Modeling Frequency of Occurrence of Toxic Concentrations of Zinc and Copper in the Upper Animas River

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ABSTRACT

Scientists participating in the USGS Abandoned Minelands Initiative have quantified metal concentrations and loadings from mining-related and natural background sources in the upper Animas River of southwestern Colorado, with the goal of guiding remediation decisions by federal land-management agencies. We have compared site-specific toxicity thresholds with frequencies of dissolved metal concentrations in stream water to evaluate the contributions of zinc and copper to toxic effects in fish and aquatic invertebrates in the upper Animas. Median lethal concentrations (LC50s) of zinc and copper were determined for fathead minnows, *Pimephales promelas*, and amphipods, *Hyalella azteca*, from seven-day toxicity tests under water quality conditions typical of the upper Animas. Frequency analysis based on hysteresis models was used to predict seasonal occurrence and daily probabilities of dissolved zinc and copper concentrations at two gaging stations near Silverton, Colorado. Results of these analyses indicate that dissolved zinc concentrations at both locations frequently exceed 7-day LC50s for amphipods, and occasionally exceed zinc LC50s for fathead minnows. In contrast, copper concentrations rarely approach lethal levels for either species. Model results are consistent with recent on-site toxicity tests with these two species. Comparison of modeled zinc and copper concentrations with published toxicity thresholds for brook trout, *Salvelinus fontinalis*, suggest that both zinc and copper contribute to chronic toxicity in resident trout in the upper Animas.

INTRODUCTION

The streams of the upper Animas River watershed receive loadings of heavy metals in water, colloids and sediment from numerous mines and associated waste deposits, as well as from natural sources in highly-mineralized portions of the watershed (Church et al. 1997). Elevated metal concentrations and other impacts associated with mining have resulted in reduction or elimination of stream fish and invertebrate communities.

The USGS Abandoned Mineland Initiative (AMLI) designated the upper Animas watershed as one of two study areas for development of scientific approaches to guide remediation of the impacts of historic mining activities (Nimick and von Guerard 1998). Studies conducted as part of the AMLI have characterized metal concentrations and loadings from mining and from natural background sources; tranformations of metals in stream ecosystems; and the bioavailability, toxicity, and habitat impacts of metals in the upper Animas.

The goal of the AMLI is to assist efforts by federal land management agencies and local stakeholders to plan and evaluate remediation efforts. Remediation with the goal of recovery of stream ecosystems requires an understanding of the mechanisms by which metals adversely affect stream biota. Zinc and copper can affect aquatic biota by a variety of mechanisms, including both acute (short-term) and chronic toxic effects of aqueous metals (USEPA 1985, 1987). Chronic toxicity can also result from exposure to metals in sediment (Kemble et al. 1994), and diet (Woodward et al. 1994). Establishing realistic thresholds for acute and chronic toxicity is necessary to determine the extent of remediation required for improvement of aquatic communities.

The flow regime of the upper Animas watershed is typical of montane stream systems, with high runoff volumes in the spring and considerably lower discharge in winter. This annual pattern of stream discharge drives trace metal concentrations in the water column. Concentrations of dissolved zinc and copper in the upper Animas River follow a hysteritic pattern that complicates modeling, as solute concentrations at a particular discharge differ between the rising and falling limbs of the hydrograph. A hysteresis model such as that suggested by Aulenbach and Hooper (1994) can use seasonality to account for similar volumes of water that contain differing concentrations of dissolved metals.

We modeled the frequency of toxic concentrations of zinc and copper in the Animas River at USGS gaging stations upstream and downstream of two tributaries, Cement and Mineral Creeks, which drain highly-mineralized watersheds with many abandoned mines (Figure 1). The extensive record of discharge and dissolved metal concentrations at these sites has been used to develop reliable models of recurrence frequency, probability of exceedance,

and duration of dissolved metal concentrations at these sites (Leib et al. 1998). Toxic concentrations of zinc and copper were determined in test waters with hardness and other ionic constituents similar to water in the upper Animas. Matching the ionic composition of test waters with site water is important for developing accurate estimates of toxicity thresholds, because metal toxicity can be strongly affected by site-specific water quality factors, such as pH, hardness, and other dissolved constituents (Diamond et al. 1997).

METHODS

Modeling Dissolved Metal Concentrations

Water quality samples were in 1997-98 at two streamflow gages on the upper Animas River (Figure 1). Gage A68, Animas River at Silverton Colorado, is located upstream of the confluence of Cement Creek. Gage A72, Animas River Below Silverton Colorado, is located downstream from the confluences of both Cement and Mineral Creeks. Samples were collected monthly during low-flow and bi-weekly or weekly during spring runoff in order to characterize variation of trace metal concentrations throughout the annual hydrographs at the current level of remediation activity in the watershed.

