper accumulations vary linearly along the centerline of the river between sampling locations; copper accumulations are constant through the treatment area upstream of Km-0; and copper accumulation can be represented with 2 cm deep sediments. Despite the considerable uncertainty introduced by these assumptions, the results provide the best available estimates of the downstream fate of the copper. This approach was applied from the treatment area to Km-28, but not beyond, because dams downstream of Km-28 likely complicate deposition dynamics and further increase uncertainty.

The toxicity of dissolved copper in the water column was estimated using the biotic ligand model (BLM), which considers the effects of the water's physiochemical characteristics on the copper's bioavailability (Di Toro et al., 2001; U.S. Environmental Protection Agency, 2007). The BLM was run using the Windward Environmental Microsoft Windows Interface Ver. 3.41.2.45 (Santore & Croteau, 2019). For each dissolved copper sample, the BLM calculated a sample-specific dissolved copper criterion maximum concentration (CMC) using the coincident water temperature, pH, DOC, calcium, magnesium, sodium, potassium, sulfate, chloride, and alkalinity (see online supplementary material Figure S3). In these calculations, the default value of 10% for the humic acid fraction of DOC was used and sulfide was assumed to be negligible. The measured concentration of dissolved copper in each sample was then divided by the sample-specific CMC to get the copper acute toxicity unit. An acute toxicity unit greater than 1.0 indicated an exceedance of the CMC and an approximate threshold for copper concentrations with potential toxicity to aquatic organisms. However, because the CMC is designed to be a concentration resulting in few if any adverse effects to the majority of aquatic taxa in short-term exposures, the consequences of exceeding the CMC are not self-evident, and the CMC cannot be thought of as a tipping point between no effects and severe effects (Mebane, 2022; Santore & Croteau, 2019). Additionally, it is not clear if or how the chelation of the copper affected its bioavailability.

As an approximate guide, assuming that species used for criteria derivation have similar copper sensitivity as closely related species occurring in the wild, reductions in the abundances of sensitive species would be anticipated when concentrations exceed the CMC by twofold. When concentrations exceed the CMC by fourfold, then severe effects or even local extirpations would be foreseeable. These estimates come from the structure of the USEPA criteria derivation process. In this process (Stephan et al., 1985), the CMC is derived by calculating the concentration causing 50% mortality (LC50) to highly sensitive taxa, defined as the 5th percentile of distribution of mean taxa sensitivities at the genus level. This 5th percentile value is then divided by two to extrapolate from a concentration lethal to half the population of sensitive taxa to a concentration killing few if any individuals (Stephan et al., 1985). Conversely, in many acute toxicity tests, concentrations twofold higher than the LC50 often kill 80%–100% of a test population (Mebane, 2015). Thus, a concentration about fourfold the CMC would be expected to produce very high mortalities in taxa with sensitivities close to the 5th percentile of the species sensitivity distribution (SSD).

The toxicity of dissolved copper in the water column was also evaluated by comparing observed concentrations with an SSD for acute toxicity from copper. The LC50 toxicity values in the SSD were from Brix et al. (2021) modified for median biogeochemical conditions in the study area during the study period (pH 8.4; DOC 1.4 mg/L; hardness 220 mg/L). In the text, we refer to these modified toxicity values as “Snake River normalized”. The LC50s for quagga mussels and Asian clams (*Corbicula*) were added to the SSD from Lake-Thompson and Hoffmann (2019) and Harrison et al. (1984), respectively.

The toxicity of copper in sediments was assessed by comparison of measured concentrations to consensus-based sediment quality guidelines from MacDonald et al. (2000). The threshold effect concentration (31.6 mg/kg dry wt) represented the concentration below which toxicity was unlikely; the probable effect concentration (149 mg/kg dry wt) represented the concentration above which toxicity was likely. Toxicity to sensitive taxa may be expected at concentrations between the threshold effect concentration (TEC) and probable effect concentration.

## Results and discussion

### Streamflow

Streamflow increased from upstream to downstream through the study reach but decreased over time (Figure 1B). Mean streamflow during the study period (September 27–November 17, 2023) was 13.5 $m^3/s$ at Km-0, increasing to 29.6 $m^3/s$ at Km-15, 51.3 $m^3/s$ at Km-28, and 196 $m^3/s$ at Km-104. Much of the increase from upstream to downstream came from the many springs that discharge to the Snake River through this reach, including at least eight with mean discharges ≥ 3.0 $m^3/s$ (Johnson et al., 2002). From the beginning to end of the 6-week study period, streamflow decreased by 28% at Km-0, 41% at Km-15, 30% at Km-28, and 21% at Km-104 (Figure 1B). There was approximately 2.4 cm of rainfall during the study period (National Weather Service, 2025).

## Copper transport and fate

Within the treatment reach, dissolved copper concentrations increased from 1.1 μg/L before the treatment to a maximum of 930 μg/L during the treatment (Km-0; Figure 1C). At Km-28, the furthest downstream water sampling location, dissolved copper concentrations increased from 1.1 μg/L before the treatment to a maximum of 119 μg/L. Given the initial sampling frequency of every 3 days at most sites, the true maxima were likely greater but not captured in our samples. The decrease in dissolved copper concentrations from Km-0 to Km-28 are attributed to a combination of (a) dilution associated with the 3.8-fold increase in streamflow through this reach (Figure 1B) and (b) loss of dissolved copper from the water column via sorption to aquatic plants/algae, biological uptake, and accumulation in sediments (Bishop et al., 2018; Rader et al., 2019; Willis et al., 2018). Dissolved copper concentrations at all downstream sites remained above background for approximately 2 weeks after the treatment ended (Figure 1C).

