PHA076

SEASONAL VARIATION OF METAL TOXICITY IN STREAMS AFFECTED BY ACID MINE DRAINAGE

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ABSTRACT

Seasonal variation of metal concentrations in the upper Animas River watershed of Colorado may strongly influence toxic effects of stream water to aquatic biota. Loadings of dissolved metals to the upper Animas River and tributaries are greatest during summer, during high stream discharge from snowmelt and monsoonal rains, but adverse effects on stream biota may be greater during winter low-flow periods, when concentrations of dissolved metals are greatest. We evaluated the toxicity of stream water from four sites to fathead minnows (*Pimephales promelas*) and amphipods (*Hyalella azteca*) in late summer 1998 and late winter 1999. Stream water was more toxic in winter than in summer, consistent with greater concentrations of dissolved zinc (Zn) and copper (Cu). Overall, amphipods were more sensitive than minnows, as undiluted water from all sites was highly toxic to amphipods during both sampling periods, but seasonal variation in toxicity was greater for minnows. Only one of five sites tested in summer 1998 caused moderate mortality of minnows (37%), whereas three of four sites tested in winter 1999 caused severe mortality (70-100%). Seasonal variation in toxicity of stream water was modeled for three sites, based on LC50s for Zn and Cu to amphipods and minnows and multiple regression models of dissolved Zn and Cu concentrations. Model predictions corresponded closely to results of toxicity tests, and indicated that the April study period was near the predicted annual maximum for toxicity at the three sites. The models also suggested that seasonal differences in toxicity to fathead minnows were influenced more strongly by variation in dissolved Cu than dissolved Zn. These results indicate that water quality objectives for remediation of the upper Animas watershed must consider seasonal variation in dissolved metal concentrations and variation in sensitivity to metal toxicity among fish and invertebrate taxa.

BACKGROUND

Aquatic biota of streams in the upper Animas River watershed of Colorado are limited by metals in acid mine drainage, from abandoned mines and deposits of mine and mill wastes, and naturally-acidic runoff from rock and soils associated with mineral deposits. Federal land managers and local stakeholders seek to remediate abandoned minelands in the watershed, with the goal of restoring aquatic ecosystem s of the upper Animas watershed. Of particular interest is the reach of the Animas near and downstream of the historic mining town of Silverton, which is located at the confluence of the three principal headwater drainages: Animas River, Cement Creek, and Mineral Creek (Figure 1).

Recent studies have documented toxic effects on fish and invertebrates associated with high concentrations of metals, especially zinc (Zn) and copper (Cu), in stream water from Cement and Mineral Creeks and from the Animas River downstream of Silverton. Development of remediation plans for the watershed requires characterization of the seasonality, duration, and causes of toxic conditions in stream reaches targeted for remediation. The biological and water resources research capabilities of the USGS, which became involved in the upper Animas watershed as part of the Abandoned Minelands Initiative, provided a unique opportunity to document the severity and causes of toxicity in stream water and to develop predictive models to guide remediation in the watershed.

Figure 1. Location of study sites in the upper Animas River watershed, Colorado USA.

STUDY OBJECTIVES:

1. Measure seasonal variation in toxicity of stream water to fish and invertebrates.
2. Evaluate contribution of Zn and Cu to toxicity of stream water .
3. Evaluate predictions of toxicity based on seasonal variation in Zn and Cu.

METHODS

1. Water sampling

Stream water for toxicity testing was collected during August-September 1998 and in early April 1999. Samples were used for toxicity testing within 48 hr (1998) or 72 hr (1999) after collection.

Samples were collected at three USGS gaging stations near Silverton, Colo. (AR1, Animas R. upstream of Cement and Mineral Cr.; AR2, Animas R. downstream; and LMC, lower Mineral Cr.) and at a reference site on the South Fork of Mineral Cr. (SMC).