Zinc and copper concentrations were estimated from this record using histeritic multiple linear regression models (Aulenbach and Hooper 1994). These models were based on discharge and date because a continuous record of each is available at the sampling sites. Although other variables might improve model predictions, a continuous record is needed for frequency analysis.

The frequency analysis used in this report is similar to that of traditional flood frequency analysis. Mean daily discharge records (1992-1993, 1995-1997) were grouped into annual data sets, each representing a seasonal cycle. Each year was distributed using a log Pearson type III technique, which helps to account for differences in water volumes during average, wet and dry years (Interagency Advisory Commitee on Water

Data 1992). Metal concentrations corresponding to these normalized discharge values were estimated using the hysterisis models. These results were averaged to estimate the daily probability that a given concentration of dissolved zinc or copper would be equaled or exceeded. Seasonality of dissolved zinc and copper was illustrated using averages of daily discharge records. This average hydrograph was converted to zinc and copper concentrations using the hysteresis models.

Toxicity Testing

The toxicity of copper and zinc to two sensitive laboratory test organisms was determined in a reconstituted water that simulated the water quality conditions in the Animas River. The reconstituted formula recommended by ASTM (1996) was modified to achieve a mixture of major ions representative of conditions in the Animas River (sulfate=100 g/L, chloride 10 mg/L, total hardness 114 mg/L, total alkalinity 16 mg/L, conductivity 255 umhos/cm). Exposure solutions containing zinc ($ZnSO_4.7H_2O$) and copper ($CuSO_4.5H_2O$) were prepared daily from stock solutions, with a series of exposure concentrations prepared by 50% serial dilutions. Metal concentrations in exposure solutions were verified by ICP-mass spectroscopy.

Toxicity tests were conducted with newly-hatched (<48 hour posthatch) fathead minnows, *Pimephales promelas*, and 7-14 day old amphipods, *Hyalella azteca*, following standard methods for testing of effuents and receiving waters (USEPA 1994). Groups of 10 minnows were tested in 500-mL test water in one-liter beakers, with two replicate beakers per concentration. Groups of 10 amphipods were tested in 250-mL test water in 300-mL beakers, with three replicate beakers per concentration. The number of surviving animals in each beaker was recorded after seven days. Median lethal concentrations for each species and each metal were determined by the moving average method (USEPA 1994).

Toxicity data derived from literature sources were used to evaluate sensitivity of several trout species to zinc and copper. Brook trout, *Salvelinus fontinalis*, have been introduced into the upper Animas watershed and are the the most widespread fish species in the watershed. Cutthroat trout, *Onchorhynchus clarki*, are native to the watershed and occur mainly in tributaries

Table 1. Median lethal concentrations (LC50) for copper and zinc to fathead minnows (*Pimephales promelas*) and amphipods (*Hyalella azteca*) in 7-day exposures in 'Animas' reconstituted water.

Species	7-d LC50, ug/L, and (95% confidence interval)	
	Zn	Cu
Amphipod	159 (125-200)	58 (48-76)
Fathead minnow	699 (550-890)	33 (25-45)

Table 2. Acute LC50s and chronic toxicity values (in parentheses) for copper and zinc toxicity to three species of trout. Values were calculated for moderately hard water (120 mg/L), based on from USEPA (1985, 1987), except (*) from Nehring and Goettl (1974).

Species	Acute and (Chronic) toxicity values, ug/L	
	Zn	Cu
Brook trout, *S. fontinalis*	4791 (855)	251 (17.4)
Cutthroat trout, *O. clarki*	1529 (--)	151 (--)
Rainbow trout, *O. mykiss*	1572 (603)	98 (11.4)

that are less affected by mining. The closely-related rainbow trout, *Onchorhynchus mykiss*, has been stocked in portions of the watershed, although it has not been found in recent surveys. Acute LC50s and thresholds for chronic toxicity of zinc and copper to brook trout and rainbow trout were obtained from water quality criteria documents (USEPA 1985, 1987). Acute LC50 values for cutthroat trout were obtained from Nehring and Goettl (1974). Acute toxicity values were adjusted for a water hardness typical of the Animas (120 mg/L as CaCO3) using exponential regression equations (USEPA 1985, 1987).