The high-frequency water samples collected at Km-15 provide additional insights into the transport and fate of the copper plume as it moved downstream. The travel time for the leading edge of the plume to reach Km-15 was 55–61 hr (Figure 2A), equivalent to a mean velocity of approximately 0.3 km/hr (the initial copper injections were 3–6 km upstream of Km-0, therefore 18+ km upstream of Km-15). This travel time represents the integration of advection, dispersion, and transient storage in pools, eddies, and the hyporheic zone (Bencala & Walters, 1983). With the arrival of the plume at Km-15, the percentage of total copper in the dissolved phase increased from 75% (median pretreatment) to 88% (median during peak of plume), reflecting the dissolved state of the copper used in the treatment. Dissolved copper concentrations reached a maximum of 260 μg/L on October 8, decreased to 140 μg/L on October 13, then again increased to 260 μg/L on October 18. The decrease on October 13 is attributed to a 1-day pause in copper injection that took place halfway through the treatment. Following the October 18 maximum, dissolved copper concentrations decreased along an exponential decay curve with a rate constant of –0.38/day ($R^2$=0.96; see online supplementary material Figure S4A). Daily loads of total copper at Km-15 reached a maximum of 811 kg/day (Figure 2B). As was observed with concentrations, daily loads at Km-15 decreased over time following an exponential decay (rate constant –0.38/day; $R^2$=0.95; see online supplementary material Figure S4B). The total copper load that reached Km-15 (i.e., the cumulative of the daily loads above background) was 11,000 kg or 57% of the original 19,300 kg of copper injected into the river upstream (Figure 2B; Table 2). Therefore, 43% (8,300 kg) of the injected copper did not reach Km-15.

Peak dissolved copper loads also appeared to decrease exponentially from upstream to downstream (rate constant –0.03/km; see online supplementary material Figure S4C). Although this

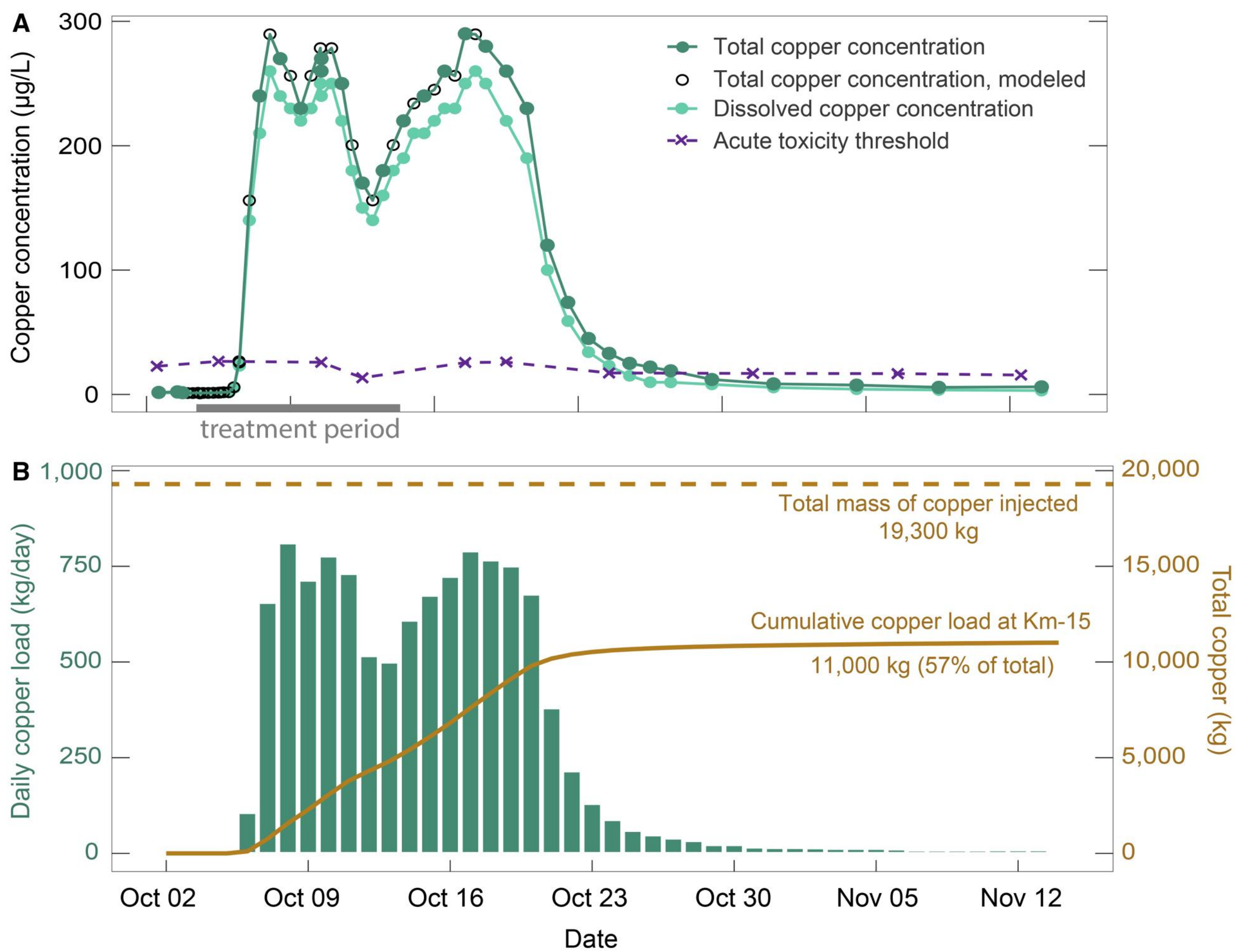


**Figure 2.** High-frequency copper concentrations (A; $n$ = 56) and daily and cumulative copper loads (B) in the water column of the Snake River at Km-15 (Pigeon Cove) during and after the 2023 copper treatment. Modeled total copper concentrations in A are estimated from a regression between dissolved and total concentrations. The acute toxicity threshold in A is the criterion maximum concentration from the biotic ligand model.

observation is based on limited data, it is supported by a previous study focused on copper algaecide dissipation in an irrigation canal (Willis et al., 2018). Extrapolating this theoretical decay rate downstream, we estimate that the dissolved copper load would return to background levels approximately 138–150 km downstream of the treatment. Future copper treatments may use this estimated decay rate as a starting point for approximating maximum expected loads (and, where streamflow is available, concentrations) at downstream locations.