Water samples were filtered through 0.45 λm teflon/polypropylene filter cartridges, acidified to 1% HNO_3, and analyzed for metals by ICP-MS.

2. Toxicity Tests

Toxicity tests were conducted on-site in 1998. Samples collected in 1999 were tested at the Columbia Environmental Research Center (CERC), Columbia MO. Stream water was tested in an abbreviated dilution series (100%, 50%, and 25%), except the 1998 amphipod test was conducted with 100% stream water only. ‘Animas' reconstituted water (ARW) was used as control and dilution water for all tests. Average characteristics of ARW were: pH 7.4, total alkalinity 16 mg/L as CaCO3, total hardness 117 mg/L as CaCO3, sulfate 83 mg/L.

Tests were started with 7-14 day old amphipods, *Hyalella azteca*, and newly-hatched (<48-hr) fathead minnows, *Pimephales promelas*. Tests were conducted at 25 °C for 7-d, except the 1998 amphipod test (14 d).

Amphipod tests were conducted following general recommendations of USEPA (1999): six replicates per treatment; ten animals per chamber; 300 mL beakers, with 250 mL exposure volume; nylon mesh substratum; fed yeast-cereal leaves-trout food suspension daily. Water additions (one-half exposure volume/d) were added using a system modified from Leppanen and Maier (1998)

Minnow tests were conducted following general recommendations of USEPA (1993/98?): 1000 mL exposure chambers with 250 mL exposure volume; ten fry per beaker; daily water renewal; fed newly-hatched brine shrimp three times/day.

Toxicity of Zn and Cu in ARW was determined using identical methods, except five concentrations of each metal were tested in 50% serial dilutions, with two (minnows) or three (amphipods) replicates per concentration.

3. Analysis of Toxicity Data

Survival data were transformed by the arcsine-square root method before analysis.

Differences between treatments and controls were tested by analysis of variance with Dunnett's test (SAS Institute 1990) .

Median lethal concentrations (LC50s) were determined by the trimmed Spearman-Karber method, using TOXSTAT software (WEST, Inc, 1994).

4. Modeling seasonal trends in dissolved metals and toxicity

Concentrations of dissolved metals in stream water were determined monthly or biweekly at three USGS gaging stations during 1997 and 1998 (Lieb et al., in prep.).

Associations of dissolved zinc and copper concentrations with stream discharge and Julian date were modeled using histeritic multiple linear regression models (Aulenbach and Hooper 1994).

Hysteresis models were used to predict seasonal variation in dissolved metal concentrations, based on average discharge by Julian dates during the period 1992-1997 (Besser and Leib 1999).

Toxic units were calculated by dividing modeled dissolved metal concentrations by LC50s (LC50 = 1 toxic unit). Cumulative toxic units for Cu and Zn were calculated assuming additive toxicity.

RESULTS AND DISCUSSION

SEASONAL DIFFERENCES IN TOXICITY

Water from all four sites was toxic to amphipods during both sampling periods (Fig. 2):

- In summer 1998, undiluted water from all four sites caused ❍90% mortality.
- In spring 1999, undiluted water from three sites (AR1, AR2, LMC) caused 100% mortality.
- Dilutions indicated toxicity varied among sites in the order: AR1> AR2 > LMC >SMC.

Toxicity to fathead minnows differed between sampling periods (Fig. 2):

- In summer 1998, water at most sites (AR1, AR2, LMC) was not toxic to fathead minnows
- In spring 1999, undiluted water from three of four sites caused significant mortality.
- Dilutions indicated toxicity varied in the order: LMC > AR2 > SMC (>?) AR1.
- Tests with water from the 'reference' site, SMC, were ambiguous in both seasons:
  - tests in summer 1998 may have been affected by high suspended solids in storm runoff;
  - effects in spring 1999 were not consistent across dilutions.

Different metals may have been responsible for toxicity at different sites (Table 1)

- Water from AR1contained high concentrations of Zn and was toxic only to amphipods.
- In spring 1999, water from AR2 and LMC had high dissolved Cu, plus Fe (LMC) or Zn and Fe (AR2).