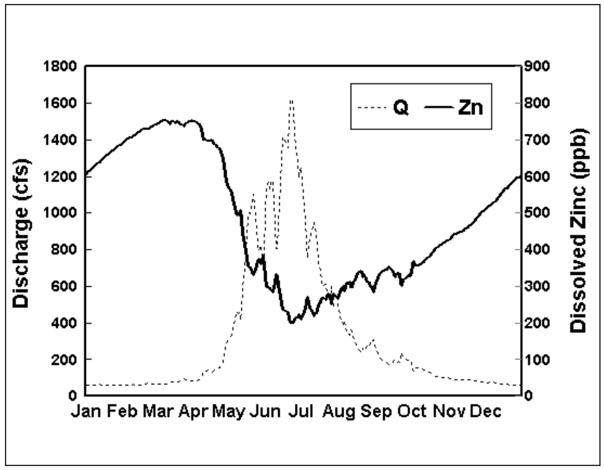
RESULTS AND DISCUSSION

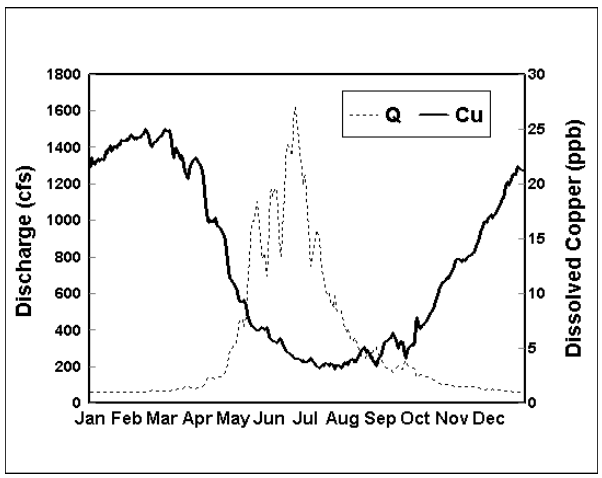
Toxicity of Zinc and Copper

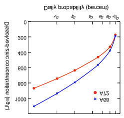
The toxicity of zinc and copper differed widely between the species tested (Table 1). Amphipods were about four times more sensitive to zinc than were fathead minnows. The relative sensitivity of the two species to copper was reversed, with fathead minnows more sensitive than amphipods. The responses of these species serve as useful benchmarks relative to toxicity thresholds for fish and benthic invertebrates that occur in the Animas watershed, or that may be restored to the watershed after remediation. Mortality of *H. azteca*, determined from seven-day exposures, is a more sensitive response to zinc than chronic toxicity to trout, determined from early life-stage or full life-cycle exposures (Table 2). The high sensitivity of amphipods to zinc is comparable to that of other sensitive taxa of invertebrates, which can be eliminated by even moderate metal pollution (USEPA 1987). The lethal concentration of zinc for fathead minnows in seven-day tests was similar to the chronic toxicity threshold for rainbow trout, which are highly sensitive to metal toxicity. Lethal concentrations of copper for fathead minnows were intermediate between acute and chronic toxicity values for all three trout species.

Frequency of Toxic Concentrations of Zinc and Copper

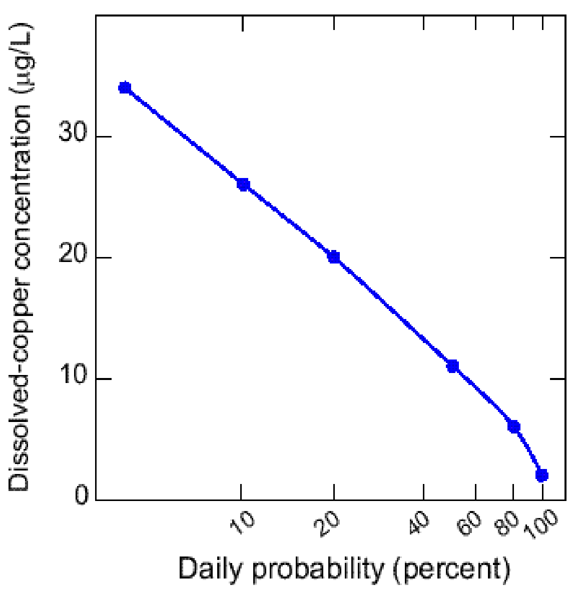
Hysteresis models based on discharge and season were developed for dissolved zinc at both A68 and A72 and for dissolved copper at A72. Coefficients of determination (r^2) indicated that these models accounted for 82% to 90% of the variation in dissolved metal concentrations. The model for copper at A68 was not used because of its low predictive ability (r^2<0.4). Predicted concentrations of dissolved zinc and copper at







A72 are plotted vs. 1997 discharge in Figures 2 and 3. Although concentrations of dissolved zinc averaged nearly ten times greater than dissolved copper, concentrations of both metals followed similar patterns of variation with stream discharge and season. Concentrations increased gradually to maxima during the winter low-flow period (November-March). Lowest concentrations occurred during the peak snowmelt period in early summer, and low concentrations persisted during the low-flow period of late summer.