Pre- and posttreatment sediment samples provide further resolution on the fate of the injected copper. Before the treatment, sediment copper concentrations at the six downstream locations averaged 10.1 mg/kg dry weight (Figure 3). Following the treatment, sediment copper concentrations at Km-0 to Km-62 increased 2.2–8.3-fold (Figure 3). The 4.1-fold increase in sediment copper concentrations at Km-62 is especially surprising given the distance and the presence of two upstream impoundments (Figure 1A) and may be explained in part by the collection of finer sediments with a greater percentage of total organic carbon in the posttreatment sample at that location (see online supplementary material Figure S5). We observed little or no accumulation of copper in sediments at Km-104. Extrapolating the observed accumulations across the entire area of the streambed, we estimate a total of approximately 1,900 kg of copper accumulated in sediments between the treatment reach and Km-15 (Table 2; see online supplementary material Figure S6). This accounts for approximately 10% of the total copper injected and 23% of the 8,300 kg of copper that was lost from the water column upstream of Km-15. This estimate implies that the remaining approximately 6,400 kg of copper lost from the water column upstream of Km-15 (33% of the total) was sorbed to aquatic plants/algae and taken up by biota (Table 2). Sorption to aquatic plants/algae was likely the dominant mechanism removing the copper from the water column based on a previous study of the fate of chelated copper in a canal (Willis et al., 2018). Extending further downstream, we estimate a total of approximately 3,300 kg of copper accumulated in sediments from the treatment reach to Km-28 (~17% of the total copper injected).

**Table 2.** Estimated fate of copper at 14.5 km downstream of the 2023 copper treatment (site Km-15/Pigeon Cove), Snake River.

| River compartment | Copper mass (kg) | % of total |
|---|---|---|
| Remaining in the water column | 11,000 | 57 |
| Accumulated in sediments | 1,900 | 10 |
| Sorbed to aquatic plants/algae and taken up by biota | 6,400 | 33 |
| Total mass of copper injected | 19,300 | 100 |

## Exposure and effects to the benthic community

### *Predicted toxicity*

Water column and sediment copper concentrations relative to toxicity thresholds suggested the likelihood of adverse effects to aquatic organisms during and after the copper treatment. In the water column, acute toxicity units based on the biotic ligand model exceeded the threshold of 1.0 for ≥15 days at least as far downstream as Km-28 (Figure 1D). Maximum acute toxicity units ranged from 32.0 at Km-0 (i.e., 32-fold greater than the criterion maximum concentration) to 6.0 at Km-28. The Snake River–normalized SSD for copper, modified from Brix et al. (2021), indicates acute toxicity to approximately 84% of the tested species at the copper concentrations observed at Km-0, and to 32% of tested species at the copper concentrations observed at Km-28 (Figure 4). Additionally, given the ≥ 15-day exposures, chronic effects may be expected in some taxa. Of the species expected to be present in the study area, Snake River–normalized LC50s were exceeded for the invertebrates *Hyalella*, *Physella*, and adult quagga mussels, as well as the fish white sturgeon, yellow perch, and northern pikeminnow. Snake River–normalized LC50s were not

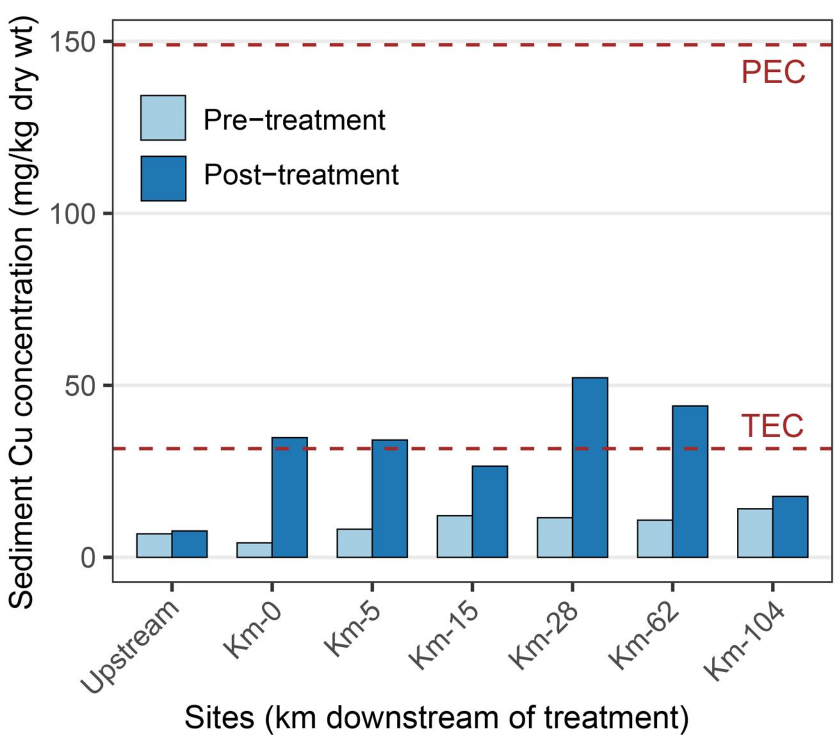


**Figure 3.** Sediment copper (Cu) concentrations in the Snake River before and after the 2023 copper treatment. PEC = probable effect concentration; TEC = threshold effect concentration.