Amphipods

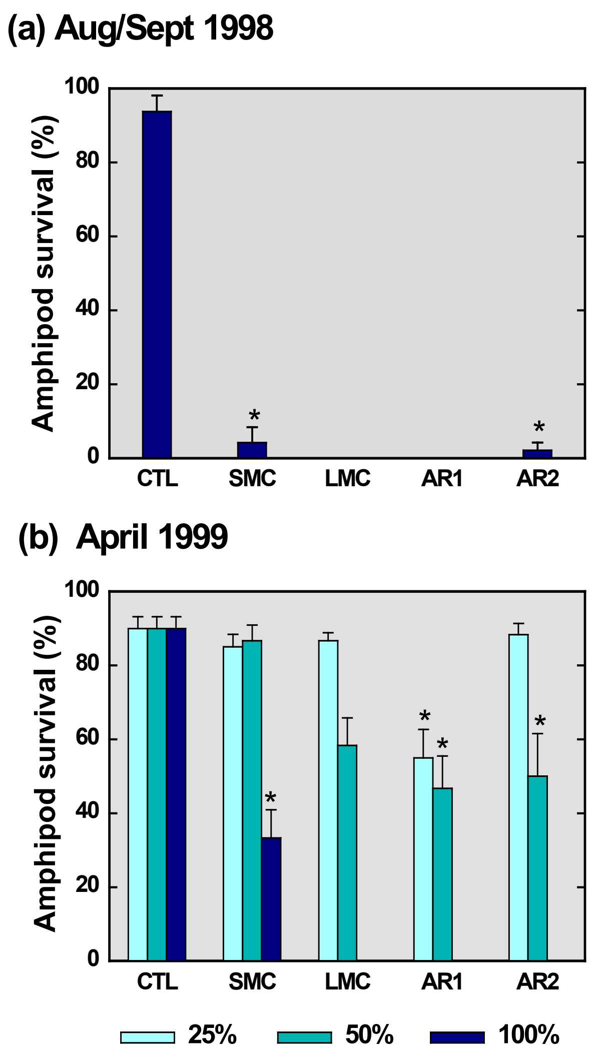

Figure 2. Survival of amphipods in stream water and dilutions: (a) summer 1998, and (b) spring 1999. Means and standard error, N=6; asterisks indicate significant difference from control.