Dissolved metal concentrations predicted over five water years were used to estimate the daily probability of exceeding toxic concentrations of dissolved zinc and copper (Figs. 4 and 5). Elevated concentrations of dissolved zinc represented a greater hazard of toxicity to amphipods and fathead minnows than did dissolved copper. Probabilities of exceeding zinc concentrations lethal to amphipods approached 100% at both A68 and A72 and probabilities of exceeding zinc concentrations toxic to the fathead minnows were approximately 40% at A68 and 15% at A72 (Fig. 4). In contrast, the probability of exceeding copper concentrations lethal to either species at A72 was close to zero (Fig. 5). Although no model of dissolved copper frequency was produced for A68, the risk of copper toxicity is even less at this site, which is located upstream of significant copper loadings from Cement and Mineral Creeks (Fig. 1).

Results of on-site toxicity tests conducted with the same two species in late summer of 1998 are consistent with modeled probabilities of toxicity. Mortality of amphipods approached 100% during 14-day exposures to stream water from A68, A72 and three other sites in the Animas watershed. Little or no mortality of fathead minnows was observed during 7-d exposures to water from either A68 or A72 (unpublished data; J. Besser). These results correspond closely to typical dissolved metal concentrations at A72 during late summer (Figs. 2 and 3)

Limits on Stream Biota of the Animas Watershed

Our results indicate that zinc toxicity is an important factor limiting biological communities in the Animas River near Silverton. High frequencies of dissolved zinc concentrations, which are toxic to invertebrates such as *H. azteca*, are consistent with observations of reduced abundance and low taxonomic diversity of invertebrates at the two study sites and elsewhere in the watershed. The occurrence of adult brook trout at A68 and in upstream reaches of the

Animas during the 1990s (unpublished data, Colorado Division of Wildlife) is also consistent with a low probability (about 10%) of zinc concentrations associated with chronic toxicity in this species. However, periods of chronic zinc toxicity during winter low-flow periods may explain the low densities and poor reproductive success of this population. The greater sensitivity of cutthroat trout to zinc (Table 1) is consistent with the distribution of this species, which occurs in less-contaminated tributaries, but is found only rarely at A68 or elsewhere in the Animas. Station A72 supported a depauperate biological community (no fish and few invertebrates) during the study period, although dissolved zinc concentrations were less at this site than at A68. This contrast suggests that factors in addition to dissolved zinc concentrations influence stream biotic communities in the study reach. Dissolved copper concentrations are greater at A72 than at A68, due to inputs from Cement and Mineral Creeks, and exceed chronic toxicity thresholds for trout for significant portions of the year (approx. 25% probability of exceeding the brook trout chronic level of 17 ug/L).

Trout may be absent from A72 and other reaches of the Animas due to mechanisms other than the direct lethality of zinc or copper that is represented by our models. Trout can detect and avoid sublethal concentrations of metals (Woodward et al. 1995). Trout may also avoid sites with very low densities of benthic invertebrates. Kiffney and Clements (1996) demonstrated that mixtures of metals (zinc, copper, and cadmium) at concentrations less than those typically occurring at A72 can result in substantial mortality of sensitive taxa and life stages of benthic invertebrates. This high sensitivity to toxic effects of metal mixtures can reflect additive or synergistic (greater than additive) toxicity of metals (Kraak et al. 1994). Additional impacts on benthic communities at A72 (and elsewhere in the watershed) can result from loadings of iron and aluminum colloids formed during neutralization of inputs from acidic tributaries. Precipitation of colloids downstream of Cement and Mineral Creeks contributes to degradation of benthic habitats at A72, due to embeddedness of stream gravels, and may also contribute to toxic effects on fish and invertebrates (Kimball et al., this document).

Our predictions of the toxicity of dissolved zinc and copper to aquatic biota are consistent with on-site toxicity evaluations and with observations of impacts on resident stream communities. We hope that this approach will prove to be useful for planning and evaluation of efforts to remediate abandoned minelands in the Animas watershed and elsewhere.

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