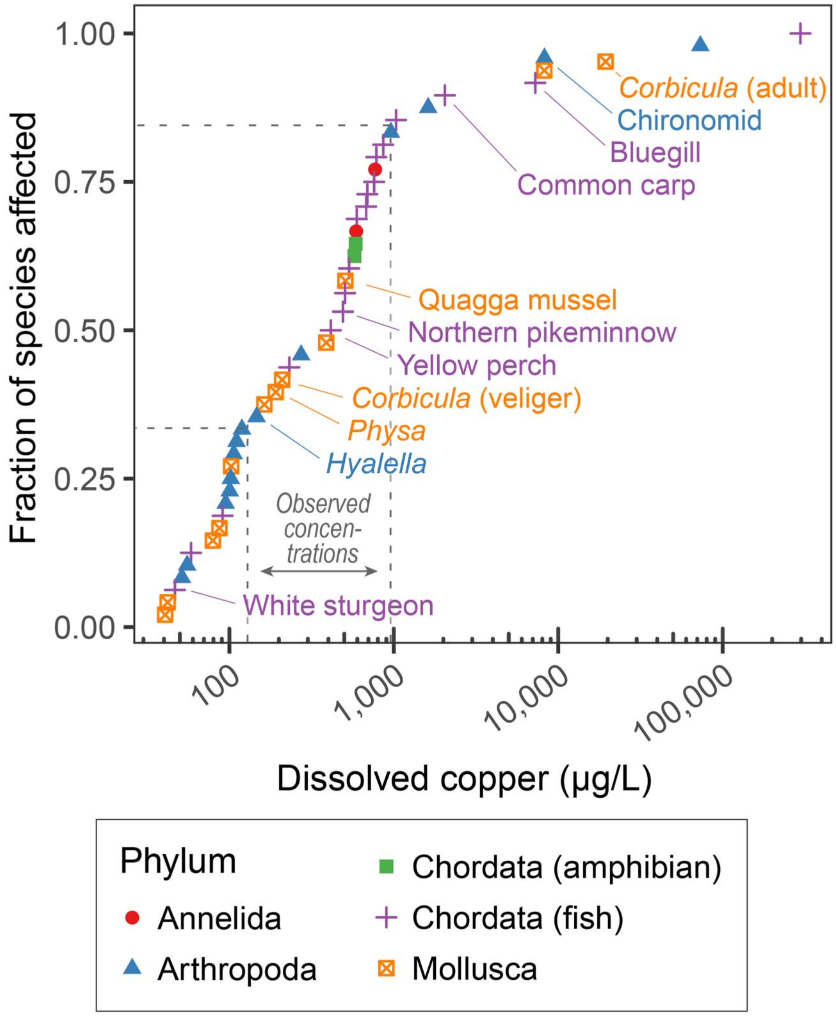


**Figure 4.** Species sensitivity distribution for Snake River–normalized acute toxicity from copper, modified from Brix et al. (2021). Values are based on the lethal concentration to 50% of individuals (LC50). Named taxa are those sampled in the current study or known to be present in the study area. Dashed lines bracket the maximum observed concentrations from Km-28 (left) to Km-0 (right). Quagga mussel data from Lake-Thompson and Hoffmann (2019); *Corbicula* data from Harrison et al. (1984). Adult *Corbicula* are shown for reference but were not included in the distribution calculation.

exceeded for adult *Corbicula*, the chironomid *Chironomus decorus*, common carp, or bluegill (Brix et al., 2021; Harrison et al., 1984; Lake-Thompson & Hofmann, 2019).

In posttreatment sediment samples, copper concentrations approached or exceeded the consensus-based TEC (MacDonald et al., 2000) of 31.6 mg/kg dry weight at all except the upstream and furthest downstream sites (Figure 3). Sediment concentrations at all sites remained below the consensus-based probable effect concentration of 149 mg/kg dry weight; MacDonald et al., 2000). Based on these results, sediment-associated toxicity may be expected at some locations but likely limited to sensitive species if present. These thresholds are estimates based on typical conditions but vary based on sediment acid-volatile sulfides, organic matter, iron and manganese oxides, aging, and other factors (Besser et al., 1996; Zhang et al., 2014).

## *Effects to periphyton*

Concentrations of periphyton biomass, pheophytin *a*, and chlorophyll *a* were sampled before and after the treatment to evaluate potential effects from the copper exposure. At the upstream control site, periphyton biomass, pheophytin *a*, and chlorophyll *a* all decreased by at least 50% in the posttreatment sample (see online supplementary material Figure S7). This likely reflected a seasonal change and confounded our interpretations of results at other sites. Downstream of the treatment, changes in periphyton biomass, pheophytin *a*, and chlorophyll *a* were mixed, with increases at some sites and decreases at others, and with no clear trends from pre- to posttreatment. However, qualitatively, we observed that periphyton at Km-0 and Km-5 easily sloughed off rocks during the posttreatment sampling, whereas scrubbing was required pretreatment. Future studies evaluating the effects of a copper treatment on periphyton may benefit from sampling at additional timepoints posttreatment and including analyses of periphyton copper concentrations and taxonomy.

## *Effects to benthic macroinvertebrates*

Effects of the copper treatment on benthic macroinvertebrates varied by site and taxa. At the upstream control site, overall macroinvertebrate abundance decreased by 69% from pre- to posttreatment (Figure 5), largely driven by reductions in *Orthocladius* chironomids, *Simulium* flies, *Petrophila*, and *Hydropsyche* (Figure 6). These reductions were likely associated with natural seasonal changes and potentially the minor reduction in streamflow (–28% at Km-0; Figure 1B) in the 6 weeks between the pre- and