Fathead Minnows

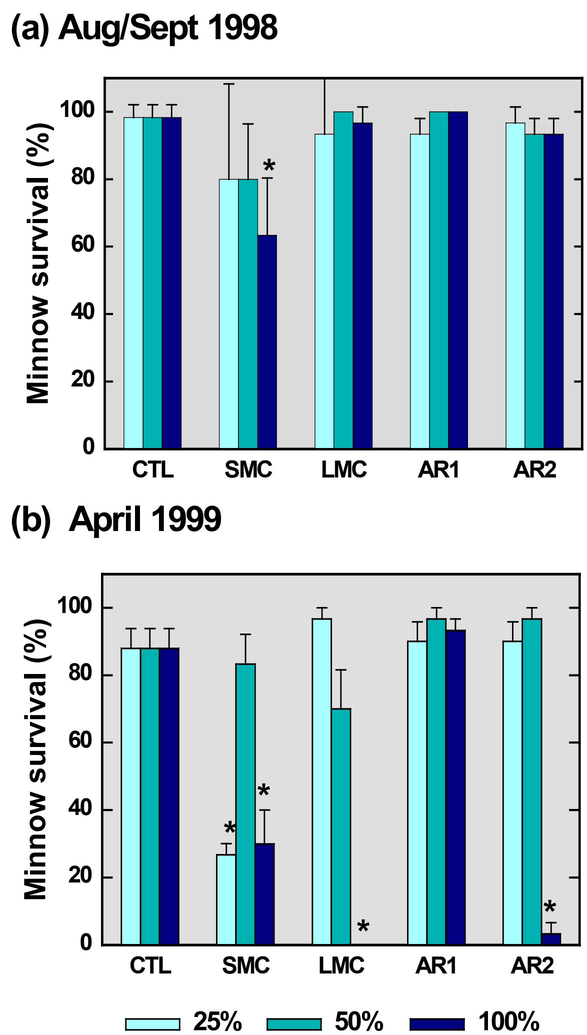

Figure 3. Survival of fathead minnows exposed to stream water and dilutions: (a) summer 1998, and (b) spring 1999. Means and standard error, N=6; asterisks indicate significant difference from control.

Table 1. Dissolved metal concentrations in stream water (µg/L), August-September 1998 and April 1999. Means, N=2.

Site	Date	Cd	Cu	Fe	Zn
SMC	8/98	0.1	3.8	355	13
	4/99	0.6	<0.1	414	7
LMC	8/98	0.7	6.7	414	210
	4/99	1.9	23	3315	397
AR1	8/98	1.1	6.4	94	275
	4/99	2.1	2.3	<30	659
AR2	8/98	0.8	5.9	402	175
	4/99	2.3	8.3	2150	625

Table 2. Median lethal concentrations (LC50) of zinc and copper for minnows and amphipods in reconstituted water, with 95% confidence intervals.

Species	LC50 (µg/L)	
	Zn	Cu
Amphipod, *H. azteca*	220 (174 - 279)	79 (62 - 102)
Fathead minnow, *P. promelas*	704 (542 - 916)	35 (25 - 51)

MODELING SEASONAL TOXICITY OF ZINC AND COPPER

Amphipods and fathead minnows had different sensitivity to Zn and Cu (Table 2):

- Zn was much more toxic to amphipods;
- Cu was more toxic to minnows.

Toxic unit models indicated differing contributions of Zn and Cu to toxicity at different sites:

- Zn contributed 86-99% of toxic units for amphipods.
- Contribution of Cu to toxic units for minnows ranged from 7% at AR1 to 56% at LMC

Amphipod toxicity was predicted (☜TU >1) year-round at two of three sites (Fig. 4a):

- Model correctly predicted toxicity in spring 1999, but underestimated toxicity of water from LMC in summer 1998.

Minnow toxicity was predicted only during the winter/spring period (Fig. 4b):

- Seasonal toxicity of water from AR2 and LMC was accurately predicted by models;
- Model overestimated toxicity of AR1 in spring 1999.