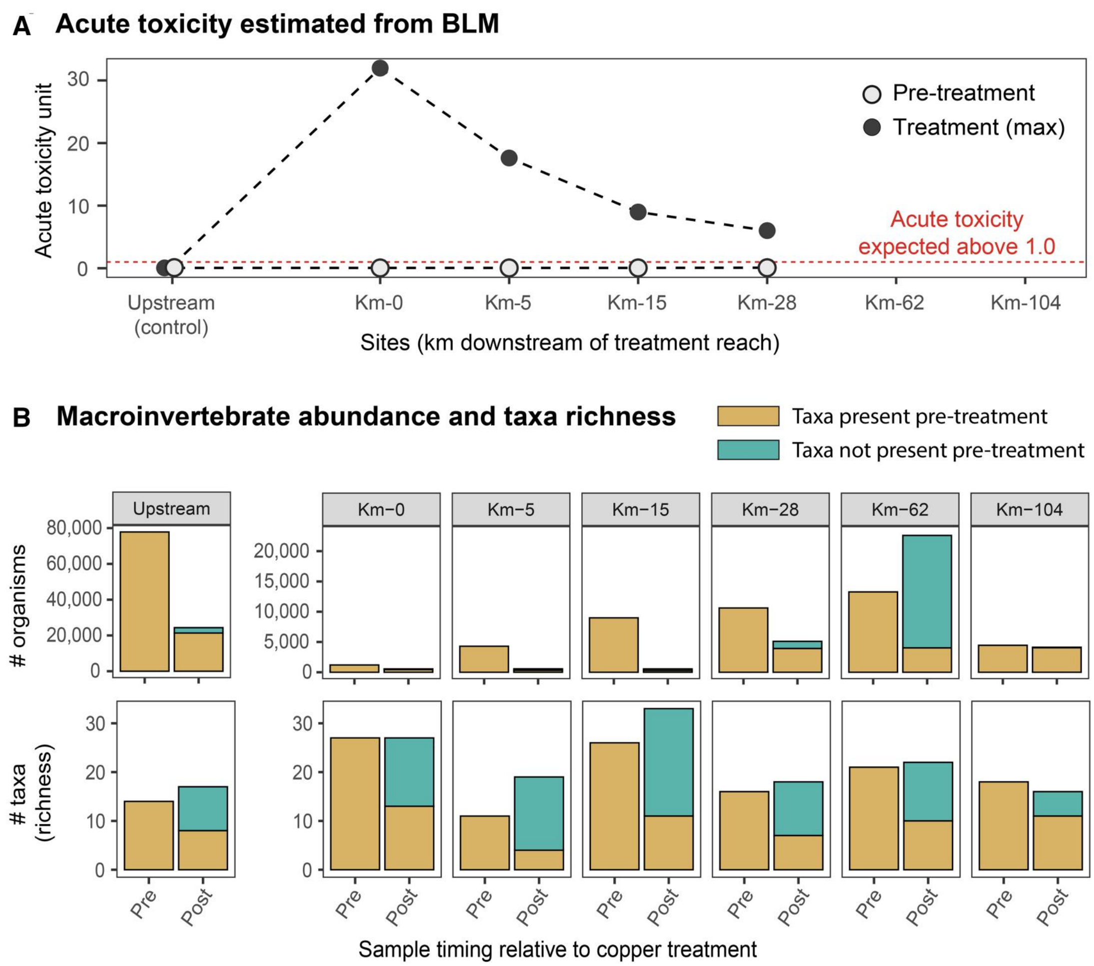


**Figure 5.** Estimated acute toxicity of copper in the water column of the Snake River (A) and observed benthic macroinvertebrate abundance and taxa richness before (pre) and after (post) the 2023 copper treatment (B). BLM = biotic ligand model.

posttreatment sampling. Although the decreases in these taxa at the control site would seem to complicate our interpretation of results downstream of the treatment, these four taxa were relatively minor in the overall abundance at downstream sites (Km-62 excepted). The downstream implications of their decreased abundance are therefore unclear. Six of the taxa in the upstream control pretreatment sample were absent in the posttreatment sample, but nine new taxa were present posttreatment (Figure 5B).

The first three macroinvertebrate sites downstream of the treatment (Km-0, Km-5, Km-15) appeared to be the most affected by the copper. Overall macroinvertebrate abundances at these sites decreased 54%–94% (Figure 5), driven by reduced numbers of *Nais* and *Turbellaria* worms; chironomids *Dicrotendipes* and *Cricotopus*; amphipods *Crangonyx* and *Hyalella*; and the gastropod *Fluminicola* (Figure 6), among others. Other taxa disappeared completely at one or more of these sites, including several gastropods (*Potamopyrgus antipodarium*, *Gyraulus*, and *Physella*; see online supplementary material Figure S8). Fewer than half of the taxa present in pretreatment samples at Km-0, Km-5, and Km-15 were found posttreatment (Figure 5B). However, small numbers of new taxa appeared in posttreatment samples, such as *Naididae* and *Paranais* worms; *Ostracods*; and numerous insects, including *Simulium*, *Sigara*, and *Orthocladius* (see online supplementary material Figure S8). These assemblage shifts were accompanied by increases of two to 15-fold in the percentage of tolerant individuals (i.e., individuals from taxa having a Hilsenhoff Biotic Index of 8 or greater; Hilsenhoff, 2017; Figure 7). Tolerant taxa in posttreatment samples included *Hyalella*, *Potamopyrgus antipodarium*, *Dicrotendipes*, and several annelids (*Quistadrilus*, *Limnodrilus*, *Nais*). Although many of these tolerant taxa had fewer individuals in posttreatment samples, their abundance relative to other taxa increased.

At Km-28, total benthic macroinvertebrate abundance decreased by 52% (Figure 5B), largely associated with decreases in the gastropod *Potamopyrgus antipodarum* and the amphipod *Crangonyx* (Figure 6). The gastropods *Fluminicola*, *Stagnicola*, and *Vorticifex* all disappeared in posttreatment samples (see online supplementary material Figure S8), echoing the apparent sensitivity of gastropods observed at Km-0, Km-5, and Km-15. Of the original unique taxa at Km-28, 56% were not found posttreatment, replaced by new taxa including *Simulium*, *Hydroptila*, *Hyalella*, and most importantly in terms of abundance, several worms (*Turbellaria*, *Limnodrilus*, *Quistadrilus*, *Helobdella*).

Total benthic macroinvertebrate abundance at Km-62 increased by 70% in the posttreatment sample (Figure 5B), driven by the appearance of large numbers of chironomids *Cardiocladius* and *Orthocladius*; and *Petrophila*, *Hydropsyche*, and *Hydroptila* (Figure 6), most of which were not found pretreatment. Their sudden appearance in such large numbers in the posttreatment sample may simply reflect a natural seasonal cycle or may have resulted from catastrophic drift from upstream sites in response to the copper exposure. Previous studies have documented catastrophic drift of various macroinvertebrates after chemical spills

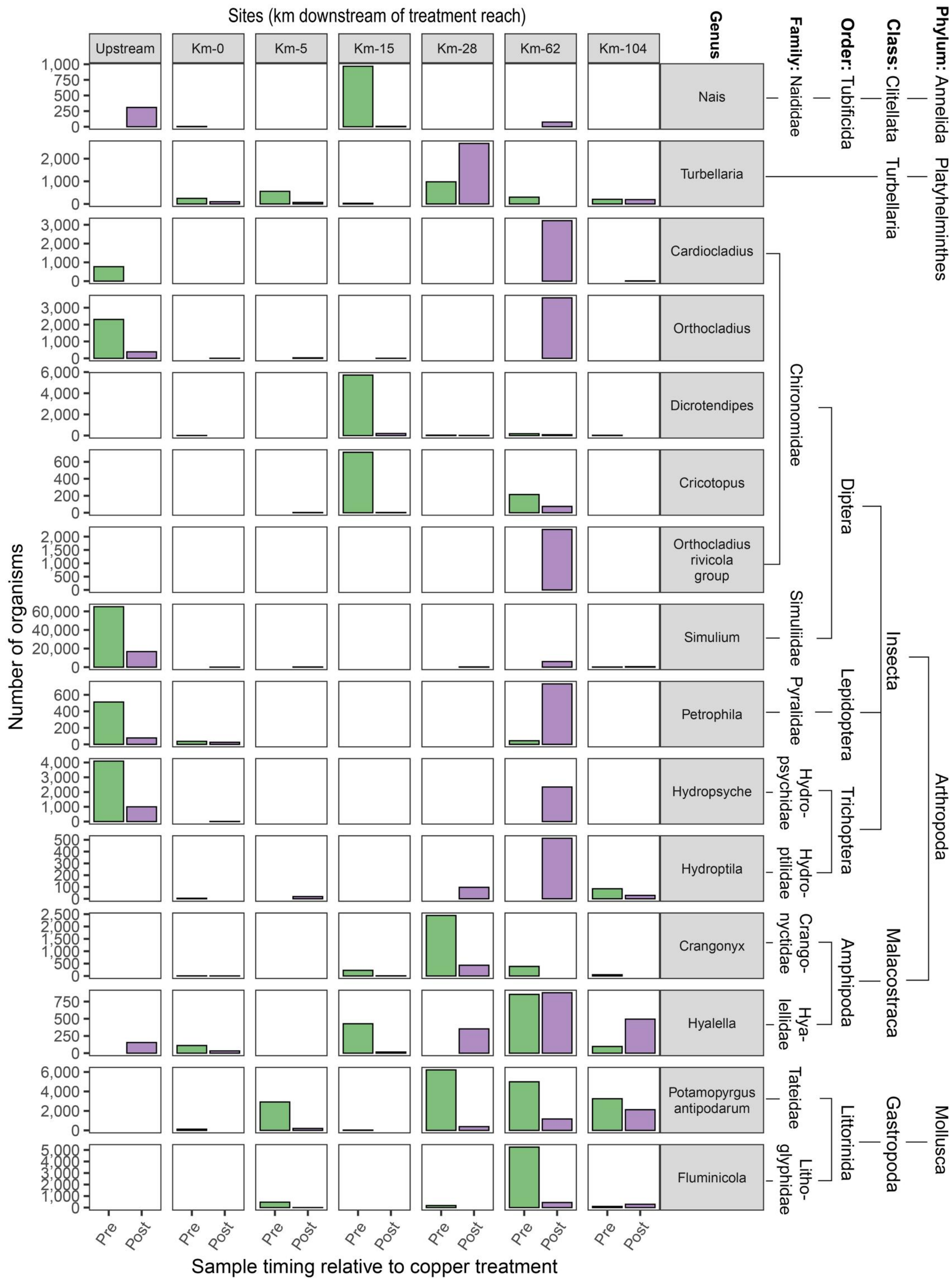


**Figure 6.** Abundances of dominant benthic macroinvertebrate taxa in the Snake River before (pre) and after (post) the 2023 copper treatment. Taxa are limited to those comprising 90% of the total abundance across all downstream sites (Km-0 to Km-104). Where no bar is shown, value is zero.

(Beketov & Liess, 2008; Davies & Cook, 1993), including pulses of copper at concentrations equivalent to those in the current study (Taylor et al., 1994). If these insects did drift to Km-62, it was from unsampled upstream areas because they were rare or absent in pretreatment samples from the studied sites (Figure 6). Half of the unique taxa present pretreatment at Km-62 were not found posttreatment, including *Turbellaria* worms, *Crangonyx*, and numerous insects (see online supplementary material Figure S8). Gastropods were also widely affected at Km-62, with decreases of 77% in *Potamopyrgus antipodarum*, 92% in *Fluminicola*, and 100% in *Vorticifex* (Figures 6, see online supplementary material Figure S8). At Km-104, both overall abundance and taxa richness were relatively stable from pre- to posttreatment (Figure 5B), and effects to individual taxa, including gastropods, were not apparent (Figure 6). Water column copper exposure at Km-62 and Km-104 is not known.