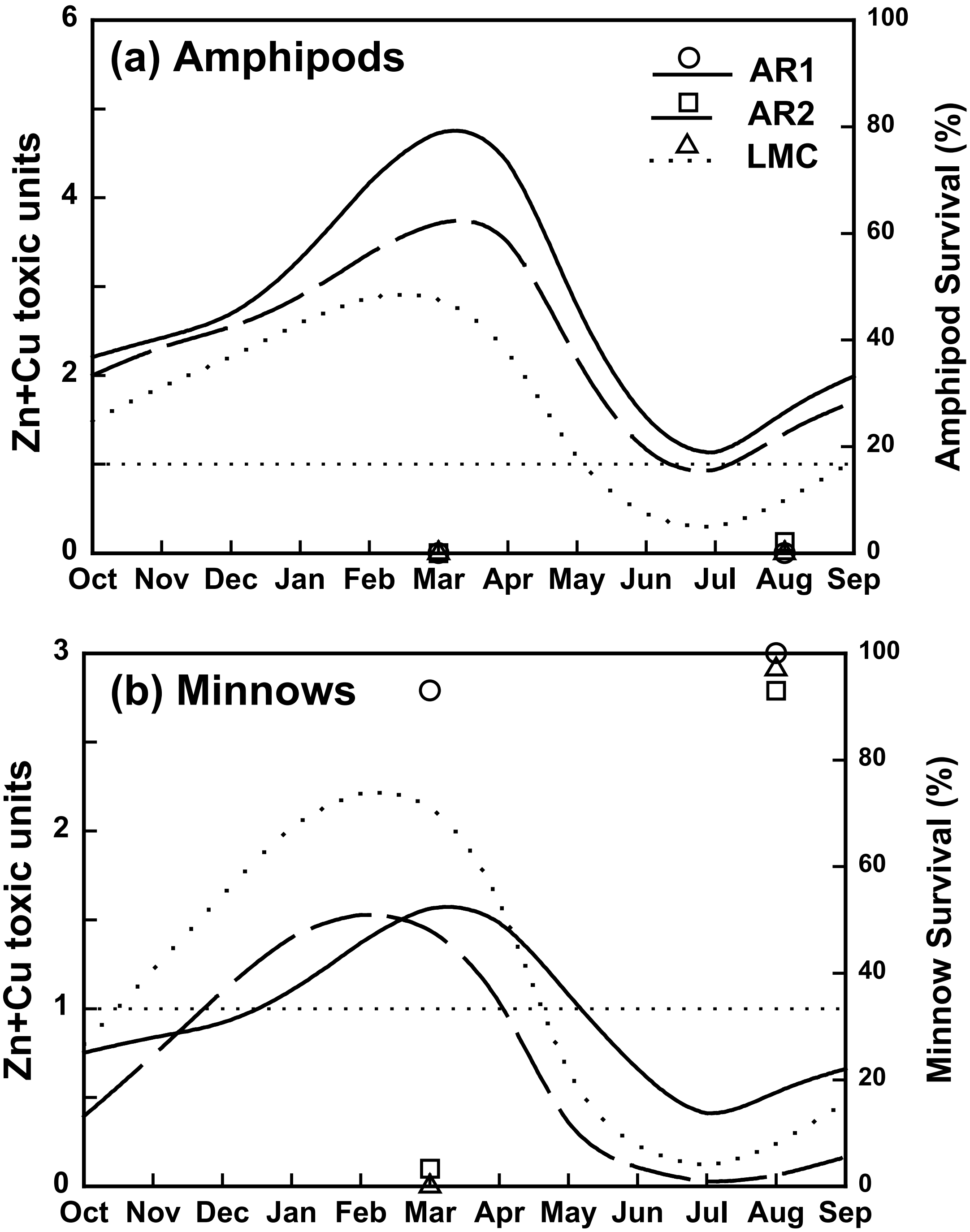

Figure 4. Modeled and observed seasonal toxicity of Zn and Cu to (a) amphipods and (b) fathead minnows. Curved lines indicate modeled toxic units for Cu+Zn; horizontal dotted line indicates 1 toxic unit. Symbols indicate survival in toxicity tests

CONCLUSIONS

1. **Toxicity of stream water from sites in the upper Animas River watershed was greater in spring 1999 than in summer 1998.**

   Seasonal variation in toxicity to fathead minnows was greatest at AR2 and LMC.

   Seasonal variation was apparently less for amphipods (but comparisons are limited by the lack of dilution series data from summer 1998).

2. **Results of toxicity tests were consistent with predictions based on seasonal variation in dissolved Zn and Cu.**

   Models correctly predicted toxicity to amphipods at two of three sites in summer 1998 and at all three sites in spring 1999.

   Models correctly predicted lack of toxicity to minnows in summer 1998 and correctly predicted toxicity at two of three sites in spring 1999.

3. **Models suggest that metals other than Zn significantly affect stream biota of the upper Animas watershed.**

   High Zn concentrations affect sensitive taxa, such as amphipods, year-round.

   Sites with high Cu concentrations exhibited greater toxicity to fathead minnows; studies with the resident species (brook trout) are ongoing.

   Dissolved Fe was also high at sites with greatest toxicity to minnows, and may contribute to observed toxicity.

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