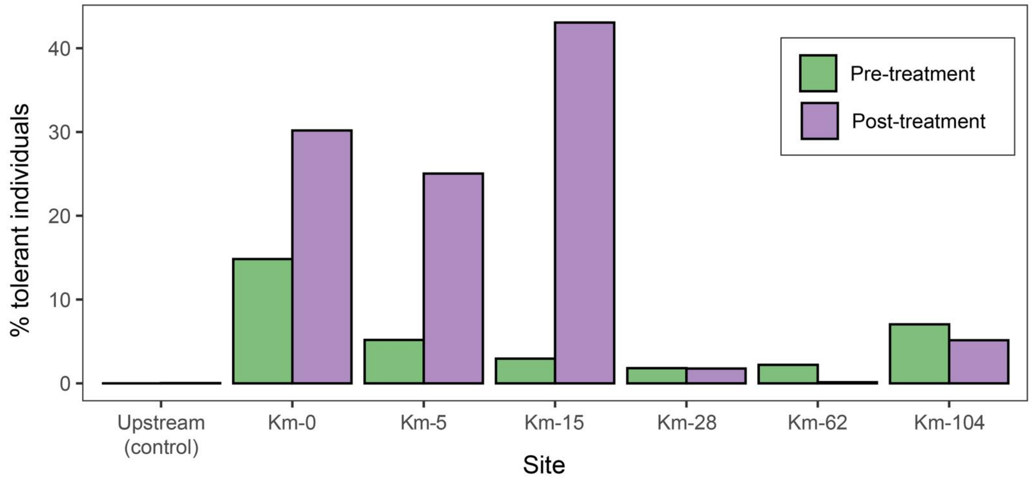


**Figure 7.** The percentage of individual Snake River benthic macroinvertebrates from tolerant taxa before and after the 2023 copper treatment. Tolerant taxa are those with a Hilsenhoff Biotic Index of 8 or greater (Hilsenhoff, 2017). Sites are defined in Table 1.

### *Predicted toxicity versus observed effects*

Dissolved copper concentrations exceeded the BLM-based acute toxicity unit of 1.0 at Km-0 through at least Km-28 and was not measured further downstream (Figure 5A). Effects in many taxa appeared to reflect this predicted toxicity, including several gastropods, *Crangonyx*, some chironomids (e.g., *Dicrotendipes*, *Cricotopus*), and *Nais* and *Prostoma* worms (Figure 6, see online supplementary material Figure S8). *Hyalella* and *Turbellaria* worms also decreased at Km-0 to Km-15 but increased at Km-28. Yet other taxa appeared to be unaffected. These results are expected given the range of copper tolerances among different taxa (Figure 4). The BLM acute toxicity unit threshold of 1.0 is meant to protect the most sensitive taxa; more tolerant taxa would be unaffected at this threshold.

Changes in the abundance of individual taxa generally appeared to follow predicted toxicity based on Snake River–normalized LC50s, as well. Taxa with known copper LC50s were limited, but included *Hyalella*, *Physa* (a genus in the family *Physidae*, included for comparison to *Physella*), *Corbicula*, and the chironomid *Chironomus decorus* (the latter not found at our sites but included for comparison to other chironomids; Figure 4). The Snake River–normalized copper LC50 for *Hyalella* (146 μg/L; Brix et al., 2021) was exceeded at two sites where *Hyalella* were present in pretreatment samples (Km-0 and Km-15). At both sites, *Hyalella* decreased in abundance by 71% and 96%, respectively. *Hyalella* also decreased by 77% at Km-28, where the Snake River–normalized LC50 was approached but not reached (maximum 114 μg/L). The Snake River–normalized copper LC50 for *Physa* (191 μg/L; Brix et al., 2021) was exceeded at Km-0, Km-5, and Km-15, and *Physella* abundances decreased from 21–85 individuals in pretreatment samples to no *Physella* in posttreatment samples (see online supplementary material Figure S8). At Km-28, where the Snake River–normalized LC50 was not exceeded, *Physella* decreased by 77% but were still present posttreatment. The Snake River–normalized LC50s for adult *Corbicula* (19,400 μg/L; Harrison et al., 1984) and *Chironomus decorus* (8,240 μg/L; Brix et al., 2021) were not exceeded at any site, and abundances of *Corbicula* and chironomids followed no clear pattern from pre- to posttreatment (see online supplementary material Figure S8).

Copper is presumed to have played a primary role in the observed losses in invertebrate abundance and shifts in assemblage in posttreatment samples, but effects from other factors cannot be discounted. For some taxa, the loss in abundance could be attributed to the changing season or life stage, or, for winged adults such as chironomids, active relocation in response to the unfavorable conditions (Thompson et al., 2016). Yet for taxa confined to the river (e.g., amphipods, gastropods, worms), the copper exposure is the most likely explanation for the loss in abundance, either via mortality or exodus to more favorable conditions via catastrophic drift (Beketov & Liess, 2008; Davies & Cook, 1993).

The apparent effect of the copper on gastropods as far as 62 km downstream of the treatment (see online supplementary material Figure S8) is especially striking and potentially consequential for federally listed threatened or endangered snails that live or may live in this reach. A population of threatened Bliss Rapids snails (*Taylorconcha serpenticola*) inhabits the Snake River at approximately Km-50 (Upper Salmon Falls Dam/Dolman Rapids; U.S. Fish and Wildlife Service, 2024), and endangered Banbury Springs limpets (*Idaholanx fresti*) inhabit a river-influenced springs area around Km-43 (Thousand Springs; U.S. Fish and Wildlife Service, 2025a). The endangered Snake River Physa (*Physa natricina*) has historically occurred throughout this reach (U.S. Fish and Wildlife Service, 2025b) but its distribution in recent years is unclear (Alyssa Bangs, U.S. Fish and Wildlife, personal communication, January 10, 2025). Additionally, the western ridged mussel (*Gonidea angulata*; not a gastropod but a bivalve), currently undergoing review for potential listing under the Endangered Species Act, is also known to live in this reach. Bliss Rapids snails are sensitive to copper (28-day LC50 15 μg/L, not Snake River–normalized; Besser et al., 2016), but posttreatment monitoring found no clear adverse effects of the copper treatment on the population around Km-50 (Idaho Power Company, 2024). Copper tolerances and the effects of the copper treatment on the Banbury Springs limpet, Snake River Physa (if present), and western ridged mussel are not known. Future invasive mussel responses may need to weigh the potential toxicity of copper to these federally protected species (and in the case of the western ridged mussel, loss of host fish) against the potential loss of their habitat if invasive mussels infest the river.

Impacts of the copper treatment on fish, although not the focus of this study, were also mixed and generally followed Snake River–normalized SSD-based predictions, where available (Figure 4). Fish surveys within and downstream of the treatment area were performed before and after the treatment by Idaho Fish and Game. Posttreatment mortalities within the treatment area were estimated at near 100% for northern pikeminnow, yellow perch, white sturgeon, and largescale suckers (Idaho Fish and Game, 2023). Common carp were moderately affected, and largemouth bass, smallmouth bass, bluegill, and green sunfish were generally unaffected. Posttreatment surveys also found increased fish populations at downstream locations (compared to pretreatment), suggesting some fish were able to flee to areas where the copper was adequately diluted. The effects of the fish kill on piscivores, such as river otter and osprey, are uncertain, as are the effects of benthic macroinvertebrate community losses or shifts on the surviving fish and other organisms.

### *Recovery and implications*

The long-term effects of the copper treatment on the Snake River ecosystem are uncertain. Although the total number of taxa were similar or even increased posttreatment at Km-0 to Km-28, the taxa assemblages were changed. Fewer than half of the unique taxa present in pretreatment samples were found posttreatment (Figures 5, see online supplementary material Figure S8), and, at Km-0 to Km-15, the percentages of individuals from tolerant taxa increased by two–15-fold (Figure 7). New taxa appeared in posttreatment samples, presumably filling some of the niches of those that disappeared. Previous studies have noted similar results following a major contamination event. Following an accidental insecticide spill, Thompson et al. (2016) observed that the loss or decrease in abundance of some taxa was compensated by an increase in other more tolerant taxa or taxa able to avoid the affected water and quickly repopulate the river (e.g., winged adult chironomids). These observations were 2 months post-spill, therefore, not too different from the timeframe in the current study.

The reorganization of the benthic community could have lasting effects on the food-web structure of the Snake River. Although some taxa will likely recover quickly (i.e., weeks to months; Mackay, 1992; Reiber et al., 2021), a full recovery of the benthic macroinvertebrate community may take many years. In a review of 50 case studies of recovery of freshwater invertebrate communities following disturbances, Mebane (2022) found that the median recovery period was 1 year, and recovery occurred within 5 years in 82% of the cases. For taxa that were locally extirpated, rate of recolonization is largely dependent on connectivity with upstream refugia and the downstream drift of organisms from these areas (Mackay, 1992; Matthaei et al., 1996). The current study area is not well-connected to upstream refugia: a reservoir lies immediately upstream of the study area, likely impeding the drift of many benthic species, and most of the inflows to the study area are from springs within the canyon.

The recovery of the Snake River ecosystem also depends on the eradication or spread of the quagga mussels. Veliger tows and environmental DNA sampling by the Idaho Department of Agriculture 1 year after the 2023 copper treatment revealed that quagga mussels were reduced in number but still present in the treatment reach (Idaho Department of Agriculture, 2024). In laboratory exposures, Lake-Thompson and Hofmann (2019) reported 100% mortality of quagga mussels after 9-day exposure at 360 μg/L (508 μg/L normalized for Snake River geochemistry). This concentration and duration of exposure were both exceeded in the treatment area (Figure 4). The reason for the quagga mussels' survival is therefore unclear but may be due to refugia created by imperfect mixing (laterally or at depth), areas of copper dilution by groundwater seeps and springs, or pools that are only connected to the main channel at higher streamflows (although disconnected pools were targeted for spot treatments). During future treatments, measuring copper concentrations at different locations and depths in the water column may help clarify the question of refugia. It is also possible that there was a reproducing population of quagga mussels upstream of the treatment area. A second copper treatment of the river (and disconnected pools) was carried out in October 2024, with the treatment reach extended further upstream. The results of the 2024 treatment are pending, and additional treatments may follow. Whether or not these treatments are successful at eradicating quagga mussels in the Snake River, introductions of invasive dreissenid mussels will continue in uninfested rivers of the western United States and elsewhere. Watershed managers will continue to face difficult decisions in how to respond, balancing the ecological, cultural, and economic risks of a dreissenid infestation with the protection of nontarget priority species. Results from this study may help inform these decisions by providing a better understanding of the downstream transport, fate, exposure, and effects of a chelated copper molluscicide in a large western river.

## Supplementary material

Supplementary material is available online at *Environmental Toxicology and Chemistry*.

## Data availability

All data are available in Murray et al., 2025: https://doi.org/10.5066/P1O3KXVM.

## Author contributions

Austin K. Baldwin (Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Visualization, Writing—original draft, Writing—review & editing), Erin M. Murray (Conceptualization, Data curation, Investigation, Methodology, Resources, Validation, Writing—review & editing), Lauren M. Zinsser (Conceptualization, Formal analysis, Investigation, Methodology, Project administration, Resources, Supervision, Validation, Visualization, Writing—review & editing), Tyler V. King (Formal analysis, Investigation, Visualization, Writing—review & editing), Scott D. Ducar (Formal analysis, Investigation, Visualization, Writing—review & editing), India Southern (Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Writing—review & editing), Theresa A Thom (Funding acquisition), and Christopher A. Mebane (Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Supervision, Validation, Writing—original draft, Writing—review & editing)

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## Conflicts of interest

The authors report no conflicts of interest.

## Disclaimer

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S.

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